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Alloying: Understanding the Basics (#06117G)

ALLOYING

UNDERSTANDING THE BASICS

Edited by
J.R. Davis
Davis & Associates



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Preface

Alloying may be defined as "the process of adding one or more elements or compounds to interact with a base metal in order to obtain beneficial changes in its mechanical, physical, or chemical properties or manufacturing/processing characteristics." For the purposes of this publication, the definition has been limited to those alloying processes that affect the *bulk* of the material; therefore, surface alloying processes such as carburizing, nitriding, ion implantation, and hot dip galvanizing are not covered. However, elements or compounds that lead to a preferential microstructure and subsequent improved properties are covered. Examples of these are grain refiners (grain refining results in better forming or higher strength), inoculants added to molten cast irons to produce changes in graphite distribution and improvements in mechanical properties, magnesium-containing nodulizing (or spheroidizing) additions in ductile irons for high strength and ductility (up to 18% elongation), and the addition of certain elements, such as calcium, sodium, strontium, and antimony, to refine the structure of aluminum-silicon casting alloys as well as improve their tensile properties and ductility. Also included are discussions of some powder metallurgy (P/M) materials that technically may fall outside the definition of alloying given above. An example is copper-base dispersion strengthened materials. Copper can be strengthened by using fine dispersed particles of aluminum oxide. Because this oxide is not immiscible in liquid copper (i.e., it does not "interact"), dispersion-strengthened copper cannot be made by conventional ingot metallurgy and alloying techniques; P/M techniques must be used. Dispersion-strengthened superalloys made by "mechanical alloying" are also described.

Although emphasis has been placed on deliberate alloying additions (minor or major alloying elements), the effects of trace or tramp elements are also summarized. Such impurities can have a profound affect on processing and properties of metals and their alloys. For example, impurity levels in the parts per million range can significantly lower the electrical conductivity of copper.

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I wish to thank a number of people who provided invaluable assistance throughout this project. The introductory article, "Principles of Alloying," was authored by Hugh Baker, consulting editor to ASM and a longtime contributor to the ASM Handbook and Phase Diagram programs. I have had the privilege of working with Hugh for some twenty years. Thanks are also extended to Larry Korb (Rockwell International), an ASM Fellow and past Chairman of the ASM Handbook Committee. Larry was instrumental in defining the scope of the book and supplied material for several articles, including those on carbon and low-alloy steels and aluminum alloys. Finally, the helpful comments and assistance from the ASM Editorial staff are acknowledged. In particular, I would like to thank Steve Lampman from Technical Publications for his involvement in the early stages of the project.

Joseph R. Davis
Davis & Associates
Chagrin Falls, Ohio

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Principles of Alloying*

Introduction and Overview

Metals are seldom used in commercial applications in their pure (unalloyed) condition. Instead, one or more chemical element is normally alloyed with the base metal to alter its characteristics to make it easier to fabricate and/or perform better in the application. Although in the broad sense, alloying covers changing the chemical composition of the surface of a part by such processes as plating, cladding, nitriding, ion implantation, carburizing, and hot dip galvanizing, this book is limited to only those alloying processes that affect the bulk of the material, while surface modification is discussed in other ASM publications. This book, however, does cover the addition of inoculant materials to the melt to alter the microstructure of the solid part. Some of the characteristics that are affected by alloying (or inoculating) are listed in Table 1.

Alloying for Mechanical Properties

Room-Temperature Strength. The most common reason for alloying is probably to improve room-temperature strength. The strength of a metal part is determined by its resistance to plastic (permanent) deformation when loaded beyond its elastic limit. Because this plastic deformation occurs by the mechanism of *slip* along the crystallographic planes in the grains of the metal (Fig. 1), the object of alloying to improve strength is that of increasing resistance to crystallographic slip. There are several ways to accomplish this increase in resistance, but before these are discussed, the internal structure (microstructure) of the metal should be examined.

*This article is written by Hugh Baker, Consulting Editor, ASM International.

Table 1 Metal characteristics affected by alloying

Mechanical properties	Processing properties
Room-temperature strength	Castability
Hardenability	Weldability, brazeability, and solderability
Fatigue resistance	Formability
Creep resistance	Machinability
Service properties	**Physical properties**
Heat resistance	Elastic modulus
Toughness and cold resistance	Density
Corrosion/oxidation resistance	Magnetic properties
Hardness and wear resistance	Electrical properties
	Thermal expansion properties
	Color

The atoms in each metal part are normally arranged into many different individual crystals (*grains*). The configuration *structure* of the crystal lattice and the distance between the atoms in the crystal (*effective atom diameter*) are those that result in the lowest energy state for the atoms in the crystal and are unique to each metallic element and temperature being considered. (Some metals have different unique crystal structures and atomic diameters at different temperatures; that is, they form different *phases* at different temperatures.) The planes of the crystals in a metal part are usually oriented in a great many different directions, many of which

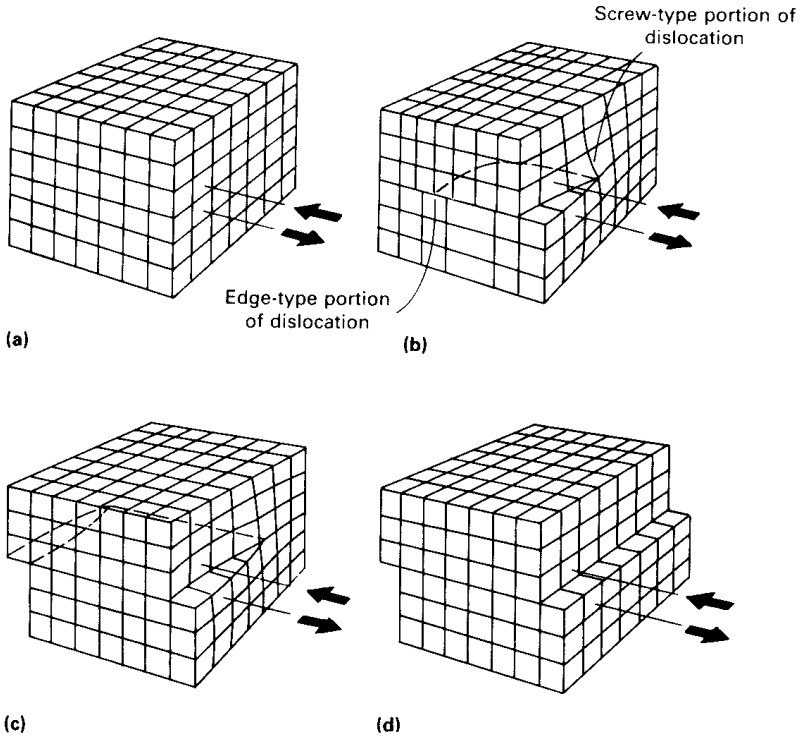


Fig. 1 Four stages of slip formation. (a) Crystal before displacement. (b) Crystal after some displacement. (c) Complete displacement across part of crystal. (d) Complete displacement across entire crystal

are not closely aligned with the direction of the external loading direction. As shown in Fig. 2, the atoms in the three-dimensional regions between the individually oriented crystals (the grain boundaries) are not aligned with either crystal and, therefore, are in a higher energy state than the crystals themselves.

All the various ways of increasing resistance to slip in a metal part are based on increasing the interference to the slip process. These include: grain refining, cold work, solid-solution hardening, age hardening, dispersion hardening, phase transformation, and duplex-structure strengthening. In multigranular parts, the orientation of the slip planes in adjoining grains is seldom aligned, and the slip path must change directions when traveling from one grain to another. Reducing grain size produces more changes in direction of the slip path and lengthens it, while the permanent deformation of the part caused by cold work results in distortion of the crystal structure, which makes slipping more difficult (*work hardening* or *strain hardening*). Vanadium, aluminum, tungsten, and nitrogen are examples of excellent grain refiners in steels, while titanium, vanadium, aluminum, and zirconium additions to carbon and low-alloy steels inhibit grain growth.

Atoms of a different element can be added to the base metal (up to the limit of solid solubility for the second element), but these new atoms will, of course, have a different effective diameter than those of the base metal. If the new atoms are quite small, they may be able to fit in the interstices between the host atoms in the crystal, but some distortion of the crystal lattice will probably result (Fig. 3a). If the difference in size of the atoms is fairly small, the new atoms can substitute for base metal atoms in the

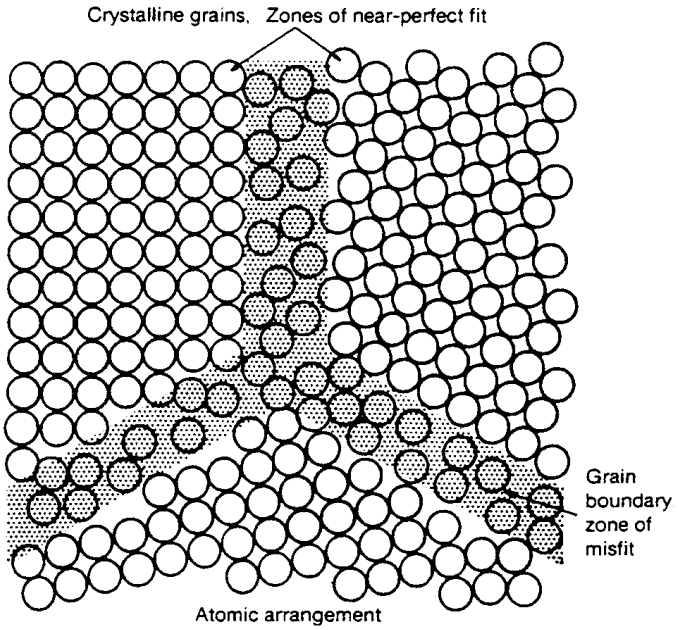


Fig. 2 Nature of grain boundaries

crystal lattice, but some distortion of the lattice will also result. In either case, the distortion caused by the *solid solution* will result in making slip more difficult (solid-solution hardening) (Fig. 3b).

When a metal solidifies from the molten state, crystal nuclei first form and then grow together to create grains, the last material to solidify forming the boundaries between the grains. When the amount of alloying atoms added exceeds the limit of solid solubility, the excess atoms of the alloying element will become trapped in the grain boundaries. Then, as the temperature is further decreased, the excess atoms try to unite with atoms of the base metal to form small regions of *intermetallic compound.* Although these regions have a different crystal structure than the base metal, the two crystal structures remain *coherent,* and the mismatch between the two lattice structures causes strain hardening of the part (Fig. 4a and 4b). At relatively low temperatures, the reaction between the base metal atoms and the excess alloying atoms is normally quite slow, and the strain-hardening phenomena is called *age hardening* (and sometimes called by the misnomer *precipitation hardening*). If the reaction is allowed to continue, the regions of intermetallic compound grow and actually precipitate out of solution (become *noncoherent*) and form discrete particles (Fig. 4c and 4d). When this happens, the mismatch straining is lost and the part becomes *overaged* and loses strength. There are many examples of alloying for age hardenability, including copper added to aluminum to form 2000-series alloys.

As stated previously, some metals have different unique crystal structures and atomic diameters at different temperatures; that is, they form different stable *phases* at different temperatures. Examples are alpha and beta titanium and alpha and gamma iron. Some metal phases are transitional rather than stable. An important example of a transitional phase is the martensite form of iron, which is a hard material that strengthens a part when it is formed (by *phase transformation* of quenched gamma iron).

If the second phase material that is finely dispersed throughout the matrix material of the alloy is a hard material, such as martensite in steel

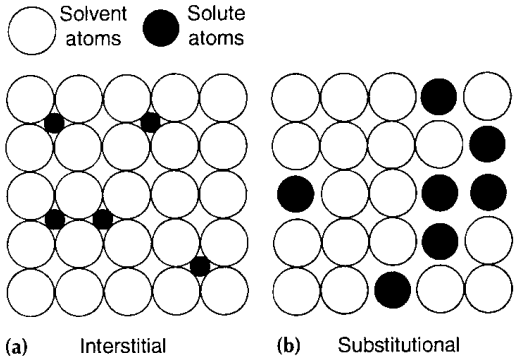


Fig. 3 Solid-solution mechanisms. (a) Interstitial. (b) Substitutional

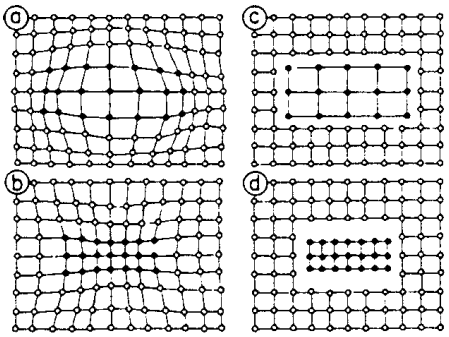


Fig. 4 Coherent (left) and noncoherent (right) precipitation. (a) and (b) A coherent or continuous structure forms when any precipitate is very small. (c) and (d) Coherency is lost after the particle reaches a certain size and forms its own crystal structure. Then a real grain boundary develops, and severe lattice stresses disappear.

or alumina (Al_2O_3) in aluminum, the alloy is strengthened by *dispersion hardening*. Another example of dispersion hardening is dispersion-strengthened copper produced by internal oxidation. These alloys, which feature a fine, uniform dispersion of aluminum oxide particles in the copper matrix, exhibit higher strength and stability at elevated temperature. Dispersion-strengthened nickel-base alloys are produced by high-energy ball milling yttria (Y_2O_3) powder and the nickel-base alloy powder together (*mechanical alloying*). The improved elevated-temperature strength of these alloys is due to a uniform dispersion of fine refractory oxide (yttria) particles in a superalloy matrix.

Austenitic stainless steels are produced by alloying with gamma-stabilizing elements, notably nickel and chromium. These alloys have been strengthened by a heat treating and working process by which a *duplex structure* containing a very intimately mixed conglomerate of alpha and gamma grains is formed that offers more resistance to slip than the gamma-only structure of standard austenitic stainless steel.

Hardenability is the relative ability of a ferrous alloy to form martensite when quenched from a temperature above the upper critical temperature. The hardenability of steel is increased by increasing the carbon content and by alloying with such elements as boron, chromium, and manganese. The hardenability of irons and steels is discussed in greater detail in the articles covering these materials. Quenching of steel in water to produce martensite, however, often results in severe cracking of the part. Adding sufficient alloying elements will allow parts to harden in room-temperature air, greatly minimizing this problem.

Fatigue Resistance. Fatigue, the damage caused to a material by cyclic stressing, results from the fact that the material is not ideally homogeneous. Therefore, in each half cycle of stressing, minute strains are produced that are not completely reversible. These strains cause incremental

slip and local strain hardening, which gradually lead to the formation of minute cracks that grow and coalesce until failure eventually occurs. While manufacturing conditions, such as cold forming, welding and brazing, plating, and surface conditions, significantly affect fatigue resistance, it is usually also directly related to the hardness and tensile strength of the material. Therefore, alloying to produce good hardness and tensile strength usually results in good fatigue resistance. In addition, reducing unwanted trace elements and inclusions to increase tensile strength also helps to increase fatigue strength.

Creep Resistance. Creep, time-dependent extension under stress, occurs by the movements of *dislocations* through the metal grains (see Fig. 1). Because their movement at lower temperatures is impeded by grain boundaries and second-phase particles, chemical compositions that help produce fine grain size and microstructures that result in "grain-boundary pinning" particles improve creep resistance. At higher temperatures, creep occurs primarily by grain-boundary sliding. Therefore, increasing grain size improves creep resistance at these temperatures.

Alloying for Service Properties

Heat Resistance. Metals for high-temperature service must be alloyed to promote improved tensile strength and/or creep strength (see previous paragraph). Steels are a good example. While at room temperature or slightly above, carbon serves admirably to increase the tensile strength of steel; at higher temperatures, carbon is less effective. For temperatures of about 350 to 550 °C (700 to 1000 °F), additions of molybdenum, tungsten, or niobium are effective in increasing the strength of chromium steels. For still higher-temperature service, it is necessary to use steels of an austenitic type, which are formed by adding sufficient nickel.

Toughness and Cold Resistance. Plain carbon and low-alloy steels, like many metals that have a body-centered cubic lattice structure at room temperature, are susceptible to a lowering of absorbed impact energy with decreasing temperature. This change is accompanied by a transition in the appearance of the fracture surface from a ductile one to a brittle one. This *ductile-to-brittle transition* occurs over a relatively narrow subfreezing temperature range (the DBTT). The composition of the steel, as well as its microstructure, significantly affects both the transition temperature and the energy absorbed during fracture at any particular temperature. For example, to avoid low-temperature brittle fracture, carbon and phosphorus should be kept low, while boron and manganese additions are helpful. Nickel additions to steel in the range of 2.25 to 9% improve low-temperature toughness and strength, because they lower the DBTT of steels.

Corrosion/Oxidation Resistance. Corrosion of metals takes several different forms, including environmental, galvanic, and stress corrosion. Environmental and stress corrosion can both be influenced by the chemical composition and microstructure of the material. For example, as stated earlier, austenitic stainless steels are produced by alloying with gamma-stabilizing elements, notably nickel and chromium. The excellent corrosion resistance of stainless steels relies mainly on the *passivity* of its surface. As such, environments that tend to break down this passivity are more detrimental to stainless steel, while environments that tend to maintain this passivity do not damage stainless steel. Chromium atoms are similar in size to iron atoms, so when chromium is alloyed in iron at a level of no more than 11% Cr, the chromium atoms replace some of the iron atoms, thus forming a substitutional solid solution (see Fig. 3b), and this iron-chromium material has much-improved corrosion resistance over iron alone. Unalloyed titanium also develops a passive surface, which allows it to be used in severely corrosive environments, but if its surface passivation is disturbed, corrosion proceeds at a high rate. Many nickel-base alloys also have long been noted for their corrosion resistance.

The most common type of environmental corrosion is oxidation, which is an electrochemical process that requires the presence of moisture (liquid) in the environment. When environmental corrosion occurs, metal atoms go into solution in the liquid as ions, which releases the excess electrons. The production of the ions and excess electrons creates an electrical potential, called an *electrode potential,* which differs from metal to metal. One of the most effective ways of countering the corrosive effects of the presence in a part of atoms of a metal having a high electrode potential is to alloy with a metal that will tie up the undesirable atoms as relatively inert compounds, for example, adding magnesium to aluminum alloys that contain iron as an impurity. Because aluminum has a relatively high electrode potential, its surface rapidly loses its shiny appearance and develops a gray oxide coating, but alloying with magnesium helps to keep it bright.

Stress-corrosion cracking (SCC) results from the combination of static tensile stress (externally applied or residual) and a particular environment. Some alloys and microstructures are more susceptible to this type of cracking than others. For example, magnesium alloys that contain more than about 1.5% Al are susceptible to SCC, and the presence of zinc in the magnesium-aluminum alloy increases this susceptibility. Stress-corrosion cracking in aluminum-magnesium alloys can be minimized by limiting the magnesium content to 3%, while SCC in brasses can be minimized by decreasing the zinc content to less than 15%.

Galvanic corrosion, which results from the contact of two dissimilar metals (alloys) in an electrically conductive liquid, is best dealt with by mechanical means (eliminating the liquid by proper design for good drainage, inserting a nonconductor between the metal parts, and/or plating

one of the contact surfaces with a more compatible metal) rather than by alloying.

Hardness and Wear Resistance. Gold is very soft and easily deformed in its pure (unalloyed) form. Therefore, when used in electrical contacts, coins, jewelry, dentistry, and other commercial applications, it is usually alloyed with harder metals, such as silver, copper, palladium, and platinum, to increase its hardness and wear resistance without an appreciable loss in oxidation resistance. The basic hardness of steel is increased by increasing the carbon content, while the *hardenability* of steel (the ability to form martensite upon quenching from above the upper critical temperature) is increased by increasing the carbon content and by alloying with such elements as boron, chromium, and manganese. The abrasion and wear resistance of steel is increased by additions of such elements as chromium, nickel, molybdenum, and tungsten. Cast iron engine parts have long been made more wear resistant by alloying with silicon. Silicon additions also increase wear resistance of aluminum alloys. High-alloy white irons have improved wear resistance due to the presence of massive chromium carbides. Austenitic manganese (Hadfield) steel has long been used in railroad "frogs" (points) and jaw-crushers because of its exceptionally high wear resistance. Lubricity of bronzes used for sleeve bearings is increased by alloying with 10% Sn.

Alloying for Processing Properties

Castability. Molten metal begins to cool as soon as it leaves the pouring ladle, and because some time is required for the metal to reach and completely fill a mold, a reasonable freezing range is necessary for a metal (alloy) to have good castability. As seen in Fig. 5, pure (unalloyed) metals and intermetallic compounds melt and freeze at a single temperature. Therefore, they are very difficult to cast into an involved shape. Alloying, however, not only decreases the melting/freezing temperature, but also extends the temperature range over which solidification occurs (see Fig. 5). Both of these effects increase castability. *Fluidity*, the ease with which the molten metal flows and fills the mold, is also increased by suitable alloying. For example, the fluidity of cast iron increases with increasing carbon content until the eutectic concentration (4.3%) is reached, and then decreases at higher carbon contents. The fluidity of aluminum is increased by additions of silicon and/or copper and magnesium and decreased by additions of nickel and/or manganese. The fluidity of brass is increased by additions of antimony.

Weldability, Brazeability, and Solderability. Although the weldability of a material depends on the welding conditions used, the composition of

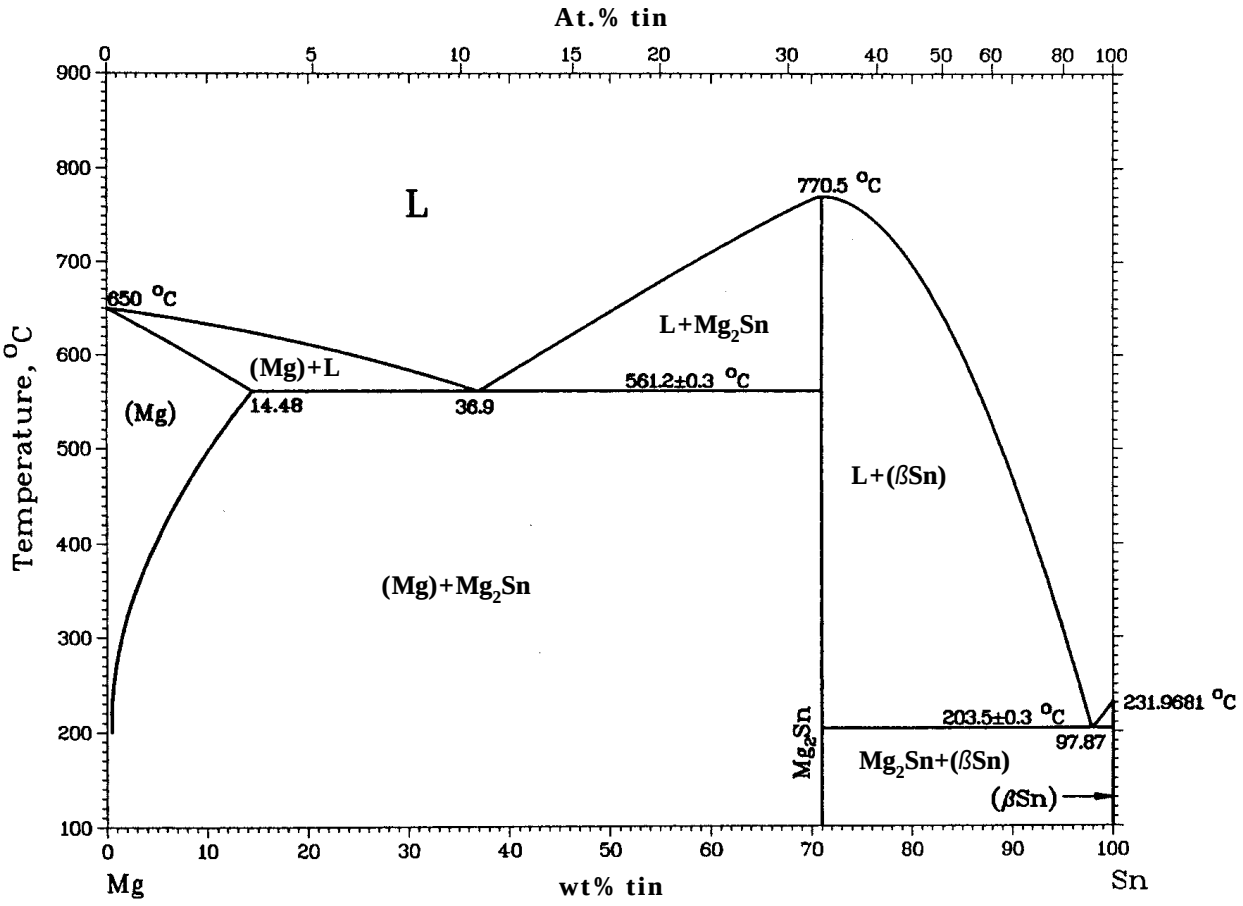


Fig. 5 Phase diagram for the magnesium-tin system, which exhibits a high-melting intermetallic compound. Source: A.A. Nayeb-Hashemi and J.B. Clark, 1988

the material is always a significant factor, as well as the composition of the filler material. Because welding is a type of casting process, the same alloy factors must be considered. For example, silicon is added to aluminum weld wire to increase its fluidity and to ensure production of sound welds. Another factor that must be considered, however, is the mechanical constraint on the freezing metal that the weld joint produces. If there are any low-melting second-phase materials in the grain boundaries, *hot tears* can form in these regions as the weld metal shrinks during cooling. High-temperature brazing fillers can be produced from alloys containing silver and other precious metals with nickel and copper, while low-temperature solder alloys are made from lead, tin, silver, indium, antimony, cadmium, and zinc.

Formability. Good formability requires that the material to be bent, drawn, stretched, ironed, or otherwise permanently deformed into a usable shape have a chemical composition that offers a combination of good ductility and strength. Low ductility and low strength both limit the amount of forming that the material can endure before tearing occurs. The

composition should also be such that there is a low tendency for formation of second-phase particles, such as sulfides in steel, which can lead to cracking or splitting during forming. The addition of 8% Ni to austenitic stainless steel lowers its rate of strain hardening, permitting deep drawing of stainless parts. Alloying, in conjunction with thermal/mechanical processing, can result in alloys that have more than 100% elongation (are *superplastic*) and that can be formed into intricate shapes.

Machinability is increased by alloying inclusions that lubricate the machine tool and break up the formed chip into small pieces. For example, lead, nitrogen, calcium, manganese, or phosphorus can be added to carbon and low-alloy steel to improve machinability, while selenium or sulfur are added to stainless steel to achieve improved machinability. Free-machining copper alloys are produced by additions of such elements as lead, sulfur, phosphorus, and tellurium.

Alloying for Physical Properties

Elastic Modulus. Several attempts have been made to take advantage of the high value of elastic modulus of beryllium in an alloy. One was an aluminum-matrix material for aerospace, called Lockalloy, after Lockheed Aircraft Company. The age-hardenable beryllium-copper alloys also have good values of elastic modulus, which are combined with high strength.

Density of an alloy is usually close to the value determined by the relative amount of the main constituents and their densities. A good estimate of the resulting value of density for an alloy can be obtained from the rule of mixtures. The addition of lithium to aluminum and magnesium is an example of producing light-weight aerospace alloys.

Magnetic Properties. All metals have magnetic properties of one type or another. *Ferromagnetic* materials are those that are strongly attracted to a magnet. Elements that are naturally ferromagnetic at room temperature include iron, nickel, and cobalt. These metals, however, lose their ferromagnetic properties when the temperature is raised above the *Curie* temperature for the metal (or alloy) in question and become *paramagnetic,* which means that they are much less strongly attracted to a magnet.

Magnetically soft materials are ferromagnetic materials that retain little or no magnetism when removed from a magnetic field. These materials are often produced by adding silicon, aluminum, or nickel to iron to increase its electrical resistivity and thereby reduce eddy-current losses and make it more suitable for alternating current motors, generators, and transformers. Cobalt additions to iron can be used to promote high permeability, while silicon additions can increase the temperature at which

grain growth occurs, allowing for more preferential grain orientation in the core material.

Magnetically hard materials for use as permanent magnets are also ferromagnetic materials, but are those that are capable by themselves of producing and maintaining relatively high magnetic induction without the aid of external magnetic fields. Permanent magnet materials are based on the cooperation of atomic and molecular moments within a magnetic body to produce a high level of retained magnetic induction. These materials are commonly hardened steels produced by phase-transformation hardening of plain (carbon) and alloyed (chromium, tungsten, or cobalt) steels, or by dispersion or precipitation agents (aluminum in iron-nickel or molybdenum in iron-cobalt). Other permanent magnet materials are alloys based on cobalt (platinum-cobalt and cobalt-rare earth) and ceramics based on hard iron oxides (ferrites).

Electrical Properties. One of the most important characteristics of a metal is the ease with which it transmits electrical current. The outer (valance) electrons in metal crystals are not tied to any specific atom and are, therefore, free to migrate in response to an electric field. However, any impediment to this free movement increases the resistance to the flow of the electrical current. These impediments include grain boundaries, second-phase particles, and lattice distortions caused by cold work, age hardening, and second elements in solid solution.

In some applications, such as electrical transmission wires, low electrical resistance coupled with adequate strength is desired. Oxygen-free copper, sometimes alloyed with minimal amounts of hardening agents (such as chromium, tellurium, beryllium, cadmium, or zirconium), is an important electric wire material. Some aluminum conductors are alloyed with silicon and magnesium to increase their strength without greatly decreasing their electrical conductivity.

In other applications, such as the magnetically soft materials described previously, greater electrical resistance is desired. In still others, such as electrical-resistance heating devices, high, uniform electrical resistance is required. Resistance-heating materials include nickel-chromium, nickel-chromium-iron, and iron-chromium-aluminum alloys.

Thermal Expansion Properties. Iron-nickel alloys have many anomalous properties, depending on the relative proportions of the two metals. For example, the coefficients of linear thermal expansion at room temperature range from a small negative value ($-0.5\ \mu m/m \cdot K$) to a large positive value ($20\ \mu m/m \cdot K$). One alloy, containing 36% Ni with small quantities of manganese, silicon, and carbon amounting to a total of less than 1%, has a coefficient so low that its length remains almost invariant (constant) for ordinary changes in room temperature. For this reason, the alloy, named Invar, has found many uses ranging from compensating

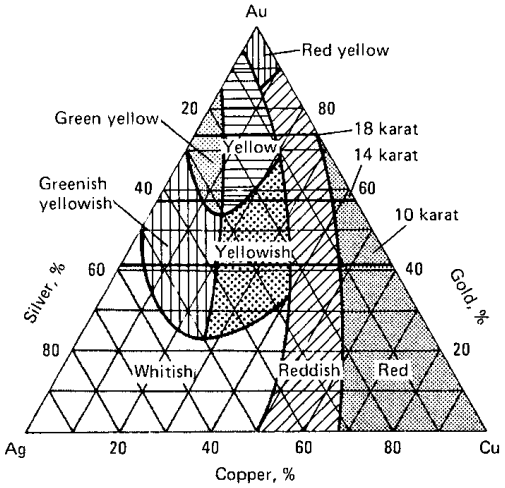


Fig. 6 Color chart for gold-silver-copper alloys for jewelry and dental applications

pendulums and balance wheels for clocks and watches to components for radios and other electronic devices.

Color. Most of the commercially important colored alloys for jewelry and dental applications are based on the gold-silver-copper system, which takes advantage of the different basic colors of these three elements to offer a wide range of color blends to suit the user (Fig. 6). Copper alloys are also available in a wide variety of colors (see the article on these alloys).

Effect of Properties on Alloying

The various techniques used for alloying and inoculation of metals have been developed to overcome physical, mechanical, and chemical problems caused by the fact that the base metal and the alloying or inoculate material have dissimilar properties. Some of these properties are discussed subsequently.

Melting Temperature. Producing a lead-tin solder alloy is fairly easy. Pieces of solid lead and tin can be melted together without much trouble, because their melting temperatures are fairly close (328 and 232 °C or 622 and 450 °F, respectively). Producing an alloy of aluminum and silicon, however, would appear to be more difficult due to the wide disparity in melting temperatures between the two constituents. Pure silicon melts at 1410 °C (2750 °F), while the melting temperature of aluminum is only 660 °C (1220 °F). If the temperature of the molten aluminum is raised to

that of molten silicon, much of the aluminum could be lost to oxidation and vaporization. However, examination of the aluminum-silicon binary phase diagram shows that a low-melting eutectic (577 °C, or 1071 °F) is formed at 12.6 wt% Si. Therefore, successful alloying of aluminum-silicon alloys is achieved by using master alloys or prealloyed ingots containing silicon contents at or near the eutectic point.

Density. If the specific weight of an alloying material is significantly different from that of the base metal, the alloying material will tend to either rise to the top or sink to the bottom of the melt, and vigorous stirring will be required to ensure a uniform chemical composition of the solid casting.

Solubility. Adding particles of inoculant material to a melt to refine the grains produced in the solid casting is often a problem. A fine grain size in the casting is produced when there are a great many grain-nucleation sites available in the melt. This usually is accomplished by use of an inoculating compound that is still solid at the temperature of the melt and that is relatively insoluble in the melt, thus remaining solid. Here again, vigorous stirring of the melt is required (to keep the solid particles from settling out).

Volatility. If the metal to be added to the melt has a high vapor pressure at the melting temperature of the base metal, much of the alloying or inoculating metal can be lost to the atmosphere. For example, special techniques must be used when adding magnesium to molten cast iron to nodulize the graphite.

Chemical Activity. Sometimes the alloying element used is quite chemically active and reacts with the atmosphere over the melt and/or with elements in it to form unwanted compounds. When this occurs, not only is some of the alloying effect lost, but the presence of the compounds formed may have an undesirable effect on the alloy if they are not removed.

Alloying Techniques

Several melting and casting techniques have been developed to overcome the problems caused by the base metal and the alloying or inoculate material having dissimilar properties.

Master Alloys, Hardeners, and Compounds. When alloying aluminum, metals having low melting temperatures, such as magnesium,

zinc, lead, bismuth, and tin, are commonly added directly to the melt and stirred in. Higher-melting metals, such as manganese, iron, titanium, and chromium, however, dissolve so slowly in the melt that they are introduced as rich (master) alloys or hardeners containing from 2 to 10% of the second metal in aluminum. When alloying magnesium, metals having low melting temperatures, such as aluminum and zinc, are once again commonly added directly to the melt and stirred in. Higher-melting metals such as manganese can be added in the metallic form, but it is usually added as manganese chloride to improve alloying efficiency.

Prealloyed Ingots. Many of the standard die casting alloys are available from suppliers already prealloyed and ready for melting and casting with little correction of chemical composition. However, in alloys containing constituents that tend to be lost during remelt, corrections must be made by adding the pure metal or a hardener having a fairly high content of the alloy element.

Mechanical Alloying. Elements that are incompatible in many ways can be alloyed through mechanical means, as described previously for the case of the dispersion-strengthened nickel-base alloys. Another example is alloying through the mixing of powdered metals. After the elements are brought together by mechanical means, they are allowed to further mingle by means of diffusion.

Surface Alloying

As stated earlier, although in the broad sense, alloying covers changing the chemical composition of the surface of a part by such processes as plating, cladding (by welding or spraying), nitriding, ion implantation, and carburizing; however, this book is limited to only those alloying processes that affect the bulk of the material, while surface modification is discussed in other ASM publications. Diffusion of the surface-alloying element into the base metal causes layers of different materials having different properties to form near the surface; these are alloys in the true sense of the word. The layers of hot dip galvanized steel are a good example. The outer surface is soft eta-phase pure zinc, next is a layer of hard, brittle zeta iron-zinc compound ($FeZn_{13}$), then a layer of ductile delta iron-zinc compound ($FeZn_7$), next a thin layer of hard, brittle gamma iron-zinc compound ($FeZn_{10}$) is formed, and finally the iron base metal. In electroplated parts, various chemical reactions occur between the plating element and the base metal that result in layers of varying composition in the plate thickness. This is also true for clad parts, such as trimetal bearings and heat exchangers. In both instances, the amount of time and temperature at which any diffusion can take place will determine the composition and

thickness of the layers. In carburizing by the pack, gas, vacuum, or plasma process, carbon is absorbed and diffused into a ferrous product to form a case capable of being subsequently hardened by quenching directly from the carburizing temperature or by cooling to room temperature and then reaustenitizing and quenching. The result is a hard case of high-carbon material surrounding a tough core of lower-carbon material. In nitriding by the gas, liquid, or plasma process, nitrogen is diffused into a ferrous product to produce a hard case with a tough core. Unlike carburizing, nitrogen is introduced at temperatures below the austenitite-formation temperature for ferretic steels, and quenching is not required. As a result of not austenitizing and quenching, nitriding produces minimum distortion and results in excellent dimension control. The case of nitrided steel contains a diffusion zone with or without a zone of iron-nitrogen compounds, such as FeN and $Fe_{2-3}N$. Other surface-modification processes for ferrous products include carbonitriding, ferritic nitrocarburizing, aluminumizing, siliconizing, chromizing, and boriding. In ion implantation, medium- to high-energy atoms bombard a solid material, and this process offers the ability to alloy almost any element into the near-surface region of any substrate. The advantage of this process is that it produces improved product properties without the limitations of dimensional changes or delamination found in conventional coatings.

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Gray Irons

Introduction and Overview

Gray irons are a group of cast irons that form flake graphite during solidification, in contrast to the spheroidal graphite morphology of ductile irons. The flake graphite in gray irons is dispersed in a matrix with a microstructure that is determined by composition and heat treatment. The usual microstructure of gray iron is a matrix of pearlite with the graphite flakes dispersed throughout (Fig. 1). The gray irons used most often and in the largest tonnages are the so-called "unalloyed" grades which are, in essence, iron-carbon-silicon alloys that usually contain 2.5 to 4% C, 1 to 3% Si, and additions of manganese, depending on the desired microstructure (as low as 0.1% Mn in ferritic gray irons and as high as 1.2% Mn in pearlitics). Sulfur and phosphorus are also present in small amounts as residual impurities.

In addition to the unalloyed gray irons described above, moderate or low-alloy gray irons and high-alloy gray irons are also produced. The total amount of alloying additions in the low-alloy gray irons is usually less than 2.0%. High-alloy gray irons contain more than 4% total alloy content and include austenitic nickel-alloyed gray irons and high-silicon gray irons. These more highly alloyed cast irons are used for corrosion-resistant and/or heat-resistant applications.

The metallurgy of gray irons is extremely complex because a wide variety of factors influence their solidification and subsequent solid-state transformations. In spite of this complexity, gray irons have found wide acceptance based on a combination of outstanding castability, excellent machinability, economics, and unique properties. An excellent review of the metallurgy and properties of gray irons can be found in Ref 1.

Classes of Gray Iron. A simple and convenient classification of the commonly used unalloyed gray irons is found in ASTM specification A 48, which classifies the various types in terms of tensile strength,

expressed in ksi. The ASTM classification by no means connotes a scale of ascending superiority from class 20 (minimum tensile strength of 140 MPa, or 20 ksi) to class 60 (minimum tensile strength of 410 MPa, or 60 ksi). In many applications, strength is not the major criterion for the choice of grade. For example, for parts such as clutch plates and brake drums, where resistance to heat checking is important, low-strength grades of iron are the superior performers. Similarly, in heat shock applications such as ingot or pig molds, a class 60 iron would fail quickly, whereas good performance is shown by class 25 iron. In machine tools and other parts subject to vibration, the better damping capacity of low-strength irons is often advantageous.

Generally, it can be assumed that the following properties of gray cast irons increase with increasing tensile strength from class 20 to class 60:

- All strengths, including strength at elevated temperature
- Ability to be machined to a fine finish
- Modulus of elasticity
- Wear resistance

On the other hand, the following properties decrease with increasing tensile strength, so that low-strength irons often perform better than high-strength irons when these properties are important:



Fig. 1 Class 30 gray cast, as-cast. Structure consists of type A graphite morphology in a pearlitic matrix. Type A graphite flakes are randomly distributed and oriented throughout the matrix and are associated with the optimum mechanical properties. Additional information on graphite morphology and its effect on properties can be found in Ref 1. Etched in 2% nital. 1000×

- Machinability
- Resistance to thermal shock
- Damping capacity
- Ability to be cast in thin sections

Applications. Gray iron is suitable for a wide range of applications because of the property changes that can be produced by controlling the characteristics of its free graphite and matrix structures. A variety of gray iron grades can be effectively used in highly competitive, low-cost applications where its founding properties are of paramount importance. Such applications include implement weights, elevator counterweights, guards and frames, enclosures for electrical equipment, and fire hydrants. Gray iron is also employed in more critical applications in which mechanical or physical property requirements determine iron selection, such as pressure-sensitive castings, automotive castings, and process furnace parts.

Standards established by ASTM, SAE, the U.S. government, and the U.S. military provide assistance in the selection of the appropriate grade or class of iron to meet specific mechanical or physical requirements. Table 1 summarizes typical applications for gray iron, based on specifications and information available in the literature.

Composition Control

For purposes of clarity and simplicity, the chemical analysis of gray iron can be broken down into three categories: the major elements; the minor, normally low-level elements that are critically related to iron solidifica-

Table 1 Typical applications for gray iron castings

Specification	Grade or class	Typical applications
ASTM A 48	20, 25	Small or thin-sectioned castings requiring good appearance, good machinability, and close dimensional tolerances
	30, 35	General machinery, municipal and waterworks, light compressors, automotive applications
	40, 45	Machine tools, medium-duty gear blanks, heavy compressors, heavy motor blocks
	50, 55, 60	Dies, crankshafts, high-pressure cylinders, heavy-duty machine tool parts, large gears, press frames
ASTM A 159, SAE J431	G1800	Miscellaneous soft iron castings (as cast or annealed) in which strength is not of primary consideration. Exhaust manifolds may be made of this grade of iron alloyed or unalloyed. These may be annealed to avoid growth cracking due to heat.
	G1800h	Brake drums and discs where very high damping capacity is required
	G2500	Small cylinder blocks, cylinder heads, air-cooled cylinders, pistons, clutch plates, oil pump bodies, transmission cases, gear boxes, clutch housings, light-duty brake drums
	G2500a	Brake drums and clutch plates for moderate service requirements, where high-carbon iron is desired to minimize heat checking

(continued)

(a) Nickel-alloyed (13.5 to 36% Ni) austenitic gray irons

Table 1 (continued)

Specification	Grade or class	Typical applications
ASTM A 159, SAE J431	G3000	Automobile and diesel cylinder blocks, cylinder heads, flywheels, differential carrier castings, pistons, medium-duty brake drums, clutch plates
	G3500	Diesel engine blocks, truck and tractor cylinder blocks and heads, heavy flywheels, tractor transmission cases, heavy gear boxes
	G3500b	Brake drums and clutch plates for heavy-duty service where both resistance to heat checking and higher strength are definite requirements
	G3500c	Extra heavy-duty service brake drums
	G4000	Diesel engine castings, liners, cylinders, pistons
	G4000d	Heavy-duty camshafts
ASTM A 126	A, B, C	Valve pressure-retaining parts, pipe fittings, flanges
ASTM A 278	40, 50, 60, 70, 80	Valve bodies, paper mill dryer rollers, chemical process equipment, pressure vessel castings
ASTM A 319	I, II, III	Stoker and firebox parts, grate bars, process furnace parts, ingot molds, glass molds, caustic pots, metal melting pots
ASTM A 823	…	Automobile, truck, appliance, and machinery castings in quantity
ASTM A 436(a)	1	Valve guides, insecticide pumps, flood gates, piston ring bands
	1b	Seawater valve and pump bodies, pump section belts
	2	Fertilizer applicator parts, pump impellers, pump casings, plug valves
	2b	Caustic pump casings, valves, pump impellers
	3	Turbocharger housings, pumps and liners, stove tops, steam piston valve rings, caustic pumps and valves
	4	Range tops
	5	Glass rolls and molds, machine tools, gages, optical parts requiring minimal expansion and good damping qualities, solder rails and pots
	6	Valves

(a) Nickel-alloyed (13.5 to 36% Ni) austenitic gray irons

tion; and the trace elements that affect the microstructure and/or properties of the material.

The major elements in gray iron are carbon, silicon, and iron. Carbon and silicon levels found in commercial irons vary widely as shown in the following table:

Type of iron	Total carbon, %	Silicon, %
Class 20	3.40–3.60	2.30–2.50
Class 30	3.10–3.30	2.10–2.30
Class 40	2.95–3.15	1.70–2.00
Class 50	2.70–3.00	1.70–2.00
Class 60	2.50–2.85	1.90–2.10

Primarily because of the development of ductile iron and some specialized grades of alloyed irons, most gray irons are produced with 3.0 to 3.5% total carbon (TC). Normal silicon levels vary from 1.8 to 2.4%.

Gray irons are normally viewed as iron-carbon-silicon ternary alloys. A section from the equilibrium phase diagram at 2.5% Si is shown in Fig. 2. As shown, the material exhibits eutectic solidification and is subject to a solid-state eutectoid transformation. These two factors dominate the metallurgy of gray iron.

Both carbon and silicon influence the nature of iron castings, so it is necessary to develop an approximation of their impact on solidification. This has been accomplished through development of the concept of carbon equivalence (CE). Using this approach, carbon equivalence is calculated as follows:

$$CE = \%C + \frac{\%Si}{3} \quad \text{(Eq 1)}$$

or more precisely, taking phosphorus into consideration:

$$CE = \%C + \frac{\%Si + \%P}{3} \quad \text{(Eq 2)}$$

Using Eq 1 and 2, it is possible to relate the effect of carbon, silicon, and phosphorus to the binary iron-carbon system. Irons with a carbon equivalent of 4.3 are considered to be of eutectic composition. Most gray irons are hypoeutectic (i.e., CE < 4.3). Nearly all of the mechanical and

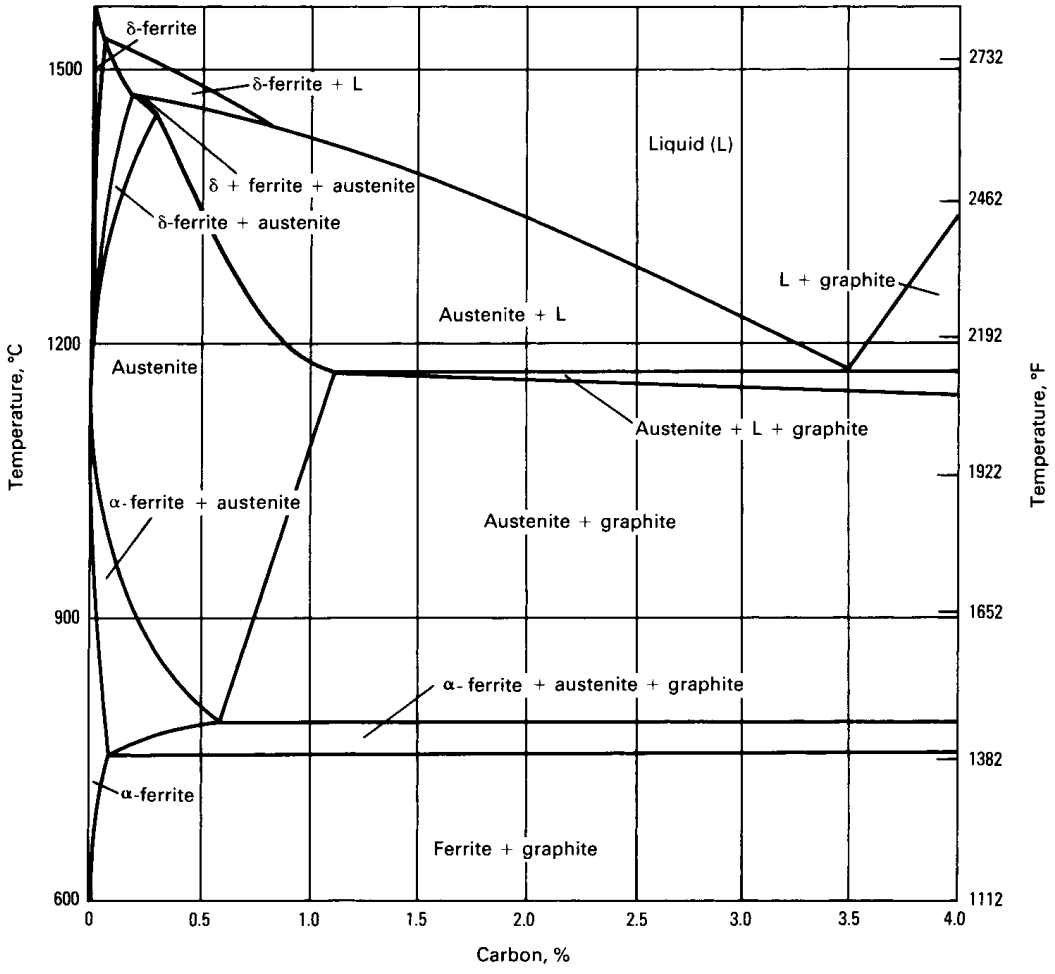


Fig. 2 Iron-carbon phase diagram at 2.5% Si

physical properties of gray iron are closely related to CE value. Figure 3 shows the influence of CE on the tensile strength of gray iron.

The minor elements in gray iron are phosphorus and the two related elements manganese and sulfur. These elements, like carbon and silicon, are of significant importance in gray iron metallurgy. Control is required for product consistency. Absolute levels vary somewhat with application and foundry process variables.

Phosphorus is found in all gray irons. It is rarely added intentionally, but it tends to come from pig iron or scrap. To some extent, it increases the fluidity of iron. Phosphorus forms a low-melting phosphide phase in gray iron that is commonly referred to as steadite. At high levels, it can promote shrinkage porosity, while very low levels can increase metal penetration into the mold (Ref 2, 3). As a result, most castings are produced with 0.02 to 0.10% P. In critical castings involving pressure tightness, it may be necessary to develop optimum levels for the application.

Sulfur levels in gray iron are very important and to some extent have been an area of technical controversy. Numerous investigators have shown that sulfur plays a significant role in the nucleation of graphite in gray iron. The impact of sulfur on cell counts and chill depth in gray iron can be seen in Fig. 4 for uninoculated and inoculated gray irons. This work indicates that sulfur levels in gray iron should be in the approximate range of 0.05 to 0.12% for optimum benefit.

The manganese content varies as a function of the desired matrix. Typically, it can be as low as 0.1% for ferritic irons and as high as 1.2% for pearlitic irons, because manganese is a strong pearlite promoter. Without manganese in the iron, undesirable iron sulfide (FeS) will form at grain boundaries. If the sulfur content is balanced by manganese, manganese sulfide (MnS) will form, but this is harmless because it is distributed within the grains. The optimum ratio between manganese and sulfur for an FeS-free structure is as follows:

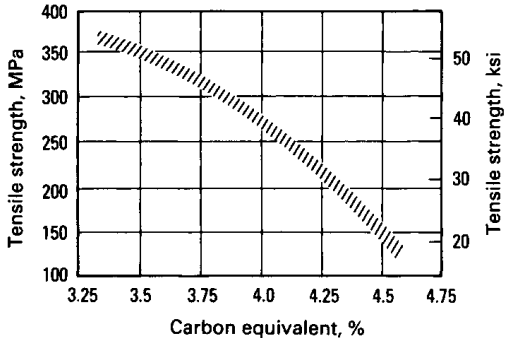


Fig. 3 General influence of carbon equivalence (CE) on the tensile strength of gray iron. Although increasing the carbon content improves graphitization potential and therefore decreases chilling tendency, the strength is adversely affected.

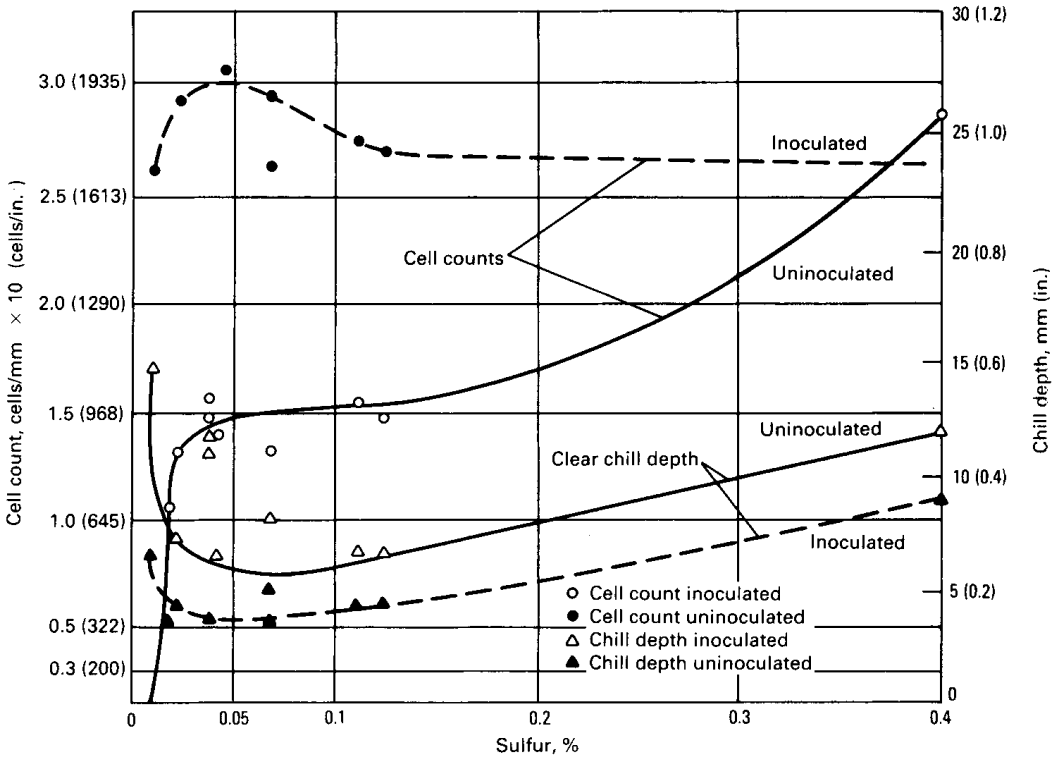


Fig. 4 Effect of sulfur content on eutectic cell count and clear chill depth for inoculated and uninoculated gray irons. Source: Ref 4

$$\%\,Mn = 1.7(\%\,S) + 0.3\% \qquad \text{(Eq 3)}$$

Recent work has indicated that the 0.3% level may be reduced slightly; some foundries add only 0.2% excess manganese.

Trace Elements. In addition to these primary elements, a number of minor elements affect the nature and properties of gray iron. Table 2, extracted in part from a tabulation by the British Cast Iron Research Association (BCIRA), shows the effects of some trace elements on gray iron as well as their possible sources. Depending on property requirements, many of these elements can be intentionally added to gray iron. For example, tin and copper are often added to promote pearlite.

Alloying Practices

Alloying practices vary considerably, depending mainly on the method of melting, the composition and product form of the alloy being added, the amount of iron being alloyed (the entire charge or only portions of the charge), and the ladling practice in the specific foundry.

Table 2 Effects, levels, and sources of some trace elements in gray iron

Element	Trace level, %	Effects	Sources
Aluminum	≤0.03	Promotes hydrogen pinhole defects, especially when green sand molds are used and at levels above 0.005%. Neutralizes nitrogen	Deliberate addition, ferrous alloys, inoculants, scrap contaminated with aluminum components
Antimony	≤0.02	Promotes pearlite. Addition of 0.01% reduces the amount of ferrite sometimes found adjacent to cored surfaces	Vitreous enameled scrap, steel scrap, white metal bearing shells, deliberate addition
Arsenic	≤0.05	Promotes pearlite. Addition of 0.05% reduces the amount of ferrite sometimes found adjacent to cored surfaces	Pig iron, steel scrap
Bismuth	≤0.02	Promotes carbides and undesirable graphite forms that reduce tensile properties	Deliberate addition, bismuth-containing molds and core coatings
Boron	≤0.01	Promotes carbides, particularly in light-section parts. Effects become significant above about 0.001%	Deliberate addition, vitreous enameled scrap
Chromium	≤0.2	Promotes chill in thin sections	Alloy steel, chromium plate, some refined pig iron
Copper	≤0.3	Trace amounts have no significant effect and can be ignored	Copper wire, nonferrous alloys, steel scrap, some refined pig iron
Hydrogen	≤0.0004	Produces subsurface pinholes and (less often) fissures or gross blowing through a section. Mild chill promoter. Promotes inverse chill when insufficient manganese is present. Promotes coarse graphite	Damp refractories, mold materials, and additions
Lead	≤0.005	Results in Widmanstätten and "spiky" graphite, especially in heavy sections with high hydrogen. Can reduce tensile strength 50% at low levels (≥0.0004%). Promotes pearlite	Some vitreous enamels, paints, free-cutting steels, nonferrous alloys, terne plate, white metal, solder, some pig irons
Molybdenum	≤0.05	Promotes pearlite	Some refined pig iron, steel scrap
Nickel	≤0.01	Trace amounts have no major effect and can be ignored	Refined pig iron, steel scrap
Nitrogen	≤0.02	Compacts graphite and increases strength. Promotes pearlite. Increases chill. Can cause pinhole and fissure defects. Can be neutralized by aluminum or titanium	Coke, carburizers, mold and core binders, some ferroalloys, steel scrap
Tellurium	≤0.003	Not usually found, but a potent carbide former	Free-cutting brasses, mold and core coatings, deliberate addition
Tin	≤0.15	Strong pearlite promoter; sometimes deliberately added to promote pearlitic structures	Solder, steel scrap, nonferrous alloys, refined pig iron, deliberate addition
Titanium	≤0.15	Promotes undercooled graphite. Promotes hydrogen pinholing when aluminum is present. Combines with nitrogen to neutralize its effects	Some pig irons, steel scrap, some vitreous enamels and paints, deliberate addition
Tungsten	≤0.05	Promotes pearlite	Tool steel
Vanadium	≤0.08	Forms carbides; promotes pearlite	Steel scrap; some pig irons

Source: Ref 5

In cupola melting, nickel, copper, chromium, and molybdenum are added to the molten metal during or after tapping, rather than being added to the cupola charge. If the ladle that receives the molten metal at the spout will pour the castings without a transfer, the alloying metal may be added to the stream at the spout. This practice generally provides reasonably thorough mixing, although the exact amount of iron tapped into the receiving ladle is sometimes difficult to control. A more common practice is to add the alloying metals to the stream from the receiving ladle (or forehearth, if used) as it is transferred to the pouring ladle, because it may not be desirable to alloy all of the metal in the receiving ladle or forehearth. The amount of mixing obtained by adding to the stream is usually sufficient, although to obtain more thorough mixing the alloyed metal is sometimes poured from the transfer ladle to another transfer ladle.

The practices described above may also be employed if the melting is done in an arc or induction furnace. However, if the entire charge of an arc or induction furnace is to be alloyed, the alloying metals may be added to the furnace, usually just a few minutes prior to tapping. Because of the stirring action in these furnaces (particularly in an induction furnace), losses of the alloying metals from oxidation may be excessive if too much time elapses between making the additions and tapping.

An advantage of adding the alloying metals to the charge in the furnace is stability of temperature. When alloying metals are added cold to the ladle after tapping, there can be a significant decrease in temperature. The amount of temperature drop increases with the amount of cold metal added. Ladle additions of cold metal that total more than 3% are not recommended.

Alloying metal should never be placed in an empty ladle; the bottom of the ladle should be covered with at least 1 in. of molten metal before any alloying metal is added. Preferably, alloy is added as a small amount at one time.

Methods of adding the cold alloying metals to a molten charge vary widely. The simplest method is to put the alloy in paper bags and toss them into the stream, or into the ladle as it fills. Mechanical devices are also used to add alloying metals.

When the alloying metals are added at the spout, and are in shot or granulated form, a funnel-like device is sometimes mounted above the spout so that the funnel outlet is directed at the stream. The funnel portion is large enough to hold the maximum amount of shot or granulated alloy that would be required for one ladle. This dispensing device is provided with a shuttle-like control so that the flow of alloy can be started, stopped, and regulated as needed.

Alloys in granulated or shot form are sometimes added from a simple sheet metal dipper-like container with a long handle that permits the operator to reach over the ladle of molten iron and pour the alloy into the stream. Although the amount of alloy is measured, the rate at which it is discharged into the stream is controlled by the operator. Another simple means of adding shot or granulated material is to pour it into a long pipe or tube that is closed at one end (an ordinary piece of downspout may be used). The tube must be long enough for the operator to hold the open end over the stream and let the alloy pour out.

Nickel is easily added, and losses are so insignificant that no allowance for loss is made. If nickel is to be added to the stream at the spout, or to a ladle, it is added as shot, an alloy that usually contains about 92% Ni. The addition is calculated on the nickel content. For instance, if it is desired to develop an alloy iron containing 1% Ni, approximately 5 kg (10.8 lb) of 92% Ni shot will be added to each 455 kg (1000 lb) of iron. When nickel is added to the molten charge of an arc or induction furnace, it is feasible to use larger pieces, because there will be more time for the nickel to become dissolved and distributed.

Copper is also simple to add, and losses are so low that no allowance for loss is made. Scrap copper wire, clippings, and various other forms of copper scrap are most commonly used. The melting temperature of copper is considerably lower than that of iron, and the specific gravity of copper is reasonably near that of iron, so copper is easily dissolved and distributed in molten iron.

Chromium is added as granulated ferrochromium, which usually contains 65 to 70% Cr. Chromium additions are subject to some loss, which must be allowed for when adding the ferroalloy. Most foundry operations allow for a loss of 5%, but experience in a particular foundry may prove the need for slightly increasing or decreasing that allowance. Ferrochromium dissolves more slowly than nickel or copper, and hence it must be given more time or more agitation, or both.

Molybdenum is also added as a granulated ferroalloy, generally one that contains 60 to 70% Mo. As for chromium, a 5% allowance for loss is made in most foundry operations.

Effects of Alloying on Properties

The properties of gray irons are influenced by a number of factors including the following (Ref 1):

- Graphite morphology
- Matrix structure. (Pearlitic structures offer greater strength and wear resistance while ferritic structures possess greater ductility.)
- The base iron composition (particularly CE)
- Section size
- Heat treatment
- Thermal properties of the mold
- Casting geometry
- Alloying additions

In most cases, minor alloying of gray iron is done to increase strength and promote formation of pearlite. The minor elements normally used in gray iron alloying are chromium, copper, nickel, molybdenum, vanadium, and tin. Table 3 summarizes the effects of various alloying elements on the properties of gray iron. Figure 5 shows the effects of minor alloying additions on hardness and strength.

Chromium. Small chromium additions (up to about 0.5 to 0.75%) cause significant increases in the strength of gray iron. Chromium also promotes a pearlitic matrix and an associated increase in hardness. Chromium is a carbide promoter, and in light-section castings or at heavy

Table 3 Effects of alloying elements on the mechanical and physical properties of gray iron

Alloying element	Effect of alloying element on: Chill propensity	Pearlite stability	Machinability	Wear resistance	Hardness level	Hardenability	Strength
Silicon	Decreases	Decreases	Increases	Decreases	Decreases	Decreases	Decreases
Manganese	…	Increases	…	…	Increases	Increases	Increases
Chromium	Increases	Increases	Decreases	Increases	Increases	Increases	Increases
Molybdenum	…	…	…	Increases	Increases	Increases	Increases
Nickel	Decreases	Increases	Increases	Increases	Increases	Increases	Increases
Copper	…	Increases	Increases	Increases	Increases	…	Increases
Vanadium	Increases	…	…	…	Increases	Increases	Increases

addition rates, it can cause chill formation. Chromium is normally added as a ferrochromium alloy. Care should be taken to ensure that the alloy is completely dissolved.

Copper also increases the tensile strength of gray iron by promoting a pearlitic matrix. Its effect is most pronounced at lower addition levels, 0.25 to 0.5%. At higher addition rates, its effects are not as dramatic. Copper has a mild graphitizing effect and therefore does not promote carbides in light sections. Copper should be added as high-purity material to avoid the introduction of tramp elements such as lead.

Nickel additions of up to 2% cause only a minor increase in the tensile strength of gray iron. Nickel does not promote the formation of carbides and in fact has a minor graphitizing effect. Nickel is normally added as elemental material, and no problems with dissolution have been reported.

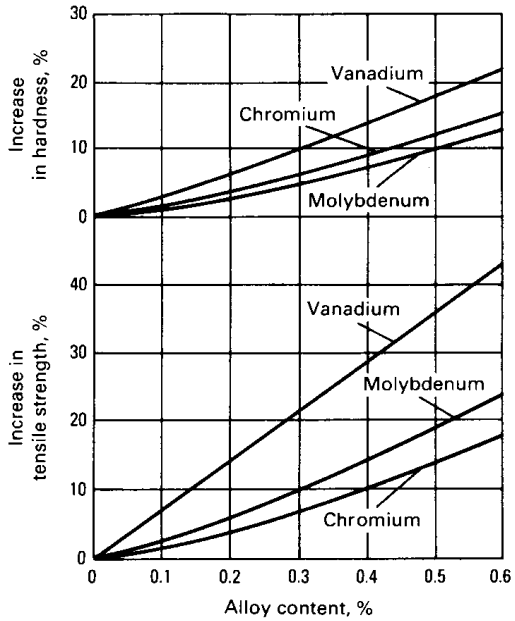


Fig. 5 Effects of alloying elements on the properties of gray cast iron. Source: Ref 6

Molybdenum. Small molybdenum additions, 0.25 to 0.75%, have a significant impact on the strength of gray iron, apparently because of matrix strengthening and graphite flake refinement. Molybdenum does not promote carbides. It is normally added as a ferromolybdenum alloy.

Tin in the range of 0.025 to 0.1% is a strong pearlite stabilizer. It does not appear to increase the strength of a fully pearlitic gray iron, but it can give a small strength increase in irons that would otherwise contain free ferrite. Additions above the levels required for pearlite stabilization should be avoided to prevent embrittlement. Tin is normally added as commercially pure tin. Care should be taken to avoid material contaminated with such elements as antimony, bismuth, or lead.

Vanadium has been suggested as a minor alloying element for gray iron. As shown in Fig. 5, vanadium has a significant effect on the hardness and strength of gray iron. The strength increases are reportedly sustained after annealing, a significant advantage. Vanadium at higher levels and in light sections can promote the formation of carbides, so good inoculation practices are suggested. Alloying can be accomplished by using ferrovanadium.

Base Irons. The selection of alloying elements to modify as-cast properties in gray iron depends to a large extent on the composition and method of manufacture of the base iron. For example, a foundry producing a base iron containing 2.3% Si and 3.4% TC for automotive castings might add 0.5 to 1.0% Cr to make heavier castings with the same hardness and strength as the normal castings. However, a foundry producing a base iron with 1.7% Si and 3.1% C for a heavy casting would add 0.5 to 0.8% Si to decrease hardness and chill when pouring this iron in light castings.

Depending on the strength desired in the final iron, the CE of the base iron may vary from approximately 4.4% for weak irons to 3.0% for high-strength irons. The method of producing the base iron will affect mechanical properties and the alloy additions to be made, because the properties are affected by factors such as type and percentage of raw materials in the metal charge, amount of superheat, and cooling rate of the iron after pouring. The base iron used for alloying varies considerably from foundry to foundry, as do the alloying elements selected to give the desired mechanical properties. However, parts produced from different base irons and alloy additions can have the same properties and performance in service.

Effects of Inoculation on Properties

In inoculation, a material is added to molten gray iron to affect the shape, size, or distribution of graphite in the casting, thereby improving mechanical properties (Fig. 6). The amount of effective element remaining in the iron is usually very small.

Inoculation should not be confused with alloying (the addition of a metal or alloy to another metal or alloy). However, when an alloy addition is made to molten gray iron there is often an incidental inoculating effect, due to the form of the addition or small quantities of other elements included in the alloy addition.

The effect of an inoculant depends on the type and amount used, the temperature and condition of the molten iron at the time of addition, and the amount of time that elapses between inoculation and the pouring of the casting. The effect will wear off or fade if the metal is not poured into the molds immediately after it is inoculated. The time required for fading is 10 to 20 min, depending on the composition of the inoculant, the iron temperature, and the amount of inoculant added.

Commercial inoculants contain various amounts of carbon, silicon, chromium, manganese, calcium, titanium-zirconium, aluminum, barium, rare earths, and strontium. Typical compositions of inoculants are listed in Table 4. Methods of introducing inoculants are discussed in Ref 8.

Graphite and high-silicon inoculants are used to decrease chill depth. Small amounts of aluminum or alkali-earth elements are the effective components of nongraphitic inoculants. High-chromium inoculants are intended to increase tensile strength by introducing chromium as an alloying element, while simultaneously adding true inoculant to control the chill-deepening effect of chromium. The amount of inoculant added to the

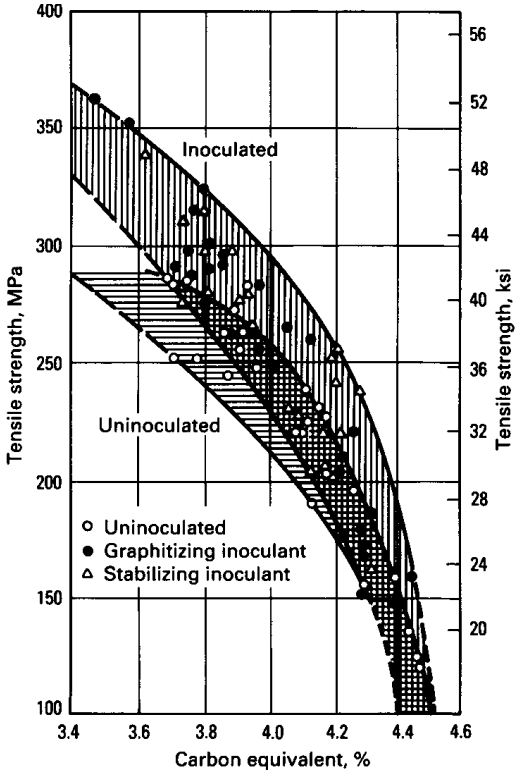


Fig. 6 Influence of inoculation on tensile strength of gray irons as a function of carbon equivalent for 30 mm (1.2 in.) diam bars. Source: Ref 7

Table 4 Compositions of ferrosilicon inoculants for gray cast iron

Performance category of inoculant	Composition, %(a)									
	Si	Al	Ca	Ba	Ce	TRE(b)	Ti	Mn	Sr	Others
Standard	46–50	0.5–1.25	0.60–0.90	…	…	…	…	…	…	…
	74–79	1.25 max	0.50–1.0	…	…	…	…	…	…	…
	74–79	0.75–1.5	1.0–1.5	…	…	…	…	…	…	…
Intermediate	46–50	1.25 max	0.75–1.25	0.75–1.25	…	…	…	1.25 max	…	…
	60–65	0.8–1.5	1.5–3.0	4–6	…	…	…	7–12	…	…
	70–74	0.8–1.5	0.8–1.5	0.7–1.3 0.75–1.25	…	…	…	…	…	…
	42–44	…	0.75–1.25	…	…	…	9–11	…	…	…
	50–55	…	5–7	…	…	…	9–11	…	…	…
	50–55	…	0.5–1.5	…	…	…	9–11	…	…	…
High	36–40	…	…	…	9–11	10.5–15	…	…	…	…
	46–50	0.50 max	0.10 max	…	…	…	…	…	0.60–1.0	…
	73–78	0.50 max	0.10 max	…	…	…	…	…	0.60–1.0	…
Stabilizing	6–11	0.50 max	0.50 max	…	…	…	…	…	…	48–52 Cr

(a) All compositions contain balance of iron. (b) TRE, total rare earth elements

metal varies from 0.10 to 0.80% by weight, depending on the anticipated time between inoculation and pouring, the composition of the base iron, and the amount of chill required. The amount of chill required is influenced by the thickness of sections cast and by the combination of tensile strength and machinability required.

Effects of Alloying on Elevated-Temperature Properties

Significant amounts of data have been generated on the elevated-temperature performance of various cast irons, including gray irons. Properties of importance include the following:

- Dimensional stability (growth)
- Resistance to scaling
- Short-time tensile properties at elevated temperatures
- Retention of hardness at elevated temperatures (hot hardness)
- Creep and stress-rupture resistance

Alloying plays a key role in improving the elevated-temperature properties of cast irons. Usually, the greatest benefits are achieved when various alloying elements are used in combination. For example, as a single alloy addition in gray irons, chromium produces the greatest increase in resistance to micro-structural decomposition, growth, and oxidation, but it has a minor effect on elevated-temperature strength and creep resistance. On the other hand, molybdenum produces the greatest increase in strength and in creep-rupture properties at elevated temperatures, but it has little or no beneficial effect on growth, structural stability, or thermal conductivity. When molybdenum and chromium are combined, the effects appear to be synergistic: structural stability is greatly increased and, as a result, both growth and creep-rupture properties are greatly increased.

Growth and Scaling

When gray cast irons are exposed for long times to elevated temperatures below the critical temperature, or when they are subject to prolonged periods of cyclic heating or cooling, they have a tendency to grow in size and exhibit oxidation at the surface. Growth may occur from one or a combination of the following causes (Ref 9, 10):

- Decomposition of carbides
- The structural breakdown of the pearlite to ferrite, a reaction which is accompanied by the formation of the bulkier graphite (graphitization)
- Internal cracking due to cyclic heating differential expansions and contractions. Formation of these fine cracks accelerates oxidation.
- Carbon deposition on graphite flakes in atmospheres containing carbon monoxide in the temperature range of 350 to 550 °C (660 to 1025 °F)

Deterioration of mechanical properties occurs concurrently with growth as a result of structural decomposition. Knowledge of the growth characteristics of cast iron is very important to the proper interpretation of creep data. Dimensional changes caused by growth must be subtracted from the elongations in creep specimens to determine the true contribution of mechanical stress to creep.

Growth occurs in gray iron more rapidly than in ductile iron, compacted graphite, or malleable irons because of the graphite structure. Growth is most rapid in irons with higher carbon content, as shown in Fig. 7. Growth can be reduced either by producing a ferritic matrix with no pearlite to decompose at elevated temperatures or by stabilizing the carbides so as to prevent their breakdown into ferrite and graphite. Growth decreases with an increase in the coarseness of the graphite flakes, probably because of a lower combined carbon content and the decrease in the rate of pearlite decomposition that results from a greater mean-free path between graphite flakes (Ref 10).

The most effective growth reduction in gray iron has been achieved with strong carbide stabilizing elements such as chromium and molybdenum. Bevan (Ref 12) demonstrated the beneficial effects of adding Cr and Cr + Mo on the dimensional stability of gray iron at 455 °C (850 °F). Growth tests were conducted for 3000 h on specimens stress relieved at 565 °C (1050 °F) in order to evaluate gray irons for potential use as housings for passenger car turbines. The results, presented in Fig. 8, show that an addition of 0.23% Mo to a chromium-bearing iron reduced growth by a factor of 4 and limited growth to an insignificant level (<0.01%).

The most extensive growth and scaling tests carried out on gray irons have been performed by BCIRA (Ref 11, 13–16). These tests, which are summarized in Table 5, were conducted at 350 to 500 °C (660 to 930 °F). The results show that no growth occured in flake graphite irons exposed at 350 °C (660 °F) for up to six years. Slight growth (<0.1%) occurred in

unalloyed gray irons exposed at 400 °C (750 °F) for 11.5 years. Additions of Cr + Mo and Cr + Ni + Mo limited growth at 400 °C (750 °F) to insignificant levels (<0.02%).

Table 5 also presents the growth test results for cast irons after 64 weeks (>10,000 h) of exposure in air at 500 and 450 °C (930 and 840 °F). Moderate alloy additions, particularly Cr + Mo and Cr + Ni + Mo, were effective in reducing growth up to 500 °C (930 °F). Similar results were demonstrated by Kattus and McPherson (Ref 17) in growth tests at 540 °C (1000 °F) for 2000 h of exposure (Fig. 9).

Scaling. Prolonged exposure of gray iron in air at elevated temperatures produces a surface scale, primarily by oxidation. The scale formed on gray iron when heating in air consists of a mixture of three iron oxides: an outer layer of Fe_2O_3, an intermediate layer of Fe_3O, and an inner layer of FeO. This scale is usually continuous and adherent up to 800 °C (1470 °F) (Ref 18). The scale may be an adherent and protective type or a cracking type that permits continued oxidation, an important consideration in matching the material and application. Generally, the relative amount of scaling is measured by the change in weight of the specimen. Absorption of oxygen during scale formation usually increases the specimen weight,

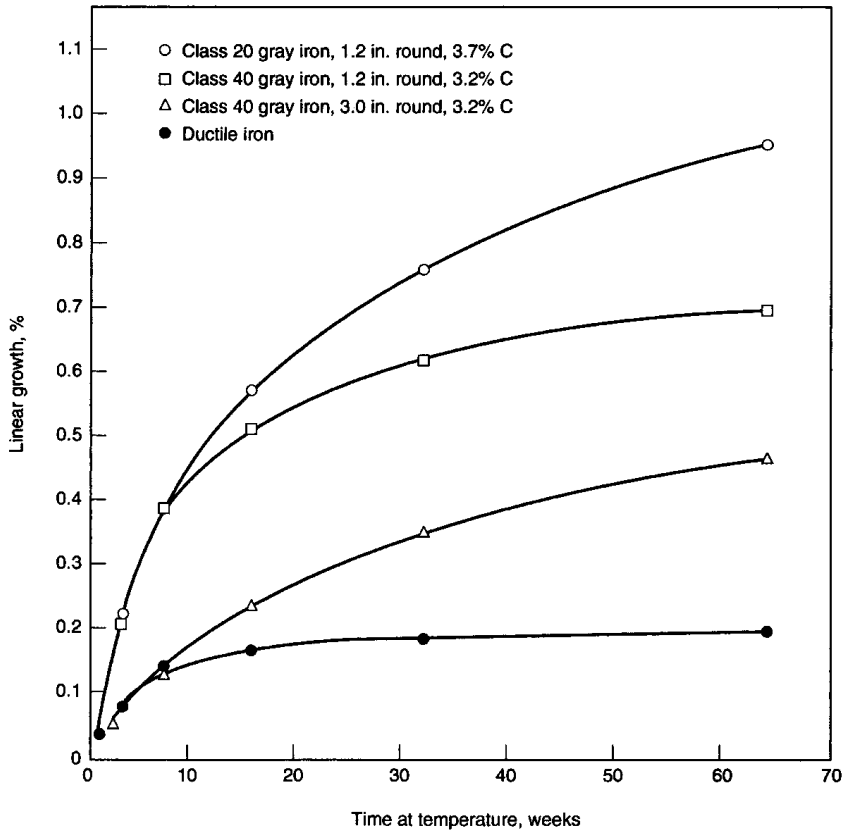


Fig. 7 Results of growth tests at 500 °C (930 °F) in air for gray and ductile irons. In gray irons, growth is greater with higher carbon contents. Source: Ref 11

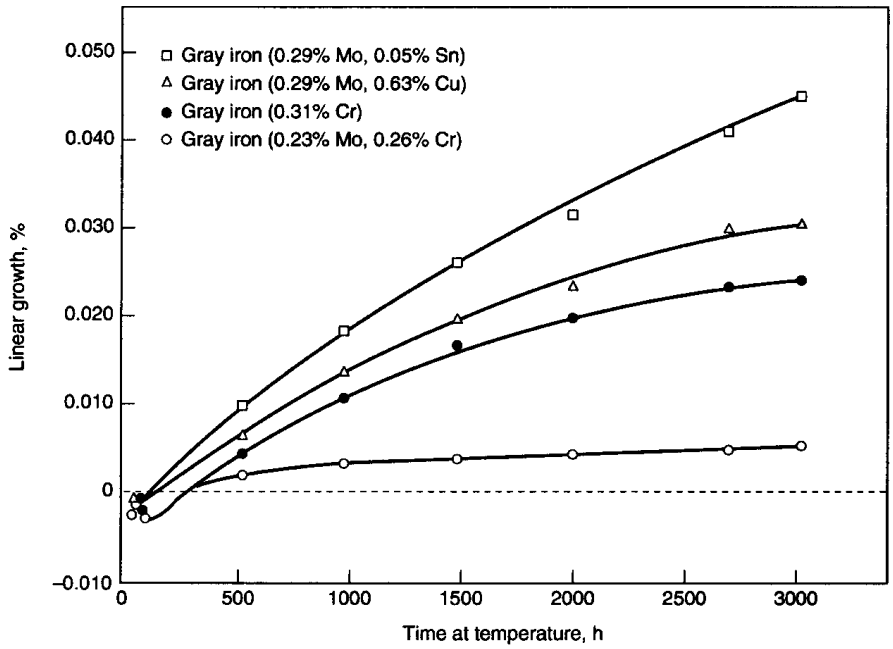


Fig. 8 Growth of four gray irons produced from the same base iron (3.3% C, 2.2% Si) and tested at 455 °C (850 °F) in air. Source: Ref 12

Table 5 Summary of growth and scaling tests carried out by BCIRA

Iron No.	Description	64 weeks(a)					6 years			$11^1/_2$ years				Alloy variations
		Growth, % increase in length		Scaling, $g/cm^2 \times 10^{-3}$			Growth, % increase in length	Scaling, $g/cm^2 \times 10^{-3}$		Growth, % increase in length		Scaling, $g/cm^2 \times 10^{-3}$		
		450 °C	500 °C	400 °C	450 °C	500 °C	400 °C	350 °C	400 °C	350 °C	400 °C	350 °C	400 °C	
1	Base iron(b)	0.31	0.72	1.86	3.24	9.93	0.035	1.70	3.24	0.005	0.075	2.03	3.90	…
2	Silicon series	0.25	0.75	1.92	4.06	11.95	0.058	1.70	3.56	0.002	0.085	2.08	4.40	2.0Si
3		0.20	0.76	1.86	3.51	8.39	0.042	1.75	3.62	0.007	0.071	2.14	4.40	1.2Si
4		0.16	0.63	2.14	3.84	7.57	0.020	1.75	3.40	0.003	0.038	2.14	4.23	1.3Si–1.2Ni
5	Carbon series	0.33	0.98	2.69	4.55	15.85	0.047	3.45	5.21	0.013	0.070	3.90	6.10	3.7C
7		0.20	0.50	2.63	4.11	10.10	0.025	2.41	4.50	0.002	0.035	2.69	5.44	3.15C
9	Mn, S, P series	0.12	0.62	1.54	2.80	10.36	0.028	1.75	2.96	0.008	0.048	1.98	3.63	1.5Mn
10		0.41	0.78	1.98	3.56	9.49	0.040	1.64	3.51	0.002	0.065	2.20	4.34	0.25S
11		0.22	0.67	1.86	3.84	8.94	0.033	1.48	3.56	0.003	0.071	1.87	4.34	0.64P
12	Cr and Cr + Ni series	0.12	0.43	2.03	4.06	8.44	0.025	1.75	3.51	0.003	0.040	2.20	4.23	0.3C
13		0.05	0.30	1.97	4.22	7.68	0.020	1.75	3.62	0	0.028	2.08	4.40	0.6Cr
14		0.11	0.49	1.64	3.73	7.24	0.035	1.75	2.85	0.003	0.053	2.08	3.52	0.3Cr + 0.6Ni
15		0.05	0.27	1.92	3.40	6.86	0.015	1.64	3.35	0	0.033	1.92	4.11	0.6Cr + 1.2Ni
16	Ni, Cr, and Mo series	0.02	0.32	2.03	3.84	8.50	0.012	1.75	3.40	0.002	0.012	2.08	4.28	0.3Cr + 0.6Mo
17		0.05	0.56	1.65	3.28	8.44	0.015	1.70	3.40	0.010	0.018	2.03	3.96	0.6Mo + 0.6Ni
18		0.02	0.27	1.81	3.56	8.12	0.012	1.70	3.35	0.008	0.008	2.14	4.07	0.4Cr + 0.6Mo + 0.6Ni
19	As and Sn series	0.21	0.73	2.14	3.29	8.78	0.030	1.64	3.29	0.018	0.058	2.03	4.07	0.07As
20		0.22	0.67	1.98	3.13	5.87	0.020	1.59	3.29	0.002	0.025	1.92	4.01	0.06Sn
21	Nodular iron	0.09	0.22	1.26	2.41	5.27	0.020	0.77	2.03	0.005	0.028	1.04	2.14	3.4C + 1.7Si + 0.4Mn

(a) Growth occurring in 64 weeks was insignificant at temperatures of 400 °C (750 °F) and below. (b) Base iron composition: 3.25% C, 1.58% Si, 0.65% Mn, 0.11% S, 0.25% P (produced from refined iron having low residual alloy levels). Source: Ref 11, 13–16

whereas removal of the scale decreases the weight because the oxidized iron is removed. A scale that is adherent is associated with a gradually diminishing rate of increase in weight, while a loose or cracked scale permits a continually rapid gain in weight (Ref 9).

The amount of scaling or gain in weight that is observed for a particular gray iron increases with the service temperature and exposure time. The relative changes depend on the atmosphere and the iron composition (Ref 9). Figure 10 illustrates the effect of temperature on four different gray irons. The surface oxidation of gray iron is considered greatest at temperatures above 760 °C (1400 °F), with the specific effect being related to the carbon, silicon, and alloy contents of the iron. Steam is typically a more aggressive atmosphere than air, as are atmospheres pro-

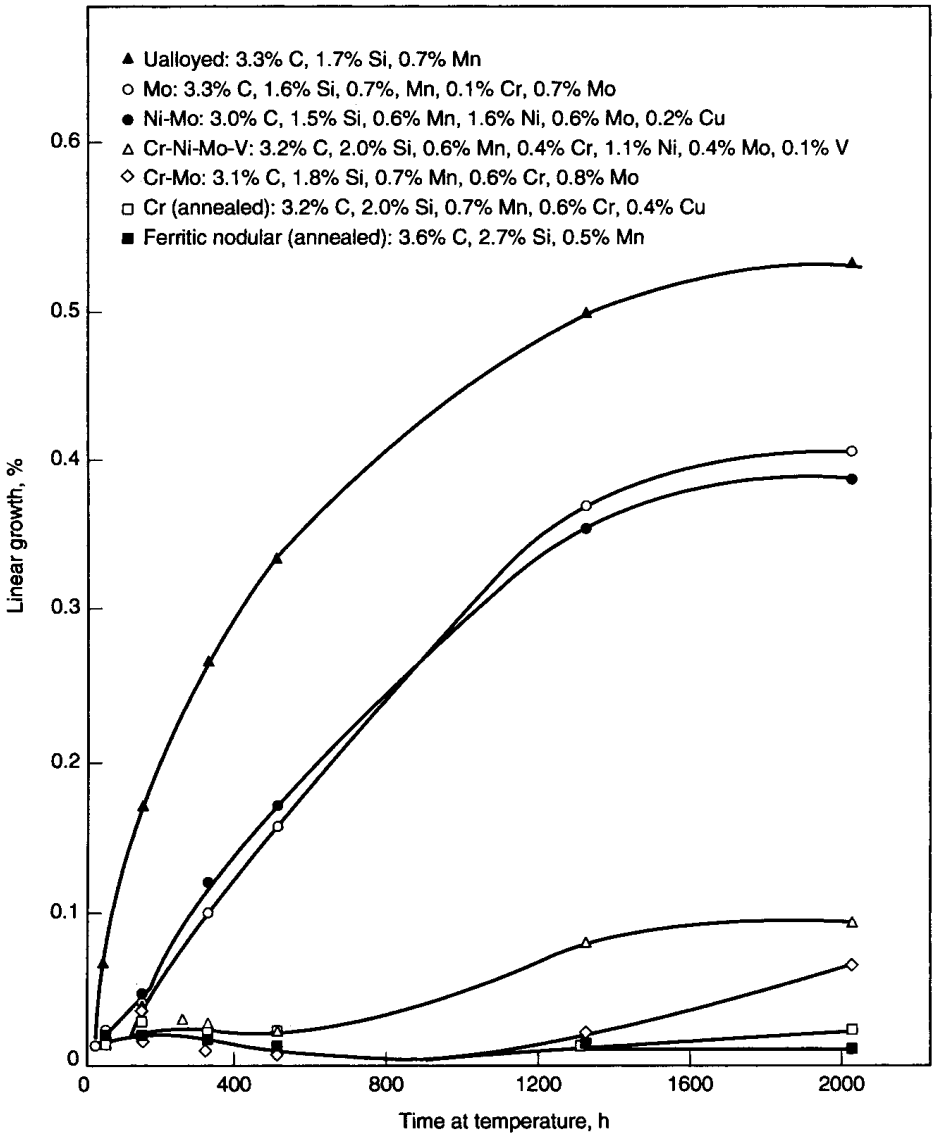
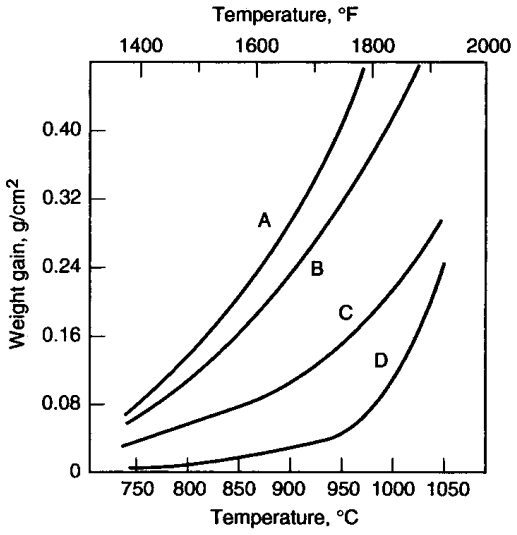


Fig. 9 Growth of six gray irons and one ductile iron tested at 540 °C (1000 °F) in air. Source: Ref 17



Iron	Type	Chemical analysis, %						
		TC	Si	Mn	P	Ni	Cr	Cu
A	Low-Si gray iron	2.98	1.14	1.07	0.18	...	...	...
B	Ni-Cr gray iron	3.45	1.64	1.03	0.15	1.18	0.92	...
C	Ni-Resist	2.74	1.93	0.89	0.04	14.62	2.11	7.16
D	Nicrosilal	1.78	4.63	0.91	0.10	22.46	2.52	...

TC, total carbon

Fig. 10 Effect of temperature and alloying on the scaling behavior of gray irons after 200 h at temperature in air. Source: Ref 19

duced by hydrogen-containing fuels such as oil or natural gas (Ref 19). Scaling can be minimized through the use of hydrogen or carbon monoxide atmospheres. Sulfur-bearing atmospheres are deleterious, but they may be resisted using higher-chromium-content irons.

The quantity and shape of the graphite has an appreciable influence on gray iron scaling, particularly up to 500 °C (900 °F) (Ref 9). In general, the degree of scaling increases markedly as the amount of graphite increases. Matrix structure apparently has little influence on the scaling of gray iron. Test results indicate that heat treatment to obtain ferritic conditions has a relatively minor effect on scaling propensity (Ref 9).

The percentage of carbon in a gray iron will affect its ability to resist scaling. Even at temperatures as low as 250 °C (500 °F), higher-carbon irons will exhibit considerably more scaling than irons having low carbon contents (Ref 11).

The most extensive study on scaling in unalloyed and low alloyed gray irons was performed at BCIRA by Gilbert (Ref 11) and Palmer (Ref 15), who monitored weight gain in specimens exposed to air for up to 11.5 years at 350 and 400 °C (660 and 750 °F) and for up to 64 weeks at 450 and 500 °C (840 and 930 °F). Their results, which are presented in Table 5, can be summarized as follows (Ref 10):

Temperature	Extent of scaling
350 °C (566 °F)	4 mg/cm^2 in 11.5 years
400 °C (750 °F)	4 mg/cm^2 in 11.5 years
450 °C (840 °F)	3–4.5 mg/cm^2 in 64 weeks
500 °C (930 °F)	6–16 mg/cm^2 in 64 weeks

There was little distinction in resistance to scaling among the 18 low-alloyed irons tested at or below 450 °C (840 °F), with the exception of a high-carbon-equivalent (3.7% C) iron that exhibited somewhat greater weight gains. At 500 °C (930 °F), the range in scaling resistance was greater, again largely due to a significantly higher graphitic carbon content in one iron. Differences in alloy content had only minor effects on scaling resistance, although all alloyed irons exhibited slightly lower weight gains (6 to 9 mg/cm^2) than the unalloyed base iron (10 mg/cm^2).

Short-Time Tensile Properties at Elevated Temperatures

The tensile properties of unalloyed gray irons exhibit small changes up to 400 °C (750 °F), as demonstrated in Fig. 11. In general, there is a slight decrease in strength as the temperature increases to about 100 °C (210 °F), then a gradual increase as the temperature increases to about 350 °C (660 °F). Above 400 °C (750 °F) the tensile strength decreases quite rapidly. The proof stress tends to follow the same trend.

Gilbert (Ref 11) conducted an extensive investigation of the tensile properties of several plain and alloyed cast irons at temperatures up to 600 °C (1110 °F). Figure 12 illustrates a series of stress-strain curves obtained at the various temperatures for two gray irons. Gilbert showed that at temperatures up to 400 °C (750 °F), the amount of curvature in the stress-strain curve increased slightly with temperature, but above 400 °C (750 °F) the ability of gray iron to resist plastic deformation decreased rapidly. The molybdenum-alloyed irons appeared to be more resistant to plastic deformation at temperatures above 400 °C (750 °F).

Turnbull and Wallace (Ref 20) determined the elevated-temperature strength of two series of gray irons alloyed with molybdenum and Cr + Mo at 425, 540, and 650 °C (800, 1000, and 1200 °F). Their tests indicated that increasing the molybdenum content, 1.4 to 1.9% Mo, increased the strength of both plain and 0.6% Cr alloyed irons to maximum values (Fig. 13).

The effects of the various alloy additions on the retention of strength at 540 °C (1000 °F) are readily seen in the ratio of tensile strength at 540 °C to that at room temperature. The strength ratios varied from 56 to 75%, and among the irons studied in Ref 10 and 21, the Cr-Mo alloyed irons exhibited the highest 540 °C (1000 °F) strengths and strength ratios. The presence of either molybdenum or chromium appeared to contribute to

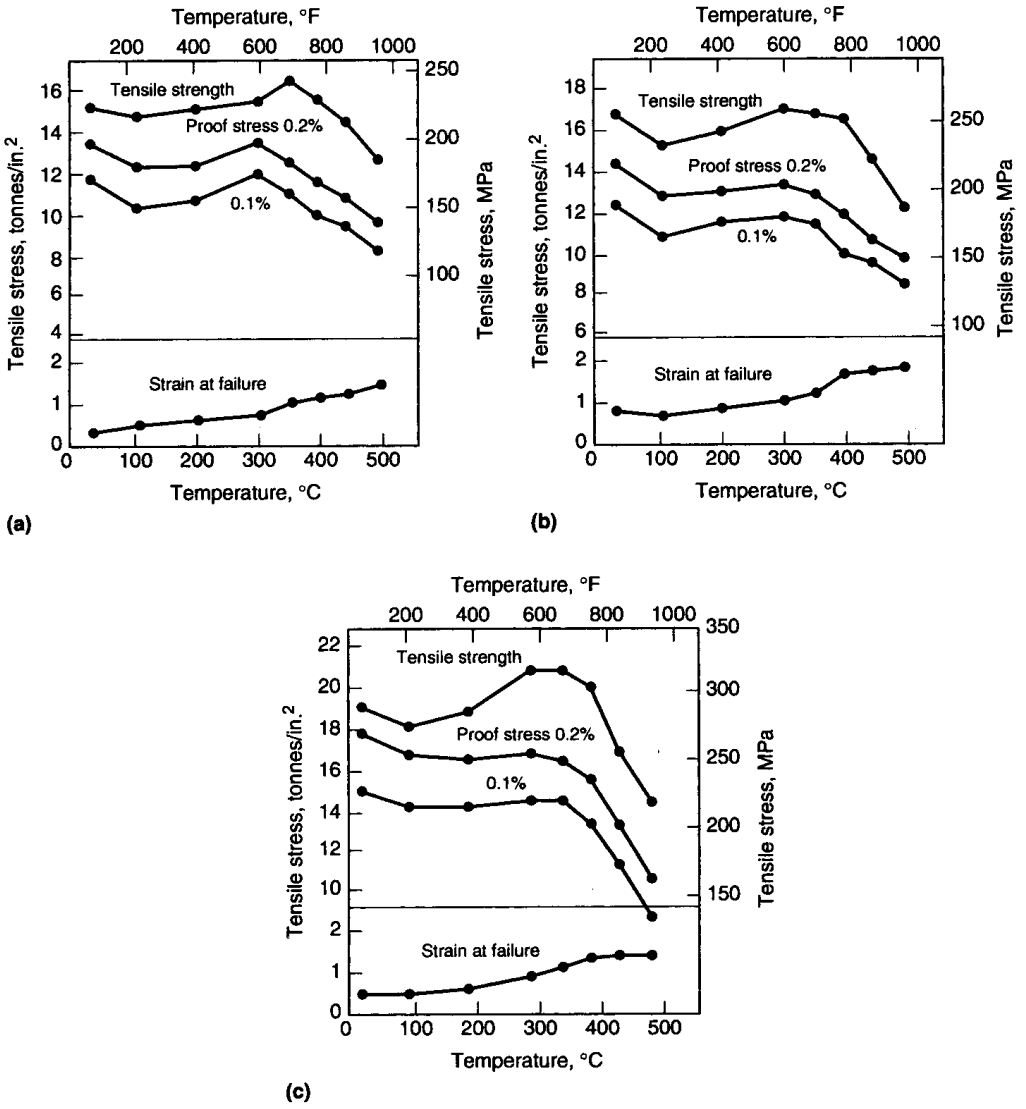


Fig. 11 Variation in tensile properties resulting from increasing temperature for three British gray iron grades. (a) Grade 14 (216 MPa, or 31 ksi, minimum tensile strength). (b) Grade 17 (263 MPa, or 38 ksi, minimum tensile strength). (c) Grade 20 (309 MPa, or 45 ksi, minimum tensile strength). Source: Ref 10

retention of strength at elevated temperatures, while additions of nickel and copper did not.

Gundlach (Ref 21) has demonstrated that the elastic modulus decreases linearly with increasing temperature (Fig. 14). As shown in Fig. 14, most alloying additions reduce the rate at which modulus changes with temperature.

Hot Hardness

Depending on alloy content, gray irons experience a loss of hardness retention at temperatures of ≥450 °C (≥840 °F). Loss of hardness corresponds to microstructural decomposition of the casting. For example,

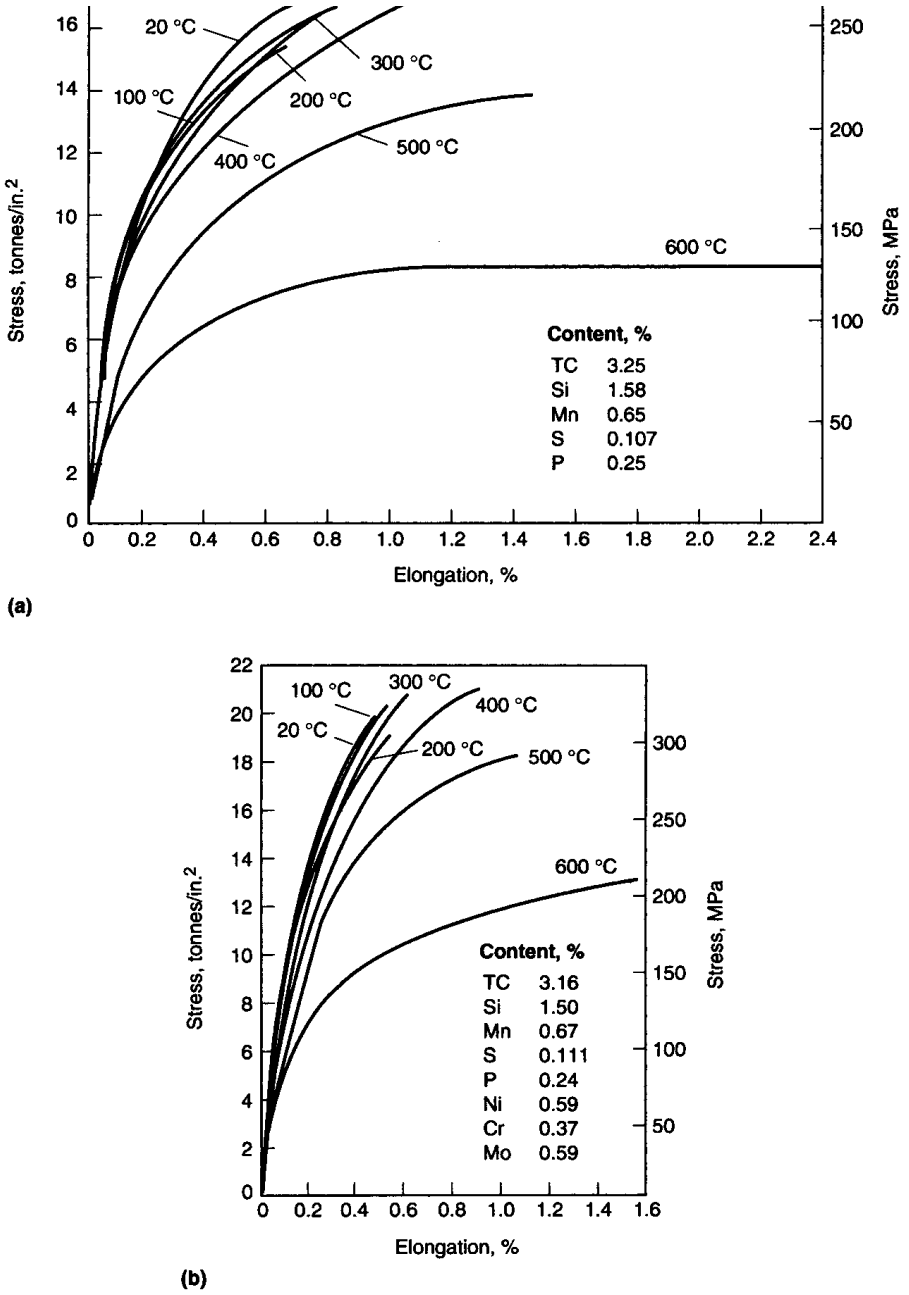
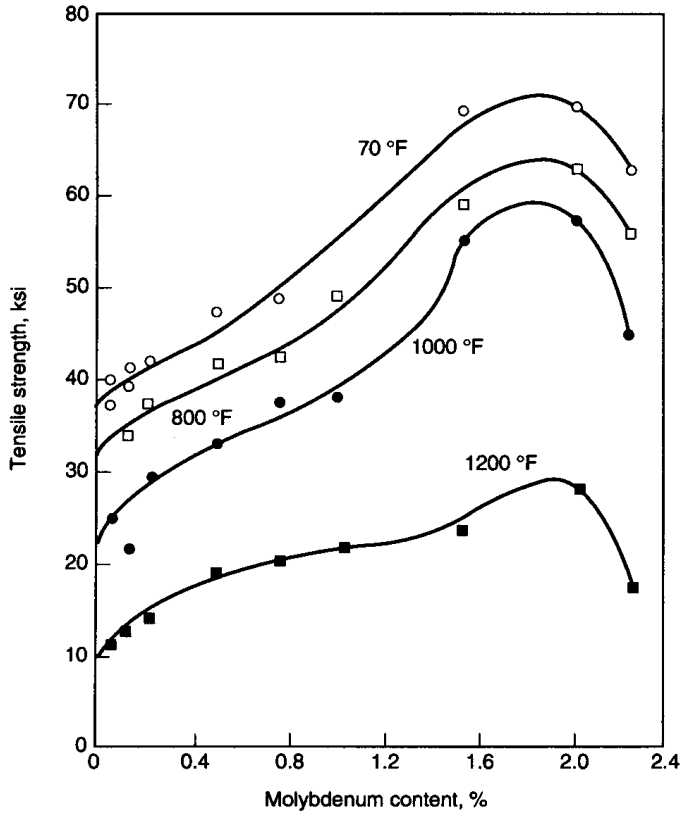


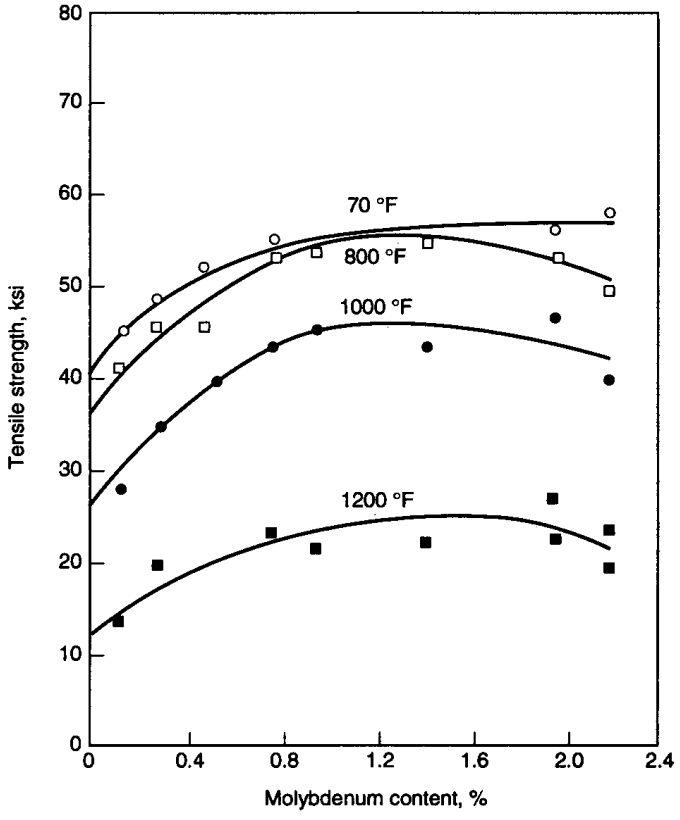
Fig. 12 Effect of temperature on the stress-strain curves of (a) unalloyed gray iron and (b) low-alloy gray iron. TC, total carbon. Source: Ref 11

pearlitic irons exposed for 64 weeks at 500 °C (930 °F) exhibited structures consisting of decomposed (spheroidized) pearlite and ferrite. The carbide in the pearlite was fine and widely dispersed, indicating that decomposition was almost complete (Ref 10). Concurrent with this microstructural decomposition is a rapid loss in hardness.

Several investigators have studied hardness of gray irons after exposure to elevated temperatures. Bevan (Ref 12) indicates no significant change in the hardness of growth test specimens of Cr, Cr-Mo, or Mo-Sn alloyed irons following 3000 h exposure at 455 °C (850 °F). Gilbert (Ref 11)



(a)



(b)

Fig. 13 Tensile strength at room and elevated temperatures as a function of molybdenum content in (a) unalloyed and (b) 0.6% Cr alloyed gray irons. Source: Ref 20

reports a significant change in hardness of unalloyed and 0.06% Sn alloyed irons at 450 °C (840 °F) after 64 weeks (> 10,000 h), but little change in hardness in Mn, Mo-Ni, Cr, Cr-Mo, and Cr-Ni-Mo alloyed irons (Fig. 15). After exposure for 64 weeks at 500 °C (930 °F), all alloys exhibited significant reduction in hardness, but chromium-containing irons exhibited the greatest resistance to softening.

Gundlach (Ref 21) studied the influence of various alloy additions to pearlitic irons on microstructural stability at 500 and 550 °C (930 and 1020 °F) for times up to 3000 h. Figure 16 illustrates the reduction in hardness with time and demonstrates the benefits of various alloying combinations. At 500 °C (930 °F), an iron alloyed with 0.5% Cr + 0.4% Mo was remarkably stable, while at 550 °C (1020 °F), none of the irons exhibited good microstructural stability.

Thwaites and Pryterch (Ref 22) studied the influence of adding tin in larger than normal amounts (>0.1%) on the structural stability of chromium-alloyed irons between 500 and 700 °C (930 and 1290 °F).

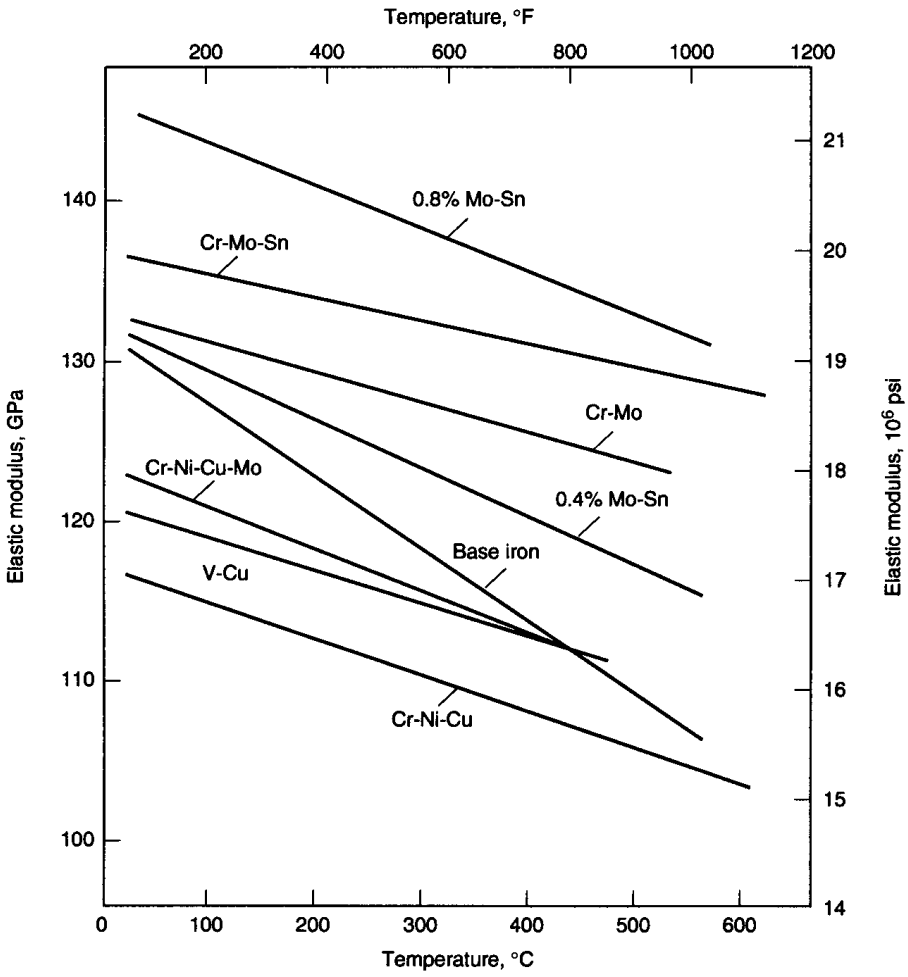
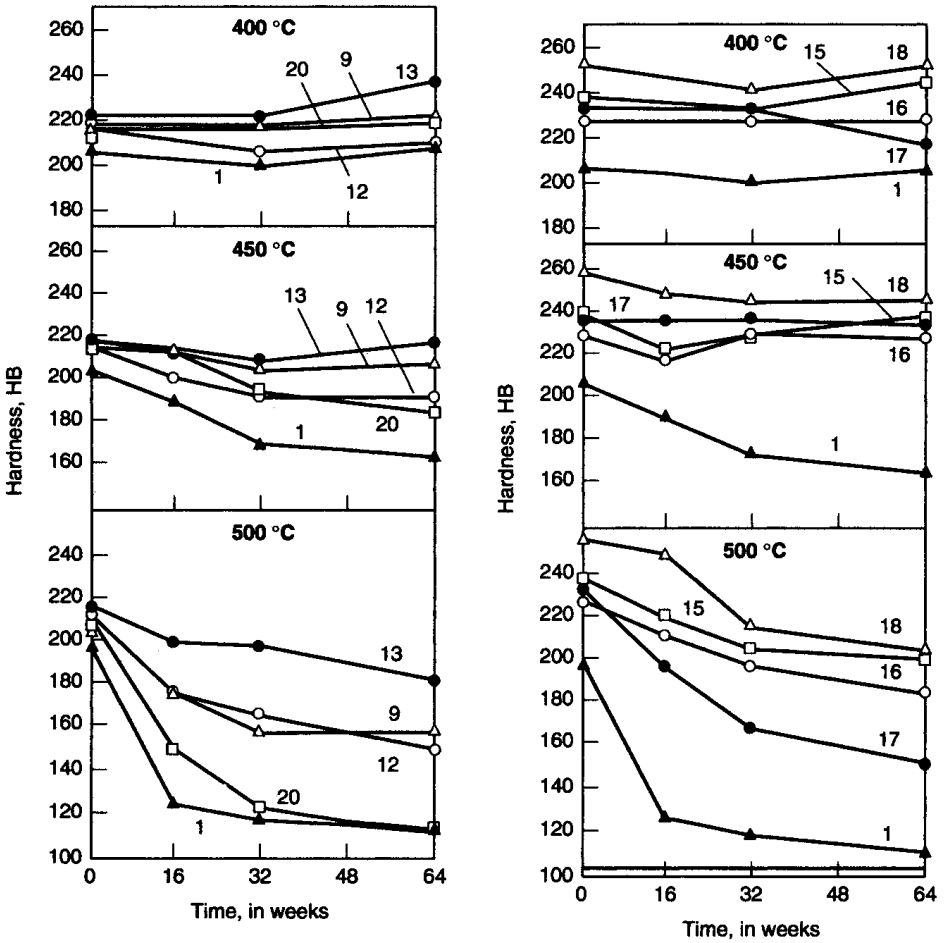


Fig. 14 Elastic modulus as a function of temperature and alloying content. Source: Ref 10

Figure 17 compares the influence of individual additions (0.3%) of tin, chromium, and molybdenum on hardness after heating at 650 °C (1200 °F) and demonstrates the potency of a 0.3% Sn addition on resistance to softening. The hardness data in Fig. 18 show that Sn + Cr is more potent than tin alone in stabilizing the structure. Thwaites and Pryterch also showed that, even at 700 °C (1290 °F), a 0.1% Sn addition significantly reduced the rate of decomposition of pearlite.

Creep and Stress-Rupture Behavior

A number of investigators have studied the influence of alloying on the creep and stress-rupture properties of gray irons. Turnbull and Wallace



Irons studied	
1	Unalloyed base iron
9	1.49% Mn
12	0.27% Cr
13	0.56% Cr
20	0.06% Sn

Irons studied	
1	Unalloyed base iron
15	0.63% Cr, 1.15% Ni
16	0.29% Cr, 0.56% Mo
17	0.55% Mo, 0.62% Ni
18	0.37% Cr, 0.59% Mo, 0.59% Ni

Fig. 15 Effect of temperature and alloying content on the hardness retention of gray irons. The base iron contained 3.06–3.25% C, 1.5–1.75% Si, and 0.5–0.8% Mn. Source: Ref 11

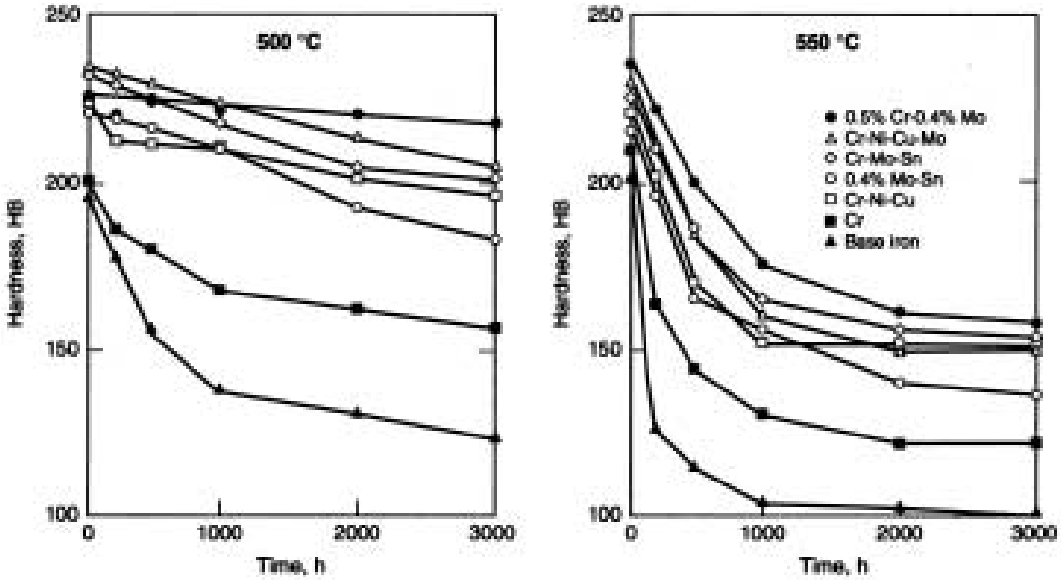


Fig. 16 Effect of temperature and alloying content on the hardness retention of gray irons. Source: Ref 21

(Ref 20) demonstrated the beneficial effects of chromium and molybdenum additions on the stress-rupture properties of gray irons at 425, 540, and 650 °C (800, 1000, and 1200 °F) (Fig. 19). Adding up to 2% Mo to an unalloyed iron continuously raised the stress-to-rupture in 100 h at all three temperatures. In a 0.6% Cr alloyed base iron, the stress-to-rupture in 100 h increased with molybdenum additions up to 0.8% Mo at the same temperatures.

Gundlach (Ref 23) demonstrated the benefits of various alloy additions on the stress-to-rupture and creep properties at 540 °C (1000 °F) in one unalloyed and four alloyed ASTM class 40 gray irons. As shown in Fig. 20, alloy additions increased 1000 h rupture strength more than 140% and dramatically reduced creep rates at a given stress level. An iron alloyed

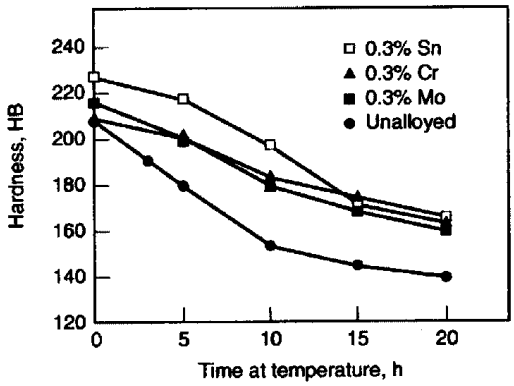


Fig. 17 Effect of tin, chromium, and molybdenum on the hardness of 50 mm (2 in.) diam gray iron bars heated to 650 °C (1200 °F). Source: Ref 22

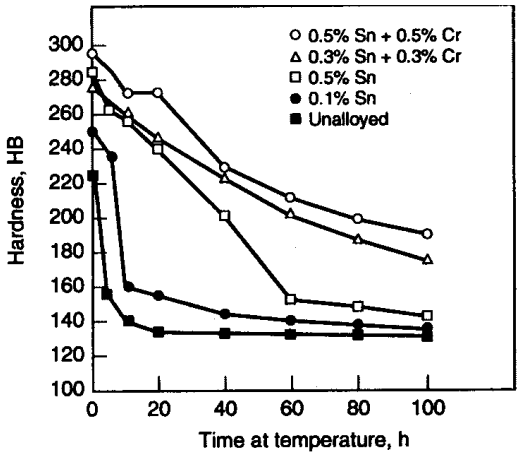


Fig. 18 The combined effects of tin and chromium on the hardness of 22 mm (0.875 in.) diam gray iron bars heated to 650 °C (1200 °F). Source: Ref 22

with 0.5% Cr + 0.4% Mo produced the highest rupture strength and resistance to creep, followed by an iron alloyed with 0.4% Mo + 0.08% Sn.

Effects of Alloying on Corrosion Behavior

Environments in which cast irons are used for their excellent corrosion resistance include water, soils, acids, alkalies, saline solutions, organic compounds, sulfur compounds, and liquid metals (Ref 24). In some services, alloyed cast irons offer the only economical alternative for constructing equipment. The alloying elements generally used to enhance the corrosion resistance of gray and ductile irons include silicon, nickel, chromium, copper, and molybdenum. Other alloying additions are sometimes used, but not to the extent of the aforementioned five primary elements.

Silicon is the most important alloying element used to improve the corrosion resistance of cast irons. Silicon is generally not considered an alloying element in cast irons until levels exceed 3%. Silicon levels between 3 and 14% result in some increase in the corrosion resistance of the alloy, but above about 14% Si, the corrosion resistance of the cast iron increases dramatically. Silicon levels up to 17% have been used to enhance the corrosion resistance of the alloy further, but silicon levels over 16% make the alloy extremely brittle and difficult to manufacture. Even at 14% Si, the strength and ductility of the material are low, and special design and manufacturing parameters are required to produce and use these alloys.

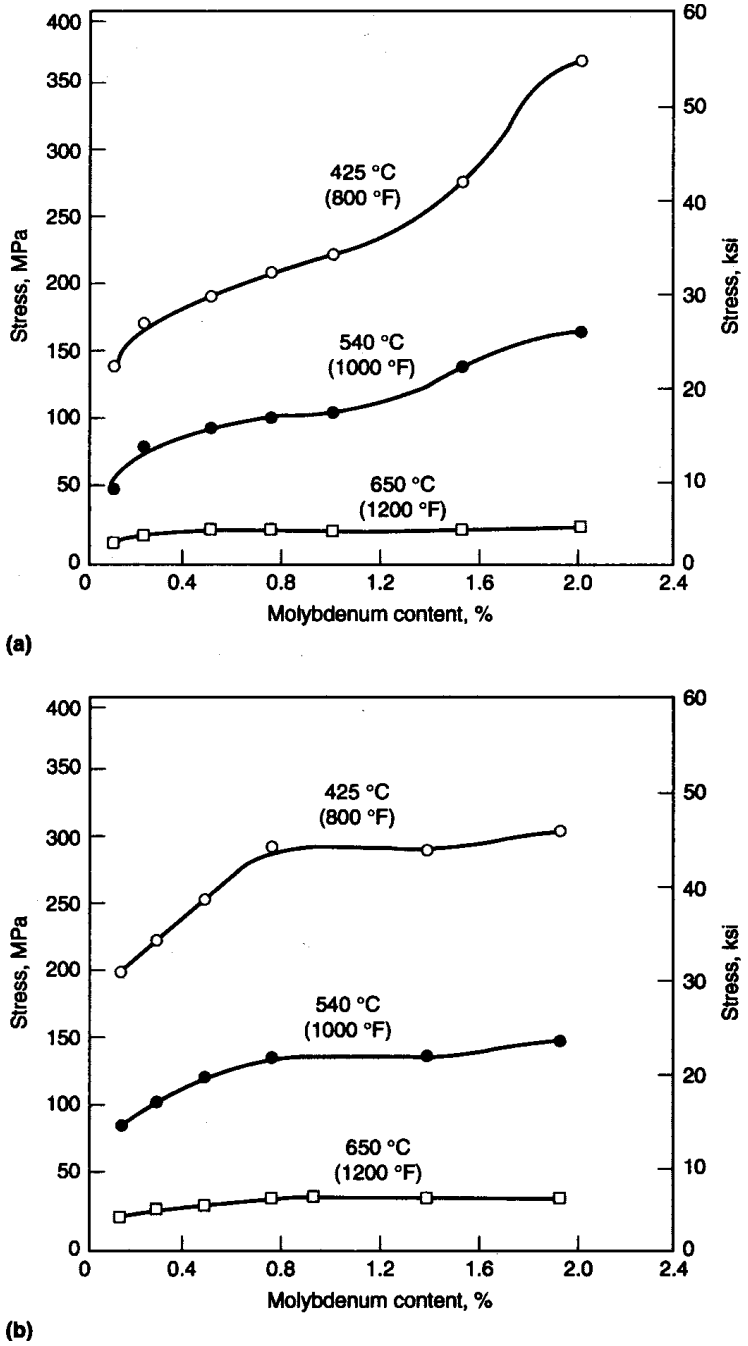


Fig. 19 Effect of molybdenum on the stress to produce rupture in 100 h in gray irons at various temperatures. (a) Unalloyed base iron. (b) 0.6% Cr alloyed base iron. Source: Ref 20

Alloying with silicon promotes strongly adherent surface films in cast irons. Considerable time may be required to establish these films fully on the castings. Consequently, in some services, corrosion rates may be relatively high for the first few hours or even days of exposure, then may decline to extremely low steady-state rates for the rest of the time the parts are exposed to the corrosive environment.

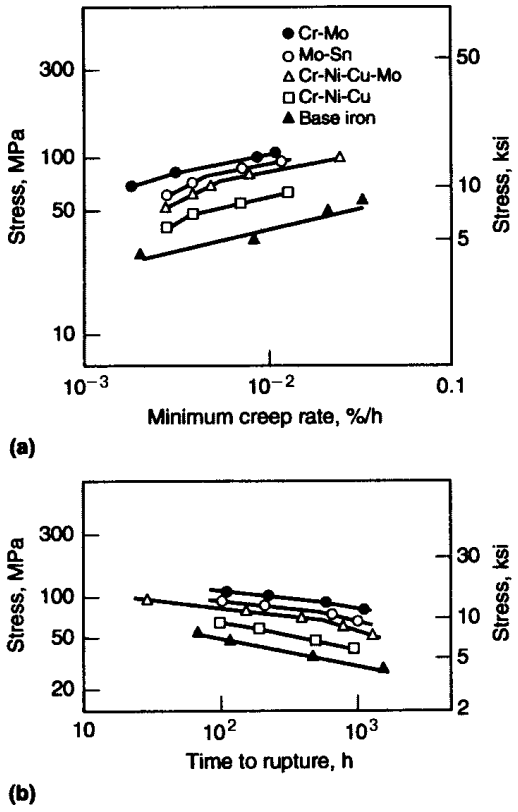


Fig. 20 Effect of alloying elements on the elevated-temperature behavior of ASTM class 40 gray irons tested at 540 °C (1000 °F) for 1000 h. (a) Stress vs. minimum creep rate. (b) Stress-rupture characteristics. Source: Ref 23

Nickel is used to enhance the corrosion resistance of cast irons in a number of applications. Nickel increases corrosion resistance by the formation of protective oxide films on the surfaces of the castings. Up to 4% Ni is added in combination with chromium to improve both strength and corrosion resistance in cast iron alloys. The enhanced hardness and corrosion resistance obtained is particularly important for improving the erosion-corrosion resistance of the material. Nickel additions enhance the corrosion resistance of cast irons to reducing acids and alkalies. Nickel additions of 12% or greater are necessary to optimize the corrosion resistance of cast irons.

Chromium is frequently added alone and in combination with nickel and/or silicon to increase the corrosion resistance of cast irons. As with nickel, small additions of chromium are used to refine graphite and matrix microstructures. These refinements enhance the corrosion resistance of cast irons in seawater and weak acids.

Chromium increases the corrosion resistance of cast iron by the formation of protective oxides on the surfaces of castings. The oxides formed will resist oxidizing acids, but will be of little benefit under reducing conditions. High chromium additions, like higher silicon additions, reduce the ductility of cast irons.

Copper is added to cast irons in special cases. Copper additions of 0.25 to 1% increase the resistance of cast iron to dilute acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl), as well as acid mine water. Small additions of copper are also made to cast irons to enhance atmospheric-corrosion resistance. Additions of up to 10% are made to some high nickel-chromium cast irons to increase corrosion resistance. The exact mechanism by which copper improves the corrosion resistance of cast irons is not known.

Molybdenum. Although an important use of molybdenum in cast irons is to increase strength, it is also used to enhance corrosion resistance, particularly in high-silicon cast irons. Molybdenum is particularly useful in HCl. As little as 1% Mo is helpful in some high-silicon irons, but for optimum resistance, 3 to 4% Mo is added.

Other Alloying Additions. In general, other alloying additions to cast irons have a minimal effect on corrosion resistance. Vanadium and titanium enhance the graphite morphology and matrix structure and impart slightly increased corrosion resistance to cast irons. Few other additions are made to cast irons that have any significant effect on corrosion resistance.

Effects of Alloying on Annealing

The heat treatment most frequently applied to gray iron, with the possible exception of stress relieving, is annealing. The annealing of gray iron consists of heating the iron to a temperature high enough to soften it and/or minimize or eliminate massive eutectic carbides, thereby improving its machinability. Gray iron is commonly subjected to one of the following three annealing treatments:

- Low-temperature (ferritizing) annealing for unalloyed or low-alloy gray irons of normal composition
- Medium-temperature (full) annealing is used when a ferritizing anneal would not be effective because of the high alloy content of a particular gray iron.
- High-temperature (graphitizing) annealing for elimination of massive carbides

Recommended practices for annealing gray irons are given in Table 6.

Effect of Alloy Content on Time at Temperature. Certain elements, such as carbon and silicon, accelerate the decomposition of pearlite and massive carbide at annealing temperatures. Therefore, when these elements are present in sufficient percentages, the time at annealing temperature may be reduced. In an investigation of the decomposition of

pearlite at various temperatures in irons containing 1.93 and 2.68% Si, it was determined that the pearlite always broke down more rapidly in the higher-silicon iron and that this iron could be effectively annealed over a greater temperature range. For example, at an annealing temperature of 750 °C (1380 °F), the complete breakdown of pearlite occurred in the higher-silicon iron in 10 min, whereas 45 min was required for the lower-silicon iron. This shows the pronounced effect of silicon as an aid to the diffusion of carbon to the flakes present in the iron.

On the other hand, the pearlite-promoting elements (antimony, tin, vanadium, chromium, manganese, phosphorus, nickel, and copper) delay pearlite decomposition. Following are the percentage increases in the time required to decompose pearlite, as affected by 0.10% additions of five of these elements:

Element	Increase in time, %
Manganese	60
Nickel	30
Copper	30
Chromium	230
Phosphorus	30

Table 6 Recommended practices for annealing gray iron castings

Type of anneal	Purpose	Temperature(a)	Time	Cooling rate(b)
Low-temperature (ferritizing) annealing	For conversion of pearlite to ferrite in unalloyed irons for maximum machinability.	700 to 760 °C (1300 to 1400 °F)	45 min per inch of cross section	Furnace cool (55 °C or 100 °F per hour) to 315 °C (600 °F). Cool in still air from 315 °C (600 °F) to room temperature.
Medium-temperature (full) annealing	For conversion of pearlite to ferrite in irons unresponsive to low-temperature annealing. For elimination of minor amounts of well-dispersed carbides in unalloyed irons.	790 to 900 °C (1450 to 1650 °F)	1 h per inch of cross section	Furnace cool to 315 °C (600 °F). Cool in still air from 315 °C (600 °F) to room temperature.
High-temperature (graphitizing) annealing	For elimination of massive carbides in mottled or chilled irons and conversion of pearlite to ferrite for maximum machinability.	900 to 950 °C (1650 to 1750 °F)	1 to 3 h plus 1 h per inch of cross section(c)	Furnace cool to 315 °C (600 °F). Cool in air from 315 °C (600 °F) to room temperature.

(a) Preferred temperature of castings is dependent on silicon, manganese and alloy contents. (b) Slow cooling from 540 to 315 °C (1000 to 600 °F) is to minimize residual stresses. (c) Time for graphitization will vary from 30 min to 1 h in unalloyed irons to several hours in irons containing carbide stabilizers. Source: Ref 25

Effects of Alloying on Normalizing

Normalizing involves heating the castings to a temperature of 875 to 900 °C (1605 to 1650 °F) and holding for about 1 h per 25 mm (1 in.) of thickness. This results in the transformation of the matrix to austenite. The castings are then air-cooled to room temperature to form a pearlitic matrix. Normalizing is used to enhance mechanical properties (e.g., hardness and strength) or to restore as-cast properties that have been modified by another heating process (e.g., graphitizing, preheating, or postheating associated with repair welding).

Effects of Composition. As shown in Table 7, both the CE and alloy content influence the response to normalizing. Bars 1, 3, 4, 6, and 7 listed in Table 7 are essentially free of alloying elements, except for residual amounts. Bars 1 and 3, characterized by high as-cast strength and low CE, virtually regained their as-cast strength as a result of normalizing for $1^1/_2$ h at 900 °C (1650 °F), air cooling, and stress relieving at 540 °C (1000 °F). The same treatment lowered the strength of bars 4, 6, and 7, all of which had higher CEs and relatively low manganese contents. Bar 2 showed an increase in strength because of the high stabilizing effect of the molybdenum, nickel, and manganese contents. Bar 5, despite a high carbon equivalent, showed quite an increase in as-cast strength because of its manganese, chromium, molybdenum, and nickel contents.

The effect of alloy content on hardness after normalizing is shown in Fig. 21 for two alloy irons with different CEs and different nickel and chromium contents. Again, it is evident that alloy content has a stabilizing effect in the graphitizing annealing range and increases hardness when the austenitizing temperature ranges from about 790 to 980 °C (1450 to 1800 °F). Thus, it can be concluded that normalizing restores as-cast properties to gray iron, and that if the CE is sufficiently low, normalizing even causes these properties to be exceeded. It can also be concluded that the alloying elements chromium, molybdenum, and nickel enhance the strengthening effect of normalizing.

Table 7 Influence of alloy content and carbon equivalent on typical properties of gray irons before and after normalizing

	Composition, %									Carbon equivalent,	As-cast			Normalized		
											Tensile strength		Hardness,	Tensile strength		Hardness,
Bar	C	Si	P	S	Mn	Cr	Ni	Mo	Cu	%	MPa	ksi	HB	MPa	ks	HB
1	2.71	2.00	0.13	0.031	0.46	0.076	0.061	0.059	…	3.37	405	59	241	380	55	241
2	3.25	2.03	0.02	0.031	0.67	0.085	0.80	0.30	0.22	3.93	380	55	241	425	62	255
3	2.66	1.90	0.03	0.018	0.63	0.063	0.092	0.042	…	3.27	400	58	255	385	56	241
4	3.15	2.20	0.38	0.018	0.44	0.074	0.071	0.071	0.39	3.88	295	43	229	235	34.3	179
5	3.45	2.16	0.09	0.077	0.84	0.39	1.21	0.50	0.10	4.17	250	36	248	405	59	311
6	3.31	2.10	0.39	0.070	0.41	0.069	0.08	0.055	0.44	4.01	275	40	212	200	29	163
7	3.42	2.44	0.42	0.058	0.56	0.063	0.058	0.057	0.108	4.23	215	31	187	180	26	143

Note: Specimens 30 mm (1.2 in.) in diameter were normalized at 900 °C (1650 °F) and then stress relieved at 540 °C (1000 °F).

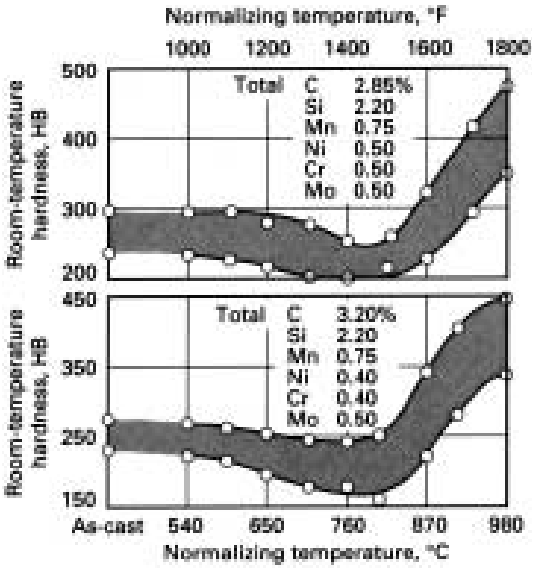


Fig. 21 Room-temperature hardness of two different low-alloy gray irons held at normalizing temperature 1 h for each 25 mm (1 in.) of thickness and air cooled on wire mesh screen. From production and experimental data

Effects of Alloying on Hardenability

As listed in Table 3, the hardenability of gray irons can be increased by the addition of chromium, molybdenum, nickel, and/or vanadium. (Manganese, found in all gray irons, is another recognized element for increasing hardenability.) Some data on the effects of various alloy additions on the hardenability of plain (unalloyed) and low-alloy gray irons are shown in Table 8 and 9. Hardenability is measured using the standard end-quench hardenability test employed for steels.

Effects of Alloying on Flame Hardening

Flame hardening is a method of selective surface hardening most commonly applied to gray irons. After flame hardening, a gray iron casting consists of a hard, wear-resistant outer layer of martensite and a core of a softer alloy.

In general, alloyed gray irons can be flame hardened with greater ease than unalloyed irons, partly because alloyed gray irons have increased hardenability. Final hardness also may be increased by alloying additions. The maximum hardness obtainable by flame hardening an unalloyed gray iron containing approximately 3% total carbon, 1.7% Si, and 0.60 to 0.80% Mn ranges from 400 to 500 HB. This is because the Brinell hardness value for gray iron is an average of the hardness of the matrix and that of the relatively soft graphite flakes. Actually, the matrix hardness on which wear resistance depends is approximately 600 HB. With the

Table 8 Hardenability data for gray irons quenched from 855 °C (1575 °F)

See Table 9 for compositions.

Distance from quenched end		Hardness, HRC					
mm	$^1/_{16}$ in. increments	Plain iron	Mo(A)	Mo(B)	Ni-Mo	Cr-Mo	Cr-Ni-Mo
3.2	2	54	56	53	54	56	55
6.4	4	53	56	52	54	55	55
9.5	6	50	56	52	53	56	54
12.7	8	43	54	51	53	55	54
15.9	10	37	52	50	52	55	53
19.0	12	31	51	49	52	54	53
22.2	14	26	51	46	52	54	52
25.4	16	26	49	45	52	54	53
28.6	18	25	46	45	52	53	52
31.8	20	23	46	44	51	50	51
34.9	22	22	45	43	47	50	50
38.1	24	22	43	44	47	49	50
41.3	26	21	43	44	47	47	49
44.4	28	20	40	41	45	47	48
47.6	30	19	39	40	45	44	50
50.8	32	17	39	40	45	41	47
54.0	34	18	36	41	44	38	46
57.2	36	18	40	40	45	36	45
60.3	38	19	38	37	45	34	46
63.5	40	22	38	36	42	35	46
66.7	42	20	35	35	42	32	45

Source: Ref 25

addition of 2.5% Ni and 0.5% Cr, an average surface hardness of 550 HB can be obtained. The same result has been achieved using 1.0 to 1.5% Ni and 0.25% Mo. Small additions of chromium are particularly valuable in preventing softening and ensuring the retention of a high content of combined carbon during austenitizing for hardening. Automotive camshafts containing 1% Cr, 0.50% Mo, and 0.8% Mn are easily flame hardened to 52 HRC to a required depth. These parts are not tempered or stress relieved.

Effects of Alloying on Stress Relieving

The purpose of stress relieving is to reduce stresses induced in the casting during solidification. In essence, the process consists of heating the

Table 9 Compositions of irons for which hardenability data are given in Table 8

Iron	Composition(a)									
	TC	CC	GC	Mn	Si	Cr	Ni	Mo	P	S
Plain	3.19	0.69	2.50	0.76	1.70	0.03	…	0.013	0.216	0.097
Mo(A)	3.22	0.65	2.57	0.75	1.73	0.03	…	0.47	0.212	0.089
Mo(B)	3.20	0.58	2.62	0.64	1.76	0.005	Trace	0.48	0.187	0.054
Ni-Mo	3.22	0.53	2.69	0.66	2.02	0.02	1.21	0.52	0.114	0.067
Cr-Mo	3.21	0.60	2.61	0.67	2.24	0.50	0.06	0.52	0.114	0.071
Cr-Ni-Mo	3.36	0.61	2.75	0.74	1.96	0.35	0.52	0.47	0.158	0.070

(a) TC, total carbon; CC, combined carbon; GC, graphite carbon.

casting to a temperature ranging from 500 to 650 °C (930 to 1200 °F), depending on the composition. The casting is held in this temperature range for 2 to 8 h, then air cooled.

Quantitative data concerning the effects of alloying elements on the optimum stress relieving temperature are meager. However, it has been reported that in one instance the addition of as little as 0.14% Cr to a 3.20 C-2.01 Si iron permitted exposure of the iron to a temperature of about 650 °C (1200 °F) for 1 h without sacrifice in room-temperature tensile strength. Figure 22 shows the effect of temperature and time on the relief of stresses for seven low-alloy irons, and the tabulation below the graphs indicates that, depending on shakeout time, these irons can be stress relieved for 8 h at 620 °C (1150 °F) with no adverse effect on hardness.

Recommended stress relieving temperatures, based on normal shakeout times in the foundry, are:

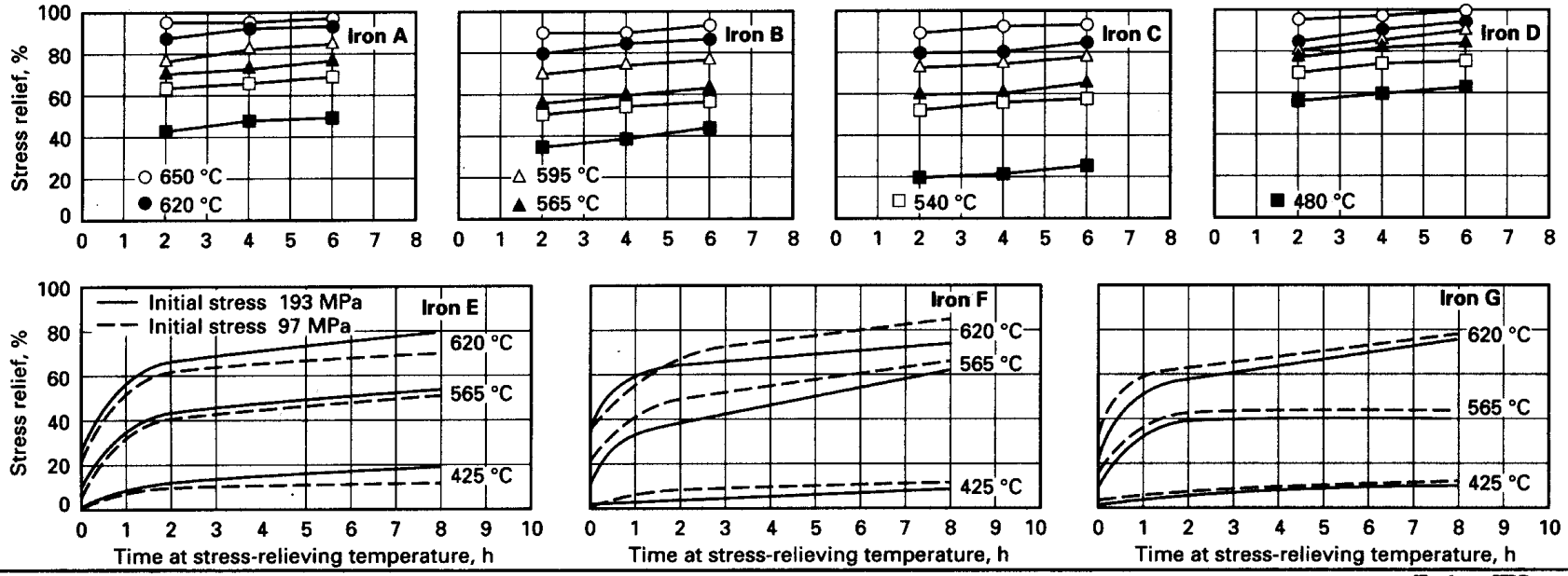
	Temperature	
Iron	**°C**	**°F**
Unalloyed, or alloyed without Cr	510–565	950–1050
0.15–0.30% Cr	595–620	1100–1150
>0.30% Cr	620–650	1150–1200

If the service requirements of a casting demand a particularly low residual stress, temperatures about 30 °C (50 °F) above those listed may be used. When these higher temperatures are used and hardness and strength are critical, it is advisable to check the hardness of the stress-relieved casting to determine whether an unacceptable decrease in hardness or strength has taken place.

High-Silicon Gray Irons for High-Temperature Service

Severe growth will occur in unalloyed or low-alloy gray cast irons at temperatures above 650 °C (1200 °F), due to oxidation. In flake graphite irons, growth may result in a 40% increase in volume, and continued growth at sufficiently elevated temperatures generally leads to complete disintegration of the component. Raising the silicon content to 4 to 6% or alloying with chromium has made it possible to increase the practical operating temperature.

High-silicon-content gray irons such as Silal (6% Si) are suitable for use at temperatures up to about 800 °C (1470 °F). In Silal, the advantages of a high critical temperature, a ferritic matrix (no combined carbon), and a



Iron	Composition, %										Hardness, HRB	
	C	Si	P	S	Mn	Ni	Cr	Mo	Cu	V	Before stress relieving	After stress relieving for 8 h at 620 °C (1150 °F)
A	2.93	2.14	0.110	0.57	0.47	0.35	0.10	...	...	...	98	94
B	3.43	2.12	0.104	0.70	0.81	0.34	0.18	0.23	...	...	98	94
C	3.24	2.55	0.107	0.62	0.87	0.51	0.20	0.22	...	...	95	95
D	3.91	1.43	0.54	0.25	0.32	1.56	0.06	...	...	...	82	80
E	3.18	2.13	0.73	0.125	0.70	1.03	0.33	0.65	...	...	98	98
F	3.12	1.76	0.075	0.097	0.78	1.02	0.41	0.58	...	...	94	95
G	2.78	1.77	0.065	0.135	0.55	0.36	0.10	0.33	0.46	0.04	96	96

Fig. 22 Effect of stress relieving time and temperature on degree of stress relief obtained in low-alloy gray irons. Table shows compositions and the negligible effect of maximum stress relieving conditions on hardness. Source: Ref 25

fine undercooled type D graphite structure combine to provide good growth and scaling resistance (Ref 10). Figure 23 shows the effect of silicon additions on the oxidation resistance of gray irons. Silicon contents from 3.0 to 4.5% are optimum for limiting growth in plain or 2% Cr gray irons for use at temperatures up to 800 °C (1470 °F) (Fig. 24).

Although quite brittle at room temperature, the high-silicon gray irons are reasonably tough at temperatures above 260 °C (500 °F). They have been successfully used for furnace and stoker parts, burner nozzles, and heat treatment trays.

High-Silicon Gray Irons for Corrosion Resistance

Irons with high silicon contents (14.5% Si) constitute a unique corrosion-resistant group of ferritic cast irons. These alloys are widely used in the chemical industry for processing and transporting highly corrosive liquids. The three most common high-silicon iron alloys are covered in ASTM A 518 (Table 10). These alloys contain 14.2 to 14.75% Si and 0.7 to 1.15% C. Grades 2 and 3 are also alloyed with 3.25 to 5% Cr, and grade 2 contains 0.4 to 0.6% Mo. Other compositions are also commercially produced with up to 17% Si.

Properties. High-silicon irons are the most universally corrosion-resistant alloys available at moderate cost. They are widely used for handling the corrosive media common in chemical plants, even when abrasive conditions are also encountered. When the silicon content is 14.2% or higher, these irons exhibit a very high resistance to boiling sulfuric acid. They are especially useful when the concentration of sulfuric acid is above 50%, at which point they are virtually immune to attack. The high-silicon irons are also very resistant to nitric acid. Increasing the silicon content to 16.5% makes the alloy quite resistant to corrosion in boiling nitric and sulfuric

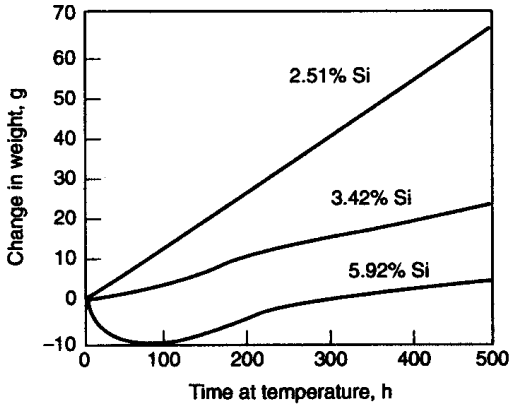


Fig. 23 Effect of silicon content on the oxidation behavior of gray irons tested at 800 °C (1470 °F). Source: Ref 26

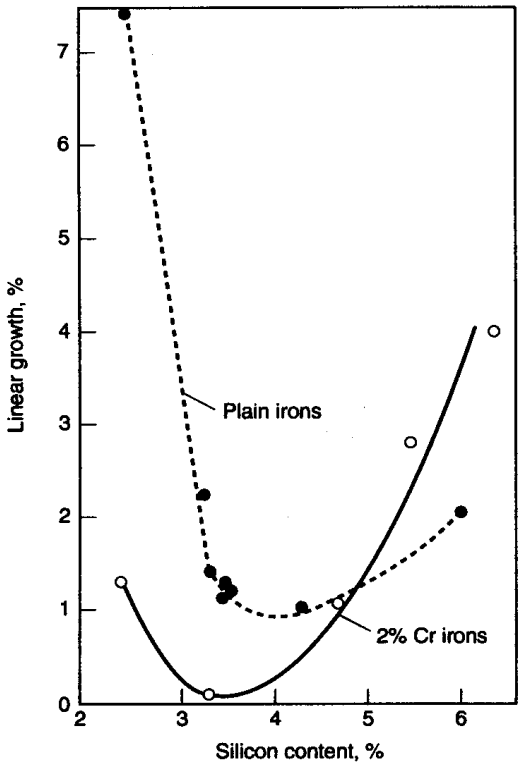


Fig. 24 Effect of silicon content on the growth of unalloyed and 2% Cr gray irons tested at 800 °C (1470 °F). Source: Ref 26

acids at nearly all concentrations. However, this is accompanied by a reduction of mechanical strength, so it is not ordinarily done in the United States.

The 14.5% Si iron is less resistant to the corrosive action of hydrochloric acid, but this resistance can be improved by additions of chromium and molybdenum and can be further enhanced by increasing the silicon content to 17%. The chromium-bearing silicon irons are very useful in contact with solutions containing copper salts, free wet chlorine, or other strongly oxidizing contaminants.

The high-silicon irons are very resistant to organic acid solutions at any concentration or temperature. However, their resistance to strong hot caustics is not satisfactory for most purposes. They are resistant to caustic solutions at lower temperatures and concentrations, and although they are no better than unalloyed gray iron in this regard, they can be used where caustics and other corrosives are mixed or alternately handled. They have no useful resistance to hydrofluoric or sulfurous acids.

Table 10 Compositions of high-silicon iron alloys per ASTM A 518

	Composition, %					
Alloy	C	Mn	Si	Cr	Mo	Cu
Grade 1	0.65–1.10	1.50 max	14.20–14.75	0.50 max	0.50 max	0.50 max
Grade 2	0.75–1.15	1.50 max	14.20–14.75	3.25–5.00	0.40–0.60	0.50 max
Grade 3	0.70–1.10	1.50 max	14.20–14.75	3.25–5.00	0.20 max	0.50 max

High-silicon irons have poor mechanical properties and particularly low thermal and mechanical shock resistance. These alloys are typically very hard and brittle, with a tensile strength of about 110 MPa (16 ksi) and a hardness of 480 to 520 HB. They are difficult to cast and are virtually unmachinable.

Austenitic Nickel-Alloyed Gray Irons

The nickel-alloyed austenitic irons (commonly referred to as Ni-Resists) are produced in both gray and ductile cast iron versions. ASTM specification A 436 defines eight grades of austenitic gray iron alloys, four of which are designed for elevated-temperature applications (2, 2b, 3, and 5 in Table 11) and four of which are designed for corrosion resistance (1, 1b, 4, and 6 in Table 11). The nickel produces a stable austenitic microstructure with good corrosion resistance and strength at elevated temperatures. The nickel-alloyed irons are additionally alloyed with chromium and silicon for wear resistance and oxidation resistance at elevated temperatures. Types 1 and 1b, which are designed exclusively for corrosion-resistant applications, are alloyed with 13.5 to 17.5% Ni and 6.5% Cu. Types 2b, 3, and 5, which are principally used for elevated-temperature service, contain 18 to 36% Ni, 1 to 2.8% Si, and 0 to 6% Cr. Type 4 is alloyed with 29 to 32% Ni, 5 to 6% Si, and 4.5 to 5.5% Cr and is recommended for stain resistance.

The gray iron Ni-Resists offer moderate strength (170 to 205 MPa, or 25 to 30 ksi minimum tensile strength) and good growth resistance in the temperature range of 650 to 900 °C (1200 to 1650 °F). In these irons, the resistance to growth is due partly to the absence of phase transformations and partly to improved oxidation resistance. Figure 10 shows the superior scaling behavior of austenitic gray irons.

Austenitic gray irons containing very high nickel contents (34 to 36%) have much lower coefficient of thermal expansion (CTE) values than

Table 11 Compositions of flake-graphite (gray) austenitic cast irons per ASTM A 436

		Composition, %					
Type	UNS number	TC(a)	Si	Mn	Ni	Cu	Cr
1(b)	F41000	3.00 max	1.00–2.80	0.50–1.50	13.50–17.50	5.50–7.50	1.50–2.50
1b	F41001	3.00 max	1.00–2.80	0.50–1.50	13.50–17.50	5.50–7.50	2.50–3.50
2(c)	F41002	3.00 max	1.00–2.80	0.50–1.50	18.00–22.00	0.50 max	1.50–2.50
2b	F41003	3.00 max	1.00–2.80	0.50–1.50	18.00–22.00	0.50 max	3.00–6.00(d)
3	F41004	2.60 max	1.00–2.00	0.50–1.50	28.00–32.00	0.50 max	2.50–3.50
4	F41005	2.60 max	5.00–6.00	0.50–1.50	29.00–32.00	0.50 max	4.50–5.50
5	F41006	2.40 max	1.00–2.00	0.50–1.50	34.00–36.00	0.50 max	0.10 max(e)
6(f)	F41007	3.00 max	1.50–2.50	0.50–1.50	18.00–22.00	3.50–5.50	1.00–2.00

(a) Total carbon. (b) Type 1 is recommended for applications in which the presence of copper offers corrosion-resistance advantages. (c) Type 2 is recommended for applications in which copper contamination cannot be tolerated, such as handling of foods or caustics. (d) Where some machining is required, 3.0 to 4.0 Cr is recommended. (e) Where increased hardness, strength, and heat resistance are desired, and where increased expansivity can be tolerated, Cr may be increased to 2.5 to 3.0%. (f) Type 6 also contains 1.0% Mo.

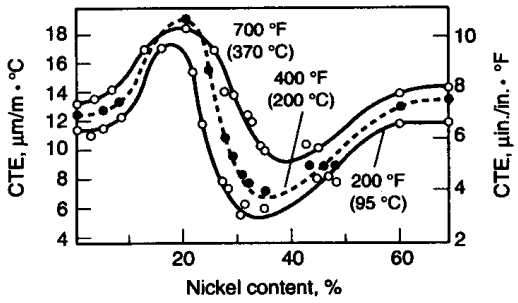


Fig. 25 Effect of nickel content and temperature on the CTE of gray irons. Source: Ref 27

those containing 14 to 22% Ni. Gray iron Ni-Resist covered by ASTM A 436 type 5 has a mean CTE value as low as 5.0 µm/m · °C (2.8 µin./in. · °F) from 20 to 200 °C (70 to 400 °F). The CTE as a function of nickel content is shown in Fig. 25 for three different temperatures.

REFERENCES

1. Metallurgy and Properties of Gray Irons, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 32–53
2. J.C. Hamaker, W.P. Wood, and F.B. Rote, Internal Porosity in Gray Iron, *Trans. AFS,* Vol 60, 1952, p 402–427
3. "The Importance of Controlling Low Phosphorus Contents in Gray Iron," Broadsheet 162, BCIRA, 1977
4. K.M. Muzumdar and J.F. Wallace, Effect of Sulfur in Cast Iron, *Trans. AFS,* Vol 81, 1973, p 412–423
5. "Effect of Some Residual or Trace Elements on Cast Iron," Broadsheet 192, BCIRA, 1981
6. J. Powell, Ferroalloys in the Production of Cast Iron, *AIME Electric Furnace Conf. Proc.,* Vol 44, Iron and Steel Society, 1986, p 215–231
7. T.E. Barlow and C.H. Loriz, Gray Cast Iron Tensile Strength, Brinell Hardness, and Composition Relationship, *Trans. AFS,* Vol 54, 1946, p 545
8. Foundry Practice for Cast Irons, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 133–154
9. Mechanical Properties of Gray Iron, *Iron Castings Handbook,* C.F. Walton and T.J. Opar, Ed., Iron Castings Society, Inc., 1981, p 203–295
10. R.B. Gundlach, The Effects of Alloying Elements on the Elevated Temperature Properties of Gray Irons, *Trans. AFS,* Vol 91, 1983, p 389–422
11. G.N.J. Gilbert, The Growth and Scaling Characteristics of Cast Irons in Air and Steam, *BCIRA J.,* Vol 7, 1959, p 478–566
12. E. Bevan, "Effect of Molybdenum on Dimensional Stability and Tensile Properties of Pearlitic Gray Irons at 600 to 850 °F (315 to 455 °C)," Internal report, Climax Molybdenum Co.

13. D.G. White, Growth and Scaling Characteristics of Cast Irons with Undercooled and Normal Flake Graphite, *BCIRA J.,* Vol 11, 1963, p 223–230
14. G.N.J. Gilbert and D.G. White, Growth and Scaling Characteristics of Flake Graphite and Nodular Graphite Cast Irons Containing Tin, *BCIRA J.,* Vol 11, 1963, p 295–318
15. K.B. Palmer, "Design with Cast Irons at High Temperatures, Part 1: Growth and Scaling," Report 1248, BCIRA
16. K.B. Palmer, "High Temperature Properties of Cast Irons," Conference on Engineering Properties and Performance of Modern Iron Castings, Loughborough, 1970 (partially reproduced in *Iron and Steel,* 1971, p 39–46)
17. J.R. Kattus and B. McPherson, Properties of Cast Iron at Elevated Temperatures, STP 248, ASTM, 1959
18. H.T. Angus, *Cast Irons*: *Physical and Engineering Properties,* Butterworths, 1976, p 253–278
19. M.M. Hallett, Tests on Heat Resisting Cast Irons, *J. Iron Steel Inst.,* Vol 70, April 1952, p 321
20. G.K. Turnbull and J.F. Wallace, Molybdenum Effect on Gray Iron Elevated Temperature Properties, *AFS Trans.,* Vol 67, 1959, p 35–46
21. R.B. Gundlach, Thermal Fatigue Resistance of Alloyed Gray Irons for Diesel Engine Components, *AFS Trans.,* Vol 87, 1979, p 551–450
22. C.J. Thwaites and J.C. Pryterch, Structural Stability of Flake Graphite Iron Alloyed with Tin and Chromium, *Foundry Trade J.,* Jan 1969, p 115–121
23. R.B. Gundlach, Elevated Temperature Properties of Alloyed Gray Irons for Diesel Engine Components, *AFS Trans.,* Vol 86, 1978, p 55–64
24. Corrosion Behavior, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 437–447
25. Heat Treating of Gray Irons, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 179–191
26. C.O. Burgess and R.W. Bishop, An Optimum Silicon Range in Plain and 2.0 Percent Chromium Cast Irons Exposed to Elevated Temperatures, *Trans. ASM,* Vol 33, 1944, p 455–476
27. Physical Properties, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 428–436

SELECTED REFERENCES

- Classification and Basic Metallurgy of Cast Irons, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 3–15
- Solidification Characteristics of Cast Irons, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 16–31

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Ductile Irons

Introduction and Overview

Ductile cast iron, also known as nodular iron or spheroidal-graphite (SG) iron, is cast iron in which the graphite is present as tiny spheres (nodules) (see Fig. 1). In ductile iron, eutectic graphite separates from the molten iron during solidification in a manner similar to that in which eutectic graphite separates in gray cast iron. However, because of additives (spheroidizing elements) introduced in the molten iron before casting, graphite grows as spheres, rather than as flakes of any of the forms characteristic of gray irons. Cast iron containing spheroidal graphite is much stronger and has higher elongation than gray iron or malleable iron. It may be considered a natural composite in which the spheroidized graphite imparts unique properties to ductile iron.

Ductile irons are used in the as-cast or heat-treated conditions. As-cast matrix microstructures usually consist of ferrite, pearlite, or both, depending on the cast section size and/or alloy composition. Common heat treatments and their purposes and resulting microstructures include:

- Annealing, to improve ductility and toughness, reduce hardness, and remove carbides. Annealed matrix microstructures are fully ferritic or contain ferrite with some pearlite.
- Normalizing, to improve strength with some ductility. Normalized matrix microstructures are predominantly pearlitic.
- Hardening and tempering, to increase hardness or improve strength with low elongation. Quenched and tempered matrix microstructures are predominantly martensitic.
- Austempering, to generate very high strength with some ductility and toughness, and improved wear resistance. Austempered matrix microstructures are a combination of acicular (bainitic) ferrite and austenite (Fig. 2).

As the matrix microstructure is progressively varied from ferrite to ferrite plus pearlite, to pearlite plus ferrite, to pearlite, to pearlite plus martensite,

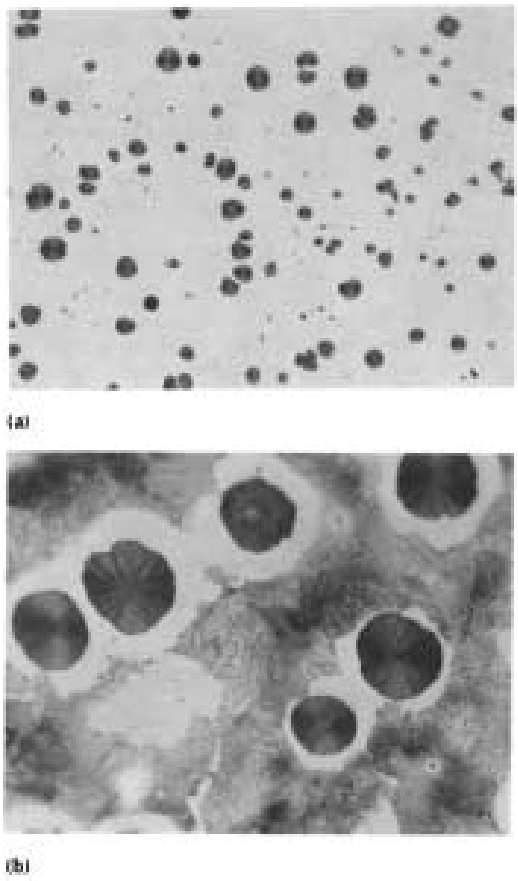


Fig. 1 Spheroidal graphite in an unetched ductile iron matrix shown at 75× (a) and in the etched (picral) condition shown at 300× (b). Etching reveals that the matrix consists of ferritic envelopes around the graphite nodules (bull's-eye structure) surrounded by a pearlitic matrix.

and finally to martensite, hardness, strength, and wear resistance increase, but impact resistance, ductility, and machinability decrease. The effect of matrix microstructure on strength and ductility is shown in Fig. 3. Overall, however, the best combination of strength, ductility, and wear resistance is achieved with austempered ductile irons (ADIs), as shown in Fig. 3 and 4.

Specifications. Most of the specifications for standard grades of ductile iron are based on properties. That is, strength and/or hardness is specified for each grade of ductile iron, and composition is either loosely specified or made subordinate to mechanical properties. Tables 1 and 2 list compositions, properties, and typical applications for most of the standard ductile irons that are defined by current standard specifications (except for the high-nickel, corrosion-resistant, and heat-resistant irons defined in ASTM A 439). As shown in Table 2, the ASTM system for designating the grade of ductile iron incorporates the numbers indicating tensile strength in ksi, yield strength in ksi, and elongation in percent. This system makes it easy to specify nonstandard grades that meet the general requirements of ASTM A 536. For example, grade 80-60-03 (552 MPa, or 80 ksi,

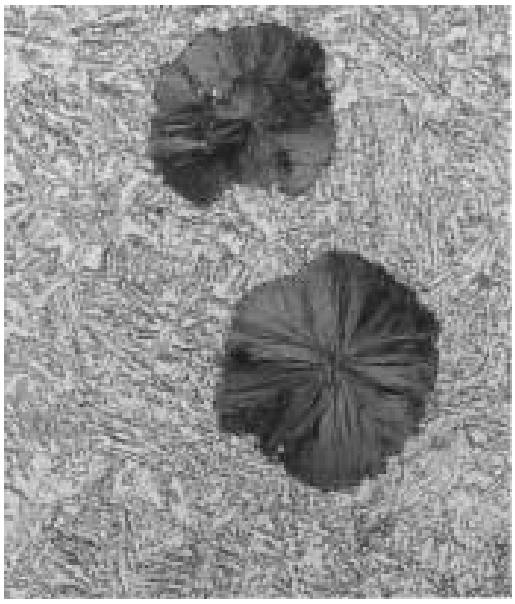


Fig. 2 Austempered ductile iron structure consisting of spheroidal graphite in a matrix of acicular ferritic plates (dark) and interplate austenitic (white)

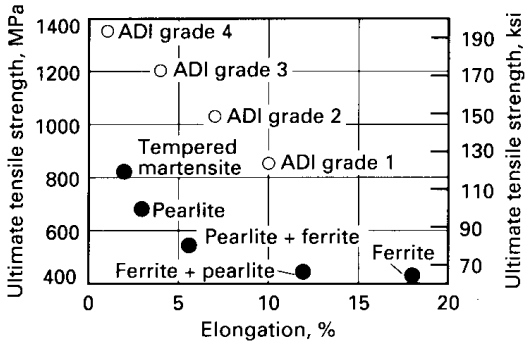


Fig. 3 Effect of matrix microstructure on the minimum values of tensile strength and elongation of ductile irons. The ADI matrix microstructure consists of acicular (bainitic) ferrite and austenite (see Fig. 2).

minimum tensile strength; 414 MPa, or 60 ksi, yield strength; and 3% elongation) is widely used in applications for which relatively high ductility is not important. Grades 65-45-12 and 60-40-18 are used in areas requiring high ductility and impact resistance. Grades 60-42-10 and 70-50-05 are used for special applications, such as annealed pipe or cast fittings. Grades other than those listed in ASTM A 536 or mentioned previously can be made to the general requirements of ASTM A 536, but with the mechanical properties specified by mutual agreement between purchaser and producer.

The Society of Automotive Engineers (now SAE International) uses a method of specifying iron for castings produced in larger quantities that is based on the microstructure and Brinell hardness of the material in the

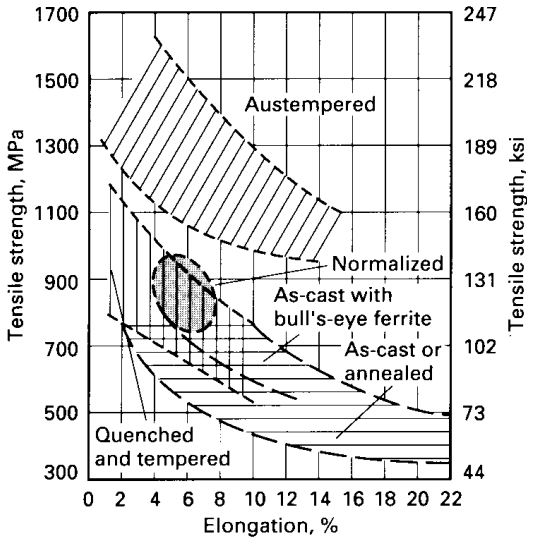


Fig. 4 Range of tensile strength and elongation values for as-cast and heat-treated ductile irons.

Table 1 Compositions and general uses for standard grades of ductile iron

Specification No.	Grade or class	UNS	TC(a)	Typical composition, %				Description	General uses
				Si	Mn	P	S		
ASTM A395; ASME SA395	60-40-18	F32800	3.00 min	2.50 max(b)	…	0.08 max	…	Ferritic; annealed	Pressure-containing parts for use at elevated temperatures
ASTM A476; SAE AMS 5316C	80-60-03	F34100	3.00 min(c)	3.0 max	…	0.08 max	0.05 max	As-cast	Paper mill dryer rolls, at temperatures up to 230 °C (450 °F)
ASTM A536	60-40-18(d)	F32800						Ferritic; may be annealed	Shock-resistant parts; low-temperature service
	65-45-12(d)	F33100						Mostly ferritic; as-cast or annealed	General service
	80-55-06(d)	F33800						Ferritic/ pearlitic; as-cast	General service
	100-70-03(d)	F34800						Mostly pearlitic; may be normalized	Best combination of strength and wear resistance and best response to surface hardening
	120-90-02(d)	F36200						Martensitic; oil quenched and tempered	Highest strength and wear resistance
ASTM A716	60-42-10	F32900						Centrifugally cast	Culvert pipe
ASTM A746	60-42-10	…						Centrifugally cast	Gravity sewer pipe
ASTM A874(e)	45-30-12	…	3.0–37	1.2–2.3	0.25 max	0.03 max	…	Ferritic	Low-temperature service
SAE J434	D4018(f)	F32800	3.20–4.10	1.80–3.00	0.10–1.00	0.015–0.10	0.005–0.035	Ferritic	Moderately stressed parts requiring good ductility and machinability

(continued)

Note: For mechanical properties and typical applications, see Table 2. (a) TC, total carbon. (b) The silicon limit may be increased by 0.08%, up to 2.75 Si, for each 0.01% reduction in phosphorus content. (c) Carbon equivalent, CE, 3.8–4.5; CE = TC + 0.3 (Si + P). (d) Composition subordinate to mechanical properties; composition range for any element may be specified by agreement between supplier and purchaser. (e) Also contains 0.07% Mg (max), 0.1% Cu (max), 1.0% Ni (max), and 0.07% Cr (max). (f) General composition given under grade D4018 for reference only. Typically, foundries will produce to narrower ranges than those shown and will establish different median compositions for different grades. (g) For castings with sections 13 mm ($\frac{1}{2}$ in.) and smaller, may have 2.75 Si max with 0.08 P max, or 3.00 Si max with 0.05 P max; for castings with section 50 mm (2 in.) and greater, CE must not exceed 4.3.

Table 1 (continued)

Specification No.	Grade or class	UNS	TC(a)	Typical composition, % Si	Mn	P	S	Description	General uses
SAE J434	D4512(f)	F33100						Ferritic/pearlitic	Moderately stressed parts requiring moderate machinability
	D5506(f)	F33800						Ferritic/pearlitic	Highly stressed parts requiring good toughness
	D7003(f)	F34800						Pearlitic	Highly stressed parts requiring very good wear resistance and good response to selective hardening
	DQ&T(f)	F30000						Martensitic	Highly stressed parts requiring uniformity of microstructure and close control of properties
SAE AMS 5315C	Class A	F33101	3.0 min	2.50 max(g)	…	0.08 max	…	Ferritic; annealed	General shipboard service

Note: For mechanical properties and typical applications, see Table 2. (a) TC, total carbon. (b) The silicon limit may be increased by 0.08%, up to 2.75 Si, for each 0.01% reduction in phosphorus content. (c) Carbon equivalent, CE, 3.8–4.5; CE = TC + 0.3 (Si + P). (d) Composition subordinate to mechanical properties; composition range for any element may be specified by agreement between supplier and purchaser. (e) Also contains 0.07% Mg (max), 0.1% Cu (max), 1.0% Ni (max), and 0.07% Cr (max). (f) General composition given under grade D4018 for reference only. Typically, foundries will produce to narrower ranges than those shown and will establish different median compositions for different grades. (g) For castings with sections 13 mm ($^1/_2$ in.) and smaller, may have 2.75 Si max with 0.08 P max, or 3.00 Si max with 0.05 P max; for castings with section 50 mm (2 in.) and greater, CE must not exceed 4.3.

Table 2 Mechanical properties and typical applications for standard grades of ductile iron

Specification No.	Grade or class	Hardness, HB(a)	Tensile strength, min(b) MPa	Tensile strength, min(b) ksi	Yield strength, min(b) MPa	Yield strength, min(b) ksi	Elongation in 50 mm (2 in.) (min), % (b)	Typical applications
ASTM A395; ASME SA395	60-40-18	143–187	414	60	276	40	18	Valves and fittings for steam and chemical plant equipment
ASTM A476(c); SAE AMS 5316	80-60-03	201 min	552	80	414	60	3	Paper mill dryer rolls
ASTM A536	60-40-18	…	414	60	276	40	18	Pressure-containing parts, such as valve and pump bodies
	65-45-12	…	448	65	310	45	12	Machine components subject to shock and fatigue loads
	80-55-06	…	552	80	379	55	6	Crankshafts, gears, and rollers
	100-70-03	…	689	100	483	70	3	High-strength gears and machine components
	120-90-02	…	827	120	621	90	2	Pinions, gears, rollers, and slides
SAE J434	D4018	170 max	414	60	276	40	18	Steering knuckles
	D4512	156–217	448	65	310	45	12	Disk brake calipers
	D5506	187–255	552	80	379	55	6	Crankshafts
	D7003	241–302	689	100	483	70	3	Gears
	DQ&T	(c)	(d)	(d)	(d)	(d)	(d)	Rocker arms
SAE AMS 5315C	Class A	190 max	414	60	310	45	15	Electric equipment, engine blocks, pumps, housings, gears, valve bodies, clamps, and cylinders

Note: For compositions, descriptions, and uses, see Table 1. (a) Measured at a predetermined location on the casting. (b) Determined using a standard specimen taken from a separately cast test block, as set forth in the applicable specification. (c) Range specified by mutual agreement between producer and purchaser. (d) Value must be compatible with minimum hardness specified for production castings.

castings themselves. Both ASTM and SAE specifications are standards for tensile properties and hardness. The tensile properties are quasi-static and may not indicate the dynamic properties, such as impact or fatigue strength.

Table 3 Hardness, toughness, and tensile properties at room temperature for austempered ductile iron grades specified in ASTM A 897 and A 897M (metric)

Grade	Minimum tensile strength		Minimum yield strength		Minimum elongation, %	Unnotched Charpy impact energy		Typical hardness, HB
	MPa	ksi	MPa	ksi		J	ft · lbf	
125/80/10 (Grade 1)	850	125	550	80	10	100	75	269–321
150/100/7 (Grade 2)	1050	150	700	100	7	80	60	302–363
175/125/4 (Grade 3)	1200	175	850	125	4	60	45	341–444
200/155/1 (Grade 4)	1400	200	1100	155	1	35	25	388–477
230/185/- (Grade 5)	1600	230	1300	185	…	…	…	444–555

Specifications for the highest-strength grades usually mention the possibility of hardened and tempered structures, but ASTM A 897 (Table 3) should be consulted for the most recently reported austempered ductile irons, which have the highest combinations of tensile strength and ductility.

Applications. The cast iron pipe industry is the largest user of ductile iron (ductile iron pipe makes up nearly 44% of the total ductile iron shipments). Ductile iron piping is made by centrifugal casting (see, e.g., ASTM A 716 and A 746 in Table 1). Many valves and fittings are also made from ductile iron.

The second largest area of ductile iron consumption is the automotive/trucking industry. About 29% of all ductile iron shipments is used in automobiles, light trucks, and medium/heavy trucks. Because of economic advantages and high reliability, ductile iron is used for such critical automotive parts as crankshafts, front wheel spindle supports, complex shapes of steering knuckles, disk brake calipers, engine connecting rods, idler arms, wheel hubs, truck axles, suspension system parts, power transmission yokes, high-temperature applications for turbo housings and manifolds, and high-security valves for many various applications. It can be rolled or spun into a desired shape or coined to an exact dimension.

Other important application areas for ductile iron components include:

- Papermaking machinery
- Farm equipment
- Construction machinery and equipment
- Power transmission components (e.g., gears)
- Oilfield equipment

Typical applications for standard grades of ductile iron are also listed in Tables 1 and 2.

Austempered ductile iron has resulted in many new applications for ductile iron. Some of the applications for ADI include:

- Gears (including side and timing gears)
- Wear-resistant parts
- High-fatigue strength applications
- High-impact strength applications

- Automotive crankshafts
- Chain sprockets
- Refrigeration compressor crankshafts
- Universal joints
- Chain links
- Dolly wheels

Composition Control and Effects of Alloying Elements

The manufacture of high-quality ductile iron begins with the careful selection of charge materials that will give a relatively pure cast iron, free of the undesirable residual elements sometimes found in other cast irons. Carbon, manganese, silicon, phosphorus, and sulfur must be held at specified levels. Magnesium, cerium, and certain other elements interfere with the nodulizing process. Such elements must be either eliminated or restricted to very low concentrations and neutralized by additions of cerium and/or rare earth elements. Alloying elements such as chromium, nickel, molybdenum, copper, vanadium, and boron act as carbide formers, as pearlite stabilizers, or as ferrite promoters. Alloys are controlled to the extent needed to obtain the required mechanical properties and/or microstructure in the critical section(s) of the castings. A summary of the effects of various elements found in ductile irons is given in Table 4.

Carbon influences the fluidity of the molten iron and the shrinkage characteristics of the cast metal. Excess carbon in suspension, not in solution, reduces fluidity. The volume of graphite is 3.5 times the volume of iron. As ductile iron solidifies, the carbon in solution precipitates out as graphite and causes an expansion of the iron, which can offset the shrinkage of the iron as it cools from liquid to solid. The amount of carbon needed to offset shrinkage and porosity is indicated by:

$$\%C + 1/7\% Si \geq 3.9\% \quad \text{(Eq 1)}$$

Carbon contents greater than this amount begin to decrease fatigue strength and affect strength before the effect is noticed on tensile strength. The size and the number of graphite nodules formed during solidification are influenced by the amount of carbon, the number of graphite nuclei, and the choice of inoculation practice. Normal graphite-containing ductile iron has 10% less weight than steel of the same section size. The graphite also provides lubricity for sliding friction, and the low coefficient of friction permits more efficiently running gears, which, furthermore, will not seize if a loss of lubricant is experienced in service. The graphite also produces ADI

Table 4 Summary of the effects of various elements found in ductile irons

Element	Typical amount	Maximum for matrix		Positive effects	Deleterious effects
		Ferrite	Pearlite		
Spheroidizing elements					
Mg	0.02–0.08%	Sufficient to ensure	spheroidal graphite	Lowers sulfur and oxygen contents; causes graphite to form spheroids	Excess promotes carbides
Rare earths	0–0.30%	About 0.035%	About 0.035%	Promotes nodule count and quality in combination with magnesium; neutralizes subversive elements	Excess promotes carbides in thin sections and chunky graphite in heavy sections
Ca	Not detected	Essentially insoluble	Essentially insoluble	Increases nodule count and improves nodule quality; optimizes inoculation	Excess promotes carbides
Ba	Not detected	Essentially insoluble	Essentially insoluble	Increases nodule count; optimizes inoculation	…
Primary elements					
C	3.00–4.00%	3.00–4.00%	3.00–4.00%	Present as spheroids or carbides	Excess results in graphite formation
Si	1.80–3.00%	1.80–3.00%	1.80–2.75%	Promotes graphitization during solidification and matrix formation	Hardens and strengthens ferrite; increases nil-ductility temperatures
P	About 0.02%	0.035% max	0.05% max	Kept as low as possible	Forms intercellular carbide network; promotes pearlite
S	0.01–0.02%	0.02% max	0.02% max	Combines with magnesium and rare earths	Limits efficiency of magnesium treatment process
Mn	0.00–1.20%	0.20%	0.80% max	Promotes pearlite in as-cast and normalized iron	Intercellular carbides when over 0.70%
Alloying elements					
Ni	0.01–2.00%	As low as possible for as-cast	To specification	Employed for hardenability (e.g., pearlitic)	…
Mo	0.01–0.75%	0.03% max	To specification	Promotes hardenability	Excess promotes intercellular carbides
Cu	0.01–0.90%	0.03% max	To specification	Promotes pearlitic hardenability	No significant effect on nodule count or quality
Tramp elements					
Te	<0.005%	0.02% max	0.02% max	Used to control pinholes	Promotes spheroid degeneration in absence of rare earths
Pb	…	0.002% max	0.002% max	Kept as low as possible	Promotes intercellular flake graphite
Ti	<0.07%	0.03% max	0.07% max	Kept as low as possible	Promotes vermicular graphite
Al	0.003–0.06%	0.05% max	0.05% max	Used in ferroalloys to suppress chill	Promotes vermicular graphite effect—greater in heavy sections; promotes pinnoles
Sb	<0.005%	0.001% max	0.001% max	Strong pearlite former; counteracts chunky graphite in heavy sections	Nodule degeneration at high levels when rare earths are not present
Bi	<0.01%	0.002% max	0.002% max	Increases nodule count and quality when rare earths are present	Promotes vermicular graphite in absence of rare earths
Zr	<0.01%	0.10% max	0.10% max	Kept as low as possible	Promotes vermicular graphite
Carbide- and pearlite-forming elements					
Cr	0.02–0.15%	0.04% max	0.10% max	Very powerful carbide former	Carbides resistant to annealing
B	<0.0005%	0.002% max	0.002% max	Kept as low as possible	Forms intercellular carbides that resist annealing
Sn	<0.10%	0.01% max	0.08% max	Very potent pearlite former	At <0.10%, forms intercellular structure with flake graphite
As	0.01% max	0.02% max	0.05% max	About 0.08% required for pearlitic matrix	…
V	<0.04%	0.04% max	0.05% max	Forms very stable carbides	Retards annealing
Gaseous elements					
O	<0.005%	About 0.003%	About 0.003%	Kept as low as possible	Combines with magnesium
H	0.0002–0.0015%	About 0.0003%	About 0.0003%	Kept as low as possible	Promotes centerline carbides and inverse chill; promotes pinholes
N	…	…	…	Kept as low as possible	Mild carbide-forming tendency; may contribute to porosity

Source: Ref 1

gears that are silent in operation. Graphite in the structure can provide good machinability of a ferritic material and then be available to redissolve into solution by heat treating to produce high strength and wear resistance.

The carbon, silicon, and phosphorus contents can be considered together as a carbon equivalent (CE) value, which can be a useful guide to foundry behavior and some properties. When CE = C% + 1/3(%Si + %P) = 4.3, the iron will be of wholly eutectic composition and structure, and the deviation of the CE value from this value is a measure of the relative amount of eutectic. If CE < 4.3, there will be a proportion of dendrites; if CE > 4.3, there will be primary graphite nodules in the structure.

Silicon (Ref 2) is a powerful graphitizing agent. Within the normal composition limits, increasing amounts of silicon promote structures that have progressively greater amounts of ferrite; furthermore, silicon contributes to the solution strengthening and hardness of ferrite. Increasing the amount of ferrite reduces the yield strength and tensile strength, but increases the elongation and impact strength. The ferrite envelope surrounding the graphite nodule in pearlitic ductile iron reduces the indicated yield strength, but increases elongation, impact strength, and fatigue strength. Silicon reduces the impact strength of ferritic ductile iron both as-cast and as subcritically annealed. To provide maximum resistance to fracture from room temperature down to –40 °C (–40 °F), silicon must be kept below 2.75% if the phosphorus content is below 0.02%. If the phosphorus content is 0.05%, the silicon content should be limited to 2.55%. As described subsequently, high-temperature application requires silicon levels of ~4%.

Manganese (Ref 3). Among the alloying elements commonly used to improve the mechanical properties of ductile iron, manganese acts as a pearlite stabilizer and increases strength, but reduces ductility and machinability (Fig. 5). It also promotes segregation to the cell boundaries and must be limited when making ADI.

Magnesium. The magnesium content required to produce spheroidal graphite usually ranges from 0.04 to 0.06%. If the initial sulfur content is below 0.015%, a lower magnesium content (in the range of 0.035 to 0.04%) may be satisfactory. Compacted graphite structures with inferior properties may be produced if the magnesium content is too low, while too high a magnesium content may promote dross defects.

Sulfur is derived from the charged metallic raw materials. In cupola melting, it is also absorbed from the coke. Before magnesium treatment, the sulfur content should be as low as possible, preferably below 0.02%. The final sulfur content of ductile iron is usually below 0.015%, but if cerium is present, it may be higher because of the presence of cerium sulfides in the iron. Excessive final sulfur contents are usually

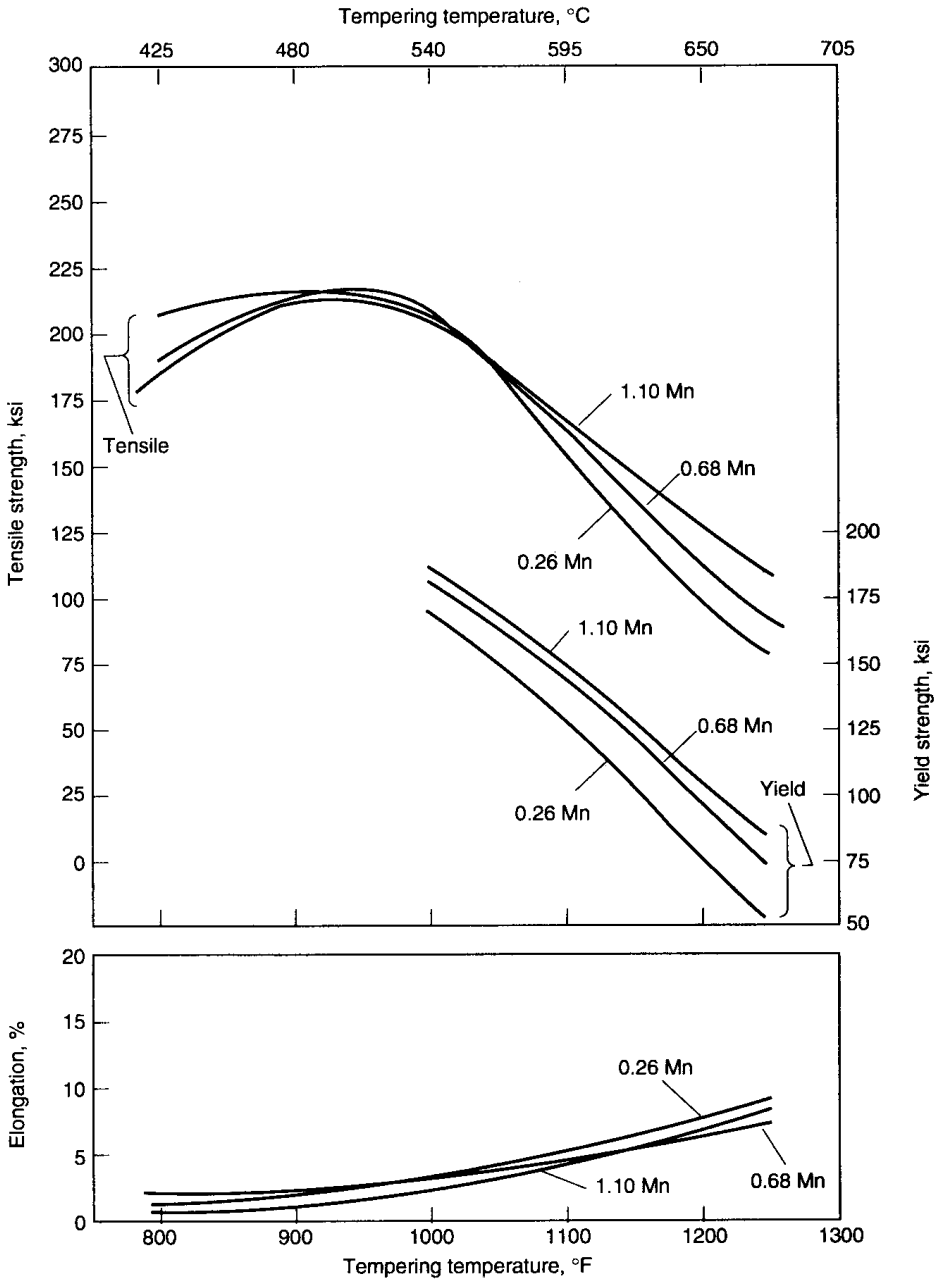


Fig. 5 Effect of varying manganese contents on the tensile properties of a ductile iron containing 3.75% C and 2.45% Si. At the normal tempering temperatures employed (540 to 675 °C, or 1000 to 1250 °F), increasing manganese content increases strength but lowers ductility. Source: Ref 4

associated with magnesium sulfide slag and dross. When using cupola-melted iron, it is common to desulfurize the metal before magnesium treatment (usually with lime or calcium carbide, either continuously or in batches) to levels of 0.02% or less. Before treatments in the mold or in the metal stream, it is advantageous to reduce the initial sulfur to 0.01% or less.

Cerium can be added to neutralize undesirable trace elements that interfere with the formation of spheroidal graphite and to aid inoculation. It may then be desirably present to the extent of 0.003 to 0.01%. In irons of very low minor element content, cerium may be undesirable and may promote chunky nonspheroidal graphite, especially in thick sections; the deliberate addition of impurities may be necessary to avoid this effect. Cerium is added as a minor constituent of a number of magnesium addition alloys and inoculants to improve graphite structure. It is removed during the remelting of scrap ductile iron.

Aluminum. The presence of even trace amounts of aluminum in ductile iron may promote subsurface pinhole porosity and dross formation and should therefore be avoided. The most common sources of aluminum are contaminants in steel and cast iron scrap, notably aluminum pistons from scrap automobile engines. Another source is aluminum-containing inoculants. Aluminum as low as 0.01% may be sufficient to cause pinholes in magnesium-containing ductile iron. It is advisable to use inoculants of low aluminum content and to practice late metal stream inoculation with very small quantities of inoculant.

Phosphorus is normally kept below 0.05%, because it promotes unsoundness and lowers ductility.

Minor Elements Promoting Nonspheroidal Graphite. Lead, antimony, bismuth, and titanium are undesirable elements that may be introduced in trace amounts with raw materials in the charge, but their effects can be neutralized by a cerium addition.

Minor Elements Promoting Pearlite. Nickel, copper, manganese, tin, arsenic, and antimony all promote pearlite and are listed here in order of increasing potency. They can enter the iron as trace constituents of raw materials. Copper up to 0.3% and tin up to 0.1% can be deliberately used as ladle additives when fully pearlitic structures are required. Almost all trace elements promote pearlite formation, and their effects are cumulative; therefore, a charge of high purity is essential for achieving fully ferritic structures as-cast or with minimal annealing.

Minor Elements Promoting Carbides. Chromium, vanadium, and boron are all carbide promoters. Manganese may accentuate the carbide-stabilizing effects of these elements, especially in heavy sections in which segregation promotes grain-boundary carbides. These elements are controlled by careful selection of metallic raw materials for melting.

Alloying Elements to Promote Hardenability. Nickel, molybdenum, manganese, and copper all promote hardenability. See the section "Effects of Alloying on Hardenability" for details.

Alloying Elements to Achieve Special Properties. Austenitic matrix structures are achieved by the addition of 20% Ni (more when resistance to heat, corrosion, or oxidation is required). Up to 5% Cr can be added to such irons. Nickel contents to 36% produce irons of controlled low-expansion properties. See the section "Austenitic Nickel-Alloyed Ductile Irons" for additional information.

Silicon contents to 6% produce ferritic matrix structures with reduced growth, scaling and thermal distortion, and cracking at elevated temperatures. The addition of up to 2% Mo to pearlitic, ferritic, and austenitic irons improves creep and elevated-temperature strength. See the section "High-Silicon Ductile Irons" for the effects of molybdenum additions.

Magnesium Treatment

Melt treatment to produce ductile iron involves the addition of magnesium to change the form of the graphite, followed by or combined with inoculation of a ferrosilicon material to ensure a graphitic structure with freedom from carbides. There are three major types of magnesium-containing nodulizing (or spheroidizing) agents: unalloyed magnesium, nickel-base nodulizers, and magnesium-containing ferrosilicons.

Unalloyed magnesium metal has been added to molten iron as wire, ingots, or pellets; as briquets in combination with sponge iron; as pellets in combination with granular lime; or in the cellular pores of metallurgical coke.

Magnesium-Containing Alloys. A nickel alloy with 14 to 16% Mg can be added to the ladle during filling or by plunging. The reaction is spectacular but not violent, and a very consistent recovery is obtained. A disadvantage lies in the accompanying increase in nickel and the cost of the alloy. Other nickel alloys containing much lower magnesium contents (down to 4%) have also been used and involve a much quieter reaction. Most alloys used to introduce magnesium into molten iron are based on ferrosilicon containing 3 to 10% Mg. The reaction varies from fairly violent (with 10% Mg) to quiet (with 3% Mg). The alloy can be plunged in a refractory bell or added in the ladle using a number of different techniques, including pouring the molten iron onto the alloy in the bottom of the ladle.

Effects of Inoculation on Properties

Following magnesium treatment, the iron is usually subjected to final inoculation, sometimes referred to as postinoculation. Inoculation is

commonly carried out in the ladle using a granular inoculant, which may be commercial ferrosilicon containing 75% Si or one of a wide range of proprietary alloys, usually containing 60 to 80% Si. The amount of inoculant added usually ranges from about 0.25 to 1.0%. A higher percentage of silicon in the magnesium-addition alloy may permit less inoculation. The inoculant can be added during reladling, stirred into the metal, placed on the bottom of the ladle before filling, or plunged in a refractory bell, as late as possible before casting. Effective stirring is necessary, and one way of achieving this is by bubbling air or nitrogen through the melt using a porous plug in the bottom of the ladle.

Inoculation reduces undercooling during solidification and helps to prevent carbides in the structure, especially in thin sections. It increases the number of graphite nodules, thus improving homogeneity, assisting in the formation of ferrite, and promoting ductility. It assists in reducing annealing time and reduces hardness.

Effects of Alloying on Hardenability

The hardenability of ductile cast iron is an important parameter for determining the response of a specific iron to normalizing, quenching and tempering, or austempering. Hardenability is normally measured by the Jominy test described in ASTM A 255 and SAE J406, in which a standard-sized bar (1 in. diameter by 4 in. in length) is austenitized and water quenched from one end. The variation in cooling rate results in micro-structural variations, giving hardness changes that are measured and recorded.

Figure 6 shows Jominy curves from an unalloyed ductile iron (3.9% C, 2.2% Si, 0.04% Mg, and residual Mn, Ni, Cu, Cr, V, Ti) that has been austenitized at 870 and 925 °C (1600 and 1700 °F). The higher carbon content in the matrix, resulting from the higher austenitizing temperature, increases the hardenability (the Jominy curve is shifted to larger distances from the quenched end) and a greater maximum hardness. The purpose of adding alloy elements to ductile cast irons is to increase hardenability.

Figure 7 shows Jominy curves for ductile irons containing variable quantities of manganese, molybdenum, nickel, and copper (Ref 6). It is clear from Fig. 7 that manganese and molybdenum are much more effective in increasing hardenability, per weight percent added, than nickel or copper. However, as is the case with steel, combinations of nickel and molybdenum, or copper and molybdenum, or copper, nickel, and manganese are more effective than the separate elements. The synergistic effects of nickel and molybdenum are shown in the Jominy curves in Fig. 8 and Table 5. Thus, heavy-section castings that require through hardening or austempering usually contain combinations of these elements. Silicon

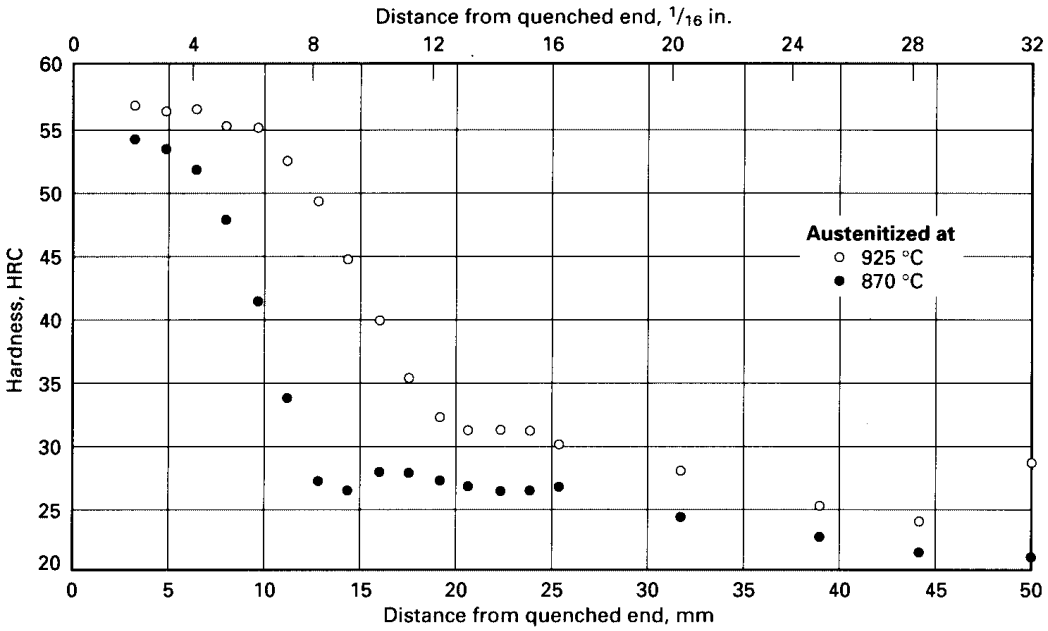


Fig. 6 Jominy curves from a ductile iron (3.9% C, 2.2% Si, 0.04% Mg, residual Mn, Ni, Cu, Cr, V, Ti), austenitized at 870 and 925 °C (1600 and 1700 °F). Source: Ref 5

does not have a large effect on hardenability, apart from its effect on matrix carbon content.

Effects of Alloying on Normalizing

Normalizing (air cooling following austenitizing) can considerably improve tensile strength and may be used in the production of ductile iron of ASTM type 100-70-03. The microstructure obtained by normalizing depends on the composition of the castings and the cooling rate. As described earlier, the composition of the casting dictates its hardenability. The cooling rate depends on the mass of the casting, but it also may be influenced by the temperature and movement of the surrounding air during cooling. Normalizing generally produces a homogeneous structure of fine pearlite, if the iron is not too high in silicon content and has at least a moderate manganese content (0.3 to 0.5% or higher). Heavier castings that require normalizing usually contain alloying elements, such as nickel, molybdenum, and additional manganese, for higher hardenability to ensure the development of a fully pearlitic structure after normalizing. Lighter castings made of alloyed iron may be martensitic or may contain an acicular structure after normalizing. Figure 9 shows the influence of various nickel contents and combinations of alloying elements on hardnesses after normalizing of different section thicknesses.

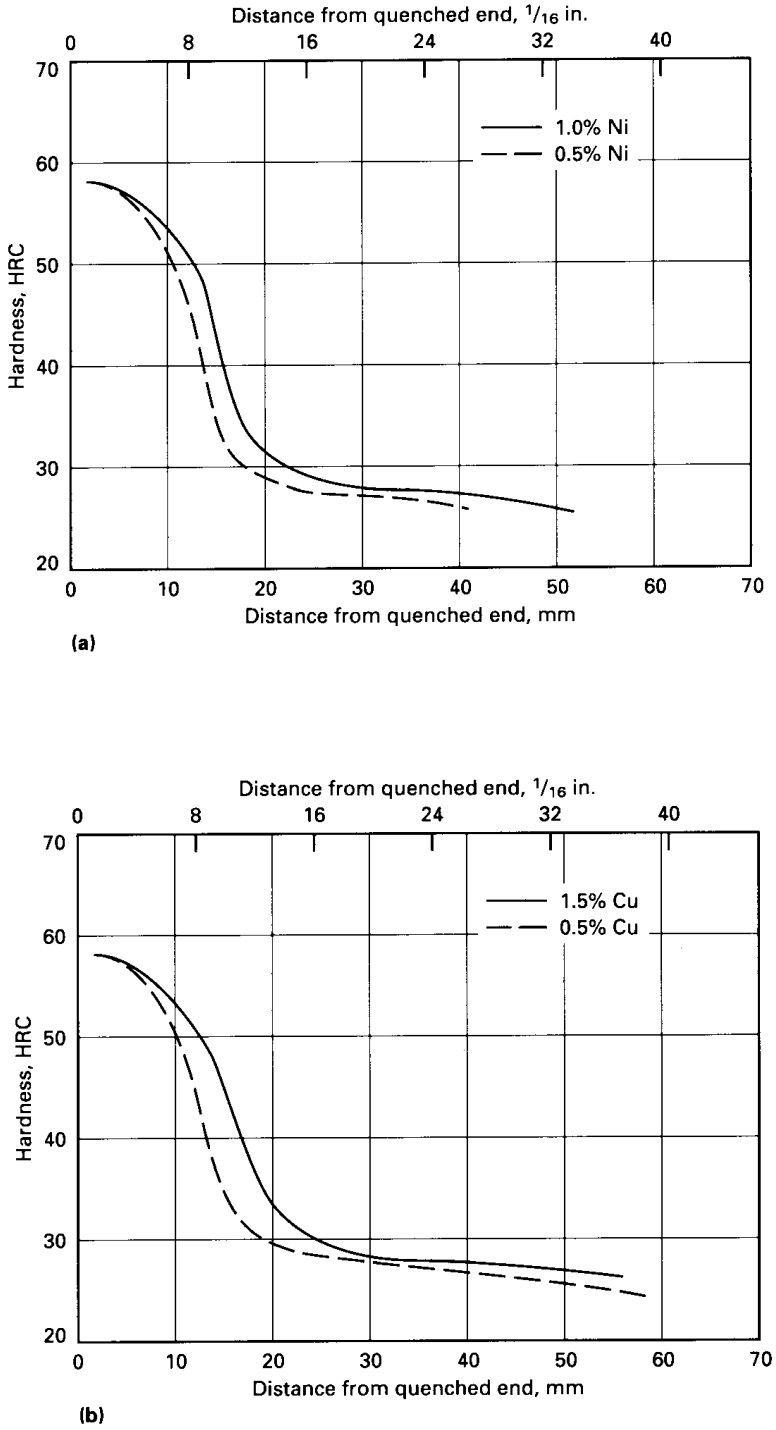
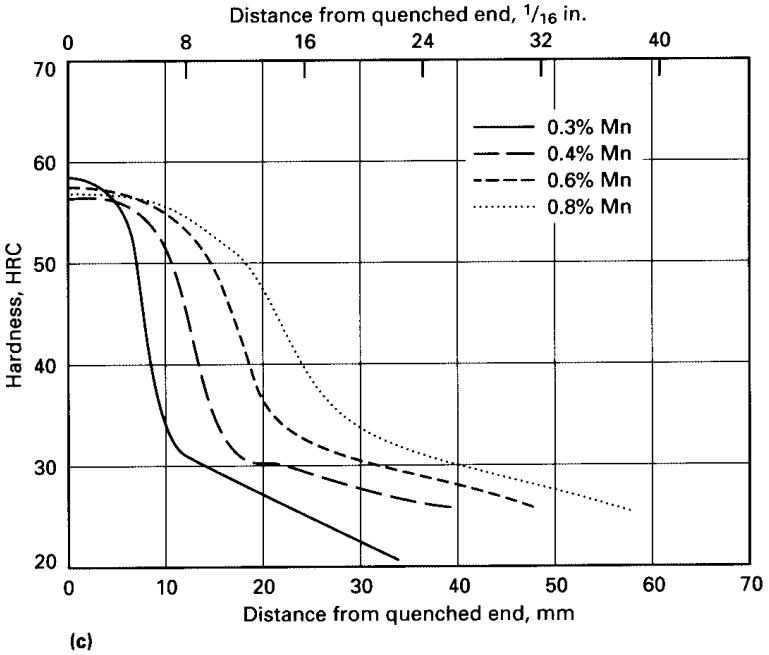


Fig. 7 Jominy curves for ductile irons containing variable quanities of (a) nickel, (b) copper, (c) manganese, and (d) molybdenum. Austenitized at 870 °C (1600 °F). Source: Ref 6



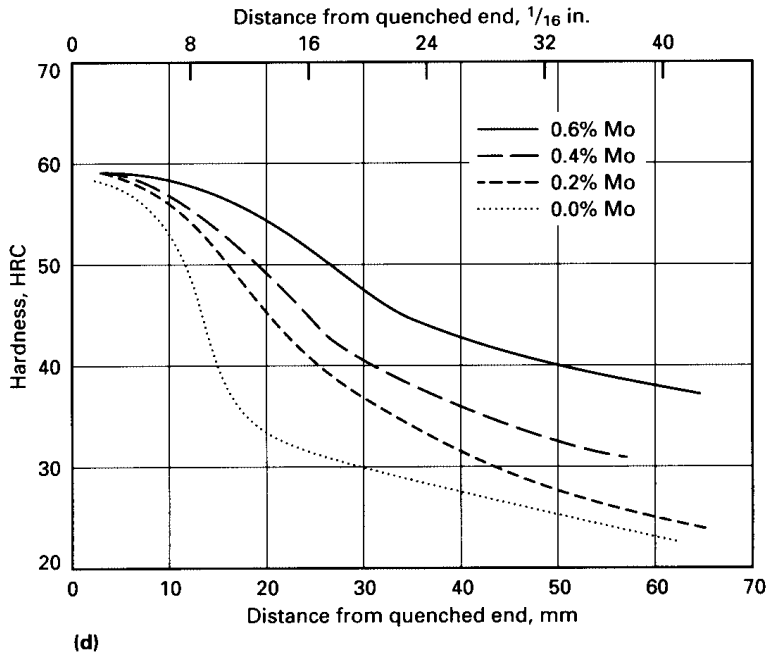


Fig. 7 (continued) (c) manganese, and (d) molybdenum. Austenitized at 870 °C (1600 °F). Source: Ref 6

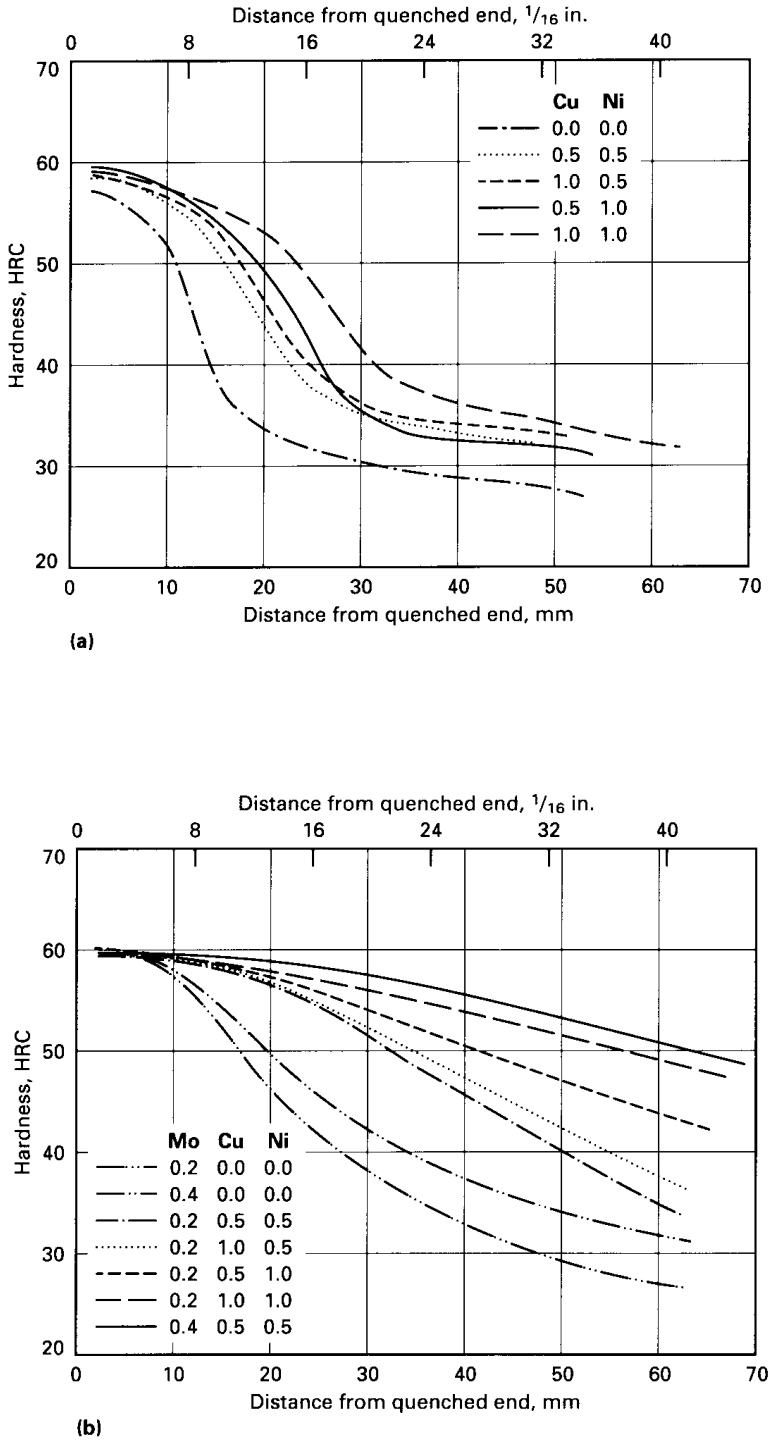


Fig. 8 Jominy curves for ductile irons containing variable combinations of (a) copper and nickel and (b) molybdenum, copper, and nickel. Austenitized at 870 °C (1600 °F). Source: Ref 6

The normalizing temperature is usually between 870 and 940 °C (1600 and 1725 °F). The standard time at temperature of 1 h per inch of section thickness or 1 h minimum is usually satisfactory. Longer times may be required for alloys containing elements that retard carbon diffusion in the austenite. For example, tin and antimony segregate to the nodules, effectively preventing the solution of carbon from the nodule sites (Ref 7).

Normalizing is sometimes followed by tempering to attain the desired hardness and relieve residual stresses that develop upon air cooling when various parts of a casting with different section sizes cool at different rates. Tempering after normalizing is also used to obtain high toughness and impact resistance. The effect of tempering on hardness and tensile properties depends on the composition of the iron and the hardness level obtained in normalizing. Tempering usually consists of reheating to temperatures of 425 to 650 °C (800 to 1200 °F) and holding at the desired

Table 5 Examples of alloying combinations used to increase the hardenability of ductile iron

Alloying elements used, %					Maximum diameter of bar that could be hardened by oil quenching	
C	Si	Mn	Ni	Mo	mm	in.
3.4	2.0	0.3	…	…	25	1
3.4	2.5	0.3	…	…	28	1.1
3.4	2.0	0.3	1.0	…	30	1.2
3.4	2.0	1.3	…	…	38	1.5
3.4	2.0	0.3	…	0.5	51	2.0
3.4	2.0	0.9	1.5	0.25	63	2.5

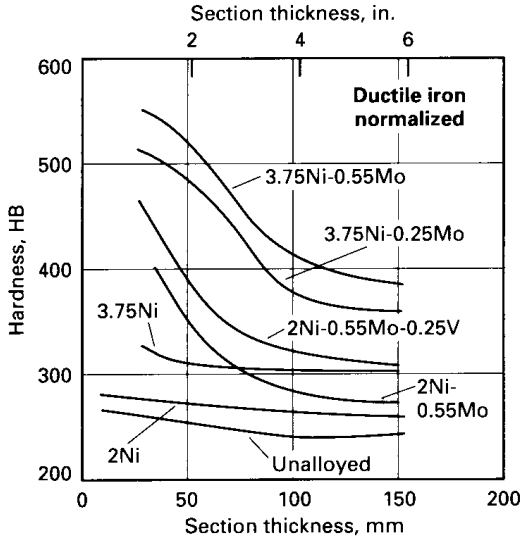


Fig. 9 Effect of alloy content and section thickness on hardness after normalizing

temperature for 1 h per inch of cross section. These temperatures are varied within the above range to meet specification limits.

Effects of Alloying on Austempering

Table 6 summarizes the effects of various alloying elements on the austempering behavior of ADI. As indicated in this table, copper, nickel, manganese, and molybdenum all enhance hardenability. However, it is important to understand that these alloying elements tend to segregate during solidification, so that a nonuniform distribution exists throughout the matrix. This has a potentially detrimental effect on the austempering reaction and therefore on mechanical properties. Ductility and impact toughness are the most severely affected.

Manganese and molybdenum have the most powerful effect on pearlite hardening but will also segregate and freeze into intercellular regions of the casting to promote iron or alloy carbides. Although nickel and copper do not affect hardenability nearly as much, they segregate to graphite

Table 6 Effects of various major alloying elements on the austempering behavior of austempered ductile iron (ADI)

Element	Alloying effects
Carbon	Increasing carbon in the range 3–4% increases the tensile strength but has negligible effect on elongation and hardness. Carbon should be controlled within the range 3.6–3.8% except when deviations are required to provide a defect-free casting.
Silicon	Silicon is one of the most important elements in ADI because it promotes graphite formation, decreases the solubility of carbon in austenite, increases the eutectoid temperature, and inhibits the formation of bainitic carbide. Increasing the silicon content increases the impact strength of ADI and lowers the ductile-brittle transition temperature. Silicon should be controlled closely within the range 2.4–2.8%.
Manganese	Manganese can be both a beneficial and a harmful element. It strongly increases hardenability, but during solidification it segregates to cell boundaries where it forms carbides and retards the austempering reaction. As a result, for castings with either low nodule counts or section sizes greater than $^3/_4$ in. (19 mm), manganese segregation at cell boundaries can be sufficiently high to produce shrinkage, carbides, and unstable austenite. These microstructural defects and inhomogeneities decrease machinability and reduce mechanical properties. To improve properties and reduce the sensitivity of ADI to section size and nodule count, it is advisable to restrict the manganese level in ADI to less than 0.3%. The use of high-purity pig iron in the ADI charge offers the twin advantages of diluting the manganese in the steel scrap to desirable levels and controlling undesirable trace elements.
Copper	Up to 0.8% Cu may be added to ADI to increase hardenability. Copper has no significant effect on tensile properties but increases ductility at austempering temperatures below 350 °C (675 °F).
Nickel	Up to 2% Ni may be used to increase the hardenability of ADI. For austempering temperatures below 350 °C (675 °F), nickel reduces tensile strength slightly but increases ductility and fracture toughness.
Molybdenum	Molybdenum is the most potent hardenability agent in ADI and may be required in heavy-section castings to prevent the formation of pearlite. However, both tensile strength and ductility decrease as the molybdenum content is increased beyond that required for hardenability. This deterioration in properties is probably caused by the segregation of molybdenum to cell boundaries and the formation of carbides. The level of molybdenum should be restricted to not more than 0.2% in heavy-section castings.

Source: Ref 8

nodule sites and do not form detrimental carbides. Combinations of these elements that segregate in opposite fashions are selected for their synergistic effect on hardenability.

Effects of Alloying on Corrosion Behavior

Although graphite shape and matrix microstructure are critical to mechanical properties, neither of these structural variables have a strong effect on corrosion resistance. Hence, there are no appreciable differences in the corrosion behavior of gray and ductile irons. As described in the article "Gray Irons," the elements that enhance the corrosion resistance of both gray and ductile irons include silicon, nickel, chromium, copper, and molybdenum. In general, low and moderately alloyed ductile irons containing some combination of these elements exhibit two to three times the service life of unalloyed ductile irons. As described in the following section, further improvements in certain environments can be achieved in the more highly alloyed nickel austenitic ductile irons.

Austenitic Nickel-Alloyed Ductile Irons

The ductile austenitic nickel-alloyed ductile irons (Ni-Resists) provide resistance to frictional wear, corrosion resistance, strength and oxidation resistance at elevated temperatures, nonmagnetic characteristics, and, in some alloys, low thermal expansivity at ambient temperatures. They have found widespread use in chemical processing equipment, food handling equipment, and components for elevated-temperature applications, such as cylinder liners, exhaust manifolds, valve guides, gas turbine housings, turbocharger housings, water pump bodies, and piston rings in aluminum pistons.

The composition and mechanical property requirements of the ductile Ni-Resist alloys are covered in ASTM A 439. Table 7 lists the compositions of the nine grades in accordance with ASTM A 439. The ductile Ni-Resists are considerably stronger and tougher than the comparable gray iron Ni-Resists. Tensile strengths of 400 to 470 MPa (58 to 68 ksi), yield strengths of 205 to 275 MPa (30 to 40 ksi), and elongations of 10 to 40% can be realized. As shown in Fig. 10(a), they also offer superior elevated-temperature properties when compared to nickel-alloyed gray irons.

Elevated-Temperature Properties. The chromium-bearing types D-2, D-2B, D-3, D-4, and D-5B and the high-silicon type D5S provide useful mechanical properties at temperatures as high as 800 °C (1475 °F). The tensile properties of type D-2 from room temperature up to 760 °C

Table 7 Compositions of nodular-graphite (ductile) austenitic cast irons in accordance with ASTM A 439

		Composition, %					
Type	UNS number	TC(a)	Si	Mn	P	Ni	Cr
D-2	F43000	3.00 max	1.50–3.00	0.70–1.25	0.08 max	18.0–22.0	1.75–2.75
D-2b	F43001	3.00 max	1.50–3.00	0.70–1.25	0.08 max	18.0–22.0	2.75–4.00
D-2c	F43002	2.90 max	1.00–3.00	1.80–2.40	0.08 max	21.0–24.0	0.50 max
D-3	F43003	2.60 max	1.00–2.80	1.00 max	0.08 max	28.0–32.0	2.50–3.50
D-3a	F43004	2.60 max	1.00–2.80	1.00 max	0.08 max	28.0–32.0	1.00–1.50
D-4	F43005	2.60 max	5.00–6.00	1.00 max	0.08 max	28.0–32.0	4.50–5.50
D-5	F43006	2.60 max	1.00–2.80	1.00 max	0.08 max	34.0–36.0	0.10 max
D-5b	F43007	2.40 max	1.00–2.80	1.00 max	0.08 max	34.0–36.0	2.00–3.00
D-5S	…	2.30 max	4.9–5.5	1.00 max	0.08 max	34.0–37.0	1.75–2.25

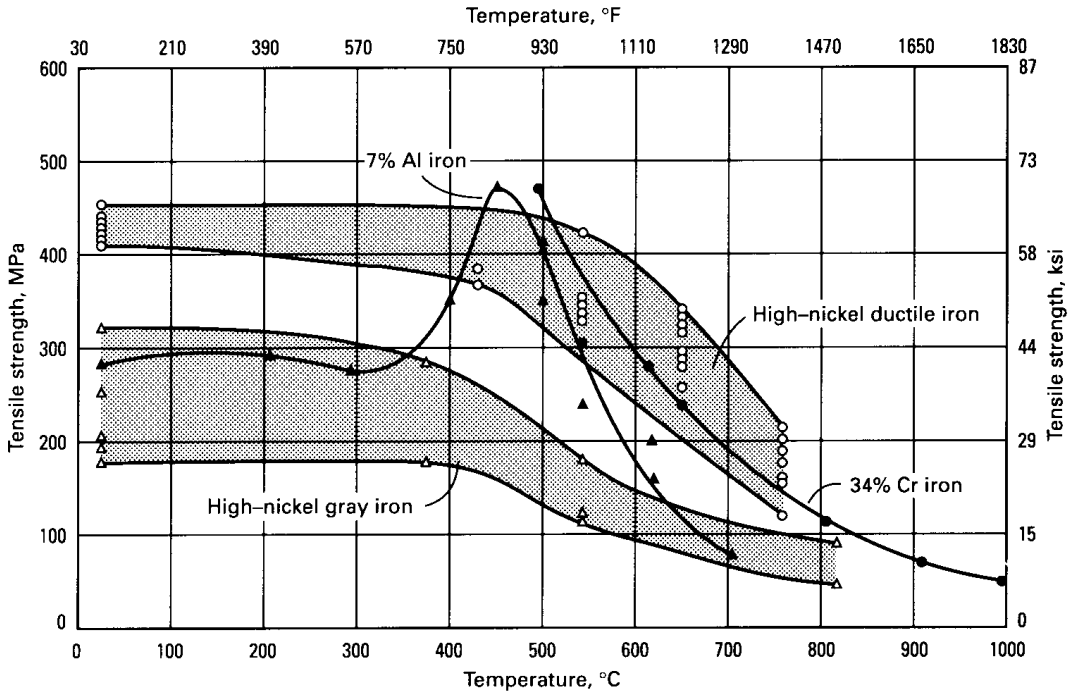
(a) Total carbon

(1400 °F) are shown in Fig. 11. Typical stress-rupture data for the austenitic 20Ni, 20Ni-1Mo, 30Ni, and 30Ni-1Mo ductile irons are given in Fig. 12, along with data for ferritic 4Si and 4Si-1Mo. For comparison, stress rupture data for a cast 19Cr-9Ni stainless steel (ASTM A 297, grade HF) are included. The addition of 1% Mo to types D-2, D-3, and D-5B increases the creep and stress-rupture strengths to levels equal or superior to those of cast stainless steels.

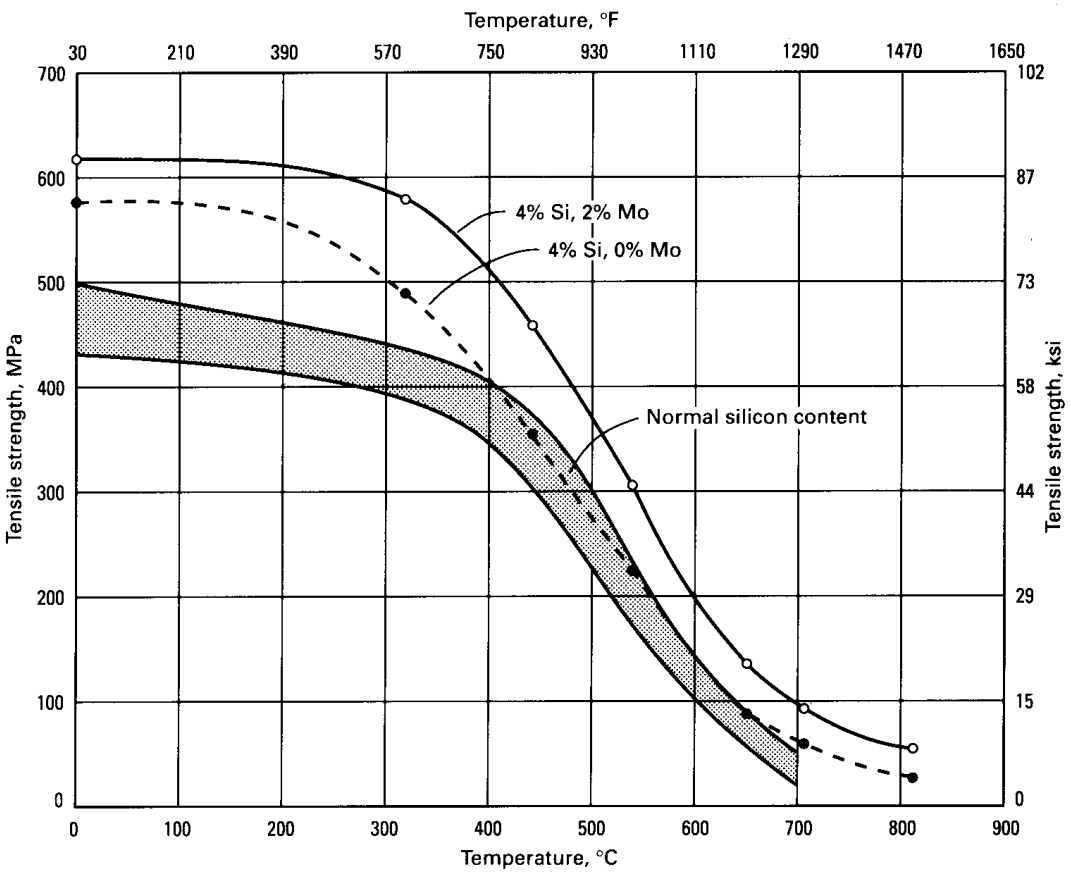
Corrosion Resistance. There is essentially no difference between the corrosion resistance of ductile and gray Ni-Resists. These materials are fairly resistant to such acids as concentrated sulfuric acid and phosphoric acid at slightly elevated temperatures, hydrochloric acid at room temperature, and organic acids such as acetic acid, oleic acid, and stearic acid. When nickel levels exceed 18%, austenitic cast irons are nearly immune to alkali or caustics, although stress corrosion can occur.

Resistance to Scaling and Growth. Ni-Resists exhibit resistance to elevated-temperature scaling and growth up to 815 °C (1500 °F) in most oxidizing atmospheres and good performance in steam service up to 530 °C (990 °F). They can withstand sour gases and liquids up to 400 °C (750 °F). The maximum temperature of use is 540 °C (1000 °F) if appreciable sulfur is present in the atmosphere. Austenitic cast iron can be employed at temperatures as high as 950 °C (1740 °F). Tables 8 and 9 provide growth and oxidation resistance data for nickel-alloyed austenitic irons.

Wear Resistance. The presence of dispersed graphite and the work-hardening character of high-alloy ductile irons provide a high level of resistance to frictional wear and galling (Ref 11). Types D-2, D-2C, D-3A, and D-4 offer good wear properties when used with a wide variety of other metals at temperatures from subzero to 815 °C (1500 °F). Tests performed from room temperature to 540 °C (1000 °F) have shown that types D-2 and D-2C have lower wear rates than bronze, unalloyed ductile iron, and Inconel 600 (Ref 11). The improved wear resistance is attributed to



(a)



(b)

Fig. 10 Short-time elevated-temperature tensile strengths of (a) alloy irons and (b) ferritic nodular irons

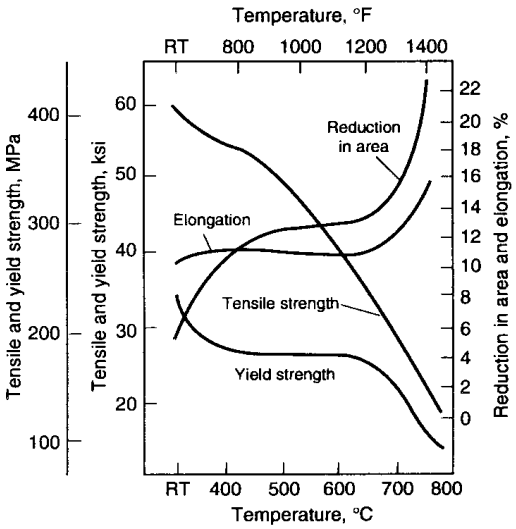


Fig. 11 Elevated-temperature tensile properties of type D-2 ductile Ni-Resist. RT, room temperature. Source: Ref 9

Table 8 Growth of high-nickel irons in superheated steam at 480 °C (900 °F)

	Growth, mm/m or 0.001 in./in., after:		
Type of iron	500 h	1000 h	2500 h
Gray iron (unalloyed)	2.3	5.2	14
High-nickel gray iron (20% Ni)	0.5	1.0	1.5
High-nickel gray iron (30% Ni)	0.3	0.45	0.48
High-nickel ductile iron (20% Ni)	0.3	0.5	0.5
High-nickel ductile iron (30% Ni)	0.3	nil	nil

Source: Ref 9

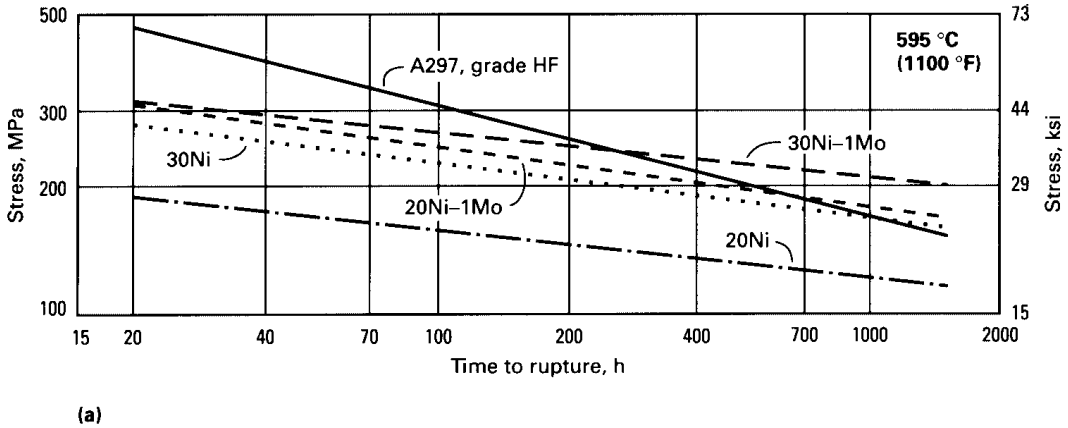
the spheroidal graphite and the formation of a nickel oxide film at higher temperatures. Types D-2B and D-3 provide inferior wear resistance compared to other high-alloy ductile irons, because they contain massive carbides that might abrade a mating material.

Ductile Ni-Resist castings, particularly those containing higher chromium levels, provide excellent service where resistance to erosion and corrosion are required, such as in the handling of wet steam, salt slurries, and relatively high-velocity corrosive liquids. Steam turbine components such as diaphragms, shaft seals, and control valves are proven examples of the excellent resistance of types D-2 and D-3 to steam erosion at high temperatures. Resistance to cavitation erosion makes high-alloy ductile irons suitable for pump impellers and small-boat propellers. Higher-chromium types D-2B, D-3, and D-4 are recommended when cavitation erosion is severe. Service results show that type D-2 is superior to straight chromium stainless steels or bronzes in resisting cavitation for applications such as boat propellers and pump impellers (Ref 11).

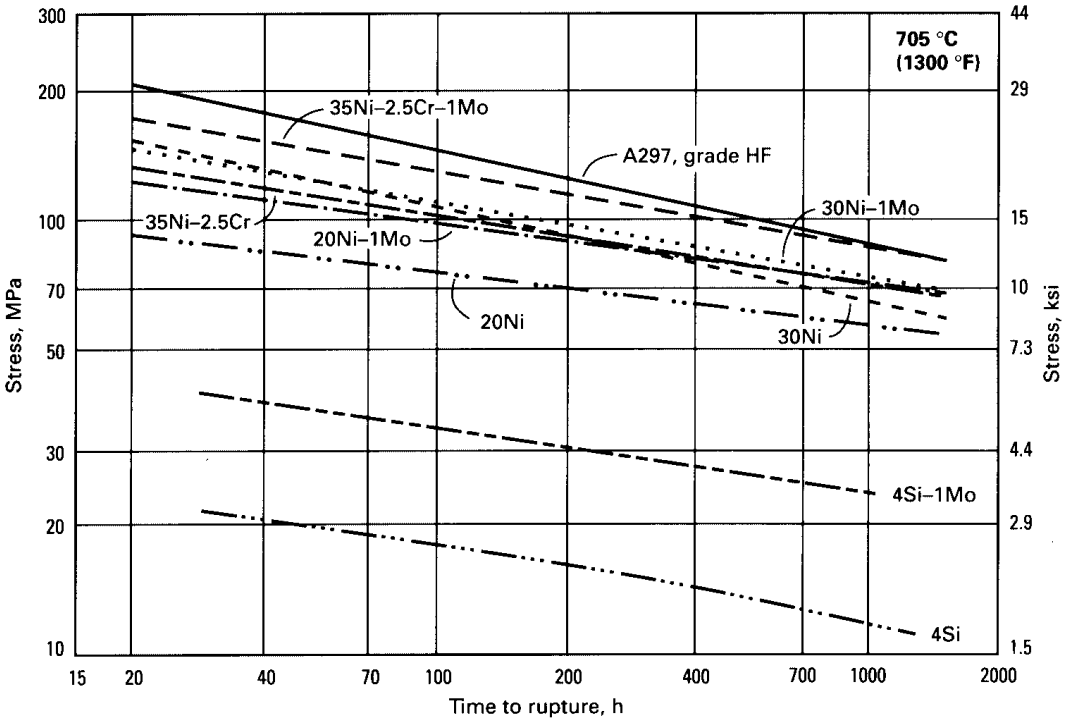
Table 9 Oxidation resistance of ductile Ni-Resist cast irons

	Oxide penetration			
	Test 1(a)		Test 2(b)	
Alloy	mm/year	mils/year	mm/year	mils/year
2.5% Si ductile iron	1.1	42	12.7	500
5.5% Si ductile iron	0.1	4	1.3	51
Ductile Ni-Resist type D-2	1.1	42	4.4	175
Ductile Ni-Resist type D-2C	1.8	70	…	…
Ductile Ni-Resist type D-4	1.1	4	nil	nil
Gray Ni-Resist type 2	2.5	98	7.6	300
Type 309 stainless steel	nil	nil	nil	nil

(a) Tested in air atmosphere, 400 h at 705 °C (1300 °F). (b) Tested in air atmosphere and exposed to a heat cycle: 600 h at 870–925 °C (1600–1700 °F); 600 h at 870–925 °C (1600–1700 °F) and 425–480 (800–900 °F); and 600 h at 425–480 °C (800–900 °F). Source: Ref 10



(a)



(b)

Fig. 12 Typical stress-rupture properties of high-nickel heat-resistant ductile irons. (a) At 595 °C (1100 °F). (b) At 705 °C (1300 °F). Source: Ref 9

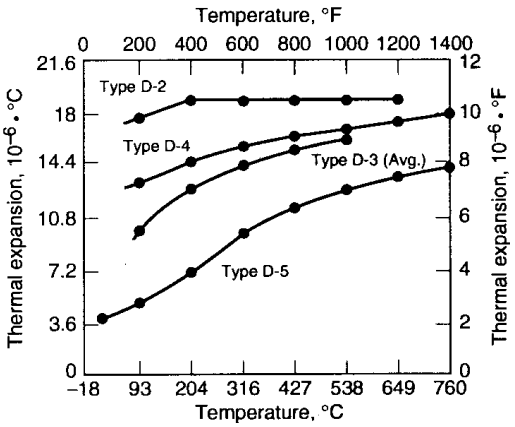


Fig. 13 Mean coefficient of thermal expansion for various types of ductile Ni-Resists. Similar behavior is exhibited by flake graphite (gray) Ni-Resists. RT, room temperature (20 °C or 70 °F). Source: Ref 9

Thermal Expansion Characteristics. Figure 13 illustrates the wide range of thermal expansion exhibited by the different types of ductile Ni-Resist irons. High-expansion types D-2 and D-4 are used to match the expansion of materials such as aluminum, copper, bronze, and austenitic stainless steels. Type D-3, with higher nickel levels, is used to obtain the controlled, intermediate thermal expansion required to match the thermal expansions of a wide variety of steels and cast irons. Types D-5 and D-5B are recommended for applications requiring maximum dimensional stability (minimum expansion), such as machine tool parts, glass molds, and gas turbine housings.

High-Silicon Ductile Irons

High-silicon ductile irons containing 4 to 6% Si, either alone or combined with up to 2% Mo, were developed to meet the increasing demands for high-strength ductile irons capable of operating at elevated temperatures in applications such as exhaust manifolds or turbocharger casings.

The primary properties required for such applications are:

- Oxidation resistance
- Structural stability
- Elevated-temperature strength
- Resistance to thermal cycling

Resistance to Oxidation and Growth. Silicon enhances the performance of ductile iron at elevated temperatures by stabilizing the ferritic matrix and forming a silicon-rich surface layer that inhibits further oxidation. Stabilization of the ferrite phase reduces elevated-temperature growth in two ways. First, silicon raises the critical temperature at which ferrite

transforms to austenite (Fig. 14). The critical temperature is considered to be the upper limit of the useful temperature range for ferritic ductile irons. Above this temperature, the expansion and contraction associated with the transformation of ferrite to austenite can cause distortion of the casting and cracking of the surface oxide layer, reducing oxidation resistance. Second, the strong ferritizing tendency of silicon stabilizes the matrix against the formation of carbides and pearlite, reducing the growth associated with the decomposition of these phases at elevated temperatures.

Silicon is highly effective in protecting ductile iron from oxidation through the formation of a silicon-rich oxide layer that inhibits further oxidation. The oxidation protection offered by silicon increases with increasing silicon content (Fig. 15). Silicon levels above 4% are sufficient to prevent any significant weight gain after the formation of an initial oxide layer.

Elevated-Temperature Strength. For most applications, alloying with 0.5 to 1% Mo provides adequate elevated-temperature strength and creep resistance. Higher molybdenum additions are used when maximum elevated-temperature strength is needed. High molybdenum additions (>1%) tend to generate interdendritic carbides of the Mo_2C type, which persist even through annealing, and tend to reduce toughness and ductility at room temperature.

Silicon lowers the eutectic carbon content, which must be controlled to avoid graphite flotation. For 4% Si irons, the carbon content should range from 3.2 to 3.5% C, depending on section size, and at 5% Si it should be about 2.9% C.

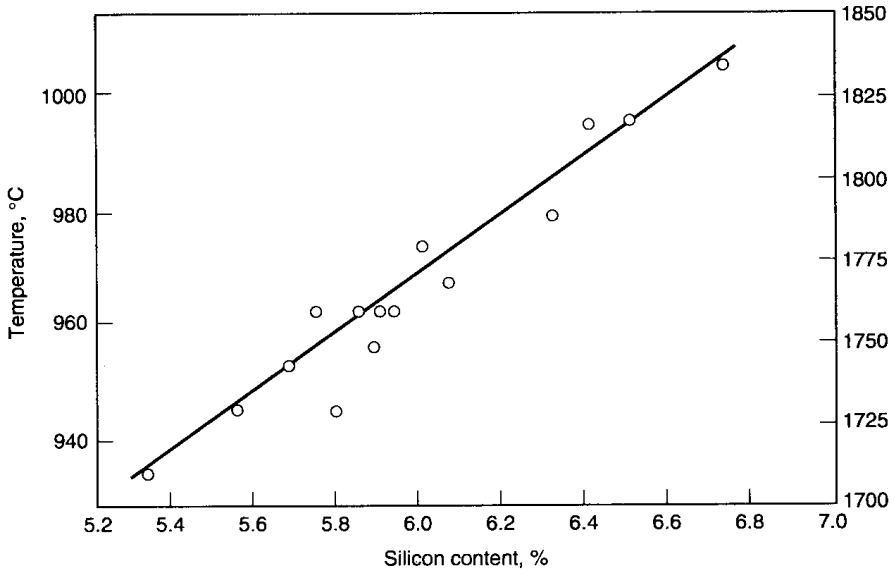


Fig. 14 Effect of silicon content on the critical temperature in cast irons. Source: Ref 10

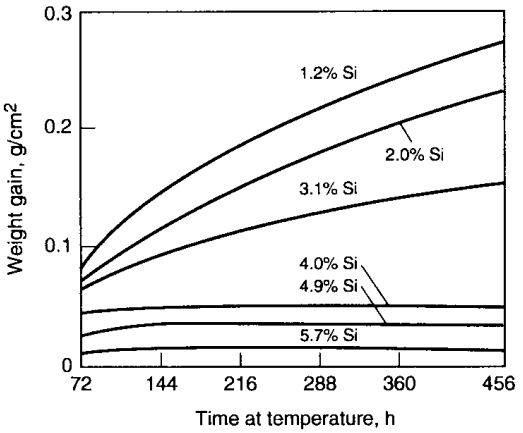


Fig. 15 Effect of silicon on the oxidation of ferritic ductile iron in air at 650 °C (1200 °F). Source: Ref 10

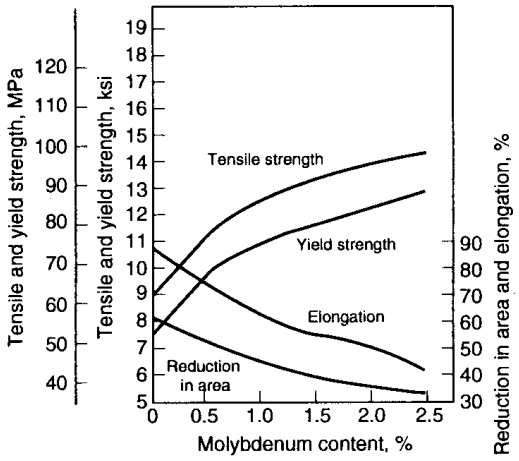


Fig. 16 Effect of molybdenum content on the elevated-temperature (705 °C, or 1300 °F) tensile properties of 4% Si ductile irons that were annealed at 790 °C (1450 °F). Source: Ref 9

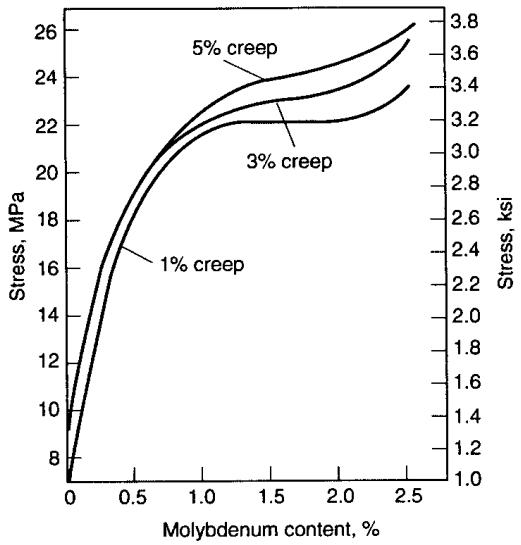


Fig. 17 Effect of molybdenum content on the creep rates of 4% Si ductile irons that were annealed at 790 °C (1450 °F) and held at 705 °C (1300 °F) for 1000 h. Source: Ref 9

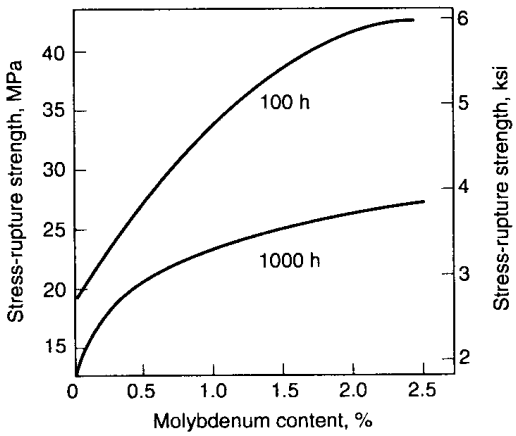


Fig. 18 Effect of molybdenum content on the stress-rupture strength at 705 °C (1300°F) for 4% Si ductile irons annealed at 790 °C (1450 °F). Source: Ref 9

Figure 10(b) shows the increase in short-time elevated temperature strength made possible by increasing the silicon content to 4% or combining silicon with molybdenum. Figure 16 illustrates the improvement in yield and tensile strengths at 700 °C (1300 °F) that can be achieved with molybdenum contents up to 2.5%.

Although there is a continuous increase in the stress-rupture strength and a reduction in creep rates as molybdenum contents are increased from 0 to 2.5%, the greatest response to increased molybdenum contents is

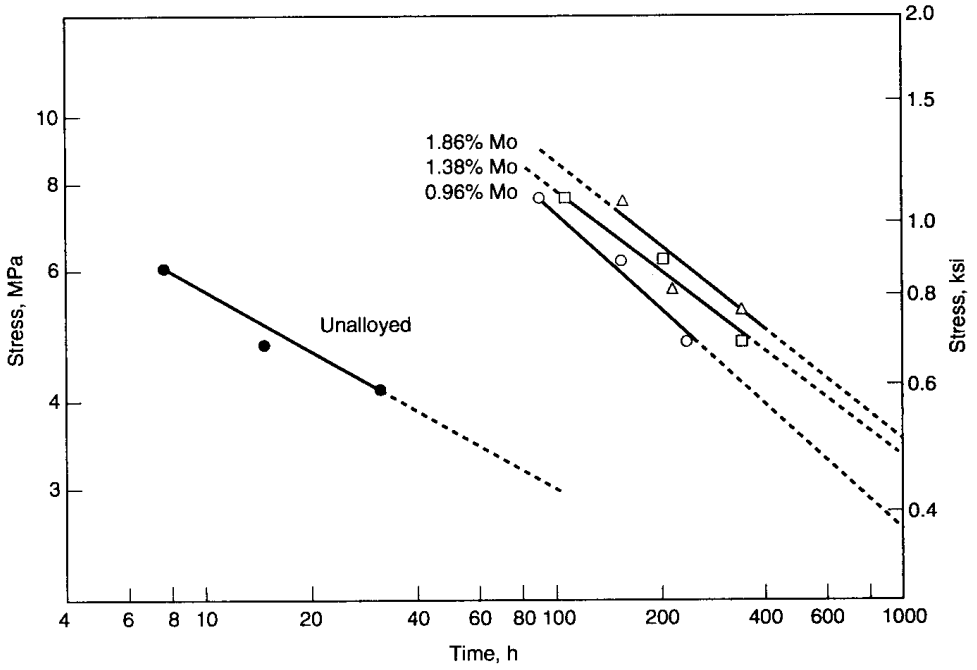


Fig. 19 Effect of molybdenum content on the time and stress to induce 1% creep at 815 °C (1500 °F) for 4% Si ductile irons. Source: Ref 9

realized from the additions of 0.5 and 1.0%. Figures 17 and 18 show the effects of molybdenum additions on the creep rates and stress-rupture properties of 4% Si ductile irons. Figure 19 shows creep data for 4% Si irons alloyed with 0.96 to 1.86% Mo.

REFERENCES

1. R.B. Gundlach, C.R. Loper, Jr., and B. Morgensteren, Composition of Ductile Irons, *Ductile Iron Handbook,* American Foundrymen's Society, 1992, p 66–109
2. "The Fatigue Life of Cast Surface of Malleable and Nodular Iron," Bulletin 177, Metals Research and Development Foundation
3. D.L. Sponseller, W.G. Scholz, and D.F. Rundle, Development of Low-Alloy Ductile Irons for Service at 1200–1500 F, *AFS Trans.,* Vol 76, 1968, p 353–368
4. J.F. Wallace and L.J. Ebert, How Composition Affects the Properties of Ductile Iron, *Met. Prog.,* Dec 1961, p 92–98
5. D.J. Moore, B.S. Shugart, K.L. Hayrynen, and K.B. Rundman, A Microstructural Determination of Isothermal Transformation Diagrams in a Low Alloy Ductile Iron, *Trans. AFS,* 1990
6. Y.H. Lee and R.C. Voight, The Hardenability of Ductile Irons, *Trans. AFS,* Vol 97, 1989, p 915–938
7. B.V. Kovacs, Pearlitic Stabilization in Cast Irons, *Trans. AFS,* Vol 89, 1981, p 79–96

8. Austempered Ductile Iron, *Ductile Iron Data for Design Engineers,* QIT-Fer et Titane Inc., 1990, p 4–1 to 4–34
9. Metallurgy and Properties of High-Alloy Graphitic Irons, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 123–130
10. Elevated-Temperature Properties, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 409–427
11. Tribological Behavior, *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 448–459

SELECTED REFERENCES

- *ASM Specialty Handbook*: *Cast Irons,* J.R. Davis, Ed., ASM International, 1996
- *Ductile Iron Handbook,* W.A. Henning, J. Mercer, and M.F. Burdin, Ed., American Foundrymen's Society, 1992

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Compacted Graphite Irons

Introduction and Overview

Compacted graphite (CG) irons are the newest member of the cast iron family. Compacted graphite irons have inadvertently been produced in the past as a result of insufficient magnesium or cerium levels in melts intended to produce ductile (spheroidal or nodular graphite) iron; however, it has only been since 1965 that CG iron has occupied its place in the cast iron family as a material with distinct properties requiring distinct manufacturing technologies. Also known as vermicular graphite cast iron, the CG irons are more widely produced in Europe than in the United States or elsewhere.

Graphite Morphology. Compacted graphite irons have a graphite shape intermediate between spheroidal and flake (gray irons) morphologies. An acceptable CG iron is one in which there is no flake graphite in the structure and for which the amount of spheroidal graphite is less than 20%; that is, 80% of all graphite is compacted. Typically, CG looks like type IV graphite described in ASTM A 247, and most of the properties of CG irons lie between those of gray iron and ductile iron.

A typical CG iron microstructure is shown in Fig. 1. Although the two-dimensional appearance (light micrograph) of compacted graphite is that of flakes with length-to-thickness ratios of 2 to 10 (Fig. 1a), the three-dimensional SEM structure (Fig. 1b) shows that the graphite does not appear in flakes, but rather in clusters interconnected within the eutectic cell.

The applications of CG irons stem from their intermediate position between gray and spheroidal graphite (SG) irons. Compared to gray irons, CG irons have certain advantages:

- Higher tensile strength at the same carbon equivalent, which reduces the need for expensive alloying elements such as nickel, chromium, copper, and molybdenum
- Higher ratio of tensile strength to hardness
- Much higher ductility and toughness, which result in a higher safety margin against fracture
- Lower oxidation and growth at high temperatures
- Less section sensitivity for heavy sections

Compared to SG irons, the advantages of CG irons are:

- Lower coefficient of thermal expansion
- Higher thermal conductivity
- Better resistance to thermal shock
- Higher damping capacity
- Better castability, leading to higher casting yield and the capability for pouring more intricate castings
- Improved machinability

Compacted graphite iron can be substituted for gray iron in all cases in which the strength of gray iron has become insufficient, but in which a change to ductile iron is undesirable because of the less favorable casting properties of the latter. Examples include bed plates for large diesel engines, crankcases, gearbox housings, turbocharger housings, connecting forks, bearing brackets, pulleys for truck servodrives, sprocket wheels, and eccentric gears.

Because the thermal conductivity of CG iron is higher than that of ductile iron, CG iron is preferred for castings operating at elevated temperature

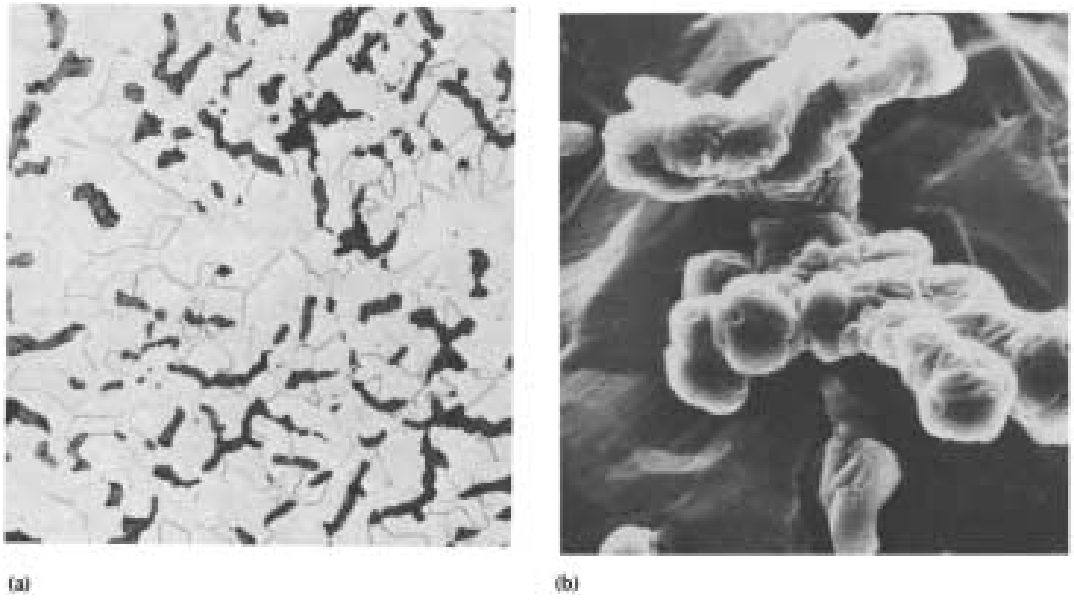


Fig. 1 Typical microstructures of CG irons. (a) Optical micrograph. Etched with nital. (b) SEM micrograph showing true shape of graphite in CG iron. Full deep etch. 395×

and/or under thermal fatigue conditions. Applications include ingot molds, crankcases, cylinder heads, exhaust manifolds, and brake disks.

Composition Requirements and Control

Carbon Equivalent. The characteristic properties of CG irons have been demonstrated over a rather wide range of carbon equivalent (CE) values, extending from hypoeutectic (CE = 3.7) to hypereutectic (CE = 4.7), with carbon contents of 3.1 to 4.0% and silicon in amounts of 1.7 to 3.0%. At constant silicon levels, a lower CE slightly increases the chilling tendency and results in lower nodularity. At constant CE, higher silicon increases nodularity. The optimum carbon and silicon contents can be selected from Fig. 2.

The optimum CE must be selected as a function of section size. For a given section size, too high a CE will result in graphite flotation, as in the case of spheroidal graphite cast iron; too low a CE may result in increased chilling tendency. For wall thicknesses ranging from 10 to 40 mm (0.4 to 1.6 in.), eutectic composition (CE = 4.3) is recommended in order to obtain optimum casting properties.

Manganese and Phosphorus Contents. The manganese content of CG iron can vary between 0.1 and 0.6%, depending on whether a ferritic or pearlitic structure is desired. The phosphorus content should be less than 0.06% in order to obtain maximum ductility from the matrix.

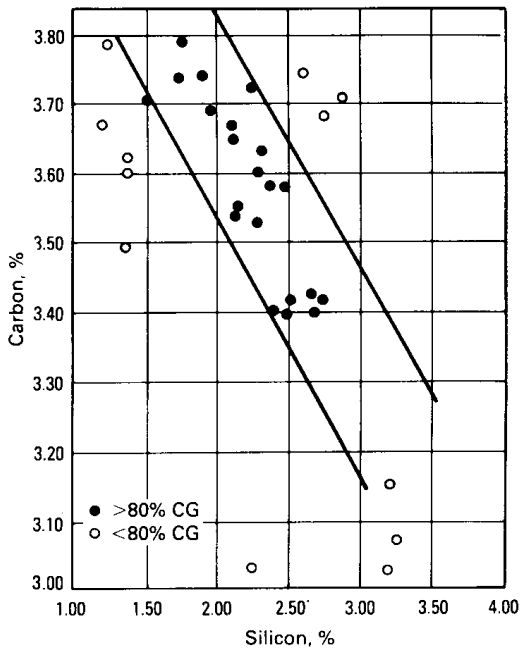


Fig. 2 Optimum range for carbon and silicon contents for CG iron

Sulfur Content. Although CG iron has been produced from base irons having sulfur contents as high as 0.07 to 0.12%, it is probably more economical to desulfurize the iron to a level of 0.01 to 0.025% before liquid treatment. The higher the sulfur content, the more alloy is required for melt treatment. Also, the risk of missing the composition window for CG iron is increased, because the residual treatment elements must be balanced with the residual sulfur. Typical residual sulfur levels after treatment are 0.01 to 0.02%.

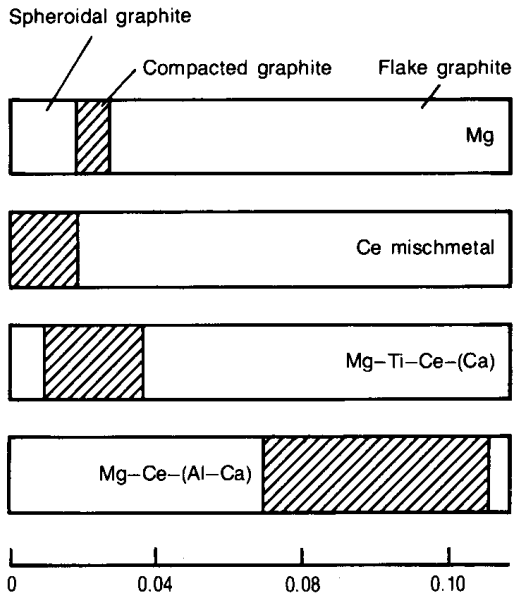
Melt Treatment Elements. The change in graphite morphology from the flake graphite in the base iron to the compacted graphite in the final iron is achieved by liquid treatment with different minor elements. These elements may include one or more of the following: magnesium, rare earths (cerium, lanthanum, praseodymium, etc.), calcium, titanium, and aluminum. Table 1 lists the compositions of typical treatment alloys used in the production of CG irons. The amounts and combinations to be used are a function of the method of liquid treatment, base sulfur, section thickness, and so forth, and are discussed in the article "Foundry Practice for Cast Irons" in the *ASM Specialty Handbook: Cast Irons*. For example, Fig. 3 shows some typical correlations between treatment method (level of minor elements), initial sulfur level, and graphite shape when producing CG irons.

Alloying elements, such as copper, tin, molybdenum, and even aluminum, can be used to change the as-cast matrix of CG iron from ferrite to pearlite. Typical ranges are 0.48% Cu or 0.033% Sn, 0.5 to 1% Mo, and up to 4.55% Al. Regardless of the alloying elements used, the high ferritizing tendency of CG iron should be taken into account. Figure 4 shows that even strong pearlite promoters such as copper or tin show reduced effectiveness in CG iron. The same is true when treating with cerium-mischmetal. A fully pearlitic structure could not be obtained even at 1.7% Cu when using high-purity charge materials. Tin, however, is effective. As shown in Fig. 5, 95% pearlite was obtained with 0.13% Sn. To produce a pearlitic

Table 1 Nominal compositions of typical melt treatment alloys for compacted graphite iron

Alloy number	Composition, %								
	Compactizing elements					Anticompactizing elements		Neutral elements	
	Mg	Ce	La	TRE(a)	Ca	Ti	Al	Si	Fe
1	5	…	…	…	1	…	<1.2	45	Balance
2	5	0.3	…	0.3	<1	9	<1.5	52	Balance
3	5	0.3	…	0.3	4.5	9	1.2	50	Balance
4	…	24	14.4	48	7.5	…	4.3	33.2	Balance
5	…	30	50	80	…	…	…	…	Balance
6	…	16	80	96	…	…	…	…	Balance
7	…	2.9	26.5	29.4	0.63	…	0.13	30.5	Balance
8	3.7	0.8	0.5	1.7	1.05	…	0.88	45.3	Balance
9	4.3	0.7	1.8	2.9	0.66	…	0.9	45.3	Balance

(a) TRE, total rare earth elements



Spheroidizer	ΔS range(a) for compacted iron, %
Mg + Ce	–0.0155 to –0.032
Mg + Ti > 0.10%	–0.0155 to –0.042
Mg + Ti 0.05 – 0.1% + Al 0.2 – 0.3%	–0.0110 to –0.055
Mg + Al > 0.35%	–0.0060 to –0.35

(a) ΔS: final % S – 0.34 (% residual elements) – 1.33 (% Mg)

Fig. 3 Optimum range of initial sulfur level as a function of type (figure) and amount (table) of minor elements used for graphite compaction. The table shows the sulfur range, ΔS, for compacted iron formation with different spheroidizers in an iron composition of 3.5% C, 2.1% Si, 0.75% Mn, and 0.03 to 0.08% P.

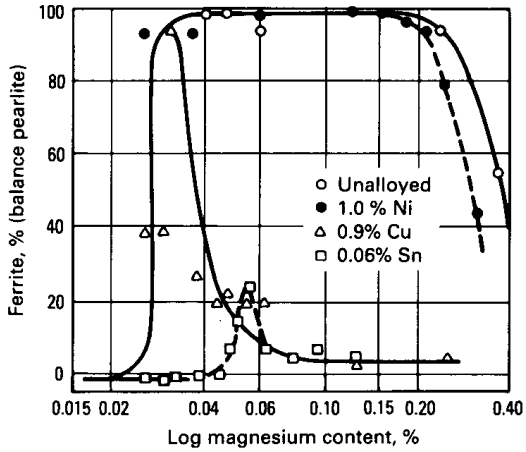


Fig. 4 The effect of copper, nickel, and tin on the type of matrix in the composition range between CG and gray iron of 25 mm (1 in.) wall thickness

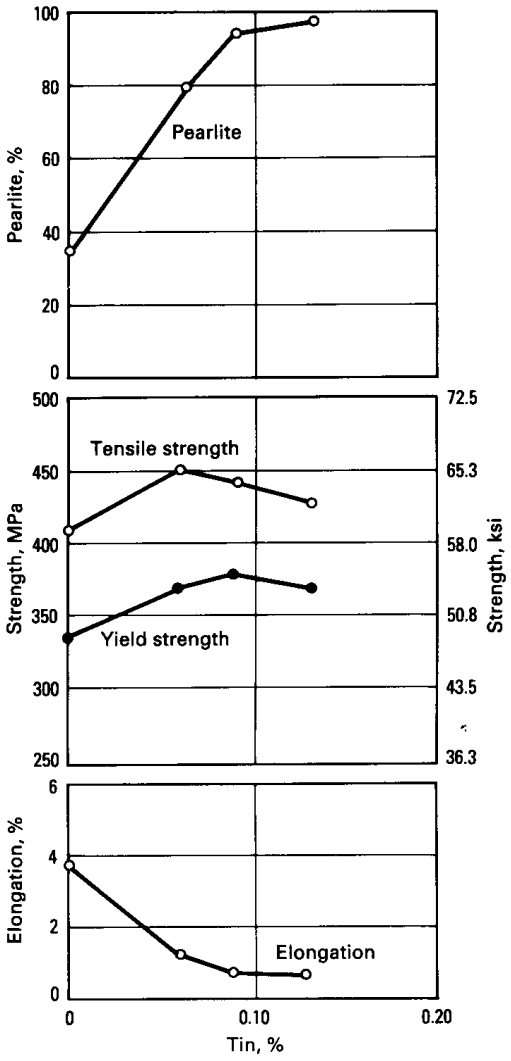


Fig. 5 The effect of tin on pearlite content and tensile properties of as-cast CG iron 25 mm (1 in.) thick

matrix, therefore, it may be necessary to add higher than usual levels of alloying elements or to make multiple additions of two or three elements.

Effects of Alloying on Properties

The tensile properties of CG irons are much less sensitive to variations in CE than those of gray irons. Even at CE near the eutectic value of 4.3, both pearlitic and ferritic CG irons have higher strengths than does low-CE, high-duty, unalloyed gray cast iron (Fig. 6).

An increase in the silicon content up to 2.6% benefits strength and hardness in both the as-cast and annealed conditions (Fig. 7). This is true even though the matrix becomes more ferritic, because silicon strengthens the

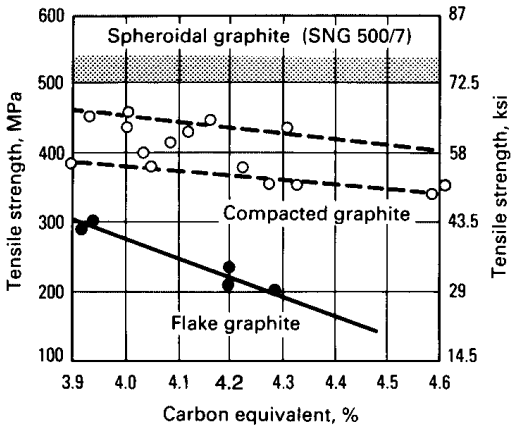


Fig. 6 Effect of carbon equivalent on the tensile strength of flake, compacted, and spheroidal graphite irons cast in 30 mm (1.2 in.) diam bars

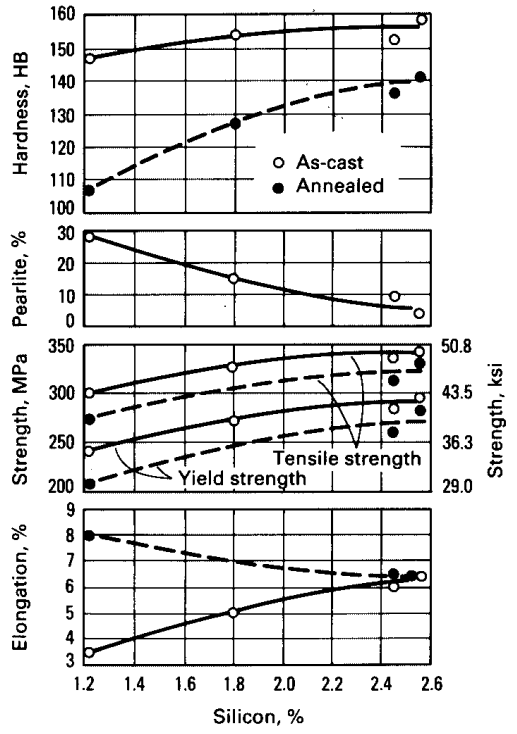


Fig. 7 The effect of silicon on mechanical properties of CG irons produced by the in-mold process. Carbon equivalents ranged from 4.33 to 4.45.

ferrite. The same is true in the case of as-cast elongation, because there is a decrease in the amount of pearlite with an increase in silicon, while elongation in the annealed condition decreases. Although increasing the phosphorus content slightly improves strength, a maximum of 0.04% P is desirable to avoid lower ductility and impact strength.

The pearlite/ferrite ratio, and thus the strength and hardness of CG irons, can be increased by the use of a number of alloying elements, such

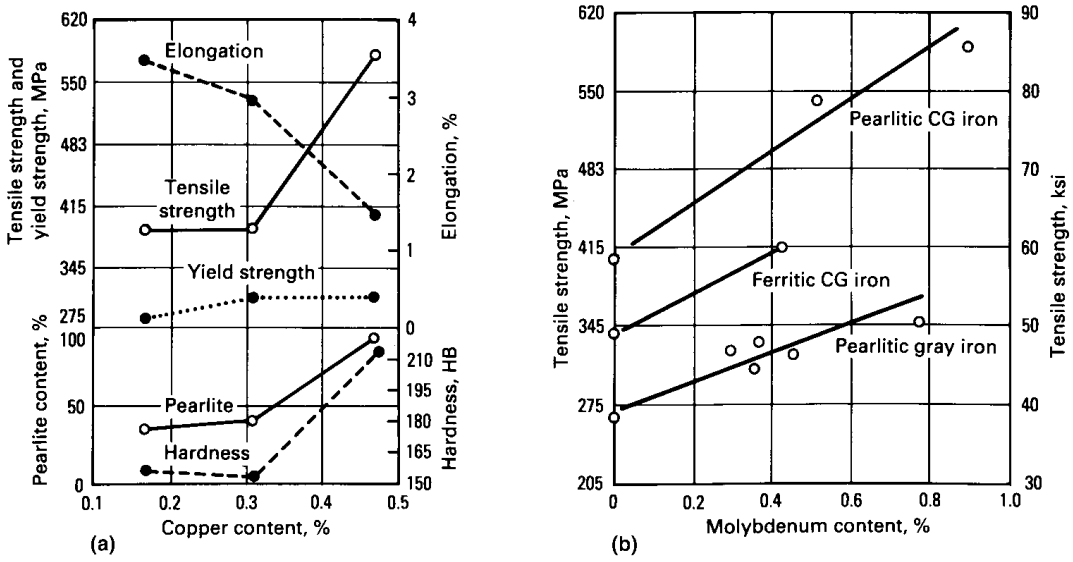


Fig. 8 Effect of (a) copper and (b) molybdenum on the tensile properties of CG iron

Table 2 Effect of heat treatment and alloying with nickel on the tensile properties of CG iron measured on a 25 mm section size

		Tensile strength		Yield strength				
Heat treatment	Iron matrix(a)	MPa	ksi	MPa	ksi	Elongation, %	Hardness, HB	Nickel, %
As-cast	60% F	325	47.1	263	38.1	2.8	153	0
Annealed(b)	100% F	294	42.6	231	33.5	5.5	121	0
Normalized(c)	90% P	423	61.3	307	44.5	2.5	207	0
As-cast	…	427	61.9	328	47.6	2.5	196	1.53
Annealed(b)	100% F	333	48.3	287	41.6	6.0	137	1.53
Normalized(c)	90% P	503	73	375	54.4	2.0	235	1.53

(a) F, ferrite; P, pearlite. (b) Annealed, 2 h at 900 °C (1650 °F), cooled in furnace to 690 °C (1275 °F), held 12 h, cooled in air. (c) Normalized, 2 h at 900 °C (1650 °F), cooled in air

as copper, nickel, molybdenum, tin, manganese, arsenic, vanadium, and aluminum. The effect of copper and molybdenum on the tensile properties of CG irons is shown in Fig. 8. After annealing to a fully ferritic structure, it is possible to increase the yield point of CG iron by 24% when using 1.5% Ni (Table 2). This is because of the strengthening of the solid solution by nickel (6). However, additions of copper, nickel, and molybdenum may increase nodularity. Figure 9 shows some correlations of microstructure and properties for iron-carbon-aluminum CG irons produced by the in-mold process.

In order to compare the quality of different types of irons, several quality indexes can be used, such as the product of tensile strength and elongation (TS × El) or the ratio of tensile strength to Brinell hardness (TS/HB). Higher values of these indexes will characterize a better iron. Figure 10 compares the TS × El product and the TS/HB ratio for unalloyed and aluminum-alloyed CG irons. It can be seen that when 2% Si is replaced by 2% Al, a much better quality CG iron is produced.

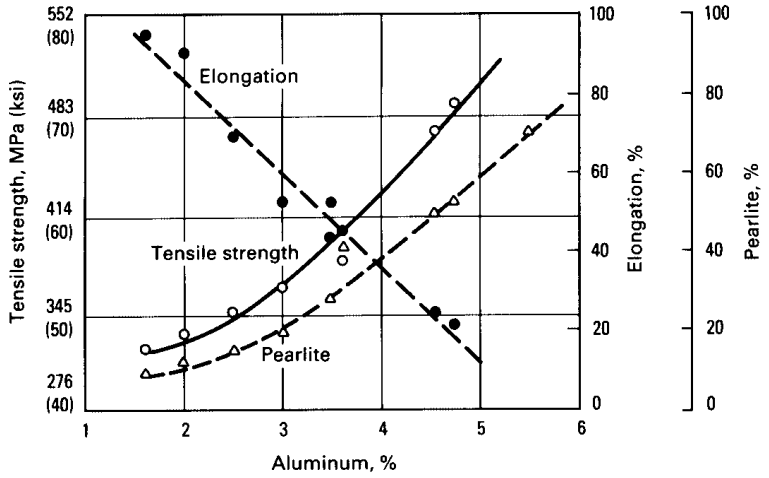


Fig. 9 The effect of aluminum on the structure and mechanical properties of CG irons produced by the in-mold process

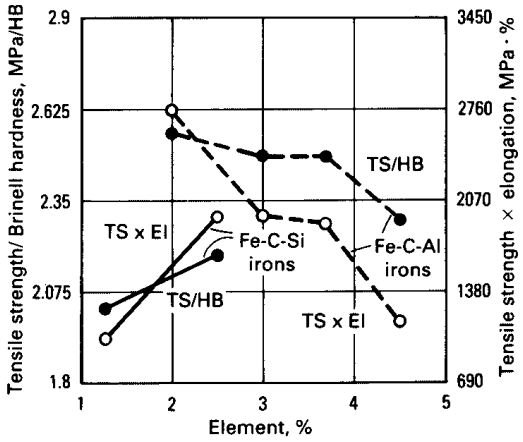


Fig. 10 Quality indexes for Fe-C-Si and Fe-C-Al irons. TS, tensile strength; El, elongation

SELECTED REFERENCES

- J. Fowler, D.M. Stefanescu, and T. Prucha, Production of Ferritic and Pearlitic Grades of Compacted Graphite Cast Iron by the In-Mold Process, *Trans. AFS,* Vol 92, 1984, p 361
- G.F. Sergeant and E.R. Evans, The Production and Properties of Compacted Graphite Irons, *Br. Foundryman,* Vol 71, 1978, p 115
- D.M. Stefanescu, R. Hummer, and E. Nechtelberger, Compacted Graphite Irons, *Casting,* Vol 15, *ASM Handbook,* ASM International, 1988, p 667–677
- D.M. Stefanescu, Compacted Graphite Iron, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook,* ASM International, 1990, p 56–70
- K.R. Ziegler and J.F. Wallace, The Effect of Matrix Structure and Alloying on the Properties of Compacted Graphite Iron, *Trans. AFS,* Vol 92, 1984, p 735

Alloying: Understanding the Basics
J.R. Davis, p100-106
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Malleable Irons

Introduction and Overview

Malleable iron is a type of cast iron that has most of its carbon in the form of irregularly shaped graphite particles instead of flakes, as in gray iron, or small graphite spherulites, as in ductile iron. Malleable iron is produced by first casting the iron as a white iron and then annealing the white cast iron to convert the iron carbide into the irregularly shaped nodules of graphite. This form of graphite in malleable iron is called *temper carbon.* Figure 1 shows the microstructure of a typical malleable cast iron. Subsequent variations in post-annealing heat treatments can produce malleable irons with ferritic, pearlitic, or martensitic microstructures.

The annealing treatment involves three important steps. The first causes nucleation of temper carbon. It is initiated during heating to a high holding temperature and occurs very early during the holding period.

The second step, first-stage graphitization (FSG), consists of holding at 900 to 970 °C (1650 to 1780 °F). During FSG, massive carbides are eliminated from the iron structure. Long holding periods at 955 °C (1750 °F) will reduce the solubility of nitrogen in iron (which should be kept at 80 to 120 ppm), thereby reducing the mechanical properties of the iron. This occurrence should be kept in mind for long, or "weekend," holding periods. When the carbides are eliminated, the iron is rapidly cooled to 740 °C (1365 °F).

The third step in the annealing treatment, second-stage graphitization (SSG), consists of slow cooling through the allotropic transformation range of the iron. During SSG, a completely ferritic matrix free of pearlite and carbides is obtained when the cooling rate is 2 to 28 °C/h (3 to 50 °F/h). This cooling rate, which depends on the silicon content of the iron and the temper carbon nodule count, may be increased to 85 °C/min (150 °F/min) by air quenching from 900 °C (1650 °F) to form a pearlitic matrix. Oil quenching from 900 °C (1650 °F) will produce a martensitic matrix. However, unless the temperature in the furnace is lowered to 845 °C



Fig. 1 Microstructure of a typical malleable cast iron showing graphite in the form of temper carbon. 4% picral etch. 250×

(1550 °F) for at least 4 h (plus 1 h for each 1 in. of section casting thickness), then raised to 900 °C (1650 °F) for 4 h (plus 1 h for each 1 in. of casting section thickness) prior to uniform quenching in oil, the matrix microstructure will not be uniform in combined carbon. This nonuniformity reduces machinability. If the hardness is reduced by extended tempering, the resulting structure may not have a good response to selective hardening.

Applications. Malleable irons have largely been replaced by ductile irons in many applications. This is due in part to the necessity of lengthy heat treatments for malleable iron and the difficulty in cooling thick sections rapidly enough to produce white iron. Malleable iron is still sometimes preferred for thin-section castings and parts that require maximum machinability and wear resistance. Examples of malleable iron applications include pipe fittings used for water, oil, steam, air, gas, and other installations, flanges and valve parts for railroad, marine, and other heavy-duty service at temperatures up to 345 °C (650 °F), and automotive components such as steering gear housings, carriers, and mounting brackets, compressor crankshafts and hubs, and surface-hardened planet carriers, transmission gears, and differential cases.

Effects of Alloying Elements

Metallurgical Control. The desired formation of temper carbon in malleable irons has two basic requirements: graphite should not form during

the solidification of the white cast iron, and graphite must be readily formed during the annealing heat treatment. These metallurgical requirements influence the useful compositions of malleable irons and the melting, solidification, and annealing procedures. Metallurgical control is based on the following criteria:

- Solidified white iron must be produced throughout the section thickness.
- An established time-temperature cycle for annealing set to minimum values in the interest of economy
- The desired graphite distribution (nodule count) must be produced upon annealing.

Changes in melting practice or composition that would satisfy the first requirement listed above are generally opposed to satisfaction of the second and third, while attempts to improve annealability beyond a certain point may result in an unacceptable tendency for the as-cast iron to be mottled instead of white.

Because of the two metallurgical requirements described above, malleable irons involve a limited range of chemical composition and the restricted use of alloys. The chemical composition of malleable iron generally conforms to the ranges given in Table 1. Small amounts of chromium (0.01 to 0.03%), boron (0.0020%), copper (~1.0%), nickel (0.5 to 0.8%), and molybdenum (0.35 to 0.5%) are also sometimes present. Table 2 summarizes the effects of various elements on the microstructural characteristics of malleable iron.

The common elements in malleable iron are generally controlled within about ±0.05 to ±0.15%. A limiting minimum carbon content is required in the interest of mechanical quality and annealability, because decreasing carbon content reduces the fluidity of the molten iron, increases shrinkage during solidification, and reduces annealability. A limiting maximum carbon content is imposed by the requirement that the casting be white as-cast. The range in silicon content is limited to ensure proper annealing during a short-cycle, high-production annealing process and to avoid the formation of primary graphite (known as mottle) during solidification of the white iron. Manganese and sulfur contents are balanced to ensure that all sulfur is combined with manganese and that only a safe, minimum quantity of excess manganese is present in the iron. An excess of either sulfur or manganese will retard annealing in the second stage and therefore

Table 1 Typical compositions for malleable iron

	Composition, %	
Element	**Ferritic**	**Pearlitic**
Total carbon	2.2-2.9	2.0-2.9
Silicon	0.9-1.9	0.9-1.9
Manganese	0.2-0.6	0.2-1.3
Sulfur	0.02-0.2	0.05-0.2
Phosphorus	0.02-0.2	0.02-0.2

Table 2 Effects of major and minor (tramp) elements on the annealing response and structure of malleable iron

Element	Principal source	Amount typically observed(a), %	Effects(b)
Carbon(c)	Pig irons, cast scrap, coke, and intentional addition	2.0–3.0	Lower levels of carbon are difficult to anneal, have strong white iron tendency, and have low fluidity. Higher levels are easier to anneal, have better fluidity, but show a tendency toward mottle
Silicon(c)	SiO_2 in ceramic linings and slags, and intentional addition (ferrosilicon). Charge materials	0.8–2.0	Acts in conjunction with carbon, and acts as a graphitizer. Silicon hardens ferrite, raising the nil-ductility transition temperature. Reduces shrinkage during solidification. Promotes ferrite in annealing
Manganese	Cast scrap and intentional addition (ferromanganese). Steel scrap	0.21–0.65	Removes the detrimental effects of sulfur: manganese in excess of $1.7 \times$ %S stabilizes carbides with little influence on solidification. Weakly retards FSG and SSG. Very high levels (8–13%) are often used in austenitic grades. Used in pearlitic grades to promote pearlite
Magnesium	Intentional addition (magnesium ferrosilicon)	ND	Promotes carbides and retards mottling
Aluminum	Ferroalloys and residual aluminum in steel, and in inoculants	0.003–0.20	0.03–0.05% decreases nodule number; over 0.05%, it increases the nodule number and increases the mottling tendency. Increases FSG and SSG
Antimony	Tramp element in cast scrap or steel. Vitreous enamel on bathtub scrap. Intentional addition	<0.005	Slightly retards FSG and SSG
Arsenic	Tramp element in cast scrap or steel	<0.011	No reported effects
Bismuth	Usually a ladle addition	0.001–0.01	Slightly retards FSG and SSG. Prevents mottling and spiking in white iron. (Note: Effect depends on section size, silicon content, etc.)
Boron	Certain pig irons, enameled scrap, and intentional addition	0.0004–0.004	Promotes FSG and SSG and increases nodule number. A large excess stabilizes carbides
Calcium	Present in ferroalloys and in inoculants	ND	Promotes mottling
Cerium	Cast scrap or intentional addition, often as mischmetal or rare-earth silicides	0.01–0.40	Retards mottling
Chromium	Alloying element in cast scrap or steel, and in some cases an intentional addition (ferrochromium)	0.02–0.10	Strongly retards FSG and SSG because of the formation of very stable carbides that are highly resistant to annealing
Copper	Nonferrous materials in scrap and intentional addition	0.11–0.21	Increases the rates of FSG and SSG. Slightly increases the nodule number
Hydrogen	Exposure to gases in melting and prior to solidification (particularly exposure to water or water vapor)	0.0002–0.0015	Retards FSG. This gas is evolved during solidification and can produce interdendritic porosity
Lead	Nonferrous materials in scrap, and may be carried in with fluorspar	<0.002	Very slight retarding effect on FSG and SSG. Causes a slight reduction in the mottling tendency
Molybdenum	Alloying element in steel or cast scrap. Intentional addition (ferromolybdenum)	0.03	Increases depth of chill and chill plus mottle. Prevents galvanic embrittlement. Slightly retards FSG and SSG
Nickel	Alloying element in cast scrap or steel, certain magnesium alloys in ductile iron production. Intentional addition	0.10	Promotes FSG and SSG while slightly increasing the nodule count. Increases strength by increasing hardenability. A nickel plus copper addition can be used to produce an austenitic grade
Nitrogen	Exposure to gases in melting, especially in arc melting operations. From core and sand binders	0.002–0.15	Stabilizes pearlite, reduces nodule number, and retards FSG and SSG
Oxygen	Gases in melting, oxides in slags	0.002–0.005	Decreases nodule number, retards FSG and SSG, and decreases mottling
Phosphorus	Certain pig irons, cast scrap, and steel	<0.20	Improves fluidity and promotes mottling. Should be less than 0.15% because it increases the nilductility transition temperature. Promotes "galvanizing" or "blue" brittleness. Effects depend on silicon content
Sulfur	Coke, carbon raisers, cast scrap	0.05–0.25	If amount present gives a Mn/S ratio >1.7%, it retards FSG and SSG and decreases the nodule number. Stabilizes carbides
Tellurium	Alloying element in steel or an intentional addition, usually in the ladle. May be present in certain "chilling" core washes	<0.004	Prevents mottling and may reduce nodule number
Tin	Usually a ladle addition. (May be present in certain types of cast scrap)	0.007–0.02	High levels retard FSG and SSG

(continued)

(a) ND, not normally detected. (b) FSG, first-stage graphitization; SSG, second-stage graphitization. (c) The individual properties associated with either carbon or silicon are interchangeable to a degree and may be assessed to some extent as a single element effect via the carbon equivalent formula CE = %C + 1/3%Si

Table 2 (continued)

Element	Principal source	Amount typically observed(a), %	Effects(b)
Titanium	Present in pig irons and in certain ferroalloys	0.01–0.02	Increases mottling tendency
Vanadium	Alloying element in scrap or steel, or an intentional addition	<0.005	Forms very stable carbides that are highly resistant to annealing
Zinc	Nonferrous materials in scrap, and in cast scrap or steel as a tramp	ND	Slightly decreases FSG and SSG
Zirconium	Present in some ferroalloys	0.005	Slightly increases annealability. Improves FSG and SSG by reacting with nitrogen, oxygen, and sulfur

(a) ND, not normally detected. (b) FSG, first-stage graphitization; SSG, second-stage graphitization. (c) The individual properties associated with either carbon or silicon are interchangeable to a degree and may be assessed to some extent as a single element effect via the carbon equivalent formula CE = %C + 1/3%Si

increase annealing costs. The chromium content is kept low because of the carbide-stabilizing effect of this element and because it retards both the first-stage and second-stage annealing reactions.

A mixture of gray iron and white iron in variable proportions that produces a mottled (speckled) appearance is particularly damaging to the mechanical properties of the annealed casting, whether ferritic or pearlitic malleable iron. Primary control of mottle is achieved by maintaining a balance of carbon and silicon contents.

Economy and castability are enhanced when the carbon and silicon contents of the base iron are in the higher proportions of their respective ranges, so some malleable iron foundries produce iron with carbon and silicon contents at levels that might produce mottle and then add a balanced, mild carbide stabilizer to prevent mottle during casting. Bismuth and boron in balanced amounts accomplish this control. A typical addition is 0.01% Bi (as metal) and 0.001% B (as ferroboron). Bismuth retards graphitization during solidification. Small amounts of boron have little effect on graphitizing tendency during solidification, but they accelerate carbide decomposition during annealing. The balanced addition of bismuth and boron permits the production of heavier sections for a given base iron or the utilization of a higher-carbon, higher-silicon base iron for a given section thickness.

Tellurium can be added in amounts from 0.0005 to 0.001% to suppress mottle. Tellurium is a much stronger carbide stabilizer than bismuth during solidification, but it also strongly retards annealing if the residual exceeds 0.003%. Less than 0.003% residual tellurium has little effect on annealing but has a significant influence on mottle control. Tellurium is more effective if added together with copper or bismuth.

Residual boron should not exceed 0.0035%, in order to avoid module alignment and carbide formation. Also, the addition of 0.005% Al to the pouring ladle significantly improves annealability without promoting mottle.

Properties. The mechanical properties of malleable iron are dominated by matrix microstructure, so the mechanical properties may relate quite well to the relative hardness levels of different matrix microstructures. This general effect of microstructure on malleable irons is similar to that of many other steels and irons. The softer ferritic matrix provides maximum

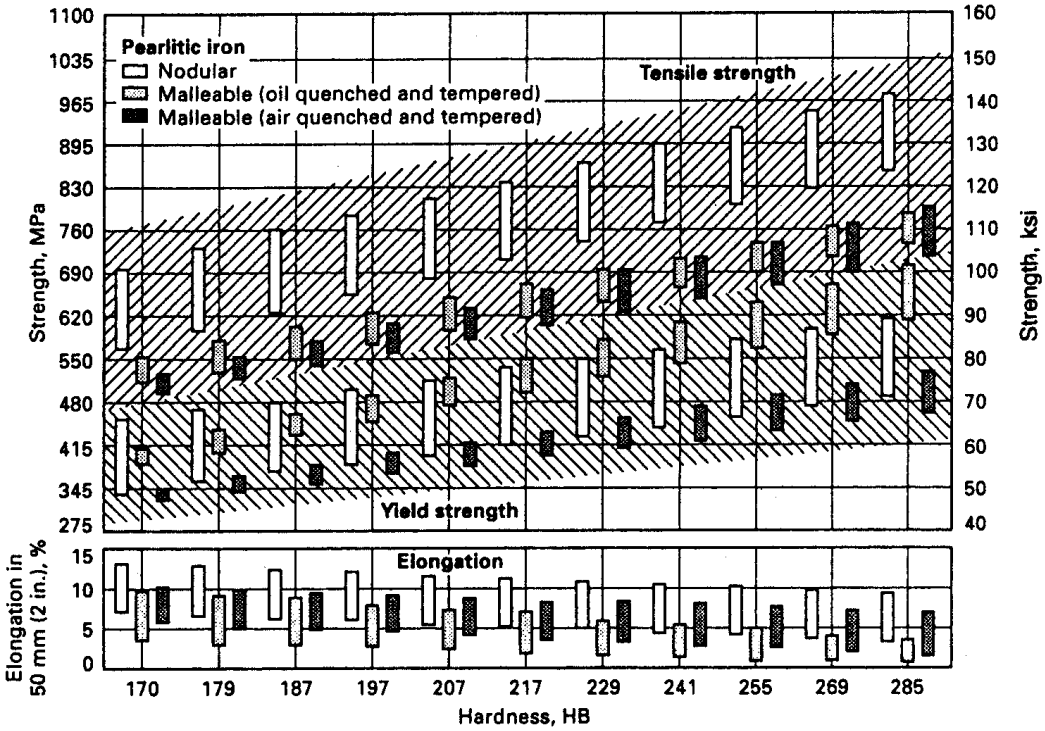


Fig. 2 Tensile properties versus hardness for two tempered pearlitic malleable cast irons and as-cast ductile iron

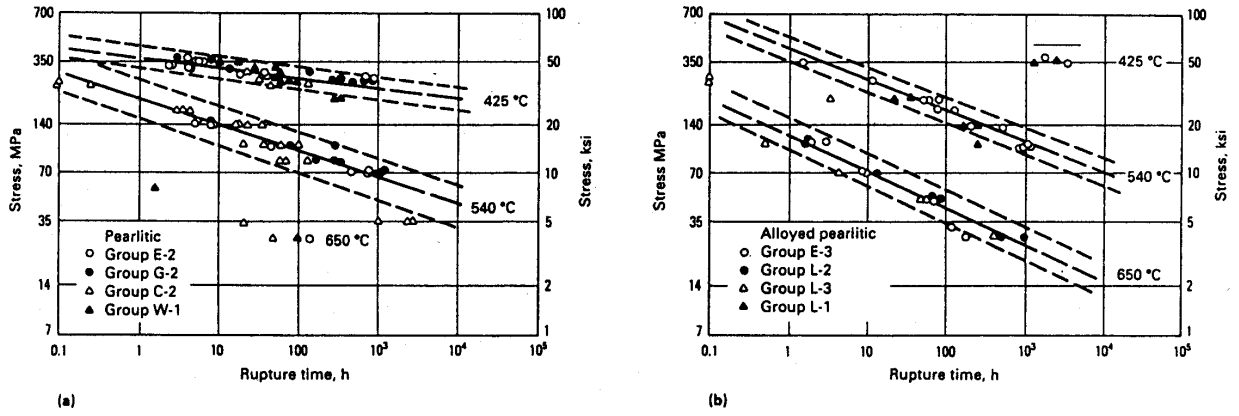
ductility with lower strength, while increasing the amount of pearlite increases hardness and strength but decreases ductility. Martensite provides further increases in hardness and strength but with additional decreases in ductility. A comparison of tensile properties with hardness of pearlitic malleable iron and as-cast ductile iron is shown in Fig. 2.

As stated earlier, metallurgical control of malleable irons is possible only by limiting their chemical compositions. Nevertheless, there are some specific alloying elements that can be added to malleable iron in rather small quantities to improve specific properties. These include:

- Copper (usually about 1%), which improves corrosion resistance
- Nickel (up to about 0.65%), which improves hardenability
- Molybdenum (up to about 0.5%), which improves high-temperature strength (Fig. 3)

SELECTED REFERENCES

- Metallurgy and Properties of Malleable Irons, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 94–106
- Heat Treating of Malleable Irons, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 205–208
- Classification and Basic Metallurgy of Cast Irons, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 3–15



Material	Composition, % C	Si	Mn	S	P	Cr	Others
Pearlitic (low carbon/high phosphorus)							
Group E-2	2.27	1.15	0.89	0.098	0.135	0.019	...
Group G-2	2.29	1.01	0.75	0.086	0.11	...	...
Pearlitic (high carbon/low phosphorus)							
Group C-2	2.65	1.35	0.41	0.15	...	0.018	0.0020 B
Group W-1	2.45	1.38	0.41	0.12	0.04	0.032	...
Alloyed pearlitic (low carbon/high phosphorus)							
Group E-3	2.21	1.13	0.88	0.110	0.122	0.021	0.47Mo, 1.03Cu
Group L-1	2.16	1.18	0.72	0.120	0.128	...	0.34Mo, 0.83Ni
Group L-2	2.16	1.18	0.80	0.123	0.128	...	0.40Mo, 0.62Ni
Group L-3	2.32	1.14	0.82	0.117	0.128	...	0.38Mo, 0.65Ni

Fig. 3 Stress-rupture plot for (a) pearlitic malleable iron and (b) alloyed pearlitic malleable iron. The solid lines are curves determined by the method of least squares from the existing data. The dashed lines define the 90% symmetrical tolerance interval. The lower dashed curve defines time and load for 95% survivors, and the upper dashed curve is the boundary for 5% survivors. Normal distribution is assumed. Note the improved performance of the molybdenum-bearing grades.

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High-Alloy White Irons

Introduction and Overview

The high-alloy white irons are primarily used for abrasion-resistant applications and are readily cast in the shapes needed in the machinery used for crushing, grinding, and general handling of abrasive materials. The large volume of eutectic carbides in their microstructures provides the high hardness needed for crushing and grinding other materials. The metallic matrix supporting the carbide phase in these irons can be adjusted by alloy content and heat treatment to develop the proper balance between resistance to abrasion and the toughness needed to withstand repeated impact.

All high-alloy white irons contain chromium to prevent formation of graphite on solidification and to ensure the stability of the carbide phase. Most also contain nickel, molybdenum, copper, or combinations of these alloying elements to prevent the formation of pearlite in the microstructure. While low-alloyed pearlitic white iron castings develop hardness in the range 350 to 550 HB, the hardness of high-alloyed white irons ranges from 450 to 800 HB. In addition, several grades contain alloy eutectic carbides (M_7C_3 chromium carbides) that are substantially harder than the iron carbide in low-alloy irons. For many applications, the increased abrasion resistance of the more expensive high-alloy white irons adds significantly to wear life, causing them to provide the most cost-effective performance.

Alloy Grades. ASTM specification A 532 covers the composition and hardness of white iron grades used for abrasion-resistant applications (Table 1). Many castings are ordered according to these specifications; however, a large number of castings are produced with modifications to composition for specific applications. It is most desirable that the designer, metallurgist, and foundry worker cooperate to specify the composition, heat treatment, and foundry practice to develop the most suitable alloy and casting design for a specific application. The standard

Table 1 Composition and hardness requirements of abrasion-resistant white irons per ASTM A 532

			Composition, wt %								
Class	Type	Designation	C	Mn	Si	Ni	Cr	Mo	Cu	P	S
I	A	Ni-Cr-HiC	2.8-3.6	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	…	0.3 max	0.15 max
I	B	Ni-Cr-LoC	2.4-3.0	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	…	0.3 max	0.15 max
I	C	Ni-Cr-GB	2.5-3.7	2.0 max	0.8 max	4.0 max	1.0-2.5	1.0 max	…	0.3 max	0.15 max
I	D	Ni-HiCr	2.5-3.6	2.0 max	2.0 max	4.5-7.0	7.0-11.0	1.5 max	…	0.10 max	0.15 max
II	A	12% Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	11.0-14.0	3.0 max	1.2 max	0.10 max	0.06 max
II	B	15% Cr-Mo	2.0-3.3	2.0 max	1.5 max	2.5 max	14.0-18.0	3.0 max	1.2 max	0.10 max	0.06 max
II	D	20% Cr-Mo	2.0-3.3	2.0 max	1.0-2.2	2.5 max	18.0-23.0	3.0 max	1.2 max	0.10 max	0.06 max
III	A	25% Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	23.0-30.0	3.0 max	1.2 max	0.10 max	0.06 max

			Hardness value													
			Sand cast, min(a) As-cast or As-cast and stress relieved			Hardened or hardened and stress relieved						Chill cast, min(b)			Softened, max		
						Level 1			Level 2								
Class	Type	Designation	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV
I	A	Ni-Cr-HiC	550	53	600	600	56	660	650	59	715	600	56	660	…	…	…
I	B	Ni-Cr-LoC	550	53	600	600	56	660	650	59	715	600	56	660	…	…	…
I	C	Ni-Cr-GB	550	53	600	600	56	660	650	59	715	600	56	660	400	41	430
I	D	Ni-HiCr	500	50	540	600	56	660	650	59	715	550	53	600	…	…	…
II	A	12% Cr	550	53	600	600	56	660	650	59	715	550	53	600	400	41	430
II	B	15% Cr-Mo	450	46	485	600	56	660	650	59	715	…	…	…	400	41	430
II	D	20% Cr-Mo	450	46	485	600	56	660	650	59	715	…	…	…	400	41	430
III	A	25% Cr	450	46	485	600	56	660	650	59	715	…	…	…	400	41	430

(a) 90% of the minimum surface hardness level shall be maintained to a depth of 40% of the casting section, with any softer material being at the thermal center of the casting. A sampling procedure should be established by agreement between the supplier and the purchaser. (b) Non-chilled areas of casting shall meet minimum hardness or sand cast requirements.

high-alloy white cast irons for abrasion-resistant applications fall into three major groups:

- The nickel-chromium white irons (class I in Table 1) are low-chromium alloys containing 3 to 5% Ni and 1 to 4% Cr, with one alloy modification that contains 7 to 11% Cr (class I, type D in Table 1). These martensitic white irons are commonly identified by the tradename of Ni-Hard types 1 to 4.
- The chromium-molybdenum white irons (class II in Table 1) contain 11 to 23% Cr and up to 3% Mo and are often additionally alloyed with nickel or copper. These white irons can be supplied either as-cast with an austenitic or austenitic-martensitic matrix (Fig. 1a), or heat treated with a martensitic matrix microstructure (Fig. 1b) for maximum abrasion resistance and toughness.
- The high-chromium irons (class III in Table 1) are commonly referred to as 25% Cr or 28% Cr white irons. These irons are alloyed with molybdenum (usually 1.5% Mo), nickel, and copper. They are selected when resistance to corrosion is also desired.

In addition to the abrasion-resistant grades covered by ASTM A 532, there are other nonstandard grades used for corrosion or high-temperature service. Alloys with improved resistance to corrosion, for applications such as pumps for handling fly ash, are produced with high chromium content (26 to 28% Cr) and low carbon content (1.6 to 2.0% C). These irons provide the maximum chromium content in the matrix. The addition

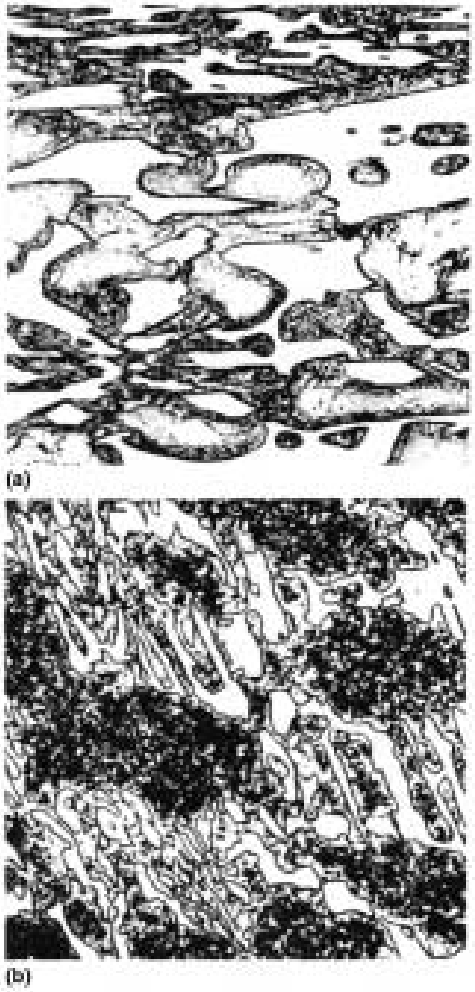


Fig. 1 High-chromium iron microstructures. (a) As-cast austenitic-martensitic matrix microstructure. (b) Heat-treated martensitic microstructure. The massive eutectic carbides are the white constituent in both figures. Both at 500×

of 2% Mo is recommended for improving resistance to chloride-containing environments. Fully austenitic matrix structures provide the best resistance to corrosion, but some reduction in abrasion resistance must be expected. Castings are normally supplied in the as-cast condition.

The high-chromium irons designated for use at elevated temperatures fall into one of three categories, depending on the matrix structure:

- Martensitic irons alloyed with 12 to 28% Cr
- Ferritic irons alloyed with 30 to 34% Cr
- Austenitic irons that contain 15 to 30% Cr, as well as 10 to 15% Ni to stabilize the austenite phase

The carbon content of these alloys ranges from 1 to 2%. The choice of an exact composition is critical to the prevention of σ-phase formation at intermediate temperatures and at the same time avoids the ferrite-to-

austenite transformation during thermal cycling, which leads to distortion and cracking.

Abrasion-Resistant Applications. Because of their low cost, the martensitic nickel-chromium white irons are consumed in large tonnages in mining operations as ball mill liners and grinding balls. Class I type A, Ni-Hard type 1, castings are used in applications requiring maximum abrasion resistance, such as ash pipes, slurry pumps, roll heads, muller tires, augers, coke crusher segments, classifier shoes, brick molds, pipe elbows carrying abrasive slurries, and grizzly disks. Class I type B, Ni-Hard type 2, is recommended for applications requiring more strength and exerting moderate impact, such as crusher plates, crusher concaves, and pulverizer pegs.

Class I type D, Ni-Hard type 4, has a higher level of strength and toughness and is therefore used for the more severe applications that justify its added alloy costs. It is commonly used for pump volutes handling abrasive slurries and coal pulverizer table segments and tires.

The class I type C alloy, Ni-Hard type 3, is specifically designed for the production of grinding balls. This grade is both sand cast and chill cast. Chill casting has the advantage of lower alloy cost, and, more important, provides a 15 to 30% improvement in life. All grinding balls require tempering for 8 h at 260 to 315 °C (500 to 600 °F) to develop adequate impact toughness.

The high-chromium class II and III white irons have excellent abrasion resistance and are used effectively in slurry pumps, brick molds, coal grinding mills, shot blasting equipment, and components for quarrying, hard-rock mining, and milling. In some applications they must also be able to withstand heavy impact loading. These alloyed white irons provide the best combination of toughness and abrasion resistance attainable among the white cast irons.

In the high-chromium irons, as with most abrasion-resistant materials, there is a tradeoff between wear resistance and toughness. By varying composition and heat treatment, these properties can be adjusted to meet the needs of most abrasive applications.

Effects of Alloying Elements and Inoculants

In most cast irons, it is the interaction among alloying elements (including carbon and silicon) that has the greatest effect on properties. This influence is exerted largely by effects on the amount and shape of graphitic carbon present in the casting. For example, in low-alloy cast irons, depth of chill or the tendency of the iron to be white as-cast depends greatly on the carbon equivalent, the silicon in the composition, and the state of inoculation. The addition of other elements can only modify the basic tendency established by the carbon-silicon relationship.

On the other hand, abrasion-resistant white cast irons are specifically alloyed with chromium to produce fully carbidic irons. One of the benefits of chromium is that it causes carbide, rather than graphite, to be the stable carbon-rich eutectic phase upon solidification. At higher chromium contents (10% or more), M_7C_3 carbide becomes the stable carbon-rich phase of the eutectic reaction.

In general, only small amounts of alloying elements are needed to improve depth of chill, hardness, and strength. Typical effects on depth of chill are given in Fig. 2 for the alloying elements commonly used in low- to moderate-alloy cast irons. High alloy contents are needed for the most significant improvements in abrasion resistance, corrosion resistance, or elevated-temperature properties.

Carbon. In chilled irons, the depth of chill decreases, and the hardness of the chilled zone increases, with increasing carbon content (Fig. 2c). Carbon also increases the hardness of white irons. Low-carbon white irons (~2.50% C) have a hardness of about 375 HB (Fig. 3), while white irons with fairly high total carbon (>3.50% C) have a hardness as high as 600 HB. In unalloyed (chilled) white irons, high total carbon is essential for high hardness and maximum wear resistance. Carbon decreases transverse breaking strength (Fig. 4) and increases brittleness. It also increases the tendency for graphite to form during solidification, especially when the silicon content is also high. As a result, it is very important to keep the silicon content low in high-carbon white irons. The normal range of carbon content for unalloyed or low-alloy white irons is about 2.2 to 3.6%. For high-chromium white irons, the normal range is from about 2.2% to the carbon content of the eutectic composition, which is about 3.5% for a 15% Cr iron and about 2.7% for a 27% Cr iron.

Silicon is present in all cast irons. In alloy cast irons, as in other types, silicon is the chief factor that determines the carbon content of the eutectic. Increasing the silicon content lowers the carbon content of the eutectic and promotes the formation of graphite upon solidification. Therefore, the silicon content is the principal factor controlling the depth of chill in unalloyed or low-chromium chilled and white irons. This effect for relatively high-carbon irons is summarized in Fig. 2(a).

In high-alloy white irons, silicon has a negative effect on hardenability; that is, it tends to promote pearlite formation in martensitic irons. However, when sufficient amounts of pearlitic-suppressing elements are present (e.g., molybdenum, nickel, manganese, or chromium), increasing the silicon content raises the M_s temperature of the alloy, thus tending to increase both the amount of martensite and the final hardness.

The silicon content of chilled and white irons is usually between 0.3 and 2.2%. In martensitic nickel-chromium white irons, the desired silicon content is usually 0.4 to 0.9%. It is necessary to select carefully the charge constituents when melting a martensitic iron so that excessive silicon

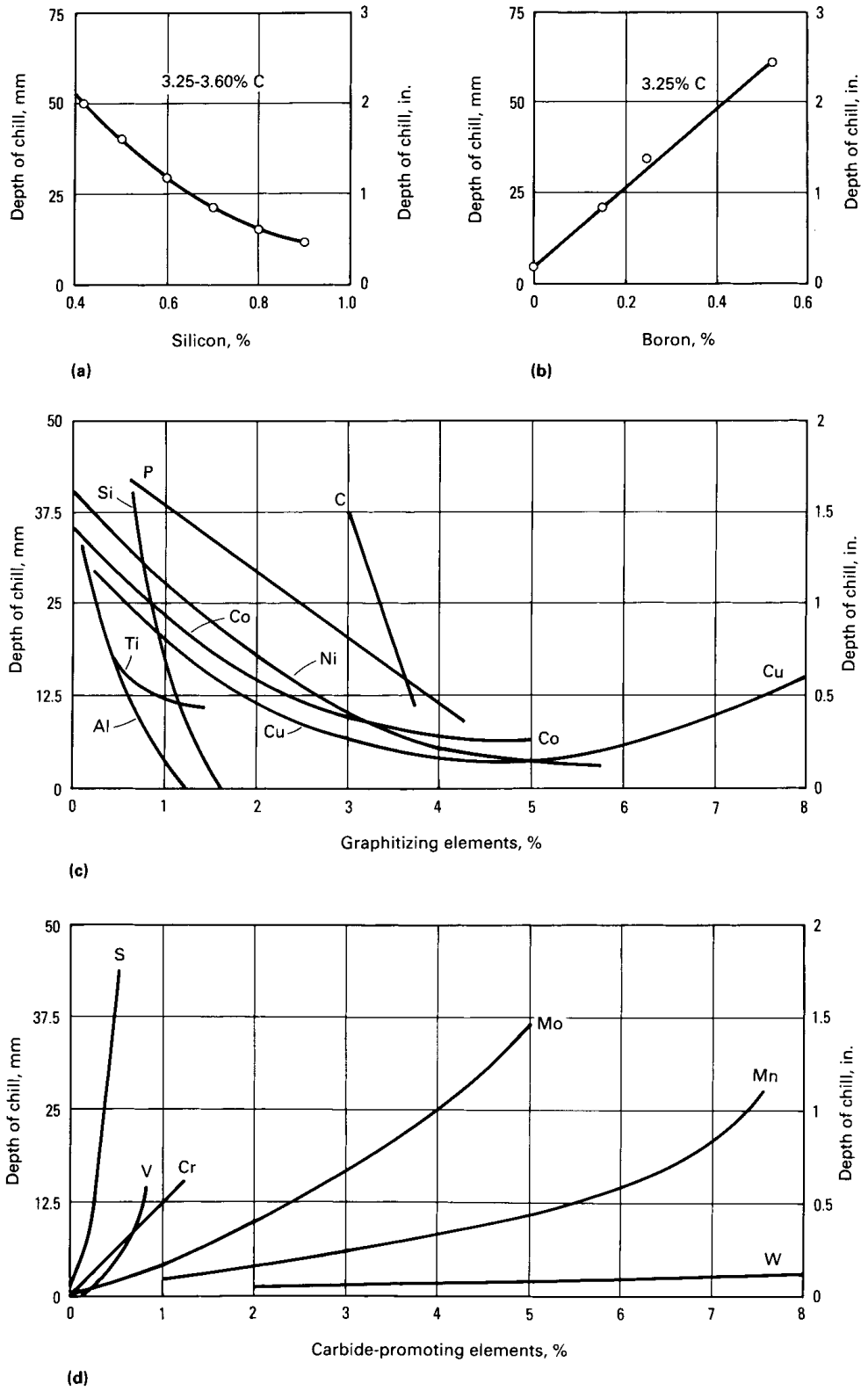


Fig. 2 Typical effects of alloying elements on depth of chill

content is avoided. In particular, it is necessary to give special attention to the silicon content of the ferrochromium used in the furnace charge.

Manganese and sulfur should be considered together in their effects on white iron. Alone, either manganese or sulfur increases the depth of chill, but when one is present, addition of the other decreases the depth of chill until the residual concentration has been neutralized by the formation of manganese sulfide. Generally, sulfur is the residual element, and excess manganese can be used to increase chill depth and hardness, as shown in Fig. 2(d). Furthermore, because it promotes the formation of finer and harder pearlite, manganese is often preferred for decreasing or preventing mottling in heavy-section castings.

Manganese, in excess of the amount needed to scavenge sulfur, mildly suppresses pearlitic formation. It is also a relatively strong austenite stabilizer and is normally kept below about 0.7% in martensitic white irons. When the manganese content exceeds about 1.3%, the strength and toughness of

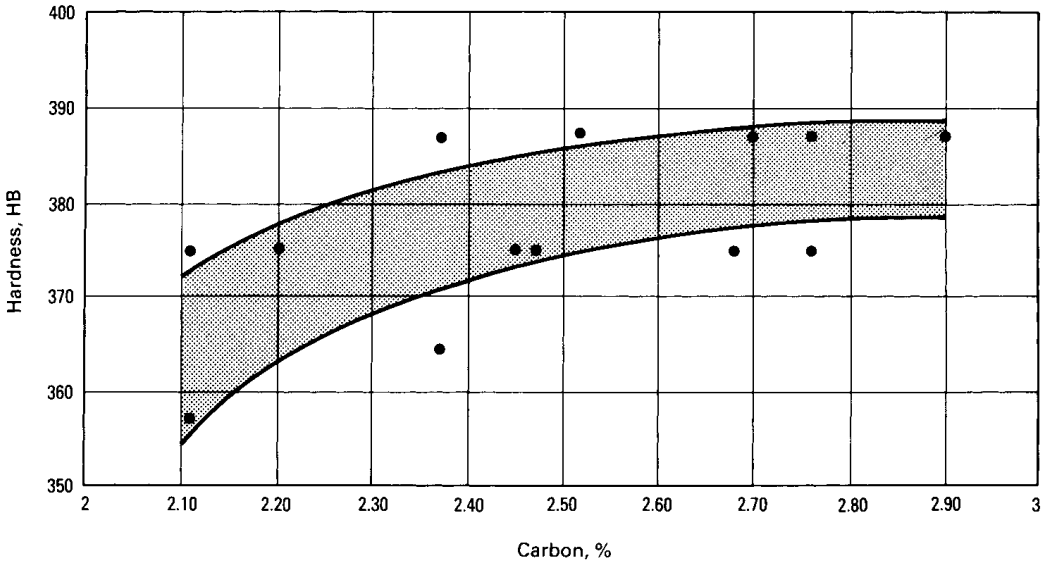


Fig. 3 Effect of carbon content on the hardness of low-carbon white iron

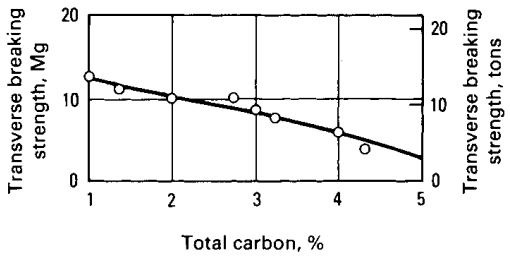


Fig. 4 Effect of total carbon on the transverse breaking strength of unalloyed white iron

martensitic irons begin to drop. Abrasion resistance also drops, mainly because of austenite retention. Molten iron with a high manganese content tends to attack furnace and ladle refractories. Consequently, the use of manganese is limited in cast irons, even though it is one of the least expensive alloying elements.

In abrasion-resistant cast irons, the sulfur content should be as low as is commercially feasible, because several investigations have shown that sulfides in the microstructure degrade abrasion resistance. A sulfur content of 0.03% appears to be the maximum that can be tolerated when optimum abrasion resistance is desired.

Phosphorus is a mild graphitizer in unalloyed irons; it mildly reduces chill depth in chilled irons (Fig. 2c). In alloyed irons, the effects of phosphorus are somewhat obscure. There is some evidence that phosphorus reduces the toughness of martensitic white irons, but no effect on abrasion resistance has been conclusively proved. In heavy-section castings made from molybdenum-containing irons, high phosphorus contents are considered detrimental because they neutralize part of the deep-hardening effect of the molybdenum. It is considered desirable to keep the phosphorus content of alloy cast irons below about 0.3%, and some specifications call for less than 0.1%. In cast irons for high-temperature or chemical service, it is customary to keep the phosphorus content below 0.15%.

Chromium has three major uses in cast irons:

- To form carbides
- To impart corrosion resistance
- To stabilize the structure for high-temperature applications

Small amounts of chromium are routinely added to control a chill depth in chilled iron, or to ensure a graphite-free structure in white iron containing less than 1% Si. At such low percentages, usually no greater than 2 to 3%, chromium has little or no effect on hardenability, chiefly because most of the chromium is tied up in carbides. However, chromium does influence the fineness and hardness of pearlite and tends to increase the amount and hardness of the eutectic carbides. Also, relatively low percentages of chromium are used to improve the hardness and abrasion resistance of pearlitic white cast irons.

When the chromium content of cast iron is greater than about 10%, eutectic carbides of the M_7C_3 type are formed, rather than the M_3C type that predominates at lower chromium contents. More significantly, however, the higher chromium content causes a change in solidification pattern to a structure in which the M_7C_3 carbides are surrounded by a matrix of austenite or its transformation products. At lower chromium contents, the M_3C carbide forms the matrix. Because of the solidification characteristics, hypoeutectic irons containing M_7C_3 carbides are normally stronger and tougher than irons containing M_3C carbides.

The relatively good abrasion resistance, toughness, and corrosion resistance of high-chromium white irons have led to the development of commercial martensitic or austenitic white irons containing 12 to 28% Cr (see Table 1). Because much of the chromium in these irons is present in combined form as carbides, chromium is much less effective than molybdenum, nickel, manganese, or copper in suppressing the eutectoid transformation to pearlite and therefore has a lesser effect on hardenability than it has in steels. Martensitic white irons usually contain molybdenum, nickel, manganese, and/or copper to give the required hardenability. These elements ensure that martensite will form upon cooling from above the upper transformation temperature, either while the casting is cooling in the mold or during subsequent heat treatment.

It is difficult to maintain a low silicon content in high-chromium irons because of the silicon introduced by high carbon, ferrochrome, and other sources. Low silicon content is advantageous in that it provides for ready response to annealing and yields high hardness when the alloy is air quenched from high temperatures. A high silicon content lessens the response to this type of heat treatment. Although high-chromium irons are sometimes used as-cast, their optimum properties are obtained in the heat-treated condition.

For developing resistance to the softening effect of heat and for protection against oxidation, chromium is the most effective element. It stabilizes iron carbide and therefore prevents the breakdown of carbide at elevated temperatures; 1% Cr gives adequate protection against oxidation up to about 760 °C (1400 °F) in many applications. For long-term oxidation resistance at elevated temperatures, white cast irons having chromium contents of 15 to 35% are employed. This percentage of chromium suppresses the formation of graphite and makes the alloy solidify as white cast iron.

Figure 5 demonstrates the beneficial effect of chromium on the oxidation resistance of cast iron at temperatures of 700 to 1000 °C (1290 to 1830 °F). The oxidation resistance of the high-chromium irons is compared with the oxidation resistance of other alloy cast irons in Fig. 6. All the irons plotted in Fig. 6 were simultaneously exposed to air and sulfurous atmospheres, simulating conditions in electric furnaces and in oil-fired or coal-fired furnaces. The controlled laboratory exposure tests were supported by testing the same irons as furnace parts under industrial conditions.

Nickel is almost entirely distributed in the austenitic phase or its transformation products. Like silicon, nickel promotes graphite formation.

When added to low-chromium white iron in amounts up to about 2.5%, nickel produces a harder and finer pearlite in the structure, which improves its abrasion resistance. Nickel in somewhat larger amounts, up to about 4.5%, is needed to completely suppress pearlite formation, thus ensuring that a martensitic iron results when the castings cool in their

molds. This latter practice forms the basis for production of the Ni-Hard cast irons. With small castings such as grinding balls, which can be shaken out of the molds while still hot, air cooling from the shakeout temperature will produce the desired martensitic structure even when the nickel content is as low as 2.7%. On the other hand, an excessively high nickel content (more than about 6.5%) will so stabilize the austenite that little martensite, if any, can be formed in castings of any size. Appreciable amounts of retained austenite in Ni-Hard cast irons can be transformed to

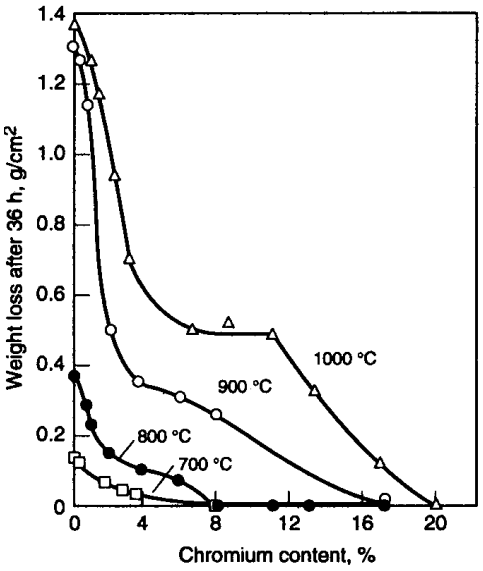


Fig. 5 Effect of chromium content on the oxidation behavior of alloy cast irons

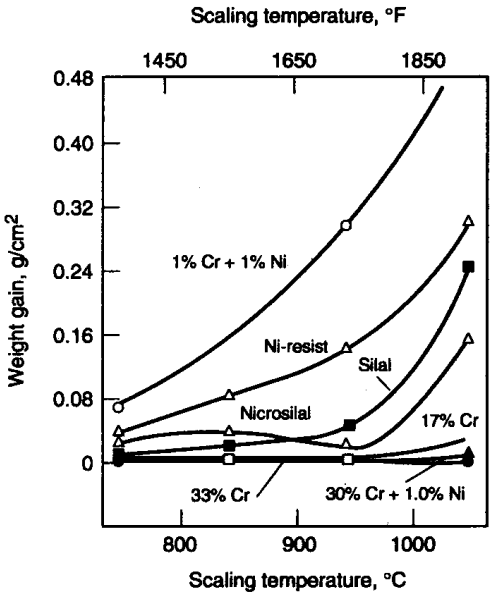


Fig. 6 Oxidation behavior of alloyed cast irons held at temperature for 200 h

martensite by refrigerating the castings at −55 to −75 °C (−70 to −100 °F) or by using special tempering treatments.

One of the Ni-Hard family of commercial alloy white irons (type 4 Ni-Hard) contains 1.0 to 2.2% Si, 5 to 7% Ni, and 7 to 11% Cr. In the as-cast condition, it has a structure of M_7C_3 eutectic carbides in a martensitic matrix. If retained austenite is present, the martensite content and hardness of the alloy can be increased by refrigeration treatment or by reaustenitizing and air cooling. Ni-Hard 4 is often specified for pumps and other equipment used for handling abrasive slurries because of its combination of relatively good strength, toughness, and abrasion resistance.

Nickel is used to suppress pearlite formation in large castings of high-chromium white iron (12 to 28% Cr). The typical amount of nickel is about 0.2 to 1.5%, and it is usually added in conjunction with molybdenum. Nickel contents higher than this range tend to excessively stabilize the austenite, leading to austenite retention. Control of composition is especially important for large castings that are intended to be martensitic, because their size dictates that they cool slowly, regardless of whether they are to be used as-cast or after heat treatment.

Copper in moderate amounts can be used to suppress pearlite formation in both low- and high-chromium martensitic white irons. The effect of copper is relatively mild compared to that of nickel, and because of the limited solubility of copper in austenite, copper additions probably should be limited to about 2.5% or less. This limitation means that copper cannot completely replace nickel in Ni-Hard-type irons. When added to chilled iron without chromium, copper narrows the zone of transition from white to gray iron, thus reducing the ratio of the mottled portion to the clear chilled portion.

Copper is most effective in suppressing pearlite when it is used in conjunction with about 0.5 to 2.0% Mo. The hardenability of this combination is surprisingly good, which indicates that there is a synergistic effect when copper and molybdenum are added together to cast iron. Combined additions appear to be particularly effective in the martensitic high-chromium irons. Here, copper content should be held to 1.2% or less; larger amounts tend to induce austenite retention.

Molybdenum in chilled and white iron compositions is distributed between the eutectic carbides and the matrix. In chilled iron compositions, molybdenum additions mildly increase depth of chill (they are about one-third as effective as chromium; see Fig. 2d). The primary purpose of small additions (0.25 to 0.75%) of molybdenum to chilled iron is to improve the resistance of the chilled face to spalling, pitting, chipping, and heat checking. Molybdenum hardens and toughens the pearlitic matrix.

Where a martensitic white iron is desired for superior abrasion resistance, additions of 0.5 to 3.0% Mo effectively suppress pearlite and other high-temperature transformation products (Fig. 7). Molybdenum is even

more effective when used in combination with copper, chromium, nickel, or both chromium and nickel. Molybdenum has an advantage over nickel, copper, and manganese in that it increases depth of hardening without appreciably overstabilizing austenite, thus preventing the retention of undesirably large amounts of austenite in the final structure. Figure 7 illustrates the influence of different amounts of molybdenum on the hardenability of high-chromium white irons and shows that the hardenability (measured as the critical diameter for air hardening) increases as the ratio of chromium to carbon increases.

The pearlite-suppressing properties of molybdenum have been used to advantage in irons of high chromium content. White irons with 12 to 18% Cr are used for abrasion-resistant castings. The addition of 1 to 4% Mo is effective in suppressing pearlite formation, even when the castings are slowly cooled in heavy sections.

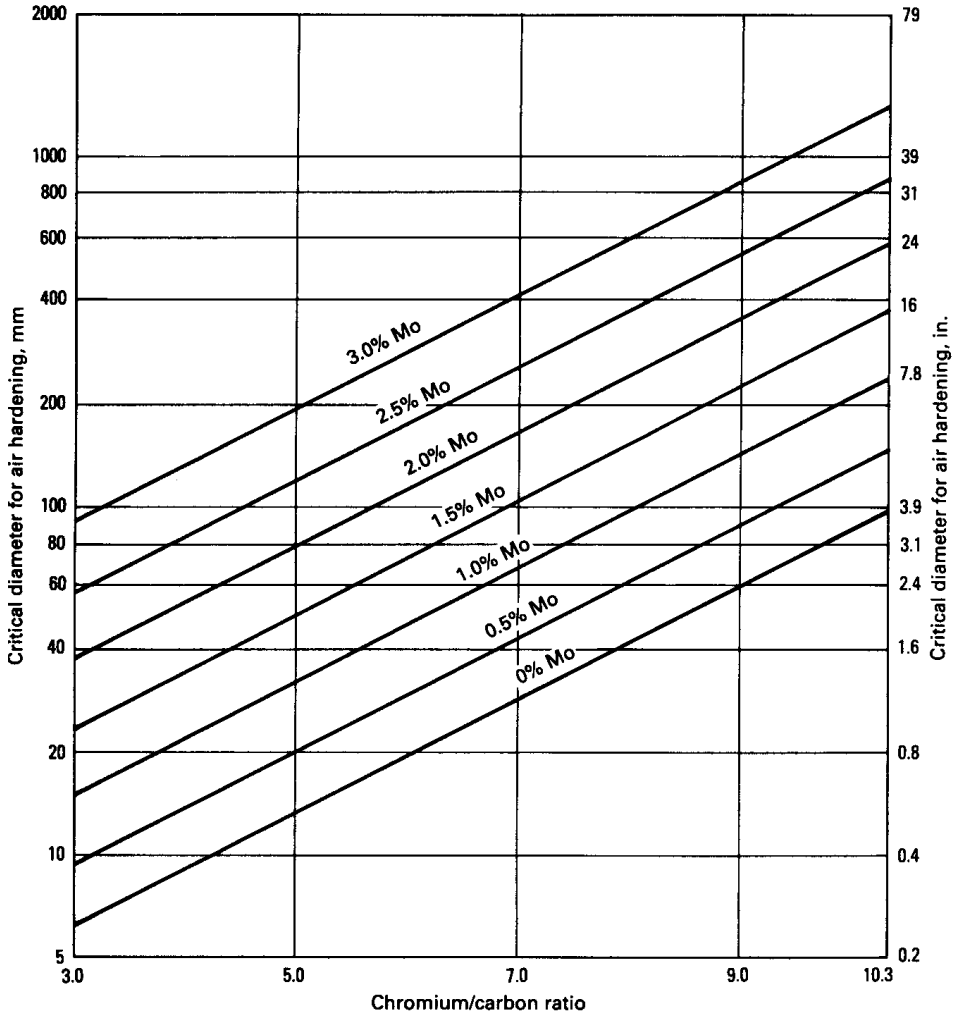


Fig. 7 Effect of molybdenum content on the hardenability of high-chromium white irons of different Cr/C ratios

Molybdenum can replace some of the nickel in the nickel-chromium type of martensitic white irons. In heavy-section castings in which 4.5% Ni would be used, the addition of 1% Mo permits a reduction of nickel content to about 3%. In light-section castings of this type, where 3% Ni would normally be used, the addition of 1% Mo permits a reduction of nickel to 1.5%.

Vanadium is a potent carbide stabilizer and increases depth of chill. The magnitude of the increase of depth of chill depends on the amount of vanadium, the composition of the iron, the section size, and the conditions of casting. The powerful chilling effect of vanadium in thin sections can be balanced by additions of nickel or copper, by a large increase in carbon or silicon, or both. In addition to its carbide-stabilizing influence, vanadium in amounts of 0.10 to 0.50% refines the structure of the chill and minimizes coarse columnar grain structure.

Effects of Inoculants. In white irons, tellurium, bismuth, and sometimes vanadium are the principal carbide-inducing inoculants. Tellurium is extremely potent; an addition of only about 5 g/tonne (5 ppm) is often sufficient. Tellurium has one major drawback: it has been found to cause tellurium halitosis in foundry workers exposed to even minute traces of its fumes. Therefore, its use as an inoculant has been discouraged and sometimes prohibited.

Bismuth, in amounts of 50 to 100 g/tonne (50 to 100 ppm), effectively suppresses graphite formation in unalloyed or low-alloy white iron. In particular, bismuth is used in the low-carbon compositions destined for malleabilizing heat treatment. It has been reported that bismuth produces a fine-grain microstructure free from spiking, a condition that is sometimes preferred in abrasion-resistant white irons.

Vanadium, in amounts up to 0.5%, is sometimes considered useful as a carbide stabilizer and grain refiner in white or chilled irons. Nitrogen and boron-containing ferroalloys have also been used as inoculants with reported beneficial effects. In general, however, the economic usefulness of inoculants in abrasion-resistant white irons has been inconsistent and remains unproved.

SELECTED REFERENCES

- Metallurgy and Properties of High-Alloy White Irons, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 107–127
- Foundry Practice for Cast Irons, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 133–154
- Heat Treating of High-Alloy Irons, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 209–213
- Tribological Behavior, *ASM Specialty Handbook: Cast Irons,* J.R. Davis, Ed., ASM International, 1996, p 448–459

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J.R. Davis, p123-192
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Carbon and Alloy Steels

Introduction and Overview

Steels constitute the most widely used category of metallic material, primarily because they can be manufactured relatively inexpensively in large quantities to very precise specifications. Carbon, microalloyed, and alloy steels are used for components requiring critical and stringent levels of ductility, strength, toughness, fatigue resistance, high-temperature creep resistance, fracture resistance, oxidation resistance, and wear resistance. These steels are also possess excellent processing characteristics (hardenability, formability, machinability, and weldability). The combination of low cost, a wide range in properties, and ease of fabrication has contributed to carbon and low-alloy steels being the material of choice for applications found throughout almost all key industries, including the automotive, aerospace, railway, power generation, defense, chemical, agriculture, shipping, and construction industries; general manufacturing; and oil, coal, and gas extraction.

Emphasis in this article has been placed on wrought carbon and alloy steels. Steels are also produced in cast and powder metallurgy (P/M) form. Alloying elements are added to cast or P/M ferrous materials for the same reasons they are added to wrought steels: primarily to improve strength and hardenability.

Carbon Steels

Carbon steels contain less than 1.65% Mn, 0.60% Si, and 0.60% Cu (less than 2.0% total alloying elements. They comprise the l*xxx* groups of the Society of Automotive Engineers (SAE)/American Iron and Steel Institute (AISI) classification system, as shown in Table 1, and are also covered in a number of ASTM specifications. Tables 2 and 3 list compositions of commonly used carbon steels. Mechanical property requirements per ASTM specifications are also given in Table 3.

Table 1 SAE-AISI system of designations for carbon and alloy steels

Numerals and digits	Type of steel and nominal alloy content, %
Carbon steels	
10*xx*(a)	Plain carbon (Mn 1.00 max)
11*xx*	Resulfurized
12*xx*	Resulfurized and rephosphorized
15*xx*	Plain carbon (max Mn range: 1.00–1.65)
Manganese steels	
13*xx*	Mn 1.75
Nickel steels	
23*xx*	Ni 3.50
25*xx*	Ni 5.00
Nickel-chromium steels	
31*xx*	Ni 1.25; Cr 0.65 and 0.80
32*xx*	Ni 1.75; Cr 1.07
33*xx*	Ni 3.50; Cr 1.50 and 1.57
34*xx*	Ni 3.00; Cr 0.77
Molybdenum steels	
40*xx*	Mo 0.20 and 0.25
44*xx*	Mo 0.40 and 0.52
Chromium-molybdenum steels	
41*xx*	Cr 0.50, 0.80, and 0.95; Mo 0.12, 0.20, 0.25, and 0.30
Nickel-chromium-molybdenum steels	
43*xx*	Ni 1.82; Cr 0.50 and 0.80; Mo 0.25
43BV*xx*	Ni 1.82; Cr 0.50; Mo 0.12 and 0.25; V 0.03 min
47*xx*	Ni 1.05; Cr 0.45; Mo 0.20 and 0.35
81*xx*	Ni 0.30; Cr 0.40; Mo 0.12
86*xx*	Ni 0.55; Cr 0.50; Mo 0.20
87*xx*	Ni 0.55; Cr 0.50; Mo 0.25
88*xx*	Ni 0.55; Cr 0.50; Mo 0.35
93*xx*	Ni 3.25; Cr 1.20; Mo 0.12
94*xx*	Ni 0.45; Cr 0.40; Mo 0.12
97*xx*	Ni 0.55; Cr 0.20; Mo 0.20
98*xx*	Ni 1.00; Cr 0.80; Mo 0.25
Nickel-molybdenum steels	
46*xx*	Ni 0.85 and 1.82; Mo 0.20 and 0.25
48*xx*	Ni 3.50; Mo 0.25
Chromium steels	
50*xx*	Cr 0.27, 0.40, 0.50, and 0.65
51*xx*	Cr 0.80, 0.87, 0.92, 0.95, 1.00, and 1.05
50*xxx*	Cr 0.50; C 1.00 min
51*xxx*	Cr 1.02; C 1.00 min
52*xxx*	Cr 1.45; C 1.00 min
Chromium-vanadium steels	
61*xx*	Cr 0.60, 0.80, and 0.95; V 0.10 and 0.15 min
Tungsten-chromium steel	
72*xx*	W 1.75; Cr 0.75
Silicon-manganese steels	
92*xx*	Si 1.40 and 2.00; Mn 0.65, 0.82, and 0.85; Cr 0 and 0.65
Boron steels	
*xx*B*xx*	B denotes boron steel
Leaded steels	
*xx*L*xx*	L denotes leaded steel
Vanadium steels	
*xx*V*xx*	V denotes vanadium steel

(a) The *xx* in the last two digits of these designations indicates that the carbon content (in hundredths of a percent) is to be inserted.

Generally speaking; carbon steels can be subdivided into the following categories:

- Low-carbon steels containing up to 0.30% C
- Medium-carbon steels containing 0.30 to 0.60% C
- High-carbon steels containing 0.60 to 1.00% C
- Free-machining grades

As will be described below, the properties and processing characteristics of these steels greatly depends on their carbon and manganese contents and impurity levels.

Low-carbon steels are comprised of two groups: group I steels with carbon contents less than approximately 0.15% and group II steels with

Table 2 Composition of selected carbon steels in the SAE-AISI system

SAE-AISI No.	Composition, wt %(a)				
	C	Mn	P	S	Other
1006	0.08	0.45	0.040	0.050	…
1010	0.08–0.13	0.30–0.60	0.040	0.050	…
1020	0.17–0.23	0.30–0.60	0.040	0.050	…
1030	0.27–0.34	0.60–0.90	0.040	0.050	…
1040	0.36–0.44	0.60–0.90	0.040	0.050	…
1050	0.47–0.55	0.60–0.90	0.040	0.050	…
1060	0.55–0.66	0.60–0.90	0.040	0.050	…
1070	0.65–0.73	0.60–0.90	0.040	0.050	…
1080	0.74–0.88	0.60–0.90	0.040	0.050	…
1095	0.90–1.04	0.30–0.50	0.040	0.050	…
Manganese-carbon					
1513	0.10–0.16	1.10–1.40	0.040	0.050	…
1527	0.22–0.29	1.20–1.50	0.040	0.050	…
1541	0.36–0.44	1.35–1.65	0.040	0.050	…
1566	0.60–0.71	0.85–1.15	0.040	0.050	…
Free-machining					
1108	0.08–0.13	0.50–0.80	0.040	0.08–0.13	…
1139	0.35–0.43	1.35–1.65	0.040	0.13–0.20	…
1151	0.48–0.55	0.70–1.00	0.040	0.08–0.13	…
1212	0.13	0.70–1.00	0.07–0.12	0.16–0.23	…
12L14	0.15	0.85–1.15	0.04–0.09	0.26–0.35	0.15–0.35 Pb

(a) Single values are maximums.

carbon contents in the range of 0.15 to 0.30%. Both groups have distinct property and processing characteristics due to their differing carbon and manganese levels.

Group I steels are selected when enhanced cold formability or drawability is required. These steels have relatively low tensile values (−205 to 240 MPa, or 30 to 35 ksi). Within the carbon range of the group, strength and hardness will increase with an increase in carbon and with cold work. Such increases in strength are at the sacrifice of ductility or the ability to withstand cold deformation.

When under 0.15% C, the steels are susceptible to grain growth and consequent brittleness if they are cold worked during forming and subsequently heated to temperatures between 595 °C (1100 °F) and the lower transformation temperature. This phenomenon is known as strain-age embrittlement. If coarse grains develop, they can be refined by heating above the A_3 transformation temperature and then cooling.

Cold-rolled sheets are made from the lower carbon content steels in the group. They have excellent surface appearance and are used in automobile panels, appliances, and so forth. The machinability of bar, rod, and wire products in this group is improved by cold drawing. In general, these steels are considered suitable for welding or brazing, but may suffer strength reductions either locally in the heat-affected zone or overall, depending on process details.

Table 3 Composition and mechanical properties of selected carbon steels covered in ASTM specifications

ASTM designation		Composition, wt %(a)			Ultimate tensile strength(b)		Yield streng1th(b)		
Specification	Grade or type	C	Mn	Si(d)	MPa	ksi	MPa	ksi	Comments(c)
Structural steels									
A 36	…	0.29	0.80–1.20	0.15–0.40	400–550	58–80	220–250	32–36	…
A 131	B	0.21	0.80–1.10	0.35	400–500	58–71	220	32	…
	E	0.18	0.70–1.35	0.10–0.35	400–500	58–71	220	32	Normalized
	CS	0.16	1.00–1.35	0.10–0.35	400–500	58–71	220	32	Normalized
A 283	A	0.14	0.90	0.04	310–415	45–60	165	24	…
	B	0.17	0.90	0.04	345–450	50–65	185	27	…
	C	0.24	0.90	0.04	380–485	55–70	205	30	…
	D	0.27	0.90	0.04	415–515	60–75	230	33	…
A 284	C	0.36	0.90	0.15–0.40	415	60	205	30	…
	D	0.35	0.90	0.15–0.40	415	60	230	33	…
A 573	58	0.23	0.60–0.90	0.10–0.35	400–500	58–71	220	32	…
	65	0.26	0.85–1.20	0.15–0.40	450–530	65–77	240	35	…
	70	0.28	0.85–1.20	0.15–0.40	485–620	70–90	290	42	…
A 285	A	0.17	0.90	0.35	310–450	45–65	165	24	…
	B	0.22	0.90	0.35	345–485	50–70	185	27	…
	C	0.28	0.90	0.35	380–515	55–75	205	30	…
A 442	55	0.24	0.80–1.10	0.15–0.40	380–515	55–75	205	30	…
	60	0.27	0.80–1.10	0.15–0.40	415–550	60–80	220	32	…
A 515	55	0.28	0.90	0.15–0.40	380–515	55–75	205	30	Normalized if *t* > 38 mm (1.5 in.)
	60	0.31	0.90	0.15–0.40	415–550	60–80	220	32	Normalized if *t* > 38 mm (1.5 in.)
	65	0.33	0.90	0.15–0.40	450–585	65–85	240	35	Normalized if *t* > 38 mm (1.5 in.)
	70	0.35	1.20	0.15–0.40	485–620	70–90	260	38	Normalized if *t* > 38 mm (1.5 in.)
A 516	55	0.26	0.60–1.20	0.15–0.40	380–515	55–75	205	30	Normalized if *t* > 38 mm (1.5 in.)
	60	0.27	0.60–1.20	0.15–0.40	415–550	60–80	220	32	Normalized if *t* > 38 mm (1.5 in.)
	65	0.29	0.85–1.20	0.15–0.40	450–585	65–85	240	35	Normalized if *t* > 38 mm (1.5 in.)
	70	0.31	0.85–1.20	0.15–0.40	485–620	70–90	260	38	Normalized if *t* > 38 mm (1.5 in.)
A 537	C1.1	0.24	0.70–1.60	0.15–0.50	450–585	65–85	310	45	Normalized
	C1.2	0.24	0.70–1.60	0.15–0.50	515–655	75–95	380	55	Quenched and tempered
A 662	A	0.14	0.90–1.50	0.15–0.40	400–540	58–78	275	40	Normalized
	B	0.19	0.85–1.60	0.15–0.40	450–585	65–85	275	40	Normalized if *t* > 38 mm (1.5 in.)
	C	0.20	1.00–1.60	0.15–0.50	485–620	70–90	295	43	Normalized if *t* > 38 mm (1.5 in.)
Pipe steels									
A 53	A	0.25	0.95	…	330	48	205	30	…
	B	0.30	1.20	…	415	60	240	35	…
A 106	A	0.25	0.27–0.93	0.10	330	48	205	30	…
	B	0.30	0.29–1.06	0.10	415	60	240	35	…
	C	0.35	0.29–1.06	0.10	485	70	275	40	…
A 381	Y42	0.26	1.40	…	415	60	290	42	…
	Y52	0.26	1.40	…	495	72	360	52	…
	Y60	0.26	1.40	…	540	78	415	60	…
Cast steels									
A 27	60–30	0.30	0.60	0.80	415	60	205	30	Heat-treated
	70–40	0.25	1.20	0.80	485	70	275	40	Heat-treated
A 216	WCA	0.25	0.70	0.60	415–585	60–85	205	30	Heat-treated
	WCB	0.30	1.00	0.60	485–655	70–95	250	36	Heat-treated
	WCC	0.25	1.20	0.50	485–655	70–95	275	40	Heat-treated
SAE J435c	0025	0.25	0.75	0.80	415	60	205	30	Heat-treated
	0050A	0.40–0.50	0.50–0.90	0.80	585	85	310	45	Heat-treated

(a) Single values are maximums. (b) Single values are minimums. (c) *t* plate thickness. (d) Silicon content varies with deoxidation practice used.

Group II steels include both the 10*xx* and 15*xx* steels listed in Table 1 and 2. Steels containing 0.15 to 0.30% C and less than about 0.75% Mn are commonly referred to as *mild steels.* Group II steels have increased strength and hardness and reduced cold formability compared with the

lowest carbon group. For heat-treating purposes, they are commonly known as carburizing or case hardening grades.

Selection of one of these steels for carburizing applications depends on the nature of the part, the properties desired, and the processing practices preferred. An increase in carbon content of the base steel results in greater core hardness for a given quench. An increase in manganese improves the hardenability of both the core and the case.

In this group, the intermediate manganese grades (0.60 to 1.00% Mn) machine better than do the lower manganese grades (0.30 to 0.60% Mn). For carburizing applications, grades 1016, 1018, and 1019 are widely used for water-quenched parts. SAE-AISI 1022 and the 1500 series in this group are used for heavier sections or with thin sections where oil quenching is desired.

In cold-formed or cold-headed parts, the lowest manganese grades offer the best formability at a given carbon level. The intermediate manganese types provide increased strength.

These steels are used for numerous forged parts. In general, these steels are suitable for welding or brazing prior to carburizing. If welding is to be performed after carburizing, the area to be welded must be protected from the carburizing media during the process. An alternative to protection is to machine away the area to be welded after carburizing, but before hardening.

A typical application for carburized plain carbon steel is for parts requiring a hard wear-resistant surface, but with little need for increased mechanical properties in the core, for example, small shafts, plungers and lightly loaded gears.

Medium-carbon steels (0.30 to ~0.60% C) are selected for uses where higher mechanical properties are needed. They are frequently further hardened and strengthened by heat treatment (quenched and tempered) or by cold working. Medium-carbon steels are suitable for a wide variety of automotive applications. Selection of the particular carbon and manganese level is governed by a number of factors. Increases in mechanical properties, section thickness, or depth of hardening normally require either higher carbon, higher manganese, or both. The heat-treating practice used, especially the quenching medium, also has a great effect on the steels selected. In general, any of the grades containing more than 0.30% C may be induction or flame hardened.

Steels in this group with lower carbon and manganese content find wide usage for certain types of cold-formed parts. In nearly all cases, the parts cold formed from these steels are annealed, normalized, or quenched and tempered prior to use. Stampings are usually-limited to flat parts or simple bends. The higher carbon grades are frequently cold drawn to specified mechanical properties for use without heat treatment for some applications.

All of these steels can be used for forgings, the selection being governed by the section size and the mechanical properties desired after heat treat-

ment. Thus SAE-AISI 1030 and 1035 are used for many small forgings where moderate properties are desired. SAE-AISI 1536 is used for more critical parts where a higher strength level and better uniformity is essential. The SAE-AISI 1038, 1052, 1053, and 1500 groups are used for larger forgings. They are also used for small forgings where high hardness after oil quenching is desired. Suitable heat treatment is necessary on forgings from this group to provide machinability.

These steels are also widely used for parts machined from bar stock. They are used both with and without heat treatment, depending on the application and the level of properties needed. As a group, they are considered good for normal machining operations. It is possible to weld these steels by most commercial methods, but precautions should be taken to avoid cracking from rapid heating or cooling.

High-carbon steels (0.60 to ~1.0% C) are used for applications where the higher carbon is needed to improve wear characteristics and where strength levels required are higher than those obtainable with the lower carbon groups.

In general, cold-forming methods are not practical with this group of steels as they are limited to flat stampings and springs coiled from small-diameter wire. Practically all parts from these steels are heat treated before use. Variations in heat-treating methods are required to obtain optimal properties for particular composition and application.

Typical uses in the spring industry include SAE-AISI 1065 for pretempered wire, 1064 for small washers and thin stamped parts, 1074 for light, flat springs formed from annealed stock, and 1080 and 1085 for thicker flat springs with the latter steel also used for heavier coiled springs.

Because of good wearing properties when properly heat treated, the high-carbon steels find wide use in the farm implement industry. Typical applications are plow beams, plow shares, scraper blades, discs, mower knives, and harrow teeth.

Free-machining grades (grades 11*xx* and 12*xx* in Tables 1 and 2) are intended for use where improved machinability is desired, compared to that for carbon steels of similar carbon and manganese content. Machinability refers to the effects of hardness, strength, ductility, grain size, microstructure, and chemical composition on cutting tool wear, chip formation, ease of metal removal, and surface finish quality of the steel being cut.

Free-machining steels contain one or more additives that enhance machining characteristics and lower machining costs. The lower costs result from either the increased production through greater machining speeds and improved tool life or the elimination of secondary operations through an improvement in surface finish.

The resulfurized 11*xx* series grades (SAE-AISI 1108 to 1151) provide improved chip formation with increased sulfur content in amounts up to

0.33% in some grades. The 12*xx* series grades (AISI 1211 to 1215) are both resulfurized and rephosphorized. Phosphorus additions increase the strength and reduce the ductility of ferrite; hence chips break up more easily. Calcium is also used to improve the shape of the sulfides. The use of other additions such as lead, bismuth, or selenium has declined due to environmental restrictions.

Sulfur and phosphorus negatively affect weld-ability, cold forming, forging, and so forth. Lead in steel wire causes a poor quality, low-strength welded or brazed joint. The lower-carbon grades can be used for case hardening operations while the grades containing more than 0.30% C can be quenched and tempered or induction hardened.

Machinability improves within the 1100 series as sulfur content increases. Sulfur combines mostly with the manganese and precipitates as sulfide inclusions. These inclusions favor machining by causing the formation of a broken chip and by providing a built-in lubricant that prevents the chips from sticking to the tool and undermining the cutting edge. By minimizing this adherence, less power is required, finish is improved, and the speed of machining may often be doubled compared with that for a similar nonresulfurized grade. The 1200 series steels are both rephosphorized and resulfurized. Phosphorus is soluble in iron and promotes chip breakage in cutting operations through increased hardness and brittleness. Steels high in phosphorus are notoriously notch sensitive. As with carbon, an excessive amount of phosphorus can raise strength and hardness levels high enough to impair machinability. Hence, the 1200 series phosphorus content is limited to either a 0.04 to 0.09% or 0.07 to 0.12% range and carbon is limited to 0.13% maximum, for the same reason.

Free-machining grades with lower carbon content (less than approximately 0.20% C) are used for applications where a combination of good machinability and response to heat treatment is needed. These steels can be used for small parts that are to be carbonitrided. SAE-AISI 1117 and 1118 contain more manganese for better hardenability, permitting oil quenching after case-hardening heat treatments.

The higher-carbon content grades are widely used for parts where a large amount of machining is necessary, or where threads, splines, grooves, or other operations offer special tooling problems. SAE-AISI 1137, for example, is widely used for nuts, bolts, and studs with machined threads. The higher-manganese grades (SAE-AISI 1137, 1141, and 1144) offer greater hardenability, the higher-carbon types being suitable for oil quenching for many parts. All of these steels may be selectively hardened by induction or flame heating, if desired.

High-Strength Low-Alloy Steels

High-strength low-alloy (HSLA) steels, which typically contain less than 0.2% C and less than 2% alloying content, are designed to provide

better mechanical properties than those of conventional carbon steels. These steels generally have yield strengths of 290 to 550 MPa (42 to 80 ksi). They are also generally of the carbon-manganese type, with very small additions of niobium and vanadium to ensure both grain refinement and precipitation hardening. The term "microalloyed steels" is often used in reference to these materials. The effects of microalloying additions to these steels are described in the following article, "High-Strength Low-Alloy Steels," in this book.

Alloy Steels

Alloy steels constitute a category of ferrous materials that exhibit mechanical properties superior to plain carbon steels as the result of additions of such alloying elements as nickel, chromium, and molybdenum. Total alloy content can range from 2.07% up to levels just below that of stainless steels, which contain a minimum of approximately 11% Cr. For many alloy steels, the primary function of the alloying elements is to increase hardenability in order to optimize mechanical properties and toughness after heat treatment. In some cases, however, alloy additions are used to reduce environmental degradation under certain specified service conditions.

Three major classes of alloy steels are described below. These include low-carbon quenched and tempered steels, low-carbon alloy steels used for pressure vessels and piping, and medium-carbon heat-treatable steels. It should be noted that the boundaries between these classes are often diffuse, they sometimes overlap (e.g., some steels are used in more than one heat-treated condition), and they are sometimes arbitrary. Nevertheless, they represent some of the most commonly used alloy steels. Table 1 lists SAE-AISI designations for various alloy steels.

Low-carbon quenched and tempered steels typically contain less than 0.25% C and less than 5% alloy. These steels combine high yield and tensile strengths with good ductility, notch toughness, atmospheric corrosion resistance, and weldability. They are strengthened primarily by quenching and tempering to produce microstructures that contain martensite, bainite, and, in some compositions, ferrite. Some types are produced with a precipitation-hardening treatment that follows hot rolling or quenching. Yield strength values range from approximately 345 to 895 MPa (50 to 130 ksi), and tensile strength values range from 485 to 1035 MPa (70 to 150 ksi), depending on chemical composition, thickness, and heat treatment.

Many of the steels are included in ASTM specifications such as A 514, A 517, and A 543. However, a few steels, such as HY-80, HY-100, and HY-130, are covered by military specifications. The low-carbon quenched and tempered steels are furnished primarily as plate, although some are produced as either forgings or castings. The chemical compositions of typical steels are given in Table 4.

Table 4 Nominal composition and tensile properties of selected low-carbon quenched and tempered low-alloy structural steels

ASTM specification or common designation	Grade	Composition, %(a)										Minimum tensile strength(c)		Minimum yield strength(c)	
		C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Other	MPa	ksi	MPa	ksi
A 514; A 517	A	0.15–0.21	0.80–1.10	0.035	0.04	0.40–0.80	0.50–0.80	…	0.18–0.28	…	Zr, 0.05–0.15; B, 0.0025	700–895; 725–930	100–130; 105–135	620–700	90–100
	B	0.12–0.21	0.70–1.00	0.035	0.04	0.20–0.35	0.40–0.65	…	0.15–0.25	…	V, 0.03–0.08; Ti, 0.01–0.03; B, 0.0005–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	C	0.10–0.20	1.10–1.50	0.035	0.04	0.15–0.30	…	…	0.20–0.30	…	B, 0.001–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	D	0.13–0.20	0.40–0.70	0.035	0.04	0.20–0.35	0.85–1.20	…	0.15–0.25	0.20–0.40	Ti, 0.004–0.10(b); B, 0.0015–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	E	0.12–0.20	0.40–0.70	0.035	0.04	0.20–0.35	1.40–2.00	…	0.40–0.60	0.20–0.40	Ti, 0.04–0.10(a); B, 0.0015–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	F	0.10–0.20	0.60–1.00	0.035	0.04	0.15–0.35	0.40–0.65	0.70–1.00	0.40–0.60	0.15–0.50	V, 0.03–0.08; B, 0.0005–0.006	700–895; 725–930	100–130; 105–135	620–700	90–100
	G	0.15–0.21	0.80–1.10	0.035	0.04	0.50–0.90	0.50–0.90	…	0.40–0.60	…	Zr, 0.05–0.15; B, 0.0025	700–895; 725–930	100–130; 105–135	620–700	90–100
	H	0.12–0.21	0.95–1.30	0.035	0.04	0.20–0.35	0.40–0.65	0.30–0.70	0.20–0.30	…	V, 0.03–0.08; B, 0.0005–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	J	0.12–0.21	0.45–0.70	0.035	0.04	0.20–0.35	…	…	0.50–0.65	…	B, 0.001–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	K	0.10–0.20	1.10–1.50	0.035	0.04	0.15–0.30	…	…	0.45–0.55	…	B, 0.001–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	L	0.13–0.20	0.40–0.70	0.035	0.04	0.20–0.35	1.15–1.65	…	0.25–0.40	0.20–0.40	Ti, 0.04–0.10(b); B, 0.0015–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	M	0.12–0.21	0.45–0.70	0.035	0.04	0.20–0.35	…	1.20–1.50	0.45–0.60	…	B, 0.001–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	N	0.15–0.21	0.80–1.10	0.035	0.04	0.40–0.90	0.50–0.80	…	0.25	…	Zr, 0.05–0.15; B, 0.0005–0.0025	700–895; 725–930	100–130; 105–135	620–700	90–100
	P	0.12–0.21	0.45–0.70	0.035	0.04	0.20–0.35	0.85–1.20	1.20–1.50	0.45–0.60	…	B, 0.001–0.005	700–895; 725–930	100–130; 105–135	620–700	90–100
	Q	0.14–0.21	0.95–1.30	0.035	0.04	0.15–0.35	1.00–1.50	1.20–1.50	0.40–0.60	…	V, 0.03–0.08	700–895; 725–930	100–130; 105–135	620–700	90–100
A 543	B	0.23	0.40	0.020	0.020	0.20–0.40	1.50–2.00	2.60–4.00	0.45–0.60	…	V, 0.03	620–930	90–135	480–700	70–100
	C	0.23	0.40	0.020	0.020	0.20–0.40	1.20–1.50	2.25–3.50	0.45–0.60	…	V, 0.03	620–930	90–135	480–700	70–100
HY-80	…	0.12–0.18	0.10–0.40	0.025	0.025	0.15–0.35	1.00–1.80	2.00–3.25	0.20–0.60	0.25	V, 0.03; Ti, 0.02	…	…	550	80
HY-100	…	0.12–0.20	0.10–0.40	0.025	0.025	0.15–0.35	1.00–1.80	2.25–3.50	0.20–0.60	0.25	V, 0.03; Ti, 0.02	…	…	700	100
HY-130	…	0.12	0.60–0.90	0.010	0.015	0.15–0.35	0.40–0.70	4.75–5.25	0.30–0.65	…	V, 0.05–0.10	…	…	895	130

(a) When a single value is shown, it is a maximum limit. (b) Vanadium may be substituted for part or all of titanium content on a one-for-one basis. (c) Limiting values vary with the plate thickness

Low-Alloy Steels for Pressure Vessels and Piping. A variety of low-alloy steels containing from 0.10 to 0.30% C and up to 10% total alloy are used for welded pressure vessels and piping. Alloy additions include manganese, silicon, molybdenum, chromium, nickel, vanadium, copper, and niobium. Table 5 gives the nominal chemical composition and minimum specified tensile strength values of representative low-alloy steels used in pressure vessels and piping. These steels are usually furnished in the as-rolled, as-forged, or annealed condition. Some steels, such as those shown in Table 6 also may be obtained in the normalized, normalized and tempered, or quenched and tempered condition to provide enhanced mechanical properties.

The choice of low-alloy steel to be used for a pressure vessel or piping system is usually made on the basis of one or more desired properties in service, such as tensile strength, resistance to hydrogen attack, resistance to creep and oxidation at elevated temperatures, or low-temperature notch ductility. Weldability is an important consideration, as well.

Heat-resisting low-alloy steels used for pressure vessels and pipe generally contain up to 0.25% C, plus alloy additions such as chromium, molybdenum, vanadium, and silicon. When compared with plain carbon steels, the heat-resisting steels offer greater tensile and creep-rupture strengths at elevated temperatures and greater resistance to oxidation and hydrogen attack. Steels with from 1 to 9% Ni provide greater resistance to

Table 5 Typical as-rolled, as-forged, or annealed low-alloy steels used for pressure vessels and piping

Product type	Base metal ASTM specification	Grade	Nominal composition, wt %			Minimum specified tensile strength	
			Cr	Mo	Ni	MPa	ksi
Plate	A 203	A	…	…	2.25	450	65
		B	…	…	2.25	480	70
		D	…	…	3.50	450	65
		E	…	…	3.50	480	70
		F (≤ 50 mm, or 2 in.)	…	…	3.50	550	80
		(> 50 mm, or 2 in.)	…	…	3.50	515	75
	A 204	A	…	0.5	…	450	65
		B	…	0.5	…	480	70
		C	…	0.5	…	515	75
	A 387	2	0.5	0.5	…	380	55
		12	1	0.5	…	380	55
		11	1.25	0.5	…	415	60
		22	2.25	1	…	415	60
		21	3	1	…	415	60
		5	5	0.5	…	415	60
		7	7	0.5	…	415	60
		9	9	1	…	415	60
Pipe	A 369	FP1	…	0.5	…	380	55
		FP2	0.5	0.5	…	380	55
		FP5	5	0.5	…	415	60
		FP7	7	0.5	…	415	60
		FP9	9	1	…	415	60
		FP11	1.25	0.5	…	415	60
		FP12	1	0.5	…	415	60
		FP21	3	1	…	415	60
		FP22	2.25	1	…	415	60

Table 6 Selected normalized, normalized and tempered, or quenched and tempered low-alloy steels used for pressure vessel and piping applications

Product type	ASTM specification	Grade	Composition, wt%					Minimum specified tensile strength	
			Ni	Cr	Cu	Mn	Mo	MPa	ksi
Pipe fittings	A 420	WPL 9	1.9	…	1	…	…	435	63
		WPL 3	3.5	…	…	…	…	450	65
		WPL 8	9	…	…	…	…	690	100
Forgings	A 508	Class 2	0.75	0.35	…	…	0.65	550	80
		Class 3	0.70	…	…	…	0.50	550	80
		Class 4	3.50	1.75	…	…	0.50	725	105
		Class 5	3.50	1.75	…	…	0.50	725	105
	A 541	Class 2	0.75	0.35	…	…	0.65	550	80
		Class 3	0.70	…	…	…	0.50	550	80
		Class 5	…	1.25	…	…	0.50	550	80
		Class 6	…	2.25	…	…	1	725	105
		Class 7	3.35	1.6	…	…	0.50	725	105
		Class 8	3.35	1.6	…	…	0.50	725	105
Flanges, fittings, and valves	A 522	Type I	9	…	…	…	…	725	100
		Type II	8	…	…	…	…	725	100
Plates	A 533	Type A	…	…	…	1.3	0.5	550(a)	80(a)
								620(b)	90(b)
								690(c)	100(c)
		Type B	0.55	…	…	1.3	0.5	550(a)	80(a)
								620(b)	90(b)
								690(c)	100(c)
		Type C	0.85	…	…	1.3	0.5	550(a)	80(a)
								620(b)	90(b)
								690(c)	100(c)
		Type D	0.30	…	…	1.3	0.5	550(a)	80(a)
								620(b)	90(b)
								690(c)	100(c)

(a) Class 1. (b) Class 2. (c) Class 3

notch embrittlement than do carbon steels or many other low-alloy steels and are widely used in low-temperature service.

The medium-carbon heat-treatable steels includes the SAE-AISI 4130, the higher-strength 4140, and the deeper hardening, higher-strength 4340. Several modifications of the basic 4340 steel have been developed. In one modification (300M), silicon content is increased to prevent embrittlement when the steel is tempered at the low temperatures required for very high strength. In AMS 6434, vanadium is added as a grain refiner to increase toughness, and the carbon is slightly reduced to promote weldability. Ladish D-6ac contains the grain refiner vanadium; slightly higher carbon, chromium, and molybdenum than 4340; and slightly lower nickel. Other less widely used steels that may be included in this family are 6150 and 8640. Chemical compositions are given in Table 7. All of these steels are capable of exhibiting yield strengths in excess of 1380 MPa (200 ksi). Applications for medium-carbon heat-treatable steels include bolts, screws, and other fasteners; gears, pinions, shafts, and similar machinery components; dies, dummy blocks, and backer blocks for forming tools; crankshafts and piston rods for engines; and landing gear and other critical structural members for aircraft.

Table 7 Compositions of medium-carbon heat-treatable high-strength steels

Designation or trade name	Composition, wt% (a)						
	C	Mn	Si	Cr	Ni	Mo	V
4130	0.28–0.33	0.40–0.60	0.20–0.35	0.80–1.10	…	0.15–0.25	…
4140	0.38–0.43	0.75–1.00	0.20–0.35	0.80–1.10	…	0.15–0.25	…
4340	0.38–0.43	0.60–0.80	0.20–0.35	0.70–0.90	1.65–2.00	0.20–0.30	…
AMS 6434	0.31–0.38	0.60–0.80	0.20–0.35	0.65–0.90	1.65–2.00	0.30–0.40	0.17–0.23
300M	0.40–0.46	0.65–0.90	1.45–1.80	0.70–0.95	1.65–2.00	0.30–0.45	0.05 min
D-6a	0.42–0.48	0.60–0.90	0.15–0.30	0.90–1.20	0.40–0.70	0.90–1.10	0.05–0.10
6150	0.48–0.53	0.70–0.90	0.20–0.35	0.80–1.10	…	…	0.15–0.25
8640	0.38–0.43	0.75–1.00	0.20–0.35	0.40–0.60	0.40–0.70	0.15–0.25	…

(a) P and S contents may vary with steelmaking practice. Usually, these steels contain no more than 0.035 P and 0.040 S.

Effects of Alloying and Residual Elements

Alloying elements are added to ordinary (plain carbon) steels to modify their behavior during thermal processing (heat treatment or thermomechanical processing), which in turn results in improvement of the mechanical and physical properties of the steel. Specifically, alloying additions are made for one or more of the following reasons:

- Improve tensile strength without appreciably lowering ductility
- Improve toughness
- Increase hardenability which permits the hardening of larger sections than possible with plan carbon steels or allows successful quenching with less drastic cooling rates, reducing the hazard of distortion and quench cracking.
- Retain strength at elevated temperatures
- Obtain better corrosion resistance
- Improve wear resistance
- Impart a fine grain size to the steel

A semantic distinction can be made between alloying elements and residual elements; the latter are not intentionally added to the steel, but result from the raw materials and steelmaking practices used to produce the steel. Any particular element can be either alloying or residual. For example, some nickel or chromium could come into steel through alloy steel scrap and so be considered residual; however, if either of these elements must be added to a steel to meet the desired composition range it might be considered an alloying element.

Both alloying and residual elements can profoundly affect steel production, manufacture into end products, and service performance of the end product. The effects of one alloying element on a steel may be affected by the presence of other elements; such interactive effects are complex. In addition, the effects of a particular element may be beneficial to steel in one respect but detrimental in others. General effects of the various alloying and residual elements commonly found in steels are summarized subsequently and in Table 8.

Table 8 Summary of the effects of alloying elements on the properties and processing of carbon and alloy steels

Property	Alloying element																							
	C	Mn	Si	Cu	Cr	Ni	Mo	V	Nb	Al	B	Ti	Zr	W	Ca	Pb	N	Co	P	Se	O	Sn	As	Sb	S
Room-temperature properties																									
Strength	✓	✓	✓(a)			✓(a)		✓(a)					✓(b)				✓		✓		✓				
Ductility	x																x		x						x
Fatigue	✓					✓									✓(c)										
Hardness	✓	✓						✓						✓			✓		✓						
Abrasion resistance	✓				✓									✓											
Hardenability	✓	✓			✓	✓(d)	✓	✓(e)			✓	✓(f)	✓(g)				x(h)								
Charpy impact	x					✓		✓							✓(c)				x		x				x
Fracture (K_{Tc}) toughness	x				✓(i)	✓		✓	x(j)						✓(c)		✓(k)	✓	x		x				
High-temperature properties																									
Strength					✓(l)		✓							✓											
Creep resistance							✓																		
Low-temperature properties																									
Strength						✓																			
Toughness	x					✓		✓																	
Corrosion																									
General corrosion resistance	x			✓(m)	✓	✓													✓						
Pitting resistance				✓			✓																		
Oxidation/scaling resistance			✓	✓																					

(continued)

✓ = effective. x = detrimental. (a) Ferrite strengthener. (b) Zirconium improves strength in the hot-rolled condition. (c) Calcium improves fatigue and toughness through inclusion shape control. (d) Nickel improves hardenability in conjunction with chromium. (e) Additions of vanadium up to 0.05% increase hardenability; larger additions result in carbide formation which is detrimental to hardenability. (f) Titanium is effective because it protects boron from nitrogen in boron-treated steels. If carbides form, it is detrimental. (g) Zirconium slightly increases hardenability unless carbides form. (h) Nitrogen can reduce the effect of boron on the hardenability of steel. (i) Chromium improves toughness in conjunction with nickel. (j) Detrimental unless grain is refined. (k) Effective in aluminium-killed steels because nitrogen forms AIN particles that control grain size and improve strength and toughness. Nitrogen lowers toughness in aluminium-free steels. (l) Chromium increases high-temperature strength in conjunction with molybdenum. (m) Copper is beneficial to atmospheric corrosion resistance when present in amounts exceeding 0.20%. (n) Segregation ratings: Mod. = moderate; sl. = slight; and Max. = Maximum. (o) Lead induces liquid metal embrittlement.

Table 8 (continued)

Property	Alloying element																							
	C	Mn	Si	Cu	Cr	Ni	Mo	V	Nb	Al	B	Ti	Zr	W	Ca	Pb	N	Co	P	Se	O	Sn	As	Sb	S
Microstructure																									
Segregation (n)	Mod.	sl.	sl.	Mod.																					Max.
Grain refiner								✓		✓				✓			✓								
Slows grain growth								✓		✓		✓	✓				✓(k)								
Deoxidizer		✓	✓							✓		✓	✓		✓										
Eliminates hot shortness		✓		x												x(o)						x			
Carbide former					✓		✓	✓	✓					✓											
Reduces temper embrittlement							✓												x			x	x	x	
Austenite stabilizer	✓	✓				✓																			
Ferrite stabilizer			✓		✓		✓		✓																
Fabrication																									
Forming	x																								
Welding	x																								
Machining	x	✓																							
Surface quality	x	✓	x	x											✓	✓			✓	✓					✓

✓ = effective. x = detrimental. (a) Ferrite strengthener. (b) Zirconium improves strength in the hot-rolled condition. (c) Calcium improves fatigue and toughness through inclusion shape control. (d) Nickel improves hardenability in conjunction with chromium. (e) Additions of vanadium up to 0.05% increase hardenability; larger additions result in carbide formation which is detrimental to hardenability. (f) Titanium is effective because it protects boron from nitrogen in boron-treated steels. If carbides form, it is detrimental. (g) Zirconium slightly increases hardenability unless carbides form. (h) Nitrogen can reduce the effect of boron on the hardenability of steel. (i) Chromium improves toughness in conjunction with nickel. (j) Detrimental unless grain is refined. (k) Effective in aluminium-killed steels because nitrogen forms AIN particles that control grain size and improve strength and toughness. Nitrogen lowers toughness in aluminium-free steels. (l) Chromium increases high-temperature strength in conjunction with molybdenum. (m) Copper is beneficial to atmospheric corrosion resistance when present in amounts exceeding 0.20%. (n) Segregation ratings: Mod. = moderate; sl. = slight; and Max. = Maximum. (o) Lead induces liquid metal embrittlement.

Alloying Elements

Carbon is the most important single alloying element in steel. It is essential to the formation of cementite, Fe_3C, (and other carbides), pearlite, spheroidite (an aggregate of spherical carbides in a ferrite matrix), bainite, and iron-carbon martensite. Microstructures comprising one or more of these components can provide a wide range of mechanical properties and fabrication characteristics. The relative amounts and distributions of these elements can be manipulated by heat treatment to alter the microstructure, and therefore the properties, of a particular piece of steel. Much of ferrous metallurgy is devoted to the various structures and transformations in iron-carbon alloys; many other alloying elements are considered largely on the basis of their effects on the iron-carbon system.

Assuming that the comparisons are made among steels having comparable microstructures, the strength and hardness are raised as the carbon content is increased; however, toughness and ductility are reduced by increases in carbon content. The influence of carbon content on mechanical properties is shown in Fig. 1. The hardness of iron-carbon martensite is increased by raising the carbon content of steel, reaching a maximum at about 0.6% C, Increasing the carbon content also increases hardenability.

The amount of carbon required in the finished steel limits the type of steel that can be made. As the carbon content of rimmed steel increases, surface quality becomes impaired. Killed steels in approximately the 0.15 to 0.30% C content level may have poorer surface quality and require special processing to obtain surface quality comparable to steels with higher or lower carbon content. Carbon has a moderate tendency to segregate, and carbon segregation is often more significant than the segregation of other elements.

Manganese is normally present in all commercial steels. It is important in the manufacture of steel because it deoxidizes the melt and facilitates hot working of the steel by reducing the susceptibility to hot shortness. Manganese also combines with sulfur to form manganese sulfide stringers, which improve the machinability of steel. It contributes to strength and hardness, but to a lesser degree than does carbon; the amount of increase depends on the carbon content. Increasing the manganese content decreases ductility and weldability but to a lesser extent than does an increase in carbon content. Manganese has a strong effect on increasing the hardenability of a steel. High levels of manganese produce an austenitic steel with improved wear and abrasion resistance.

Manganese has less of a tendency toward macrosegregation than any of the common elements. Steels with more than 0.60% Mn cannot be readily rimmed. Manganese is beneficial to surface quality in all carbon ranges (with the exception of extremely low-carbon rimmed steels).

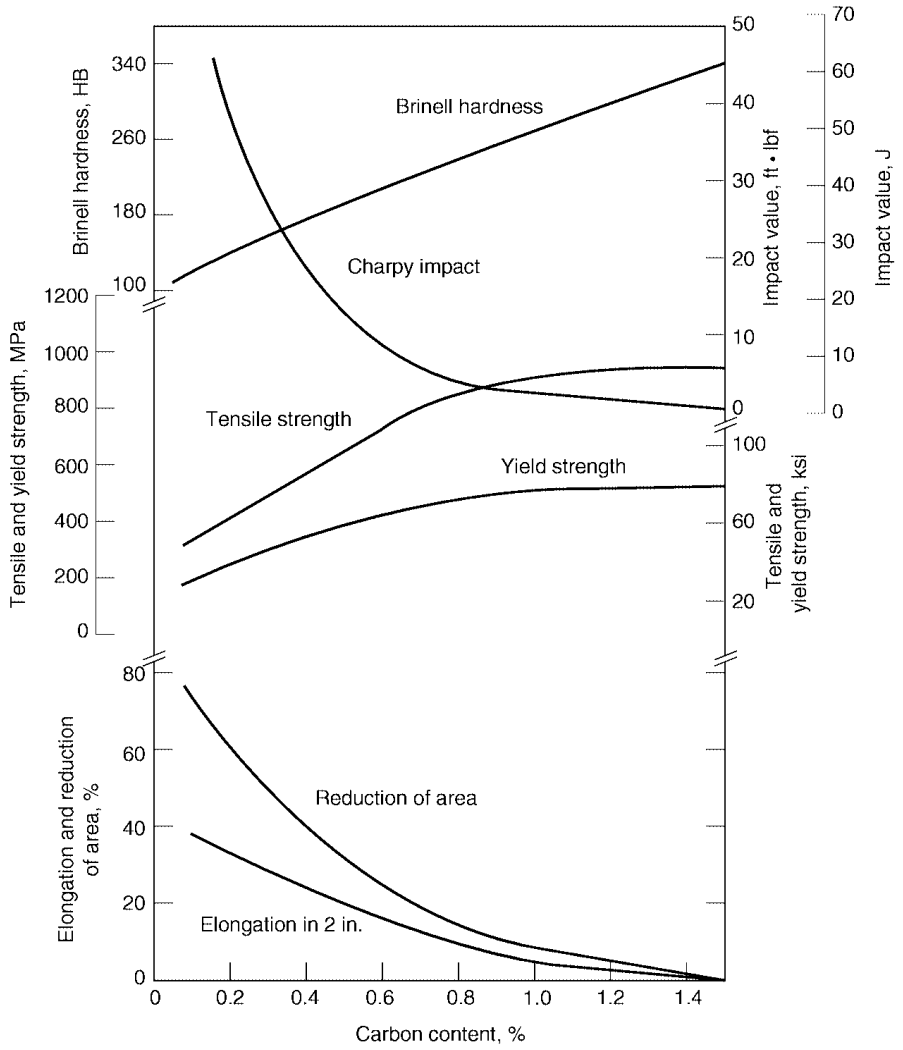


Fig. 1 Variations in average mechanical properties of as-rolled 25 mm (1 in.) diam bars of plain carbon steels as a function of carbon content

Silicon is one of the principal deoxidizers used in steelmaking. The amount of this element in a steel, which is not always noted in the chemical composition specifications, depends on the deoxidation practice specified for the product. Rimmed and capped steels contain minimal silicon, usually less than 0.05%. Fully killed steels usually contain 0.15 to 0.30% silicon for deoxidation; if other deoxidants are used, the amount of silicon in the steel may be reduced. Silicon has only a slight tendency to segregate. In low-carbon steels, silicon is usually detrimental to surface quality, and this condition is more pronounced in low-carbon resulfurized grades.

Silicon slightly increases the strength of ferrite, without causing a serious loss of ductility. In larger amounts, it increases the resistance of steel to scaling in air (up to about 260 °C, or 500 °F) and decreases the magnetic hysteresis loss. Such high-silicon steels are generally difficult to process.

Copper has a moderate tendency to segregate. Copper in appreciable amounts is detrimental to hot-working operations. Copper adversely affects forge welding, but it does not seriously affect arc or oxyacetylene welding. Copper is detrimental to surface quality and exaggerates the surface defects inherent in resulfurized steels. Copper is, however, beneficial to atmospheric corrosion resistance when present in amounts exceeding 0.20%. Steels containing these levels of copper are referred to as weathering steels and are described in the section "Effects of Alloying on Corrosion Behavior."

Chromium is generally added to steel to increase resistance to corrosion and oxidation, to increase hardenability, to improve high-temperature strength, or to improve abrasion resistance in high-carbon compositions. Chromium is a strong carbide former. Complex chromium-iron carbides go into solution in austenite slowly; therefore, a sufficient heating time before quenching is necessary.

Chromium can be used as a hardening element and is frequently used with a toughening element such as nickel to produce superior mechanical properties. At higher temperatures, chromium contributes increased strength; it is ordinarily used for applications of this nature in conjunction with molybdenum.

Nickel, when used as an alloying element in constructional steels, is a ferrite strengthener, Because nickel does not form any carbide compounds in steel, it remains in solution in the ferrite, thus strengthening and toughening the ferrite phase. Nickel steels are easily heat treated because nickel lowers the critical cooling rate. In combination with chromium, nickel produces alloy steels with greater hardenability, higher impact strength, and greater fatigue resistance than can be achieved in carbon steels. Nickel alloy steels also have superior low-temperature strength and toughness.

Molybdenum increases the hardenability of steel and is particularly useful in maintaining the hardenability between specified limits. This element, especially in amounts between 0.15 and 0.30%, minimizes the susceptibility of a steel to temper embrittlement. Hardened steels containing molybdenum must be tempered at a higher temperature to achieve the same amount of softening. Molybdenum is unique in the extent to which it increases the high-temperature tensile and creep strengths of steel. It retards the transformation of austenite to pearlite far more than it does the transformation of austenite to bainite; thus, bainite can be produced by continuous cooling of molybdenum-containing steels.

Vanadium is generally added to steel to inhibit grain growth during heat treatment. In controlling grain growth, it improves both the strength and toughness of hardened and tempered steels. Additions of vanadium of

up to about 0.05% increase the hardenability of the steel; larger additions appear to reduce the hardenability, probably because vanadium forms carbides that have difficulty dissolving in austenite. Vanadium is also an important element in microalloyed steels.

Niobium. Small additions of niobium increase the yield strength and, to a lesser degree, the tensile strength of carbon steel. The addition of 0.02% Nb can increase the yield strength of medium-carbon steel by 70 to 100 MPa (10 to 15 ksi). This increased strength may be accompanied by considerably impaired notch toughness unless special measures are used to refine grain size during hot rolling. Grain refinement during hot rolling involves special thermomechanical processing techniques such as controlled-rolling practices, low finishing temperatures for final reduction passes, and accelerated cooling after rolling is completed.

Aluminum is widely used as a deoxidizer and for control of grain size. When added to steel in specified amounts, it controls austenite grain growth in reheated steels. Of all the alloying elements, aluminum is the most effective in controlling grain growth prior to quenching. Titanium, zirconium, and vanadium are also effective grain growth inhibitors; however, for structural grades that are heat treated (quenched and tempered), these three elements may have adverse effects on hardenability because their carbides are quite stable and difficult to dissolve in austenite prior to quenching.

Aluminum is also an important alloying element in nitrided steels. Aluminum is beneficial in nitriding because it forms a nitride (AIN) that is stable at nitriding temperatures. Because aluminum is the strongest nitride-former of the common alloying elements, aluminum-containing steels (typically about 1.4% Al) yield the best nitriding results in terms of total alloy content.

Titanium increases the strength and hardness of steel by grain size control. It is also a very strong carbide and nitride former. Titanium may be added to boron steels because it combines readily with any oxygen and nitrogen in the steel, thereby increasing the effectiveness of the boron in increasing the hardenability of the steel. Titanium is also a strong deoxidizer.

Boron is added to fully killed steel to improve hardenability. Boron-treated steels are produced in a range of 0.0005 to 0.003%. Whenever boron is substituted in part for other alloys, it should be done only with hardenability in mind because the lowered alloy content may be harmful for some applications. Boron is most effective in lower carbon steels. Boron is also added to steel for nuclear reactor applications because of its high cross-section for neutrons.

Tungsten increases hardness, promotes a fine-grain structure, and is excellent for resisting heat. At elevated tempering temperatures, tungsten forms tungsten carbide, which is very hard and stable. The tungsten carbide helps prevent the steel from softening during tempering. Tungsten is used extensively in high-speed tool steels and has been proposed as a substitute for molybdenum in reduced-activation ferritic steels for nuclear applications.

Zirconium inhibits grain growth and is used as a deoxidizer in killed steels. Its primary use is to improve hot-rolled properties in HSLA steels. Zirconium in solution also improves hardenability slightly.

Calcium is sometimes used to deoxidize steels. In HSLA steels, it helps to control the shape of nonmetallic inclusions, thereby improving toughness. Steels deoxidized with calcium generally have better machinability than do steels deoxidized with silicon or aluminum.

Cerium is added to steel for sulfide shape control. It is also a strong deoxidizer.

Lead is sometimes added to carbon and alloy steels through mechanical dispersion during teeming for the purpose of improving the machining characteristics of the steels. These additions are generally in the range of 0.15 to 0.35%.

Lead does not dissolve in the steel during teeming, but is retained in the form of microscopic globules. At temperatures near the melting point of lead, it can cause liquid embrittlement.

Bismuth, like lead, is added to special steels for improved machinability.

Nitrogen increases the strength, hardness, and machinability of steel, but it decreases the ductility and toughness. In aluminum-killed steels, nitrogen forms aluminum nitride particles that control the grain size of the steel, thereby improving both toughness and strength. Nitrogen can reduce the effect of boron on the hardenability of steels.

Residual Elements

Any of the alloying elements mentioned above may inadvertently appear in steel as a result of the presence in raw materials used to make the steel. As such, they would be known as “residual” elements. Because of possible undesired (though not necessarily undesirable) effects of these elements on the finished products, most steelmakers are careful to minimize the amount of these elements in the steel, primarily through separation of steel scrap by alloy content.

Several other elements, generally considered to be undesirable impurities, may be introduced into steel from pig iron. For certain specific purposes, however, they may be deliberately added; in this case, they would be considered alloying elements. A brief description of each of these follows.

Phosphorus increases strength and hardness of steel, but severely decreases ductility and toughness. It increases the susceptibility of medium-carbon alloy steels, particularly straight chromium steels, to temper embrittlement. Phosphorus may be deliberately added to steel to improve its machinability or corrosion resistance.

Sulfur. Increased sulfur content lowers transverse ductility and notch impact toughness but has only a slight effect on longitudinal mechanical properties. Weldability decreases with increasing sulfur content. This element is very detrimental to surface quality, particularly in the lower-carbon and lower-manganese steels. For these reasons, only a maximum limit is specified for most steels. The only exception is the group of free-machining steels, where sulfur is added to improve machinability; in this case, a range is specified. Sulfur has a greater segregation tendency than do any of the other common elements. Sulfur occurs in steel principally in the form of sulfide inclusions. Obviously, a greater frequency of such inclusions can be expected in the resulfurized grades.

Oxygen. Although oxygen can slightly increase the strength of steel, it is generally considered an undesirable element. Oxygen combines with other elements (e.g., Mn, Si, Al, and Ti) to form oxide inclusions that can degrade toughness and fatigue resistance. It is usually minimized in steel by deoxidation with aluminum and/or silicon and vacuum degassing.

Hydrogen dissolved in steel during manufacture can seriously embrittle it. This effect is not the same as the embrittlement that results from electroplating or pickling. Embrittlement resulting from hydrogen dissolved during manufacture can cause flaking during cooling from hot rolling temperatures. Dissolved hydrogen rarely affects finished mill products, for reheating the steel prior to hot forming bakes out nearly all of the hydrogen.

Tin can render steel susceptible to temper embrittlement and hot shortness.

Arsenic and antimony also increase susceptibility of a steel to temper embrittlement.

Effects of Carbon Content and Alloying on Hardenability

Hardenability of steel is the property that determines the depth and distribution of hardness induced by quenching. Steels that exhibit deep hardness penetration are considered to have high hardenability, while those that exhibit shallow hardness penetration are of low hardenability. Because the primary objective in quenching is to obtain satisfactory hardening to some desired depth, it follows that hardenability is usually the most important single factor in the selection of steel for heat treated parts.

Hardenability should not be confused with hardness as such or with maximum hardness. The maximum attainable hardness of any steel depends solely on carbon content. Also, the maximum hardness values that can be obtained with small test specimens under the fastest cooling rates of water quenching are nearly always higher than those developed under production heat treating conditions, because hardenability limitations in quenching larger sizes may result in less than 100% martensite formation. Effects of carbon and martensite content on hardness are shown in Fig. 2.

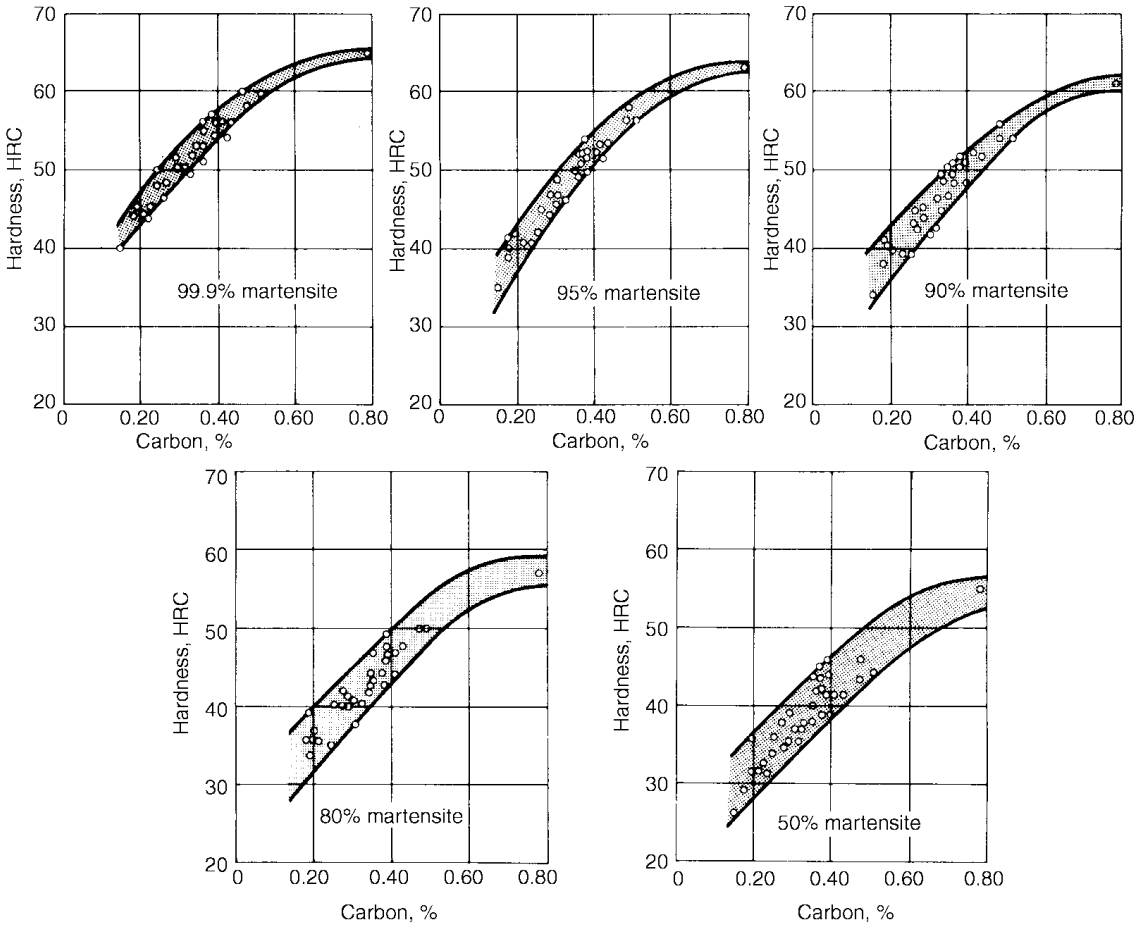


Fig. 2 Effect of carbon on hardness of martensite structures

The hardenability of steel is governed almost entirely by the chemical composition (carbon and alloy content) at the austenitizing temperature and the austenite grain size at the moment of quenching. In some instances, the chemical composition of the austenite may not be the same as that determined by chemical analysis, because some carbide may be undissolved at the austenitizing temperature. Such carbides would be reflected in the chemical analysis, but, being undissolved in the austenite, neither their carbon nor alloy content can contribute to hardenability. Also, by nucleating transformation products, undissolved carbides can actively decrease hardenability. This is especially important in high-carbon (0.50 to 1.10%) and alloy carburizing steels, which may contain excess carbides at the austenitizing temperature. Consequently, such factors as austenitizing temperature, time at temperature, and prior microstructure are sometimes very important variables when determining the basic hardenability of a specific steel composition.

Hardenability Testing

Hardenability of a steel is best assessed by studying the hardening response of the steel to cooling in a standardized configuration in which a variety of cooling rates can be easily and consistently reproduced from one test to another.

The end-quench, or Jominy, test fulfills the cooling rate requirements of hardenability testing most conveniently. The test specimen, a 1 in. (25.4 mm) diam bar 4 in. (102 mm) in length, is water quenched on one end face. The bar from which the specimen is made must be normalized before the test specimen is machined. The test involves heating the test specimen to the proper austenitizing temperature and then transferring it to a quenching fixture designed so that the specimen is held vertically 12.7 mm ($\frac{1}{2}$ in.) above an opening through which a column of water may be directed against the bottom face of the specimen. While the bottom end is being quenched by the column of water, the opposite end is cooling slowly in air, and intermediate positions along the specimen are cooling at intermediate rates. After the specimen has been quenched, parallel flats 180° apart are ground 0.015 in. (0.38 mm) deep on the cylindrical surface, Rockwell C hardness is measured at intervals of $\frac{1}{16}$ in. (1.59 mm) for alloy steels and $\frac{1}{32}$ in. (0.79 mm) for carbon steels, starting from the water-quenched end. A plot of these hardness values and their positions on the test bar, as shown in Fig. 3, indicates the relation between hardness and cooling rate, which, in effect, is the hardenability of the steel. Figure 3 also shows the cooling rate for the designated test positions. Details of the standard test method are contained in ASTM A 255 and SAE J406.

The measured hardenability, curve shown in Fig. 3 for one specimen of 8650 steel falls about midway between the minimum and maximum hard-

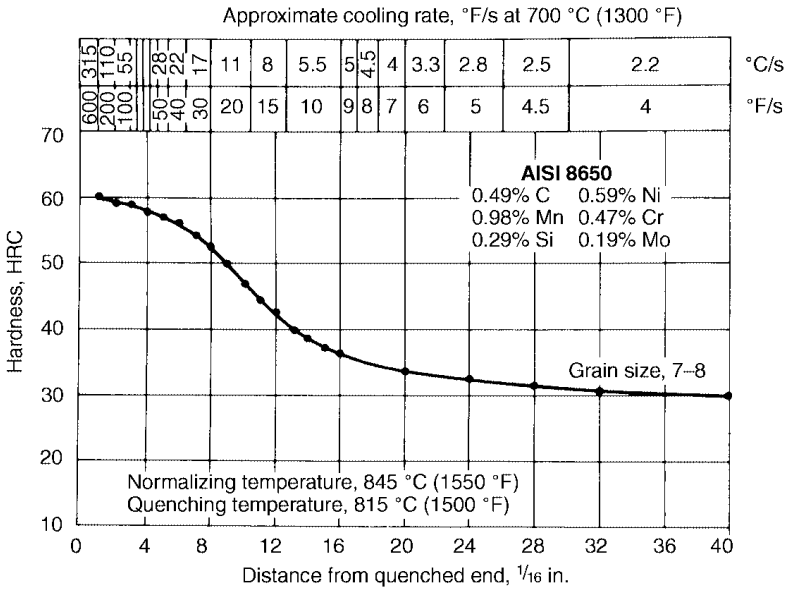


Fig. 3 Method for presenting end-quench hardenability data

enability curves that would be obtained from many heats of 8650 steel, and that define the limits of the so-called H-band for the 8650 steel. (Each grade of steel purchased to hardenability limits is represented by such an H-band that defines these limits.

Effect of Carbon Content

Carbon has a dual effect in hardenable alloy steels: It controls maximum attainable hardness and contributes substantially to hardenability. The latter effect is enhanced by the quantity and type of alloying elements present. It might be concluded, therefore, that increasing the carbon content is the least expensive approach to improving hardenability. This is true to a degree, but several factors weigh against the use of large amounts of carbon:

- High carbon content generally decreases toughness at room and subzero temperatures.
- It produces harder and more abrasive microstructures in the annealed conditions, which makes cold shearing, sawing, machining, and other forms of cold processing more difficult.
- It makes the steel more susceptible to hot shortness in hot working.
- It makes the steel more prone to cracking and distortion in heat treatment. Because of these disadvantages, more than 0.60% C is seldom used in steels for machine parts, except for springs and bearings, and steels with 0.50 to 0.60% C are used less frequently than those containing less than 0.50% C.

Figure 4 shows the differences between minimum hardenability curves for six series of steels. In each series, alloy content is essentially constant,

and the effect of carbon content on hardenability can be observed over a range from 0.15 to 0.60%. The hardness effect is shown by the vertical distance between the curves at any position on the end-quenched specimen, that is, for any cooling rate. This effect varies significantly, depending on the type and amounts of alloying elements. For example, referring to Fig. 4(d) to (f), an increase in carbon content from 0.35 to 0.50% in each of the three series of steels causes hardness increases (in Rockwell C points) at four different end-quench positions, as shown below:

	Distance from quenched surface, in.			
Series	$^{1}/_{16}$	$^{4}/_{16}$	$^{2}/_{16}$	$^{12}/_{16}$
41*xx*H	8	10	17	20
51*xx*H	8	13	9	8
86*xx*H	8	12	18	12

The hardenability effect of carbon content is read on the horizontal axes in Fig. 4. If the inflection points of the curves are used to approximate the position of 50% martensite transformation, the effect of carbon content on hardenability in 8650 versus 8630 steel can be expressed as $+\,^{4}/_{16}$; that is, the inflection point is moved from the $^{5}/_{16}$ position to the $^{9}/_{16}$ position. Similarly, with nominal carbon contents of 0.35 and 0.50%, the hardenability effect of carbon is seen to be less ($^{2}/_{16}$) in 51*xx* series steels and more ($^{6}/_{16}$) in 41*xx* series steels.

Considering the combined hardening and hardenability effects in terms of quenching speed, the cooling rate (or quenching speed) required to produce 45 HRC is affected more by 0.15% C with certain combinations of alloying elements than it is by other combinations. For example, in a steel containing 0.75% Cr and 0.15% Mo (a 41*xx*H series steel, for example), increasing the carbon content by 0.15% lowers the required or critical cooling rate to obtain 45 HRC from 25 to 4.6 °C/s (45 to 83 °F/s), while in a steel containing 0.75% Cr and no molybdenum (51*xx*H series), the same increase in carbon content lowers the cooling rate from 47 to 21 °C/s (85 to 37 °F/s).

The practical significance of the effect of carbon and alloy content on cooling rate is considerable. In a 50 mm (2 in.) diam bar of 4150 steel, a hardness of 45 HRC can be obtained at half-radius using an oil quench without agitation. In a 4135 steel bar of the same diameter, to obtain the same hardness at half-radius would require a strongly agitated water quench. Comparing 32 mm ($1^{1}/_{4}$ in.) diam bars of 5135 and 5150 steel, an agitated water quench will produce a hardness of 45 HRC at half-radius in the 5135 bar, the identical condition can be obtained in the 5150 bar using an oil quench with moderate agitation. Thus, an increase or decrease in carbon content or an alloying addition, such as 0.15% Mo, affects the results obtained both in terms of the quenching severity required and the section size in which the desired results can be obtained.

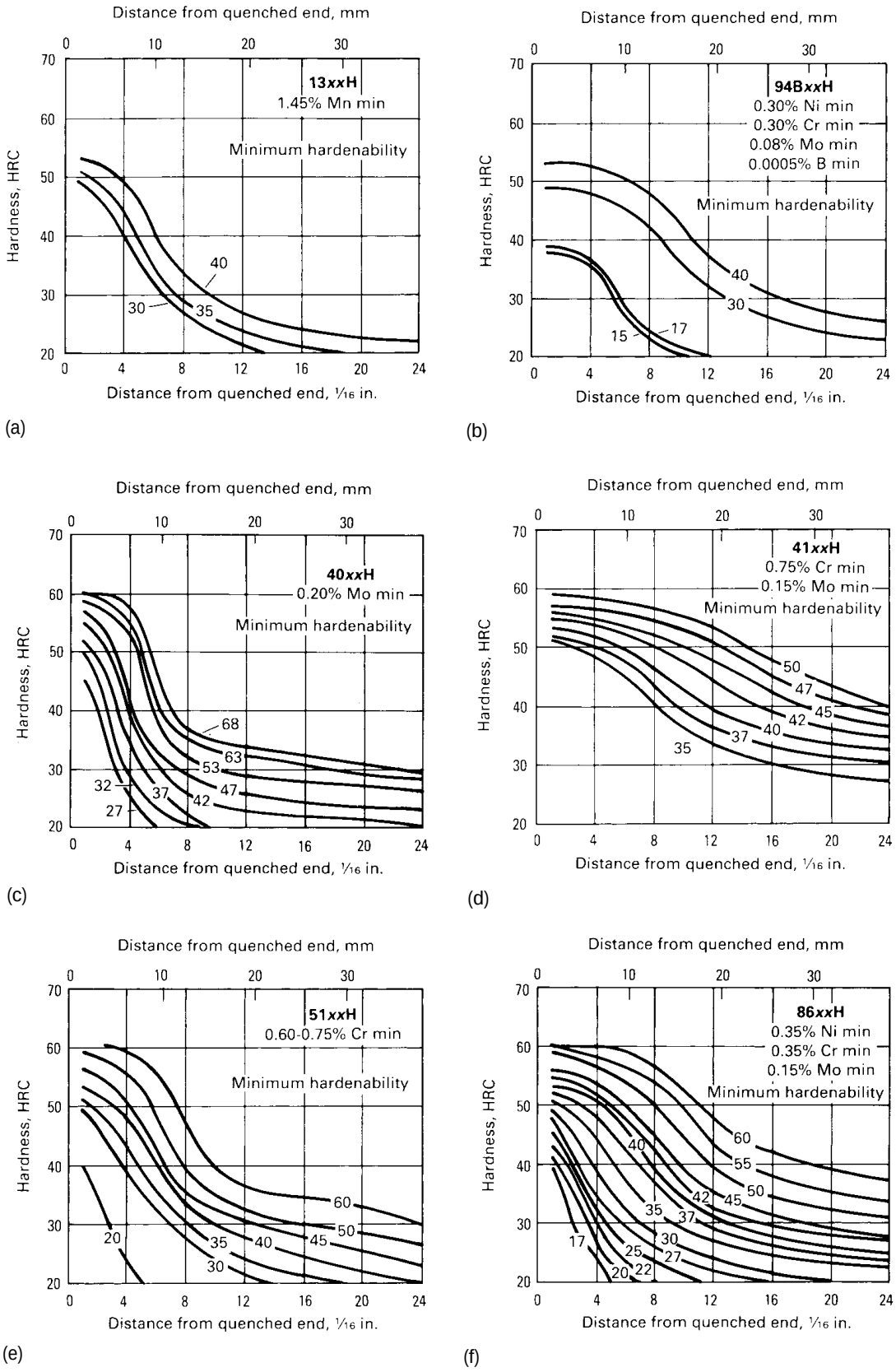


Fig. 4 Effect of carbon content on the minimum end-quench hardenability of six series of alloy H-steels. The number adjacent to each curve is inserted in place of *xx* in the alloy designation to indicate the carbon content of the steel

The above method of rating differs from rating in terms of ideal critical diameter, which is based on hardening not to a given hardness but to 50% martensite at the center of a section, the hardness of which varies according to carbon content. Therefore, a part that must be hardened to a minimum hardness regardless of carbon content requires a steel rated in terms of that hardness and not in terms of 50% martensite, which varies in hardness. Figure 5 shows how steels are rated on the basis of ideal critical diameter by expressing the effect of carbon and alloy content on the section size that will harden to 50% martensite at the center, assuming an ideal quench. An ideal quench is defined as one that removes heat from the surface of the steel as fast as it is delivered to the surface.

Effects of Alloying Elements

The most important function of the alloying elements in heat-treatable steel is to increase hardenability. Increased hardenability makes possible the hardening of larger sections and the use of an oil rather than a water quench to minimize distortion and to avoid quench cracking.

When the standard alloy steels are considered, it is found that, for practical purposes, all compositions develop the same tensile properties when quenched to martensite and tempered to the same hardness below 50 HRC. However, it should not be inferred that all tempered martensites

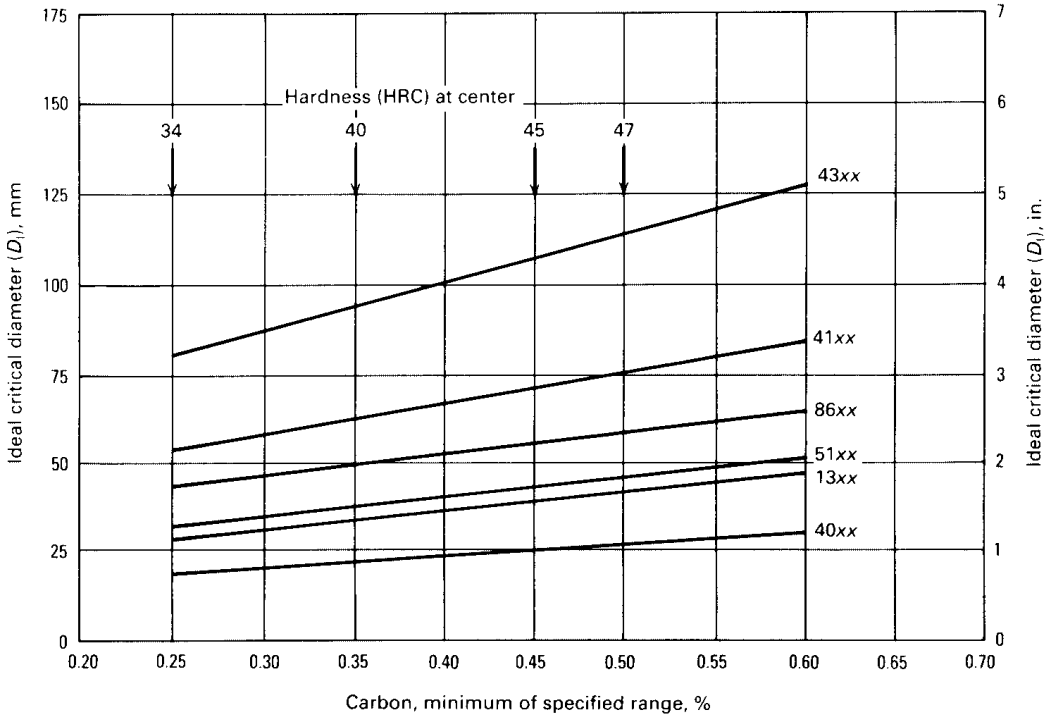


Fig. 5 Effect of carbon content on ideal critical diameter, calculated for the minimum chemical composition of each grade

of the same hardness are alike in all respects. For example, plain carbon martensites have lower reduction-in-area values than alloy martensites. A further difference, sometimes important, is that fully quenched alloy steels require, for the same hardness levels, higher tempering temperatures than carbon steels. This difference in tempering temperature may serve to reduce the residual stress level in finished parts. The stress reduction could be an advantage or a disadvantage, depending on whether a controlled compressive stress is desired in the part. Although tensile properties may not differ significantly from one alloy steel to another, considerable differences may exist in fracture toughness and low-temperature impact properties. In general, steels with a higher nickel content, such as 4320, 3310, and 4340, offer much greater toughness at a given hardness level. In some applications, the toughness factor rather than hardenability may dictate steel selection, but hardenability is still important, because steels that can be fully quenched to 100% martensite are much tougher than those that cannot.

Specific Alloying Elements. Usually, the least expensive means of increasing hardenability at a given carbon content is by increasing the manganese content. Chromium and molybdenum, already referred to as increasing hardenability, are also among the most economical elements per unit of increased hardenability. Nickel is the most expensive per unit, but is warranted when toughness is a primary consideration.

Important synergistic effects, not yet fully defined, can also occur when combinations of alloying elements are used in place of single elements. Some examples of known synergistic combinations are nickel plus manganese, molybdenum plus nickel, and silicon plus manganese.

Boron. Another potent and economical alloying element is boron, which markedly increases hardenability when added to a fully deoxidized steel. The effects of boron on hardenability are unique in several respects:

- A very small amount of boron (about 0.001%) has a powerful effect on hardenability.
- The effect of boron on hardenability is much less in high-carbon than in low-carbon steels.
- Nitrogen and deoxidizers influence the effectiveness of boron.
- High-temperature treatment reduces the hardenability effect of boron.

Figure 6 illustrates the very small amount of boron required for an optimal hardenability effect when appropriate protection of the boron is afforded by additions of titanium or zirconium. In carburizing steels, the effect of boron on case hardenability may be completely lost if nitrogen is abundant in the carburizing atmosphere. The cost of boron is usually much less than that of other alloying elements having approximately the same hardenability effect.

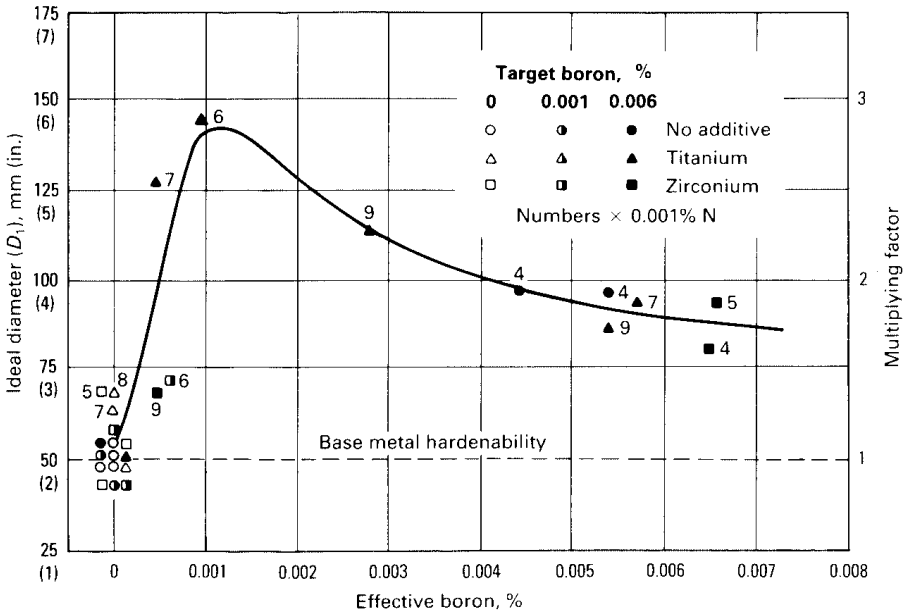


Fig. 6 Influence of effective boron content (B_{eff}) on the hardenability of an 8620 type steel. B_{eff} = B-[(N-0.002)-Ti/5-Zr/15] ≥ 0.

Effects of Alloying on Notch Toughness

The composition of a steel, as well as its microstructure and processing history, significantly affect both the ductile-to-brittle transition temperature range and the energy absorbed during fracture at any particular temperature. The effect of the various alloying elements and those of microstructural and processing variables are intimately interrelated; in practice, it is difficult to change one variable without affecting another. Each individual alloying element contributes to notch toughness to varying degrees.

Carbon. Increasing carbon content increases transition temperature and decreases upper-shelf fracture energy primarily as a result of increased strength and hardness. These effects, measured by Charpy V-notch impact tests, are shown in Fig. 7. Carbon is one of the most potent alloying elements in its effect on notch toughness and strength. Consequently, for maximum toughness, the carbon content should be kept as low as possible, consistent with strength requirements. Low-carbon steels tend to have very steep transition curves.

Manganese has a variety of effects on transition temperature. In low-carbon steels, it can substantially reduce the transition temperature, as shown in Fig. 8. In higher-carbon steels, manganese may be less beneficial. As illustrated in Fig. 9, increasing the manganese content of a normalized medium-carbon steel lowered the ductile-to-brittle fracture transition temperature, probably because the additional manganese reduced the pearlite interlamellar spacing (the spacing between the alter-

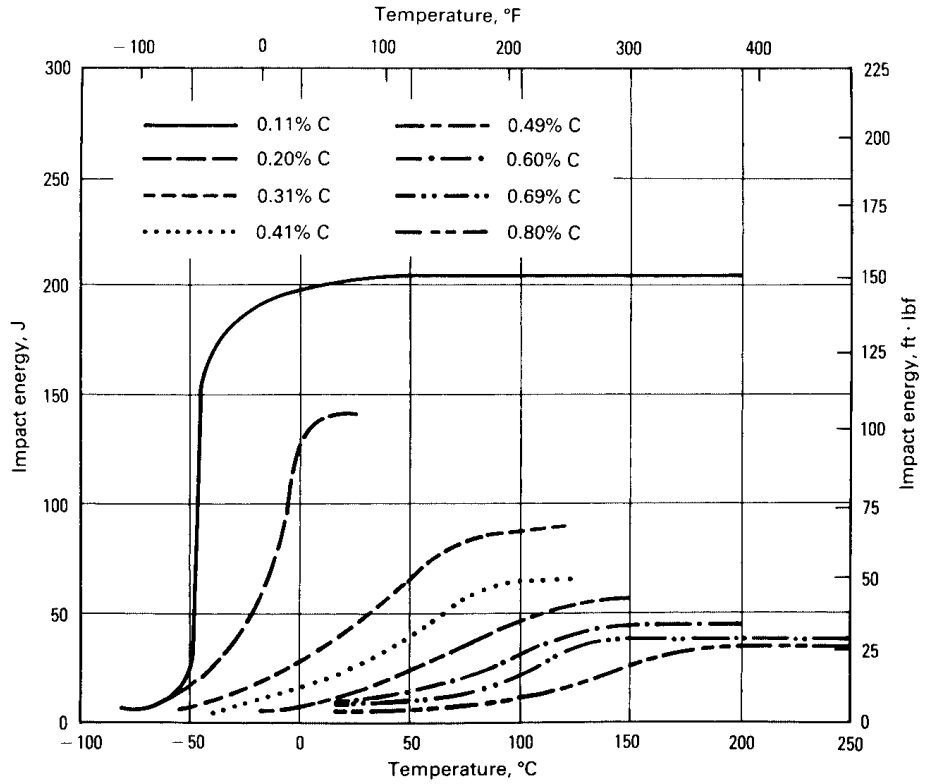


Fig. 7 Variation in Charpy V-notch impact energy with temperature for normalized plain carbon steels of varying carbon content

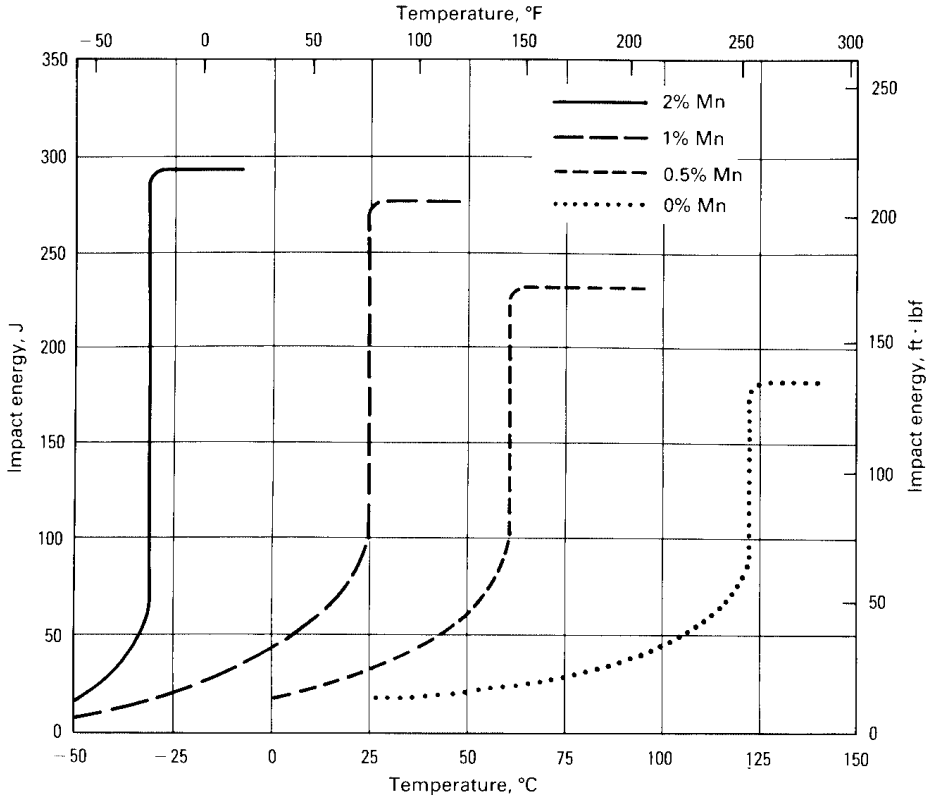


Fig. 8 Variation in Charpy V-notch impact energy with temperature for furnace-cooled Fe-Mn-0.05C alloys containing varying amounts of manganese

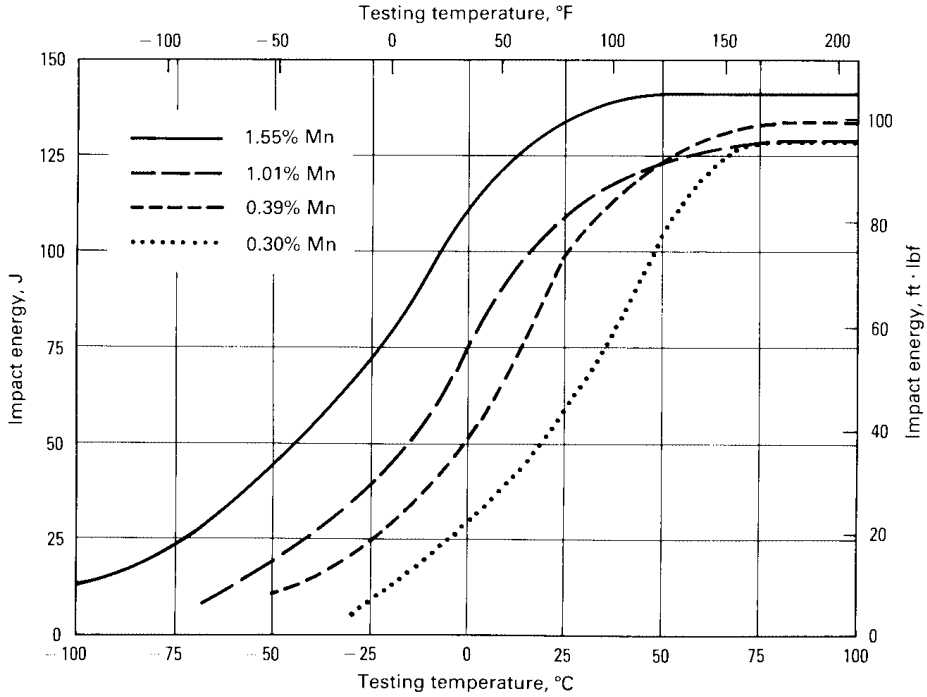


Fig. 9 Variation in Charpy V-notch impact energy with temperature for 0.30% C steels containing varying amounts of manganese. The specimens were austenitized at 900 °C (1650 °F) and cooled at approximately 14 °C/min (25 °F/min). The microstructures of these steels were pearlitic.

nating plates of ferrite and cementite in pearlite). In a hardened and tempered steel, manganese can have the opposite effect, as illustrated in Fig. 10. Manganese can make the steel susceptible to temper embrittlement, and it may cause the formation of less tough upper bainite (rather than fine pearlite) during normalizing.

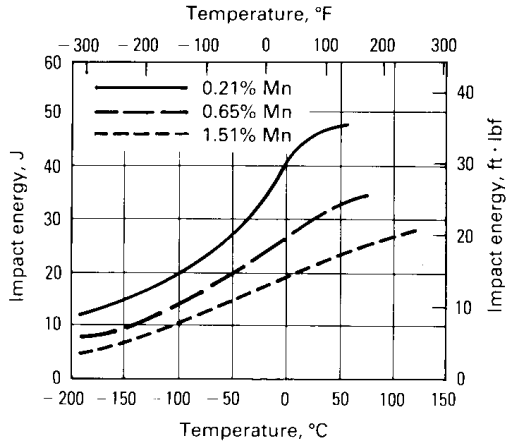


Fig. 10 Variation in Charpy V-notch impact energy with temperature for alloy steels containing 0.35% C, 0.35% Si, 0.80% Cr, 3.00% Ni, 0.30% Mo, 0.10% V, and the indicated amounts of manganese. The steels were hardened and tempered to a yield strength of approximately 1175 MPa (170 ksi). The microstructures of these steels contained tempered martensite.

Sulfur. The effect of sulfur on the notch toughness of steels is directly related to deoxidation practice. For rimmed, semikilled, and silicon-killed steels, sulfur in amounts up to about 0.04% has a negligible effect on notch toughness. Sulfur has a strong directional effect on Charpy results depending on the inclusion types present (for example, sulfides, oxides, and complex non-metallics). Charpy tests taken perpendicular to the working or rolling direction have lower absorbed energies when manganese sulfide stringers are present. Steel ladle treatments, used to reduce sulfur and to provide inclusion shape control, minimize Charpy test directionality. For silicon-aluminum-killed steels, a reduction in sulfur content can substantially increase upper-shelf energy, as shown in Fig. 11. This improvement in energy absorption results from a reduction in the number of sulfide stringers in the steel. Room-temperature Charpy results taken transverse to the rolling direction in plate steels show substantial improvement in energy absorbed only when sulfur levels are reduced below about 0.010% (Fig. 12).

Phosphorus has a strongly deleterious effect on the notch toughness of steel. It raises the 50% fracture appearance transition temperature (FATT) about 7 °C (13 °F) for each 0.01% P and reduces upper shelf energy. In addition, phosphorus increases the susceptibility of some steels to temper embrittlement.

Silicon, used in amounts of 0.15 to 0.30% to deoxidize steels, generally lowers the ductile-to-brittle fracture transition and raises upper-shelf energy. Compared with rimmed or semikilled steels, silicon-killed steels are cleaner and have more uniform ferrite grains. These effects are probably caused by variations in steelmaking practice characteristic of the deoxidation methods used, rather than by the silicon content.

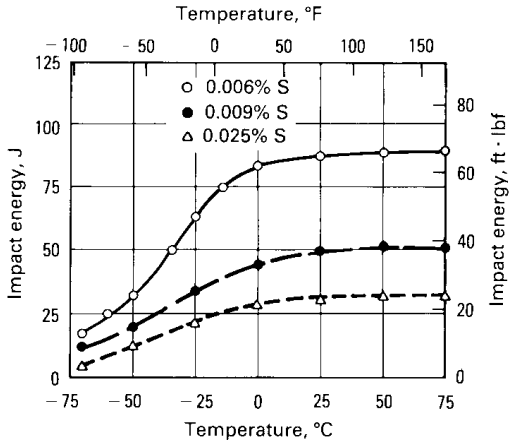


Fig. 11 Variation in transverse Charpy V-notch impact energy with temperature for HSLA steels containing varying amounts of sulfur. The steels were silicon-aluminum killed with a minimum yield strength of 450 MPa (65 ksi).

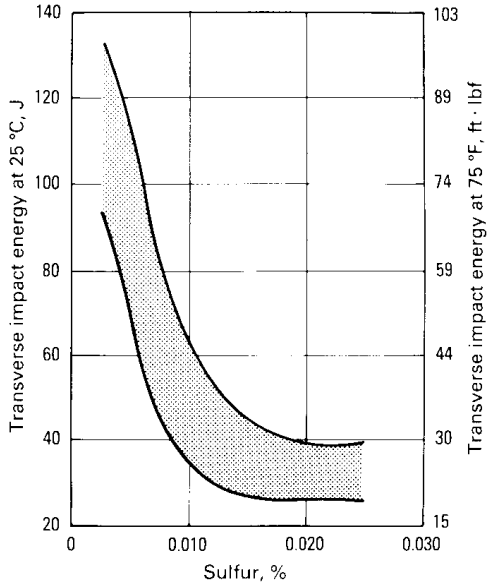


Fig. 12 Effect of sulfur content on transverse impact energy at room temperature in a silicon-aluminum killed steel

Aluminum. The effect of aluminum on the notch toughness of a medium-carbon steel is illustrated in Fig. 13. Note that increasing the aluminum content above that needed for forming aluminum nitrides (≈0.075% Al) impairs notch toughness.

Nitrogen, by itself, lowers the upper-shelf energy and raises the transition temperature. However, most nitrogenized steels are deoxidized with silicon and aluminum, both of which combine with nitrogen. Aluminum

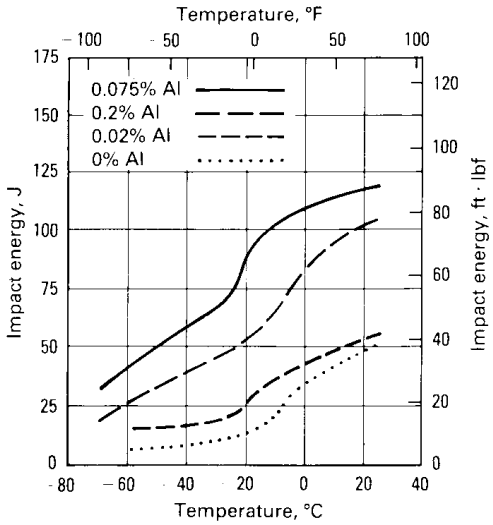


Fig. 13 Variation in Charpy V-notch impact energy with temperature for normalized and tempered medium-carbon steels containing varying amounts of aluminum

nitrides formed during deoxidation serve to stabilize grain size and thus improve the notch toughness of these steels.

Nickel, like manganese, is useful for improving the notch toughness of steels at low temperatures. Nickel is less effective in improving the toughness of medium-carbon steels than low-carbon steels. Some high-nickel alloy steels, such as maraging steels and austenitic stainless steels, do not exhibit the typical ductile-to-brittle transition (austenitic steels, being face-centered cubic, do not have a ductile-to-brittle transition). The high nickel content reduces upper-shelf fracture energy—but to a level that is still quite acceptable for most applications. The effect of varying nickel content on the low-temperature notch toughness of steels is discussed in the section "Alloying for Low-Temperature Service."

Chromium raises the transition temperature slightly. In steels having chromium contents in excess of 0.90%, it is very difficult to develop those microstructures and mechanical properties that are typical of plain carbon steels; therefore, impact test results are not comparable. Chromium is usually added to increase hardenability. The increase in hardenability is often sufficient to develop a martensitic microstructure, which provides high upper-shelf energy. Medium-carbon, straight chromium alloy steels, such as 5140, are susceptible to embrittlement when quenched to martensite and tempered between 370 and 575 °C (700 and 1070 °F).

Molybdenum in the typical quantities in alloy steels (up to about 0.40%) raises the 50% FATT. Molybdenum is frequently used to increase hardenability, and it influences notch toughness primarily through its effect on microstructure. About 0.5 to 1.0% Mo can be added to alloy steels to reduce their susceptibility to temper embrittlement, but it is effective only for relatively short heating times at embrittling temperatures. Molybdenum appears to delay rather than eliminate temper embrittlement, because steels containing small amounts of this element have become embrittled upon prolonged exposure within the embrittling temperature range.

Boron. For quenched and tempered steals, a practical way of improving toughness without reducing strength is to use a boron-containing grade of steel with a lower carbon content. As shown in Fig. 14, 10B2I steel has greater toughness than 1038 steel at all strength levels. However, the benefit of boron is applicable only to quenched and tempered steels; boron reduces the toughness of as-rolled, as-annealed, and as-normalized steels.

Copper in steels that have not been subjected to precipitation hardening appears to be moderately beneficial to low-temperature notch tough-

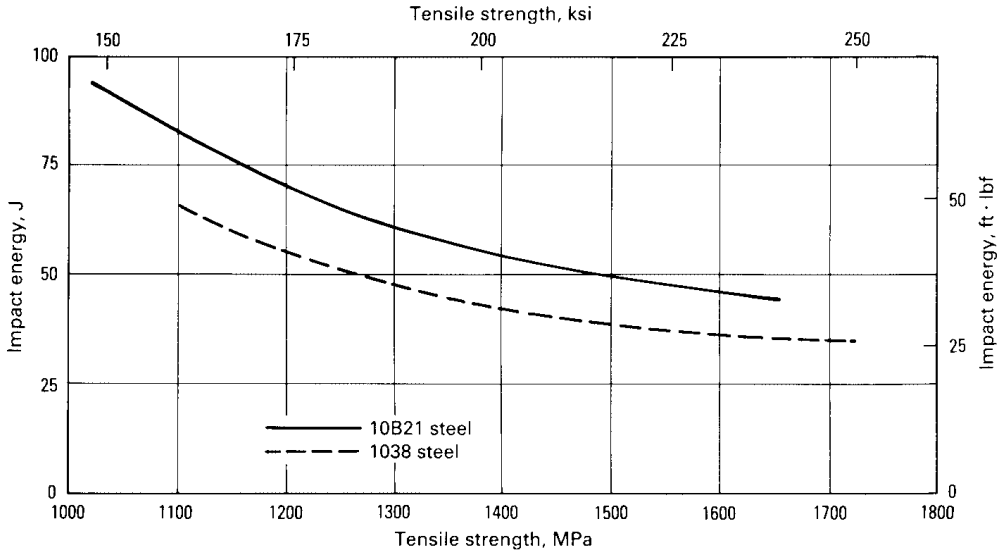


Fig. 14 Effect of boron content on notch toughness. Room-temperature Charpy V-notch impact energy varies with tensile strength for 10B21 and 1038 steels having tempered martensile structures.

ness. However, copper promotes precipitation hardening in steel and, as a result, may adversely affect notch toughness, particularly if the tempering temperature is between 400 and 565 °C (750 and 1050 °F).

Vanadium, niobium, and titanium are most often used in steels that receive controlled thermomechanical treatment. Consequently, the toughness of steels containing these elements is largely a function of mill processing. When the steel is finished at temperatures below about 925 °C (1700 °F) (which is characteristic of certain HSLA steels), vanadium, niobium, and titanium improve toughness primarily by refining the ferrite grain size. At higher finishing temperatures, these elements may be detrimental to toughness. The effect of niobium on toughness in a low-carbon normalized steel is shown in Fig. 15.

Zirconium, titanium, calcium, and the rare earths can be used to control the shape of manganese sulfide inclusions, causing the inclusions to be spherical rather than elongated. Spherical inclusions raise upper-shelf energy and minimize the anisotropic nature of notch toughness; these effects are particularly useful in HSLA sheet and plate. Figure 16 shows the effect of calcium treatment on the notch toughness of HSLA plate steels.

Interstitial elements, such as carbon, oxygen, nitrogen, and hydrogen, generally reduce the notch toughness of steels. This effect is especially evident in maraging steels, as shown in Fig. 17. Oxygen content in steels is usually determined by the deoxidation practice used in manufacturing

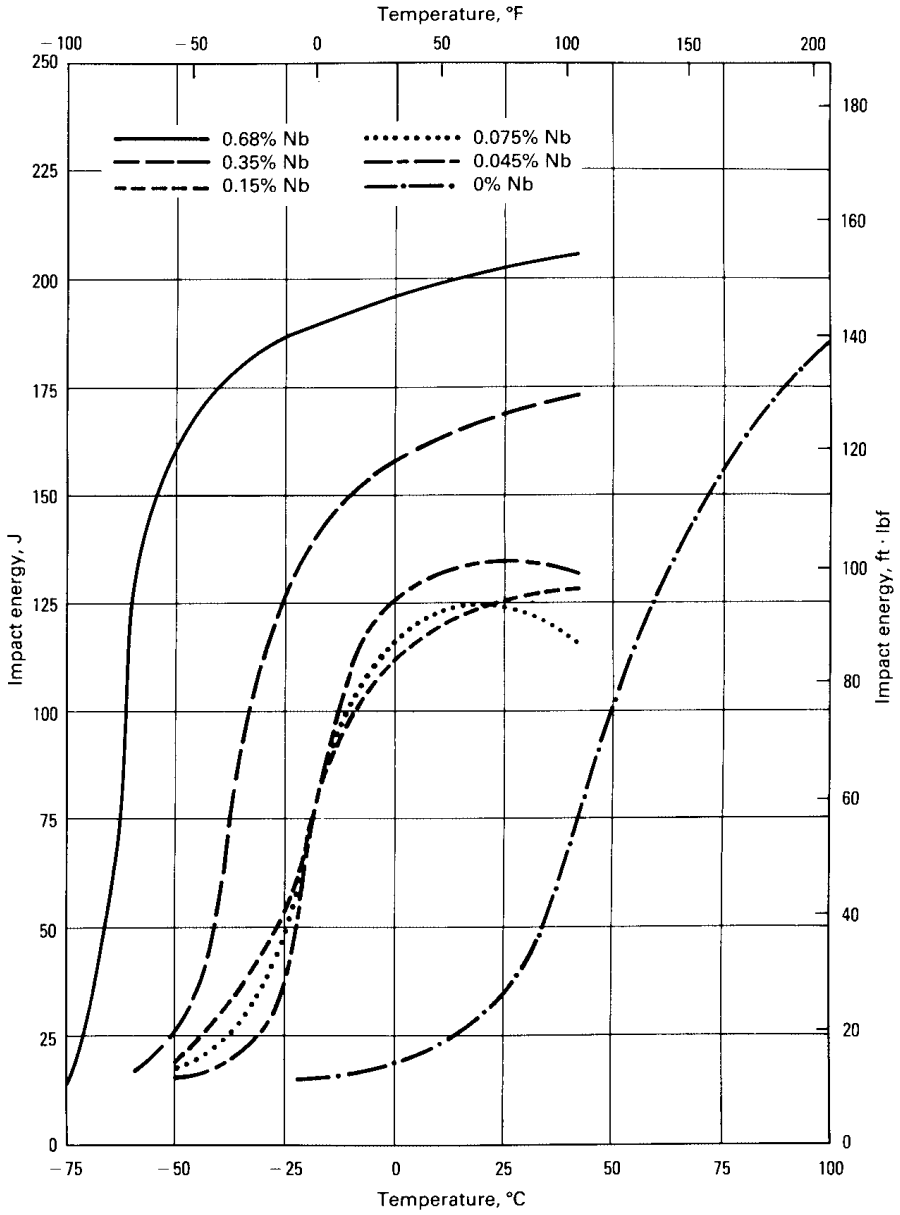


Fig. 15 Variation in Charpy V-notch impact energy with temperature for low-carbon steels containing varying amounts of niobium that were normalized from 955 °C (1750 °F)

the steel; rimmed steels have higher oxygen contents and higher transition temperatures than killed steels. Hydrogen reduces the notch toughness of steels; its chief deleterious effect occurs under conditions of slow or static loading.

Antimony, Arsenic, and Tin. In trace amounts, these elements reduce the notch toughness of steels and greatly increase the susceptibility of nickel- and chromium-alloy steels to temper embrittlement.

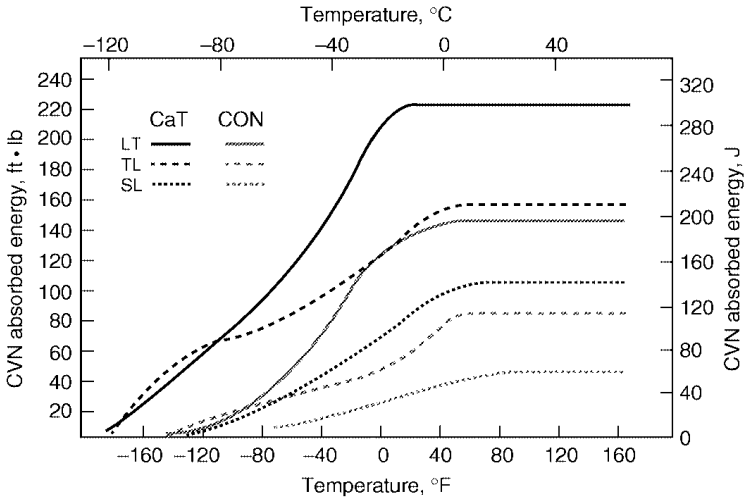


Fig. 16 Effect of calcium treatment and inclusion shape control on the Charpy V-notch (CVN) transition curves of two 100 mm (4 in.) A 633 grade C HSLA plate steels tested in the longitudinal (LT), transverse (TL), and short-transverse through thickness (SL) orientations. CON, conventional processing; CaT, calcium treatment

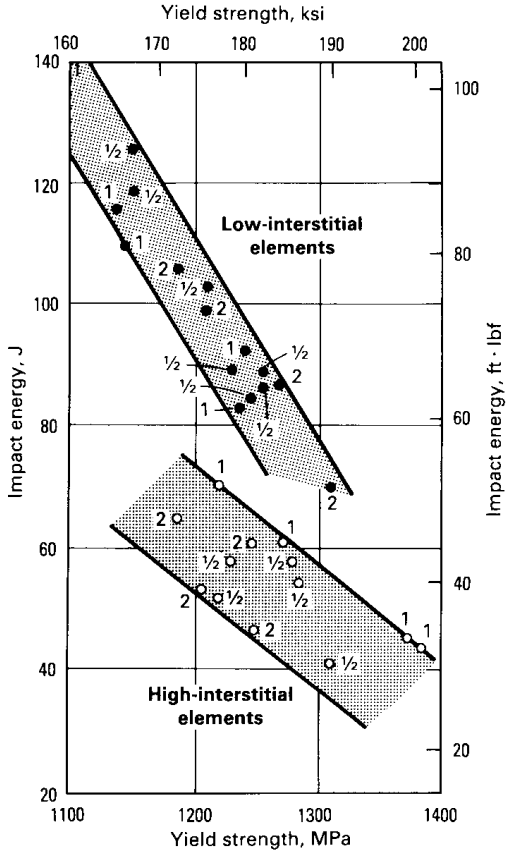


Fig. 17 Effect of interstitial elements on notch toughness. The notch toughness at −18 °C (0 °F) of 12% Ni maraging steel can be significantly raised by controlling the amount of interstitial alloying elements in the steel, regardless of the strength level. Numbers indicate plate thickness in inches.

Interactive effects of alloying elements are very common, particularly between the interstitial elements carbon and nitrogen and the strong carbide or nitride formers, such as aluminum, vanadium, manganese, niobium, molybdenum, and titanium. Some interactive effects are described in the sections "Sulfur" and "Aluminum" in this article; other examples are shown in Fig. 18 and 19.

Effects of Alloying on Fatigue Resistance

Carbon Content. An increase in carbon content can increase the fatigue limit of steels, particularly when the steels are hardened to 45 HRC or higher (Fig. 20). Other alloying elements may be required to attain the desired hardenability, but they generally have less of an effect on fatigue behavior than does carbon content.

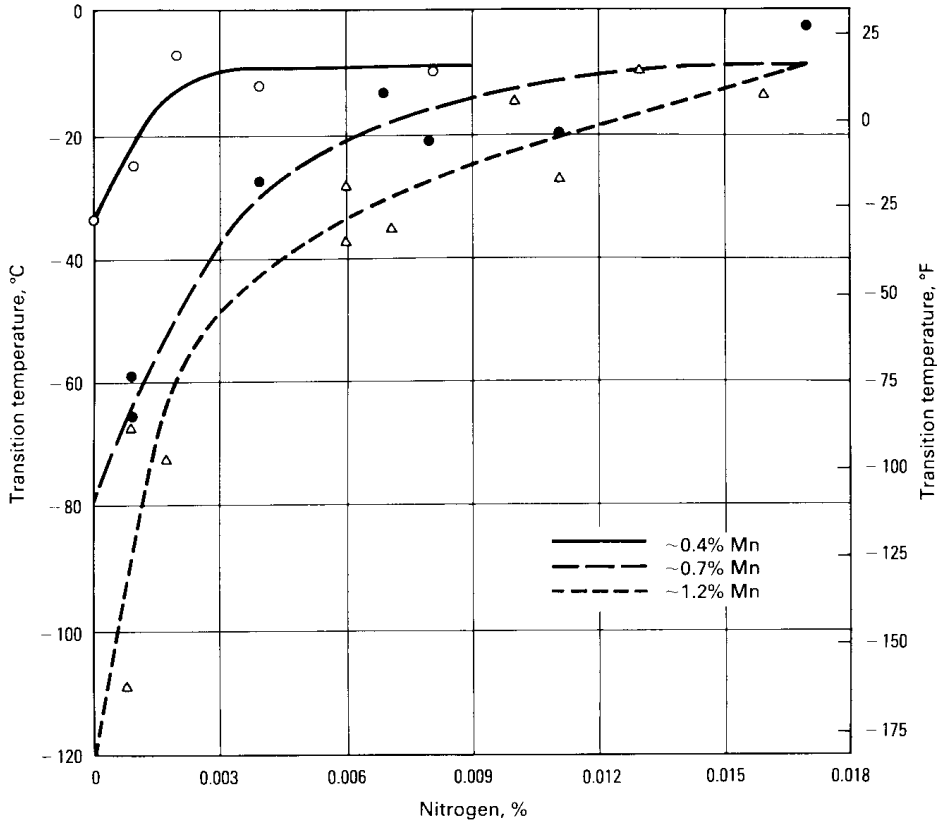


Fig. 18 Interactive effect of manganese and nitrogen on notch toughness. Fracture appearance transition temperature (50% shear FATT) in plain carbon steel (0.10% C) at three manganese levels (0.4, 0.7, and 1.2% Mn) varies with nitrogen content. The beneficial effect of manganese is particularly evident at low levels of nitrogen.

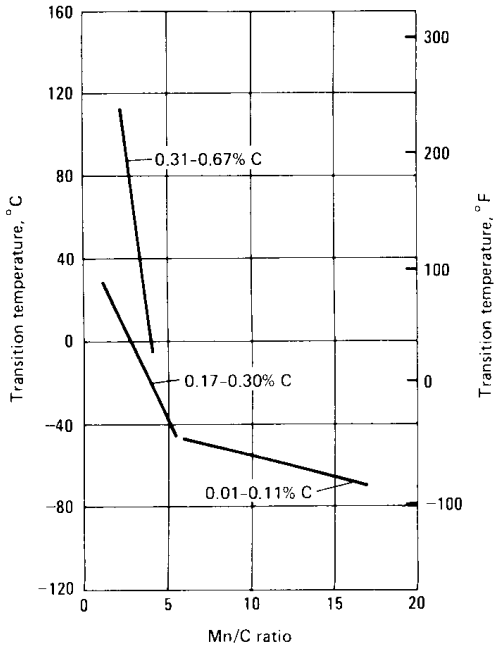


Fig. 19 Interactive effect of carbon and manganese on notch toughness. Manganese-to-carbon ratio affects the transition temperature of ferritic steels.

Steel cleanliness has been shown to have a significant influence on fatigue crack growth rate behavior within a steel. For example, significant anisotropy or directionality of behavior between conventional and calcium-treated A588A steels is detailed in Fig. 21. It has been demon-

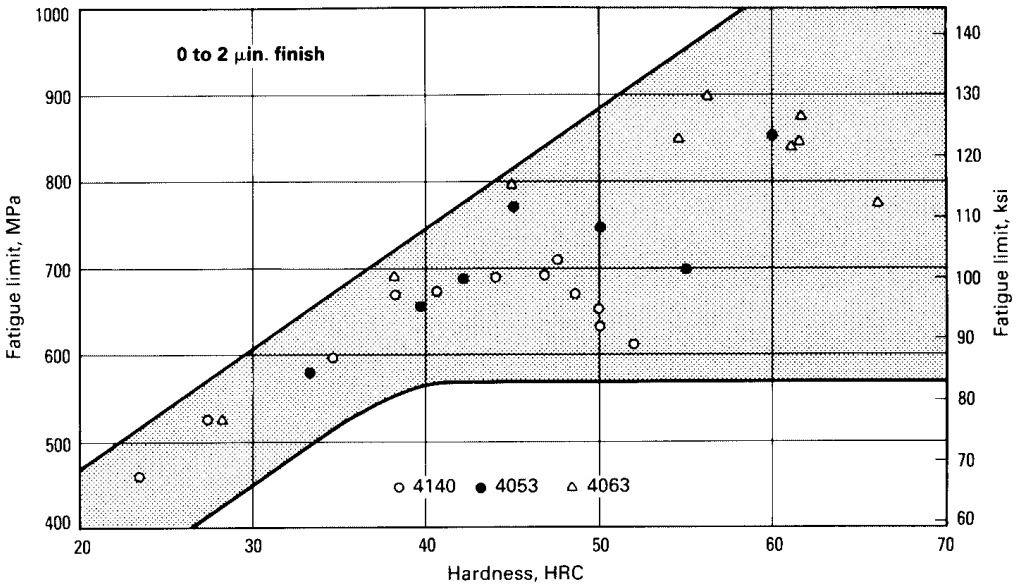


Fig. 20 Effect of carbon content and hardness on fatigue limit of through-hardened and tempered 4140, 4053, and 4063 steels

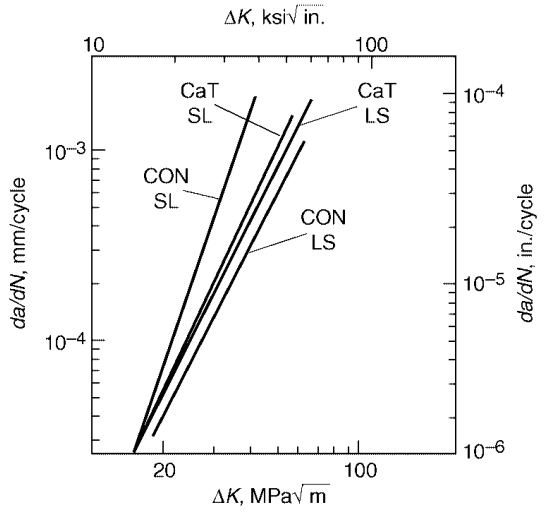


Fig. 21 Fatigue crack growth rate results for two A588 grade A HSLA steels showing comparison of LS and SL testing orientations. CON, conventional; CaT, calcium treatment. Improved isotropy of the calcium-treated steel is noted.

strated that nonmetallic inclusions can accelerate fatigue crack growth, particularly in the through-thickness (SL, ST) and transverse (TL) testing orientations, and particularly at higher stress intensity (ΔK) levels. Figure 22 demonstrates this for three other steel grades.

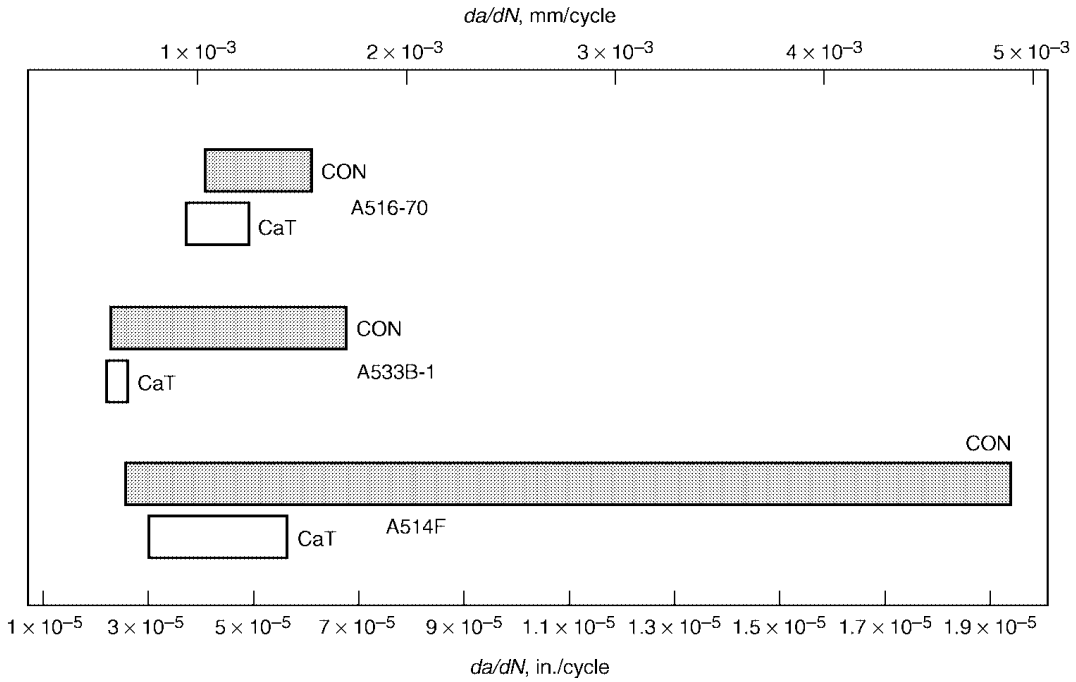


Fig. 22 Range of fatigue crack growth notes at Δk = 55 MPa $\sqrt{m}$ (50 ksi $\sqrt{in.}$) in six testing orientations for conventional (CON) and calcium-treated (CaT) quality plates of A516-70, A533B-1, and A514F. Improved isotropy of quality levels is demonstrated for calcium-treated plate.

Alloying for Low-Temperature Service

Steels selected for low-temperature service are often nickel-bearing low-carbon plate steels containing $2^1/_4$, $3^1/_2$, 5, 8, and 9% Ni. These steels are used for applications involving exposure to temperatures from 0 to −195 °C (32 to −320 °F), for example, storage and transportation of liquefied natural gas.

Effects of Nickel. The ability of nickel to improve the low-temperature properties of low-carbon steel has been associated with several observed effects. Essentially these effects involve the ferrite grain size, carbide distribution, generation of dislocations, and with higher nickel content, the retention of austenite.

Since ferrite is the predominant phase in low-carbon steel, its grain size has an important effect on the notch toughness of the steel. Nickel has been found to exert a refining effect on the ferrite grain size. By its hardenability effect, nickel suppresses proeutectoid ferrite and favors bainitic and martensitic structures of higher notch toughness. Also in solid solution, nickel is reported to facilitate dislocation generation at low temperatures and thus lower flow stresses relative to the cohesive strength level with resultant gains in toughness. At higher nickel levels, the transformation temperature range is lowered and considerable retained austenite may be present to enhance notch toughness. Figure 23 illustrates the effect of nickel additions on the Charpy impact toughness of carbon steel. As this figure shows, the nil-ductility transition temperature decreases from approximately −75 °C (−100 °F) for the unmodified specimen to less than −185 °C (−300 °F) for the specimen containing 9% Ni.

Alloying for High-Temperature Service

Creep-resistant low-alloy steels usually contain $^1/_2$ to 1% Mo for enhanced creep strength, along with chromium contents between $^1/_2$ and 9% for

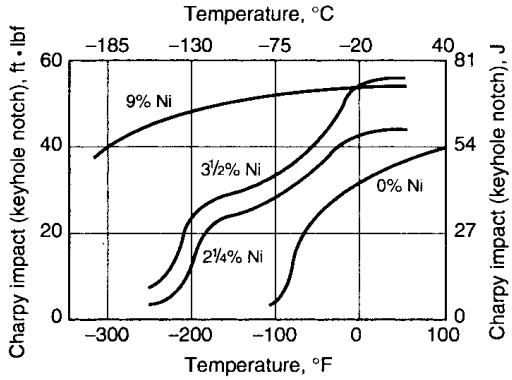


Fig. 23 Effect of nickel on toughness of normalized and tempered 13 mm ($^1/_2$ in.) plates of carbon steel

improved corrosion resistance, rupture ductility, and resistance against graphitization. Small additions of carbide formers such as vanadium, niobium, and titanium may also be added for precipitation strengthening and/or grain refinement. The effects of alloy elements on transformation hardening and weldability are of course, additional factors.

The three general types of creep-resistant low-alloy steels are chromium-molybdenum steels, chromium-molybdenum-vanadium steels, and modified chromium-molybdenum steels. Chromium-molybdenum steels are used primarily for tube, pipe, and pressure vessels, where the allowable stresses may permit creep deformation up to about 5% over the life of the component. Typical creep strengths of various chromium-molybdenum steels are shown in Fig. 24. Figure 24 also shows the creep strength of a chromium-molybdenum steel with vanadium additions. Chromium-molybdenum-vanadium steels provide higher creep strengths and are used for high-temperature bolts, compressor wheels, or steam turbine rotors, where allowable stresses may require deformations less than 1% over the life of the component.

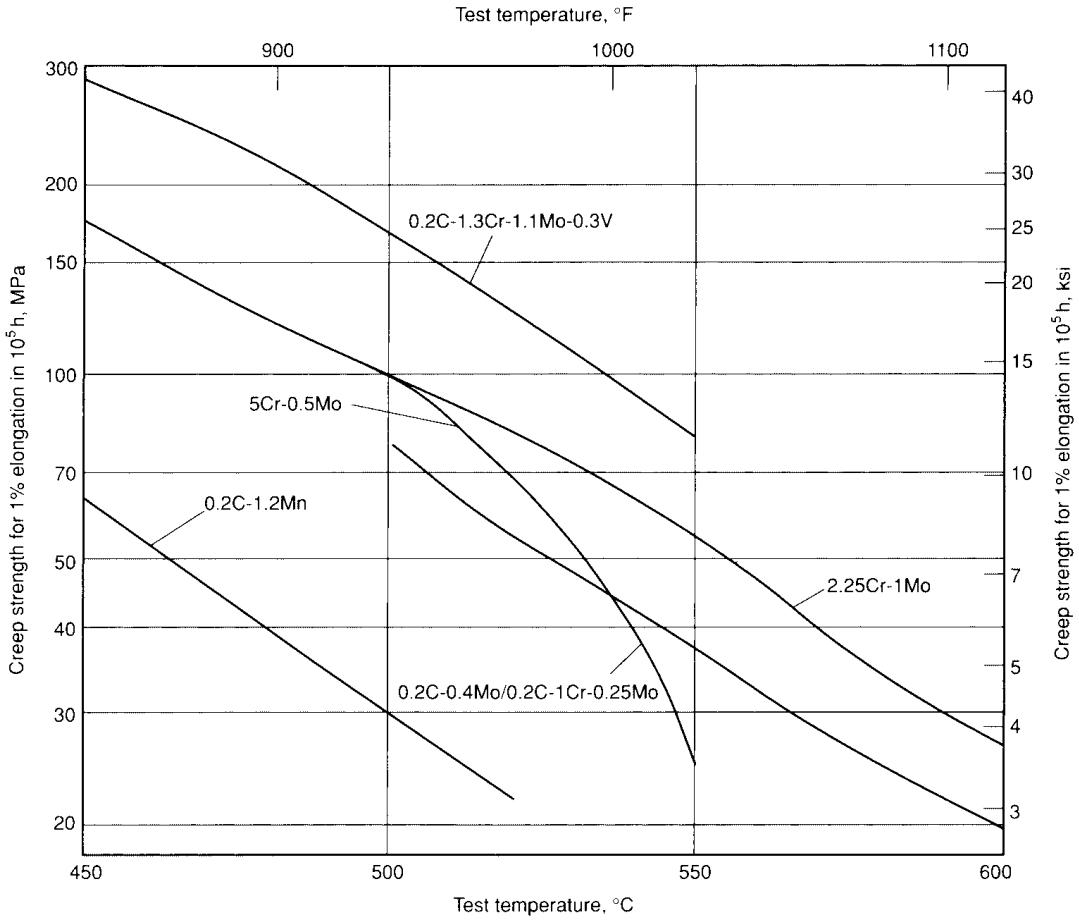


Fig. 24 General comparison of creep strengths of various creep-resistant low-alloy steels

Effects of Alloying on Temper Embrittlement

Temper embrittlement (also known as temper brittleness, two-step temper embrittlement, or reversible temper embrittlement) is associated with tempered alloy steels that are heated within, or slowly cooled through, a critical temperature range, generally 300 to 600 °C (570 to 1110 °F) for low-alloy steels. This treatment causes a decrease in toughness as determined with Charpy V-notch impact specimens. It is a particular problem for heavy-section components, such as pressure vessels and turbine rotors, that are slowly cooled through the embrittling range after tempering and also experience service at temperatures within the critical range.

Temper embrittled steels exhibit an increase in their ductile-to-brittle transition temperature (DBTT) and a change in fracture mode in the brittle test temperature range from cleavage to intergranular. The DBTT can be assessed in several ways. The most common is the temperature for 50% ductile and 50% brittle fracture (50% fracture appearance transition temperature, or FATT), or the lowest temperature at which the fracture is 100% ductile (100% fibrous criterion). Transition temperatures based on absorbed energy values are not normally employed. Temper embrittlement is reversible; that is, the toughness of embrittled steels can be restored by tempering them above the critical region, followed by rapid cooling (e.g., water quenching). This decreases the DBTT and changes the low-temperature (that is, below the 50% FATT) intergranular brittle appearance back to the cleavage mode.

Temper embrittlement occurs only in alloy steels, not in plain carbon steels, and the degree of embrittlement varies with alloy steel composition. Therefore, the alloying elements present and their combinations and levels, are important. Impurities, in decreasing order of influence in terms of weight percent, are antimony, phosphorus, tin, and arsenic. Of these elements, phosphorus is most commonly present in alloy steels, and it has captured the most attention in research studies. Manganese and silicon also increase the susceptibility to embrittlement. Although alloy steels are ferritic in the tempered condition, fracture below the DBTT occurs along prior-austenite grain boundaries where both alloying elements and impurity elements are concentrated.

Effect of Alloying on Change in FATT. Proof that antimony, phosphorus, tin, and/or arsenic are essential ingredients for temper embrittlement was obtained in the late 1950s (Ref 1, 2). Studies determined the change in 50% FATT and 100% fibrous FATT with isothermal aging (450 °C, or 840 °F, for up to 1000 h) for Ni-Cr and Ni-Cr-Mo laboratory heats with controlled compositions and impurity levels. Figures 25 and 26 show some test results for the influence of antimony, phosphorus, tin, and arsenic. Embrittlement was greater for the Ni-Cr steels than for the Ni-Cr-Mo steels because of the beneficial influence of molybdenum. The Ni-Cr

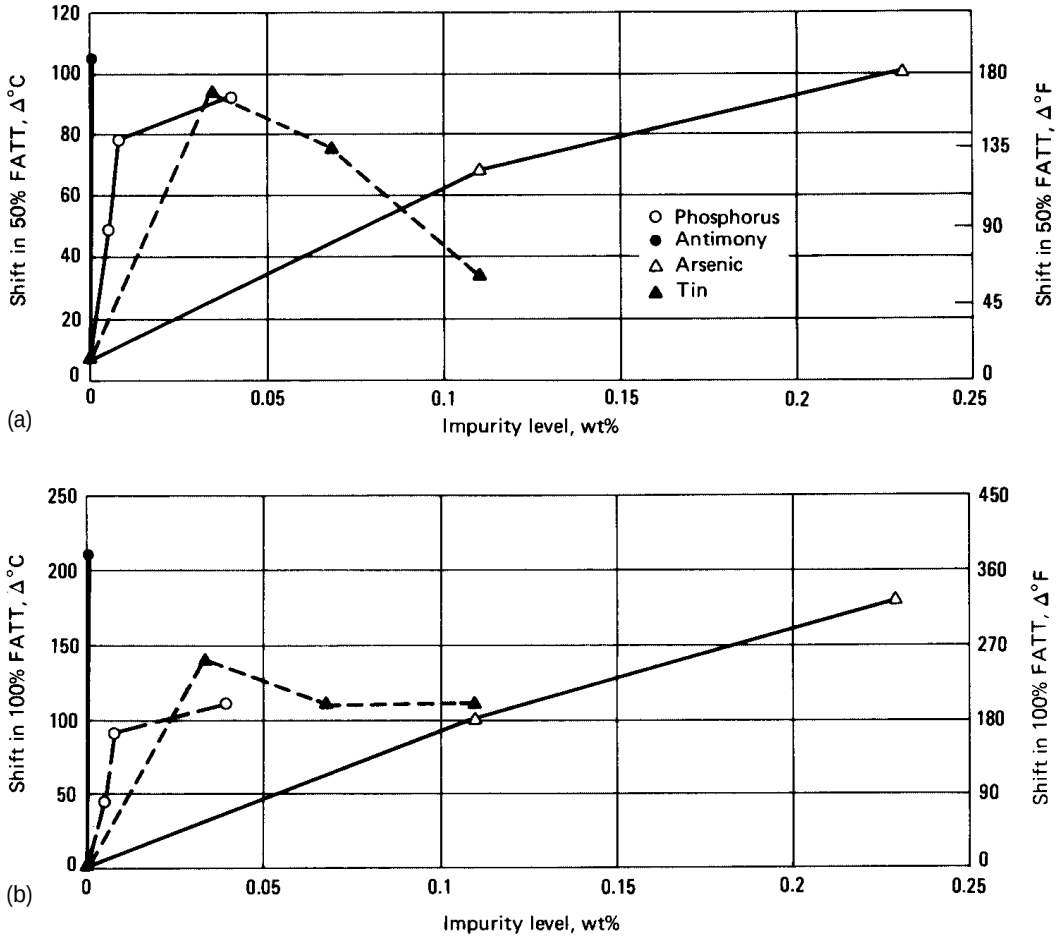


Fig. 25 Influence of phosphorus, antimony, arsenic, and tin impurity elements on the temper embrittlement susceptibility of nickel-chromium experimental steels based on the change in (a) 50% fracture appearance transition temperature (FATT) and (b) 100% fibrous FATT after aging at 450 °C (840 °F) for 1000 h. Source: Ref 1

steels also showed substantially greater embrittlement from the manganese addition than the Ni-Cr-Mo steels. The addition of about 0.7% Si had a smaller embrittling influence that was similar for both grades.

The important role of alloying elements has been clearly demonstrated in tests that also used heats of controlled composition (Ref 3). The tests were performed using 0.4% C alloy steels containing nickel, chromium, or nickel and chromium, as well as a plain carbon steel. Controlled additions of antimony, phosphorus, tin, and arsenic were made to these compositions. The 50% FATT was evaluated for each composition after heat treatment (870 °C, or 1600 °F, for 1 h, oil quench; 625 °C, or 1155 °F, for 1 h, water quench) and after step-cool embrittlement. Figure 27 shows the results for additions of antimony to plain carbon and alloy steels of various analyses. The bars show the 50% FATT after tempering at 625 °C (1155 °F) (left end, not embrittled) and after step cooling (right end, embrittled). The value under the bar is the shift in 50% FATT. The addition of 600 to 800 ppm Sb to the 0.4C-3.5Ni-1.7Cr steel caused a shift in

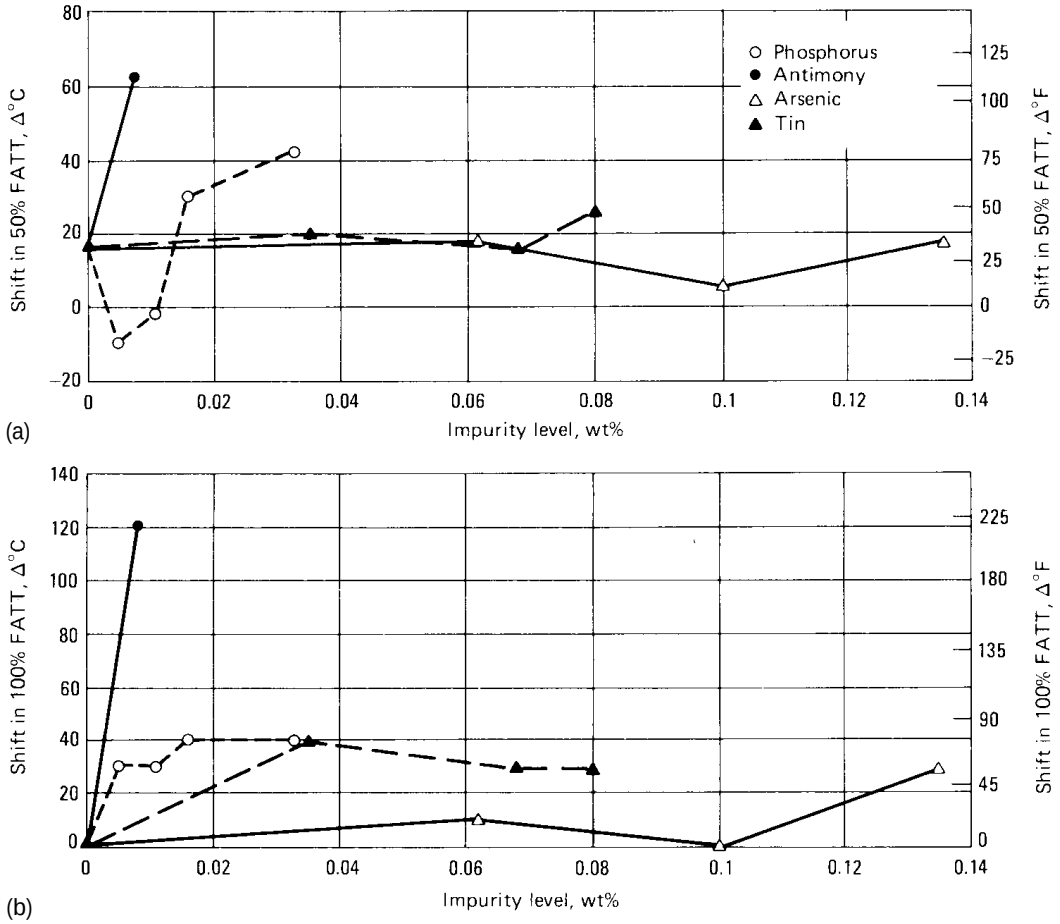
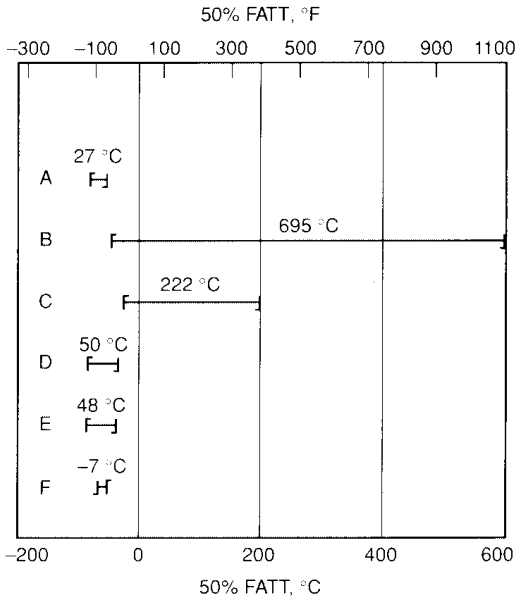


Fig. 26 Influence of phosphorus, antimony, arsenic, and tin Impurity elements on the temper embrittlement susceptibility of nickel-chromium-molybdenum experimental steels based on the change in (a) 50% fracture appearance transition temperature (FATT) and (b) 100% fibrous FATT after aging at 450 °C (840 °F) for 1000 h. Source: Ref 1

transition temperature of 695 °C (1285 °F). The same steel, but without carbon, exhibited a shift of 222 °C (432 °F), but its hardness was much lower (~80 HRB vs. 27 HRC). The steels with only nickel and carbon, or chromium and carbon, and 600 to 800 ppm Sb exhibited much less embrittlement, while the plain carbon steel was not embrittled by antimony.

Figure 28 shows the results for additions of about 500 ppm each of phosphorus, tin, and antimony to the Ni-Cr-C, Ni-C, and Cr-C steels. The nonembrittled toughnesses of the Ni-Cr-C-P and Cr-C-P alloys were poorer than those of the other alloys shown, probably because of the segregation of phosphorus in austenite. Phosphorus also embrittled the Cr-C-P alloy much more than the Ni-C-P alloy. This is due to an interaction between chromium and phosphorus. Tin appears to embrittle the Ni-Cr-C alloy more than phosphorus, in that the change in FATT was greater. However, the grain size of the Ni-Cr-C-P alloy was ASTM No. 8, while that of the Ni-Cr-C-Sn alloy was ASTM No. 6. Also, the nonembrittled toughness



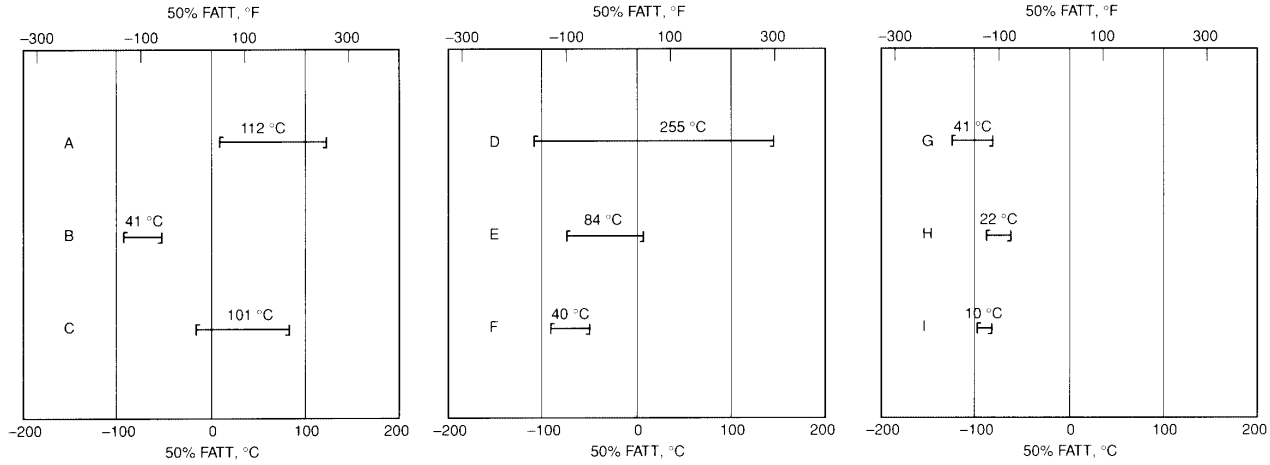
Steel	Composition, wt % Ni	Cr	C	Sb
Alloy				
Line A	3.5	1.7	0.4	…
Line B	3.5	1.7	0.4	0.06-0.08
Line C	3.5	1.7	…	>0.08
Line D	3.5	…	0.4	0.06-0.08
Line E	…	1.7	0.4	0.06-0.08
Plain carbon				
Line F	…	…	0.4	>0.08

Fig. 27 Influence of alloying elements on the temper embrittlement of steels (compositions given in accompanying table) containing 600 to 800 ppm Sb. The left end of each bar gives the nonembrittled ductile-to-brittle transition temperature (DBTT); the right end of the bar gives the DBTT after embrittlement (except for line F, which is reversed). The values between bar ends are the shifts in 50% FATT. Source: Ref 2

of the alloy containing phosphorus was much poorer. The 50% FATT values for these two compositions are nearly identical and would be even closer if the grain sizes were the same. Otherwise, it appears that tin embrittled the Ni-C alloy more than phosphorus, while phosphorus embrittled the Cr-C alloy more than tin. Arsenic was a much weaker embrittler.

The data in Fig. 27 and 28 clearly show that the combination of nickel and chromium results in much greater embrittlement, particularly for additions of antimony and tin. The data for phosphorus show that a strong interaction exists between chromium and phosphorus, while phosphorus causes little embrittlement in nickel steels that do not contain chromium.

The beneficial influence of molybdenum on phosphorus-induced temper embrittlement has been known for many years (Ref 4, 5). It has also been known that carbon steels are immune to temper embrittlement, but that substantial additions of manganese cause susceptibility to this



Steel	Composition, wt %			
	Ni	Cr	C	P
Line A	3.5	1.7	0.4	0.05-0.06
Line B	3.5	…	0.4	0.05-0.06
Line C	…	1.7	0.4	0.05-0.06

(a)

Steel	Composition, wt %			
	Ni	Cr	C	Sn
Line D	3.5	1.7	0.4	0.046-0.048
Line E	3.5	…	0.4	0.046-0.048
Line F	…	1.7	0.4	0.046-0.048

(b)

Steel	Composition, wt %			
	Ni	Cr	C	As
Line G	3.5	1.7	0.4	0.05-0.053
Line H	3.5	…	0.4	0.05-0.053
Line I	…	1.7	0.4	0.05-0.053

(c)

Fig. 28 Influence of alloying elements on the temper embrittlement of steels (compositions given in accompanying tables). (a) Steel containing 500 to 600 ppm P. (b) Steel containing 460 to 480 ppm Sn. (c) Steel containing 500 to 530 ppm As. The left end of each bar gives the nonembrittled ductile-to-brittle transition temperature (DBTT); the right end gives the DBTT after embrittlement. The values between bar ends are the shifts in 50% fracture appearance transition temperature. Source: Ref 2

problem. In addition, high levels of manganese in alloy steels have been known to render them more susceptible to temper embrittlement.

Reference 6 includes an evaluation of the addition of 0.6% Mo, along with controlled antimony, phosphorus, tin, arsenic, and other elements, to AISI 3304 (3.5Ni-1.7Cr-0.4C). The addition of molybdenum eliminated or greatly reduced embrittlement due to step cooling for additions of antimony, tin, and arsenic, but not for additions of phosphorus. The addition of 0.7% Mn to this steel produced substantial embrittlement, which was largely eliminated when 0.6% Mo was added. In this work, it was shown that phosphorus segregates to the austenite grain boundaries during austenitization: antimony does not. This work also clearly showed that manganese is an embrittling element, not merely an enhancer of embrittlement.

Later work was conducted to clarify these results (Ref 7). The earlier work employed specimens with a very coarse grain size (Ref 6). Results with somewhat finer grain sizes showed that 0.5 to 0.6% Mo additions prevented temper embrittlement caused by phosphorus in 3.5Ni-1.7 Cr-0.2C steels for aging times up to 1000 h at 475 and 500 °C (885 and 930 °F). The influence of molybdenum on the prevention of temper embrittlement appears to depend on how much of it is dissolved in the matrix as opposed to how much is tied up in carbides. As more molybdenum becomes tied up in carbides, its beneficial influence decreases. Therefore, depending on the temperatures experienced and the presence of other strong carbide formers, molybdenum may or may not be able to suppress temper embrittlement.

Effects of Alloying on Corrosion Behavior

This section examines the effects of alloying in three critical areas: atmospheric corrosion, high-temperature oxidation, and stress-corrosion cracking (SCC). In all three of these types of corrosion, key alloying additions can have a significant influence on corrosion behavior.

Atmospheric Corrosion

Because carbon steels are by definition not very highly alloyed, it is not surprising that most grades do not exhibit large differences in atmospheric-corrosion rate. Nevertheless, alloying can make changes in the atmospheric-corrosion rate of carbon steel. The elements generally found to be most beneficial in this regard are copper, nickel, silicon, chromium, and phosphorus. Of these, the most striking example is that of copper, increases from 0.01 to 0.05% have been shown to decrease the corrosion rate by a factor of two to three. Additions of the above elements in combination are

generally more effective than when added singly, although the effects are not additive. The effectiveness of these elements in retarding corrosion also appears to depend on the corrosive environment, with the most benefit appearing in industrial atmosphere.

The weathering steels had their origin in the early studies of D.M. Buck. After a decade of effort, Buck established the efficacy of copper as a means of enhancing the atmospheric-corrosion resistance of unpainted carbon steel in a variety of environments. While this work was going on, a large study was initiated in 1916 by ASTM (formerly the American Society for Testing and Materials) to evaluate the atmospheric performance of a variety of ferrous materials.

By 1929, United States Steel Corporation had initiated studies to enhance the performance of copper-bearing steel further through the addition of a number of alloying elements. By 1933, the first commercially available HSLA steel was introduced into the railroad industry for coal hopper car use in the unpainted condition. These HSLA steels were capable of resisting the leachates from sulfur-bearing coals better than the existing carbon and copper-bearing steel cars. Since that time, the original architectural grade has been covered by ASTM A 242. When the heavier structural grades of high-strength low-alloy steels became available, they were covered by ASTM A 588. Chemical composition variations among the four grades of A 588 are listed in Table 9.

Through the exposure of small test panels in various atmospheres, the performance of the steel composition as well as the aggressiveness of the particular location were both calibrated. Other characteristics of the HSLA steels were studied, such as the ability to develop the protective oxide film under sheltered conditions in the atmosphere, in the soil, and immersed in freshwater and seawater. Studies were conducted on the staining characteristics and the ability to perform in contact with other materials. Finally, studies were performed to determine the manner in which protective coatings would function.

Copper-Bearing Steel. To appreciate the nature of the current composition of the weathering steels, it is useful to recall some of Buck's findings. In the early days, scrap steel was not in common use. Thus, Buck

Table 9 Compositional limits for weathering steel grades (ASTM A 588) used in building and bridge construction

Grade	UNS designation	Heat compositional limits(a), %									
		C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
A	K11430	0.10–0.19	0.90–1.25	0.04	0.05	0.15–0.30	0.40–0.65	…	0.25–0.40	0.02–0.10	…
B	K12043	0.20	0.75–1.25	0.04	0.05	0.15–0.30	0.40–0.70	0.25–0.50	0.20–0.40	0.01–0.10	…
C	K11538	0.15	0.80–1.35	0.04	0.05	0.15–0.30	0.30–0.50	0.25–0.50	0.20–0.50	0.01–0.10	…
K	…	0.17	0.5–1.20	0.04	0.05	0.25–0.50	0.40–0.70	0.40	0.30–0.50	…	0.10 Mo, 0.005–0.05 Nb

(a) If a single value is shown, it is a maximum unless otherwise stated.

accidently noticed that one test sheet outperformed the others. Upon examination, the copper level of this sheet was found to exceed the 0.01 to 0.02% common to the remainder of the test sheets. This finding resulted in Buck's initiating a series of studies to identify the minimum amount of copper (found to be 0.20%) necessary to effect an improvement in performance and to determine the relationship of the copper content to the sulfur content of the steel. From 1929 to 1933, much effort was expended toward developing compositions with superior atmospheric-corrosion resistance to the accepted 0.20%-Cu-containing steels.

High-Strength Low-Alloy Steels. In 1962, the results of a comprehensive 15.5-year study were published in which some 270 different steels were exposed in three atmospheres beginning in the late 1940s (Ref 8). The sites were at Kearny, NJ (industrial); South Bend, PA (semirural): and Kure Beach, NC (250 m, or 800 ft, from the ocean). Table 10 lists the performance of 18 representative compositions in which the different levels of copper are combined with one of the four alloying elements (nickel, chromium, silicon, and phosphorus) to show their respective influences on corrosion in the industrial and marine sites. In addition, this group contains seven compositions in which one of the alloying elements is omitted, the purpose being to demonstrate how the remaining elements are capable of contributing to a satisfactory performance in the various atmospheres. Figure 29 summarizes some of the results from industrial environments. The carbon steel corrosion rate becomes constant after about five years. The corrosion rate of the copper steel levels off to a constant value after about three years, and the HSLA steel, which uses several alloy elements, exhibits a constant rate after approximately two years. Corrosion of the high-strength low-alloy steel eventually ceases.

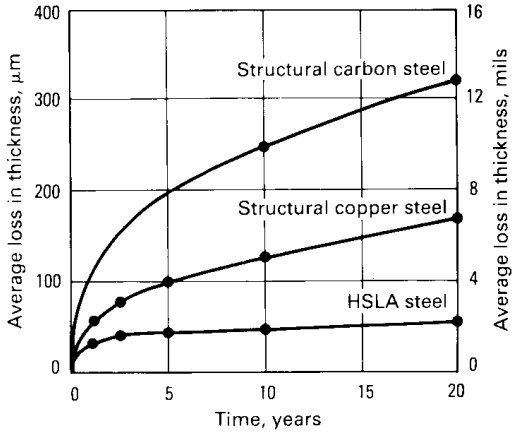


Fig. 29 Atmospheric corrosion versus time in a semi-industrial or industrial environment. Source: Ref 9

The significance of copper levels is shown in compositions 1, 2, and 3 in Table 10. Compositions 4 and 5 show how nickel can compensate for a low copper level. In contrast, compositions 6 and 7 show that chromium requires copper except in the marine environment. In compositions 8 and 9, silicon shows useful properties in the absence of copper. Phosphorus also contributes to this effect (compositions 10 and 11). Compositions 12 through 18 show the results of combining all of the alloying elements or omitting one of the elements. Additional research revealed that lower concentrations of the alloying elements were still effective.

Effects of Alloying on Oxidation Resistance. The oxidation behavior of carbon steel in air at 425, 540, 650, and 760 °C (800, 1000, 1200, and 1400 °F) is summarized in Fig. 30. After 700 h of exposure at 425 and 540 °C (800 and 1000 °F), carbon steel suffered negligible oxidation attack, with less than 20 mg/cm of weight loss. As the temperature was increased to 650 °C (1200 °F), the oxidation rate was significantly increased. At 760 °C (1400 °F), carbon steel suffered rapid oxidation, exhibiting essentially a linear rate of attack. These results suggest that carbon steel may not be suitable in air or highly oxidizing atmospheres at temperatures in excess of 650 °C (1200 °F). This was substantiated by the results of Vrable et al. (Ref 11), as illustrated in Fig. 31. At 650 °C (1200 °F), carbon steel suffered an oxidation rate of about 1.3 mm/yr (53 mils/yr). The oxidation rate is expected to be much higher when carbon steel is exposed to temperatures higher than 650 °C (1200 °F). Figure 31 also illustrates that HSLA steel is significantly better than carbon steel in oxidation resis-

Table 10 Average reduction in thickness of steel specimens after 15.5-year exposure in different atmospheres

						Thickness reduction			
	Composition, wt%					Kearny, NJ (industrial)		Kure Beach, NC, 250 m (800 ft) lot (moderate marine)	
Specimen No.	Cu	Ni	Cr	Si	P	μm	mils	μm	mils
1	0.012	…	…	…	…	731	28.8	1321	52.0
2	0.04	…	…	…	…	223	8.8	363	14.3
3	0.24	…	…	…	…	155	6.1	284	11.2
4	0.008	1	…	…	…	155	6.1	244	9.6
5	0.2	1	…	…	…	112	4.4	203	8.0
6	0.01	…	0.61	…	…	1059	41.7	401	15.8
7	0.22	…	0.63	…	…	117	4.6	229	9.0
8	0.01	…	…	0.22	…	373	14.7	546	21.5
9	0.22	…	…	0.20	…	152	6.0	251	9.9
10	0.02	…	…	…	0.06	198	7.8	358	14.1
11	0.21	…	…	…	0.06	124	4.9	231	9.1
12	…	1	1.2	0.5	0.12	66	2.6	99	3.9
13	0.21	…	1.2	0.62	0.11	48	1.9	84	3.3
14	0.2	1	…	0.16	0.11	84	3.3	145	5.7
15	0.18	1	1.3	…	0.09	48	1.9	97	3.8
16	0.22	1	1.3	0.46	…	48	1.9	94	3.7
17	0.21	1	1.2	0.48	0.06	48	1.9	84	3.3
18	0.21	1	1.2	0.18	0.10	48	1.9	97	3.8

Source: Ref 9

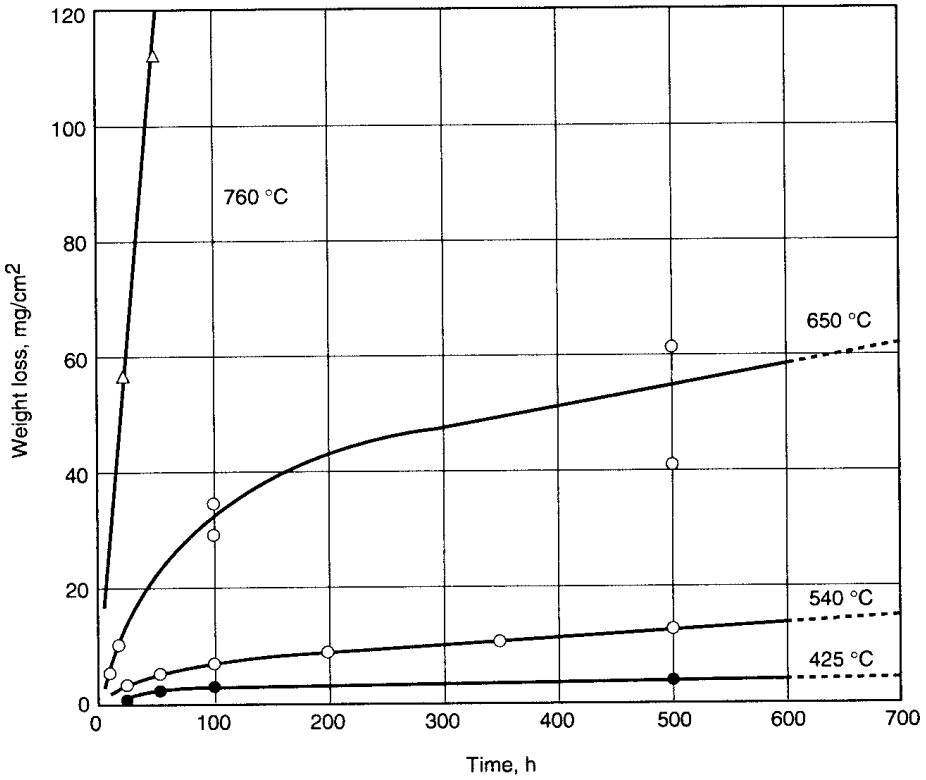


Fig. 30 Oxidation behavior of plain low-carbon steel in air at 430, 540, 650, and 760 °C (800, 1000, 1200, and 1400 °F). Source: Ref 10

tance, presumably due to minor alloying elements such as manganese, silicon, chromium, and nickel.

Chromium-molybdenum steels are used at higher temperatures than carbon steel because of higher tensile and creep-rupture strengths. Molybdenum and chromium provide not only solid solution strengthening

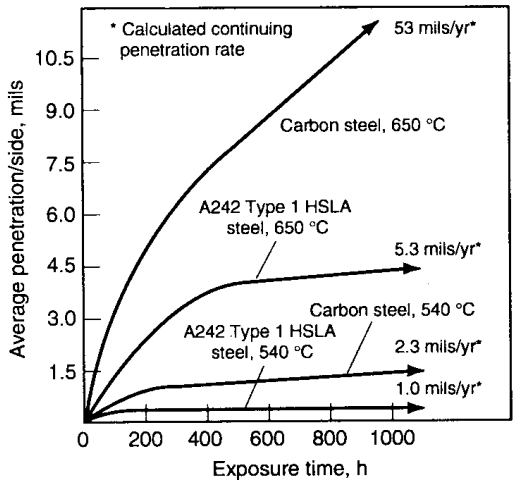


Fig. 31 Oxidation of carbon steel and HSLA steel in air. Source: Ref 11, 12

but also carbide strengthening. Some of the major applications for chromium-molybdenum steels include superheater tubes and steam pipes.

Low-alloy steels with chromium and silicon additions exhibit better oxidation resistance than carbon steel. The beneficial effects of chromium and silicon additions to carbon steel are summarized in Fig. 32. Silicon is very effective in improving the oxidation resistance of chromium-molybdenum steels. Addition of 1.5% Si to 5Cr-0.5Mo steel significantly improved its oxidation resistance, although silicon additions also reduce creep strength and may promote temper embrittlement when other impurities are present. The most important alloying element for improving oxidation resistance is chromium. As shown in Fig. 32, for 0.5% Mo-containing steels, increasing chromium from 1 to 9% significantly increases oxidation resistance. The 7Cr-0.5Mo and 9Cr-1Mo steels showed negligible oxidation rates at temperatures up to 680 °C (1250 °F) and 700 °C (1300 °F), respectively. Further increases in chromium improve oxidation resistance even more.

Effects of Alloying on SCC Resistance (Ref 14)

An overview of compositional effects on the SCC of two low-alloy steels in aqueous chlorides is given in Table 11. Although similar trends are sometimes observed for other steels and for other environments, the situation is much more complex in that composition can greatly influence heat treatment response, strength, and welding characteristics, which also affect SCC.

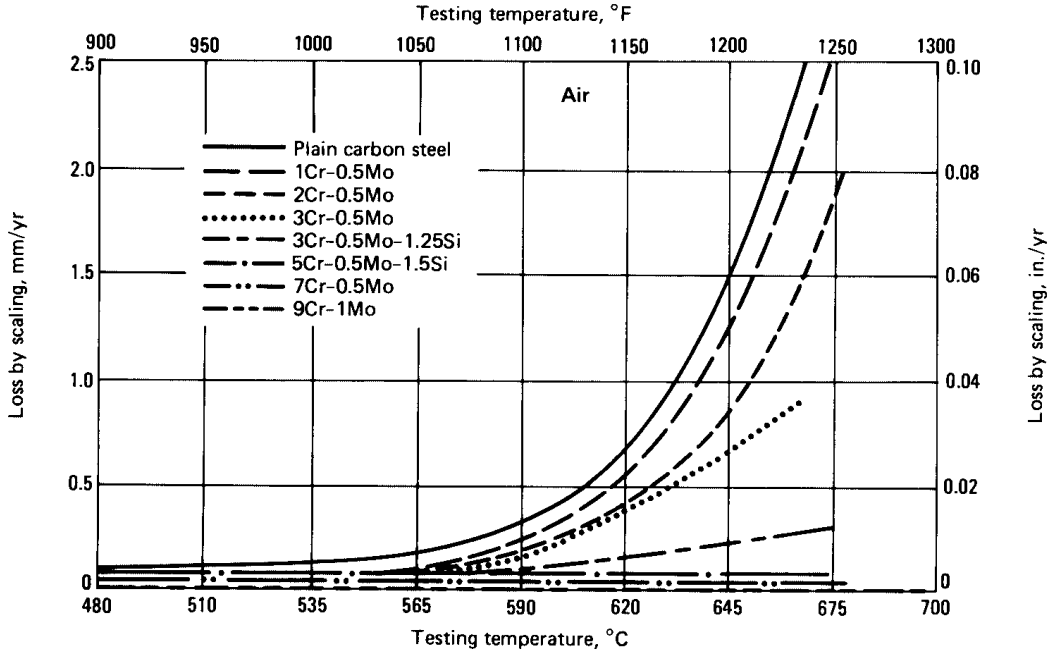


Fig. 32 Effect of chromium and/or silicon on the oxidation resistance of steels in air. Source: Ref 13

Table 11 Effect of alloying within normal limits on the stress-corrosion cracking resistance of martensitic low-alloy steels to chloride

Element	AISI 4120 (yield strength = 1034 MPa, or 150 ksi)	AISI 4340 (yield strength = 1172-1448 MPa, or 170-210 ksi)
Carbon	Decrease	Decrease
Manganese	No effect	Decrease
Nickel	Increase	No effect
Chromium	Increase	No effect
Molybdenum	Increase	No effect
Vanadium	Increase	…
Niobium	Increase	…
Titanium	Increase	…
Zirconium	Increase	…
Boron	No effect	…
Copper	No effect	…
Silicon	No effect	…
Sulfur	Beneficial	No effect
Phosphorus	Decrease	No effect
Oxygen	Decrease	…
Nitrogen	Decrease	No effect

Source: Ref 14

Carbon. As carbon content increases, the SCC resistance of steels in aqueous chlorides is reduced, with the most dramatic effects seen in the 0.2 to 0.4% range. Increases in carbon content also increase the magnitude of the drop in SCC resistance with increasing yield strength, with lower carbon steels showing a lesser effect.

For quenched and tempered steels in aqueous hydrogen sulfide, carbon does not have a significant influence on SCC resistance. Some researchers have reported that carbon causes a slight improvement; others have noted slightly detrimental effects.

Susceptibility of annealed and normalized carbon steels to SCC in nitrate solutions is determined primarily by carbon content. Steels are resistant at carbon contents below about 0.001% and at carbon contents above about 0.18%, but they are susceptible between these values. SCC susceptibility is thought to be largely due to carbide morphology and distribution. By contrast, SCC resistance of alloy steels appears to be independent of carbon content. Although all plain carbon steels are susceptible to SCC in hydroxide solutions, susceptibility to caustic cracking increases with carbon content, except that a beneficial effect is reported at levels above 0.2%.

Manganese has an adverse effect on the chloride SCC of medium-carbon steels, but not on low-carbon materials. Increases in the manganese content of steels are reportedly detrimental to SCC resistance in hydrogen sulfide environments, possibly due to manganese segregation. The resistance of carbon steels to SCC in nitrate solutions is also adversely affected by increased manganese content, especially when steels are annealed at high temperatures for extended periods.

Nickel. Some investigators have reported that nickel contents above 1% reduce the SCC resistance of steels in hydrogen-sulfide-containing environments, while others report no significant effect. This contradiction may be related to heat treatment, because increasing the nickel content increases the likelihood that untempered martensite will be present. No effect of nickel on SCC in nitrate solutions has been reported.

Chromium contents below about 1.4% reportedly improve SCC resistance to aqueous hydrogen sulfide. Above this level, detrimental effects are generally observed. In nitrate solutions, a similar beneficial effect of chromium on SCC resistance has been reported at least to about 1.0%.

Carbide-Forming Elements. Molybdenum is believed to increase SCC resistance to hydrogen sulfide by producing fine carbides during tempering. Vanadium is thought to be beneficial by causing a similar carbide effect, as well as grain refinement. Titanium additions produce comparable results, but at higher levels, SCC can be promoted through the presence of second-phase titanium carbonitride precipitation. A beneficial effect of titanium on SCC resistance in nitrate solutions has been reported.

Copper and Silicon. Copper has been observed to adversely affect the SCC resistance of steels in nitrate solutions. By contrast, silicon appears to be beneficial in such environments. Silicon contents of 1.58% or more have been reported to decrease SCC propagation rates in chloride solutions.

Aluminum in amounts of 0.3 to 0.6% reportedly increases SCC resistance to hydrogen sulfide. In nitrate solutions, aluminum does not affect SCC at typical deoxidizing levels, that is, less than about 0.01%. Improvements in SCC resistance are reported at levels above about 0.3%. A possible beneficial effect of aluminum on caustic cracking has also been reported.

Residual Elements. High sulfur and phosphorus contents have reduced the SCC resistance of steels in hydrogen sulfide and can also affect SCC in nitrate solutions. No influence of oxygen or nitrogen has been reported for SCC in hydrogen sulfide solutions. Nitrogen levels below 0.01% promote SCC of steels in nitrate solutions, but higher levels appear to be beneficial.

Effects of Alloying on Wear Behavior

As shown in Fig. 33, carbon and alloy steels with low-to-medium carbon contents are not considered wear-resistant materials. Improved wear resistance can be achieved by:

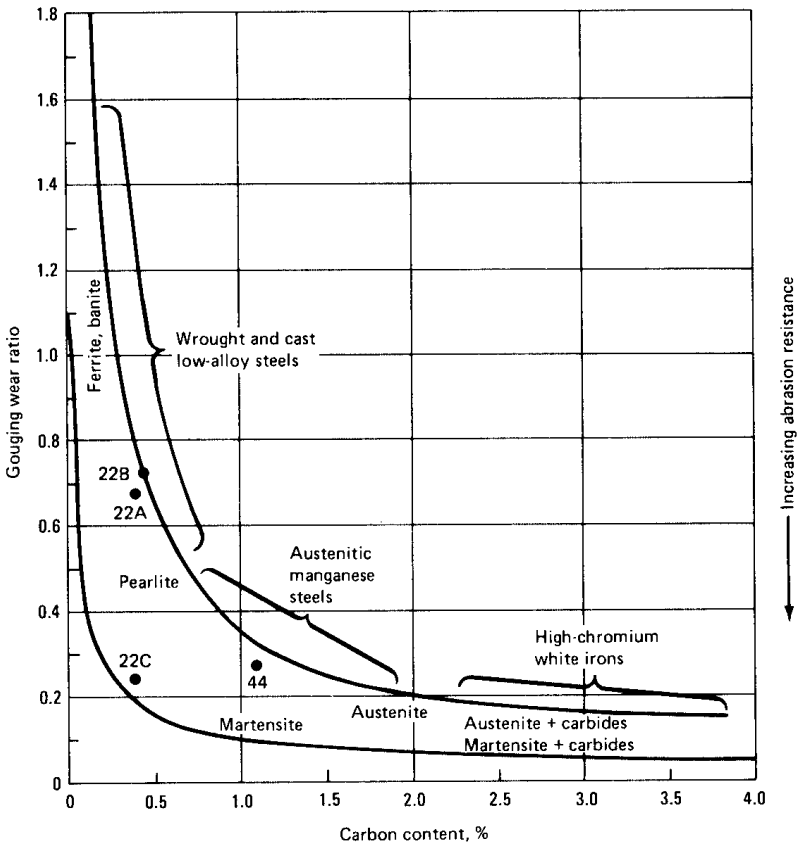


Fig. 33 Relation between gouging wear and carbon content for various types of steel and cast iron

- Raising the carbon content, i.e., high-carbon steels
- Surface alloying (e.g., carburizing, nitriding, or ion implantation)
- Raising the carbon content in conjunction with adding high amounts of carbide-forming elements (Cr, V, Mo, and W). See, for example, the article "Tool Steels."
- Raising the carbon content in conjunction with adding high amounts of manganese. See, for example, the article "Austenitic Manganese Steels."

Carbon Content. The wear resistance of ferritic steel is improved by hardening, either throughout the section or superficially. The maximum hardness depends on the carbon content of the steel and the amount of martensite (efficiency of quenching), as shown in Fig. 2.

Standard hardness measurements may indicate that a martensitic steel is largely transformed, although it may retain some austenite. Exposure to ultralow temperatures (followed by tempering) can help complete the transformation to martensite and improve wear resistance. Because martensite is a metastable structure, it begins to transform to more stable structures as the temperature is raised. Consequently, martensitic steels

are not suitable for wear resistance at elevated temperatures or for applications in which the heat of friction can raise the temperature significantly. They should not be used at temperatures above 200 °C (390 °F). Special alloy steels, such as tool steels or martensitic stainless steels, are appropriate for service at higher temperatures. The thermal instability of martensite should also be considered during finishing operations (such as grinding), when a heat-affected zone could be produced at the surface. The resultant tempering effects could be localized or general; in either case, wear resistance is likely to be reduced.

Carbon content also affects hardness and wear resistance through the formation of various simple and complex carbides. Wear properties depend on the type, amount, shape, size, and distribution of carbides present, as well as the properties of the matrix (hardness, toughness, and stability). Despite this complexity, correlation of relative wear rates with carbon content is possible. An example of gouging wear is shown in Fig. 33. Because most carbides are relatively stable compared to martensite, wear resistance achieved with the aid of these hard microconstituents is retained at higher temperatures.

Effects of Alloying on Formability

Low-carbon sheet steels are generally preferred for forming. These steels typically contain less than 0.10% C and less than 1% total intentional and residual alloying elements. The amount of manganese, the principal alloying addition, normally ranges from 0.15 to 0.35%. Controlled amounts of silicon, niobium, titanium, or aluminum may be added either as deoxidizers or to develop certain properties. Residual elements, such as sulfur, chromium, nickel, molybdenum, copper, nitrogen, and phosphorus, are usually limited as much as possible. In steelmaking shops, these amounts are based on the quality of sheet being produced. Alloy sheet steels (including HSLA grades), however, contain specified amounts of one or more of these elements.

Carbon content is particularly significant in steels that are intended for complex forming applications. An increase in the carbon content of steel increases the strength of the steel and reduces its formability. These effects are caused by the formation of carbide particles in the ferrite matrix and by the resulting small grain size. The amount of carbon in steel sheet is generally limited to 0.10% or less to maximize the formability of the sheet.

Manganese enhances the hot-working characteristics of the steel and facilitates the development of the desired grain size. Some manganese is also necessary to neutralize the detrimental effects of sulfur, particularly for hot workability. Typical manganese contents for low-carbon steel sheet

range from 0.15 to 0.35%; manganese contents up to 2.0% may be specified in HSLA steels. When the sulfur content of the steel is very low, the manganese content also can be low, which allows the steel to be processed to develop high *r* (drawability) values.

Phosphorus and sulfur are considered undesirable in steel sheet intended for forming, drawing, or bending because their presence increases the likelihood of cracking or splitting. Allowable levels of phosphorus and sulfur depend on the desired quality level. For example, commercial-quality cold-rolled sheet must contain less than 0.035% P and 0.040% S. For some applications, phosphorus may be added to the steel to increase the strength. Sulfur usually appears as manganese sulfide stringers in the microstructure. These stringers can promote splitting, particularly whenever an unrestrained edge is deformed.

Silicon content in low-carbon steel varies according to the deoxidation practice used during production. In rimmed steels (so called because of the rimming action caused by outgassing during solidification from the molten state), the silicon content is generally less than 0.10%. When silicon rather than aluminum is used to kill the rimming action, the silicon content may be as high as 0.40%. Silicon may cause silicate inclusions, which increase the likelihood of cracking during bending. Silicon also increases the strength of the steel and thus decreases its formability.

Chromium, nickel, molybdenum, vanadium, and other alloying elements are present in low-carbon steel only as residual elements. With proper scrap selection and control of steelmaking operations, these elements are generally held to minimum amounts. Each of these elements increases the strength and decreases the formability of steel sheet. High-strength low-alloy steels may contain specified amounts of one or more of these elements.

Copper is generally considered an innocuous residual element in steel sheet. The strengthening effect of copper is almost negligible in typical residual amounts of less than 0.10%. However, copper is added to steel in amounts exceeding 0.20% to improve resistance to atmospheric corrosion.

Niobium strengthens HSLA steel through the formation of niobium carbides and nitrides. It can also be used either alone or in combination with titanium to develop high *r* values in interstitial-free steels. These alloying elements remove the interstitial elements carbon and nitrogen from solid solution. Consequently, the steel shows no yield point elongation.

Titanium is a strong carbide and nitride former. It helps develop high *r* values and eliminates yield point elongation and the aging of cold-rolled annealed steel sheet. Titanium streaks may be a problem in some grades, especially in the form of surface defects in exposed applications.

Aluminum is added to steel to kill the rimming action and thus produce a very clean steel known as an aluminum-killed or special-killed, steel. Aluminum combines with both the oxygen and nitrogen to stop the outgassing of the molten steel when it is added to the ladle or mold. Aluminum also aids the development of preferred grain orientations to attain high *r* values in cold-rolled and annealed steel sheet. Elongated grains of an approximate ASTM 7 size are found in most well-processed aluminum-killed steels. Because the aluminum combines with the nitrogen, the steel is not subject to strain aging.

Nitrogen can significantly strengthen low-carbon steel. It also causes strain aging of the steel. The effects of nitrogen can be controlled by deoxidizing the melt with aluminum.

Cerium and other rare-earth elements may be added to steel to change the shape of manganese sulfide inclusions from being needlelike or ribbonlike to being globular. Globular inclusions reduce the likelihood of cracking if the sheet is formed without restraining the edges.

Oxygen content of molten steel determines its solidification characteristics in the ingot. Excessive amounts of oxygen impede nitride formation and thus negate the effects of alloying elements added to minimize strain aging. Deoxidizers such as silicon, aluminum, and titanium will control the oxygen content. When oxygen combines with these deoxidants, complex nonmetallics are formed. Although most nonmetallics dissolve in the slag, some may become trapped in the steel, causing the surface defects of seams and slivers.

Effects of Alloying on Forgeability

Forgeability varies considerably among the various grades of carbon and alloy steels. Carbon and alloy content, forging temperature, and strength at forging temperature determine forgeability. Low-carbon steels are the most forgeable, partly because they can be forged at higher temperatures than high-carbon steels (Table 12) and partly because of their low strength at elevated temperatures. As carbon and alloy contents increase, the strength of the metal at any temperature increases, as do the forging load requirements. Figure 34 shows the effects of steel composition on the forging loads and forging pressures required to effect upset reductions of increasing severity at different forging temperatures.

Microalloyed forging steels often can be forged at lower temperatures than conventional carbon or alloys steels. The combination of metal displacement and heating during forging, followed by controlled cooling, strengthens the workpiece thermomechanically. This eliminates the need for subsequent quenching and tempering.

Table 12 Maximum safe forging temperatures for carbon and alloy steels of various carbon contents

Carbon content, %	Maximum safe forging temperature			
	Carbon steels		Alloy steels	
	°C	°F	°C	°F
0.10	1290	2350	1260	2300
0.20	1275	2325	1245	2275
0.30	1260	2300	1230	2250
0.40	1245	2275	1230	2250
0.50	1230	2250	1230	2250
0.60	1205	2200	1205	2200
0.70	1190	2175	1175	2150
0.90	1150	2100	…	…
1.10	1110	2025	…	…

Effects of Alloying on Weldability

There are a number of metallurgical factors that determine the weldability of a carbon or alloy steel. These include hardenability, carbon content (and to a lesser extent alloying content), weld metal microstructure, heat-affected zone (HAZ) microstructure, and preweld and postweld heat treatments.

Hardenability in steels is generally used to indicate austenite stability with alloy additions. However, it has also been used as an indicator of weldability and as a guide for selecting a material and welding process to

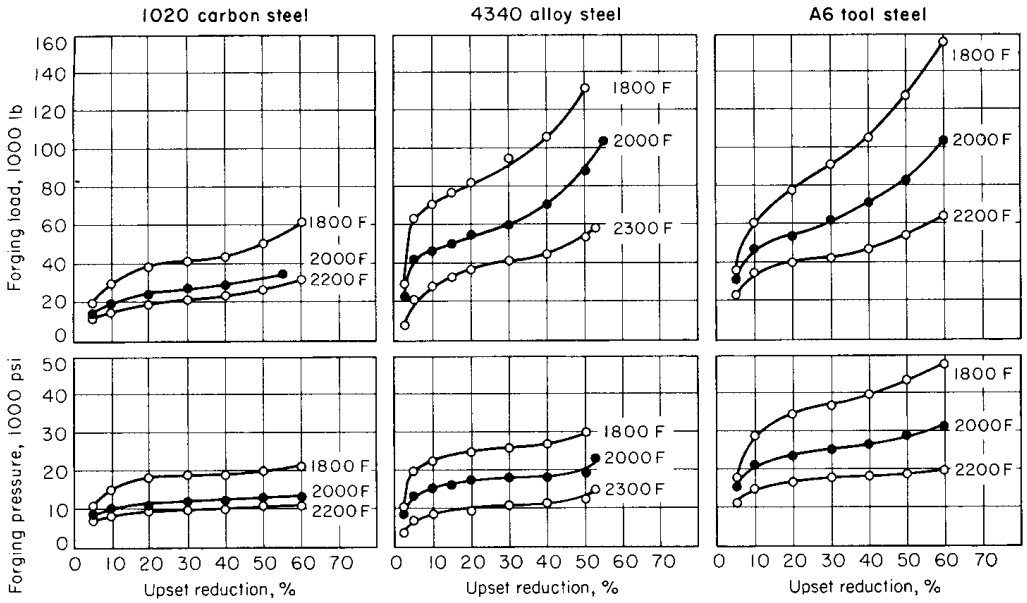


Fig. 34 Effects of compositions of three different steels on loads and pressures required for upset reductions of increasing severity at various temperatures

avoid excessive hardness and cracking in the HAZ. Steels with high hardness often contain a high volume fraction of martensite, which is extremely susceptible to cracking during processing. Hardenability is also used to indicate the susceptibility of a steel to hydrogen-induced cracking.

Effects of Carbon Content and Alloying Elements. Traditionally, empirical equations have been developed experimentally to express weldability. Carbon equivalent (CE) is one such expression; it was developed to estimate the cracking susceptibility of a steel during welding and to determine whether the steel needs preweld and postweld heat treatment to avoid cracking. Carbon equivalent equations do include the hardenability effect of the alloying elements by expressing the chemical composition of the steel as a sum of weighted alloy contents. To date, several CE expressions with different coefficients for the alloying elements have been reported. The International Institute of Welding (IIW) carbon equivalent equation is:

$$CE = C + \frac{Mn}{6} + \frac{Ni}{15} + \frac{Cu}{15} + \frac{Cr}{5} + \frac{Mo}{5} + \frac{V}{5} \qquad \text{(Eq 1)}$$

where the concentration of the alloying elements is given in weight percent. It can be seen in Eq 1 that carbon is the element that most affects weldability. Together with other chemical elements, carbon may affect the solidification temperature range, hot tear susceptibility, hardenability, and cold-cracking behavior of a steel weldment. Figure 35 summarizes the CE

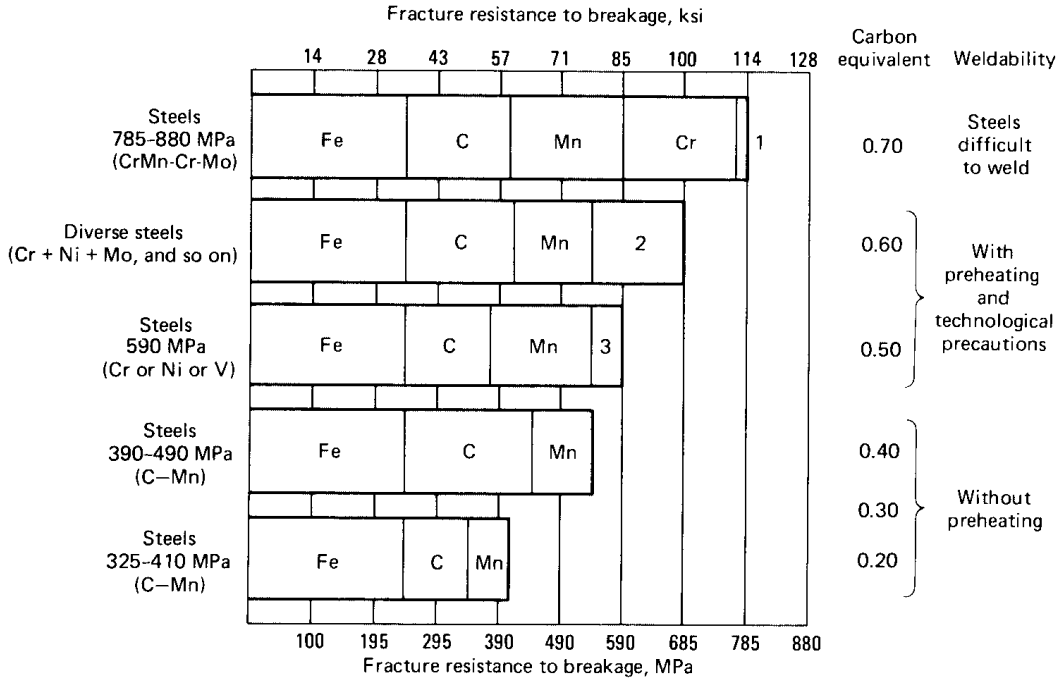


Fig. 35 Weldability of several families of steels as a function of carbon equipment. 1, Mo; 2, Cr + Ni + Mo + Si, and so on; 3, Cr or V or Ni + Si, and so on

and weldability description of some steel families. Because of the simplification and generalization involved in Fig. 35, it should be used cautiously for actual welding situations.

Weldability of Low-Carbon Steels. At low carbon levels (less than 0.15% C), the steels are nonhardening and weldability is excellent. The bulk of the steels in this carbon range are used for flat-rolled products (sheet and strip), which may contain up to 0.5% Mn. Most of these steels are now aluminum-killed, continuous-cast product supplied in the cold-rolled and annealed condition. The lower available oxygen in the killed sheet makes it easier to arc weld without porosity formation.

Weldability of Mild Steels. In the range of 0.15 to 0.30% C, carbon, or mild steels, are generally easily welded, but because hardening is a possibility, precautions such as preheating may be required higher manganese levels, in thicker sections, or at high levels of joint restraint. The welding of sections that are more than 25 mm (1 in.) thick, particularly if the carbon content of the base metal exceeds 0.22 wt%, may require that the steel be preheated to approximately 40 °C (100 °F) and stress relieved at approximately 525 to 675 °C (1000 to 1250 °F).

Weldability of Medium-Carbon Steels. Steels containing 0.30 to 0.60% C can be successfully welded by all of the arc welding processes, provided suitable precautions are taken. The higher carbon content of these steels, along with manganese from 0.6 to 1.65%, makes these steels more hardenable. For this reason, they are commonly used in the quenched and tempered condition. Because of the greater likelihood of martensite formation during welding, and the higher hardness of the martensite formed, preheating and postheating treatments are necessary. Low-hydrogen consumables and procedures should also be used to reduce the likelihood of hydrogen-induced cracking. The higher strength level of these steels may require the use of an alloyed electrode to match the base-metal properties. It may also be necessary to postweld heat treat the part in order to restore the strength and/or toughness of the HAZ.

Weldability of High-Carbon Steels. Steels containing 0.60 to 2.00% C have poor weldability because of the likelihood of formation of a hard, brittle martensite upon weld cooling. Steels of this type are used for springs, cutting tools, and abrasion-resistant applications. Low-hydrogen consumables and procedures, preheating, interpass control, and stress relieving are essential if cracking is to be avoided. Austenitic stainless steel electrodes are sometimes used to weld high-carbon steels. These electrodes will reduce the risk of hydrogen-induced cracking but may not match the strength of the high-carbon steel base metal.

Preheat and postheat will not actually retard the formation of brittle high-carbon martensite in the weld. However, preheating can minimize shrinkage stresses, and postheating can temper the martensite that forms.

Successful welding of high-carbon steel requires the development of a specific welding procedure for each application. The composition, thickness, and configuration of the component parts must be considered in process and consumable selections.

Weldability of Free-Machining Steels. The 11*xx* and 12*xx* series steels contain large amounts of sulfur, phosphorus, or lead for improved machinability. Both series are difficult to weld because of solidification cracking and porosity formation.

Weldability of HSLA Steels. For all practical purposes, welding these steels is the same as welding plain carbon steels that have similar carbon equivalents. Preheating may sometimes be required, but postheating is almost never required.

Weldability of Quenched and Tempered Steels. These steels are furnished in the heat-treated condition with yield strengths ranging from approximately 350 to 1000 MPa (50 to 150 ksi), depending on the composition. The base metal is kept at less than 0.22% C for good weldability. Preheating must be used with caution when welding quenched and tempered steels because it reduces the cooling rate of the weld HAZ. If the cooling rate is too slow, the reaustenitized zone adjacent to the weld metal can transform either to ferrite with regions of high-carbon martensite, or to coarse bainite, of lower strength and toughness. A moderate preheat, however, can ensure against cracking, especially when the joint to be welded is thick and highly restrained. A postweld stress-relief heat treatment is generally not required to prevent brittle fracture in weld joints in most quenched and tempered steels.

Weldability of Heat-Treatable Low-Alloy Steels. Examples of heat-treatable low-alloy steels include AISI 4140, AISI 4340, AISI 5140, AISI 8640, and 300M. The high hardness of these steels requires that welding be conducted on materials in an annealed or overtempered condition, followed by heat treatment to counter martensite formation and cold cracking. However, high preheating is often used with a low-hydrogen process on these steels in a quenched and tempered condition, as in motor shaft applications. Preheating, or interpass heating, for both the weld metal and the HAZ are recommended. Hydrogen control is also essential to prevent weld cracking. Extremely clean vacuum-melted steels are preferred for welding.

Low sulfur and phosphorus are required to reduce hot cracking. Segregation, which occurs because of the extended temperature range at which solidification takes place, reduces high-temperature strength and ductility. Fillers of lower carbon and alloy content are highly recommended. Preheat and interpass temperatures of 315 °C (600 °F) or higher are very harsh environments for welders because of the physical discom-

fort. However, the cooling rate must be controlled to allow the formation of a bainitic microstructure instead of the hard martensite. The bainitic microstructure can be heat treated afterward to restore the original mechanical properties of the structure. Specifications and procedures should be followed rigorously for difficult-to-weld materials.

Weldability of Chromium-Molybdenum Steels. The weldability of chromium-molybdenum steels is very similar to that of quenched and tempered and hardenable low-alloy steels. The major problem in the HAZ is cracking in the hardened coarse-grained region, as well as HAZ softening between Ac_1 and Ac_3. Reheat cracking during postweld heat treatment and long-term exposure in elevated-temperature service conditions also can cause severe problems. The appropriate preheat and interpass temperature should be selected, and low-hydrogen practice should be used.

Although a postweld heat treatment is not required for chromium-molybdenum steels with lower chromium contents and thinner gages, it is often conducted immediately after welding as part of the welding procedure. The postweld heat treatment of a chromium-molybdenum weldment is also referred to as a stress-relief heat treatment.

Effects of Alloying on Machinability

Carbon steels nearly always have better machinability than alloy steels of comparable carbon content and hardness. Steels hardened and tempered to hardness levels greater than 300 HB are an exception to this observation; under such conditions, alloy steels have superior machinability, which is usually attributed to, first, the higher tempering temperature required to temper an alloy steel to a specified hardness level and, second, nonuniformity of microstructure due to limited hardenability in carbon steels.

Carbon Steels

Effect of Carbon Content. Relative machinability ratings for some plain carbon steels are given in Table 13. Carbon content has a dominant effect on the machinability of carbon steels, chiefly because it governs strength, hardness, and ductility. Increasing the carbon content of steel increases its strength and the unit power consumption for cutting. Data in Fig. 36 show the effects of increasing carbon content and manganese content on unit power consumption.

Low-carbon steels containing less than 0.15% C are low in strength in the annealed condition; they machine poorly because they are soft and

Table 13 Machinability ratings of plain carbon steels

Machinability ratings are from the percentage of cutting speed for 1212 steel at 50 m/min (160 stm).

SAE/AISI grade (a)	Machinability rating	Hardness, HB
1212	100	175
1005	45	95
1006	50	95
1010	55	105
1015	60	111
1017	65	116
1019	70	131
1030	70	149
1038	65	163
1040	60	170
1045	55	179
1045	60(b)	170
1050	45	197
1050	55(b)	189
1065	60(b)	183
1070	55(b)	187
1075	48	192
1085	45(c)	192
1095	45(c)	197
1524	60	163
1536	55	187
1541	45	207
1547	40	207
1547	45(b)	187

(a) Values are for steel cold drawn from the hot-rolled condition, unless otherwise indicated. (b) Annealed, then cold drawn. (c) Spheroidized, then cold drawn

gummy and adhere to the cutting tools. The machinability of these grades can best be improved by work hardening to raise the strength level and lower the ductility.

Steels in the 0.15 to 0.30% C range are usually machined satisfactorily in the as-rolled, as-forged, annealed, or normalized condition with a predominantly pearlitic structure. The medium-carbon grades, containing up to about 0.55% C, machine best if an annealing treatment

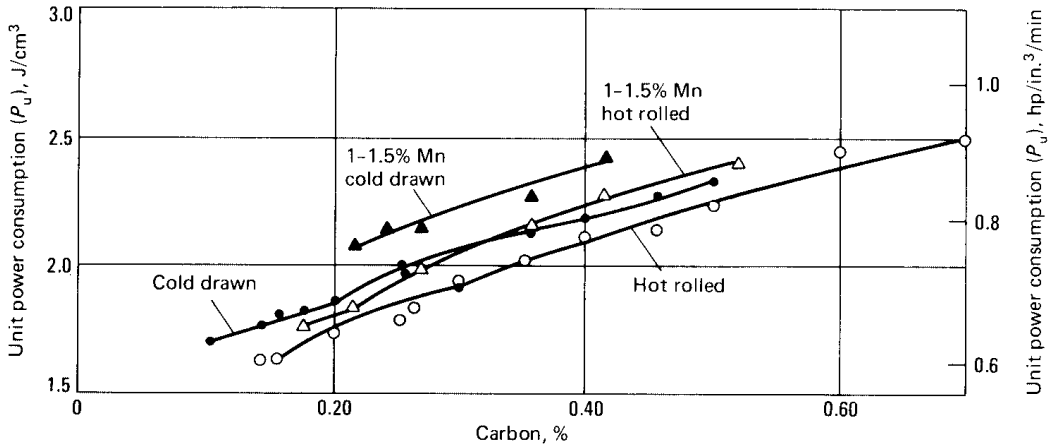


Fig. 36 Effect of carbon content on unit power consumption. Unit power consumption for hot-rolled and cold-drawn steels of two different manganese levels containing various amounts of carbon

that produces a mixture of lamellar pearlite and spheroidite is used. If the structure is not partially spheroidized, the strength and hardness may be too high for optimal machinability. For steels with carbon content higher than about 0.55%, a completely spheroidized structure is preferred. Hardened and tempered structures are generally not desired for machining.

Carbon content also affects surface finish in machining, although its effect can be greatly modified by the nature of the cutting operation or by the cutting conditions. Low values of surface roughness resulting from machining can be most easily achieved with carbon steels containing approximately 0.25 to 0.35% C.

Resulfurized Carbon Steels

There is a significant improvement in machinability when a resulfurized carbon steel is substituted for a plain carbon steel of approximately the same carbon content. In carbon steels, the sulfur content is ordinarily restricted to a maximum of 0.05%. In the manufacture of resulfurized steels, sulfur is deliberately added to achieve the desired sulfur level. The most common range of sulfur content in resulfurized steels is 0.08 to 0.13%, but some grades permit sulfur content as high as 0.35%. Machinability ratings for standard resulfurized steels are given in Table 14.

Sulfur is added to steel for the sole purpose of decreasing machining costs, either by increasing productivity through greater machining speeds and improved tool life or by eliminating secondary operations through an improvement in finish. Sulfide inclusions, depending on their size, shape,

Table 14 Machinability ratings of resulfurized and rephosphorized carbon steels, percent of cutting speed for B1112/1212 at 50 m/min (160 sfm)

Grade (a)	Machinability rating, %	Hardness, HB
1117	90	137
1118	85	143
1137	70	197
1140	70	170
1141	70	212
1144	80	217
1146	70	187
1151	65	207
1212	100	…
1213	136	…
1215	136	…
12L14	160	163
12L14(b)	190	137
12L14(c)	235	137
12L14(d)	295	137

(a) All values are for cold-drawn steels. (b) Proprietary free-machining variant of 12L14. (c) Proprietary free-machining variant of 12L14 containing bismuth. (d) Proprietary free-machining variants of 12L14 containing bismuth, selenium, or tellurium

and orientation, improve machining by causing the formation of a broken chip instead of a stringy or continuous chip and by providing a built-in lubricant that prevents the chips from sticking to the tool and undermining the cutting edge. By minimizing this adherence, less power is required, finish is improved, and the speed of machining can often be doubled, compared with machining a similar, nonresulfurized grade. A tightly curled chip that breaks readily is also particularly helpful in milling, deep drilling, tapping, slotting, and reaming because the chip is forced to move within a confined area in these operations.

The reduced friction, lower specific power requirements, and improved chip characteristics when machining resulfurized steels all contribute to increased production rates. The advantage of free-machining steels over carbon and alloy grades in terms of unit power consumption is shown in Fig. 37. The difference is important because almost all the energy of cutting is converted into heat in the cutting zone.

The manganese content of resulfurized steels must be high enough to ensure that all the sulfur is present in the form of manganese sulfide (MnS) particles. When a high sulfur content is accompanied by an increase in manganese content, a better surface finish is obtainable, which usually results in an improvement in dimensional accuracy.

Control of Sulfide Morphology. The control of MnS particle shape, size, and distribution is a critical aspect of steelmaking. Elemental additions of calcium and calcium change the shape of nonmetallic inclusions (make them more globular) and improve both toughness and machinability.

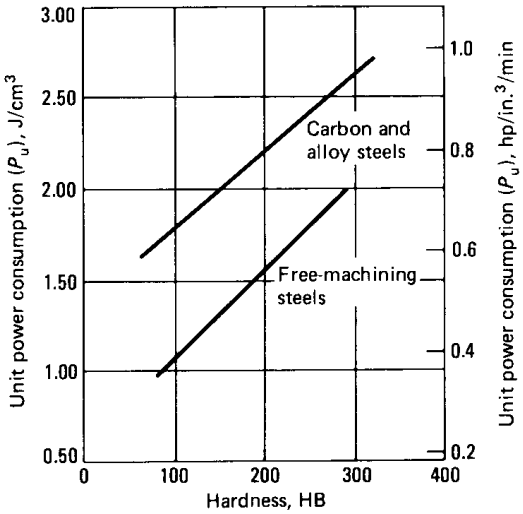


Fig. 37 Unit power consumption for free-machining and standard grades of carbon and alloy steels as a function of hardness

Carbon Steels with Other Additives

Phosphorus, as well as sulfur, is often added to improve the machining characteristics of low-carbon steels. The phosphorus range for 12L14 and 1215 is 0.04 to 0.09%. The phosphorus limits are 0.07 to 0.12% for other steels in the 12*xx* series. The limits are set because phosphorus, like carbon, increases the hardness and strength of the steel. Consequently, excessive phosphorus contents impair machining characteristics and some other properties of steel.

Phosphorus is soluble in iron and increases the strength of ferrite, an effect that promotes chip breaking in cutting operations. The phosphorus helps to avoid the formation of long, stringy chips in some operations and may result in a better surface finish.

Selenium, tellurium, and bismuth additions improve machinability but are not available in standard grades of steel. These additions are expensive (selenium treatment increases the cost of steel by about 15%). When they are used, it is often in combination with sulfur or lead. Typical percentages of these elements would be 0.04 or 0.05%. They seem to exert beneficial effects by promoting the retention of globular-shaped sulfide-type inclusions. For the same reason, they are considered to have a less deleterious effect than sulfur on mechanical properties.

Leaded Carbon and Resulfurized Steels

The addition of lead to carbon steels is another means of increasing the machinability of the steel and improving the surface finish of machined parts. Lead is added to the molten steel during teeming of ingots or sometimes, to the ladle. Because lead is insoluble, or nearly so, in molten steel, a fine dispersion of lead particles develops as the steel solidifies. The lead is usually found near or surrounding the sulfide inclusions. On special order, nearly all carbon steels in the 10*xx* and 11*xx* series can be produced with 0.15 to 0.35% Pb. The grades are identified by inserting the letter "L" between the second and third numerals of the grade designation, for example, 10L45. It is generally believed that lead has a minimal effect on the yield or ultimate strength, ductility, or fatigue properties of steels at room temperature and moderate strength levels. Lead can also be added to alloy steels to improve machinability without sacrificing room-temperature mechanical properties. Environmental considerations may restrict the manufacture or use of leaded steels.

Leaded steels cost about 5% more than similar nonleaded compositions. Because requirements of machinability and finish are the only reasons for using leaded grades, the extra cost for these steels must be justified by either or both of these factors.

Through-Hardening Alloy Steels

The steels chosen for parts that must be hardened throughout must contain enough carbon to achieve the desired hardness after quenching and sufficient alloy content to obtain the desired percentage martensite in the thickest section of the part. The combination of carbon and alloy contents can make these steels difficult to machine. The extent of the difficulties encountered in machining these steels depends primarily on the microstructure and hardness of the steel and secondarily on its alloy content. Machinability ratings for several alloy steels are given in Table 15.

A comparison of the machinability ratings with the compositions of these steels indicates that all of the alloying elements that increase the hardenability of the steel decrease machinability; ferrite-strengthening elements such as nickel and silicon decrease the machinability more than equivalent amounts of carbide-forming elements such as chromium and molybdenum.

Table 15 Machinability ratings for alloy steels compared to 1212 steel at 50 m/min (160 sfm)

The machinability rating of 1212 steel is assigned at 100.

Grade	Machinability rating(a)	Hardness, HB
1330	55(b)	179–235
1340	50(b)	183–241
1345	45(c)	183–241
4024	75(c)	156–207
4028	75(c)	167–212
4042	65(b)	179–229
4130	70(b)	187–229
4140	65(b)	187–229
41L40	85(b)	185–230
4150	55(b)	187–240
4340	50(b)	187–240
4620	65(c)	183–229
50B40	65(b)	174–223
50B60	55(d)	170–212
5130	70(b)	174–212
5140	65(b)	179–217
5160	55(d)	179–217
51B60	55(d)	179–217
50100	40(d)	183–240
51100	40(d)	183–240
52100	40(d)	183–240
8115	65(c)	163–202
81B45	65(b)	179–223
8630	70(b)	179–229
8620	65(c)	179–235
86L20	85(c)	…
8660	55(d)	179–217
8645	65(b)	184–217
86B45	65(b)	184–217
8740	65(b)	184–217

(a) Ratings are for cold-finished bars. (b) Microstructure composed of ferrite and lamellar pearlite. (c) Microstructure composed mainly of acicular pearlite and bainite. (d) Microstructure composed primarily of spheroidite

Effects of Sulfur. The sulfur content of through-hardening alloy steels can significantly affect machining behavior. Variations in residual sulfur level can account for unexplained differences in the machining behavior of different lots of the same material. Many grades of hardenable alloy steels can be obtained in the resulfurized condition. The differences in tool life and cutting speed between standard and high-sulfur 4150 steels are substantial Raising the sulfur content from 0.04 to 0.09% increases the cutting speed for 60-min tool life by 25%. Alloy steels containing lead are available and useful. As indicated in Table 15, the machinability rating of the leaded grade 41L40 is 85, while the rating for 4140 is only 65.

Another important factor that can affect the choice of steel for a through-hardening application is the effect of alloying elements added for machinability on the mechanical properties of the steel. These steels are often used at high-strength levels, where the deleterious effects of inclusions, particularly on transverse properties, might not be permissible. The effect of sulfur, in the amounts usually specified for enhanced machinability, is generally considered to be more damaging than that of lead. For some applications, neither machinability additive can be tolerated.

REFERENCES

1. K. Balajiva et al., Effects of Trace Elements on Embrittlement of Steels, *Nature,* Vol 178, 1956, p 433
2. W. Steven and K. Balajiva, The Influence of Minor Elements on the Isothermal Embrittlement of Steels, *J. Iron Steel Inst.,* Vol 193, Oct 1959, p 141–147
3. J.R. Low et al., Alloy and Impurity Effects on Temper Brittleness of Steel. *Trans. AIME,* Vol 242, Jan 1968, p 14–24
4. R.H. Greaves and J.A. Jones, Temper-Brittleness of Nickel-Chromium Steels, *J. Iron Steel Inst.,* Vol 102, 1920, p 171–222
5. R.H. Greaves and J.A. Jones, Temper-Brittleness of Steel: Susceptibility to Temper-Brittleness in Relation to Chemical Composition, *J. Iron Steel Inst.,* Vol III, 1925, p 231–255
6. B.J. Schulz and C.J. McMahon, Jr., Alloy Effects in Temper Embrittlement, *Temper Embrittlement of Alloy Steels,* STP 499, American Society for Testing and Materials, 1972, p 104–135
7. C.J. McMahon, Jr. et al., The Influence of Moon P-Induced Temper Embrittlement in Ni-Cr Steel, *Metall Trans. A,* Vol 8, July 1977, p 1055–1057
8. P.W. Brown and L.W. Masters, Factors Affecting the Corrosion of Metals in the Atmosphere, *Atmospheric Corrosion,* W.H. Ailor, Ed., John Wiley & Sons, 1982, p 31–47
9. C.P. Larrabee and S.K. Coburn, The Atmospheric Corrosion of Steels as Influenced by Changes in Chemical Composition. *Proc. Ist International Congress on Metallic Corrosion,* Butterworths, 1962, p 276–285

10. W.R. Patterson, in *Designing for Automotive Corrosion Prevention,* Proceedings P-78, Nov 8–10, 1978 (Troy, MI), Society of Automotive Engineers, p 71
11. J.B. Vrable, R.T. Jones, and E.H. Phelps, "The Application of Corrosion-Resistant High-strength Low-Alloy Steels in the Chemical Industry," presented at Fall Meeting (Chicago), American Society for Metals, 1977
12. R.T. Jones, in *Process Industry Corrosion,* National Association of Corrosion Engineers, Houston, 1986, p 373
13. A.W. Zeuthen, *Heating, Piping and Air Conditioning,* Vol 42 (No. 1), 1970, p 152
14. S.W. Ciraldi, Stress-Corrosion Cracking of Carbon and Low-Alloy Steels, *Stress-Corrosion Cracking*: *Materials Performance and Evaluation,* R.H. Jones, Ed., ASM International, 1992, p 41–61

SELECTED REFERENCES

- E.C. Bain and H.W. Paxton, *Alloying Elements in Steel,* American Society for Metals, 1966
- B.L. Bramfitt, Structure/Property Relationships in Irons and Steels, *Metals Handbook Desk Edition,* 2nd ed., J.R. Davis, Ed., ASM International, 1998, p 153–173
- R.W.K. Honeycombe, *Steels—Microstructure and Properties,* Edward Arnold Ltd., 1982
- G. Krauss, *Steels—Heat Treatment and Processing Principles,* ASM International, 1989
- W.C. Leslie, *The Physical Metallurgy of Steels,* McGraw-Hill, 1981
- *Properties and Selection*: *Irons, Steels, and High-Performance Alloys,* Vol 1, ASM Handbook, ASM International, 1990
- A.K. Sinha, *Ferrous Physical Metallurgy,* Butterworths, 1989
- *ASM Specialty Handbook*: *Carbon and Alloy Steels,* J.R. Davis, Ed., ASM International, 1996

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High-Strength Low-Alloy Steels

Introduction and Overview

High-strength low-alloy (HSLA) steels, or microalloyed steels, are designed to provide better mechanical properties and/or greater resistance to atmospheric corrosion than conventional carbon steels. They are not considered to be alloy steels in the normal sense because they are designed to meet specific mechanical properties rather than a chemical composition (HSLA steels have yield strengths greater than 275 MPa, or 40 ksi). The chemical composition of a specific HSLA steel may vary for different product thicknesses to meet mechanical property requirements. The HSLA steels in sheet or plate form have low carbon content (0.05 to –0.25% C) in order to produce adequate formability and weldability, and they have manganese content up to 2.0%. Small quantities of chromium, nickel, molybdenum, copper, nitrogen, vanadium, niobium, titanium, and zirconium are used in various combinations.

HSLA Steel Categories. High-strength low-alloy steels include many standard and proprietary grades designed to provide specific desirable combinations of properties such as strength, toughness, formability, weldability, and atmospheric corrosion resistance. These steels are not considered alloy steels, even though their desired properties are achieved by the use of small alloy additions. Instead, HSLA steels are classified as a separate steel category, which is similar to as-rolled mild-carbon steel with enhanced mechanical properties obtained by the addition of small amounts of alloys and, perhaps, special processing techniques such as controlled rolling and accelerated cooling methods. This separate product recognition of HSLA steels is reflected by the fact that HSLA steels are generally priced from the base price for carbon steels, not from the base price for alloy steels. Moreover, HSLA steels are often sold on the basis

of minimum mechanical properties, with the specific alloy content left to the discretion of the steel producer.

HSLA steels can be divided into six categories:

- *Weathering steels,* which contain small amounts of alloying elements such as copper and phosphorus for improved atmospheric corrosion resistance and solid-solution strengthening (see the article "Carbon and Alloy Steels").
- *Microalloyed ferrite-pearlite steels,* which contain very small (generally, less than 0.10%) additions of strong carbide or carbonitride-forming elements such as niobium, vanadium, and/or titanium for precipitation strengthening, grain refinement, and possibly transformation temperature control
- *As-rolled pearlitic steels,* which may include carbon-manganese steels but which may also have small additions of other alloying elements to enhance strength, toughness, formability, and weldability
- *Acicular ferrite (low-carbon bainite) steels,* which are low-carbon (less than 0.05% C) steels with an excellent combination of high yield strengths, (as high as 690 MPa, or 100 ksi) weldability, formability, and good toughness
- *Dual-phase steels,* which have a microstructure of martensite dispersed in a ferritic matrix and provide a good combination of ductility and high tensile strength
- *Inclusion-shape-controlled steels,* which provide improved ductility and through-thickness toughness by the small additions of calcium, zirconium, or titanium, or perhaps rare earth elements so that the shape of the sulfide inclusions is changed from elongated stringers to small, dispersed, almost spherical globules

These categories are not necessarily distinct groupings, as an HSLA steel may have characteristics from more than one grouping. For example, all the above types of steels can be inclusion shape controlled. Microalloyed ferrite-pearlite steel may also have additional alloys for corrosion resistance and solid-solution strengthening. Table 1 lists compositions of some HSLA steels covered in ASTM specifications.

Applications of HSLA steels include oil and gas pipelines, heavy-duty highway and off-road vehicles, construction and farm machinery, industrial equipment, storage tanks, mine and railroad cars, barges and dredges, snowmobiles, lawn mowers, and passenger car components. Bridges, offshore structures, power transmission towers, light poles, and building beams and panels are additional uses of these steels.

The choice of a specific high-strength steel depends on a number of application requirements including thickness reduction, corrosion resistance, formability, and weldability. For many applications, the most important factor in the steel selection process is the favorable strength-to-weight

Table 1 Compositional limits for HSLA steel grades described in ASTM specifications

ASTM specification(a)	Type or grade	UNS designation	Heat computational limits, % (b)									
			C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
A 242	Type 1	K11510	0.15	1.00	0.45	0.05	…	…	…	0.20 min	…	…
A 572	Grade 42	…	0.21	1.35(c)	0.04	0.05	0.30(c)	…	…	0.20 min(d)	…	(e)
	Grade 50	…	0.23	1.35(c)	0.04	0.05	0.30(c)	…	…	0.20 min(d)	…	(e)
	Grade 60	…	0.26	1.35(c)	0.04	0.05	0.30	…	…	0.20 min(d)	…	(e)
	Grade 65	…	0.23(c)	1.65(c)	0.04	0.05	0.30	…	…	0.20 min(d)	…	(e)
A 588	Grade A	K11430	0.10–0.19	0.90–1.25	0.04	0.05	0.15–0.30	0.40–0.65	…	0.25–0.40	0.02–0.10	…
	Grade B	K12043	0.20	0.75–1.25	0.04	0.05	0.15–0.30	0.40–0.70	0.25–0.50	0.20–0.40	0.01–0.10	…
	Grade C	K11538	0.15	0.80–1.35	0.04	0.05	0.15–0.30	0.30–0.50	0.25–0.50	0.20–0.50	0.01–0.10	…
	Grade D	K11552	0.10–0.20	0.75–1.25	0.04	0.05	0.50–0.90	0.50–0.90	…	0.30	…	0.04 Nb, 0.05–0.15 Zr
	Grade K	…	0.17	0.5–1.20	0.04	0.05	0.25–0.50	0.40–0.70	0.40	0.30–0.50	…	0.10 Mo, 0.005–0.05 Nb
A 606	…	…	0.22	1.25	…	0.05	…	…	…	…	…	…
A 607	Grade 45	…	0.22	1.35	0.04	0.05	…	…	…	0.20 min(d)	…	(e)
	Grade 50	…	0.23	1.35	0.04	0.05	…	…	…	0.20 min(d)	…	(e)
	Grade 55	…	0.25	1.35	0.04	0.05	…	…	…	0.20 min(d)	…	(e)
	Grade 60	…	0.26	1.50	0.04	0.05	…	…	…	0.20 min(d)	…	(e)
	Grade 65	…	0.26	1.50	0.04	0.05	…	…	…	0.20 min(d)	…	(e)
	Grade 70	…	0.26	1.65	0.04	0.05	…	…	…	0.20 min(d)	…	(e)
A 618	Grade Ia	…	0.15	1.00	0.15	0.05	…	…	…	0.20 min	…	…
	Grade Ib	…	0.20	1.35	0.04	0.05	…	…	…	0.20 min(f)	…	…
	Grade II	K12609	0.22	0.85–1.25	0.04	0.05	0.30	…	…	…	0.02 min	…
	Grade III	K12700	0.23	1.35	0.04	0.05	0.30	…	…	…	0.02 min	0.005 Nb min(g)
A 633	Grade A	K01802	0.18	1.00–1.35	0.04	0.05	0.15–0.30	…	…	…	…	0.05 Nb
	Grade C	K12000	0.20	1.15–1.50	0.04	0.05	0.15–0.50	…	…	…	…	0.01–0.05 Nb
	Grade D	K02003	0.20	0.70–1.60(c)	0.04	0.05	0.15–0.50	0.25	0.25	0.35	…	0.08 Mo
	Grade E	K12202	0.22	1.15–1.50	0.04	0.05	0.15–0.50	…	…	…	0.04–0.11	0.01–0.05 Nb(d), 0.01–0.03 N

(continued)

(a) For characteristics and intended uses, see Table 2. (b) If a single value is shown, it is a maximum unless otherwise stated. (c) Values may vary, or minimum value may exist, depending on product size und mill form. (d) Optional or when specified. (e) May be purchased as type 1 (0.005–0.05 Nb), type 2 (0.01–0.15 V), type 3 (0.05 Nb, max, plus 0.02–0.15 V) or type 4 (0.015 N, max, plus V ≥ 4N). (f) If chromium and silicon are each 0.50% min, the copper minimum does not apply. (g) May be substituted for all or part of V. (h) Niobium plus vanadium, 0.02 to 0.15%. (i) Nitrogen with vanadium content of 0.015% (max) with a minimum vanadium-to-nitrogen ratio of 4:1. (j) When silicon-killed steel is specified. (k) For plate under 40 mm (1.5 in.), manganese contents are 0.70 to 1.35% or up to 1.60% if carbon equivalents do not exceed 0.47%. For plate thicker than 40 mm (1 to 5 in.), ASTM A 841 specifies manganese contents of 1.00 to 1.60%.

Table 1 (continued)

ASTM specification(a)	Type or grade	UNS designation	Heat computational limits, % (b)									
			C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
A 656	Type 3	…	0.18	1.65	0.025	0.035	0.60	…	…	…	0.08	0.020 N, 0.005–0.15 Nb
	Type 7	…	0.18	1.65	0.025	0.035	0.60	…	…	…	0.005–0.15	0.020 N, 0.005–0.10 Nb
A 690	…	K12249	0.22	0.60–0.90	0.08–0.15	0.05	0.10	…	0.40–0.75	0.50 min	…	…
A 709	Grade 50, type 1	…	0.23	1.35	0.04	0.05	0.40	…	…	…	…	0.005–0.05 Nb
	Grade 50, type 2	…	0.23	1.35	0.04	0.05	0.40	…	…	…	0.01–0.15	…
	Grade 50, type 3	…	0.23	1.35	0.04	0.05	0.40	…	…	…	(h)	0.05 Nb max
	Grade 50, type 4	…	0.23	1.35	0.04	0.05	0.40	…	…	…	(i)	0.015 N max
A 715	…	…	0.15	1.65	0.025	0.035	…	…	…	…	Added as necessary	Ti, Nb added as necessary
A 808	…	…	0.12	1.65	0.04	0.05 max or 0.010 max	0.15–0.50	…	…	…	0.10	0.02–0.10 Nb, V + Nb = 0.15 max
A 812	65	…	0.23	1.40	0.035	0.04	0.15–0.50(j)	…	…	…	V + Nb = 0.02–0.15	0.05 Nb max
	80	…	0.23	1.50	0.035	0.04	0.15–0.50	0.35	…	…	V + Nb = 0.02–0.15	0.05 Nb max
A 841	…	…	0.20	(k)	0.030	0.030	0.15–0.50	0.25	0.25	0.35	0.06	0.08 Mo, 0.03 Nb, 0.02 Al total
A 871	…	…	0.20	1.50	0.04	0.05	0.90	0.90	1.25	1.00	0.10	0.25 Mo, 0.15 Zr, 0.05 Nb, 0.05 Ti

(a) For characteristics and intended uses, see Table 2. (b) If a single value is shown, it is a maximum unless otherwise stated. (c) Values may vary, or minimum value may exist, depending on product size und mill form. (d) Optional or when specified. (e) May be purchased as type 1 (0.005–0.05 Nb), type 2 (0.01–0.15 V), type 3 (0.05 Nb, max, plus 0.02–0.15 V) or type 4 (0.015 N, max, plus V ≥ 4N). (f) If chromium and silicon are each 0.50% min, the copper minimum does not apply. (g) May be substituted for all or part of V. (h) Niobium plus vanadium, 0.02 to 0.15%. (i) Nitrogen with vanadium content of 0.015% (max) with a minimum vanadium-to-nitrogen ratio of 4:1. (j) When silicon-killed steel is specified. (k) For plate under 40 mm (1.5 in.), manganese contents are 0.70 to 1.35% or up to 1.60% if carbon equivalents do not exceed 0.47%. For plate thicker than 40 mm (1 to 5 in.), ASTM A 841 specifies manganese contents of 1.00 to 1.60%.

ratio of HSLA steels compared with conventional low-carbon steels. This characteristic of HSLA steels has lead to their increased use in automobile components. Table 2 describes mill forms, characteristics, and applications for selected HSLA steels.

Effects of Microalloying Additions

Emphasis in this section is placed on microalloyed ferrite-pearlite steels, which use additions of alloying elements such as niobium and vanadium to increase strength (and thereby increase load-carrying ability) of hot-rolled steel without increasing carbon and/or manganese contents. Extensive studies during the 1960s on the effects of niobium and vanadium on the properties of structural-grade materials resulted in the discovery that very small amounts of niobium and vanadium (<0.10% each) strengthen the standard carbon-manganese steels without interfering with subsequent processing. Carbon content thus could be reduced to improve both weldability and toughness because the strengthening effects of niobium and vanadium compensated for the reduction in strength due to the reduction in carbon content.

The mechanical properties of microalloyed HSLA steels result, however, from more than just the mere presence of microalloying elements. Austenite conditioning, which depends on the complex effects of alloy design and rolling techniques, is also an important factor in the grain refinement of hot-rolled HSLA steels. Grain refinement by austenite conditioning with controlled rolling methods has resulted in improved toughness and high yield strengths in the range of 345 to 620 MPa (50 to 90 ksi). This development of controlled-rolling processes coupled with alloy design has produced increasing yield strength levels accompanied by a gradual lowering of the carbon content. Many of the proprietary microalloyed HSLA steels have carbon contents as low as 0.06% or even lower, yet are still able to develop yield strengths of 485 MPa (70 ksi). The high yield strength is achieved by the combined effects of fine grain size developed during controlled hot rolling and precipitation strengthening that is due to the presence of vanadium, niobium, and titanium.

The various types of microalloyed ferrite-pearlite steels include:

- Vanadium-microalloyed steels
- Niobium-microalloyed steels
- Niobium-molybdenum steels
- Vanadium-niobium microalloyed steels
- Vanadium-nitrogen microalloyed steels
- Titanium-microalloyed steels
- Niobium-titanium microalloyed steels
- Vanadium-titanium microalloyed steels

Table 2 Summary of characteristics and intended uses of HSLA steels described in ASTM specifications

ASTM specification	Title	Alloying elements[a]	Available mill forms	Special characteristics	Intended uses
A 242	High-strength low-alloy structural steel	Cr, Cu, N, Ni, Si, Ti, V, Zr	Plate, bar, and shapes ≤100 mm (4 in.) in thickness	Atmospheric-corrosion resistance four times that of carbon steel	Structural members in welded, bolted, or riveted construction
A 572	High-strength low-alloy niobium-vanadium steels of structural quality	Nb, V, N	Plate, bar, shapes, and sheet piling ≤150 mm (6 in.) in thickness	Yield strengths of 290 to 450 MPa (42 to 65 ksi) in six grades	Welded, bolted, or riveted structures, but mainly bolted or riveted bridges and buildings
A 588	High-strength low-alloy structural steel with 345 MPa (50 ksi) minimum yield point ≤100 mm (4 in.) inthickness	Nb, V, Cr, Ni, Mo, Cu, Si, Ti, Zr	Plate, bar, and shapes ≤200 mm (8 in.) in thickness	Atmospheric-corrosion resistance four times that of carbon steel; nine grades of similar strength	Welded, bolted, or riveted structures, but primarily welded bridges and buildings in which weight savings or added durability is important
A 606	Steel sheet and strip, hot-rolled and cold-rolled, high-strengthlow-alloy with improved corrosion resistance	Not specified	Hot-rolled and cold-rolled sheet and strip	Atmospheric-corrosion resistance twice that of carbon steel (type 2) or fourtimes that of carbon steel(type 4)	Structural and miscellaneous purposes for which weight savings or added durability is important
A 607	Steel sheet and strip, hot-rolled and cold-rolled, high strength low-alloy niobium and/or vanadium	Nb, V, N, Cu	Hot-rolled and cold-rolled sheet and strip	Atmospheric-corrosion resistance twice that of carbon steel, but only when copper content is specified; yield strengths of 310 to 485 MPa (45 to 70 ksi) in six grades	Structural and miscellaneous purposes for which greater strength or weight savings is important
A 618	Hot-formed welded and seamless high-strength low-alloy structural tubing	Nb, V, Si, Cu	Square, rectangular, round, and special-shape structural welded or seamless tubing	Three grades of similar yield strength; may be purchasedwith atmospheric-corrosion resistance twice that of carbon steel	General structural purposes, included welded, bolted, or riveted bridges and buildings
A 633	Normalized high-strength low-alloy structural steel	Nb, V, Cr, Ni, Mo, Cu, N, Si	Plate, bar, and shapes ≤150 mm (6 in.) in thickness	Enhanced notch toughness; yield strengths of 290 to 415 MPa (42 to 60 ksi) in five grades	Welded, bolted, or riveted structures for service at temperatures at or above −45 °C (−50 °F)
A 656	High-strength, low-alloy, hot-rolled structural vanadium-aluminum-nitrogen and titanium-aluminum steels	V, Al, N, Ti, Si	Plate, normally ≤16 mm ($^5/_8$ in.) in thickness	Yield strength of 552 MPa (80 ksi)	Truck frames, brackets, crane booms, rail cars, and other application for which weight savings is important
A 690	High-strength low-alloy steel H-piles and sheet piling	Ni, Cu, Si	Structural-quality H-piles and sheet piling	Corrosion resistance two to three times greater than that of carbon steel in the splash zone of marine structures	Dock walls, sea walls, bulkheads, excavations, and similar structures exposed to seawater

(a) In addition to carbon, manganese, phosphorus, and sulfur. A given grade may contain one or more of the listed elements, but not necessarily all of them; for specified compositional limits, see Table 1. (b) Obtained by producing killed steel, made to fine grain practice, and with microalloying elements such as niobium, vanadium, titanium, and zirconium in the composition

Table 2 (continued)

ASTM specification	Title	Alloying elements[a]	Available mill forms	Special characteristics	Intended uses
A 709, grade 50 and 50W	Structural steel	V, Nb, N, Cr, Ni, Mo	All structural-shape groups and plate ≤100 mm (4 in.) in thickness	Minimum yield strength of 345 MPa (50 ksi). Grade 50W is a weathering steel	Bridges
A 714	High-strength low-alloy welded and seamless steel pipe	V, Ni, Cr, Mo, Cu, Nb	Pipe with nominal pipe size diameters of 13 to 660 mm ($^1/_2$ to 26 in.)	Minimum yield strengths ≤345 MPa (50 ksi) and corrosion resistance two to four times that of carbon steel	Piping
A 715	Steel sheet and strip, hot-rolled, high-strength low-alloy with improved formability	Nb, V, Cr, Mo, N, Si, Ti, Zr, B	Hot-rolled sheet and strip	Improved formability(c) compared to A606 and A607; yield strengths of 345 to 550 MPa (50 to 80 ksi) in four grades	Structural and miscellaneous applications for which high strength, weight saving improved formability, and good weldability are important
A 808	High-strength low-alloy steel with improved notch toughness	V, Nb	Hot-rolled steel plate ≤65 mm ($2^1/_2$ in.) in thickness	Charpy V-notch impact energies of 40–60 J (30–45 ft.-Ibl) at −45 °C (−50 °F)	Railway tank cars
A 812	High-strength low-alloy steels	Y, Nb	Steel sheet in coil form	Yields strengths of 450–550 MPa (65–85 ksi)	Welded layered pressure vessels
A 841	Plate produced by thermomechanical controlled processes	V, Nb, Cr, Mo, Ni	Plates ≤100 mm (4 in.) in thickness	Yield strengths of 310–345 MPa (45–50 ksi)	Welded pressure vessels
A 847	Cold-formed welded and seamless high-strength low-alloy structural tubing with improved atmospheric-corrosion resistance	Cu, Cr, Ni, Si, V, Ti, Zr, Nb	Welded tubing with maximum periphery of 1625 mm (64 in.) and wall thickness of 16 mm (0.625 in.) or seamless tubing with maximum periphery of 810 mm (32 in.) and wall thickness of 13 mm (0.50 in.)	Minimum yield strengths ≤345 MPa (50 ksi) with atmospheric-corrosion resistance twice that of carbon	Round, square, or specially shaped structural tubing for welded, riveted, or bolted construction of bridges and buildings
A 860	High-strength butt-welding fittings of wrought high-strength low-alloy steel	Cu, Cr, Ni, Mo, V, Nb, Ti	Normalized or quenched-and-tempered wrought fittings	Minimum yield strengths ≤485 MPa (70 ksi)	High-pressure gas and oil transmission lines
A 871	High-strength low-alloy steel with atmospheric corrosion resistance	V, Nb, Ti, Cu, Mo, Cr	As-rolled plate ≤35 mm ($1^3/_8$ in.) in thickness	Atmospheric-corrosion resistance four times that of carbon structural steel	Tubular structures and poles

(a) In addition to carbon, manganese, phosphorus, and sulfur. A given grade may contain one or more of the listed elements, but not necessarily all of them; for specified compositional limits, see Table 1. (b) Obtained by producing killed steel, made to fine grain practice, and with microalloying elements such as niobium, vanadium, titanium, and zirconium in the composition

These steels may also include other elements for improved corrosion resistance and solid-solution strengthening, or enhanced hardenability (if transformation products other than ferrite-pearlite are desired).

Vanadium Microalloyed Steels. The development of vanadium-containing steels occurred shortly after the development of weathering steels, and flat-rolled products with up to 0.10% V are widely used in the hot-rolled condition. Vanadium-containing steels are also used in the controlled-rolled, normalized, or quenched and tempered condition.

Vanadium contributes to strengthening by forming fine precipitate particles (5 to 100 nm in diameter) of V(CN) in ferrite during cooling after hot rolling. These vanadium precipitates, which are not as stable as niobium precipitates, are in solution at all normal rolling temperatures and thus are very dependent on the cooling rate for their formation. Niobium precipitates, however, are stable at higher temperatures, which is beneficial for achieving fine-grain ferrite (see the section "Niobium Microalloyed Steels" in this article).

The strengthening from vanadium averages between 5 and 15 MPa (0.7 and 2 ksi) per 0.01 wt% V, depending on carbon content and rate of cooling from hot rolling (and thus section thickness). The cooling rate, which is determined by the hot-rolling temperature and the section thickness, affects the level of precipitation strengthening in a 0.15% V steel, as shown in Fig. 1. An optimum level of precipitation strengthening occurs at a cooling rate of about 170 °C/min (306 °F/min) (Fig. 1). At cooling rates lower than 170 °C/min (306 °F/min), the V(CN) precipitates coarsen and are less effective for strengthening. At higher cooling rates, more V(CN) remains in solution, and thus a smaller fraction of V(CN) particles precipitate and strengthening is reduced. For a given section thickness and cooling medium, cooling rates can be increased or decreased by increasing or decreasing, respectively, the temperature before cooling. Increasing

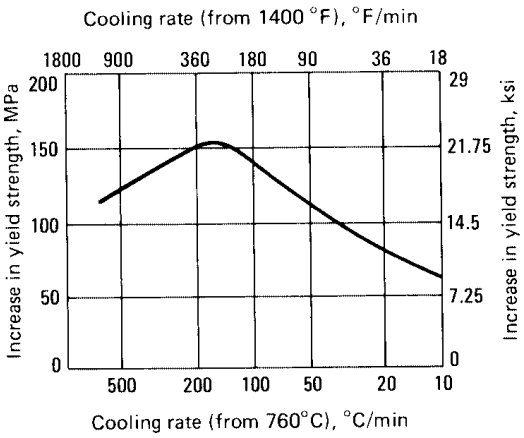


Fig. 1 Effect of cooling rate on the increase in yield strength due to precipitation strengthening in a 0.15% V steel

the temperature results in larger austenite grain sizes, while decreasing the temperature makes rolling more difficult.

Manganese content also affects the strengthening of vanadium microalloyed steels. The effect of manganese on a hot-rolled vanadium steel is shown in Table 3. The 0.9% increase in manganese content increased the strength of the matrix by 34 MPa (5 ksi) because of solid-solution strengthening. The precipitation strengthening by vanadium was also enhanced because manganese lowered the austenite-to-ferrite transformation temperature, thereby resulting in a finer precipitate dispersion. This effect of manganese on precipitation strengthening is greater than its effect in niobium steels. However, the absolute strength in a niobium steel with 1.2% Mn is only about 50 MPa (7 ksi) less than that of vanadium steel but at a much lower alloy level (that is, 0.06% Nb versus 0.14% V).

The third factor affecting the strength of vanadium steels is the ferrite grain size produced after cooling from the austenitizing temperature. Finer ferrite grain sizes (which result in not only higher yield strengths but also improved toughness and ductility) can be produced by either lower austenite-to-ferrite transformation temperatures or by the formation of finer austenite grain sizes prior to transformation. Lowering the transformation temperature, which affects the level of precipitation strengthening as mentioned above, can be achieved by alloy additions and/or increased cooling rates. For a given cooling rate, further refinement of ferrite grain size is achieved by the refinement of the austenite grain size during rolling.

The austenite grain size of hot-rolled steels is determined by the recrystallization and grain growth of austenite during rolling. Vanadium hot-rolled steels usually undergo conventional rolling but are also produced by recrystallization controlled rolling. With conventional rolling, vanadium steels provide moderate precipitation strengthening and relatively little strengthening from grain refinement. The maximum yield strength of conventionally hot-rolled vanadium steels with 0.25% C and 0.08% V is about 450 MPa (65 ksi). The practical limit of yield strengths for hot-rolled vanadium-microalloyed steel is about 415 MPa (60 ksi),

Table 3 Effect of manganese content on the precipitation strengthening of a vanadium-microalloyed steel with a base composition of 0.08% C and 0.30% Si

	Yield strength		Change in yield strength	
Vanadium content, %	MPa	ksi	MPa	ksi
0.3% Mn				
0.00	297	43	0	0
0.08	352	51	55	8
0.14	380	55	83	12
1.2% Mn				
0.00	331	48	0	0
0.08	462	67	131	19
0.14	552	80	221	32

even when controlled rolling techniques are used. Vanadium steels subjected to recrystallization controlled rolling require a titanium addition so that a fine precipitate of TiN is formed that restricts austenite grain growth after recrystallization. Yield strengths from conventional controlled rolling are limited to a practical limit of about 415 MPa (60 ksi) because of the lack of retardation of recrystallization. When both strength and impact toughness are important factors, controlled-rolled low-carbon niobium steel (such as X-60 hydrogen-induced cracking resistant plate) is preferable.

Niobium Microalloyed Steels. Like vanadium, niobium increases yield strength by precipitation hardening; the magnitude of the increase depends on the size and amount of precipitated niobium carbides (Fig. 2). However, niobium is also a more effective grain refiner than vanadium. Thus, the combined effect of precipitation strengthening and ferrite grain refinement makes niobium a more effective strengthening agent than vanadium. The usual niobium addition is 0.02 to 0.04%, which is about one-third the optimum vanadium addition.

Strengthening by niobium is 35 to 40 MPa (5 to 6 ksi) per 0.01% addition. This strengthening was accompanied by a considerable impairment of notch toughness until special rolling procedures were developed and carbon contents were lowered to avoid formation of upper bainite. In general, high finishing temperatures and light deformation passes should be avoided with niobium steels because that may result in mixed grain sizes or Widmanstätten ferrite, which impair toughness.

Niobium steels are produced by controlled rolling, recrystallization controlled rolling, accelerating cooling, and direct quenching. The recrystal-

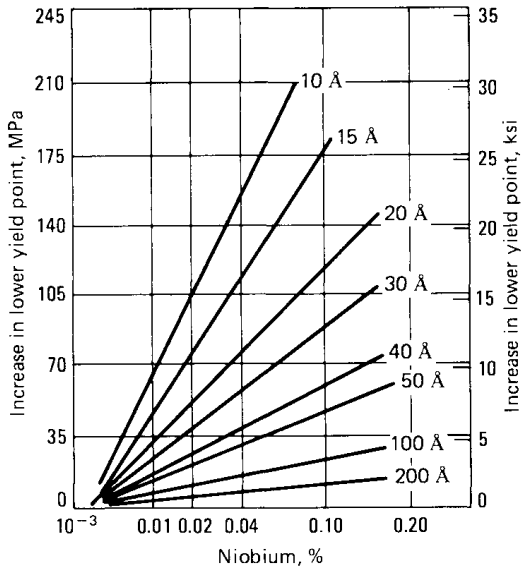


Fig. 2 Effect of niobium carbide on yield strength for various sizes of niobium carbide particles

lization controlled rolling of niobium steel can be effective without titanium, while recrystallization rolling of vanadium steels requires titanium for grain refinement. Also, much less niobium is needed, and niobium-titanium steels can be recrystallization controlled rolled at higher temperatures. At present, offshore platform steels up to 75 min (3 in.) thick with yield strengths of 345 to 415 MPa (50 to 60 ksi) are routinely produced.

Vanadium-Niobium Microalloyed Steels. Steels microalloyed with both niobium and vanadium provide a higher yield strength in the conventionally hot-rolled condition than that achievable with either element alone. As conventionally hot rolled, the niobium-vanadium steels derive almost all of their increased strength from precipitation strengthening and therefore have high ductile-brittle transition temperatures. If the steel is controlled rolled, the addition of both niobium and vanadium together is especially advantageous for increasing the yield strength and lowering ductile-brittle transition temperatures by grain refinement.

Usually niobium-vanadium steels are made with relatively low carbon contents (<0.10% C). This reduces the amount of pearlite and improves toughness, ductility, and weldability. These steels are frequently referred to as pearlite-reduced steels.

Niobium-molybdenum microalloyed steels may have either a ferrite-pearlite microstructure or an acicular ferrite microstructure. In ferrite-pearlite niobium steels, the addition of molybdenum increases the yield strength and tensile strength by about 20 MPa (3 ksi) and 30 MPa (4.5 ksi), respectively, per 0.1% Mo, over an investigated range of 0% to 0.27% Mo. The principal effect of molybdenum on the microstructure is to alter the morphology of the pearlite and to introduce upper bainite as a partial replacement for pearlite. However, because the individual strength values of pearlite and bainite are somewhat similar, it has been proposed that the strength increase is due to solid-solution strengthening and enhanced Nb(CN) precipitation strengthening caused by a molybdenum-niobium synergism. The interaction between molybdenum and niobium (or vanadium) has been proposed as an explanation for the increase in precipitation strengthening by the addition of molybdenum. This effect has been attributed to the reduced precipitation in austenite from an increase in solubility arising from a decrease in carbon activity brought about by molybdenum. With less precipitation in austenite, more precipitates could form in the ferrite, resulting in enhanced strength. Also, molybdenum has been identified in the precipitates themselves; its presence may increase their strengthening effectiveness by increasing coherency strains and/or by increasing the volume fraction of precipitation. These metallurgical factors, when considered in conjunction with the effectiveness of controlled rolling to temperatures just below the Ar_3 temperature, have led to the development of a more economical X-70 molybdenum-niobium linepipe steel.

Vanadium-Nitrogen Microalloyed Steels. Vanadium combines more strongly with nitrogen than does niobium and forms VN precipitates in vanadium-nitrogen steel. Nitrogen additions to high-strength steels containing vanadium have become commercially important because the additions enhance precipitation hardening. Precipitation hardening may be accompanied by a drop in notch toughness, but this can often be overcome by lowering the carbon content. The precipitation of vanadium nitride also acts as a grain refiner.

Some producers use nitrogen additions to assist in the precipitation strengthening of controlled-cooled sheet and plate with thicknesses above 9.5 mm (0.375 in.). Hot-rolled plates with vanadium and 0.018 to 0.022% N have been produced by controlled cooling in thicknesses up to 16 mm (0.625 in.) with yield strengths of 550 MPa (80 ksi). However, delayed cracking is a major problem in these steels. The use of nitrogen is not recommended for steels that will be welded because of its detrimental effect on notch toughness in the heat-affected zone.

Titanium-Microalloyed Steels. Titanium in low-carbon steels forms into a number of compounds that provide grain refinement, precipitation strengthening, and sulfide shape control. However, because titanium is also a strong deoxidizer, titanium can be used only in fully killed (aluminum deoxidized) steels so that titanium is available for forming into compounds other than titanium oxide. Commercially, steels precipitation strengthened with titanium are produced in thicknesses up to 9.5 mm (0.375 in.) in the minimum yield strength range from 345 to 550 MPa (50 to 80 ksi), with controlled rolling required to maximize strengthening and improve toughness.

Like niobium and/or vanadium steels, titanium microalloyed steels are strengthened by mechanisms that involve a combination of grain refinement and precipitation strengthening; the combination depends on the amount of alloy additions and processing methods. In reheated or continuously cast steels, small amounts of titanium (≤0.025% Ti) are effective grain refiners because austenite grain growth is retarded (Fig. 3a) by titanium nitride. Small amounts of titanium are also effective in recrystallization controlled rolling because titanium nitride retards the grain growth of recrystallized austenite. In conventional controlled rolling, however, titanium is a moderate grain refiner, causing less refinement than niobium but more than vanadium.

In terms of precipitation strengthening (Fig. 3b), a sufficient amount of titanium is required to form titanium carbide. Small percentages of titanium (<0.025% Ti) form mainly into TiN, which has an effect on austenite grain growth but little effect on precipitation strengthening because the precipitates formed in the liquid are too coarse. Increasing the titanium content leads to the formation first of titanium-containing manganese sulfide inclusions (Mn, Ti)S, and then of globular carbosulfides, $Ti_4C_2S_2$ (which provide sul-

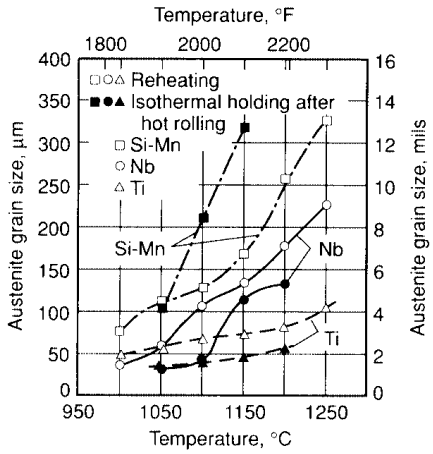


Fig. 3(a) Austenite grain coarsening during reheating and after hot rolling for a holding time of 30 min. Titanium contents were between 0.008 and 0.022% Ti.

fide shape control). The formation of $Ti_4C_2S_2$ is accompanied by and followed by titanium carbide (TiC) formation, which can be used for the precipitation strengthening of low-carbon steels. To determine the amount of titanium that is available for precipitation strengthening, the total titanium content must be adjusted for the formation of the coarse, insoluble titanium nitride and carbosulfides that do not participate in precipitation strengthening.

Experimentally observed strength increases from TiC precipitation have ranged up to 440 MPa (64 ksi) for very fine particles (less than 30 Å) and a relatively large fraction of precipitate (Fig. 3b). If sufficient amounts of titanium are used, titanium carbide can provide more precipitation strengthening than either niobium or vanadium. However, because higher levels of precipitation strengthening are generally associated with reduced toughness, grain refinement would be necessary to improve toughness. Titanium is a moderate grain refiner (compared to niobium and vanadium

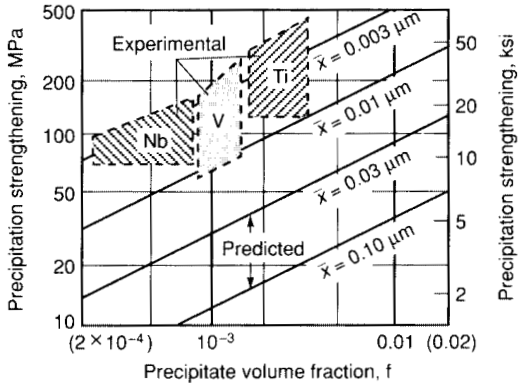


Fig. 3(b) The dependence of precipitation strengthening on average precipitate size $(\overline{X})$ and fraction according to theory and experimental observations for given microalloying additions. Source: Ref 22

in hot-rolled steels), and the high levels of precipitation strengthening of titanium microalloyed steels result in a severe penalty in toughness. Using only titanium as a strengthener in high-strength hot-rolled strip has also resulted in unacceptable variability in mechanical properties.

Titanium-Niobium Microalloyed Steels. Although precipitation-strengthened titanium steels have limitations in terms of toughness and variability of mechanical properties, research has shown that an addition of titanium to low-carbon niobium steels results in an overall improvement in properties. Titanium increases the efficiency of niobium because it combines with the nitrogen-forming titanium nitrides, thus preventing the formation of niobium nitrides. This allows for increased solubility of niobium in the austenite resulting in subsequent increased precipitation of Nb(C,N) particles in the ferrite. The addition of 0.04% titanium to steel strip containing various amounts of niobium consistently produced a yield strength increase of about 105 MPa (15 ksi) for a coiling temperature of 675 °C (1250 °F). Hot-rolled niobium-titanium steel strip is effective in achieving yield strengths of 550 MPa (80 ksi) in ferrite-pearlite steels. An addition of either vanadium or molybdenum can raise yield strengths to 690 MPa (100 ksi).

Effects of Microalloying on Processing Characteristics

The combination of low-carbon and very low alloying content in HSLA steels does not affect processing significantly. For example, niobium or niobium-titanium HSLA steels develop high *r* (drawability) values in interstitial-free steels (Fig. 4). Dual-phase steels, which feature hard martensite particles in a soft ductile ferrite matrix are also highly formable (Fig. 4). The low-carbon content of HSLA also makes them highly weldable. In fact, the weldability of most HSLA steels is similar to that of mild steels. The machinability of HSLA steels is also comparable to carbon steels. Improved machining characteristics can be achieved by using inclusion-shape-controlled HSLA steels. The only challenge associated with processing of HSLA steels has been associated with forging. The application of microalloying technology to forging steels has lagged behind that of flat-rolled products because of the different property requirements and thermomechanical processing of forging steels. Forging steels are commonly used in applications in which high strength, fatigue resistance, and wear resistance are required. These requirements are most often filled by medium-carbon steels. Thus, the development of microalloyed forging steels has centered on grades containing 0.30 to 0.50% C, although steels with carbon contents as low as 0.20% have also been developed.

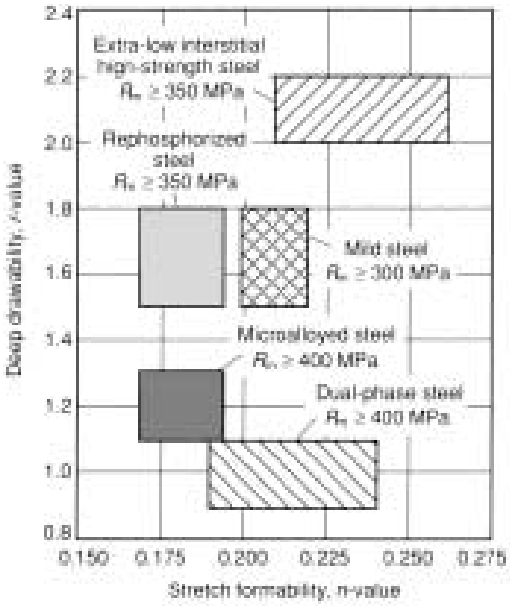


Fig. 4 Deep-drawing properties of steel sheet grades

Processing of Microalloyed Forging Steels

The driving force behind the development of microalloyed forging steels has been the need to reduce manufacturing costs. This is accomplished in these materials by means of a simplified thermomechanical treatment (that is, a controlled cooling following hot forging) that achieves the desired properties without the separate quenching and tempering treatments required by conventional carbon and alloy steels. Figure 5 shows typical thermal cycles for conventional quench and temper and for microalloy process routes.

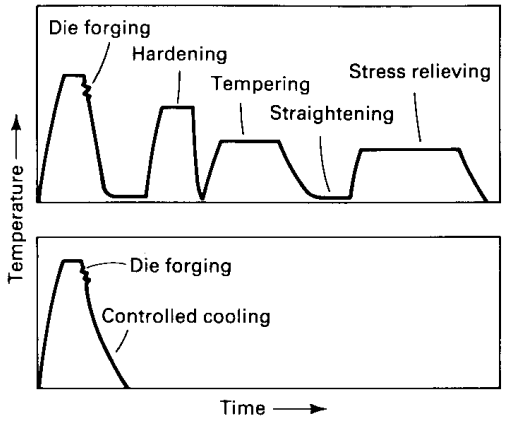


Fig. 5 Processing cycles for conventional (quenched-and-tempered: top) and microalloyed steels (bottom)

Control of Properties. In order to realize the full strengthening potential of microalloying additions, it is necessary to use a soaking temperature prior to forging that is high enough to dissolve all vanadium-bearing precipitates. A soaking temperature above 1100 °C (2010 °F) is preferred. Rapid induction heating methods for bar and billet to conventional commercial forging temperatures of 1250 °C (2280 °F) are acceptable and allow sufficient time for the dissolution of the microalloying constituents.

Tensile strength decreases slightly as the finish forging temperature is reduced, but there is not significant effect on yield strength. Ductility and toughness show a significant increase with a reduction in finishing temperature; this is due to grain refinement of the austenite and increased ferrite content. Forgers are beginning to use this approach to enhance the toughness of as-forged microalloyed steel: however, low finish forging temperatures are often avoided to minimize die wear. The specified properties of microalloyed forging steels can be achieved over a wide range of finishing temperatures.

One of the most important processing factors affecting the properties of as-forged microalloyed steels is the postforging cooling procedure. Increasing the cooling rate generally increases the yield and tensile strength because it enhances grain refinement and precipitation hardening. At high cooling rates, an optimum can be reached; above this rate the strength reduces due to the suppression of precipitation and the introduction of low-temperature transformation products.

The optimal cooling rate and maximum hardness are significantly influenced by the alloy and residual element content of the steel. Nevertheless, through control of the steel composition it is possible to ensure that the specified mechanical properties are achieved over a wide range of section sizes and cooling conditions.

Effects of Microalloying Elements on Forging

Carbon. Most of the microalloyed steels developed for forging have carbon contents ranging from 0.30 to 0.50%, which is high enough to form a large amount of pearlite. The pearlite is responsible for substantial strengthening. This level of carbon also decreases the solubility of the microalloying constituents in austenite.

Niobium, Vanadium, and Titanium. Formation of carbonitride precipitates is the other major strengthening mechanism of microalloyed forging steels. Vanadium, in amounts ranging from 0.05 to 0.2%, is the most common microalloying addition used in forging steels. Niobium and titanium enhance strength and toughness by providing control of austenite grain size. Often niobium is used in combination with vanadium to obtain the benefits of austenite grain size control (from niobium) and carbonitride precipitation (from vanadium).

Manganese is used in relatively large amounts (1.4 to 1.5%) in many microalloyed forging steels. It tends to reduce the cementite plate thickness while maintaining the interlamellar spacing of pearlite developed; thus high manganese levels require lower carbon contents to retain the large amounts of pearlite required for high hardness. Manganese also provides substantial solid solution strengthening, enhances the solubility of vanadium carbonitrides, and lowers the solvus temperature for these phases.

The silicon content of most commercial microalloyed forging steels is about 0.30%; some grades contain up to 0.70%. Higher silicon contents are associated with significantly higher toughness, apparently because of an increased amount of ferrite relative to that formed in ferrite-pearlite steels with lower silicon contents.

Sulfur. Many microalloyed forging steels, particularly those destined for use in automotive forgings in which machinability is critical, have relatively high sulfur contents. The higher sulfur contents contribute to their machinability, which is comparable to that of quenched-and-tempered steels.

Aluminum and Nitrogen. As in hardenable fine-grain steels, aluminum is important for austenite grain size control in microalloyed steels. The mechanism of aluminum grain size control is the formation of aluminum nitride particles. It has been shown that nitrogen is the major interstitial component of vanadium carbonitride. For this reason, moderate to high nitrogen contents are required in vanadium-containing microalloyed steels to promote effective precipitate strengthening.

SELECTED REFERENCES

- *High-Strength Low-Alloy Steels: Status, Selection and Physical Metallurgy,* Battelle Press, 1979
- High-Strength Structural and High-Strength Low-Alloy Steels, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook,* ASM International, 1990, p 389–423
- *HSLA Steels: Metallurgy and Applications,* American Society for Metals, 1986
- *HSLA Steels—Technology and Applications,* American Society for Metals, 1984
- *Microalloyed HSLA Steels,* ASM International, 1988

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Tool Steels

Introduction and Overview

A tool steel is any steel used to make tools for cutting, forming, or otherwise shaping a material into a part or component adapted to a definite use. The earliest tool steels were simple, plain carbon steels, but by 1868 and increasingly in the early 20th century, many complex, highly alloyed tool steels were developed. These tool steels contain, among other elements, relatively large amounts of tungsten, molybdenum, vanadium, manganese, and chromium, and they make it possible to meet increasingly severe service demands and to provide greater dimensional control and freedom from cracking during heat treatment. Many alloy tool steels are also widely used for machinery components and structural applications in which particularly stringent requirements must be met, such as high-temperature springs, ultrahigh-strength fasteners, special-purpose valves, and bearings of various types for elevated-temperature service.

In service, most tools are subjected to extremely high loads that are applied rapidly. The tools must withstand these loads a great number of times without breaking and without undergoing excessive wear or deformation. In many applications, tool steels must provide this capability under conditions that produce high temperatures in the tool. No single tool material combines maximum wear resistance, toughness, and resistance to softening at elevated temperatures. Consequently, the selection of the proper tool material for a given application often requires a tradeoff to achieve the optimum combination of properties.

Most tool steels are wrought products, but powder metallurgy (P/M) processing, where gas-atomized powders are consolidated to full density by hot isostatic pressing (HIP), is also used in making tool steels. Powder metallurgy processing provides, first, a more uniform carbide size and distribution in large sections, and, second, special compositions that are difficult or impossible to produce by melting and casting and then mechanically working the cast product.

Classification and Characteristics. Table 1 gives composition limits for the wrought tool steels most commonly used. Each group of tool steels of similar composition and properties is identified by a capital letter; within each group, individual tool steel types are assigned code numbers.

Table 1 Composition limits of principal types of wrought tool steels

Designation		Composition(a), %								
AISI	UNS	C	Mn	Si	Cr	Ni	Mo	W	V	Co
Molybdenum high-speed steels										
M1	T11301	0.78–0.88	0.15–0.40	0.20–0.50	3.50–4.00	0.30 max	8.20–9.20	1.40–2.10	1.00–1.35	…
M2	T11302	0.78–0.88 0.95–1.05	0.15–0.40	0.20–0.45	3.75–4.50	0.30 max	4.50–5.50	5.50–6.75	1.75–2.20	…
M3, class 1	T11313	1.00–1.10	0.15–0.40	0.20–0.45	3.75–4.50	0.30 max	4.75–6.50	5.00–6.75	2.25–2.75	…
M3, class 2	T11323	1.15–1.25	0.15–0.40	0.20–0.45	3.75–4.50	0.30 max	4.75–6.50	5.00–6.75	2.75–3.75	…
M4	T11304	1.25–1.40	0.15–0.40	0.20–0.45	3.75–4.75	0.30 max	4.25–5.50	5.25–6.50	3.75–4.50	…
M7	T11307	0.97–1.05	0.15–0.40	0.20–0.55	3.50–4.00	0.30 max	8.20–9.20	1.40–2.10	1.75–2.25	…
M10	T11310	0.84–0.94; 0.95–1.05	0.10–0.40	0.20–0.45	3.75–4.50	0.30 max	7.75–8.50	…	1.80–2.20	…
M30	T11330	0.75–0.85	0.15–0.40	0.20–0.45	3.50–4.25	0.30 max	7.75–9.00	1.30–2.30	1.00–1.40	4.50–5.50
M33	T11333	0.85–0.92	0.15–0.40	0.15–0.50	3.50–4.00	0.30 max	9.00–10.00	1.30–2.10	1.00–1.35	7.75–8.75
M34	T11334	0.85–0.92	0.15–0.40	0.20–0.45	3.50–4.00	0.30 max	7.75–9.20	1.40–2.10	1.90–2.30	7.75–8.75
M35	T11335	0.82–0.88	0.15–0.40	0.20–0.45	3.75–4.50	0.30 max	4.50–5.50	5.50–6.75	1.75–2.20	4.50–5.50
M36	T11336	0.80–0.90	0.15–0.40	0.20–0.45	3.75–4.50	0.30 max	4.58–5.50	5.50–6.50	1.75–2.25	7.75–8.75
M41	T11341	1.05–1.15	0.20–0.60	0.15–0.50	3.75–4.50	0.30 max	3.25–4.25	6.25–7.00	1.75–2.25	4.75–5.75
M42	T11342	1.05–1.15	0.15–0.40	0.15–0.65	3.50–4.25	0.30 max	9.00–10.00	1.15–1.85	0.95–1.35	7.75–8.75
M43	T11343	1.15–1.25	0.20–0.40	0.15–0.65	3.50–4.25	0.30 max	7.50–8.50	2.25–3.00	1.50–1.75	7.75–8.75
M44	T11344	1.10–1.20	0.20–0.40	0.30–0.55	4.00–4.75	0.30 max	6.00–7.00	5.00–5.75	1.85–2.20	11.00–12.25
M46	T11346	1.22–1.30	0.20–0.40	0.40–0.65	3.70–4.20	0.30 max	8.00–8.50	1.90–2.20	3.00–3.30	7.80–8.80
M47	T11347	1.05–1.15	0.15–0.40	0.20–0.45	3.50–4.00	0.30 max	9.25–10.00	1.30–1.80	1.15–1.35	4.75–5.25
M47	T11348	1.42–1.52	0.15–0.40	0.15–0.40	3.50–4.00	0.30 max	4.75–5.50	9.50–10.50	2.75–3.25	8.00–10.00
M62	T11362	1.25–1.35	0.15–0.40	0.15–0.40	3.50–4.00	0.30 max	10.00–11.00	5.75–6.50	1.80–2.10	…
Tungsten high-speed steels										
T1	T12001	0.65–0.80	0.10–0.40	0.20–0.40	3.75–4.50	0.30 max	…	17.25–18.75	0.90–1.30	…
T2	T12002	0.80–0.90	0.20–0.40	0.20–0.40	3.75–4.50	0.30 max	1.0 max	17.50–19.00	1.80–2.40	…
T4	T12004	0.70–0.80	0.10–0.40	0.20–0.40	3.75–4.50	0.30 max	0.40–1.00	17.50–19.00	0.80–1.20	4.25–5.75
T5	T12005	0.75–0.85	0.20–0.40	0.20–0.40	3.75–5.00	0.30 max	0.50–1.25	17.50–19.00	1.80–2.40	7.00–9.50
T6	T12006	0.75–0.85	0.20–0.40	0.20–0.40	4.00–4.75	0.30 max	0.40–1.00	18.50–21.00	1.50–2.10	11.00–13.00
T8	T12008	0.75–0.85	0.20–0.40	0.20–0.40	3.75–4.50	0.30 max	0.40–1.00	13.25–14.75	1.80–2.40	4.25–5.75
T15	T12015	1.50–1.60	0.15–0.40	0.15–0.40	3.75–5.00	0.30 max	1.00 max	11.75–13.00	4.50–5.25	4.75–5.25
Intermediate high-speed steels										
M50	T11350	0.78–0.88	0.15–0.45	0.20–0.60	3.75–4.50	0.30 max	3.90–4.75	…	0.80–1.25	…
M52	T11352	0.85–0.95	0.15–0.45	0.20–0.60	3.50–4.30	0.30 max	4.00–4.90	0.75–1.50	1.65–2.25	…
Chromium hot-work steels										
H10	T20810	0.35–0.45	0.25–0.70	0.80–1.20	3.00–3.75	0.30 max	2.00–3.00	…	0.25–0.75	…
H11	T20811	0.33–0.43	0.20–0.50	0.80–1.20	4.75–5.50	0.30 max	1.10–1.60	…	0.30–0.60	…
H12	T20812	0.30–0.40	0.20–0.50	0.80–1.20	4.75–5.50	0.30 max	1.25–1.75	1.00–1.70	0.50 max	…
H13	T20813	0.32–0.45	0.20–0.50	0.80–1.20	4.75–5.50	0.30 max	1.10–1.75	…	0.80–1.20	…
H14	T20814	0.35–0.45	0.20–0.50	0.80–1.20	4.75–5.50	0.30 max	…	4.00–5.25	…	…
H19	T20819	0.32–0.45	0.20–0.50	0.20–0.50	4.00–4.75	0.30 max	0.30–0.55	3.75–4.50	1.75–2.20	4.00–4.50
Tungsten hot-work steels										
H21	T20821	0.28–0.36	0.15–0.40	0.15–0.50	3.00–3.75	0.30 max	…	8.50–10.00	0.30–0.60	…
H22	T20822	0.30–0.40	0.15–0.40	0.15–0.40	1.75–3.75	0.30 max	…	10.00–11.75	0.25–0.50	…
H23	T20823	0.25–0.35	0.15–0.40	0.15–0.60	11.00–12.75	0.30 max	…	11.00–12.75	0.75–1.25	…

(continued)

(a) All steels except group W contain 0.25 max Cu, 0.30 max P, and 0.03 max S; group W contains 0.20 max Cu, 0.025 max P, and 0.025 max S. Where specified, sulfur may be increased to 0.06 to 0.15% to improve machinability of group A, D, H, M, and T steels. (b) Available in several carbon ranges. (c) Contains free graphite in the microstructure. (d) Optional. (e) Specified carbon ranges are designated by suffix numbers.

Table 1 (continued)

Designation		Composition(a), %								
AISI	UNS	C	Mn	Si	Cr	Ni	Mo	W	V	Co
H24	T20824	0.42–0.53	0.15–0.40	0.15–0.40	2.50–3.50	0.30 max	…	14.00–16.00	0.40–0.60	…
H25	T20825	0.22–0.32	0.15–0.40	0.15–0.40	3.75–4.50	0.30 max	…	14.00–16.00	0.40–0.60	…
H26	T20826	0.45–0.55(b)	0.15–0.40	0.15–0.40	3.75–4.50	0.30 max	…	17.25–19.00	0.75–1.25	…
Molybdenum hot-work steels										
H42	T20842	0.55–0.70(b)	0.15–0.40	…	3.75–4.50	0.30 max	4.50–5.50	5.50–6.75	1.75–2.20	…
Air-hardening, medium-alloy, cold-work steels										
A2	T30102	0.95–1.05	1.00 max	0.50 max	4.75–5.50	0.30 max	0.90–1.40	…	0.15–0.50	…
A3	T30103	1.20–1.30	0.40–0.60	0.50 max	4.75–5.50	0.30 max	0.90–1.40	…	0.80–1.40	…
A4	T30104	0.95–1.05	1.80–2.20	0.50 max	0.90–2.20	0.30 max	0.90–1.40	…	…	…
A6	T30106	0.65–0.75	1.80–2.50	0.50 max	0.90–1.20	0.30 max	0.90–1.40	…	…	…
A7	T30107	2.00–2.85	0.80 max	0.50 max	5.00–5.75	0.30 max	0.90–1.40	0.50–1.50	3.90–5.15	…
A8	T30108	0.50–0.60	0.50 max	0.75–1.10	4.75–5.50	0.30 max	1.15–1.65	1.00–1.50	…	…
A9	T30109	0.45–0.55	0.50 max	0.95–1.15	4.75–5.50	1.25–1.75	1.30–1.80	…	0.80–1.40	…
A10	T30110	1.25–1.50(c)	1.60–2.10	1.00–1.50	…	1.55–2.05	1.25–1.75	…	…	…
High-carbon, high-chromium, cold-work steels										
D2	T30402	1.40–1.60	0.60 max	0.60 max	11.00–13.00	0.30 max	0.70–1.20	…	1.10 max	…
D3	T30403	2.00–2.35	0.60 max	0.60 max	11.00–13.50	0.30 max	…	1.00 max	1.00 max	…
D4	T30404	2.05–2.40	0.60 max	0.60 max	11.00–13.00	0.30 max	0.70–1.20	…	1.00 max	…
D5	T30405	1.40–1.60	0.60 max	0.60 max	11.00–13.00	0.30 max	0.70–1.20	…	1.00 max	2.50–3.50
D7	T30407	2.15–2.50	0.60 max	0.60 max	11.50–13.50	0.30 max	0.70–1.20	…	3.80–4.40	…
Oil-hardening cold-work steels										
O1	T31501	0.85–1.00	1.00–1.40	0.50 max	0.40–0.60	0.30 max	…	0.40–0.60	0.30 max	…
O2	T31502	0.85–0.95	1.40–1.80	0.50 max	0.50 max	0.30 max	0.30 max	…	0.30 max	…
O6	T31506	1.25–1.55(c)	0.30–1.10	0.55–1.50	0.30 max	0.30 max	0.20–0.30	…	…	…
O7	T31507	1.10–1.30	1.00 max	0.60 max	0.35–0.85	0.30 max	0.30 max	1.00–2.00	0.40 max	…
Shock-resisting steels										
S1	T41901	0.40–0.55	0.10–0.40	0.15–1.20	1.00–1.80	0.30 max	0.50 max	1.50–3.00	0.15–0.30	…
S2	T41902	0.40–0.55	0.30–0.50	0.90–1.20	…	0.30 max	0.30–0.60	…	0.50 max	…
S5	T41905	0.50–0.65	0.60–1.00	1.75–2.25	0.50 max	…	0.20–1.35	…	0.35 max	…
S6	T41906	0.40–0.50	1.20–1.50	2.00–2.50	1.20–1.50	…	0.30–0.50	…	0.20–0.40	…
S7	T41907	0.45–0.55	0.20–0.90	0.20–1.00	3.00–3.50	…	1.30–1.80	…	0.20–0.30(d)	…
Low-alloy special-purpose tool steels										
L2	T61202	0.45–1.00(b)	0.10–0.90	0.50 max	0.70–1.20	…	0.25 max	…	0.10–0.30	…
L6	T61206	0.65–0.75	0.25–0.80	0.50 max	0.60–1.20	1.25–2.00	0.50 max	…	0.20–0.30(d)	…
Low-carbon mold steels										
P2	T51602	0.10 max	0.10–0.40	0.10–0.40	0.75–1.25	0.10–0.50	0.15–0.40	…	…	…
P3	T51603	0.10 max	0.20–0.60	0.40 max	0.40–0.75	1.00–1.50	…	…	…	…
P4	T51604	0.12 max	0.20–0.60	0.10–0.40	4.00–5.25	…	0.40–1.00	…	…	…
P5	T51605	0.10 max	0.20–0.60	0.40 max	2.00–2.50	0.35 max	…	…	…	…
P6	T51606	0.05–0.15	0.35–0.70	0.10–0.40	1.25–1.75	3.25–3.75	…	…	…	…
P20	T51620	0.28–0.40	0.60–1.00	0.20–0.80	0.40–2.00	…	0.30–0.55	…	…	…
P21	T51621	0.18–0.22	0.20–0.40	0.20–0.40	0.50 max	3.90–4.25	…	…	0.15–0.25	1.05–1.25A1
Water-hardening tool steels										
W1	T72301	0.70–1.50(e)	0.10–0.40	0.10–0.40	0.15 max	0.20 max	0.10 max	0.15 max	0.10 max	…
W2	T72302	0.85–1.50(e)	0.10–0.40	0.10–0.40	0.15 max	0.20 max	0.10 max	0.15 max	0.15–0.35	…
W3	T72305	1.05–1.15	0.10–0.40	0.10–0.40	0.40–0.60	0.20 max	0.10 max	0.15 max	0.10 max	…

(a) All steels except group W contain 0.25 max Cu, 0.30 max P, and 0.03 max S; group W contains 0.20 max Cu, 0.025 max P, and 0.025 max S. Where specified, sulfur may be increased to 0.06 to 0.15% to improve machinability of group A, D, H, M, and T steels. (b) Available in several carbon ranges. (c) Contains free graphite in the microstructure. (d) Optional. (e) Specified carbon ranges are designated by suffix numbers.

Tool steels are produced to various standards, including several ASTM specifications. The *Steel Products Manual* covering tool steels, which is published by the Iron and Steel Society, Inc. (Ref 1), contains much useful information that essentially represents the normal manufacturing practices of most tool steel producers. Frequently, more stringent chemical and/or metallurgical standards are invoked by the individual producers or consumers to achieve certain commercial goals. Where appropriate, standard specifications for tool steels, ASTM A600, A681, and A686, may be used as a basis for procurement. ASTM A600 sets forth standard requirements for tungsten and molybdenum high-speed steels; A681 applies to hot-work, cold-work, shock-resisting, special-purpose, and mold steels; and A686 covers water-hardening tool steels. In many instances, however, tool steels are purchased by tradename because the user has found that a particular tool steel from a certain producer gives better performance in a specific application than does a tool steel of the same AISI type classification purchased from another source.

Wrought High-Speed Tool Steels

High-speed tool steels are so named primarily because of their ability to machine materials at high cutting speeds. They are complex iron-base alloys of carbon, chromium, vanadium, molybdenum, or tungsten, or combinations thereof, and, in some cases, substantial amounts of cobalt. The carbon and alloy contents are balanced at levels to give high attainable hardening response, high wear resistance, high resistance to the softening effect of heat, and good toughness for effective use in industrial cutting operations.

M and T Classification

There are presently more than 40 classifications of high-speed tool steels, according to the American Iron and Steel Institute (AISI). When these are compounded by the number of domestic manufacturers, the total number of individual steels in the high-speed tool steels category exceeds 150.

The AISI established its own classification system for high-speed tool steels many years ago. It designates with a T those steels that have tungsten as one of their primary alloying elements and with an M those steels that have molybdenum additions as one of their primary alloying elements. A number follows either the M or the T (e.g., M1, M2, M41, T1, T15), but it has no significance other than to distinguish one high-speed tool steel from another. For example, M1 is not more highly alloyed than M2, or more hardenable, or more wear resistant and so on. Table 1 lists composition limits for M and T types.

Effects of Alloying Elements

The T-series contains 12 to 20% W with chromium, vanadium, and cobalt as the other major alloying elements. The M-series contains approximately 3.5 to 10% Mo, with chromium, vanadium, tungsten, and cobalt as the other alloying elements. All types, whether molybdenum or tungsten, contain about 4% Cr; the carbon and vanadium contents vary. As a general rule, when the vanadium content is increased, the carbon content is usually increased (Ref 1).

Type T1 does not contain molybdenum or cobalt. Cobalt-base tungsten types range from T4 through T15 and contain from 5 to 12% Co.

Types M1 through M10 (except M6) contain no cobalt, but most contain some tungsten. The cobalt-base, molybdenum-tungsten, premium types are generally classified in the M30 and M40 series. Super high-speed steels normally range from M40 upward; they are capable of being heat treated to high hardnesses.

Compared to the T-type steels, the M-type steels generally have higher abrasion resistance, are less prone to distortion in heat treatment, and are less expensive (Ref 2). Tools made of high-speed tool steels can also be coated with titanium nitride, titanium carbide, and numerous other coatings by physical vapor deposition for improved performance and increased tool life.

Various elements are added to M- and T-type steels to impart certain properties. These elements and their effects are discussed in the following paragraphs.

Carbon is by far the most important of the elements and is very closely controlled. The carbon content of any one high-speed tool steel is usually fixed within narrow limits, but variations within these limits can cause important changes in the mechanical properties and the cutting ability. As the carbon concentration is increased, the working hardness rises, the elevated temperature hardness rises, and the number of hard, stable, complex carbides rises. The latter contribute much to the wear resistance and other properties of the high-speed tool steels.

Silicon. Up to about 1.00%, the influence of silicon on high-speed tool steels is slight. Increasing the silicon content from 0.15 to 0.45% gives a slight increase in maximum attainable tempered hardness and has some influence on carbide morphology, although there seems to be a concurrent slight decrease in toughness. Some manufacturers produce at least one grade with silicon up to 0.65%, but this level requires a lower maximum austenitizing temperature than a lower silicon level in the same grade, to prevent overheating. In general, the silicon content is kept below 0.45% on most grades.

Manganese concentration is generally not high in high-speed tool steels because of its marked effect in increasing brittleness and the danger of cracking upon quenching.

Phosphorus has no effect on any of the desired properties of high-speed tool steels. However, because of its well-known effect in causing cold shortness, or room-temperature brittleness, the concentration of phosphorus is kept to a minimum.

Chromium is always present in high-speed tool steels in amounts ranging from 3 to 5%. It is mainly responsible for the hardenability. Generally, the addition is 4%, because it appears that this concentration gives the best compromise between hardness and toughness. In addition, chromium reduces oxidation and scaling during heat treatment.

Tungsten. In the high-speed tool steels, tungsten is of vital importance. It is found in all T-type steels and in all but two of the M-type steels. The complex carbide of iron, tungsten, and carbon that is found in high-speed tool steels is very hard and significantly contributes to wear resistance. Tungsten improves hot hardness, causes secondary hardening, and imparts marked resistance to tempering. When the tungsten concentration is lowered in high-speed tool steels, molybdenum is usually added to make up for its loss.

Molybdenum forms the same double carbide with iron and carbon as tungsten does, but it has half the atomic weight of tungsten. As a consequence, molybdenum can be substituted for tungsten on the basis of approximately one part of molybdenum, by weight, for two parts of tungsten.

The melting point of M-type steels is somewhat lower than that of T-type steels, and they thus require a lower hardening temperature and have a narrower hardening range. The M-type steels are tougher than the T-type steels, but the hot hardness is slightly lower. Compensation for this reduced hot hardness is partially accomplished by the addition of tungsten (and, to a lesser extent, vanadium) to the plain molybdenum grades. This is one important reason for the popularity of the tungsten-molybdenum grades, such as M2, M3, and M4: they afford good hot hardness, which is so desirable in high-speed tool steels.

Vanadium was first added to high-speed tool steels as a scavenger to remove slag impurities and to reduce nitrogen levels in the melting operation. It was soon found that this element materially increases the cutting efficiency of tools. The addition of vanadium promotes the formation of very hard, stable carbides, which significantly increase wear resistance and, to a lesser extent, hot hardness. When properly balanced by carbon additions, an increase in vanadium has relatively little effect on the tough-

ness. For this reason, vanadium-bearing grades are a very good choice when very fast cutting operations are demanded, as in finishing cuts, or when the surface of the material is hard and scaly.

Several specially developed steels with high vanadium additions have been developed for very severe service requiring high toughness, as well as exceptional hot hardness and wear resistance. The T15, M4, and M15 grades are in this category; their vanadium contents are 4.88, 4.13, and 5.00%, respectively.

Cobalt. The main effect of cobalt in high-speed tool steels is to increase the hot hardness (Fig. 1 and 2) and thus increase the cutting efficiency when high tool temperatures are attained during the cutting operation. Cobalt raises the heat-treating temperatures because it elevates the melting point. Hardening temperatures for cobalt high-speed tool steels can be 14 to 28 °C (25 to 50 °F) higher than would be normal for similar grades without cobalt. Cobalt additions slightly increase the brittleness of high-speed tool steels.

Cobalt steels are especially effective on rough or hogging cuts, but they are not usually suited to finishing cuts that do not involve high temperatures. They usually perform quite well for operations involving deep cuts and fast speeds, hard and scaly materials, or materials that have discontinuous chips, such as cast iron or nonferrous metals.

Sulfur, in normal concentrations of 0.03% or less, has no effect on the properties of high-speed tool steels. However, sulfur is added to certain high-speed tool steels to contribute free-machining qualities, as it does in low-alloy steels. The consumption of free-machining high-speed tool steels is a small but significant percentage of the total consumption of high-speed tool steels. One of the major applications for free-machining high-speed tool steels is in larger-diameter tools such as hobs, broaches, and so on.

Sulfur forms complex sulfides, containing chromium, vanadium, and manganese, that are distributed throughout the steel as stringer-type inclusions, interrupting the steel structure and acting as notches. These notches aid the metal-removing action of a cutting tool when a high-speed steel is machined, because the resulting chip is discontinuous, a characteristic of free-machining steels. Very high sulfur additions (up to 0.30%) are made to some P/M high-speed tool steels for improved machinability/ grindability by forming globular sulfides rather than stringers. (See the section "P/M High-Speed Tool Steels" in this article.)

Nitrogen is generally present in air-melted high-speed tool steels in amounts varying from approximately 0.02 to 0.03%. The nitrogen content of some high-speed tool steels is deliberately increased to about 0.04 to 0.05%. This addition, when combined with higher-than-usual amounts of silicon, results in a slight increase of maximum attainable tempered hardness and some change in carbide morphology.

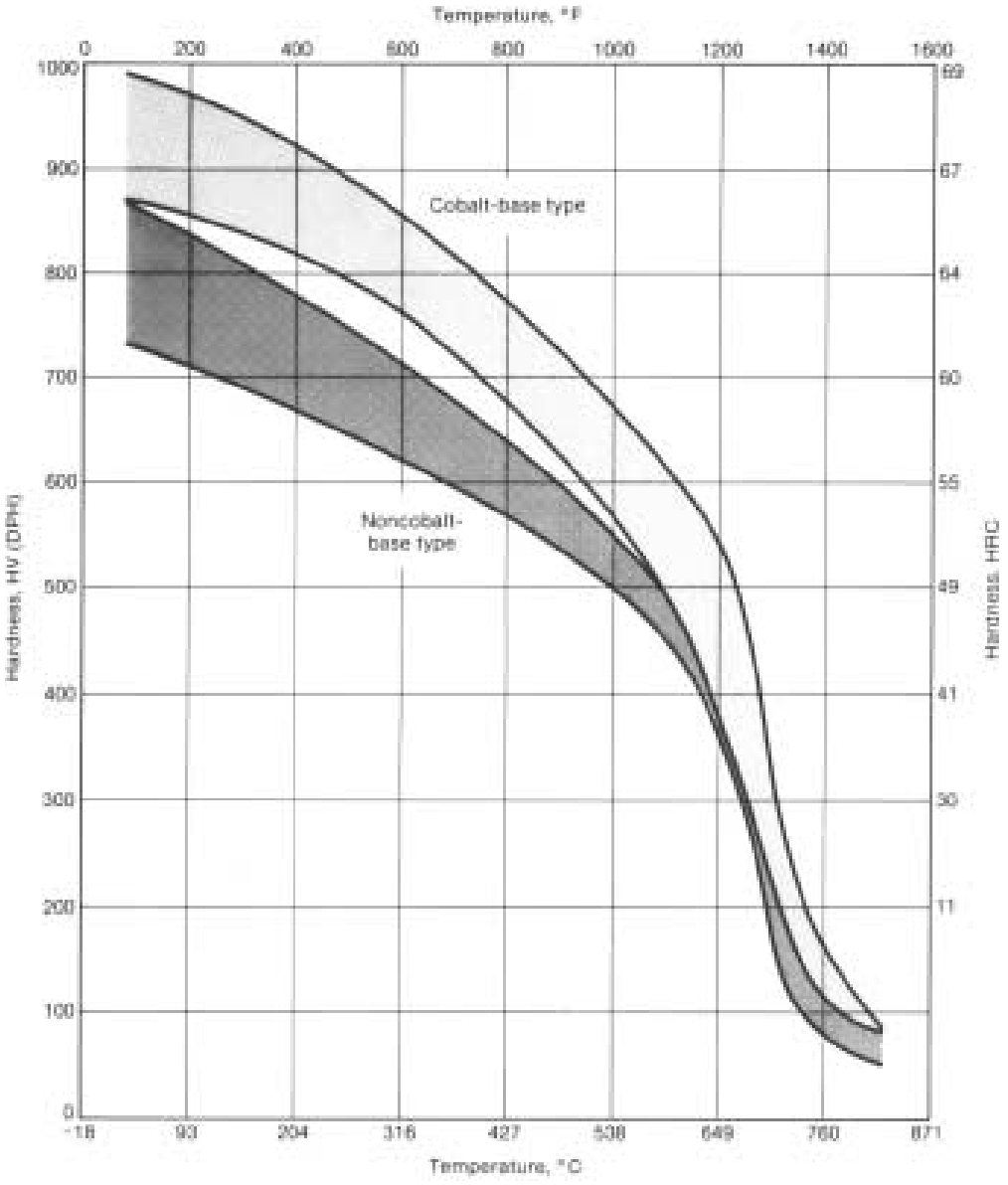


Fig. 1 Comparison of the hot hardness of cobalt-bearing (M4, M33, M36, and T15)vs. that of noncobalt-bearing (M1, M2, M4, M7, and T1) high-speed tool steels

Effects of Alloying and Alloy Carbides on Wear Resistance

Wear resistance of high-speed tool steels is affected by the matrix hardness and composition, precipitated M_2C and MC carbides responsible for secondary hardness, the volume of excess alloy carbides, and the nature of these excess carbides. Table 2 lists the types of carbides, the crystal lattice types, and some characteristics of each of the various carbides found in tool steels. The wear resistance of tool steels increases with increasing carbide volume fraction and carbide hardness.

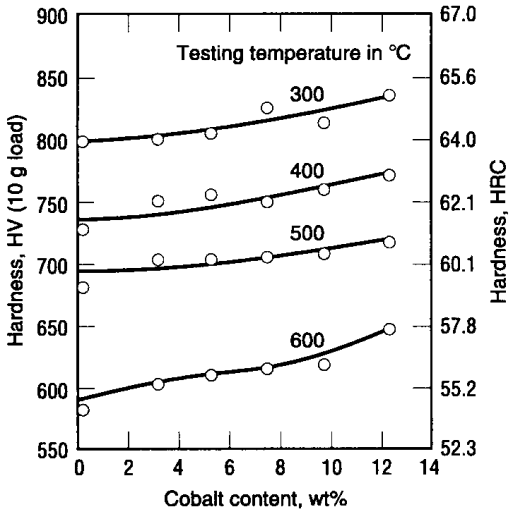


Fig. 2 Effect of cobalt content on the hot hardness of T1 high-speed steel. Initial hardness of 66 HRC at different testing temperatures. Source: Ref 3

Figure 3 is a graphical comparison of the hardness of various alloy carbides relative to the hardness of martensite and cementite (Fe_3C), the carbide typically found in plain carbon and low-alloy carbon steels. As shown, the precipitated metal carbides such as MC and M_2C attain very high hardness, and they contribute significant wear resistance to tool steels that are alloyed to contain large volume fractions of carbides. For example, high-speed tool steels may contain as much as 30 vol% of carbides, consisting of a mixture of MC, $M_{23}C_6$ and M_6C (Ref 6).

In practically any given high-speed tool steels, wear resistance strongly depends on the hardness of the steel. Higher hardness, however achieved, is an aim when highly abrasive cutting conditions will be encountered.

For the ultimate in wear resistance, carbon content can be increased simultaneously with vanadium content, introducing a greater quantity of total carbide and a greater percentage of extremely hard vanadium carbide. Steels T15, M3 (class 2), M4, and M15 are in this category, and all have extremely high wear resistance.

Table 2 Characteristics of alloy carbides found in tool steels

Type of carbide	Lattice type	Remarks
M_3C	Orthorhombic	This is a carbide of the cementite (Fe_3C) type, M, maybe Fe, Mn, Cr with a little W, Mo, V.
M_7C_3	Hexagonal	Mostly found in Cr alloy steels. Resistant to dissolution at higher temperatures. Hard and abrasion resistant. Found as a product of tempering high-speed steels.
$M_{23}C_6$	Face-centered cubic	Present in high-Cr steels and all high-speed steels. The Cr can be replaced with Fe to yield carbides with W and Mo.
M_6C	Face-centered cubic	Is a W- or Mo-rich carbide. May contain moderate amounts of Cr, V, Co. Present in all high-speed steels. Extremely abrasion resistant.
M_2C	Hexagonal	W- or Mo-rich carbide of the W_2C type. Appears after temper. Can dissolve a considerable amount of Cr.
MC	Face-centered cubic	V-rich carbide. Resists dissolution. Small amount that does dissolve reprecipitates on secondary hardening.

Source: Ref 4

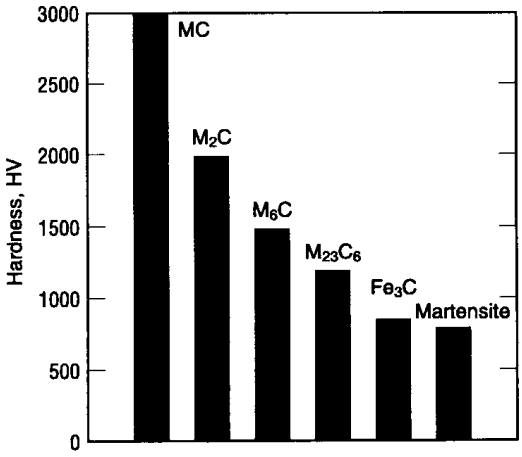


Fig. 3 Relative hardness of alloy carbides, cementite, and martensite in high-speed steels. Source: Ref 5

Wrought Hot-Work Tool Steels

Many manufacturing operations involve punching, shearing, or forming of metals at high temperatures. Hot-work steels (group H) have been developed to withstand the combinations of heat, pressure, and abrasion associated with such operations.

Group H tool steels usually have medium carbon contents (0.35 to 0.45%) and chromium, tungsten, molybdenum, and vanadium contents of 6 to 25%. These steels are divided into three subgroups: chromium hot-work steels (types H10 to H19), tungsten hot-work steels (types H21 to H26), and molybdenum hot-work steels (types H42 and H43). Composition limits for hot-work steels are listed in Table 1.

Effects of Alloying Elements

Chromium hot-work steels (types H10 to H19) have good resistance to heat softening because of their medium chromium content and the addition of carbide-forming elements such as molybdenum, tungsten, and vanadium. The low carbon and low total alloy contents promote toughness at the normal working hardnesses of 40 to 55 HRC. Higher tungsten and molybdenum contents increase hot strength but slightly reduce toughness. Vanadium is added to increase resistance to washing (erosive wear) at high temperatures. An increase in silicon content improves oxidation resistance at temperatures up to 800 °C (1475 °F). The most widely used types in this group are H11, H12, H13, and, to a lesser extent, H19.

Tungsten Hot-Work Steels. The principal alloying elements of tungsten hot-work steels (types H21 to H26) are carbon, tungsten, chromium, and vanadium. The higher alloy contents of these steels make them more

resistant to high-temperature softening and washing than H11 and H13 hot-work steels. However, high alloy content also makes them more prone to brittleness at normal working hardnesses (45 to 55 HRC) and makes it difficult for them to be safely water cooled in service.

Molybdenum Hot-Work Steel. There are only two active molybdenum hot-work steels: type H42 and type H43. These alloys contain molybdenum, chromium, vanadium, carbon, and varying amounts of tungsten. They are similar to tungsten hot-work steels, having almost identical characteristics and uses. Although their compositions resemble those of various molybdenum high-speed steels, they have a low carbon content and greater toughness. The principal advantage of types H42 and H43 over tungsten hot-work steels is their lower initial cost. They are more resistant to heat checking than are tungsten hot-work steels, but in common with all high-molybdenum steels, they require greater care in heat treatment, particularly with regard to decarburization and control of austenitizing temperature.

Wrought Cold-Work Tool Steels

Cold-work tool steels, because they do not have the alloy content necessary to make them resistant to softening at elevated temperature, are restricted in application to those uses that do not involve prolonged or repeated heating above 205 to 260 °C (400 to 500 °F). There are three categories of cold-work steels: air-hardening steels, also called group A; high-carbon, high-chromium steels, also called group D; and oil-hardening steels, also called group O. Composition limits for cold-work steels are listed in Table 1.

Effects of Alloying Elements

Air-hardening, medium-alloy, cold-work steels (group A) contain enough alloying elements to enable them to achieve full hardness in sections up to about 100 mm (4 in.) in diameter upon air cooling from the austenitizing temperature. (Type A6 through-hardens in sections as large as a cube 175 mm, or 7 in., on a side.) Because they are air hardening, group A tool steels exhibit minimum distortion and the highest safety (least tendency to crack) in hardening. Manganese, chromium, and molybdenum are the principal alloying elements used to provide this deep hardening. Types A2, A3, A7, A8, and A9 contain a high percentage of chromium (5%), which provides moderate resistance to softening at elevated temperatures.

Types A4, A6, and A10 are lower in chromium content (1%) and higher in manganese content (2%). They can be hardened from temperatures

about 110 °C (200 °F) lower than those required for the high-chromium types, further reducing distortion and undesirable surface reactions during heat treatment.

To improve toughness, silicon is added to type A8, and both silicon and nickel are added to types A9 and A10. Because of the high carbon and silicon contents of type A10, graphite is formed in the microstructure. As a result, A10 has much better machinability in the annealed condition, and somewhat better resistance to galling and seizing in the fully hardened condition, than other group A tool steels.

Typical applications for group A tool steels include shear knives, punches, blanking and trimming dies, forming dies, and coining dies. The inherent dimensional stability of these steels makes them suitable for gages and precision measuring tools. In addition, the extreme abrasion resistance of type A7 makes it suitable for brick molds, ceramic molds, and other highly abrasive applications.

The complex chromium or chromium-vanadium carbides in group A tool steels enhance the wear resistance provided by the martensitic matrix. Therefore, these steels perform well under abrasive conditions at less than full hardness. Although cooling in still air is adequate for producing full hardness in most tools, massive sections should be hardened by cooling in an air blast or by interrupted quenching in hot oil.

High-carbon, high-chromium, cold-work steels (group D) contain 1.50 to 2.35% C and 12% Cr. With the exception of type D3, they also contain 1% Mo. All group D tool steels except type D3 are air hardening and attain full hardness when cooled in still air. Type D3 is almost always quenched in oil (small parts can be austenitized in vacuum and then gas quenched). Therefore, tools made of D3 are more susceptible to distortion and are more likely to crack during hardening.

Group D steels have high resistance to softening at elevated temperatures. These steels also exhibit excellent resistance to wear, especially type D7, which has the highest carbon and vanadium contents. All group D steels, particularly the higher-carbon types D3, D4, and D7, contain massive amounts of carbides, which make them susceptible to edge brittleness.

Typical applications of group D steels include long-run dies for blanking, forming, thread rolling, and deep drawing; dies for cutting laminations; brick molds; gages; burnishing tools; rolls; and shear and slitter knives.

Oil-hardening cold-work steels (group O) have high carbon contents, plus enough other alloying elements that small-to-moderate sections can attain full hardness when quenched in oil from the austenitizing temperature. Group O tool steels vary in type of alloy, as well as in alloy content, even though they are similar in general characteristics and are used for similar applications. Type O1 contains manganese, chromium, and tungsten. Type O2 is alloyed primarily with manganese. Type O6 contains silicon,

manganese, and molybdenum. It has a high total carbon content that includes free carbon, as well as sufficient combined carbon to enable the steel to achieve maximum as-quenched hardness. Type O7 contains manganese and chromium and has a tungsten content higher than that of type O1.

The most important service-related property of group O steels is high resistance to wear at normal temperatures, a result of high carbon content. On the other hand, group O steels have a low resistance to softening at elevated temperatures.

The ability of group O steels to harden fully upon relatively slow quenching yields lower distortion and greater safety (less tendency to crack) in hardening than is characteristic of the water-hardening tool steels. Tools made from these steels can be successfully repaired or renovated by welding if proper procedures are followed. In addition, graphite in the microstructure of type O6 greatly improves the machinability of annealed stock and helps reduce galling and seizing of fully hardened steel.

Group O steels are used extensively in dies and punches for blanking, trimming, drawing, flanging, and forming. Surface hardnesses of 56 to 62 HRC, obtained through oil quenching followed by tempering at 175 to 315 °C (350 to 600 °F), provide a suitable combination of mechanical properties for most dies made from type O1, O2, or O6. Type O7 has lower hardenability but better general wear resistance than any other group O tool steel, and it is more often used for tools requiring keen cutting edges. Oil-hardening tool steels are also used for machinery components (e.g., cams, bushings, and guides) and for gages, where good dimensional stability and wear resistance properties are needed.

Effects of Alloying on the Characteristics of Other Non-Machining Wrought Tool Steel Grades

In addition to the hot- and cold-work steels described previously, shock-resisting steels, low-alloy special-purpose steels, mold steels, and water-hardening steels are also used for non-machining applications. Table 1 lists composition limits for these steels.

Shock-Resisting Steels. The principal alloying elements in shock-resisting steels, also called group S steels, are manganese, silicon, chromium, tungsten, and molybdenum, in various combinations. Carbon content is about 0.50% for all group S steels, which produces a combination of high strength, high toughness, and low-to-medium wear resistance. Group S steels are used primarily for chisels, rivet sets, punches, driver bits, and other applications requiring high toughness and resistance to shock loading. Types S1 and S7 are also used for hot punching and shearing, which require some heat resistance.

Low-alloy special-purpose steels, also called group L steels, contain small amounts of chromium, vanadium, nickel, and molybdenum. At one time, seven steels were listed in this group, but because of falling demand, only types L2 and L6 remain. Type L2 is available in several carbon contents, from 0.50 to 1.10%. Its principal alloying elements are chromium and vanadium, which make it an oil-hardening steel of fine grain size. Type L6 contains small amounts of chromium and molybdenum, as well as 1.50% Ni for increased toughness. Group L steels are generally used for machine parts, such as arbors, cams, chucks, and collets, and for other special applications requiring good strength and toughness.

Mold steels, also called group P steels, contain chromium and nickel as principal alloying elements. Their low-carbon content facilitates mold impression by cold hubbing. Group P steels are used for low-temperature die casting dies and in molds for the injection of compression molding of plastics.

Water-hardening steels, also called group W steels, contain carbon as the principal alloying element. Small amounts of chromium are added to most of the group W steels to increase hardenability and wear resistance, and small amounts of vanadium are added to maintain fine grain size and thus enhance toughness. Group W tool steels are made with various nominal carbon contents (~0.60 to 1.40%); the most popular grades contain approximately 1.00% C.

Group W steels have low resistance to softening at elevated temperatures. They are suitable for cold heading, striking, coining, and embossing tools; woodworking tools; hard metal-cutting tools, such as taps and reamers; wear-resistant machine tool components; and cutlery.

P/M High-Speed Tool Steels

Powder metallurgy tool steels used in the cutting tool industry are high-speed steel compositions capable of both achieving high room-temperature hardness for wear resistance (at least 64 HRC after heat treatment) and maintaining high hardness when exposed to the frictional heating encountered at the tool/workpiece interface during the cutting operation (commonly referred to as hot hardness or “red hardness”).

Effects of Alloying and Alloy Carbides on Properties

The relative performance of the P/M high-speed steels is strongly influenced by the alloy composition and heat treatment. The principal alloying elements found in varying amounts in high-speed steels are carbon,

tungsten, molybdenum, vanadium, and cobalt. All high-speed steels also contain about 4% Cr to provide good hardenability in larger cross sections during heat treatment. Carbon is necessary for heat treat response, and it combines with the carbide-forming elements to form wear-resistant primary carbides. Tungsten and/or molybdenum are essential alloying elements for developing sufficient temper resistance to enable these materials to perform at high speeds in cutting operations. Both elements form wear-resistant M_6C primary carbides that partially dissolve during heat treatment to provide a strong precipitation or "secondary" hardening response on tempering. In high molybdenum compositions (e.g., containing 9 to 10% Mo), it is also possible to form some M_2C carbides. Recognizing that tungsten and molybdenum can often be used interchangeably for alloying on an atomic basis and that their atomic weights differ by a factor of two, the combined effects of tungsten and molybdenum are often compared by calculating a "tungsten equivalency" (W_{eq}) equal to the tungsten content plus twice the molybdenum content (W + 2 Mo). Vanadium also contributes to secondary hardening during heat treatment, but its main function is to form primary MC carbides for wear resistance. Niobium would be expected to have an effect similar to that of vanadium, but it is not a commonly used alloying element for high-speed steels. Cobalt does not form carbides in tool steels, but significantly contributes to the hot hardness and tempering resistance of the matrix in compositions containing 5 to 8% Co and higher.

Table 3 lists a number of the commonly recognized P/M high-speed steel compositions that are currently produced internationally. The table also includes the calculated W_{eq} and the attainable hardness capability for each alloy. Some of the compositions listed are P/M modifications of traditional high-speed-steel grades (e.g., M3, M4, and T15) that are also produced conventionally. Notably absent from this table are the 1 to 2% V commodity high-speed steels such as M1, M2, M7, and M42. Although several of the latter materials have been periodically produced in P/M form for specialized applications, the general trend in the cutting tool industry has been to take advantage of the grindability and toughness properties resulting from P/M processing to upgrade to higher-performance higher-vanadium alloy compositions. Thus, the base alloy compositions listed are P/M M3 and P/M M4, which are essentially high-carbon and high-vanadium modifications of M2. With the exception of P/M M35 (M2 + 5 Co), the balance of the compositions listed are generally classified as "super-high-speed" steels, which have high attainable hardness capability (66 HRC minimum) and excellent temper resistance for a combination of good wear resistance and high red hardness properties.

The wear resistance of a P/M high-speed steel is determined by the heat treated hardness and by the amount and type (hardness) of primary carbide present in the heat treated microstructure. As discussed earlier, all

Table 3 Nominal compositions of P/M high-speed steels

Tradename(s)	Designation				Composition, wt%					W_{eq}	Hardness, HRC
	AISI	UNS	JIS	Werk. No.	C	W	Mo	V	Co		
Wear-resistant high-speed steels containing 3 to 4% V											
ASP23, APM 23, CPM M3, Micromelt M3, FAX 31, DEX 20, KHA 32	M3	T11323	SKH53	1.3344	1.3	6.25	5	3	…	16.25	65–67
CPM M4, Micromelt M4, Isomatrix S690, HAP M4	M4	T11304	SKH54	…	1.4	5.75	5	4	…	15.75	65–67
Heat-resistant and super-high-speed steels containing 5 to 12% Co and 2 to 6.5% V											
CPM M35	M35	…	SKH 55	1.3243	1	6	5	2	5	16	65–67
CPM Rex 54	…	…	…	…	1.5	5.75	5	4	5	15.75	66–68
ASP30, APM30, CPM Rex 45, Micromelt HS 30, Isomatrix S790, FAX 38, DEX 40, HAP 40, KHA 30	…	…	…	…	1.3	6.25	5	3	8	16.25	66–68
CPM T15, Micromelt T15, FAX 55, DEX 61, HAPT15, KHA 50	T15	T12015	SKH10	1.3202	1.6	12	…	5	5	12	66–68
CPM Rex 76, Micromelt HS 76	M48	T11348	…	…	1.5	10	5.25	3	8.5	20.5	67–69
HAP 50, DEX 62	…	…	…	…	1.5	8	6	4	8	20	67–69
Isomatrix S390	…	…	…	…	1.6	11	2	5	8	15	66–68
ASP60, APM60, KHA 60	…	…	…	1.3241	2.3	6.5	7	6.5	10.5	20.5	67–69
DEX 80	…	…	…	…	2.1	14	6	5.5	12	26	68–70
HAP 70	…	…	…	…	2.2	12	9	5	12	30	69–71
Cobalt-free super-high-speed steels											
CPM Rex 20	M62	T11362	…	…	1.3	6.25	10.5	2	…	27.25	66–68
CPM Rex 25	M61	T11361	…	…	1.8	12.5	6.5	5	…	25.5	67–69

Note: All of the P/M high-speed steels contain about 4% Cr for hardenability in large sections. Silicon, manganese, and sulfur contents are typically 0.50%, 0.30%, and 0.03% maximum, respectively. For select applications requiring improved machinability, sulfur contents are increased to 0.10 or 0.22% with corresponding increases in the manganese contents.

of the P/M high-speed steels contain significant amounts of tungsten and/or molybdenum as well as vanadium, which combine with carbon to form tungsten or molybdenum-rich M_6C (occasionally some M_2C) and vanadium-rich MC primary carbides, respectively. The approximate microhardnesses of these complex carbides, as well as the chromium-rich M_7C_3-type primary carbide found in some cold-work die steels, which are discussed later, are given in Table 4. It follows that for a given heat treated hardness and a similar total primary carbide volume fraction, a high-speed steel with a higher percentage of the harder vanadium-rich (or niobium-rich) MC carbide exhibits better wear resistance. It is therefore very often possible to rank the P/M high-speed steels in Table 3 in order of increasing wear resistance by simply looking at the relative vanadium contents. Thus, the P/M high speed steels with 4% V generally outwear P/M or con-

Table 4 Microhardness of primary carbides in P/M tool steels

Carbide type	Knoop hardness
M(V,Nb)C	2200–2800
$M(W,Mo)_6C$	1550–1750
$M(Cr)_7C_3$	1300–1600

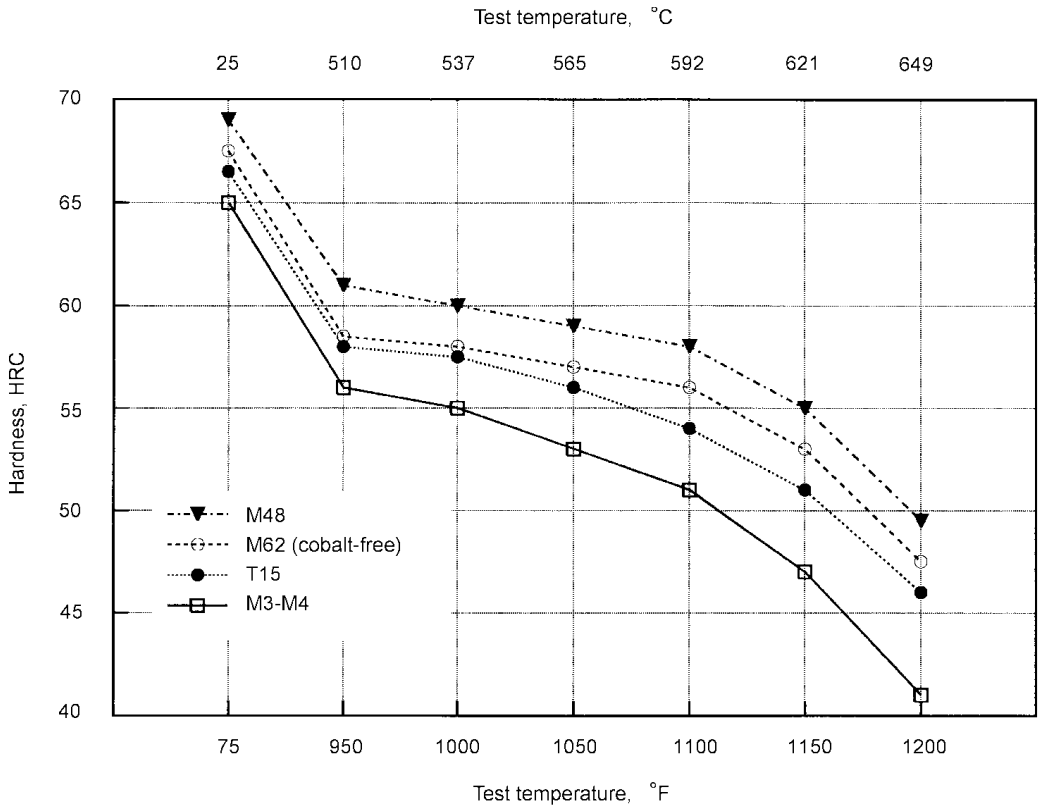


Fig. 4 Hot hardness of P/M high-speed steels

ventional high-speed steels with 2 to 3% V, and steels with 5 to 6% V generally outwear the materials with 4% V. Exceptions to this vanadium content "rule of thumb" are special cases where the alloying results in a significant increase in the total volume fraction of primary carbides as well as the attainable hardness capability. An example of the latter is P/M M48 (1.5C-10W-5Mo-3V-8.5Co), which contains about 33% total alloy content. This material is capable of attaining 67 to 69 HRC and also has a significantly greater volume fraction of primary carbides than the lower alloyed P/M M3, P/M M4, and P/M M3 + 8Co grades. Other exceptions to this rule are the cobalt-free P/M super high-speed steels, which by design also have significantly increased volume fractions of the M_6C primary carbide compared to the cobalt-bearing materials they were designed to replace. These materials are discussed in a later section.

The red hardness characteristic of a high-speed steel is dependent on the effect of alloying on the initial attainable hardness as well as on resistance to softening as the tempering or exposure temperature is increased. A measure of the relative red hardness capability is laboratory hot hardness, which is shown in Fig. 4 for a number of the P/M high-speed steels. Note that the materials that exhibit higher initial attainable hardness also exhibit higher hot hardness as the testing temperature is increased. These same materials also exhibit greater resistance to tempering during heat treatment.

Cobalt-Free High-Speed Steels. A unique class of materials are the cobalt-free P/M super-high-speed steels that were first developed by the Crucible Materials Corporation in the late 1970s in direct response to a serious curtailment in the worldwide availability of cobalt raw materials. P/M M61 (1.8C-12.5W-6.5Mo-5V) and P/M M62 (1.3C-6.25W-10.5Mo-2V) were simultaneously designed as cobalt-free substitutes for T15 (1.5C-12W-5V-5Co) and M42 (1.1C-1.5W-9.5Mo-1V-8Co), which have historically been two of the more important cobalt-bearing cutting tool materials used in the aerospace industry and elsewhere. Replacing the solid-solution effects of cobalt on heat treating response and elevated-temperature properties was accomplished primarily by alloying with tungsten and/or molybdenum to form a significantly greater number of alloy carbides in the annealed microstructure, which partially dissolve during austenitizing for heat treatment to provide a strong secondary or precipitation hardening response on tempering. Thus, the P/M M61 composition with a W_{eq} = 25.5 and no cobalt has heat treat response and temper-resistance characteristics comparable to T15 with 5% Co, and also better wear resistance due to a greater volume fraction of primary carbides in the heat treated microstructure. Similarly, the P/M M62 composition with a W_{eq} = 27.25 and no cobalt has about the same attainable hardness, somewhat better temper resistance, and significantly better wear resistance compared to M42 with 8% Co. These highly alloyed cobalt-free compositions could not be economically produced or fabricated into tools without the benefits of P/M processing.

Property Comparisons. The relative effects of attainable hardness, vanadium carbide content, and total alloying on the properties of the P/M high-speed steels are summarized in the qualitative comparison chart shown in Fig. 5. As illustrated in the graph, red hardness increases as the total alloy content and corresponding attainable hardness capability increase. Wear resistance also generally increases with total alloy content and attainable hardness, but the most wear-resistant materials in each classification of high-speed steels are the higher vanadium compositions, for example, P/M M4 and P/M T15. The graph also shows that as the alloy content increases, the relative toughness decreases. The generally improved toughness of the P/M materials compared to conventionally produced high-speed steels often enables upgrading without serious concerns about the actual toughness in service.

P/M Cold-Work Tool Steels

Effects of Alloying and Alloy Carbides. Several of the international tool steel producers have also taken advantage of P/M processing to develop new cold-work tooling materials alloyed primarily with high vanadium to maximize wear resistance. The first such material designed specifical-

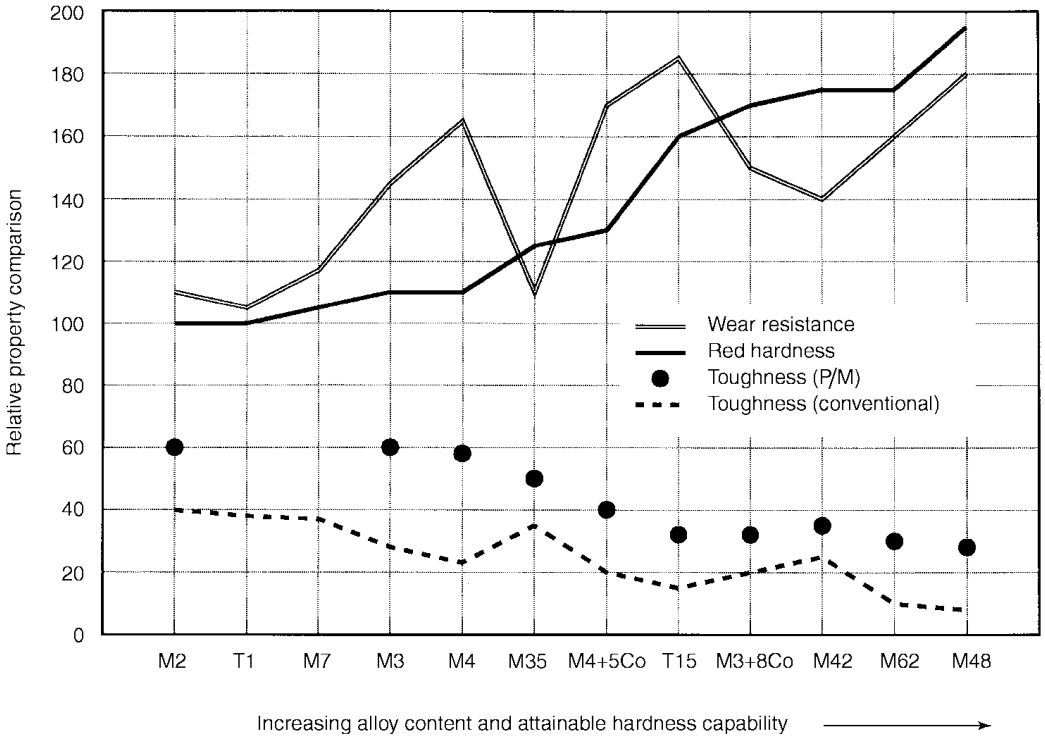


Fig. 5 Graphical comparison of high-speed steel properties

ly for high-performance wear applications was Crucible particle metallurgy CPM 10V (hereafter referred to as P/M 10V), which was introduced commercially in 1978. Also developed at about the same time was a lower-matrix carbon and slightly lower vanadium modification of P/M 10V, called CPM 9V (hereafter referred to as P/M 9V), which has lower attainable hardness but better toughness than P/M 10V and can also be used in warm-working applications requiring resistance to heat checking. More recent P/M tool steel development work has focused on the following: (a) even more wear-resistant ultrahigh vanadium compositions containing 15 to 18% V with up to 30% by volume of primary MC-type carbides, (b) low-to-intermediate carbide volume fraction materials moderately alloyed with vanadium and chromium to optimize the toughness properties while still maintaining good wear resistance, and (c) high-vanadium high-chromium compositions for wear applications that also require good corrosion resistance. The wear/corrosion-resistant P/M tool steels are discussed in a later section.

Table 5 lists the nominal compositions for several of the commercially available P/M cold-work tool steels as well as the P/M M4 high-speed steel discussed previously. Also included are the compositions of conventionally produced A2, D2, and D7 cold-work tool steels. With the exception of P/M 9V, all of the tool steels listed in the table are capable of attaining 58 to 62 HRC during heat treatment, which is the typical application hardness range for cold-work tooling.

Table 5 Nominal compositions of P/M cold-work tool steels

Steel	AISI designation	Commercial equivalent	Composition, wt%				
			C	Cr	Mo	W	V
P/M cold-work tool steels							
P/M 3V	…	CPM 3V	0.80	7.50	1.00	…	2.75
P/M M4	M4	CPM M4HC	1.40	4.00	5.25	5.75	4.00
P/M 8Cr4V	…	Vanadis 4	1.50	8.00	1.00	…	4.00
P/M 12Cr4V	D2	K190 P/M	2.30	12.00	1.00	…	4.00
P/M 9V	…	CPM 9V	1.80	5.25	1.30	…	9.00
P/M 10V	A11	CPM 10V	2.45	5.25	1.30	…	9.75
P/M 8Cr10V	…	Vanadis 10	2.90	8.00	1.50	…	9.80
P/M 15V	…	CPM 15V	3.50	5.25	1.30	…	14.50
P/M 18V	…	CPM 18V	3.90	5.25	1.30	…	17.50
Conventionally produced (ingot-cast) cold-work tool steels							
A2	A2	…	1.00	5.25	1.15	…	0.30
D2	D2	…	1.55	11.50	0.80	…	0.90
D7	D7	…	2.35	12.00	1.00	…	4.00

For a given hardness, the relative wear resistance of both the P/M and conventional cold-work tool steels is a function of the amount and type (hardness) of primary carbide present in the heat treated microstructure. Carbide size is only a factor under abrasive wear conditions and generally only applies to conventionally produced tool steels that have inherently coarser carbide size compared to the P/M tool steels. Table 6 shows the results of SEM and image analysis of the primary carbides observed in heat treated samples of the alloys listed in Table 5. The total volume percent of primary carbides ranges from approximately 5% in P/M 3V to

Table 6 SEM image analysis of the primary carbides in P/M cold-work tool steels

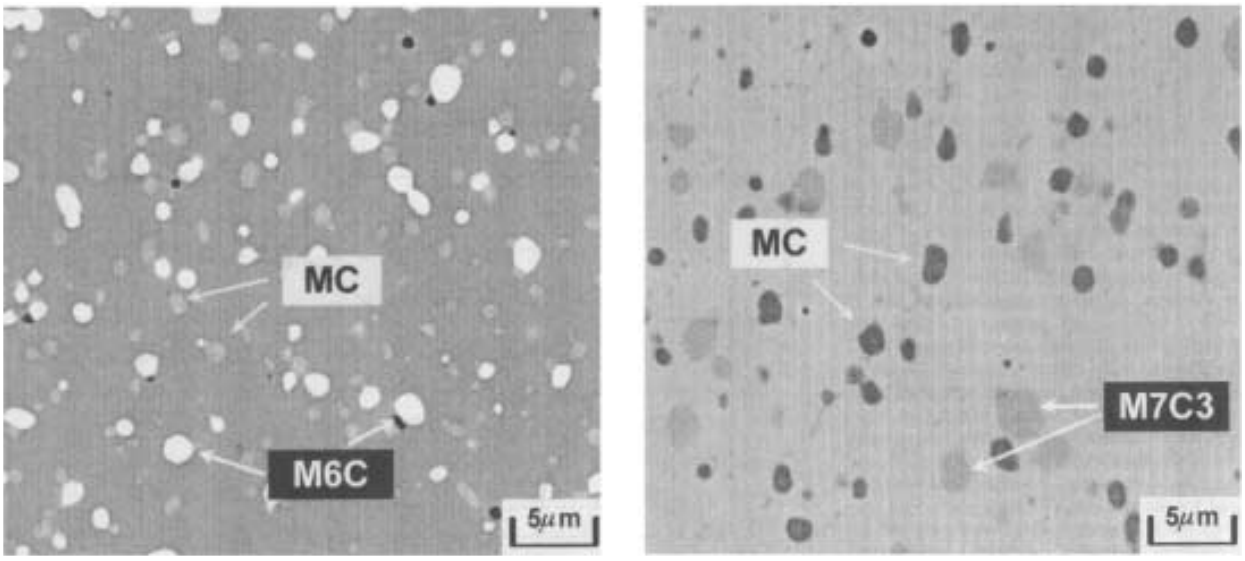
Steel	Heat treatment	Hardness, HRC	Carbide content, vol%			
			MC	M_7C_3	M_6C	Total
P/M cold-work tool steels						
P/M 3V	1121 °C (2050 °F)/30 min + air cool + 524 °C (975 °F) temper (3 × 2h)	60	4.7	0.4	…	5.1
P/M M4	1163 °C (2125 °F)/4 min + oil quench + 565 °C (1050 °F) temper (3 × 2h)	62	3.8	…	8.8	12.6
P/M 8Cr4V	1021 °C (1870 °F)/30 min + air cool + 524 °C (975 °F) temper (2 × 2h)	60	6.6	5.7	…	12.3
P/M 12Cr4V	1121 °C (2050 °F)/30 min + oil quench + 260 °C (500 °F) temper (2 × 2h)	59	3	20	…	23
P/M 9V	1121 °C (2050 °F)/30 min + air cool + 565 °C (1050 °F) temper (2 × h)	54	14.4	…	…	14.4
P/M 10V	1121 °C (2050 °F)/30 min + oil quench + 552 °C (1025 °F) temper (2 × 2h)	61	17.4	…	…	17.4
P/M 8Cr10V	1060 °C (1940 °F)/30 min + air cool + 552 °C (1025 °F) temper (2 × 2h)	60	13	14	…	27
P/M 15V	1177 °C (2150 °F)/10 min + oil quench + 552 °C (1025 °F) temper (3 × 2h)	62	22.7	…	…	22.7
P/M 18V	1121 °C (2050 °F)/30 min + oil quench + 552 °C (1025 °F) temper (2 × 2h)	62	30.5	…	…	30.5
Conventionally ingot cast cold-work tool steels						
A1	Not reported	60	…	6	…	6
D2	Not reported	61	…	15.5	…	15.5
D7	Not reported	61	3	21	…	24

30% in P/M 18V. The relative percentages of the primary carbide types present (MC, M_6C, M_7C_3) vary according to the alloying balance, with only P/M 3V, P/M 9V, P/M 10V, P/M 15V, and P/M 18V having essentially all MC carbides. Although P/M M4 and P/M 8Cr4V have similar vanadium contents and total carbide volumes (about 12.5%), about two-thirds of the carbides in P/M M4 are M_6C and about half the carbides in P/M 8Cr4V are M_7C_3-type. These microstructural differences are illustrated in the photomicrographs in Fig. 6, where it can be seen that the various carbide types exhibit characteristically different electronic imaging in the SEM. Figure 7 shows a similar SEM metallographic comparison between P/M 12Cr4V and P/M 15V both of which contain about 23% total primary carbide volume. Whereas P/M 15V contains all vanadium-rich MC-type carbides, P/M 12Cr4V has predominantly M_7C_3-type due to the high chromium content. Table 6 also lists the approximate total primary carbide volumes for conventionally produced A2, D2, and D7. With less than 1% V, A2 and D2 tool steels contain predominantly M_7C_3-type primary carbides. Conventional D7 has essentially the same alloy composition as P/M 12Cr4V and very similar carbide volumes as determined by SEM analysis. More detailed information on the influence of carbide content and total primary carbide volume on the wear resistance of P/M cold-work tool steels can be found in Ref 7.

P/M Wear/Corrosion-Resistant Tool Steels

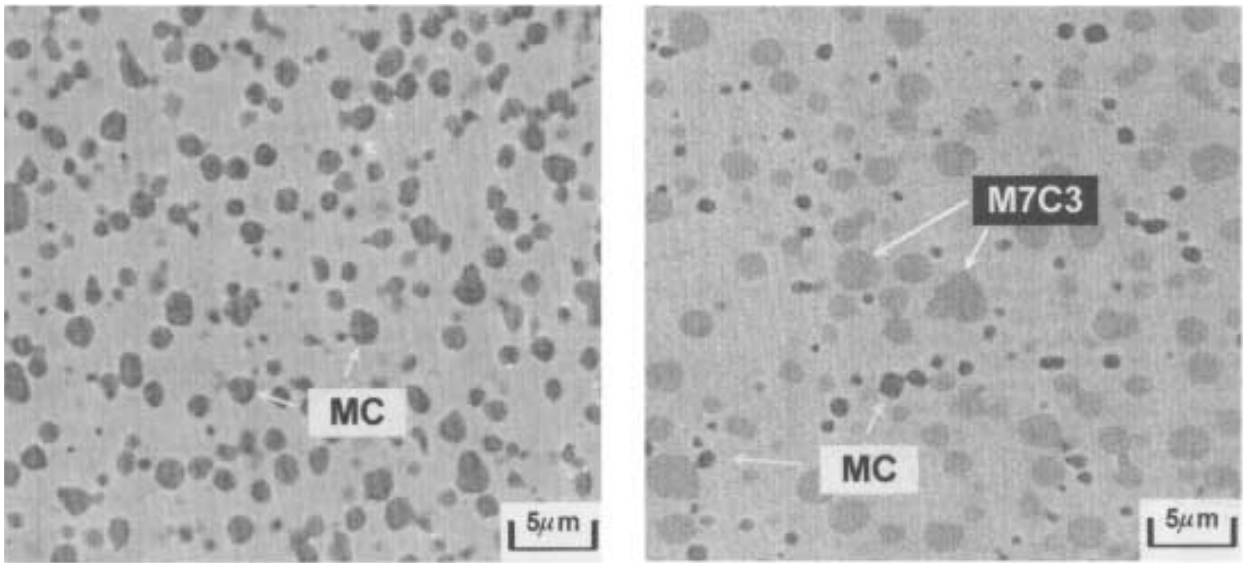
Effects of Alloying and Alloy Carbides. A number of high-performance wear/corrosion-resistant P/M tool steels have been developed containing the following: (a) significant amounts of vanadium and chromium to form wear-resistant primary carbides, (b) a minimum of 11% matrix Cr after heat treatment to provide increased corrosion resistance compared to the P/M tool steels containing 5 to 8% total Cr, and (c) an optimal level of carbon and/or nitrogen to form the wear-resistant carbides and to achieve a minimum of 56 to 58 HRC after heat treatment without forming excessive amounts of retained austenite or precipitating additional chromium-rich carbides, which would lower the desired matrix chromium. These materials usually also contain a minimum of 1% Mo to improve hardenability and resistance to pitting corrosion.

Table 7 lists the nominal compositions of several commercially available P/M wear/corrosion-resistant tool steel grades along with the compositions of conventionally produced T440C stainless steel and D2 tool steel. As shown, the P/M wear/corrosion-resistant materials have total chromium contents ranging from about 14 to 24%, vanadium contents ranging from about 3 to 15%, molybdenum contents ranging from about



(a) (b)

Fig. 6 Primary carbides in (a) heat treated P/M M4 and (b) P/M 8Cr4V wear-resistant tool steels containing approximately 12.5% total carbide volume



(a) (b)

Fig. 7 Primary carbides in (a) heat treated P/M 15V and (b) P/M 12Cr4V wear-resistant tool steels containing approximately 23% total carbide volume

Table 7 Nominal compositions of wear/corrosion-resistant tool steels

Steel	Commercial equivalent	Composition, wt %				
		C	Cr	V	Mo	Other
P/M steels						
P/M 14Cr-9V	CPM 420V (9V)	2.30	14	9	1	…
P/M 14Cr-12V	CPM 420V (12V)	2.85	14	12	1	…
P/M 14Cr-15V	CPM 420V (15V)	3.25	14	14.5	1	…
P/M 17Cr-6V	CPM 440VM	1.90	17	6	1	…
P/M 17Cr-3V	Elmax P/M	1.70	17	3	1	…
P/M 20Cr-4V	Isomatrix M390	1.90	20	4	1	0.60%W
P/M 24Cr-9V	Supracor	3.75	24	9	3	…
Conventional steel						
T440C	…	1.05	17	…	0.5	…
D2	…	1.55	11.5	0.8	…	…

1 to 3%, and carbon contents ranging from about 1.7 to 3.75%. The relative wear and corrosion resistance of these materials is strongly influenced by the partitioning of the alloying elements between the matrix and the primary carbides during solidification from the melt, by the volume fraction of primary carbides, and by heat treatment (Ref 7).

REFERENCES

1. *Steel Products Manual: Tool Steels,* Iron and Steel Society, April 1988
2. S. Kalpakjian, *Manufacturing Processes for Engineering Materials,* Addison-Wesley, 1984, p 524
3. G. Hoyle, *High Speed Steels,* Butterworths, 1988, p 152
4. R. Wilson, *Metallurgy and Heat Treatment of Tool Steels,* McGraw-Hill, London, 1975
5. H. Brandis, E. Haberling, and H.H. Weigard, Metallurgical Aspects of Carbides in High Speed Steels, *Processing and Properties of High Speed Tool Steels,* M.G.H. Wells and L.W. Lherbier, Ed., TMS-AIME, 1980, p 1–18
6. G.A. Roberts and R.A. Cary, *Tool Steels,* 4th ed., American Society for Metals, 1980
7. R.B. Dixon, W. Stasko, and K.E. Pinnow, Particle Metallurgy Tool Steels, *Powder Metal Technologies and Applications,* Vol 7, *ASM Handbook,* ASM International, 1998, p 786–802

SELECTED REFERENCES

- *ASM Specialty Handbook: Tool Materials,* J.R. Davis, Ed., ASM International, 1995
- G. Roberts, G. Krauss, and R. Kennedy, *Tool Steels,* 5th ed., ASM International, 1998

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Maraging Steels

Introduction and Overview

Maraging steels comprise a special class of high-strength steels that differ from conventional steels in that they are hardened by a metallurgical reaction that does not involve carbon. Instead, these steels are strengthened by the precipitation of intermetallic compounds at temperatures of about 480 °C (900 °F). The term maraging is derived from martensite age hardening and denotes the age hardening of a low-carbon, iron-nickel lath martensite matrix.

Commercial maraging steels are designed to provide specific levels of yield strength from 1030 to 2420 MPa (150 to 350 ksi). Some experimental maraging steels have yield strengths as high as 3450 MPa (500 ksi). These steels typically have very high nickel, cobalt, and molybdenum contents and very low carbon contents. Carbon, in fact, is an impurity in these steels and is kept as low as commercially feasible in order to minimize the formation of titanium carbide (TiC), which can adversely affect strength, ductility, and toughness. Other varieties of maraging steel have been developed for special applications. Maraging steels are commercially produced by various steel companies in the United States and abroad.

General Characteristics. The absence of carbon and the use of intermetallic precipitation to achieve hardening produce several unique characteristics that set maraging steels apart from conventional steels. Hardenability is of no concern. The low-carbon martensite formed after annealing is relatively soft—about 30 to 35 HRC. During age hardening, there are only very slight dimensional changes. Therefore, fairly intricate shapes can be machined in the soft condition and then hardened with a minimum of distortion. Weldability is excellent. Fracture toughness is considerably better than that of conventional high-strength steels (Fig. 1).

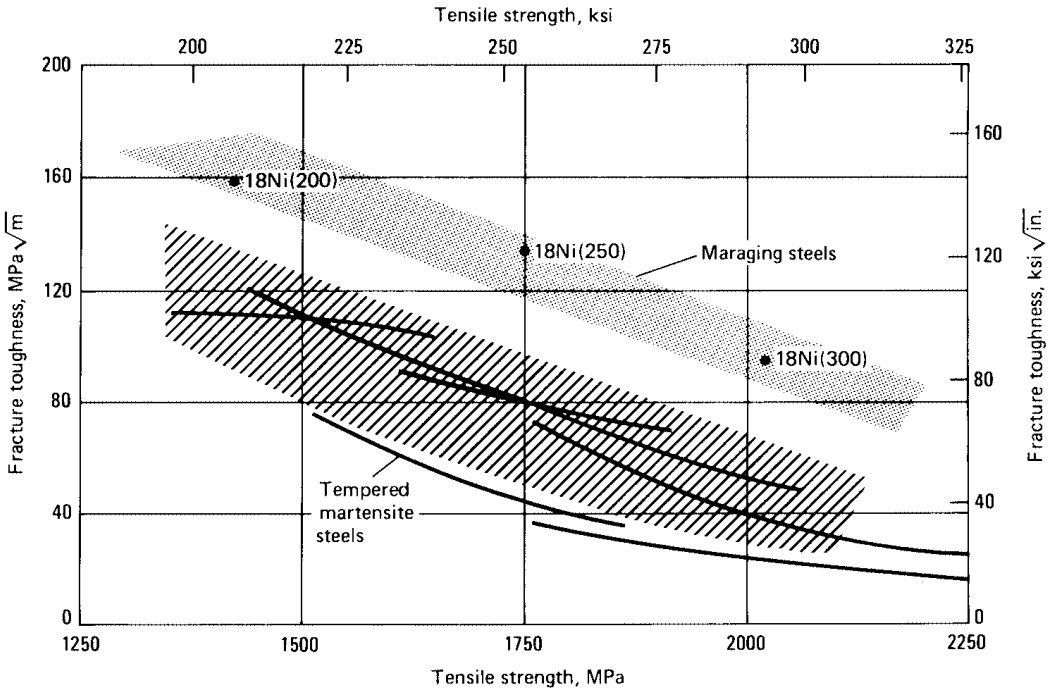


Fig. 1 Plane-strain fracture toughness of maraging steels compared with fracture toughness of several ultrahigh strength steels as a function of tensile strength.

Applications. Maraging steels have been used extensively in two general types of applications:

- Aircraft and aerospace applications, in which the superior mechanical properties and weldability of maraging steels are the most important characteristics
- Tooling applications, in which the excellent mechanical properties and superior fabricability (in particular, the lack of distortion during age hardening) are important

Commercial Alloys

Table 1 lists the chemical compositions of the more common grades of maraging steel. The nomenclature that has become established for these steels is nominal yield strength (ksi units) in parentheses. Thus, for example, 18Ni(200) steel is normally age hardened to a yield strength of 1380 MPa (200 ksi). The first three steels in Table 1—18Ni(200), 18Ni(250), and 18Ni(300)—are the most widely used and most commonly available grades. The 18Ni(350) grade is an ultrahigh-strength variety made in limited quantities for special applications. Two 18Ni(350) compositions have been produced (see the footnote in Table 1). The 18Ni(Cast) grade was developed specifically as a cast composition.

Table 1 Nominal compositions of commercial maraging steels

Grade	Composition, %(a)					
	Ni	Mo	Co	Ti	Al	Nb
Standard grades						
18Ni(200)	18	3.3	8.5	0.2	0.1	…
18Ni(250)	18	5.0	8.5	0.4	0.1	…
Low-cobalt 18Ni(250)	18.5	2.6	2.0	1.2	0.1	0.1
18Ni(300)	18	5.0	9.0	0.7	0.1	…
18Ni(350)	18	4.2(b)	12.5	1.6	0.1	…
18Ni(Cast)	17	4.6	10.0	0.3	0.1	…
12-5-3(180)(c)	12	3	…	0.2	0.3	…

(a) All grades contain no more than 0.03% C. (b) Some producers use a combination of 4.8% Mo and 1.4% Ti, nominal. (c) Contains 5% Cr

Special varieties of maraging steels have been developed, including stainless grades, other cast grades, grades of other strength levels, low-cobalt or cobalt-free grades, a grade especially suited for heavy sections, and a grade with superior magnetic characteristics. Some of these steels have been made and used commercially, but only in limited amounts for specific applications.

Effects of Alloying Elements on Physical Metallurgy

Maraging steels can be considered highly alloyed low-carbon, iron-nickel lath martensites. These alloys also contain small but significant amounts of titanium (Table 1). The phase transformations in these steels can be explained with the help of the two phase diagrams shown in Fig. 2, which depict the iron-rich end of the iron-nickel binary system. Figure 2(a) is the metastable diagram plotting the austenite-to-martensite transformation upon cooling and the martensite-to-austenite reversion upon heating. Figure 2(b) is the equilibrium diagram showing that at higher nickel contents the equilibrium phases at low temperatures are austenite and ferrite.

The metastable diagram indicates the typical behavior of these steels during cooling from the austenitizing or solution annealing temperature. No phase transformations occur until the M_s temperature, the temperature at which martensite starts to transform from austenite, is reached. Even very slow cooling of heavy sections produces a fully martensitic structure, so there is no lack of hardenability in these alloys.

Alloying Effects on the M_s Temperature. Alloying elements alter the M_s temperature significantly, but do not alter the characteristic that transformation is independent of cooling rate. In addition to nickel, the other alloy elements present in maraging steels generally lower the martensite transformation range, with the exception of cobalt, which raises it. One of the roles of cobalt in maraging steels is to raise the M_s temperature so that greater amounts of other alloying elements (that is, titanium and molybdenum,

which lower the M_s temperature) can be added while still allowing complete transformation to martensite before the steel cools to room temperature.

Most grades of maraging steel have M_s temperatures of the order of 200 to 300 °C (390 to 570 °F) and are fully martensitic at room temperature. Therefore, retained austenite is generally not a problem in these alloys, and as a result, refrigeration treatments are not needed prior to aging. The martensite is normally a low-carbon, body-centered cubic (bcc) lath martensite containing a high dislocation density but no twinning. This martensite is relatively soft (~30 HRC), ductile, and machinable.

Alloying Effects on Age Hardening. Age hardening in maraging steels results primarily from the precipitation of intermetallic compounds. Precipitation takes place preferentially on dislocations and within the lath martensite to produce a fine uniform distribution of coherent particles. The major hardener is molybdenum, which upon aging initially forms Ni_3Mo, with an orthorhombic Cu_3Ti-type structure. The metastable Ni_3Mo phase forms initially because of its better lattice fit with the bcc martensitic matrix. Growth of the Ni_3Mo is restricted by coherency strains, and as such, further aging results in the in situ transformation of Ni_3Mo to the equilibrium Fe_2Mo phase, which has a hexagonal *C*14-type structure. Titanium, which is generally present in maraging steels, promotes additional age hardening through the precipitation of Ni_3Ti, which has a $D0_{24}$ ordered hexagonal structure.

Cobalt does not directly participate in the age-hardening reaction, because this element does not form a precipitate with iron, nickel, molybdenum, or titanium in the 18Ni maraging alloy system. The main contribution of cobalt is to lower the solubility of molybdenum in the martensitic matrix and thus increase the amount of Ni_3Mo precipitate

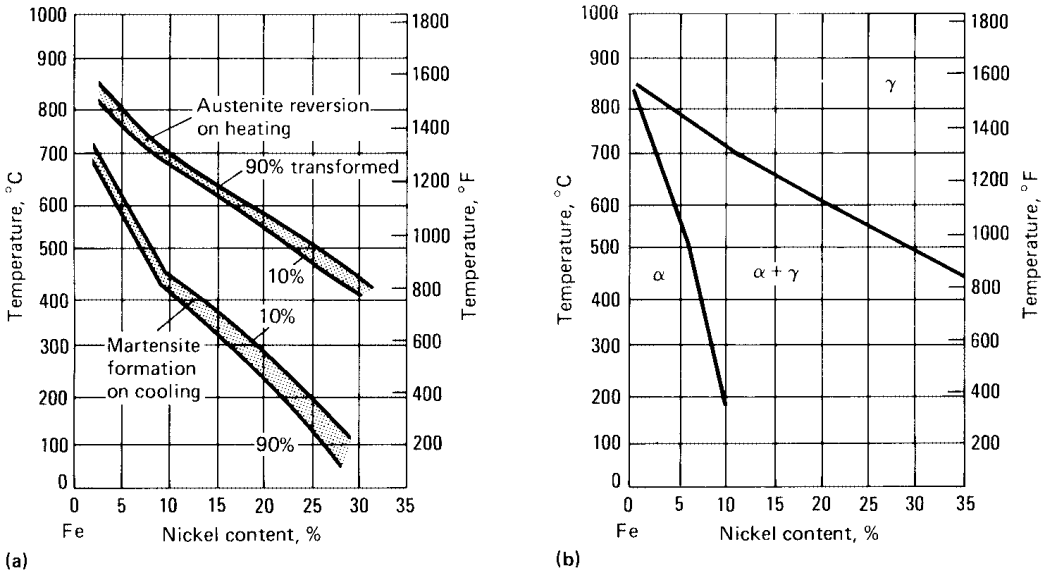


Fig. 2 Phase relationships in the iron-nickel system. (a) Metastable. (b) Equilibrium.

formed during age hardening. Some hardening also results from a short-range ordering reaction in the matrix that involves cobalt.

Molybdenum also plays the necessary supplemental role of minimizing localized grain-boundary precipitation by lowering the diffusion coefficients of a number of elements in solid solution. Precipitation of these grain-boundary phases severely impairs the toughness of most molybdenum-free ferrous alloys. Discrete particles of austenite are also present on the grain and subgrain boundaries in molybdenum-free 18Ni(300). It has been theorized that the precipitation of these discrete particles of austenite at the grain and subgrain boundaries results in a nickel-depleted zone, which adversely affects the toughness and ductility of the molybdenum-free 18Ni(300) alloy on a localized scale.

The precipitate particles are of a lattice size comparable to that of the martensite matrix and cause little distortion of the matrix. This characteristic, together with the absence of carbon, allows the steel to be age hardened to very high strength levels while minimizing changes in the shape of the part being hardened.

Effects of Alloying on Properties

The mechanical properties of 18Ni(250), cobalt-free 18Ni(250), and low-cobalt-bearing 18Ni(250) are compared in Table 2. These data show that all three alloys exhibit comparable strength when aged at 480 °C (900 °F) for 5 h. However, these data also show that, in general, the cobalt-free 18Ni(250) material displays reduced localized ductility as measured by the percentage of reduction in area, and reduced plane-strain fracture toughness compared to the standard 18Ni(250) and low-cobalt-bearing 18Ni(250) alloys. The reduced ductility and toughness of the cobalt-free 18Ni(250) alloy is related to the absence of cobalt in this material. The lack of cobalt eliminates the previously discussed cobalt/molybdenum interaction and thus necessitates a higher level of titanium, which is a

Table 2 Comparison of the longitudinal, room-temperature mechanical properties of standard, cobalt-free, and low-cobalt-bearing 18Ni(250) maraging steels

Heat treatment: solution heat 1 h at 815 °C (1500 °F), then age 5 h at 480 °C (900 °F). Testing was conducted on 63.5 × 88.9 mm (2.5 × 3.5 in.) billets produced from 200 mm (8 in.) diam vacuum induction melted/vacuum arc remelted ingots.

Grade	Ultimate tensile strength		0.2% offset yield strength		Elongation in 25 mm (1 in.), %	Reduction in area, %	Charpy V-notch impact toughness(a)		Plane-strain fracture toughness(a)	
	MPa	ksi	MPa	ksi			J	ft · lbf	MPa $\sqrt{m}$	ksi $\sqrt{in.}$
18Ni(250)	1870	271	1825	265	12	64.5	37	27	138	125
Cobalt-free 18Ni(250)	1895	275	1825	265	11.5	58.5	34	25	127	115
Low-cobalt 18Ni(250)	1835	266	1780	258	11	63.5	43	32	149	135

(a) Longitudinal-short transverse orientation tested (L-S orientation)

more potent embrittling agent than either cobalt or molybdenum when present at levels significantly in excess of 1.3%.

Resistance to Stress-Corrosion Cracking. Maraging steels are susceptible to stress-corrosion cracking (SCC) in most aqueous environments; their resistance to cracking increases significantly at lower yield strengths. Maraging steels, however, have better resistance to SCC than tempered martensitic steels of comparable strength.

For the 18Ni maraging steels, the prime competing factor for a given strength level is whether the material is a standard grade (8% Co, nominal) or a cobalt-free or low-cobalt-bearing grade (2% Co, nominal). At the 1720 MPa (250 ksi) yield strength level, the influence of cobalt level can be seen in Fig. 3 for a marine atmosphere. Cobalt exerts a mixed influence on plain-strain fracture toughness (K_{Ic}) and the threshold stress intensity for SCC (K_{ISCC}). The highest value of K_{Ic} is obtained for the low-cobalt grade, while the two cobalt-bearing grades are not significantly different in terms of K_{ISCC}. The cobalt-free grade has lower resistance to SCC. Consistent with improved K_{ISCC}, cobalt additions increase time-to-failure for maraging steels (Fig. 4). Based on Fig. 4, the apparent threshold stress levels for 18Ni(250), low-cobalt 18Ni(250), and cobalt-free 18Ni(250) in stagnant 3.5% NaCl are 1.035 GPa (150 ksi), 0.86 GPa (125 ksi), and 0.515 GPa (75 ksi), respectively. In conclusion, Fig. 3 and 4 show that the lower value of K_{ISCC} for the cobalt-free grades accompanies a relatively high value of crack velocity.

Effect of Residual Elements on Thermal Embrittlement. Maraging steels fracture intergranularly at low impact energies if improperly processed after hot working. This problem, known as thermal embrittlement, occurs when maraging steels that have been heated above 1095 °C (2000 °F) are slowly cooled through, or held within, the temperature range of 980 to 815 °C (1800 to 1500 °F). The embrittlement is caused by the

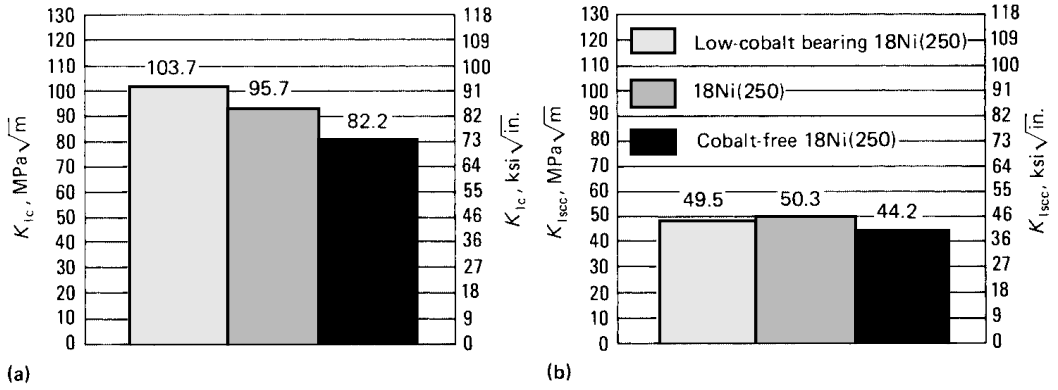


Fig. 3 Bar graphs comparing (a) K_{Ic} and (b) K_{ISCC} (circumferential-radial specimen orientation) of low-cobalt-bearing, standard, and cobalt-free 18Ni-250 maraging steels. K_{ISCC} testing was conducted in a marine atmosphere.

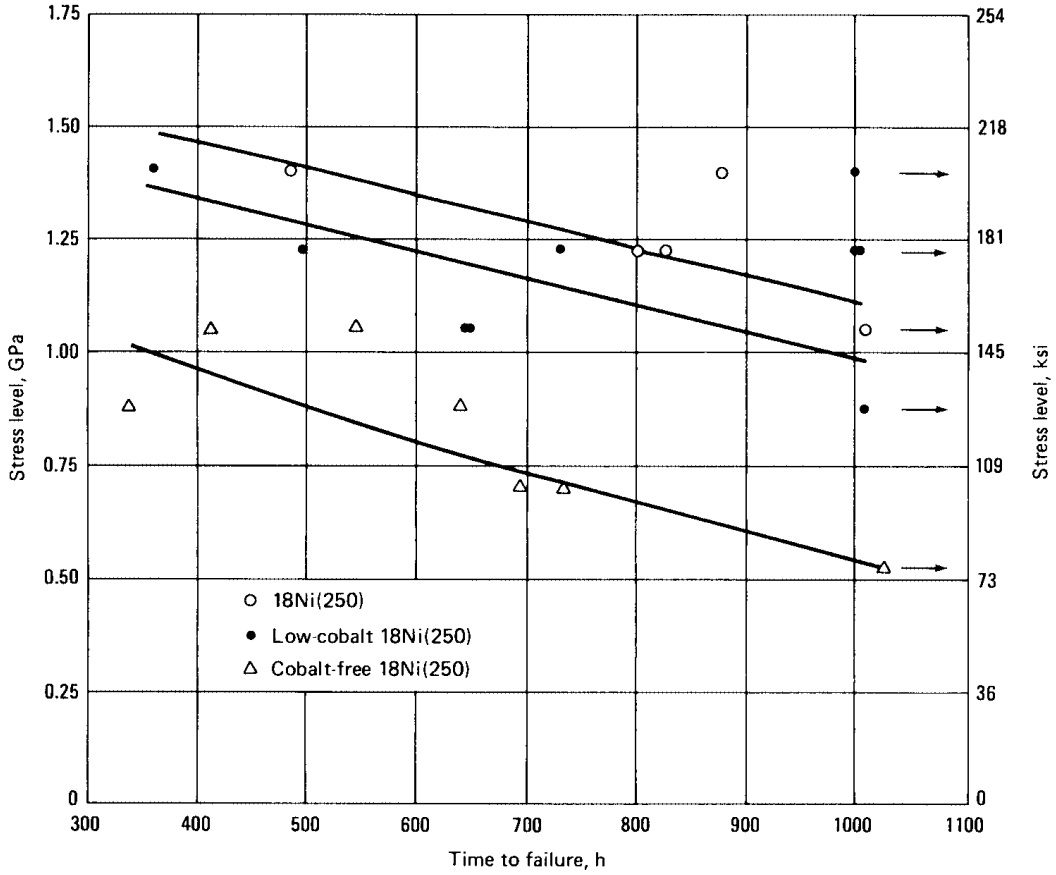


Fig. 4 Plot of stress level vs. time to failure to compare behavior of low-cobalt-bearing, standard, and cobalt-free 18Ni-250 maraging steels, tested in stagnant 3.5% NaCl solution for 1000 h using proof-ring tensile specimens

precipitation of TiC and/or Ti(C,N) on the austenite grain boundaries during cooling through, or holding within, the critical temperature range. The degree of embrittlement increases with time within the critical range. Increased levels of carbon and nitrogen render maraging steels more susceptible to thermal embrittlement.

Effects of Alloying on Processing

The two manufacturing or processing characteristics most influenced by alloying in maraging steels are weldability and hot workability.

Weldability in maraging steels is enhanced, because the low carbon content produces a soft, ductile martensite in the weld zone on cooling. This results in low residual stresses and a low susceptibility to weld cracking.

Hot Workability. Maraging steels can be hot worked by conventional steel mill techniques, even though allowances must be made for several unique characteristics. Steels with high titanium contents have greater hot

strength than conventional steels and require higher hot-working loads or higher working temperatures. Working above about 1260 °C (2300 °F) should be avoided. To maximize their mechanical properties, maraging steels should be hot worked at the lowest temperatures that equipment power limitations permit.

The precipitation of TiC films at austenite grain boundaries must be avoided. This phenomenon first came to light in billets that had been worked at very high temperatures and then allowed to cool slowly through the temperature range of 750 to 1095 °C (1380 to 2000 °F) or to cool with inadvertent thermal arrests in this range. It is essential that long dwell times in this temperature range be avoided after working is completed, so that the titanium and carbon remain in solution.

However, one should keep in mind that it is safe to heat into the 750 to 1095 °C (1380 to 2000 °F) range from room temperature, because stable carbides will already have precipitated. This temperature range should be avoided only when cooling from temperatures above 1150 °C (2100 °F).

SELECTED REFERENCES

- K. Rohrbach and M. Schmidt, Maraging Steels, *Properties and Selection*: *Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook,* ASM International, 1990, p 793–800
- *Maraging Steels*: *Recent Developments and Applications.* The Minerals, Metals and Materials Society, 1988
- *Source Book on Maraging Steels,* American Society for Metals, 1979

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Austenitic Manganese Steels

Introduction and Overview

The original austenitic manganese steel, containing about 1.25% C and 12% Mn, was invented by Sir Robert Hadfield in 1882. Hadfield's steel was unique in that it combined high toughness and ductility with high work-hardening capacity and, usually, good resistance to wear. Consequently, it rapidly gained acceptance as a very useful engineering material.

Hadfield's austenitic manganese steel is still used extensively, with minor modifications in composition and heat treatment, primarily in the fields of earthmoving, mining, quarrying, oil well drilling, steelmaking, railroading, dredging, lumbering, and in the manufacture of cement and clay products. Austenitic manganese steel is used in equipment for handling and processing earthen materials (such as rock crushers, grinding mills, dredge buckets, power shovel buckets and teeth, and pumps for handling gravel and rocks). Other applications include fragmentizer hammers and grates for automobile recycling and military applications such as tank track pads. Another important use is in railway trackwork at frogs, switches, and crossings, where wheel impacts at intersections are especially severe. Because austenitic manganese steel resists metal-to-metal wear, it is used in sprockets, pinions, gears, wheels, conveyor chains, wear plates, and shoes.

Austenitic manganese steel has certain properties that tend to restrict its use. It is difficult to machine and usually has a yield strength of only 345 to 415 MPa (50 to 60 ksi). Consequently, it is not well suited for parts that require close-tolerance machining or that must resist plastic deformation when highly stressed in service. However, hammering, pressing, cold rolling, or explosion shocking of the surface raises the yield strength to provide a hard surface on a tough core structure.

Composition Requirements and Control

Many variations of the original austenitic manganese steel have been proposed, often in unexploited patents, but only a few have been adopted as significant improvements. These usually involve variations of carbon and manganese, with or without additional alloys such as chromium, nickel, molybdenum, vanadium, titanium, and bismuth. The most common of these compositions, as listed in ASTM A 128, are given in Table 1.

The available assortment of wrought grades is smaller and usually approximates ASTM composition B-3. Some wrought grades contain about 0.8% C and either 3% Ni or 1% Mo. Large heat orders are usually required for the production of wrought grades, while cast grades and their modifications are more easily obtained in small lots. A manganese steel foundry may have several dozen modified grades on its production list. Modified grades are usually produced to meet the requirements of application, section size, casting size, cost, and weldability considerations.

Carbon and Manganese. The ASTM A 128 compositions in Table 1 do not permit any austenite transformation when the alloys are water quenched from above the A_{cm} (that is, the temperature that corresponds to the boundary between the cementite-austenite and the austenite fields). However, this does not preclude lower ductility in heavy sections because of slower quenching rates. The effect is due to the formation of carbides along grain boundaries and other interdendritic areas and, to some degree, affects nearly all commercial castings except the very smallest. Figure 1 shows A_{cm} temperatures for 13% Mn steels containing between 0.6 and 1.4% C. Figure 2 shows the effects of carbon and manganese content on the M_s temperature, that is, the temperature at which martensite starts to form from austenite upon cooling, of a homogeneous austenite with all carbon and manganese in solid solution.

The mechanical properties of austenitic manganese steel vary with both carbon and manganese content. Figure 3 indicates that carbon increases strength up to the range of ASTM A 128, grade A. A pleateau is indicated at 1.05 to 1.35% C content. Any departure from this curve can be attributed

Table 1 Standard composition ranges for austenitic manganese steel castings

ASTM A 128 grade	Composition, %						
	C	Mn	Cr	Mo	Ni	Si (max)	P (max)
A	1.05–1.35	11.0 min	…	…	…	1.00	0.07
B-1	0.9–1.05	11.5–14.0	…	…	…	1.00	0.07
B-2	1.05–1.2	11.5–14.0	…	…	…	1.00	0.07
B-3	1.12–1.28	11.5–14.0	…	…	…	1.00	0.07
B-4	1.2–1.35	11.5–14.0	…	…	…	1.00	0.07
C	1.05–1.35	11.5–14.0	1.5–2.5	…	…	1.00	0.07
D	0.7–1.3	11.5–14.0	…	…	3.0–4.0	1.00	0.07
E-1	0.7–1.3	11.5–14.0	…	0.9–1.2	…	1.00	0.07
E-2	1.05–1.45	11.5–14.0	…	1.8–2.1	…	1.00	0.07
F	1.05–1.35	6.0–8.0	…	0.9–1.2	…	1.00	0.07

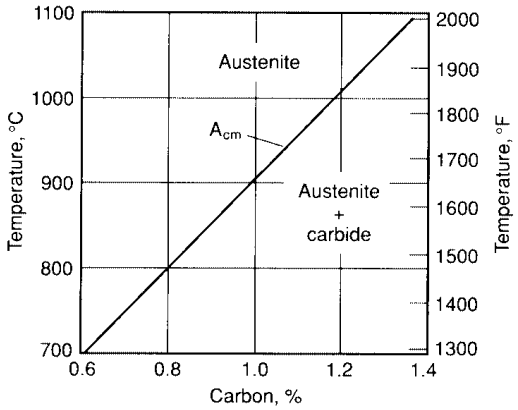


Fig. 1 Solubility of carbon in 13% Mn steels. Source: Ref 1

to grain size unless good statistical evidence is found. The plateau at 827 MPa (120 ksi) is based on the 97-heat, 270-test scatter graph shown in Fig. 4. The data points in Fig. 4 were used to calculate the standard deviation, σ, data in Fig. 3. As carbon is increased it becomes increasingly difficult to retain all of the carbon in solid solution, which may account for reductions in tensile strength and ductility. Nevertheless, because abrasion resistance tends to increase with carbon, carbon content higher than the 1.20% midrange of grade A may be preferred even when ductility is lowered. Carbon content above 1.4% is seldom used because of the difficulty of obtaining an austenitic structure sufficiently free of grain boundary carbides, which are detrimental to strength and ductility. The effect can also be observed in 13% Mn steels containing less than 1.4% C because

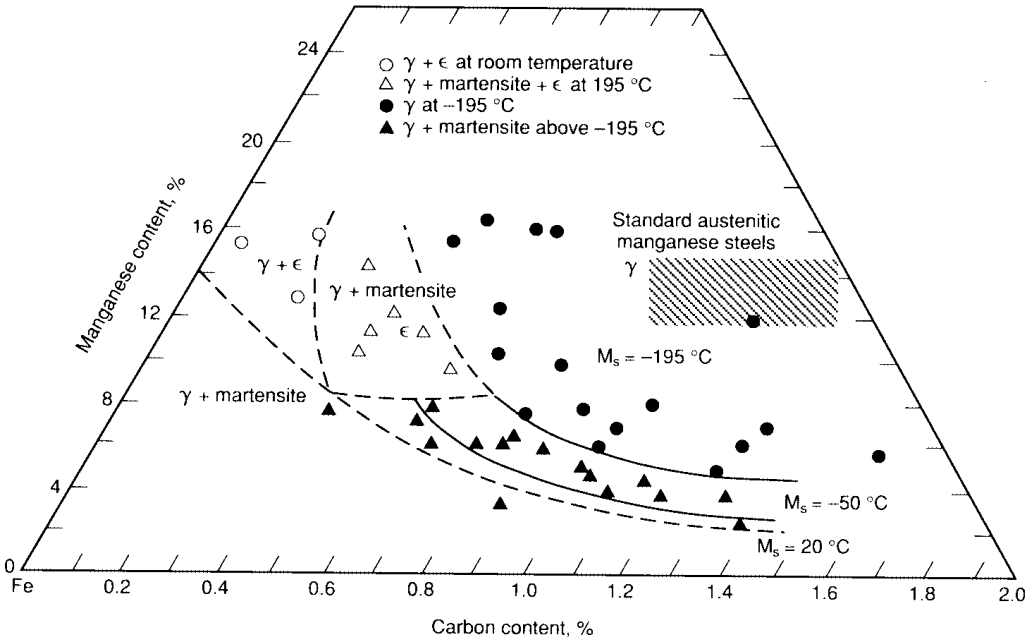


Fig. 2 Variation of M_S temperature with carbon and manganese contents. Source: Ref 2

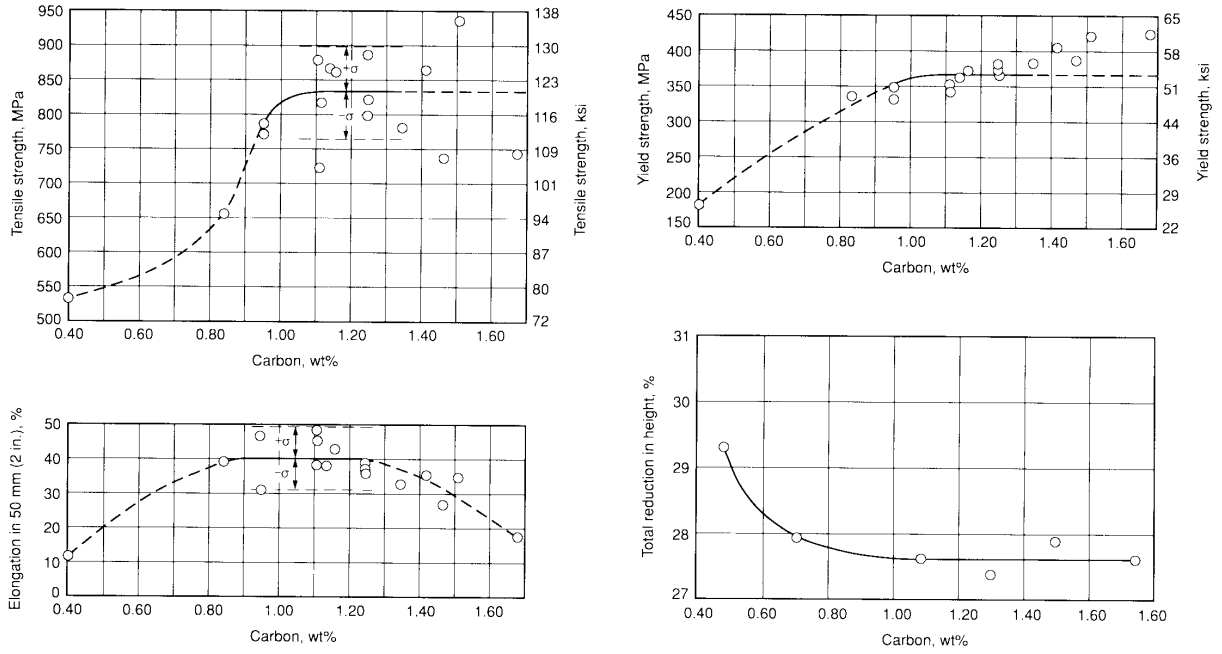


Fig. 3 Variation of properties with carbon content for austenitic manganese steel containing 12.2 to 13.8% Mn. Data are for castings weighing 3.6 to 4.5 kg (8 to 10 lb) and about 25 mm (1 in.) in section size that were water quenched from 1040 to 1095 °C (1900 to 2000 °F). Flow under impact is the total reduction in height sustained by a cylindrical specimen 25 mm (1 in.) in both diameter and length after absorbing 20 blows of 680 J (500 ft · lbf) each. Source: Abex Research Center

segregation may result in local variations of ±17% (±0.2% C) from the average carbon level determined by chemical analysis.

The 0.7% C (min) of grades D and E-1 may be used to minimize carbide precipitation in heavy castings or in weldments, and similar low carbon contents are specified for welding filler metal. Carbides form in castings that are cooled slowly in the molds. In fact, carbides form in practically all ascast grades containing more than 1.0% C, regardless of mold cooling rates. They form in heavy-section castings during heat treatment if quenching is ineffective in producing rapid cooling throughout the entire section thickness. Carbides can form during welding or during service at temperatures above about 275 °C (530 °F).

If carbon and manganese are lowered together, for instance to 0.53% C with 8.3% Mn or 0.62% C with 8.1% Mn, the work-hardening rate is increased because of the formation of strain-induced α (body-centered cubic, or bcc) martensite. However, this does not provide enhanced abrasion resistance (at least to high-stress grinding abrasion) as is often hoped (Ref 4).

Manganese contributes the vital austenite-stabilizing effect of delaying transformation (but not eliminating it). Thus, in a simple steel that

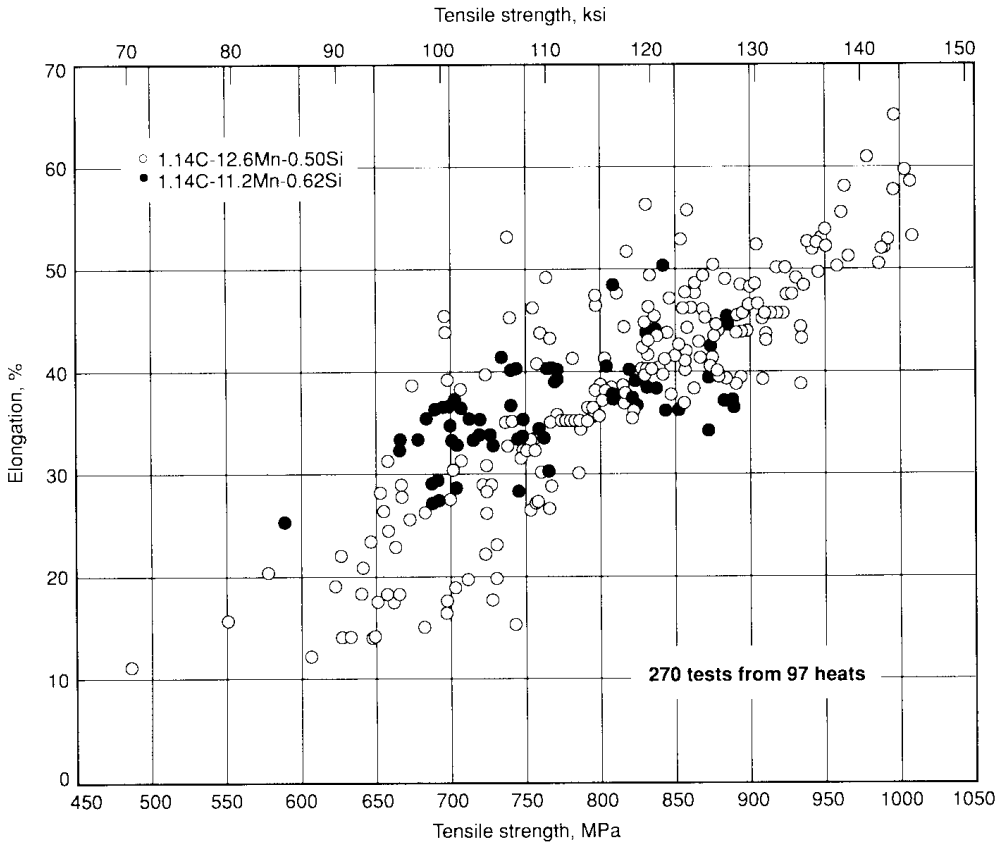


Fig. 4 Distribution of tensile strength and ductility values for 97 heats of manganese steel. The chemical compositions indicated are average for the specific data points plotted. Test specimens were 25 mm (1 in.) diam bars, austenitized and quench-annealed from 1010 °C (1850 °F) or above. Source: Ref 3

contains 1.1% Mn, isothermal transformation at 370 °C (700 °F) begins about 15 s after the steel is quenched to that temperature, whereas in a 13% Mn steel, transformation at the same temperature does not begin until after 48 h (Ref 1). Below 260 °C (500 °F), phase changes and carbide precipitation are so sluggish that for all practical purposes they may be neglected, in the absence of deformation, if manganese content exceeds 10%.

Figure 5 shows the influence of manganese content on the strength and ductility of cast austenitic steel that has been solution treated and water quenched. It confirms the observations of many investigators, including Sir Robert Hadfield (Ref 5), who studied the influence of manganese content up to about 22%. Manganese content has little effect on yield

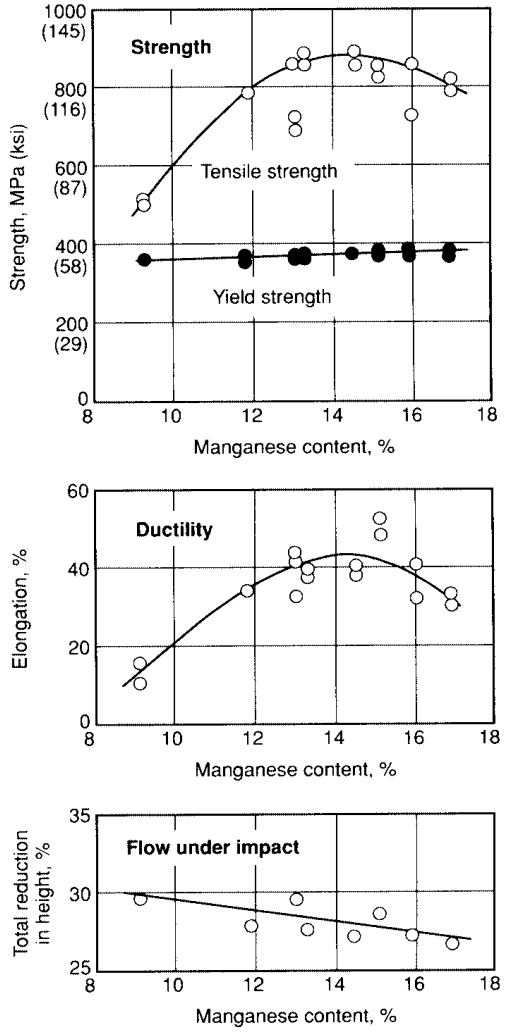


Fig. 5 Variation of properties with manganese content for austenitic manganese steel containing 1.15% C. Data are for castings weighing 3.6 to 4.5 kg (8 to 10 lb) and about 25 mm (1 in.) in section size that were water quenched from 1040 to 1095 °C (1900 to 2000 °F). Flow under impact is the total reduction in height sustained by a cylindrical specimen 25 mm (1 in.) in both diameter and length after absorbing 20 blows of 680 J (500 ft · lbf) each. Source: Abex Research Center

strength. In tensile testing, ultimate strength and ductility increase fairly rapidly with increasing manganese content up to about 12% and then tend to level off, although small improvements normally continue up to about 13% Mn.

Silicon and Phosphorus. As noted in Table 1, silicon and phosphorus are present in all ASTM A 128 grades of austenitic manganese steel. Silicon is seldom added except for steelmaking purposes. Silicon content exceeding 1% is uncommon, because foundries do not like to have the silicon pyramid in melts containing returned scrap. A silicon content of 1 to 2% might be used to increase yield strength to a moderate degree, but other elements are preferred for this effect. Loss of strength is abrupt above 2.2% Si, and Mn steel containing more than 2.3% Si may be worthless. On the other hand, silicon levels below 0.10% show decreased fluidity during casting.

The availability of low-phosphorus ferromanganese since about 1960 has enabled steelmakers to reduce phosphorus levels in manganese steel to a large extent. The preferred practice is to hold the phosphorus content below 0.04% even though 0.07% is permitted by ASTM A 128. Levels above 0.06%, which formerly were prevalent, contribute to hot shortness and low elongation at very high temperatures and frequently are the cause of hot tears in castings and underbead cracking in weldments. It is particularly advantageous to keep phosphorus at the lowest possible level in the grades that are welded, and in manganese steel welding electrodes, and in heavy section castings.

Effects of Alloying Elements

The most common alloying elements are chromium, molybdenum, and nickel (Table 1). When added to the usual carbon level of about 1.15%, both chromium and molybdenum increase yield strength (Fig. 6) and flow resistance under impact.

Chromium additions are less expensive for a given increase, and chromium grades (ASTM A 128, grade C, for instance) are probably the most common modifications. ASTM A 128, grade B, often contains some chromium also. The 2% chromium addition in grade C does not significantly lower toughness in light sections. However, in heavier sections, its effect is similar to that of raising the carbon level; the result is a decrease in ductility due to an increase in the volume fraction of carbides in the microstructure. Chromium additions have been used up to 6% for some applications, sometimes in combination with copper, but these grades no longer receive much attention. Chromium enhances resistance to both atmospheric corrosion and abrasion, although the latter effect is not

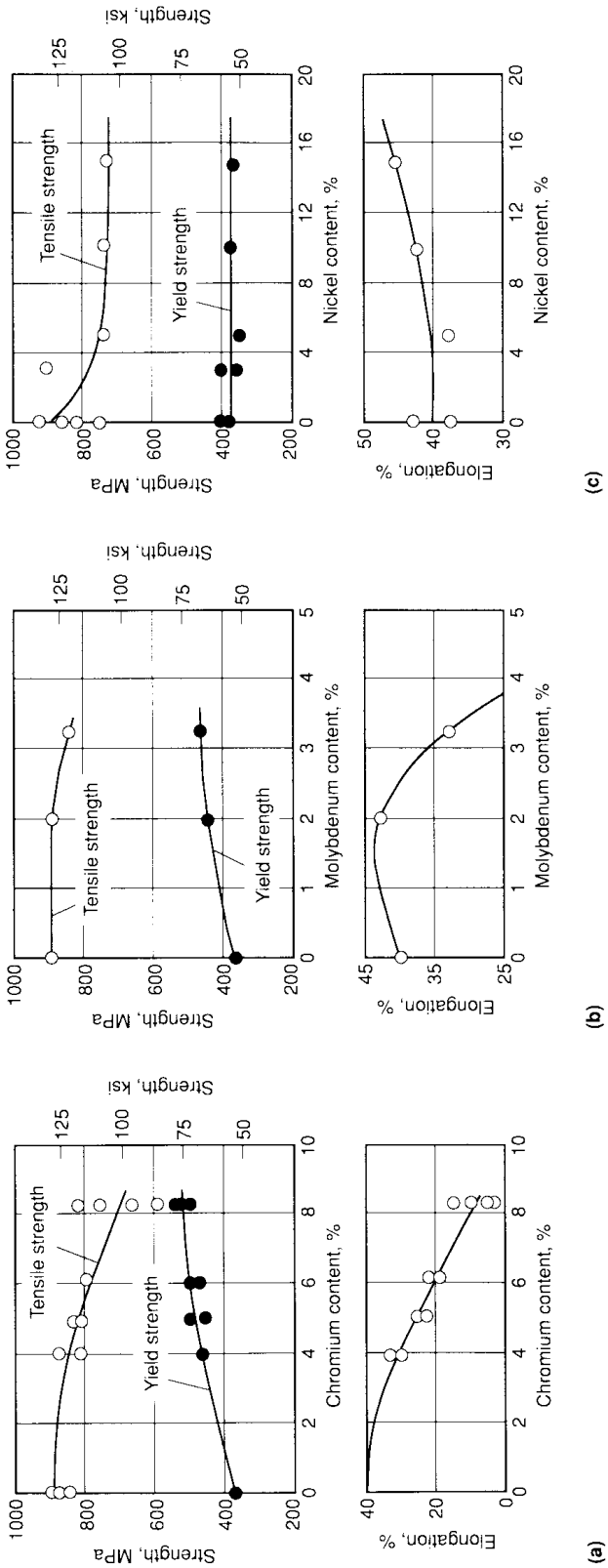


Fig. 6 Effects of (a) chromium, (b) molybdenum, and (c) nickel contents on the tensile properties of cast manganese steel. Steel was cast in 25 mm (1 in.) diam test bars, reheated to 1095 °C (2000 °F), and water quenched. Source: Ref 6

always consistent and depends on the individual application. It is also used up to 18% in low-carbon electrodes for welding manganese steel. Because of the stabilizing effect of chromium on iron carbide, higher heat-treatment (solutionizing) temperatures are often necessary prior to water quenching.

Molybdenum additions, usually 0.5 to 2%, are made to improve the toughness and resistance to cracking of castings in the as-cast condition and to raise the yield strength (and possibly toughness) of heavy-section castings in the solution-treated and quenched condition. These effects occur because molybdenum in manganese steel is distributed partly in solution in the austenite and partly in primary carbides formed during solidification of the steel. The molybdenum in solution effectively suppresses the formation of both embrittling carbide precipitates and pearlite, even when the austenite is exposed to temperatures above 275 °C (530 °F) during welding or in service. The molybdenum in primary carbides tends to change the morphology from continuous envelopes around austenite dendrites to a less harmful nodular form, especially when the molybdenum content exceeds 1.5%.

The 1% molybdenum grades (ASTM A 128, grade E-1, and AWS A5.13, grade EFeMn-B) are resistant to the reheating effect that limits the usefulness of the standard B-2, B-3, and B-4 grades. Grade E-1 is adapted to heavy-section castings used in roll and impact crushers that are frequently reheated during weld buildup and overlays.

Grade E-2, which contains about 2% Mo, may be given a special heat treatment to develop a structure of finely dispersed carbides in austenite. This heat treatment entails a partial grain refinement (U.S. Patent 1,975,746) by pearlitizing near 595 °C (1105 °F) for 12 h and water quenching from 980 °C (1800 °F). This type of microstructure has been found to enhance abrasion resistance in crusher applications. The tensile properties of specimens removed from worn cone crusher parts ranged from 440 to 485 MPa (64 to 70 ksi) in yield strength, 695 to 850 MPa (100 to 125 ksi) in tensile strength, and 15 to 25% in elongation.

The addition of molybdenum in amounts greater than 1% can increase the susceptibility of the manganese steel to incipient fusion during heat treatment. Incipient melting refers to a liquation phenomenon that occurs because of the presence of low-melting constituents in interdendritic areas, both within individual grains and along grain boundaries. This tendency is aggravated by higher P levels (>0.05%), higher pouring temperatures (which promote segregation in the casting), and higher carbon levels (>1.3%) in the steel.

As a further use, molybdenum is added to the lean manganese steel grade F partly to suppress embrittlement in both as-cast and heat-treated conditions.

Nickel Additions. Nickel, in amounts up to 4%, stabilizes the austenite because it remains in solid solution. It is particularly effective for suppressing precipitates of carbide platelets, which can form between about 300 to 550 °C (570 to 1020 °F). Therefore, the presence of nickel helps retain nonmagnetic qualities in the steel, especially in the decarburized surface layers. Nickel additions increase ductility, decrease yield strength slightly, and lower the abrasion resistance of manganese steel. Nickel is used primarily in the lower-carbon or weldable grades of cast manganese steel and in wrought manganese steel products (including welding electrodes). In wrought products, nickel is sometimes used in conjunction with molybdenum.

Alloying Elements for Unique Applications

Vanadium is a strong carbide former, and its addition to manganese steels substantially increases yield strength, but with a corresponding decrease in ductility. Vanadium is used in precipitation-hardening manganese steels in amounts ranging from 0.5 to 2%. Because of the stability of vanadium carbonitrides, a higher solutionizing temperature 1120 to 1175 °C (2050 to 2150 °F) is recommended prior to aging (usually between 500 to 650 °C or 930 to 1200 °F). Yield strengths of over 700 MPa (100 ksi) are obtainable depending on the level of ductility that can be tolerated for a given application. Tests of an age-hardened manganese-nickel-molybdenum-vanadium austenitic alloy demonstrated that the abrasion resistance of this steel is not as good as that of the standard grades (Ref 7).

Copper. Like nickel, copper in amounts of 1 to 5% has been used in austenitic manganese steels to stabilize the austenite. The effects of copper on mechanical properties have not been clearly established. Scattered reports indicate that it may have an embrittling effect, which may be due to the limited solubility of copper in austenite.

Bismuth is added to standard manganese steels to improve machinability, especially when coupled with high manganese levels (> 13%).

Titanium can reduce carbon in austenite by forming very stable carbides. The resulting properties may simulate those of a lower-carbon grade. Titanium may also somewhat neutralize the effect of excessive phosphorus; some European practice is apparently based on this idea. Microalloying additions (<0.1%) of titanium, vanadium, boron, zirconium, and nitrogen have been reported to promote grain refinement in manganese steels. The effect, however, is inconsistent. Higher levels of these elements can result in serious losses in ductility. Nitrogen in amounts

greater than 0.20% can cause gas porosity in castings. An overall reduction in grain size lowers the susceptibility of the steel to hot tearing.

Sulfur. The sulfur content in manganese steels seldom influences its properties, because the scavenging effect of manganese operates to eliminate sulfur by fixing it in the form of innocuous, rounded, sulfide inclusions. The elongation of these inclusions in wrought steels may contribute to directional properties; in cast steels, such inclusions are harmless. However, it is best to keep sulfur as low as is practically possible to minimize the number of inclusions in the microstructure that would be potential sites for the nucleation of fatigue cracks in service.

Special Grades of Manganese Steels

Lower Manganese Content Steels. ASTM A 128, grade F, has reduced manganese (6 to 8%) to make the austenite less stable, but this requires compensation with 1% Mo to gain acceptable properties. Work-hardening rates are reported to be higher than that of the standard 13% Mn grades, with some loss in toughness. This grade has been used in scoop lips, ball mill end liners, discharge grates, and grizzly screens for siliceous ore milling. One record indicates 45% longer life in ball mill discharge grates compared to pearlitic chromium-molybdenum steel used previously. Average properties reported were 415 MPa (60 ksi) yield strength, 585 MPa (85 ksi) tensile strength, and 12% elongation for carbon levels of 1.2 to 1.4%. ASTM A 128, grade F, is not adapted to heavy sections or to service involving temperatures above 315 °C (600 °F). It has poor weldability and should be avoided if a casting must be hardfaced or rebuilt.

Several other elements not listed in Table 1 (for example, vanadium, copper, titanium, and bismuth) are added to manganese steel for unique applications.

Higher Manganese Content Steels. Austenitic steels with a higher manganese content (15 to 30%) have been developed for applications requiring low magnetic permeability, low-temperature (cryogenic) strength, and low-temperature toughness (Ref 8). These applications stem from the development of superconducting technologies used in transportation systems and nuclear fusion research; they also satisfy the need for structural materials that are able to store and transport liquified gas.

For low magnetic permeability, these alloys have a lower carbon content than the standard manganese steels. The corresponding loss in yield strength is compensated for by alloying with vanadium, nitrogen, chromium, molybdenum, and titanium. Chromium also imparts corrosion resistance, as required in some cryogenic applications. Additions of calcium, sulfur,

and aluminum are made to enhance the machinability of these alloys where required. Phosphorus levels are generally maintained below 0.02%.

REFERENCES

1. E.C. Bain, E.S. Davenport, and W.S.N. Waring, The Equilibrium Diagram of Iron-Manganese-Carbon Alloys of Commercial Purity, *Trans. AIME,* Vol 100, 1932, p 228
2. C.H. Shih, B.L. Averbach, and M. Cohen, Work Hardening and Martensite Formation in Austenitic Manganese Alloys, Research Report, Massachusetts Institute of Technology, 1953
3. H.S. Avery, Austenitic Manganese Steel, *Metals Handbook,* Vol 1, 8th ed., American Society for Metals, 1961
4. H.S. Avery, Work Hardening in Relation to Abrasion Resistance, in *Proceedings of the Symposium on Materials for the Mining Industry,* published by Climax Molybdenum Company, 1974, p 43
5. *Manganese Steel,* Oliver and Boyd, for Hadfields Ltd., 1956
6. H.S. Avery and H.J. Chapin, Austenitic Manganese Steel Welding Electrodes, *Weld. J.,* Vol 33, 1954, p 459
7. F. Borik and W.G. Scholz, Gouging Abrasion Test for Materials Used in Ore and Rock Crushing, Part II, *J. Mater.,* Vol 6 (No. 3), Sept 1971, p 590
8. M. Fujikura, Recent Developments of Austenitic Manganese Steels for Non-Magnetic and Cryogenic Applications in Japan, The Manganese Center, Paris 1984

SELECTED REFERENCES

- D.K. Subramanyam, A.E. Swansiger, and H.S. Avery, Austenitic Manganese Steels, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook,* ASM International, 1990, p 822–841
- D.K. Subramanyam, G.W. Grube, and H.J. Chapin, Austenitic Manganese Steel Castings, *Metallography and Microstructures,* Vol 9, *ASM Handbook,* ASM International, 1985, p 237–241

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Stainless Steels

Introduction and Overview

Stainless steels are iron-base alloys that contain a minimum of about 11% Cr, the amount needed to prevent the formation of rust in unpolluted atmospheres (hence the designation *stainless*). Most stainless steels contain less than 30% Cr or more than 50% Fe. They achieve their stainless characteristics through the formation of an invisible and adherent chromium-rich oxide passive film. This oxide forms and heals itself in the presence of oxygen. Other elements added to improve particular characteristics include nickel, manganese, molybdenum, copper, titanium, silicon, niobium, aluminum, sulfur, and selenium. Carbon is normally present in amounts ranging from less than 0.03% to over 1.0% in certain grades. Figure 1 provides a useful summary of some of the compositional and property linkages in the stainless steel family.

Designations for Stainless Steels. In the United States, wrought grades of stainless steels are generally designated by the American Iron and Steel Institute (AISI) numbering system, the Unified Numbering System (UNS), at the proprietary name of the alloy. In addition, designation systems have been established by most of the major industrial nations. Of the two institutional numbering systems used in the United States, AISI is the older and more widely used. Most of the grades have a three-digit designation; the 200 and 300 series are generally austenitic stainless steels, whereas the 400 series are either ferritic or martensitic. Some of the grades have a one-letter or two-letter suffix that indicates a particular modification of the composition.

The UNS system includes a considerably greater number of stainless steels than AISI because it incorporates all of the more recently developed stainless steels. The UNS designation for a stainless steel consists of the letter S, followed by a five-digit number. For those alloys that have an AISI designation, the first three digits of the UNS designation usually correspond to an AISI number. When the last two digits are 00, the number

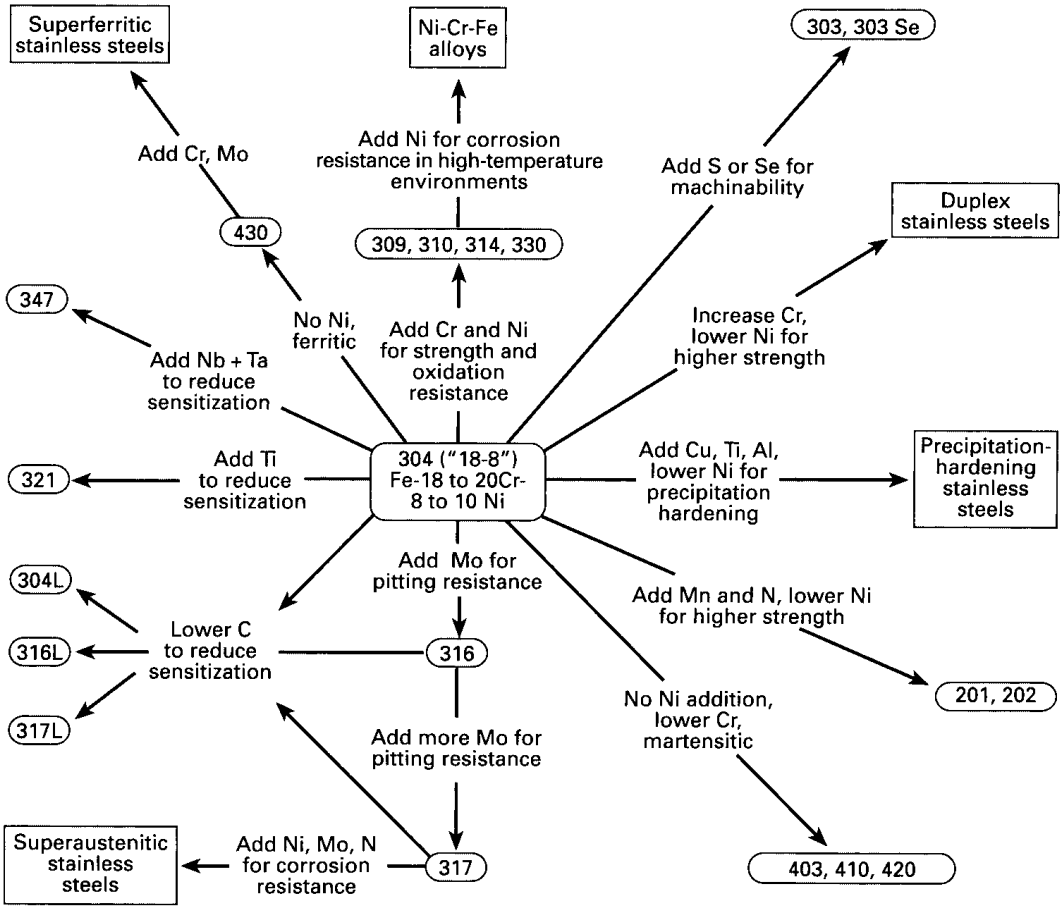


Fig. 1 Composition and property linkages in the stainless steel family of alloys

designates a basic AISI grade. Modifications of the basic grades use two digits other than zeroes.

For stainless steels that contain less than 50% iron, the UNS designation consists of the letter N (for nickel-base alloys), followed by a five-digit number. Examples include some of the more highly alloyed austenitic grades.

Applications. Stainless steels are used in a wide variety of applications. Most of the structural applications occur in the chemical and power engineering industries, which account for more than a third of the market for stainless steel products (see the following table). These applications include an extremely diversified range of uses, including nuclear reactor vessels, heat exchangers, oil industry tubulars, components for chemical processing and pulp and paper industries, furnace parts, and boilers used in fossil fuel electric power plants. The relative importance of the major fields of application for stainless steel products are as follows:

Application	Percentage
Industrial equipment	
Chemical and power engineering	34
Food and beverage industry	18
Transportation	9
Architecture	5
Consumer goods	
Domestic appliances, household utensils	28
Small electrical and electronic appliances	6

Families of Stainless Steels

There are five major families of stainless steels, as defined by crystallographic structure. Each family is distinct with regard to its typical mechanical properties. Furthermore, each family tends to share a common nature in terms of resistance/susceptibility to particular forms of corrosion. However, within each family, it is possible to have a substantial range of composition. Therefore, each family is applicable to a broad range of corrosion environments.

Ferritic Stainless Steels. The simplest stainless steels contain only iron and chromium. Chromium is a ferrite stabilizer; therefore, the stability of the ferritic structure increases with chromium content. Ferrite has a body-centered cubic crystal structure, and it is characterized as magnetic and relatively high in yield strength but low in ductility and work hardenability. Ferrite shows an extremely low solubility for such interstitial elements as carbon and nitrogen. The ferritic grades exhibit a transition from ductile to brittle behavior over a rather narrow temperature range. At higher carbon and nitrogen contents, especially at higher chromium levels, this ductile-to-brittle transition can occur above ambient temperature. This possibility severely limited the use of ferritic grades before the use of argon-oxygen-decarburization (AOD). The ferritic family was then limited to AISI type 446 for oxidation-resistant applications and to AISI types 430 and 434 for such corrosion applications as automotive trim. The fact that these grades were readily sensitized to intergranular corrosion as a result of welding or thermal exposure further limited their use.

With AOD, it was possible to reduce the levels of carbon and nitrogen significantly. The activity of carbon and nitrogen could further be reduced by the use of stabilizers, which are highly reactive elements, such as titanium and niobium, that precipitate the remaining interstitials. This newer generation of ferritic stainless steels includes AISI type 444 and the more highly alloyed ferritic grades containing very low interstitial element contents or stabilizing elements for improved corrosion resistance and weldability.

With control of interstitial elements, it is possible to produce grades with unusually high chromium and molybdenum contents. At these low effective carbon levels, these grades are tougher and more weldable than the first generation of ferritic stainless steels. Nevertheless, their limited toughness generally restricts use of these grades to sheet or lighter-gage tubulars.

Ferritic stainless steels are highly resistant and are in some cases immune to chloride stress-corrosion cracking (SCC). These grades are frequently considered for thermal transfer applications.

The same properties and advantages are also responsible for the extraordinary development of the lowest-alloyed grade of the ferritics, AISI type 409. This grade, developed for automotive muffler and catalytic converter service, has gained in technical sophistication. It is increasingly used in automotive exhaust systems and in other moderately severe atmospheric-exposure applications.

Tables 1 through 4 list compositions of ferritic stainless steels. These include Group I (first generation) alloys, Group II (second generation) alloys, which are modified versions of Group I alloys, and Group III high-purity alloys, which are referred to as superferritic stainless steels (Fig. 1).

Tabel 1 Nominal chemical composition of representative Group I standard-grade 400-series ferritic stainless steels

		Composition(a),wt%			
UNS No.	Type	C	Cr	Mo	Other
S42900	429	0.12	14.0–16.0	…	…
S43000	430	0.12	16.0–18.0	…	…
S43020	430F	0.12	16.0–18.0	0.6	0.06 P; 0.15 min S
S43023	430FSe	0.12	16.0–18.0	…	0.15 min Se
S43400	434	0.12	16.0–18.0	0.75–1.25	…
S43600	436	0.12	16.0–18.0	0.75–1.25	Nb + Ta = 5 × %C min
S44200	442	0.20	18.0–23.0	…	…
S44600	446	0.20	23.0–27.0	…	…

(a) Single values are maximum values unless otherwise indicated.

Table 2 Chemical compositions of Group II ferritic stainless steels

		Composition(a), wt%				
UNS No.	Alloy designation	C	Cr	Mo	Ni	Other
S40500	405	0.08	11.5–14.5			0.10–0.30 Al
S40900	409	0.08	10.5–11.75	…	0.5	Ti = 6 × C min to 0.75 max
…	409Cb	0.02(b)	12.5(b)	…	0.2(b)	0.4 Nb(b)
S40975	409Ni	0.02(b)	11.0(b)	…	0.85(b)	0.20 Ti(b)
…	11Cr-Cb	0.01(b)	11.35(b)	…	0.2(b)	0.35 Nb(b), 0.35 Al(b), 0.2 Ti(b)
S41050	E-4	0.04(b)	11.5(b)	…	0.85(b)	…
S44100	441	0.02(b)	18.0(b)	…	0.3(b)	0.7 Nb(b), 0.3 Ti(b)
…	AL433	0.02(b)	19.0(b)	…	0.3(b)	0.4 Nb(b), 0.5 Si(b), 0.4 Cu(b)
…	AL446	0.01(b)	11.5(b)	…	0.2(b)	0.2 Nb(b), 0.1 Ti(b)
…	AL468	0.01(b)	18.2(b)	…	0.2(b)	0.2 Nb(b), 0.1 Ti(b)
…	YUS436S	0.01(b)	17.4(b)	1.2(b)	…	0.2 Ti(b)
S43035	439	0.07	17.00–19.00	…	0.5	Ti = 0.20 + 4 (C + N) min to 1.0 max
…	12SR	0.2	12.0	…	…	1.2 Al; 0.3 Ti
…	18SR	0.04	18.0	…	…	2.0 Al; 0.4 Ti
K41970	406	0.06	12.0–14.0	…	0.5	2.75–4.25 Al; 0.6 Ti

(a) Single values are maximum values unless otherwise indicated. (b) Typical value

Table 3 Nominal chemical compositions of Group III intermediate-purity ferritic stainless steels

UNS No.	Alloy designation	Composition(a), (wt%)					
		C	N	Cr	Mo	Ni	Ti
S44626	26-1 Ti	0.02(b)	0.025(b)	26(b)	1(b)	0.25(b)	0.5(b)
S44400	AISI 444	0.02(b)	0.02(b)	18(b)	2(b)	0.4(b)	0.5(b)
S44660	Sea-Cure	0.025	0.035	25–27	2.5–3.5	1.5–3.5	$[0.20 + 4 (C + N)] \leq (Nb + Ti) \leq 0.80$
S44635	Monit	0.025	0.035	24.5–26	3.5–4.5	3.5–4.5	$[0.20 + 4 (C + N)] \leq (Nb + Ti) \leq 0.80$
S44735	Al29-4C	0.030	0.045	28–30	3.6–4.2	1.0	$6(C + N) \leq (Nb + Ti) \leq 1.0$

(a) Single values are maximum values unless otherwise stated. (b) Typical value.

Table 4 Nominal chemical compositions of Group III ultrahigh-purity ferritic stainless steel

UNS No.	Alloy designation	Composition(a), wt%						
		C	N	Cr	Mo	Ni	Nb	Other
S44726	E-Brite 26-1 (XM-27)	0.010	0.015	25–27	0.75–1.5	0.30	0.05–0.20	0.4 Mn
S44800	AL 29-4.2	0.010	0.020	28–30	3.5–4.2	2.0–2.5	…	…
S44700	AL 29-4	0.010	0.020	28–30	3.5–4.2	0.15	…	0.3 Mn
…	SHOMAC 30-2	0.003(b)	0.007(b)	30(b)	2(b)	0.2(b)	…	0.3 Mn
S44400	YUS 190L	0.004(b)	0.0085(b)	18(b)	2(b)	0.4(b)	…	…

(a) Single values are maximum unless otherwise stated. (b) Typical value

The Group III alloys can be further divided into intermediate-purity alloys (Table 3) and ultrahigh-purity alloys (Table 4). Figure 2 shows the effects of alloying on the properties and processing characteristics of the standard AISI ferritic stainless steels.

Austenitic Stainless Steels. The detrimental effects of carbon and nitrogen in ferrite can be overcome by changing the crystal structure to austenite, a face-centered cubic crystal structure. This change is accomplished by adding austenite stabilizers—most commonly nickel but also manganese and nitrogen. Austenite is characterized as nonmagnetic, and it is usually relatively low in yield strength with high ductility, rapid work-hardening rates, and excellent toughness. These desirable mechanical properties, combined with ease of fabrication, have made the austenitic grades, especially AISI type 304, the most common of the stainless grades. Processing difficulties tend to limit increases in chromium content; therefore, improved corrosion resistance is usually obtained by adding molybdenum. The use of nitrogen as an intentional alloy addition stabilizes the austenite phase, particularly with regard to the precipitation of intermetallic compounds. With the nitrogen addition, it is possible to produce austenitic grades with up to 6% Mo for improved corrosion resistance in chloride environments. Other special grades include the high-chromium grades for high-temperature applications and the high-nickel grades for inorganic acid environments.

The austenitic stainless steels can be sensitized to intergranular corrosion by welding or by longer-term thermal exposure. These thermal exposures lead to the precipitation of chromium carbides in grain boundaries and to the depletion of chromium adjacent to these carbides. Sensitization

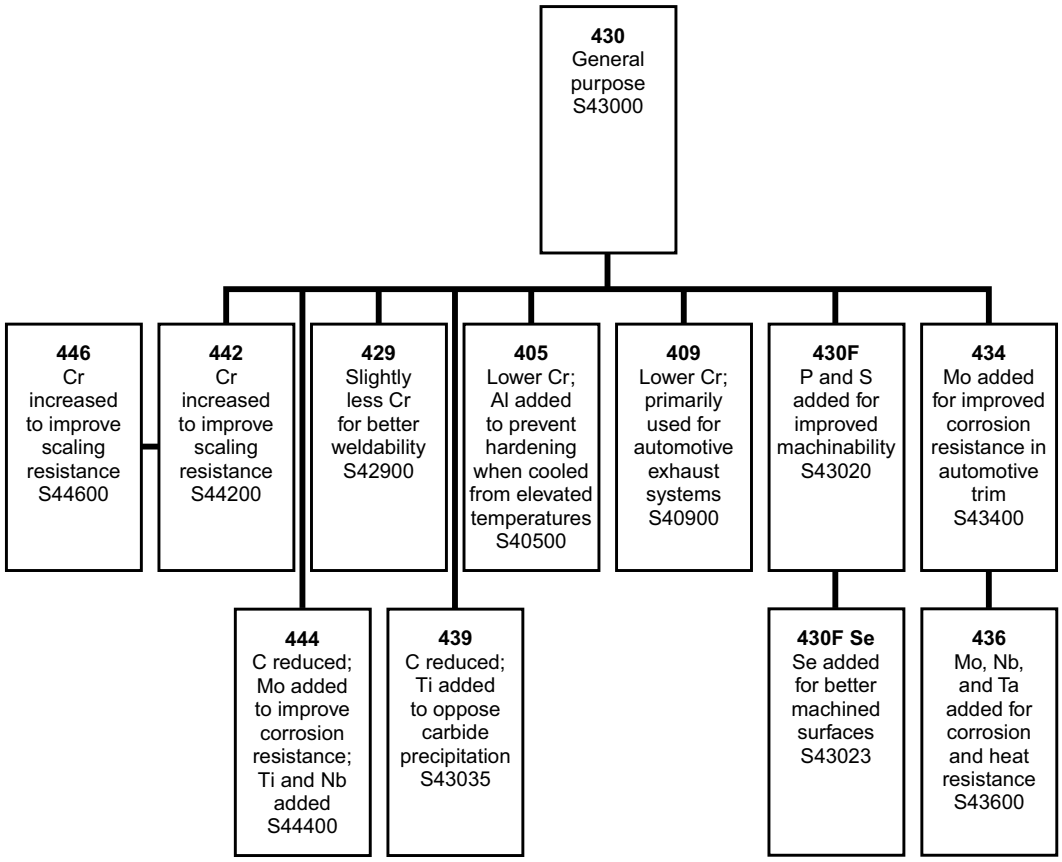


Fig. 2 Family relationships for standard AISI ferritic stainless steels

can be greatly delayed or prevented by the use of lower-carbon L-grades (<0.03% C) or stabilized grades, such as AISI types 321 and 347, which include additions of carbide-stabilizing elements (titanium and niobium, respectively).

The common austenitic grades, AISI types 304 and 316, are especially susceptible to chloride SCC. All austenitic stainless steels exhibit some degree of susceptibility, but several of the high-nickel high-molybdenum grades are satisfactory with respect to stress-corrosion attack in most engineering applications.

Table 5 lists the compositions of the standard AISI austenitic stainless steel grades. As this table indicates, the standard grades can be further subdivided into 300-series (Fe-Cr-Ni) and 200-series (Fe-Cr-Mn-Ni) alloys. Figure 3 shows the effects of alloying on the properties and processing characteristics of the standard AISI austenitic stainless steels.

Table 6 lists the compositions of nonstandard austenitic stainless steels. Included in this table are some of the more highly alloyed grades that contain less than 50% Fe. The high-alloy stainless steels were developed for applications where corrosive conditions are too severe for the standard or modified 300-series austenitic grades. A good example of a high-alloy stainless steel is 20Cb-3 (N08020), which was designed for improved

Table 5 Chemical compositions of standard AISI austenitic stainless steels

UNS No.	Type/ designation	Composition(a), wt%							
		C	Mn	Si	Cr	Ni	P	S	Other
S20100	201	0.15	5.5–7.5	1.00	16.0–18.0	3.5–5.5	0.06	0.03	0.25 N
S20200	202	0.15	7.5–10.0	1.00	17.0–19.0	4.0–6.0	0.06	0.03	0.25 N
S20500	205	0.12–0.25	14.0–15.5	1.00	16.5–18.0	1.0–1.75	0.06	0.03	0.32–0.40 N
S30100	301	0.15	2.0	1.00	16.0–18.0	6.0–8.0	0.045	0.03	…
S30200	302	0.15	2.0	1.00	17.0–19.0	8.0–10.0	0.045	0.03	…
S30215	302B	0.15	2.0	2.0–3.0	17.0–19.0	8.0–10.0	0.045	0.03	…
S30300	303	0.15	2.0	1.00	17.0–19.0	8.0–10.0	0.20	0.15 min	0.6 Mo(b)
S30323	303Se	0.15	2.0	1.00	17.0–19.0	8.0–10.0	0.20	0.06	0.15 min Se
S30400	304	0.08	2.0	1.00	18.0–20.0	8.0–10.5	0.045	0.03	…
S30403	304L	0.03	2.0	1.00	18.0–20.0	8.0–12.0	0.045	0.03	…
S30451	304N	0.08	2.0	1.00	18.0–20.0	8.0–10.5	0.045	0.03	0.10–0.16 N
S30500	305	0.12	2.0	1.00	17.0–19.0	10.5–13.0	0.045	0.03	…
S30800	308	0.08	2.0	1.00	19.0–21.0	10.0–12.0	0.045	0.03	…
S30900	309	0.20	2.0	1.00	22.0–24.0	12.0–15.0	0.045	0.03	…
S30908	309S	0.08	2.0	1.00	22.0–24.0	12.0–15.0	0.045	0.03	…
S31000	310	0.25	2.0	1.50	24.0–26.0	19.0–22.0	0.045	0.03	…
S31008	310S	0.08	2.0	1.50	24.0–26.0	19.0–22.0	0.045	0.03	…
S31400	314	0.25	2.0	1.5–3.0	23.0–26.0	19.0–22.0	0.045	0.03	…
S31600	316	0.08	2.0	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo
S31620	316F	0.08	2.0	1.00	16.0–18.0	10.0–14.0	0.20	0.10 min	1.75–2.5 Mo
S31603	316L	0.03	2.0	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo
S31651	316N	0.08	2.0	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo; 0.10–0.16 N
S31700	317	0.08	2.0	1.00	18.0–20.0	11.0–15.0	0.045	0.03	3.0–4.0 Mo
S31703	317L	0.03	2.0	1.00	18.0–20.0	11.0–15.0	0.045	0.03	3.0–4.0 Mo
S32100	321	0.08	2.0	1.00	17.0–19.0	9.0–12.0	0.045	0.03	5 × %C min Ti
S34700	347	0.08	2.0	1.00	17.0–19.0	9.0–13.0	0.045	0.03	10 × %C min Nb
S34800	348	0.08	2.0	1.00	17.0–19.0	9.0–13.0	0.045	0.03	0.2 Co; 10 × %C min Nb; 0.10 Ta
S38400	384	0.08	2.0	1.00	15.0–17.0	17.0–19.0	0.045	0.03	…

(a) Single values are maximum values unless otherwise indicated. (b) Optional

resistance to sulfuric acid. This alloy has been used in many applications in a wide variety of chemical and allied industry environments. The presence of niobium in the alloy minimizes weld sensitization (intergranular corrosion), and the higher nickel content (32.5 to 35%) confers resistance to chloride SCC. The molybdenum content (2 to 3%) increases resistance to pitting and crevice corrosion, and copper (3 to 4%) provides resistance to sulfuric acid. Other important examples of high-alloy stainless steels are the 6% Mo superaustenitic stainless steels (Fig. 1) and high-nickel-content grades for heat-resistant applications.

Martensitic Stainless Steels. With lower chromium levels and relatively high carbon levels, it is possible to obtain austenite at elevated temperatures and then, with accelerated cooling, to transform this austenite to martensite, which has a body-centered tetragonal structure. Just as with plain carbon and low-alloy steels, this strong, brittle martensite can be tempered to favorable combinations of high strength and adequate toughness. Because of the ferrite-stabilizing character of chromium, the total chromium content, and thus the corrosion resistance, of the martensitic grades is somewhat limited. In recent years, nitrogen, nickel, and molybdenum additions at somewhat lower carbon levels have produced martensitic stainless steels of improved toughness and corrosion resistance.

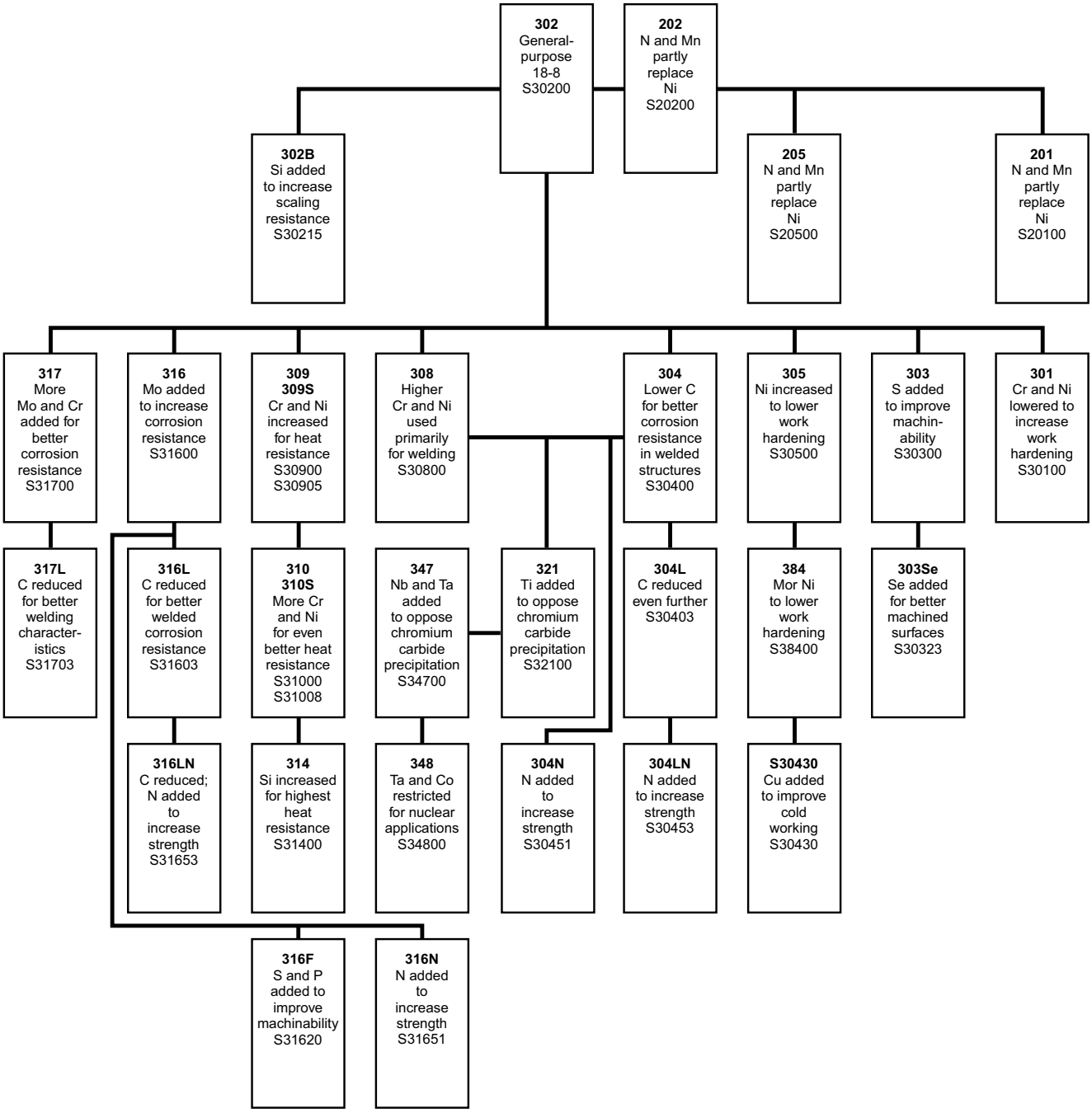


Fig. 3 Family relationships for standard AISI austenitic stainless steels

Table 6 Compositions of some proprietary and nonstandard stainless steels

UNS designation	Common name	Composition, %(a)								
		C	Mn	P	S	Si	Cr	Ni	Mo	Others
Austenitic grades										
S24100	18Cr-2Ni-12Mn	0.15	11.0–14.0	0.060	0.03	1.00	16.50–19.50	0.5–2.50	…	0.2–0.45N
S20910	Nitronic 50 (22-13-5)	0.06	4.0–6.0	0.040	0.03	1.00	20.50–23.50	11.50–13.50	1.50–3.00	0.1–0.3Nb, 0.2–0.4N, 0.1–0.3V
S30345	303 Al MODIFIED	0.15	2.00	0.050	0.11–0.16	1.00	17.00–19.00	8.00–10.00	0.40–0.60	0.60–1.00Al
	302BV(b)	0.11	1.75	0.03	0.14	0.35	17.75	9.00	0.50	0.75Al
	302 HQ–FM	0.06	2.00	0.04	0.14	1.00	16.00–19.00	9.00–11.00	…	1.3–2.4Cu
S30430	302 HQ	0.10	2.00	0.045	0.03	1.00	17.00–19.00	8.00–10.00	…	3.0–4.0Cu
S30453	304LN	0.03	2.00	0.045	0.03	1.00	18.00–20.00	8.00–12.00	…	0.1–0.16N
S31653	316LN	0.03	2.00	0.045	0.03	1.00	16.00–18.00	10.00–14.00	2.00–3.00	0.1–0.16N
S31753	317LN	0.03	2.00	0.045	0.30	1.00	18.00–20.00	11.00–15.00	3.00–4.00	0.1–0.2N
S31725	317LM	0.03	2.00	0.045	0.03	0.075	18.00–20.00	13.00–17.00	4.00–5.00	0.1N, 0.75Cu
	317LMN	0.03	2.00	0.045	0.03	0.075	18.00–20.00	13.00–17.00	4.00–5.00	0.1–0.2N
N08904	904L	0.02	2.00	0.045	0.035	1.00	19.00–23.00	23.0–28.0	4.00–5.00	1.0–2.0Cu
N08700	JS700	0.04	2.00	0.04	0.03	1.00	19.00–23.00	24.0–26.0	4.3–5.0	0.5Cu, Nb: (8 × C)–1.00, 0.005Pb, 0.035Sn
	JS777	0.025	1.70	0.03	0.03	0.50	19.00–23.00	24.0–26.0	4.00–5.00	2.10Cu, 0.25Nb
N08020	20Cb-3	0.07	2.00	0.045	0.035	1.00	19.00–21.00	32.00–38.00	2.00–3.00	3.0–4.0Cu, (8 × C)Nb
N08024	20Mo-4	0.03	1.00	0.035	0.035	0.50	22.5–25.00	35.00–40.00	3.50–5.00	0.5–1.5Cu, 0.15–0.35Nb
N08026	20Mo-6	0.03	1.00	0.03	0.03	0.50	22.00–26.00	33.00–37.20	5.00–6.70	2.0–4.0Cu
N08028	Alloy 28	0.03	2.50	0.03	0.03	1.00	26.00–28.00	29.5–32.5	3.0–4.0	0.6–1.4Cu
N08367	AL–6 × N	0.03	2.0	0.04	0.03	1.00	20.0–22.0	23.50–25.50	6.0–7.0	0.18–0.25N
S31254	254SMO	0.02	1.00	0.03	0.01	0.80	19.50–20.50	17.50–18.50	6.0–6.5	0.5–1.0Cu, 0.18–0.22N

(a) Maximum unless otherwise indicated; all compositions contain balance of iron. (b) Nominal composition

Table 7 lists the compositions of both standard (AISI) and representative nonstandard martensitic stainless steel grades. Figure 4 shows the effects of alloying on the properties and processing of the standard grades.

The duplex stainless steels can be thought of as chromium-molybdenum ferritic stainless steels to which sufficient austenite stabilizers have been added to produce steels in which a balance of ferrite and austenite is present at room temperature. Such grades can have the high chromium and molybdenum responsible for the excellent corrosion resistance of ferritic stainless steels as well as the favorable mechanical properties of austenitic stainless steels. In fact, the duplex grades with about equal amounts of ferrite and austenite have excellent toughness and their strength exceeds either phase present singly.

First-generation duplex grades, such as AISI type 329, achieved this phase balance primarily by nickel additions. These early duplex grades have superior properties in the annealed condition, but segregation of chromium and molybdenum between the two phases as re-formed after welding often significantly reduced corrosion resistance. The addition of nitrogen to the second generation of duplex grades restores the phase balance more rapidly and minimizes chromium and molybdenum segregation without annealing. The newer duplex grades combine high strength, good

Table 7 Chemical compositions of martensitic stainless steels

UNS No.	Type/ designation	Composition(a), %							
		C	Mn	Si	Cr	Ni	P	S	Other
Standard (AISI) grades									
S40300	403	0.15	1.00	0.50	11.5–13.0	…	0.04	0.03	…
S41000	410	0.15	1.00	1.00	11.5–13.5	…	0.04	0.03	…
S41400	414	0.15	1.00	1.00	11.5–13.5	1.25–2.50	0.04	0.03	…
S41600	416	0.15	1.25	1.00	12.0–14.0	…	0.06	0.15 min	0.6 Mo(b)
S41623	416Se	0.15	1.25	1.00	12.0–14.0	…	0.06	0.06	0.15 min Se
S42000	420	0.15 min	1.00	1.00	12.0–14.0	…	0.04	0.03	…
S42020	420F	0.15 min	1.25	1.00	12.0–14.0	…	0.06	0.15 min	0.6 Mo(b)
S42200	422	0.20–0.25	1.00	0.75	11.5–13.5	0.5–1.0	0.04	0.03	0.75–1.25 Mo; 0.75–1.25 W; 0.15–0.3 V
S43100	431	0.20	1.00	1.00	15.0–17.0	1.25–2.50	0.04	0.03	…
S44002	440A	0.60–0.75	1.00	1.00	16.0–18.0	…	0.04	0.03	0.75 Mo
S44003	440B	0.75–0.95	1.00	1.00	16.0–18.0	…	0.04	0.03	0.75 Mo
S44004	440C	0.95–1.20	1.00	1.00	16.0–18.0	…	0.04	0.03	0.75 Mo
Nonstandard grades									
S41008	Type 410S	0.08	1.00	1.00	11.5–13.5	0.60	0.040	0.030	…
S41040	Type 410Cb (XM-30)	0.15	1.00	1.00	11.5–13.5	…	0.040	0.030	0.05–0.20 Nb
DIN 1.4935(c)	HT9	0.17–0.23	0.30–0.80	0.10–0.50	11.0–12.5	0.30–0.80	0.035	0.035	0.80–1.20 Mo; 0.25–0.35 V; 0.4–0.6 W
S41500	Moly Ascoloy	0.05	0.50–1.00	0.60	11.5–14.0	3.50–5.50	0.030	0.030	0.50–1.00 Mo
S41610	416 Plus X (XM-6)	0.15	1.5–2.5	1.00	12.0–14.0	…	0.060	0.15 min	0.6 Mo
S41800	Greek Ascoloy	0.15–0.20	0.50	0.50	12.0–14.0	1.8–2.2	0.040	0.030	2.5–3.5 W
S42010	TrimRite	0.15–0.30	1.00	1.00	13.5–15.0	0.25–1.00	0.040	0.030	0.40–1.00 Mo
S42023	Type 429 F Se	0.3–0.4	1.25	1.00	12.0–14.0	…	0.060	0.060	0.15 min Se; 0.6 Zr; 0.6 Cu
S42300	Lapelloy	0.27–0.32	0.95–1.35	0.50	11.0–12.0	0.50	0.025	0.025	2.5–3.0 Mo; 0.2–0.3 V
S42670	Pyrowear 675	0.05–0.09	0.50–1.00	0.10–0.70	12.0–14.0	2.00–3.00	0.015	0.010	4.00–7.00 Co; 1.50–2.50 Mo; 0.40–0.80 V
S42700	BG42	1.10–1.20	0.30–0.60	0.20–0.40	14.0–15.0	0.40	0.015	0.010	3.75–4.25 Mo; 0.35 Cu; 1.10–1.30 V
S44020	Type 440F	0.95–1.20	1.25	1.00	16.0–18.0	0.75	0.040	0.10–0.35	0.08 N
S44023	Type 440F Se	0.95–1.20	1.25	1.00	16.0–18.0	0.75	0.040	0.030	0.15 min Se; 0.60 Mo

(a) Single values are maximum values unless otherwise indicated. (b) Optional. (c) German (DIN) specification

toughness, high corrosion resistance, good resistance to chloride SCC, and good production economy in the heavier product forms.

Table 8 lists the duplex stainless steels currently covered by UNS designations. There are three basic categories of duplex stainless steels—low-alloy, intermediate alloy, and highly alloyed- (or "superduplex") grades—grouped according to their pitting resistance equivalent number (PREN), which is derived from:

$$\mathrm{PREN} = \%\mathrm{Cr} + 3.3 \times (\%\mathrm{Mo}) + 16 \times (\%\mathrm{N})$$

When tungsten is introduced into duplex grades, a modified form of the PREN relationship has been proposed, namely:

$$\mathrm{PREN_w} = \%\mathrm{Cr} + 3.3 \times (\%\mathrm{Mo} + 0.5 \times \%\mathrm{W}) + 16 \times (\%\mathrm{N})$$

Low-alloy duplex grades have PRENs of <32, intermediate alloy grades have PRENs between 32 and 39. Superduplex grades have PRENs ≥40.

The precipitation-hardening stainless steels are chromium-nickel grades that can be hardened by an aging treatment at a moderately elevated temperature. These grades may have austenitic, semiaustenitic, or martensitic crystal structures. Semiaustenitic structures are transformed from a readily formable austenite to martensite by a high-temperature austenite-conditioning treatment. Some grades use cold work to facilitate transformation. The strengthening effect is achieved by adding such elements as copper and aluminum, which form intermetallic precipitates during aging. In the solution-annealed condition, these grades have properties similar to those of the austenitic grades and are therefore readily

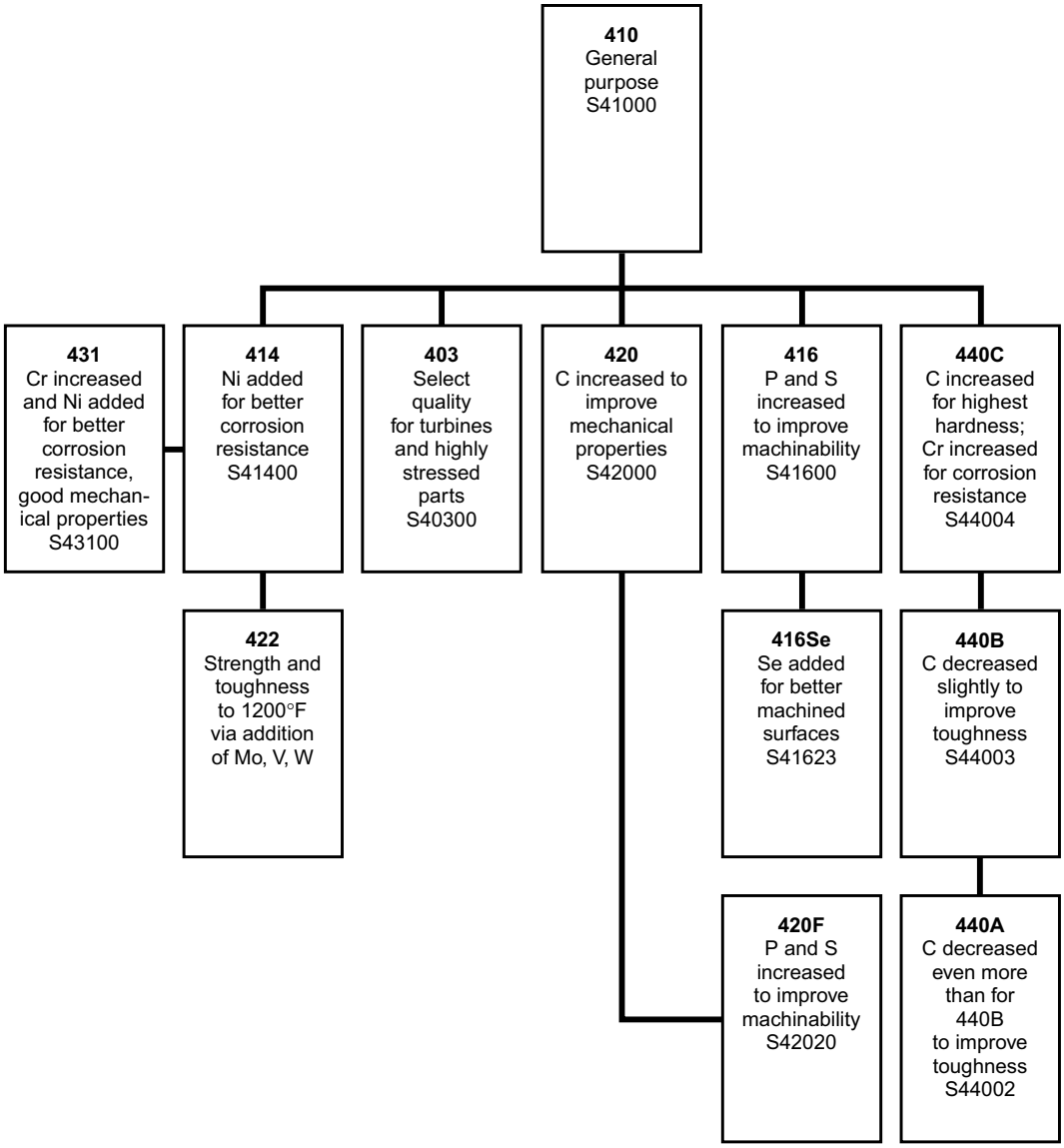


Fig. 4 Family relationships for standard martensitic stainless steels

Table 8 Composition and pitting resistance equivalent numbers (PREN) of wrought duplex stainless steels covered by UNS designations

UNS No.	Common designation	Composition(a), wt%											PREN
		C	Mn	S	P	Si	Cr	Ni	Mo	Cu	W	N_2	
Low-alloy grades (PREN <32)													
S31500	3RE60	0.03	1.2–2.0	0.03	0.03	1.4–2.0	18.0–19.0	4.25–5.25	2.5–3.0	…	…	0.05–0.10	28
S32001	19D	0.03	4.0–6.0	0.03	0.04	1.00	19.5–21.5	1.0–3.0	0.60	1.00	…	0.05–0.17	23.6
S32304	2304	0.03	2.5	0.04	0.04	1.00	21.5–24.5	3.0–5.5	0.05–0.60	0.05–0.60	…	0.05–0.20	25
S32404	UR50	0.04	2.0	0.010	0.030	1.00	20.5–22.5	5.5–8.5	2.0–3.0	1.0–2.0	…	0.20	31
Intermediate-alloy grades (PREN 32–39)													
S31200	44LN	0.03	2.00	0.03	0.045	1.00	24.0–26.0	5.5–6.5	1.2–2.0	…	…	0.14–2.0	33
S31260	DP3	0.03	1.00	0.030	0.030	0.75	24.0–26.0	5.5–7.5	2.5–3.5	0.20–0.80	0.10–0.50	0.10–0.30	38
S31803	2205	0.03	2.00	0.02	0.03	1.00	21.0–23.0	4.5–6.5	2.5–3.5	…	…	0.08–0.20	34
S32205	2205+	0.03	2.00	0.02	0.030	1.00	22.0–23.0	4.5–6.5	3.0–3.5	…	…	0.14–0.20	35–36
S32550	255	0.03	1.5	0.03	0.04	1.00	24.0–27.0	4.5–6.5	2.9–3.9	1.5–2.5	…	0.10–0.25	38
S32900	10RE51	0.06	1.00	0.03	0.04	0.75	23.0–28.0	2.5–5.0	1.0–2.0	…	…	…	33
S32950	7-Mo Plus	0.03	2.00	0.01	0.035	0.60	26.0–29.0	3.5–5.20	1.0–0.5	…	…	0.15–0.35	35
Superduplex grades (PREN ≥40)													
S32520	UR52N+	0.03	1.5	0.020	0.035	0.80	24.0–26.0	5.5–8.0	3.0–5.0	0.50–3.00	…	0.20–0.35	41
S32750	2507	0.03	1.2	0.02	0.035	1.00	24.0–26.0	6.0–8.0	3.0–5.0	0.5	…	0.24–0.32	≥41
S32760	Zeron 100	0.03	1.0	0.01	0.03	1.00	24.0–26.0	6.0–8.0	3.0–4.0	0.5–1.0	0.5–1.0	0.30	≥40
S32906	Safurex	0.030	0.80–1.50	0.03	0.03	0.50	28.0–30.0	5.8–7.5	1.50–2.60	0.80	…	0.30–0.40	≥41
S39274	DP3W	0.030	1.0	0.020	0.030	0.80	24.0–26.0	6.0–8.0	2.50–3.50	0.20–0.80	1.50–2.50	0.24–0.32	42(b)
S39277	AF918	0.025	…	0.002	0.025	0.80	24.0–26.0	4.5–6.5	3.0–4.0	1.2–2.0	0.80–1.20	0.23–0.33	≥41

(a) Single values are maximum. (b) $PREN_w$ value

formed. Hardening is achieved after fabrication within a relatively short time at 480 to 620 °C (900 to 1150 °F). The precipitation-hardened grades must not be subjected to further exposure to elevated temperature by welding or environment, because the strengthening can be lost by overaging of the precipitates. The precipitation-hardened grades have corrosion resistance generally comparable to that of the chromium-nickel grades.

While the AISI numbering system (600 series) exists for some of these steels, they are more frequently described by their UNS designation or proprietary alloy name. Table 9 lists the chemical compositions of the common PH stainless steels.

Effects of Alloying on Corrosion Behavior

With increasing chromium content and the presence or absence of some ten to fifteen other alloying elements, stainless steels can provide an extraordinary range of corrosion resistance. Various grades have been used for many years in environments as mild as open air in architectural applications and as severe as the chemically active product streams in the chemical processing industries.

Stainless steels are susceptible to several forms of localized corrosive attack including:

- Pitting corrosion
- Crevice corrosion
- Sensitization and intergranular corrosion
- Stress-corrosion cracking

The avoidance of such localized corrosion is the focus of most of the effort involved in selecting stainless steels. As such, the primary focus of this article is on the alloying elements that help mitigate these forms of corrosion. Information regarding mechanical and electrical properties, wear resistance, and processing characteristics of stainless steels can be found in a number of excellent texts listed in the Selected References at the conclusion of this article.

General Effects of the Major Alloying Elements

Chromium is the one element essential in forming the passive film. Other elements can influence the effectiveness of chromium in forming or maintaining the film, but no other element can, by itself, create the properties of stainless steel. The film is first observed at about 10.5% Cr, but it is rather weak at this composition and affords only mild atmospheric protection. Increasing the chromium content to 17 to 20%, as typical of

Table 9 Compositions of PH stainless steels covered by UNS designations

			Composition(b), %									
UNS No.	AISI	Name(a)	C	Cr	Ni	Mn	Si	Ti	Al	Mo	N	Others
Martensitic grades												
S17600	635	Stainless W	0.08	15.0–17.5	6.0–7.5	1.0	1.0	0.4–1.2	0.40	…	…	…
S17400	630	17.4PH	0.07	15.5–17.5	3.0–5.0	1.0	1.0	…	…	…	…	0.15–0.45 Nb, 3.0-5.0 Cu
S15500	…	15-5 PH (XM-12)	0.07	14.0–15.5	3.5–5.5	1.0	1.0	…	…	…	…	0.15–0.45 Nb, 2.5–4.5 Cu
S16600	…	Croloy 16-6 PH	0.045	15.0–16.0	7.0–8.0	0.70–0.90	0.5	0.3–0.5	0.25–0.40	…	…	…
S45000	…	Custom 450 (XM-25)	0.05	14.0–16.0	5.0–7.0	1.0	1.0	…	…	0.5–1.0	…	1.25–1.75 Cu, Nb = 8 × C min
S45500	…	Custom 455 (XM-16)	0.05	11.0–12.5	7.5–9.5	0.50	0.50	…	…	0.50	…	0.10–0.50 Nb, 1.5–2.5 Cu
S13800	…	PH 13-8 Mo (XM-13)	0.05	12.25–13.25	7.5–8.5	0.20	0.10	…	0.90–1.35 Al	2.0–2.5	0.01	…
S36200	…	Almar 362 (XM-9)	0.05	14.0–14.5	6.25–7.0	0.50	0.30	0.55–0.9	…	…	…	…
Semiaustenitic grades												
S17700	631	17-7 PH	0.09	16.0–18.0	6.5–7.75	1.0	1.0	…	0.75–1.5	…	…	…
S15700	632	PH 15-7 Mo	0.09	14.0–16.0	6.5–7.25	1.0	1.0	…	0.75–1.5	2.0–3.0	…	…
S35000	633	AM-350	0.07–0.11	16.0–17.0	4.0–5.0	0.50–1.25	0.50	…	…	2.5–3.25	0.07–0.13	…
S35500	634	AM-355	0.10–0.15	15.0–16.0	4.0–5.0	0.50–1.25	0.50	…	…	2.5–3.25	0.07–0.13	…
S14800	…	PH 14-8 Mo (XM-24)	0.05	13.75–15.0	7.5–8.75	1.0	1.0	…	0.75–1.5	2.0–3.0	…	…
Austenitic grades												
S66286	660	A-286	0.08	13.5–16.0	24.0–27.0	2.0	1.0	1.9–2.35	0.35	1.0–1.5	…	0.10–0.50 V, 0.001–0.01 B

(a) Designations in parentheses are ASTM designations. (b) Single values are maximum unless otherwise indicated.

the austenitic stainless steels, or to 26 to 29%, as possible in the newer ferritic stainless steels, greatly increases the stability of the passive film. However, higher chromium may adversely affect mechanical properties, fabricability, weldability, or suitability for applications involving certain thermal exposures. Therefore, it is often more efficient to improve corrosion resistance by altering other elements, with or without some increase in chromium.

Nickel in sufficient quantities, will stabilize the austenitic structure; this greatly enhances mechanical properties and fabrication characteristics. Nickel is effective in promoting repassivation, especially in reducing environments. Nickel is particularly useful in resisting corrosion in mineral acids. Increasing nickel content to about 8 to 10% decreases resistance to SCC, but further increases begin to restore SCC resistance. Resistance to SCC in most service environments is achieved at about 30% Ni. In the newer ferritic grades, in which the nickel addition is less than that required to destabilize the ferritic phase, there are still substantial effects. In this range, nickel increases yield strength, toughness, and resistance to reducing acids, but it makes the ferritic grades susceptible to SCC in concentrated magnesium chloride ($MgCl_2$) solutions.

Manganese in moderate quantities and in association with nickel additions will perform many of the functions attributed to nickel. However, total replacement of nickel by manganese is not practical. Very high manganese steels have some unusual and useful mechanical properties, such as resistance to galling. Manganese interacts with sulfur in stainless steels to form manganese sulfides. The morphology and composition of these sulfides can have substantial effects on corrosion resistance, especially pitting resistance.

Molybdenum in combination with chromium is very effective in terms of stabilizing the passive film in the presence of chlorides. Molybdenum is especially effective in increasing resistance to the initiation of pitting and crevice corrosion.

Carbon is useful to the extent that it permits hardenability by heat treatment, which is the basis of the martensitic grades, and that it provides strength in the high-temperature applications of stainless steels. In all other applications, carbon is detrimental to corrosion resistance through its reaction with chromium. In the ferritic grades, carbon is also extremely detrimental to toughness.

Nitrogen is beneficial to austenitic stainless steels in that it enhances pitting resistance, retards the formation of the chromium-molybdenum σ phase, and strengthens the steel. Nitrogen is essential in the newer duplex grades for increasing the austenite content, diminishing chromium and

molybdenum segregation, and for raising the corrosion resistance of the austenitic phase. Nitrogen is highly detrimental to the mechanical properties of the ferritic grades and must be treated as comparable to carbon when a stabilizing element is added to the steel.

Effects of Alloying on Pitting Corrosion (Ref 1)

Pitting is a localized attack that can produce penetration of a stainless steel with almost negligible weight loss to the total structure. Pitting is associated with a local discontinuity of the passive film. It can be a mechanical imperfection, such as an inclusion or surface damage, or it can be a local chemical breakdown of the film. Chloride is the most common agent for initiation of pitting. Once a pit is formed, it in effect becomes a crevice; the local chemical environment is substantially more aggressive than the bulk environment. This explains why very high flow rates over a stainless steel surface tend to reduce pitting corrosion; the high flow rate prevents the concentration of corrosive species in the pit. The stability of the passive film with respect to resistance to pitting initiation is controlled primarily by chromium and molybdenum. Minor alloying elements can also have an important effect by influencing the amount and type of inclusions (for example, sulfides) in the steel that can act as pitting sites.

Austenitic Stainless Steels. Both the major alloying elements of austenitic stainless steels, chromium and nickel, increase resistance to pitting. Other important alloying elements that increase resistance to pitting are molybdenum and nitrogen.

In Fig. 5 the relationship between pitting resistance and molybdenum content is clearly seen. The highest critical pitting temperature is exhibited by the highest molybdenum-containing alloys tested, namely, 254SMO and AL-6X. However, the amount of molybdenum that can be added to austenitic stainless steels is limited by the onset of sigma and chi phase precipitation, which embrittle the alloys and reduce pitting resistance. Therefore, the extent to which pitting resistance can be improved by molybdenum additions is limited.

Although nitrogen additions to molybdenum-free austenitic stainless steels improve pitting resistance, the effect of nitrogen is significantly enhanced in the presence of molybdenum. The mechanisms providing these benefits are complex, involving the enrichment of chromium below the passive film, the formation of a nitride layer at the film-metal interface, and the formation of a ferrous molybdate layer in the outer regions of the passive film. The combined beneficial effects of nitrogen and molybdenum are used in the 200-series alloys containing manganese and in the superaustenitics containing 6% Mo.

The effects of various other elements on the pitting resistance of austenitic stainless steels in chloride solutions is summarized in Fig. 6. As

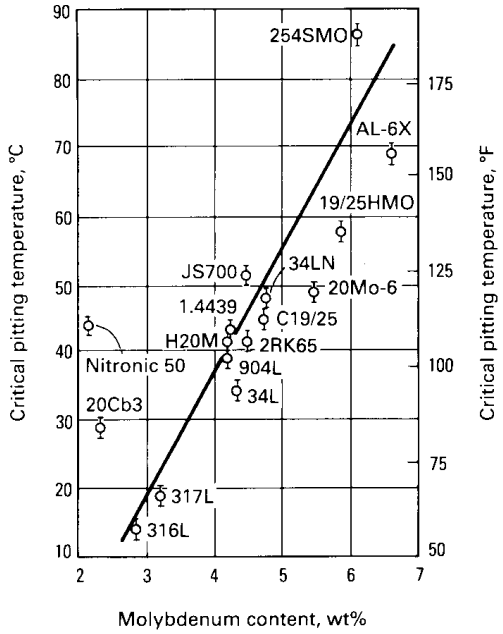


Fig. 5 Effect of molybdenum content on the $FeCl_3$ critical pitting temperature of commercial stainless steels. The more resistant steels have tighter critical pitting temperatures.

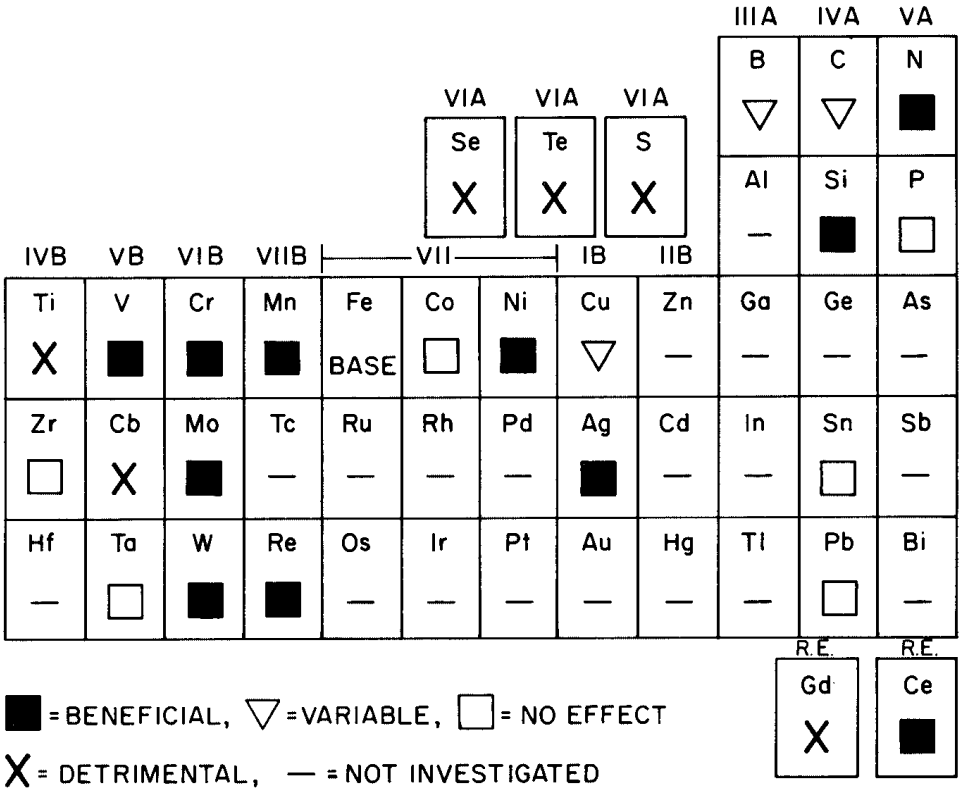


Fig. 6 Effect of various elements on resistance of stainless steels to pitting in chloride solutions. Source: Ref 1

this figure shows, other beneficial alloying elements include vanadium, silicon, and tungsten. More detailed information can be found in Ref 1.

Ferritic Stainless Steels. In considering the pitting resistance of ferritic stainless steels, a distinction must be made between the standard grades (e.g., types 430 and 434) and the proprietary superferritic grades (e.g., 29-4C, Sea-Cure, and Monit). The superferritics such as 29-4 have very high pitting resistance in chloride solutions, whereas the 400-grades exhibit relatively low pitting potentials.

In superferritics the very high chromium contents together with about 4% molybdenum would be expected to give a highly pitting-resistant structure, since both of these alloying elements significantly raise the pitting potential in the noble direction. Studies of high-purity, inclusion-free ferritic stainless steels have shown that increasing the chromium content from 18% to 28% results in thinner passive films and increased chromium enrichment within the films. The exact mechanism by which molybdenum improves pitting resistance in ferritic stainless steel is still not understood despite a significant research effort to resolve this question.

The effects of other alloying elements have been explored for the lower-chromium ferritic stainless steels, with tungsten, vanadium, and silicon having been identified as beneficial for both 13%Cr and 24%Cr ferritics. Other studies have shown that the beneficial chromium plus molybdenum effect is synergistic (Fig. 7). Thus, while molybdenum additions are

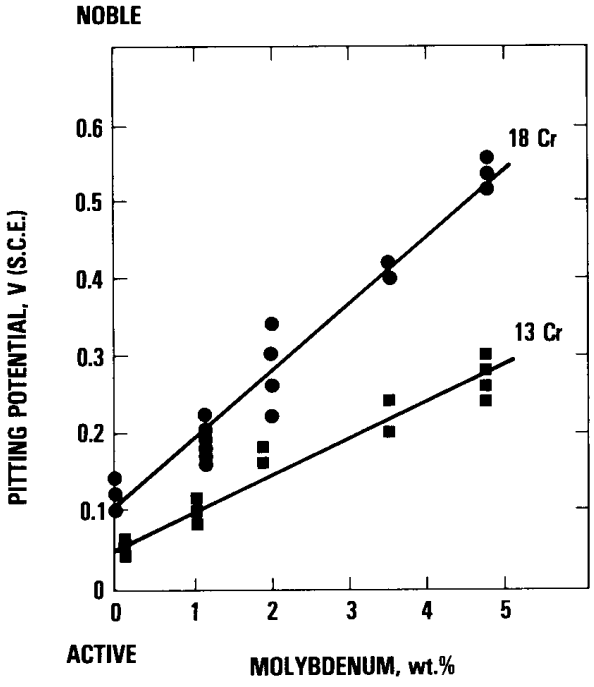


Fig. 7 Pitting potentials of vacuum-melted 13%Cr and 18%Cr ferritic stainless steels in 1*M* NaCl solution at 25°C (75°F). Source: Ref 1

beneficial for both the 13%Cr and 18%Cr ferritics, at the higher chromium content the increase in pitting potential in the noble direction caused by each increment of molybdenum is considerably greater (Fig. 7).

It has also been shown that for a given carbon plus nitrogen level, the addition of titanium is beneficial and that the titanium benefit increases with increasing molybdenum content (Fig. 8). It is also evident from Fig. 8 that the pitting potentials of alloys with low carbon plus nitrogen levels are more noble than those with higher carbon plus nitrogen levels.

Duplex stainless steels usually contain austenite and ferrite in a 50:50 ratio. Therefore the alloying elements that improve the pitting resistance of both austenitic and ferritic stainless steels will also improve the pitting resistance of duplex stainless steels. Thus, chromium, molybdenum, and nitrogen are used to provide pitting resistance, whereas nickel is used to adjust the austenite and ferrite contents to the 50:50 ratio. Since both chromium and molybdenum promote the formation of the embrittling sigma phase, chromium is usually kept in the range 22 to 26% and molybdenum is kept in the range 2 to 5%.

Other alloying additions that increase pitting resistance are copper, tungsten, and silicon. Carbon is detrimental to pitting resistance at low nitrogen contents, but has no effect at high nitrogen levels.

Martensitic and Precipitation-Hardening Stainless Steels. Martensitic stainless steels exhibit pitting potentials in aqueous chloride solutions that are considerably less noble than those exhibited by type 304 stainless steel (Table 10). Their pitting resistance in humid atmospheres

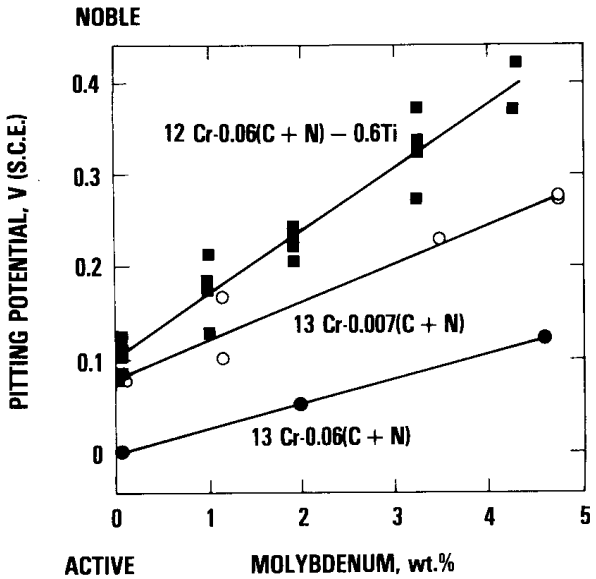


Fig. 8 Effect of titanium and carbon plus nitrogen content on pitting potentials of ferritic stainless steels in 1*M* NaCl solution at 25 °C (75 °F). Source: Ref 1

increases with increasing chromium content, and alloying with molybdenum is beneficial.

The higher chromium martensitic precipitation-hardening stainless steels such as Custom 450 (15%Cr) and 17-4 PH (16%Cr) exhibit pitting potentials that are slightly less noble than those of type 304 (18%Cr), as noted in Table 10.

Crevice Corrosion (Ref 2)

Crevice corrosion can be considered a severe form of pitting. Any crevice, whether the result of a metal-to-metal joint, a gasket, fouling, or deposits, tends to restrict oxygen access, resulting in attack. In practice, it is extremely difficult to prevent all crevices, but every effort should be made to do so. Higher-chromium and, in particular, higher-molybdenum grades are more resistant to crevice attack. Just as there is a critical pitting temperature for a particular environment, there is also a critical crevice temperature (CCT). This temperature is specific to the geometry and nature of the crevice and to the precise corrosion environment for each grade. The CCT can be useful in selecting an adequately resistant grade for particular applications.

Austenitic Stainless Steels. As in pitting resistance, the major alloying elements, nickel and chromium, increase resistance to crevice corrosion. Other important elements that increase resistance to crevice corrosion are molybdenum, nitrogen in the presence of molybdenum, silicon, and copper. Of these alloying elements, molybdenum provides the greatest improvement in crevice corrosion resistance. Figure 9 shows the effect of molybdenum additions on the CCT of various stainless steels.

For ferritic stainless steels, increasing the chromium and molybdenum contents result in increased resistance to crevice corrosion. The beneficial effect of increasing chromium content can be inferred from the data

Table 10 Pitting potentials for various stainless steels in 3.5% NaCl solution, pH = 5, at 25 °C (75 °F), and weight loss in 5% $FeCl_3$ at 24 °C after 3 h exposure

Steel	Category	Heat treatment	Pitting potential (volts vs. SCE)	Weight loss (mg)
Type 430	Ferritic	Annealed	−0.08	151
Type 410	Martensitic	Annealed	−0.06	…
17-4 PH	PH	Annealed	+0.17	…
		Aged 482 °C	+0.16	57
		Aged 621 °C	+0.15	62
Custom 450	PH	Annealed	+0.22	35
		Aged 482 °C	+0.20	36
		Aged 621 °C	+0.16	39
Type 304	Austenitic	Annealed	+0.29	26

SCE, standard calomel electrode. PH, precipitation hardenable

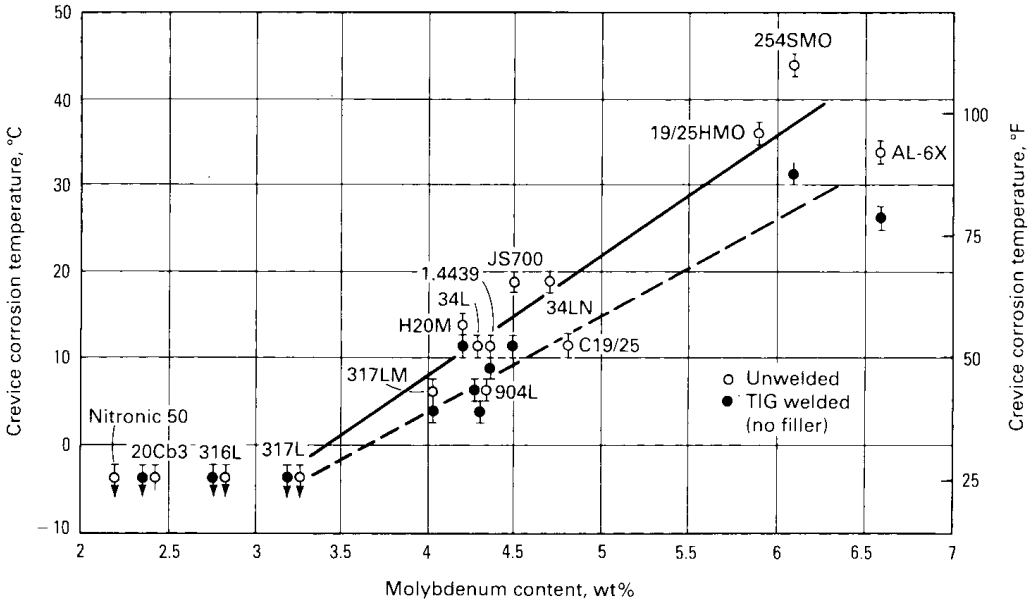


Fig. 9 Effect of molybdenum content on the crevice corrosion temperature of commercial stainless steels. The more resistant steels have higher crevice corrosion temperatures in the $FeCl_3$ test.

shown in Table 11, where it is seen that type 446 (26% Cr) is more resistant to crevice corrosion in seawater than type 430 (17.5% Cr).

The beneficial effect of increasing molybdenum content can be inferred from the data shown in Table 12. It can be seen that at a constant chromium level of 25%, increasing the molybdenum content from 0 to 5% results in a progressive increase in the temperature at which crevice attack is observed.

Duplex Stainless Steels. The data of Table 13 show that increasing molybdenum and nitrogen contents result in major increases in CCT. The observed beneficial effect of nitrogen supports the view that nitrogen both improves the crevice corrosion resistance of the austenite phase and reduces the partitioning of chromium, enabling a higher chromium content to be maintained in the austenite. Tungsten additions in the range 0.5–1.0% have been shown to improve the crevice corrosion resistance of duplex stainless steels.

Table 11 Probability of crevice corrosion initiation and maximum depth of attack of various stainless steels exposed for 30 days to seawater at 15 °C (60 °F): Multiple crevice technique, 120 crevices per material

Steel	Composition, wt%			Probability of crevice corrosion initiation, %	Maximum depth of attack, mm
	Cr	Ni	Mo		
Type 430	17.5	0.26	0.02	52	1.17
Type 446	25.9	0.03	…	7	0.23
Type 304	18.4	9.4	…	13	0.28
Type 316	17.5	13.5	2.3	2	0.03
Type 317	19.0	13.5	3.8	0	0

Table 12 Crevice corrosion tests in 10% $FeCl_3 \cdot 6H_2O$ + 0.1 N HCl: weight loss in mg/dm² per day computed over entire coupon area (test duration in days given in parentheses)

Nominal composition, wt%	Test temperature (°C)			
	25	30	40	50
Fe–20Cr–2Mo	64 (1)	197 (1)	…	…
Fe–22.5Cr–2Mo	0 (7)	3 (1)	…	…
Fe–25Cr	670 (2.5)	…	…	…
Fe–26Cr–1Mo	0 (23)	6.2 (4)	229 (1)	764 (1)
Fe–25Cr–2Mo	0 (7)	0 (1)	0 (1)	210 (1)
Fe–28Cr–2Mo	0 (7)	0 (4)	0 (1)	13 (1)
Fe–25Cr–3.5Mo	0 (24)	…	…	7 (5)
Fe–25Cr–5Mo	0 (63)	…	…	0 (11)

Table 13 Listing of CCTs in 10% ferric chloride (ASTM G-48, Method B) for a number of commercial duplex stainless steels

Stainless steel	Cr,%	Ni,%	Mo,%	N,% (max)	CCT (°C)
Type 329	26	4.5	1.5	—	5
44 LN	25	6	1.7	0.2	5
DP-3	25	7	3	0.3	10
7-Mo Plus	26.5	4.8	1.5	0.35	15
2205	22	5	3	0.2	17.5
Ferralium 255	25	6	3	0.25	22.5
SAF 2507	25	7	4	0.32	37.5
Zeron 100	25	7	4	0.3	40 (min)

Note: Zeron 100 also contains 0.7% W, and DP-3 contains 0.5% W.

Sensitization and Intergranular Corrosion

Sensitization, or carbide precipitation at grain boundaries, can occur when austenitic stainless steels are heated for a period of time in the range of about 425 to 870 °C (800 to 1600 °F). Time at temperature will determine the amount of carbide precipitation. When the chromium carbides precipitate in grain boundaries, the area immediately adjacent is depleted of chromium. When the precipitation is relatively continuous, the depletion renders the stainless steel susceptible to intergranular corrosion, which is the dissolution of the low-chromium layer or envelope surrounding each grain. Sensitization also lowers resistance to other forms of corrosion, such as pitting, crevice corrosion, and SCC.

Time-temperature-sensitization curves are available that provide guidance for avoiding sensitization and illustrate the effect of carbon content on this phenomenon (Fig. 10). The curves shown in Fig. 10 indicate that a type 304 stainless steel with 0.062% C would have to cool below 595 °C (1100 °F) within about 5 min to avoid sensitization, but a type 304L with 0.030% C could take about 20 h to cool below 480 °C (900 °F) without becoming sensitized. These curves are general guidelines and should be verified before they are applied to various types of stainless steels.

Another method of avoiding sensitization is to use stabilized steels. Such stainless steels contain titanium and/or niobium. These elements

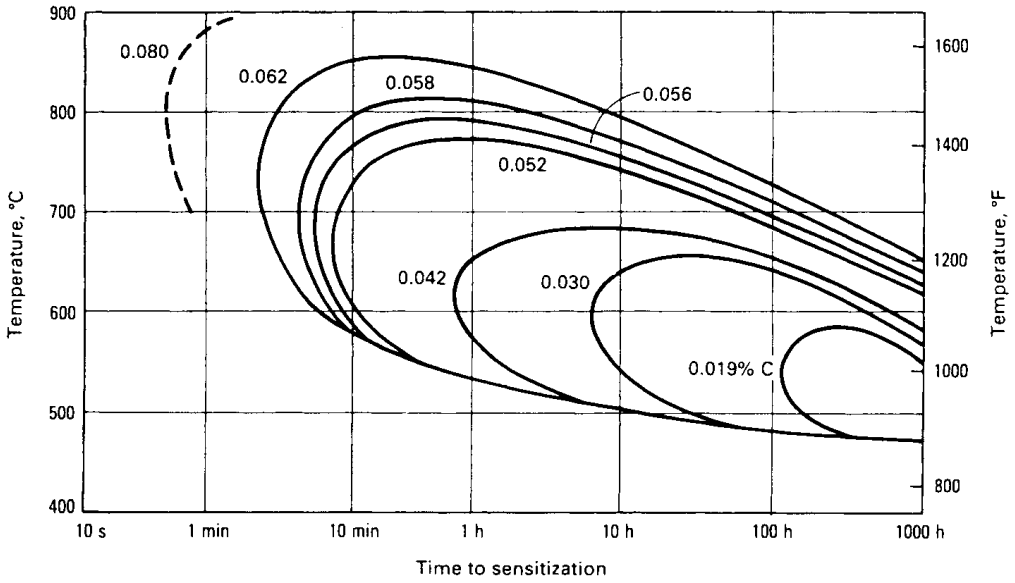


Fig. 10 Time-temperature-sensitization curves for type 304 stainless steel in a mixture of $CuSO_4$ and H_2SO_4 containing free copper. Curves show the times required for carbide precipitation in steels with various carbon contents. Carbides precipitate in the areas to the right of the various carbon content curves.

have an affinity for carbon and form carbides readily; this allows the chromium to remain in solution even for extremely long exposures to temperatures in the sensitizing range. Type 304L can avoid sensitization during the relatively brief exposure of welding, but it will be sensitized by long exposures.

Stress-Corrosion Cracking (Ref 3)

Stress-corrosion cracking is a corrosion mechanism in which the combination of a susceptible alloy, sustained tensile stress, and a particular environment leads to cracking of the metal. Stainless steels are particularly susceptible to SCC in chloride environments; temperature and the presence of oxygen tend to aggravate chloride SCC of stainless steels. More ferritic and duplex stainless steels are either immune or highly resistant to SCC. All austenitic grades, especially types 304 and 316, are susceptible to some degree. Most martensitic and precipitation-hardening steels are also particularly susceptible. Stress corrosion is difficult to detect while in progress (even when pervasive) and can lead to rapid catastrophic failures of pressurized equipment.

Austenitic Stainless Steels. There has been extensive research, often employing boiling magnesium chloride environments, on the effects of alloying additions on the chloride SCC resistance of stainless steels. Figure 11 summarizes the effects of various elements. It is evident from

Fig. 11 that many alloying additions appear to be detrimental to chloride SCC, but there are also those that can be categorized as *beneficial* and *variable.* Those designated *beneficial* in Fig. 11 are nickel, cadmium, zinc, silicon, beryllium, and copper. It should be emphasized that the beneficial effect of nickel relates only to austenitic stainless steels. When present in relatively small quantities in ferritic stainless steels, nickel is detrimental to chloride SCC resistance. The beneficial effect of nickel on chloride SCC resistance of austenitic stainless steels and higher alloys has been extensively studied and is well documented.

Figure 12 shows the effect of nickel content on the susceptibility to chloride SCC of stainless steel wire specimens tested in boiling magnesium chloride. The data of Fig. 12 suggest that very high nickel contents (about 50%) would be required for resistance to chloride SCC. This is at variance with general industrial experience, which is that chloride SCC is not usually observed at nickel contents at or above 42%. In fact, Alloy 825 (42% Ni), Alloy G (44% Ni), and 20Cb3 (33% Ni) are often specified for applications requiring resistance to chloride SCC. Recent evaluations

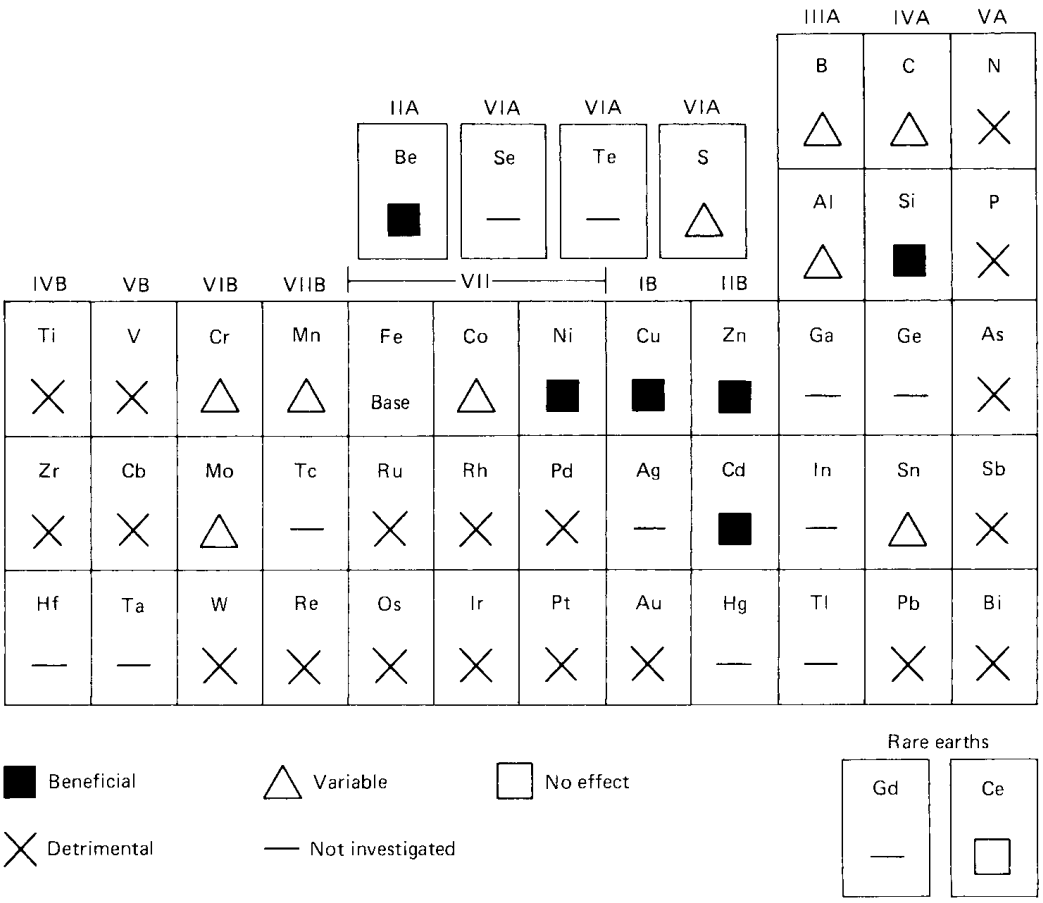


Fig. 11 Effect of various elements on resistance of austenitic stainless steels to stress-corrosion cracking in chloride solutions. Source: Ref 3

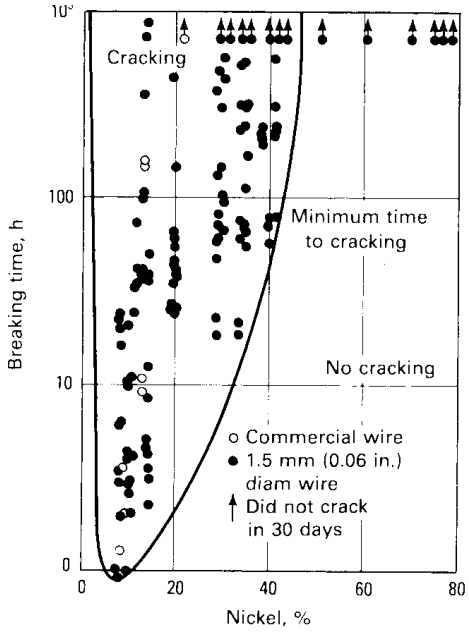


Fig. 12 Effect of nickel content on stress–corrosion cracking susceptibility of stainless steel wires containing 18 to 20% Cr in a magnesium chloride solution boiling at 154 °C (309 °F)

using precracked fracture-mechanics specimens support the view that magnesium chloride is a much more severe environment than sodium chloride (Fig. 13), and they suggest that the nickel level required for lack of susceptibility to SCC in sodium chloride may be between 30 and 40% (Fig. 14). In these tests, absence of crack propagation at a stress intensity of 60 MPa$\sqrt{m}$ (55 ksi$\sqrt{in.}$) is equated with resistance to SCC.

Additions of cadmium and zinc are also designated as beneficial (Fig. 11). Actually, there is very little information about the effects of these alloying elements. A 0.2% Cd addition to type 304 inhibited cracking in a vapor test that readily cracked type 304, and a 1% Zn addition to an Fe-20Cr-15Ni alloy led to a fivefold improvement in SCC resistance. Therefore, the designation of these elements as beneficial must be regarded as tentative.

Alloying with silicon has been shown to be beneficial to chloride SCC resistance in boiling 42% $MgCl_2$. However, other studies, summarized in Table 14, have shown that the beneficial effect of silicon noted in magnesium chloride tests is barely detectable, if at all, in sodium chloride solutions at higher temperatures. Beryllium and copper alloying additions have been shown to be beneficial, although the effect of copper is slight.

The elements designated in Fig. 11 as having a variable effect on chloride SCC can be divided into the three categories shown in Table 15. Boron, aluminum, and cobalt appear to be detrimental in small quantities but beneficial in larger amounts; tin and manganese appear to have no effect in certain ranges and beneficial or detrimental effects in other ranges; carbon and chromium show minimal effect on chloride SCC resistance. The effect of molybdenum appears to depend on the test

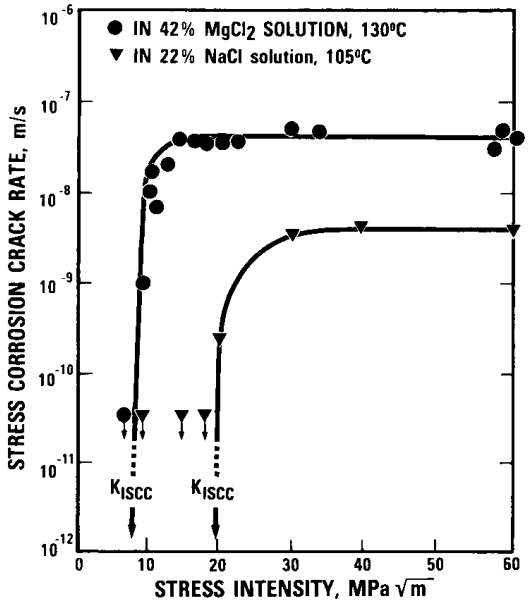


Fig. 13 Effect of stress intensity on the growth rate of stress-corrosion cracks in type 304L stainless steel exposed to magnesium chloride and sodium chloride solutions

environment. The magnesium chloride data suggest that molybdenum additions first decrease and then increase resistance to cracking, with a minimum resistance at about 1.5% Mo. No such pattern is in evidence in sodium chloride tests (Fig. 15), which show cracking resistance increasing with increasing molybdenum content.

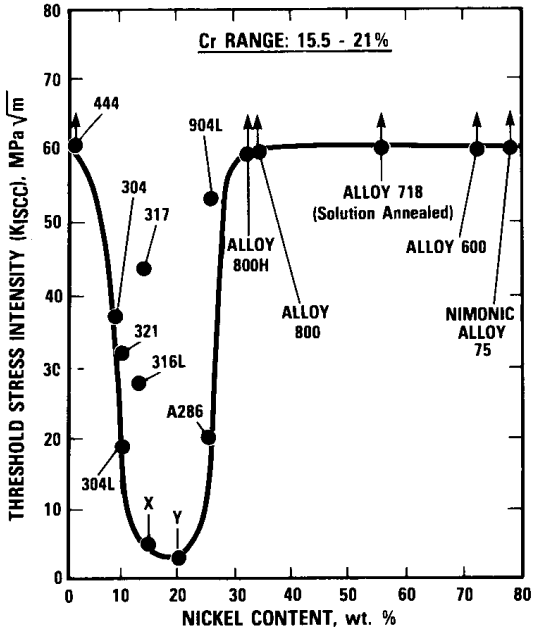


Fig. 14 Effect of nickel content on the stress-corrosion threshold stress intensity of various alloys in an aerated aqueous 22% NaCl solution at 105 °C (220 °F). Alloys X and Y are German heat-resistant grades.

Table 14 Effect of silicon on SCC resistance of austenitic stainless steels in various chloride media

Analysis, wt%(a)						Ferrite content, %	Time to failure, h		
C	Si	Mn	Cr	Ni	N		42% $MgCl_2$ at boiling point(b)	100 ppm NaCl at 250 °C (480 °F)	1000 ppm NaCl at 250 °C (480 °F)
0.020	0.46	0.83	18.28	15.10	0.07	0.5	219	28	10
0.022	0.80	0.77	18.54	15.20	0.08	0.5	292	24	5
0.031	2.48	0.83	18.58	15.23	0.07	1	1000 NF	92	32
0.031	3.69	0.88	18.46	15.20	0.07	1	1000 NF	81	15
0.031	4.53	0.86	18.42	15.28	0.08	2.5	1000 NF	54	50

(a) Balance iron. (b) 1000 NF, no failure in 1000 h. Source: Ref 3

Table 15 Effects of various elements on resistance of austenitic stainless steels to chloride cracking

Element	Beneficial	Detrimental
Boron	>0.1%	0.01%
Aluminum	0.1%	0.04%
Cobalt	>1.8%	1.50%
Tin	0.001–0.02%	No effect at 0.4%
Manganese	No effect at 0–2%	>2%
	Minimum in cracking resistance at:	
Carbon	0.06–0.1%	
Molybdenum	~1.5%	
Chromium	12–25%	

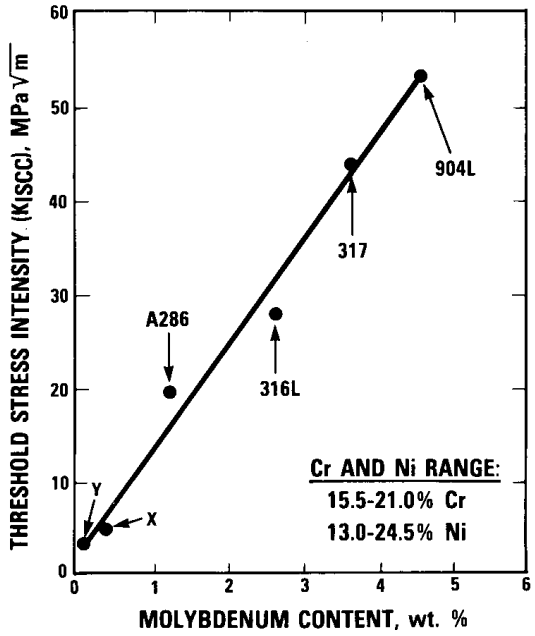


Fig. 15 Effect of molybdenum content on the stress-corrosion threshold stress intensity of Fe-Cr-Ni-Mo alloys in an aerated aqueous 22% NaCl solution at 105 °C (220 °F). Alloys X and Y are German heat-resistant grades.

The foregoing survey of the effects of alloying additions on the chloride SCC resistance of austenitic stainless steels pertains to materials made by conventional melting practice, which contain many impurities. In this regard it has been shown that austenitic (as well as ferritic) stainless steels of very high purity are highly resistant to SCC in boiling magnesium chloride. Two examples are Fe-16Cr-20Ni and Fe-18Cr-14Ni high-purity alloys. In the latter case, the total metallic impurities were quoted at 1 ppm and the total nonmetal impurities (oxygen, nitrogen, sulfur, and phosphorus) at 10 ppm, the material having been prepared by plasma furnace melting. Other studies have shown that decreasing the phosphorus content of an Fe-18Cr-10Ni stainless steel down to 0.003 wt% produces a material that is highly resistant to chloride SCC in a magnesium chloride solution boiling at 154 °C (309 °F) (Fig. 16). It has been suggested that these high-purity alloys are resistant because their corrosion potentials are outside the potential range where SCC occurs.

Ferritic Stainless Steels. Alloying elements that have been identified as detrimental to the chloride SCC resistance of ferritic stainless steels include copper, nickel, molybdenum (in the presence of nickel), cobalt (in

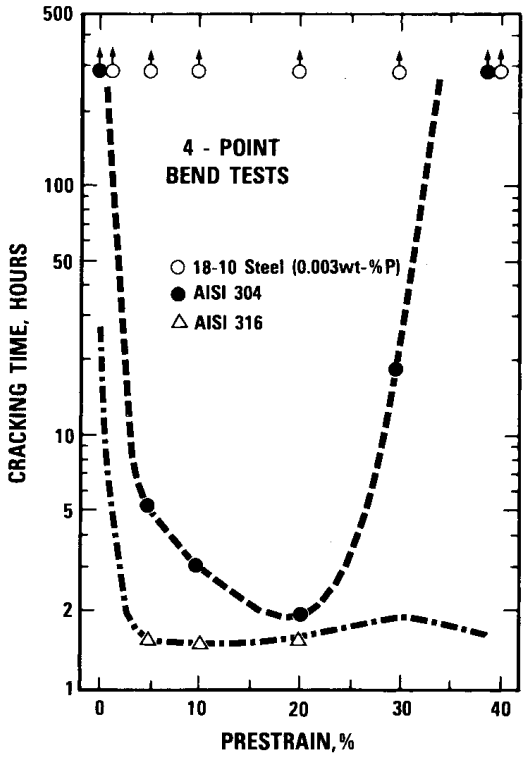


Fig. 16 Effect of phosphorus content on the cracking time of an 18Cr-10 Ni-0.003P stainless steel and types 304 and 316 in magnesium chloride solutions boiling at 154 °C (309 °F) under an applied tensile stress of 196 MPa (28 ksi)

the presence of molybdenum), ruthenium, and carbon. Sulfur, either in the alloy or as sulfur-containing gases in the environment, may also facilitate SCC in chloride environments.

The copper and nickel levels that introduce susceptibility to SCC in magnesium chloride environments in annealed and in welded Fe-18Cr-2Mo alloy are shown in Fig. 17. The detrimental effect of molybdenum in the presence of nickel is shown in Fig. 18. Because molybdenum can be an alloying addition, and copper, nickel, and cobalt can be present if scrap is used in the melt charge, these effects could become technologically significant. The reported detrimental effect of ruthenium is of more academic interest, because significant amounts of this element are not generally found as an impurity in stainless steels. Regarding carbon, it has been shown that, for a 28.5Cr-4.0Mo stainless steel, increasing the carbon content from 20 to 171 ppm leads to SCC in a magnesium chloride solution boiling at 155 °C (310 °F). Sulfur is also detrimental; type 430F (0.15% S) has exhibited cracking in marine atmospheres.

Duplex Stainless Steels. There have been no reports of systematic studies of the effects of single-alloying-element additions on chloride SCC for duplex stainless steels. There are, however, significant variations in chloride SCC resistance among the different commercial grades (Fig. 19). The data of Fig. 19 suggest that increasing the total chromium, nickel,

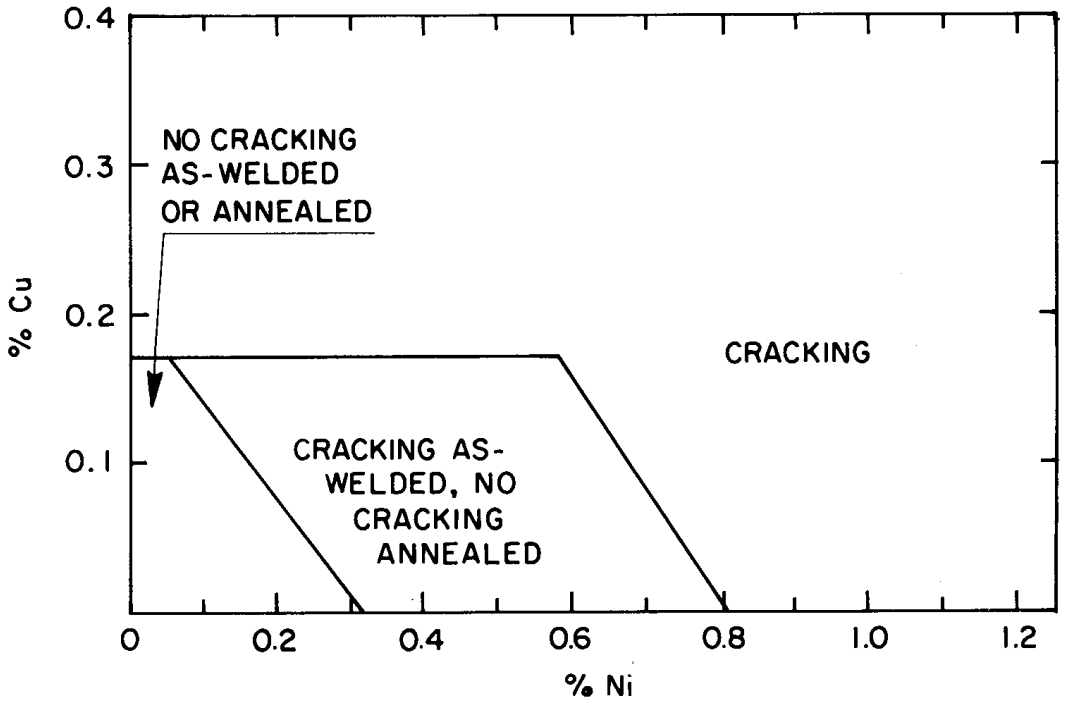


Fig. 17 Effect of copper and nickel contents on the stress-corrosion cracking resistance of U-bend specimens of ferritic Fe-18Cr-2Mo-0.35Ti-0.015C-0.015N stainless steels exposed to a magnesium chloride solution boiling at 140 °C (284 °F)

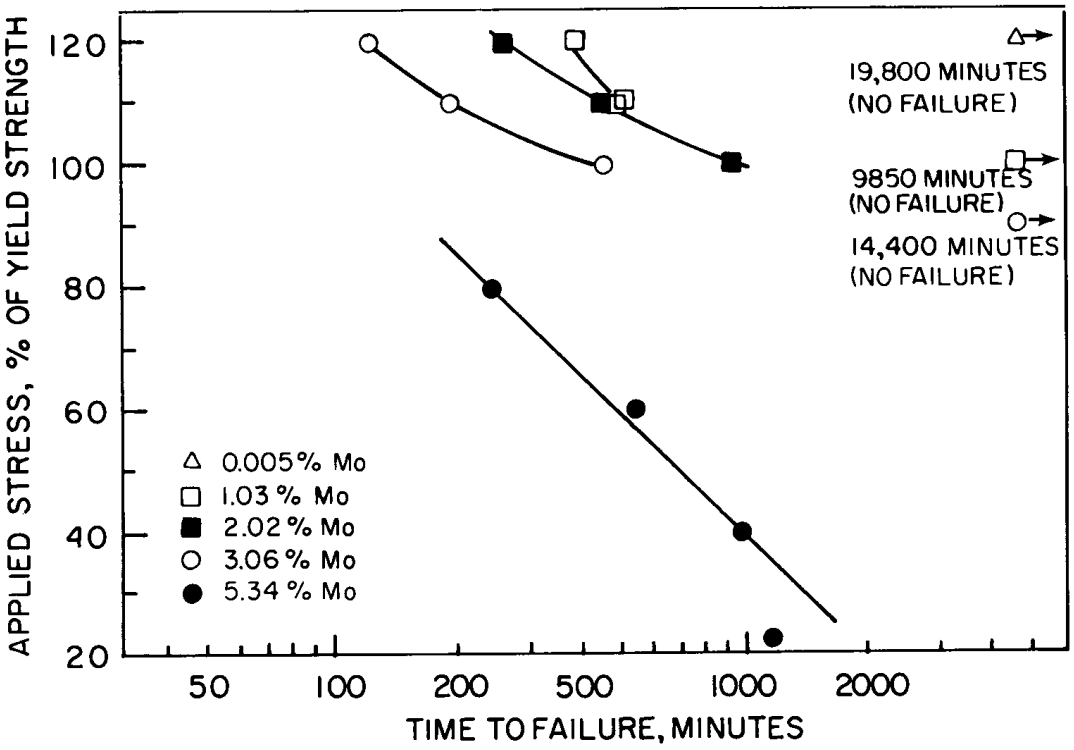


Fig. 18 Effect of applied stress on the times to failure of tensile specimens of experimental ferritic Fe-17Cr-1Ni stainless steels containing various amounts of molybdenum in a magnesium chloride solution boiling at 140 °C (284 °F)

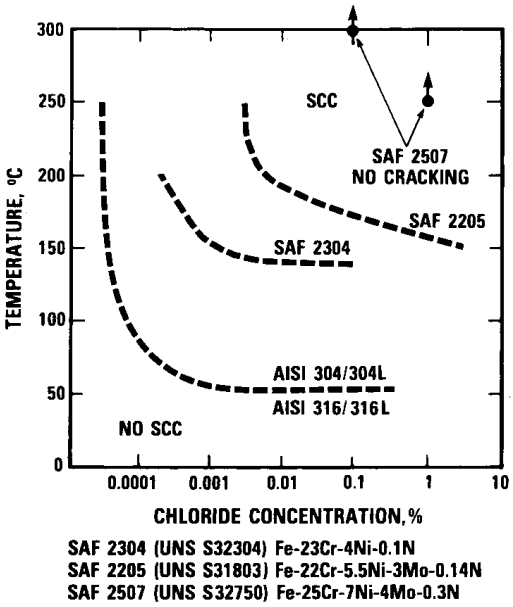


Fig. 19 Stress-corrosion cracking susceptibility of various stainless steels as a function of temperature and chloride concentration. Materials designated as 2304, 2205, and 2507 are duplex grades.

molybdenum, and nitrogen contents results in increased chloride SCC resistance. These data do not differentiate between effects due to individual alloying elements.

Effects of Alloying on Oxidation Resistance (Ref 4)

The effects of various alloying elements on the oxidation resistance of stainless steels are summarized in Fig. 20. In stainless steels, chromium is by far the most important element for increasing oxidation resistance. The formation of the protective Cr_2O_3 scale involves the selective oxidation of chromium at the metal surface, resulting in the depletion of chromium at the metal–oxide interface. To maintain or stabilize the Cr_2O_3 scale, it is important that the bulk chromium content be sufficiently high so that it does not fall below certain minimum values in this interface region. These minimum values for various laboratory Fe-Cr-Ni and Fe-Cr alloys have been determined and vary with alloy composition. For commercial stainless steels, bulk chromium contents approaching those of type 310 (e.g., 25% Cr) are needed to ensure good oxidation resistance at temperatures approaching 1000°C under cyclic temperature exposures, as indicated in Fig. 21.

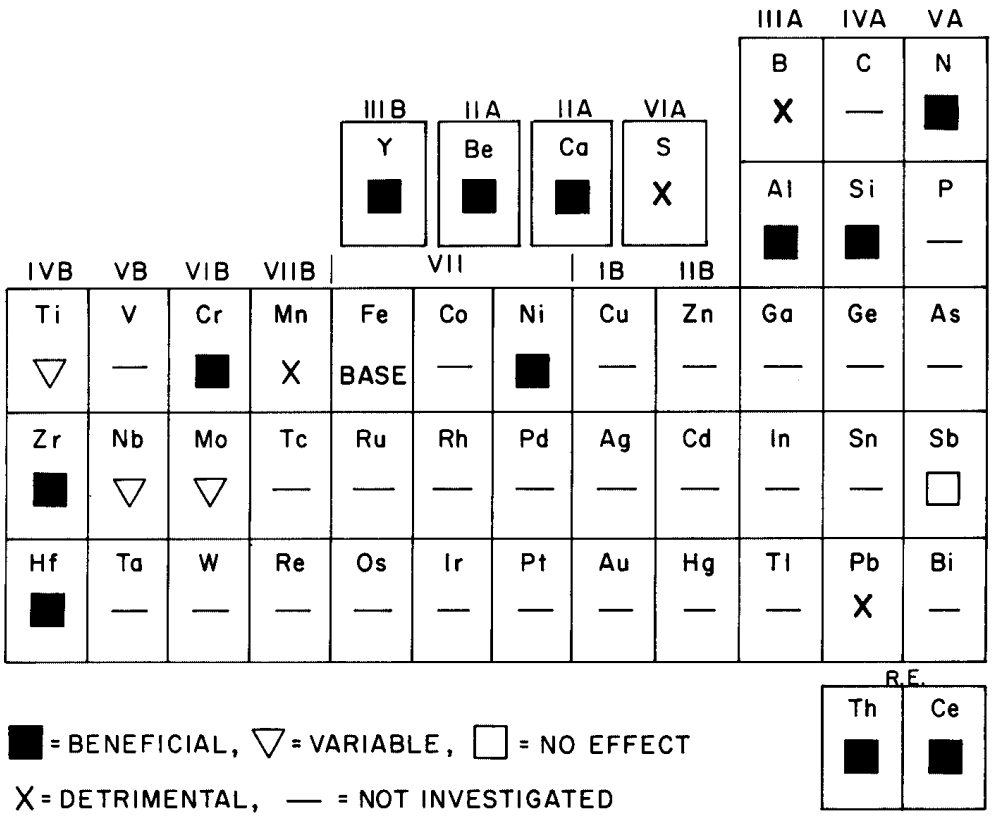


Fig. 20 Effect of various elements on the oxidation resistance of stainless steels. Source: Ref 4

Table 16 compares the oxidation resistance of stainless steels containing the same amounts of chromium and silicon, but varying amounts of nickel. These data show a pronounced beneficial effect of nickel, which influences the adhesion of the protective scale, reduces the rate of cation diffusion in Cr_2O_3 scales, and inhibits the breakdown of the scale. Nickel also stabilizes the fcc austenitic structure. The austenitic structure is inherently stronger and more creep resistant than ferrite.

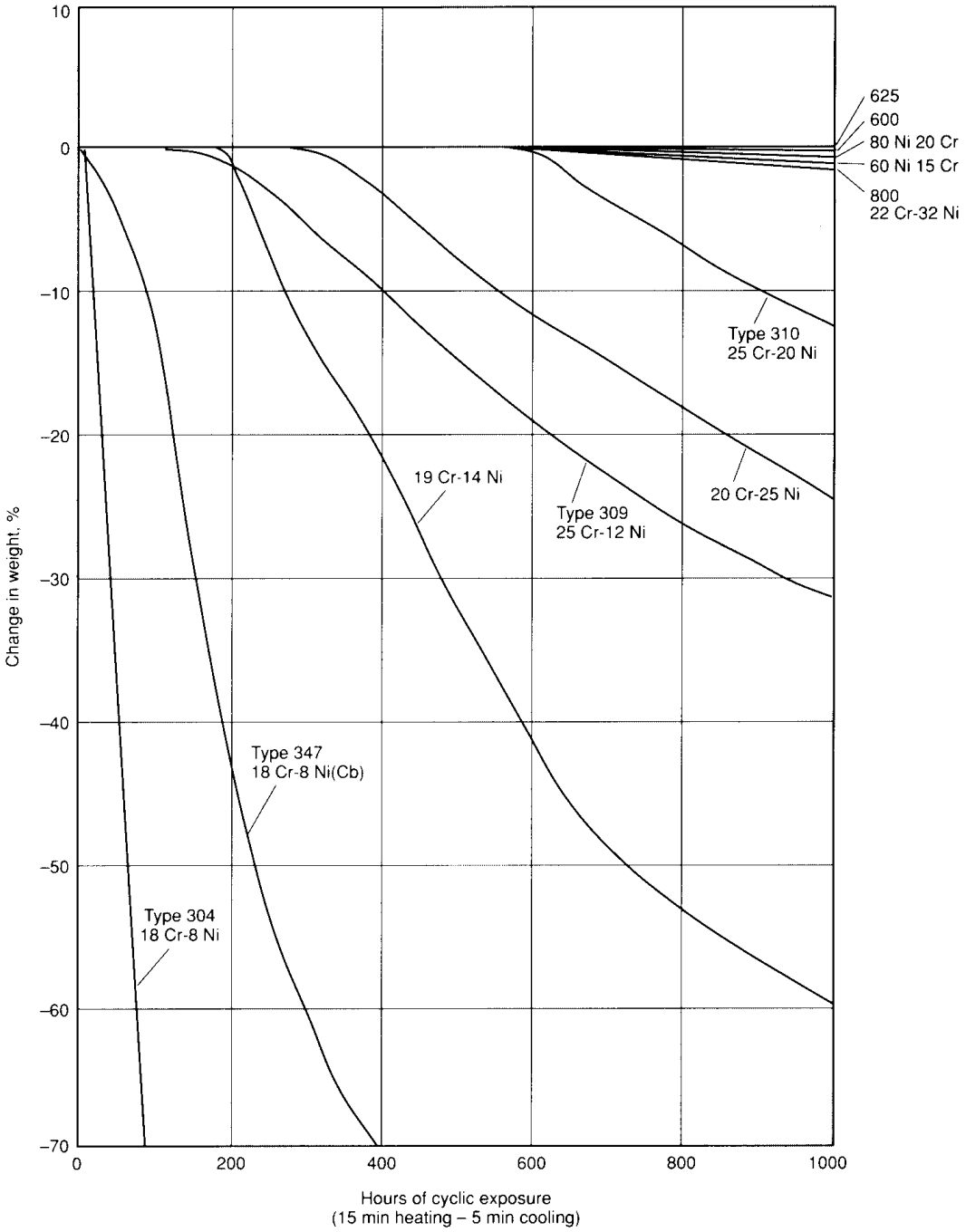


Fig. 21 Cyclic oxidation resistance of several stainless steels and nickel-base alloys in air at 980 °C (1800 °F)

Table 16 Effect of nickel content on the generally accepted maximum service temperature in air for two cast stainless steels

Stainless steel	Composition, wt% Ni	Cr	Si	Maximum continuous service temperature, °C
HF	10.5	21	2	900
HN	25	21	2	1095

The effect of silicon is also designated as beneficial in Fig. 20. While there is some question as to whether small amounts of silicon (0.5%) improve the oxidation resistance of laboratory-prepared Fe-26% Cr ferritic alloys, there is good evidence that silicon improves the oxidation resistance of commercial austenitic stainless steels, as shown in Fig. 22. The increased oxidation resistance of type 302B (3% Si maximum) over type 302 (1% Si maximum) is readily in evidence, although it falls short of the oxidation resistance exhibited by the high-chromium type 310. Increasing the silicon level to 3.5% in austenitic stainless steels results in oxidation rates comparable to type 310.

Additions of aluminum also improve the oxidation resistance of stainless steels due to the formation of protective alumina scales. However, aluminum also promotes the formation of delta ferrite and the brittle sigma phase and may reduce cold formability. Therefore, the use of aluminum additions to improve oxidation resistance should be carefully

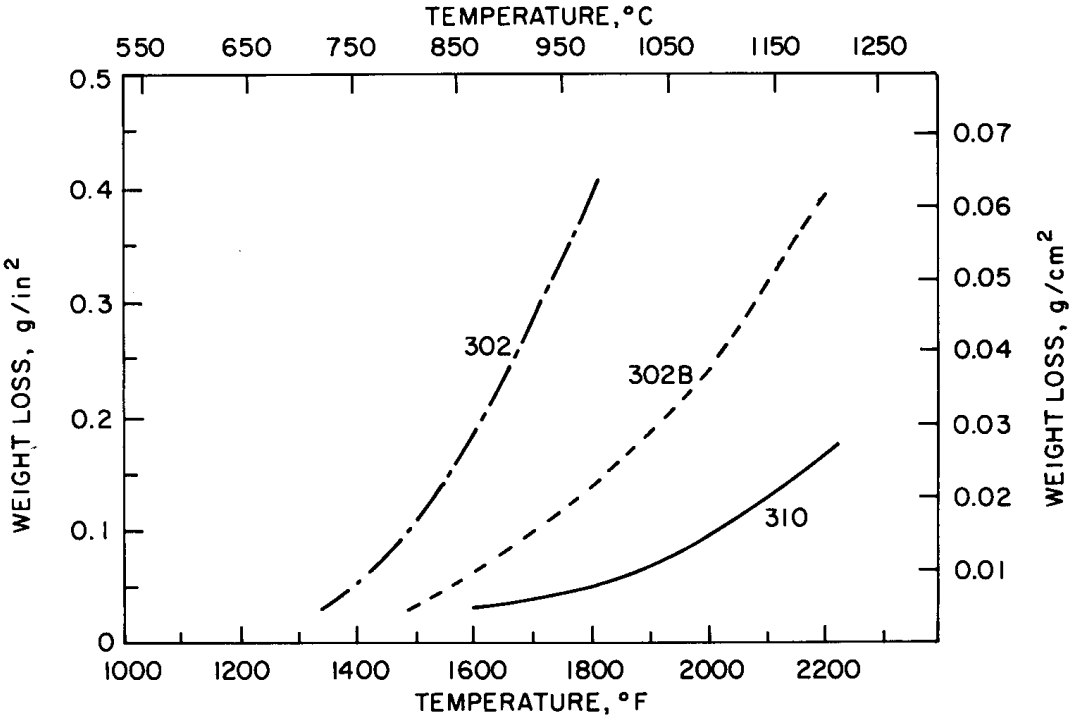


Fig. 22 Scaling losses developed in 12 intermittent heating and cooling cycles by various stainless steels

weighed against other metallurgical requirements. Because of this, proprietary stainless steels and higher alloys that employ aluminum to enhance oxidation resistance either contain relatively low chromium levels [e.g., type 406 (13% Cr)] or high nickel levels [e.g., alloy 601 (59% Ni)]. Also, ferritic stainless steels such as Fe-22Cr-5Al can become embrittled by prolonged exposure at temperatures on the order of 1000 °C (1830 °F) due to grain coarsening.

REFERENCES

1. A.J. Sedriks, Pitting, *Corrosion of Stainless Steels*, 2nd ed., John Wiley & Sons, Inc., 1996, p 102–175
2. A.J. Sedriks, Crevice Corrosion, *Corrosion of Stainless Steels*, 2nd ed., John Wiley & Sons, Inc., 1996, p 176–230
3. A.J. Sedriks, Stress-Corrosion Cracking of Stainless Steels, *Stress-Corrosion Cracking*: *Materials Performance and Evaluation*, R.H. Jones, Ed., ASM International, 1992, p 91–130
4. A.J. Sedriks, Corrosion by Hot Gases and Molten Compounds, *Corrosion of Stainless Steels*, 2nd ed., John Wiley & Sons, Inc., 1996, p 388–423

SELECTED REFERENCES

- A.J. Sedriks, *Corrosion of Stainless Steels*, 2nd ed., John Wiley & Sons, Inc., 1996
- J.R. Davis, Ed., *Alloy Digest Sourcebook*: *Stainless Steels*, ASM International, 2000
- J.R. Davis, Ed., *ASM Specialty Handbook*: *Stainless Steels*, ASM International, 1994
- P. Lacombe, B. Baroux, and G. Beranger, Ed., *Stainless Steels,* Les Éditions de Physique, 1993
- R. Lula, Ed., *Stainless Steel*, American Society for Metals, 1986
- D. Peckner and I.M. Bernstein, Ed., *Handbook of Stainless Steels,* McGraw-Hill, 1977

Alloying: Understanding the Basics
J.R. Davis, p290-307
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Superalloys

Introduction and Overview

General Characteristics. Superalloys are nickel-, iron-nickel-, and cobalt-base alloys generally used at temperatures above approximately 540 °C (1000 °F). They have a face-centered cubic (fcc, austenitic) structure. Iron, cobalt, and nickel are transition metals with consecutive positions in the periodic table of elements. The iron-nickel-base superalloys are an extension of stainless steel technology and generally are wrought, whereas cobalt- and nickel-base superalloys may be wrought or cast, depending on the application/composition involved. The more highly alloyed compositions are normally processed as castings. Cast alloys may have equiaxed grain structures or directionally solidified columnar grains; they may also be cast as single crystals (more accurately, a single grain or primary dendrite). Some highly alloyed nickel-base compositions are also processed by powder metallurgy (P/M) techniques. Fabricated structures can be built up by welding or brazing, but many highly alloyed compositions containing a high volume fraction (V_f) of hardening phase are difficult to weld.

A noteworthy feature of nickel-base alloys is their use in load-bearing applications at temperatures in excess of 80% of their incipient melting temperatures (0.85 T_m), a fraction that is higher than for any other class of engineering alloys. Superalloys exhibit some combination of high strength at temperature; resistance to environmental attack (including nitridation, carbonization, oxidation, and sulfidation); excellent creep resistance, stress-rupture strength, toughness, and metallurgical stability; useful thermal expansion characteristics; and resistance to thermal fatigue and corrosion. The aforementioned properties can be controlled by adjustments in composition and by processing (including heat treatment and thermomechanical processing). Figure 1 compares stress-rupture behavior of the three alloy classes.

Superalloys were initially developed for use in aircraft piston engine turbosuperchargers, and their development over the last 60 years has been

paced by the demands of advancing gas turbine engine technology. The vast majority of use by tonnage of nickel-base superalloys is found in turbines, both for aerospace applications and for land-based power generation. These applications require a material with high strength, good creep and fatigue resistance, good corrosion resistance, and the ability to be operated continuously at elevated temperatures. Figure 2 traces the historical development of superalloys and lists some of the important alloying additions that increased temperature capability.

Applications. Superalloys have been used in cast, rolled, extruded, forged, and powder-processed forms. Sheet, bar, plate, tubing, shafts, airfoils, disks, and pressure vessels (cases) are some of the shapes that have been produced. These metals have been used in aircraft, industrial, and marine gas turbines; nuclear reactors; aircraft skins; spacecraft structures; petrochemical production; orthopedic and dental prostheses; and environmental protection applications. Although developed for high-temperature use, some are used at cryogenic temperatures and others at body temperature. Applications continue to expand, but at lower rates than in previous decades. Aerospace usage remains the predominant application on a volume basis.

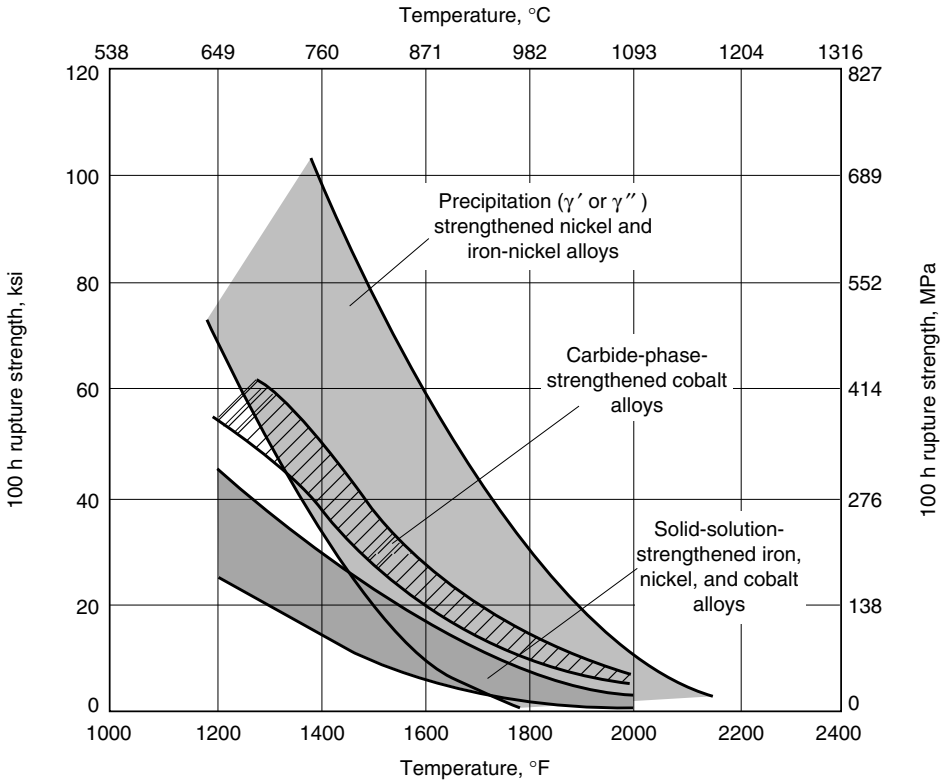


Fig. 1 General stress rupture behavior of superalloys

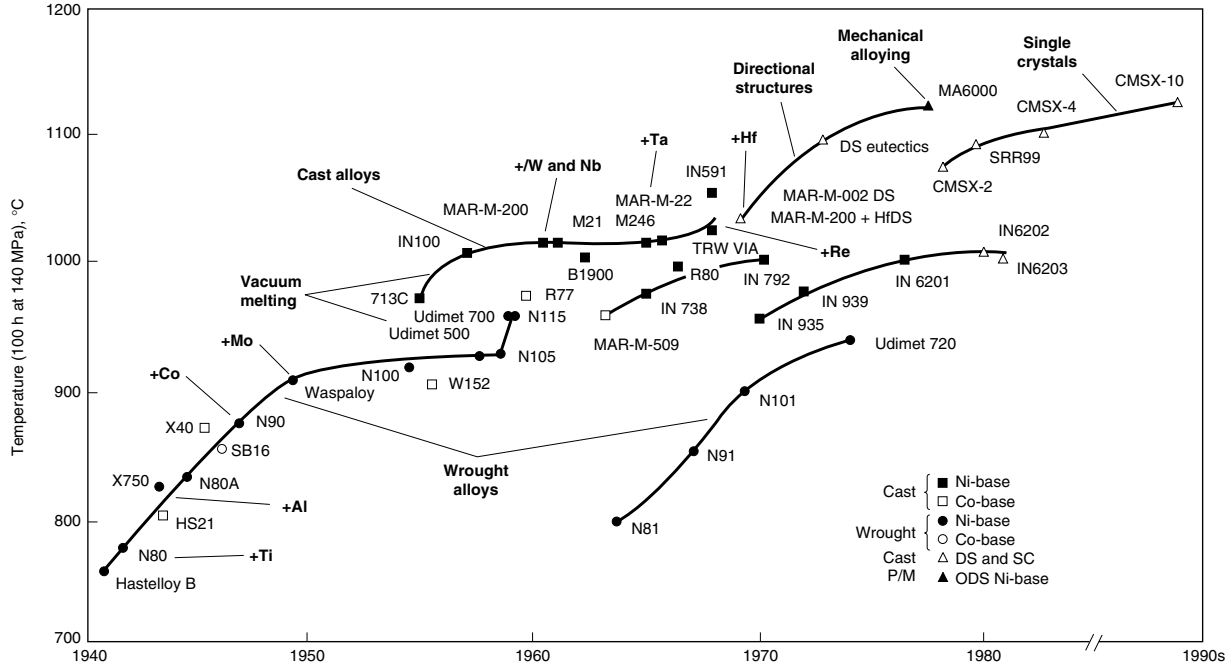


Fig. 2 Temperature capability of superalloys with approximate year of introduction. DS, directionally solidified; SC, single-crystal; P/M, powder metallurgy; ODS, oxide-dispersion-strengthened

Phases, Structures, and Alloying Elements Associated with Superalloys

Superalloys consist of the austenitic fcc matrix phase γ plus a variety of secondary phases. Secondary phases of value in controlling properties are the carbides MC, $M_{23}C_6$, M_6C, and M_7C_3 (rare) in all superalloy types; the γ′ fcc ordered $Ni_3(Al, Ti)$, γ″ bct (body-centered tetragonal) ordered Ni_3Nb, η hexagonal ordered Ni_3Ti, and δ orthorhombic Ni_3Nb intermetallic compounds in nickel- and iron-nickel-base superalloys. The superalloys derive their strength from solid-solution hardeners and precipitated phases. Principal strengthening precipitate phases are γ′ and γ″. Carbides may provide limited strengthening directly (e.g., through dispersion hardening) or, more commonly, indirectly (e.g., by stabilizing grain boundaries against excessive shear). The δ and η phases are useful (along with γ′) in controlling the structure of wrought superalloys during processing. The extent to which they directly contribute to strengthening depends on the alloy and its processing.

In addition to those elements that produce solid-solution hardening and/or promote carbide and γ′ formation, other elements (e.g., boron, zirconium, and hafnium) are added to enhance mechanical or chemical properties. Some carbide- and γ′-forming elements may contribute significantly to chemical properties as well. Tables 1(a) and (b), respectively, give a generalized list of the ranges of alloying elements and their effects in superalloys. Similar information is provided in Fig. 3.

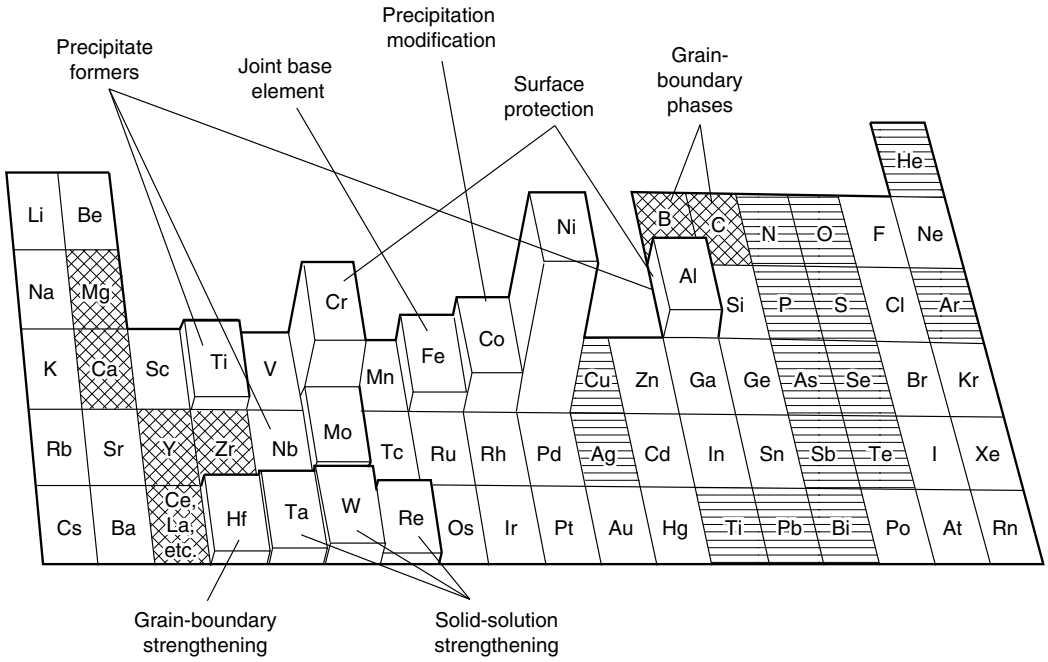


Fig. 3 Alloying elements used in nickel-base superalloys. The height of the element blocks indicates the amount that may be present. Beneficial trace elements are marked with cross hatching and harmful trace elements are marked with horizontal line hatching.

Table 1(a) Common ranges of major alloying additions in superalloys

	Range, %	
Element	**Fe-Ni- and Ni-base**	**Co-base**
Chromium	5–25	19–30
Molybdenum, tungsten	0–12	0–11
Aluminum	0–6	0–4.5
Titanium	0–6	0–4
Cobalt	0–20	…
Nickel	…	0–22
Niobium	0–5	0–4
Tantalum	0–12	0–9
Rhenium	0–6	0–2

Table 1(b) Role of alloying elements in superalloys

Effect(a)	Iron-base	Cobalt-base	Nickel-base
Solid-solution strengtheners	Cr, Mo	Nb, Cr, Mo, Ni, W, Ta	Co, Cr, Fe, Mo, W, Ta, Re
fcc matrix stabilizers	C, W, Ni	Ni	…
Carbide form:			
MC	Ti	Ti	W, Ta, Ti, Mo, Nb, Hf
M_7C_3	…	Cr	Cr
$M_{23}C_6$	Cr	Cr	Cr, Mo, W
M_6C	Mo	Mo, W	Mo, W, Nb
Carbonitrides: M(CN)	C, N	C, N	C, N
Promotes general precipitation of carbides	P	…	…
Forms γ' Ni_3(Al, Ti)	Al, Ni, Ti	…	Al, Ti
Retards formation of hexagonal η (Ni_3Ti)	Al, Zr	…	…
Raises solvus temperature of γ'	…	…	Co
Hardening precipitates and/or intermetallics	Al, Ti, Nb	Al, Mo, Ti(b), W, Ta	Al, Ti, Nb
Oxidation resistance	Cr	Al, Cr	Al, Cr, Y, La, Ce
Improve hot corrosion resistance	La, Y	La, Y, Th	La, Th
Sulfidation resistance	Cr	Cr	Cr, Co, Si
Improves creep properties	B	…	B, Ta
Increases rupture strength	B	B, Zr	B(c)
Grain-boundary refiners	…	…	B, C, Zr, Hf
Facilitates working	…	Ni_3Ti	…
Retard γ' coarsening	…	…	Re

(a) Not all these effects necessarily occur in a given alloy. (b) Hardening by precipitation of Ni_3Ti also occurs if sufficient Ni is present. (c) If present in large amounts, borides are formed

Superalloy Systems

The three types of superalloys—iron-nickel-, nickel-, and cobalt-base—may be further subdivided into cast and wrought. A large number of alloys have been invented and studied; many have been patented. However, the many alloys have been winnowed down over the years, and only a few are extensively used. Alloy usage is a function of industry (gas turbines, steam turbines, etc.). Not all alloys can be mentioned; examples of older and newer alloys will be used to demonstrate the physical metallurgy response of superalloy systems. Representative superalloys and compositions emphasizing alloys developed in the United States are listed in Tables 2 and 3.

Table 2 Nominal compositions of wrought superalloys

Alloy	UNS No.	Composition, %										
		Cr	Ni	Co	Mo	W	Nb	Ti	Al	Fe	C	Other
Solid-solution alloys												
Iron-nickel-base												
Alloy N-155 (Multimet)	R30155	21.0	20.0	20.0	3.00	2.5	1.0	…	…	32.2	0.15	0.15 N, 0.2 La, 0.02 Zr
Haynes 556	R30556	22.0	21.0	20.0	3.0	2.5	0.1	…	0.3	29.0	0.10	0.50 Ta, 0.02 La, 0.002 Zr
19-9 DL	S63198	19.0	9.0	…	1.25	1.25	0.4	0.3	…	66.8	0.30	1.10 Mn, 0.60 Si
Incoloy 800	N08800	21.0	32.5	…	…	…	…	0.38	0.38	45.7	0.05	…
Incoloy 800H	N08810	21.0	33.0	…	…	…	…	…	…	45.8	0.08	…
Incoloy 800HT	N08811	21.0	32.5	…	…	…	…	0.4	0.4	46.0	0.08	0.8 Mn, 0.5 Si, 0.4 Cu
Incoloy 801	N08801	20.5	32.0	…	…	…	…	1.13	…	46.3	0.05	…
Incoloy 802	N08802	21.0	32.5	…	…	…	…	0.75	0.58	44.8	0.35	…
Nickel-base												
Haynes 214	N07214	16.0	76.5	…	…	…	…	…	4.5	3.0	0.03	
Haynes 230	N06230	22.0	55.0	5.0 max	2.0	14.0	…	…	0.35	3.0 max	0.10	0.015 max B, 0.02 La
Inconel 600	N06600	15.5	76.0	…	…	…	…	…	…	8.0	0.08	0.25 Cu
Inconel 601	N06601	23.0	60.5	…	…	…	…	…	1.35	14.1	0.05	0.5 Cu
Inconel 617	N06617	22.0	55.0	12.5	9.0	…	…	…	1.0	…	0.07	…
Inconel 625	N06625	21.5	61.0	…	9.0	…	3.6	0.2	0.2	2.5	0.05	…
RA 333	N06333	25.0	45.0	3.0	3.0	3.0	…	…	…	18.0	0.05	…
Hastelloy B	N10001	1.0 max	63.0	2.5 max	28.0	…	…	…	…	5.0	0.05 max	0.03 V
Hastelloy N	N10003	7.0	72.0	…	16.0	…	…	0.5 max	…	5.0 max	0.06	
Hastelloy S	N06635	15.5	67.0	…	15.5	…	…	…	0.2	1.0	0.02 max	0.02 La
Hastelloy W	N10004	5.0	61.0	2.5 max	24.5	…	…	…	…	5.5	0.12 max	0.6 V
Hastelloy X	N06002	22.0	49.0	1.5 max	9.0	0.6	…	…	2.0	15.8	0.15	…
Hastelloy C-276	N10276	15.5	59.0	…	16.0	3.7	…	…	…	5.0	0.02 max	…
Haynes HR-120	N08120	25.0	37.0	3.0	2.5	2.5	0.7	…	0.1	33.0	0.05	0.7 Mn, 0.6 Si, 0.2 N, 0.004 B
Haynes HR-160	N12160	28.0	37.0	29.0	…	…	…	…	…	2.0	0.05	2.75 Si, 0.5 Mn
Nimonic 75	N06075	19.5	75.0	…	…	…	…	0.4	0.15	2.5	0.12	0.25 max Cu
Nimonic 86	…	25.0	65.0	…	10.0	…	…	…	…	…	0.05	0.03 Ce, 0.015 Mg
Cobalt-base												
Haynes 25 (L605)	R30605	20.0	10.0	50.0	…	15.0	…	…	…	3.0	0.10	1.5 Mn
Haynes 188	R30188	22.0	22.0	37.0	…	14.5	…	…	…	3.0 max	0.10	0.90 La
Alloy S-816	R30816	20.0	20.0	42.0	4.0	4.0	4.0	…	…	4.0	0.38	…
MP35-N	R30035	20.0	35.0	35.0	10.0	…	…	…	…	…	…	…
MP159	R30159	19.0	25.0	36.0	7.0	…	0.6	3.0	0.2	9.0	…	…
Stellite B	N07718	30.0	1.0	61.5	…	4.5	…	…	…	1.0	1.0	…
UMCo-50	…	28.0	…	49.0	…	…	…	…	…	21.0	0.12	…
Precipitation-hardening alloys												
Iron-nickel-base												
A-286	S66286	15.0	26.0	…	1.25	…	…	2.0	0.2	55.2	0.04	0.005B, 0.3 V
Discaloy	S66220	14.0	26.0	…	3.0	…	…	1.7	0.25	55.0	0.06	…
Incoloy 903	N19903	0.1 max	38.0	15.0	0.1	…	3.0	1.4	0.7	41.0	0.04	…
Pyromet CTX-1	…	0.1 max	37.7	16.0	0.1	…	3.0	1.7	1.0	39.0	0.03	…
Incoloy 907	N19907	…	38.4	13.0	…	…	4.7	1.5	0.03	42.0	0.01	0.15 Si
Incoloy 909	N19909	…	38.0	13.0	…	…	4.7	1.5	0.03	42.0	0.01	0.4 Si
Incoloy 925	N09925	20.5	44.0	…	2.8	…	…	2.1	0.2	29	0.01	1.8 Cu
V-57	…	14.8	27.0	…	1.25	…	…	3.0	0.25	48.6	0.08 max	0.01 B, 0.5 max V
W-545	S66545	13.5	26.0	…	1.5	…	…	2.85	0.2	55.8	0.08 max	0.05 B
Nickel-base												
Astroloy	N13017	15.0	56.5	15.0	5.25	…	…	3.5	4.4	<0.3	0.06	0.03 B, 0.06 Zr
Custom Age 625 PLUS	N07716	21.0	61.0	…	8.0	…	3.4	1.3	0.2	5.0	0.01	…
Haynes 242	…	8.0	62.5	2.5 max	25.0	…	…	…	0.5 max	2.0 max	0.10 max	0.006 max B
Haynes 263	N07263	20.0	52.0	…	6.0	…	…	2.4	0.6	0.7	0.06	0.6 Mn, 0.4 Si, 0.2 Cu
Haynes R-41	N07041	19.0	52.0	11.0	10.0	…	…	3.1	1.5	5.0	0.09	0.5 Si, 0.1 Mn, 0.006 B
Inconel 100	N13100	10.0	60.0	15.0	3.0	…	…	4.7	5.5	<0.6	0.15	1.0 V, 0.06 Zr, 0.015 B
Inconel 102	N06102	15.0	67.0	…	2.9	3.0	2.9	0.5	0.5	7.0	0.06	0.005 B, 0.02 Mg, 0.03 Zr

(continued)

Table 2 (continued)

Alloy	UNS No.	Composition, %										
		Cr	Ni	Co	Mo	W	Nb	Ti	Al	Fe	C	Other
Precipitation-hardening alloys (continued)												
Nickel-base (continued)												
Incoloy 901	N09901	12.5	42.5	…	6.0	…	…	2.7	…	36.2	0.10 max	…
Inconel 702	N07702	15.5	79.5	…	…	…	…	0.6	3.2	1.0	0.05	0.5 Mn, 0.2 Cu, 0.4 Si
Inconel 706	N09706	16.0	41.5	…	…	…	…	1.75	0.2	37.5	0.03	2.9 (Nb + Ta), 0.15 max Cu
Inconel 718	N07718	19.0	52.5	…	3.0	…	5.1	0.9	0.5	18.5	0.08 max	0.15 max Cu
Inconel 721	N07721	16.0	71.0	…	…	…	…	3.0	…	6.5	0.04	2.2 Mn, 0.1 Cu
Inconel 722	N07722	15.5	75.0	…	…	…	…	2.4	0.7	7.0	0.04	0.5 Mn, 0.2 Cu, 0.4 Si
Inconel 725	N07725	21.0	57.0	…	8.0	…	3.5	1.5	0.35 max	9.0	0.03 max	
Inconel 751	N07751	15.5	72.5	…	…	…	1.0	2.3	1.2	7.0	0.05	0.25 max Cu
Inconel X-750	N07750	15.5	73.0	…	…	…	1.0	2.5	0.7	7.0	0.04	0.25 max Cu
M-252	N07252	19.0	56.5	10.0	10.0	…	…	2.6	1.0	<0.75	0.15	0.005 B
Nimonic 80A	N07080	19.5	73.0	1.0	…	…	…	2.25	1.4	1.5	0.05	0.10 max Cu
Nimonic 90	N07090	19.5	55.5	18.0	…	…	…	2.4	1.4	1.5	0.06	…
Nimonic 95	…	19.5	53.5	18.0	…	…	…	2.9	2.0	5.0 max	0.15 max	+B, +Zr
Nimonic 100	…	11.0	56.0	20.0	5.0	…	…	1.5	5.0	2.0 max	0.30 max	+B, +Zr
Nimonic 105	…	15.0	54.0	20.0	5.0	…	…	1.2	4.7	…	0.08	0.005 B
Nimonic 115	…	15.0	55.0	15.0	4.0	…	…	4.0	5.0	1.0	0.20	0.04 Zr
C-263	N07263	20.0	51.0	20.0	5.9	…	…	2.1	0.45	0.7 max	0.06	…
Pyromet 860	…	13.0	44.0	4.0	6.0	…	…	3.0	1.0	28.9	0.05	0.01 B
Pyromet 31	N07031	22.7	55.5	…	2.0	…	1.1	2.5	1.5	14.5	0.04	0.005 B
Refractaloy 26	…	18.0	38.0	20.0	3.2	…	…	2.6	0.2	16.0	0.03	0.015 B
René 41	N07041	19.0	55.0	11.0	10.0	…	…	3.1	1.5	<0.3	0.09	0.01B
René 95	…	14.0	61.0	8.0	3.5	3.5	3.5	2.5	3.5	<0.3	0.16	0.01 B, 0.05 Zr
René 100	…	9.5	61.0	15.0	3.0	…	…	4.2	5.5	1.0 max	0.16	0.015 B, 0.06 Zr, 1.0 V
Udimet 500	N07500	19.0	48.0	19.0	4.0	…	…	3.0	3.0	4.0 max	0.08	0.005 B
Udimet 520	…	19.0	57.0	12.0	6.0	1.0	…	3.0	2.0	…	0.08	0.005 B
Udimet 630	…	17.0	50.0	…	3.0	3.0	6.5	1.0	0.7	18.0	0.04	0.004 B
Udimet 700	…	15.0	53.0	18.5	5.0	…	…	3.4	4.3	<1.0	0.07	0.03 B
Udimet 710	…	18.0	55.0	14.8	3.0	1.5	…	5.0	2.5	…	0.07	0.01 B
Unitemp AF2-1DA	N07012	12.0	59.0	10.0	3.0	6.0	…	3.0	4.6	<0.5	0.35	1.5 Ta, 0.015 B, 0.1 Zr
Waspaloy	N07001	19.5	57.0	13.5	4.3	…	…	3.0	1.4	2.0 max	0.07	0.006 B, 0.09 Zr

Iron-Nickel-Base. The most important class of iron-nickel-base superalloys includes those strengthened by intermetallic compound precipitation in an fcc matrix. The most common precipitate is γ′, typified by A-286, V-57, or Incoloy 901. Some alloys, typified by Inconel (IN) 718, which precipitate γ″, were formerly classed as iron-nickel-base but now are considered to be nickel-base. Other iron-nickel-base superalloys consist of modified stainless steels primarily strengthened by solid-solution hardening. Alloys in this last category vary from 19-9DL (18-8 stainless with slight chromium and nickel adjustments, additional solution hardeners, and higher carbon) to Incoloy 800H (21% chromium, high nickel with small additions of titanium and aluminium, which yields some γ′ phase).

Nickel-Base. The most important class of nickel-base superalloys is that strengthened by intermetallic-compound precipitation in an fcc matrix. For nickel-titanium/aluminum alloys, the strengthening precipitate is γ′. Such alloys are typified by the wrought alloys Waspaloy and Udimet (U) 720, or by the cast alloys René 80 and IN 713. For nickel-niobium alloys, the strengthening precipitate is γ″. These alloys are typified by IN 718. Some nickel-base alloys may contain both niobium plus

Table 3 Nominal compositions of cast superalloys

Alloy designation	Nominal composition, %												
	C	Ni	Cr	Co	Mo	Fe	Al	B	Ti	Ta	W	Zr	Other
Nickel base													
B-1900	0.1	64	8	10	6	…	6	0.015	1	4(a)	…	0.10	…
CMSX-2	…	66.2	8	4.6	0.6	…	56	…	1	6	8	6	…
Hastelloy X	0.1	50	21	1	9	18	…	…	…	…	1	…	…
Inconel 100	0.18	60.5	10	15	3	…	5.5	0.01	5	…	…	0.06	1 V
Inconel 713C	0.12	74	12.5	…	4.2	…	6	0.012	0.8	1.75	…	0.1	0.9 Nb
Inconel 713LC	0.05	75	12	…	4.5	…	6	0.01	0.6	4	…	0.1	…
Inconel 738	0.17	61.5	16	8.5	1.75	…	3.4	0.01	3.4	…	2.6	0.1	2 Nb
Inconel 792	0.2	60	13	9	2.0	…	3.2	0.02	4.2	…	4	0.1	2 Nb
Inconel 718	0.04	53	19	…	3	18	0.5	…	0.9	…	…	…	0.1 Cu, 5 Nb
X-750	0.04	73	15	…	…	7	0.7	…	2.5	…	…	…	0.25 Cu, 0.9 Nb
M-252	0.15	56	20	10	10	…	1	0.005	2.6	…	…	…	…
MAR-M 200	0.15	59	9	10	…	1	5	0.015	2	…	12.5	0.05	1 Nb(b)
MAR-M 246	0.15	60	9	10	2.5	…	5.5	0.015	1.5	1.5	10	0.05	…
MAR-M 247	0.15	59	8.25	10	0.7	0.5	5.5	0.015	1	3	10	0.05	1.5 Hf
PWA 1480	…	bal	10	5.0	…	…	5.0	…	1.5	12	4.0	…	…
René 41	0.09	55	19	11.0	10.0	…	1.5	0.01	3.1	…	…	…	…
René 77	0.07	58	15	15	4.2	…	4.3	0.015	3.3	…	…	0.04	…
René 80	0.17	60	14	9.5	4	…	3	0.015	5	…	4	0.03	…
René 80 Hf	0.08	60	14	9.5	4	…	3	0.015	4.8	…	4	0.02	0.75 Hf
René 100	0.18	61	9.5	15	3	…	5.5	0.015	4.2	…	…	0.06	1 V
René N4	0.06	62	9.8	7.5	1.5	…	4.2	0.004	3.5	4.8	6	…	0.5 Nb, 0.15 Hf
Udimet 500	0.1	53	18	17	4	2	3	…	3	…	…	…	…
Udimet 700	0.1	53.5	15	18.5	5.25	…	4.25	0.03	3.5	…	…	…	…
Udimet 710	0.13	55	18	15	3	…	2.5	…	5	…	1.5	0.08	…
Waspaloy	0.07	57.5	19.5	13.5	4.2	1	1.2	0.005	3	…	…	0.09	…
WAX-20 (DS)	0.20	72	…	…	…	…	6.5	…	…	…	20	1.5	…
Cobalt-base													
AiResist 13	0.45	…	21	62	…	…	3.4	…	…	2	11	…	0.1 Y
AiResist 213	0.20	0.5	20	64	…	0.5	3.5	…	…	6.5	4.5	0.1	0.1 Y
AiResist 215	0.35	0.5	19	63	…	0.5	4.3	…	…	7.5	4.5	0.1	0.1 Y
FSX-414	0.25	10	29	52.5	…	1	…	0.010	…	…	7.5	…	…
Haynes 21	0.25	3	27	64	…	1	…	…	…	…	…	…	5 Mo
Haynes 25; L-605	0.1	10	20	54	…	1	…	…	…	…	15	…	…
J-1650	0.20	27	19	36	…	…	…	0.02	3.8	2	12	…	…
MAR-M 302	0.85	…	21.5	58	…	0.5	…	0.005	…	9	10	0.2	…
MAR-M 322	1.0	…	21.5	60.5	…	0.5	…	…	0.75	4.5	9	2	…
MAR-M 509	0.6	10	23.5	54.5	…	…	…	…	0.2	3.5	7	0.5	…
MAR-M 918	0.05	20	20	52	…	…	…	…	…	7.5	…	0.1	…
NASA Co-W-Re	0.40	…	3	67.5	…	…	…	…	1	…	25	1	2 Re
S-816	0.4	20	20	42	…	4	…	…	…	…	4	…	4 Mo, 4 Nb, 1.2 Mn, 0.4 Si
V-36	0.27	20	25	42	…	3	…	…	…	…	2	…	4 Mo, 2 Nb, 1 Mn, 0.4 Si
WI-52	0.45	…	21	63.5	…	2	…	…	…	…	11	…	2 Nb + Ta
X-40 (Stellite alloy 31)	0.50	10	22	57.5	…	1.5	…	…	…	…	7.5	…	0.5 Mn, 0.5 Si

(a) B-1900 + Hf also contains 1.5% Hf. (b) MAR-M 200 + Hf also contains 1.5% Hf.

titanium and/or aluminum and utilize both γ' and γ'' precipitates in strengthening. Alloys of this type are IN 706 and IN 909. Another class of nickel-base superalloys is essentially solid-solution strengthened. Such alloys are Hastelloy X and IN 625. The solid-solution strengthened nickel-base alloys may derive some additional strengthening from carbide and/or intermetallic-compound precipitation. A third class includes oxide-dispersion strengthened (ODS) alloys such as IN MA-754 and IN MA-6000, which are strengthened by dispersion of inert particles such as yttria, coupled in some cases with γ' precipitation (MA 6000).

Nickel-base superalloys are utilized in both cast and wrought forms, although special processing (powder metallurgy/isothermal forging) is frequently used to produce wrought versions of the more highly alloyed compositions (René 95, Astroloy, IN 100). An additional dimension of nickel-base superalloys has been the introduction of grain-aspect ratio and orientation as a means of controlling properties. In some instances, in fact, grain boundaries have been removed (e.g., investment cast single crystal alloys). Wrought P/M alloys of the ODS class and cast alloys such as MAR-M 247 have demonstrated property improvements owing to control of grain morphology by directional recrystallization or solidification.

Cobalt-Base. The cobalt-base superalloys are invariably strengthened by a combination of carbides and solid-solution hardeners. The essential distinction in these alloys is between cast and wrought structures. Cast alloys are typified by X-40 and wrought alloys by alloy 25 (also known as L605). No intermetallic compound possessing the same degree of utility as the γ' precipitate in nickel- or iron-nickel-base superalloys has been found to be operative in cobalt-base systems.

Properties and Microstructure

The principal microstructural variables of superalloys are the precipitate amount and morphology, grain size and shape, and carbide distribution. Nickel and iron-nickel-base alloys of the titanium/aluminum type have their properties controlled by all three variables; nickel-niobium alloys have the additional variable of δ-phase distribution; cobalt-base superalloys are not affected by the first variable. Structure control is achieved through composition selection/modification and by processing. For a given nominal composition, there are property advantages and disadvantages of the structures produced by deformation processing and by casting. Cast superalloys generally have coarser grain sizes, more alloy segregation, and improved creep and rupture characteristics. Wrought superalloys generally have more uniform, and usually finer, grain sizes and improved tensile and fatigue properties.

Nickel- and iron-nickel-base superalloys of the Ni-Ti/Al type typically consist of γ' dispersed in a γ matrix, and the strength increases with increasing V_f γ'. The lowest V_f amounts of γ' are found in iron-nickel-base and first-generation nickel-base superalloys, where V_f γ' is generally less than about 0.25 (25 vol%). The γ' is commonly spheroidal in lower V_f γ' alloys but often cuboidal in higher V_f γ' ($\geq$0.35) nickel-base superalloys. The nickel-niobium-type superalloys typically consist of γ'' dispersed in a γ matrix, with some γ' present as well. The inherent strength capability of the γ'-and γ''-hardened superalloys is controlled by the intragranular distribution of the hardening phases; however, the usable strength in polycrystalline

alloys is determined by the condition of the grain boundaries, particularly as affected by the carbide-phase morphology and distribution, and in the case of nickel-niobium alloys, additionally by the distribution of the δ phase.

Satisfactory properties in Ni-Ti/Al alloys are achieved by optimizing the γ′ V_f and morphology (not necessarily independent characteristics) in conjunction with securing a dispersion of discrete globular carbides along the grain boundaries. Discontinuous (cellular) carbide or γ′ at grain boundaries increases surface area and drastically reduces rupture life, even though tensile and creep strength may be relatively unaffected.

Wrought nickel- and iron-nickel-base superalloys generally are processed to have optimal tensile and fatigue properties. At one time, when wrought alloys were used for creep-limited applications, such as gas turbine high-pressure turbine blades, heat treatments different from those used for tensile-limited uses were applied to the same nominal alloy composition to maximize creep-rupture life. Occasionally, the nominal composition of an alloy such as IN-100 or U-700/Astroloy varies according to whether it is to be used in the cast or the wrought condition.

Effects of Alloying Elements. Superalloys contain a variety of elements in a large number of combinations to produce desired effects. Some elements go into solid solution to provide one or more of the following: strength (molybdenum, tantalum, tungsten, rhenium); oxidation resistance (chromium, aluminum); phase stability (nickel); and increased volume fractions of favorable secondary precipitates (cobalt). Other elements are added to form hardening precipitates such as γ′ (aluminum, titanium) and γ″ (niobium). Minor elements (carbon, boron) are added to form carbides and borides; these and other elements (magnesium) are added for purposes of tramp-element control. Some elements (boron, zirconium, hafnium) also are added to promote grain-boundary effects other than precipitation or carbide formation. Lanthanum has been added to some alloys to promote oxidation resistance, and yttrium has been added to coatings to enhance oxidation resistance. A major addition to nickel-base superalloy chemistry in recent years has been the element rhenium, which has extended the temperature capability of the directionally solidified, columnar grain and single crystal alloys. Rhenium appears to produce these improvements by significantly reducing the coarsening rate for γ′. Many elements (cobalt, molybdenum, tungsten, rhenium, chromium, etc.), although added for their favorable alloying qualities, can participate, in some circumstances, in undesirable phase formation (σ, μ, Laves, etc.).

Some of these elements produce readily discernible changes in microstructure; others produce more subtle microstructural effects. The precise microstructural effects produced are functions of processing and heat treatment. The most obvious microstructural effects involve precipitation of geometrically close-packed (gcp) phases such as γ′, formation of carbides, and formation of topologically close-packed (tcp) phases such as σ.

Even when the type of phase is specified, microstructure morphology can vary widely—for example, script versus blocky carbides, cuboidal versus spheroidal γ', cellular versus uniform precipitation, acicular versus blocky σ, and discrete γ' versus γ' envelopes. Typical nickel-base superalloy microstructures, as they evolved from spheroidal to cuboidal γ', are depicted in Fig. 4.

The γ' phase is an ordered ($L1_2$) intermetallic fcc phase having the basic composition $Ni_3(Al,Ti)$. Alloying elements affect γ' mismatch with the matrix γ phase, γ' antiphase-domain-boundary (APB) energy, γ' morphology, and γ' stability. A related phase, η, is an ordered ($D0_{24}$) hexagonal phase of composition Ni_3Ti that may exist in a metastable form as γ' before transforming to η. Other types of intermetallic phases, such as δ, orthorhombic Ni_3Nb, or γ'', bct ordered ($D0_{22}$) Ni_3Nb strengthening precipitate, have been observed.

Carbides also are an important constituent of superalloys. They are particularly essential in the grain boundaries of cast polycrystalline alloys for production of desired strength and ductility characteristics. Carbide levels in wrought alloys always have been below those in cast alloys, but some carbide has been deemed desirable for achieving optimal strength properties. As cleanliness of superalloys has increased, the carbide levels in wrought alloys have been lowered. Carbides, at least large ones, become the limiting fracture mechanics criteria for modern wrought superalloy application.

Carbides may provide some degree of matrix strengthening, particularly in cobalt-base alloys, and are necessary for grain-size control in some wrought alloys. Some carbides are virtually unaffected by heat treatment, while others require such a step to be present. Various types of carbides are possible depending on alloy composition and processing. Some of the

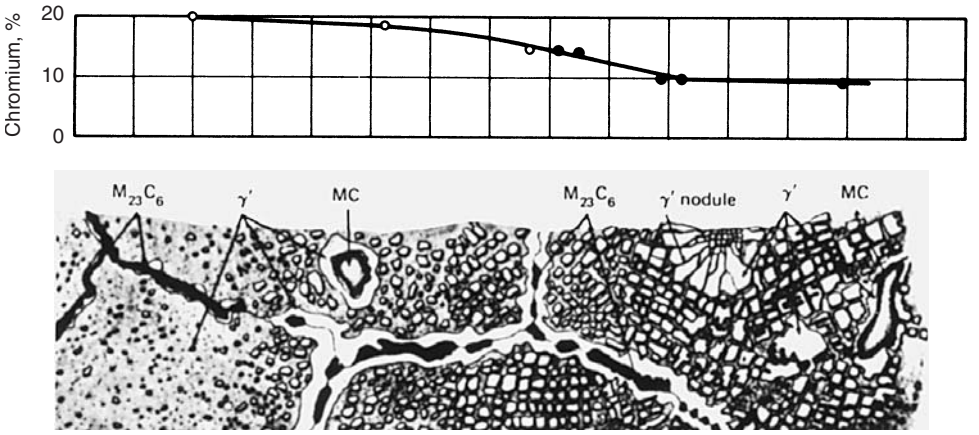


Fig. 4 Qualitative description of the evolution of microstructure and chromium content of nickel-base superalloys

important types are MC, M_6C, $M_{23}C_6$, and M_7C_3, where M stands for one or more types of metal atom. In many cases, the carbides exist jointly; however, they usually are formed by sequential reactions in the solid state following break-down of the MC that normally is formed in the molten state. The common carbide-reaction sequence for many superalloys is MC to $M_{23}C_6$, and the important carbide-forming elements are chromium ($M_{23}C_6$, M_7C_3); titanium, tantalum, niobium, and hafnium (MC); and molybdenum and tungsten (M_6C). Boron may participate somewhat interchangeably with carbon and produces such phases as MB_{12}, M_3B_2, and others. One claim made for boron is that primary borides formed by adjustment of boron/carbon ratio are more amenable to morphological modification through heat treatment.

Alloying Elements to Improve Oxidation Resistance. All superalloys contain some chromium plus other elements to promote resistance to environmental degradation. The role of chromium is to promote Cr_2O_3 formation on the external surface of an alloy. When sufficient aluminum is present, formation of the more protective oxide Al_2O_3 is promoted when oxidation occurs. A chromium content of 6 to 22 wt% generally is common in nickel-base superalloys, whereas a level of 20 to 30 wt% Cr is characteristic of cobalt-base superalloys, and a level of 15 to 25 wt% Cr is found in iron-nickel-base superalloys. Amounts of aluminum up to approximately 6 wt% can be present in nickel-base superalloys. High tantalum (>3%) and low titanium (<1%) contents are also recommended for oxidation-resistant nickel-base alloys.

Effect of Boron, Zirconium, and Hafnium. Within limits, significant improvements in mechanical properties can be achieved by additions of boron, zirconium, and hafnium. However, only limited microstructural correlations can be made. The presence of these elements may modify the initial grain-boundary carbides or tie up deleterious elements such as sulfur and lead. Reduced grain-boundary diffusion rates may be obtained, with consequent suppression of carbide agglomeration and creep cracking. Hafnium contributes to the formation of more γ-γ' eutectic in cast alloys; the eutectic at grain boundaries is thought (in modest quantities) to contribute to alloy ductility. The effects of these elements are limited to nickel- and iron-nickel-base alloys; virtually no cobalt-base alloys contain them. Hafnium in particular contributes strongly to improved ductility in transverse boundaries in directionally solidified, columnar grain alloys.

Effect of Trace Elements. The main trace elements present in superalloys are shown in Figure 3. A simple classification of the trace and minor element additions in superalloys is given in Table 4.

The presence of gases can give rise to void formation via migration and coalescence with the subsequent weakening of the alloy. For example, oxygen has been shown to react with carbides to form either CO or CO_2

Table 4 Classification of trace and minor elements found in superalloys

Category	Elements
Detrimental elements	
Residual gases	O, H, N, Ar, He
Nonmetallic impurities	S, P
Metallic or metalloid impurities	Pb, Bi, Sb, As, Se, Ag, Cu, Tl, Te
Beneficial elements	
Refining aids	Ca, Mg, Ce, La
Minor and ppm alloying additions	B, Zr, Hf, Mg, C
Alloying addition up to 1.5%	Hf, Zr

bubbles at grain boundaries. Of the residual gases, oxygen introduced during heat treatment, high-temperature testing, or service, is known to cause reductions in ductility while oxides picked up from the melting crucible can limit the useful strength of alloys subjected to cyclic stressing.

Most superalloys contain strong nitride formers such as titanium; the effects of small amounts of TiN can be beneficial in cobalt-base alloys (e.g., acting as nuclei for the formation of MC type carbides or inducing strain aging to increase the strength of the alloy, although at the expense of ductility). Nickel-base superalloys that contain large amounts of nitrogen are, however, prone to excessive microporosity, which leads to reduced ductility and rupture life. This problem is most frequently associated with revert alloys, that is, alloys made from superalloy scrap. A study of MAR-M002 doped with 24 and 50 ppm of nitrogen showed the increased porosity and a change in the carbide morphology from an acicular to a blocky form. Many of these blocky carbides have cored structures with a titanium-rich central region, which means that the reaction between titanium and nitrogen to form TiN particles is the first stage leading to high-porosity castings. These nitride particles act as profuse nucleants for carbide formation and influence the final solidification behavior by inhibiting the liquid flow.

Both sulfur and phosphorous form eutectics with nickel. Sulfur in particular has long been known to adversely affect ductility. Elements such as titanium, zirconium and hafnium, which are commonly present in superalloys, reduce the effects of sulfur by forming carbosulfides of the type M_2SC, which crystallize as flakes or plates away from the grain boundaries. However, excessive additions of zirconium and hafnium can also lead to embrittlement.

The effects of the harmful metallic and metalloid elements listed in Table 4 have been studied extensively and with the aim of minimizing their concentrations in nickel-base alloys. The stress-rupture properties of alloys IN-100 and MAR-M002 have been investigated after deliberate contamination with bismuth, lead, silver, tin, and tellurium. By far the most damaging element was found to be bismuth, followed by tellurium, selenium, lead, and silver; the presence of tin had almost no harmful effects. The presence of only 0.2 ppm bismuth in IN-100 was shown to reduce its creep life by 20%.

Elements such as calcium, magnesium, cerium, and lanthanum have been added to superalloy melts as deoxidizers or desulfurizers, although large residual amounts of calcium and magnesium may cause problems of their own. Magnesium is beneficial in terms of castability, but detrimental to the high-temperature creep-properties. As mentioned earlier, minor additions of lanthanum or yttrium improve the oxidation resistance of superalloys.

Mechanical Alloying

Mechanical alloying (MA) is a dry, high-energy ball-milling process for producing composite metallic powders with a controlled, fine microstructure. It is carried out in a highly agitated ball charge by repeated cold welding and fracturing of a mixture of metal powders to which some nonmetal powders may be added. Its widest use has been in the production of ODS nickel- and iron-base superalloys for service at 1000 °C (1830 °F) and above.

Unlike mechanical mixing processes, MA produces a material whose internal homogeneity is independent of starting powder particle size. Thus, ultrafine dispersions (<1 μm interparticle spacing) can be obtained with relatively coarse initial powder (50–100 μm average diameter).

The Processing Path. Figure 5 is a schematic showing the path of raw materials using the MA process. The raw materials, the type of mill used, the process of consolidation, and the details of heat treatment differ depending on the type of product desired, but the processing route remains essentially the same. It is possible that some minor steps are either added or deleted in some special circumstances. The actual process of MA starts with mixing of powders in the right proportion and loading the powder into the high-energy ball mill, along with the grinding medium (generally steel balls). This mix is then milled for the desired length of time until a

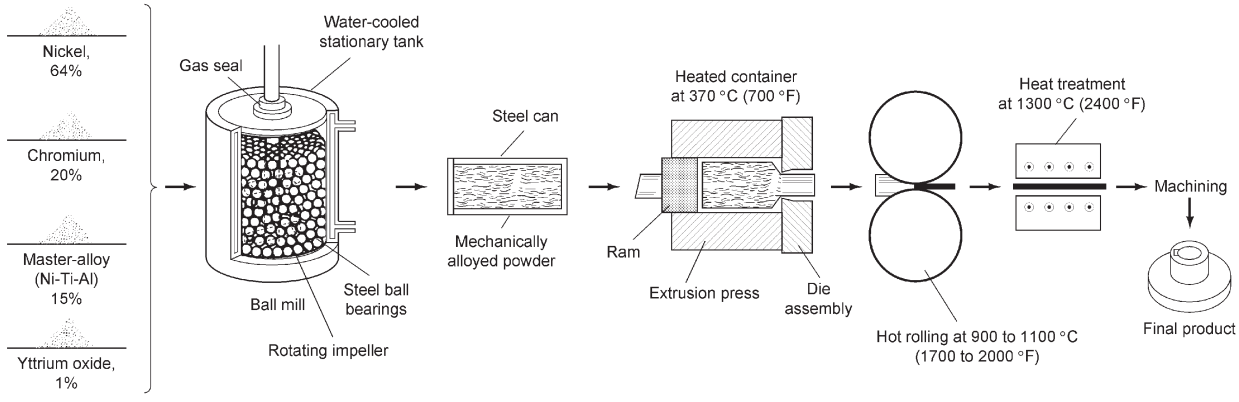


Fig. 5 Processing path in producing a product from powders by mechanical alloying

steady state is reached. A steady state occurs when the composition of every powder particle is the same as the proportion of the elements in the starting powder mix. Sometimes, the powder is milled to an intermediate state either to form metastable phases or to achieve certain desired properties. The milled powder is then consolidated into a bulk shape and heat treated to obtain the desired microstructure and properties.

The raw materials used for mechanically alloyed dispersion-strengthened superalloys are widely available commercially pure powders that have particle sizes that vary from about 1 to 200 μm. These powders fall into the broad categories of pure metals, master alloys, and refractory compounds. The pure metals include nickel, chromium, iron, cobalt, tungsten, molybdenum, and niobium. The master alloys include nickel-base alloys with relatively large amounts of combinations of aluminum, titanium, zirconium, or hafnium.

These master alloys are relatively brittle when cast and easily milled into powder. In addition, because they consist of relatively exothermic intermetallic compounds, the thermodynamic activity of the reactive alloying elements, such as aluminum and titanium, is considerably reduced compared to that of the pure metals.

A typical powder mixture may consist of fine (4–7 μm) nickel powder, −150 μm chromium, and −150 μm master alloy. The master alloy may contain a wide range of elements selected for their role as alloying constituents or for gettering of contaminants. About 2 vol% of very fine yttria, Y_2O_3 (25 nm, or 250 Å) is added to form the dispersoid. The yttria becomes entrapped along the weld interfaces between fragments in the composite metal powders. After completion of the power milling, a uniform interparticle spacing of about 0.5 μm is achieved.

The oxygen contents of the commercially pure metal powders and the master alloys range from 0.05 to 0.2 wt%. The refractory compounds that can be added include carbides, nitrides, and oxides. For the production of dispersion-strengthened materials, such additions are limited to very stable oxides, such as yttria, alumina, or, less frequently, thoria. These oxides, which are prepared by calcination of oxalate precipitates, consist of crystallites of about 50 nm agglomerated into pseudomorphs of about 1 μm.

The only restriction on the mixture of powder particles for mechanical alloying (other than the particle size range mentioned above and the need to minimize excessive oxygen) is that at least 15 vol% of the mix should consist of a compressibly deformable metal powder. The function of this component, which can consist of any one or all of the pure metals, is to act as a host or binder for the other constituents during the process.

Commercial Alloys. The most commercially important nickel-base mechanically alloyed ODS alloys include MA 754, MA 758, MA 6000, and, to a lesser extent, MA 760 (the latter alloy is in limited production). Compositions of these alloys are given in Table 5.

Table 5 Nominal compositions (wt%) of mechanically alloyed nickel-base superalloys

Alloy	Ni	Cr	Al	Ti	Mo	W	Y_2O_3	Ta
MA 754	bal	20	0.3	0.5	…	…	0.6	…
MA 757	bal	16	4.0	0.5	…	…	0.6	…
MA 758	bal	30	0.3	0.5	…	…	0.6	…
MA 760	bal	20	6.0	…	2.0	3.5	0.95	…
MA 6000	bal	15	4.5	0.5	2.0	4.0	1.1	2.0
TMO-2(a)	bal	6	4.2	0.8	2.0	12.4	1.1	4.7

(a) This alloy additionally contains 9.7 wt% cobalt.

The most significant advantage of ODS superalloys is the increased stress rupture properties. Figure 6 compares the 1000 h specific rupture strength (strength/density) for two ODS alloys (MA 6000 and thoria-dispersed nickel) and two cast alloys (directionally solidified Mar-M200 + Hf) and single-crystal PWA 454). It is clear from this figure that the MA 6000 alloy can maintain a given stress for a much longer time than a casting alloy for similar vane applications. This is mainly due to the benefits of the combined strengthening modes (γ' and ODS) in the mechanically alloyed material.

Effects of Alloying Elements and Intermetallic Phases on Welding

Nickel- and iron-nickel-base superalloys are considerably less weldable than cobalt-base superalloys. Because of the presence of the γ' strengthening

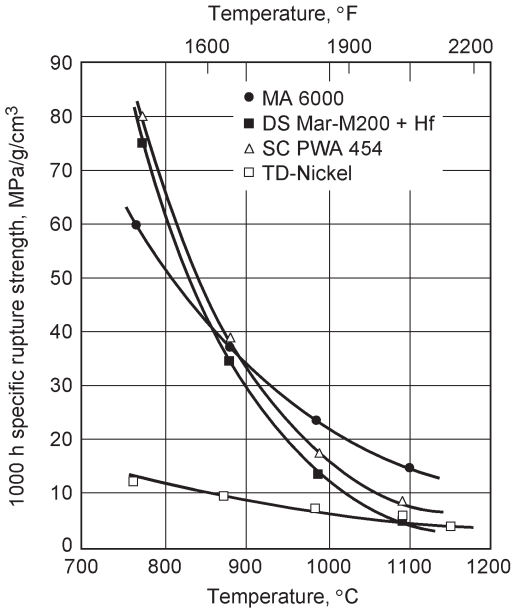


Fig. 6 Comparison of 1000 h specific rupture strength of MA 6000 with directionally solidified Mar-M200 + Hf, TD-Ni, and single-crystal PWA 454

phase, the alloys tend to be susceptible to hot cracking (weld cracking) and postweld heat treatment (PWHT) cracking (strain age or delay cracking). The susceptibility to hot cracking is directly related to the aluminum and titanium contents (γ' formers). Hot cracking occurs in the weld heat-affected zone (HAZ), and the extent of cracking varies with alloy composition and weldment restraint. Welding is normally restricted to the lower V_f γ' (≤ 0.35) alloys generally in the wrought condition.

Figure 7 shows a plot of weldability as a function of (Al + Ti) content. Those alloys with low aluminum and titanium contents, shown below the diagonal line, are more readily weldable and less susceptible to strain-age cracking. However, as combined aluminum and titanium is increased, welding becomes more difficult, and strain-age cracking is more likely. Alloys like René 41 and Waspaloy are borderline; they weld with relatively little difficulty but sometimes crack during postweld heat treating. Casting alloys with high aluminum and titanium, like 713C and IN-100, have low ductility at all temperatures and usually crack during welding, although repair welding (e.g., turbine-blade and vane-tip restoration) can be carried out if nonhardenable filler metal is used.

Because of their γ' strengthening mechanism and capability, many nickel- and iron-nickel-base superalloys are welded in the solution heat treated condition. Special preweld heat treatments have been used for some alloys. Nickel-niobium alloys, as typified by IN-718, have unique welding characteristics. The hardening phase, γ'', is precipitated more sluggishly at a lower temperature than is γ' so that the attendant welding-associated strains that must be redistributed are more readily accommodated in the weld metal and HAZ. The alloy is welded in the solution-treated condition and then given a postweld stress-relief-and-aging treatment that

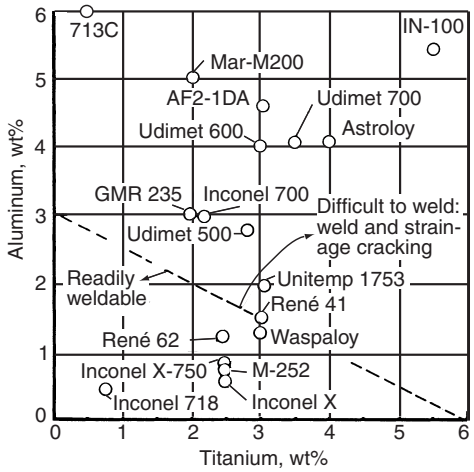


Fig. 7 Weldability diagram for some γ'-strengthened iron-nickel- and nickel-base superalloys, showing influence of total aluminum + titanium hardeners

causes γ' precipitation. The superior weldability of IN-718 has largely contributed to the popularity of the alloy. It is one of the most widely used superalloys.

SELECTED REFERENCES

- M.J. Donachie and S.J. Donachie, Superalloys, *Metals Handbook Desk Edition*, 2nd ed., J.R. Davis, Ed., ASM International, 1998, p 394–413 (Note: this article contains an extensive bibliography on superalloy processing, microstructures, and properties.)
- M.J. Donachie and S.J. Donachie, Ed., *Superalloys*: *A Technical Guide*, 2nd ed., ASM International, to be published in 2002
- J.R. Davis, Ed., *ASM Specialty Handbook*: *Heat-Resistant Materials*, ASM International, 1997

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Refractory Metal Alloys

Introduction and Overview

Property Characteristics. The refractory metals include molybdenum, tungsten, niobium (also known as columbium), tantalum, and rhenium. The refractory metals and their alloys have been so named for their heat resistance, which is attributable to their characteristic high melting points, good elevated-temperature strength and mechanical stability, and good resistance to softening. They also have high densities, low vapor pressures, and relatively low thermal expansion coefficients compared to other common structural metals and alloys. With the exception of rhenium, which has a hexagonal close-packed (hcp) crystal structure, the refractory metals have body-centered cubic (bcc) crystal structures. Table 1 compares some of the physical properties refractory metals with those iron, aluminum, and copper.

All of the refractory metals are readily degraded by oxidizing environments at relatively low temperatures; this property has restricted their use as high-temperature materials. Protective coating systems have been developed, mostly for niobium alloys, to permit their use in high-temperature oxidizing aerospace applications. While the refractory metals have high oxidation tendencies, some of these metals (most notably niobium and tantalum) have exceptionally good resistance to certain corrosion environments. For example, tantalum is immune to attack by almost all acids except hydrofluoric acid.

The refractory metals with a bcc crystal structure display a ductile-to-brittle transition temperature (DBTT) behavior typical of such metals. When tested below the transition temperature (that is, where cleavage or the intergranular fracture mode prevails) these metals behave in a brittle, glasslike manner. The bcc crystal structure refractory alloys show DBTTs at and above room temperature. Moreover, ductility is sensitive to the presence of impurity elements segregated to recrystallized grain boundaries.

Table 1 Properties of the refractory metals compared to those of iron, copper, and aluminum

Metal	Crystal structure	Density, g/cm^3	Melting point		Elastic modulus		Thermal expansion coefficient at room temperature	
			°C	°F	GPa	10^6 psi	ppm/°C	ppm/°F
Refractory metals								
Niobium	bcc	8.57	2468	4474	102	15	7.3	4.1
Tantalum	bcc	16.6	2996	5425	186	27	6.5	3.6
Molybdenum	bcc	10.2	2610	4730	324	47	4.9	2.7
Tungsten	bcc	19.2	3410	6170	400	58	4.6	2.6
Rhenium	hcp	21.0	3180	5755	460	67	6.7	3.7
Metals for comparison								
Iron	bcc	7.87	1538	2798	208	30	11.8	6.5
Copper	fcc	8.93	1085	1981	115	17	16.5	9.2
Aluminum	fcc	2.70	660	1220	62	9	23.6	13.1

Applications. At one time, refractory metals were limited to use in lamp filaments, electron tube grids, heating elements, and electrical contacts. However, they have since found widespread application in the aerospace, electronics, nuclear and high-energy physics, and chemical process industries. Each of the refractory metals, with the exception of rhenium, is consumed in quantities exceeding 900 metric tonnes annually worldwide.

Molybdenum and Molybdenum Alloys

Molybdenum combines a high melting point (2610 °C, or 4730 °F) with strength retention at high temperatures. Molybdenum also boasts a high specific elastic modulus, which makes it attractive for applications that require both high stiffness and low weight. The high thermal conductivity, low coefficient of thermal expansion, and low specific heat of this metal provide resistance to thermal shock and fatigue, and these properties are also important in electronic applications. In addition, molybdenum is stable in a wide variety of chemical environments, and it has good electrical conductivity, although this physical property is seldom the critical factor in materials selection.

Molybdenum is generally commercially available in the worked/stress-relieved, annealed condition. These molybdenum products have a DBTT of –20 to 40 °C (–4 to 104 °F). Should the wrought/stress-relief/annealed product be heated above its recrystallization temperature (about 1100 °C, or 2010 °F), the DBTT rises to 40 to 80 °C (100 to 175 °F), making the metal brittle when cooled to room temperature.

Molybdenum mill products are produced by vacuum-arc casting (VAC) or powder metallurgy (P/M) processing. P/M billets are subsequently pressed and sintered followed with extruding, rolling, or forging. Cast ingots are first hot-extruded and then processed into mill products by

conventional forming processes. More molybdenum is consumed annually than any other refractory metal. Most molybdenum is used as an alloying element in irons, steels, and superalloys. Molybdenum-base mill products represent about 5% of total usage.

Classes of Molybdenum-Base Alloys

As shown in Table 2, there are several classes of commercial molybdenum-base alloys:

- *Carbide-strengthened alloys* rely on the formation of fine reactive-metal carbides to dispersion strengthen the material, and to increase the recrystallization temperature above that of pure molybdenum by stabilizing the dislocation structure formed during processing. These alloys are produced in both VAC and P/M grades.
- *Solid-solution alloys* are produced in both VAC and P/M grades.
- *Combination alloys,* such as HWM-25 (Mo-W-Hf-C), contain both carbide-forming and substitutional elements to provide improved high-temperature strength.
- *Dispersion-strengthened P/M alloys* rely on second-phase particles, introduced or produced during powder processing, to increase the resistance to recrystallization and stabilize the recrystallized grain structure. These alloys have enhanced high-temperature strength and improved low-temperature ductility.

Table 2 Compositions of selected commercial molybdenum alloys

Alloy	Alloying additions, wt %	Recrystallization temperature, °C (°F)
Unalloyed Mo	…	1100 (2010)
Reactive-metal-carbide alloys		
TZM (MT-104)	0.5 Ti, 0.08 Zr, 0.03 C	1400 (2550)
TZC	1.2 Ti, 0.3 Zr, 0.1 C	1550 (2820)
MHC (HCM)	1.2 Hf, 0.05 C	1550 (2820)
ZHM	0.5 Zr, 1.5 Hf, 0.2 C	1550 (2820)
Solid-solution alloys		
25W	25 W	1200 (2190)
30W	30 W	1200 (2190)
5 Re	5 Re	1200 (2190)
41 Re	41 Re	1300 (2370)
50 Re	47.5 Re	1300 (2370)
Combination alloy		
HWM-25 (Mo25WH)	1 Hf, 0.07 C, 25 W	1650 (3000)
Dispersion-strengthened alloys		
Z-6	0.5 ZrO_2	1250 (2280)
MH (HD)	150 K, 300 Si (ppm)	1800 (3270)
KW	200 K, 300 Si, 100 Al (ppm)	1800 (3270)

Source: Ref 1

Some of the important properties of molybdenum and its alloys are compared in Table 3. Not listed in Tables 2 and 3 are composite molybdenum-silver alloys made by P/M processing. These materials are described in the article "Electrical Contact Alloys.

Table 3 Property comparison of refractory metal alloys

Nominal alloy additions, wt %	Common designation	Most common product form	Usual condition(a)	Low-temperature ductility class(b)	Typical high-temperature strength			
					Temperature, °C	Tensile, MPa	Temperature, °C	10 h rupture, MPa
Niobium and its alloys								
None	Unalloyed Nb	All	Rx	A	1095	69	1095	37
1 Zr	Nb-1Zr	All	Rx	A	1095	158	1095	96
1 Zr, 0.1 C	PWC-11	All	Rx	A	1095	130	…	…
10 Hf, 1 Ti, 0.7 Zr	C-103 (KBI 3)	All	Rx	A	1095	186	…	…
10 Ta, 10 W	SCb-291	Bar, sheet	Rx	A	1095	220	1095	62
10 W, 10 Hf, 0.1 Y	C-129Y	Sheet	Rx	A	1315	179	1095	103
28 Ta, 11 W, 0.8 Zr	FS-85	Sheet	Rx	A	1315	158	1315	83
Molybdenum and its alloys								
None	Unalloyed Mo(c)	All	SRA	B-C	1000	50	980	175
0.5 Ti, 0.08 Zr, 0.03 C	TZM (MT-104)(c)	All	SRA	B-C	1000	600	1315	140
1.2 Ti, 0.3 Zr, 0.1 C	TZC	All	SRA	B-C	1000	800	1315	190
1.2 Hf, 0.05 C	MHC (HCM)	All	SRA	B-C	1000	800	1315	210
0.5 Zr, 1.5 Hf, 0.2 C	ZHM	All	SRA	B-C	1000	800	1400	200
25 W	25W	All	SRA	B-C	1000	330	…	…
30 W	30W(c)	All	SRA	B-C	1000	350	1095	140
1 Hf, 0.07 C, 25 W	HWM-25 (Mo25WH)	All	SRA	C	1000	900	1300	200
5 Re	5 Re	All	SRA or Rx	B	1000	400	1650	7
41 Re	41 Re	All	SRA or Rx	B	1000	600	…	…
47.5 Re	50 Re	All	SRA or Rx	B	1000	580	1600	27
0.5 ZrO_2	Z-6	All	SRA	B-C	1000	280	…	…
150 K, 300 Si (ppm)	MH (HD)	Wire, sheet	CW, SRA	B	1000	300	…	…
200 K, 300 Si, 100 Al (ppm)	KW	Wire, sheet	CW, SRA	B	1000	300	…	…
Tantalum and its alloys								
None	Unalloyed Ta	All	Rx	A	1315	59	1315	7
7.5 W (P/M alloy)	FS-61	Wire, strip	CW	A	25	1140	…	…
2.5 W, 0.15 Nb	FS-63	All	Rx	A	95	315	…	…
25 W	KBI-6	All	Rx	A	95	315	…	…
10 W	Ta-10W	All	Rx	A	1315	345	1315	140
8 W, 2 Hf	T-111	All	Rx	A	1315	255	…	…
8 W, 1 Re, 1 Hf, 0.025 C	Astar 811C	All	Rx	A	1315	275	…	…
40 Nb	KBI-40	All	Rx	A	260	290	…	…
37.5 Nb, 2.5 W, 2 Mo	KBI-41	All	Rx	A	260	515	…	…
Tungsten and its alloys								
None	Unalloyed W	Wrought bar	SRA	D	1000	620	…	…
		Sheet, wire	SRA	D	1650	120	1650	50
None	Unalloyed W	CVD sheet	Rx	D	1000	565	…	…
Al, K, Si (ppm levels)	Doped AKS W	Wire	CW	C	1650	650	…	…
1 ThO_2	W-1% ThO_2	Bar, sheet, wire	SRA	D	1650	255	…	…
2 ThO_2	W-2% ThO_2	Bar, sheet, wire	SRA	D	1650	205	1650	125
15 Mo	W-15Mo	Bar, sheet	SRA	D	1650	250	1650	85
4 Re	W-4Re	Wire, ribbon	SRA or Rx	C	1650	150	…	…
25 Re	W-25Re	All	SRA or Rx	B	1650	275	1650	95
4 Re, HfC	W-4Re-HfC	Wire	SRA	C	1650	620	…	…
Rhenium								
None	Unalloyed Re(c)	All	Rx	A	20	1172/2324(d)	1600	56
					500	786/1196(d)	2200	21
					1000	588/855(d)	2800	4.2
					1500	262/276(d)	…	…
					2000	…/103(d)	…	…
					2300	53/…(d)	…	…

(a) CW, cold worked; Rx, recrystallized; SRA, stress-relief annealed. (b) A, excellent cryogenic ductility; B, excellent room-temperature ductility; C, may have marginal ductility at room temperature; D, normally brittle at room temperature. (c) Available in both powder metallurgy and arc-cast forms. (d) First value, annealed material; second value, wrought material cold worked 15% Source: Ref 2

Effects of Alloying Elements

Carbide-strengthened alloys were the first molybdenum alloys to be commercialized. Mo-0.5Ti, the initial alloy, is no longer commercially available. Its high-temperature strength and recrystallization resistance were improved by adding about 0.08% zirconium, resulting in the alloy known as TZM. A higher-alloy-content modification of TZM, TZC, has improved properties and responds to an age-hardening heat treatment. However, TZC has not replaced TZM as the commercial alloy of choice, primarily due to economic considerations. More recently, alloys strengthened with hafnium carbide (MHC) and combinations of reactive metal carbides (ZHM) have been marketed. Figure 1 compares elevated-temperature properties of carbide-strengthened alloys. Additional property data are listed in Table 3. The carbide-strengthened molybdenum alloys are used in making tooling materials, rotating discs for rapid solidification processing, and glassmaking equipment.

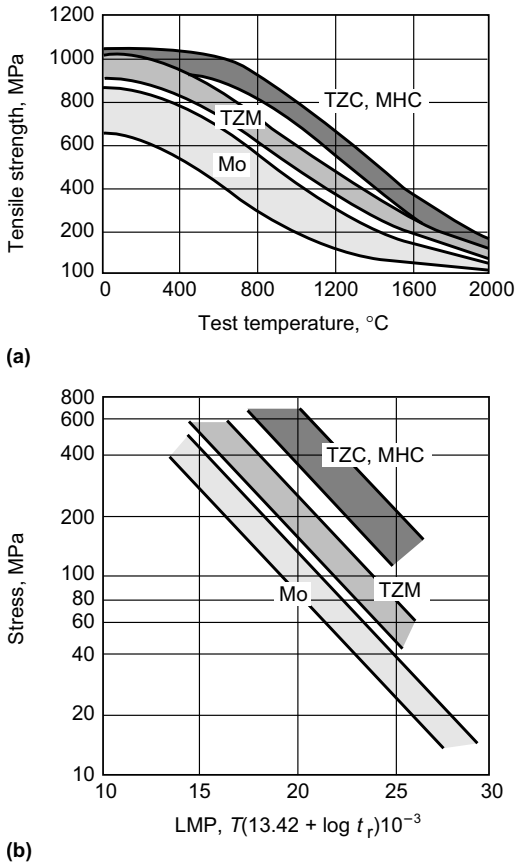


Fig. 1 Elevated-temperature properties of molybdenum and molybdenum alloys. (a) Tensile strength. (b) Larson-Miller parameter (LMP) with temperature given in degrees Kelvin and the time to rupture, t_r, given in hours. Source: Ref 1

Solid-Solution Alloys. Tungsten and rhenium are the substitutional elements of interest in solid-solution molybdenum alloys. In addition to several "standard" alloys, other compositions can be special ordered. With the exception of Mo-30W, which is also available as a VAC product, the solid-solution molybdenum alloys are normally made via P/M.

The molybdenum-tungsten alloys were developed for their chemical resistance, and they are primarily used in equipment for handling molten zinc. They are lower-cost, lighter-weight alternatives to pure tungsten in these applications. The commercial importance of molybdenum-rhenium alloys is due to the so-called "rhenium effect", which results in the material's having a significantly lower DBTT. The most common alloys contain 5, 41, and 50% (actually 47.5%) Re. The 5Re and 41Re alloys are used for thermocouple wire and for structural applications in the aerospace market. The W-50Re alloy is typically specified for high-temperature structural components.

Dispersion-Strengthened Alloys. Doped molybdenum alloys were the first dispersion-strengthened materials. They are analogous to the Al-K-Si-doped tungsten alloys (AKS tungsten), developed for lamp filaments. They were initially designed to satisfy lighting industry requirements for creep-resistant molybdenum parts. Doped alloys such as MH and KW (see Tables 2 and 3) do not have particularly high strength at low temperatures, but these materials are extremely resistant to recrystallization and have excellent creep resistance.

The dopant strengthening mechanism is unique. Small "bubbles" of dopant are retained in the sintered ingot and are highly elongated by subsequent deformation. Annealing causes the elongated dopant regions to "pinch off," forming arrays of extremely fine bubbles that impede grain boundary motion during recrystallization. The result is recrystallized material having an elongated, interlocked grain structure, which is much more ductile at ambient temperatures than the equiaxed recrystallized structure of pure molybdenum and other molybdenum alloys. This stable grain structure also reduces grain boundary creep, producing a one-to-two order of magnitude decrease in steady-state creep rate, compared with that of pure molybdenum.

Dispersions of reactive-metal oxides also are used to improve the elevated-temperature strength and creep resistance of molybdenum. An example is the zirconia-dispersion-strengthened alloy Z-6 (0.5% ZrO_2). A fine, initial oxide dispersion is critical to alloy performance, because the "pinching-off" mechanism of doped alloys is not operative. The improvement in steady-state creep rate provided by the zirconia-stabilized grain structure is similar to that produced by doping.

Tungsten and Tungsten Alloys

The key characteristics and properties of tungsten are its high melting point (3410 °C, or 6170 °F), high stability (strength and softening resistance,

low vapor pressure) at elevated temperatures, high elastic modulus (400 GPa, or 58×10^6 psi), good electrical and thermal conductivity, and high density (19.2 g/cm^3, or 0.697 lb/in.^{3}).

Tungsten suffers from brittleness and notch sensitivity, with a DBTT above room temperature (150 to 300 °C, or 300 to 570 °F). In unalloyed tungsten with low impurity content, cold working lowers the DBTT to below room temperature.

Tungsten and tungsten mill products are produced primarily by P/M techniques. Tungsten sheet has also been produced by chemical vapor deposition (CVD). Tungsten and tungsten alloys may also be produced by arc casting and electron beam melting, but these processes are not of significant importance.

Basic commerical processing involves extrusion and forging with rolling and drawing used as follow-up for making the finish forms. The alloys are "warm" worked at about 1200 °C (2190 °F), that is, at temperatures above the DBTT (about 300 °C, or 572 °F, for unalloyed tungsten) and below the recrystallization temperature (about 1370 °C, or 2500 °F) in order to avoid embrittlement caused by the crack sensitivity of recrystallized grain boundaries. Processing sequences of warm working at temperatures above about 650 °C (1200 °F) with interpass softening anneals (recovered, not recrystallized) intentionally develops a microstructure with elongated, cold-worked grains, with interlocked boundaries and with a recovered dislocation substructure, providing alternate, less-embrittling sites for interstitial impurity segregation. In this condition, the material can be further worked or can be used in applications requiring hardness and strength at moderate, subrecrystallization temperatures. Such a cold-worked structure exhibits property anisotropy in sheet form. For higher-temperature use, the more stable, recrystallized grain structure needed to provide creep resistance and mechanical stability is obtained by alloy-doping techniques.

In terms of refractory metal consumption, tungsten ranks second to molybdenum, with more than 8500 metric tonnes consumed annually. Cutting tools account for 59% of the total; mill products, 26%; alloying in steels and superalloys, 9%; and chemicals and miscellaneous applications, 6%.

Classes of Tungsten-Base Alloys

- *Doped tungsten* containing minute quantities of aluminum (15 ppm), silicon (50 ppm), potassium (90 ppm), and oxygen (35 ppm)
- *Solid-solution alloys* containing various amounts of molybdenum (2 to 20%) or rhenium (1 to 25%)
- *Dispersion-strengthened alloys* containing 1 to 2% ThO_2, or tungsten-rhenium alloys with a dispersion of ThO_2 or HfC added
- *Tungsten heavy alloys,* which consist of tungsten-nickel-iron, tungsten-nickel-iron, and tungsten-nickel-cobalt

- *Composite tungsten-copper or tungsten-silver alloys* for electrical contacts. These composite P/M materials are discussed in the article "Electrical Contact Alloys".

Properties of various tungsten alloys are compared in Table 3.

Effects of Alloying Elements

The doped tungsten alloys, or AKS alloys, are made by adding aluminum, potassium, and silicon compounds at dopant levels to the tungsten powder before pressing. During the sintering treatment at about 3000 °C (5430 °F) in hydrogen, the oxides are reduced and the dopants volatilized. Potassium, in particular, at residual levels of about 85 wt ppm (400 at. ppm) is entrapped in stringers of nanometer-size bubbles that become aligned along grain boundaries, creating jagged boundaries during grain growth during in-process recrystallization anneals (Fig. 2). The resulting interlocking of recrystallized grain boundaries promotes good creep resistance, providing a more stable structure that shows less deflection and distortion during repeated heating cycles at high temperatures, making them suitable for common electric lamp filaments that can reach temperatures as high as 2500 °C (4530 °F) in service.

Solid-Solution Alloys. Both tungsten-molybdenum and tungsten-rhenium alloys have been extensively studied. Tungsten-molybdenum alloys are of interest because molybdenum helps refine the grain size of arc-cast tungsten. They also are less dense than unalloyed tungsten, which is a plus for aerospace applications. In addition, molybdenum lowers the melting point of tungsten, which makes it easier to produce material by melt processing. On the other hand, tungsten-molybdenum alloys have lower maximum useful operating temperatures than unalloyed tungsten. The effects of various molybdenum additions on the properties of tungsten-molybdenum alloys are shown in Table 4 and Fig. 3. A current application of tungsten-molybdenum alloys is a rotating shaft that operates in a corrosive environment. Other materials met requirements for corrosion resistance, but the tungsten-base alloy also offered superior wear resistance.

Tungsten-rhenium alloys are of tremendous interest because of the ductilizing effect achieved by the rhenium addition. Tungsten-rhenium alloys are stronger than unalloyed tungsten, and they have a lower DBTT and higher recrystallization temperature. (Rhenium is the only alloying element known to lower the DBTT of tungsten.) The effects of various rhenium additions on the properties of tungsten-rhenium alloys are shown in Fig. 4 and 5. Applications of tungsten-rhenium alloys include high-temperature thermocouple elements, propulsion-system components, and rotating anodes for x-ray tubes (the rhenium addition provides increased resistance to thermal shock and thermal fatigue).

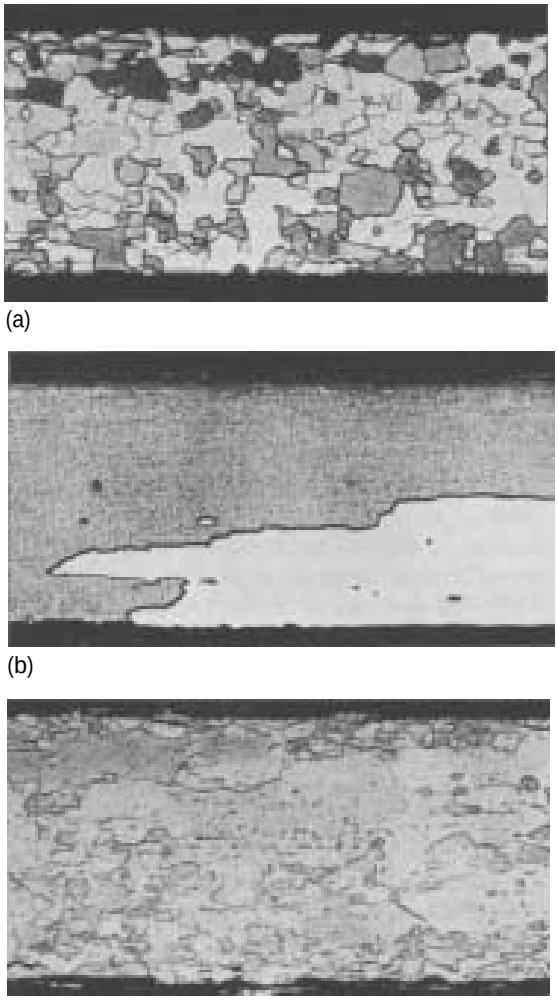


Fig. 2 Photomicrographs comparing (a) the fully recrystallized, equiaxed grains in undoped tungsten wire to (b) the "interlocked" recrystallized grain structure of doped tungsten wire and to (c) the recrystallized structure of mixed grain size due to ThO_2 particles (black dots) in thoriated tungsten wire. Wire diam., 0.2 mm (0.007 in.); annealed at 2700 °C (4890 °F) for 5 min. 200×

Table 4 Properties of tungsten-molybdenum alloys

Alloy content, wt %		Melting point, °C	Density, g/cm^3	Thermal coefficient, µm/m · K, at 20 to 100 °C	Brinell hardness
Molybdenum	Tungsten				
100	0	2600	10.2	4.75×10^{-3}	200
90	10	2620	11.2	4.02×10^{-3}	210
80	20	2640	12.1	3.50×10^{-3}	230
72.5	27.5	2675	12.8	3.25×10^{-3}	250
51	49	2850	14.8	2.90×10^{-3}	300
20	80	3075	17.5	3.20×10^{-3}	330
0	100	3370	19.3	4.82×10^{-3}	350

Source: Ref 3

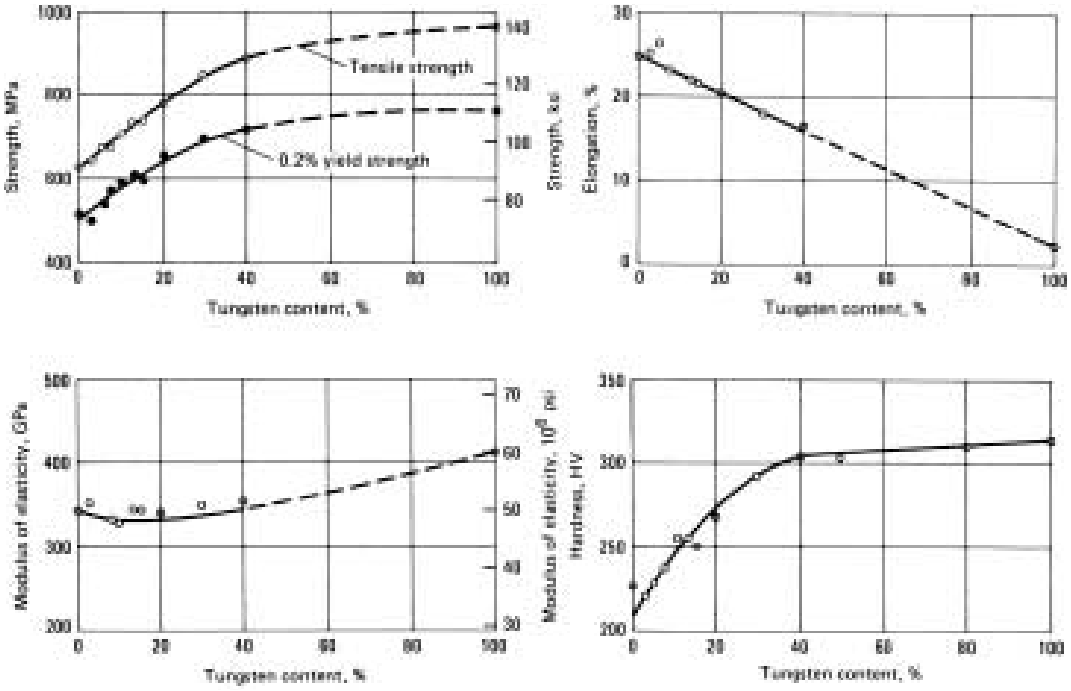


Fig. 3 Effect of tungsten content on the room-temperature mechanical properties of tungsten-molybdenum alloys

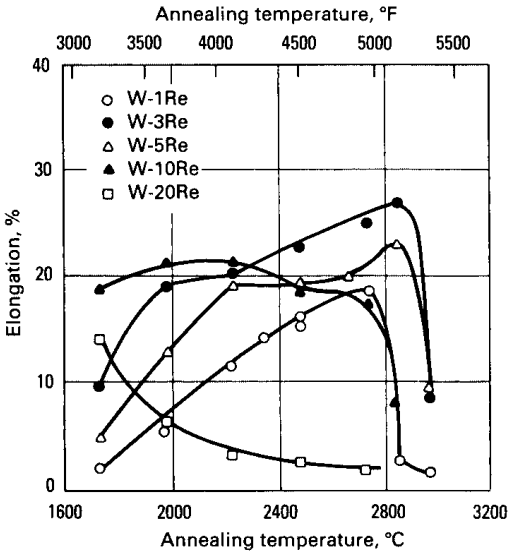


Fig. 4 Room-temperature ductility of annealed wire for five tungsten-rhenium alloys

Dispersion-Strengthened Alloys. Thoriated tungsten was originally developed as a filament alloy for the lighting industry. The ThO_2 dispersion modifies the grain structure, resulting in extended filament life. ThO_2 also increases the high-temperature strength and lowers the work function of tungsten. (A lower work function translates into less evaporative loss of tungsten at the high filament operating temperature.)

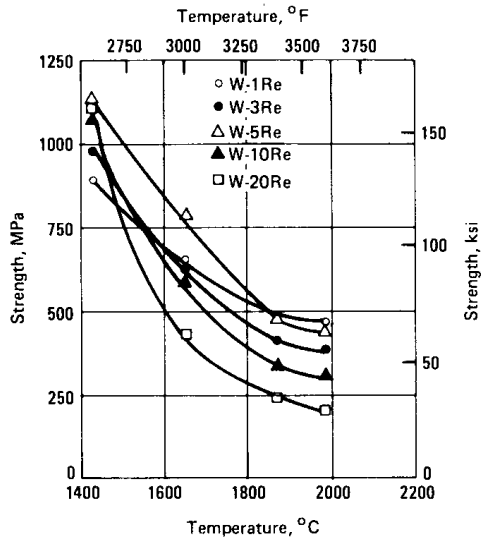


Fig. 5 Short-time tensile strengths of five tungsten-rhenium alloys

Today, thoriated tungsten is also used as a high-temperature structural material. The ThO_2 particles retard recrystallization in wrought tungsten, which inhibits grain growth at high temperatures and results in a maximum temperature capability that is several hundred degrees higher than that of unalloyed tungsten. ThO_2 particles also interact with dislocations during deformation, which strengthens the material via the classical dispersion-hardening mechanism. Thoriated tungsten is stronger than unalloyed tungsten at all temperatures.

As noted above, the addition of rhenium to tungsten simultaneously raises high-temperature strength (via solid-solution strengthening) and low-temperature ductility. To further improve the strength of tungsten-rhenium alloys, a dispersion of ThO_2 or HfC may be added. Research also has been conducted on the strengthening effects of zirconia particles formed by internal oxidation of tungsten-zirconium alloys.

Dispersion-strengthened tungsten alloys are among the strongest materials ever produced for service at temperatures up to 2000 °C (3630 °F). Of the tungsten alloys, those in the W-Re-HfC system have the highest strength (Fig. 6). W-Re-HfC alloys currently are in an advanced stage of development and are being evaluated for a number of applications, including reinforcing fibers in cast nickel-base superalloy turbine blades (to increase the temperature capability) and as structural materials in space-based power generating systems.

Tungsten heavy alloys (WHAs) typically consist of 90 to 98 wt% W in combination with a binder phase of some combination of nickel, iron, and/or cobalt. These high-density alloys (17.0 to 18.5 g/cm^3) are used for such applications as counterweights and balances, radiation shielding, antiarmor kinetic energy penetrators, and fragmentation warheads.

The bulk of WHA produced falls into the 90 to 95% W range. The majority of current uses for WHAs are best satisfied with the W-Ni-Fe

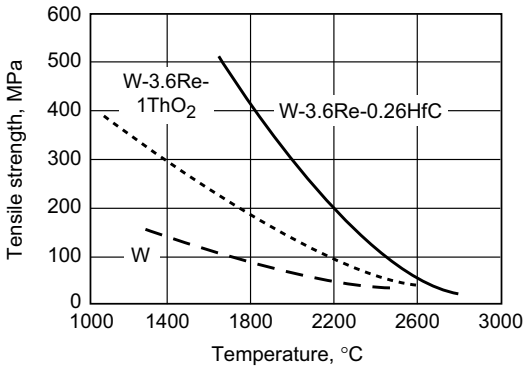


Fig. 6 Elevated-temperature tensile strength of dispersion-strengthened tungsten alloys. Source: Ref 4

system. Alloys such as 93W-4.9Ni-2.1Fe and 95W-4Ni-1Fe represent common compositions. Nickel-iron ratios in the range of 2 to 4 are most common and produce optimum mechanical properties. The W-Ni-Fe alloys are produced by the liquid-phase sintering process, which results in a microstructure consisting of tungsten spheroids (approximately 40 to 60 μm in size) in a binder phase of transition metals plus dissolved tungsten (Fig. 7).

The addition of cobalt to a W-Ni-Fe alloy is a common approach for slight enhancement of both strength and ductility. The presence of cobalt within the alloy provides solid-solution strengthening of the binder and slightly enhanced tungsten-matrix interfacial strength. Cobalt additions of 5 to 15% of the nominal binder weight fraction are most common.

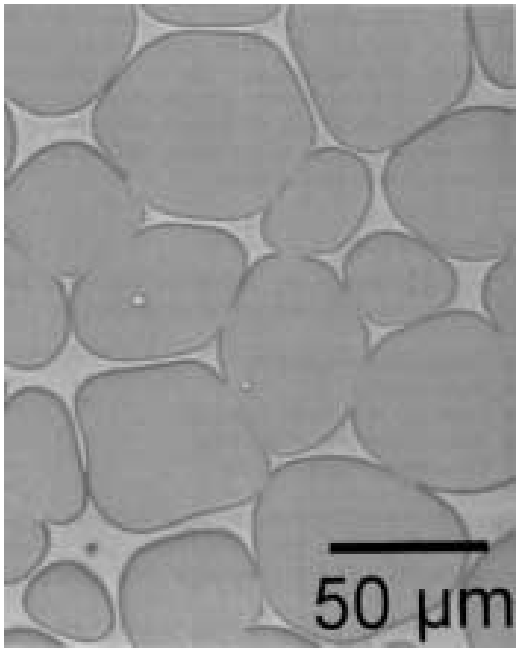


Fig. 7 Typical microstructure of a liquid-phase sintered W-7Ni-3Fe heavy alloy showing the spheroidized tungsten phase in a solid solution binder

Niobium and Niobium Alloys

Niobium, formerly called columbium in the United States, has a lower density (8.57 g/cm^3, or 0.310 lb/in.^{3}), a lower melting point (2468 °C, or 4474 °F) and a lower modulus of elasticity (102 GPa, or 15×10^6 psi) than the other refractory metals. Because niobium and its alloys are relatively light and high in elevated-temperature strength, they are used extensively for aerospace applications. Niobium is also quite corrosion resistant, especially in nitric and hydrochloric acids, and can be used in contact with liquid metals such as lithium, sodium, and sodium-potassium. Niobium-base materials, most notably a binary NbTi composition containing 45 to 50% Ti and the intermetallic compound Nb_3Sn, are used in superconducting applications.

The DBTT of commercially pure, polycrystalline niobium sheet ranges from approximately −160 to −200 °C (−255 to −330 °F), lower than that of all refractory metals except tantalum. The DBTT increases with higher impurity content. Tight control of impurities is also important during manufacture of niobium and its alloys to guarantee processing capability.

Niobium and niobium alloys can be made by P/M techniques, but are usually made by consumable electrode vacuum arc melting and electron beam melting ingot techniques. Fabrication of the common alloys is generally accomplished by high-temperature extrusion or forging near the alloy recrystallization temperature, which is typically 1095 to 1370 °C (2000 to 2500 °F). Secondary fabrication is completed by warm working and cold working to final shapes with appropriate stops for recrystallization annealing, which is performed under vacuum. Most commercial alloys are ductile enough to be processed into various mill products, such as sheet, foil, rod, wire, and tubing.

Presently, the use of niobium as an alloying element in steels, superalloys, and nonferrous alloys accounts for about 95% of production; the consumption of niobium and niobium-base alloys accounts for the remaining 5%. Niobium ranks third, behind molybdenum and tungsten, in terms of refractory metal production.

Classes of Niobium-Base Alloys

Most of the niobium-base alloys discussed in this section were developed during the 1960s and early 1970s for a number of high-temperature applications. As listed in Table 5, niobium alloys can be categorized as follows:

- *Low-strength, high-ductility alloys,* which are highly fabricable and weldable. Included in this group are Nb-1Zr and PWC-11 (Nb-1Zr-0.1C), used for containment of liquid alkali metals in space nuclear power systems. These alloys typically contain additions of zirconium

Table 5 Compositions of selected niobium alloys

Common designation	Nominal alloy additions, %
Low strength and high ductility	
Nb-1Zr	1 Zr
D-14, B-33	5 Zr
C-103	10 Hf, 1 Ti, 0.7 Zr
Cb-753	5 V, 1.25 Zr
D-36	10 Ti, 5 Zr
Moderate strength and ductility	
PWC-11	1 Zr, 0.1 C
SCb-291	10 W, 10 Ta
C-129Y	10 W, 10 Hf, 0.1 Y
Cb-752	10 W, 2.5 Zr
D-43	10 W, 1 Zr, 0.1 C
FS-85	28 Ta, 11 W, 0.8 Zr
SU-16	10 W, 3 Mo, 2 Hf
B-66	5 Mo, 5 V, 1 Zr
AS-55	10 W, 1 Zr, 0.06 Y
High strength	
Cb-1	30 W, 1 Zr, 0.05 C
B-88	28 W, 2 Hf, 0.07 C
SU-31	17 W, 3.5 Hf, 0.12 C, 0.05 Si
Cb-132M	20 Ta, 15 W, 5 Mo, 1 Zr, 0.1 C
F-48	15 W, 5 Mo, 1 Zr, 0.05 C
F-50	15 W, 5 Mo, 5 Ti, 1 Zr, 0.05 C
WC-3009	30 Hf, 9 W

or hafnium, which remove oxygen from solution in niobium by precipitation of ZrO_2 or HfO_2.

- *Moderate strength, fabricable alloys,* generally produced in the form of sheet for aerospace applications. Alloys such as FS-85 (Nb-28Ta-10W), C129Y (Nb-10W-10Hf-0.2Y), and B-66 (Nb-5Mo-5V-1Zr) are typical of this group.
- *Higher-strength alloys,* developed for gas turbine blades. Examples include B-88 (Nb-28W-2Hf-0.07C) and Cb-1 (Nb-30W-1Zr-0.06C).

Properties of these alloys are listed in Table 3.

Effects of Alloying Elements

The alloying additions used in commercial and advanced developmental niobium alloys include:

- Substitutional solutes (Mo, W, V, Ta)
- Reactive elements that have a higher negative free energy of formation for carbides, nitrides, and/or oxides than the matrix element (Zr, Hf, Ti)
- Interstitials (C, N)

The effects of these alloying elements on the DBTT, elevated-temperature yield strength, and creep strength of niobium alloys are reviewed below.

A key objective in developing alloys for structural applications is to achieve appropriately high strength levels while maintaining satisfactory

fabricability and ductility. Niobium, in common with other metals having a bcc crystal structure, undergoes a ductile-to-brittle transition at low temperatures. In pure niobium, the tensile transition temperature is quite low, on the order of –200 °C (–325 °F), but solutes can increase the transition temperature rather dramatically. Figure 8 shows the effect of binary alloy additions on the fracture transition temperature of niobium. In early studies, the group VA elements (chromium, molybdenum, and tungsten) had a pronounced effect in raising this temperature, as did rhenium and aluminum. The reactive elements zirconium and hafnium had much less effect, and titanium and tantalum had no significant influence. These studies indicated that only a limited number and range of substitutional solutes could be used if a balanced combination of properties was to be achieved.

Similar data on elevated-temperature (1095 °C, or 2000 °F) yield strength are shown in Fig. 9. Again, significant strengthening was exhibited by alloys containing additions of tungsten, molybdenum, chromium, rhenium, and vanadium, while titanium had no effect on short-time elevated-temperature strength properties. However, in these tests appreciable strengthening was exhibited by alloys containing zirconium and hafnium. Because these alloys were produced with niobium of moderate interstitial level (250 ppm C, 150 ppm N, and 450 ppm O), part of the strengthening may be attributed to the interaction of the interstitials with the reactive solutes zirconium and hafnium.

The relative effect of alloy additions on the creep strength of niobium is quite different. McAdam (Ref 6) investigated the effects of various substitutional solutes on the creep strength of niobium. The strengthening contributions of the individual elements are summarized in Fig. 10, where the contributions are expressed as a percentage of the effect of tungsten,

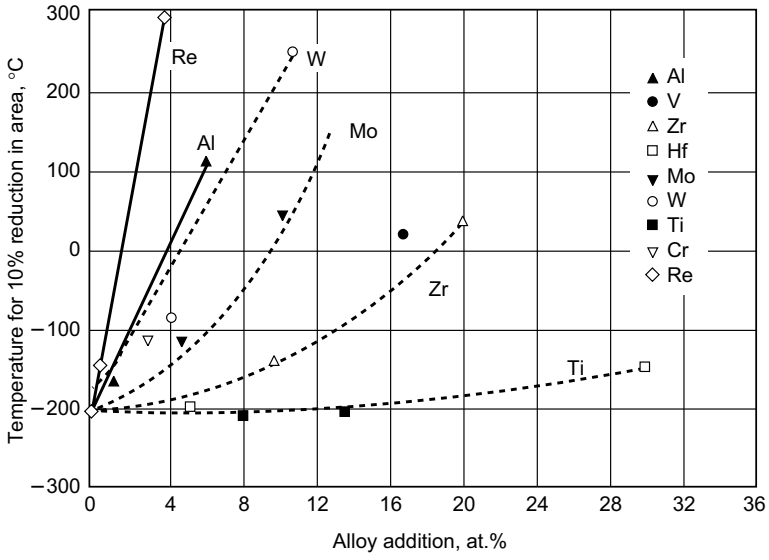


Fig. 8 Effect of binary alloy additions on the transition temperature of niobium. Source: Ref 5

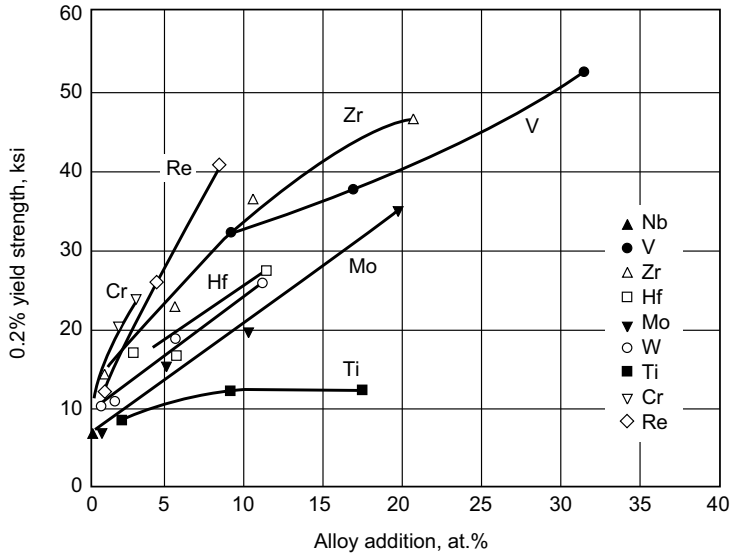


Fig. 9 Effect of binary alloy additions on the yield strength of niobium at 1095 °C (2000 °F). Source: Ref 5

the most potent solute. The data are for 1200 °C (2190 °F). McAdam's results showed that the group VIA elements, particularly tungsten and molybdenum, improved the creep strength of niobium, as did rhenium and tantalum. Unfortunately these elements, with the exception of tantalum, also raised the fracture transition temperature of niobium significantly. McAdam also observed that vanadium, hafnium, zirconium, and titanium make a negative contribution to the creep strength of niobium alloys, even though, as stated above, vanadium has a potent effect in increasing the short-time elevated-temperature strength of niobium. The weakening of niobium by titanium additions has been observed by a number of investigators. McAdam showed that the precious metals osmium, iridium, and ruthenium were effective strengthening elements, but they were not considered for engineering alloys because of the obvious cost and availability problems.

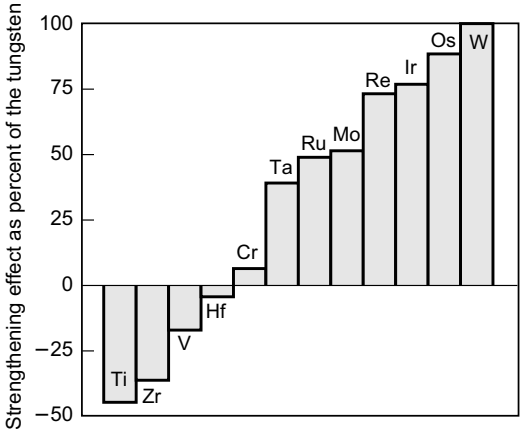


Fig. 10 Creep strengthening effect of alloying elements in niobium at 1200 °C (2190 °F). Source: Ref 5

In summary, only a limited number and range of alloy additions can be effectively used in niobium alloys intended for high-temperature applications (Ref 5). Tungsten and molybdenum are effective strengtheners but significantly degrade low-temperature ductility and weldability. Rhenium has the same characteristics and provides no benefit compared to tungsten as an alloy addition. Furthermore, all of these elements increase alloy density. Tantalum provides moderate strengthening without degrading low-temperature ductility or fabricability, but this benefit is achieved at the expense of alloy density. Vanadium is a very effective strengthener with respect to short-time properties, but it degrades creep strength. Titanium additions result in ductile and fabricable alloys but greatly degrade strength properties. Alloy additions of zirconium and hafnium are used primarily to form carbides and carbonitrides for dispersed-phase strengthening. Strengthening of niobium alloys arising from the precipitation of reactive metal carbides and nitrides has been shown by many investigators, and this strengthening mechanism is a key contributor to the properties of the higher-strength niobium alloys, such as B-88, Cb-1, and Cb-132M. Experience with high-strength niobium alloys indicates that hafnium additions are equally effective carbide formers as zirconium, and that they provide somewhat superior fabricability than zirconium at equivalent additions.

Tantalum and Tantalum Alloys

Tantalum provides a combination of properties not found in other refractory metals. Its high melting point (2996 °C, or 5425 °F), tolerance for interstitial elements, and reasonable modulus of elasticity make it an attractive alloy base material. Tantalum also possesses excellent room-temperature ductility (>20% tensile elongation), is readily weldable, has a very low DBTT (about 25 K, or about –250 °C) in both the welded and unwelded conditions, and exhibits relatively high-solid solubility for other refractory and reactive metals.

The production of tantalum and its alloys starts with tantalum powder, which is isostatically pressed into bars. The bars are then electron-beam-melted into ingots or sintered at high temperature under vacuum. Alloying can take place either in the electron beam furnace or during a subsequent vacuum arc remelting operation. The ingots are broken down by either forging or extruding. Vacuum sintered bars can be rolled directly without any prior breakdown. Tantalum products can subsequently be manufactured by standard cold-working techniques such as rolling, drawing, tube reducing, and swaging.

About 25% of annual production appears as mill products in the form of plate/sheet, rod/bar, and tube. Because of its relatively good thermal conductivity and its remarkably good corrosion resistance to many industrial

chemicals and body fluids, tantalum mill products are used in the chemical process industry as heat exchangers and tank liners, as well as for prosthetic devices. It is clad to copper, aluminum, or steel to take advantage of the combination of properties available with a composite, including lower cost. In elevated-temperature service, tantalum and its alloys are used in various aerospace applications and in heating elements in vacuum furnaces to take advantage of the good forming and welding capability as well as its good elevated-temperature strength. Its high density and excellent formability are called upon for shape-charge liner components of armor penetrators. About 50% of annual tantalum production is used in the electronics industry as capacitors to take advantage of the uniquely high value and temperature stability (over the range −55 to 125 °C, or −67 to 257 °F) of the dielectric constant of its oxide. In terms of total refractory metal consumption, tantalum ranks behind molybdenum, tungsten, and niobium.

Effects of Alloying on Mechanical Properties

Table 6 lists the most common tantalum alloys developed to date. As with niobium alloys, most of these alloys were developed prior to 1973.

Tantalum shows complete solid solubility for tungsten, niobium, and molybdenum and rather extensive solubility for hafnium, zirconium, rhenium, and vanadium, giving a wide choice of alloying elements available for solution hardening of the base metal. Ta-2.5 W (Tantaloy 63), for example, is used in heat exchangers and in welded-tube applications requiring high formability. The tungsten addition adds solid-solution hardening, increasing the room-temperature tensile strength by about 25%, or by 35 to 70 MPa (5 to 10 ksi), but doubling the elevated-temperature yield strength at 200 °C (390 °F) over that of unalloyed tantalum. At 1000 °C (1830 °F), this alloy has tensile properties of 69 MPa (10 ksi) yield strength, 124 MPa (18 ksi) tensile strength, and 20% elongation. The alloy Ta-10W (UNS R05255) offers still higher room-temperature tensile strength (482 MPa, or 70 ksi, min) and a higher elastic modulus (207 GPa, or 30×10^6 psi) than unalloyed tantalum. This alloy is used in aerospace applications and can be used at temperatures up to 2480 °C (4500 °F).

Table 6 Compositions of selected tantalum alloys

Common designation	Nominal alloy additions, %
Tantaloy 63	2.5 W, 0.15 Nb
Ta-5W	5 W
FS-61	7.5 W
Ta-10W	10 W
T-111	8 W, 2 Hf
T-222	10 W, 2.5 Hf, 0.01 C
Astar-811C	8 W, 1 Re, 1 Hf, 0.025 C
Astar-1211C	12 W, 1 Re, 1 Hf, 0.025 C
Astar-1511C	15 W, 1 Re, 1 Hf, 0.025 C
KBI40	40 Nb
WC-640	40 Nb, 0.5 W
Ta-Mo	Various Mo contents ranging from 10 to <50%

Still other tantalum alloys are available that combine solution-hardening elements, such as alloy T-111, containing 8W-2Hf, and alloy T-222, containing 10W-2.5Hf-0.01C. In addition, the solid-solution alloy Ta-40Nb is regarded as an inexpensive substitute for alloys richer in tantalum. This solution-hardened alloy combines the tensile strength of Ta-2.5W with a lower density (12.1 g/cm^3, or 0.437 lb/in.^{3}) and elastic modulus (152 GPa, or 22×10^6 psi), falling proportionally between the values of the pure metals, as one would expect for a solid solution.

As indicated in Table 3, the elevated-temperature properties of tantalum alloys are generally superior to those of niobium alloys but lower than those of either molybdenum or tungsten alloys. Alloys strengthened from a dispersed second phase by the addition of carbon exhibit superior creep and high-temperature yield properties (Table 7). Some of these alloys (e.g., Astar-811C) have creep properties similar to those of molybdenum and tungsten alloys. High-temperature annealing treatments are recommended for carbide-strengthened alloys in order to increase grain size, which in turn improves creep strength.

Effects of Alloying on Corrosion Resistance

Tantalum has excellent resistance to corrosion by a large number of acids, by most aqueous solutions of salts, by organic chemicals, and by various combinations and mixtures of these agents. Tantalum also exhibits good resistance to many corrosive and common gases and to many liquid metals. At moderate temperatures (below about 150 °C, or 300 °F), the only media that can affect it are fluorine, hydrofluoric acid, sulfur trioxide (including fuming sulfuric acid), concentrated strong alkalis, and certain molten salts. The corrosion resistance of tantalum is about the same as that of glass, but it withstands higher temperatures and offers the intrinsic fabrication advantages of a metal. Additional information can be found in Ref 8.

Although the majority of corrosion studies on tantalum have been performed on the unalloyed metal, several tantalum-base alloys have also demonstrated excellent corrosion resistance in various environments. As described below, these include various tantalum-tungsten alloys (most

Table 7 Mechanical behavior of tantalum alloys at 1316 °C (2400 °F)

Alloy	Carbon content	Yield strength		Stress for 1 % creep elongation in 10,000 h
		MPa	ksi	
Ta-10W	(a)	120	17.4	5
T-111	(a)	190	27.6	4
T-222	0.01	260	37.7	20
Astar-811C	0.025	215	31.2	60
Astar-1211C	0.025	267	38.7	90
Astar-1511C	0.025	288	41.8	96

(a) No carbon deliberately added to alloys. Source: Ref 7

Table 8 Corrosion rates for tantalum materials exposed to concentrated H_2SO_4 at 175 to 200 °C (345 to 392°F)

Material	Metallurgical condition	Temperature °C	Temperature °F	Exposure, days	Corrosion rate mm/yr	Corrosion rate mils/yr
Ta, electron beam melted	Recrystallized	175	345	60	0.005	0.189
Ta, P/M	Recrystallized	175	345	60	0.0055	0.217
Tantaloy 63	Recrystallized	175	345	60	0.0058	0.229
Tantaloy 63	As-rolled	181	360	7	0.0026	0.104
Tantaloy 63	Stress-relieved	181	360	7	0.0022	0.087
Tantaloy 63	Recrystallized	181	360	7	0.0022	0.087
Ta, electron beam melted	As-rolled	199	390	3	0.018	0.72
Ta, electron beam melted	Recrystallized	199	390	3	0.024	0.96
Tantaloy 63	As-rolled	199	390	3	0.0048	0.19
Tantaloy 63	Stress-relieved	199	390	3	0.0043	0.17
Tantaloy 63	Recrystallized	199	390	3	0.0045	0.18
Ta, electron beam melted	Recrystallized	200	392	32	0.057	2.24
Ta, (P/M)	Recrystallized	200	392	32	0.058	2.27
Tantaloy 63	Recrystallized	200	392	32	0.029	1.15
Tantaloy 63	Recrystallized	200	392	13	0.03	1.24
Ta-5W	Recrystallized	200	392	13	0.034	1.34
Ta-10W	Recrystallized	200	392	13	0.05	1.98

notably Ta-2.5W-0.15Nb), tantalum-molybdenum alloys, tantalum-niobium alloys, and tantalum-titanium alloys.

Tantalum-Tungsten Alloys. Samples of 0.18 to 0.75 mm (0.007 to 0.03 in.) thick strip or sheet of the following materials were exposed for selected times in concentrated (95.5 to 98%) sulfuric acid (H_2SO_4) at chosen temperatures ranging from 175 to 200 °C (345 to 390 °F):

- Tantalum, electron beam melted
- Tantalum, powder metallurgy
- Tantaloy 63 (Ta-2.5W-0.15Nb)
- Ta-5W
- Ta-10W

Some tests on electron-beam-melted tantalum and Tantaloy 63 were conducted on materials in the as-rolled, stress-relieved, and fully recrystallized conditions. The average corrosion rates observed in these tests are listed in Table 8. Corrosion rate as a function of tungsten content is plotted in Fig. 11 for additional tests on electron-beam-melted tantalum,

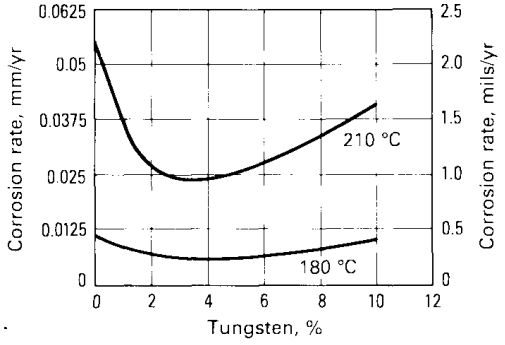


Fig. 11 Corrosion rate versus tungsten content for tantalum-tungsten alloys exposed to concentrated H_2SO_4 at 180 °C (360 °F) and 210 °C (405 °F)

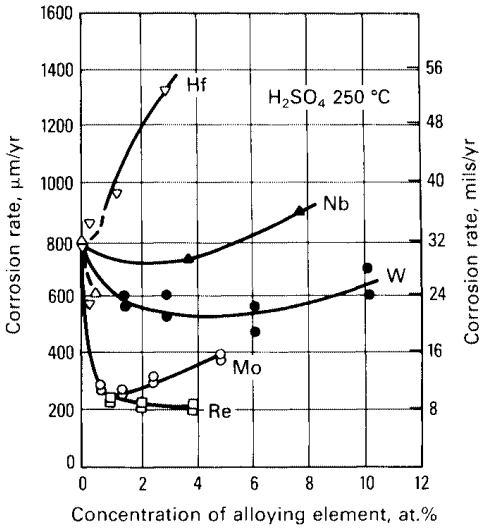


Fig. 12 Influence of alloying elements on the corrosion rate of binary tantalum alloys exposed 3 days to 95% H_2SO_4 at 250 °C (480 °F). Source: Ref 9

Tantaloy 63 (Ta-2.5W-0.15Nb), Ta-5W, and Ta-10W exposed to concentrated H_2SO_4 at 180 and 210 °C (360 and 405 °F).

The corrosion behavior of substitutional tantalum-molybdenum, tantalum-tungsten, tantalum-niobium, tantalum-hafnium, tantalum-zirconium, tantalum-rhenium, tantalum-nickel, tantalum-vanadium, tantalum-tungsten- molybdenum, tantalum-tungsten-niobium, tantalum-tungsten-hafnium, and tantalum-tungsten-rhenium alloys was studied in various corrosive mediums, including concentrated H_2SO_4 at 200 and 250 °C (390 and 480 °F) (Ref 8). Figure 12 gives corrosion data in 95% H_2SO_4 for several binary tantalum alloys. Tantalum became embrittled in concentrated H_2SO_4 at 250 °C (480 °F). Additions of tungsten reduced the corrosion rate and hydrogen absorption, but additions of molybdenum and rhenium were more effective in reducing both effects. Additions of niobium and vanadium had only a slight influence on the corrosion rate of tantalum; lower-valence elements, such as hafnium, increased the corrosion rate (Ref 9).

Hydrochloric Acid. Samples of recrystallized sheet of electron beam melted tantalum and Tantaloy 63 were exposed in the same test in a tantalum autoclave to concentrated (37 to 38%) HCl at 100 °C (212 °F) for 24 h. The corrosion rates of these materials were:

	Corrosion rate	
Alloy	**mm/yr**	**mils/yr**
Tantalum	0.04	1.6
Tantaloy 63	0.023	0.9

Corrosion rates for Tantaloy 63 in three metallurgical conditions exposed to concentrated HCl at 100 °C (212 °F) for 24 h in another autoclave test were about tenfold lower:

Condition	Corrosion rate	
	μm/yr	mils/yr
As-rolled	0.8	0.032
Stress relieved	1.0	0.039
Fully recrystallized	1.0	0.039

Researchers in other tests also found that tantalum and substitutional tantalum-base alloys became hydrogen embrittled in concentrated HCl at 150 °C (300 °F) (Ref 9).

Nitric Acid. Samples of unalloyed, electron beam melted tantalum and Tantaloy 63 were exposed to concentrated (70%) HNO_3 for 3 days at about 200 °C (390 °F). Following this test, neither material showed any measurable weight loss. Additional tests on Tantaloy 63 tested in 70% HNO_3 at about 200 °C (390 °F) for 72 h in an autoclave reactor gave the following corrosion rates for material in three metallurgical conditions:

Condition	Corrosion rate	
	μm/yr	mils/yr
As-rolled	0.1	0.0038
Stress-relieved	0.04	0.0016
Fully recrystallized	0.038	0.0015

Other Aqueous Media. The Ta-10W binary solid-solution alloy, has been used in some applications, such as pump and valve parts, for which a material appreciably harder and stronger than the pure metal is desired. For example, Ta-10W alloy is used as an insert in the plug of a tantalum-lined split-body valve to give a hard plug to soft seat combination when used with a tantalum seat.

A search of the literature indicated that very little corrosion data were available on the Ta-10W alloy (Ref 10). This alloy is of interest as a repair metal for glass-lined steel equipment because it is of much higher strength than unalloyed tantalum. Consequently, corrosion tests were conducted on the Ta-10W alloy in various environments (Ref 10).

Figure 13 shows the corrosion rate as a function of H_2SO_4 concentration for tests at 205 and 230 °C (400 and 450 °F). These data indicate that either unalloyed tantalum or Ta-10W alloy can be used at 230 °C (450 °F) to handle H_2SO_4 in concentrations below 90%. Although the corrosion rates at 205 °C (450 °F) are similar for the two materials, on the basis of this graph, the corrosion weight loss of the Ta-10W alloy is about twice

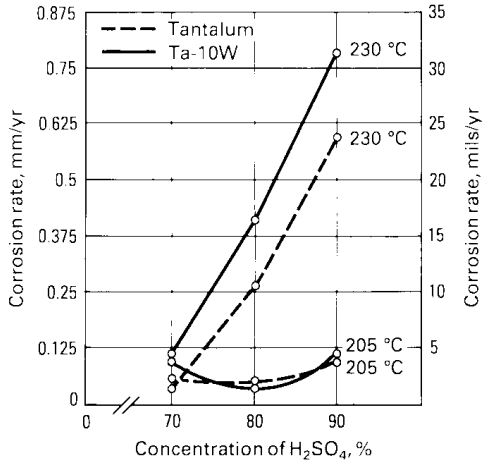


Fig. 13 Corrosion rate versus concentration for tantalum and Ta-10W alloy exposed to H_2SO_4 at various temperatures. Source: Ref 10

that of unalloyed tantalum at 230 °C (450 °F) in H_2SO_4 over the concentration range of 70 to 90%.

Little or no weight loss occurred below 175 °C (350 °F) in HCl, even at 30% concentration. At 190 °C (375 °F), a small amount of attack was detected, with that for the Ta-10W alloy being more severe.

In the HNO_3 corrosion tests, even up to 175 °C (350 °F) in concentrations to 60%, it was concluded that neither the tantalum nor the Ta-10W alloy showed any perceptible loss in weight (Ref 11). No comments were made regarding the small weight gains observed in most cases.

Tests were also conducted in 5% sodium hydroxide (NaOH) solution at 100 °C (212 °F). Considerable weight losses occurred on both the unalloyed tantalum and the alloy under caustic conditions. The difference, if any, in the corrosion rates of the two materials appears small.

The NaOH corrosion test was conducted because tantalum is known to be susceptible to caustic embrittlement; therefore, it was desired to determine whether the Ta-10W alloy suffered embrittlement also. Unalloyed tantalum showed approximately a 25% increase in yield strength and a 10% increase was attributed to a pickup of interstitial elements (oxygen, nitrogen, and hydrogen), although chemical analyses of the materials before and after exposure were not conducted. With the Ta-10W alloy, the exposure to 5% NaOH at 100 °C (212 °F) produced embrittlement as evidenced by the premature fracture in the tensile test. Reportedly, such embrittlement was not evident on the sample of the Ta-10W alloy to which a platinum spot had been welded before the test.

The corrosion resistance of tantalum-tungsten alloys was also studied in 50% potassium hydroxide (KOH) at 30 and 80 °C (85 and 175 °F), 20% hydrofluoric acid (HF) at 20 °C (70 °F), and KOH:$3K_3Fe(CN)_6$ mixture (concentration not given) (Ref 12). In the hydroxide solutions, a maximum corrosion rate was obtained at about 60 at.% tantalum. Although the alloy system reportedly represents a continuous series of solid solutions,

a maximum electrical resistance also was found at the same composition. In 20% HF solution, the tantalum-tungsten alloy system essentially exhibits the relatively low corrosion rates associated with tungsten, except when the tantalum concentration exceeds 80 at.%, at which concentration the corrosion increases markedly. Alloys containing more than 18% W show no corrosion in 20% HF, thus offering an advantage over pure tantalum. Other tests have been conducted on tantalum and tantalum-tungsten alloys having tungsten contents ranging from 8.7 to 20.4% in 20% HF. This work showed that tantalum and tantalum-tungsten alloys containing less than about 20% W were more susceptible to attack by 20% HF than was previously reported. Tantalum-tungsten alloys showed little improvement over tantalum when tested in the $KOH:3Fe(CN)_6$ mixture.

Combined Reagents. In a proposed dehydrator application, the exposure was to be to an environment containing 61.5% HNO_3 plus 7% magnesium nitrate ($Mg(NO_3)_2$) at 115 °C (238 °F). Although no significant corrosion on tantalum would be expected upon exposure to the separate reagents, tests were conducted on the mixture to determine corrosion rates. Base metal and weldment specimens of tantalum and Tantaloy 63 were used. Within the precision of the weight measurements, no specimen of either tantalum or Tantaloy 63 showed any weight loss in these corrosion tests.

Phosphoric Acid Plus Residual Hydrofluoric Acid. The use of tantalum in H_3PO_4, other than the high-purity Food Grade acid, has always been questioned because fluoride compounds are usually present. The observation has been made in several publications and bulletins that the presence of a small amount of HF (<5 ppm) in commercial H_3PO_4 causes severe corrosion of tantalum (Ref 13). Therefore, tantalum has not been considered resistant to H_3PO_4 containing more than a trace of F^- ion.

In one test, a sample of Tantaloy 63 was exposed to a wet-process H_3PO_4 at an average temperature of 155 °C (310 °F) for a total of 283.5 h. Following the corrosion exposure, the sample (0.64 mm, or 0.025 in., thick) was fully ductile and withstood bending flat on itself with no evidence of cracking. There was no indication of corrosion on the surface of the specimen, and metallographic examination of a cross section of the specimen showed no evidence of corrosion attack. The weight loss data for the exposure equated to a corrosion penetration rate of 0.004 mm/yr (0.15 mils/yr). These data suggested that the tantalum alloy showed good corrosion resistance to the hot-wet process H_3PO_4.

Tantalum-Molybdenum Alloys. Corrosion resistance was studied on tantalum-molybdenum alloys that form a continuous series of solid solutions (Ref 14). The entire alloy system is extremely corrosion resistant, and the corrosion resistance of tantalum is generally retained when the alloy contains more than about 50% Ta. Table 9 gives weight loss data for

Table 9 Corrosion rates of tantalum-molybdenum alloys in concentrated H_2SO_4 at 150 °C (300 °F)

Solutions were saturated with oxygen.

Tantalum in molybdenum, at. %	Average corrosion rate, $mg/cm^2/d$	
	Concentrated H_2SO_4 (98 %)	Concentrated HCl (37 %)
0	0.008	0.018
10.1	0.009	0.017
20.1	0.008	0.018
30.0	0.010	0.009
40.0	0.009	0.010
50.0	0.000	0.010
61.2	0.000	0.000
71.5	0.000	…
82.8	0.000	0.000
91.4	0.000	0.000
100.0	0.000	0.000

tantalum-molybdenum alloys in concentrated H_2SO_4 and concentrated HCl at 150 °C (300 °F).

Tantalum-Niobium Alloys. Corrosion tests were conducted in hot and cold concentrated HCl and H_2SO_4 on alloys having various proportions of tantalum and niobium (Ref 15). The corrosion rates increased roughly in proportion to the niobium content in the alloy. Even though the 95Ta-5Nb alloy showed excellent resistance in all exposures, the attack was three times that obtained on pure tantalum. Additional corrosion data on binary tantalum-niobium alloys are given in Ref 16 and 17.

Other data were reported on corrosion tests of binary tantalum-niobium alloys and ternary alloys based on the Ta-Nb system (Ref 18). Tests on the materials were carried out in 75% H_2SO_4 at 185 °C (360 °F), in 70% H_2SO_4 at 165 °C (330 °F), in 75% H_2SO_4 at room temperature, and in 20% HCl at room temperature. The tantalum-niobium alloys containing approximately 60% or more tantalum appeared promising for boiling 70% H_2SO_4. Ternary alloys containing elements of groups IVA, VA, and VIA with tantalum and niobium did not offer any advantages in fabricability, and addition of zirconium, hafnium, chromium, and vanadium lowered the corrosion resistance.

One manufacturer developed an alloy designated WC-640 for corrosion-resistant applications (Ref 19). Analysis of a sheet sample showed that the chemical composition actually corresponded to a ternary tantalum-niobium-tungsten alloy, nominally Ta-40Nb-0.5W. Tensile properties of WC-640 were found to be similar to those of Tantaloy 63. The alloy exhibited excellent resistance to all test environments except concentrated H_2SO_4 at 200 °C (390 °F) and 40% NaOH at 100 °C (212 °F).

Tantalum-Titanium Alloys. Considerable data have been accumulated on the corrosion resistance of tantalum-titanium alloys (Ref 14). Dilution of tantalum with titanium shows considerable promise for the possibility

of providing a lower-cost alloy with corrosion resistance almost comparable to that of tantalum in some selected environments. In addition to dilution with a lower-cost material, the resulting marked reduction in density is particularly advantageous because corrosion applications generally require materials on a volume rather than a weight basis. Corrosion tests in 10 to 70% HNO_3 at the boiling point and at 190 °C (375 °F) (in sealed glass tubes) were conducted on tantalum-titanium alloys ranging from pure tantalum to Ta-90Ti. All of these materials showed excellent behavior, with corrosion rates less than 0.025 mm/yr (1 mil/yr) and no indication of embrittlement.

Hydrogen embrittlement may occur when this alloy system is exposed to reducing corrosive conditions in tests conducted in sealed capsules. The tendency for hydrogen damage is markedly decreased as the tantalum concentration is increased (Ref 12).

Other Tantalum Alloys. It has been observed that the presence of a small amount of iron or nickel, for example, in a tantalum weld makes that site subject to about the same acid attack as would be experienced by iron or nickel alone (Ref 12). Galvanic action, as well as simple chemical attack, is undoubtedly involved.

Rhenium and Rhenium-Bearing Alloys

Rhenium is a strong, ductile, refractory metal with an hcp crystal structure. It has a very high density (21.0 g/cm^3, or 0.760 lb/in.^{3}) and melting point (3180 °C, or 5755 °F). It has good mechanical stability at elevated temperatures, offering good resistance to thermal shock and wear, and higher creep resistance and strength than the other refractory elements. Elevated-temperature properties of unalloyed rhenium are listed in Table 3.

Rhenium does not have a DBTT, as it retains its ductility from subzero to high temperatures. Rhenium also has a very high modulus of elasticity that, among metals, is second only to those of iridium and osmium (Ref 20). As temperature increases from room temperature to 725 °C (1340 °F), the modulus decreases only about 20%. This implies that structures made of rhenium will have excellent mechanical stability and rigidity, permitting the design of parts having thin sections.

Rhenium is primarily made using P/M techniques. Rhenium powder is cold pressed into and sintered in inert atmospheres to produce compacts with densities more than 90%. Electron beam melting is sometimes used to reduce the impurity content of rhenium compacts. Chemical vapor deposition is an alternative fabrication method. Rhenium can be cold-worked, but because of its high work hardening rate, it must be annealed frequently between cold-working reduction steps. Primary working is done by rolling, swaging, or forging.

Platinum-rhenium reforming catalysts are the major rhenium end-use products and account for about 85% of rhenium consumption. Rhenium is also used for heating elements, electrical contacts, thermocouples, and filaments for electrical devices, including large-diameter lamp filaments. Because it is in short supply and costly, rhenium is used mostly as an alloying addition to the other refractory alloys in non-catalyst applications.

Rhenium Alloying Additions. Because of its hcp structure, rhenium has a high solubility in transition metals having bcc and face-centered cubic (fcc) structures. This characteristic was used to advantage in the development of tungsten-rhenium and molybdenum-rhenium alloys, which derive their properties from the so-called "rhenium effect": A rhenium addition simultaneously improves strength, plasticity, and weldability, lowers the DBTT of wrought products, and reduces the degree of recrystallization embrittlement. A rhenium addition changes the deformation mechanism during warm and cold working from slipping only to twinning and slipping, and it neutralizes the embrittling effects of carbon and oxygen. The greatest improvements in properties are obtained with additions of 10 to 26 wt% Re to tungsten and 11 to 50 wt% Re to molybdenum.

Data for 7 to 12 mm (0.3 to 0.5 in.) thick rolled plates of molybdenum-rhenium and tungsten-rhenium alloys show that hardness increases with increasing amounts of rhenium beyond about 5% (Ref 20). The hardness of W-26Re is 20% greater than that of pure tungsten, and the tensile strength is more than twice as high, with an elongation of 15 to 18%. The recrystallized grain size decreases from 62 μm (0.002 in.) for pure tungsten to 32 μm (0.001 in.) for W-26Re. The hardness of Mo-41Re is 60% greater than that of pure molybdenum, and the strength of the alloy is 75% higher, while its elongation is an acceptable 17%.

Rhenium is also a solid-solution-strengthening alloying element in superalloys. A number of directionally solidified and single-crystal nickel-base superalloys contain up to 3% Re. One recently developed single-crystal superalloy (CMSX-10) contains 6% Re as well as 0.25 to 0.20% Mo, 3.5 to 7.5% W, 7.0 to 10.0% Ta, and 0.5% Nb.

REFERENCES

1. J.A. Shields, Jr., Molybdenum and Its Alloys, *Advanced Materials & Processes*, Vol 142 (No. 4), Oct 1992, p 28–36
2. Datasheet: Typical Properties of Refractory Metals and Their Alloys, *Advanced Materials & Processes*, Vol 142 (No. 3), Sept 1992, p 54
3. R.L. Heestand, A History of Tungsten- and Molybdenum-Base Alloys, *Evolution of Refractory Metals and Alloys*, TMS-AIME, 1994, p 109–117

4. J.P. Wittenaurer, T.G. Nieh, and J. Wadsworth, Tungsten and Its Alloys, *Advanced Materials & Processes*, Vol 142 (No. 3), Sept 1992, p 28–37
5. R.T. Begley, Columbium Alloy Development at Westinghouse, *Evolution of Refractory Metals and Alloys*, TMS-AIME, 1994, p 29–48
6. G.D. McAdam, Substitutional Niobium Alloys of High Creep Strength, *J. Inst. Met.*, Vol 93, 1964–65, p 59–564
7. R.W. Buckman, Jr. and R.L. Ammon, Evolution of Tantalum Alloy Development, *Evolution of Refractory Metals and Alloys*, TMS-AIME, 1994, p 49–79
8. M. Schussler and C. Pokross, Corrosion of Tantalum, *Corrosion*, Vol 13, *ASM Handbook*, ASM International, 1987, p 725–739
9. L.A. Gypen, M. Brabers, and A. Deruyttere, Corrosion Resistance of Tantalum Base Alloys, Elimination of Hydrogen Embrittlement in Tantalum by Substitutional Alloying, *Werkst. Korros.*, Vol 35, 1984, p 37–46
10. B.G. Staples and W.S. Galloway, Jr., Recent Results of Testing Corrosion Performance of 90-10 Tantalum-Tungsten Alloy, Pfaudler Reprint 581, reprinted from *Mater. Protect.*, Vol 7 (No. 7), July 1968, p 34–39
11. N.D. Tomashov, T.V. Chukalovskaya et al., "Investigation of the Corrosion Resistance of Alloys of the Ti-Ta-Nb Systems," translation of the Foreign Technology Division, Air Force Systems Command, FTD-HT-149-74
12. C.A. Hampel, Ed., *Tantalum in Rare Metals Handbook*, 2nd ed., Reinhold, 1967
13. Corrosionomics, Vol 3 (No. 1), Fansteel Inc., 1958
14. M. Stern and C.R. Bishop, Corrosion and Electrochemical Behavior, in *Columbium and Tantalum*, F.T. Sisco and E. Epremian, Ed., John Wiley & Sons, 1963
15. G.L. Miller, *Tantalum and Columbium*, Academic Press, 1959
16. A.V. Mosolov, I.D. Nefedova, and I.Y. Klinov, Corrosion and Electrochemical Behavior of Niobium-Tantalum Alloys in HCl at Elevated Temperatures and Pressures, *Z. Metallov.*, Vol 4 (No. 3), May-June 1968, p 248–251 (in English)
17. A.P. Gulyaev and I.Y. Georgieva, Corrosion Resistance of Binary Niobium Alloys, *Z. Metallov.*, Vol 1 (No. 6) Nov–Dec 1965, p 652–657 (in English)
18. D. Lupton and F. Aldinger, Possible Substitutes for Tantalum in Chemical Plant Handling Mineral Acids, in *Trends in Refractory Metals*, *Hard Metals*, *and Special Materials and Their Technology*, Proceedings of the 10th Plansee Seminar, Reutte, Austria, 1981, p 101–130
19. "Columbium (niobium)," TWCA-8204 Cb Teledyne Wah Chang Albany

20. B.D. Bryskin, Rhenium and Its Alloys, *Advanced Materials & Processes*, Vol 142 (No. 3), Sept 1992, p 22–27

SELECTED REFERENCES

- Refractory Metals and Alloys, *ASM Specialty Handbook*: *Heat-Resistant Materials*, J.R. Davis, Ed., ASM International, 1997, p 361–382
- J.B. Lambert et al., Refractory Metals and Alloys, *Properties and Selection*: *Nonferrous and Special-Purpose Alloys*, Vol 2, *ASM Handbook*, ASM International, 1990, p 557–585

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Ordered Intermetallics

Introduction and Overview

Alloys based on ordered intermetallic compounds constitute a unique class of metallic material that form long-range ordered crystal structures (Fig. 1) below a critical temperature, generally referred to as the critical ordering temperature (T_c). These ordered intermetallics usually exist in relatively narrow compositional ranges around simple stoichiometric ratio (see the phase diagrams shown in this article).

The search for new high-temperature structural materials has stimulated much interest in ordered intermetallics. Recent interest has been focused on nickel aluminides based on Ni_3Al and NiAl, iron aluminides based on Fe_3Al and FeAl, and titanium aluminides based on Ti_3Al and TiAl. These aluminides possess many attributes that make them attractive for high-temperature structural applications. They contain enough aluminum to form, in oxidizing environments, thin films of alumina (Al_2O_3) that are compact and protective. They have low densities, relatively high melting points, and good high-temperature strength properties (Tables 1 and 2).

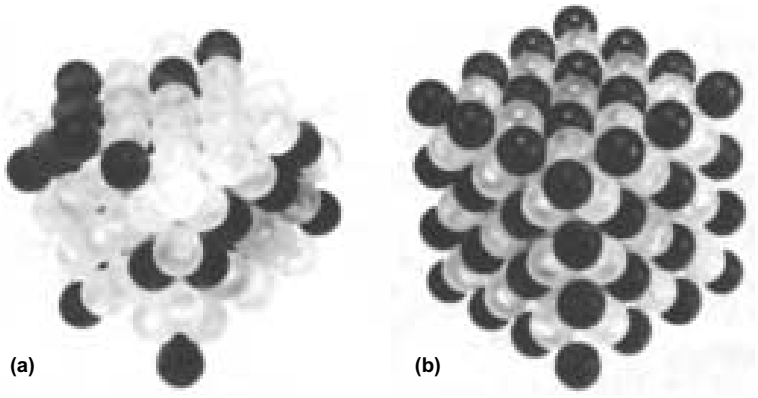


Fig. 1 Atomic arrangements of conventional alloys and ordered intermetallic compounds. (a) Disordered crystal structure of a conventional alloy. (b) Long-range ordered crystal structure of an ordered intermetallic compound

Table 1 Properties of nickel, iron, and titanium aluminides

Alloy	Crystal structure(a)	Critical ordering temperature (T_c)		Melting point (T_m)		Material density, g/cm^3	Young's modulus	
		°C	°F	°C	°F		GPa	10^6 psi
Ni_3Al	$L1_2$ (ordered fcc)	1390	2535	1390	2535	7.50	179	25.9
NiAl	$B2$ (ordered bcc)	1640	2985	1640	2985	5.86	294	42.7
Fe_3Al	$D0_3$ (ordered bcc)	540	1000	1540	2805	6.72	141	20.4
	$B2$ (ordered bcc)	760	1400	1540	2805	…	…	…
FeAl	$B2$ (ordered bcc)	1250	2280	1250	2280	5.56	261	37.8
Ti_3Al	$D0_{19}$ (ordered hcp)	1100	2010	1600	2910	4.2	145	21.0
TiAl	$L1_0$ (ordered tetragonal)	1460	2660	1460	2660	3.91	176	25.5
$TiAl_3$	$D0_{22}$ (ordered tetragonal)	1350	2460	1350	2460	3.4	…	…

(a) fcc, face-centered cubic; bcc, body-centered cubic; hcp, hexagonal close packed

Nickel, iron, and titanium aluminides, like other ordered intermetallics, exhibit brittle fracture and low ductility at ambient temperatures. It has also been found that a large number of ordered intermetallics, such as iron aluminides, exhibit environmental embrittlement at ambient temperatures. The embrittlement involves the reaction of water vapor in air with reactive elements (aluminum, for example) in intermetallics to form atomic hydrogen, which drives into the metal and causes premature fracture. Thus, the poor fracture resistance and limited fabricability have restricted the use of aluminides as engineering materials in most cases. However, in recent years, alloying and processing have been employed to overcome the brittleness problem of ordered intermetallics. Success in this work has inspired parallel efforts aimed at improving strength properties. The results have led to the development of a number of attractive intermetallic alloys that have useful ductility and strength.

Table 2 Attributes and upper use temperature limits for nickel, iron, and titanium aluminides

Alloy	Attributes	Maximum use temperature, °C (°F)	
		Strength limit	Corrosion limit
Ni_3Al	Oxidation, carburization, and nitridation resistance; high-temperature strength	1000 (1830)	1150 (2100)
NiAl	High melting point; high thermal conductivity; oxidation, carburization, and nitridation resistance	1200 (2190)	1400 (2550)
Fe_3Al	Oxidation and sulfidation resistance	600 (1110)	1100 (2010)
FeAl	Oxidation, sulfidation, molten salt, and carburization resistance	800 (1470)	1200 (2190)
Ti_3Al	Low density; good specific strength	760 (1400)	650 (1200)
TiAl	Low density; good specific strength; wear resistance	1000 (1830)	900 (1650)

Nickel Aluminides

As indicated in the "Introduction and Overview," nickel aluminide alloys based on both Ni_3Al and NiAl have been developed. However, because NiAl has not yet been developed into an engineering material for structural use, it will not be examined further in this section.

The aluminide Ni_3Al is of interest because of its excellent strength and oxidation resistance at elevated temperatures (see Table 2). This intermetallic has long been used as a strengthening constituent in high-temperature, nickel-base superalloys, which owe their outstanding strength properties to a fine dispersion of precipitation particles of the ordered γ' phase (Ni_3Al), embedded in a ductile disordered matrix. (See the article "Superalloys" in this book.)

Single crystals of Ni_3Al are ductile at ambient temperatures, but polycrystalline Ni_3Al fails by brittle grain-boundary fracture with very little plasticity. This effect persists even in very high-purity materials, where no grain-boundary segregation of impurities can be detected. The observation of this characteristic turned attention toward a search for segregants that might act in a beneficial way.

Microalloying and Macroalloying Additions. Studies of segregants led to the discovery that small (~0.1 wt%) boron additions not only eliminated the brittle behavior of Ni_3Al, but converted the material to a highly malleable form exhibiting tensile ductility as high as 50% at room temperature. The beneficial effect of boron is, however, dependent on stoichiometry, and boron is effective in increasing the ductility of Ni_3Al only in alloys containing less than 25 at.% aluminum. Since gaining the knowledge that microalloying with boron can ductilize polycrystalline Ni_3Al, a number of Ni_3Al alloy compositions have been developed. As shown in Table 3, macroalloying additions include chromium, iron, zirconium, and molybdenum. These alloying additions were made to improve strength, castability, hot workability, and corrosion resistance.

Table 3 Nominal compositions of selected Ni_3Al alloys

	Composition, wt %						
Alloy (a)	Al	Cr	Fe	Zr	Mo	B	Ni
IC-50	11.3	…	…	0.6	…	0.02	bal
IC-74M	12.4	…	…	…	…	0.05	bal
IC-218	8.5	7.8	…	0.8	…	0.02	bal
IC-218 LZr	8.7	8.1	…	0.2	…	0.02	bal
IC-221	8.5	7.8	…	1.7	…	0.02	bal
IC-221M	8.0	7.7	…	0.7	1.3	0.02	bal
IC-357	9.5	7.0	11.2	0.4	1.3	0.02	bal
IC-396M	8.0	7.7	…	0.8	3.0	0.01	bal

(a) Designations used by Oak Ridge National Laboratory, Oak Ridge, TN

Anomalous Dependence of Yield Strength on Temperature. Ni_3Al is one of a number of intermetallic alloys that exhibit an engineering yield strength (0.2% offset) that increases with increasing temperature. This is shown in Fig. 2, which is a plot of 0.2% yield stress as a function of test temperature for two Ni_3Al-base alloys and a cast HU alloy (Fe-20Cr-39Ni-2.5Si). The anomalous yielding effect, which is lower at lower strains, occurs because of the extremely rapid work hardening. As indicated in Fig. 2, the yield strength does not begin to decline until temperature exceeds approximately 800 °C (1470 °F).

Effects of Alloying Elements on Properties. The study of ductility and strength of Ni_3Al has led to the development of ductile nickel aluminide alloys for structural applications with the following composition range (in atomic percent):

$$\text{Ni-(14–18)Al-(6–9)Cr-(1–4)Mo-(0.01–1.5)Zr/Hf-(0.01–0.20)B}$$

In these aluminide alloys, 6 to 9 at.% Cr is added to reduce environmental embrittlement in oxidizing environments at elevated temperatures. Zirconium and hafnium additions most effectively improve high-temperature strength via solid-solution hardening effects. Molybdenum additions improve strength at ambient and elevated temperatures. Microalloying with boron reduces moisture-induced hydrogen embrittlement and enhances grain-boundary cohesive strength, resulting in sharply increased ductility at ambient temperatures. In some cases, certain amounts (<20 at.%) of cobalt and iron are added to replace nickel, and aluminum and nickel, respectively, in order to further improve hardness and corrosion resistance. Iron additions also improve weldability. The alloys with optimum properties usually contain 5 to 15 vol% of the disordered γ phase, which has the beneficial effect of reducing environmental embrittlement in oxidizing atmospheres and improving creep properties at elevated temperatures.

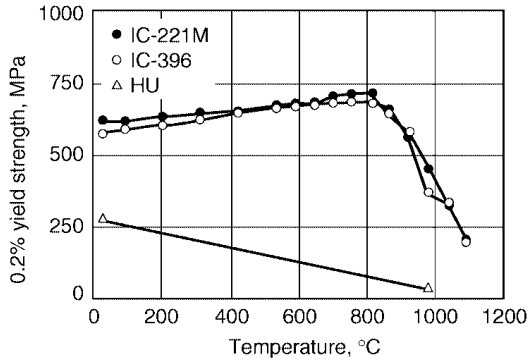
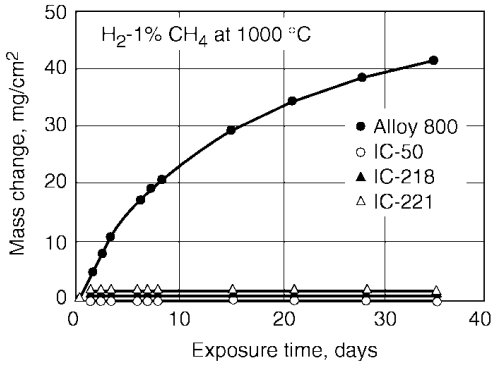


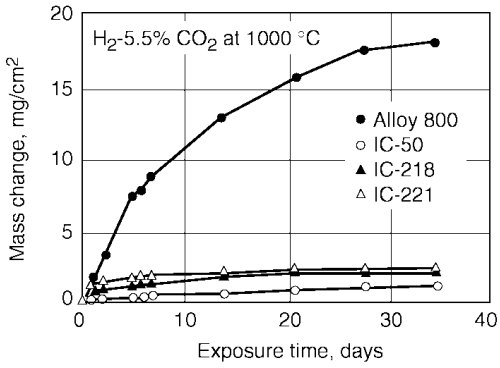
Fig. 2 Comparison of yield strength versus temperature of cast Ni_3Al-base alloys with cast HU alloy

Structural Applications. The first successful commercial applications for Ni_3Al-base alloys were heat treating (carburizing) furnace trays, support posts, and fixtures. Such parts require superior carburization resistance (Fig. 3), high-temperature strength, and thermal fatigue resistance. Other potential applications for Ni_3Al-base alloys include the following:

- Gas, water, and steam turbines (the excellent cavitation, erosion, and oxidation resistance of the alloys)
- Aircraft fasteners (low density and ease of achieving the desired strength)
- Automotive turbochargers (high fatigue resistance and low density)
- Pistons and valves (wear resistance and capability of developing a thermal barrier by high-temperature oxidation treatment)
- Bellows for expansion joints to be used in corrosive environments (good aqueous corrosion resistance)
- Tooling (high-temperature strength and wear resistance developed through preoxidation)
- Permanent molds (the ability to develop a thermal barrier coating by high-temperature oxidation)



(a)



(b)

Fig. 3 Comparison of the carburization resistance of Ni_3Al-base alloys with that of alloy 800. (a) Oxidizing carburizing environment. (b) Reducing carburizing environment

Iron Aluminides

The iron aluminides based on Fe_3Al and FeAl possess unique properties and have development potential as new materials for structural use. This potential is based on the capability of the aluminides to form protective Al_2O_3 scales in oxidizing and sulfidizing environments at elevated temperatures. In addition to excellent corrosion resistance, the aluminides offer low material cost, low density, and conservation of strategic elements. However, the major drawbacks of the iron aluminides are their low ductility and fracture toughness at ambient temperature, their poor strength at temperatures above 600 °C (1110 °F), and their susceptibility to environmental embrittlement.

Alloying Effects in Fe_3Al Aluminides. Grain structure refinement by material processing and alloy additions has been shown to be useful in increasing ductility in Fe_3Al (Fe-28Al at.%) aluminides. Additions of titanium diboride (TiB_2) to Fe_3Al powders are very effective in reducing grain size, and they increase the tensile ductility of recrystallized materials from 2 to 5 to 7%. Stress relief following hot working of the same materials results in ductilities as high as 18%. The presence of TiB_2 particles increases the recrystallization temperature from 650 to 1100 °C (1200 to 2010 °F), which means that wrought materials will retain room-temperature ductility even after exposure to temperatures as high as 1000 °C (1830 °F). For these materials, ductility is very high at temperatures above 600 °C (1110 °F), and conventional hot fabrication techniques can be employed without difficulty.

Strength properties of these aluminides are also sensitive to microstructure and the level of aluminum. Room-temperature yield strength drops sharply with an increase of aluminum above 25%. Additions of TiB_2, which reduce the grain size of recrystallized material and stabilize the wrought structure, increase the strength significantly and cause it to be retained to higher temperatures.

One alloy design of Fe_3Al showed that the ductility of the aluminide prepared by melting and casting and fabricated by hot rolling can be substantially improved by increasing the aluminum content from 25 to 28 or 30 at.% and by adding chromium at a level of 2 to 6%. The increase in the aluminum concentration sharply decreases the yield strength of the aluminide. The beneficial effect of chromium may come from modifying the surface composition and reducing the water vapor and aluminum atom reaction, (that is, by reducing environmental embrittlement). The mechanical properties of the chromium-modified Fe_3Al alloys can be further improved by thermomechanical treatment and alloy additions of molybdenum and niobium. Some of these alloys show a tensile ductility of more than 15% at room temperature and a yield strength of close to 500 MPa (72.5 ksi) at 600 °C (1110 °F). These ductile Fe_3Al alloys are much

stronger than austenitic and ferritic steels such as type 314 stainless steel and Fe-9Cr-1Mo steel. The refractory elements also substantially enhance the creep properties of the Fe_3Al alloys. Table 4 lists several Fe_3Al alloys that have been developed.

Alloying Effects in FeAl Aluminides. FeAl aluminides containing 40 at.% or more aluminum fail at room temperature by intergranular fracture with little tensile ductility. Small additions of boron (0.05 to 0.2%) suppress grain-boundary fracture and allow a small increase in ductility (~3%) in Fe-40Al, but not in Fe-50Al. The beneficial effect of boron is not nearly as dramatic in FeAl as it is in Ni_3Al, but it is nevertheless significant. The ductility of boron-doped FeAl aluminides remains low, because the alloys are still embrittled by the test environment (air). It has been found that boron-doped FeAl (40% Al) exhibits a high ductility (18%) when tested in dry oxygen to avoid environmental embrittlement.

Boron additions also increase the elevated-temperature strength of FeAl, especially in combination with niobium and zirconium. For example, the creep rate can be lowered by an order of magnitude at 825 °C (1520 °F) by the combination of 0.1% Zr and 0.2% B.

More recent alloy development studies have focused on a base alloy of Fe-36Al (at.%) alloyed with the elements listed in Table 5. The most effective elements for increasing high-temperature strength and room-temperature ductility of these FeAl alloys were small additions of molybdenum, zirconium, and boron in combination; the synergistic effects are much more potent than the single element effects. While zirconium and boron additions were very important for improved room-temperature ductility, Mo + Zr + B additions produced the best tensile and creep-rupture strength at 600 °C (1110 °F) in an alloy designated FA-362 (Table 5). The FA-362 alloy also showed the highest room-temperature ductility in air (11.8%). Preoxidation at 700 °C (1290 °F) further increased the tensile ductility to 14.7%.

Potential applications for iron aluminides include molten salt systems for chemical air separation, automotive exhaust systems, immersion heaters, heat exchangers, catalytic conversion vessels, chemical production systems, coal conversion systems, and so on.

Table 4 Chemical compositions of selected Fe_3Al aluminides

	Composition, wt %						
Alloy (a)	Al	Cr	B	Zr	Nb	C	Fe
FAS	15.9	2.20	0.01	…	…	…	bal
FAL	15.9	5.5	0.01	0.15	…	…	bal
FA-129	15.9	5.5	…	…	1.0	0.05	bal

(a) Designations used by Oak Ridge National Laboratory, Oak Ridge, TN

Table 5 Chemical compositions of developmental FeAl (Fe-35.8 at.% Al) alloys

	Composition, at.%						
Alloy (a)	Cr	Nb	Ti	Mo	Zr	C	B
FA-350	…	…	…	…	0.05	…	0.24
FA-362	…	…	…	0.2	0.05	…	0.24
FA-372	…	…	…	0.2	0.05	…	…
FA-383	…	…	…	…	0.05	…	…
FA-384	2	…	…	0.2	0.05	…	…
FA-385	…	…	…	0.2	0.05	0.13	…
FA-386	…	…	…	0.2	0.05	0.24	…
FA-387	…	…	…	0.2	…	…	0.24
FA-388	…	…	…	0.2	…	0.25	…
FA-385M1	…	…	…	0.2	0.05	0.13	0.01
FA-385M2	…	…	…	0.2	0.05	0.13	0.021
FA-385M3	2	…	…	0.2	0.05	0.13	…
FA-385M4	…	0.5	…	0.2	0.05	0.13	…
FA-385M5	2	0.5	…	0.2	0.05	0.13	…
FA-385M6	2	0.5	…	0.2	0.05	0.25	…
FA-385M7	2	0.5	…	0.2	0.1	0.25	…
FA-385M8	2	0.5	0.05	0.2	0.05	0.13	…
FA-385M9	2	0.5	0.05	0.2	0.05	0.25	…
FA-385M10(b)	2	0.5	0.05	0.2	0.05	0.13	…
FA-385M11(c)	2	0.5	0.05	0.2	0.05	…	…

(a) Designations used by Oak Ridge National Laboratory, Oak Ridge, TN. (b) Also contains 0.5% Ni, 0.3% Si, and 0.016% P (at.%), (c) Also contains 0.25% W (at.%)

Titanium Aluminides

Because of their low density, titanium aluminides based on Ti_3Al and TiAl are attractive candidates for applications in advanced aerospace engine components (latter stages of the compressor or turbine sections), airframe components, and automotive valves and turbochargers. Table 1 presents the characteristics of titanium aluminides alongside those of other aluminides. Despite a lack of fracture resistance (low ductility, fracture toughness, and fatigue crack growth rate), the titanium aluminides Ti_3Al (α-2) and TiAl (γ) have great potential for enhanced performance. Table 6 compares properties of these aluminides with those of conventional titanium alloys and superalloys. Because they have slower diffusion rates than conventional titanium alloys, the titanium aluminides feature enhanced high-temperature properties such as strength retention, creep and stress rupture, and fatigue resistance.

Another negative feature of titanium aluminides, in addition to their low ductility at ambient temperatures, is their oxidation resistance, which is lower than desirable at elevated temperatures. The titanium aluminides are characterized by a strong tendency to form TiO_2, rather than the protective Al_2O_3, at high temperatures. Because of this tendency, a key factor in increasing the maximum-use temperatures of these aluminides is enhancing their oxidation resistance while maintaining adequate levels of creep and strength retention at elevated temperatures.

Table 6 Properties of titanium aluminides, titanium-base conventional alloys, and nickel-base superalloys

Property	Conventional titanium alloys	Ti_3Al	TiAl	Nickel-base superalloys
Density, g/cm³	4.5	4.1–4.7	3.7–3.9	8.3
Modulus, GPa (10^6 psi)	96–100 (14–14.5)	100–145 (14.5–21)	160–176 (23.2–25.5)	206 (30)
Yield strength(a), MPa (ksi)	380–1150 (55–167)	700–990 (101–144)	400–650 (58–94)	…
Tensile strength(a), MPa (ksi)	480–1200 (70–174)	800–1140 (116–165)	450–800 (65–116)	…
Creep limit, °C (°F)	600 (1110)	760 (1400)	1000 (1830)	1090 (1995)
Oxidation limit, °C (°F)	600 (1110)	650 (1200)	900 (1650)	1090 (1995)
Ductility at room temperature, %	20	2–10	1–4	3–5
Ductility at high temperature, %	High	10–20	10–60	10–20
Structure	hcp/bcc	$D0_{19}$	$L1_0$	fcc/L_2

(a) At room temperature

Alpha-2 (Ti_3Al) Alloys

Compositions. The semicommercial and experimental α-2 alloys developed are two phase (α-2 + β/*B*2), with contents of 23 to 25 at.% Al and 11 to 18 at.% Nb. Alloy compositions with current engineering significance are Ti-24Al-11Nb, Ti-25Al-10Nb-3V-1Mo, Ti-25Al-17Nb-1Mo, and modified alloy compositions such as Ti-24.5Al-6Nb-6 (Ta,Mo,Cr,V). Increasing the niobium content generally enhances most material properties, although excessive niobium can degrade creep performance. Niobium can be replaced by specific elements for improved strength (molybdenum, tantalum, or chromium), creep resistance (molybdenum), and oxidation resistance (tantalum, molybdenum). However, for full optimization of mechanical properties, control of the microstructure must be maintained, particularly for tensile, fatigue, and creep performance. Microstructural features, such as primary α-2 grain size and volume fraction and secondary α-2 plate morphology and thickness, are varied by thermomechanical processing.

Alloying Effects on Properties. Mechanical properties for a number of α-2 alloys are listed in Table 7. Production of two-phase alloys by alloying Ti_3Al with β-stabilizing elements results in up to a doubling of strength. Interface strengthening of the two-phase mixture appears to be predominantly responsible for the increased strength, but other strengthening factors, such as long-range order, solid solution, and texture effects, also contribute.

Additions of silicon and zirconium appear to improve creep resistance, but the most significant improvement is attained by increasing the aluminum content to 25 at.% and limiting β-stabilizing elements to approximately 12 at.%. However, the Ti-24.5Al-17Nb-1Mo alloy exhibits a rupture life superior to that of other α-2 alloys.

Orthorhombic Alloys. At higher niobium levels, the α-2 phase evolves to a new ordered orthorhombic structure that is based on the composition

Table 7 Properties of α-2 Ti_3Al alloys with various microstructures

Alloy	Microstructure(a)	Yield strength		Ultimate tensile strength		Elongation, %	Plane-strain fracture toughness (K_{Ic})		Creep rupture(b)
		MPa	ksi	MPa	ksi		MPa $\sqrt{m}$	ksi $\sqrt{in.}$	
Ti-25Al	E	538	78	538	78	0.3	…	…	…
Ti-24Al-11Nb	W	787	114	824	119	0.7	…	…	44.7
	FW	761	110	967	140	4.8	…	…	…
Ti-24Al-14Nb	W	831	120	977	142	2.1	…	…	59.5
Ti-25Al-10Nb-3V-1Mo	W	825	119	1042	151	2.2	13.5	12.3	>360
	FW	823	119	950	138	0.8	…	…	…
	C + P	745	108	907	132	1.1	…	…	…
	W + P	759	110	963	140	2.6	…	…	…
	FW + P	942	137	1097	159	2.7	…	…	…
Ti-24.5Al-17Nb	W	952	138	1010	146	5.8	28.3	25.7	62
	W + P	705	102	940	136	10.0	…	…	…
Ti-25Al-17Nb-1Mo	FW	989	143	1133	164	3.4	20.9	19.0	476

(a) E, equiaxed α-2; W, Widmanstätten; FW, fine Widmanstätten; C, colony structure; P, primary α-2 grains. (b) Time to rupture, h, at 650 °C (1200 °F) and 380 MPa (55 ksi)

Ti_2AlNb (O phase). This has been observed in titanium aluminides with compositions near Ti-(21–25)Al-(21–27)Nb (at.%).

Although the orthorhombic alloys have a lower use temperature than the γ aluminides described in the section "Gamma (TiAl) Alloys" (approximately 650 °C, or 1200 °F), they offer much higher absolute strengths. Room-temperature tensile strengths on the order of 1380 MPa (200 ksi) with close to 5% elongation have been reported. In addition, 0.2% yield strengths in the range of 590 to 690 MPa (86 to 100 ksi) at 700 °C (1290 °F) have also been reported for Ti-21Al-25Nb (at.%) alloy. This material had a room-temperature yield strength of approximately 1070 MPa (155 ksi) with 3.5% elongation.

The ordered orthorhombic alloys having the best combination of tensile, creep, and fracture toughness properties are two-phase O + β alloys such as Ti-22Al-27Nb (at.%).

Gamma (TiAl) Alloys

Compositions. The γ alloys of engineering importance contain approximately 45 to 48 at.% Al and 1 to 10 at.% M, with M being at least one of the following: vanadium, chromium, manganese, niobium, tantalum, and tungsten. These alloys can be divided into two categories: single-phase (γ) alloys and two-phase (γ + α-2) materials. The (α-2 + γ)/γ phase boundary at 1000 °C (1830 °F) occurs at an aluminum content of approximately 49 at.%, depending on the type and level of solute M. Single-phase γ alloys contain third alloying elements, such as niobium or tantalum, that promote strengthening and further enhance oxidation resistance. Third alloying elements in two-phase alloys can raise ductility (vanadium, chromium, and manganese), increase oxidation resistance (niobium and tantalum) or enhance combined properties.

Alloying Effects on Properties. Table 8 lists tensile properties and fracture toughness of γ alloys as functions of composition, processing/

microstructure, and temperature. Ternary alloys of Ti-48Al with approximately 1 to 3% V, Mn, or Cr exhibit enhanced ductility, but Ti-48Al alloys with approximately 1 to 3% Nb, Zr, Hf, Ta, or W show lower ductility than binary Ti-48Al. The brittle-ductile transition (BDT) occurs at 700 °C (1290 °F) in Ti-56Al and at lower temperatures with decreasing aluminum levels. Increased room-temperature ductility generally results in a reduced

Table 8 Tensile properties and fracture toughness values of gamma titanium aluminides tested in air

Alloy designation and composition, at.%	Processing and microstructure	Temperature		Yield strength		Tensile strength		Elongation, %	Fracture toughness(a), K_q	
		°C	°F	MPa	ksi	MPa	ksi		MPa $\sqrt{m}$	ksi $\sqrt{in.}$
48-1(0.3C)/Ti-48Al-1V-0.3C-0.2O	Forging + HT/duplex	RT	RT	392	57	406	59	1.4	12.3	11.2
		437	819	…	…	…	…	…	22.8	20.7
		760	1400	320	46	470	68	10.8	…	…
	Casting/duplex	RT	RT	490	71	…	…	…	24.3	22.1
48-1(0.2C)/Ti-48Al-1V-0.2C-0.14O	Forging + HT/duplex + NL	RT	RT	480	70	530	77	1.5	…	…
		815	1500	360	52	450	65	…	…	…
48-2-2/Ti-48Al-2Cr-2Nb	Casting + HIP + HT/duplex	RT	RT	331	48	413	60	2.3	20–30	18–27
		760	1400	310	45	430	62	…	…	…
	Extrusion + HT/duplex	RT	RT	480	70	…	…	3.1	…	…
		760	1400	403	58	…	…	40	…	…
		870	1600	330	48	…	…	53	…	…
	Extrusion + HT/FL	RT	RT	454	66	…	…	0.5	…	…
		760	1400	405	59	…	…	3.0	…	…
		870	1600	350	51	…	…	19	…	…
	P/M extrusion + HT/NL	RT	RT	510	74	597	87	2.9	…	…
		700	1290	421	61	581	84	5.2	…	…
G1/Ti-47Al-1Cr-1V-2.6Nb	Forging + HT/duplex	RT	RT	480	70	548	79	2.3	12	10.8
		600	1110	383	56	507	74	3.1	16	14.6
		800	1470	324	47	492	71	55	…	…
	Forging + HT/FL	RT	RT	330	48	383	56	0.8	30–36	27–33
		800	1470	290	42	378	55	1.5	40–70	36–64
Sumitomo/Ti-45Al-1.6Mn	Reactive sintering/NL	RT	RT	465	67	566	82	1.4	…	…
		800	1470	370	54	540	78	14	…	…
ABB alloy/Ti-47Al-2W-0.5Si	Casting + HT/duplex	RT	RT	425	62	520	75	1.0	22	20
		760	1400	350	51	460	67	2.5	…	…
47XD/Ti-47Al-2Mn-2Nb-0.8TiB_2	Casting + HIP + HT/NL + TiB_2	RT	RT	402	58	482	70	1.5	15–16	13.6–14.6
		760	1400	344	50	458	66	…	…	…
45XD/Ti-45Al-2Mn-2Nb-0.8TiB_2	Casting + HIP + HT	RT	RT	570	83	695	101	1.5	15–19	13.6–17.3
		600	1110	440	64	650	94	…	…	…
		760	1400	415	60	510	74	19	…	…
GE alloy 204b/Ti-46.2Al-*x* Cr-*y* (Ta,Nb)	Casting + HIP + HT/NL	RT	RT	442	64	575	83	1.5	34.5	31.4
		760	1400	382	55.4	560	81	12.4	…	…
		840	1545	381	55.2	549	80	12.2	…	…
Ti-47Al-2Nb-2Cr-1Ta	Casting + HIP + HT/duplex	RT	RT	430	62	515	75	1.0	…	…
		800	1470	363	53	495	72	23.3	…	…
		870	1600	334	48	403	58	14.6	…	…
Ti-47Al-2Nb-1.75Cr	PM casting + HIP + HT	RT	RT	429	62	516	75	1.4	…	…
		760	1400	286	41	428	62	13.3	…	…
		815	1500	368	53	531	77	23.3	…	…
Alloy 7/Ti-46Al-4Nb-1W	Extrusion + HT/NL	RT	RT	648	94	717	104	1.6	…	…
		760	1400	517	75	692	100	…	…	…
Alloy K5/Ti-46.5Al-2Cr-3Nb-0.2W	Forging + HT/duplex	RT	RT	462	67	579	84	2.8	11	10
		800	1470	345	50	468	68	40	…	…
	Forging + HT/RFL	RT	RT	473	69	557	81	1.2	20–22	18–20
		800	1470	375	54	502	73	3.2	…	…
		870	1600	362	53	485	70	12.0	…	…

HT, heat treated; HIP, hot-isostatically pressed; P/M, powder metallurgy; PM, permanent mold (casting); NL, nearly lamellar; FL, fully lamellar; RFL, refined fully lamellar; RT, room temperature. (a) K_q = the provisional K_{Ic} value

BDT temperature. Above the BDT temperature, ductility increases rapidly with temperature, approaching 100% at 1000 °C (1830 °F) for the most ductile γ alloy compositions.

Creep properties of γ alloys, when normalized by density, are better than those of superalloys, but they are strongly influenced by alloy chemistry and thermomechanical processing. Increased aluminum content and additions of tungsten or carbon increase creep resistance. Increasing the volume fraction of the lamellar structure enhances creep properties, but lowers ductility. The level of creep strain from elongation upon initial loading and primary creep is of concern because it can exceed projected design levels for maximum creep strain in the part.

Effects of Alloying on Oxidation Resistance. Although the γ class of titanium aluminides offers oxidation and interstitial (oxygen, nitrogen) embrittlement resistance superior to that of the α-2 and orthorhombic (Ti_2AlNb) classes of titanium aluminides, environmental durability is still a concern, especially at temperatures approximately 750 to 800 °C (1380 to 1470 °F) in air. This is because, as stated earlier in this article, all titanium aluminides are characterized by a strong tendency to form TiO_2, rather than the protective Al_2O_3 scale, at elevated temperature. To improve the oxidation resistance of γ aluminides, two areas are being explored: alloy development and the development of improved protective coatings.

Ternary and higher-order alloying additions can reduce the rate of oxidation of γ alloys. Of particular benefit are small (1 to 4%) ternary additions of tungsten, niobium, and tantalum. When combined with quaternary additions of 1 to 2% Cr or Mn, further improvement in oxidation resistance is gained. However, it is important to stress that these small alloying additions do not result in continuous Al_2O_3 scale formation. Rather, a complex intermixed Al_2O_3/TiO_2 scale is still formed, but the rate of growth of this scale is reduced. Further improvements in oxidation resistance can be obtained via protective coatings.

SELECTED REFERENCES

- R. Darolia, J.J. Lewandowski, C.T. Liu, P.L. Martin, D.B. Miracle, and M.V. Nathal, Ed., *Structural Intermetallics,* TMS-AIME, 1993
- T. Grobstein and J. Doychale, Ed., *Oxidation of High-Temperature Intermetallics,* TMS-AIME, 1989
- C.T. Liu, J.O. Stiegler, and F.H. Froes, Ordered Intermetallics, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 911–942
- M.V. Nathal, Ed., *Structural Intermetallics 1997,* TMS-AIME, 1998
- Structural Intermetallics, *ASM Specialty Handbook*: *Heat-Resistant Materials,* J.R. Davis, Ed., ASM International, 1997, p 389–41
- S.H. Whang, C.T. Liu, D.P. Pope, and J.O. Stiegler, Ed., *High-Temperature Aluminides and Intermetallics,* TMS-AIME, 1990

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Aluminum and Aluminum Alloys

Introduction and Overview

General Characteristics. The unique combinations of properties provided by aluminum and its alloys make aluminum one of the most versatile, economical, and attractive metallic materials for a broad range of uses—from soft, highly ductile wrapping foil to the most demanding engineering applications. Aluminum alloys are second only to steels in use as structural metals.

Aluminum has a density of only 2.7 g/cm^3, approximately one-third as much as steel (7.83 g/cm^3). One cubic foot of steel weighs about 490 lb; a cubic foot of aluminum, only about 170 lb. Such light weight, coupled with the high strength of some aluminum alloys (exceeding that of structural steel), permits design and construction of strong, lightweight structures that are particularly advantageous for anything that moves—space vehicles and aircraft as well as all types of land- and water-borne vehicles.

Aluminum resists the kind of progressive oxidization that causes steel to rust away. The exposed surface of aluminum combines with oxygen to form an inert aluminum oxide film only a few ten-millionths of an inch thick, which blocks further oxidation. And, unlike iron rust, the aluminum oxide film does not flake off to expose a fresh surface to further oxidation. If the protective layer of aluminum is scratched, it will instantly reseal itself.

The thin oxide layer itself clings tightly to the metal and is colorless and transparent—invisible to the naked eye. The discoloration and flaking of iron and steel rust do not occur on aluminum.

Appropriately alloyed and treated, aluminum can resist corrosion by water, salt, and other environmental factors, and by a wide range of other chemical and physical agents. The corrosion characteristics of aluminum alloys are examined in the section “Effects of Alloying on Corrosion Behavior” in this article.

Aluminum surfaces can be highly reflective. Radiant energy, visible light, radiant heat, and electromagnetic waves are efficiently reflected, while anodized and dark anodized surfaces can be reflective or absorbent. The reflectance of polished aluminum, over a broad range of wave lengths, leads to its selection for a variety of decorative and functional uses.

Aluminum typically displays excellent electrical and thermal conductivity, but specific alloys have been developed with high degrees of electrical resistivity. These alloys are useful, for example, in high-torque electric motors. Aluminum is often selected for its electrical conductivity, which is nearly twice that of copper on an equivalent weight basis. The requirements of high conductivity and mechanical strength can be met by use of long-line, high-voltage, aluminum steel-cored reinforced transmission cable. The thermal conductivity of aluminum alloys, about 50 to 60% that of copper, is advantageous in heat exchangers, evaporators, electrically heated appliances and utensils, and automotive cylinder heads and radiators.

Aluminum is nonferromagnetic, a property of importance in the electrical and electronics industries. It is nonpyrophoric, which is important in applications involving inflammable or explosive-materials handling or exposure. Aluminum is also non-toxic and is routinely used in containers for food and beverages. It has an attractive appearance in its natural finish, which can be soft and lustrous or bright and shiny. It can be virtually any color or texture.

The ease with which aluminum may be fabricated into any form is one of its most important assets. Often it can compete successfully with cheaper materials having a lower degree of workability. The metal can be cast by any method known to foundrymen. It can be rolled to any desired thickness down to foil thinner than paper. Aluminum sheet can be stamped, drawn, spun, or roll formed. The metal also may be hammered or forged. Aluminum wire, drawn from rolled rod, may be stranded into cable of any desired size and type. There is almost no limit to the different profiles (shapes) in which the metal can be extruded.

Alloy Categories. It is convenient to divide aluminum alloys into two major categories: wrought compositions and cast compositions. A further differentiation for each category is based on the primary mechanism of property development. Many alloys respond to thermal treatment based on phase solubilities. These treatments include solution heat treatment, quenching, and precipitation, or age, hardening. For either casting or wrought alloys, such alloys are described as heat treatable. A large number of other wrought compositions rely instead on work hardening through mechanical reduction, usually in combination with various annealing procedures for property development. These alloys are referred to as work hardening. Some casting alloys are essentially not heat treatable and are

used only in as-cast or in thermally modified conditions unrelated to solution or precipitation effects.

Cast and wrought alloy nomenclatures have been developed. The Aluminum Association system is most widely recognized in the United States. Their alloy identification system employs different nomenclatures for wrought and cast alloys, but divides alloys into families for simplification. For wrought alloys a four-digit system is used to produce a list of wrought composition families as follows:

- 1*xxx:* Controlled unalloyed (pure) composition, used primarily in the electrical and chemical industries
- 2*xxx:* Alloys in which copper is the principal alloying element, although other elements, notably magnesium, may be specified. 2*xxx*-series alloys are widely used in aircraft where their high strength (yield strengths as high as 455 MPa, or 66 ksi) is valued.
- 3*xxx:* Alloys in which manganese is the principal alloying element, used as general-purpose alloys for architectural applications and various products
- 4*xxx:* Alloys in which silicon is the principal alloying element, used in welding rods and brazing sheet
- 5*xxx:* Alloys in which magnesium is the principal alloying element, used in boat hulls, gangplanks, and other products exposed to marine environments
- 6*xxx:* Alloys in which magnesium and silicon are the principal alloying elements, commonly used for architectural extrusions and automotive components
- 7*xxx:* Alloys in which zinc is the principal alloying element (although other elements, such as copper, magnesium, chromium, and zirconium, may be specified), used in aircraft structural components and other high-strength applications. The 7*xxx* series are the strongest aluminum alloys, with yield strengths ≥500 MPa (≥73 ksi) possible.
- 8*xxx:* Alloys characterizing miscellaneous compositions. The 8*xxx* series alloys may contain appreciable amounts of tin, lithium, and/or iron.
- 9*xxx:* Reserved for future use

Wrought alloys that constitute heat-treatable (precipitation-hardenable) aluminum alloys include the 2*xxx,* 6*xxx,* 7*xxx,* and some of the 8*xxx* alloys. The various combinations of alloying additions and strengthening mechanisms used for wrought aluminum alloys are shown in Table 1. The strength ranges achievable with various classes of wrought and cast alloys are given in Tables 2 and 3.

Casting compositions are described by a three-digit system followed by a decimal value. The decimal .0 in all cases pertains to casting alloy limits. Decimals .1, and .2 concern ingot compositions, which after melting and processing should result in chemistries conforming to casting specification requirements. Alloy families for casting compositions include the following:

- 1*xx.x:* Controlled unalloyed (pure) compositions, especially for rotor manufacture
- 2*xx.x:* Alloys in which copper is the principal alloying element. Other alloying elements may be specified.
- 3*xx.x:* Alloys in which silicon is the principal alloying element. The other alloying elements such as copper and magnesium are specified. The 3*xx.x* series comprises nearly 90% of all shaped castings produced.
- 4*xx.x:* Alloys in which silicon is the principal alloying element.
- 5*xx.x:* Alloys in which magnesium is the principal alloying element.
- 6*xx.x:* Unused
- 7*xx.x:* Alloys in which zinc is the principal alloying element. Other alloying elements such as copper and magnesium may be specified.
- 8*xx.x:* Alloys in which tin is the principal alloying element.
- 9*xx.x:* Unused

Heat-treatable casting alloys include the 2*xx,* 3*xx,* and 7*xx* series.

Tables 4 and 5 list nominal compositions for representative wrought and cast aluminum alloys. It should be noted that the alloy compositions listed in these tables make up a rather small percentage of the total amount of compositions developed. More than 500 alloy designations/compositions have been registered by the Aluminum Association Inc. for aluminum alloys. Composition limits for these alloys can be found in the *Metals Handbook Desk Edition,* 2nd ed., (see the article "Chemical Compositions and International Designations on pages 426–436) and in Registration Records on wrought alloys, castings, and ingots published by the Aluminum Association.

Table 1 Classification of wrought aluminum alloys according to their strengthening mechanism

Alloy system	Aluminum series
Work-hardenable alloys	
Pure Al	1*xxx*
Al-Mn	3*xxx*
Al-Si	4*xxx*
Al-Mg	5*xxx*
Al-Fe	8*xxx*
Al-Fe-Ni	8*xxx*
Precipitation-hardenable alloys	
Al-Cu	2*xxx*
Al-Cu-Mg	2*xxx*
Al-Cu-Li	2*xxx*
Al-Mg-Si	6*xxx*
Al-Zn	7*xxx*
Al-Zn-Mg	7*xxx*
Al-Zn-Mg-Cu	7*xxx*
Al-Li-Cu-Mg	8*xxx*

Applications. Aluminum alloys are economical in many applications. They are used in the automotive industry, aerospace industry, in construction of machines, appliances, and structures, as cooking utensils, as covers for housings for electronic equipment, as pressure vessels for cryogenic applications, and in innumerable other areas. Tables 6 and 7 list typical applications for some of the more commonly used wrought and cast alloys, respectively.

Table 2 Strength ranges of various wrought aluminum alloys

Aluminum Association series	Type of alloy composition	Strengthening method	Tensile strength range	
			MPa	ksi
1*xxx*	Al	Cold work	70–175	10–25
2*xxx*	Al-Cu-Mg (1–2.5% Cu)	Heat treat	170–310	25–45
2*xxx*	Al-Cu-Mg-Si (3–6% Cu)	Heat treat	380–520	55–75
3*xxx*	Al-Mn-Mg	Cold work	140–280	20–40
4*xxx*	Al-Si	Cold work (some heat treat)	105–350	15–50
5*xxx*	Al-Mg (1–2.5% Mg)	Cold work	140–280	20–40
5*xxx*	Al-Mg-Mn (3–6% Mg)	Cold work	280–380	40–55
6*xxx*	Al-Mg-Si	Heat treat	150–380	22–55
7*xxx*	Al-Zn-Mg	Heat treat	380–520	55–75
7*xxx*	Al-Zn-Mg-Cu	Heat treat	520–620	75–90
8*xxx*	Al-Li-Cu-Mg	Heat treat	280–560	40–80

Table 3 Strength ranges of various cast aluminum alloys

Alloy system (AA designation)	Tensile strength range	
	MPa	ksi
Heat treatable sand cast alloys (various tempers)		
Al-Cu (201–206)	353–467	51–68
Al-Cu-Ni-Mg (242)	186–221	27–32
Al-Cu-Si (295)	110–221	16–32
Al-Si-Cu (319)	186–248	27–36
Al-Si-Cu-Mg (355, 5% Si, 1.25% Cu, 0.5% Mg)	159–269	23–39
Al-Si-Mg (356, 357)	159–345	23–50
Al-Si-Cu-Mg (390, 17% Si, 4.5% Cu, 0.6% Mg)	179–276	26–40
Al-Zn (712, 713)	241	35
Non-heat treatable die cast alloys		
Al-Si (413, 443, F temper)	228–296	33–43
Al-Mg (513, 515, 518, F temper)	276–310	40–45
Non-heat treatable permanent mold cast alloys		
Al-Sn (850, 851, 852, T5 temper)	138–221	20–32

Table 4 Product forms and nominal compositions of common wrought aluminum alloys

AA number	Product(a)	Composition, %							
		Al	Si	Cu	Mn	Mg	Cr	Zn	Others
1050	DT	99.50 min	…	…	…	…	…	…	…
1060	S, P, ET, DT	99.60 min	…	…	…	…	…	…	…
1100	S, P, F, E, ES, ET, C, DT, FG	99.00 min	…	0.12	…	…	…	…	…
1145	S, P, F	99.45 min	…	…	…	…	…	…	…
1199	F	99.99 min	…	…	…	…	…	…	…
1350	S, P, E, ES, ET, C	99.50 min	…	…	…	…	…	…	…
2011	E, ES, ET, C, DT	93.7	…	5.5	…	…	…	…	0.4 Bi; 0.4 Pb
2014	S, P, E, ES, ET, C, DT, FG	93.5	0.8	4.4	0.8	0.5	…	…	…
2024	S, P, E, ES, ET, C, DT	93.5	…	4.4	0.6	1.5	…	…	…
2036	S	96.7	…	2.6	0.25	0.45	…	…	…
2048	S, P	94.8	…	3.3	0.4	1.5	…	…	…
2124	P	93.5	…	4.4	0.6	1.5	…	…	…
2218	FG	92.5	…	4.0	…	1.5	…	…	2.0 Ni
2219	S, P, E, ES, ET, C, FG	93.0	…	6.3	0.3	…	…	…	0.06 Ti; 0.10 V; 0.18 Zr
2319	C	93.0	…	6.3	0.3	…	…	…	0.18 Zn; 0.15 Ti; 0.10 V
2618	FG	93.7	0.18	2.3	…	1.6	…	…	1.1 Fe; 1.0 Ni; 0.07 Ti
3003	S, P, F, E, ES, ET, C, DT, FG	98.6	…	0.12	1.2	…	…	…	…
3004	S, P, ET, DT	97.8	…	…	1.2	1.0	…	…	…
3105	S	99.0	…	…	0.55	0.50	…	…	…
4032	FG	85.0	12.2	0.9	…	1.0	…	…	0.9 Ni
4043	C	94.8	5.2	…	…	…	…	…	…
5005	S, P, C	99.2	…	…	…	0.8	…	…	…
5050	S, P, C, DT	98.6	…	…	…	1.4	…	…	…
5052	S, P, F, C, DT	97.2	…	…	…	2.5	0.25	…	…
5056	F, C	95.0	…	…	0.12	5.0	0.12	…	…
5083	S, P, E, ES, ET, FG	94.7	…	…	0.7	4.4	0.15	…	…
5086	S, P, E, ES, ET, DT	95.4	…	…	0.4	4.0	0.15	…	…
5154	S, P, E, ES, ET, C, DT	96.2	…	…	…	3.5	0.25	…	…
5182	S	95.2	…	…	0.35	4.5	…	…	…
5252	S	97.5	…	…	…	2.5	…	…	…
5254	S, P	96.2	…	…	…	3.5	0.25	…	…
5356	C	94.6	…	…	0.12	5.0	0.12	…	0.13 Ti
5454	S, P, E, ES, ET	96.3	…	…	0.8	2.7	0.12	…	…
5456	S, P, E, ES, ET, DT, FG	93.9	…	…	0.8	5.1	0.12	…	…
5457	S	98.7	…	…	0.3	1.0	…	…	…
5652	S, P	97.2	…	…	…	2.5	0.25	…	…
5657	S	99.2	…	…	…	0.8	…	…	…
6005	E, ES, ET	98.7	0.8	…	…	0.5	…	…	…
6009	S	97.7	0.8	0.35	0.5	0.6	…	…	…
6010	S	97.3	1.0	0.35	0.5	0.8	…	…	…
6061	S, P, E, ES, ET, C, DT, FG	97.9	0.6	0.28	…	1.0	0.2	…	…
6063	E, ES, ET, DT	98.9	0.4	…	…	0.7	…	…	…
6066	E, ES, ET, DT, FG	95.7	1.4	1.0	0.8	1.1	…	…	…
6070	E, ES, ET	96.8	1.4	0.28	0.7	0.8	…	…	…
6101	E, ES, ET	98.9	0.5	…	…	0.6	…	…	…
6151	FG	98.2	0.9	…	…	0.6	0.25	…	…
6201	C	98.5	0.7	…	…	0.8	…	…	…
6205	E, ES, ET	98.4	0.8	…	0.1	0.5	0.1	…	0.1 Zr
6262	E, ES, ET, C, DT	96.8	0.6	0.28	…	1.0	0.09	…	0.6 Bi; 0.6 Pb
6351	E, ES	97.8	1.0	…	0.6	0.6	…	…	…
6463	E, ES	98.9	0.4	…	…	0.7	…	…	…
7005	E, ES	93.3	…	…	0.45	1.4	0.13	4.5	0.04 Ti; 0.14 Zr
7049	P, E, ES, FG	88.2	…	1.5	…	2.5	0.15	7.6	…
7050	P, E, ES, FG	89.0	…	2.3	…	2.3	…	6.2	0.12 Zr
7072	S, F	99.0	…	…	…	…	…	1.0	…
7075	S, P, E, ES, ET, C, DT, FG	90.0	…	1.6	…	2.5	0.23	5.6	…
7175	S, P, FG	90.0	…	1.6	…	2.5	0.23	5.6	…
7178	S, P, E, ES, C	88.1	…	2.0	…	2.7	0.26	6.8	…
7475	S, P, FG	90.3	1.5	…	…	2.3	0.22	5.7	…

(a) S, sheet; P, plate; F, foil; E, extruded rod, bar and wire; ES, extruded shapes; ET, extruded tubes; C, cold finished rod, bar and wire; DT, drawn tube; FG, forgings

Wrought Alloy Classes

As described in the "Introduction and Overview" to this article, aluminum alloys are commonly grouped into an alloy designation series. The general characteristics of the wrought alloy groups are described below. Strength ranges, nominal compositions, and applications for wrought aluminum alloys are listed in Tables 2, 4, and 6, respectively.

1*xxx* Series. Aluminum of 99.00% or higher purity has many applications, especially in the electrical and chemical fields. These grades of aluminum are characterized by excellent corrosion resistance, high thermal

Table 5 Designations and nominal compositions of common aluminum alloys used for casting

AA number	Product(a)	Composition, %				
		Cu	Mg	Mn	Si	Others
201.0	S	4.6	0.35	0.35	…	0.7 Ag, 0.25 Ti
206.0	S or P	4.6	0.25	0.35	0.10(b)	0.22 Ti, 0.15 Fe(b)
A206.0	S or P	4.6	0.25	0.35	0.05(b)	0.22 Ti, 0.10 Fe(b)
208.0	S	4.0	…	…	3.0	…
242.0	S or P	4.0	1.5	…	…	2.0 Ni
295.0	S	4.5	…	…	0.8	…
96.0	P	4.5	…	…	2.5	…
308.0	S or P	4.5	…	…	5.5	…
319.0	S or P	3.5	…	…	6.0	…
336.0	P	1.0	1.0	…	12.0	2.5 Ni
354.0	P	1.8	0.50	…	9.0	…
355.0	S or P	1.2	0.50	0.50(b)	5.0	0.6 Fe(b), 0.35Zn(b)
C355.0	S or P	1.2	0.50	0.10(b)	5.0	0.20 Fe(b), 0.10Zn(b)
356.0	S or P	0.25(b)	0.32	0.35(b)	7.0	0.6 Fe(b), 0.35 Zn(b)
A356.0	S or P	0.20(b)	0.35	0.10(b)	7.0	0.20 Fe(b), 0.10 Zn(b)
357.0	S or P	…	0.50	…	7.0	…
A357.0	S or P	…	0.6	…	7.0	0.15 Ti, 0.005 Be
359.0	S or P	…	0.6	…	9.0	…
360.0	D	…	0.50	…	9.5	2.0 Fe(b)
A360.0	D	…	0.50	…	9.5	1.3 Fe(b)
\380.0	D	3.5	…	…	8.5	2.0 Fe(b)
A380.0	D	3.5	…	…	8.5	1.3 Fe(b)
383.0	D	2.5	…	…	10.5	…
384.0	D	3.8	…	…	11.2	3.0 Zn(b)
A384.0	D	3.8	…	…	11.2	1.0 Zn(b)
390.0	D	4.5	0.6	…	17.0	1.3 Zn(b)
A390.0	S or P	4.5	0.6	…	17.0	0.5 Zn(b)
413.0	D	…	…	…	12.0	2.0 Fe(b)
A413.0	D	…	…	…	12.0	1.3 Fe(b)
4430	S	0.6(b)	…	…	5.2	…
A443.0	S	0.30(b)	…	…	5.2	…
B443.0	S or P	0.15(b)	…	…	5.2	…
C443.0	D	0.6(b)	…	…	5.2	2.0 Fe(b)
514.0	S	…	4.0	…	…	…
518.0	D	…	8.0	…	…	…
520.0	S	…	10.0	…	…	…
535.0	S	…	6.8	0.18	…	0.18 Ti
A535.0	S	…	7.0	0.18	…	…
B535.0	S	…	7.0	…	…	0.18 Ti
712.0	S or P	…	0.6	…	…	5.8 Zn, 0.5 Cr, 0.20 Ti
713.0	S or P	0.7	0.35	…	…	7.5 Zn, 0.7 Cu
771.0	S	…	0.9	…	…	7.0 Zn, 0.13 Cr, 0.15 Ti
850.0	S or P	1.0	…	…	…	6.2 Sn, 1.0 Ni

(a) S, sand casting; P, permanent mold casting; D, die casting. (b) Maximum

Table 6 Selected applications for wrought aluminum alloys

Alloy	Description and selected applications
1100	Commercially pure aluminum highly resistant to chemical attack and weathering. Low cost, ductile for deep drawing, and easy to weld. Used for high-purity applications such as chemical processing equipment. Also for nameplates, fan blades, flue lining, sheet metal work, spun holloware, and fin stock
1350	Electrical conductors
2011	Screw machine products. Appliance parts and trim, ordnance, automotive, electronic, fasteners, hardware, machine parts
2014	Truck frames, aircraft structures, automotive, cylinders and pistons, machine parts, structurals
2017	Screw machine products, fittings, fasteners, machine parts
2024	For high-strength structural applications. Excellent machinability in the T-tempers. Fair workability and fair corrosion resistance. Alclad 2024 combines the high strength of 2024 with the corrosion resistance of the commercially pure cladding. Used for truck wheels, many structural aircraft applications, gears for machinery, screw machine products, automotive parts, cylinders and pistons, fasteners, machine parts, ordnance, recreation equipment, screws and rivets
2219	Structural uses at high temperature (to 315 °C, or 600 °F). High-strength weldments
3003	Most popular general-purpose alloy. Stronger than 1100 with same good formability and weldabilty. For general use including sheet metal work, stampings, fuel tanks, chemical equipment, containers, cabinets, freezer liners, cooking utensils, pressure vessels, builder's hardware, storage tanks, agricultural applications, appliance parts and trim, architectural applications, electronics, fin stock, fan equipment, name plates, recreation vehicles, trucks and trailers. Used in drawing and spinning.
3004	Sheet metal work, storage tanks, agri cultural applications, building products, containers, electronics, furniture, kitchen equipment, recreation vehicles, trucks and trailers
3105	Residential siding, mobile homes, rain-carrying goods, sheet metal work, appliance parts and trim, automotive parts, building products, electronics, fin stock, furniture, hospital and medical equipment, kitchen equipment, recreation vehicles, trucks and trailers
5005	Specified for applications requiring anodizing; anodized coating is cleaner and lighter in color than 3003. Uses include appliances, utensils, architectural, applications requiring good electrical conductivity, automotive parts, containers, general sheet metal, hardware, hospital and medical equipment, kitchen equipment, name plates, and marine applications
5052	Stronger than 3003 yet readily formable in the intermediate tempers. Good weldability and resistance to corrosion. Uses include pressure vessels, fan blades, tanks, electronic panels, electronic chassis, medium-strength sheet metal parts, hydraulic tube, appliances, agricultural applications, architectural uses, automotive parts, building products, chemical equipment, containers, cooking utensils, fasteners, hardware, highway signs, hospital and medical equipment, kitchen equipment, marine applications, railroad cars, recreation vehicles, trucks and trailers
5056	Cable sheathing, rivets for magnesium, screen wire, zippers, automotive applications, fence wire, fasteners
5083	For all types of welded assemblies, marine components, and tanks requiring high weld efficiency and maximum joint strength. Used in pressure vessels up to 65 °C (150 °F) and in many cryogenic applications, bridges, freight cars, marine components, TV towers, drilling rigs, transportation equipment, missile components, and dump truck bodies. Good corrosion resistance
5086	Used in generally the same types of applications as 5083, particularly where resistance to either stress corrosion or atmospheric corrosion is important
5454	For all types of welded assemblies, tanks, pressure vessels. ASME code approved to 205 °C (400 °F). Also used in trucking for hot asphalt road tankers and dump bodies; also, for hydrogen peroxide and chemical storage vessels
5456	For all types of welded assemblies, storage tanks, pressure vessels, and marine components. Used where best weld efficiency and joint strength are required. Restricted to temperatures below 65 °C (150 °F)
5657	For anodized auto and appliance trim and name plates
6061	Good formability, weldability, corrosion resistance, and strength in the T-tempers. Good general-purpose alloy used for a broad range of structural applications and welded assemblies including truck components, railroad cars, pipelines, marine applications, furniture, agricultural applications, aircrafts, architectural applications, automotive parts, building products, chemical equipment, dump bodies, electrical and electronic applications, fasteners, fence wire, fan blades, general sheet metal, highway signs, hospital and medical equipment, kitchen equipment, machine parts, ordnance, recreation equipment, recreation vehicles, and storage tanks
6063	Used in pipe railing, furniture, architectural extrusions, appliance parts and trim, automotive parts, building products, electrical and electronic parts, highway signs, hospital and medical equipment, kitchen equipment, marine applications, machine parts, pipe, railroad cars, recreation equipment, recreation vehicles, trucks and trailers
7050	High-strength alloy in aircraft and other structures. Also used in ordnance and recreation equip ment
7075	For aircraft and other applications requiring highest strengths. Alclad 7075 combines the strength advantages of 7075 with the corrosion-resisting properties of commercially pure aluminum-clad surface. Also used in machine parts and ordnance

and electrical conductivities, low mechanical properties, and excellent workability. Moderate increases in strength may be obtained by strain hardening. Iron and silicon are the major impurities.

2*xxx* Series. Copper is the principal alloying element in 2*xxx* series alloys, often with magnesium as a secondary addition. These alloys require solution heat treatment to obtain optimum properties; in the solution heat-treated condition, mechanical properties are similar to, and sometimes exceed, those of low-carbon steel. In some instances, precipitation heat treatment (aging) is employed to further increase mechanical properties. This treatment increases yield strength, with attendant loss in elongation; its effect on tensile strength is not as great.

The alloys in the 2*xxx* series do not have as good corrosion resistance as most other aluminum alloys, and under certain conditions they may be subject to intergranular corrosion. Therefore, these alloys in the form of sheet usually are clad with a high-purity aluminum, a magnesium-silicon alloy of the 6*xxx* series, or an alloy containing 1% Zn. The coating, usually from $2\frac{1}{2}$ to 5% of the total thickness on each side, provides galvanic protection of the core material and thus greatly increases resistance to corrosion.

Alloys in the 2*xxx* series are particularly well suited for parts and structures requiring high strength-to-weight ratios and are commonly used to

Table 7 Selected applications for aluminum casting alloys

Alloy	Representative applications
100.0	Electrical rotors larger than 152 mm (6 in.) in diameter
201.0	Structural members; cylinder heads and pistons; gear, pump, and aerospace housings
208.0	General-purpose castings; valve bodies, manifolds, and other pressure-tight parts
222.0	Bushings; meter parts; bearings; bearing caps; automotive pistons; cylinder heads
238.0	Sole plates for electric hand irons
242.0	Heavy-duty pistons; air-cooled cylinder heads; aircraft generator housings
A242.0	Diesel and aircraft pistons; air-cooled cylinder heads; aircraft generator housings
B295.0	Gear housings; aircraft fittings; compressor connecting rods; railway car seat frames
308.0	General-purpose permanent mold castings; ornamental grilles and reflectors
319.0	Engine crankcases; gasoline and oil tanks; oil pans; typewriter frames; engine parts
332.0	Automotive and heavy-duty pistons; pulleys, sheaves
333.0	Gas meter and regulator parts; gear blocks; pistons; general automotive castings
354.0	Premium-strength castings for the aerospace industry
355.0	Sand: air compressor pistons; printing press bedplates; water jackets; crankcases. Permanent: impellers; aircraft fittings; timing gears; jet engine compressor cases
356.0	Sand: flywheel castings; automotive transmission cases; oil pans; pump bodies. Permanent: machine tool parts; aircraft wheels; airframe castings; bridge railings
A356.0	Structural parts requiring high strength; machine parts; truck chassis parts
357.0	Corrosion-resistant and pressure-tight applications
359.0	High-strength castings for the aerospace industry
360.0	Outboard motor parts; instrument cases; cover plates; marine and aircraft castings
A360.0	Cover plates; instrument cases; irrigation system parts; outboard motor parts; hinges
380.0	Housings for lawn mowers and radio transmitters; air brake castings; gear cases
A380.0	Applications requiring strength at elevated temperature
384.0	Pistons and other severe service applications; automatic transmissions
390.0	Internal combustion engine pistons, blocks, manifolds, and cylinder heads
413.0	Architectural, ornamental, marine, and food and dairy equipment applications
A413.0	Outboard motor pistons; dental equipment; typewriter frames; street lamp housings
443.0	Cookware; pipe fittings; marine fittings; tire molds; carburetor bodies
514.0	Fittings for chemical and sewage use; dairy and food handling equipment; tire molds
A514.0	Permanent mold casting of architectural fittings and ornamental hardware
518.0	Architectural and ornamental castings; conveyor parts; aircraft and marine castings
520.0	Aircraft fittings; railway passenger care frames; truck and bus frame sections
535.0	Instrument parts and other applications where dimensional stability is important
A712.0	General-purpose castings that require subsequent brazing
713.0	Automotive parts; pumps; trailer parts; mining equipment
850.0	Bushings and journal bearings for railroads
A850.0	Rolling mill bearings and similar applications

make truck and aircraft wheels, truck suspension parts, aircraft fuselage and wing skins, structural parts, and those parts requiring good strength at temperatures up to 150 °C (300 °F). Figure 1 shows the relationships between some of the more commonly used alloys in the 2*xxx* series.

3*xxx* Series. Manganese is the major alloying element of 3*xxx* series alloys. These alloys generally are non-heat-treatable but have about 20% more strength than 1*xxx* series alloys. Because only a limited percentage of manganese (up to about 1.5%) can be effectively added to aluminum, manganese is used as a major element in only a few alloys. However, one of these, the popular 3003 alloy, is widely used as a general-purpose alloy for moderate-strength applications requiring good workability.

4*xxx* Series. The major alloying element in 4*xxx* series alloys is silicon, which can be added in sufficient quantities (up to 12%) to cause substantial lowering of the melting range without producing brittleness. For this reason, aluminum-silicon alloys are used in welding wire and as brazing

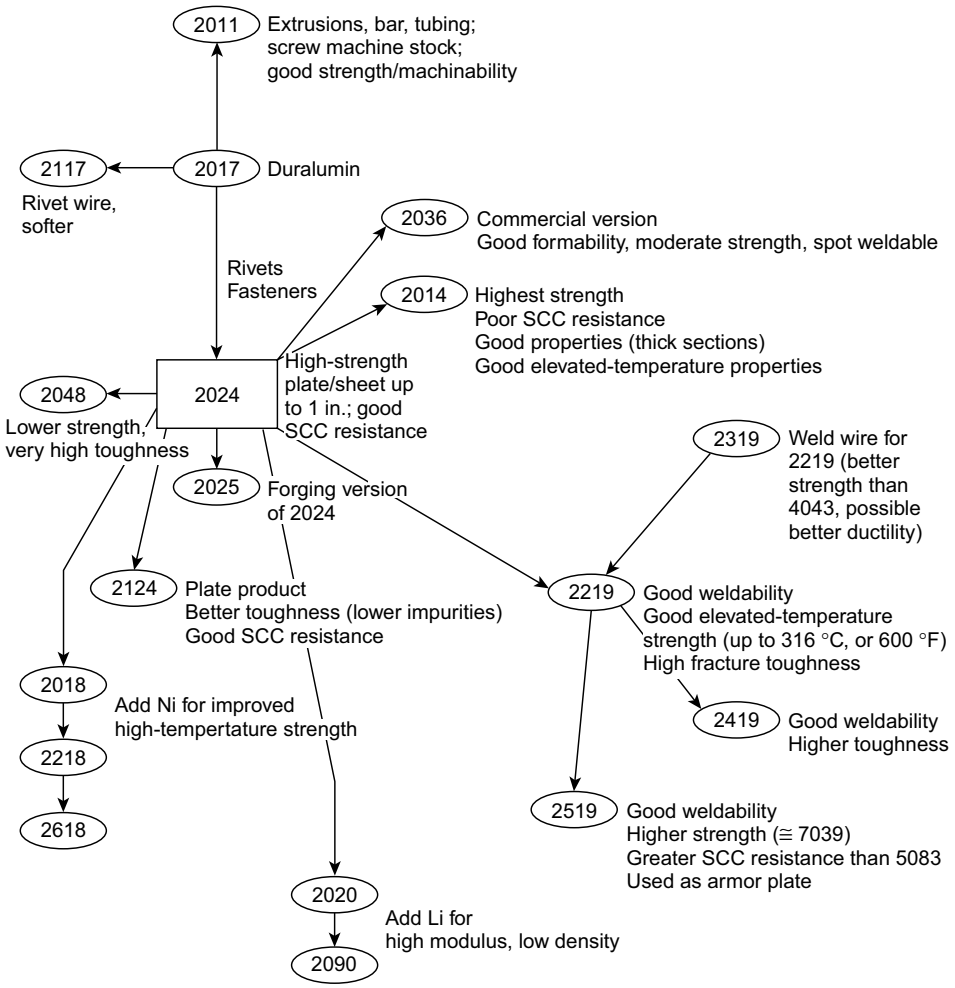


Fig. 1 Relationships among commonly used alloys in the 2*xxx* series (Al-Cu)

alloys for joining aluminum, where a lower melting range than that of the base metal is required. Most alloys in this series are non-heat treatable, but when used in welding heat-treatable alloys, they pick up some of the alloying constituents of the latter and so respond to heat treatment to a limited extent. The alloys containing appreciable amounts of silicon become dark gray to charcoal when anodic oxide finishes are applied and hence are in demand for architectural applications. Alloy 4032 has a low coefficient of thermal expansion and high wear resistance; thus it is well suited to production of forged engine pistons.

5*xxx* Series. The major alloying element in 5*xxx* series alloys is magnesium. When it is used as a major alloying element or with manganese, the result is a moderate-to-high-strength workhardenable alloy. Magnesium is considerably more effective than manganese as a hardener, about 0.8% Mg being equal to 1.25% Mn, and it can be added in considerably higher quantities. Alloys in this series possess good welding characteristics and good resistance to corrosion in marine atmospheres. However, certain limitations should be placed on the amount of cold work and the safe operating temperatures permissible for the higher-magnesium alloys (over ~3.5% for operating temperatures above ~65 °C, or 150 °F) to avoid susceptibility to stress-corrosion cracking. Figure 2 shows the relationships between some of the more commonly used alloys in the 5*xxx* series.

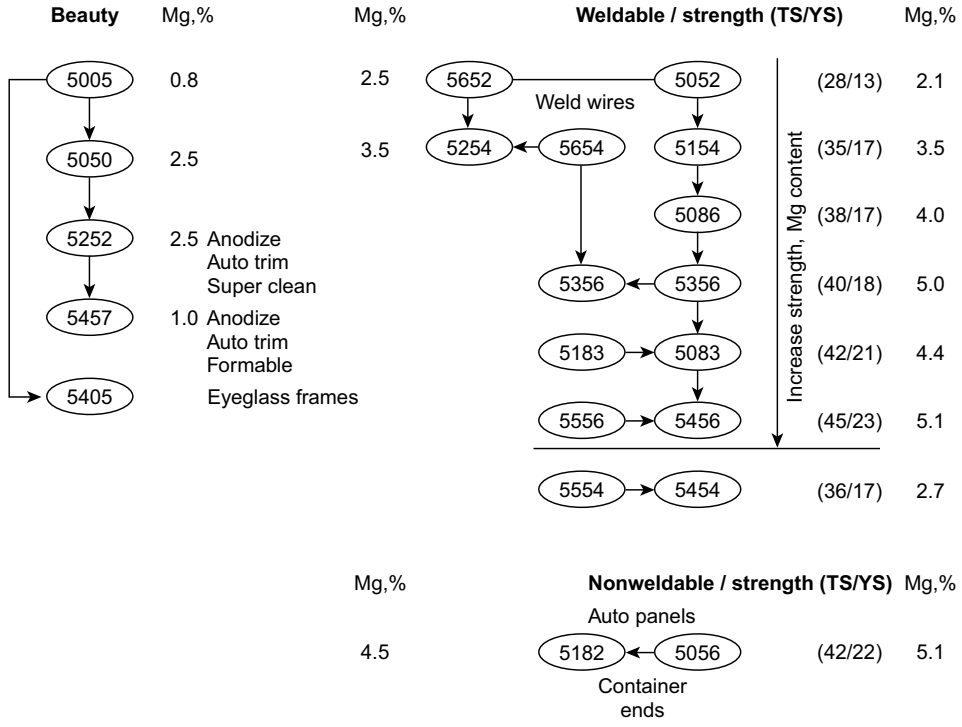


Fig. 2 Relationships among commonly used alloys in the 5*xxx* series (Al-Mg). Tensile strength (TS) and yield strength (YS) are in ksi units.

6*xxx* Series. Alloys in the 6*xxx* series contain silicon and magnesium approximately in the proportions required for formation of magnesium silicide (Mg_2Si), thus making them heat treatable. Although not as strong as most 2*xxx* and 7*xxx* alloys, 6*xxx* series alloys have good formability, weldability, machinability, and corrosion resistance, with medium strength. Alloys in this heat-treatable group may be formed in the T4 temper (solution heat treated but not precipitation heat treated) and strengthened after forming to full T6 properties by precipitation heat treatment. Figure 3 shows the relationships between some of the more commonly used alloys in the 6*xxx* series.

7*xxx* Series. Zinc, in amounts of 1 to 8%, is the major alloying element in 7*xxx* series alloys, and when coupled with a smaller percentage of magnesium results in heat-treatable alloys of moderate to very high strength. Usually other elements, such as copper and chromium, are added in small quantities. Dilute additions of scandium also improve properties. 7*xxx* series alloys are used in airframe structures, mobile equipment, and other highly stressed parts.

Higher strength 7*xxx* alloys exhibit reduced resistance to stress corrosion cracking and are often utilized in a slightly overaged temper to provide better combinations of strength, corrosion resistance, and fracture

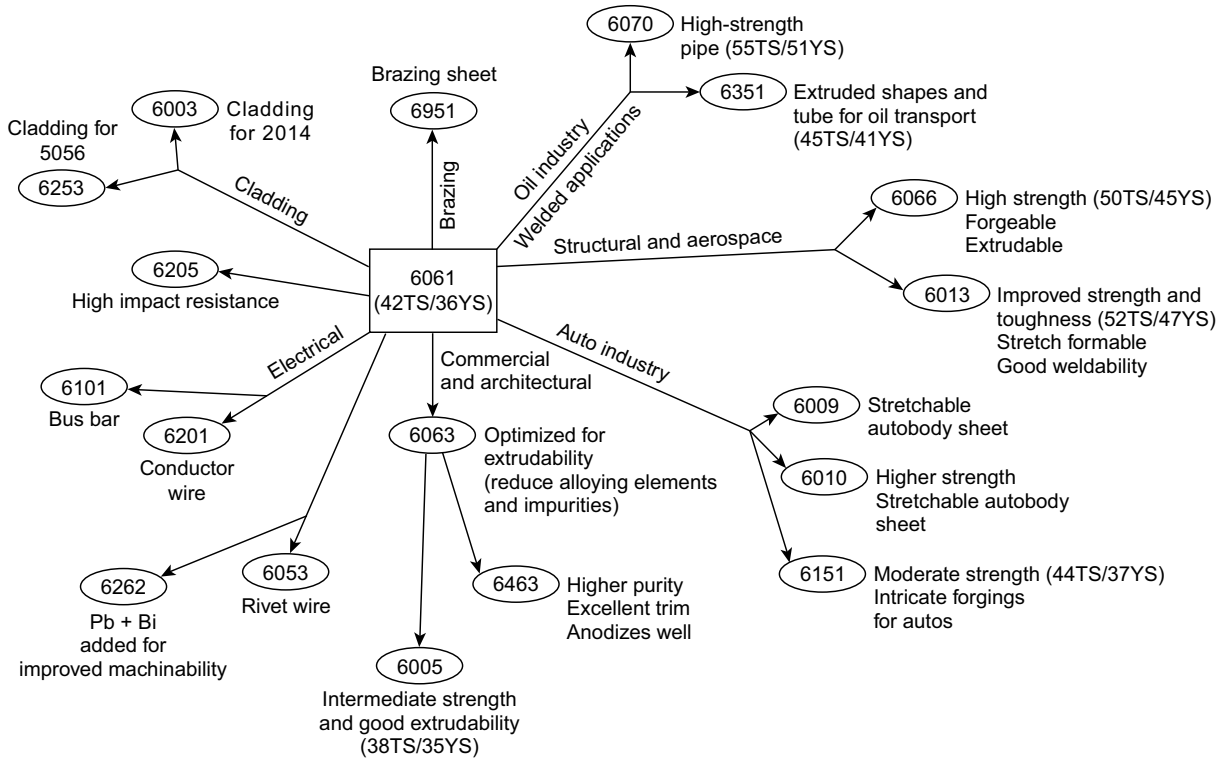


Fig. 3 Relationships among commonly used alloys in the 6*xxx* series (Al-Mg-Si). Tensile strength (TS) and yield strength (YS) are in ksi units

toughness. Figure 4 shows the relationships between some of the more commonly used alloys in the 7*xxx* series.

8*xxx* series alloys constitute a wide range of chemical compositions. For example, improved elevated-temperature performance is achieved through the use of dispersion-strengthened Al-Fe-Ce alloys (e.g., 8019) or Al-Fe-V-Si alloys (e.g., 8009) made by powder metallurgy processing. Lower density and higher stiffness can be achieved in lithium-containing alloys (e.g., 8090). The latter alloy, which is precipitation hardenable, has replaced medium-to-high strength 2*xxx* and 7*xxx* alloys in some aircraft/aerospace applications (e.g., helicopter components).

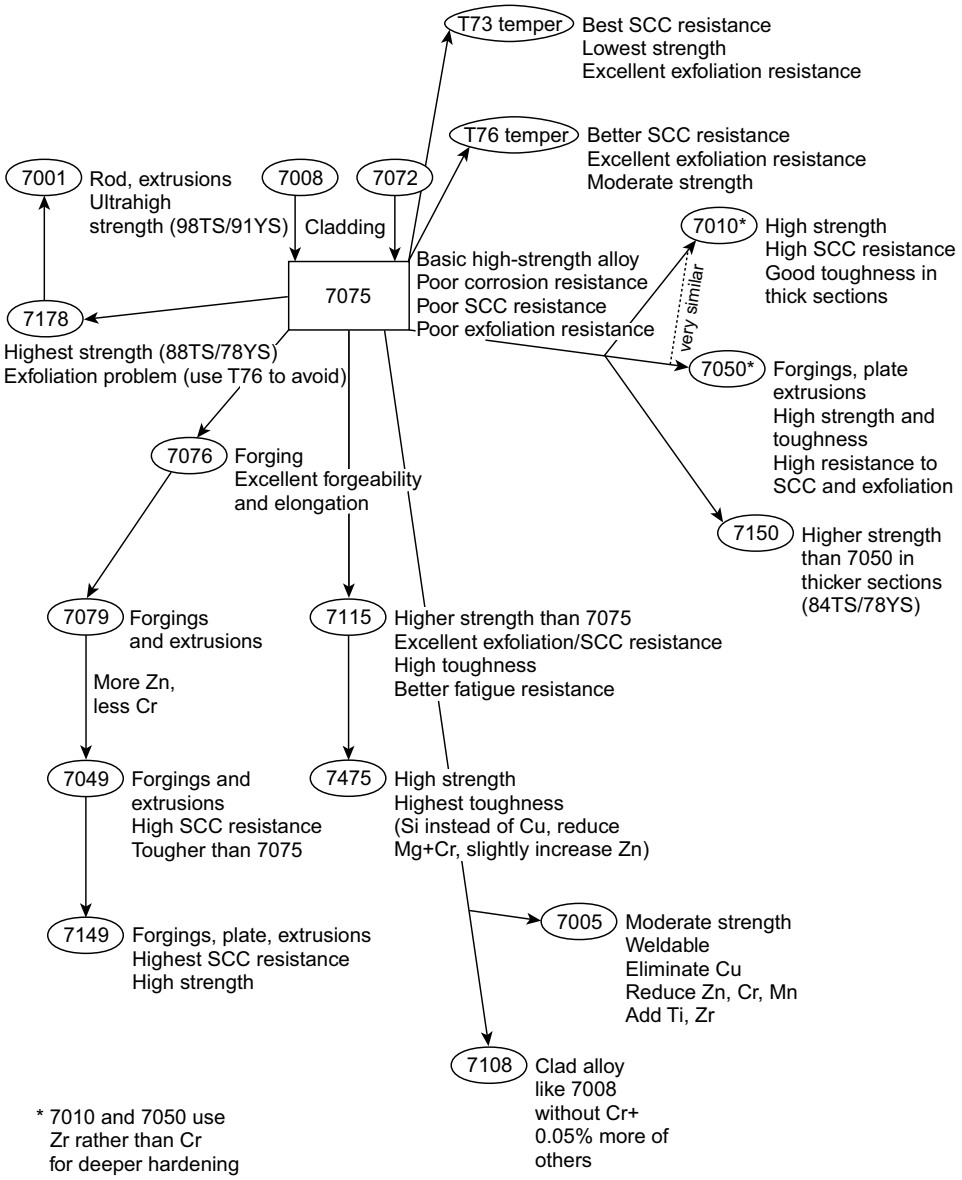


Fig. 4 Relationships among commonly used alloys in the 7*xxx* series (Al-Zn-Cu-Mg-Cr). Tensile strength (TS) and yield strength (YS) are in ksi units

Cast Alloy Classes

Aluminum casting alloys are based on the same alloy systems as those of wrought aluminum alloys, are strengthened by the same mechanisms (with the general exception of strain hardening), and are similarly classified into non-heat-treatable and heat treatable types. The major difference is that the casting alloys used in the greatest volumes contain alloying additions of silicon far in excess of the amounts in most wrought alloys. Silicon is the alloying element that literally makes the commercial viability of the high-volume aluminum casting industry possible. Silicon contents from ~4% to the eutectic level of ~12% reduce scrap losses, permit production of much more intricate designs with greater variations in section thickness, and yield castings with higher surface and internal quality. These benefits derive from the effects of silicon in increasing fluidity, reducing cracking, and improving feeding to minimize shrinkage porosity.

Figure 5 shows the complete phase diagram of the binary aluminum-silicon system. This is a simple eutectic system with limited terminal solubility and is the basis for the 4*xx.x* alloys. Metallographic structures of the pure components and of several intermediate compositions show typical morphologies. The intermediate compositions are mixtures of aluminum

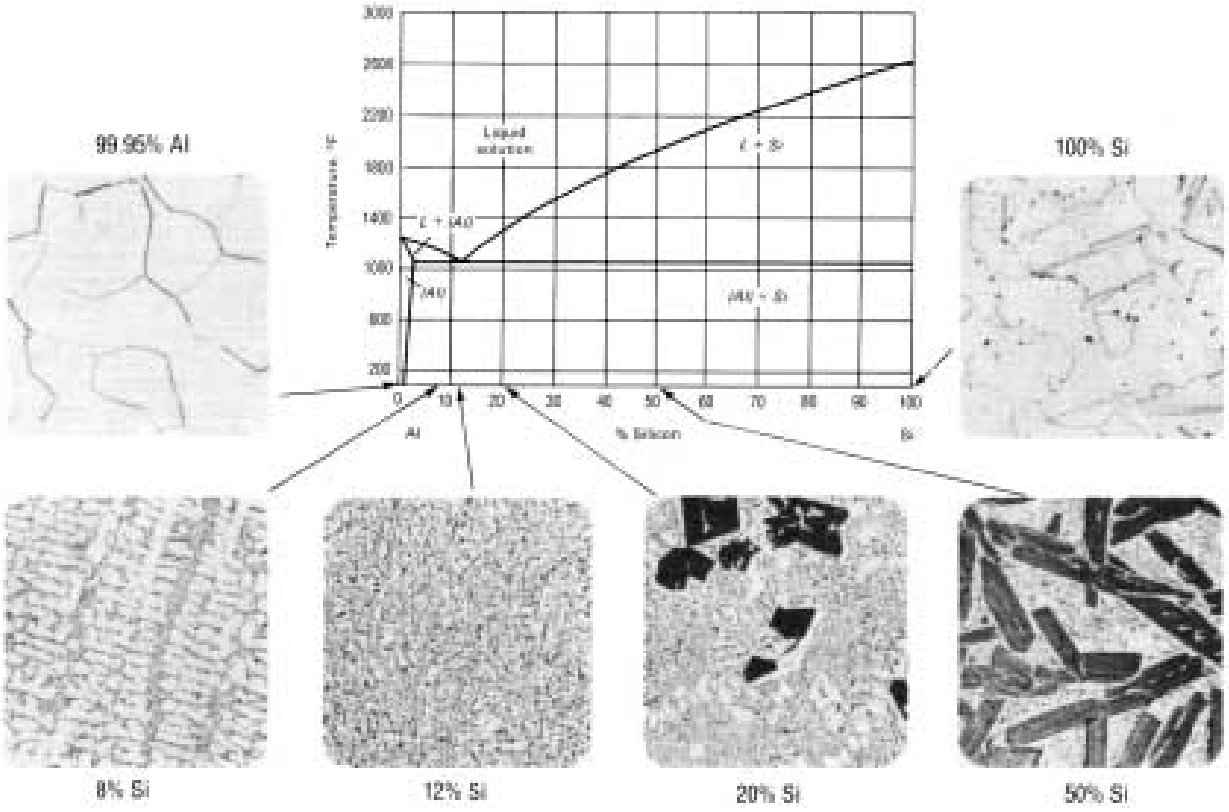


Fig. 5 Aluminum-silicon phase diagram and cast microstructures of pure components and of alloys of various compositions. Alloys with less than 12% Si are referred to as hypoeutectic, those with close to 12% Si as eutectic, and those with over 12% Si as hypereutectic

containing ~1% Si in solid solution as the continuous phase, with particles of essentially pure silicon. Alloys with <12% Si are referred to as "hypoeutectic," those with close to 12% Si as "eutectic," and those with >12% Si as "hypereutectic."

The general characteristics of the cast alloy series are described below. Strength ranges, nominal compositions, and applications for cast aluminum alloys are listed in Tables 3, 5, and 7, respectively.

2*xx.x* Series. The 2*xx.x* aluminum-copper group includes compositions capable of developing the highest strengths among all casting alloys, and these alloys are used where this is a predominant requirement. These alloys (A201.0, 202.0, 204.0, and A206.0) contain 4 to 6% Cu and 0.25 to 0.35% Mg, with highly restrictive impurity (iron and silicon) limits, and in some cases also contain 0.25 to 0.35% Mn or Cr and (in alloys 201.0, A201.0, and 202.0) 0.7% Ag. Good casting design and foundry techniques must be employed to realize full mechanical-property capabilities and consistently high quality for these alloys.

The 2*xx.x* alloys also have the highest strengths and hardnesses of all casting alloys at elevated temperatures (to 300 °C, or 600 °F), and this factor accounts for their use in some applications. Alloys 222.0, 224.0, 238.0, 240.0, 242.0, and 243.0, some with higher copper contents up to 2% Mg (6% in alloy 240.0) and additions of manganese, nickel, vanadium, and/or zirconium, are used primarily at elevated temperatures.

Heat treatment is required with the 2*xx.x* alloys for development of highest strength and ductility and must be properly applied to ensure high resistance to stress-corrosion cracking. General corrosion resistance of these alloys is lower than those of other types of casting alloys, and protection by surface coatings is required in critical applications.

3*xx.x* Series. The highest-volume-usage alloys are those in the 3*xx.x* group, which, in addition to silicon, contain magnesium, copper, or both, and in specific cases, supplementary additions of nickel or beryllium. In general, they fall into one of three types: Al-Si-Mg, Al-Si-Cu, or Al-Si-Cu-Mg. Silicon contents range from 5 to 22%. Copper contents range from 0% (alloys 356.0 through 361.0) to a maximum of 4.5%. Most of these alloys have nominal magnesium contents ranging from as low as 0.3% to ~0.6% for the high-strength compositions and 1.0% for the piston alloys 332.0 and 336.0. The principal alloys of this group requiring low magnesium contents (0.10% maximum) are the die casting compositions 380.0 through 384.0.

Both copper and magnesium increase strength and hardness in the as-cast (F) temper through increased solid-solution hardening. Much greater increases are afforded by artificial aging only (T5-type tempers) or by complete solution plus artificial aging treatments (T6- or T7-type tempers). Depending on composition, the precipitation hardening is the result of precipitate structures based on Mg_2Si, Al_2Cu, Al_2CuMg, or combinations of

these phases. The alloys containing both copper and magnesium have higher strengths at elevated temperatures.

Higher-silicon-content alloys are preferred for casting by the permanent mold and die casting processes. The thermal expansion coefficient decreases with increasing silicon and nickel contents. A low expansion coefficient is beneficial for engine applications such as pistons and cylinder blocks. When the silicon content exceeds 12%, as in alloys 390.0 through 393.0, primary silicon crystals are present and, if fine and well distributed, enhance wear resistance.

4*xx.x* Series. Alloys of the 4*xx.x* group, based on the binary aluminum-silicon system and containing from 5 to 12% Si, find many applications where combinations of moderate strength and high ductility and impact resistance are required. Bridge railing support castings are a representative example.

5*xx.x* Series. The aluminum-magnesium alloys in the 5*xx.x* group are essentially single phase binary alloys with moderate-to-high strength and toughness properties. High corrosion resistance, especially to seawater and marine atmospheres, is the primary advantage of castings made of Al-Mg alloys. Best corrosion resistance requires low impurity content (both solid and gaseous), and thus alloys must be prepared from high-quality metals and handled with great care in the foundry. These alloys are suitable for welded assemblies and are often used in architectural and other decorative or building needs. Aluminum-magnesium alloys also have good machinability and an attractive appearance when anodized.

7*xx.x* Series. The 7*xx.x* aluminum-zinc-magnesium alloys are notable for their combinations of good finishing characteristics, good general corrosion resistance, and the capability of developing high strength through natural aging without heat treatment.

8*xx.x* Series. Alloys of the 8*xx.x* group contain ~6% Sn and small amounts of copper and nickel for strengthening. These alloys were developed for bearing applications (tin imparts lubricity), for example, connecting rods and crankcase bearings for diesel engines.

Alloying and Second-Phase Constituents

The predominant reason for alloying is to increase strength, hardness, and resistance to wear, creep, stress relaxation or fatigue. Effects on these properties are specific to the different alloying elements and combinations of them, and are related to their alloy phase diagrams and to the

microstructures and substructures that they form as a result of solidification, thermomechanical history, heat treatment and/or cold working.

The tensile yield strength of super-purity aluminum in its annealed (softest) state is approximately 10 MPa (1.5 ksi), whereas those of some heat treated commercial high-strength alloys exceed 550 MPa (80 ksi). When the magnitude of this difference (an increase of over 5000%) is considered, this practical, everyday accomplishment, which is just one aspect of the physical metallurgy of aluminum, is truly remarkable. Higher strengths, up to a yield strength of 690 MPa (100 ksi) and over, may be readily produced, but the fracture toughness of such alloys does not meet levels considered essential for aircraft or other critical-structure applications.

The elements that are most commonly present in commercial alloys to provide increased strength—particularly when coupled with strain hardening by cold working or with heat treatment, or both—are copper, magnesium, manganese, silicon, and zinc (Fig. 6). These elements all have significant solid solubility in aluminum, and in all cases the solubility increases with increasing temperature (see Fig. 7).

For those elements that form solid solutions, the strengthening effect when the element is in solution tends to increase with increasing difference in the atomic radii of the solvent (Al) and solute (alloying element) atoms. This factor is evident in data obtained from super-purity binary solid-solution alloys in the annealed state, presented in Table 8, but it is evident that other effects are involved, chief among which is an electronic bonding factor. The effects of multiple solutes in solid solution are somewhat less than additive and are nearly the same when one solute has a larger and the other a smaller atomic radius than that of aluminum as

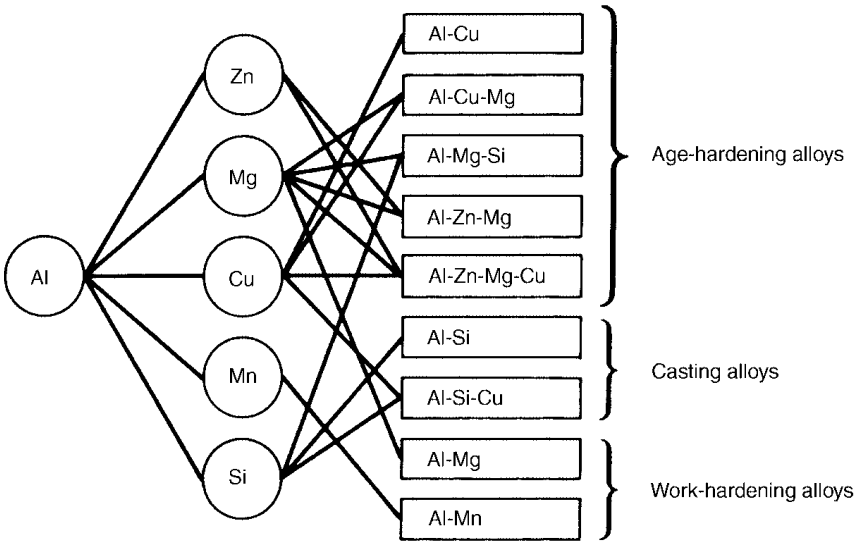


Fig. 6 The principal aluminum alloys

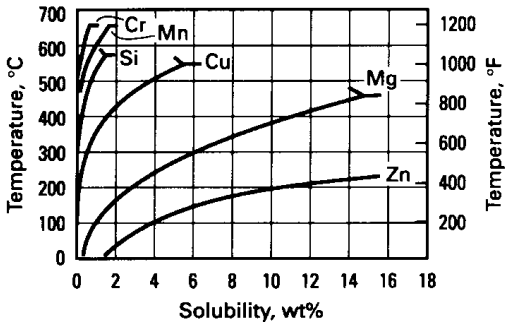


Fig. 7 Equilibrium binary solid solubility as a function of temperature for alloying elements most frequently added to aluminum

when both are either smaller or larger. Manganese in solid solution is highly effective in strengthening binary alloys. Its contribution to the strength of commercial alloys is less, because in these compositions, as a result of commercial mill fabricating operations, the manganese is largely precipitated.

The principal alloys that are strengthened by alloying elements in solid solution (often coupled with cold work) are those in the aluminum-magnesium series, ranging form 0.5 to 6 wt% Mg. These alloys often contain small additions of transition elements, such as chromium or manganese, and less frequently zirconium, to control the grain or subgrain structure, and iron and silicon impurities that usually are present in the form of intermetallic particles. Figure 8 illustrates the effect of magnesium in solid solution on the yield strength and tensile elongation for most of the common aluminum-magnesium commercial alloys.

Second-Phase Constituents. Elements and combinations that form predominantly second-phase constituents with relatively low solid solubility include iron, silicon, magnesium, copper, manganese and chromium, and combinations thereof (see also the section "Alloying Effects on Phase Formation"). The presence of increasing volume fractions of the intermetallic-compound phases formed by these elements and the elemental silicon constituent formed by silicon during solidification or by

Table 8 Solid-solution effects on strength of principal solute elements in super-purity aluminum

Element	Difference in atomic radii, $r_x - r_{Al}$ % (a)	Strength/addition values(b)							
		Yield strength/% addition(c)				Tensile strength/% addition(d)			
		MPa/at. %	ksi/at. %	MPa/wt %	ksi/wt %	MPa/at. %	ksi/at. %	MPa/wt %	ksi/wt %
Si	−3.8	9.3	1.35	9.2	1.33	40.0	5.8	39.6	5.75
Zn	−6.0	6.6	0.95	2.9	0.42	20.7	3.0	15.2	2.2
Cu	−10.7	16.2	2.35	13.8	2.0	88.3	12.8	43.1	6.25
Mn	−11.3	(e)	(e)	30.3	4.4	(e)	(e)	53.8	7.8
Mg	+11.8	17.2	2.5	18.6	2.7	51.0	7.4	50.3	7.3

(a) Listed in order of increasing percent difference in atomic radii. (b) Some property to percent addition relationships are nonlinear, Generally, the unit effects of smaller additions are greater. (c) Increase in yield strength (0.2% offset) for 1% (atomic or weight basis) alloy addition. (d) Increase in ultimate tensile strength for 1% (atomic or weight basis) alloy addition. (e) 1 at.% of manganese is not soluble.

precipitation in the solid state during postsolidification heating also increases strength and hardness. The rates of increase per unit weight of alloying element added are frequently similar to but usually lower than those resulting form solid solution. This "second-phase" hardening occurs even though the constituent particles are of sizes readily resolved by optical microscopy. These irregularly shaped particles form during solidification and occur mostly along grain boundaries and between dendrite arms.

Manganese and chromium are included in the group of elements that form predominantly second phase constituents, because in commercial alloys they have very low equilibrium solid solubilities. In the case of many compositions containing manganese, this is because iron and silicon are also present and form the quaternary phase Al_{12} $(Fe, Mn)_3Si$. In alloys containing copper and manganese, the ternary phase $Al_{20}Cu_2Mn_3$ is formed. Most of the alloys in which chromium is present also contain magnesium, so that during solid-state heating they form $Al_{12}Mg_2Cr$, which also has very low equilibrium solid solubility. The concentrations of manganese and/or chromium held in solid solution in as-cast ingot that has been rapidly solidified and cooled from the molten state greatly exceed the equilibrium solubility. The solid solution is thus supersaturated and metastable. Ingot preheating for wrought commercial alloys containing these elements is designed to cause solid-state precipitation of the complex phase containing one or the other of these elements that is appropriate to the alloy composition. This precipitation does not cause appreciable hardening, nor is it intended that it should. Its purpose is to produce finely divided and dispersed particles that retard or inhibit recrystallization

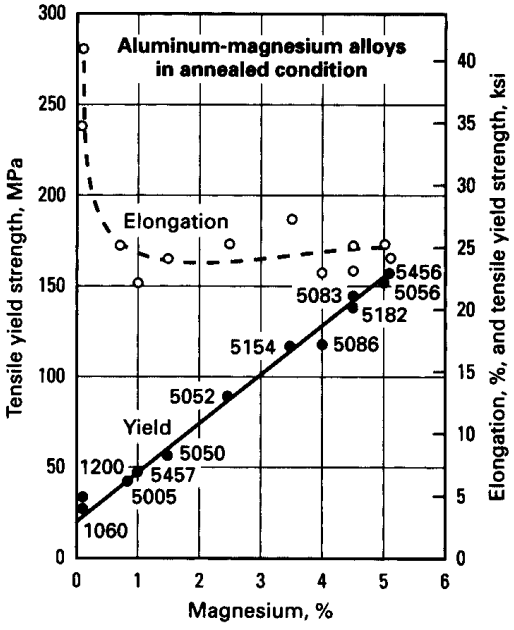


Fig. 8 Correlation between tensile yield, strength elongation, and magnesium content for some commercial aluminum alloys

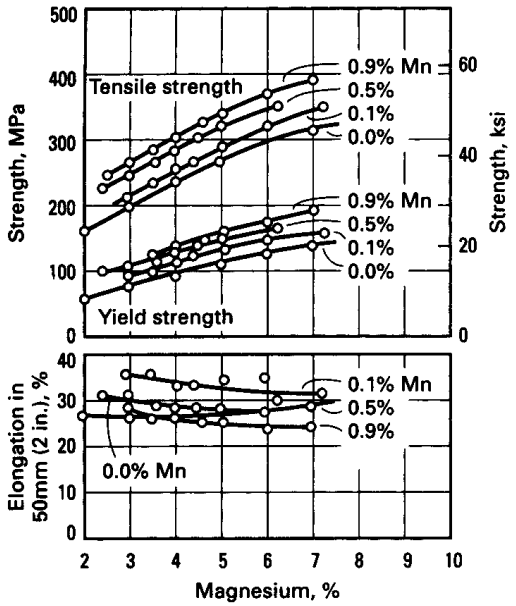


Fig. 9 Tensile properties in Al-Mg-Mn alloys in the form of annealed (O temper) plate 13 mm (0.5 in.) thick

and grain growth in the alloy during subsequent heatings. The precipitate particles of $Al_{12}(Fe,Mn)_3Si$, $Al_{20}Cu_2Mn_3$, or $Al_{12}Mg_2Cr$ are incoherent with the matrix, and concurrent with their precipitation the original solid solution becomes less concentrated. These conditions do not provide appreciable precipitation hardening. Changes in electrical conductivity constitute an effective measure of the completeness of these precipitation reactions that occur in preheating.

For alloys that are composed of both solid-solution and second-phase constituents and/or dispersoid precipitates, all of these components of microstructure contribute to strength, in a roughly additive manner. This is shown in Fig. 9 for Al-Mg-Mn alloys in the annealed condition.

Effects of Specific Alloying Elements and Impurities

The mechanical, physical, and chemical properties of aluminum alloys depend upon composition and microstructure. The addition of selected elements to pure aluminum greatly enhances its properties and usefulness. Because of this, most applications for aluminum utilize alloys having one or more elemental additions. The major alloying additions used with aluminum are copper, manganese, silicon, magnesium, and zinc. The total amount of these elements can constitute up to 10% of the alloy composition (all percentages given in weight percent unless otherwise noted). Impurity elements are also present, but their total percentage is usually less than 0.15% in aluminum alloys.

The important alloying elements and impurities are listed here alphabetically as a concise review of major effects. Some of the effects, particularly with respect to impurities, are not well documented and are specific to particular alloys or conditions.

Antimony is present in trace amounts (0.01 to 0.1 ppm) in primary commercial-grade aluminum. Antimony has a very small solid solubility in aluminum (<0.01%). It has been added to aluminum-magnesium alloys because it was claimed that by forming a protective film of antimony oxychloride, it enhances corrosion resistance in salt water. Some bearing alloys contain up to 4 to 6% Sb. Antimony can be used instead of bismuth to counteract hot cracking in aluminum-magnesium alloys.

Arsenic. The compound AsAl is a semiconductor. Arsenic is very toxic (as AsO_3) and must be controlled to very low limits where aluminum is used as foil for food packaging.

Beryllium is used in aluminum alloys containing magnesium to reduce oxidation at elevated temperatures. Up to 0.1% Be is used in aluminizing baths for steel to improve adhesion of the aluminum film and restrict the formation of the deleterious iron-aluminum complex. The mechanism of protection is attributed to beryllium diffusion to the surface and the formation of a protective layer. Oxidation and discoloration of wrought aluminum-magnesium products are greatly reduced by small amounts of beryllium because of the diffusion of beryllium to the surface and the formation of an oxide of high-volume ratio. Beryllium does not affect the corrosion resistance of aluminum. Beryllium is generally held to 8 ppm in welding filler metal, and its content should be limited in wrought alloys that may be welded.

Beryllium poisoning is an allergic disease, a problem of individual hypersensitivity that is related to intensity and duration of exposure. Inhalation of dust containing beryllium compounds may lead to acute poisoning. Beryllium is not used in aluminum alloys that may contact food or beverages.

Bismuth. The low-melting-point metals such as bismuth, lead, tin, and cadmium are added to aluminum to make free-machining alloys. These elements have a restricted solubility in solid aluminum and form a soft, low-melting phase that promotes chip breaking and helps to lubricate the cutting tool. An advantage of bismuth is that its expansion on solidification compensates for the shrinkage of lead. A 1-to-1 lead-bismuth ratio is used in the aluminum-copper alloy, 2011, and in the aluminum-Mg_2Si alloy, 6262. Small additions of bismuth (20 to 200 ppm) can be added to aluminum-magnesium alloys to counteract the detrimental effect of sodium on hot cracking.

Boron is used in aluminum and its alloys as a grain refiner and to improve conductivity by precipitating vanadium, titanium, chromium, and molybdenum (all of which are harmful to electrical conductivity at their usual impurity level in commercial-grade aluminum). Boron can be used alone (at levels of 0.005 to 0.1%) as a grain refiner during solidification, but it becomes more effective when used with an excess of titanium. Commercial grain refiners commonly contain titanium and boron in a 5-to-1 ratio. Boron has a high-neutron-capture cross section and is used in aluminum alloys for certain atomic energy applications, but its content has to be limited to very low levels in alloys used in reactor areas where this property is undesirable.

Cadmium is a relatively low-melting element that finds limited use in aluminum. Up to 0.3% Cd may be added to aluminum-copper alloys to accelerate the rate of age hardening, increase strength, and increase corrosion resistance. At levels of 0.005 to 0.5%, it has been used to reduce the time of aging of aluminum-zinc-magnesium alloys. It has been reported that traces of cadmium lower the corrosion resistance of unalloyed aluminum. In excess of 0.1%, cadmium causes hot shortness in some alloys. Because of its high neutron absorption, cadmium has to be kept very low for atomic energy use. It has been used to confer free-cutting characteristics, particularly to aluminum-zinc-magnesium alloys; it was preferred to bismuth and lead because of its higher melting point. As little as 0.1% provides an improvement in machinability. Cadmium is used in bearing alloys along with silicon. The oral toxicity of cadmium compounds is high. In melting, casting, and fluxing operation, cadmium oxide fume can present hazards.

Calcium has very low solubility in aluminum and forms the intermetallic $CaAl_4$. An interesting group of alloys containing about 5% Ca and 5% Zn have superplastic properties. Calcium combines with silicon to form $CaSi_2$, which is almost insoluble in aluminum and therefore will increase the conductivity of commercial-grade metal slightly. In aluminum-magnesium-silicon alloys, calcium will decrease age hardening. Its effect on aluminum-silicon alloys is to increase strength and decrease elongation, but it does not make these alloys heat-treatable. At the 0.2% level, calcium alters the recrystallization characteristics of 3003. Very small amounts of calcium (10 ppm) increase the tendency of molten aluminum alloys to pick up hydrogen.

Carbon may occur infrequently as an impurity in aluminum in the form of oxycarbides and carbides, of which the most common is Al_4C_3, but carbide formation with other impurities such as titanium is possible. Al_4C_3 decomposes in the presence of water and water vapor, and this may lead to surface pitting. Normal metal transfer and fluxing operations usually reduce carbon to the ppm level.

Cerium, mostly in the form of misch metal (rare earths with 50 to 60% Ce), has been added experimentally to casting alloys to increase fluidity and reduce die sticking. In alloys containing high iron (0.7%), it is reported to transform acicular $FeAl_3$ into a nonacicular compound. Cerium has also been added to rapidly solidified powder metallurgy (RS-P/M) alloys (e.g., 8019, an Al-9Fe-4Ce alloy). Cerium forms thermally stable dispersoid particles in these alloys.

Chromium occurs as a minor impurity in commercial-purity aluminum (5 to 50 ppm). It has a large effect on electrical resistivity. Chromium is a common addition to many alloys of the aluminum-magnesium, aluminum-magnesium-silicon, and aluminum-magnesium-zinc groups, in which it is added in amounts generally not exceeding 0.35%. In excess of these limits, it tends to form very coarse constituents with other impurities or additions such as manganese, iron, and titanium. This limit is decreased as the content of transition metals increases. In casting alloys, excess chromium will produce a sludge by peritectic precipitation on holding.

Chromium has a slow diffusion rate and forms finely dispersed phases in wrought products. These dispersed phases inhibit nucleation and grain growth. Chromium is used to control grain structure, to prevent grain growth in aluminum-magnesium alloys, and to prevent recrystallization in aluminum-magnesium-silicon or aluminum-zinc alloys during hot working or heat treatment. The fibrous structures that develop reduce stress corrosion susceptibility and/or improve toughness. Chromium in solid solution and as a finely dispersed phase increases the strength of alloys slightly. The main drawback of chromium in heat-treatable alloys is the increase in quench sensitivity when the hardening phase tends to precipitate on the pre-existing chromium-phase particles. Chromium imparts a yellow color to the anodic film.

Cobalt is not a common addition to aluminum alloys. It has been added to some aluminum-silicon alloys containing iron, where it transforms the acicular β (aluminum-iron-silicon) into a more rounded aluminum-cobalt-iron phase, thus improving strength and elongation. Aluminum-zinc-magnesium-copper alloys containing 0.4 to 1.5% Co are produced by RS-P/M (e.g., alloys 7090 and 7091). Cobalt forms Co_2Al_9 or $(Co,Fe)_2Al_9$ particles, which are homogeneously dispersed. These dispersoids refine the grain size for improved high strength and ductility and enhance resistance to stress-corrosion cracking.

Copper. Aluminum-copper alloys containing 2 to 10% Cu, generally with other additions, form important families of alloys. Both cast and wrought aluminum-copper alloys respond to solution heat treatment and subsequent aging with an increase in strength and hardness and a decrease in elongation. The strengthening is maximum between 4 and 6% Cu, depending upon the influence of other constituents present. The properties

of aluminum-copper alloy sheet in a number of thermal conditions are assembled in Fig. 10. The aging characteristics of binary aluminum-copper alloys have been studied in greater detail than any other system, but there are actually very few commercial binary aluminum-copper alloys. Most commercial alloys contain other alloying elements.

Copper-Magnesium. The main benefit of adding magnesium to aluminum-copper alloys is the increased strength possible following solution heat treatment and quenching. In wrought material of certain alloys of this type, an increase in strength accompanied by high ductility occurs on aging at room temperature. On artificial aging, a further increase in strength, especially in yield strength, can be obtained, but at a substantial sacrifice in tensile elongation.

On both cast and wrought aluminum-copper alloys, as little as about 0.5% Mg is effective in changing aging characteristics. In wrought products, the effect of magnesium additions on strength can be maximized in artificially aged materials by cold working prior to aging (Fig. 11). As shown in Fig. 12, cold working also influences the strength of naturally aged aluminum-copper alloys, with or without magnesium additions. The effect of magnesium on the corrosion resistance of aluminum-copper alloys depends on the type of product and the thermal treatment.

Copper-Magnesium Plus Other Elements. The cast aluminum-copper-magnesium alloys containing iron are characterized by dimensional stability and improved bearing characteristics, as well as by high strength and hardness at elevated temperatures. However, in a wrought Al-4%-Cu-0.5%Mg alloy, iron in concentrations as low as 0.5% lowers the tensile properties in the heat-treated condition, if the silicon content is less than that required to tie up the iron as the αFeSi constituent. In this event, the

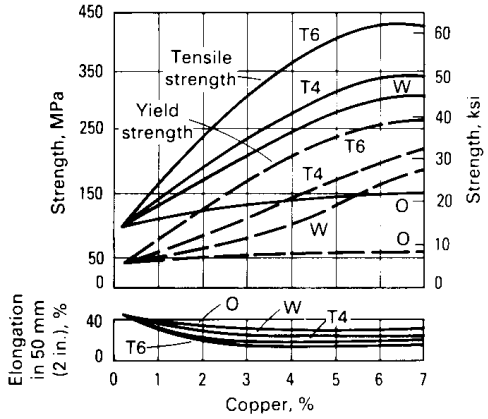


Fig. 10 Tensile properties of high-purity, wrought aluminum-copper alloys. Sheet specimen was 13 mm (0.5 in.) wide and 1.59 mm (0.0625 in.) thick. O, annealed; W, tested immediately after water quenching from a solution heat treatment; T4, as in W, but aged at room temperature; T6, as in T4, followed by precipitation treatment at elevated temperature

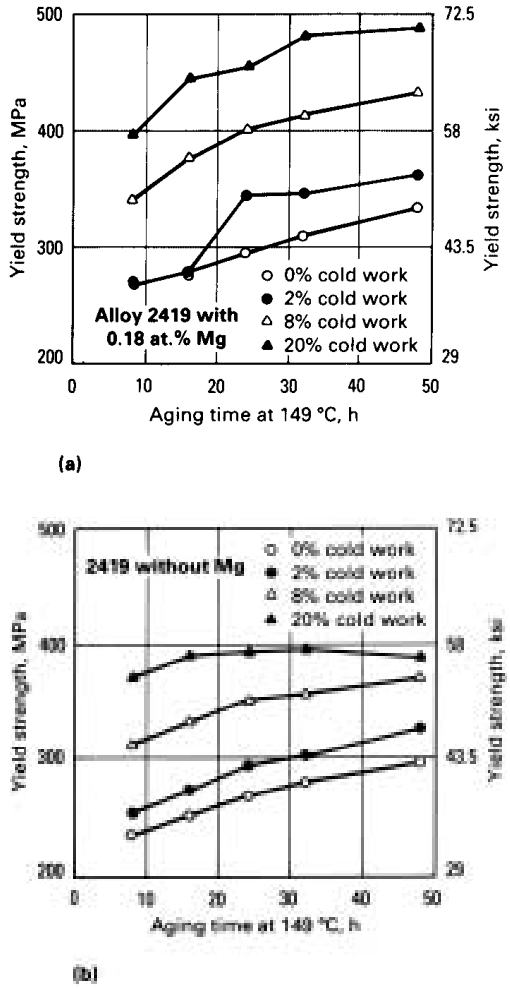


Fig. 11 Effect of cold work and Mg addition on alloy 2419. (a) The effect of cold work on the yield strength response to aging at 149 °C (300 °F) for the alloy with 0.18 at.% Mg. (b) The effect of cold work on the yield strength response to aging at 149 °C (300 °F) for the alloy without Mg.

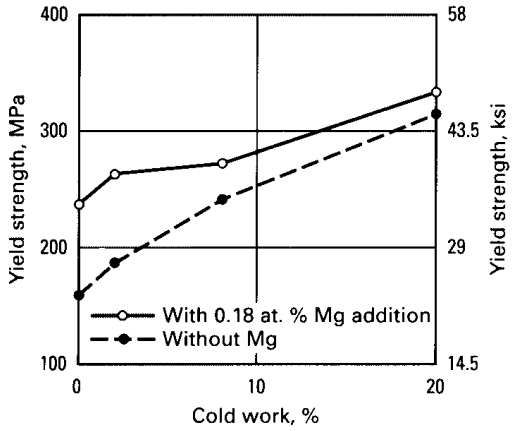


Fig. 12 The effect of cold work on yield strength of aluminum-copper alloy 2419 in naturally aged materials

excess iron unites with copper to form the Cu_2FeAl_7 constituent, thereby reducing the amount of copper available for heat-treating effects. When sufficient silicon is present to combine with the iron, the properties are unaffected. Silicon also combines with magnesium to form Mg_2Si precipitate and contributes in the age-hardening process.

Silver substantially increases the strength of heat-treated and aged aluminum-copper-magnesium alloys. Nickel improves the strength and hardness of cast and wrought aluminum-copper-magnesium alloys at elevated temperatures. Addition of about 0.5% Ni lowers the tensile properties of the heat-treated, wrought Al-4%-Cu-0.5%Mg alloy at room temperature.

The alloys containing manganese form the most important and versatile system of commercial high-strength wrought aluminum-copper-magnesium alloys. The substantial effect exerted by manganese on the tensile properties of aluminum-copper alloys containing 0.5% Mg is shown in Fig. 13. It is apparent that no one composition offers both maximum strength and ductility. In general, tensile strength increases with separate or simultaneous increases in magnesium and manganese, and the yield strength also increases, but to a lesser extent. Further increases in tensile and particularly yield strength occur on cold working after heat treatment. Additions of manganese and magnesium decrease the fabricating characteristics of the aluminum-copper alloys, and manganese also causes a loss in ductility; hence, the concentration of this element does not exceed about 1% in commercial alloys. Additions of cobalt, chromium, or molybdenum to the wrought Al-4%-Cu-0.5%Mg type of alloy increase the tensile properties of heat treatment, but none offers a distinct advantage over manganese.

Alloys with lower copper content than the conventional 2024 and 2014 type alloys were necessary to provide the formability required by the automobile industry. Copper-magnesium alloys developed for this purpose are 2002 and 2036 variations. These have acceptable formability, good spot weldability, reasonable fusion weldability, good corrosion resistance, and freedom from Lüders lines. The paint-baking cycle serves as a precipitation treatment to give final mechanical properties.

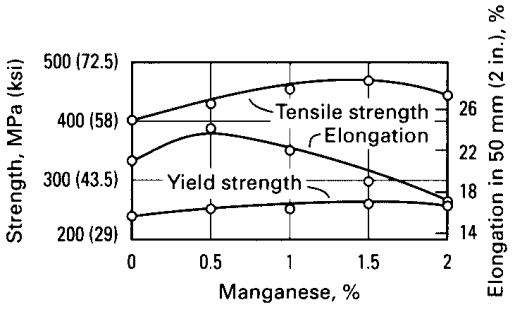


Fig. 13 Relationship between tensile properties and manganese content of Al-4%Cu-0.5%Mg alloy, heat treated at 525 °C (980 °F)

Copper and Minor Additions. In the wrought form, an alloy family of interest is the one containing small amounts of several metals known to raise the recrystallization temperature of aluminum and its alloys, specifically manganese, titanium, vanadium, or zirconium. An alloy of this nature retains its properties well at elevated temperatures, fabricates readily, and has good casting and welding characteristics. Figure 14 illustrates the effect of 3 to 8% Cu on an alloy of Al-0.3%Mn-0.2%Zr-0.1%V at room temperature and after exposure at 315 °C (600 °F) for two different periods of time. The stability of the properties should be noted, as reflected in the small reduction in strength with time at this temperature.

Gallium is an impurity in aluminum and is usually present at levels of 0.001 to 0.02%. At these levels its effect on mechanical properties is quite small. At the 0.2% level, gallium has been found to affect the corrosion characteristics and the response to etching and brightening of some alloys. Liquid gallium metal penetrates very rapidly at aluminum grain boundaries and can produce complete grain separation. In sacrificial anodes, an addition of gallium (0.01 to 0.1%) keeps the anode from passivating.

Hydrogen has a higher solubility in the liquid state at the melting point than in the solid at the same temperature. Because of this, gas porosity can form during solidification. Hydrogen is produced by the reduction of water vapor in the atmosphere by aluminum and by the decomposition of hydrocarbons. Hydrogen pickup in both solid and liquid aluminum is enhanced by the presence of certain impurities, such as sulfur compounds, on the surface and in the atmosphere. Hydride-forming elements in the

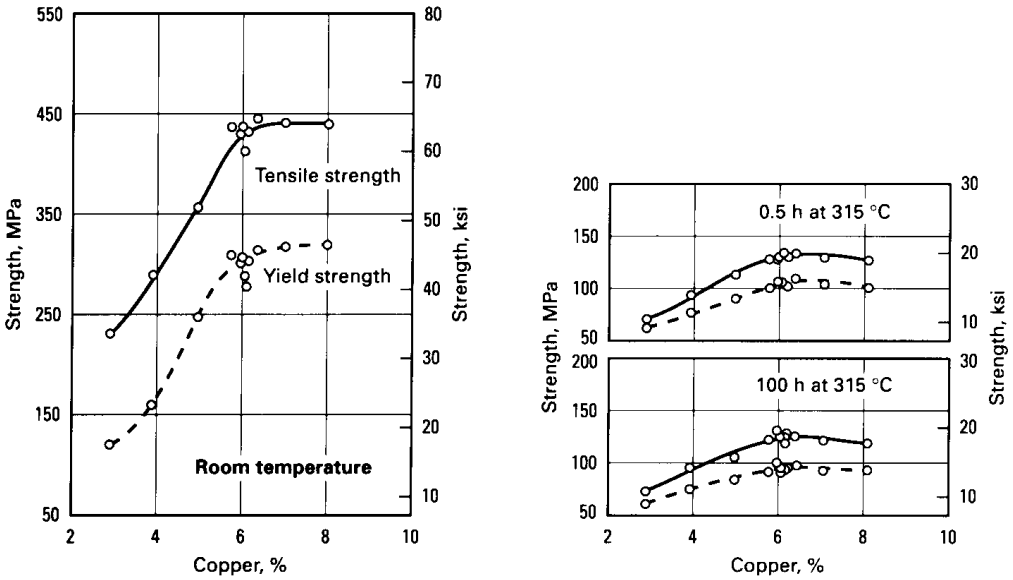


Fig. 14 Variation of tensile properties with copper content in Al-0.3%Mn-0.2%Zr-0.1%V alloy in the T6 temper

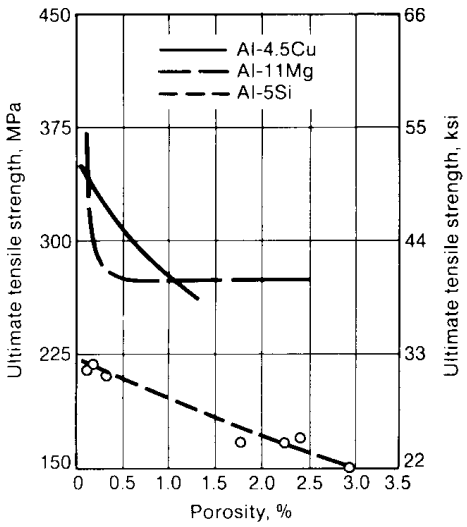


Fig. 15 Ultimate tensile strength versus hydrogen porosity for sand-cast bars of three aluminum alloys

metal increase the pickup of hydrogen in the liquid. Other elements, such as beryllium, copper, tin, and silicon, decrease hydrogen pickup.

Hydrogen porosity adversely affects mechanical properties in a manner that varies with the alloy. Figures 15 and 16 show the effect of porosity on the ultimate tensile strength of selected compositions.

In addition to causing primary porosity in casting, hydrogen causes secondary porosity, blistering, and high-temperature deterioration (advanced internal gas precipitation) during heat treating. It probably plays a role in

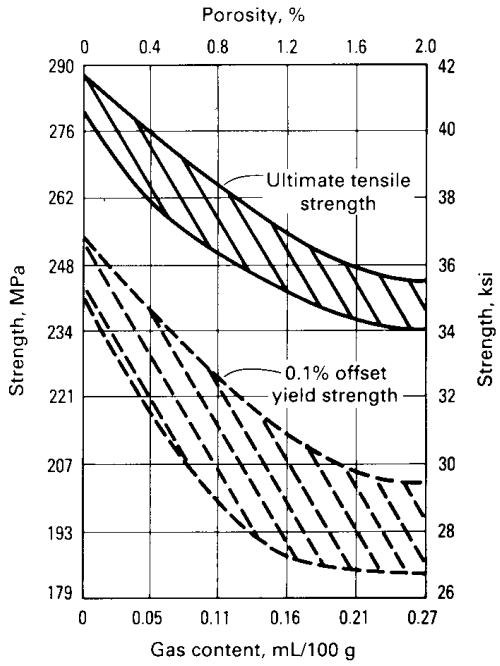


Fig. 16 Influence of gas content on the tensile and yield strengths of aluminum alloy 356

grain-boundary decohesion during stress-corrosion cracking. Its level in melts is controlled by fluxing with hydrogen-free gases or by vacuum degassing.

Indium. Small amounts (0.05 to 0.2%) of indium have a marked influence on the age hardening of aluminum-copper alloys, particularly at low copper contents (2 to 3% Cu). In this respect, indium acts very much like cadmium in that it reduces room-temperature aging but increases artificial aging. The addition of magnesium decreases the effect of indium. Small amounts of indium (0.03 to 0.5%) are claimed to be beneficial in aluminum-cadmium bearing alloys.

Iron is the most common impurity found in aluminum. It has a high solubility in molten aluminum and is therefore easily dissolved at all molten stages of production. The solubility of iron in the solid state is very low (~0.05%); therefore, most of the iron present in aluminum over this amount appears as an intermetallic second phase in combination with aluminum and often other elements. Because of its limited solubility, it is used in electrical conductors in which it provides a slight increase in strength (Fig. 17) and better creep characteristics at moderately elevated temperatures.

Iron reduces the grain size in wrought products. Alloys of iron and manganese near the ternary eutectic content, such as 8006, can have useful combinations of strength and ductility at room temperature and retain strength at elevated temperatures. The properties are due to the fine grain size that is stabilized by the finely dispersed iron-rich second phase. Iron is added to the aluminum-copper-nickel group of alloys to increase strength at elevated temperatures.

Lead. Normally present only as a trace element in commercial-purity aluminum, lead is added at about the 0.5% level with the same amount as bismuth in some alloys (2011 and 6262) to improve machinability. Additions of lead may be troublesome to the fabricator as lead will tend to segregate during casting and cause hot shortness in aluminum-copper-magnesium alloys. Lead compounds are toxic.

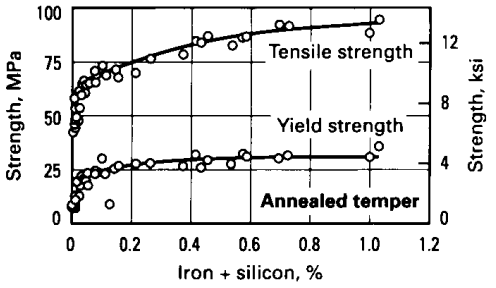


Fig. 17 Effect of iron plus silicon impurities on tensile strength and yield strength of aluminum

Lithium. The impurity level of lithium is of the order of a few ppm, but at a level of less than 5 ppm it can promote the discoloration (blue corrosion) of aluminum foil under humid conditions. Traces of lithium greatly increase the oxidation rate of molten aluminum and alter the surface characteristics of wrought products. Binary aluminum-lithium alloys age harden but are not used commercially. Present interest is on the aluminum-copper-magnesium-lithium alloys, which can be heat-treated to strengths comparable to those of 7*xxx* alloys. In addition, the density is decreased and the modulus is increased. This type of alloy has a high volume fraction of coherent, ordered $LiAl_3$ precipitate. In addition to increasing the elastic modulus, the fatigue crack growth resistance is increased at intermediate levels of stress intensity.

Magnesium is the major alloying element in the 5*xxx* series of alloys. Its maximum solid solubility in aluminum is 17.4%, but the magnesium content in current wrought alloys does not exceed 5.5%. Magnesium precipitates preferentially at grain boundaries as a highly anodic phase (Mg_5Al_3 or Mg_5Al_8), which produces susceptibility to intergranular cracking and to stress corrosion. Wrought alloys containing up to 5% Mg, properly fabricated, are stable under normal usage. The addition of magnesium markedly increases the strength of aluminum without unduly decreasing the ductility. Corrosion resistance and weldability are good. In the annealed condition, magnesium alloys form Lüders lines during deformation.

Magnesium-Manganese. In wrought alloys, this system has high strength in the work-hardened condition, high resistance to corrosion, and good welding characteristics. Increasing amounts of either magnesium or manganese intensify the difficulty of fabrication and increase the tendency toward cracking during hot rolling, particularly if traces of sodium are present. The two main advantages of manganese additions are that the precipitation of the magnesium phase is more general throughout the structure, and that for a given increase in strength, manganese allows a lower magnesium content and ensures a greater degree of stability to the alloy.

The tensile properties of 13 mm (0.5 in.) plate at various magnesium and manganese concentrations are shown in Fig. 9 for the O temper and in Fig. 18 for a work-hardened temper. Increasing magnesium raises the tensile strength by about 35 MPa (5 ksi) for each 1% increment; manganese is about twice as effective as magnesium.

Magnesium-Silicide. Wrought alloys of the 6*xxx* group contain up to 1.5% each of magnesium and silicon in the approximate ratio to form Mg_2Si, that is, 1.73:1. The maximum solubility of Mg_2Si is 1.85%, and this decreases with temperature. Precipitation upon age hardening occurs by formation of Guinier-Preston (G-P) zones and a very fine precipitate. Both confer an increase in strength to these alloys, though not as great as in the case of the 2*xxx* or the 7*xxx* alloys.

Al-Mg_2Si alloys can be divided into three groups. In the first group, the total amount of magnesium and silicon does not exceed 1.5%. These elements are in a nearly balanced ratio or with a slight excess of silicon. Typical of this group is 6063, widely used for extruded architectural sections. This easily extrudable alloy nominally contains 1.1% Mg_2Si. Its solution heat-treating temperature of just over 500 °C (930 °F) and its low quench sensitivity are such that this alloy does not need a separate solution treatment after extrusion but may be air-quenched at the press and artificially aged to achieve moderate strength, good ductility, and excellent corrosion resistance.

The second group nominally contains 1.5% or more of magnesium plus silicon and other additions such as 0.3% Cu, which increases strength in the T6 temper. Elements such as manganese, chromium, and zirconium are used for controlling grain structure. Alloys of this group, such as the structural alloy 6061, achieve strengths about 70 MPa (10 ksi) higher than in the first group in the T6 temper. Alloys of the second group require a higher solution-treating temperature than the first and are quench-sensitive. Therefore, they generally require a separate solution treatment followed by rapid quenching and artificial aging.

The third group contains an amount of Mg_2Si overlapping the first two but with a substantial excess of silicon. An excess of 0.2% Si increases the strength of an alloy containing 0.8% Mg_2Si by about 70 MPa (10 ksi). Larger amounts of excess silicon are less beneficial. Excess magnesium, however, is of benefit only at low Mg_2Si contents because magnesium lowers the solubility of Mg_2Si. In excess silicon alloys, segregation of silicon to the boundary causes grain-boundary fracture in recrystallized

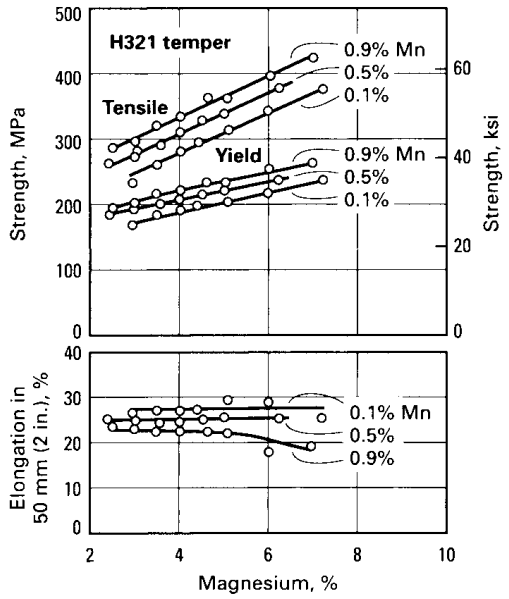


Fig. 18 Tensile properties of 13 mm (0.5 in.) aluminum-magnesium-manganese plate in H321 temper

structures. Additions of manganese, chromium, or zirconium counteract the effect of silicon by preventing recrystallization during heat treatment. Common alloys of this group are 6009, 6010, and 6351. Additions of lead and bismuth to an alloy of this series (6262) improves machinability. This alloy has a better corrosion resistance than 2011, which also is used as a free-machining alloy.

Manganese is a common impurity in primary aluminum, in which its concentration normally ranges from 5 to 50 ppm. It decreases resistivity. Manganese increases strength either in solid solution or as a finely precipitated intermetallic phase. It has no adverse effect on corrosion resistance. Manganese has a very limited solid solubility in aluminum in the presence of normal impurities but remains in solution when chill cast, so that most of the manganese added is substantially retained in solution, even in large ingots. As an addition, it is used to increase strength and to control the grain structure (Fig. 19). The effect of manganese is to increase the recrystallization temperature and to promote the formation of fibrous structure upon hot working. As a dispersed precipitate it is effective in slowing recovery and in preventing grain growth. The manganese precipitate increases the quench sensitivity of heat-treatable alloys.

Manganese is also used to correct the shape of acicular or of platelike iron constituents and to decrease their embrittling effect. Up to the 1.25% level, manganese is the main alloying addition of the 3*xxx* series of alloys, in which it is added alone or with magnesium. This series of alloys is used in large tonnages for beverage containers and general utility sheet. Even

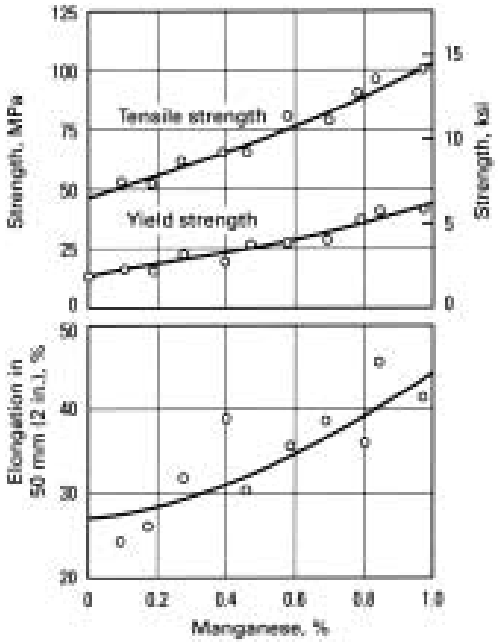


Fig. 19 Effect of manganese on tensile properties of wrought 99.95% Al, 1.6 mm (0.064 in.) thick specimens, quenched in cold water from 565 °C (1050 °F)

after high degrees of work hardening, these alloys are used to produce severely formed can bodies.

The combined content of manganese, iron, chromium, and other transition metals must be limited, otherwise large primary intermetallic crystals precipitate from the melt in the transfer system or in the ingot sump during casting. In alloys 3003 and 3004 the iron plus manganese content should be kept below about 2.0 and 1.7%, respectively, to prevent the formation of primary $(Fe,Mn)Al_6$ during casting.

Mercury has been used at the level of 0.05% in sacrificial anodes used to protect steel structures. Other than for this use, mercury in aluminum or in contact with it as a metal or a salt will cause rapid corrosion of most aluminum alloys. The toxic properties of mercury must be kept in mind when adding it to aluminum alloys.

Molybdenum is a very low level (0.1 to 1.0 ppm) impurity in aluminum. It has been used at a concentration of 0.3% as a grain refiner, because the aluminum end of the equilibrium diagram is peritectic, and also as a modifier for the iron constituents, but it is not in current use for these purposes.

Nickel. The solid solubility of nickel in aluminum does not exceed 0.04%. Over this amount, it is present as an insoluble intermetallic, usually in combination with iron. Nickel (up to 2%) increases the strength of high-purity aluminum but reduces ductility. Binary aluminum-nickel alloys are no longer in use, but nickel is added to aluminum-copper and to aluminum-silicon alloys to improve hardness and strength at elevated temperatures and to reduce the coefficient of expansion. Nickel promotes pitting corrosion in dilute alloys such as 1100. It is limited in alloys for atomic reactor use, due to its high neutron absorption, but in other areas it is a desirable addition along with iron to improve corrosion resistance to high-pressure steam.

Niobium. As with other elements forming a peritectic reaction, niobium would be expected to have a grain-refining effect on casting. It has been used for this purpose, but the effect is not marked.

Phosphorus is a minor impurity (1 to 10 ppm) in commercial-grade aluminum. Its solubility in molten aluminum is very low (~0.01% at 660 °C, or 1220 °F) and considerably smaller in the solid. Phosphorus is used as a modifier for hypereutectic aluminum-silicon alloys where aluminum-phosphide acts as nucleus for primary silicon, thus refining silicon and improving machinability. The aluminum-phosphorus compounds reacts with water vapor to give phosphine (PH_3), but the level of phosphorus in aluminum is sufficiently low that this does not constitute a health hazard if adequate ventilation is used when machining phosphorus-nucleated

castings. Phosphine can be a problem in furnace teardowns where phosphate-bonded refractories are used.

Silicon, after iron, is the highest impurity level in electrolytic commercial aluminum (0.01 to 0.15%). In wrought alloys, silicon is used with magnesium at levels up to 1.5% to produce Mg_2Si in the 6*xxx* series of heat-treatable alloys.

High-purity aluminum-silicon alloys are hot short up to 3% Si, the most critical range being 0.17 to 0.8% Si, but additions of silicon (0.5 to 4.0%) reduce the cracking tendency of aluminum-copper-magnesium alloys. Small amounts of magnesium added to any silicon-containing alloy will render it heat-treatable, but the converse is not true because excess magnesium over that required to form Mg_2Si sharply reduces the solid solubility of this compound. Modification of the silicon can be achieved through the addition of sodium in eutectic and hypoeutectic alloys and by phosphorus in hypereutectic alloys. Up to 12% Si is added in wrought alloys used as cladding for brazing sheet. Hypereutectic casting alloys used for wear applications contain up to 23% Si. Alloys containing about 5% Si acquire a black color when anodized and are used for ornamental purposes.

Silver has an extremely high solid solubility in aluminum (up to 55%). Because of cost, no binary aluminum-silver alloys are in use, but small additions (0.1 to 0.6% Ag) are effective in improving the strength and stress-corrosion resistance of aluminum-zinc-magnesium alloys.

Sodium is a chemical modifier in hypoeutectic aluminum-silicon alloys (see the section "Alloying Elements that Modify and Refine Hypoeutectic Al-Si Alloys").

Strontium. Traces of strontium (0.01 to 0.1 ppm) are found in commercial-grade aluminum. Strontium is also a chemical modifier in hypoeutectic aluminum-silicon alloys (see the section "Alloying Elements that Modify and Refine Hypoeutectic Al-Si Alloys").

Sulfur. As much as 0.2 to 20 ppm sulfur is present in commercial-grade aluminum. It has been reported that sulfur can be used to modify both hypo- and hypereutectic aluminum-silicon alloys.

Tin is used as an alloying addition to aluminum—from concentrations of 0.03 to several percent in wrought alloys, to concentrations of about 25% in casting alloys. Small amounts of tin (0.05%) greatly increase the response of aluminum-copper alloys to artificial aging following a solution heat treatment. The result is an increase in strength and an improvement in corrosion resistance. Higher concentrations of tin cause hot cracking in aluminum-copper alloys. If small amounts of magnesium are

present, the artificial aging characteristics are markedly reduced, probably because magnesium and tin form a noncoherent second phase.

The aluminum-tin bearing alloys, with additions of other metals such as copper, nickel, and silicon, are used where bearings are required to withstand high speeds, loads, and temperatures. The copper, nickel, and silicon additions improve load-carrying capacity and wear resistance, and the soft tin phase provides antiscoring properties.

As little as 0.01 % Sn in commercial-grade aluminum will cause surface darkening on annealing and increase the susceptibility to corrosion, which appears to be due to migration of tin to the surface. This effect may be reduced by small additions (0.2%) of copper. Aluminum-zinc alloys with small additions of tin are used as sacrificial anodes in salt water.

Titanium. Amounts of 10 to 100 ppm Ti are found in commercial-purity aluminum. Titanium depresses the electrical conductivity of aluminum, but its level can be reduced by the addition of boron to the melt to form insoluble TiB_2. Titanium is used primarily as a grain refiner of aluminum alloy castings and ingots. When used alone, the effect of titanium decreases with time of holding in the molten state and with repeated remelting. The grain-refining effect is enhanced if boron is present in the melt or if it is added as a master alloy containing boron largely combined as TiB_2. Titanium is a common addition to weld filler wire; it refines the weld structure and prevents weld cracking. It is usually added alone or with TiB_2 during the casting of sheet or extrusion ingots to refine the as-cast grain structure and to prevent cracking.

Vanadium. There is usually 10 to 200 ppm V in commercial-grade aluminum, and because it lowers conductivity, it generally is precipitated from electrical conductor alloys with boron. The aluminum end of the equilibrium diagram is peritectic, and therefore the intermetallic $VA1_{11}$ would be expected to have a grain-refining effect on solidification, but it is less efficient than titanium and zirconium. The recrystallization temperature is raised by vanadium.

Zinc. The aluminum-zinc alloys have been known for many years, but hot cracking of the casting alloys and the susceptibility to stress-corrosion cracking of the wrought alloys curtailed their use. Aluminum-zinc alloys containing other elements offer the highest combination of tensile properties in wrought aluminum alloys. Efforts to overcome the aforementioned limitations have been successful, and these aluminum-zinc alloys are being used commercially to an increasing extent. The presence of zinc in aluminum increases its solution potential, hence its use in protective cladding (7072) and in sacrificial anodes.

Zinc-Magnesium. The addition of magnesium to the aluminum-zinc alloys develops the strength potential of this alloy system, especially in the

range of 3 to 7.5% Zn. Magnesium and zinc form $MgZn_2$, which produces a far greater response to heat treatment than occurs in the binary aluminum-zinc system.

The strength of the wrought aluminum-zinc alloys also is substantially improved by the addition of magnesium. Increasing the $MgZn_2$ concentration from 0.5 to 12% in cold-water-quenched 1.6 mm (0.062 in.) sheet continuously increases the tensile and yield strengths. The addition of magnesium in excess (100 and 200%) of that required to from $MgZn_2$ further increases tensile strength, as shown in Fig. 20.

On the negative side, increasing additions of both zinc and magnesium decrease the overall corrosion resistance of aluminum to the extent that close control over the microstructure, heat treatment, and composition are often necessary to maintain adequate resistance to stress corrosion and to exfoliatory attack. For example, depending on the alloy, stress corrosion is controlled by some or all of the following:

- Overaging
- Cooling rate after solution treatment
- Maintaining a nonrecrystallized structure through the use of additions such as zirconium
- Copper or chromium additions (see zinc-magnesium-copper alloys below)
- Adjusting the zinc-magnesium ratio closer to 3:1

Zinc-Magnesium-Copper. The addition of copper to the aluminum-zinc-magnesium system, together with small but important amounts of chromium and manganese, results in the highest-strength aluminum-base alloys commercially available. The properties of a representative group of these compositions, after one of several solution and aging treatments to which they respond, are shown in Fig. 21.

In this alloy system, zinc and magnesium control the aging process. The effect of copper is to increase the aging rate by increasing the degree of

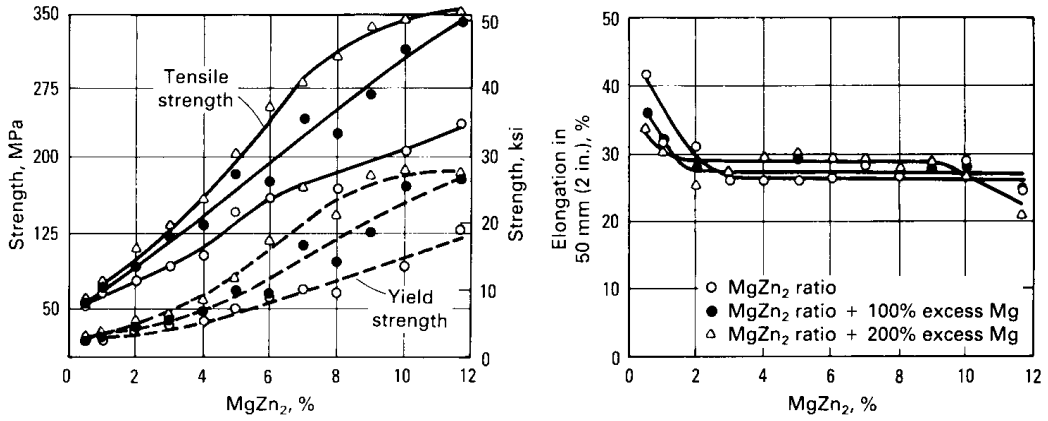


Fig. 20 Effect of $MgZn_2$ and $MgZn_2$ with excess magnesium on tensile properties of wrought 95% Al; 1.59 mm (0.0625 in.) specimens, quenched in cold water from 470 °C (875 °F)

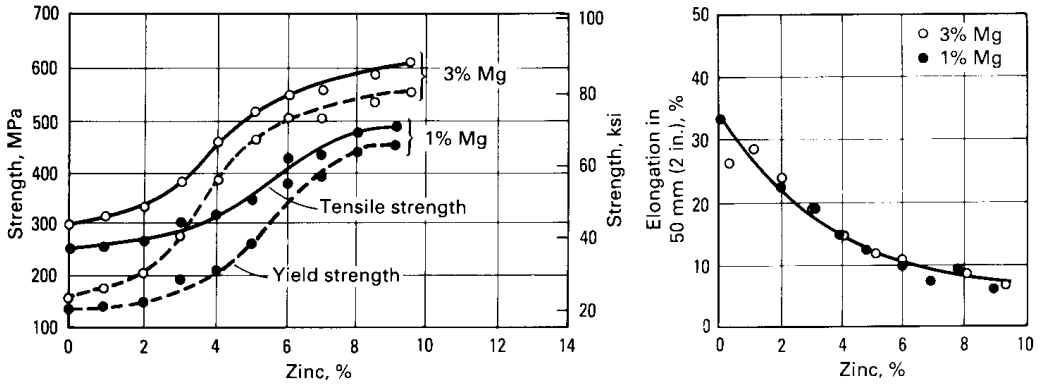


Fig. 21 Effect of zinc on aluminum alloy containing 1.5% Cu and 1 and 3% Mg; 1.6 mm (0.064 in.) thick sheet. Alloy with 1% Mg heat treated at 495°C (920 °F); that with 3% Mg heat treated at 460 °C (860 °F). All specimens quenched in cold water, aged 12 h at 135 °C (275 °F)

supersaturation and perhaps through nucleation of the $CuMgAl_2$ phase. Copper also increases quench sensitivity upon heat treatment. In general, copper reduces the resistance to general corrosion of aluminum-zinc-magnesium alloys, but increases the resistance to stress corrosion. The minor alloy additions, such as chromium and zirconium, have a marked effect on mechanical properties and corrosion resistance.

Zirconium additions in the range of 0.1 to 0.3% are used to form a fine precipitate of intermetallic particles that inhibit recovery and recrystallization. An increasing number of alloys, particularly in the aluminum-zinc-magnesium family, use zirconium additions to increase the recrystallization temperature and to control the grain structure in wrought products. Zirconium additions leave this family of alloys less quench-sensitive than similar chromium additions. Higher levels of zirconium (0.3 and 0.4%) are employed in some superplastic alloys to retain the required fine substructure during elevated-temperature forming. Zirconium additions have been used to reduce the as-cast grain size, but its effect is less than that of titanium. In addition, zirconium tends to reduce the grain-refining effect of titanium plus boron additions, so that it is necessary to use more titanium and boron to grain refine zirconium-containing alloys.

Alloying Effects on Phase Formation

All commercial aluminum alloys contain iron and silicon as well as two or more elements intentionally added to enhance properties. The phases formed and the function of the alloying elements are described below. Figure 6 summarizes the most common alloying additions in aluminum alloys.

Iron. Virtually all aluminum alloys contain some iron that is an impurity remaining after refining bauxite and smelting. The phase diagram predicts

that during solidification of an aluminum-iron alloy containing a few tenths of a percent of iron, most of the iron remains in the liquid phase until a eutectic of solid solution plus Al_3Fe intermetallic constituent particles having a monoclinic crystal structure freezes. Depending on solidification rate and on the presence of other elements such as manganese, constituent particles of the metastable orthorhombic Al_6Fe phase can form instead of the equilibrium Al_3Fe. The maximum solid solubility of iron in aluminum is 0.05%, but the solubility is much lower in most structural alloys.

Silicon. This element is also a ubiquitous impurity in commercial aluminum alloys. Two ternary phases, cubic $\alpha Al_{12}Fe_3Si$ and monoclinic β-$Al_9Fe_2Si_2$, form by a eutectic reaction. At low silicon contents, almost all of the iron is present as Al_3Fe. With increasing silicon contents, first the α- then the β-Al-Fe-Si phases appear. Phases in commercial products may not be those predicted by the equilibrium phase diagrams because of the long times at high temperatures required to approach equilibrium. In large amounts, silicon improves castability and fluidity. Consequently, it is used in 4*xxx* brazing sheet and in 3*xx.x* and 4*xx.x* casting alloys. Silicon ranges from about 5 to 20% in casting alloys. Hypereutectic alloys (those containing >12.6% Si, the eutectic composition) are used for engine blocks because the primary silicon particles are wear resistant. Some 3*xx.x* casting alloys contain small additions of magnesium to render them capable of being age hardened.

Silicon is deliberately added to some alloys containing magnesium to provide precipitation hardening. The Al-Mg-Si system is the basis for the 6*xxx* alloys. At low magnesium contents, elemental silicon may be present as second-phase particles. As magnesium increases, both silicon particles and equilibrium hexagonal Mg_2Si constituents may be present. At higher magnesium contents, only Mg_2Si is present. Ternary alloys are strengthened by precipitation of metastable precursors to Mg_2Si. With the addition of copper, a complex quaternary $Al_4CuMg_5Si_4$ phase can form. A precursor to this quaternary phase strengthens Al-Cu-Mg-Si alloys.

Manganese. The aluminum-manganese system is the basis for the oldest aluminum alloys. Such alloys, known as 3*xxx,* are the most widely used wrought alloys because of their excellent formability and resistance to corrosion. Commercial aluminum-manganese alloys contain both iron and silicon. During solidification of commercial size ingots, some of the manganese forms $Al_6(Mn,Fe)$ and cubic $Al_{12}(Fe,Mn)Si$ by eutectic reactions. The remaining manganese remains in solution and is precipitated during the ingot preheat as $Al_{12}(Mn,Fe)Si$ and $Al_6(Mn,Fe)$ dispersoids. These dispersoids strengthen the material and control recrystallized grain size. In alloys containing copper, manganese precipitates as $Al_{20}Cu_2Mn_3$

dispersoid particles. Effects on strength are minor, but the dispersoids aid in grain size control after solution heat treatment.

Magnesium. The aluminum-magnesium system is the basis for the wrought 5*xxx* and cast 5*xx.x* non-heat-treatable aluminum alloys, which provide excellent combinations of strength and corrosion resistance by solid-solution strengthening and work hardening. Although in principle this phase diagram exhibits a positively sloping solvus, a necessary condition for a precipitation-hardening system, difficulty in nucleating the face-centered cubic (fcc) Al_3Mg_2 precipitates has precluded commercialization of heat-treatable aluminum-magnesium alloys, unless they contain enough silicon, copper, or zinc to form Mg_2Si, Al-Cu-Mg, or Al-Zn-Mg precipitates.

Copper. The aluminum-copper system is the basis for the wrought 2*xxx* and cast 2*xx.x* alloys, and many other heat-treatable alloys contain copper. In commercial aluminum-copper alloys, some of the copper chemically combines with aluminum and iron to form either tetragonal Al_7Cu_2Fe or orthorhombic α(Al,Cu,Fe) constituent particles during solidification. These constituents cannot be dissolved during subsequent thermal treatments, but one can transform to the other during thermal treatments of ingots or castings. During heat treatment of aluminum-copper alloys containing little magnesium, Al_2Cu precipitates as the strengthening phase.

Adding magnesium to aluminum-rich aluminum-copper alloys results in the formation of the Al_2CuMg phase by eutectic decomposition. Metastable precursors to face-centered orthorhombic Al_2CuMg precipitates are used to strengthen several structural alloys used in the aerospace industry because they confer a desirable combination of strength, fracture toughness, and resistance to the growth of fatigue cracks.

Zinc. This element confers little solid-solution strengthening or work hardening to aluminum, but Al-Zn-Mg precipitates provide the basis for the 7*xxx* wrought alloys and the 7*xx.x* cast alloys. Two phases can form by eutectic decomposition in commercial Al-Zn-Mg alloys: hexagonal $MgZn_2$ and body-centered cubic (bcc) $Al_2Mg_3Zn_3$. Depending on the zinc/magnesium ratio, copper-free alloys are strengthened by metastable precursors to either $MgZn_2$ or $Al_2Mg_3Zn_3$. In Al-Zn-Mg-Cu alloys, copper and aluminum substitute for zinc in $MgZn_2$ to form $Mg(Zn,Cu,Al)_2$. Al_2CuMg particles can also form in these alloys by eutectic decomposition and solid-state precipitation.

Chromium. In commercial alloys, the solubility can be reduced to such an extent that Al_7Cr primary particles can form by a peritectic reaction at chromium contents lower than that indicated by the binary aluminum-chromium phase diagram. Because coarse primary particles are harmful to

ductility, fatigue, and fracture toughness, the upper limits of chromium depend on the amount and nature of the other alloying and impurity elements. In 5*xxx* alloys, fcc cubic $Al_{18}Mg_3Cr_2$ dispersoids precipitate during ingot preheating. In 7*xxx* alloys, the composition of the dispersoids is closer to $Al_{12}Mg_2Cr$. Chromium dispersoids contribute to strength in non-heat-treatable alloys and control grain size and degree of recrystallization in heat-treatable alloy products.

Zirconium. This element also forms a peritectic with aluminum. The phase diagram predicts that the equilibrium Al_3Zr phase is tetragonal, but fine dispersoids of metastable cubic Al_3Zr form during ingot preheating treatments. Most 7*xxx* and some 6*xxx* and 5*xxx* alloys developed since the 1960s contain small amounts of zirconium, usually less than 0.15%, to form Al_3Zr dispersoids for recrystallization control.

Lithium. This element reduces the density and increases the modulus of aluminum alloys. In binary alloys it forms metastable Al_3Li precipitates and combines with aluminum and copper in Al-Cu-Li alloys to form a large number of Al-Cu-Li phases. Because of its high cost relative to other alloying elements, lithium alloys have been found to be cost effective thus far only in space and military applications.

Grain Refiners

All aluminum alloys can be made to solidify with a fully equiaxed, fine-grain structure through the use of suitable grain-refining additions. The most widely used grain refiners are master alloys of titanium, boron, or titanium and boron, in aluminum. Aluminum-titanium refiners generally contain from 3 to 10% Ti. The same range of titanium concentrations is used in Al-Ti-B refiners, with boron contents from 0.2 to 2.5% and titanium-to-boron ratios ranging from about 5:1 to 50:1. Although grain refiners of these types can be considered conventional hardeners or master alloys, they differ from master alloys added to the melt for alloying purposes alone. To be effective, grain refiners must introduce controlled, predictable, and operative quantities of aluminides (and borides) in the correct form, size, and distribution for grain nucleation. Wrought refiner in rod form, developed for the continuous treatment of aluminum in primary operations, is available in sheared lengths for foundry use. The same grain-refining compositions are furnished in waffle form. In addition to grain-refining master alloys, salts (usually in compacted form) that react with molten aluminum to form combinations of $TiAl_3$ and TiB_2 are also available.

Despite the successful use of titanium as a grain refiner for foundry alloys, it has recently been found that boron alone may be a more effec-

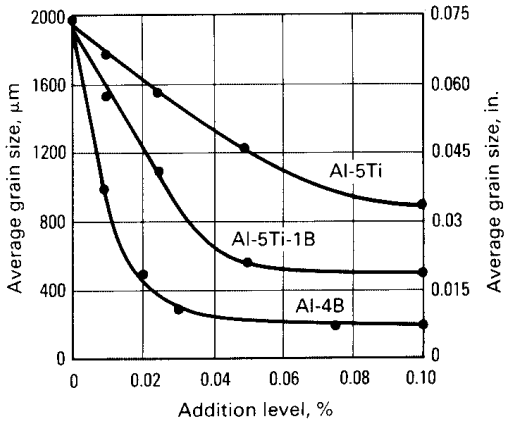


Fig. 22 Comparison of the effectiveness of various master alloy grain refiners in aluminum alloy 356

tive refiner than titanium in aluminum-silicon alloys. Figure 22 compares the grain sizes achieved with additions of boron, titanium, and a titanium-boron mixture on alloy 356.

Figure 23 demonstrates the effectiveness of Al-2.5Ti-2.5B master alloys to 356 and 319 foundry alloys compared to the Al-5Ti-1B alloys previously used. Clearly, the use of higher levels of boron and lower levels of titanium than those previously used can have substantial

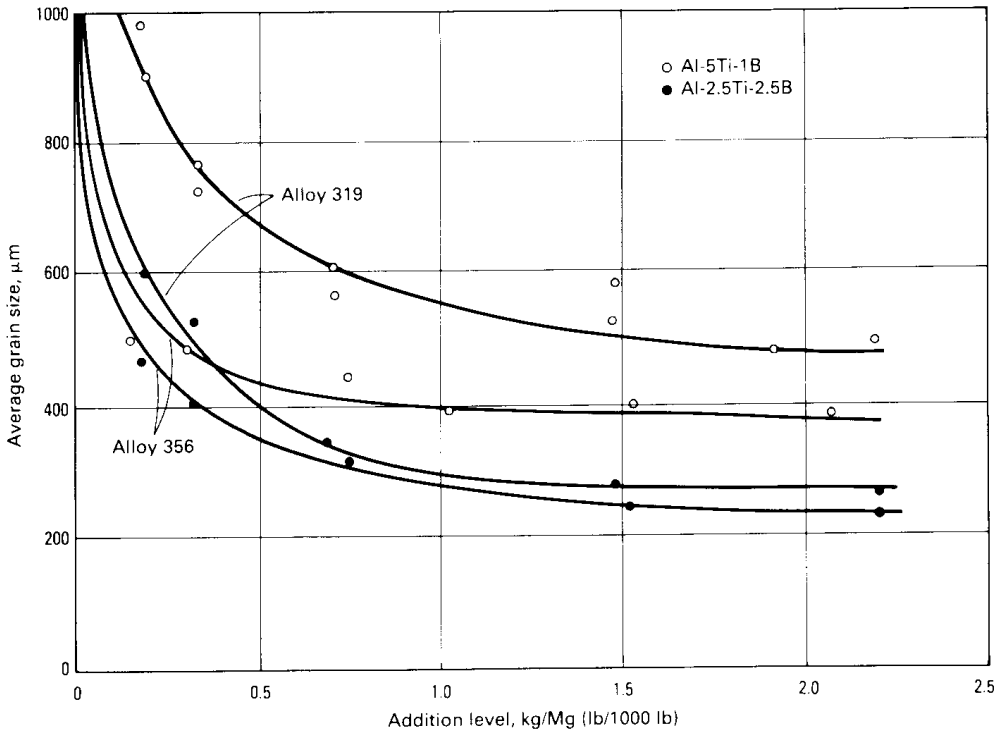


Fig. 23 Effectiveness of titanium-boron grain refiners in aluminum alloys 356 and 319

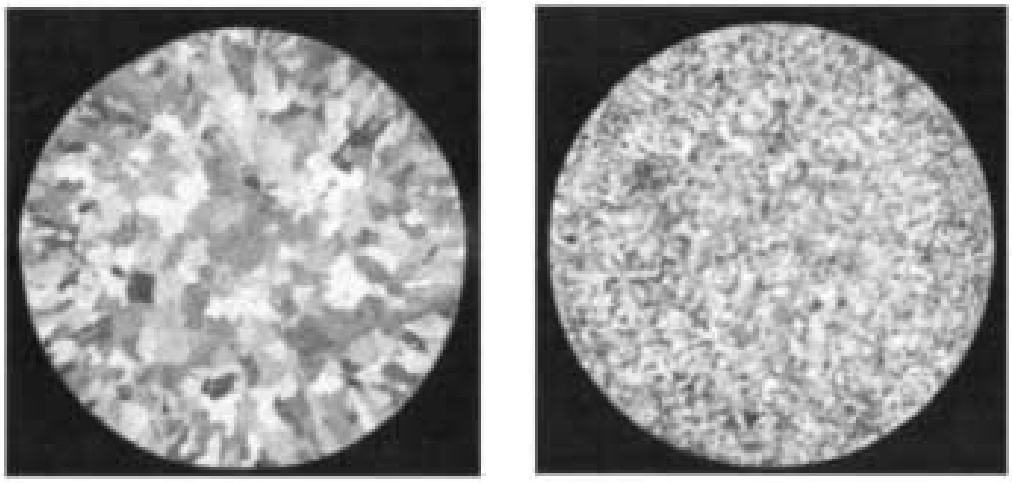


Fig. 24 As-cast Al-7Si ingots showing the effects of grain refinement. (a) No grain refiner. (b) Grain-refined. Both etched using Poulton's etch; both 2x

benefits for foundry alloys. Figure 24 illustrates the comparison of an adequately grain-refined Al-7Si alloy before and after grain-refining addition.

Alloying Elements that Modify and Refine Hypoeutectic Al-Si Alloys

Hypoeutectic aluminum-silicon alloys can be improved by inducing structural modification of the normally occurring eutectic. In general, the greatest benefits are achieved in alloys containing from 5% Si to the eutectic concentration; this range includes most common gravity cast compositions.

Chemical Modifiers. The addition of certain elements, such as calcium, sodium, strontium, and antimony, to hypoeutectic aluminum-silicon alloys results in a finer lamellar or fibrous eutectic network. It is also understood that increased solidification rates are useful in providing similar structures. There is, however, no agreement on the mechanisms involved. The most popular explanations suggest that modifying additions suppress the growth of silicon crystals within the eutectic, providing a finer distribution of lamellae relative to the growth of the eutectic. Various degrees of eutectic modification are shown in Fig. 25.

The results of modification by strontium, sodium, and calcium are similar. Sodium has been shown to be the superior modifier, followed by strontium and calcium, respectively. Each of these elements is mutually compatible so that combinations of modification additions can be made without adverse effects. Eutectic modification is, however, transient when artificially promot-

ed by additions of these elements. Figure 26 illustrates the relative effectiveness of various modifiers as a function of time at temperature.

Antimony has been advocated as a permanent means of achieving structural modification. In this case, the modified structure differs; a more acicular refined eutectic is obtained compared to the uniform lace-like dispersed structures of sodium-, calcium-, or strontium-modified metal. As a result, the improvements in castability and mechanical properties offered by this group of elements are not completely achieved. Structural

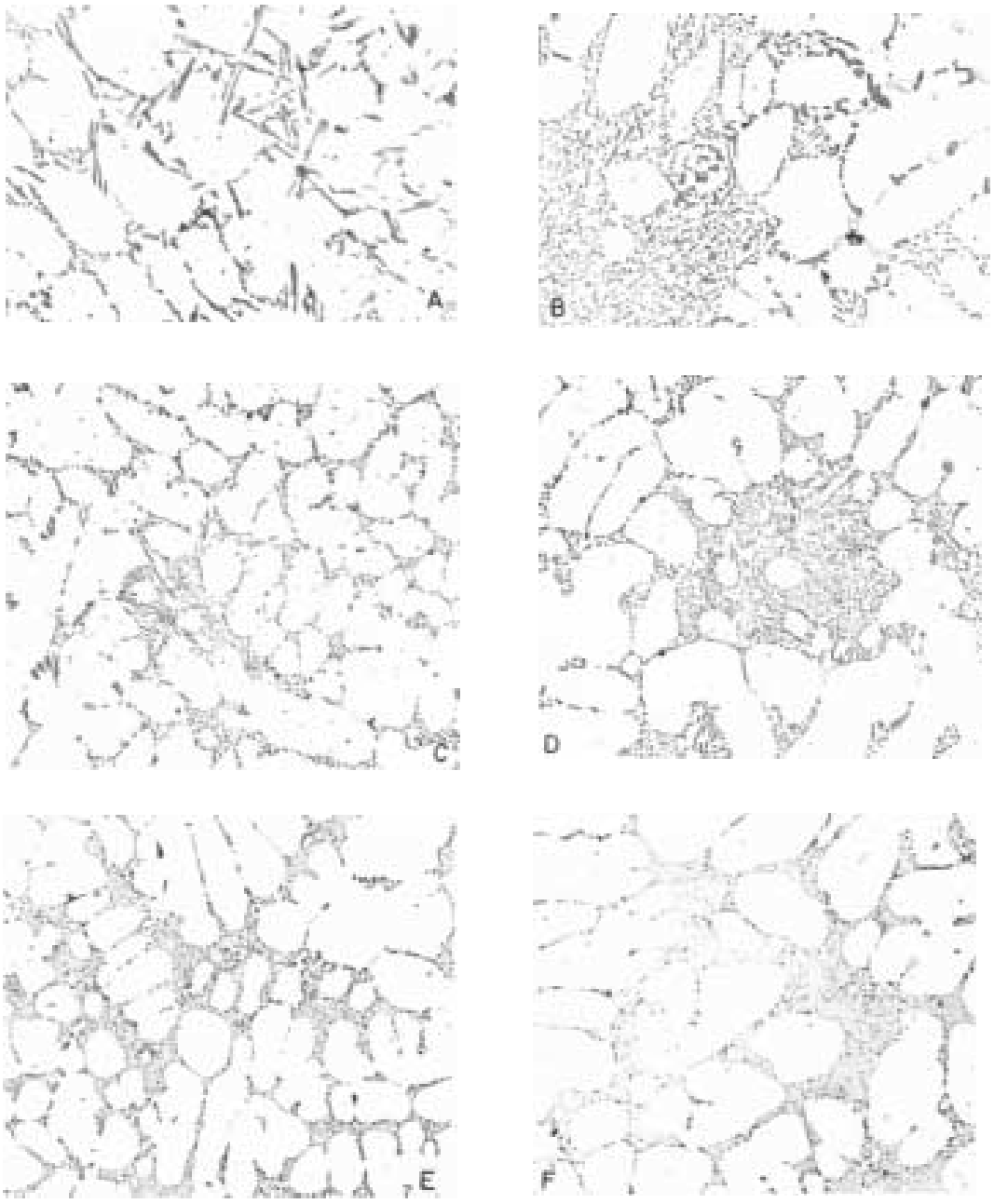


Fig. 25 Varying degrees of aluminum-silicon eutectic modification ranging from unmodified (A) to well modified (F). See Fig. 26 for the effectiveness of various modifiers

refinement is obtained that is time-independent when two conditions are satisfied. First, the metal to be treated must be essentially phosphorus-free, and second, the velocity of the solidification front must exceed a minimum value approximately equal to that obtained in conventional permanent mold casting.

Antimony is not compatible with other modifying elements. In cases in which antimony and other modifiers are present, coarse antimony-containing intermetallics are formed that preclude the attainment of an effectively modified structure and adversely affect casting results.

Modifier additions are usually accompanied by an increase in hydrogen content (Fig. 27). In the case of sodium and calcium, the reactions involved in element solution are invariably turbulent or are accompanied by compound reactions that increase dissolved hydrogen levels. In the case of strontium, master alloys may be highly contaminated with hydrogen, and there are numerous indications that hydrogen solubility is increased after alloying.

For sodium, calcium, and strontium modifiers, the removal of hydrogen by reactive gases also results in the removal of the modifying element. Recommended practices are to obtain modification through additions of modifying elements added to well-processed melts, followed by inert gas

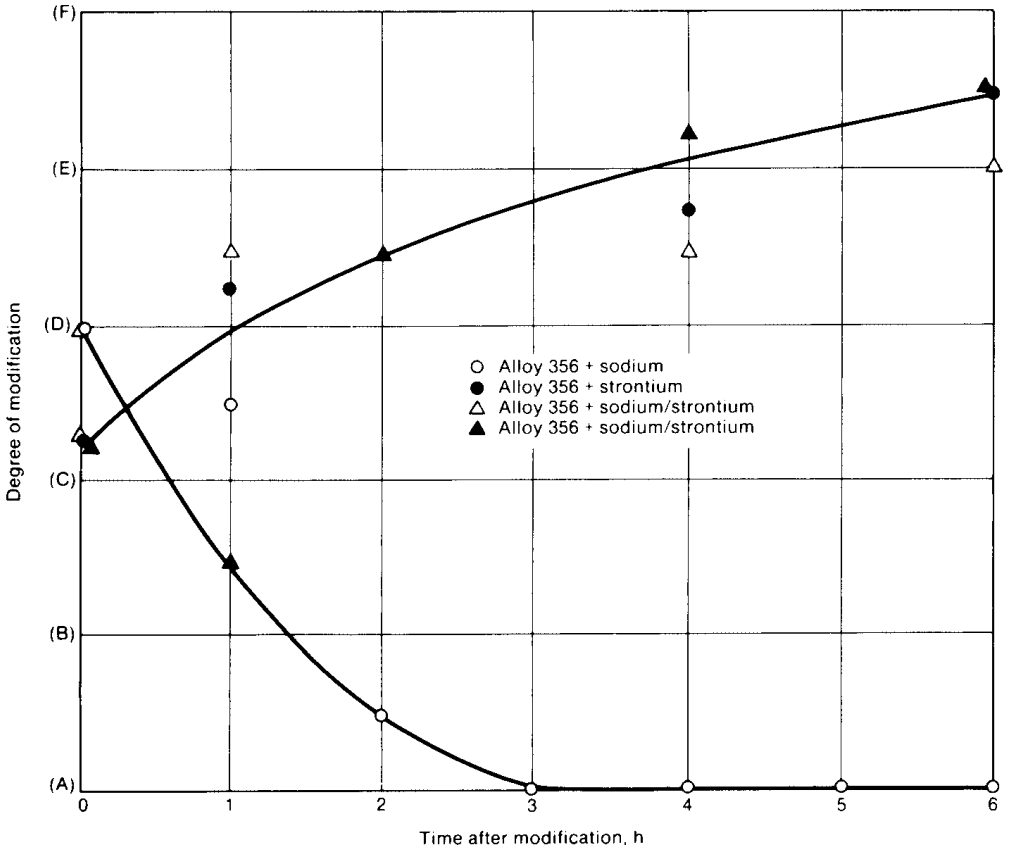


Fig. 26 Effectiveness of sodium and strontium modifiers as a function of time. See Fig. 25 for degrees of modification

fluxing to acceptable hydrogen levels. No such disadvantages accompany antimony use.

Calcium and sodium can be added to molten aluminum in metallic or salt form. Vacuum-prepackaged sodium metal is commonly used. Strontium is currently available in many forms, including aluminum-strontium master alloys ranging from approximately 10 to 90% Sr and Al-Si-Sr master alloys of varying strontium contents.

Very low sodium concentrations (~0.001%) are required for effective modification. More typically, additions are made to obtain a sodium content in the melt of 0.005 to 0.015%. Remodification is performed as required to maintain the desired modification level.

A much wider range of strontium concentrations is in use. In general, addition rates far exceed those required for effective sodium modification. A range of 0.015 to 0.050% Sr is standard industry practice. Normally, good modification is achievable in the range of 0.008 to 0.015% Sr. Remodification through strontium additions may be required, although retreatment is less frequent than for sodium.

To be effective in modification, antimony must be alloyed to approximately 0.06%. In practice, antimony is employed in the much higher range of 0.10 to 0.50%.

It is possible to achieve a state of overmodification, in which eutectic coarsening occurs, when sodium and/or strontium are used in excessive amounts. The corollary effects of reduced fluidity and susceptibility to hydrogen-related problems are usually encountered well before overmodification may be experienced.

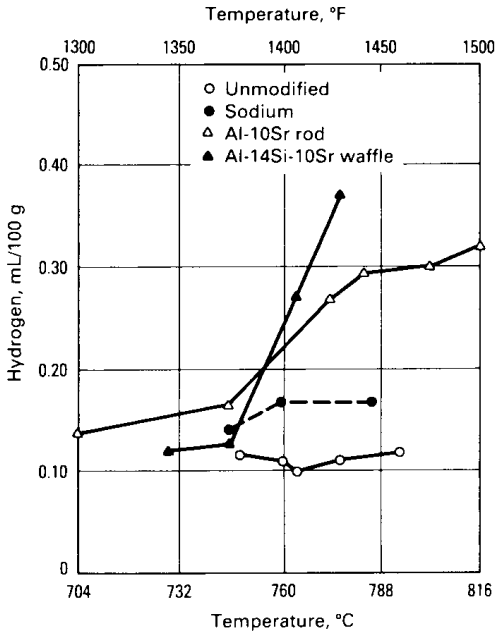


Fig. 27 Hydrogen content as a function of holding temperature for aluminum alloy 356 melts with various modifiers.

The Importance of Phosphorus. It has been well established that phosphorus interferes with the modification mechanism. Phosphorus reacts with sodium and probably with strontium and calcium to form phosphides that nullify the intended modification additions. It is therefore desirable to use low-phosphorus metal when modification is a process objective and to make larger modifier additions to compensate for phosphorus-related losses.

Primary producers may control phosphorus contents in smelting and processing to provide less than 5 ppm of phosphorus in alloyed ingot. At these levels, normal additions of modification agents are effective in achieving modified structures. However, phosphorus contamination may occur in the foundry through contamination by phosphate-bonded refractories and mortars and by phosphorus contained in other melt additions, such as master alloys and alloying elements including silicon.

Effects of Modification. Typically, modified structures display somewhat higher tensile properties and appreciably improved ductility when compared to similar but unmodified structures. Figure 28 illustrates the

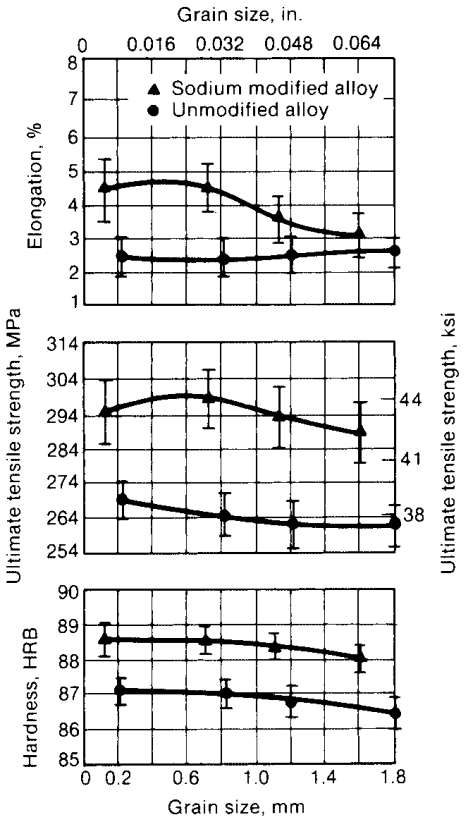


Fig. 28 Mechanical properties of as-cast A356 alloy tensile specimens as a function of modification and grain size

desirable effects on mechanical properties that can be achieved by modification. Improved performance in casting is characterized by improved flow and feeding as well as by superior resistance to elevated-temperature cracking.

Use of Phosphorus to Refine Hypereutectic Al-Si Alloys

The elimination of large, coarse primary silicon crystals that are harmful in the casting and machining of hypereutectic silicon alloy compositions is a function of primary silicon refinement. Phosphorus added to molten alloys containing more than the eutectic concentration of silicon, made in the form of metallic phosphorus or phosphorus-containing compounds such as phosphor-copper and phosphorus pentachloride, has a marked effect on the distribution and form of the primary silicon phase. Investigations have shown that retained trace concentrations as low as 0.0015 through 0.03% P are effective in achieving the refined structure. Disagreements on recommended phosphorus ranges and addition rates have been caused by the extreme difficulty of accurately sampling and analyzing for phosphorus. More recent developments employing vacuum stage spectrographic or quantometric analysis now provide rapid and accurate phosphorus measurements.

Following melt treatment by phosphorus-containing compounds, refinement can be expected to be less transient than the effects of conventional modifiers on hypoeutectic modification. Furthermore, the solidification of phosphorus-treated melts, cooling to room temperature, reheating, remelting, and resampling in repetitive tests have shown that refinement is not lost; however, primary silicon particle size increases gradually, responding to a loss in phosphorus concentration. Common degassing methods accelerate phosphorus loss, especially when chlorine or Freon is used. In fact, brief inert gas fluxing is frequently employed to reactivate aluminum phosphide nuclei, presumably by resuspension.

Practices that are recommended for melt refinement are:

- Melting and holding temperatures should be held to a minimum.
- The alloy should be thoroughly chlorine- or Freon-fluxed before refining to remove phosphorus-scavenging impurities such as calcium and sodium.
- Brief fluxing after the addition of phosphorus is recommended to remove the hydrogen introduced during the addition and to distribute the aluminum phosphide nuclei uniformly in the melt.

Figure 29 illustrates the microstructural differences between refined and unrefined structures.

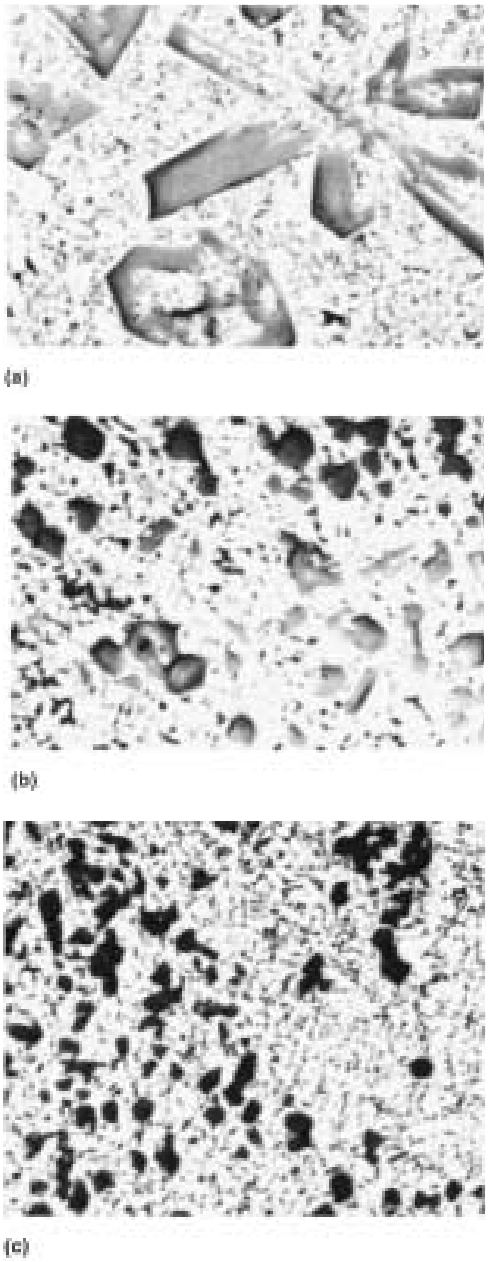


Fig. 29 Effect of phosphorus refinement on the microstructure of Al-22Si-1Ni-1Cu alloy. (a) Unrefined. (b) Phosphorus-refined. (c) Refined and fluxed. All 100x

Effects of Alloying on Corrosion Behavior

Aluminum, as indicated by its position in the electromotive force series, is a thermodynamically reactive metal; among structural metals, only beryllium and magnesium are more reactive. Aluminum owes its excellent corrosion resistance and its usage as one of the primary metals of commerce to the barrier oxide film that is bonded strongly to its surface. The

normal surface film formed in air at ambient temperature is only about 5 nm (50 Å) thick. If damaged, this thin film re-forms immediately in most environments and continues to protect the aluminum from corrosion. When the film is removed or damaged under conditions such that self repair cannot occur, corrosion takes place.

The corrosion resistance of an aluminum alloy depends on both metallurgical and environmental variables. Metallurgical variables that affect corrosion are composition (as described below), heat treatment (proper temper selection), and mechanical working. These determine the microstructure, which decides whether localized corrosion occurs and the method of attack.

Both chemical and physical environmental variables affect corrosion. The chemical influence of the environment depends on its composition and the presence of impurities such as heavy metal ions. Physical variables are temperature, degree of movement and agitation, and pressure. Another physical variable that can cause corrosion of aluminum is the presence of stray electrical currents (alternating or direct).

Because many variables influence corrosion, the suitability of aluminum cannot be considered solely on the basis of a specific product or environment. A detailed knowledge of traces of impurities, conditions of operation, design of a piece of equipment, and alloy microstructure is essential. Experience gained from previously successful service applications is most valuable.

1*xxx* Wrought Alloys. Pure aluminum (99.00% or purer) is more corrosion resistant than any of the aluminum alloys. Rapid dissolution will occur in highly acidic or alkaline solutions, but in the oxide stable range of pH 4 to 9, aluminum is subject only to water staining of the surface and to localized pitting corrosion. Pure aluminum does not incur any of the more drastic forms of localized corrosion such as intergranular corrosion, exfoliation, or SCC.

Wrought aluminums of the 1*xxx* series conform to composition specifications that set maximum individual, combined, and total contents for several elements present as natural impurities in the smelter-grade or refined aluminum used to produce these products. Aluminums 1100 and 1135 differ somewhat from the others in this series in having minimum and maximum specified copper contents. Corrosion resistance of all 1*xxx* compositions is very high, but under many conditions, it decreases slightly with increasing alloy content. Iron, silicon, and copper are the elements present in the largest percentages. The copper and part of the silicon are in solid solution. The second-phase particles present contain either iron or iron and silicon—Al_6Fe, Al_3Fe, and $Al_{12}Fe_3Si_2$—all of which are cathodic to the aluminum matrix. When these particles are present at the surface, the oxide film over them is thin or nonexistent. The local cells produced by these impurities promote pitting attack of the surface in a conductive

liquid. The number and/or size of such corrosion sites is proportional to the area fraction of the second-phase particles.

Not all impurity elements are detrimental to corrosion resistance of 1*xxx* series aluminum alloys, and detrimental elements can reduce the resistance of some types of alloys but have no ill effects in others. Therefore, specification limitations established for impurity elements are often based on maintaining consistent and predictable levels of corrosion resistance in various applications rather than on their effects in any specific application.

2*xxx* wrought alloys and 2*xx.x* casting alloys, in which copper is the major alloying element, are less resistant to corrosion than alloys of other series, which contain much lower amounts of copper. Alloys of this type were the first heat treatable high-strength aluminum-base materials, dating back to Duralumin developed in Germany in 1919 and subsequently produced in the United States as alloy 2017 (see Fig. 1). Much of the thin sheet made of these alloys is produced as an alclad composite, but thicker sheet and other products in many applications require no protective cladding.

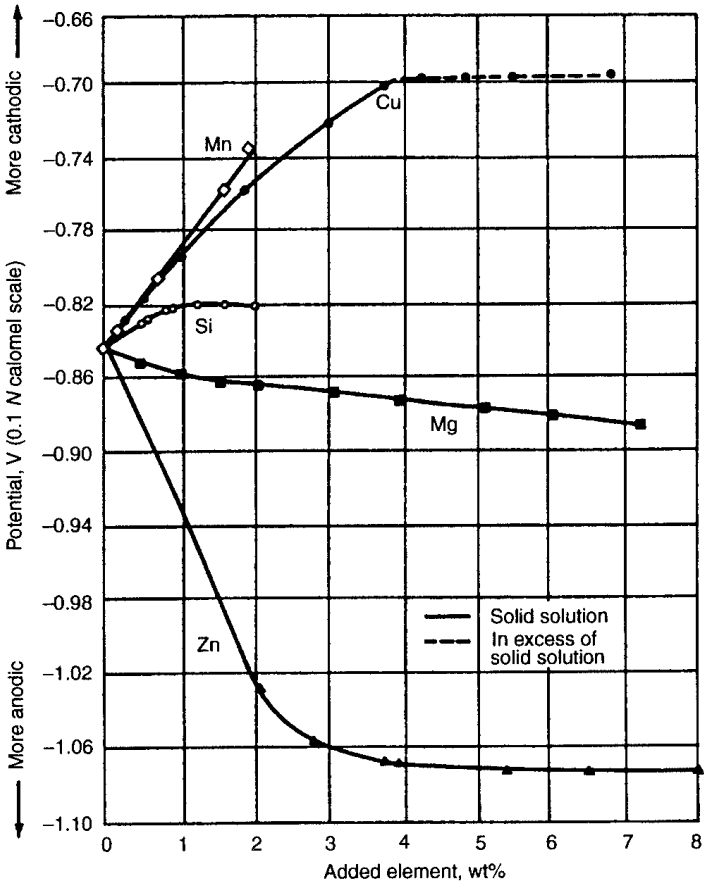


Fig. 30 Effects of principal alloying elements on electrolytic solution potential of aluminum. Potentials are for high-purity binary alloys solution heat treated and quenched. Measured in a solution of 53 g/L NaCl plus 3 g/L H_2O_2 maintained at 25 °C (77 °F)

Electrochemical effects on corrosion can be stronger in these alloys than in alloys of many other types because of two factors: greater change in electrode potential with variations in amount of copper in solid solution (Fig. 30) and, under some conditions, the presence of nonuniformities in solid-solution concentration. However, general resistance to corrosion decreasing with increasing copper content is not primarily attributable to these solid-solution or second-phase solution-potential relationships. The decrease in general corrosion resistance is attributable to galvanic cells created by formation of minute copper particles or films deposited on the alloy surface as a result of corrosion. As corrosion progresses, copper ions, which initially go into solution, replate onto the alloy to form metallic copper cathodes. Reduction of copper ions and increased efficiency of O_2 and H^+ reduction reactions in the presence of copper increase the corrosion rate.

These alloys are invariably solution heat treated and are used in either the naturally aged or the precipitation heat treated temper. Development of these tempers using good heat treating practice can minimize electrochemical effects on corrosion resistance. The rate of quenching and the temperature and time of artificial aging both can affect the corrosion resistance of the final product. Principal strengthening phases of artificially aged 2*xxx* alloys are $CuAl_2$ for alloys with <1% Mg (e.g., 2014 and 2219), $CuMgAl_2$ for a magnesium content above 1% (e.g., 2024 and 2034), $CuLiAl_2$ when lithium is present (e.g., 2090 as described below), and Mg_2Si for low-copper-content alloys (e.g., 2008 and 2117).

Wrought Aluminum-Lithium Alloys. Lithium additions decrease the density and increase the elastic modulus of aluminum alloys, making aluminum-lithium alloys good candidates for replacing the existing high-strength alloys, primarily in aerospace applications. Both 2*xxx* and 8*xxx* series alloys based on the Al-Cu-Mg-Li system have been developed.

One of the earliest aluminum alloys containing lithium was 2020. This alloy in the T6 temper was commercially introduced in 1957 as a structural alloy with good strength properties up to 175 °C (350 °F). It has a modulus 8% higher and a density 3% lower than alloy 7075-T6. Alloy 2020 was rarely used in aircraft because of its relatively low fracture toughness. It was used in the thrust structure of the Saturn S-II, the second stage of the Saturn V launch vehicle.

Two more recently registered lithium-bearing alloys are 2090 and 8090. Alloy 2090, in T8-type tempers, has a higher resistance to exfoliation than 7075-T6 has, and the resistance to SCC is comparable (Ref 23). The corrosion resistance of alloy 8090, which was developed to meet a combination of mechanical property goals, is a strong function of the degree of artificial aging and the microstructure. Alloy 8090 generally displays good exfoliation resistance in atmospheric exposure.

Although lithium is highly reactive, addition of up to 3% Li to aluminum shifts the pitting potential of the solid solution only slightly in the anodic direction in 3.5% NaCl solution. In an extensive corrosion investigation of several binary and ternary aluminum-lithium alloys, modifications to the microstructure that promote formation of the δ phase (AlLi) were found to reduce the corrosion resistance of the alloy in 3.5% NaCl solution. It was concluded that an understanding of the nucleation and growth of the δ phase is central to an understanding of the corrosion behavior of these alloys.

3*xxx* Wrought Alloys. Wrought alloys of the 3*xxx* series (aluminum-manganese and aluminum-manganese-magnesium) have very high resistance to corrosion. The manganese is present in the aluminum solid solution, in submicroscopic particles of precipitate, and in larger particles of $Al_6(Mn,Fe)$ or $Al_{12}(Mn,Fe)_3Si$ phases, both of which have solution potentials almost the same as that of the solid-solution matrix. Hence, these constituents are not significant sites for corrosion initiation. Like pure aluminum, 3*xxx* alloys do not incur any of the more drastic forms of localized corrosion, and pitting corrosion is the principal type of corrosion encountered. Such alloys are widely used for cooking and food-processing equipment, chemical equipment, and various architectural products requiring high resistance to corrosion.

4*xxx* Wrought Alloys and 3*xx.x* and 4*xx.x* Casting Alloys. Elemental silicon is present as second-phase constituent particles in wrought alloys of the 4*xxx* series, in brazing and welding alloys, and in casting alloys of the 3*xx.x* and 4*xx.x* series. Silicon is cathodic to the aluminum solid-solution matrix by several hundred millivolts and accounts for a considerable volume fraction of most of the silicon-containing alloys. However, the effects of silicon on the corrosion resistance of these alloys are minimal because of low corrosion current density resulting from the fact that the silicon particles are highly polarized.

Corrosion resistance of 3*xx.x* casting alloys is strongly affected by copper content, which can be as high as 5% in some compositions, and by impurity levels. Modifications of certain basic alloys have more restrictive limits on impurities, which benefit corrosion resistance and mechanical properties.

5*xxx* Wrought Alloys and 5*xx.x* Casting Alloys. Wrought alloys of the 5*xxx* series (Al-Mg-Mn, Al-Mg-Cr, and Al-Mg-Mn-Cr) and casting alloys of the 5*xx.x* series have high resistance to corrosion. This accounts in part for their use in a wide variety of building products and chemical-processing and food-handling equipment, as well as applications involving exposure to seawater.

Alloys in which the magnesium is present in amounts that remain in solid solution or is partially precipitated as Al_8Mg_5 particles dispersed uniformly throughout the matrix are generally as resistant to corrosion as

commercially pure aluminum. These alloys also are more resistant to salt water and some alkaline solutions, such as those of sodium carbonate and amines. The wrought alloys containing about 3% or more magnesium under conditions that lead to an almost continuous intergranular Al_8Mg_5 precipitate, with very little precipitate within grains, can be susceptible to exfoliation or SCC. Tempers have been developed for these higher-magnesium wrought alloys to produce microstructures having extensive Al_8Mg_5 precipitate within the grains, thus eliminating such susceptibility.

In the 5*xxx* alloys that contain chromium, this element is present as a submicroscopic precipitate, $Al_{12}Mg_2Cr$. Manganese in these alloys is in the form of $Al_6(Mn,Fe)$ as both submicroscopic and larger particles. Such precipitates and particles do not adversely affect corrosion resistance of these alloys.

6*xxx* Wrought Alloys. Moderately high strength and very good resistance to corrosion make the heat-treatable wrought alloys of the 6*xxx* series (Al-Mg-Si) highly suitable in various structural, building, marine, machinery, and process-equipment applications. The Mg_2Si phase, which is the basis for precipitation hardening, is unique in that it is an ionic compound and is not only anodic to aluminum but also reactive in acidic solutions. However, either in solid solution or as submicroscopic precipitate, Mg_2Si has a negligible effect on electrode potential. Because these alloys are normally used in the heat treated condition, no detrimental effects result from the major alloying elements or from the supplementary chromium, manganese, or zirconium, which are added to control grain structure. Copper additions, which augment strength in many of these alloys, are limited to small amounts to minimize effects on corrosion resistance. At copper levels higher than 0.5% some intergranular corrosion can occur in some tempers (e.g., T4 and T6). However, this intergranular corrosion does not result in susceptibility to exfoliation or SCC.

When the magnesium and silicon contents in a 6*xxx* alloy are balanced (in proportion to form only Mg_2Si), corrosion by intergranular penetration is slight in most commercial environments. If the alloy contains silicon beyond that needed to form Mg_2Si or contains a high level of cathodic impurities, susceptibility to intergranular corrosion increases.

7*xxx* wrought alloys and 7*xx.x* casting alloys contain major additions of zinc, along with magnesium or magnesium plus copper in combinations that develop various levels of strength. Those containing copper have the highest strengths and have been used as construction materials, primarily in aircraft applications, for more than 50 years. The copper-free alloys of the series have many desirable characteristics: moderate-to-high strength; excellent toughness; and good workability, formability, and weldability. Use of these copper-free alloys has increased in recent years and now includes automotive applications (such as bumpers), structural

members and armor plate for military vehicles, and components of other transportation equipment.

The 7*xxx* wrought and 7*xx.x* casting alloys, because of their zinc contents, are anodic to 1*xxx* wrought aluminums and to other aluminum alloys. They are among the aluminum alloys most susceptible to SCC. However, SCC can be avoided by proper alloy and temper selection and by observing appropriate design, assembly, and application precautions.

Resistance to general corrosion of the copper-free wrought 7*xxx* alloys is good, approaching that of the wrought 3*xxx,* 5*xxx,* and 6*xxx* alloys. The copper-containing alloys of the 7*xx.x* series, such as 7049, 7050, 7075, and 7178, have lower resistance to general corrosion than those of the same series that do not contain copper. All 7*xxx* alloys are more resistant to general corrosion than 2*xxx* alloys but less resistant than wrought alloys of other groups.

Although the copper in both wrought and cast alloys of the Al-Zn-Mg-Cu type reduces resistance to general corrosion, it is beneficial from the standpoint of resistance to SCC. Copper allows these alloys to be precipitated at higher temperatures without excessive loss in strength and thus makes possible the development of T73 tempers, which couple high strength with excellent resistance to SCC.

Effects of Additional Alloying Elements. In addition to the major elements that define the alloy systems discussed, commercial aluminum alloys can contain other elements that provide special characteristics. Lead and bismuth are added to alloys 2011 and 6262 to improve chip breakage and other machining characteristics. Nickel is added to wrought alloys 2018, 2218, and 2618, which were developed for elevated-temperature service, and to certain 3*xx.x* cast alloys used for pistons, cylinder blocks, and other engine parts subjected to high temperatures. Cast aluminum bearing alloys of the 850.0 group contain tin. In all cases, these alloying additions introduce constituent phases that are cathodic to the matrix and decrease resistance to corrosion in aqueous saline media. However, these alloys are often used in environments in which they are not subject to corrosion.

Effects of Alloying on Wear Behavior

Aluminum alloys for wear resistance applications are based on the aluminum-silicon alloy system. This binary system is a simple eutectic alloy system with the eutectic composition at 12.5% Si (Fig. 5). Standard alloys, of course, contain a number of alloying ingredients. Selected commercial alloy compositions are shown in Table 9.

At room temperature, the hypoeutectic alloys consist of the soft, ductile primary aluminum phase and the very hard, brittle silicon phase associated

Table 9 Nominal compositions of selected commercial aluminum-silicon alloys recommended for wear applications

Alloy	Composition, wt%					
	Si	Fe	Cu	Mg	Mn	Other
Hypereutectic alloys						
390.0	16–18	1.3	4–5	0.45–0.65	0.1	…
A390.0	16–18	0.5	4–5	0.45–0.65	0.1	…
B390.0	16–18	1.3	4–5	0.45–0.65	0.5	1.5 Zn
392.0	18–20	1.5	0.4–0.8	0.8–1.2	0.2–0.6	0.5 Ni, 0.5 Zn, 0.3 Sn
393.0	21–23	1.3	0.7–1.1	0.7–1.3	0.1	2–2.5 Ni
Eutectic alloys						
384.0	10.5–12	1.3	3–4.5	0.1	0.5	0.5 Ni, 3 Zn, 0.35 Sn
336.0	11–13	1.2	0.5–1.5	0.7–1.3	0.35	2–3 Ni, 0.35 Zn
339.0	11–13	1.2	1.5–3	0.5–1.5	0.5	0.5–1.5 Ni, 1 Zn
413.0	11–13	2	1	0.1	0.35	0.5 Ni, 0.5 Zn
4032	11–13.5	1	0.5–1.3	0.8–1.3	…	0.5–1.3 Ni
Hypoeutectic alloys						
319.0	5.5–6.5	1	3–4	0.1	0.5	0.35 Ni, 1 Zn
356.0	6.5–7.5	0.6	0.25	0.2–0.45	0.35	0.35 Zn
364.0	7.5–9.5	1.5	0.2	0.2–0.4	0.1	0.25–0.5 Cr, 0.15 Ni, 0.15 Sn
380.0	7.5–9.5	2	3–4	0.1	0.5	0.5 Ni, 3 Zn, 0.35 Sn
333.0	8–10	1	3–4	0.05–0.5	0.5	0.5 Ni, 1 Zn
332.0	8.5–10.5	1.2	2–4	0.5–1.5	0.5	0.5 Ni, 1 Zn
360.0	9–10	2	0.6	0.4–0.6	0.35	0.5 Ni, 0.5 Zn
383.0	9.5–11.5	1.3	2–3	0.1	0.5	0.3 Ni, 3 Zn, 0.15 Sn

Source: Ref 8, 9

with eutectic reaction. It is this silicon phase that contributes to the very good wear resistance of these alloys. The silicon phase is diamond cubic with a density of ~2.6 g/cm^2 (0.094 lb/in.^{2}) and a Vickers hardness of approximately 10 GPa (1.5×10^6 psi). Silicon is essentially insoluble in aluminum. Figure 31 illustrates the typical microstructure of a common hypoeutectic alloy, A357.0 (Al-7Si-0.5Mg). Hypereutectic alloys, the most commonly used wear-resistant alloys, contain coarse, angular, primary silicon particles as well as eutectic silicon. These primary silicon particles impart excellent wear resistance to the alloys. A typical microstructure of hypereutectic alloy A390 (Al-17Si-4.5Cu-0.6Mg) is shown in Fig. 32.

Commercial aluminum-silicon alloys generally contain other alloying elements to further enhance or modify the wear resistance or impart additional properties to these alloys.

Iron. The most common alloying element is iron, which can be tolerated up to levels of 1.5 to 2.0% Fe. The presence of iron modifies the silicon phase by introducing several Al-Fe-Si phases. The most common of these are the α and β phases. The α phase has a cubic crystal structure and appears in the microstructure as a "Chinese script" eutectic. The less common β phases generally appear as needles and/or platelets in the structure. Other iron-bearing phases such as Al_6Fe and $FeAl_3$ can also be found in these alloys. Aluminum-silicon alloys intended for die castings typically

have higher minimum iron levels to reduce sticking between the mold and the casting.

Magnesium is added to provide strengthening through precipitation of Mg_2Si in the matrix. In an Al-Fe-Si-Mg alloy, the Al-Si-Fe phases will not be affected by the addition of magnesium. However, magnesium can combine with insoluble aluminum-iron phases, resulting in a loss of strengthening potential.

Copper. The most common aluminum wear-resistant alloys also contain copper. Copper additions impart additional strengthening of the matrix through the aging or precipitation-hardening process ($AlCu_2$ phase) or through modification of the hard, brittle Al-Fe-Si phases by substitution in these intermetallic phases. As the strength of these alloys increases through magnesium and copper additions, some sacrifice in ductility and corrosion resistance occurs.

Manganese. Many of the important aluminum-silicon alloys also contain low (<1 wt%), but significant, amounts of manganese. The presence of manganese can reduce the solubility of iron and silicon in aluminum and alter the composition and morphology of the Al-Fe-Si primary constituent phases. For example, manganese additions can favor the formation of constituents such as $Al_{12}(Fe,Mn)_3Si$ rather than the $Al_9Fe_2Si_2$-type constituents. The manganese-bearing constituents are typically less needle-

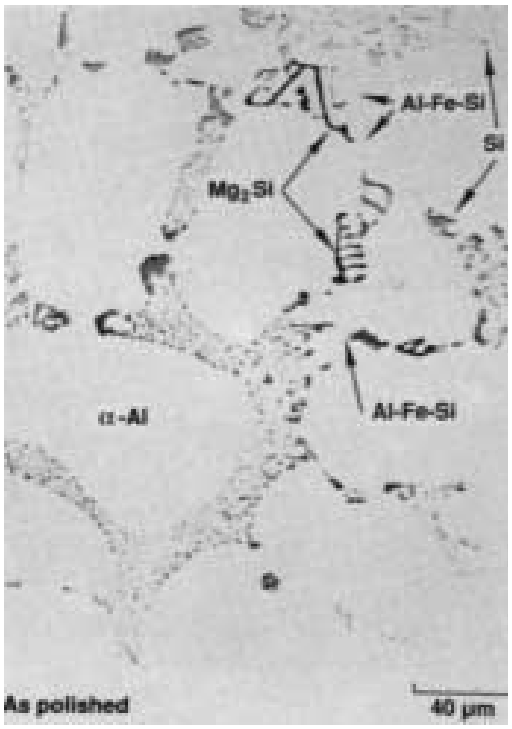


Fig. 31 Typical microstructure of type A357.0 hypoeutectic alloy

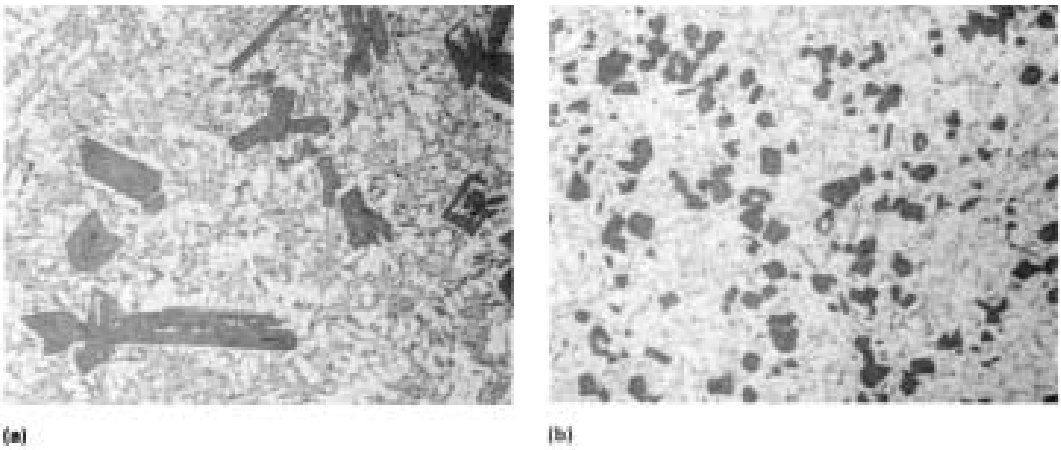


Fig. 32 Microstructure of type A390.0 hypereutectic alloy. (a) Unrefined (Graff-Sargent etch). Dark regions contain coarse primary silicon particles in addition to eutectic silica. (b) Refined (as polished). 120x

like or platelike than the manganese-free iron- or iron/silicon-bearing primary constituents. Manganese additions also improve elevated-temperature properties of the aluminum-silicon alloys.

Cumulative Effect of Alloying Elements. In summary, aluminum wear-resistant alloys are based on alloys containing the hard, brittle silicon phase. Alloying elements such as iron, manganese, and copper increase the volume fraction of the intermetallic silicon-bearing phases, contributing to increased wear resistance compared to binary aluminum-silicon alloys. In addition, magnesium and copper also provide additional strengthening by producing submicroscopic precipitates within the matrix through an age-hardening process.

Effects of Alloying on Processing

Forming

The formability of a material is the extent to which it can be deformed in a particular process before the onset of failure. Aluminum sheet or aluminum shapes usually fail by localized necking or by ductile fracture. Necking is governed largely by bulk material properties such as work hardening and strain-rate hardening and depends critically on the strain path followed by the forming process. In dilute alloys, the extent of necking or limit strain is reduced by cold work, age hardening, gross defects, a large grain size, and the presence of alloying elements in solid solution. Ductile fracture occurs as a result of the nucleation and linking of microscopic voids at particles and the concentration of strain in narrow shear bands. Fracture usually occurs at larger strains than does localized necking and therefore is usually important only when necking is suppressed.

Common examples where fracture is encountered are at small radius bends and at severe drawing, ironing, and stretching near notches or sheared edges.

Considerable advances have been made in developing alloys with good formability, but in general, an alloy cannot be optimized on this basis alone. The function of the formed part must also be considered, and improvements in functional characteristics, such as strength and ease of machining, often tend to reduce the formability of the alloy.

The principal alloys that are strengthened by alloying elements in solid solution (often coupled with cold work) are those in the aluminum-magnesium (5*xxx*) series, ranging from 0.5 to 6 wt% Mg. Figure 8 illustrates the effect of magnesium in solid solution on the yield strength and tensile elongation for most of the common aluminum-magnesium commercial alloys. Note the large initial reduction in the tensile elongation with the addition of small amounts of magnesium.

The reductions in the forming limit produced by additions of magnesium and copper appear to be related to the tendency of the solute atoms to migrate to dislocations (strain age). This tends to increase work hardening at low strains, where dislocations are pinned by solute atoms, but it decreases work hardening at large strains. Small amounts of magnesium or copper also reduce the strain-hardening rate, which will reduce the amount of useful diffuse necking that occurs after the uniform elongation. Zinc in dilute alloys has little effect on work hardening or necking, and it does not cause strain aging.

Elements that have low solid solubilities at typical processing temperatures, such as iron, silicon, and manganese, are present in the form of second-phase particles and have little influence on either strain hardening or strain-rate hardening and thus a relatively minor influence on necking behavior. Second-phase particles do, however, have a large influence on fracture, as is shown in Fig. 33 and 34. In these examples an increase in the iron, nickel, or manganese content produces an increase in the number of microscopic particles that promote fracture. The addition of magnesium promotes an additional reduction in fracture strain because the higher flow stresses aid in the formation and growth of voids at the intermetallic particles. Magnesium in solid solution also promotes the localization of strain into shear bands, which concentrates the voids in a thin plane of highly localized strain.

Precipitation-strengthened alloys are usually formed in the naturally aged (T4) condition, or in the annealed (O) condition, but only very rarely in the peak strength (T6) condition where both the necking and fracture limits are low. In Fig. 35 the effect of a wide range of precipitate structures on some of the forming properties is illustrated for alloy 2036 (2.5% Cu-0.5% Mg). Curves similar in shape can be drawn for most of the precipitation-strengthened alloys in the 2*xxx* and 6*xxx* series. The properties in Fig. 35 were obtained from sheet tensile specimens, first solution heat-

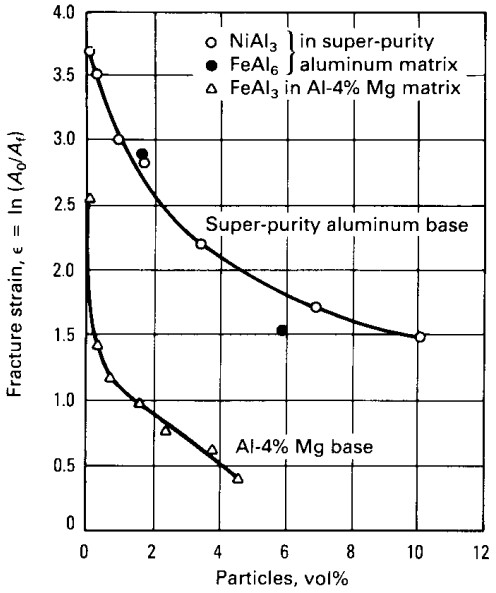


Fig. 33 Effect of volume percent fraction of micronsize intermetallic particles and composition of the matrix on the fracture strain of 5 mm (0.2 in.) diam tensile specimens. A_0 is initial cross-sectional area. A_f is area of fracture

treated, then aged at temperatures ranging from room temperature to 350 °C (660 °F). This produced a full range of structures from solid solution (as quenched) through T4 and T6 tempers to various degrees of overaging and precipitate agglomeration.

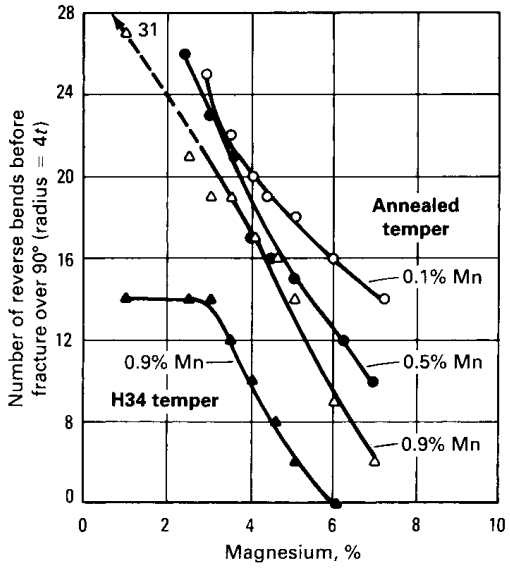


Fig. 34 Effect of magnesium and manganese on the formability of aluminum alloys in the annealed and H34 tempers; 1.6 mm (0.064 in.) thick sheet

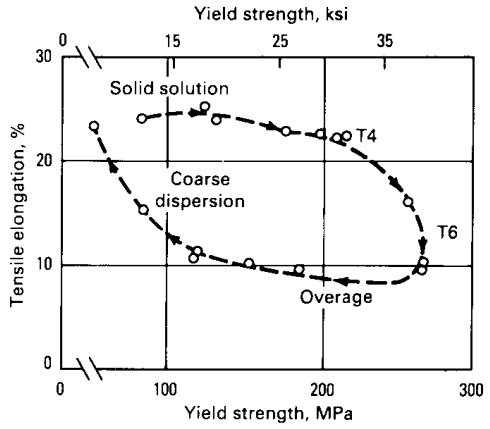


Fig. 35 Effect of precipitation on yield strength and elongation in alloy 2036

Forging

Commercial purity (or higher purity) aluminum is readily forgeable into intricate shapes over a wide range of temperatures. While many aluminum alloys are also readily forgeable, difficulty tends to increase because the addition of alloying elements increases flow strength. The formation of discrete phases that interrupt continuity of the structure also adversely affects forgeability. The higher deformation strength increases pressure requirements, while the discrete phases make flow less uniform and increase the likelihood of cracking. Alloying additions that significantly increase solid solution strength are copper, magnesium, and silicon. Chromium, manganese, titanium, vanadium, and zirconium form insoluble phases. The presence of these elements strengthens the aluminum at elevated temperature, but they have less effect than the higher solid solubility elements. If the low-solubility elements are present in sufficient quantity, massive primary particles may form. These particles can promote local cracking during forging or other hot working operations. Figure 36 shows the effect of several common additions on forgeability in the range of 370 to 455 °C (700 to 850 °F). This figure indicates that forgeability, as measured by deformation resistance, is nearly linear for the temperature and alloy range shown. Forgeability as measured by freedom from cracking falls off abruptly near or at temperature where initial melting occurs in an alloy.

Sound aluminum direct-chilled ingot with a low alloy content can be forged as-cast. Where the alloying content is higher, it is usually advantageous to homogenize the ingots before forging and, in the case of some high-content alloys, heavy sections and intricate finished shapes, it may be desirable to hot roll, extrude, or preforge the stock to obtain a uniform structure more suitable for forging. Thermal treatments should be used to maximize solid solution and to spheroidize the remaining constituents.

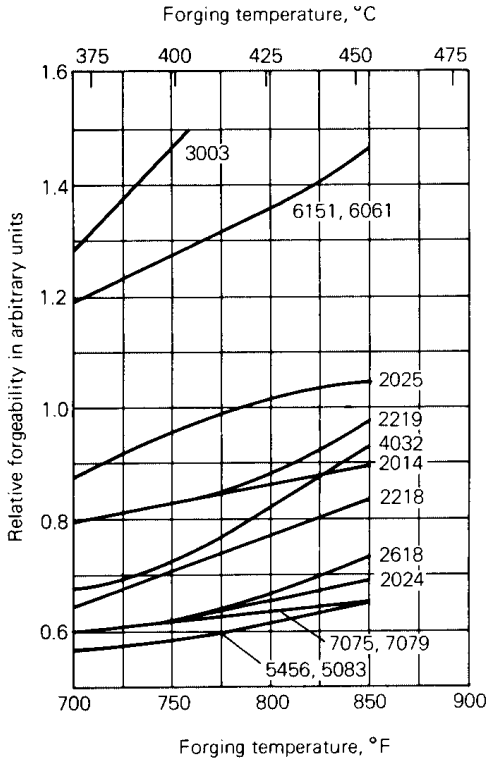


Fig. 36 Effect of temperature on relative forgeability of various aluminum alloys. Vertical scale is based on deformation per unit of energy absorbed estimated from production experience.

Machining

Pure, unalloyed aluminum is relatively soft and ductile and tends to adhere to a cutting tool, forming a builtup edge and long chips. It requires special machining techniques to avoid producing rough surfaces and heavy burrs. Alloying aluminum improves its machinability. Elements in solid solution that make an alloy heat-treatable or work-hardenable increase the hardness of the aluminum matrix and thereby reduce the builtup edge on the cutting tool; formation of burrs, roughness and tearing on the machined surface; and the length of chips.

Elements out of solution can act as chip breakers, thereby reducing the length of chips. Elements such as lead or bismuth form small insoluble globules and are effective chip breakers. If present in sufficient quantity (generally about 0.5% each), lead and bismuth permit increased machining speeds and reduce the need for cutting fluids. Intermetallic constituents such as $CuAl_2$ or $FeAl_3$ similarly act as chip breakers without significantly reducing the life of cutting tools. However, the very hard constituents, such as silicon or the complex intermetallics that contain chromium or manganese, while effectively acting as chip breakers, noticeably decrease tool life. The presence of primary silicon in hypereutectic aluminum-silicon cast alloys is

especially harmful in terms of tool life, but at the same time, it produces very short chips, minimum tool edge buildup, and excellent machined surface finish. The elements sodium, strontium, antimony, and phosphorus also effect machinability because they affect the cast microstructure. Sodium, strontium, or antimony modify the eutectic silicon morphology, changing it from acicular or needlelike to a very fine, lacy, or spheroidized structure. Phosphorus refines primary silicon in hypereutectic alloys, reducing its size by a factor of approximately 10 to 1. Modification and refinement both tend to increase tool life significantly.

In summary, the alloys having the poorest machining characteristics are of low alloy content and are in the softest condition. Cold working, increasing alloy concentration, and/or heat treatment all harden an alloy and tend to reduce the built-up edge on the tool. Elements and constituents out of solution promote chip breaking. Hard constituents, especially if large and unrefined, can significantly reduce tool life.

Welding

Aluminum has several chemical and physical properties that need to be understood when using the various joining processes. The specific properties that affect welding are its oxide characteristics; the solubility of hydrogen in molten aluminum; its thermal, electrical, and nonmagnetic characteristics; its lack of color change when heated; and its wide range of mechanical properties and melting temperatures that result from alloying with other metals.

Non-Heat-Treatable Alloys. The absence of precipitate-forming elements in these low- to moderate-strength non-heat-treatable alloys becomes a positive attribute when considering weldability, because many of the alloy additions needed for precipitation hardening (for example, copper plus magnesium, or magnesium plus silicon) can lead to hot cracking, which results from heat-affected zone (HAZ) liquidation during the welding operation. In addition, joint efficiencies are higher in non-heat-treatable alloys because the HAZ is not compromised by the coarsening or dissolution of precipitates. This obviates the need for thick joint lands or postweld heat treatment and favors the use of welded structures in the as-welded condition.

The 2*xxx* series alloys, having copper as the primary alloying addition, possess high strength but somewhat lower corrosion resistance than most other aluminum alloys. Many of these alloys also possess relatively good elevated-temperature strength. Magnesium is also added to the 2*xxx* series alloys for increased strength but results in greater weld crack sensitivity. Alloy 2024 is one of the highest-strength 2*xxx* alloys and is used exten-

sively in the aircraft industry; however, the 1.5% nominal Cu content of 2024 hinders its weldability due to increased weld crack sensitivity. Alloys having controlled levels of magnesium, such as 2014, 2219, and 2519, are used for applications requiring good weldability. Generally, these alloys provide good machinability but less formability than other heat-treatable aluminum alloys.

The 6*xxx* series alloys containing magnesium and silicon provide moderate strengths and good corrosion resistance in relation to other heat-treatable aluminum alloys. Because they are easily extruded, they are available in a wide range of structural shapes, as well as sheet and plate products. The versatility of these alloys is represented in 6061, which is one of the most commonly used aluminum alloys. Typically, the 6*xxx* alloys have good formability and good weldability.

The 7*xxx* series provides the highest strength of all aluminum alloys, although this claim is being challenged by aluminum-lithium alloys. High strength in the 7*xxx* alloys is achieved by alloying additions of zinc, magnesium, and often copper, combined with controlled thermal and mechanical processing. Copper, in combination with zinc and magnesium in the 7*xxx* series alloys, increases strength but hampers weldability due to increased susceptibility to weld cracking. Alloy 7075, containing nominally 5.6% Zn, 2.5% Mg, and 1.6% Cu, is a commonly used alloy of this system, but it has a propensity for weld cracking. Alloys 7004, 7005, and 7039 were designed for applications requiring high strength and good weldability. These alloys have limited amounts of copper that reduce the sensitivity to weld cracking. One important characteristic of the 7*xxx* series is the ability of the HAZ in these alloys to naturally age, or become precipitation-strengthened at room temperature, after welding. Because of this, weld properties continue to improve for up to 30 days after welding.

Brazing

Base Metals. The non-heat-treatable wrought alloys typically used as base metals are listed in Table 10. Those that are most successfully brazed are the 1*xxx* and 3*xxx* series and the low-magnesium members of the 5*xxx* series. The alloys containing a higher magnesium content, such as 5083, 5086, 5154, and 5456, are more difficult to braze by the usual flux methods because of poor wetting and excessive penetration by the filler metal. Filler metals are available that melt below the solidus temperatures of most commercial, non-heat-treatable wrought alloys.

The commonly brazed heat-treatable wrought alloys are the 6*xxx* series. Because the 2*xxx* and 7*xxx* series of aluminum alloys have melting points that are too low, they are not normally brazeable. Exceptions are the 7072

Table 10 Melting ranges and brazeability of some common aluminum alloys

Alloy	Melting range °C	Melting range °F	Brazeability(a)
Non-heat-treatable wrought alloys			
1350	646–657	1195–1215	A
1100	643–657	1190–1215	A
3003(b)	643–654	1190–1210	A
3004	629–652	1165–1205	B
5005	632–652	1170–1205	B
5050	627–652	1160–1205	B
5052	593–649	1100–1200	C
Heat-treatable wrought alloys			
6053	593–652	1100–1205	A
6061	593–649	1100–1200	A
6063	616–654	1140–1210	A
6951(c)	616–654	1140–1210	A
7005	607–649	1125–1200	B
Casting alloys(d)			
443.0	574–632	1065–1170	B
356.0	557–613	1035–1135	B
710.0	596–646	1105–1195	B
711.0	604–643	1120–1190	A

(a) A, generally brazeable by all commercial procedures; B brazeable with special techniques or in specific applications that justify preliminary trials or testing to develop the procedure and to check the performance of brazed joints; C, limited brazeability. (b) Used both plain and as the core of brazing sheet. (c) Used only as the core of brazing sheet. (d) Sand and permanent mold castings only

alloy, which is used for cladding material only, and 7005 alloy. Alloys with a solidus temperature above 595 °C (1100 °F) are readily brazed using the aluminum-silicon filler metals.

There are several brazeable cast aluminum alloys, which are listed in Table 10 along with their melting range and degree of brazeability. The most readily brazeable are those with the higher solidus temperatures, such as the 710 and 711 alloys.

Filler Metals. Commercial filler metals for brazing aluminum are aluminum-silicon alloys containing 7 to 12% Si. Lower melting points are attained, with some sacrifice in resistance to corrosion, by adding copper and zinc. Filler metals for vacuum (fluxless) brazing of aluminum usually contain magnesium to enhance oxide film modification, to promote wetting, and to reduce the partial pressures of oxygen-bearing gases in the chamber. The compositions and the solidus, liquidus, and brazing temperatures of the most frequently used brazing filler metals for aluminum are given in Table 11.

Soldering

Wrought Alloys. Although all aluminum alloys can be soldered, alloy composition greatly affects ease of soldering, type of solder, method employed, and ultimate service acceptability of the assembly. The relative solderability of the principal wrought aluminum alloys is listed below:

- *Excellent solderability:* 1100, 1200, 1235, 1350, and 3003
- *Good solderability:* 3004, 5357, 6003, 6061, 6063, 6101, 6151, 6253, 6951, 7072, and 8112
- *Fair solderability:* 2011, 2014, 2017, 2018, 2024, 2025, 2117, 2214, 2218, 2225, 5050, and 7005
- *Poor solderability:* 5052, 5056, 5083, 5086, 5154, 5254, 5356, 5652, 7075, 7178, and 7277

Alloys containing more than 1% Mg cannot be soldered satisfactorily with an organic flux, and alloys containing more than 2.5% Mg are difficult to solder with reaction fluxes. Alloys containing more than 5% Si are difficult to solder by any flux method.

Aluminum alloys containing more than 0.5% Mg are subject to intergranular penetration by molten tin solders. Zinc also penetrates the aluminum-magnesium alloys intergranularly, but the extent of penetration usually is not significant until the magnesium content exceeds 0.7%. Intergranular penetration by molten solder is aggravated if magnesium-containing alloys are prestressed. This can be reduced if the assembly is stress-relieved before soldering. However, when using high-temperature zinc or zinc-aluminum solders that have a solidus temperature of 370 °C (700 °F) or greater, complete stress relief occurs in non-heat-treatable alloys before molten solder contacts the surface of the aluminum. Partial stress relief occurs in the heat-treatable alloys, thus reducing solder penetration.

Aluminum-magnesium-silicon alloys are less susceptible to intergranular penetration than binary aluminum-magnesium alloys and are more solderable than binary aluminum-silicon alloys.

Aluminum alloys containing copper or zinc as a major alloying element generally contain appreciable quantities of other elements. Most such alloys are subject to intergranular penetration by solder and generally are not soldered. Solderability of the highly alloyed materials can be improved, however, by employing an aluminum alloy cladding or by plating the surface.

Table 11 Compositions and solidus, liquidus, and brazing temperature ranges of brazing filler metals for use on aluminum alloys

AWS classification	Composition(a), %						Temperature					
							Solidus		Liquidus		Brazing	
	Si	Cu	Mg	Zn	Mn	Fe	°C	°F	°C	°F	°C	°F
BAlSi-2	6.8–8.2	0.25	…	0.20	0.10	0.8	577	1070	613	1135	599–621	1110–1150
BAlSi-3(b)	9.3–10.7	3.3–4.7	0.15	0.20	0.15	0.8	521	970	585	1085	571–604	1060–1120
BAlSi-4	11.0–13.0	0.30	0.10	0.20	0.15	0.8	577	1070	582	1080	582–604	1080–1120
BAlSi-5(c)	9.0–11.0	0.30	0.05	0.10	0.05	0.8	577	1070	591	1095	588–604	1090–1120
BAlSi-6(d)	6.8–8.2	0.25	2.0–3.0	0.20	0.10	0.8	559	1038	607	1125	599–621	1110–1150
BAlSi-7(d)	9.0–11.0	0.25	1.0–2.0	0.20	0.10	0.8	559	1038	596	1105	588–604	1090–1120
BAlSi-8(d)	11.0–13.0	0.25	1.0–2.0	0.20	0.10	0.8	559	1038	579	1075	582–604	1080–1120
BAlSi-9(d)	11.0–13.0	0.25	0.10–0.5	0.20	0.10	0.8	562	1044	582	1080	582–604	1080–1120
BAlSi-10(d)	10.0–12.0	0.25	2.0–3.0	0.20	0.10	0.8	559	1038	582	1080	582–604	1080–1200
BAlSi-11(d)(e)	9.0–11.0	0.25	1.0–2.0	0.20	0.10	0.8	559	1038	596	1105	582–604	1080–1120

(a) Principal alloying elements. (b) Contains 0.15% Cr. (c) Contains 0.20% Ti. (d) Solidus and liquidus temperature ranges vary when used in vacuum. (e) Contains 0.02–0.20% Bi

Thermally treated alloys develop a heavier oxide film than forms naturally; this can hinder soldering. With the heat-treated alloys, it usually is necessary to pretreat the surface chemically before soldering.

Cast Alloys. The substantial amounts of alloying elements present in most casting alloys increase the probability that these elements will be dissolved in the solder, which will reduce its wetting capacity and capillary action. The casting alloys, as a group, thus have poor solderability. The time at soldering temperature must be held to a minimum to reduce penetration of molten solder. Electroplating the cast surface facilitates soldering by controlling solder penetration and improving solder wetting capacity and capillary action.

Any roughness, minute cavity, or porosity in a cast surface can entrap flux and make flux removal difficult. Permanent-mold, plaster mold, and die castings generally present a good surface condition for soldering. However, because die castings are subject to surface blistering when exposed to temperatures over 315 °C (600 °F), they generally cannot be high-temperature soldered. Because most die casting alloys contain a high percentage of silicon and a tenacious oxide film, they are difficult to wet and normally are soldered by fluxless methods.

The three aluminum casting alloys that are relatively easily wetted by solder are 443.0, 443.2, and 356. Casting alloys that are less responsive but still solderable are 213.0, 710.0, and 711.0.

SELECTED REFERENCES

- *Corrosion of Aluminum and Aluminum Alloys*, J.R. Davis, Ed., ASM International, 1999
- *ASM Specialty Handbook*: *Aluminum and Aluminum Alloys,* J.R. Davis, Ed., ASM International, 1993
- Aluminum and Aluminum Alloys, in *Metals Handbook Desk Edition,* 2nd ed., J.R. Davis, Ed., ASM International, 1998, p 417–505
- D.G. Altenpohl, *Aluminum*: *Technology, Applications, and Environment,* 6th ed., The Aluminum Association Inc. and TMS, 1998
- *Aluminum: Properties and Physical Metallurgy,* J.E. Hatch, Ed., American Society for Metals, 1984

Alloying: Understanding the Basics
J.R. Davis, p417-431
DOI:10.1361/autb2001p417
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Titanium and Titanium Alloys

Introduction and Overview

General Characteristics. Titanium is a low-density element (≅ 4.5 g/cm^3, which is about 60% of the density of iron) that can be highly strengthened by alloying and deformation processing. Titanium is nonmagnetic and has good heat-transfer properties. Its coefficient of thermal expansion is somewhat lower than that of steels and less than half that of aluminum. Titanium and its alloys have melting points higher than those of steels, but maximum useful temperatures for structural applications generally range from 425 to 595 °C (800 to 1100 °F). Titanium aluminide alloys show promise for applications at temperatures up to 760 °C (1400 °F). Titanium has the ability to passivate and thereby exhibits a high degree of immunity to attack by most mineral acids and chlorides. Titanium is nontoxic and generally biologically compatible with human tissues and bones. The combination of high strength, stiffness, good toughness, low density, and good corrosion resistance provided by various titanium alloys at very low to elevated temperatures allows weight savings in aerospace structures and other high-performance applications. The excellent corrosion resistance and biocompatibility coupled with good strength make titanium and its alloys useful in chemical and petrochemical applications, marine environments, and biomaterial applications.

Applications. Titanium and its alloys are used primarily in two areas of application where the unique characteristics of these metals justify their selection: corrosion-resistant service and strength-efficient structures. For these two diverse areas, selection criteria differ markedly. Corrosion applications normally utilize low-strength "unalloyed" titanium mill products fabricated into tanks, heat exchangers, or reactor vessels for chemical-processing, desalination, or power-generation plants. In contrast,

high-performance applications typically utilize high-strength titanium alloys in a very selective manner depending on factors such as thermal environment, loading parameters, available product forms, fabrication characteristics, and inspection and/or reliability requirements. Examples of high-performance applications include offshore drilling components and geothermal piping, gas turbine engine components, aerospace pressure vessels, submarine hulls and submersible research vehicles, and heat exchangers for power generation. As a result of their specialized usage, alloys for high-performance applications normally are processed to more stringent and costly requirements than "unalloyed" titanium for corrosion service.

Historically, titanium alloys have been used instead of iron or nickel alloys in aerospace applications because titanium saves weight in highly loaded components that operate at low to moderately elevated temperatures. Many titanium alloys have been custom designed to have optimal tensile, compressive, and/or creep strength at selected temperatures and, at the same time, to have sufficient workability to be fabricated into mill products suitable for specific applications. During the life of the titanium industry, various compositions have had transient usage, but one alloy, Ti-6Al-4V, has been consistently responsible for about 45% of industry application. Ti-6Al-4V is unique in that it combines attractive properties with inherent workability (which allows it to be produced in all types of mill products, in both large and small sizes), good shop fabricability (which allows the mill products to be made into complex hardware), and the production experience and commercial availability that lead to reliable and economic usage. Thus Ti-6Al-4V has become the standard alloy against which other alloys must be compared when selecting a titanium alloy (or custom designing one) for a specific application. Ti-6Al-4V also is the standard alloy selected for castings and powder metallurgy (P/M) products that must exhibit superior strength. For elevated-temperature applications, the most commonly used alloy is Ti-6Al-2Sn-4Zr-2Mo + Si. This alloy is primarily used for turbine components and in sheet form for afterburner structures and various "hot" airframe applications.

Physical Metallurgy

Titanium undergoes an allotropic transformation at about 885 °C (1625 °F), changing from a close-packed hexagonal (cph) crystal structure (α phase) to a body-centered cubic (bcc) crystal structure (β-phase). The transformation temperature (β-transus—completion of transformation to β on heating) is strongly influenced by the interstitial elements oxygen, nitrogen, and carbon (α-stabilizers), which raise the transformation temperature; by hydrogen (β-stabilizer), which lowers the transformation temperature; and by metallic impurity or alloying elements, which may either raise or lower the transformation temperature.

Depending on their microstructure, titanium alloys fall into one of four classes: α, near-α, α-β, or β. These classes denote the general type of microstructure after processing. Most α-alloys will have a minimal amount of β-phase, sometimes as a result of tramp iron, as in commercially pure titanium, and sometimes due to minor β-stabilizer additions to enhance workability (e.g., the molybdenum and vanadium additions in Ti-8Al-1Mo-1V). A near-α or super-α alloy may appear microstructurally similar to an α-alloy. An α-β alloy consists of α and retained or transformed β, and commercial β-alloys tend to retain the β-phase on initial cooling to room temperature, but precipitates secondary phases during heat treatment.

Effects of Alloy Elements

In titanium alloys, the principal effect of an alloying element is its effect on the alpha-to-beta transformation temperature. Some elements stabilize the alpha crystal structure by raising the alpha-to-beta transformation temperature, while other elements stabilize the beta structure by lowering the alpha-to-beta transformation temperature.

Table 1 classifies the common alloying elements as alpha or beta stabilizers. The addition of alloying elements also divides the single temperature for equilibrium transformation into two temperatures—the alpha transus, above which the alpha phase begins transformation to beta, and the beta transus, above which the alloy is all-beta. Between these temperatures, both alpha and beta are present. Transus temperatures vary with impurity levels and the range of alloy additions.

Alpha Stabilizers. Aluminum is the primary alpha stabilizer in titanium alloys. Other alloying elements that favor the alpha crystal structure and stabilize it by raising the alpha-beta transformation temperatures include gallium, germanium, carbon, oxygen, and nitrogen.

Beta stabilizers are classified into two groups: beta isomorphous and beta eutectoid. Isomorphous alpha phase results from the decomposition

Table 1 Ranges and effects of some alloying elements used in titanium

Alloying element	Range (approx), wt%	Effect on structure
Aluminum	3–8	α-stabilizer
Tin	2–4	α-stabilizer
Vanadium	2–15	β-stabilizer
Molybdenum	2–15	β-stabilizer
Chromium	2–12	β-stabilizer
Copper	~2	β-stabilizer
Zirconium	2–5	α- and β-strengthener
Silicon	0.05–0.5	Improves creep resistance

of the metastable beta in the first group, whereas in the second group, an intimate eutectoid mixture of alpha and a compound form.

The isomorphous group consists of elements that are completely miscible in the beta phase; included in this group are molybdenum, vanadium, tantalum, and niobium.

The eutectoid-forming group, which has eutectoid temperatures as much as 335 °C (600 °F) below the transformation temperature of unalloyed titanium, includes manganese, iron, chromium, cobalt, nickel, copper, and silicon. Active eutectoid formers (for example, nickel or copper) promote rapid decomposition; sluggish eutectoid formers (for example, iron or manganese) induce a slower reaction.

Aluminum is a principal alpha stabilizer in titanium alloys that increases tensile strength, creep strength, and the elastic moduli. The maximum solid solution strengthening that can be achieved by aluminum is limited, because above 6% Al promotes ordering and Ti_3Al (α_2) formation, which is associated with embrittlement. Thus, aluminum content of most titanium alloys is typically below 7%. Formation of α_2, which is closely related to O_2 content, can actually occur at lower levels of aluminum.

Tin has extensive solid solubilities in both alpha and beta phases and is often used as a solid solution strengthener in conjunction with aluminum to achieve higher strength without embrittlement. Tin is a less potent alpha stabilizer than aluminum, but does retard the rates of transformation.

Zirconium forms a continuous solid solution with titanium and increases strength at low and intermediate temperatures. The use of zirconium above 5 to 6% may reduce ductility and creep strength. Zirconium is a weak beta stabilizer, but does retard the rates of transformation.

Molybdenum is an important beta stabilizer that promotes hardenability and short-time elevated-temperature strength. Molybdenum makes welding more difficult and reduces long-term, elevated-temperature strength.

Niobium is a beta stabilizer that is added primarily to improve oxidation resistance at high temperatures.

Silicon is added to titanium alloys to improve creep resistance. Depending on the alloy, silicon contents range from about 0.08 to 0.45%. Figure 1 shows the effect of silicon content on the creep behavior of two high-performance titanium alloys.

Alloying elements to improve corrosion resistance include nickel, molybdenum, palladium, and ruthenium. See the section “Effects of Alloying on Corrosion Behavior” for additional information.

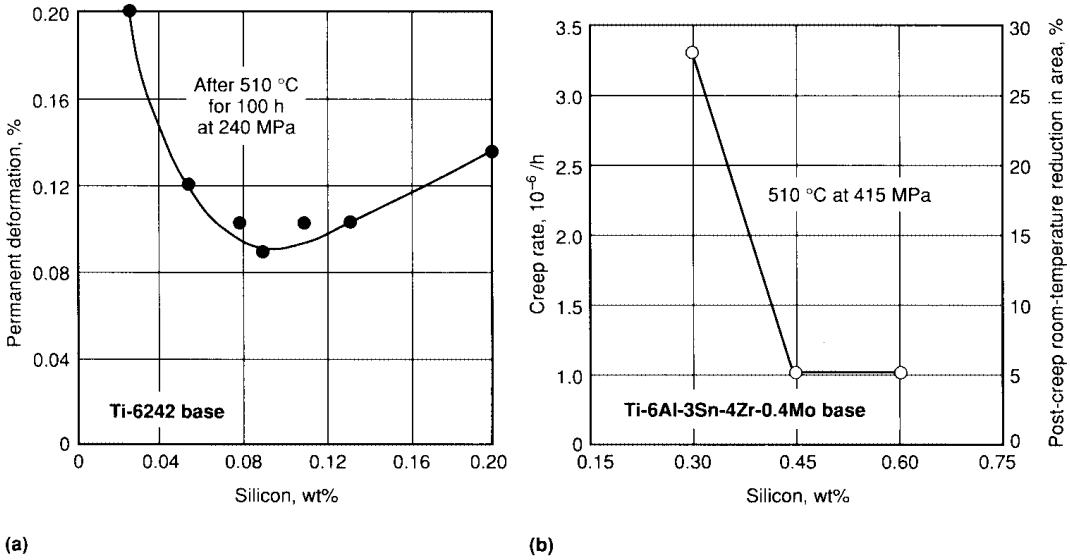


Fig. 1 Effect of silicon content on the creep behavior of (a) Ti-6Al-2Sn-4Zr-2Mo base composition and (b) Ti-6Al-3Sn-4Zr-0.4Mo base composition

Alloy Systems and Their Processing Characteristics

Table 2 lists some commercial and semicommercial titanium grades and alloys currently available, which are subdivided into four groups: unalloyed (commercially pure) grades, α- and near-α alloys, α-β alloys, and β-alloys. Selection of an unalloyed grade or higher strength alloy depends on desired mechanical properties, service requirements, processing considerations (e.g., forming and welding requirements) and other factors that enter into the materials selection process.

Unalloyed Titanium. There are a number of grades of unalloyed titanium; the primary difference between grades is oxygen and iron content. Grades of higher purity (lower interstitial content) are lower in strength, hardness, and transformation temperature than those higher in interstitial content, and have greater formability. The high solubility of the interstitial elements oxygen and nitrogen makes titanium unique among metals and also creates problems not of concern in most other metals. For example, heating titanium in air at high temperature results not only in oxidation but also in solid-solution hardening of the surface as a result of inward diffusion of oxygen (and nitrogen). A surface-hardened zone of "α-case" (or "air contamination layer") is formed. Normally, this layer is removed by machining, chemical milling, or other mechanical means prior to placing a part in service because the presence of α-case reduces fatigue strength and ductility.

Unalloyed titanium usually is selected for its excellent corrosion resistance, especially in applications where high strength is not required. Yield

Table 2 Summary of commercial and semicommercial grades and alloys of titanium

Designation	Tensile strength (min)		0.2% Yield strength (min)		Impurity limits, wt% (max)					Nominal composition, wt%				
	MPa	ksi	MPa	ksi	N	C	H	Fe	O	Al	Sn	Zr	Mo	Others
Unalloyed grades														
ASTM grade 1	240	35	170	25	0.03	0.08	0.015	0.20	0.18	…	…	…	…	…
ASTM grade 2	340	50	280	40	0.03	0.08	0.015	0.30	0.25	…	…	…	…	…
ASTM grade 3	450	65	380	55	0.05	0.08	0.015	0.30	0.35	…	…	…	…	…
ASTM grade 4	550	80	480	70	0.05	0.08	0.015	0.50	0.40	…	…	…	…	…
ASTM grade 7	340	50	280	40	0.03	0.08	0.015	0.30	0.25	…	…	…	…	0.2Pd
ASTM grade 11	240	35	170	25	0.03	0.08	0.015	0.20	0.18	…	…	…	…	0.2Pd
α and near-α alloys														
Ti-0.3Mo-0.8Ni (ASTM grade 12)	480	70	380	55	0.03	0.10	0.015	0.30	0.25	…	…	…	0.3	0.8Ni
Ti-5Al-2.5Sn	790	115	760	110	0.05	0.08	0.02	0.50	0.20	5	2.5	…	…	…
Ti-5Al-2.5Sn-ELI	690	100	620	90	0.07	0.08	0.0125	0.25	0.12	5	2.5	…	…	…
Ti-8Al-1Mo-1V	900	130	830	120	0.05	0.08	0.015	0.30	0.12	8	…	…	1	1V
Ti-6Al-2Sn-4Zr-2Mo	900	130	830	120	0.05	0.05	0.0125	0.25	0.15	6	2	4	2	0.08Si
Ti-6Al-2Nb-1Ta-0.8Mo	790	115	690	100	0.02	0.03	0.0125	0.12	0.10	6	…	…	1	2Nb, 1Ta
Ti-2.25Al-11Sn-5Zr-1Mo	1000	145	900	130	0.04	0.04	0.008	0.12	0.17	2.25	11	5	1	0.2Si
Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si	1030	149	910	132	0.03	0.08	0.006	0.05	0.15	5.8	4	3.5	0.5	0.7Nb, 0.35Si
α-β alloys														
Ti-6Al-4V(a)	900	130	830	120	0.05	0.10	0.0125	0.30	0.20	6	…	…	…	4V
Ti-6Al-4V-ELI(a)	830	120	760	110	0.05	0.08	0.0125	0.25	0.13	6	…	…	…	4V
Ti-6Al-6V-2Sn(a)	1030	150	970	140	0.04	0.05	0.015	1.0	0.20	6	2	…	…	0.75Cu, 6V
Ti-6Al-2Sn-4Zr-6Mo(b)	1170	170	1100	160	0.04	0.04	0.0125	0.15	0.15	6	2	4	6	…
Ti-5Al-2Sn-2Zr-4Mo-4Cr(b)	1125	163	1055	153	0.04	0.05	0.0125	0.30	0.13	5	2	2	4	4Cr
Ti-6Al-2Sn-2Zr-2Mo-2Cr(a)	1030	150	970	140	0.03	0.05	0.0125	0.25	0.14	5.7	2	2	2	2Cr, 0.25Si
Ti-3Al-2.5V(c)	620	90	520	75	0.015	0.05	0.015	0.30	0.12	3	…	…	…	2.5V
Ti-4Al-4Mo-2Sn-0.5Si	1100	160	960	139	(d)	0.02	0.0125	0.20	(d)	4	2	…	4	0.5Si
β alloys														
Ti-10V-2Fe-3Al	1170	170	1100	160	0.05	0.05	0.015	2.5	0.16	3	…	…	…	10V
Ti-3Al-8V-6Cr-4Mo-4Zr	900	130	830	120	0.03	0.05	0.020	0.25	0.12	3	…	4	4	6Cr, 8V
Ti-15V-3Cr-3Al-3Sn	1000(b) 1241(e)	145(b) 180(e)	965(b) 1172(e)	140(b) 170(e)	0.05	0.05	0.015	0.25	0.13	3	3	…	…	15V, 3Cr
Ti-15Mo-3Al-2.7Nb-0.2Si	862	125	793	115	0.05	0.05	0.015	0.25	0.13	3	…	…	15	2.7Nb, 0.2Si

(a) Mechanical properties given for the annealed condition; may be solution treated and aged to increase strength. (b) Mechanical properties given for the solution-treated-and-aged condition; alloy not normally applied in annealed condition. (c) Primarily a tubing alloy; may be cold drawn to increase strength. (d) Combined $O_2 + 2N_2 = 0.27\%$. (e) Also solution treated and aged using an alternative aging temperature (480 °C, or 900 °F)

strengths of unalloyed (commercially pure) grades (see Table 2) vary from 170 MPa (25 ksi) to 480 MPa (70 ksi), simply as a result of variations in the interstitial and impurity levels.

Alpha and Near-α Alloys. Alpha alloys that contain aluminum, tin, and/or zirconium are preferred for high-temperature, as well as cryogenic applications. Alpha-rich alloys generally are more resistant to creep at high temperature than α-β or β-alloys. The extra-low-interstitial α alloys (ELI grades) retain ductility and toughness at cryogenic temperatures, and Ti-5Al-2.5Sn-ELI has been used extensively in such applications.

Unlike α-β and β-alloys, α-alloys cannot be significantly strengthened by heat treatment. Generally, α alloys are annealed or recrystallized to remove residual stresses induced by cold working. Alpha alloys have good weldability because they are insensitive to heat treatment. They generally have poorer forgeability and narrower forging temperature ranges than

α-β or β-alloys, particularly at temperatures below the β-transus. This poorer forgeability is manifested by a greater tendency for strain-induced porosity or surface cracks to occur, which means that small reduction steps and frequent reheats must be incorporated in forging schedules.

Alpha alloys that contain small additions of β-stabilizers (Ti-8Al-1Mo-1V or Ti-6Al-2Nb-1Ta-0.8Mo, for example) sometimes have been classed as "super-α" or "near-α" alloys. Although they contain some retained β-phase, these alloys consist primarily of α and behave more like conventional α-alloys than α-β alloys.

Alpha-beta alloys contain one or more α stabilizers or α-soluble elements plus one or more β-stabilizers. These alloys retain more β-phase after solution treatment than do near-α alloys, the specific amount depending on the quantity of β-stabilizers present and on heat treatment.

Alpha-beta alloys can be strengthened by solution treating and aging. Solution treating usually is done at a temperature high in the two-phase α-β field and is followed by quenching in water, oil, or other suitable quenchant. As a result of quenching, the β-phase present at the solution-treating temperature may be retained or may be partly, or fully, transformed during cooling by either martensitic transformation or nucleation and growth. The specific response depends on alloy composition, solution treating temperature (β-phase composition at the solution temperature), cooling rate, and section size. Solution treatment is followed by aging, normally at 480 to 650 °C (900 to 1200 °F), to precipitate α and produce a fine mixture of α and β in the retained or transformed β-phase. Transformation kinetics, transformation products, and specific response of a given alloy can be quite complex; a detailed review of the subject is beyond the scope of this article.

Solution treating and aging can increase the strength of α-β alloys 30 to 50%, or more, over the annealed or overaged condition. Response to solution treating and aging depends on section size; alloys relatively low in β-stabilizers (Ti-6Al-4V, for example) have poor hardenability and must be quenched rapidly to achieve significant strengthening. For Ti-6Al-4V, the cooling rate of a water quench is not rapid enough to significantly harden sections thicker than about 25 mm (1 in.). As the content of β-stabilizers increases, hardenability increases; Ti-5Al-2Sn-2Zr-4Mo-4Cr, for example, can be through hardened with relatively uniform response throughout sections up to 150 mm (6 in.) thick. For some alloys of intermediate β-stabilizer content, the surface of a relatively thick section can be strengthened, but the core may be 10 to 20% lower in hardness and strength. The strength that can be achieved by heat treatment is also a function of the volume fraction of β-phase present at the solution-treating temperature. Alloy composition, solution temperature, and aging conditions must be carefully selected and balanced to produce the desired mechanical properties in the final product.

Although the ability of α-β alloys to be precipitation hardened has been studied in laboratory programs since the early days of the titanium industry, there have been relatively few production applications of solution-treated and precipitation-(age)-hardened alloys. This situation appears to be changing, because alloys such as Ti-6Al-2Sn-4Zr-6Mo, Ti-5Al-2Sn-2Zr-4Mo-4Cr, and certain high-hardenability β alloys have been developed specifically to be age hardened for improved strength—about 30 to 40% above that of annealed alloys.

Beta alloys are richer in β-stabilizers and leaner in α stabilizers than α-β alloys. They are characterized by high hardenability, with β-phase completely retained on air cooling of thin sections or water quenching of thick sections. Beta alloys have excellent forgeability, cold-rolling capabilities, and, in sheet form, can be cold brake-formed more readily than high-strength α-β or α alloys. It is more difficult to perform more complex triaxial-strain-type forming operations with β-alloys because they exhibit almost no work hardening, and necking occurs early. After solution treating, β-alloys are aged at temperatures of 450 to 650 °C (850 to 1200 °F) to partially transform the β-phase to α. The α forms as finely dispersed particles in the retained β, and strength levels comparable or superior to those of aged α-β alloys can be attained. The chief disadvantages of β-alloys in comparison with α-β alloys include higher density, lower creep strength, and lower tensile ductility in the aged condition. Although tensile ductility is lower, the fracture toughness of an aged β-alloy generally is higher than that of an aged α-β alloy of comparable yield strength.

In the solution-treated condition (100% retained β), β alloys have good ductility and toughness, relatively low strength, and excellent formability. Solution-treated β-alloys begin to precipitate α phase at slightly elevated temperatures and thus are unsuitable for elevated-temperature service without prior stabilization or overaging treatment.

Beta alloys (at least commerical β-alloys), despite the name, actually are metastable, because cold work at ambient temperature can induce a martensitic transformation, or heating to a slightly elevated temperature can cause partial transformation to α or other transformation products. The principal advantages of β-alloys are that they have high hardenability, excellent forgeability, and good cold formability in the solution-treated condition.

Effects of Alloying on Corrosion Behavior

Titanium is highly resistant to corrosion by many natural environments, including seawater, body fluids, and fruit and vegetable juices. Titanium is used extensively for handling salt solutions (including chlorides, hypochlorides, sulfates, and sulfides), wet chlorine gas, and nitric acid

solutions. On the other hand, hot concentrated low-pH chloride salts (such as boiling 30% $AlCl_3$ and boiling 70% $CaCl_2$) corrode titanium. Warm or concentrated solutions of HCl, H_2SO_4, H_3PO_4, and oxalic acid also are damaging. In general, all acidic solutions that are reducing in nature corrode titanium unless they contain inhibitors. Strong oxidizers, including anhydrous red fuming nitric acid and 90% H_2O_2, also cause attack. Ionizable fluoride compounds, such as NaF and HF, activate the surface and can cause rapid corrosion; dry chlorine gas is especially harmful.

Mechanism of Corrosion Resistance. The excellent corrosion resistance of titanium alloys results from the formation of very stable, continuous, highly adherent, and protective oxide films on metal surfaces. Because titanium metal itself is highly reactive and has an extremely high affinity for oxygen, these beneficial surface oxide films form spontaneously and instantly when fresh metal surfaces are exposed to air and/or moisture. In fact, a damaged oxide film can generally reheal itself instantaneously if at least traces (that is, parts per million) of oxygen or water (moisture) are present in the environment. However, anhydrous conditions in the absence of a source of oxygen may result in titanium corrosion, because the protective film may not be regenerated if damaged.

The nature, composition, and thickness of the protective surface oxides that form on titanium alloys depend on environmental conditions. In most aqueous environments, the oxide is typically TiO_2, but may consist of mixtures of other titanium oxides, including TiO_2, Ti_2O_3, and TiO.

Effects of Alloying on the Oxide Films. The nature of the oxide film on titanium alloys basically remains unaltered in the presence of minor alloying constituents; thus, small additions (<2 to 3%) of most commercially used alloying elements or trace alloy impurities generally have little effect on the basic corrosion resistance of titanium in normally passive environments. For example, despite small differences in interstitial element (carbon, oxygen, and nitrogen) and iron content, all unalloyed grades of titanium possess the same useful range of resistance in environments in which corrosion rates are normally very low. However, under active conditions in which titanium exhibits significant general corrosion, certain alloying elements may accelerate corrosion. Increasing the alloy iron and sulfur content, for example, increases corrosion rates when corrosion rates exceed 0.13 mm/yr (5 mils/yr). Thus, minor variations in alloy chemistry may be of concern only under conditions in which the passivity of titanium is borderline or when the metal is fully active.

Effects of Specific Elements. Anodic control of the corrosion reaction predominates when titanium is exposed to a reducing acid such as hydrochloric or sulfuric. Alloying with elements that reduce anodic activity therefore should improve corrosion resistance. This can be accomplished

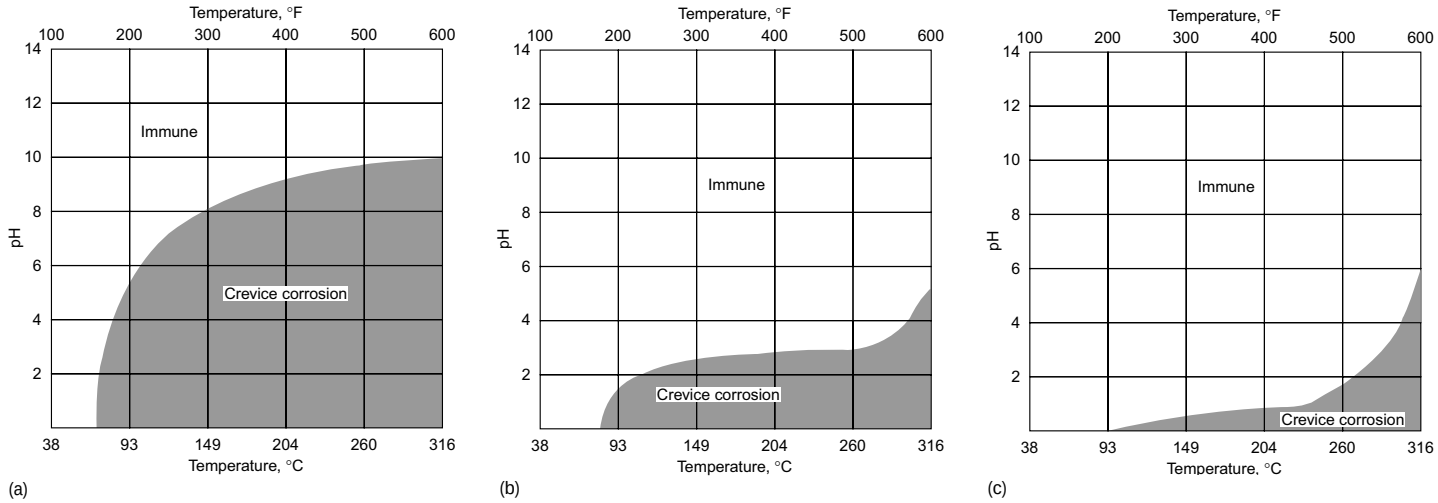


Fig. 2 Effects of alloying on the crevice corrosion of titanium in saturated sodium chloride brines. (a) Unalloyed grades 1, 2, 3, and 4. (b) ASTM grade 12 containing 0.3% Mo and 0.8% Ni. (c) ASTM grades 7 and 11 containing 0.15% Pd. The same resistance can be achieved with ruthenium (0.10%) additions.

by using alloying elements that: (a) shift the corrosion potential of the alloy in the positive direction (cathodic alloying), (b) increase the thermodynamic stability of the alloy and thus reduce the ability of the titanium to dissolve anodically, or (c) increase the tendency of titanium to passivate. The first group includes noble metals such as platinum, palladium, and rhodium. The second includes nickel, molybdenum, and tungsten. The third group includes zirconium, tantalum, chromium, and possibly molybdenum. Considerable work has been done on the use of noble metals as alloying additions in titanium. An outgrowth of this work has been the development of Ti-0.2Pd, which has considerably greater resistance to corrosion in reducing environments than does unalloyed titanium (ruthenium additions of 0.10% have been found to have the same effect). In addition, work on alloying for thermodynamic stability has resulted in Ti-2Ni, which was developed for service in hot brine environments where crevice corrosion is sometimes a problem. Figure 2 shows the effects of palladium additions on the crevice corrosion in saturated NaCl brine.

Various studies have shown that crevice corrosion resistance of titanium is improved by addition of molybdenum. The commercial alloy Ti Code 12 (ASTM grade 12 in Table 2), which contains 0.3% Mo and 0.8% Ni, combines some of the favorable properties of nickel and molybdenum additions while avoiding the negative aspects. This alloy has excellent resistance to pitting and crevice corrosion in high-temperature brines, which sometimes attack commercially pure titanium, and also has better resistance to oxidizing environments such as nitric acid. Figure 2 shows the effects of molybdenum and nickel additions on the crevice corrosion of grade 12 in saturated NaCl brine.

Effects of Alloying on Resistance to Stress-Corrosion Cracking

Unalloyed titanium generally is immune to stress-corrosion cracking (SCC) unless it has a high oxygen content (0.3% or more). For this reason, SCC is of little concern in the chemical-process industries, where unalloyed titanium is most commonly used. On the other hand, certain alloys of titanium used principally in the aerospace industry are subject to SCC. Table 3 provides an overview of the types of environments that are known to stimulate SCC in certain titanium alloys, along with the specific alloys that have exhibited finite susceptibility in laboratory and service exposures. It should be noted that the alloys listed in Table 3 represent only those reported in the literature; it should not be assumed that other titanium alloys are necessarily resistant to SCC under similar conditions. It also should be noted that the alloys listed were susceptible to SCC in at

Table 3 Environments known to promote stress-corrosion cracking of commercial titanium alloys

Environment			
Medium	Temperature °C	Temperature °F	Titanium alloys with known susceptibility
Oxidizers			
Nitric acid (red-fuming)	Room temperature		Ti,Ti-8Mn, Ti-6Al-4V, Ti-5Al-2.5Sn
Nitrogen tetroxide (no excess NO)	30–75	86–167	Ti-6Al-4V
Organic compounds			
Methyl alcohol (anhydrous)	Room temperature		Ti-6Al-4V, grade 2, grade 4, Ti-4Al-3Mo-1V, Ti-3Al-8V-6Cr-4Zr-4Mo, Ti-8Al-1Mo-1V, Ti-13V-11Cr-3Al,Ti-5Al-2.5Sn
Methyl chloroform	370	700	Ti-8Al-1Mo-1V, Ti-6Al-4V, Ti-5Al-2.5Sn, Ti-13V-11Cr-3Al
Ethyl alcohol (anhydrous)	Room temperature		Ti-8Al-1Mo-1V,Ti-5Al-2.5Sn
Ethylene glycol	Room temperature		Ti-8Al-1Mo-1V
Trichloroethylene	370,620,815	700,1150,1500	Ti-8Al-1Mo-1V,Ti-5Al-2.5Sn
Trichlorofluorethane	788	1450	Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn,Ti-6Al-4V,Ti-13V-11Cr-3Al
Chlorinated diphenyl	315–370	600–700	Ti-5Al-2.5Sn
Hot salt			
Chloride and other halide salts/residues	230–430	450–805	Most commercial alloys, except grades 1,2,7,11,12, and 9
Metal embrittlement			
Cadmium (solid + liquid)	25–600	77–1110	Ti-8Mn,Ti-13V-11Cr-3Al, grade 2, Ti-6Al-4V
Mercury (liquid)	Room temperature		Grade 4, Ti-6Al-4V
	370	700	Ti-13V-11Cr-3Al, Ti-8Al-1Mo-1V
	232–480	450–900	Ti-7Al-4Mo, Ti-5Al-2.5Sn
Silver (solid) and AgC			
Ag-5Al-2.5Mn (braze alloy)	340	645	Ti-6Al-4V, Ti-8Al-1Mo-1V
Miscellaneous			
Seawater/NaCl solution	Room temperature		Unalloyed Ti (with >0.3% O), Ti-2.5Al-1Mo-11Sn-5Zr-0.2Si (IMI-679), Ti-3Al-11Cr-13V, Ti-5Al-2.5Sn, Ti-8Mn, Ti-6Al-4V, Ti-6Al-6V-2Sn, Ti-7Al-2Nb-1Ta, Ti-4Al-3Mo-1V, Ti-8Al-1Mo-1V, Ti-6Al-Sn-4Zr-6Mo
Distilled water	Room temperature		Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn, Ti-11.5Mo-6Zr-4.5Sn
Chlorine gas	288	550	Ti-8Al-1Mo-1V
10% HCl	35, 340	95, 645	Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V
LiCl, KBr, and Na_2SO_4 solution (0.6 *M*)	Room temperature		Ti-6Al-4V, Ti-6Al-6V-2Sn
Molten chloride/bromide salts	300–500	570–930	Ti-8Al-1Mo-1V

least one metallurgical condition (not indicated in the table). This means that changes in alloy composition (within specifications) and/or metallurgical conditions (i.e., processing and/or final heat treatment) may or may not eliminate susceptibility to SCC.

The following paragraphs deal with the metallurgical factors (composition and structure) that influence SCC behavior in titanium alloys. Emphasis is placed on data generated in 3.5% NaCl and seawater media at ambient temperature.

In α titanium alloys, SCC behavior is primarily composition dependent, with grain morphology, size, and texture playing a secondary role. Stress-corrosion cracking behavior is especially sensitive to aluminum and oxygen content in the alloy, and also to nitrogen, carbon, and/or tin

levels. Alloy SCC susceptibility increases at aluminum levels of ≥ 5 wt%, which stems from the increased tendency to form the highly ordered Ti_3Al (α_2) phase. This low-ductility ordered phase forms in the 400 to 700 °C (750 to 1290 °F) temperature range and increases crack velocity and decreases threshold stress intensity for SCC (K_{ISCC}) as volume fraction increases. Oxygen levels above 0.20 to 0.25 wt% also promote SCC. This means that although grades 1 and 2 titanium fully resist aqueous SCC, certain higher interstitial chemistries of the grade 3 (or grade 4) alloy may not, as indicated by the following ambient saltwater data:

Grade 2 (0.12% O_2) →

K_{Ic} = 66 MPa$\sqrt{m}$ (60 ksi$\sqrt{in.}$)

K_{ISCC} = 66 MPa $\sqrt{m}$ (60 ksi $\sqrt{in.}$)

Grade 4 (0.38% O_2) →

K_{Ic} = 110 MPa $\sqrt{m}$ (100 ksi $\sqrt{in.}$)

K_{ISCC} = 38 MPa $\sqrt{m}$ (35 ksi $\sqrt{in.}$)

The influence of aluminum and oxygen on titanium alloy SCC is synergistic in a negative fashion, as indicated in Fig. 3. Tin additions also promote ordered structures and thus are also negative in this regard, as evidenced by the susceptible Ti-5Al-2.5Sn alloy. Zirconium additions, in contrast, are somewhat beneficial.

Compositionally susceptible α alloys generally remain so, whether the structure is equiaxed α or martensitic (quenched from the β-phase field). In general, SCC susceptibility of equiaxed α alloys diminishes with decreasing grain size. Depending on the alloy, transformation to martensitic phase

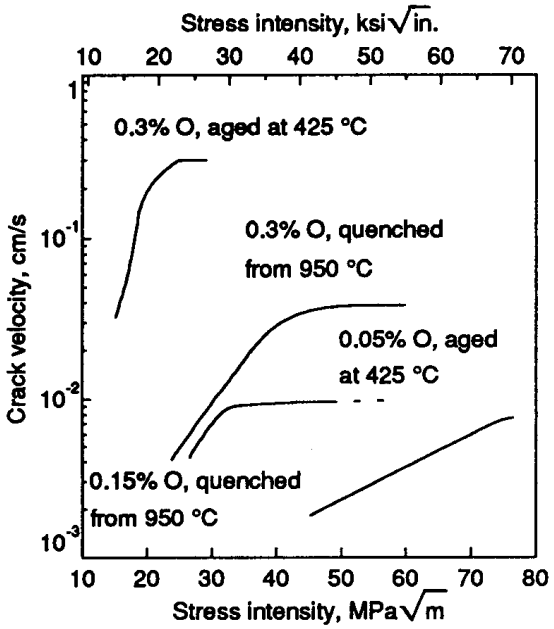


Fig. 3 Influence of oxygen and heat treatment on crack velocity (*V*) versus stress intensity (*K*) relationships for Ti-6Al binary alloys tested in 0.6 *M* KCl at 24 °C (75 °F)

structure may or may not improve SCC resistance. The SCC fracture mode in α alloys is transgranular, with the fracture path highly oriented in unidirectionally processed (textured) material and more random in martensitic structures.

In α-β alloys, it is also the α phase that can exhibit SCC susceptibility in aqueous media. Thus, dependence of alloy SCC susceptibility on aluminum, tin, and O_2 content is still relevant. The strong negative effect of increasing aluminum content is evident in the α-β alloy K_{ISCC} data plotted in Fig. 4. Similarly, oxygen levels above 0.10 to 0.12 wt% generally diminish α-β alloy SCC resistance significantly. It is for optimized K_{Ic} and K_{ISCC} values that extra-low-interstitial (ELI) grades of certain α-β alloys, such as ELI Ti-6A1-4V, are often specified for critical saltwater applications. On the other hand, most isomorphous β-phase stabilizer additions, such as molybdenum, vanadium, niobium, and tantalum, tend to reduce or eliminate SCC susceptibility in aqueous halide solutions. The β-eutectoid additions, such as iron, manganese, chromium, silicon, and copper, however, tend to degrade SCC resistance. Increasing hydrogen content may also reduce SCC resistance in α-β alloys.

Phase structure is also vital in dictating SCC behavior in α-β alloys. The degree of susceptibility is directly related to the grain size, volume fraction, and mean free path of the susceptible α phase. Increasing α grain size increases susceptibility. Because the β-phase acts as a ductile, SCC-resistant crack arrester, structures that have an increased β-phase volume fraction and that break up or disperse α phase tend to be beneficial. Thus,

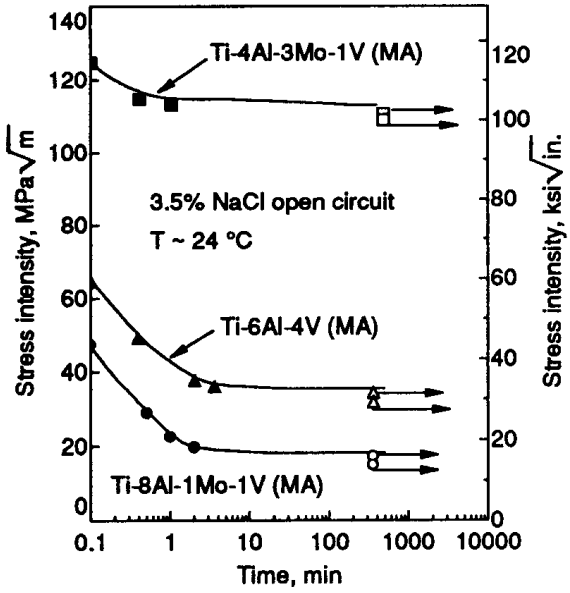


Fig. 4 Variation of time to failure with stress intensity, *K*, for three mill-annealed (MA) commercial α-β alloys of varying aluminum contents tested in 3.5% NaCl

the fine, equiaxed β-phase which results from processing in the α-β field is much less effective than the lamellar, randomly oriented β-phase produced by β-processing. Beta processing and/or final β-heat-treatment improves both air and aqueous toughness by improving chemical homogeneity, randomizing crystallographic texture, and providing a structure with greatest crack-path tortuosity.

As discussed previously for α-alloys, α-β alloys containing higher aluminum levels (≥5 wt%) may form Ti_3Al (α_2) phase (1) when aged in the 400 to 700 °C (750 to 1290 °F) range. Increasing oxygen and/or tin levels further aggravates the phenomenon, which can severely sensitize the alloy to SCC (see Fig. 3). Slow or step-cooled Ti-8Al-1Mo-1V is a classic example of an α-β alloy sensitized to SCC by this effect.

The SCC fracture mode in α-β alloys consists of transgranular cleavage through the α-phase and ductile tearing (dimples and tear ridges) through the β-phase. Crack velocities are high, and in the range of 1 to 50 mm/min (0.04 to 2 in./min).

In β-titanium alloys, the β-phase may be susceptible to either transgranular or intergranular SCC, depending on alloy composition and microstructure. Intergranular cracking has been observed only in a few aged β-alloys, particularly with fine α-precipitates formed at lower aging temperatures. Beta phase alloys stabilized by either molybdenum, vanadium, niobium, or tantalum is immune to SCC. Exceptions include β-phase stabilized by the eutectoid elements manganese and chromium. Transgranular cleavage of β-phase is known to occur in the Ti-8Mn alloy with a β + α structure and in solution-treated Ti-13V-11Cr-3Al. Stress-corrosion cracking susceptibility in this case is mitigated by decreasing the grain size and mean free path of the β-phase. Although β + ω phase structures appear to be highly resistant, the precipitation of compounds, such as $TiCr_2$, with the β-phase can be expected to degrade cracking resistance.

SELECTED REFERENCES

- R.R. Boyer, Titanium and Titanium Alloys, *Metals Handbook Desk Edition,* 2nd ed., J.R. Davis, Ed., ASM International, 1998, p 574–588
- *Materials Properties Handbook: Titanium Alloys,* R.R. Boyer, G. Welsch, and E.W. Collings, Ed., ASM International, 1994
- R.W. Schutz, Stress-Corrosion Cracking of Titanium Alloys, *Stress-Corrosion Cracking: Materials Performance and Evaluation,* R.H. Jones, Ed., ASM International, 1992, p 265–297
- R.W. Schutz and D.E. Thomas, Corrosion of Titanium and Titanium Alloys, *Corrosion,* Vol 13, *ASM Handbook,* ASM International, 1987, p 669–706
- *Titanium: A Technical Guide,* 2nd ed., M.J. Donachie Jr., Ed., ASM International, 2000

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J.R. Davis, p432-453
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Magnesium and Magnesium Alloys

Introduction and Overview

Magnesium and magnesium alloys have been employed in a wide variety of structural applications because of their favorable combination of tensile strength 160 to 365 MPa, or 23 to 53 ksi), elastic modulus (45 GPa, or 6.5×10^6 psi), and low density (1.74 g/cm^3, which is the lowest density of all structural metals). Magnesium alloys have high strength-to-weight ratios (tensile strength/density), comparable to those of other structural metals. Magnesium has relatively good electrical conductivity (38.6% IACS) and thermal conductivity (154.5 W/m · K, or 89.2 Btu/ft · h · °F) values. It also has a very high damping capacity, that is, the ability to absorb elastic vibrations.

Uses of Magnesium

Magnesium and magnesium alloys are used in a wide variety of structural and nonstructural applications. Figure 1 summarizes recent end-use statistics for magnesium and magnesium alloys.

Structural uses, mostly die castings, account for ~30% of total reported consumption. Applications include automotive, industrial, materials-handling, commercial, and aerospace equipment. The automotive applications include instrument panel support beams, brake and clutch pedal brackets, air intake grills, steering column support brackets, steering wheels, seat back frames and seat bottoms, and battery cases for electric vehicles. In industrial machinery, such as textile and printing machines, magnesium alloys are used for parts that operate at high speeds and thus must be lightweight to minimize inertial forces. Materials-handling equipment includes dockboards, grain shovels, and gravity conveyors.

Commercial applications include hand-held tools, computer housings, and mobile-phone cases. Magnesium alloys are valuable for aerospace applications because they are lightweight and exhibit good strength and stiffness at both room and elevated temperatures. Aerospace components produced from magnesium alloys include main transmission housings for helicopters and gearboxes and gearbox housings for commercial and military aircraft.

Nonstructural Uses. Magnesium is an important constituent in aluminum alloys; in fact, the largest usage of magnesium (44% of reported consumption) is for alloying with aluminum. Additions of up to 5% in wrought alloys and 10% in cast alloys result in aluminum alloys with favorable combinations of strength, formability (wrought products), and corrosion resistance. Magnesium is also used as an oxygen scavenger and desulfurizer in the manufacture of nickel and copper alloys; as a desulfurizer in the iron and steel industry; and as a reducing agent in the production of beryllium, titanium, zirconium, hafnium, and uranium. Another important nonstructural use of magnesium is in the Grignard reaction in organic chemistry. In finely divided form, magnesium finds some use in pyrotechnics, both as pure magnesium and alloyed with 30% or more aluminum. The relative position of magnesium in the electromotive series allows it to be used for cathodic protection of other metals from corrosion and in construction of dry-cell, seawater, and reserve-cell batteries. Cast iron foundries use magnesium and magnesium-containing alloys as ladle addition agents introduced just before the casting is poured. The magnesium makes the graphite particles nodular and greatly improves the toughness and ductility of the cast iron. Because of its rapid but controllable response to etching and its light weight, magnesium is also used in photoengraving.

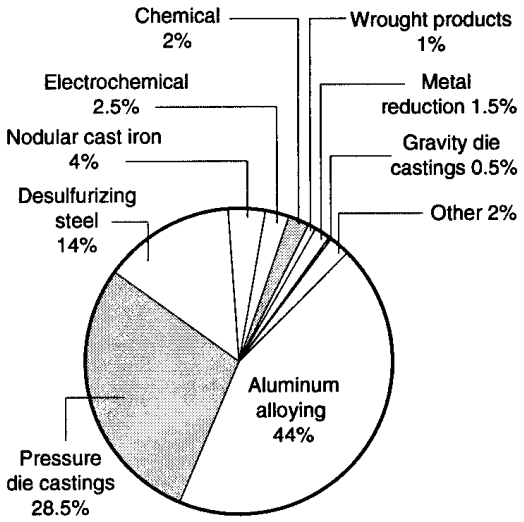


Fig. 1 Consumption of magnesium in Western world in 1997 (total 333,700 tonnes). Amount used for magnesium alloys is shown shaded. Courtesy of International Magnesium Association

Alloy Designations and Tempers

Alloy Designations. No international system for designating magnesium alloys exists, although there has been a trend toward adopting the naming method used by ASTM for magnesium alloys. This method is a three-part letter-number-letter system. The first part consists of code letters indicating the two principal alloying elements, listed in order of decreasing alloying content. These code letters are listed in Table 1. The second part consists of the weight percentages of these two elements, rounded off to the nearest whole number and listed in the same order as the code letters. (Note that some alloys have only one principal alloying element.) The third part consists of an assigned letter (beginning with "A") to distinguish between alloys having the same nominal designation, or an "X" to indicate that the alloy is still experimental. For example, AZ91C is a magnesium alloy containing approximately 9% aluminum and 1% zinc, and is the third specific composition registered having this nominal composition.

Temper Designations. The ASTM method also includes a code system for the temper of magnesium (and other) alloys. This consists of a letter plus one or more digits (see Table 2). The temper designation follows the alloy designation and is separated from it by a hyphen. For example, AZ91C-F indicates that the part (in this instance, a die casting) is made from the "C" version of Mg-9Al-1Zn alloy and is in the as-fabricated (as-cast) condition.

Product Forms

As discussed previously, the primary product forms for magnesium alloys are pressure die castings, which make up 28.5% of magnesium consumption (Fig. 1). Magnesium alloys are also produced by sand casting, permanent mold casting, investment casting, and thixotropic molding (semisolid injection molding). Wrought products, which account for only

Table 1 Code letters for the designation system of magnesium alloys

Letter	Alloying element
A	Aluminum
C	Copper
E	Rare earth metals
H	Thorium
K	Zirconium
L	Lithium
M	Manganese
Q	Silver
S	Silicon
W	Yttrium
Z	Zinc

Table 2 Temper designations for magnesium alloys

General divisions	
F	As fabricated
O	Annealed, recrystallized (wrought products only)
H	Strain-hardened
T	Thermally treated to produce stable tempers other than F, O, or H
W	Solution heat treated (unstable temper)
Subdivisions of H	
H1, plus one or more digits	Strain-hardened only
H2, plus one or more digits	Strain-hardened and then partially annealed
H3, plus one or more digits	Strain-hardened and then stabilized
Subdivisions of T	
T1	Cooled and naturally aged
T2	Annealed (cast products only)
T3	Solution heat treated and then cold worked
T4	Solution heat treated
T5	Cooled and artificially aged
T6	Solution heat treated and artificially aged
T7	Solution heat treated and stabilized
T8	Solution heat treated, cold worked, and artificially aged
T9	Solution heat treated, artificially aged, and cold worked
T10	Cooled, artificially aged, and cold worked

1% of magnesium consumption, are available as forgings, extruded bars and shapes, and sheet and plate.

Commercial Alloy Systems

Magnesium is rarely used for engineering applications without being alloyed with other metals. The vast majority of the alloy systems currently being commercially produced contain aluminum, manganese, zinc, zirconium, rare earths, and silver in order to obtain the strong, light weight alloys needed for structural uses. Magnesium alloys systems can be subdivided as follows:

- Magnesium-manganese
- Magnesium-aluminum-manganese
- Magnesium-aluminum-zinc-manganese
- Magnesium-zirconium
- Magnesium-zinc-zirconium
- Magnesium-rare earth metal-zirconium
- Magnesium-silver-rare earth metal-zirconium
- Magnesium-yttrium-rare earth metal-zirconium

Until fairly recently, thorium was also a constituent in some magnesium alloy systems. These included:

- Magnesium-thorium-zirconium
- Magnesium-thorium-zinc-zirconium
- Magnesium-silver-thorium-rare earth metal-zirconium

Table 3 Nominal compositions and typical room-temperature tensile properties of magnesium alloys

Alloy	Composition, %						Tensile strength		Tensile yield strength		Elongation in 50 mm (2 in.), %	Hardness, HR(c)
	Al	Mn(a)	Th	Zn	Zr	Other(b)	MPa	ksi	MPa	ksi		
Sand and permanent mold castings												
AM100A-T61	10.0	0.10	…	…	…	…	275	40	150	22	1	69
AZ63A-T6	6.0	0.15	…	3.0	…	…	275	40	130	19	5	73
AZ81A-T4	7.6	0.13	…	0.7	…	…	275	40	83	12	15	55
AZ91C and E-T6(d)	8.7	0.13	…	0.7	…	…	275	40	145	21	6	66
AZ92A-T6	9.0	0.10	…	2.0	…	…	275	40	150	22	3	84
EQ21A-T6	…	…	…	…	0.7	1.5 Ag, 2.1 Di	235	34	195	28	2	65–85
EZ33A-T5	…	…	…	2.7	0.6	3.3 RE	160	23	110	16	2	50
HK31A-T6	…	…	3.3	…	0.7	…	220	32	105	15	8	55
HZ32A-T5	…	…	3.3	2.1	0.7	…	185	27	90	13	4	57
K1A-F	…	…	…	…	0.7	…	180	26	55	8	1	…
QE22A-T6	…	…	…	…	0.7	2.5 Ag, 2.1 Di	260	38	195	28	3	80
QH21A-T6	…	…	1.0	…	0.7	2.5 Ag, 1.0 Di	275	40	205	30	4	…
WE43A-T6	…	…	…	…	0.7	4.0 Y, 3.4 RE	250	36	165	24	2	75–95
WE54A-T6	…	…	…	…	0.7	5.2 Y, 3.0 RE	250	36	172	25	2	75–95
ZC63A-T6	…	0.25	…	6.0	…	2.7 Cu	210	30	125	18	4	55–65
ZE41A-T5	…	…	…	4.2	0.7	1.2 RE	205	30	140	20	3.5	62
ZE63A-T6	…	…	…	5.8	0.7	2.6 RE	300	44	190	28	10	60–85
ZH62A-T5	…	…	1.8	5.7	0.7	…	240	35	170	25	4	70
ZK51A-T5	…	…	…	4.6	0.7	…	205	30	165	24	3.5	65
ZK61A-T5	…	…	…	6.0	0.7	…	310	45	185	27	…	68
ZK61A-T6	…	…	…	6.0	0.7	…	310	45	195	28	10	70
Die castings												
AE42-F	4.0	0.1	…	…	…	2.5 RE	230	34	145	21	11	60
AM20-F	2.1	0.1	…	…	…	…	210	31	90	13	20	45
AM50A-F	4.9	0.26	…	…	…	…	230	33	125	18	15	60
AM60A and B-F(e)	6.0	0.13	…	…	…	…	240	35	130	19	13	65
AS21-F	2.2	0.1	…	…	…	1.0 Si	220	32	120	17	13	55
AS41A-F(f)	4.2	0.20	…	…	…	1.0 Si	240	35	140	20	15	60
AZ91A, B, and D-F(g)	9.0	0.13	…	0.7	…	…	250	36	160	23	7	70
Forgings												
AZ31B-F	3.0	0.20	…	1.0	…	…	260	38	170	25	15	50
AZ61A-F	6.6	0.15	…	1.0	…	…	295	43	180	26	12	55
AZ80A-T5	8.5	0.12	…	0.5	…	…	345	50	250	36	6	72
AZ80A-T6	8.5	0.12	…	0.5	…	…	345	50	250	36	11	75
M1A-F	…	1.2	…	…	…	…	250	36	160	23	7	47
ZK31-T5	…	…	…	3.0	0.6	…	290	42	210	30	7	…
ZK60A-T5	…	…	…	5.5	0.45(a)	…	305	44	215	31	16	65
ZK61-T5	…	…	…	6.0	0.8	…	275	40	160	32	7	…
ZM21-F	…	0.5	…	2.0	…	…	200	29	125	18	9	…
Extruded bars and shapes												
AZ10A-F	1.2	0.2	…	0.4	…	…	240	35	145	21	10	…
AZ31B and C-F(h)	3.0	0.20	…	1.0	…	…	255	37	200	29	12	49
AZ61A-F	6.5	0.15	…	1.0	…	…	305	44	205	30	16	60
AZ80A-T5	8.5	0.12	…	0.5	…	…	380	55	275	40	7	80
M1A-F	…	1.2	…	…	…	…	255	37	180	26	12	44
ZC71-T6	…	0.5	…	6.5	…	1.25 Cu	295	43	324	47	3	70–80
ZK21A-F	…	…	…	2.3	0.45(a)	…	260	38	195	28	4	…
ZK31-T5	…	…	…	3.0	0.6	…	295	43	210	30	7	…
ZK40A-T5	…	…	…	4.0	0.45(a)	…	275	40	255	37	4	…
ZK60A-T5	…	…	…	5.5	0.45(a)	…	350	51	285	41	11	82
ZM21-F	…	0.5	…	2.0	…	…	235	34	155	22	8	…
Sheet and plate												
AZ31B-H24	3.0	0.20	…	1.0	…	…	290	42	220	32	15	73
ZM21-0	…	0.5	…	2.0	…	…	240	35	120	17	11	…
ZM21-H24	…	0.5	…	2.0	…	…	250	36	165	24	6	…

(a) Minimum. (b) RE, rare-earth; Di, didymium (a mixture of rare earth elements made up chiefly of neodymium and praseodymium). (c) 500 kg load, 10 mm ball. (d) Properties of C and E are identical, but AZ91E casting have 0.17% minimum Mn and maximum contaminant levels of 0.005% Fe, 0.0010% Ni, and 0.015% Cu. (e) Properties of A and B are identical, but AM60B castings have maximum contaminant levels of 0.005% Fe, 0.002% Ni and 0.010% Cu. (f) Properties of A and XB are identical, but AS41B castings have maximum contaminant levels of 0.0035% Fe, 0.002% Ni, and 0.002 Cu. (g) Properties of A, B, and D are identical, except that 0.30% maximum residual Cu is allowable in AZ91B, and AZ91D castings have maximum contaminant levels of 0.005% Fe, 0.002% Ni, and 0.030% Cu. (h) Properties of B and C are identical, but AZ31C has 0.15% minimum Mn, 0.1% maximum Cu, and 0.03% maximum Ni.

Although thorium-containing alloys have found applications in missiles and spacecraft, they have lost favor because of environmental considerations and are generally considered obsolete.

All of the alloy systems listed previously can be generally grouped into those that contain aluminum as an alloying element and those that do not. Because most alloys that do not contain aluminum as an alloying element contain zirconium additions to refine the grain structure (magnesium-manganese alloys are the main exception), commercial magnesium alloy systems can be alternatively grouped as zirconium-free and zirconium-containing. The specific alloys can also be classified as to product from: cast, wrought, or filler metal. The nominal compositions and typical tensile properties of the most common commercial magnesium alloys are presented in Table 3.

Alloying Practices

Alloys of magnesium can be produced by melting magnesium pigs in oil- or gas-fired steel pots and then adding the alloying metals, such as aluminum and zinc. Manganese can be added in the metallic form, but it is usually added as manganese chloride to improve alloying efficiency.

Most foundries, however, purchase prealloyed ingot, which is subsequently charged into the melting furnace with a proportion of process scrap. In some die-casting operations, the amount of process scrap generated is low, and it becomes economically feasible to have this scrap remelted and ingotted before it is reused.

With the magnesium-aluminum-zinc alloys used in the sand-casting and die-casting operations, little correction to the composition is necessary. However, the magnesium-zirconium alloys contain alloying constituents that tend to be lost during each remelt operation and need to be added each time the material is remelted. Such corrections can be made by adding the pure metals themselves (such as zinc, misch metal, and so forth), or hardener alloys with a fairly high content of the alloying element. Examples include zirconium added as a master alloy of about 30% in magnesium and cerium or other rare earths added as a master alloy with a content of 20% rare earths in magnesium. Composition control, however, must allow for the fact that the addition of a master alloy to correct one element can lead to a dilution of the melt, causing the content of other elements to be reduced.

Normally, alloying metals and master alloys are added into the melt, which is held at about 700 °C (1300 °F), as sawed pieces of ingot.

When alloying with zirconium, a “puddling” technique involving either manual or mechanical stirring, followed by a settling procedure to allow acid-insoluble zirconium complexes to settle, is required to produce the required degree of supersaturation of the melt with zirconium. Care must be taken not to hold the melt too long or to allow the melt temperature to fall, however, because losses of zirconium will result.

Effects of Alloying Elements on Properties and Processing

Emphasis in this section is placed on the effects of alloying on mechanical properties and castability. Subsequent sections in this article discuss how alloying influences corrosion behavior, physical properties, weldability, and machinability.

Aluminum has the most favorable effect on magnesium of any of the alloying elements. It improves strength and hardness, and it widens the freezing range and makes the alloy easier to cast. When present in amounts in excess of 6 wt%, the alloy becomes heat treatable, but commercial alloys rarely exceed 10 wt% aluminum. An aluminum content of 6% yields the optimum combination of strength and ductility.

Beryllium. Although only slightly soluble in magnesium, adding up to about 0.001 wt% beryllium decreases the tendency for the surface of the molten metal to oxidize during melting, casting, and welding. It can be used successfully in die-cast and wrought alloys, but must be used judiciously in sand-casting alloys because of its grain-coarsening effect.

Calcium is a special alloying ingredient added in very small amounts by some manufacturers to assist in metallurgical control. It serves a dual purpose: when added to casting alloys immediately prior to pouring, it reduces oxidation in the molten condition, as well as during subsequent heat treatment of the casting, and it improves the rollability of magnesium sheet. The addition of calcium must be controlled to below about 0.3 wt%, however, or the sheet will be susceptible to cracking during welding.

Copper adversely affects the corrosion resistance of magnesium alloys if present in quantities exceeding 0.05 wt%. However, it improves high-temperature strength.

Iron is one of the more harmful impurities in magnesium alloys in that it greatly reduces the corrosion resistance if present in even small amounts. In ordinary commercial-grade alloys, the iron content can average as high as 0.01 to 0.03 wt%. For maximum resistance to corrosion, however, 0.005% is specified as the upper limit for iron content.

Lithium has relatively high solid solubility in magnesium (5.5 wt%, 17.0 at.%), and because of its low relative density of 0.54, it has attracted interest as an alloying element in magnesium alloys to lower the density to values even lower than that of unalloyed magnesium. Moreover, only some 11 wt% of lithium is needed to form the β phase, which has a body-centered cubic (bcc) crystal structure (rather than a hexagonal close-

packed, or hcp, structure), thereby improving formability of wrought products. The addition of lithium decreases strength, but increases ductility. Mg-Li alloys are also amenable to age hardening, although they tend to overage at only slightly elevated temperatures (e.g., 60 °C, or 140 °F). So far, Mg-Li alloys have found only limited application.

Manganese does not have much effect on tensile strength, but it does increase yield strength slightly. Its most important function is to improve the saltwater resistance of Mg-Al and Mg-Al-Zn alloys by removing iron and other heavy-metal elements into relatively harmless intermetallic compounds, some of which separate out during melting. The amount of manganese that can be added is limited by its relatively low solubility in magnesium. Commercial alloys containing manganese rarely contain over 1.5 wt%, and in the presence of aluminum, the solid solubility of manganese is reduced to about 0.3 wt%.

Nickel is like iron in that it is another of the more harmful impurities in magnesium alloys; it also greatly reduces the corrosion resistance if present in even small amounts. In ordinary commercial-grade alloys, the nickel content can average as high as 0.01 to 0.03 wt%, but for maximum resistance to corrosion, 0.005% is specified as the upper limit for nickel content.

Rare earth metals are added to magnesium alloys either as mischmetal or as didymium. Mischmetal is a natural mixture of the rare earths containing about 50 wt% cerium, with the remainder being principally comprised of lanthanum and neodymium; didymium is a natural mixture of approximately 85% neodymium and 15% praseodymium.

Additions of the rare earths increase the strength of magnesium alloys at elevated temperatures. They also reduce weld cracking and porosity in casting because they narrow the freezing range of the alloys.

Silicon. The addition of silicon to magnesium alloys has been found to increase fluidity of the metal in the molten state. However, it decreases corrosion resistance of magnesium alloys if iron is also present in the alloy.

Silver additions improve the mechanical properties of magnesium alloys by increasing response to age hardening.

Thorium additions increase the creep strength of magnesium alloys at temperatures up to 370 °C (700 °F). The most common alloys contain 2 to 3 wt% thorium in combination with zinc, zirconium, or manganese. Thorium improves the weldability of alloys containing zinc.

Tin is useful when alloyed with magnesium in combination with small amounts of aluminum. The tin serves to increase the ductility of the alloy and makes it better for hammer forging because it reduces the tendency for the alloy to crack while being hot worked.

Zinc is next to aluminum in effectiveness as an alloying ingredient in magnesium. Zinc is often used in combination with aluminum to produce improvement in room-temperature strength; however, it increases hot shortness when added in amounts greater than 1 wt% in magnesium alloys containing 7 to 10 wt% aluminum. Zinc is also used in combination with zirconium, rare earths, or thorium to produce precipitation-hardenable magnesium alloys with good strength. Zinc also helps overcome the harmful corrosive effect of iron and nickel impurities that might be present in the magnesium alloy.

Zirconium has a powerful grain-refining effect on magnesium alloys. It is thought that because the lattice parameters of α-zirconium (a = 0.323 nm, c = 0.514 nm) are very close to those of magnesium (a = 0.320 nm, c = 0.520 nm), zirconium-rich solid particles produced early in the freezing of the melt may provide sites for the heterogeneous nucleation of magnesium grains during solidification.

Zirconium is added to alloys containing zinc, rare earths, thorium, or a combination of these elements, where it serves as a grain refiner (up to its limit of solid solubility). However, it cannot be used in alloys containing aluminum or manganese because it forms stable compounds with these elements and is thus removed from solid solution. It also forms stable compounds with any iron, silicon, carbon, nitrogen, oxygen, and (mainly) hydrogen present in the melt. Because only the portion of the zirconium content available for grain refining is that which is in solid solution, the soluble zirconium content, rather than the total zirconium content, is the value important to the alloy.

Yttrium has a relatively high solid solubility in magnesium (12.4 wt%) and is added with other rare earth elements to promote creep resistance at temperatures up to 300 °C (570 °F). About 4 to 5% Zr is added to magnesium to form commercial alloys such as WE54 and WE43, where it imparts good elevated-temperature properties up to about 250 °C (480 °F).

Effects of Alloying on Properties of Specific Die Casting Alloys

The number of alloys that can be successfully cast by die casting is much more restricted than gravity-casting alloys. The current commercial magnesium die-casting alloys (Table 3) contain aluminum as the main alloying element, which improves the castability, strength, and corrosion resistance. In addition, they also contain manganese to improve their corrosion resistance. Zinc additions to the most common die-casting alloy, AZ91, around 0.7 wt% result in minor improvements in strength and corrosion resistance. AZ91 has excellent castability and high strength

combined with moderate ductility, and it should always be considered the first choice for an application unless it is ruled out by specific property requirements.

Because ductility and fracture toughness are gradually reduced with increasing aluminum content, the AM series of alloys with reduced aluminum contents (and reduced zinc contents) is now used extensively for automotive safety-related components. AM60 and AM50 have found widespread application in safety parts, such as automotive panel supports, steering-wheel armatures, and seat parts. To some extent, the castability is diminished as the aluminum content is reduced, so the alloys having the highest aluminum content with the required mechanical properties should be chosen.

Because heavy-element impurities are detrimental to the saltwater corrosion resistance of magnesium-alloy parts, a series of higher-purity die-casting alloys have been introduced in which the levels of heavy-element impurities are strictly controlled. For example, AZ91A and AZ91B, two versions of AZ91 alloy, have been used in die castings for many years. The only difference between them is that a higher level of copper is allowed in AZ91B than in AZ91A.

In addition, a high-purity version of AZ91, AZ91D, is also now available for die casting. Because tight limits have been placed on levels of copper, nickel, and iron impurities allowed in AZ91D, this alloy has saltwater corrosion rates 100 times lower than sand-cast AZ91C, making it comparable to the rates of aluminum casting alloys.

Two versions of AM60 are also available. Similar to AZ91B and AZ91A, the main differences between AM60A and AM60B is that higher copper levels are allowed in AM60A than in AM60B. Therefore, AM60B has better saltwater corrosion resistance than AM60A.

Manganese content in magnesium die-casting alloys varies from one alloy to another, depending on the mutual solubilities of iron and manganese in the presence of other alloying elements. A basic requirement for the high-purity alloys is that the iron content of die-cast parts be limited to a maximum of 0.005 wt%.

Efforts to improve the creep strength of magnesium die-casting alloys at temperatures exceeding 120 °C (250 °F) have resulted in the introduction of alloys containing silicon or rare earth metals. These alloying elements form intermetallic constituents that stabilize the grain boundaries. As a result, these alloys show good creep properties at temperatures up to 150 °C (300 °F), as well as good room-temperature mechanical properties. In these alloys, aluminum must be kept at relatively low levels. Once again, two versions of one of the AS-series alloys, AS41, are available. The main difference between AS41A and AS41B is that higher copper levels are allowed in AS41A than in AS41B. Therefore, AS41B has better saltwater corrosion resistance than AS41A.

Beryllium is added to the magnesium die-casting alloys to levels of 5 to 15 ppm to reduce the oxidation rate in the molten metal.

Effects of Alloying on Corrosion Behavior

Magnesium is the most active of metals used for structural applications; it is more active than either zinc or aluminum. Because of this activity, magnesium is widely used as sacrificial anodes for cathodic protection in waters and soils. However, the electrochemical activity of magnesium and its alloys also makes them very susceptible to galvanic corrosion. Unfortunately, alloying is not an effective means of mitigating galvanic corrosion. Only proper design and protection of assemblies can prevent galvanic corrosion.

Because chloride solutions are particularly corrosive to magnesium and magnesium alloys, the following discussion will address the effects of various alloying/residual elements on salt water/salt spray corrosion performance. More detailed information on the corrosion behavior of magnesium alloys in various environments can be found in Ref 1.

Importance of Composition Control. Figure 2 shows the effects of 14 elements on the saltwater corrosion performance of magnesium in binary alloys with increasing levels of the individual elements. Six of the elements included in Fig. 2 (aluminum, manganese, sodium, silicon, tin, and lead) plus thorium, zirconium, beryllium, cerium, praseodymium, and yttrium are known to have little if any deleterious effect on the basic saltwater corrosion performance of pure magnesium when present at levels exceeding their solid solubility or up to a maximum of 5%. Four elements in Fig. 2 (cadmium, zinc, calcium, and silver) have mild to moderate accelerating effects on corrosion rates, whereas four others (iron, nickel, copper, and cobalt) have extremely deleterious effects because of their low solid-solubility limits and their ability to serve as active cathodic sites for

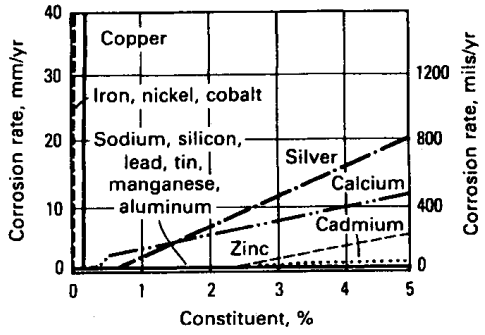


Fig. 2 Effect of alloying and contaminant metals on the corrosion rate of magnesium as determined by alternate immersion in 3% NaCl solution. Source: Ref 2

the reduction of water at the sacrifice of elemental magnesium. Although cobalt is seldom encountered at detrimental levels and cannot be introduced, even through the long immersion of cobalt steels in magnesium melts, iron, nickel, and copper are common contaminants that can be readily introduced through poor molten-metal handling practices. These elements must be held to levels under their individual solubility limits (or their activity moderated through the use of alloying elements such as manganese or zinc) to obtain good corrosion resistance.

Figure 3 illustrates the effect of increasing iron, nickel, and copper contamination on the standard ASTM salt-spray performance of die-cast AZ91 test specimens, as compared to the range of performance observed for cold-rolled steel and die-cast aluminum alloy 380 samples. Such results have led to the definition of the critical contaminant limits for magnesium-aluminum alloys in both low- and high-pressure cast form and the introduction of improved high-purity versions of the alloys. Table 4 lists the critical contaminant limits for magnesium die castings. The iron tolerance for the magnesium-aluminum alloys depends on the manganese present, a fact suggested many years ago, but only recently proved. For AZ91 with a manganese content of 0.15%, this means that the iron tolerance would be 0.0048% (0.032 × 0.15%) (Ref 4).

It should also be noted that the nickel tolerance depends strongly on the cast form, which influences grain size, with the low-pressure cast alloys showing just a 10 ppm tolerance for nickel in the as-cast (F) temper. Therefore, alloys intended for low-pressure cast applications should be of the lowest possible nickel level. The low tolerance limits for the contaminants in AM60 alloy when compared to AZ91 alloy can be related to the absence of zinc. Zinc is thought to improve the tolerance of magnesium-aluminum alloys for all three contaminants, but it is limited to 1 to 3%

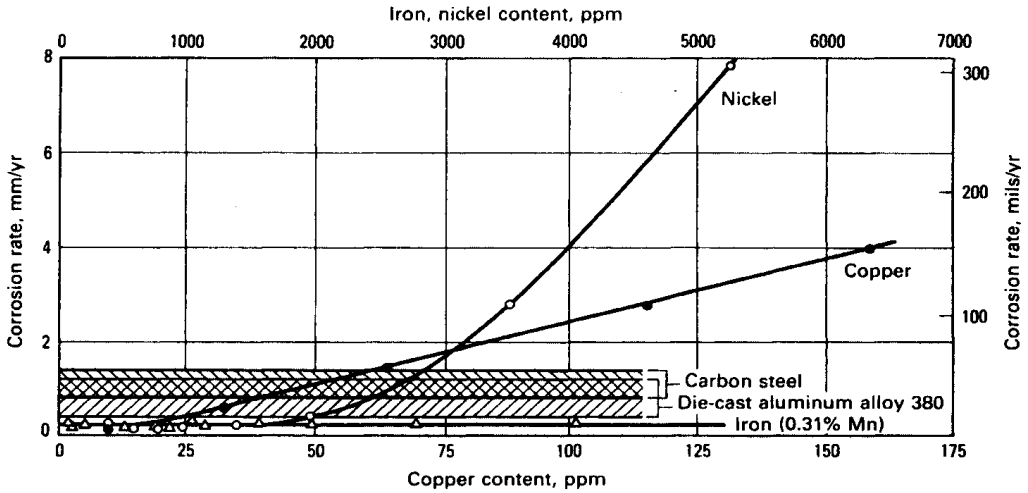


Fig. 3 Effect of nickel and copper contamination on the salt-spray-corrosion performance of die-cast AZ91 alloy. Source: Ref 3

Table 4 Contaminant tolerances and manganese limits for magnesium die castings

Alloy	Critical contaminant limit (max), %			Mn limit, %
	Cu	Ni	Fe	
AM50A	0.010	0.002	0.004(a)	0.26–0.6(a)
AM60A	0.35	0.03	…	0.13–0.6
AM60B	0.10	0.002	0.005(a)	0.24–0.6(a)
AS41A	0.06	0.03	…	0.20–0.50
AS41B	0.02	0.002	0.0035	0.35–0.7
AZ91A	0.10	0.03	0.30(b)	0.13–0.50
AZ91B	0.35	0.03	0.3(b)	0.13–0.50
AZ91D	0.30	0.002	0.005(a)	0.15–0.50(b)

Per ASTM B 94. (a) In alloys AS41B, AM50A, AM60B, and AZ91D, if either the minimum manganese limit or the maximum iron limit is not met, then the iron/manganese ratio shall not exceed 0.010, 0.015, 0.021, and 0.032, respectively. (b) Not specified, but included in the limits for "other metals"

because of its detrimental effects on microshrinkage porosity and its accelerating effect on corrosion above 3%.

For the rare earth, thorium, and zinc alloys containing zirconium, the normal saltwater corrosion resistance is only moderately reduced when compared to high-purity magnesium-aluminum alloys—0.5 to 0.76 mm/year (20 to 30 mils/year) as opposed to less than 0.25 mm/year (10 mils/year) in 5% salt spray—but contaminants must again be controlled. The zirconium alloying element is effective in this situation because it serves as a strong grain refiner for magnesium alloys, and it precipitates the iron contaminant from the alloys before casting. However, if alloys containing more than 0.5 to 0.7% Ag or more than 2.7 to 3% Zn are used, a sacrifice in corrosion resistance should be expected (Fig. 2). Nevertheless, when properly finished, these alloys provide excellent service in harsh environments.

Effects of Residual Elements on Heat-Treated or Grain-Refined Alloys. Heating or aging temperature also exerts an effect on salt-spray corrosion rate of diecast commercial magnesium-aluminum alloys, and this is an interactive effect with contaminant levels. Figure 4 shows the adverse effect of aging temperature on salt-spray corrosion rate. Alloys having higher contents of residual elements (iron, nickel, and copper) were much more adversely affected by temperature exposure.

Using controlled-purity AZ91 alloy cast in both high- and low-pressure forms, the contaminant tolerance limits have been defined as summarized in Table 5 for the as-cast (F), the solution-treated (T4, held 16 h at 410 °C, or 775 °F, and quenched), and the solution treated and aged (T6, held 16 h at 410 °C, or 775 °F, quenched, and aged 4 h at 215 °C, or 420 °F).

Table 6 compares the average 5% salt-spray corrosion performance of sand-cast samples produced in a standard AZ91C and a high-purity AZ91E composition. The alloys were cast with and without standard grain-refining practices used to evaluate physical and compositional

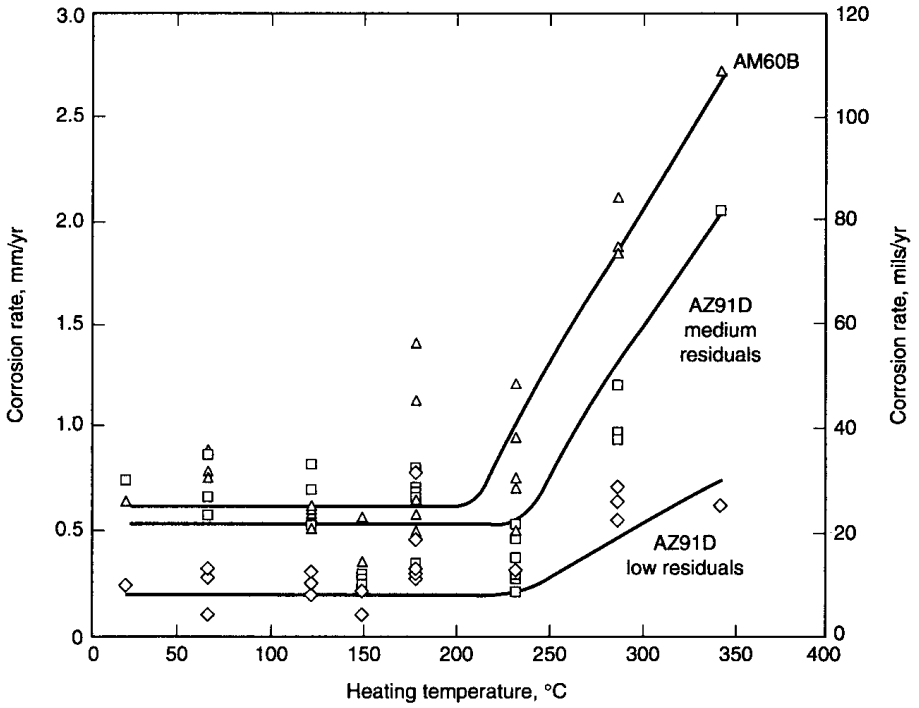


Fig. 4 Effect of heating temperature on corrosion rate of die-cast AZ91D and AM60B in salt-spray test for 10 days according to ASTM B 117. Data are for test specimens that were heated for 0.5 to 36 h. Source: Ref 5

effects. The cast samples were then tested in the F, T4, T6, and T5 (aged 4 h at 215 °C, or 420 °F) tempers. With the high-iron-containing AZ91C, none of the variations tested significantly affected the poor corrosion performance resulting from an iron level 2 to 3 times the alloy tolerance. With the high-purity alloy, however, the T5 and T6 tempers consistently gave salt-spray corrosion rates under 0.25 mm/year (10 mils/year), whereas the as-cast and solution-treated samples exhibited an inverse response to grain size and/or the grain-refining agents.

Table 5 Contaminant tolerance limits versus temper and cast form for AZ91 alloy

High-pressure die cast, 5–10 mm average grain size; low-pressure cast, 100–200 mm average grain size

Contaminant, %	Critical contaminant limit (a)			
	High pressure, F	Low pressure		
		F	T4	T6
Iron	0.032 Mn	0.032 Mn	0.035 Mn	0.046 Mn
Nickel	0.0050	0.0010	0.001	0.001
Copper	0.040	0.040	<0.010	0.040

(a) Tolerance limits expressed in wt% except for iron, which is expressed as the fraction of the manganese content (for example, the iron tolerance of 0.2% Mn alloy = 0.0064% Fe in F temper)

Table 6 Typical corrosion rates versus temper and grain size for two magnesium alloys with varying iron contents

ASTM B 117 salt-spray test

Alloy	Grain size, μm	Mn, %	Fe(a)	Temper and corrosion rate							
				F		T4		T6		T5	
				mm/yr	mil/yr	mm/yr	mil/yr	mm/yr	mils/yr	mm/yr	mil/yr
AZ91C (untreated)	187	0.18	0.087	18	700	15	600	15	600	…	…
AZ91C (degassed and grain refined)	66	0.16	0.099	17	690	18	700	15	600	…	…
AZ91E(b) (untreated)	146	0.23	0.008	0.64	25	4	160	0.15	6	0.12	5
AZ91E (degassed and grain refined)	78	0.26	0.008	2.2	90	1.7	70	0.12	5	0.12	5
AZ91E (untreated)	160	0.33	0.004	0.35	14	3	120	0.22	9	0.12	5
AZ91E (degassed and grain refined)	73	0.35	0.004	0.72	29	0.82	33	0.1	4	0.1	4

(a) Iron is expressed as a fraction of analyzed manganese content. (b) AZ91E alloy pending ASTM approval. Source: Ref 6–8

Effects of Alloying on Stress-Corrosion Cracking Behavior

Commercially pure magnesium is not susceptible to stress-corrosion cracking (SCC) when loaded up to its yield strength in atmospheric and most aqueous environments. The only reports of SCC of commercially pure magnesium have emanated from laboratory tests in which specimens were immersed in very severe corrosive solutions.

Aluminum-containing magnesium alloys have the highest SCC susceptibility, with the sensitivity generally increasing with increasing aluminum content, as illustrated in Fig. 5. An aluminum content above a threshold of 0.15 to 2.5% is reportedly required to induce SCC behavior, with the effect peaking at approximately 6% Al. In contrast, a study of magnesium-

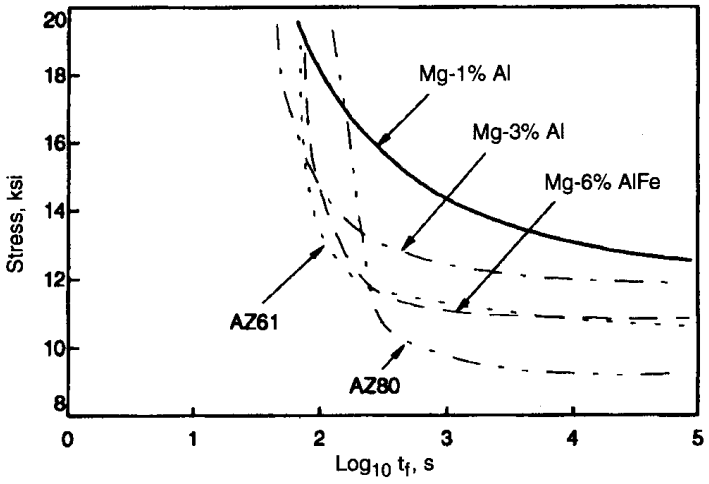


Fig. 5 Stress versus time to failure (t_f) for magnesium-aluminum alloys in aqueous 40 g/L NaCl + 40 g/L Na_2CrO_4. Source: Ref 9

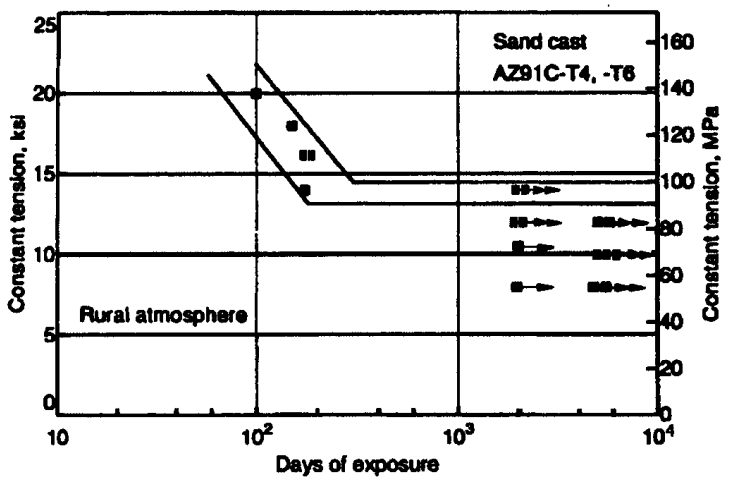


Fig. 6 Stress corrosion of sand-cast AZ91C (T4 and T6) in rural atmosphere. Source: Ref 10

aluminum die-casting alloys revealed no significant increase in SCC susceptibility between 4 and 9% Al.

Zinc also induces SCC susceptibility in magnesium alloys, so it is not surprising that the aluminum- and zinc-bearing AZ alloys, which are the most commonly used magnesium alloys, have the greatest susceptibility to SCC. Alloys with higher aluminum content, such as AZ61, AZ80, and AZ91, can be very susceptible to SCC in atmospheric and more severe environments.

For example, Fig. 6 and 7 show that AZ91 is quite susceptible to SCC in rural atmosphere, and very susceptible when partially immersed in

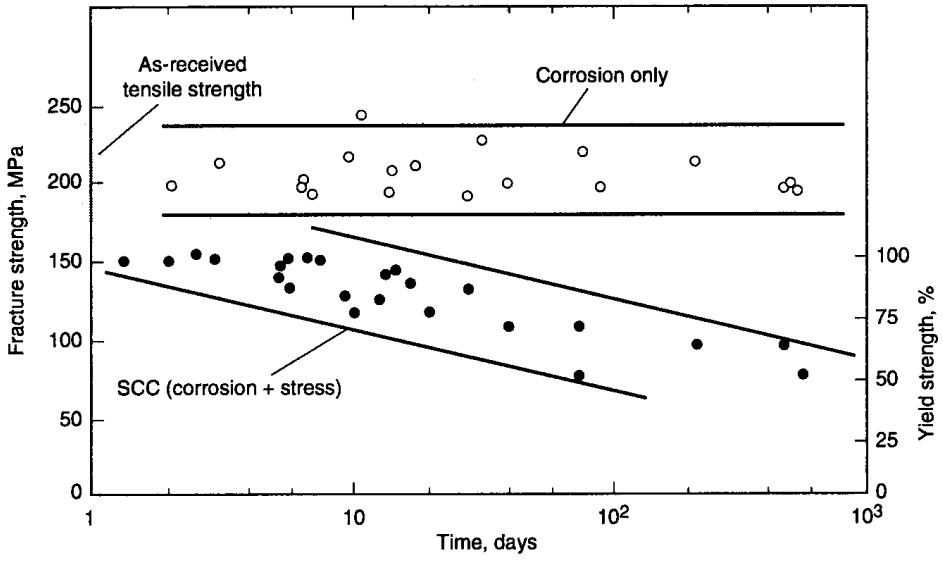


Fig. 7 Stress-corrosion cracking behavior of AZ91 in distilled water. Stress-corrosion cracking tests on standard ASTM B 577 die-cast tensile specimens were conducted on a dead-weight tension-loading apparatus. Source: Ref 11

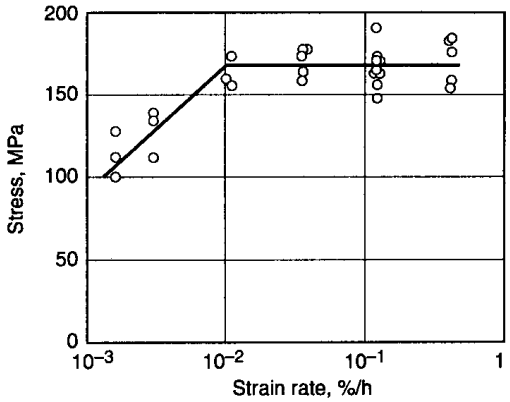


Fig. 8 Stress at fracture versus strain rate in slow-strain-rate SCC tests of AZ91. The specimens were partially immersed in distilled water. Strain was controlled with a linear ramp to maintain the desired strain rate. Source: Ref 11

distilled water, with fractures occurring at stresses at least 50% of the yield strength. The SCC fractures plotted in Fig. 7 generally occurred at, or very close to, the tip of the meniscus formed at the water-air interface. Figure 8 shows the stress at fracture versus strain rate in the slow-strain-rate SCC tests. Fracture stress during these tests was a function of strain rate when it was below 0.01%/h, indicating the effects of a rate-dependent SCC interaction. The mechanism may be a cathodically driven, film-rupture SCC process. The effect of immersion in an electrolytic solution ($NaCl + Na_2CrO_4$) is shown in Fig. 9.

In contrast to the magnesium alloys that contain higher amounts of aluminum, lower-aluminum AZ31 is generally more resistant. However, it too can suffer SCC under certain conditions (Fig. 10).

Magnesium-zinc alloys that are alloyed with either zirconium or rare earths, but not with aluminum, such as ZK60 and ZE10, have intermediate

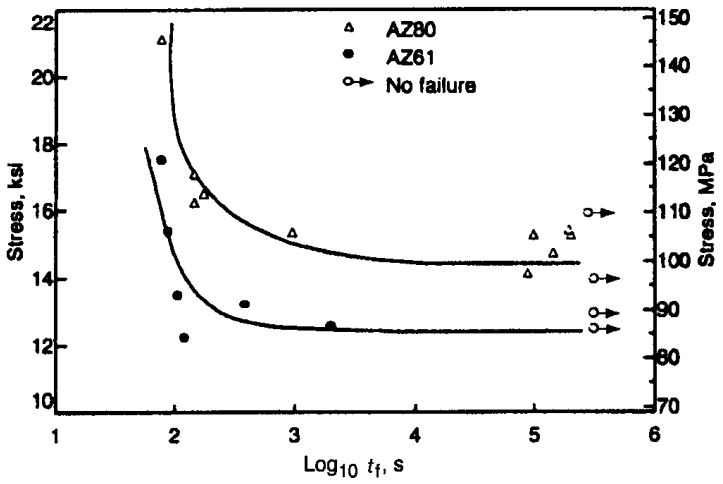


Fig. 9 Stress versus time to failure (t_f) for the two-phase alloys AZ80 (Mg-8.5Al-0.5Zn) and AZ61 (Mg-6Al-1Zn) in aqueous 40 g/L NaCl + 40 g/L Na_2CrO_4

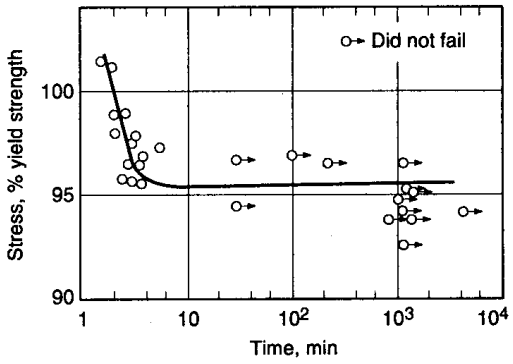


Fig. 10 Stress-corrosion cracking behavior of AZ31 in an aqueous solution of 3.5% NaCl + 2% K_2CrO_4. Source: Ref 12

SCC resistance (Fig. 11). SCC has not been a serious problem in some applications. However, SCC can still occur in atmospheric environments at stresses as low as 50% of the yield strength, although life is significantly longer than for Mg-Al-Zn alloys.

Magnesium alloys that contain neither aluminum nor zinc are the most SCC resistant. Magnesium-manganese alloys, such as M1, are among the alloys with the highest resistance to SCC, and they are generally considered to be immune when loaded up to the yield strength in normal environments. In fact, SCC of Mg-Mn alloys has been reported only in tests involving stresses higher than the yield strength and/or exposure to very severe laboratory environments. Alloy QE22 is also resistant to SCC, exhibiting SCC thresholds at approximately 70 to 80% of the yield strength in rural-atmosphere tests.

Magnesium-lithium alloys are of commercial interest because of their higher stiffness and lower density compared with other magnesium alloys. Tests in humid air have resulted in SCC failures of Mg-Li-Al alloys, but

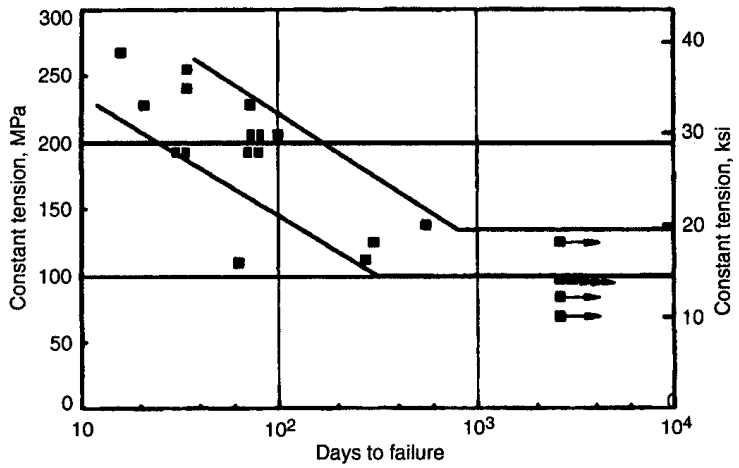


Fig. 11 Stress corrosion of ZK60A-T5 extrusion in rural atmosphere. Source: Ref 10

SCC did not occur during testing of magnesium-lithium alloys strengthened with zinc, silicon, and/or silver instead of aluminum.

Iron is found in commercial magnesium alloys in small, residual amounts and, although iron is known to reduce general corrosion resistance, its effect on SCC remains unclear. Early investigations indicated that iron was associated with decreased SCC resistance in Mg-Al-Zn alloy. Later studies, however, found that iron had minimal or no effect.

The effects of other alloying elements have had limited study. It has been reported that additions of cadmium increase SCC susceptibility, while cerium, tin, lead, copper, nickel, and silicon have no effect. Other researchers, however, have indicated that the addition of cerium or tin to Mg-Al-Mn alloys somewhat increases SCC susceptibility.

Alloying Effects on Physical Properties

The physical properties of magnesium are, of course, affected by the amount of each alloying constituent added to it. In many instances, the effect is more or less directly proportional to the amount added, up to the limits of solid solubility at the temperature at which the property is measured. The processing and property effects of the individual alloying elements, however, are more important in most structural applications than the physical properties. Figure 12 shows the effects of various alloying elements on the electrical resistivity of magnesium.

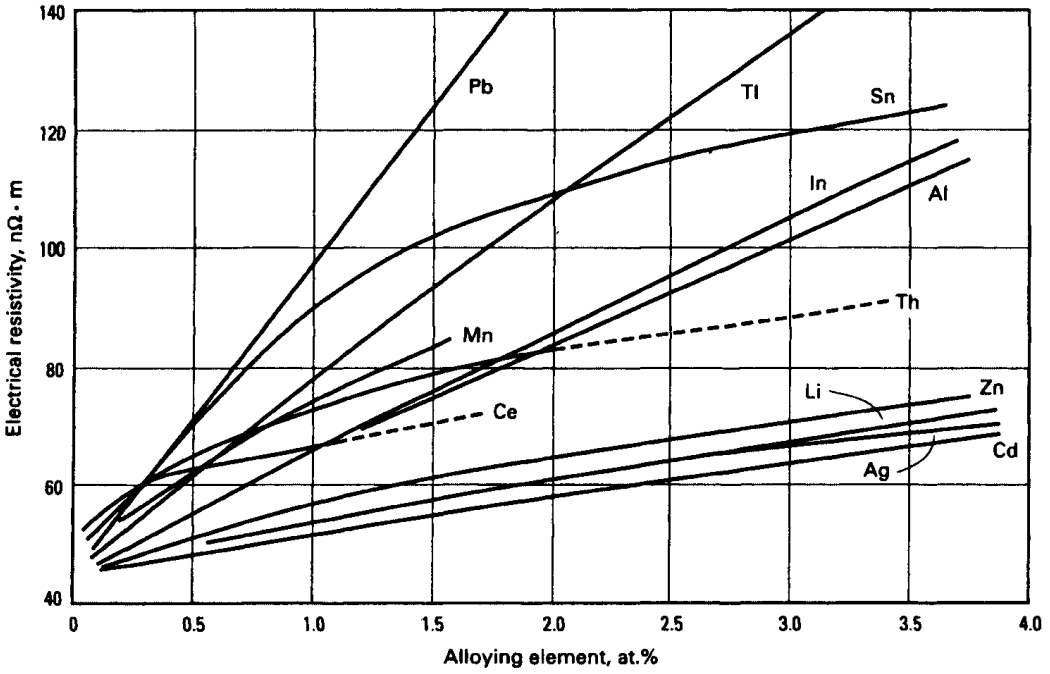


Fig. 12 Effect of alloying additions on the electrical resistivity of magnesium. Source: Ref 13, 14

Effects of Alloying on Processing

This section reviews the effects of alloying on weldability, formability, and machinability. Alloying additions that influence castability were discussed earlier in the section "Effects of Alloying Elements on Properties and Processing."

Weldability. Table 7 lists some magnesium alloys that are weldable, along with their respective weldability ratings based on a scale of A (excellent) to D (limited). This rating is based largely on freedom from susceptibility to cracking, and to some extent on joint efficiency. Under optimal welding conditions, including favorable joint design, joint efficiencies of 60 to 100% can be obtained for virtually all of the magnesium alloys. Alloys rated A in Table 7 are likely to have high joint efficiency ratings.

In the Mg-Al-Zn alloys (AZ31B, AZ61A, AZ63A, AZ80A, AZ81A, AZ91C, and AZ92A), aluminum content up to about 10% aids weldability by helping to refine the grain structure, while zinc content of more than 1% increases hot shortness, which may cause weld cracking. Alloys with high zinc content (ZH62A, ZK51A, ZK60A, and ZK61A) are highly susceptible to cracking and have poorer weldability.

Table 7 Relative arc weldability of magnesium alloys

A, excellent; B, good; C, fair; D, limited weldability

Alloy	Rating
Casting alloys	
AM100A	B+
AZ63A	C
AZ81A	B+
AZ91C	B+
AZ92A	B
EK30A	B
EK41A	B
EQ21	B
EZ33A	A
K1A	A
QE22A	B
ZE41A	B
WE43	B–
WE54	B–
ZC63	B–
ZK51A	D
ZK61A	D
Wrought alloys	
AZ10A	A
AZ31B, C	A
AZ61A	B
AZ80A	B
M1A	A
ZE10A	A
ZK21A	B
ZK60A	D

Welds in magnesium alloys are characterized by a fine grain size averaging less than 0.25 mm (0.01 in.). Magnesium alloys containing more than 1.5% Al are susceptible to stress corrosion, and residual welding stresses must be relieved.

Formability. Magnesium alloys are readily formed at elevated temperatures. Alloying does not play a significant role in terms of formability.

Machinability. There are no significant differences in machinability among magnesium alloys. Therefore, a specific magnesium alloy rarely, if ever, is selected in place of another magnesium alloy solely on the basis of machinability.

REFERENCES

1. D.L. Hawke, J.E. Hillis, M. Pekguleryuz, and I. Nakatsugawa, Corrosion Behavior, *ASM Specialty Handbook*: *Magnesium and Magnesium Alloys,* M.M. Avedesian and H. Baker, Ed., ASM International, 1999, p 194–210
2. J.D. Hanawalt, C.E. Nelson, and J.A. Peloubet, Corrosion Studies of Magnesium and Its Alloys, *Trans. AIME,* Vol 147, 1942, p 273–299
3. J.E. Hillis and K.N. Reichek, Paper 870288, Society of Automotive Engineers, 1986
4. I. Lunder, T.K. Aune, and K. Nisancioglu, Paper 382, presented at Corrosion/85 Conference, National Association of Corrosion Engineers, 1985
5. C. Suman, Paper 900794, Society of Automotive Engineers, 1990
6. K.N. Reichek, K.J. Clark, and J.E. Hillis, Paper 850417, Society of Automotive Engineers, 1985
7. The Dow Chemical Company, unpublished research
8. E.F. Emley, *Principles of Magnesium Technology,* Pergamon Press, 1966
9. J.A. Beavers, G.H. Koch, and W.E. Berry, "Corrosion of Metals in Marine Environments," Metals and Ceramics Information Center, Battelle Columbus Laboratories, July 1986
10. R.S. Busk, *Magnesium Products Design,* Marcel Dekker, 1987
11. W. Miller, *Mater. Res. Symp. Proc.,* Vol 125, 1988, p 253
12. H.L. Logan, What We Don't Know about Stress Corrosion Cracking, *The Coupling of Basic and Applied Corrosion Research—A Dialogue,* National Association of Corrosion Engineers, 1969, p 57–62
13. A. Beck, *The Technology of Magnesium and Its Alloys,* F.A. Hughes and Company, Ltd., 1943, p 122
14. E.J. Salkovitz, A.J. Schindler, and F.W. Kammer, *Phys. Rev.,* Vol 105, 1967, p 855

SELECTED REFERENCES

- *ASM Specialty Handbook*: *Magnesium and Magnesium Alloys,* M.M. Avedesian and H. Baker, Ed., ASM International, 1999
- I.J. Polmear, *Magnesium Alloys and Applications,* Materials Science and Technology, The Institute of Materials, London, 1994
- G.V. Raynor, *The Physical Metallurgy of Magnesium and Its Alloys,* Pergamon Press, 1959
- C.S. Roberts, *Magnesium and Its Alloys,* John Wiley & Sons, 1960

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Copper and Copper Alloys

Introduction and Overview

Characteristics and Applications. Copper and copper alloys form one of the major groups of commercial metals, ranking third behind only iron/steel and aluminum in production and consumption. They are widely used because of their excellent electrical and thermal conductivities, outstanding resistance to corrosion, ease of fabrication, and good strength and fatigue resistance. They are generally nonmagnetic. They can be readily soldered and brazed, and many coppers and copper alloys can be welded by various gas, arc, and resistance methods. For decorative parts, standard alloys having specific colors are readily available. Copper alloys can be polished and buffed to almost any desired texture and luster. They can be plated, coated with organic substances, or chemically colored to further extend the variety of available finishes.

Pure copper is used extensively for cables and wires, electrical contacts, and a wide variety of other parts that are required to pass electrical current. Coppers and certain brasses, bronzes, and cupronickels are used extensively for automobile radiators, heat exchangers, home heating systems, panels for absorbing solar energy, and various other applications requiring rapid conduction of heat across or along a metal section. Because of their outstanding ability to resist corrosion, coppers, brasses, some bronzes, and cupronickels are used for pipes, valves, and fittings in systems carrying potable water, process water, or other aqueous fluids.

In all classes of copper alloys, certain alloy compositions for wrought products have counterparts among the cast alloys; this enables the designer to make an initial alloy selection before deciding on the manufacturing process. Most wrought alloys are available in various cold-worked conditions, and the room-temperature strengths and fatigue resistances of these alloys depend on the amount of cold work as well as the alloy content.

Typical applications of cold-worked wrought alloys (cold-worked tempers) include springs; fasteners, hardware, small gears, cams, electrical contacts, and electronic components, such as connectors and lead frames.

Certain types of parts, most notably plumbing fittings and valves, are produced by hot forging simply because no other fabrication process can produce the required shapes and properties as economically. Copper alloys containing 1 to 6% Pb are free-machining grades. These alloys are widely used for machined parts, especially those produced in screw machines.

Alloy Designations. Under the Unified Numbering Systems (UNS), copper and copper alloys are designated by five-digit numbers preceded by the letter "C." The format is essentially the Copper Development Association's former three-digit system expanded to accommodate new compositions. Using the UNS system, numbers ranging from C10000 through C79999 denote wrought alloys; numbers ranging from C80000 through C99999 denote cast alloys. As shown in Table 1, within these two categories, the compositions are grouped into distinct families of copper and copper alloys, including the six major branches—coppers, high-copper

Table 1 Generic classification of coppers and copper alloys

Generic name	UNS No.	Composition
Wrought alloys		
Coppers (a)	C10100–C15815	> 99% Cu
High-copper alloys (b)	C16200–C19900	> 96% Cu
Brasses	C20100–28000	Cu-Zn
Leaded brasses	C31200–C38500	Cu-Zn-Pb
Tin brasses	C40400–C48600	Cu-Zn-Sn-Pb
Phosphor bronzes	C50100–C52480	Cu-Sn-P
Leaded phosphor bronzes	C53400–C54400	Cu-Sn-Pb-P
Copper-phosphorus and copper-silver-phosphorus alloys (c)	C55180–C55284	Cu-P-Ag
Aluminum bronzes	C60800–C64210	Cu-Al-Ni-Fe-Si-Sn
Silicon bronzes	C64700–C66100	Cu-Si-Sn
Other copper-zinc alloys	C66300–C69710	Cu-Zn-Mn-Fe-Sn-Al-Si-Cu
Copper nickels	C70100–C72950	Cu-Ni-Fe
Nickel silvers	C73500–C79830	Cu-Ni-Zn
Cast alloys		
Coppers (a)	C80100–C81200	> 99% Cu
High-copper alloys (d)	C81400–C82800	> 94% Cu
Red and leaded red brasses	C83300–C83810	Cu-Sn-Zn-Pb (82-94% Cu)
Semi-red and leaded semi-red brasses	C84200–84800	Cu-Sn-Zn-Pb (75-82% Cu)
Yellow and leaded yellow brasses	C85200–C85800	Cu-Zn-Pb
Manganese bronzes and leaded manganese bronzes (e)	C86100–C86800	Cu-Zn-Mn-Fe-Pb
Silicon brasses/bronzes	C87300–C87800	Cu-Zn-Si
Copper-bismuth and copper-bismuth-selenium alloys	C89320–C89940	Cu-Sn-Bi-Se
Tin bronzes	C90200–C91700	Cu-Sn-Zn
Leaded tin bronzes	C92200–94500	Cu-Sn-Zn-Pb
Nickel-tin bronzes	C94700–C94900	Cu-Ni-Sn-Zn-Pb
Aluminum bronzes	C95200–C95900	Cu-Al-Fe-Ni
Copper nickels	C96200–C96950	Cu-Ni-Fe
Nickel silvers	C97300–C97800	Cu-Ni-Zn-Pb-Sn
Leaded coppers	C98200–C98840	Cu-Pb
Special alloys	C99300–C99750	Cu-Zn-Mn-Al-Fe-Co-Sn-Pb

(a) Metals which have a designated Cu content of 99.3% or higher. (b) For wrought products, those alloys with designated Cu contents less than 99.3%, but more than 96% which do not fall into any other copper alloy group. (c) Brazing filler metal alloys. (d) Cast high-copper alloys have designated Cu contents in excess of 94%, to which Ag may be added for special properties. (e) Also referred to as high-strength and leaded high-strength yellow brasses

alloys, brasses, bronzes, copper nickels, and nickel silvers. Alloys not falling into one of these six branches are classified as "Other Copper-Zinc Alloys" (wrought compositions) or "Special Alloys" (cast compositions).

Wrought Copper and Copper Alloy Families

The most common way to catalog copper and copper alloys is to divide them into six families: coppers, high-copper (or dilute) alloys, brasses, bronzes, copper-nickels, and nickel silvers. The first family, the coppers, is essentially commercially pure copper, which ordinarily is soft and ductile and contains less than about 0.7% total impurities. The high-copper alloys contain small amounts of various alloying elements, such as beryllium, cadmium, chromium, and iron, each having less than 8 at.% solid solubility; these elements modify one or more of the basic properties of copper. Each of the remaining families contains one of five major alloying elements as its primary alloying ingredient:

Family	Alloying element	Solid solubility, at.%(a)
Brasses	Zinc	37
Phosphor bronzes	Tin	9
Aluminum bronzes	Aluminum	19
Silicon bronzes	Silicon	8
Copper-nickels, nickel silvers	Nickel	100

(a) At 20 °C (70 °F)

The purpose of adding alloying elements to copper is to optimize the strength, ductility (formability), and thermal stability, without inducing unacceptable loss in fabricability, electrical/thermal conductivity, or corrosion resistance. Copper alloys show excellent hot and cold ductility, although usually not to the same degree as the unalloyed parent metal. Even alloys with large amounts of solution-hardening elements—zinc, aluminum, tin, and silicon—that show rapid work hardening are readily commercially processed beyond 50% cold work before a softening anneal is required to permit additional processing. The amount of cold working and the annealing parameters must be balanced to control grain size and crystallographic texturing. These two parameters are controlled to provide annealed strip products at finish gage that have the formability needed in the severe forming and deep drawing commonly done in commercial production of copper, brass, and other copper alloy hardware and cylindrical tubular products.

Tables 2 and 3 list physical and mechanical properties of representative wrought coppers and copper alloys, as well as their nominal compositions.

Table 2 Physical properties of representative wrought copper alloys

UNS No.	Nominal composition, %	Density, g/cm^3 (lb/in.^{3})	Coefficient of thermal expansion 10^{-6}/ °C (10^{-6} °F), 20–300 °C (70–570 °F)	Thermal conductivity W/m · K, at 293 K (Btu/ft · h · °F at 70 °F	Electrical conductivity, %IACS, at 20 °C (70 °F)	Specific heat, cal/g · °C at 20 °C (Btu/lb · °F, at 70 °F)
Coppers (C10100–C15999)						
C10200	99.95 Cu	8.94 (0.323)	17.7 (9.8)	391 (226)	101	0.092
C11000	99.9 Cu	8.94 (0.323)	17.7 (9.8)	391 (226)	101	0.092
C12200	99.90 Cu, 0.02 P	8.94 (0.323)	17.7 (9.8)	339 (196)	85	0.092
C15760	Cu, 0.6 Al, 0.57 O	8.80 (0.318)	16.6 (9.2)	322 (186)	78	0.092
High-copper alloys (C16200–C19199)						
C17200	98.1 Cu, 1.9 Be, 0.2 (Ni+Co) min.	8.25 (0.298)	17.8 (9.9)	107 (62)	22	0.10
C17410	Cu, 0.5 Co, 0.3 Be	8.80 (0.318)	17.7 (9.8)	208 (120)	45	0.08
C18100	Cu, 0.04 Mg, 0.15 Zr, 0.8 Cr	8.83 (0.319)	19.4 (10.7)	324 (187)	80	0.094
C19400	97.4 Cu, 2.4 Fe, 0.13 Zn, 0.04 P	8.91 (0.322)	17.9 (9.2)	262 (150)	65	0.092
C19500	97 Cu, 1.5 Fe, 0.6 Sn, 0.1 P, 0.8 Co	8.92 (0.322)	16.9 (9.4)	197 (115)	50	0.092
Copper-zinc alloys (brasses, C21000–C28000)						
C23000	85 Cu, 15 Zn	8.74 (0.316)	18.7 (10.4)	159 (92)	37	0.09
C26000	70 Cu, 30 Zn	8.52 (0.308)	20.1 (11.1)	121 (70)	28	0.09
C28000	60 Cu, 40 Zn	8.39 (0.303)	21.0 (11.6)	123 (71)	28	0.09
Copper-zinc-lead alloys (leaded brasses, C31200–C38500)						
C34500	63.5 Cu, 34.5 Zn, 2 Pb	8.49 (0.307)	20.3 (11.3)	116 (67)	26	0.09
C35300	61.5 Cu, 36.5 Zn, 2.8 Pb	8.47 (0.306)	20.4 (11.3)	116 (67)	26	0.09
C36000	61.5 Cu, 35.4 Zn, 3.1 Pb	8.50 (0.307)	20.6 (11.4)	116 (67)	26	0.09
C37700	59.5 Cu, 38 Zn, 2 Pb	8.44 (0.305)	20.8 (11.5)	119 (69)	27	0.09
Copper-zinc-tin alloys (tin brasses, C40400–C48600)						
C42500	88.5 Cu, 9.5 Zn, 2 Sn, 0.2 P	8.78 (0.317)	18.4 (10.2)	121 (69)	28	0.09
C44400	71 Cu, 28 Zn, 1 Sn, 0.02 Sb min.	8.53 (0.308)	20.2 (11.2)	109 (64)	28	0.09
C46400	60 Cu, 39.2 Zn, 0.8 Sn	8.41 (0.304)	21.3 (11.8)	116 (67)	26	0.09
Copper-tin-phosphorus alloys (phosphor bronzes, C50100–C54200)						
C50500	98.7 Cu, 1.3 Sn	8.89 (0.321)	17.8 (9.9)	87 (50)	48	0.09
C51000	94.8 Cu, 5 Sn, 0.2 P	8.86 (0.320)	17.9 (9.9)	69 (40)	15	0.09
C51100	95.6 Cu, 4.2 Sn, 0.2 P	8.86 (0.320)	17.8 (9.9)	84 (48.4)	20	0.09
Copper-tin-lead-phosphorus alloys (leaded phosphor bronzes, C53400–C53500)						
C54400	88 Cu, 4 Sn, 4 Pb, 4 Zn, 0.5 P max.	8.88 (0.321)	17.4 (9.6)	87 (50)	19	0.09
Copper-aluminum alloys (aluminum bronzes, C60800–C64210)						
C61300	90.3 Cu, 6.8 Al, 2.5 Fe, 0.35 Sn	7.94 (0.287)	16.3 (9.0)	55 (32)	12	0.09
C63000	82 Cu, 10 Al, 5 (Ni + Co), 3 Fe	7.58 (0.274)	16.3 (9.0)	39 (22)	7	0.09
C63020	74.5 Cu min., 10.5 Al, 5 Ni, 4.75 Fe	7.45 (0.269)	16.3 (9.0)	47 (27)	6	...
C63800	95 Cu, 2.8 Al, 1.8 Si, 0.4 Co	8.28 (0.299)	17.1 (9.5)	41 (23)	10	0.09
Copper-silicon alloys (silicon bronzes, C64700–C66100)						
C65500	97 Cu, 3 Si	8.52 (0.308)	18.0 (10.0)	36 (21)	7	0.09
Other copper-zinc alloys (C66400–C69710)						
C67500	58.5 Cu, 39 Zn, 1.4 Fe, 1 Sn, 0.1 Mn	8.36 (0.302)	21.3 (11.8)	105 (61)	24	0.09
C69400	81.5 Cu, 14.5 Zn, 4 Si	8.19 (0.296)	20.3 (11.2)	26 (15)	6	0.09
Copper-nickel alloys (copper nickels, C70100–C72950)						
C70600	88.6 Cu, 10 Ni, 1.4 Fe	8.94 (0.323)	17.1 (9.5)	45 (26)	9	0.09
C71500	69.5 Cu, 30 Ni, 0.5 Fe	8.94 (0.323)	16.2 (9.0)	29 (17)	4	0.09
C72200	82.2 Cu, 16.5 (Ni + Co), 0.8 Fe, 0.5 Cr	8.94 (0.323)	15.8 (8.8)	34 (20)	6.5	0.094
Copper-zinc-nickel alloys (nickel silvers, C73500–C79800)						
C74500	65 Cu, 25 Zn, 10 Ni	8.69 (0.314)	16.4 (9.1)	45 (26)	9	0.09
C77000	55 Cu, 27 Zn, 18 Ni	8.70 (0.314)	16.7 (9.3)	29 (17)	5.5	0.09

Table 3 Nominal mechanical properties of representative wrought copper alloys

UNS No.	Product form and section size, mm (in.)/ condition, % cold work (c.w.)/temper	Tensile strength, MPa (ksi)	Yield strength, MPa (ksi) 0.2% offset	Yield strength, MPa (ksi) 0.5% extension	Elongation, in 51 mm (2 in.), %	Hardness	Fatigue strength, 10^8 cycles, MPa (ksi)	Elastic modulus, GPa (10^6 psi)
Coppers (C10100–C15999)								
C10200	Strip, 1 (0.04)/spring/H08	379 (55)	…	345 (50)	4	60 HRB	96.5 (14)	117 (17)
C11000	Strip, 1 (0.04/spring/H08	379 (55)	…	345 (50)	4	60 HRB	96.5 (14)	117 (17)
C12200	Tube/hard drawn, c.w. 40%/H08	379 (55)	…	345 (50)	8	60 HRB	131 (19)(a)	117 (17)
C15760	Rod, 7 (0.275)/c.w. 74%	621 (90)	600 (87)	…	14	14 HRB	248 (36)(b)	117 (17)
High-copper alloys (C16200–C19199)								
C17200	Rod, <9.5 (<0.375)/c.w. & aged/TH04	1485 (215)	1345 (195)	…	5	44 HRC	380 (55)	128 (18.5)
C17410	Rod, <9.5 (<0.375)/c.w. & aged/TH04	825 (120)	760 (110)	…	8	102 HRB	…	131 (19)
C18100	Strip, 1 (0.04)/c.w. 40% & aged/TH04	496 (72)	455 (66)	…	10	…		125 (18.2)
C19400	Strip, 1 (0.04)/extra spring/H10	524 (76)	503 (73)	…	2	77 HRB	141 (20.5)	121 (17.5)
C19500	Strip, 1 (0.04)/spring, c.w. & aged/TD08	641 (93)	621 (90)	…	4	…	200 (29)	119 (17.3)
Copper-zinc alloys (brasses, C21000–C28000)								
C23000	Strip, 1 (0.04)/half hard/H02	393 (57)	…	338 (49)	12	65 HRB	…	117 (17)
C26000	Strip, 1 (0.04)/half hard/H02	427 (62)	…	359 (52)	25	70 HRB	124 (128)	110 (16)
C28000	Rod, 25 (1)/quarter hard/H01	496 (72)	…	345 (50)	25	78 HRB	…	103 (15)
Copper-zinc-lead alloys (leaded brasses, C31200–C38500)								
C34500	Rod, 25 (1)/half hard/H02	483 (70)	…	400 (58)	25	80 HRB	…	…
C35300	Rod, 25 (1)/half hard, c.w. 20%/H02	400 (58)	…	310 (45)	25	75 HRB	…	103 (15)
C36000	Rod, 25 (1)/half hard, c.w. 20%/H02	400 (58)	…	310 (45)	25	78 HRB	…	96.5 (14)
C37700	Rod, 25 (1)/as extruded/M30	359 (52)	…	138 (20)	45	78 HRF	…	…
Copper-zinc-tin alloys (tin brasses, C40400–C48600)								
C42500	Strip, 1 (0.04)/spring/H08	614 (89)	586 (85)	517 (75)	4	92 HRB	…	110 (16)
C44400	Tube, 25 × 1.65 (1 × 0.065)/OS025	365 (53)	…	152 (22)	65	75 HRF	…	110 (16)
C46400	Rod, 25 (1)/half hard, c.w. 20%/H02	517 (75)	…	365 (53)	20	82 HRB	…	103 (15)
Copper-tin-phosphorus alloys (phosphor bronzes, C50100–C54200)								
C50500	Strip, 1 (0.04)/hard/H04	448 (65)	…	345 (50)	8	75 HRB	…	117 (17)
C51000	Strip, 1 (0.04)/spring/H08	690 (100)	…	552 (80)	4	95 HRB	152 (22)	110 (16)
C51100	Strip, 1 (0.04)/spring/H08	679 (98)	655 (90)	552 (80)	3	93 HRB	…	110 (16)
Copper-tin-lead-phosphorus alloys (leaded phosphor bronzes, C53400–C53500)								
C54400	Rod, 25 (1)/hard, c.w. 25%/H04	469 (68)	…	393 (57)	20	80 HRB	…	103 (15)
Copper-aluminum alloys (aluminum bronzes, C60800–C64210)								
C61300	Rod, 25 (1)/hard, c.w. 25%/H04	669 (82)	…	276 (40)	35	90 HRB	…	117 (17)
C63000	Rod, 25 (1)/half hard, c.w. 10%/H02	814 (118)	…	517 (75)	15	98 HRB	262 (38)	121 (17.5)
C63020	Rod, <25 (<1)/quenched & tempered/TQ30	1000 (145)	793 (115)	…	8	29 HRC	352 (51)	124 (18)
C63800	Strip, 1 (0.04)/spring/H08	883 (128)	758 (110)	…	4	101 HRB	241 (35)	115 (16.7)
Copper-silicon alloys (silicon bronzes, C64700–C66100)								
C65500	Rod, 25 (1)/hard, c.w. 36%/H04	634 (92)	…	379 (55)	22	90 HRB	…	103 (15)
Other copper-zinc alloys (C66400–C69710)								
C67500	Rod, 25 (1)/half hard, c.w. 20%/H02	579 (60)	…	414 (60)	19	90 HRB	…	103 (15)
C69400	Rod, 25 (1)/soft anneal/O60	586 (85)	…	296 (43)	25	85 HRB	…	115 (16)
Copper-nickel alloys (copper nickels, C70100–C72950)								
C70600	Tube, 25 × 1.65 (1 × 0.065)/light drawn/H55	414 (60)	…	393 (57)	10	72 HRB	…	124 (18)
C71500	Rod, 25 (1)/half hard, c.w. 20%/H02	517 (75)	…	483 (70)	15	80 HRB	…	152 (22)
C72200	Tube, all sizes/light drawn/H55	483 (70)	455 (66)	…	…	…	…	138 (20)
Copper-zinc-nickel alloys (nickel silvers, C73500–C79800)								
C74500	Strip, 1 (0.04)/extra hard/H06	655 (95)	…	524 (76)	3	92 HRB	…	121 (17.5)
C77000	Wire, 2 (0.08)/spring, c.w. 68%/H08	1000 (145)	…	…	2	…		124 (18)

(a) Rod sample, rotating beam, 20 million cycles. (b) 10 million cycles

Nominal properties of all the standard grades are provided in publications distributed by the Copper Development Association. (CDA), the Canadian Copper and Brass Development Association (CCBDA), and similar organizations around the world. Extensive property data can also be found in the *ASM Specialty Handbook*: *Copper and Copper Alloys.*

Coppers

Wrought coppers (C10100 to C15999) must contain at least 99.3% Cu, but may include residual deoxidizers or minor alloying elements. The normally soft, ductile metals can be strengthened by cold working. However, exposure to elevated temperatures readily anneals the cold-worked microstructure. Coppers are inherently resistant to atmospheric and aqueous corrosion and are relatively insensitive to stress-corrosion cracking (SCC). Their most important characteristic is superior electrical conductivity. They are primarily used for electrical and electronic products.

Oxygen-free coppers (C10100 to C10700) are generally reserved for applications requiring the highest electrical conductivity. Their conductivity is at least 100% IACS (International Annealed Copper Standard, as described in the section "Effects of Impurities and Alloying Elements on Electrical Conductivity.") Electrolytic tough pitch (ETP) copper (C11000) is commonly used for electrical wire and cable, as well as for roofing and architectural trim, while phosphorus-deoxidized copper (C12200) is the standard material for household water tube. Oxygen-free and deoxidized coppers can be welded without danger of embrittlement.

Silver imparts modest annealing resistance to copper without significantly affecting its electrical conductivity. This is why coppers containing residual silver have been used for electrical products that must not soften as a result of exposure to soldering temperatures. Arsenic, cadmium, and zirconium coppers (C14200, C14300, and C15000, respectively) have similar properties. Cadmium also imparts wear resistance, a useful property for sliding electrical contacts. Arsenic improves resistance to both corrosion and high-temperature oxidation; these properties are required for products such as heat-exchanger tubing. Tellurium-bearing coppers (C14500 and C14510) and sulfur-bearing copper (C14700) are free-machining, and are supplied as rods for making high-conductivity parts by screw machining.

Coppers C15715 through C15760 are dispersion-strengthened with aluminum oxide to inhibit softening at elevated temperatures (Fig. 1). The combination of thermal stability and high electrical conductivity is useful in applications such as heavy-duty electrical connectors, vacuum tube components, and resistance welding electrodes.

High-Copper Alloys

As stated earlier, the high-copper or dilute alloys (C16200 to C19900) contain ~94% Cu and small amounts of various alloying elements, such as beryllium, cadmium, chromium, or iron, each having less than 8 at.% solid solubility. Some high-copper alloys also contain up to ~2% of nickel, cobalt, and tin. Because dilute copper alloys retain copper's face-centered cubic (fcc) α structure, their physical properties are similar to those of the pure metal. Alloying generally serves to impart higher strength, thermal stability, or other mechanical attributes, while retaining sufficient electrical conductivity for the intended use. Typical applications for high-copper alloys include electrical/electronic connectors, integrated circuit lead frames, electronic components for severe, automotive, under-the-hood environments, circuit breaker components, and resistance welding equipment.

Age-hardening alloys are also included in the high-copper alloy category. Age hardening produces very high strengths but is limited to those few copper alloys in which the solubility of the alloying element decreases sharply with decreasing temperature. The beryllium-coppers can be considered typical of the age-hardenable copper alloys.

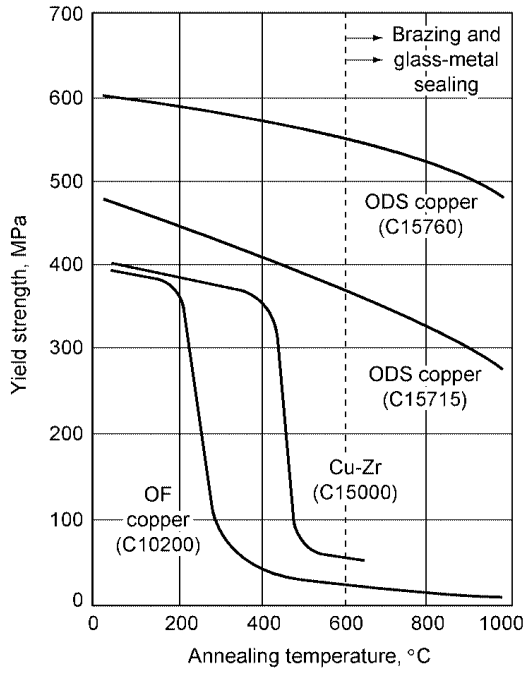


Fig. 1 Softening behavior of dispersion-strengthened copper compared to oxygen-free copper and copper-zirconium alloy

Wrought beryllium-coppers can be precipitation hardened to the highest strength levels attainable in copper-base alloys. There are two commercially significant alloy families employing two ranges of beryllium with additions of cobalt or nickel. The so-called red alloys contain beryllium at levels ranging from approximately 0.2 to 0.7 wt%, with additions of nickel or cobalt totaling 1.4 to 2.7 wt%, depending on the alloy. Alloys C17500 and C17510 are examples of red alloys; these low-beryllium alloys achieve relatively high conductivity (for example, 50% IACS) and retain the pink luster of other low-alloy coppers. The red alloys achieve yield strengths ranging from about 170 to 550 MPa (25 to 80 ksi) with no heat treatment to greater than 895 MPa (130 ksi) after precipitation hardening, depending on degree of cold work.

The more highly beryllium-alloyed systems can contain from 1.6 to 2.0 wt% Be and about 0.25 wt% Co, for example, alloys C17000 and C17200. These alloys frequently are called the gold alloys because of the shiny luster imparted by the substantial amount of beryllium present (~12 at.%). The gold alloys are the high-strength beryllium-coppers because they can attain yield strengths ranging from approximately 205 to 690 MPa (30 to 100 ksi) in the age-hardenable condition to above 1380 MPa (200 ksi) after aging. The conductivity of the gold alloys is lower than that of the red alloy family by virtue of the high beryllium content. However, conductivity ranging from about 20% to higher than 30% IACS is obtained in wrought products depending on the amount of cold work and the heat treatment schedule. For enhanced machinability in rod and wire, lead is added (as in alloy C17300).

Other age-hardenable alloys include C15000; C15100 (zirconium-copper); C18200, C18400, and C18500 (chromium-coppers); C19000 and C19100 (copper-nickel-phosphorus alloys). Some age-hardening alloys have different desirable characteristics, such as high strength combined with better electrical conductivity than the beryllium-coppers.

Brasses

The common brasses (C21000 to C28000) are copper alloys in which zinc is the principal alloying element. Low-zinc alloys, such as gilding (C21000), retain the fcc α-structure, while high-zinc brasses (>39% Zn), such as Muntz metal (C28000), contain mostly the hard body-centered cubic (bcc) β-phase. Brasses containing between 32 and 39% Zn may have a duplex $\alpha + \beta$ structure, which makes them easier to hot work and machine. Increasing zinc content produces stronger and "springier" alloys, at the expense of a moderate decrease in corrosion resistance. Although produced in all product forms, brasses are primarily used as sheet, for stampings (springs, and components of electrical switches and sockets, for example); as tube, for lamp components, drain pipe, and plumbing goods; and as rod, for cold-headed fasteners and forgings.

The corrosion resistance of brass is adequate for service in most atmospheric environments. However, the alloys are subject to dezincification in stagnant, acidic aqueous environments, and may fail by SCC in the presence of moist ammonia, amines, and mercury compounds. Electrical conductivity of brass is reasonably high, ranging from 56% IACS for C21000 to 28% IACS for high-zinc alloys. The cartridge brass (C26000) used in common electrical hardware has a conductivity of 28% IACS. (The conductivities of carbon steel and austenitic stainless steel are about 8.5% and 2.3% IACS, respectively.)

Alloy selection among the brasses is normally made on the basis of formability (C26000 is generally regarded as having optimum forming characteristics), corrosion resistance (which favors low-zinc alloys that have more copper-like properties), or color (which ranges from reddish pink to pale yellow, depending on zinc content). Hot forged products, if they must be lead-free, should be made from duplex alloys, or mostly-β-phase compositions such as alloy C28000.

Leaded (Cu-Zn-Pb) Brasses. The lead in wrought leaded brasses (C31200 to C38500) provides high machinability by acting as a microscopic chip breaker and tool lubricant. Leaded brasses are produced primarily as rod, bar, shapes, and mechanical tubing. The alloys have the same atmospheric corrosion resistance as their unleaded counterparts. Alloy C35330 also contains arsenic to inhibit dezincification.

Free-cutting brass (C36000) containing ~3% Pb is normally the first choice for a copper-base screw-machine material. The alloy's theoretical machinability is more than five times that of leaded low-carbon steel (AISI 12L14), which the brass approaches in terms of mechanical properties and far surpasses in corrosion resistance. With the high scrap value of turnings and no need for expensive electroplating, the total cost of brass screw-machine products can be significantly lower than that of leaded-steel parts. For products that require both machining and cold forming, reduced-lead (~2% Pb) copper alloys such as C34500 or C35300 should be considered.

Alloy C37700 is primarily specified for corrosion-resistant forgings, such as valves and fittings, architectural hardware, and specialty fasteners. A modest lead content (~2% Pb) makes the alloy free-cutting. Like most brasses, it can be finished to a high luster and readily accepts decorative electroplated coatings.

Tin (Cu-Zn-Sn) brasses (C40400 to C48600) are essentially high-zinc brasses containing tin for better corrosion resistance and somewhat higher strength. Tin, like arsenic, antimony, and phosphorus, reduces susceptibility to dezincification. These economical alloys have properties somewhat better than those of the straight Cu-Zn brasses.

Tin brasses have good hot forgeability and reasonably good cold formability. In rod form, they can be cold-headed to produce high-strength

fasteners and similar parts. Leaded alloys C48200 and C48500 are free-machining. Alloy C42500 is supplied as strip for fabricating into electrical connectors, springs, and related products. The admiralty brasses (C44300, C44400, and C44500) and naval brasses (C46400, C46500, and C46600) are used for corrosion-resistant mechanical products. Leaded naval brasses (C48200 and C48500) are supplied in rod form for marine hardware, pump shafts, valve stems, and corrosion-resistant screw-machine parts.

Copper-Zinc Alloys (C66300 to C69710). These miscellaneous Cu-Zn alloys form a subgroup of high-strength brasses in which mechanical properties are enhanced by additions of manganese, iron, tin, aluminum, silicon, and/or cobalt. The alloys display a wide range of properties, but they are best known for their combination of high strength and moderately high corrosion resistance. Alloy C67300 is a familiar bearing material best used at high speeds and medium loads. It machines well and has reasonably good corrosion resistance. Alloy C68800 in strip form is a common electrical connector.

Bronzes

Bronzes are copper alloys in which the major alloying addition is neither zinc nor nickel. Although there are exceptions, bronzes are generally classified by their major alloying element or elements.

Tin (Cu-Sn-P) bronzes (C50100 to C52480), also commonly referred to as phosphor bronzes, have superb spring qualities, high fatigue resistance, excellent formability and solderability, and high corrosion resistance. They are primarily produced as strip for electrical products. Other uses include corrosion-resistant bellows, diaphragms, and spring washers.

Leaded (Cu-Sn-P-Pb) tin or phosphor bronzes (C53400 and C54400) combine high strength and fatigue resistance with good machinability, high wear resistance, and excellent corrosion resistance, especially in seawater. They are frequently used for sleeve bearings, thrust washers, cam followers, and similar parts. Leaded tin bronze bearings resist pounding, but should be used against hardened journals (300 to 400 HB min.), and only in applications where reliable lubrication is assured.

Aluminum (Cu-Al) bronzes (C60800 to C64210) are best known for their combination of high strength and excellent corrosion resistance. Their stress-corrosion fatigue resistance exceeds that of austenitic stainless steels. They are readily weldable, and can be machined or ground, although good lubrication and cooling are essential to obtain fine surface finishes.

Aluminum bronzes containing less than about 9.5% Al are hardened through a combination of solid-solution strengthening, cold work, and the precipitation of an iron-rich phase. Tensile strengths range between 480 and 690 MPa (70 and 100 ksi), depending on composition and temper. High-aluminum alloys (9 to 11% Al), such as C63000 and C63020, can be quenched and tempered much like steels to produce tensile strengths higher than 1000 MPa (145 ksi).

Aluminum bronzes have a very wide range of applications. Common uses include marine hardware, shafts, and pump and valve components for handling seawater, sour mine waters, nonoxidizing acids, and industrial process fluids. The alloys' good wear resistance makes them excellent choices for heavy-duty sleeve bearings and machine-tool ways. Because the aluminum reduces density in addition to raising strength, these bronzes have relatively high strength-to-weight ratios. This explains why nickel-aluminum bronze (C63020) is sometimes substituted for beryllium copper in aircraft landing-gear bearings.

Silicon (Cu-Si) bronzes (C64700 to C66100) resemble the lower-aluminum bronzes in mechanical properties, having nominal tensile strengths up to about 690 MPa (100 ksi). The alloys exhibit the good corrosion resistance characteristic of all copper metals, although their resistance to SCC is somewhat lower than that of the aluminum bronzes. Silicon bronzes are produced in relatively low volumes for products such as hydraulic fluid lines, high-strength fasteners, wear plates, and marine and pole-line hardware. The alloys have excellent weldability, and are commonly used as welding filler wire.

Copper-Nickel Alloys and Nickel Silvers

The copper-nickel alloys (C70100 to C72950) inhabit the copper-rich end of the binary Cu-Ni system that also includes the Monel (67Ni-30Cu) alloys; furthermore their properties are similar to those of nickel-rich alloys. Copper nickels are among the most corrosion resistant and thermally stable of all the copper alloys; they are virtually immune to SCC. Like nickel-base alloys, copper nickels exhibit high oxidation resistance in steam and moist air. Their moderate to high strength is retained well at elevated temperatures.

Low-nickel alloys (2 to 4% Ni) are used in strip form for electrical/electronic products, where strength, thermal stability, and good bend formability are needed. Alloys C70600 (10% Ni), C72200 (16% Ni, plus iron and chromium), and C71500 (30% Ni) are mostly produced as tubes for condensers in ships and seacoast power stations. Rod and plate are used for a variety of marine products, including valves, pumps, fittings, and fouling-resistant sheathing for ship hulls and offshore oil/gas platforms.

Nickel Silvers. These Cu-Ni-Zn alloys (C73500 to C79830) can be thought of as nickel brasses, because they generally contain more zinc than nickel. Nickel silvers combine good corrosion resistance with moderately high strength, which accounts for their wide use in food and beverage handling equipment. Their attractive silver luster is exploited for decorative hardware, electroplated tableware, optical and photographic equipment, and musical instruments.

Copper Casting Alloy Families

Copper casting alloys are primarily selected for either their corrosion resistance, or their combination of corrosion resistance and mechanical properties. These materials also feature good castability, high machinability, and compared with other corrosion-resistant alloys, reasonable cost. Additional benefits include biofouling resistance—important in marine applications—and a spectrum of attractive colors. Many of the alloys also have favorable tribological properties, which explains their widespread use for sleeve bearings, wear plates, gears, and wear-prone components. Table 4 lists nominal compositions and properties of representative copper casting alloys.

Cast Versus Wrought Compositions

Compositions of copper casting alloys may differ from those of their wrought counterparts for various reasons. Generally, casting permits greater latitude in the use of alloying elements because the effects of composition on hot- or cold-working properties are not important. However, imbalances among certain elements and trace amounts of certain impurities in some alloys, will diminish castability and can result in castings of lower quality.

Lead Additions. Lead is commonly added to many cast copper alloys and many alloys have lead contents of 5% or more. Alloys containing such high percentages of lead are not suited to hot working, but they offer several advantages as castings. Because of the low solubility of lead in copper, true alloying does not occur to any measurable degree. During the solidification of castings, some constituents in a given alloy form crystals at higher temperatures relative to others, resulting in tree-like structures called dendrites. The small spaces between the dendrites can interconnect to form micropores. This microporosity is a consequence of the solidification process. The role of lead is to seal these intradendritic pores. This results in a pressure tight casting, which is important for fluid handling applications.

Table 4 Compositions and properties of selected copper casting alloys

UNS No.	Nominal composition, %	Typical tensile strength, MPa (ksi)	Typical yield strength 0.5% extension, MPa (ksi)	Hardness	Electrical conductivity, % IACS, at 20 °C (70 °F)	Thermal conductivity, W/m · K at 293 K (Btu/ft^2/ft/h/°F, at 70 °F)
Coppers						
C80100	99.95 Cu	172 (25)	62 (9)	44 HB (a)	100	391 (226)
C81200	99.9 Cu	…	…	…	…	…
High-copper alloys						
C81500	Cu, 1 Cr	352 (51)	276 (40)	105 HB(a)	82	315 (182)
C82200	Cu, 0.6 Be, 1.5 Ni	345 (50)	172 (25)(b)	55 HRB	45	183 (106)
C82500	97.2 Cu, 2 Be, 0.5 Co, 0.25 Si	517 (75)	276 (40)(b)	81 HRB	20	130 (74.9)
Leaded red brasses						
C83600	85 Cu, 5 Sn, 5 Pb, 5 Zn	255 (37)	117 (17)	60 HB(a)	15	72 (41.6)
Leaded semired brasses						
C84400	81 Cu, 3 Sn, 7 Pb, 9 Zn	234 (34)	103 (15)	55 HB(a)	16	72.4 (41.8)
C84800	76 Cu, 3 Sn, 6 Pb, 15 Zn	255 (37)	97 (14)	55 HB(a)	16	72 (41.6)
Leaded yellow brasses						
C85200	72 Cu, 1 Sn, 3 Pb, 24 Zn	262 (38)	90 (13)	45 HB(a)	18	83.9 (48.5)
C85800	58 Cu, 1 Sn, 1 Pb, 40 Zn	379 (55)	207 (30)(b)	55 HRB, 102 HB(a)	20	83.9 (48.5)
High-strength brasses (manganese bronzes)						
C86200	64 Cu, 26 Zn, 4 Al, 3 Fe, 3 Mn	655 (95)	331 (48)(b)	180 HB(d)	8	20.5 (35.5)
C86500	58 Cu, 39.5 Zn, 1 Al, 1 Fe, 0.5 Sn	490 (71)	200 (29)	100 HB(a), 130 HB(d)	22	85.5 (49.6)
Silicon bronzes						
C87300	Cu, 4 Si	379 (55)	172 (25)	85 HB(a)	6	28.4 (16.4)
Tin bronzes						
C90300	88 Cu, 8 Sn, 4 Zn	310 (45)	145 (21)	70 HB(a)	12	74.8 (43.2)
Leaded tin bronzes						
C92200	88 Cu, 6 Sn, 1.5 Pb, 4.5 Zn	276 (40)	138 (20)	65 HB(a)	14	69.6 (40.2)
High-leaded tin bronzes						
C93200	83 Cu, 7 Pb, 3 Zn	241 (35)	124 (18)	65 HB(a)	12	58.8 (33.6)
Nickel-tin bronzes						
C94700	88 Cu, 5 Sn, 2 Zn, 5 Ni	345 (50)	159 (23)	85 HB(a)	…	31.2 (54.0)
Aluminum bronzes						
C95400	85 Cu, 11 Al, 4 Fe	586 (85)	241 (35)	170 HB(d)	13	58.7 (33.9)
C95800	81 Cu, 9 Al, 4 Fe, 5 Ni, 1 Mn	655 (95)	262 (38)	159 HB(d)	7	36.0 (20.8)
Copper nickels						
C96200	88.6 Cu, 10 Ni, 1.4 Fe	310 (45)(c)	172 (25)(c)	…	11	45.2 (26.1)
C96400	69.1 Cu, 30 Ni, 0.9 Fe	469 (68)	255 (37)	140 HB(a)	5	28.5 (16.4)
Nickel silvers						
C97600	64 Cu, 4 Sn, 4 Pb, 8 Zn, 20 Ni	310 (45)	165 (24)	80 HB(a)	5	31.4 (13)

(a) 10 mm ball, 500 kg load. (b) 0.2% offset. (c) Minimum values. (d) 10 mm ball, 3000 kg load

Lead also allows the machining of castings to be performed at higher speeds without the aid of coolants, because it acts as a lubricant for cutting tool edges and promotes the formation of small, discontinuous chips that can easily be cleared. This results in improved machine surface finishes. Lead also plays a role in providing lubricity during service as in cast copper bearings and bushings. Lead does not have an adverse effect on strength unless present in high concentrations, but it does reduce ductility. Although lead-containing copper alloys can be soldered and brazed, they cannot be welded.

Coppers

Cast coppers (C80100 to C81200) are high-purity metals containing at least 99.3% Cu. (Wrought coppers have a slightly higher minimum copper content.) Trace amounts of silver or phosphorus (a deoxidizer) may be present. Silver imparts annealing resistance, while phosphorus facilitates welding. Neither element affects electrical conductivity significantly when present in such small concentrations. Electrical conductivity can be as high as 100% IACS, while thermal conductivity can reach 391 W/m · K (226 Btu/ft · h · °F). Coppers have very modest strength and cannot be hardened by heat treatment.

Oxygen-free copper (C80100) has the highest electrical and thermal conductivity among the cast copper alloys, but it is essentially identical to phosphorus-deoxidized copper (C81200) in other respects. Both oxygen-free and deoxidized coppers are readily weldable.

Ironically, while copper alloys are among the most easily cast engineering materials, unalloyed copper presents a number of casting difficulties: coarse, often columnar grain structures; rough surfaces; and a tendency to form shrinkage cavities. Although these problems can be overcome by proper foundry practice, use of cast pure copper is generally reserved for applications that demand the highest electrical and/or thermal conductivities. Typical products include large electrical connectors and water-cooled, hot-metal handling equipment such as blast furnace tuyeres.

High-Copper Alloys

Compared with pure copper, the dilute alloys (C81400 to C82800) have significantly higher strengths, higher hardness and wear resistance, higher fatigue resistance, and better castability, yet they retain most of copper's electrical and thermal conductivity. Corrosion and oxidation resistance of these alloys are as good or better than those of pure copper, because alloying improves the chemical and mechanical properties of their protective oxide films. Within their useful temperature range, which extends from the cryogenic region to 400 °C (750 °F), depending on composition, no

other engineering materials can match their combination of conductivity, strength, and corrosion resistance.

Age-Hardening Alloys. Several of the high-copper alloys can be age hardened. In the fully aged condition, the strength of chromium copper (C81500) is roughly twice that of pure copper, and its electrical conductivity remains higher than 80% IACS. Chromium copper is used for electromechanical products such as welding-machine clamps, resistance welding electrodes, and high-strength electrical cable connectors.

The age-hardening beryllium coppers can be further categorized as high-conductivity alloys, such as C82200 (nominally 0.6% Be), and high-strength grades, such as C82500 (2% Be). Alloy selection depends on whether electrical or mechanical properties are more important. In the fully aged condition (TF00 temper), the high-conductivity alloy develops about 60% of the strength, but twice the conductivity, of the high-strength alloy.

Beryllium coppers are relatively expensive, but they can be very cost effective when properly used. Plastic injection molds, a common application, are a good example. Cu-Be casting alloys have high fluidity and can reproduce fine details in master patterns. Their high conductivity enables high production speed, while their good corrosion/oxidation resistance promotes long die life. Other applications for beryllium copper alloys include inlet guide vanes for helicopter turbine engines (C82200), pitot tube housings for high-speed aircraft, golf club heads (C82500), and components of undersea-cable repeater housings.

Brasses

Brasses (C83300 to C87900 and C89320 to C89940) are copper alloys in which zinc is the dominant alloying addition. Because of their excellent castability, relatively low cost, and favorable combination of strength and corrosion resistance, brasses are by far the most commonly cast copper alloys. There are six subcategories of cast brasses: red and leaded red, semi-red and leaded semi-red, yellow and leaded yellow, high-strength and leaded high-strength yellow (manganese bronzes), silicon brasses/silicon bronzes, and copper-bismuth/copper-selenium-bismuth brasses.

Red and Leaded Red Brasses. The cast red brasses (C83300 to C83810) are alloys of copper, zinc, tin, and in some cases, lead. A "red" copper-like color is evident in alloys containing less than about 8% Zn. These moderate-strength alloys retain the face-centered cubic (alpha) structure of pure copper. Their electrical conductivity, while not extremely high, is adequate for electromechanical equipment such as pole-line hardware. The leaded red brasses may contain up to 7% Pb. The element's primary function is to provide pressure tightness by sealing the interdendritic shrinkage pores that form as these wide-freezing-range alloys solidify.

Lead also improves machinability, but high levels of the element diminish mechanical properties, particularly at elevated temperatures.

With their high aqueous and atmospheric corrosion resistance, the red brasses are widely used for plumbing goods, valves, fittings, pump housings and impellers, water meters, plaques and statuary, and countless other products. The workhorse alloy is C83600, which is also known as 85-5-5-5 (85Cu-5Sn-5Pb-5Zn), ounce metal, and composition metal. C83600 has been used commercially for several hundred years, and currently accounts for more tonnage than any other copper casting alloy.

Semi-Red and Leaded Semi-Red Brasses. These alloys (C84200 to C84800) differ from the red brasses primarily by their higher zinc contents, which range up to 15%. Zinc reduces corrosion resistance (and cost) somewhat compared with red brasses, but it has little effect on strength. Higher zinc also lightens the alloys' color. The microstructure remains mostly single-phase alpha, although some body-centered cubic beta phase may appear as a result of coring. The leaded alloys C84400 and C84800 are the most widely used members of this family. Like the red brasses, the semi-red alloys are primarily specified for plumbing fixtures, fittings, and low-pressure valves.

The yellow and leaded yellow brasses (C85200 to C85800) span a broad range of zinc contents (20 to 40%). As a result, the alloys have microstructures that range from essentially all-alpha to ones with substantial amounts of the hard beta phase. Properties vary accordingly, since beta is a potent strengthener. Although beta slightly impairs room-temperature ductility, it also markedly improves ductility at temperatures approaching the solidus. This feature is put to use in alloy C85800 (40% Zn), which is suitable for both permanent mold casting and pressure die casting because it can accommodate the high shrinkage strains that arise in rigid molds.

Yellow brasses have a pleasing light color and can be polished to a high luster. Their corrosion resistance and cost are somewhat lower than those of the semi-red brasses, but properties are well suited for the architectural trim, decorative hardware, and plumbing fixtures for which these alloys are commonly used. The most widely used yellow brasses are C85200, C85400, and C85700. Alloy C85700 is essentially a cast version of the familiar 60Cu-40Zn Muntz metal (C28000).

High-Strength Brasses. Also called manganese bronzes and high-tensile brasses, these Cu-Zn-Fe-Al-Mn alloys (C86100 to C86800) are among the strongest (as cast) copper-base materials. The mechanical properties of the high-strength yellow brasses derive primarily from a high beta-phase content. Beta is stable in binary alloys containing more than 39.5% Zn, but strong beta stabilizers such as aluminum promote its pres-

ence at lower zinc contents, as in alloys C86200 (25 Zn, 4 Al) and C86300 (26 Zn, 6 Al). Additional strength is provided by iron, a grain refiner that appears as precipitates of an iron-rich intermetallic compound. Manganese also contributes to strength, but its principal functions may have more to do with castability. The high-zinc, low-aluminum alloys C86400 and C86500 have duplex (alpha + beta) structures. Their mechanical properties fall between those of yellow brasses and fully beta alloys such as C86200 and C86300.

The high-strength yellow brasses are mainly used for gears, bolts, valve stems, bridge trunnions, and other mechanical products requiring high strength, good wear resistance, and reasonably good corrosion resistance. Where economically feasible, however, the high-strength brasses have increasingly been replaced by the more corrosion-resistant and equally strong aluminum bronzes.

Silicon Brasses/Bronzes. The foundry characteristics of silicon brasses (C87300 to C87900) include favorably low melting points and high fluidity. They are amenable to most casting methods, including permanent mold and pressure die casting processes. Castings exhibit moderate strength and very good aqueous and atmospheric corrosion resistance, although susceptibility to stress-corrosion cracking in severe environments has been reported. Silicon brasses have been considered as possible lead-free replacements for common plumbing brasses, but limited machinability restricts their widespread acceptance. Current applications include bearings, gears, pole-line hardware, and intricately shaped pump and valve components.

Copper-Bismuth and Copper-Selenium-Bismuth Brasses. The copper-bismuth and copper-selenium-bismuth (SeBiLoy) red brasses (alloys C89510 and C89520, respectively) are low-lead sand-cast alloys that are used in food process and potable water applications such as faucets and other plumbing fixtures. These alloys were developed to minimize lead leaching into potable water and to replicate the high machinability and pressure tightness of leaded brass.

A selenium-bismuth-containing yellow brass (C89550) has also been developed for the permanent mold casting process. It too was developed for use in potable water systems.

Bronzes

Under the UNS system, the term bronze applies to a broad class of alloys (C90200 to C95900) in which the principal alloying element is neither zinc nor nickel. There are four broad categories of cast bronzes: tin bronzes, leaded and high-leaded tin bronzes, nickel-tin bronzes, and aluminum bronzes.

Tin Bronzes. Tin is a potent solid-solution strengthener in copper. It also increases corrosion resistance, as the hundreds of surviving Bronze Age relics dramatically illustrate. In fact, today's tin bronzes (C90200 to C91700) are not materially different from those cast more than 3500 years ago in Europe and China.

Binary Cu-Sn alloys retain the alpha solid solution up to 15.8% Sn at 520°C (968°F), and while tin's solubility is much lower at room temperature, low-temperature transformations are very sluggish and can usually be ignored. Tin broadens the freezing range far more than zinc does, and the tin bronzes therefore tend to undergo an extended mushy stage during solidification. Castings must be designed with this behavior in mind.

Tin bronzes are stronger and more ductile than red and semi-red brasses, and are usable at higher temperatures than leaded alloys. Their high wear resistance and low friction coefficient against steel are useful in bearings, gears, and piston rings. Other applications include valves, fittings, and bells. Alloys C90300 and C90500 can be used for pressure-retaining products at temperatures up to 260°C (500°F).

Leaded Tin Bronzes. Lead's principal functions in Cu-Sn and Cu-Sn-Zn alloys are to improve machinability and pressure tightness. With proper foundry practice, most copper alloys can produce pressure-tight castings, but extended-freezing-range alloys such as the high-tin bronzes often require some lead to seal interconnected microporosity. As little as 1% Pb is usually sufficient, although more may be present if it is needed to improve machinability or bearing properties. Lead does reduce tensile strength and ductility; however, the amount added can be balanced with regard to machinability and strength requirements.

Many mechanical products are routinely cast in leaded tin bronzes (C92200 to C92900). Alloys C92200 (Navy "M" bronze, steam bronze) and C92300 (Navy "G" bronze) are specified for corrosion-resistant valves, fittings, and other pressure-retaining products. C92200 may be used for pressure-retaining parts at temperatures up to 290°C (550°F), whereas alloy C92300 is limited to temperatures below 260°C (500°F) as a precaution against a form of embrittlement that can occur at higher temperatures. Alloys C92600 through C92900, which contain 10% Sn, are slightly stronger and more corrosion resistant than leaner alloys such as C92200. None of the leaded alloys can be welded, but all can be soldered and many can be brazed, provided they can cool without constraint so as to avoid hot shortness (brittleness).

High-leaded tin bronzes (C93100 to C94500) are primarily used for sleeve bearings. Should the flow of lubricant in such bearings be interrupted, lead exudes from the alloy, smears over the surface of the journal, and prevents galling and seizing, at least temporarily. This "slow-fail" feature is one of the principal advantages that leaded-bronze sleeve bearings hold over rolling-element bearings.

Nickel-Tin Bronzes. The nickel-tin bronze alloys C94700 and C94800 combine strength (585 MPa, 85 ksi tensile strength) and toughness with good bearing properties and high corrosion resistance. They are amenable to most foundry processes, including permanent mold and investment (precision) casting. Bearings, rings, and gear blanks can be produced by centrifugal and/or continuous casting. The alloys are soft and ductile in the as-cast or solution-annealed and quenched condition, but low-temperature aging (at 315°C, 600°F) causes a spinodal decomposition that sharply raises mechanical properties. The alloys find numerous uses as specialty bearings, pistons, nozzles, shifter forks, feed mechanisms, mechanical actuators, and machinery components.

Aluminum bronzes (C95200 to C95900) are best known for their combination of exceptional corrosion resistance; high mechanical strength, toughness, and wear resistance; and good casting and welding characteristics. They comprise a large family of alloys ranging from ductile, moderate-strength grades to some of the strongest copper-base compositions available. Alloys with less than about 9.25% Al display primarily alpha-phase microstructures, which can be strengthened via precipitation of iron- or nickel-rich phases. Alloys with more than about 8.5% Al can contain mixtures of several phases in the as-cast condition. The nature and occurrence of these phases are controlled by composition, cooling rate, and heat treatment.

Simple aluminum bronzes such as C95200 to C95500 are actually Cu-Al-Fe ternary alloys. Of these, C95300, C95400, and C95500 can be quenched and tempered, although C95400, the most widely used of the three, is usually not heat treated.

Alloy C95600 is a silicon-aluminum bronze with reportedly improved machinability and bearing properties. C95700 is a high-strength manganese-nickel-iron-aluminum bronze originally developed as a marine propeller alloy. It has largely been replaced in this application by C95800, a nickel-aluminum bronze. Alloy C95800 cannot be heat treated to improve mechanical properties, but it is commonly temper annealed to enhance its corrosion resistance.

The corrosion resistance of aluminum bronzes is generally very high, especially in sea-water, chlorides, and dilute acids, including sulfuric, phosphoric, hydrochloric and hydrofluoric. Aluminum bronzes are much less susceptible to crevice corrosion than stainless steels, and resist both pitting and stress-corrosion cracking. Largely because of the high alumina (Al_2O_3) content of their protective corrosion-product films, aluminum bronzes have very high erosion-corrosion and cavitation resistance.

Aluminum bronzes have a wide range of uses. They have replaced other copper-base alloys in traditional applications such as pump and valve components, bearings, and wear rings. In many other cases, they have

proven to be technically viable and cost-effective alternatives to stainless steels and nickel-base alloys. Because the alloys resist biofouling, they are widely used in marine equipment, such as seawater piping, fittings, valves, pumps, propellers, and propeller hubs. Other applications include: bearings and pump/valve components in the chemical process industries, wear rings for hydroelectric turbines, and large-diameter landing-gear bearings for commercial and military aircraft.

Other Alloys

Copper-Nickel Alloys. The Cu-Ni binary system includes the copper nickels (C96200 to C96900) at its copper-rich end and the Monel alloys (e.g., Ni-30Cu) in its nickel-rich section. Copper nickels, also called cupronickels, are solid-solution alloys to which iron, chromium, niobium and/or manganese are added for improved strength and corrosion resistance, particularly under conditions of high-velocity liquid flow. They are noted for their exceptional corrosion resistance in seawater, and for their virtual immunity to stress-corrosion cracking in media that attack other copper alloys (ammonia, amines, and nitrites, for example). Biofouling resistance is highest in low-nickel alloys such as C96200 (10% Ni), but other properties generally improve with nickel content. Highest corrosion resistance is observed in C96400 (30% Ni). Since nickel content strongly affects alloy price, use of these alloys should be justified by the severity of service conditions and the required product life.

Copper-nickel alloys are typically used aboard ships, on offshore platforms, and in coastal power plants. They are acknowledged to be the best materials for evaporative desalination plants. Cast copper nickels have also been considered as candidate materials for spent-nuclear-fuel burial containers, along with pure copper and aluminum bronze.

Nickel Silvers. These Cu-Sn-Pb-Zn-Ni alloys (C97300 to C97800), some of which are actually leaded nickel brasses, are named for their bright silvery luster. They have low to moderate strength, depending on grade. The alloys exhibit high fluidity during casting and can reproduce fine details. Tin and nickel impart good aqueous corrosion resistance, while lead provides pressure tightness and machinability. The nickel silvers are often thought of as ornamental alloys, and architectural trim and musical-instrument valves are indeed two of their better known uses. However, alloy C97600 (20% Ni), which has a nominal as-cast tensile strength of 310 MPa (45 ksi), is also used for marine hardware and low-pressure valves and fittings for the food, dairy, and beverage industries.

Leaded coppers (C98200 to C98840) are essentially pure copper or high-copper alloys containing lead. The leaded coppers offer the moder-

ate corrosion resistance and high conductivity of the copper alloys, in addition to the lubricity and low friction characteristics of high-leaded bronzes. Applications include auto main and connecting rod bearings.

Special alloys (C99300 to C99750) are those with unique characteristics, such as C99300 (Incramet 800), which has high oxidation resistance due to aluminum, good thermal fatigue resistance, and high hot hardness. This alloy was developed for glass processing including glassmaking molds and plate glass rolls. Other alloys falling under the "special alloy" category include the manganese white brasses (C99700 and C99750) which are used in musical instrument components, decorative hardware requiring silver color, and components which have good damping characteristics and attenuate noise well.

Effects of Impurities or Alloying on Electrical Conductivity

More than 60% of all copper and copper alloys consumed in the United States are used because of their high electrical conductivity. The bulk of these applications are wire cable, e.g., telecommunications wire and cable, electronic wire and cable, building wire, magnet wire, power cable, and automotive wire and cable.

The electrical conductivity scale established in 1913 was based on a copper standard defined as 100%, and the electrical conductivity of any material is still expressed as percent IACS, which is equal to 100 times the ratio of the volume resistivity of the annealed copper standard (0.017241 $\mu\Omega \cdot$ m) at 20 °C (68 °F) to the value measured for the material concerned. The highest purity copper produced today (99.999% Cu) has been found to have a room-temperature IACS value of 103.06%. Only silver, with 106% IACS, has a higher electrical conductivity than copper. Current practically attainable conductivity values for electrolytic tough pitch and deoxidized low residual phosphorus coppers stand at about 101% IACS. Oxygen-free copper is certified by ASTM standards to meet this as a minimum value.

Effect of Composition. All additives to pure copper reduce its electrical conductivity, depending upon the element and amount in solid solution. Only small decreases are caused by elements added in excess of solubility. The data in Table 5 show the solubility of each element in copper at room temperature and the degree to which each element decreases electrical conductivity by indicating the resistivity increase per 1 wt% added. There is a cumulative effect when more than one element is added. The drop in electrical conductivity caused by additions of commonly used

alloying elements is illustrated by Fig. 2, which shows the strongly detrimental effects of phosphorus and iron and the relatively mild decreases caused by silver and zinc additions. Oxygen in standard-grade copper

Table 5 Solubility limits and electrical resistivity effects of copper alloying elements

Element	Solubility at 293 K, wt%	Resistivity increase per 1 wt% addition, μΩ · cm
Ag	0.1	0.355
Al	9.4	2.22
As	6.5	5.67
Au	100	0.185
B	0.06	8.25
Be	0.2	4.57
Ca	…	4.77
Cd	0.5	0.172
Co	0.2	7.3
Cr	0.03	4.9
Fe	0.14	10.6
Ga	20	1.27
Ge	11	3.2
Hg	…	0.32
In	3	0.615
Ir	1.5	2
Mg	1	4.2
Mn	24	3.37
Ni	100	1.2
O	0.0002	21
P	0.5	14.3
Pb	0.02	1.02
Pd	40	9.57
Pt	100	0.635
Rh	20	1.5
S	<0.0025	18.6
Sb	2	2.9
Se	<0.002	8.5
Si	2	7
Sn	1.2	1.65
Te	<0.0005	4
Ti	0.4	21.6
Zn	30	0.286
Zr	<0.01	8

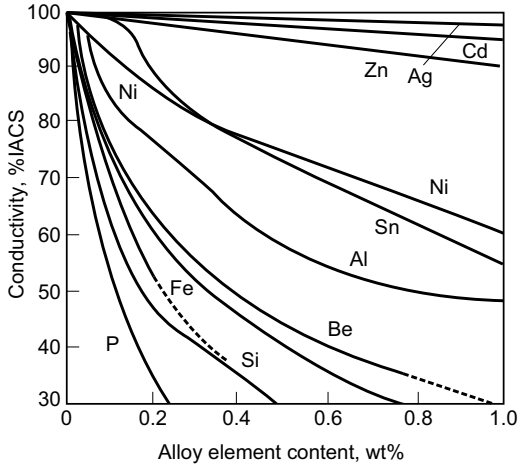


Fig. 2 Effect of alloying elements on the conductivity of oxygen-free high-conductivity copper

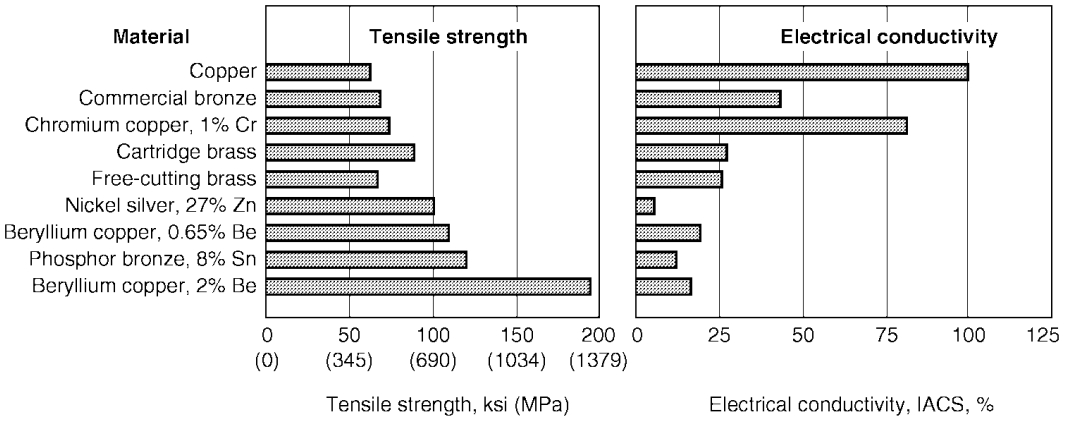


Fig. 3 Relationship between strength and electrical conductivity for copper and copper alloys

reacts with many impurities, yielding insoluble oxides and thereby greatly reducing the harmful effects. Where oxygen-free or deoxidized copper is used, impurity levels must be reduced below those in cathode copper to achieve >100% IACS.

Effect of Alloying and Condition. As with other metal systems, copper is intentionally alloyed to improve strength without unduly degrading ductility or workability. However, it should be recognized that additions of alloying elements also degrade electrical and thermal conductivity by various amounts depending on the alloying element and the concentration and location in the microstructure (solid solution, precipitate, dispersoid). The choice of alloy and condition is most often based on the tradeoff between strength and conductivity (Fig. 3). Figure 4 shows the general tradeoff between strength and conductivity for solid-solution, dispersion, and precipitation hardening. The optimum tradeoff is achieved by precipitation hardening, which is usually the most costly, because of either the alloy additions or extra processing. Precipitation hardening alloys exhibit increases in electrical conductivity, along with increased strength during the aging heat treatment, as elements are removed from supersaturated solid solution to form precipitates of intermetallic compounds.

Effects of Alloying on Corrosion Resistance

Coppers and high-copper alloys have similar corrosion resistance. They have excellent resistance to seawater corrosion and biofouling, but are susceptible to erosion-corrosion at high water velocities. The high-copper alloys are primarily used in applications that require enhanced mechanical performance, often at slightly elevated temperature, with good thermal or electrical conductivity. Processing for increased strength in the

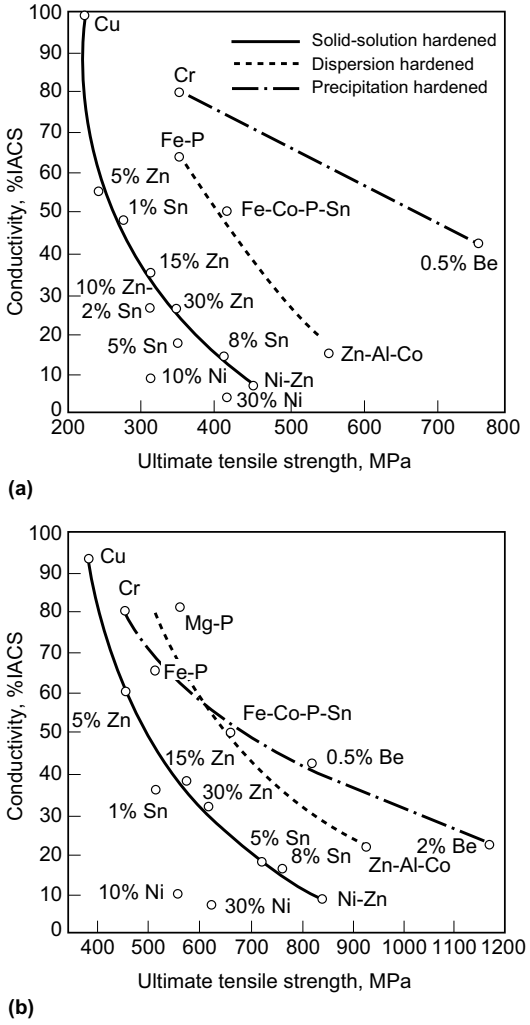


Fig. 4 Electrical conductivity as a function of tensile strength for (a) annealed and (b) 60% cold-reduced copper alloy strip

high-copper alloys generally improves their resistance to erosion-corrosion. A number of alloys in this category have been developed for electronic applications—such as contact clips, springs, and lead frames—that require specific mechanical properties, relatively high electrical conductivity, and atmospheric-corrosion resistance.

Brasses. The resistance of brasses to corrosion by aqueous solutions does not change markedly, as long as the zinc content does not exceed about 15%; above 15% Zn, dezincification may occur. Quiescent or slowly moving saline solutions, brackish waters, and mildly acidic solutions are environments that often lead to the dezincification of unmodified brasses.

Susceptibility to SCC is significantly affected by zinc content; alloys that contain more zinc are more susceptible. Resistance increases substantially as zinc content decreases from 15 to 0%. Stress-corrosion cracking is rare in commercial copper.

Elements such as lead, tellurium, beryllium, chromium, phosphorus, and manganese have little or no effect on the corrosion resistance of coppers and binary copper-zinc alloys. These elements are added to enhance such mechanical properties as machinability, strength, and hardness.

Tin Brasses. Tin additions significantly increase the corrosion resistance of some brasses, especially resistance to dezincification. Examples of this effect are two tin-bearing brasses: uninhibited admiralty metal (no active UNS number) and naval brass (C46400). Uninhibited admiralty metal was once widely used to make heat-exchanger tubes; it has largely been replaced by inhibited grades of admiralty metal (C44300, C44400, and C44500), which have even greater resistance to dealloying. Admiralty metal is a variation of cartridge brass (C26000) that is produced by adding about 1% Sn to the basic 70Cu-30Zn composition. Similarly, naval brass is the alloy resulting from the addition of 0.75% Sn to the basic 60Cu-40Zn composition of Muntz metal (C28000).

Cast brasses for marine use are also modified by the addition of tin, lead, and, sometimes, nickel. This group of alloys is known by various names, including composition bronze, ounce metal, and valve metal. These older designations are used less frequently, because they have been supplanted by alloy numbers under the UNS system. The cast marine brasses are used for plumbing goods in moderate-performance seawater piping systems or in deck hardware, for which they are subsequently chrome plated.

Aluminum Brasses. An important constituent of the corrosion film on a brass that contains a few percent aluminum in addition to copper and zinc is aluminum oxide (Al_2O_3), which markedly increases resistance to impingement attack in turbulent high-velocity saline water. For example, the arsenical aluminum brass C68700 (76Cu-22Zn-2Al) is frequently used for marine condensers and heat exchangers in which impingement attack is likely to pose a serious problem. Aluminum brasses are susceptible to dezincification unless they are inhibited, which is usually done by adding 0.02 to 0.10% As.

Inhibited Alloys. Addition of phosphorus, arsenic, or antimony (typically 0.02 to 0.10%) to admiralty metal, naval brass, or aluminum brass effectively produces high resistance to dezincification. Inhibited alloys have been extensively used for such components as condenser tubes, which must accumulate years of continuous service between shutdowns for repair or replacement.

Phosphor Bronzes. Addition of tin and phosphorus to copper produces good resistance to flowing seawater and to most nonoxidizing acids except hydrochloric (HCl). Alloys containing 8 to 10% Sn have high resistance to impingement attack. Phosphor bronzes are much less susceptible to SCC than brasses and are similar to copper in resistance to sulfur attack. Tin bronzes tend to be used primarily in the cast form, in which

they are modified by further alloy additions of lead, zinc, and nickel. Like the cast brasses, the cast tin bronzes are occasionally identified by older, more colorful names that reflect their historic uses, such as G Bronze, Gun Metal, Navy M Bronze, and steam bronze. Contemporary uses include pumps, valves, gears, and bushings. Wrought tin bronzes are known as phosphor bronzes and find use in high strength wire applications, such as wire rope. This group of alloys has fair resistance to impingement and good resistance to biofouling.

Copper Nickels. Alloy C71500 (Cu-30Ni) has the best general resistance to aqueous corrosion of all the commercially important copper alloys, but C70600 (Cu-10Ni) is often selected because it offers good resistance at lower cost. Both of these alloys, although well suited to applications in the chemical industry, have been most extensively used for condenser tubes and heat-exchanger tubes in recirculating steam systems. They are superior to coppers and to other copper alloys in resisting acid solutions and are highly resistant to SCC and impingement corrosion.

Nickel Silvers. The two most common nickel silvers are C75200 (65Cu-18Ni-17Zn) and C77000 (55Cu-18Ni-27Zn). They have good resistance to corrosion in both fresh and salt waters. Primarily because their relatively high nickel contents inhibit dezincification, C75200 and C77000 are usually much more resistant to corrosion in saline solutions than brasses of similar copper content.

Copper-silicon alloys generally have the same corrosion resistance as copper, but they have higher mechanical properties and superior weldability. These alloys appear to be much more resistant to SCC than the common brasses. Silicon bronzes are susceptible to embrittlement by high-pressure steam and should be tested for suitability in the service environment before being specified for components to be used at elevated temperature.

Aluminum bronzes containing 5 to 12% Al have excellent resistance to impingement corrosion and high-temperature oxidation. Aluminum bronzes are used for beater bars and for blades in wood pulp machines because of their ability to withstand mechanical abrasion and chemical attack by sulfite solutions.

In most practical commercial applications, the corrosion characteristics of aluminum bronzes are primarily related to aluminum content. Alloys with up to 8% Al normally have completely face-centered cubic (fcc) α structures and good resistance to corrosion attack. As aluminum content increases above 8%, α-β duplex structures appear. The β phase is a high-temperature phase retained at room temperature upon fast cooling from 565 °C (1050 °F) or above. Slow cooling for long exposure at temperatures from 320 to 565 °C (610 to 1050 °F) tends to decompose the β phase into a brittle $\alpha + \gamma_2$ eutectoid having either a lamellar or a nodular structure.

The β phase is less resistant to corrosion than the α phase, and eutectoid structures are even more susceptible to attack.

Depending on specific environmental conditions, β phase or eutectoid structure in aluminum bronze can be selectively attacked by a mechanism similar to the dezincification of brasses. Proper quench-and-temper treatment of duplex alloys, such as C62400 and C95400, produces a tempered β structure with reprecipitated acicular α crystals, a combination that is often superior in corrosion resistance to the normal annealed structures.

Iron-rich particles are distributed as small round or rosette particles throughout the structures of aluminum bronzes containing more than about 0.5% Fe. These particles sometimes impart a rusty tinge to the surface, but have no known effect on corrosion rates.

Nickel-aluminum bronzes are more complex in structure with the introduction of the κ phase. Nickel appears to alter the corrosion characteristics of the β phase to provide greater resistance to dealloying and cavitation-erosion in most liquids. For C63200 and perhaps C95800, quench-and-temper treatments may yield even greater resistance to dealloying. Alloy C95700, a high-manganese cast aluminum bronze, is somewhat inferior in corrosion resistance to C95500 and C95800, which are low in manganese and slightly higher in aluminum.

Aluminum bronzes are generally suitable for service in nonoxidizing mineral acids, such as phosphoric (H_3PO_4) sulfuric (H_2SO_4), and HCl; organic acids, such as lactic, acetic (CH_3COOH), or oxalic; neutral saline solutions, such as sodium chloride (NaCl) or potassium chloride (KCl); alkalies, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and anhydrous ammonium hydroxide (NH_4OH); and various natural waters including sea, brackish, and potable waters. Environments to be avoided include nitric acid (HNO_3); some metallic salts, such as ferric chloride ($FeCl_3$) and chromic acid (H_2CrO_4); moist chlorinated hydrocarbons; and moist ammonia (HN_3). Aeration can result in accelerated corrosion in many media that appear to be compatible.

Exposure under high tensile stress to moist NH_3 can result in SCC. In certain environments, corrosion can lower the fatigue limit to 25 to 50% of the normal atmospheric value.

Effects of Alloying on SCC Resistance

Most of the literature on SCC of copper-base alloys has been concerned with copper-zinc alloys (brasses) in ammoniacal solutions. However, a number of other copper-base alloys are susceptible to SCC (see Table 6). In general, the susceptible alloys are solid-solution α-phase copper alloys containing other elements such as manganese, aluminum, and even gold. The rate and path of failure (intergranular or transgranular) depend on the nature of the solute and the environment.

Table 6 Copper-base alloys that have experienced stress-corrosion cracking

Alloy	Environment
Pure copper	Ammonia
	Sodium nitrite
DHP copper	Sodium nitrite
OFHC copper	Sodium nitrite
Cu-Zn alloys	Ammonia
Cu-10Mn	Mattsson's solution
Cu-5Zn-5Mn	Mattsson's solution
Cu-5Zn-10Mn	Mattsson's solution
Cu-20Zn-5Ni	Mattsson's solution
Aluminum brass	Acidic chloride-citrate
Cu-2Be	Ammonia
Cu-4Ti	Ammonia
Cu-6Mn	Ammonia
Cu-12Mn	Ammonia
Cu-18Mn	Ammonia
Cu-4Al	Ammonia
Cu-8Al	Ammonia
Cu-Au	Aqua regia
	$FeCl_3$
	Ammonia
Cu-Al	Ammonia
Cu-Ga	Ammonia
Cu-Ge	Ammonia
Cu-Zn	Ammonia
	Water
Cu-Zn-Sn	Water
β-brass	Water
Cusil (Cu-72 Ag)	Mattsson's solution

Several researchers have investigated the effect of zinc content of binary Cu-Zn alloys on SCC susceptibility in ammoniacal solutions (e.g., Ref 1, 2). Data from Ref 2, presented in Fig. 5, show that susceptibility to SCC in constant-load tests increased with increasing zinc content for both tarnishing and nontarnishing solutions. These data also show that the fracture-mode was intergranular for tarnishing solutions, while a fracture-mode transition from intergranular to transgranular occurred at approximately 15% Zn for the nontarnishing solutions. This transition has been attributed to a change in the dislocation structure as solute addition increases.

While SCC susceptibility of Cu-Zn alloys increases monotonically with increasing zinc content, susceptibility appears to reach a maximum with increasing alloy content for other α-phase copper alloys. Data showing the effect of aluminum and nickel on time to failure of binary alloys in moist ammonia are given in Fig. 6. The Cu-Zn alloys also are more susceptible to SCC than the other binary alloys, as comparison of the data in Fig. 5 and 6 demonstrates.

The effects on SCC of minor alloy additions to Cu-Zn alloys also have been investigated. Syrett and Parkins (Ref 3) studied the effects of tin and arsenic on the SCC of Cu-20Zn alloys in Mattsson's solutions of pH 7.3 and 11.3 and found that additions of both elements increased cracking resistance. These tests were performed under freely corroding conditions. It also was observed that the alloy additions promoted a fracture-mode transition from intergranular to transgranular. The results were attributed to the effects of the solute on the passivation characteristics of the alloys,

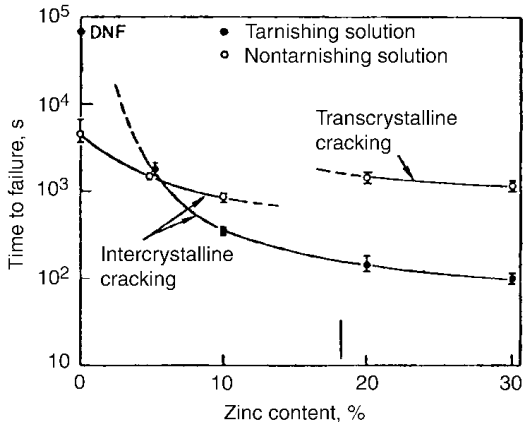


Fig. 5 Effect of zinc content on time to failure for specimens tested at 10% proof stress in tarnishing and nontarnishing ~15 N ammoniacal solutions containing 8 g/L Cu. DNF, did not fail. Source: Ref 2

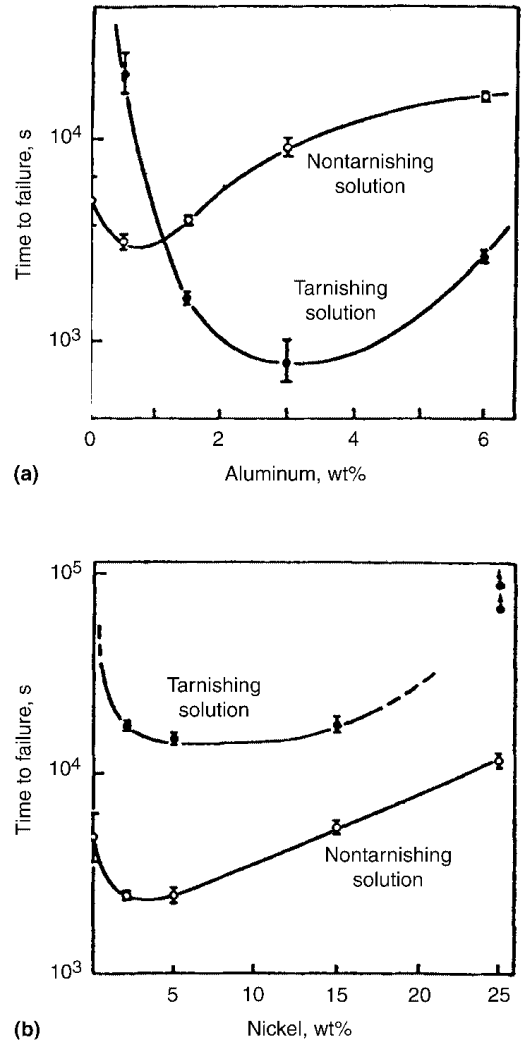


Fig. 6 Effect of aluminum content (a) or nickel content (b) on time to failure of copper-base alloys tested in tarnishing and nontarnishing ~15 N aqueous ammonia containing 8 g/L Cu. Source: Ref 2

as opposed to a change in their stacking-fault energy. On the other hand, Torchio (Ref 4) found that additions of arsenic and phosphorus to aluminum brass decreased the SCC resistance of the alloy in an acidified citrate chloride solution. The crack path was transgranular in the presence of arsenic, in agreement with the studies of Syrett and Parkins (Ref 3), but was intergranular when only phosphorus was present. Thus, alloying effects in copper-base alloys appear to be environment specific. This conclusion greatly complicates alloy selection for SCC resistance.

A significant finding of SCC research on copper-base alloys over the past 20 years is that pure copper undergoes SCC (Ref 5, 6). (Pure copper was long thought to be immune to cracking.) Cracking was transgranular and was observed in sodium nitrite solutions. More recently, Cassagne et al. (Ref 7) have reported transgranular SCC of pure copper in sodium acetate solutions as well.

Effects of Alloying on Weldability

Several alloying elements have pronounced effects on the weldability of copper and copper alloys. Small amounts of volatile, toxic alloying elements are often present in copper and its alloys. As a result, the requirement of an effective ventilation system to protect the welder and/or the welding machine operator is more critical than when welding ferrous metals.

Zinc reduces the weldability of all brasses in relative proportion to the percent of zinc in the alloy. Zinc has a low boiling temperature, which results in the production of toxic vapors when welding copper-zinc alloys. Effective forced ventilation is mandatory, and source-capture systems are necessary to contend with the fumes.

Tin increases the hot-crack susceptibility during welding when present in amounts from 1 to 10%. These alloys are typically the phosphor bronzes and tin brasses. Tin, when compared with zinc, is far less volatile and toxic. During welding, tin may preferentially oxidize relative to copper. The results will be an oxide entrapment, which may reduce the strength of the weldment.

Beryllium, aluminum, and nickel form tenacious oxides that must be removed prior to welding. The formation of these oxides during the welding process must be prevented by shielding gas or by fluxing, in conjunction with the use of the appropriate welding current. The oxides of nickel interfere with arc welding less than those of beryllium or aluminum. Consequently, the nickel silvers and copper-nickel alloys are less sensitive to the type of welding current used during manufacture. Beryllium-containing alloys also produce toxic fumes during welding.

Silicon has a beneficial effect on the weldability of copper-silicon alloys because of its deoxidizing and fluxing actions. The combination of this effect and the low thermal conductivity makes silicon bronzes the most weldable of the copper alloys for any arc welding process.

Phosphorus is beneficial to certain copper and copper alloys as a strengthener and deoxidizer. When added to brass, phosphorus inhibits dezincification corrosion. In the amounts normally present in most copper alloys, phosphorus does not adversely affect or hinder welding.

Chromium, like beryllium and aluminum, can form a refractory oxide on the surface of the molten weld pool. Arc welding should be done in an inert protective atmosphere to prevent formation of chromium oxides.

Cadmium has no serious effect on the weldability of copper. However, the low boiling temperature of cadmium does result in evaporation of this alloy at welding temperatures, thereby creating a potential health hazard. Cadmium will also form an oxide in the molten weld metal, but the oxide can be easily reduced by fluxing agents.

Oxygen can cause porosity and reduce the strength of welds made in certain copper alloys that do not contain sufficient quantities of phosphorus or other deoxidizers. Oxygen may be found as a free gas or as cuprous oxide. Most commonly welded copper alloys contain deoxidizing elements—usually phosphorus, silicon, aluminum, iron, or manganese. These elements will readily combine with oxygen and eliminate the potential for porosity. The same deoxidizers are also included in the filler metals. The soundness and strength of arc welds made in commercial coppers depend upon the cuprous oxide content. As the oxide content decreases, weld soundness increases. Deoxidized coppers provide the best results because they are free from cuprous oxides and contain residual amounts of phosphorus.

Iron and manganese do not significantly affect the weldability of the alloys that contain them. Iron is typically present in some special brasses, aluminum bronzes, and copper-nickel alloys in amounts of 1.4 to 3.5%. Manganese is commonly used in these same alloys, but at lower concentrations than iron.

Free-Machining Additives. Lead, selenium, tellurium, and sulfur are added to copper alloys to improve machinability. Bismuth is beginning to be used for this purpose as well when lead-free alloys are desired. These minor alloying agents, while improving machinability, adversely affect the weldability of copper alloys by rendering the alloys hot-crack susceptible. The adverse effect on weldability begins to be evident at about 0.05% of the additive and is more severe with larger concentrations.

Lead is the most harmful of the alloying agents with respect to hot-crack susceptibility. Alloys that contain 0.5 to 4% Pb are not ordinarily welded.

Effects of Alloying on Brazeability and Solderability

Brazeability. As shown in Table 7, the brazeability of copper and copper alloys generally ranges from good to excellent. With some alloys, however, some difficulties may be encountered. For example, some lead-containing alloys can form a dross that interferes with wetting; tin-containing alloys, if not stress relieved before brazing, may crack when subjected to rapid localized heating; aluminum bronzes containing more than 8% Al require special techniques because of the tenacious refractory oxides that form on their surface.

Solderability. Copper and copper alloys are among the most frequently soldered engineering materials. In fact, copper joining is practically synonymous with soldering. With most copper and copper alloys, the copper surface oxide is easily disrupted and displaced by most flux types. The presence of alloying elements such as beryllium, chromium, silicon, and aluminum modifies the nature of the oxide, making it more tenacious. For these alloys, a special flux is recommended to remove the oxide from the surface and enhance the solderability of the base metal groups. As shown in Table 6, the degree of solderability for copper and copper alloys generally ranges from good to excellent.

Table 7 Brazing and soldering characteristics of the major classes of coppers and copper alloys

Alloy	UNS No.	Rating (a)	
		Brazing	Soldering
ETP copper	C11000–C11900	E	G
Oxygen-free copper	C102000	E	E
Deoxidized copper	C12000–C12300	E	E
Beryllium copper	C17000–C17500	G	G
Cadmium/chromium copper	C16200–C18200	G	G
Red brass - 85%	C23000	E	E
Low brass - 80%	C24000	E	E
Cartridge brass - 70%	C26000	E	E
Leaded brasses	C31400–C38590	E	G
Phosphor bronzes	C50100–C52400	E	E
Copper-nickel - 30%	C71500	E	E
Copper-nickel - 10%	C70600	E	E
Nickel-silvers	C75200	E	E
Aluminum bronze	C61300, C61400	F	NR
Silicon bronzes	C65100–C65500	E	G

(a) E, excellent; G, good; F, fair; NR, not recommended

Effects of Alloying on Machinability

Lead, tellurium, sulfur, bismuth, and selenium are added to copper base metals to improve machinability. Free-cutting alloys containing such additions yield small, fragmented chips, making them well suited for high-speed machining operations (i.e., screw machine production).

Lead-Bearing Copper Alloys. Strictly speaking, lead-bearing copper alloys are composite structures rather than true alloys. This is because lead is insoluble in copper and appears as a dispersion of microscopic globules, as shown in Fig. 7. The stress-raising effect of these lead particles causes chips to break up into tiny flakes as the metal passes over the tool face. (This is what is meant by the term "free-cutting.")

Careful observations have shown that chips from leaded alloys remain in contact with the tool face for only a very short time before the energy of fracture actually propels them away from the cutting tool. The short contact time reduces friction, which in turn minimizes tool wear and energy consumption. It has been suggested that lead also acts as an "internal lubricant" as it smears over the tool face.

The beneficial effect of lead on free-cutting behavior increases with lead content, but the rate of improvement decreases as lead content rises. Significantly improved machinability can be measured in leaded alloys containing less than 0.5% Pb, although optimum free-cutting behavior

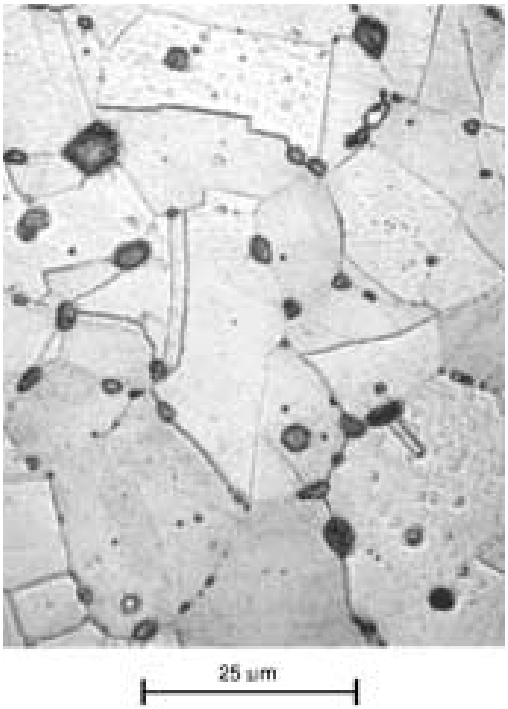


Fig. 7 Microstructure of alloy C36000 (free-cutting brass) showing globules of lead (dark) and alpha grains (light)

occurs at concentrations between 0.5% and 3.25% (Fig. 8). The specified nominal lead content in C36000 is 3.1%.

The ASTM test method E 618, "Standard Method for Evaluating Machining Performance Using an Automatic Screw/Bar Machine," is used to assess a material's machinability by determining the effect of production rate (spindle speed and cutting tool feed rate) on tool wear. Tool wear is measured indirectly by monitoring the test pieces' dimensions and surface finish, just as in commercial machine shop practice, where tools are resharpened when parts go out of tolerance. The ASTM test method makes it possible to interpolate the production rate that provides an "optimum" eight-hour tool life, and that production rate is taken as the test material's machinability rating (Fig. 9a).

The most important advantage of the ASTM E 618 method is that it permits a fair comparison of completely different materials. Such a comparison, particularly between free-cutting brass and leaded AISI/SA E 12L14 steel, has always been difficult, and the several machinability indexes currently in use only confuse the issue. When rated according to ASTM E 618, brass is nearly five times as machinable as the leaded steel, meaning that if C36000 were assigned an index rating of 100, AISI/SAE 12L14 would have a rating of 21. ASTM E 618-based machinability ratings of free-machining steel (AISI 12L14), aluminum alloy 2011, free-cutting brass (C36000), medium-leaded brass (C34000), and Naval brass (C46400) are shown in Fig. 9(b).

Alternative Free-Cutting Additives. Additions of tellurium, sulfur, and bismuth also produce free-cutting behavior in copper alloys. These elements can be more effective than lead in terms of the amounts needed to produce optimum improvements, but they are not without shortcomings. Bismuth and tellurium can cause serious embrittlement and/or directionally sensitive ductility when present in uncontrolled concentrations, while sulfur cannot be used in many alloy systems because of its reactivity. Generally, unleaded free-cutting alloys are considerably more expensive than leaded versions and therefore should be considered only when lead must be avoided entirely. Such is the case with plumbing fixtures, which have strict regulations regarding lead contents. Sand-cast faucets and other plumbing components have traditionally been made from leaded red or semi-red brasses, which no longer meet the lead content restrictions

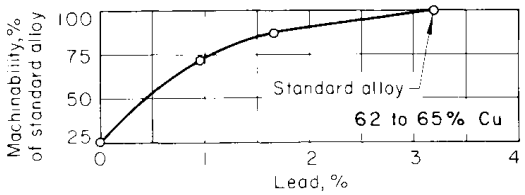
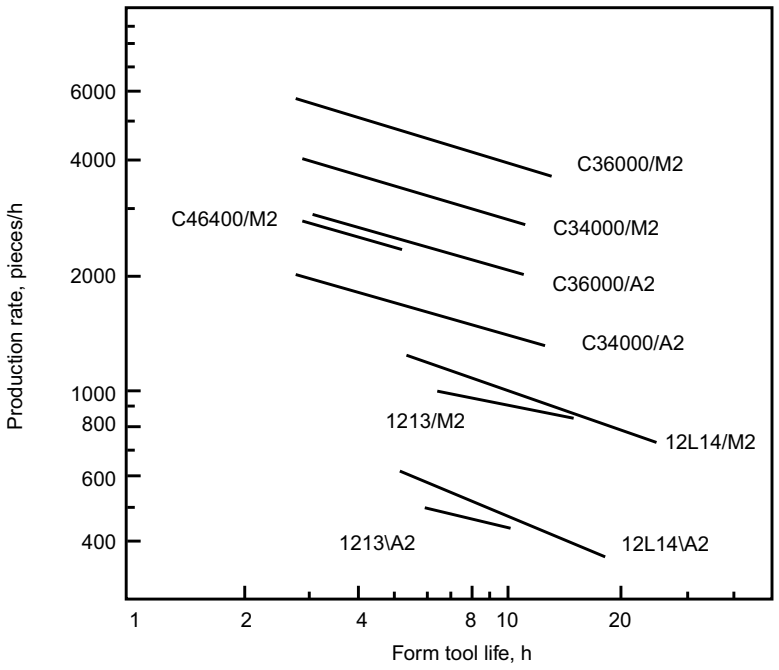
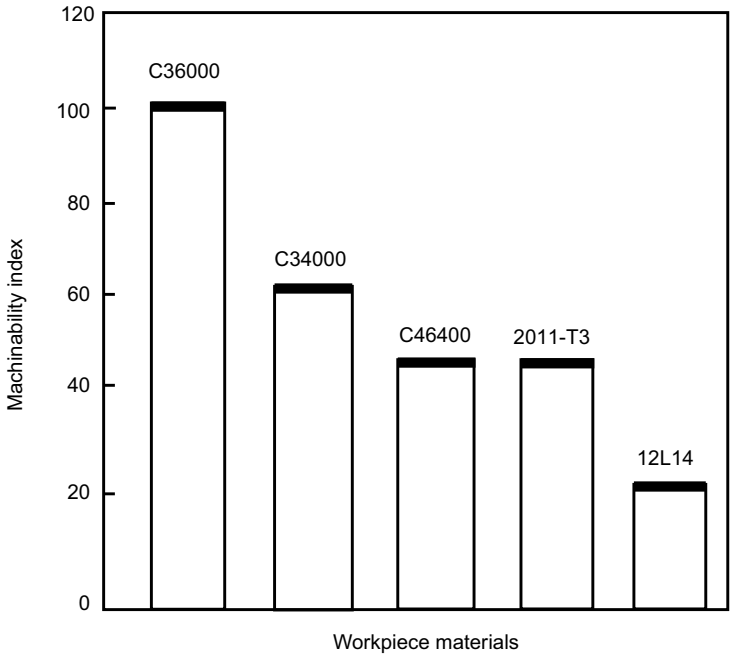


Fig. 8 Effect of lead content on the machinability of yellow brass



(a)



(b)

Fig. 9 Results of a universal machinability index test for various alloys. (a) Tool life data plotted to determine the maximum theoretical production rate for an 8-h hour tool life. This value of production rate is taken as the machinability rating of the material under test. (b) Universal machinability ratings (maximum theoretical production rates for 8-h M2 tool life) of common automatic screw machine materials using ASTM E 618. Data are normalized to alloy C36000 (free-cutting brass = 100).

established by the Environmental Protection Agency or the National Sanitation Foundation. This has led to the development of low-lead red brass casting alloys containing bismuth and selenium. Examples include C89510 and C89520, which contain between 0.5 and 2.2% Bi and 0.35 to 1.1% Se (Bi:Se ratio ≥2:1). These alloys have machinability ratings between 75 and 85 (C36000 = 100). Selenium enhances the effect of bismuth in red brasses; therefore, it reduces the amount of bismuth needed to improve machinability and lessens the chances of embrittlement.

Effects of Alloying on Workability and Castability

Workability. Copper itself is very easily hot or cold worked, with reductions in thickness of more than 99% possible before annealing is required. Workability is usually impaired by the presence of impurities and by alloying. The effects are particularly strong when impurities segregate to grain boundaries, which can lead to embrittlement, and when alloying gives rise to the formation of a brittle phase such as β in the copper-zinc system.

Soluble impurities such as silver, gold, nickel, and arsenic have no effect on hot workability. Because these elements do not form stable oxides in copper, they are benign in both oxygen-bearing and deoxidized or OF copper. Cadmium and antimony, which are also soluble in copper but do form stable oxides, are also innocuous, in this case because their concentration is normally too low to cause concern. Oxides of iron, tin, zinc, phosphorus, silicon, and aluminum are not deleterious because they are rarely entrained during solidification. Selenium and tellurium form brittle sulfides and oxides, and the presence of these compounds in copper seriously degrades both hot and cold workability.

Zinc improves cold formability, which reaches optimum levels at the familiar 70Cu-30Zn composition of cartridge brass, C26000. The presence of β phase in higher zinc brasses impedes cold formability, but hot workability (forgeability) is markedly improved. Forging brass, C37700, is one example of a material that takes advantage of this effect. The alloy's hot forgeability is high enough to overcome the detrimental effect of the small amount of lead added to improve machinability. Table 8 compares the forgeability ratings of the most commonly forged coppers and copper alloys. Forging brass (C37700), the least difficult alloy to forge, has been assigned an arbitrary forgeability rating of 100%.

Some copper alloys cannot be forged to any significant degree, because they will crack. Leaded copper-zinc alloys, such as architectural bronze, which may contain more than 2.5% Pb, are seldom recommended for hot forging. Although lead content improves metal flow, it promotes cracking

Table 8 Relative forgeability ratings of commonly forged copper alloys

Ratings are in terms of the most forgeable alloy, forging brass (C37700).

Alloy	Nominal composition	Relative forgeability(a), %
C10200	99.95 min Cu	65
C10400	Cu-0.027 Ag	65
C11000	99.9 min Cu	65
C11300	Cu-0.027 Ag + O	65
C14500	Cu-0.65Te-0.008P	65
C18200	Cu-0.10Fe-0.90Cr-0.10 Si-0.05Pb	80
C37700	Cu-38Zn-2Pb	100
C46400	Cu-39.2Zn-0.8Sn	90
C48200	Cu-38Zn-0.8Sn-0.7Pb	90
C48500	Cu-37.5Zn-1.8Pb-0.7Sn	90
C62300	Cu-10Al-3Fe	75
C63000	Cu-10Al-5Ni-3Fe	75
C63200	Cu-9Al-5Ni-4Fe	70
C64200	Cu-7Al-1.8Si	80
C65500	Cu-3Si	40
C67500	Cu-39Zn-1.4Fe-1Si-0.1Mn	80

(a) Takes into consideration such factors as pressure, die wear, and hot plasticity

in those areas of a forging, particularly deep-extruded areas, that are not completely supported by, or enclosed in, the dies. This does not mean that the lead-containing alloys cannot be forged, but rather that the design of the forging may have to be modified to avoid cracking.

The solubility of lead in β-brass at forging temperatures is about 2% maximum, but lead is insoluble in β-brass at all temperatures. Consequently, although a lead content of up to 2.5% is permissible in Cu-40Zn α-β brasses, lead in excess of 0.10% in a Cu-30Zn α-brass will contribute to catastrophic cracking.

Other copper alloys, such as the copper-nickels, can be forged only with greater difficulty and at higher cost. The copper-nickels, primarily because of their higher forging temperatures, are sometimes heated in a controlled atmosphere, thus complicating the process. The silicon bronzes, because of their high forging temperatures and their compositions, cause more rapid die deterioration than the common forging alloys.

Castability. Copper is alloyed with other elements for foundry applications because pure copper is extremely difficult to cast and it is prone to surface cracking, porosity problems, and the formation of internal cavities. The casting characteristics of copper can be improved by the addition of small amounts of elements including beryllium, silicon, nickel, tin, zinc, chromium, silver, and lead. Because they do not have to withstand mechanical working stresses, cast copper metals generally tolerate higher lead levels than their wrought counterparts. For example, lead is severely detrimental to hot workability, and high-leaded wrought brasses seldom contain more than 3.5 to 4% of the element. Cast leaded brasses normally contain as much as 6 to 8% Pb, and lead content may be as high as

25% in certain bearing bronzes and leaded coppers. Leaded red brasses and leaded tin bronzes, all of which have wide freezing ranges, are among the most castable copper alloys.

Lead improves the fluidity of casting alloys, making it easier to reproduce fine detail. Lead also seals the microscopic pores formed when certain alloys solidify; this sealing action renders such alloys pressure-tight. On the other hand, even small amounts of lead are severely detrimental to strength and ductility in cast high-strength yellow brasses. Phosphorus also improves fluidity, but allowable concentrations are severely restricted if aluminum is also present.

REFERENCES

1. D.H. Thompson and A.W. Tracy, Influence of Composition on the Stress-Corrosion Cracking of Some Copper-base Alloys, *Trans. AIME*, Vol 185, 1949, p 100
2. E.N. Pugh, J.V. Craig, and A.J. Sedriks, The Stress-Corrosion Cracking of Copper, Silver, and Gold Alloys, in *Proc. Conf. Fundamental Aspects of Stress Corrosion Cracking*, R.W. Staehle, A.J. Forty, and D. Van Rooyen, Ed., National Association of Corrosion Engineers, 1969, p 118
3. B.C. Syrett and R.N. Parkins, The Effect of Sn and As on the Stress Corrosion of Cu-Zn Alloys, *Corros. Sci.*, Vol 10, 1970, p 197
4. S. Torchio, The Influence of Arsenic and Phosphorus on the Stress Corrosion Cracking of Aluminum Brass in Chloride-Citrate Solution, *Corros. Sci.*, Vol 21, 1981, p 425
5. Y. Suzuki and Y. Hisamatsu, Stress Corrosion Cracking of Pure Copper in Dilute Ammoniacal Solutions, *Corros. Sci.*, Vol 21, 1981, p 353
6. S.P. Pednekar et al., Transgranular Cracking of Copper in 1M $NaNO_2$ Solution, *J. Electrochem. Soc.*, Vol 126, 1979, p 701
7. T.B. Cassagne, J. Kruger, and E.N. Pugh, Role of the Oxide Film in the Transgranular Stress Corrosion Cracking of Copper, in *Environmentally Assisted Cracking*: *Science and Engineering*, STP 1049, W.B. Lisagor, T.W. Crooker, and B.N. Leis, Ed., ASTM, 1990, p 59

SELECTED REFERENCES

- *ASM Specialty Handbook*: *Copper and Copper Alloys*, J.R. Davis, Ed., ASM International, 2001
- *Copper*: *Its Trade*, *Manufacture*, *Use*, *and Environmental Status*, G. Joseph and K.J.A. Kundig, Ed., International Copper Association, Ltd. and ASM International, 1999
- E.G. West, *Copper and Its Alloys*, Ellis Horwood Ltd, 1982

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Nickel and Nickel Alloys

Introduction and Overview

General Characteristics. Nickel and nickel-base alloys are vitally important to modern industry because of their ability to withstand a wide variety of severe operating conditions involving corrosive environments, high temperatures, high stresses, and combinations of these factors. There are several reasons for these capabilities. Pure nickel is ductile and tough because it possesses a face-centered cubic (fcc) structure up to its melting point (1453 °C, or 2647 °F). Therefore, nickel and nickel alloys are readily fabricated by conventional methods—wrought, cast, and powder metallurgy (P/M) products are available—and they offer freedom from the ductile-to-brittle transition behavior of other metals and alloys, including steels. Nickel has good resistance to corrosion in the normal atmosphere, in natural freshwaters, and in deaerated nonoxidizing acids, and it has excellent resistance to corrosion by caustic alkalies. Therefore, nickel offers very useful corrosion resistance, and it is an excellent base on which to develop specialized alloys that can capitalize on the unique properties of specific alloying elements.

Because nickel has an extensive solid solubility for many alloying elements, the micro-structure of nickel alloys consists of the fcc solid-solution austenite (γ) in which dispersoid and precipitate particles can form. Nickel forms a complete solid solution with copper and has nearly complete solubility with iron. It can dissolve ~35% Cr, 20% each of molybdenum and tungsten, and 5 to 10% each of aluminum, titanium, manganese, and vanadium. Thus, the tough, ductile fcc matrix can dissolve extensive amounts of elements in various combinations to provide solution hardening, as well as improved corrosion and oxidation resistance. The degree of solution hardening has been related to the atomic size difference between nickel and the alloying element, and therefore the ability of the solute to interfere with dislocation motion. Tungsten, molybdenum, niobium, tantalum, and aluminum, when aluminum is left in solution, are strong solution hardeners, with tungsten, niobium, tantalum, and molybdenum

also being effective at temperatures above 0.6 T_m (T_m is melting temperature), where diffusion-controlled creep strength is important. Iron, cobalt, titanium, chromium, and vanadium are weaker solution-hardening elements.

Finally, unique intermetallic phases can form between nickel and some nickel alloying elements. For example, aluminum and titanium are usually added together for the age-hardening gamma prime, γ', precipitate $Ni_3(Al, Ti)$. This enables the formation of alloys with very high strengths for both low- and high-temperature services.

Applications. Nickel and nickel alloys are used for a wide variety of applications, the majority of which involve corrosion resistance and/or heat resistance. Some of these include components used in the chemical and petrochemical industries, pollution control equipment, coal gasification and liquefaction systems, parts used in pulp and paper mills, aircraft gas turbines, team turbine power plants, turbochargers and valves in reciprocating engines, electrical and electronic applications, and heat-treating equipment. A number of other applications for nickel alloys involve the unique physical properties of special-purpose alloys, such as controlled-expansion alloys, electrical-resistance alloys, soft-magnetic alloys, and shape-memory alloys. Compositions, mechanical properties, and the corrosion resistance of nickel and nickel alloys are described in the following paragraphs.

Categories of Nickel and Nickel Alloys

Nickel and nickel alloys are often classified as either corrosion resistant or heat resistant alloys. This somewhat arbitrary distinction centers on whether the alloy composition and microstructure is optimized for aqueous corrosion resistance or elevated-temperature service. Heat resistant alloys can be further subdivided according to whether they are designed primarily for corrosion resistance to hot aggressive environments or for optimal strength and metallurgical stability. In practice, there is considerable overlap, and some versatile alloys are capable of serving effectively in multiple capacities. For example, alloy 718 (UNS N07718) resists corrosion in organic acids, alkalies and salts, and seawater; it is resistant to high-temperature oxidation, carburization, and nitridation; and it exhibits high strength at temperatures up to 700 °C (1300 °F). As a result, alloy 718 can be considered a corrosion resistant alloy, a heat resistant alloy, and/or a high-performance superalloy.

The alloys described in this article are resistant to aqueous corrosion, high-temperature corrosion, or both. Although emphasis has been placed on wrought alloys, it should be noted that cast counterparts exist for many

wrought compositions. Additional information on alloying of nickel-base high-strength alloys used for elevated-temperature applications can be found in the article "Superalloys."

The Nickel and Nickel Alloy Family

The nickel alloy family consists of:

- Commercially pure nickels
- Low-alloy nickels
- Nickel-copper alloys
- Nickel-molybdenum alloys
- Nickel-chromium-iron alloys
- Iron-nickel-chromium alloys
- Nickel-chromium-molybdenum alloys
- Nickel-chromium-iron-molybdenum alloys
- Nickel-chromium-tungsten alloys
- Nickel-iron-chromium alloys
- Nickel-cobalt-chromium-silicon alloys
- Precipitation-hardening (PH) alloys

Table 1 lists the compositions of commonly used alloys. As this table indicates, nickel-base alloys range in composition from ≥99% pure to complex alloys containing as many as 12 or more alloying elements. Figure 1 shows the many alloying combinations that make up the nickel alloy family. The effects of alloying elements on the corrosion resistance, strength, and structure of nickel-base alloys are listed in Table 2.

The commercially pure nickel grades, Nickel 200 to 205, are highly resistant to many corrosive media, especially in reducing environments, but also in oxidizing environments where they can maintain the passive nickel oxide surface film. They are used in the chemical processing and electronics industries. The most significant attribute of commercially pure nickels is their outstanding resistance to caustic alkalies—for example, sodium hydroxide (NaOH)—over a wide range of temperatures and concentrations. Figure 2 compares the corrosion rate of Nickel 200 and nickel-base alloys in 50% NaOH at ~150 °C (300 °F).

Commercially pure nickel grades are hot worked at 650 to 1230 °C (1200 to 2250 °F), annealed at 700 to 925 °C (1300 to 1700 °F), and are hardened by cold working. For processed sheet, for example, the tensile properties in the annealed condition (460 MPa, or 67 ksi, tensile strength; 148 MPa, or 22 ksi, yield strength; and 47% elongation) can be increased by cold rolling up to 760 MPa (110 ksi) tensile strength, 635 MPa (92 ksi) yield strength, and 8% elongation. Because of nominal 0.08% C content

Table 1 Compositions of commonly used wrought corrosion-resistant nickel and nickel alloys

Alloy	UNS No.	Composition(a), wt%							
		Ni	Cu	Fe	Mn	C	Si	S	Other
Commercially pure nickels									
Nickel 200	N02200	99.0 min	0.25	0.40	0.35	0.15	0.35	0.01	…
Nickel 201	N02201	99.0 min	0.25	0.40	0.35	0.02	0.35	0.01	…
Nickel 205	N02205	99.0 min(b)	0.15	0.20	0.35	0.15	0.15	0.008	0.01–0.08 Mg, 0.01–0.05 Ti
Nickel 212	…	97.0 min	0.20	0.25	1.5–2.5	0.10	0.20	…	0.20 Mg
Nickel 220	N02220	99.0 min	0.10	0.10	0.20	0.15	0.01–0.05	0.008	0.01–0.08 Mg
Nickel 225	N02225	99.0 min	0.10	0.10	0.20	0.15	0.15–0.25	0.008	0.01–0.08 Mg, 0.01–0.05 Ti
Nickel 230	N02230	99.0 min	0.10	0.10	0.15	0.15	0.01–0.035	0.008	0.04–0.08 Mg, 0.005 Ti
Nickel 270	N02270	99.97 min	0.001	0.005	0.02	0.02	0.001	0.001	0.001 Co, 0.001 Cr, 0.001 Ti
Low-alloy nickels									
Nickel 211	N02211	93.7 min	0.25	0.75	4.25–5.25	0.20	0.15	0.015	…
Duranickel 301	N03301	93.00 min	0.25	0.60	0.50	0.30	1.00	0.01	4.00–4.75 Al, 0.25–1.00 Ti
Alloy 360	N03360	bal	…	…	…	…	…	…	1.85–2.05 Be, 0.4–0.6 Ti
Nickel-copper alloys									
Alloy 400	N04400	63.0 min(b)	28.0–34.0	2.5	0.20	0.3	0.5	0.024	…
Alloy 401	N04401	40.0–45.0(b)	bal	0.75	2.25	0.10	0.25	0.015	…
Alloy 404	N04404	52.0–57.0	bal	0.50	0.10	0.15	0.10	0.024	0.05 Al
Alloy R-405	N04405	63.0 min(b)	28.0–34.0	2.5	2.0	0.3	0.5	0.25–0.060	…
Alloy K-500	N05500	63.0 min(b)	27.0–33.0	2.0	1.5	0.25	0.5	0.01	2.30–3.15 Al, 0.35–0.85 Ti

Alloy	UNS No.	Composition(a), wt%													
		Ni	Cr	Fe	Co	Mo	W	Nb	Ti	Al	C	Mn	Si	B	Other
Nickel-molybdenum alloys															
Hastelloy B	N10001	bal	1.0	6.0	2.5	26.0–33.0	…	…	…	…	0.12	1.0	1.0	…	0.60 V
Hastelloy B-2	N10665	bal	1.0	2.0	1.0	26.0–30.0	…	…	…	…	0.02	1.0	0.10	…	…
Hastelloy B-3	N10675	65.0	1.0–3.0	1.0–3.0	3.0	27.0–32.0	3.0	0.20	0.20	0.50	0.01	3.0	0.10	…	0.20 Ta
Nicrofer 6629 (B-4)	N10629	bal	0.5–1.5	1.0–6.0	2.5	26.0–30.0	…	…	…	0.1–0.5	0.01	1.5	0.05	…	…

(continued)

(a) Single values are maximum unless otherwise indicated. (b) Nickel plus cobalt content

Table 1 (continued)

Alloy	UNS No.	Composition(a), wt%												
		Ni	Cr	Fe	Co	Mo	W	Nb	Ti	Al	C	Mn	Si	B	Other
Nickel-chromium-iron alloys															
Inconel 600	N06600	72.0 min(b)	14.0–17.0	6.0–10.0	…	…	…	…	…	…	0.15	1.0	0.5	…	0.5 Cu
Inconel 601	N06601	58.0–63.0	21.0–25.0	bal	…	…	…	…	…	1.0–1.7	0.10	1.0	0.50	…	1.0 Cu
Inconel 690	N06690	58.0 min	27.0–31.0	7.0–11.0	…	…	…	…	…	…	0.05	0.50	0.50	…	0.50 Cu
Haynes 214	N07214	bal	15.0–17.0	2.0–4.0	2.0	0.5	0.5	…	0.5	4.0–5.0	0.05	0.5	0.2	0.006	0.05 Zr, 0.002–0.040Y
Iron-nickel-chromium alloys															
Incoloy 800	N08800	30.0–35.0	19.0–23.0	39.5 min	…	…	…	…	0.15–0.60	0.15–0.60	0.10	1.5	1.0	…	…
Incoloy 800HT	N08811	30.0–35.0	19.0–23.0	39.5 min	…	…	…	…	0.15–0.60	0.15–0.60	0.06–0.10	1.5	1.0	…	0.895–1.20 Al + Ti
Incoloy 801	N08801	30.0–34.0	19.0–22.0	bal	…	…	…	…	0.75–1.5	…	0.10	1.5	1.0	…	0.5 Cu
Incoloy 803	S35045	32.0–37.0	25.0–29.0	37.0 min	…	…	…	…	0.15–0.60	0.15–0.60	0.06–0.10	1.5	1.0	…	0.75 Cu
Nickel-chromium-molybdenum alloys															
Hastelloy C	N10002	bal	14.5–16.50	4.0–7.0	2.5	15.0–17.0	3.0–4.5	…	…	…	0.08	1.0	1.0	…	0.35 V
Hastelloy C-4	N06455	bal	14.0–18.0	3.0	2.0	14.0–17.0	…	…	0.70	…	0.015	1.0	0.08	…	…
Hastelloy C-22	N06022	bal	20.0–22.5	2.0–6.0	2.5	12.5–14.5	2.5–3.5	…	…	…	0.015	0.5	0.08	…	0.35 V
Hastelloy C-276	N10276	bal	14.5–16.50	4.0–7.0	2.5	15.0–17.0	3.0–4.5	…	…	…	0.02	1.0	0.08	…	0.35 V
Hastelloy C-2000	N06200	bal	22.0–24.0	3.0	2.0	15.0–17.0	…	…	…	0.5	0.010	0.5	0.08	…	1.3–1.9 Cu
Nicrofer 5923 (Alloy 59)	N06059	bal	22.0–24.0	1.5	0.3	15.0–16.5	…	…	…	0.1–0.4	0.010	0.5	0.10	…	…
Inconel 617	N06617	44.5 min	20.0–24.0	3.0	10.0–15.0	8.0–10.0	…	…	0.6	0.8–1.5	0.05–0.15	1.0	1.0	0.006	0.5 Cu
Inconel 625	N06625	58.0 min	20.0–23.0	5.0	1.0	8.0–10.0	…	3.15–4.15	0.40	0.40	0.10	0.50	0.50	…	…
Inconel 686	N06686	bal	19.0–23.0	5.0	…	15.0–17.0	3.0–4.4	…	0.02–0.25	…	0.010	0.75	0.08	…	…
Hastelloy S	N06635	bal	14.5–17.0	3.0	2.0	14.0–16.5	1.0	…	…	0.1–0.50	0.02	0.3–1.0	0.20–0.75	0.015	0.35 Cu, 0.01–0.10 La
Allcorr	N06110	bal	27.0–33.0	…	12.0	8.0–12.0	4.0	2.0	1.50	1.50	0.15	…	…	…	…

(continued)

(a) Single values are maximum unless otherwise indicated. (b) Nickel plus cobalt content

Table 1 (continued)

Alloy	UNS No.	Composition(a), wt%													
		Ni	Cr	Fe	Co	Mo	W	Nb	Ti	Al	C	Mn	Si	B	Other
Nickel-chromium-iron-molybdenum alloys															
Incoloy 825	N08825	38.0–46.0	19.5–23.5	bal	…	2.5–3.5	…	…	0.6–1.2	0.2	0.05	1.0	0.5	…	…
Hastelloy G	N06007	bal	21.0–23.5	18.0–21.0	2.5	5.5–7.5	1.0	1.75–2.5	…	…	0.05	1.0–2.0	1.0	…	…
Hastelloy G-2	N06975	47.0–52.0	23.0–26.0	bal	…	5.0–7.0	…	…	0.70–1.5	…	0.03	1.0	1.0	…	0.7–1.20 Cu
Hastelloy G-3	N06985	bal	21.0–23.5	18.0–21.0	5.0	6.0–8.0	1.5	…	…	…	0.015	1.0	1.0	…	1.5–2.5 Cu, 0.50 Nb + Ta
Hastelloy G-30	N06030	bal	28.0–31.5	13.0–17.0	5.0	4.0–6.0	1.5–4.0	0.3–1.5	…	…	0.03	1.5	0.8	…	1.0–2.4 Cu
Hastelloy G-50	N06950	50.0 min	19.0–21.0	15.0–20.0	2.5	8.0–10.0	1.0	0.5	…	…	0.015	1.0	1.0	…	0.5 Cu
Hastelloy D-205	…	65.0	20.0	6.0	…	2.5	…	…	…	…	0.03	…	5.0	…	2.0 Cu
Hastelloy N	N10003	bal	6.0–8.0	5.0	0.2	15.0–18.0	0.5	…	…	…	0.010	1.0	1.0	0.010	0.50 V, 0.35 Cu
Hastelloy X	N06002	bal	20.5–23.0	17.0–20.0	0.5–2.5	8.0–10.0	0.20–1.0	…	…	…	0.05–0.15	1.0	1.0	…	…
Nicrofer 3033 (Alloy 33)	R20033	30.0–33.0	31.0–35.0	bal	…	0.5–2.0	…	…	…	…	0.015	2.0	0.5	…	0.3–1.2 Cu
Nickel-chromium-tungsten, nickel-iron-chromium, and nickel-cobalt-chromium-silicon alloys															
Haynes 230	N06230	bal	20.0–24.0	3.0	…	1.0–3.0	13.0–15.0	…	…	0.20–0.50	0.05–0.15	0.3–1.0	0.25–0.75	0.015	0.005–0.05 La
Haynes HR-120	N08120	35.0–39.0	23.0–27.0	bal	3.0	2.5	2.5	0.4–0.9	0.20	0.40	0.02–0.1	1.5	1.0	0.010	0.5 Cu
Haynes HR-160	N12160	bal	26.0–30.0	3.5	27.0–33.0	1.0	1.0	…	0.20–0.80	…	0.15	1.5	2.4–3.0	…	…
Precipitation-hardening alloys															
Alloy 625 Plus	N07716	57.0–63.0	19.0–22.0	bal	…	7.0–9.50	…	2.75–4.0	1.0–1.60	0.35	0.03	0.20	0.20	…	…
Inconel 718	N07718	50.0–55.0	17.0–21.0	bal	1.0	2.80–3.30	…	4.75–5.50	0.35	0.20–0.80	0.08	0.35	0.35	0.06	0.3 Cu
Inconel 725	N07725	55.0–59.0	19.0–22.5	bal	…	7.0–9.50	…	2.75–4.0	1.0–1.70	0.35	0.03	0.35	0.50	…	…
Inconel 925	N09925	38.0–46.0	19.5–23.5	22.0 min	…	2.50–3.50	…	0.50	1.9–2.40	0.10–0.50	0.03	1.0	0.50	…	1.5–3.0 Cu

(a) Single values are maximum unless otherwise indicated. (b) Nickel plus cobalt content

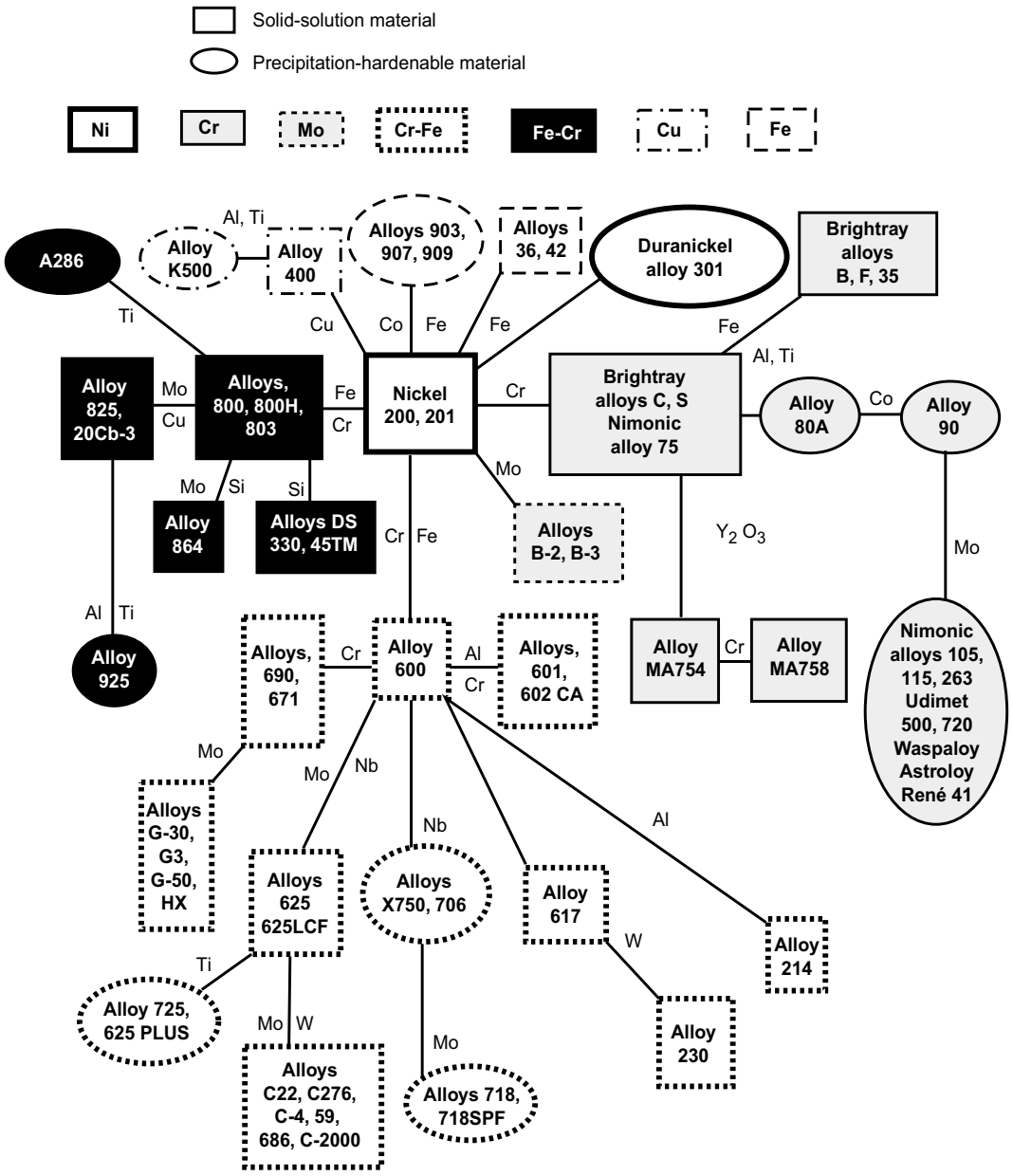


Fig. 1 Development of the nickel alloy family

(0.15% max), Nickel 200 (N02200) should not be used above 315 °C (600 °F) because embrittlement results from the precipitation of graphite in the temperature range 425 to 650 °C (800 to 1200 °F). The more widely used low-carbon alloy Nickel 201 (N02201), with 0.02% max C, can be used at temperatures above 290 °C (550 °F).

Higher-purity nickel is commercially available for various electrical and electronic applications. For example, Nickel 270 (N02270) contains a minimum of 99.9% Ni.

Effects of Impurities. In general, minor constituents or impurities that exist in solid solution in nickel tend to increase hardness, strength, and

Table 2 Effects of alloying elements on the corrosion resistance, strength, and structure of nickel alloys

Element	Effect
Nickel	Improves high-temperature strength
	Improves resistance to oxidation, nitridation, carburization, and halogenation
	Detrimental to sulfidation
	Improves metallurgical stability
	Improves resistance to reducing acids and caustic
	Improves resistance to stress-corrosion cracking
Aluminum	Improves oxidation and sulfidation resistance
	Age-hardening component
Iron	Improves economy of alloy
	Controlled thermal expansion addition
Rare earth elements lanthanum and yttrium	Improves adherence of oxide layer
Copper	Improves resistance to reducing acids and salts (Ni-Cu alloys)
	Improves resistance to sulfuric acid
Niobium	Improves high-temperature strength
	Improves resistance to pitting
	Carbide stabilization component
	Age-hardening component
Sulfur	Improves machinability
Chromium	Improves oxidation and sulfidation resistance
	Below 18% can improve resistance to halogens or high-temperature halides
	Improves aqueous corrosion resistance
Carbon	High-temperature strength
Silicon	Improves oxidation and carburization resistance, especially under alternating oxidizing and reducing conditions
Cobalt	Improves high-temperature strength and oxidation resistance
	Controlled thermal expansion addition
Molybdenum	Improves high-temperature strength
	May reduce oxidation resistance
	Improves resistance to pitting and crevice corrosion
	Improves resistance to reducing acids
Nitrogen	Can improve high-temperature strength by precipitation of stable nitrides
	Improves pitting and crevice corrosion resistance
	Improves metallurgical stability by acting as an austenitizer
Titanium	Detrimental to oxidation due to titanium oxides disrupting primary oxide scale
	Age-hardening component
	Carbide stabilization component
Tungsten	Improves resistance to pitting and crevice corrosion
	Improves high-temperature strength
Yttrium oxide	Improves high-temperature strength
	Improves grain size control
	Improves resistance to oxidation

electrical resistivity; they also decrease thermal expansion and thermal conductivity, and, except for iron and cobalt, lower the Curie temperature. Nickel will form solid solutions with elements whose atomic radii differ from that of nickel by not more than 11 percent. Impurities that are present in excess of the solid solubility in nickel chiefly affect the workability, particularly the hot workability, and affect the resistance to corrosive attack. Of the minor constituents listed in the commercially pure nickel grades in Table 1, only small amounts of manganese and magnesium are sometimes *deliberately* added. These elements act in concert to control the harmful effects of sulfur and to enhance hot workability and extend the hot working range.

Low-alloy nickels contain 94% min Ni. The 5% Mn solid-solution addition in Nickel 211 (N02211) protects against sulfur in service environments. As little as 0.005% S can cause liquid embrittlement at unal-

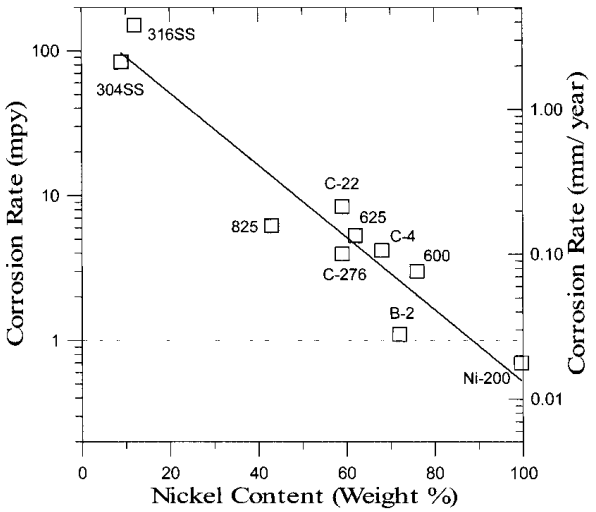


Fig. 2 Effect of nickel content on the corrosion resistance of various alloys in 50% NaOH (caustic soda) at ~150 °C (300 °F). As the nickel content increases, the corrosion rate in caustic solutions decreases.

loyed nickel grain boundaries in the range between 640 and 740 °C (1185 and 1365 °F).

Duranickel alloy 301 (N03301), which contains 4.5% Al and 0.6% Ti, offers the corrosion resistance of commercially pure nickel with the strengthening provided by the precipitation of γ'. There are sufficient alloying additions in alloy 301 to lower the Curie temperature, making the alloy weakly ferromagnetic at room temperature.

Another low-alloy nickel of commercial importance is the nickel-beryllium alloy 360 (N03360). Containing about 2 wt% Be and 0.5% Ti, this precipitation-hardening alloy is used primarily as mechanical and electrical/electronic components that must exhibit good spring properties at elevated temperatures.

Nickel-Copper Alloys. The first useful corrosion resistant nickel-base alloy was the nickel-copper alloy Monel 400 (N04400), which was developed in 1905. Strong and tough, it was found to be resistant to corrosion in various environments, including brine, sulfuric acid, and other acids, and was immune to stress-corrosion cracking (SCC). Alloy 400 and other nickel-copper alloys are used in chemical processing and pollution equipment.

Capable of precipitating γ', $Ni_3(Al,Ti)$ with 2.7Al-0.6Ti alloy addition, alloy K-500 (N05500) adds an age-hardening component to the good solution-strengthening and work-hardening characteristics already available with the nominal 30% Cu in alloy 400. The composition of these alloys can be adjusted to decrease the Curie temperature to below room temperature.

Nickel-Molybdenum Alloys. The original nickel-molybdenum alloy, Hastelloy B (N10001), was introduced in 1923. It displays excellent resistance to hydrochloric acid and other reducing environments. A minimum molybdenum content of 26% is needed for very low corrosion rates in boiling hydrochloric acid even when dilute. In 1974 an improved version of alloy B with low-iron and low-carbon contents was introduced. Called Hastelloy B-2 (N10665), it contains nominal 28% Mo, 0.8% Fe, and 0.002% C. Twenty years later, Hastelloy B-3 (N10675) (with nominal 28.5% Mo, 1.5% Cr, 1.5% Fe, and 0.003% C) and Nicrofer 6628 or B-4 (N10629) (with nominal 28% Mo, 1.3% Cr, 3% Fe, and 0.005% C) were introduced. These alloys provide a level of thermal stability superior to alloy B-2.

Slightly lowering the molybdenum content to a nominal 24% Mo and adding 6% Fe, 5% Cr, and 2.5% Co produces Hastelloy W (N10004). This alloy is widely used as a weld filler metal used to join dissimilar high-temperature alloys. It is used extensively in aircraft engine repair and maintenance.

The Ni-Cr-Fe alloys might simply be thought of as nickel-base analogs of the iron-base austenitic stainless steel alloys, with an interchange of the iron and nickel contents. In these commercially important alloys, the chromium content in general ranges from 15 to 30%, and iron ranges from 3 to 20%. With a well-maintained Cr_2O_3 surface film, these alloys offer excellent corrosion resistance in many severe environments, showing immunity to chloride-ion SCC. They also offer good oxidation and sulfidation resistance with good strength at elevated temperatures. These nickel-rich Ni-Cr-Fe alloys have maximum operating temperatures of approximately 1200 °C (2200 °F). Alloy 600 (N06600), which was developed in 1931 and contains a nominal 15% Cr and 8% Fe, is a single-phase alloy that can be used at temperatures from cryogenic to 1093 °C (2000 °F). The modest yield strength of strip in the annealed condition (207 to 310 MPa, or 30 to 45 ksi) can be readily work hardened by cold rolling to reach yield strengths of 827 to 1100 MPa (120 to 160 ksi) and can retain most of this strength up to approximately 540 °C (1000 °F).

Other alloys in this family include the higher-chromium-content (29% Cr) alloy 690 (N06690) developed for improved performance in nuclear steam generators, aluminum-containing (1.4% Al) alloy 601 (N06601) developed for improved oxidation resistance, and the Ni-Cr-Al-Fe alloy 214 (N07214) that contains 4.5% Al and has the highest oxidation resistance of any wrought alloy at temperatures of 955 °C (1750 °F) and above.

The Fe-Ni-Cr alloys are also an extension of stainless steel technology. Incoloy alloy 800 (N08810) was designed as a leaner nickel version of the Ni-Cr-Fe series of materials described previously. It offers good oxidation resistance and was introduced as a sheathing material for electric stove

elements. The 800 alloy series has also found extensive use in high-temperature petrochemical environments, where sulfur-containing feedstocks (naptha and heavy oils) are cracked into component distillate parts. Not only are they resistant to chloride-ion SCC, but they also offer resistance to polythionic acid cracking. (Alloy 801 offers optimum resistance.) The Fe-Ni-Cr alloys also offer excellent strength at elevated temperature (creep and stress rupture).

The Ni-Cr-Mo alloys consist of a large family of alloys that are used in the chemical processing, pollution control, and waste treatment industries due to their excellent heat and corrosion resistance. As indicated in Table 1, these alloys contain a nominal 52 to 60% Ni, 15 to 31% Cr, 9 to 16% Mo, and smaller additions of other elements, such as iron and tungsten.

The Hastelloy C series of alloys was introduced in the 1930s. The original alloy C (N30002) served the chemical processing industry for approximately 30 years. However, it had several serious limitations. In many applications, vessels fabricated from alloy C had to be solution heat treated to remove detrimental weld heat-affected zone (HAZ) precipitates. When used in the as-welded condition, alloy C was often susceptible to serious intergranular corrosion attack in many oxidizing and chloride-containing environments. The first modification of alloy C was an alloy that had carbon and silicon contents reduced more than tenfold, typically 0.005% C and 0.04% Si. This alloy came to be known as C-276 (N10276).

Several variants of C-276 have also been introduced, including:

- *Alloy C-4 (N06455)*, which has improved thermal stability. In this alloy, the tungsten was totally omitted and the iron content was reduced to approximately 1%. The alloy also contains approximately 0.3% Ti.
- *Alloy C-22 (N06022)*, which has better resistance to chloride-induced localized corrosion and SCC. In this alloy, the chromium content was raised to approximately 21% and molybdenum content reduced to approximately 13%. It also contains approximately 0.2% V and 1.7% Co.
- *Alloy 59 (N06059)*, with a chromium content of approximately 23%, iron less than 1%, and approximately 0.2% Al for very severe corrosive applications
- *Alloy C-2000 (N06200)*, with approximately 1.6% Cu added for improved corrosion resistance in sulfuric acid and reducing media

Alloys 625 and 617, which were introduced in the 1960s, were developed for aircraft engines but have found wide use in other applications requiring high-temperature strength and corrosion resistance. Alloy 625 (N06625) contains a nominal 20% Cr, 9% Mo, and 2.5% Fe and is stabilized with approximately 3.5% Nb. In alloy 617 (N06617), some of the nickel has been replaced with cobalt (~12.5% Co). Other 600-series

Ni-Cr-Mo alloys include alloys 622 (N06022) and 686 (N06686), both of which contain tungsten additions.

Hastelloy S (N06635) contains a nominal 67% Ni, 16% Cr, and 15% Mo, as well as other alloying elements that improve its thermal stability, fatigue life, oxidation resistance, and low-expansion characteristics. It is used in low-stress gas turbine parts and is an excellent dissimilar filler metal.

The Ni-Cr-Fe-Mo alloys constitute another large family of nickel alloys. Alloy 825 (N08825) was developed in the 1950s for sulfuric acid service. It contains a nominal 42% Ni, 22% Cr, 32% Fe, 2.5% Mo, and 2% Cu, and is stabilized with 0.8% Ti. The Hastelloy G series of alloys was developed for use in wet-process phosphoric acid service. They contain a nominal 22 to 30% Cr, 15 to 20% Fe, 5 to 7% Mo, and smaller additions of cobalt and niobium. The lower carbon variants of the predecessor alloy G (N06007), which include G-3 (N06985) and G-30 (N06039), have improved resistance to HAZ carbide precipitation, improved resistance to hot cracking, and improved weld metal bend ductility. Alloy G-50 was developed for use in sour gas environments.

Other alloys in the Ni-Cr-Fe-Mo family include:

- *Hastelloy X (N06002)*, which contains a nominal 47% Ni, 22% Cr, 18% Fe, and 9% Mo and is widely used for aircraft, marine, and industrial gas turbine combustors and fabricated parts
- *Hastelloy N (N10003)*, which contains a nominal 71% Ni, 7% Cr, 5% Fe, and 16% Mo and is highly resistant to molten fluoride salts
- *Hastelloy D-205 (UNS No. pending)*, which contains a nominal 65% Ni, 20% Cr, 6% Fe, and 2.5% Mo, plus additions of 5% Si and 2% Cu, and is highly resistant to hot concentrated sulfuric acid
- *Nicrofer 3033*, also referred to as alloy 33 (R20033), which contains a nominal 31% Ni, 33% Cr, 32% Fe, and 1.6% Mo, plus an addition of 0.4% N, and is highly resistant to sulfuric acid.

Miscellaneous Solid-Solution Alloys. Some of the more recently developed alloys that exhibit excellent resistance to high-temperature corrosion do not fit into the alloy families described above. Three examples are:

- *Alloy 230 (N06230)*, which is a Ni-Cr-W alloy (see Table 1 for the composition). It has an excellent balance of strength, thermal stability, oxidation resistance, thermal cycling resistance, and fabricability. It is used in gas turbine combustors and other key stationary components. It is also used for heat treating and industrial heating applications, and in the chemical/petrochemical process industry and in fossil fuel energy plants.
- *HR-120 (N08120)*, which is a Ni-Fe-Cr alloy containing a wide variety of alloying elements (see Table 1). Because of its high iron content

(33% Fe), this is an economical alloy that exhibits high strength and excellent resistance to carburization and sulfidation. It is used in heat-treating fixtures and industrial heating applications.

- *HR-160 (N12160)*, which is a Ni-Co-Cr-Si-Fe alloy (see Table 1). It has outstanding resistance to sulfidation and chloride attack and is used in a variety of fabricated components that are used in municipal, industrial, and nuclear waste incinerators.

Precipitation-Hardening Alloys. The increasing use of nickel alloys in natural gas production led to the development of high-strength, corrosion resistant, age-hardenable alloy 925 (N09925) and age-hardening variations of alloy 625, including alloy 725 (N07725) and 626 PLUS (N07716). Alloy 925 offers corrosion resistance comparable with that of alloy 825, but with higher strength obtained by age hardening (see Table 3). A similar relationship exists between alloys 725 and 625 PLUS and solid-solution strengthened alloy 625.

As stated earlier in this article, alloy 718 (N07718) is another age-hardenable alloy that is highly corrosion resistant. Its high strength, corrosion resistance, and ease of weld fabrication have made alloy 718 the most popular superalloy used in industry.

Effects of Alloying on Corrosion Resistance

The roles of the major alloying elements are summarized below. Figure 3 shows some compositional modifications that result in improved corrosion resistance.

Copper. Additions of copper provide improvement in the resistance of nickel to nonoxidizing acids. In particular, alloys containing 30 to 40% Cu offer useful resistance to nonaerated sulfuric acid (H_2SO_4) and offer excellent resistance to all concentrations of nonaerated hydrofluoric acid (HF). Additions of 2 to 3% Cu to Ni-Cr-Mo-Fe alloys have also been found to improve resistance to hydrochloric acid (HCl) H_2SO_4, and phosphoric acid (H_3PO_4).

Chromium additions impart improved resistance to oxidizing media such as nitric (HNO_3) and chromic (H_2CrO_4) acids. Improved resistance to hot H_3PO_4 has also been shown. Chromium also improves resistance to high-temperature oxidation and to attack by hot sulfur-bearing gases. Although alloys have been formulated containing up to 50% Cr, alloying additions are usually in the range of 15 to 30%.

Iron is typically used in nickel-base alloys to reduce costs, not to promote corrosion resistance. However, iron does provide nickel with

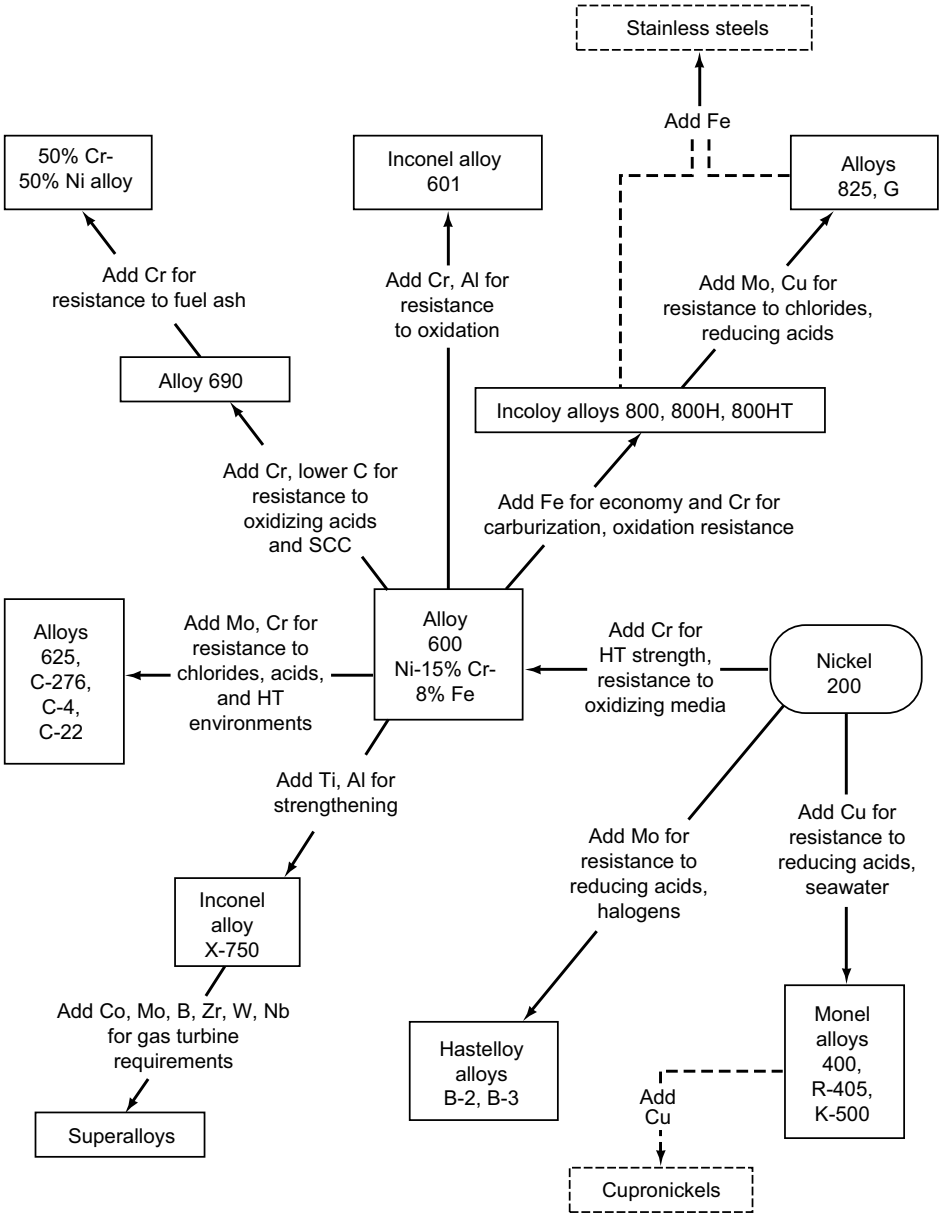


Fig. 3 Effects of alloying additions on the corrosion resistance of nickel alloys. HT, high-temperature

improved resistance to H_2SO_4 in concentrations above 50%. Iron also increases the solubility of carbon in nickel; this improves resistance to high-temperature carburizing environments.

Molybdenum in nickel substantially improves resistance to nonoxidizing acids. Commercial alloys containing up to 28% Mo have been developed for service in nonoxidizing solutions of HCl, H_3PO_4, and HF, as well as in H_2SO_4 in concentrations below 60%. Molybdenum also markedly improves the pitting and crevice corrosion resistance of nickel-base

alloys. In addition, it is an important alloying element for imparting strength in metallic materials designed for high-temperature service.

Tungsten behaves similarly to molybdenum in providing improved resistance to nonoxidizing acids and to localized corrosion. However, because of its atomic weight, approximately twice as much tungsten as molybdenum must be added by weight to achieve atomically equivalent effects. Because of the negative impact this would have on alloy density and because of the typically higher cost and lower availability of tungsten, additions of molybdenum are generally preferred. However, additions of tungsten of the order of 3 to 4% in combination with 13 to 16% Mo in a nickel-chromium base result in alloys with outstanding resistance to localized corrosion.

Silicon is typically present only in minor amounts in most nickel-base alloys as a residual element from deoxidation practices or as an intentional addition to promote high-temperature oxidation resistance. In alloys containing significant amounts of iron, cobalt, molybdenum, tungsten, or other refractory elements, the level of silicon must be carefully controlled because it can stabilize carbides and harmful intermetallic phases. On the other hand, the use of silicon as a major alloying element has been found to improve greatly the resistance of nickel to hot, concentrated H_2SO_4. Alloys containing 9 to 11% Si are produced for such service in the form of castings (e.g., Hastelloy D containing 9.5% Si).

Cobalt. The corrosion resistance of cobalt is similar to that of nickel in most environments. Because of this and because of its higher cost and lower availability, cobalt is not generally used as a primary alloying element in materials designed for aqueous corrosion resistance. On the other hand, cobalt imparts unique strengthening characteristics to alloys designed for high-temperature service. Cobalt, like iron, increases the solubility of carbon in nickel-base alloys, and this increases resistance to carburization. Further, the melting point of cobalt sulfide is higher than that of nickel sulfide; therefore, alloying with cobalt also tends to improve high-temperature sulfidation resistance.

Niobium and Tantalum. In corrosion resistant alloys, both niobium and tantalum were originally added as stabilizing elements to tie up carbon and prevent intergranular corrosion attack due to grain-boundary carbide precipitation. However, the advent of argon-oxygen decarburization melting technology made it possible to achieve very low levels of residual carbon, and such additions of niobium and tantalum are no longer necessary. In high-temperature alloys, both elements are used to promote high-temperature strength through solid-solution and precipitation-hardening mechanisms. Additions of these elements are also considered to

be beneficial in reducing the tendency of nickel-base alloys toward hot cracking during welding.

Aluminum and titanium are often used in minor amounts in corrosion resistant alloys for the purpose of deoxidation or to tie up carbon and/or nitrogen, respectively. When added together, these elements enable the formulation of age-hardenable high-strength alloys for low- and elevated-temperature service. Additions of aluminum can also be used to promote the formation of a tightly adherent alumina scale at high temperature that resists attack by oxidation, carburization, and chlorination.

Carbon and Carbides. Carbide precipitation is an important factor affecting corrosion of nickel-base alloys. In nickel, carbon is known to form Ni_3C, but it decomposes to graphite, which weakens the grain boundaries. This is why low-carbon forms of nickel are usually preferred in corrosion-resistant applications. The addition of copper reduces the tendency to graphitization. In the other nickel-base alloys, the type and composition of carbides depend on the composition of the alloy.

In corrosion-resistant alloys, many types of carbides are considered harmful because they can precipitate at grain boundaries during heat treatment or weld fabrication and subsequently promote intergranular corrosion or cracking in service. This results from the depletion of matrix elements essential to corrosion resistance during the carbide precipitation process. In high-temperature alloys, the presence of carbides is generally desired to control grain size and to enhance elevated-temperature strength and ductility. However, careful attention must be paid to the carbide types and morphologies after solution heat treatment or postfabrication heat treatment in order to avoid cracking during component manufacture or loss of strength and/or ductility in service.

Primary and Secondary Carbides. In discussing carbides, it is necessary to distinguish between primary and secondary types. Primary carbides form during the solidification process. They are interdendritic and form from the last liquid to freeze, which is generally enriched in alloying elements. These carbides are typically metastable and would dissolve if given sufficient time at elevated temperatures. However, during metal manufacture, this is usually not the case; therefore, they can persist in the final product as stringers in the direction of predominant metal flow. Some level of carbide stringers usually must be tolerated because they cannot be economically avoided in complex alloy systems. However, large amounts of such stringers should be avoided, because they can adversely affect formability, weld fabrication, and service performance characteristics.

Secondary carbides are those that precipitate as the result of thermal exposures during metal manufacture and component fabrication operations or during component service life. These carbides precipitate preferentially on grain boundaries and internal structural defects, such as twin

boundaries and dislocations. The quantity of secondary carbides that precipitate depends on the amount of carbon in solution, the exposure temperature, and the time at temperature. Therefore, conditions that generate a supersaturated solution of carbon followed by slow cooling or thermal arrests below carbide solvus temperatures will produce heavy secondary carbide precipitation. It is also possible to generate aligned or stringer-type structures of secondary carbides. This can occur if an alloy with secondary precipitates is mechanically worked and annealed below the solvus temperature. Heavy secondary carbide precipitation generally reduces ductility and toughness, and this adversely affects fabrication and service performance.

Chromium-Rich and Refractory Metal Carbides. The carbide types occurring in nickel-base alloys can be separated into two broad categories: those that are chromium rich and those that are rich in refractory alloying elements. The chromium-rich carbides are of the forms Cr_7C_3 and $M_{23}C_6$. The Cr_7C_3 carbide forms only in a few simple alloys that are low in chromium as well as reactive and refractory alloying elements. It occurs as a blocky, intergranular precipitate, and it is stable only at temperatures of the order of 1050 to 1150 °C (1920 to 2100 °F). It decomposes into $M_{23}C_6$ at lower temperatures.

The $M_{23}C_6$ carbide can range in chemistry from $Cr_{23}C_6$ in simple nickel-chromium alloys to $Cr_{21}(Mo, W)_2C_6$ in alloys containing molybdenum and tungsten. Other elements, such as nickel, iron, and cobalt, can partially substitute for chromium. The $M_{23}C_6$ carbide can assume a variety of morphologies, such as discrete, globular particles, continuous grain-boundary films, or a cellular grain-boundary structure. In some alloys, the latter two forms can seriously reduce ductility. Depending on alloy chemistry, $M_{23}C_6$ carbides can be stable to temperatures of 1150 °C (2100 °F) or above. Precipitation kinetics are particularly rapid in the temperature range of 760 to 980 °C (1400 to 1800 °F), which may be encountered during heat treatment or in-service exposure.

The common refractory metal carbides take on the forms of MC, M_6C, and $M_{12}C$. The MC carbides are formed by the reactive metal elements, such as titanium, zirconium, and hafnium, and by the refractory metal elements, such as vanadium, niobium, and tantalum. The MC carbides can contain mixtures of these elements (for example, (Ti,Nb)C) as well as less refractory elements, such as molybdenum and tungsten (for example, (TiMo)C). If nitrogen is present in the alloy, carbonitride forms, such as Nb(C,N), are also possible. When present, these carbonitrides exhibit yellow to orange coloration, as opposed to the steel gray appearance of the simple monocarbide. The MC carbides are usually formed as primary carbides. In wrought alloys, they are present as discrete, angularly shaped particles within grains and at grain boundaries. In cast alloys, they are usually present in a script morphology at interdendritic locations. The MC carbides are extremely stable and do not break down easily unless

weakened by molybdenum or tungsten substitution. Decomposition of the MC carbide can yield the $M_{23}C_6$ or M_6C carbide forms.

The M_6C carbides, also known as the eta (η) carbides, are usually formed between the refractory elements molybdenum and tungsten and the major matrix elements of nickel, iron, cobalt, and chromium. Carbide chemistries can vary widely from forms such as $(Ni,Co)_3Mo_3C$ to $(Ni,Co)_2W_4C$, and carbon contents may range above and below that required for stoichiometry. Silicon is also known to enter the carbide in large amounts. The M_6C carbides can form both as primary and secondary precipitates in a globular morphology. Their solvus temperatures are high, typically of the order of 1175 °C (2150 °F) or higher. In the temperature range of 760 to 980 °C (1400 to 1800 °F), they can decompose into the $M_{23}C_6$ or $M_{12}C$ carbide forms, depending on the alloy system.

The $M_{12}C$ carbides are closely related to the M_6C carbides. They usually form between the refractory elements molybdenum and tungsten and the matrix elements nickel, iron, cobalt, and chromium. However, unlike M_6C, the $M_{12}C$ carbides exhibit a very narrow chemistry range, with a composition such as Ni_6Mo_6C representing a typical example. Silicon is also known to enter the carbide preferentially in large quantities. The $M_{12}C$ carbide is usually observed as a secondary carbide after the dissolution or decomposition of primary M_6C carbides. Once formed, the $M_{12}C$ carbides are very stable, with solvus temperatures of 1175 °C (2150 °F) and above.

Intermetallic Phases. The occurrence of intermetallic phases in nickel-base alloys carries both good and bad connotations. On the positive side, the nickel-base system has been the most widely and successfully exploited of any alloy base in the development of high-strength high-temperature alloys because of the occurrence of unique intermetallic phases such as gamma prime (γ') and gamma double prime (γ''). On the negative side, the precipitation of certain intermetallic phases such as sigma (σ), mu (μ), and Laves phase can seriously degrade ductility and corrosion resistance. This latter effect results from the fact that intermetallics, like carbides, can rob the matrix of elements vital to service performance.

In the case of corrosion resistant alloys, especially the solid-solution type, the formulation of alloy chemistry to avoid intermetallic precipitation altogether is not necessary, because service temperatures are usually well below those at which precipitation kinetics become important. In such cases, it is necessary only to restrict alloy composition sufficiently to ensure successful manufacturing, fabrication, and use capabilities. For high-temperature alloys, the precipitation of undesired intertmetallics can be a major concern, especially for applications requiring a long service life or ease of repair. Therefore, much effort has been devoted to understanding intermetallics and their effects on properties and to determining how to avoid their occurrence through alloy design. Additional information on intermetallic phases can be found in the article “Superalloys” in this book.

Effects of Alloying and Intermetallic Phases on Processing

Most of the difficulties in processing nickel-base alloys are associated with the higher strength solid-solution-strengthened alloys and heat-resistant alloys strengthened by the γ' precipitate. In general, the commercially pure nickels, low-alloy nickels, and nickel-coppers do not pose serious challenges during forming, forging, welding, and machining.

Forming

The ductility of nickel-base alloys in the annealed condition makes them adaptable to virtually all methods of cold forming. Within this group of alloys, which includes the commercially pure nickels, the nickel-coppers, and the more highly alloyed solid-solution-strengthened and precipitation-hardenable alloys, other engineering properties vary sufficiently to cause the alloys to range from moderately easy to difficult to form, compared to other materials.

Alloying and Strain Hardening. Because strain hardening is related to the solid-solution strengthening afforded by alloying elements, the strain-hardening rate generally increases with the complexity of the alloy. Accordingly, strain-hardening rates range from moderately low for nickel and nickel-copper alloys to moderately high for the nickel-chromium, nickel-chromium-cobalt, and nickel-iron-chromium alloys. Similarly, the precipitation-hardenable alloys have higher strain-hardening rates than their solid-solution equivalents. Figure 4 compares the strain-hardening rates of six nickel alloys, in terms of the increase in hardness with increasing cold reduction, with those of four other materials. Note that the strain-hardening rates of the nickel-base alloys are greater than that of 1020 steel, and most are less than that of AISI-type 304 stainless steel.

Special Considerations for Heat-Resistant Alloys. The differences in composition of the various heat-resistant alloys cause differences in their formability. Most alloys that contain substantial amounts of molybdenum or tungsten for strengthening, such as alloy 230 (UNS N06230), which contains 14% W and 2% Mo, or alloy 41 (UNS N07041), which contains 10% Mo, are harder to form than alloys containing lesser amounts of these elements. Alloys that contain aluminum and titanium are strengthened by precipitation of the γ' phase. The volume fraction γ' depends strongly on the amounts of aluminum and titanium present and an overall composition. Examples of alloys that contain γ' include alloy 80A (UNS N07080), Waspaloy alloy (UNS N07011), and alloy 214 (UNS N07214). These typically contain 15, 20, and 33% γ', respectively. Many precipitation-hardenable alloys require complex production steps to produce satisfactory

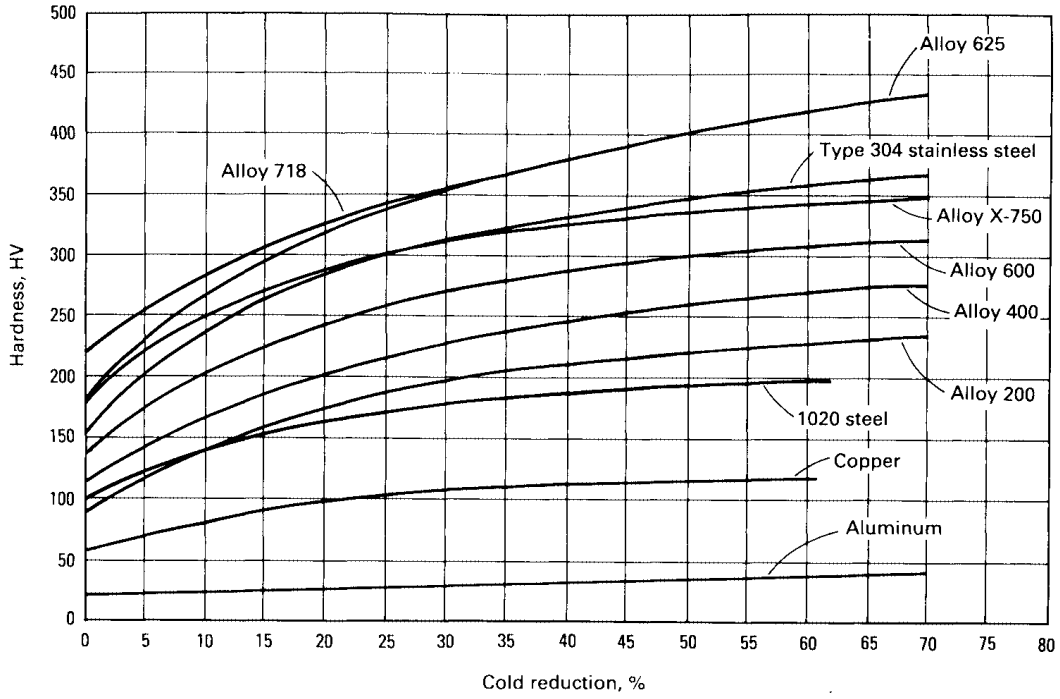


Fig. 4 Effect of cold work on the hardness of various nickel-base alloy sheet materials

components. Most of the iron-base and nickel-base alloys contain less than 0.15% C; more carbon than this causes excessive carbide precipitation, which can severely reduce ductility. Small amounts of boron (up to 0.03% B) are used in some of the heat treatable nickel-base alloys, such as alloy 41 and Udimet 700, to prevent carbide precipitation at grain boundaries; too much boron, however, can cause cracking during forming.

Sulfur causes hot shortness of nickel-base alloys. Silicon content should be below 0.60% and preferably less than 0.30%. More than 0.60% Si causes cracking of cold-drawn alloys and may cause weld cracking in others. Silicon at levels of less than 0.30% usually does not contribute to difficulties in forming.

Forging

As with forming operations, the stronger, more highly alloyed nickel-base alloys are more difficult to forge than are nickels, low-alloy nickels, and nickel-coppers. The γ' strengthened alloys are the most difficult to forge. In fact, some age-hardening alloys with high volume fractions of γ' cannot be forged by conventional forging processes due to hot cracking of the forged ingot. These materials must be manufactured by special forging methods—for example, isothermal forging—by powder metallurgy (P/M) processing, or by investment casting.

Welding

Nickel and nickel alloys can be joined reliably by a wide variety of welding processes. The more ductile solid-solution-strengthened nickels and nickel alloys are the more readily welded, and, to these, almost all welding processes have been successfully applied at some time. The weld fabrication of these materials is straightforward in that they usually do not require preheat or postheat, and interpass temperature control during welding is normally not critical. The precipitation-hardenable alloys are less weldable and, because of the presence of the γ' strengthening phase, tend to be susceptible to what is called "strainage cracking." These materials are usually welded in the annealed (or solution-annealed condition) and are postweld heat treated to precipitate the γ' phase as a final or near-final production step. More detailed information on the weldability of precipitation-hardenable alloys can be found in the article "Superalloys." The effects of major and minor alloying elements on the weldability of corrosion-resistant nickel alloys are described in the paragraphs that follow.

Copper forms a complete series of solid-solution alloys with nickel and has little effect on the weldability of nickel. Metallurgically, the binary high-nickel-content alloys that contain from 15 to 40% Cu behave much like commercially pure nickel when welded. The nickel-copper alloys have about the same susceptibility to embrittlement by elements such as sulfur as does commercially pure nickel. The need for alloying to control gaseous porosity is not significantly reduced in the nickel-copper alloys, compared to that required for commercially pure nickel. As copper is increased up to the range of the copper-nickel alloys, such as 70Cu-30Ni and 80Cu-20Ni, the alloy behaves more like a copper alloy, and reduced amounts of deoxidizers can be used. The presence of copper changes the high-temperature solubility of carbon to the point where graphitization is not encountered.

Chromium. The chromium addition in alloys of commercial importance does not exceed the limit of solid-solution alloys and presents an attractively narrow freezing range. Chromium has the ability to form stable oxides and nitrides, which, in turn, greatly reduce the tendency for weld porosity compared to that encountered in commercially pure nickel and nickel-copper welds. The chromium-bearing alloys are more susceptible than other high-nickel-content alloys to hot cracking when other elements, notably silicon, are present. For example, the hot-cracking susceptibility of a nickel-base weld metal containing 15% Cr is sharply increased as silicon increases from a few tenths of a percent to 1% and higher, whereas levels on the order of 1% Si are relatively innocuous in nickel and nickel-copper alloys.

Iron is commonly present in the nickel-chromium alloys, such as alloy 600, in amounts up to 8 wt%. It is not intended to enhance mechanical properties or weldability but is added as a ferroalloy (along with other additives) and helps keep the cost of these alloys down. Up to this level, iron is not believed to appreciably affect welding behavior. As the amount of iron increases to the composition range of nickel-chromium-iron alloys (such as alloy 800, which contains about 46% Fe), the alloy becomes increasingly hot-crack sensitive. When steel is melted into a high-nickel-content alloy weld, such as in an overlay or in dissimilar metal welding, there is some reason to believe that residual elements such as sulfur and phosphorus, which are normally present in more abundant quantities in steel than in nickel-base alloys, are more damaging to the properties of the weld than the iron itself.

Molybdenum is added to nickel in amounts ranging from 5 to 28% to substantially improve resistance to nonoxidizing acid environments. Early versions of these alloys suffered from grain boundary precipitation of carbides leading to intergranular corrosion or HAZ corrosion degradation. More recently developed lower carbon versions with more balanced compositions, however, have effectively eliminated such problems and molybdenum poses no serious problems during welding operations.

Carbon is usually present in nickel and high-nickel-content weld metals in amounts ranging from 0.01 to 0.15 or 0.20%. The effect of carbon is a major concern with commercially pure nickel. The limit of carbon solubility in the temperature range from 370 to 650 °C (700 to 1200 °F) is about 0.02 to 0.03%. During welding, any graphitic carbon present in the HAZ is dissolved and held in a super-saturated solution as the metal rapidly cools. Subsequent exposure to the temperature range from 370 to 650 °C (700 to 1200 °F) causes carbon to precipitate in the form of intergranular graphite. Unwelded, high-carbon, commercially pure nickel would be similarly embrittled in this temperature range by carbon migration to the grain boundaries, but it would require a much longer time. Therefore, when the wrought commercially pure alloys are to be used at temperatures above 370 °C (700 °F), a maximum of 0.02% carbon is used, as in alloy 201. In weld metal, titanium is added to tie carbon up in the form of titanium carbide, thus preventing the formation of graphitic carbon.

In the nickel-base alloys, copper alters solubility to the point where graphitic embrittlement is not encountered up to carbon levels of 0.15 to 0.20%. The carbon content in nickel-copper alloys does have an effect on hot-cracking tendencies when iron is present. For example, nickel-copper alloys with over 0.20% C can tolerate only about 5% Fe; hot cracking may result at higher levels. Low-carbon nickel-copper alloys with less than 0.10% C can tolerate up to about 30 wt% Fe.

In nickel-chromium alloys, carbon combines with chromium to form chromium carbides, unless titanium or niobium are present to form their

respective carbides. Although chromium depletion may occur in the HAZ of welds, as it does with the iron-base alloys in the absence of titanium or niobium, corrosion resistance is impaired only in extremely corrosive media.

Manganese was considered to be relatively unimportant to welding metallurgy for many years. It is now well established that in both the nickel-chromium and nickel-copper alloys, manganese is beneficial in minimizing fissuring and in preventing hot cracking in welds of heavy sections, as well as in cases where excessive iron dilution may be encountered. Additions of up to 9 wt% Mn have been used in some commercially available welding electrodes.

Magnesium in wrought materials forms a stable high-melting-point magnesium sulfide preferentially to the extremely low-melting-point nickel-nickel sulfide eutectic. In welding, magnesium in the base metal serves to prevent hot cracking in the HAZ.

Silicon may be present in nickel-base alloys in amounts ranging from 0.01 to 4.0%. However, it is generally considered to have an adverse effect on welding because it increases the tendency for hot cracking. Therefore, wrought materials generally have less than 1% Si. The adverse behavior is associated with a eutectic melting that is more damaging to weld metal than to base metal. Pure nickel is most resistant, followed by nickel-copper alloys. Nickel-chromium alloys are the least resistant to the effects of silicon.

Both titanium and aluminum can be added to the weld metal and the base material to promote age hardening. In smaller amounts, the addition of titanium to nickel and nonchromium-bearing nickel-base alloys helps control gas porosity. Aluminum is added to wrought alloys as a deoxidizer. If substantial amounts of titanium and aluminum are added, the sensitivity of the weld metal to hot cracking increases.

Boron amounts that range from 0.003 to 0.10% improve the high-temperature mechanical properties of certain wrought and cast nickel-base alloys. These alloys are usually intended for elevated-temperature service, where grain boundary strengths are enhanced by boron additions. Unfortunately, boron contents of 0.03% or higher have a grossly damaging effect on weldability. At higher boron levels, the weld metal and HAZ are extremely hot-crack sensitive, and considerable care must be exercised with respect to heat input and stress levels.

Zirconium acts similarly to boron in nickel-base alloys by promoting hot cracking in the weld metal and HAZ. However, the tolerance for zirconium is somewhat higher than it is for boron.

Sulfur is perhaps the most damaging of all elements that are involved in the welding metallurgy of nickel and high-nickel-content alloys. Sulfur is particularly damaging to nickel because of its extremely limited solid solubility and because of a nickel-nickel sulfide eutectic reaction that occurs at 649 °C (1200 °F).

Sulfur is different from most other elements that adversely affect weldability because it affects both the HAZ and the weld metal. Penetration occurs at the weld HAZ area that is heated above a threshold temperature while being in contact with sulfur-bearing material. The threshold temperature varies from 316 °C (600 °F) for pure nickel to about 649 °C (1200 °F) for chromium-bearing alloys. Magnesium and manganese are alloying additions that are used to control the effects of sulfur. Unusual diligence is required when handling the nickel-base alloys to avoid contamination from sulfur-containing compounds, which can include such commonly used materials as machining lubricants, marking crayons, temperature-indicating sticks, and shop dirt.

Lead causes hot shortness in high-nickel-content weld metal at about the same level as sulfur. The metallurgical explanation of the subversive effect of lead is very similar to that of sulfur. In practice, lead contamination is less common than sulfur contamination, but probably only because there are fewer common sources of lead-containing contaminants in fabricating shops than there are sources of sulfur-containing contaminants.

Phosphorus can exhibit an effect similar to lead and sulfur in high-nickel-content weld metals. The solubility of phosphorus is quite limited and undergoes a eutectic reaction at about 870 °C (1600 °F). Severe weld metal cracking has been attributed to as little as a few hundredths of a percent of phosphorus.

Machining

In decreasing order of ease of machining, nickel alloys can be ranked as follows:

- *Group A alloys* include the commercially pure nickels, which have the lowest strength and work hardening rates in the nickel alloy family. These metals exhibit gummy behavior when machined in the annealed condition and should be cold worked prior to machining.
- *Group B alloys* include the nickel-coppers. These alloys have higher strengths and work hardening rates than Group A nickels and are more difficult to machine. Best machining is obtained in the cold-drawn condition.
- *Group C alloys* include the solid-solution-strengthened nickel-chromium and nickel-iron-chromium alloys. These alloys have machining charac-

teristics similar to austenitic stainless steels. They should also be machined in the cold-drawn condition.

- *Group D alloys* are those in the age hardened condition. They contain strong solution strengtheners and hard abrasive precipitates, which make them difficult to machine. These alloys should be rough machined in the annealed condition and then finish machined after aging.

SELECTED REFERENCES

- *ASM Specialty Handbook: Nickel*, *Cobalt*, *and Their Alloys*, J.R. Davis, Ed., ASM International, 2000
- W. Betteridge, *Nickel and Its Alloys*, Ellis Horwood Ltd., 1984
- R.B. Rebak and P. Crook, Nickel Alloys for Corrosive Environments, *Advanced Materials & Processes*, Vol 157 (No. 2), 2000

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Zinc and Zinc Alloys

Introduction and Overview

Zinc, its alloys, and its chemical compounds represent the fourth most industrially used metal (behind iron, aluminum, and copper). Zinc is used in five principal applications: in coatings and anodes for corrosion protection of irons and steels; in zinc casting alloys; as an alloying element in copper, aluminum, magnesium, and other alloys; in wrought zinc alloys; and in zinc chemicals. In the corrosion-protection category, hot dip or continuous galvanizing accounts for the majority of zinc consumption (Hot dip zinc and zinc alloy coatings are described in *Surface Engineering,* Volume 5, of *ASM Handbook.*) Almost all of the zinc used in zinc casting alloys is used in die-casting compositions, although more recently developed alloys have spurred growth in sand and permanent mold casting. Among zinc-containing alloys, copper alloys such as brasses are the largest zinc consumers. Rolled zinc is the principal form in which wrought zinc alloys are supplied, although drawn zinc wire for thermal spraying (metallizing) is used increasingly often. In the zinc-chemical category, zinc oxide is the major compound.

Cast Product Applications. Zinc is used extensively in the transportation industry for parts such as carburetors, fuel pump bodies, wiper parts, speedometer frames, grilles, horns, shift levers, load-bearing transmission cases, heater components, brake parts, radio bodies, electronic heat sinks, lamp and instrument bezels, steering wheel hubs, alternator brackets, exterior and interior hardware, instrument panels and body moldings. The average U.S. manufactured passenger car contains about 7.7 kg (17 lb) of die cast parts. Zinc castings are also extensively used in general hardware and electronic and electrical fittings of all kinds, including parts for domestic appliances (for example, washing machines, vacuum cleaners, mixers, and so on), oil burners, motor housings, locks, and clocks. Zinc castings are frequently and increasingly being specified for hardware used

in the computer industry, in business machines (photocopiers, facsimile machines, cash registers, and typewriters), and in such items as recording machines, projectors, vending machines, cameras, gasoline pumps, many hand tools, and machinery such as larger drill presses and lathes. The higher aluminum content alloys (the ZA alloys described) are increasingly being specified for bearings and bushings in low-speed, high-load applications.

Wrought Product Applications. In addition to the use of wrought zinc in roofing and flashing, rolled zinc is drawn into many different products, including:

Alloy	Applications
Pure zinc	Deep-drawn hardware, expanded metal
Zn-Cu	Building construction materials, deep-drawn hardware, coinage
Zn-Cu-Ti	Roofing, gutters, and downspouts; building construction materials; deep-drawn hardware; address plates; solar collectors
Zn-Pb-Cd-Fe	Building construction materials, dry-cell battery cans, deep-drawn hardware, address plates, electrical components
Zn-Al (superplastic zinc)	Shaped components such as typewriter casings, computer panels, and covers

Zinc Casting Alloys

Zinc casting alloys can be divided into two principal classes based on aluminum content: the hypoeutectic die casting alloys containing about 4% Al and the hypereutectic alloys containing >5% Al. The hypereutectic alloys are produced by pressure die casting and gravity casting (sand and permanent mold casting). The standard die-casting alloys (No. 2 to 7 in Table 1) are basically a family of Zn-4Al alloys, because this composition provides excellent casting characteristics and optimal strength and ductility. The alloys with higher aluminum content (the ZA alloys in Table 2) offer higher strength and creep and fatigue resistance than the 4% Al alloys. The improved creep resistance is directly related to the coarser cast grain structure. These alloys are also more dimensionally stable and have lower densities than the 4% Al alloys. However, they offer lower ductility than the 4% Al alloys. Table 3 compares the properties of 4% Al and ZA casting alloys.

Table 1 Nominal compositions of 4% Al hypoeutectic zinc alloy die castings and zinc alloy ingot for die casting

Alloy(a)			Composition, %								
UNS No.	ASTM designation	Common designation	Cu	Al	Mg	Fe max	Pb max	Cd max	Sn max	Ni	Zn
Castings (ASTM B 86)											
Z33520(b)	AG40A	No. 3	0.25 max (d)	3.5–4.3	0.020–0.05(e)	0.100	0.005	0.004	0.003	…	bal
Z33523(b)	AG40B	No. 7	0.25 max	3.5–4.3	0.005–0.020	0.075	0.0030	0.0020	0.0010	0.005–0.020	bal
Z35531(b)	AC41A	No. 5	0.75–1.25	3.5–4.3	0.03–0.08(e)	0.100	0.005	0.004	0.003	…	bal
Z35541	AC43A	No. 2	2.5–3.0	3.5–4.3	0.020–0.050	0.100	0.005	0.004	0.003	…	bal
Ingot form (ASTM B 240)											
Z33521(c)	AG40A	No. 3	0.10 max	3.9–4.3	0.025–0.05	0.075	0.004	0.003	0.002	…	bal
Z33522(c)	AG40B	No. 7	0.10 max	3.9–4.3	0.010–0.02	0.075	0.002	0.002	0.001	0.005–0.020	bal
Z35530(c)	AC41A	No. 5	0.75–1.25	3.9–4.3	0.03–0.06	0.075	0.004	0.003	0.002	…	bal
Z35540	AC43A	No. 2	2.6–2.9	3.9–4.3	0.025–0.05	0.075	0.004	0.003	0.002	…	bal

Note: For purposes of acceptance and rejection, the observed value or calculated value obtained from analysis should be rounded to the nearest unit in the last right-hand place of figures used in expressing the specified limit, in accordance with the rounding procedure described in ASTM E 29. (a) ASTM alloy designations were established in accordance with ASTM B275. UNS designations were established in accordance with ASTM E 527. The last digit of a UNS number differentiates between alloys of similar composition. UNS designations for ingot and casting versions of an alloy were not assigned in the same sequence for all alloys. (b) Zinc alloy die castings may contain nickel, chromium, silicon, and manganese in amounts of 0.02, 0.02, 0.35, and 0.06%, respectively. No harmful effects have ever been noted from the presence of these elements in these concentrations; therefore, analyses are not required for these elements. (c) Zinc alloy ingot for die casting may contain nickel, chromium, silicon, and manganese in amounts of up to 0.02, 0.02, 0.035, and 0.05%, respectively. No harmful effects have ever been noted from the presence of these elements up to these concentrations; therefore, analyses are not required for these elements, except that nickel analysis is required for Z33522. (d) For the majority of commercial applications, a copper content in the range of 0.25–0.075% will not adversely affect the serviceability of die castings and should not serve as a basis for rejection. (e) Magnesium may be as low as 0.015% provided that the lead, cadmium, and tin do not exceed 0.003, 0.003, and 0.001%, respectively.

Effects of Alloying Elements (Ref 1)

Of the eleven elements exhibiting a reasonable level of solubility in zinc, silver and gold are too costly, while cadmium, mercury, and as little as 0.08% Mg lead to hot shortness. Aluminum and copper, with minute amounts of magnesium (<0.08%), and more recently titanium, are mainly added to casting and wrought zinc alloys. The principal role of the alloy elements is, in general, to provide second-phase particles or precipitates to increase mechanical strength, while restraining recrystallization, grain growth, and creep processes.

Table 2 Nominal compositions of hypereutectic zinc-aluminum (>5% Al) casting alloys and zinc-alumium ingot for casting

Alloy		Composition, %							
		Additions				Impurities (c)			
Common designation	UNS No. (a)	Al	Cu	Mg	Zn(b)	Fe max	Pb max	Cd max	Sn max
Castings (ASTM B 791)									
ZA-8	Z35636	8.0–8.8	0.8–1.3	0.015–0.030	bal	0.075	0.006	0.006	0.003
ZA-12	Z35631	10.5–11.5	0.5–1.2	0.015–0.030	bal	0.075	0.006	0.006	0.003
ZA-27	Z35841	25.0–28.0	2.0–2.5	0.010–0.020	bal	0.075	0.006	0.006	0.003
Ingot form (ASTM B 669)									
ZA-8	Z35635	8.2–8.8	0.8–1.3	0.020–0.030	bal	0.065	0.005	0.005	0.002
ZA-12	Z35630	10.8–11.5	0.5–1.2	0.020–0.030	bal	0.065	0.005	0.005	0.002
ZA-27	Z35840	25.5–28.0	2.0–2.5	0.012–0.020	bal	0.072	0.005	0.005	0.002

(a) UNS alloy designations have been established in accordance with ASTM E 527. (b) Determined arithmetically by difference. (c) Zinc-aluminum ingot for foundry and pressure die casting may contain chromium, manganese, or nickel in amounts of up to 0.01% each or 0.03% total. No harmful effects have ever been noted from the presence of these elements in these concentrations; therefore, analyses are not required for these elements.

Table 3 Compositions and properties of selected zinc alloys

UNS No.	Common name	Nominal composition, %	Tensile strength		Elongation, %	Hardness HB(a)
			MPa	ksi		
Die-casting alloys						
Z35541	No. 2,AC43A	Zn-4Al-2.5Cu-0.04Mg	359	52	7	100
Z33520	No. 3,AG40A	Zn-4Al-0.04Mg	283	41	10	82
Z35531	No. 5,AC41A	Zn-4Al-1Cu-0.05Mg	329	48	7	91
Z33523	No. 7,AG40B	Zn-4Al-0.015Mg-0.012Ni	283	41	14	76
Z35635	ZA-8	Zn-8Al-1Cu-0.025Mg	374	54	8	103
Z35630	ZA-12	Zn-11Al-1Cu-0.025Mg	404	58	5	100
Z35840	ZA-27	Zn-27Al-2Cu-0.015Mg	426	62	2	119
Wrought alloys (hot-rolled condition)						
Z21220	…	Zn-0.06Pb-0.06Cd	150–170	21–25	52–30	43
Z44330	…	Zn-1Cu	170–210	24–30	50–35	52
Z41320	…	Zn-0.8Cu-0.15Ti	221–290	32–42	38–21	61

(a) Test duration, 30 s

The purposes served by the alloying elements and the effects of using these elements in amounts exceeding specified limits are summarized in the following paragraphs. Strict control of chemical composition is absolutely essential for avoiding any chance of intergranular (intercrystalline) corrosion, dimensional changes, or loss of mechanical properties. It should be noted that emphasis has been placed on the standard 4% die casting alloys. This is because extensive studies have been carried out on the effects of various alloying additions on the properties and processing of zinc die casting alloys. For example, one report available from the International Lead Zinc Research Organization (ILZRO) provides data from experiments with 29 different addition elements, consisting of approximately 750 alloys (Ref 2). This survey evaluated the effects of alloying additions on mechanical properties and aging stability, as well as solubility and retention in the melt. Base alloys used in this 50 year study were Alloys 3 and 5 listed in Table 1.

Aluminum is added to zinc for die casting to strengthen the alloy, reduce grain size, and minimize the attack of the molten metal on the iron and steel in the casting and handling equipment. Aluminum adds to the fluidity of the molten metal and improves its castability. As indicated in Table 1, aluminum contents range from 3.5 to 4.3% for Alloys 3 and 5. An aluminum content lower than 3.5% requires higher-than-normal metal temperatures for satisfactory castability. The higher temperatures result in undue attack on the dies. Other disadvantages of low aluminum are lower strength and less dimensional stability than alloys containing aluminum within the specified range.

When the aluminum content exceeds 4.3%, it lowers the impact strength of the castings (Fig. 1). The zinc-aluminum eutectic forms at about 5% Al. This eutectic alloy is extremely brittle and must be avoided.

Magnesium content must be carefully maintained within the ranges shown in Table 1. Magnesium is added primarily to minimize susceptibility to intergranular corrosion caused by the presence of impurities. Excessive amounts of magnesium lower the fluidity of the melt, promote hot cracking, increase hardness, and decrease elongation. Cracking is generally confined to castings of complex form that are free to shrink in the die.

Copper, like magnesium, minimizes the undesirable effects of impurities and, to a small extent, increases the hardness and strength of the castings. Castings containing more than about 1.25% Cu are dimensionally less stable than those with less copper. The copper range for Alloy 5 is 0.6 to 1.25%. The lower limit places the alloy into the high-tensile and high-hardness range, while the upper limit is safely under the copper content that produces aging changes in castings at room temperature.

Iron, in amounts up to 0.10%, has little detrimental effect, but may contribute to problems in buffing or machining. Iron under 0.02% is in solid solution. Greater amounts form hard iron-aluminum compounds, which can produce comet tails during buffing and can dull tools during machining.

Nickel, chromium, silicon, and manganese are not harmful in amounts up to the solubility limit of each (0.02% Ni, 0.02% Cr, 0.035% Si, and 0.5% Mn). When these metals exceed their solubility limits, they form

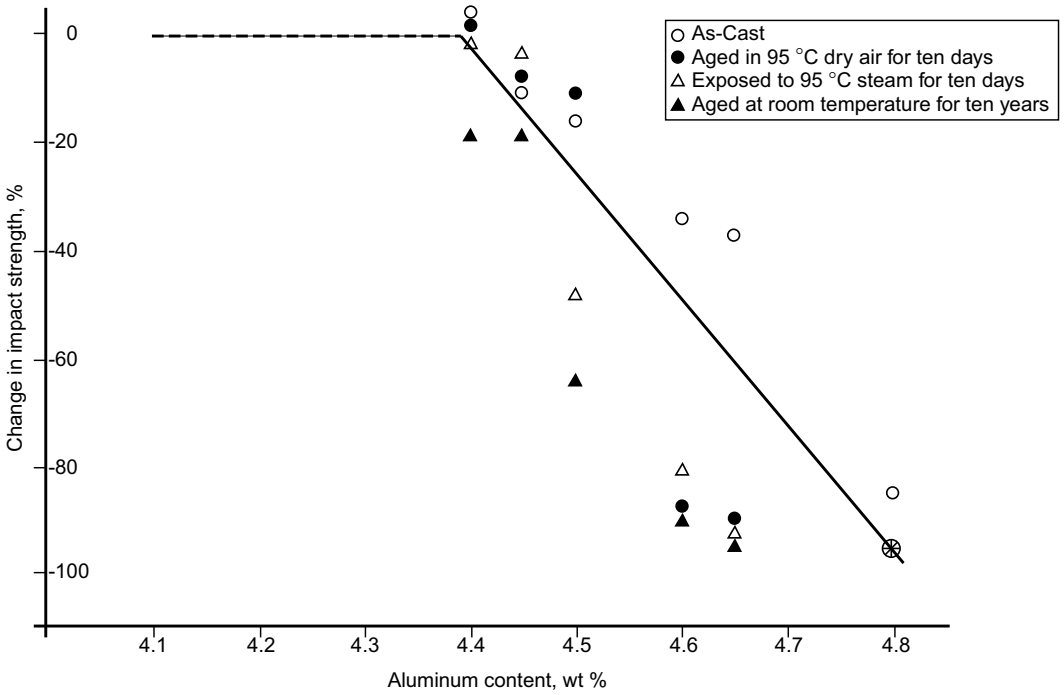


Fig. 1 The effect of high aluminum content on the impact strength of Alloy 3 (see Table 1). Source: Ref 2

light intermetallic compounds with aluminum and can be skimmed off the surface of the melt.

Lead, cadmium, and tin at levels exceeding the limits shown in Table 1 can cause die cast parts to swell, crack, or distort. These defects can occur within one year. The maximum limit for lead, which can promote the occurrence of subsurface network corrosion, is 0.005%. Cadmium is detrimental in its effect at some concentrations and is neutral at others. As such, the maximum limit for cadmium is set at 0.004%. Tin, like lead, can promote subsurface network corrosion, and therefore is also restricted to the maximum safe limit of 0.003%.

Wrought Zinc and Zinc Alloys

Zinc, in pure form or with small alloying additions, is used in three main types of wrought products: flat-rolled products, wire-drawn products, and extruded and forged products. Wrought zinc is readily machined, joined, and finished. Properties of selected wrought alloys are listed in Table 3.

Effects of Alloying Elements (Ref 3)

As listed in Table 4, the wrought alloys are relatively lean in alloy content and the strict impurity control noted for the casting alloys also applies to the wrought alloys.

Rolled Zinc Alloys. In addition to pure zinc, there are seven commercial rolled zinc alloys (see Table 4). They are readily formable, provided that the temperature is kept above 21 °C (70 °F), and are generally hot worked at 120 to 275 °C (250 to 525 °F). Higher strength and creep resistance are obtainable with the alloys in which copper is used as a hardening agent, through the precipitation of the ε-copper-zinc phase. The alloy Zn-0.8Cu-0.15Ti offers higher room-temperature tensile strength (200 to 262 MPa, or 29 to 38 ksi) and creep resistance than the other wrought

Table 4 Nominal compositions of rolled zinc alloys per ASTM B 69

Alloy		Composition, %						
Common designation	UNS No.	Cu	Pb	Cd	Fe max	Al max	Other max	Zn
Zn-0.08Pb	Z21210	0.001 max	0.10 max	0.005 max	0.012	0.001	0.001 Sn	bal
Zn-0.06Pb-0.06Cd	Z21220	0.005 max	0.05–0.10	0.05–0.08	0.012	0.001	0.001 Sn	bal
Zn-0.3Pb-0.3Cd	Z21540	0.005 max	0.25–0.50	0.25–0.45	0.002	0.001	0.001 Sn	bal
Zn-1Cu	Z44330	0.85–1.25	0.10 max	0.005 max	0.012	0.001	0.001 Sn	bal
Zn-1Cu-0.010Mg	Z45330	0.85–1.25	0.15 max	0.04 max	0.015	0.001	0.006–0.016Mg 0.001 Sn	bal
Zn-0.8Cu-0.15Ti	Z41320	0.50–1.50	0.10 max	0.05 max	0.012	0.001	0.12–0.50 Ti 0.001 Sn	bal
Zn-0.8Cu	Z40330	0.70–0.90	0.02 max	0.02 max	0.01	0.005	0.02 Ti	bal

alloys, provided that the alloy is heat treated after rolling (typically at 250 °C, or 480 °F, for 45 min) to precipitate the intermetallic compounds that zinc forms with copper and titanium. In this latter alloy, the precipitation of $TiZn_{15}$ at grain boundaries restrains grain growth. Controlled amounts of cadmium are added to rolled alloys to increase strength, hardness, and creep resistance. Cadmium also raises the recrystallization temperature of zinc alloys.

Superplastic Zinc. One of the most-studied superplastic materials is the Zn-22Al eutectoid alloy, to which 0.5% Cu and 0.02% Mg can be added for enhanced creep strength. When solutionized, quenched, and annealed, this alloy forms a microstructure comprising small equiaxed grains of zinc and aluminum terminal solid solution phases. It is this fine-grained structure that exhibits a tensile elongation in excess of 2500% when tensile tested in the superplastic regime at 250 °C (480 °F) and is easily formed into complex shapes at 250 to 270 °C (480 to 520 °F). When heated above 275 °C (527 °F) and slowly cooled to room temperature, it loses its superplastic properties. The alloy has the directionality in properties of a wrought product, with tensile properties in the rolling direction of 255 MPa (37 ksi) yield strength, 310 MPa (45 ksi) tensile strength, and 27% elongation; in the orientation transverse to the rolling direction, 295 MPa (43 ksi) yield strength, 380 MPa (55 ksi) tensile strength, and 25% elongation.

Wire-Drawn Products. Zinc alloy wire is widely used in thermal spraying, or metallizing, where the wire is melted and sprayed onto a substrate using a special gun. This process is used primarily for the corrosion protection of steel. In addition to pure zinc, zinc alloys containing 15% Al are used in thermal spraying because the zinc-aluminum alloy provides increased corrosion protection. In addition to its thermal spraying applications, zinc alloy wire is used in nail and screw production and in zinc-base solders.

Forged and extruded products are primarily made of either the zinc-aluminum alloy, Zn-14.5Al-0.75Cu-0.02Mg, or the zinc-copper-titanium alloy, Zn-1.0Cu-0.1Ti. The zinc-aluminum alloy has higher impact strength at low temperatures, while the titanium-containing alloy has better creep strength. The ZA alloys can also be extruded.

REFERENCES

1. D.C.H. Nevison, Zinc and Zinc Alloys, *Casting,* Vol 15, *ASM Handbook,* ASM International, 1988, p 786–797
2. "ILZRO Project ZM-246, Survey of the NJZ Die Casting Research Data Files, Final Report", April 1976 to June 1977, International Lead Zinc Research Organization, Inc., Research Triangle Park, NC

3. R.N. Caron and J.T. Staley, Effects of Composition, Processing, and Structure on Properties of Nonferrous Alloys, *Materials Selection and Design,* Vol 20, *ASM Handbook*, ASM International, 1997, p 383–415

SELECTED REFERENCES

- R.J. Barnhurst, Zinc and Zinc Alloys, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 527–542
- *Engineering Properties of Zinc Alloys,* 3rd ed., International Lead Zinc Research Organization, 1988
- F. Porter, *Zinc Handbook*: *Properties, Processing, and Use in Design,* International Lead Zinc Research Organization, 1991
- *Zinc Alloy Castings*: *Product Design and Development,* International Lead Zinc Research Organization, 1993

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Lead, Tin, and Their Alloys

Introduction and Overview

Lead and tin are low melting point metals that are often alloyed together. For example, solders in the tin-lead system are the most widely used of all joining materials. Lead and tin are also important alloy constituents in a number of ferrous and nonferrous alloys.

Lead is a high density (11.34 g/cm^3) metal with a melting point of 327.4 °C (621.3 °F). The most significant applications of lead and lead alloys are lead-acid storage batteries (in the grid plates, posts, and connector straps), ammunition, cable sheathing, and building construction materials (such as sheet, pipe, solder, and wool for caulking). Other important applications include counterweights, battery clamps and other cast products such as: bearings, ballast, gaskets, type metal, terneplate, and foil. Lead in various forms and combinations is finding increased application as a material for controlling sound and mechanical vibrations. Also, in many forms it is important as shielding against x-rays and, in the nuclear industry, gamma rays. In addition, lead is used as an alloying element in steel and in copper alloys to improve machinability and other characteristics, and it is used in fusible (low-melting) alloys for fire sprinkler systems.

Tin is a soft, brilliant white metal with a melting point of 231.9 °C (449.4 °F). The single largest application of tin worldwide is in the manufacture of tinplate (steel sheet electrolytically coated with tin). Most of the tinplate produced is used for containers (tin cans). Tin and a number of tin alloy coatings are also deposited by electroplating and hot dip coating onto a variety of substrates. In addition to coatings, tin is used in chemicals, solders, bearing alloys, and pewter. Large amounts of tin are used in copper-base alloys (copper-tin bronzes). Tin is a potent solid-solution

strengthener in copper and also increases corrosion resistance. In addition, tin is used as an alloying element in dental amalgams, cast irons, fusible alloys, titanium alloy, and zirconium alloys. Tin is also an important alloying element in lead-base battery grid alloys. The use of ternary lead-calcium-tin alloys containing up to 1.3% Sn has substantially reduced gassing, and thus batteries with grids made of these alloys do not require water additions during their working life.

Alloying Elements in Lead

Because lead is soft and ductile, it is normally used commercially as lead alloys. Antimony, tin, arsenic, and calcium are the most common alloying elements. Copper is also sometimes employed. Table 1 lists the nominal compositions of various lead-base alloys.

Table 1 UNS categories and nominal compositions of various lead grades and lead-base alloys

Lead alloy type(a)	UNS designations
Pure leads (UNS L50000–L50099)	
Zone-refined lead (99.9999% Pb min)	L50001
Refined soft lead (99.999% Pb min)	L50005
Refined soft lead (99.99% Pb min)	L50011, L50012, L50013, L50014
Corroding lead (99.94% Pb min)	L50042
Common lead (99.94% Pb min)	L50045
Lead-silver alloys (UNS L50100–L50199)	
Cable-sheathing alloy (0.2% Ag, 99.8% Pb)	L50101
Electrowinning alloys (0.5–1.0% Ag, 99.5–99% Pb)	L50110, L50115, L50120
Electrowinning alloy (1.0% Ag, 1.0% As, 98% Pb)	L50122
Cathodic protection anode alloy (2.0% Ag, 98% Pb)	L50140
Solder alloys (1.0–1.5% Ag, 1.0 Sn, bal Pb)	L50121, L50131
Solder alloys (1.5–2.5% Ag, with no tin)	L50132, L50150, L50151
Solder alloy (1.5% Ag, 5.0% Sn, 93.5% Pb)	L50134
Solder alloy (2.5% Ag, 2.0% Sn, 95.5% Pb)	L50152
Solder alloy (5.0% Ag, 95% Pb)	L50170
Solder alloys (5.0% Ag, with 5% Sn or 5% In)	L50171, L50172
Solder alloy (5.5% Ag)	L50180
Lead-arsenic alloys (UNS L50300–L50399)	
Arsenical lead cable-sheathing alloy (0.15% As, 0.10% Bi, 0.10% Sn, 99.6% Pb)	L50310
Lead-barium alloys (UNS L50500–L50599)	
Lead-barium alloy (0.05% Ba, 99.9% Pb)	L50510
Lead-tin-barium alloys (0.05–0.10% Ba, 1.0–2.0% Sn, 97.9–99% Pb)	L50520–L50522, L50530, L50535
Frary metal (0.4–1.2% Ba, 0.5–0.8% Ca, 97.2–98.8% Pb)	L50540–L50543
Lead-calcium alloys (UNS L50700–L50899)	
Lead-calcium alloys (99.9% Pb, 0.008–0.03% Ca)	L50710, L50720
Cable-sheathing alloys (0.025% Ca, 99.7–99.9% Pb, 0.0–0.025% Sn)	L50712, L50713
Lead-copper-calcium alloy (99.9% Pb, 0.06% Cu, 0.03% Ca)	L50722
Electrowinning anode alloy (0.5% Ag, 99.4% Pb, 0.05% Ca)	L50730
Battery grid alloy (99.9% Pb, 0.06% Ca)	L50735
Battery grid alloys (0.065% Ca, 0.2–1.5% Sn, 99.7–98.4% Pb)	L50736, L50737, L50740, L50745, L50750, L50755
Battery grid alloys (0.07% Ca, 0.0–0.7% Sn, 99.2–99.9% Pb)	L50760, L50765
Battery grid alloys (0.10% Ca, 0.0–1.0% Sn, 98.9–99.9% Pb)	L50770, L50775, L50780, L50790
Battery grid alloys (0.12% Ca, 0.3% Sn, 99.6% Pb)	L50795, L50800
Bearing metal (0.02% Al, 0.04% Li, 0.7% Ca, 0.6% Na, 98.7% Pb)	L50810
Bearing metal (0.02% Al, 0.04% Li, 0.7% Ca, 0.2% Na, 0.4% Ba, 98.7% Pb)	L50820
Lead-calcium alloys (1.0–6.0% Ca, 94.0–99.0% Pb)	L50840, L50850, L50880
Lead-cadmium alloys (UNS L50900–L50999)	
Lead-cadmium eutectic alloy (17.0% Cd, 83.0% Pb)	L50940
Lead-copper alloys (UNS L51100–L51199)	
Copperized lead (0.05% Cu, 99.9% Pb)	L51110
Chemical lead (99.90% Pb min)	L51120
Copper-bearing lead (0.06% Cu, 99.90% Pb min)	L51121
Lead-tellurium-copper alloys (0.06% Cu, 0.045–0.055% Te, 99.82–99.85% Pb min)	L51123, L51124

(continued)

(a) Unless otherwise specified as a minimum (min) or balance (bal), the listed compositions represent nominal values (or the range of nominal values when several alloy designations are grouped together). (b) See Table 3 for compositions of specific lead-antimony alloys. (c) See Table 4 for compositions of specific lead-tin alloys.

Table 1 UNS categories and nominal compositions of various lead grades and lead-base alloys (continued)

Lead alloy type(a)	UNS designations
Copperized soft lead (0.06% Cu, 99.9% Pb min)	L51125
Copper-bearing alloy (51% Pb, 3.0% Sn, other 0.8% max, bal Cu) (alloy 485 in SAE J460)	L51180
Lead-indium alloys (UNS L51500–L51599)	
Lead-indium-silver solder alloys (2.38–2.5% Ag, 4.76–5.0% In, 92.5–92.8% Pb)	L51510, L51512
Lead-indium solder alloys (5.0% In, 95.0% Pb)	L51511
Lead-indium alloys (19.0–70% In, 30–81% Pb)	L51530, L51532, L51535, L51540, L51550, L51560, L51570
Indium-tin-lead alloy (40% In, 40% Sn, 20% Pb)	L51545
Indium-silver-lead alloy (80% In, 5% Ag, 15% Pb)	L51585
Lead-lithium alloys (UNS L51700–L51799)	
Lead-lithium alloys (0.01–0.07% Li, 99.9% Pb)	L51705, L51708, L51710, L51720, L51730
Lead-tin-lithium alloys (0.02–0.04% Li, 0.35–0.7% Sn, 99.2–99.9% Pb)	L51740, L51748
Lead-tin-lithium-calcium alloys (0.08–0.065% Li, 1–2% Sn, 0.02–0.15% Ca, 97.8–99.6% Pb)	L51770, L51775, L51778, L51780, L51790
Lead-antimony alloys (UNS L52500–L53799)	
Lead-antimony alloys (<1.0% Sb)	L52500–L52599
Lead-antimony alloys (1.0–1.99% Sb)	L52600–L52699
Lead-antimony alloys (2.0–2.99% Sb)	L52700–L52799
Lead-antimony alloys (3.0–3.99% Sb)	L52800–L52899
Lead-antimony alloys (4.0–4.99% Sb)	L52900–L52999
Lead-antimony alloys (5.0–5.99% Sb)	L53000–L53099
Lead-antimony alloys (6.0–6.99% Sb)	L53100–L53199
Lead-antimony alloys (7.0–8.99% Sb)	L53200–L53299
Lead-antimony alloys (9.0–10.99% Sb)	L53300–L53399
Lead-antimony alloys (11.0–12.99% Sb)	L53400–L53499
Lead-antimony alloys (13.0–15.99% Sb)	L53500–L53599
Lead-antimony alloys (16.0–19.99% Sb)	L53600–L53699
Lead-antimony alloys (>20% Sb)	L53700–L53799
Lead-tin alloys (UNS L54000–L55099)	
Lead-tin alloys (<1.0% Sn)	L54000–L54099
Lead-tin alloys (1.0–1.99% Sn)	L54100–L54199
Lead-tin alloys (2.0–3.99% Sn)	L54200–L54299
Lead-tin alloys (4.0–7.99% Sn)	L54300–L54399
Lead-tin alloys (8.0–11.99% Sn)	L54400–L54499
Lead-tin alloys (12.0–15.99% Sn)	L54500–L54599
Lead-tin alloys (16.0–19.99% Sn)	L54600–L54699
Lead-tin alloys (20.0–27.99% Sn)	L54700–L54799
Lead-tin alloys (28.0–37.99% Sn)	L54800–L54899
Lead-tin alloys (38.0–47.99% Sn)	L54900–L54999
Lead-tin alloys (48.0–57.99% Sn)	L55000–L55099
Lead-strontium alloys (UNS L55200–L55299)	
Battery alloys (0.06–0.2% Sr, 0.0–0.03% Al, 0.0–0.08% Sn, 0.0–0.6% Ca, 99–99.8% Pb)	L55210, L55230, L55260
Lead-strontium alloy (2% Sr, 98% Pb)	L55290

(a) Unless otherwise specified as a minimum (min) or balance (bal), the listed compositions represent nominal values (or the range of nominal values when several alloy designations are grouped together).

Antimony generally is used to give greater hardness and strength, as in storage battery grids, sheet, pipe, and castings. Antimony contents of lead-antimony alloys can range from 0.5 to 25%, but they are usually 2 to 5%.

Within the past decade, lead-calcium alloys have replaced lead-antimony alloys in a number of applications, in particular, storage battery grids and casting applications. These alloys contain 0.03 to 0.15% Ca for strengthening. More recently, aluminum has been added to calcium-lead and calcium-tin-lead alloys as a stabilizer for calcium.

Adding tin to lead or lead alloys increases hardness and strength, but lead-tin alloys are more commonly used for their good melting, casting, and wetting properties, as in type metals and solders. Tin gives the alloy the ability to wet and bond with metals such as steel and copper; unalloyed lead has poor wetting characteristics. Tin combined with lead and bismuth or cadmium forms the principal ingredient of many low-melting alloys.

Arsenical lead (UNS L50310) is used for cable sheathing. Arsenic is often used to harden lead-antimony alloys and is essential to the production of round dropped shot.

Battery Grid Alloys. The largest use of lead is in the manufacture of lead-acid storage batteries. These batteries consist of a series of grid plates

made from either cast or wrought calcium lead or antimonial lead that is pasted with a mixture of lead oxides and immersed in sulfuric acid.

The length of the active life of a battery depends on the resistance of the lead alloy grids to corrosion under repeated cycling (charge and discharge) in the sulfuric acid. Automotive positive battery plates are usually made from antimony-lead alloys containing 1.5 to 3% antimony and other elements such as tin, arsenic, copper, sulfur, and selenium. Other automotive battery grids are made from lead-calcium-tin-aluminum alloys. The exact composition used varies with the manufacturer. Table 2 lists some typical compositions of lead alloys used for battery applications. Hybrid automotive batteries are made from 1 to 2% Sb-Pb alloys for the positive grid and lead-calcium alloys (0.04 to 0.15% Ca) for the negative grid. Battery grid alloys may also include 0.1 to 0.8% Sn (Table 2). In addition, some lead-calcium alloys contain 0.01 to 0.03% Al. Industrial batteries usually are made from alloys containing 5 to 8% Sb and various other elements. For all of these alloys, long battery life requires close control of impurities. Large standby stationary batteries can be made with grids of relatively pure lead of special design. This type of battery normally contains lead calcium.

Type metals, a class of metals used in the printing industry, generally consist of lead-antimony and tin alloys. Small amounts of copper are added to increase hardness for some applications. Compositions of type metals in present commercial use are given in Table 3. The lead base provides low cost, a low melting point, and ease of casting— properties that are desirable for all type metals. Additions of antimony harden the alloy, make it more resistant to compressive impact and wear, lower the casting temperature, and minimize contraction during freezing. Tin adds fluidity, improves castability, reduces brittleness, and imparts a finer structure—a characteristic that helps type reproduce fine detail.

Table 2 Compositions of selected lead alloys for battery grids

	Composition, %						
UNS designation	As max	Ag max	Ca	Pb	Sb	Sn	Other
Calcium-lead alloys							
L50760	0.0005	0.001	0.06–0.08	bal	0.0005 max	0.0005 max	(a)
L50770	0.0005	0.001	0.10 nom	bal	0.0005 max	0.0005 max	(a)
L50775	0.0005	0.001	0.08–0.11	bal	0.0005 max	0.2–0.4	(a)
L50780	0.0005	0.001	0.08–0.11	bal	0.0005 max	0.4–0.6	(a)
L50790	0.0005	0.001	0.08–0.10	bal	0.0005 max	0.9–1.1	(a)
Antimony-lead alloys							
L52760	0.18 nom	…	…	bal	2.75 nom	0.2 nom	…
L52765	0.3 nom	…	…	bal	2.75 nom	0.3 nom	…
L52770	0.15 nom	…	…	bal	2.9 nom	0.3 nom	…
L52840	0.15 nom	…	…	bal	2.9 nom	0.3 nom	…

(a) 0.005% max Bi and 0.0005% max each for Cu, Zn, Cd, Ni, and Fe

Table 3 Typical compositions and properties of type metals

Item	Composition, %			Hardness, HB(a)	Liquidus temperature		Solidus temperature	
	Pb	Sn	Sb		°C	°F	°C	°F
Electrotype								
General	95	2.5	2.5	…	303	578	246	475
General	94	3	3	12.4	298	568	246	475
Curved plates	93	4	3	12.5	294	561	245	473
Stereotype								
Flat plate	80	6	14	23	256	493	239	462
General	80.5	6.5	13	22	252	485	239	462
Curved plates	77	8	15	25	263	505	239	462
Linotype								
Standard	86	3	11	19	247	477	239	462
Special	84	5	11	22	246	475	239	462
Ternary eutectic alloy	84	4	12	22	239	463	239	462
Monotype								
Ordinary	78	7	15	24	262	503	239	462
Display	75	8	17	27	271	520	239	462
Case type(b)	72	9	19	28.5	286	546	239	462
Case type	64	12	24	33	330	626	239	462
Rules	75	10	15	26	270	518	239	462
Foundry type								
Hard (1.5% Cu)	60.5	13	25	…	…	…	…	…
Hard (1.5% Cu)	58.5	20	20	…	…	…	…	…
Hard (2.0% Cu)	61	12	25	…	…	…	…	…

(a) 10 mm ball, 250 kg load. (b) Lanston standard

Lead-base bearing alloys, which are called lead-base babbitt metals, vary widely in composition, but can be categorized into two groups:

- Alloys of lead, tin, antimony, and, in many instances, arsenic
- Alloys of lead, calcium, tin, and one or more of the alkaline earth metals

Many alloys of the first group have been used for centuries as type metals. They most likely were chosen for use as bearing materials because of the properties they were known to possess. The advantages of arsenic additions in this type of bearing alloy have been generally recognized since 1938. Alloys of the second type were developed early in the 20th century.

Nominal compositions of the most widely used lead babbitts according to ASTM, SAE, and ISO specifications are listed in Table 4. In the absence of arsenic, the microstructures of these alloys comprise cuboid primary crystals of SbSn or of antimony embedded in a ternary mixture of Pb-Sb-SbSn in which lead forms the matrix. The number of these cuboids per unit volume of alloy increases as antimony content increases. If antimony content is more than about 15%, the total amount of the hard constituents increases to such an extent that the alloys become too brittle to be useful as bearing materials.

Arsenic is added to lead babbitts to improve their mechanical properties, particularly at elevated temperatures. All lead babbitts are subject to soft-

Table 4 Designations and nominal composition of lead-base bearing alloys

Designation				Composition, %						
UNS	SAE	ISO	ASTM (B 23)	Pb	Sb	Sn	As	Other	Product form	Applications
53346	Alloy 13	PbSb10Sn6	Alloy 13	84	10	6	…	…	Cast on steel or steel-backed bronze	Bimetal and tri-metal surface layer
53581	Alloy 14	PbSb15Sn10	Alloy 7	75	15	10	…	…	Cast on steel back	Bimetal surface layer
53620	Alloy 15	PbSb15SnAs	Alloy 15	84	15	1	1	…	Cast on steel back	Bimetal surface layer
…	…	PbSb14Sn9CuAs	…	77	14	9	0.5	1 Cu	Cast on steel back	Bimetal surface layer
53565	…	…	Alloy 8	80	15	5	0.5	…	Cast on steel back	Bimetal surface layer
…	…	…	(a)	87.5	9	3.5	…	…	Cast on bronze back	Bimetal surface layer

(a) ASTM B 67

ening or loss of strength during prolonged exposure to the temperatures (95 to 150 °C, 200 to 300 °F) at which they serve as bearings in internal-combustion engines. The addition of arsenic minimizes such softening. Under suitable casting conditions, the arsenical lead babbitts—for example, SAE 15 (ASTM grade 15)—develop remarkably fine and uniform structures. They also have better fatigue strength than arsenic-free alloys.

Arsenical babbitts give satisfactory service in many applications. The use of these alloys increased greatly during the Second World War, particularly in the automobile industry and in the manufacture of diesel engines. The most widely used alloy is SAE 15 (ASTM grade 15), which contains 1% arsenic. Automobile bearings of this alloy are usually made from continuously cast bimetal (steel and babbitt) strip. When properly handled, this alloy can withstand the considerable strain that results from forming the bimetal strip into bearings.

Diesel engine bearings often are cast as individual bearing shells by either centrifugal or gravity methods. A lead-antimony alloy that contains 3% arsenic has been used successfully for applications where higher hardness is required and where formability requirements are less severe (rolling mill bearings, for example).

For many years, lead-base bearing alloys were considered to be only inferior low-cost substitutes for tin alloys. However, the two groups of alloys do not differ greatly in antiseizure characteristics, and when lead-base alloys are used with steel backs and in thicknesses below 0.75 mm (0.03 in.), they have a fatigue resistance that is equal to, if not better than, that of tin alloys. Bearings of any of these alloys remain serviceable longest when they are no more than 0.13 mm (0.005 in.) thick. The superiority of lead alloys over tin-alloys becomes more marked as operating temperatures increase. For this reason, automotive engineers generally favor lead-base alloys of compositions that approximate ASTM alloys 7 and 15, and SAE alloy 16. The SAE alloy is cast into and on a porous

sintered matrix, usually of copper-nickel, that is bonded to steel. The surface layer of the babbitt is 0.025 to 0.13 mm (0.001 to 0.005 in.) thick.

The use of lead babbitts containing calcium and alkaline earth metals is confined almost entirely to railway applications, although these babbitts also are employed to some extent in certain diesel engine bearings. One of the more widely used alloys contains 1.0 to 1.5% Sn, 0.50 to 0.75% Ca, and small amounts of various other elements. The strength of this alloy approximates that of a tin alloy containing 90% Sn, 8% Sb, and 2% Cu. The hardness of this lead alloy is about 20 HB, the solidus temperature is 321 °C (610 °F), and the liquidus temperature is probably near 338 °C (640 °F). The pouring temperature, which varies from 500 to 520 °C (930 to 970 °F), is relatively high. The high temperature and reactive nature of calcium accounts for the formation of a much larger volume of dross than that encountered in the melting of lead-antimony-tin alloys. Care must be taken to avoid contamination of the alloy with antimonial lead babbitts, and vice versa. Deformability and resistance to wear are of the same order as those of the other lead babbitts. Most alloys of this type are subject to corrosion by acidic oils.

Tin-Lead Solders

Solders account for the largest consumption of tin in the United States. Tin is an important constituent in solders because it wets and adheres to many common base metals at temperatures considerably below their melting points. Industrial tin-lead solder alloys contain a combination of materials from 100% tin to 100% lead, as demanded by the particular application. The utility of the tin-lead combination is highlighted by examination of the constitution diagram between these two materials, shown in Fig. 1. Solder alloys can be obtained with melting temperatures as low as 182 °C (360 °F) and as high as 315 °C (600 °F) within this system. Except for the pure metals and the eutectic solder at 63%Sn-37%Pb, all solder alloys melt within a temperature range that varies according to the alloy composition. Each alloy has unique characteristics. In general, properties are influenced by the melting characteristics of the alloys, which in some measure are related to their load-carrying and temperature capabilities.

Table 5 lists the compositions and melting ranges of tin-lead, tin-lead antimony, tin-lead-silver, and lead-silver solders. The high-lead solders, which have a 5 to 20 wt% Sn content, are used extensively in microelectronics packaging or in high-temperature applications. Other applications include radiator assembly and automobile body repair, which utilize torch heating techniques. A drop in the liquidus temperature is obtained when tin content increases from 20 to 30 wt%. The 5 to 20 wt% Sn alloys have a wider pasty range that provides greater workability,

whereas the higher tin content improves the wetting and flow of the solder. On the other hand, increased concentrations of tin also raise the price of the solder.

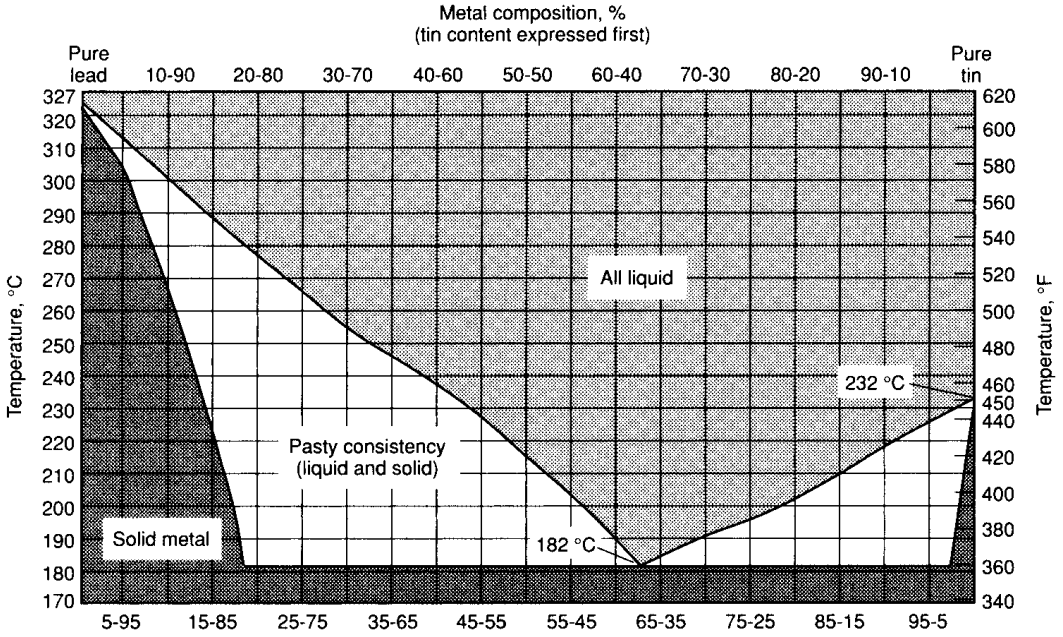


Fig. 1 Tin-lead phase diagram

Table 5 ASTM B 32 specification for tin-lead, tin-lead-antimony, tin-lead-silver, and lead-silver solders

	Composition, %(a)											Melting range(b)			
												Solidus		Liquidus	
Alloy grade	Sn	Pb	Sb	Ag	Cu	Cd	Al	Bi	As	Fe	Zn	°C	°F	°C	°F
Sn70	69.5–71.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.03	0.02	0.005	183	361	193	377
Sn63	62.5–63.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.03	0.02	0.005	183	361	183	361
Sn62	61.5–62.5	bal	0.50	1.75–2.25	0.08	0.001	0.005	0.25	0.03	0.02	0.005	179	354	189	372
Sn60	59.5–61.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.03	0.02	0.005	183	361	190	374
Sn50	49.5–51.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.025	0.02	0.005	183	361	216	421
Sn45	44.5–46.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.025	0.02	0.005	183	361	227	441
Sn40A	39.5–41.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	183	361	238	460
Sn40B	39.5–41.5	bal	1.8–2.4	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	185	365	231	448
Sn35A	34.5–36.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	183	361	247	447
Sn35B	34.5–36.5	bal	1.6–2.0	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	185	365	243	470
Sn30A	29.5–31.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	183	361	255	491
Sn30B	29.5–31.5	bal	1.4–1.8	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	185	365	250	482
Sn25A	24.5–26.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	183	361	266	511
Sn25B	24.5–26.5	bal	1.1–1.5	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	185	365	263	504
Sn20A	19.5–21.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	183	361	277	531
Sn20B	19.5–21.5	bal	0.8–1.2	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	184	363	270	517
Sn15	14.5–16.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	225	437	290	554
Sn10A	9.0–11.0	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	268	514	302	576
Sn10B	9.0–11.0	bal	0.20	1.7–2.4	0.08	0.001	0.005	0.03	0.02	0.02	0.005	268	514	299	570
Sn5	4.5–5.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	308	586	312	594
Sn2	1.5–2.5	bal	0.50	0.015	0.08	0.001	0.005	0.25	0.02	0.02	0.005	316	601	322	611
Ag1.5	0.75–1.25	bal	0.40	1.3–1.7	0.30	0.001	0.005	0.25	0.02	0.02	0.005	309	588	309	588
Ag2.5	0.25	bal	0.40	2.3–2.7	0.30	0.001	0.005	0.25	0.02	0.02	0.005	304	580	304	580
Ag5.5	0.25	bal	0.40	5.0–6.0	0.30	0.001	0.005	0.25	0.02	0.02	0.005	304	580	380	716

(a) Limits are maximum percentages, unless shown as a range or stated otherwise. For purposes of determining conformance to these limits, an observed value or calculated value obtained from analysis shall be rounded to the nearest unit in the last right-hand place of figures used in expressing the specified limit, in accordance with the rounding method of ASTM Recommended Practice E 29. (b) Temperatures given are approximations and are for information only.

The most widely used solders are the eutectic 63Sn-37Pb and the near-eutectic alloys, 60Sn-40Pb and 50Sn-50Pb. These solders are used in electronics and structural applications, such as the assembly of conduit for nonpotable water, industrial fluids, compressed gas products, and vacuum assemblies. The narrow pasty range of these alloys limits their workability prior to solidification. The largest use of the eutectic and near-eutectic solder is in the assembly of circuit boards for electronic products.

The alloys with higher tin contents of 65 to 100 wt% have more limited applications, because the melting temperatures and pasty range needed for structural applications can be provided by the less expensive lead-rich compositions. However, the tin-rich alloys have improved wettability for hard-to-solder substrates.

Impurities in Tin-Lead Solders

Impurities in solders can affect their performance and must be kept to a minimum. Standards of ASTM for solder alloys set maximum tolerable impurities in alloys as provided by the supplier or refinery. Impurities can be inadvertently picked up during normal usage of the alloys, especially when solder pots with recirculation systems and passage of components through the molten materials are used. The purity of solders supplied by reputable manufacturers usually is adequate for most applications. Particular soldering operations may require the use of super-purity materials that can be supplied upon request. Impurities present in sufficient quantities can affect wetting properties, flow within the joint, melting temperature of the solder, strength capabilities of joints, and oxidation characteristics of the solder alloys. The most common impurity elements are listed below with their principal levels and effects.

Aluminum. Traces of aluminum in a tin-lead solder bath can seriously affect soldering qualities. More than 0.005% of the metal can cause grittiness, lack of adhesion, and surface oxidation of the solder alloy. A deterioration in surface brightness of a molten bath sometimes is an indication of the presence of aluminum.

Antimony may be found in solders for any one of three reasons: as an impurity that reduces the effective spread of the solder alloy; as a minor addition of 0.25 wt%, minimum, to try to prevent the formation of the low-temperature allotrope of tin (α of tin at 13.2 °C, or 55.8 °F); and as a principal component, representing 1 to 5 wt%, to improve monotonic and creep strength of the solder. The levels of added antimony should be less than 7 wt% of the tin component of the solder (the solubility limit of antimony in tin) in order to prevent the formation of tin-antimony intermetallic compounds, which can severely impact the fluidity of the molten solder or reduce the ductility of the solidified joint. The ASTM designation

for antimony levels in the solders are: Class A (alloys with tin content greater than 35 wt%), maximum of 0.12 wt%; Class B, 0.2 to 0.5 wt%; and Class C (tin content, 20 to 40 wt%), maximum of 6 wt%.

Arsenic. A progressive deterioration in the quality of the solder is observed with increases in arsenic content. As little as 0.005% As induces some dewetting, which becomes more severe as the percentage of arsenic is increased to 0.02%. Arsenic levels should be kept within this range.

Bismuth. Low levels of bismuth in the solder alloy generally do not cause any difficulties, although some discoloration of soldered surfaces occurs at levels above 0.5%.

Cadmium. A progressive decrease in wetting capability occurs with additions of cadmium to tin-lead solders. While there is no significant change in the molten solder appearance, small amounts of cadmium can increase the risk of bridging and icicle formation in printed circuits. For this and health reasons, cadmium levels should be kept to a minimum.

Copper. The role of copper as a contaminant in solder appears to be variable and related to the particular product. A molten tin-lead solder bath is capable of dissolving copper at a high rate, easily reaching 0.3% Cu. Copper in liquid solder does not appear to have any deleterious effect upon wetting rate or joint formation. Excess copper settles to the bottom of a solder bath as an intermetallic compound sludge. New solder alloy allows a maximum copper content of 0.08%.

Iron and nickel are not naturally present in solder alloy. The presence of iron-tin compounds in tin-lead solders can be identified as a grittiness. Generally, iron is limited to 0.02% maximum in new solder. There are no specification limits for nickel, but levels as low as 0.02% can produce some reduction in wetting characteristics.

Phosphorus and Sulfur. Phosphorus at a 0.01% level is capable of producing dewetting and some grittiness. At higher levels, surface oxidation occurs, and some identifiable problems such as grittiness and dewetting become readily discernible. Sulfur causes grittiness in solders at a very low level, and should be held to 0.001%. Discrete particles of tin-sulfide can be formed. Both of these elements are detrimental to good soldering.

Zinc. The ASTM new solder alloy specification states that zinc content must be kept to 0.005% maximum in tin-lead solders. At this maximum limit, even with new solders in a molten bath, some surface oxidation can be observed and oxide skins may form, encouraging icicles and bridging. Up to 0.01% Zn has been identified as the cause of dewetting on copper surfaces.

The combined effects of the above impurity elements can be significant. Excessive contamination in solder baths or dip pots generally can be identified through surface oxidation, changes in the product quality, and the appearance of grittiness or frostiness in joints made in this bath. A general sluggishness of the solder also is observed. In addition to analysis, experience with solder bath operation is helpful in determining the point at which the material should be renewed for good solder joint production. Specifications of ASTM, which specify maximum allowable concentrations, are useful in purchasing solder for general use. In particular applications, specific contaminants or a combination of elements may be detrimental to a particular soldered product. A determination of a revised or limited specification for solder materials sometimes is required. Impurities of a metallic and nonmetallic nature can be found in raw materials and in scrap solder sometimes used by reclaimers. Reclaimed solder is used in many industrial applications where impurities may not be detrimental. However, correct selection of solder grade becomes important for economical production. Manufacturing problems are sometimes the result of inappropriate solder selection, use of solder baths for longer periods than contamination buildup will tolerate, or processing methods that rapidly contaminate a solder bath. Determination of suitable specifications, allowable impurities in new materials, and allowable impurities through deterioration to the point at which a solder bath is discarded should be included in any soldering quality-control program.

Other Solder Alloys

Tin-zinc solders are used to join aluminum. Tin-antimony and tin-silver solders are employed in applications requiring joints with high creep resistance and in applications requiring a lead-free solder composition, such as potable-water plumbing. Also, tin solders that contain 5% Sb (or 5% Ag) are more suitable for use at higher temperatures than are the tin-lead solders. A tin-copper-silver solder containing 0.25 to 0.75% Ag and 3.0 to 5.0% Cu is used extensively in plumbing applications for potable water and in food handling equipment. Silver improves strength and spreading and lowers the melting temperature, when compared with pure tin. The copper addition further improves strength.

Tin-Base Bearing Alloys

Tin-base bearing materials (babbitts) are alloys of tin, antimony, and copper that contain limited amounts of zinc, aluminum, arsenic, bismuth, and iron. The compositions of tin-base bearing alloys, according to ASTM B 23, SAE, and ISO specifications, are shown in Table 6.

Table 6 Designations and nominal composition of tin-base bearing alloys

Designation				Composition, %					
UNS	SAE	ISO	ASTM (B 23)	Sn	Sb	Cu	Other	Product form	Applications
55191	…	…	Alloy 1	91	4.5	4.5	…	Cast on steel or bronze back	Bimetal surface layer
55188	…	…	Alloy 11	87	7	6	…	Cast on steel; bronze or steel-backed bronze	Bimetal and trimetal surface layer
55193	Alloy 12	SnSb8Cu4	Alloy 2	89	7.5	3.5	…	Cast on steel; bronze or steel-backed bronze	Bimetal and trimetal surface layer
55189	…	…	Alloy 3	84	8	8	…	Cast on steel or bronze back	Bimetal surface layer
…	…	SnSb12Cu6Pb	…	80	12	6	2 Pb	Cast on steel back	Bimetal surface layer

The presence of zinc in tin-base bearing metals generally is not favored. Arsenic increases resistance to deformation at all temperatures; zinc has a similar effect at 38 °C (100 °F), but causes little or no change at room temperature. Zinc has a marked effect on the microstructures of some of these alloys. Small quantities of aluminum (even less than 1%) will modify their microstructures. Bismuth is objectionable because, in combination with tin, it forms a eutectic that melts at 137 °C (279 °F). At temperatures above this eutectic, alloy strength is appreciably decreased.

In high-tin alloys, such as ASTM grades 1, 2, and 3, and SAE 11 and 12, lead content is limited to 0.50% or less because of the deleterious effect of higher percentages on the strength of these alloys at temperatures of 150 °C (300 °F) and above. Lead and tin form a eutectic that melts at 183 °C (361 °F). At higher temperatures, bearings become fragile as a result of the formation of a liquid phase within them.

SELECTED REFERENCES

- W.B. Hampshire, Tin and Tin Alloys, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials*, Vol 2, *ASM Handbook,* ASM International, 1990, p 517–526
- P.T. Vianco, General Soldering, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook*, ASM International, 1991, p 964–984
- A.W. Worcester and J.T. O'Reilly, Lead and Lead Alloys, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook*, ASM International, 1990, p 543–536

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Cobalt and Cobalt Alloys

Introduction and Overview

Elemental Cobalt. Falling between iron and nickel in the periodic table, cobalt has many similar properties as these other two more familiar transition metals. Its melting temperature (1493 °C, or 2719 °F), density (8.85 g/cm^3, or 0.322 lb/in.^{3}), thermal expansion coefficient (13.8/K, or 7.66/°F), thermal conductivity (69.0 W/m · K), and elastic modulus (210 GPa, or 30×10^6 psi) are all rather similar to the respective values of iron and nickel. All three are ferromagnetic, but the Curie temperature of cobalt, 1123 °C (2050 °F), is significantly higher than that of iron (770 °C, or 1418 °F) or nickel (358 °C, or 676 °F). The crystal structure and chemical and mechanical properties differ enough to give cobalt a viable commercial life of its own.

Crystal Structure. At temperatures below 417 °C (783 °F), cobalt exhibits a hexagonal close-packed (hcp) structure (ε-cobalt). Between 417 °C (783 °F) and its melting point of 1493 °C (2719 °F), cobalt has a face-centered cubic (fcc) structure (α-cobalt). Although the principal alloying elements affect the temperature of this transition (chromium, tungsten, and molybdenum stabilize the hcp phase, and iron and nickel stabilize the fcc structure), the fcc-to-hcp transformation is notably sluggish especially in alloyed cobalt. The alloys usually go into service at room temperature in the metastable fcc form. The α-to-ε transformation usually occurs by the strain-induced martensitic (or shear) reaction, which also contributes to the high work-hardening rates generally seen with cobalt alloys. Carbon, one of the principal alloying elements, has a profound influence on hardness, elevated-temperature strength, and creep resistance, as well as resistance to abrasive wear through formation of carbide phases.

Uses of cobalt can be broadly classified as metallurgical and non-metallurgical. Metallurgical uses include the wear resistant, corrosion

resistant, and heat resistant cobalt-base alloys, the use of cobalt in nickel-base superalloys (the largest end-use sector for cobalt), iron-base superalloys, cemented carbides, magnetic materials, low-expansion alloys, steels, and, to a lesser extent, nonferrous alloys and cobalt coatings. Nonmetallurgical uses include the use of cobalt compounds in chemicals (for example, pigments, catalysts, driers, and adhesives) and electronic applications (for example, cobalt-containing magnetic recording media and batteries). Consumption statistics for cobalt are listed in Tables 1 and 2.

Table 1 Worldwide consumption of cobalt by market segment

Market	Percentage	Form
Superalloys (Ni-base/Co-base/Fe-base)	24.3	Metal
Hardfacing and other alloys	6.9	Powder, metal
Magnets	8.5	Metal, powder
Cemented carbides and diamond tooling	15.2	Powder
Catalysts	8.0	Salts (carbonate, sulfate, nitrate, acetate), metal
Colorizers(a)	11.6	Oxide plus some sulfate, hydroxide, and carbonate
Feedstuff, anodizing, magnetic recording, electrolysis, and copper electrowinning	5.0	Mainly sulfate, but some carbonate and hydroxide
Batteries	9.5	Hydroxide, powder, $LiCoO_2$
Tire adhesives, soaps, and driers (for paint and/or ink)	11.0	Soaps and complexes made from metal starting point
Total	**100**	

(a) For coloring glass, enamels, plastics, ceramics, and fabrics. Source: Cobalt Development Institute

Table 2 Consumption of cobalt in the United States by end use

	Metric tonnes(a)(b)(c)	
End use	**1997**	**1998**
Steel		
Stainless and heat resisting	38	38
Tool	112	96
Superalloys	4,170	4,110
Alloys (excludes steels and superalloys)		
Magnetic alloys	879	771
Other alloys(d)	342	421
Cemented carbides(e)	789	844
Chemical and ceramic uses		
Catalysts	734	W
Driers in paints or related usage	556	W
Ground coat frit	490	W
Pigments	201	W
Miscellaneous and unspecified(f)	602	2,900
Total	**8,910**	**9,180**

(a) Data are rounded to three significant digits; may not add to totals shown. (b) Includes estimates. (c) W, withheld to avoid disclosing company proprietary data; included with "Miscellaneous and unspecified." (d) Includes nonferrous alloys, welding materials, and wear-resistant alloys. (e) Includes diamond bit matrices, cemented and sintered carbides, and cast carbide dies or parts. (f) Includes feed or nutritive additive, alloy steel, glass decolorizer, and mill products made from metal powder. Source: U.S. Geological Survey

Cobalt-base alloys can conveniently be categorized as follows:

- High-carbon alloys designed for wear service
- Low-carbon alloys designed for high-temperature service
- Low-carbon alloys designed to combat corrosion or simultaneous corrosion and wear

Table 3 lists typical compositions of present-day cobalt-base alloys in these three application areas. Many of the properties of the alloys arise from the crystallographic nature of cobalt, Co (in particular its response to stress), the solid-solution-strengthening effects of chromium, Cr, tungsten, W, and molybdenum, Mo, the formation of metal carbides, and the corrosion

Table 3 Compositions of various cobalt-base alloys

Alloy tradename	UNS No.	Nominal composition, wt%									
		Co	Cr	W	Mo	C	Fe	Ni	Si	Mn	Others
Cast, P/M, and weld overlay wear resistant alloys											
Stellite 1	R30001	bal	30	13	0.5	2.5	3	1.5	1.3	0.5	…
Stellite 3 (P/M)	R30103	bal	30.5	12.5	…	2.4	5 (max)	3.5 (max)	2 (max)	2 (max)	1 B (max)
Stellite 4	R30404	bal	30	14	1 (max)	0.57	3 (max)	3 (max)	2 (max)	1 (max)	…
Stellite 6	R30006	bal	29	4.5	1.5 (max)	1.2	3 (max)	3 (max)	1.5 (max)	1 (max)	…
Stellite 6 (P/M)	R30106	bal	28.5	4.5	1.5 (max)	1	5 (max)	3 (max)	2 (max)	2 (max)	1 B (max)
Stellite 12	R30012	bal	30	8.3	…	1.4	3 (min)	1.5	0.7	2.5	…
Stellite 21	R30021	bal	27	…	5.5	0.25	3 (max)	2.75	1 (max)	1 (max)	0.007 B (max)
Stellite 98M2 (P/M)	…	bal	30	18.5	0.8 (max)	2	5 (max)	3.5	1 (max)	1 (max)	4.2 V, 1 B (max)
Stellite 703	…	bal	32	…	12	2.4	3 (max)	3 (max)	1.5 (max)	1.5 (max)	…
Stellite 706	…	bal	29	…	5	1.2	3 (max)	3 (max)	1.5 (max)	1.5 (max)	…
Stellite 712	…	bal	29	…	8.5	2	3 (max)	3 (max)	1.5 (max)	1.5 (max)	…
Stellite 720	…	bal	33	…	18	2.5	3 (max)	3 (max)	1.5 (max)	1.5 (max)	0.3 B
Stellite F	R30002	bal	25	12.3	1 (max)	1.75	3 (max)	22	2 (max)	1 (max)	…
Stellite Star J (P/M)	R30102	bal	32.5	17.5	…	2.5	3 (max)	2.5 (max)	2 (max)	2 (max)	1 B (max)
Stellite Star J	R31001	bal	32.5	17.5	…	2.5	3 (max)	2.5 (max)	2 (max)	2 (max)	…
Tantung G	…	bal	29.5	16.5	…	3	3.5	7 (max)	…	2 (max)	4.5 Ta/Nb
Tantung 144	…	bal	27.5	18.5	…	3	3.5	7 (max)	…	2 (max)	5.5 Ta/Nb
Laves-phase wear resistant alloys											
Tribaloy T-400	R30400	bal	9	…	29	…	…	…	2.5	…	…
Tribaloy T-800	…	bal	18	…	29	…	…	…	3.5	…	…
Wrought wear resistant alloys											
Stellite 6B	R30016	bal	30	4	1.5 max	1	3 (max)	2.5	0.7	1.4	…
Stellite 6K	…	bal	30	4.5	1.5 max	1.6	3 (max)	3 (max)	2 (max)	2 (max)	…
Wrought heat resistant alloys (see Table 5 for cast alloy compositions)											
Haynes 25 (L605)	R30605	bal	20	15	…	0.1	3 (max)	10	0.4 (max)	1.5	…
Haynes 188	R30188	bal	22	14	…	0.1	3 (max)	22	0.35	1.25	0.03 La
Inconel 783	R30783	bal	3	…	…	0.03 (max)	25.5	28	0.5 (max)	0.5 (max)	5.5 Al, 3 Nb, 3.4 Ti (max)
UMCo-50	…	bal	28	…	…	0.02 (max)	21	…	0.75	0.75	…
S-816	R30816	40 (min)	20	4	4	0.37	5 (max)	20	1 (max)	1.5	4 Nb
Corrosion resistant alloys											
Ultimet (1233)	R31233	bal	26	2	5	0.06	3	9	0.3	0.8	0.08 N
MP159	R30159	bal	19	…	7	…	9	25.5	…	…	3 Ti, 0.6 Nb, 0.2 Al
MP35N	R30035	35	20	…	10	…	…	35	…	…	…
Duratherm 600	R30600	41.5	12	3.9	4	0.05 (max)	8.7	bal	0.4	0.75	2 Ti, 0.7 Al, 0.05 Be
Elgiloy	R30003	40	20	…	7	0.15 (max)	bal	15.5	…	2	1 Be (max)
Havar	R30004	42.5	20	2.8	2.4	0.2	bal	13	…	1.6	0.06 Be (max)

P/M, powder metallurgy; bal, balance

resistance imparted by chromium. Generally, the softer and tougher compositions are used for high-temperature applications, such as gas-turbine vanes and buckets. The harder grades are used for resistance to wear.

Historically, many of the commercial cobalt-base alloys are derived from the Co-Cr-W and Co-Cr-Mo ternaries first investigated by Elwood Haynes at the turn of the century. He discovered the high strength and stainless nature of the binary cobalt-chromium alloy, and he later identified tungsten and molybdenum as powerful strengthening agents within the cobalt-chromium system. When he discovered these alloys, Haynes named them the Stellite alloys after the Latin, *stella*, for star because of their star-like luster. Having discovered their high strength at elevated temperatures, Haynes also promoted the use of Stellite alloys as cutting tool materials.

Following the success of cobalt-base tool materials during World War I, they were then used from about 1922 in weld overlay form to protect surfaces from wear. These early cobalt-base "hardfacing" alloys were used on plowshares, oil well drilling bits, dredging cutters, hot trimming dies, and internal combustion engine valves and valve seats.

Later in the 1930s and early 1940s, cobalt-base alloys for corrosion and high-temperature applications were developed in a series of related events involving the Austenal Laboratories and the Haynes Stellite Division of Union Carbide. Of the corrosion resistant alloys, a Co-Cr-Mo alloy with a moderately low carbon content was developed to satisfy the need for a suitable investment-cast dental material. This biocompatible material, which has the tradename Vitallium, is in use today for surgical implants. In the 1940s, this same alloy also underwent investment casting trials for World War II aircraft turbocharger blades, and, with modifications to enhance structural stability, was used successfully for many years in this and other elevated-temperature applications. This early high-temperature material, Stellite alloy 21, is still in use today, but predominantly as an alloy for wear resistance.

Cobalt-Base Wear Resistant Alloys

The cobalt-base wear alloys of today are little changed from the early alloys of Elwood Haynes. The most important differences relate to the control of carbon and silicon (which were impurities in the early alloys). Indeed, the main differences in the current Stellite alloy grades are carbon and tungsten contents (hence the amount and type of carbide formation in the microstructure during solidification).

Effects of Carbides and Alloying Elements

Carbides. As can be deduced from Table 3, the chief difference among the individual Stellite wear resistant alloys is carbon content and, thus,

carbide volume fraction in the material. For example, at a carbon level of 2.4 wt% (Stellite 3), the carbides constitute about 30 wt% of the material. These are of the M_7C_3 (chromium-rich primary) and M_6C (tungsten-rich eutectic) types, where M represents the metal component (e.g., M_7C_3 corresponds to C_7C_3). At 1 wt% carbon (Stellite 6B), the carbides constitute approximately 13 wt% of the material, these being predominantly chromium-rich eutectic carbides of the M_7C_3 type.

The size and shape of the carbide particles within the Stellite alloys are strongly influenced by cooling rate and subtle chemistry changes. Such changes markedly affect abrasion resistance because there is a distinct relationship among the size of abrading species, the size of the structural hard particles, and the rate of abrasive wear.

Chromium has a dual function in the Stellite alloys. It is both the predominant carbide former (i.e., most of the carbides are chromium rich) and the most important alloying element in the matrix, where it provides added strength (as a solute) and resistance to corrosion and oxidation. The most common carbide in the Stellite alloys is a chromium-rich M_7C_3 type, although chromium-rich $M_{23}C_6$ carbides are abundant in low-carbon alloys such as Stellite alloy 21.

Tungsten and molybdenum in the Stellite alloys serve to provide additional strength to the matrix. They do so by virtue of their large atomic size (i.e., they impede dislocation flow when present as solute atoms). When present in large quantities (e.g., in Stellite alloy 1), they participate in the formation of carbides during alloy solidification and promote the precipitation of M_6C. They also improve general corrosion resistance of the alloys. Although these alloying elements are critical to the performance of the Stellite alloys in service, the main reason for the commercial success of the Stellite alloys is the cobalt.

Cobalt imparts to its alloys an unstable fcc crystal structure with a very low stacking fault energy. The instability arises from the fact that elemental cobalt, if cooled extremely slowly, transforms from an fcc to a hcp crystal structure at 417 °C (783 °F). In most cobalt alloys, the transformation temperature is somewhat higher.

Because of the sluggish nature of the transformation, the fcc structure in cobalt and its alloys is usually retained to room temperature, and hcp formation is triggered only by mechanical stress or time at elevated temperature. The unstable fcc structure and its associated low stacking fault energy are believed to result in:

- High yield strengths
- High work-hardening rates (due to the interaction between stacking faults)
- Limited fatigue damage under cyclic stresses (due to the lack of cell walls within plastically deformed material)

- The ability to absorb stresses (through transformation of the structure to hcp)

The first three of these attributes are believed to be important in preventing metallic damage during sliding wear. The last two are believed to be responsible for the outstanding resistance to cavitation and erosion-corrosion of the cobalt alloys.

The Stellite alloys listed in Table 3 are generally used in the form of castings or weld overlays (hardfacing alloys). Some alloys (e.g., Stellite alloys 1, 6, and 12) are derivatives of the original Co-Cr-W alloys developed by Haynes. These alloys are characterized by their carbon and tungsten contents, with Stellite alloy 1 being the hardest, most abrasion resistant, and least ductile. The carbides in the Co-Cr-W-base Stellites are generally of the chromium-rich M_7C_3 type, although in high-tungsten alloys (such as Stellite alloy 1) tungsten-rich M_6C carbides usually are present also.

Stellite alloy 21 differs from the three alloys mentioned above in that it employs molybdenum, rather than tungsten, to strengthen the solid solution. Stellite alloy 21 also contains considerably less carbon. By virtue of the high molybdenum content, and the fact that most of the chromium is in solution (rather than in C_7C_3 carbides), the alloy is more resistant to corrosion than Stellite alloys 1, 6, and 12.

The most recently developed alloys in the Stellite family are those in the 700 series (alloys 703, 706, 712, and 720 in Table 3). As with Stellite alloy 21, the tungsten in these alloys has been replaced by molybdenum (molybdenum contents range from 5 to 18%). The 700 series alloys possess excellent corrosion resistance in reducing environments. Molybdenum also partitions in the carbides formed in these alloys to enhance the wear resistance.

Powder metallurgy (P/M) versions of several Stellite alloys (typically containing low levels of boron—1.0% max as listed in Table 3—to enhance sintering) are available for applications where the P/M process is cost effective (e.g., high-volume production of small simple shapes). The microstructure of P/M Stellite alloys contains complex combinations of M_7C_3, M_6C, and $M_{23}C_6$ carbides embedded in a Co-Cr-W matrix.

Laves-phase alloys include the Tribaloy family of wear resistant materials. Two cobalt-base Laves-type alloy compositions (T-400 and T-800) are listed in Table 3. In these materials, molybdenum and silicon are added at levels in excess of their solubility limit with the objective of inducing the precipitation of the hard (and corrosion resistant) Laves phase (CoMoSi or Co_3Mo_2Si). Carbon is held as low as possible in these alloys to discourage carbide formation.

Because the Laves intermetallic phase is so abundant in these alloys (35–70 vol%), its presence governs all the material properties.

Accordingly, the effects of the matrix composition in these alloys are less pronounced than in the case for the cobalt-base carbide-type alloys (Stellite), for example. The Laves phase is specifically responsible for outstanding abrasion resistance, but it severely limits the material ductility and the impact strength. In fact, it is difficult to attain crack-free overlays on all but the smallest components given adequate preheat. For this reason, these alloys have been more successful as thermal (plasma) spray coatings.

Wrought Alloys. The high-carbon alloys, such as Stellite alloys 6B and 6K in Table 3, are essentially wrought versions of the hardfacing (Stellite) alloys described above. Wrought processing improves chemical homogeneity (important in a corrosion sense), markedly increases ductility, and modifies substantially the geometry of the carbide precipitates within the alloys (blocky carbides within the microstructure enhance abrasion resistance). In terms of composition, the alloys are essentially Co-Cr-W-C quaternaries with chromium providing strength and corrosion resistance to the solid solution in addition to functioning as the chief carbide former (during alloy solidification). Tungsten provides additional solid-solution strength. Alloy 6B contains approximately 12.5 wt% carbides of the M_7C_3 and $M_{23}C_6$ types in the ratio 9 to 1. Alloy 6K exhibits an even greater carbide volume fraction, again with the M_7C_3 as the predominant type.

Cobalt-Base Heat Resistant Alloys

For many years, the predominant user of heat resistant alloys was the gas turbine industry. In the case of aircraft gas turbine power plants, the chief material requirements were elevated-temperature strength, resistance to thermal fatigue, and oxidation resistance. For land-base gas turbines, which typically burn lower grade fuels and operate at lower temperatures, sulfidation resistance was the major concern. Today, the use of heat resistant alloys is more diversified, as more efficiency is sought from the burning of fossil fuels and waste, and as new chemical processing techniques are developed.

Although cobalt-base alloys are not as widely used as nickel and nickel-iron alloys in high-temperature applications, cobalt-base heat resistant alloys nevertheless play an important role, by virtue of their excellent resistance to sulfidation, hot corrosion, and their strength at temperatures exceeding those at which the gamma-prime and gamma-double-prime precipitates in the nickel and nickel-iron alloys dissolve.

Effects of Carbides and Alloying Elements

As previously noted, Stellite 21 was an early type of cobalt-base heat resistant alloy that is used now primarily for wear resistance. Since the

early use of Stellite 21, cobalt-base heat resistant materials have gone through various stages of development to increase their high-temperature capability. The use of tungsten (or tantalum) rather than molybdenum, moderate nickel and chromium contents, lower carbon contents, and rare-earth additions typify cobalt-base high-temperature alloys of today. Table 4 summarizes some of the effects various alloying elements can produce in cobalt-base heat resistant alloys.

Wrought Heat Resistant Alloys. Table 3 lists typical wrought compositions developed for high-temperature use. Alloys 25 and 188 are considerably more ductile, oxidation resistant, and microstructurally stable than the wear resistant wrought cobalt alloys. Both alloys contain approximately 0.1 wt% C (about one-tenth of that in wrought, wear-resistant alloy 6B), which is sufficient to provide carbide strengthening, yet low enough to maintain ductility. Carbide precipitation, which is predominately of the M_6C type, is important to the high-temperature properties of these materials, partially because it restricts grain growth during heat treatment and service. Structural stability is enhanced in these alloys by nickel, which decreases the fcc/hcp transformation temperature in cobalt-base alloys.

Cast heat resistant alloys, such as alloys MAR-509, FSX-414, and the others listed in Table 5, are designed around a cobalt-chromium matrix with chromium contents ranging from approximately 18 to 30%. The high chromium content contributes to oxidation resistance, hot corrosion resistance, and sulfidation resistance, but also participates in carbide formation (Cr_7C_3 and $M_{23}C_6$) and solid-solution strengthening. Carbon content generally ranges from 0.25 to 1.0%, with nitrogen occasionally substituting for carbon.

These alloys also contain significant levels of both nickel and tungsten. The addition of nickel helps to stabilize the desired fcc matrix, while tungsten provides solid-solution strengthening and promotes carbide formation. Other alloying elements contributing to the solid-solution and/or carbide formation are tantalum, niobium, zirconium, vanadium, and titanium. Yttrium is also added to some alloys for improved oxidation resistance.

Table 4 Effects of alloying elements in cobalt-base heat resistant alloys

Element	Effect(a)
Chromium	Oxidation and sulfidation resistance, carbide former (M_7C_3 and $M_{23}C_6$)
Molybdenum, tungsten	Solid-solution strengtheners, carbide former (M_6C), intermetallic compound (Co_3M)
Tantalum, niobium	Solid-solution strengtheners, carbide former (MC) and (M_6C), intermetallic compound (Co_3M)
Aluminum	Oxidation resistance, intermetallic compound (CoAl)
Titanium	Carbide former (MC), intermetallic compound (Co_3Ti and with sufficient nickel Ni_3Ti)
Nickel	Stabilize fcc form of matrix, intermetallic compound (Ni_3Ti) facilitates working
Boron, zirconium	Increase stress-rupture strength
Carbon	Formation of carbides (MC, M_7C_3, M_6C, $M_{23}C_6$)
Yttrium, lanthanum	Oxidation resistance

(a) Not all these effects necessarily occur in a given alloy.

Table 5 Nominal compositions of cast cobalt-base heat resistant alloys

Alloy designation	Nominal composition, %												
	C	Ni	Cr	Co	Mo	Fe	Al	B	Ti	Ta	W	Zr	Other
AiResist 13	0.45	…	21	62	…	…	3.4	…	…	2	11	…	0.1Y
AiResist 213	0.20	0.5	20	64	…	0.5	3.5	…	…	6.5	4.5	0.1	0.1Y
AiResist 215	0.35	0.5	19	63	…	0.5	4.3	…	…	7.5	4.5	0.1	0.1Y
FSX-414	0.25	10	29	52.5	…	1	…	0.010	…	…	7.5	…	…
Haynes 25 (L-605)	0.1	10	20	54	…	1	…	…	…	…	15	…	…
J-1650	0.20	27	19	36	…	…	…	0.02	3.8	2	12	…	…
MAR-M 302	0.85	…	21.5	58	…	0.5	…	0.005	…	9	10	0.2	…
MAR-M 322	1.0	…	21.5	60.5	…	0.5	…	…	0.75	4.5	9	2	…
MAR-M 509	0.6	10	23.5	54.5	…	…	…	…	0.2	3.5	7	0.5	…
NASA Co-W-Re	0.40	…	3	67.5	…	…	…	…	1	…	25	1	2 Re
S-816	0.4	20	20	42	…	4	…	…	…	…	4	…	4 Mo, 4 Nb, 1.2 Mn, 0.4 Si
V-36	0.27	20	25	42	…	3	…	…	…	…	2	…	4 Mo, 2 Nb, 1 Mn, 0.4 Si
WI-52	0.45	…	21	63.5	…	2	…	…	…	…	11	…	2 Nb + Ta
Stellite 23	0.40	2	24	65.5	…	1	…	…	…	…	5	…	0.3 Mn, 0.6 Si
Stellite 27	0.40	32	25	35	5.5	1	…	…	…	…	…	…	0.3 Mn, 0.6 Si
Stellite 30	0.45	15	26	50.5	6	1	…	…	…	…	…	…	0.6 Mn, 0.6 Si
Stellite 31 (X-40)	0.50	10	22	57.5	…	1.5	…	…	…	…	7.5	…	0.5 Mn, 0.5 Si

Cobalt-Base Corrosion Resistant Alloys

To satisfy the industrial need for alloys that exhibit outstanding resistance to aqueous corrosion, yet share the attributes of cobalt as an alloy base (resistance to various forms of wear and high strength over a wide range of temperatures), several low-carbon, Co-Ni-Cr-Mo alloys are produced (see Table 3). These include the "multiphase" alloys MP35N (R30035) and MP159 (R30159), which possess the unique combination of ultrahigh strength, toughness, ductility, and corrosion resistance; and Ultimet (R31233), which combines excellent corrosion resistance to pitting (especially in oxidizing acids) with very high wear resistance (cavitation erosion, galling, and abrasion). These alloys are provided in various wrought forms, in the work-hardened or work-plus-age-hardened condition. The alloys work-harden rapidly due to strain-induced transformation, that provide a dispersion of fine hcp platelets.

Effects of Alloying Elements

Carbon in corrosion-resistant alloys is minimized to avoid carbide precipitation along grain boundaries, maximizing corrosion resistance.

Chromium. The presence of chromium in cobalt alloys permits them to passivate by forming adherent films of Cr_2O_3 as do stainless steels, thereby providing excellent resistance to elevated-temperature oxidation, sulfidation, and chemical salt reactions.

Nickel serves to stabilize the fcc structure with a view toward improved ductility during service. Nickel also improves resistance to mineral acids

and stress-corrosion cracking (SCC). The quaternary alloy MP35N (35Co-35Ni-20Cr-10Mo) resists corrosion in hydrogen sulfide, salt water, and other chloride solutions, as well as mineral acids (nitric, hydrochloric, and sulfuric). In addition, it has excellent resistance to crevice corrosion and SCC. MP35N is also biocompatible and is used for surgical implants.

Molybdenum enhances resistance to corrosion within the active regime and improves resistance to crevice corrosion.

SELECTED REFERENCES

- Cobalt-Base Alloys, *ASM Specialty Handbook: Nickel, Cobalt, and Their Alloys*, J.R. Davis, Ed., ASM International, 2000, p 362–370
- Properties of Cobalt Alloys, *ASM Specialty Handbook*: *Nickel, Cobalt, and Their Alloys*, J.R. Davis, Ed., ASM International, 2000, p 373–386
- Wear Behavior of Cobalt Alloys, *ASM Specialty Handbook*: *Nickel, Cobalt, and Their Alloys*, J.R. Davis, Ed., ASM International, 2000, p 387–394
- Corrosion Behavior of Cobalt Alloys, *ASM Specialty Handbook*: *Nickel, Cobalt, and Their Alloys*, J.R. Davis, Ed., ASM International, 2000, p 395–400

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J.R. Davis, p550-569
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Noble Metal Alloys

Introduction and Overview

The noble metals include silver, gold, and the six platinum group metals—platinum, palladium, ruthenium, rhodium, osmium, and iridium—so named because they commonly occur together in nature. The use of noble metals, also commonly referred to as precious metals, pervades our everyday life. Gold, silver, and platinum are used extensively in making jewelry; gold, silver, and other alloys are used in restorative dentistry; and sterling silver is used for making tableware. Less obvious, but equally pervasive, are the use of platinum-group metals as catalysts in automotive pollution-control equipment and for making the spinnerettes used in the manufacture of synthetic fibers for clothing; the use of silver for photographic processes; the use of gold, palladium, and their alloys in printed circuit board assemblies; silver, gold, and platinum-group metals for electrical contacts; the use of organometallic compounds containing platinum for cancer chemotherapy drugs; and many other applications.

Table 1 lists structural and physical properties of the eight noble metals. As described subsequently, for most industrial applications, an alloy is more suitable than the pure metal because of the increased strength and other property changes brought about by alloying additions.

Silver and Silver Alloys

Silver is characterized by its bright appearance, high thermal and electrical conductivities, reflectivity, and very high malleability. It is resistant to corrosion in many organic acids and in sodium and potassium hydroxide, but it is susceptible to corrosion in mineral acids. It resists oxidation at room temperature, but is susceptible to attack by sulfur. In addition, oxygen diffuses more freely through solid silver than through any metal. This fact has made it feasible to internally oxidize certain alloying ele-

Table 1 Selected properties of the noble metals

Property	Metal							
	Platinum	Palladium	Iridium	Rhodium	Osmium	Ruthenium	Gold	Silver
Crystal structure	fcc	fcc	fcc	fcc	hcp	hcp	fcc	fcc
Density at 20 °C (70 °F), g/cm^3(lb/in.^{3})	21.45 (0.774)	12.02 (0.434)	22.65 (0.818)	12.41 (0.448)	22.61 (0.816)	12.45 (0.449)	19.32 (0.697)	10.49 (0.378)
Melting point, °C (°F)	1769 (3216)	1554 (2829)	2447 (4437)	1963 (3565)	3045 (5513)	2310 (4190)	1064.4 (1948)	961.9 (1763.4)
Boiling point, °C (°F)	3800 (6870)	2900 (5250)	4500 (8130)	3700 (6690)	5020 ± 100 (9070 ± 180)	4080 ± 100 (7375 ± 180)	2808 (5086)	2210 (4010)
Electrical resistivity, μΩ · cm at 0 °C (32 °F)	9.85	9.93	4.71	4.33	8.12	6.80	2.06	1.59
Linear coefficient of thermal expansion, μin./in./°C	9.1	11.1	6.8	8.3	6.1	9.1	14.16	19.68
Tensile strength, MPa (ksi)								
As-worked wire	207–241 (30–35)	324–414 (47–60)	2070–2480(a) (300–360)	1379–1586(a) (200–230)	… …	496 (72)(a) …	207–221 (30–32)	290 (42)
Annealed wire	124–165 (18–24)	145–228 (21–33)	1103–1241 (160–180)	827–896 (120–130)	…	…	124–138 (18–20)	125–186 (18.2–27)
Elongation in 50 mm (2 in.), %								
As-worked wire	1–3	1.5–2.5	15–18(a)	2	…	3(a)	4	3–5
Annealed wire	30–40	29–34	20–22	30–35	…	…	39–45	43–50
Hardness, HV								
As-worked wire	90–95	105–110	600–700(a)	…	…	…	55–60	…
Annealed wire	37–42	37–44	200–240	120–140	300–670	200–350	25–27	25–30
As-cast	43	44	210–240	…	800	170–450	33–35	…
Young's modulus at 20 °C (70 °F), GPa (10^{6}psi)								
Static	171 (24.8)	115 (16.7)	517 (75)	319 (46.5)	558 (81)	414 (60)	77 (11.2)	74 (10.8)
Dynamic	169 (24.5)	121 (17.6)	527 (76.5)	378 (54.8)	…	476 (69)	…	…
Poisson's ratio	0.39	0.39	0.26	0.26	…	…	0.42	0.37(b)

fcc, face-centered cubic; hcp, hexagonal close-packed. (a) Hot worked. (b) Annealed. Source: Engelhard Industries Division, Engelhard Corporation

ments, such as cadmium, in order to dispersion strengthen silver for use in electrical contacts.

Brazing Alloys. A very wide range of silver-based brazing filler metal alloys is described by various standards, most notably American Society of Mechanical Engineers (ASME) SFA5.8 and American Welding Society (AWS) A5.8, which give alloy designations in the form BAg-*x*. These alloys are characterized by low melting temperatures and the ability to wet the solid base metals; hence, they are suitable filler metals for brazing steel, cast iron, stainless steel, and copper alloys to themselves and each other. They are also used in the brazing of some reactive and refractory metals, although the latter are restricted to low-temperature use.

These brazing alloys are generally Ag-Cu-Zn alloys, some with additions of cadmium, manganese, nickel, tin, or lithium (Table 2). The most widely used are the alloys BAg-1 (UNS P07450, which contains 45% Ag, 15% Cu, 16% Zn, 24% Cd) and BAg-1a (UNS P07500, containing 50% Ag, 15% Cu, 16% Zn, 18% Cd). The cadmium additions give these alloys particularly low melting temperatures, narrow melting temperature ranges, and high fluidities. Other brazing alloys include BAg-2 (UNS P07350 with 35% Ag, 26% Cu, 21% Zn, 18% Cd), and BAg-2a (UNS P07300 with 30% Ag, 27% Cu, 23% Zn, 20% Cd), which contain less silver and are therefore less expensive, but have higher melting temperatures and are less fluid. For food-processing applications, where toxicity must

Table 2 Nominal composition and solidification temperatures for silver-base brazing filler metals

		Composition, wt%									Solidification temperatures					
AWS designation(a)	UNS No.	Ag	Cu	Zn	Cd	Ni	Sn	Li	Mn	Other elements, total(b)	Solidus °C	Solidus °F	Liquidus °C	Liquidus °F	Brazing temperature range °C	Brazing temperature range °F
BAg-1	P07450.....	44.0–46.0	14.0–16.0	14.0–18.0	23.0–25.0	…	…	…	…	0.15	607	1125	618	1145	618–760	1145–1400
BAg-1a	P07500.....	49.0–51.0	14.5–16.5	14.5–18.5	17.0–19.0	…	…	…	…	0.15	627	1160	635	1175	635–760	1175–1400
BAg-2	P07350.....	34.0–36.0	25.0–27.0	19.0–23.0	17.0–19.0	…	…	…	…	0.15	607	1125	702	1295	702–843	1295–1550
BAg-2a	P07300.....	29.0–31.0	26.0–28.0	21.0–25.0	19.0–21.0	…	…	…	…	0.15	607	1125	710	1310	710–843	1310–1550
BAg-3	P07501.....	49.0–51.0	14.5–16.5	13.5–17.5	15.0–17.0	2.5–3.5	…	…	…	0.15	632	1170	688	1270	688–816	1270–1500
BAg-4	P07400.....	39.0–41.0	29.0–31.0	26.0–30.0	…	1.5–2.5	…	…	…	0.15	671	1240	779	1435	779–899	1435–1650
BAg-5	P07453.....	44.0–46.0	29.0–31.0	23.0–27.0	…	…	…	…	…	0.15	663	1225	743	1370	743–843	1370–1550
BAg-6	P07503.....	49.0–51.0	33.0–35.0	14.0–18.0	…	…	…	…	…	0.15	688	1270	774	1425	774–871	1425–1600
BAg-7	P07563.....	55.0–57.0	21.0–23.0	15.0–19.0	…	…	4.5–5.5	…	…	0.15	618	1145	652	1205	652–760	1205–1400
BAg-8	P07720.....	71.0–73.0	bal	…	…	…	…	…	…	0.15	779	1435	779	1435	779–899	1435–1650
BAg-8a	P07723.....	71.0–73.0	bal	…	…	…	…	0.25–0.50	…	0.15	766	1410	766	1410	766–871	1410–1600
BAg-9	P07650.....	64.0–66.0	19.0–21.0	13.0–17.0	…	…	…	…	…	0.15	671	1240	718	1325	718–843	1325–1550
BAg-10	P07700.....	69.0–71.0	19.0–21.0	8.0–12.0	…	…	…	…	…	0.15	691	1275	738	1360	738–843	1360–1550
BAg-13	P07540.....	53.0–55.0	bal	4.0–6.0	…	0.5–1.5	…	…	…	0.15	718	1325	857	1575	857–968	1575–1775
BAg-13a	P07560.....	55.0–57.0	bal	…	…	1.5–2.5	…	…	…	0.15	771	1420	893	1640	871–982	1600–1800
BAg-18	P07600.....	59.0–61.0	bal	…	…	…	9.5–10.5	…	…	0.15	602	1115	718	1325	718–843	1325–1550
BAg-19	P07925.....	92.0–93.0	bal	…	…	…	…	0.15–0.30	…	0.15	760	1400	891	1635	877–982	1610–1800
BAg-20	P07301.....	29.0–31.0	37.0–84.0	30.0–34.0	…	…	…	…	…	0.15	677	1250	766	1410	766–871	1410–1600
BAg-21	P07630.....	62.0–64.0	27.5–29.5	…	…	2.0–3.0	5.0–7.0	…	…	0.15	691	1275	802	1475	802–899	1475–1650
BAg-22	P07490.....	48.0–50.0	15.0–17.0	21.0–25.0	…	4.0–5.0	…	…	7.0–8.0	0.15	680	1260	699	1290	699–830	1290–1525
BAg-23	P07850.....	84.0–86.0	…	…	…	…	…	…	bal	0.15	960	1760	970	1780	970–1038	1780–1900
BAg-24	P07505.....	49.0–51.0	19.0–21.0	26.0–30.0	…	1.5–2.5	…	…	…	0.15	660	1220	705	1305	705–843	1305–1550
BAg-26	P07250.....	24.0–26.0	37.0–39.0	31.0–35.0	…	1.5–2.5	…	…	1.5–2.5	0.15	705	1305	800	1475	800–870	1475–1600
BAg-27	P07251.....	24.0–26.0	34.0–36.0	24.5–28.5	12.5–14.5	…	…	…	…	0.15	605	1125	745	1375	745–860	1375–1575
BAg-28	P07401.....	39.0–41.0	29.0–31.0	26.0–30.0	…	…	1.5–2.5	…	…	0.15	650	1200	710	1310	710–843	1310–1550
BAg-33	P07252.....	24.0–26.0	29.0–31.0	26.5–28.5	16.5–18.5	…	…	…	…	0.15	607	1125	682	1260	682–760	1260–1400
BAg-34	P07380.....	37.0–39.0	31.0–33.0	26.0–30.0	…	…	1.5–2.5	…	…	0.15	650	1200	721	1330	721–843	1330–1550

(a) AWS, American Welding Society. (b) The brazing alloy shall be analyzed for the specific elements for which values are shown in this table. If the presence of other elements is indicated in the course of this work, the amount of those elements shall be determined to ensure that their total does not exceed the limit specified for other elements.

be considered, it is necessary to use brazing alloys that are free of cadmium; these alloys include BAg-4 (UNS P07400 with 40% Ag, 30% Cu, 28% Zn, 2% Ni), BAg-5 (UNS P07453 with 45% Ag, 30% Cu, 25% Zn), BAg-20 (UNS P07301 with 30% Ag, 38% Cu, 32% Zn), and BAg-28 (UNS P07401 with 40% Ag, 30% Cu, 28% Zn, 2% Sn). For the brazing of stainless steel, the nickel-bearing alloy BAg-3 (UNS P07501 with 50% Ag, 15% Cu, 16% Zn, 16% Cd, 3% Ni) is most commonly used, but many other silver-base brazing alloys are applicable as well. Vacuum brazing grades, BVAg-*x,* are also available. These filler metals have maximum contents specified for a number of impurities—notably cadmium, phosphorus, and zinc—and have high vapor pressures.

Electrical Contact Alloys. Silver is a useful material for medium- and heavy-duty electrical contacts, particularly when alloyed with a dispersion of cadmium oxide. Here, advantage is taken of the high thermal and electrical conductivity and low surface contact resistance of silver and the ability of the particles of cadmium oxide to prevent sticking and welding and to minimize arc erosion. Under light-duty conditions (low voltage, low current) these materials are not suitable because of the tendency of silver to react with sulfur in the atmosphere to form a sulfide surface layer. The cadmium oxide dispersion can be formed either by powder metallur-

gical processing or by internal oxidation (e.g., the Ag-15%CdO alloy). Silver alloys containing approximately 0.25% each of magnesium, nickel, and in some cases copper, can also be dispersion strengthened by internal oxidation for use as electrical contact materials. Other silver-base alloys used for electrical contact purposes include fine silver, for low-current applications, and alloys of silver with copper, palladium, platinum, or gold. These alloying elements increase the hardness, but decrease the electrical conductivity. Additional information on silver-base alloys used for electrical contacts can be found in the article "Electrical Contact Alloys."

Silver-Copper Alloys for Jewelry, Tableware, and Coinage. The high reflectivity of silver makes it particularly attractive for applications in jewelry and tableware. Strength, hardness, and wear resistance are obtained through the use of alloys, in particular sterling silver, which contains 92.5% Ag and 7.5% Cu. There are two grades of sterling silver—the standard grade (UNS P07931) and silversmiths grade (P07932), which has closer limits on the allowable silver and copper contents. Silver alloys containing copper (e.g., Ag-10%Cu) are traditional coinage alloys.

Effect of Copper Content on Mechanical and Physical Properties. Copper is effective in hardening and strengthening silver, but lowers the melting point considerably and lowers electrical and thermal conductivities. Figure 1 shows the effects of copper content on the properties of silver-copper alloys.

Effect of Copper Content on Corrosion Behavior. At ordinary temperatures, the presence of copper in solid solution in silver will have little effect on the resistance of the metal to corrosion. The presence of small areas of the slightly less noble copper-rich phase might be expected to cause difficulty because of electrolytic effects, but apparently the difference between the potentials is small enough for the duplex alloys to behave satisfactorily in their usual applications. In seawater, however, and in similar electrolytes, some selective attack may be anticipated. At slightly elevated temperatures, copper oxidizes selectively. This behavior is of some consequence in electrical contacts, because it necessitates higher contact pressure. At approximately 595 °C (1100 °F), oxidizing atmospheres will cause rapid oxidation of the copper, and oxygen will diffuse to a considerable depth. One hour of exposure to air at this temperature will oxidize the 7.5% Cu alloy to a depth of 0.08 mm (0.003 in.). This was formerly very troublesome, but with the production of well-deoxidized alloys and the use of nonoxidizing atmospheres, effects from the oxidation of copper have been minimized.

Dental amalgam is a silver-mercury alloy for restoring lost tooth structure. In this application it is commonly referred to as a silver filling. It is

essentially a metallic composite consisting mainly of the intermetallic compounds $\gamma(Ag_3Sn)$ and $\gamma_1(Ag_2Hg_3)$, with smaller amounts of either $\gamma_2(Sn_7Hg)$ or $\eta'(Cu_6Sn_5)$, depending on the copper content. It is prepared by grinding silver-tin alloy particles with liquid mercury.

Dental amalgam typically contains 40 to 50% Hg, 20 to 35% Ag, 12 to 15% Sn, 2 to 15% Cu, and under 1% Zn. The applicable specifications,

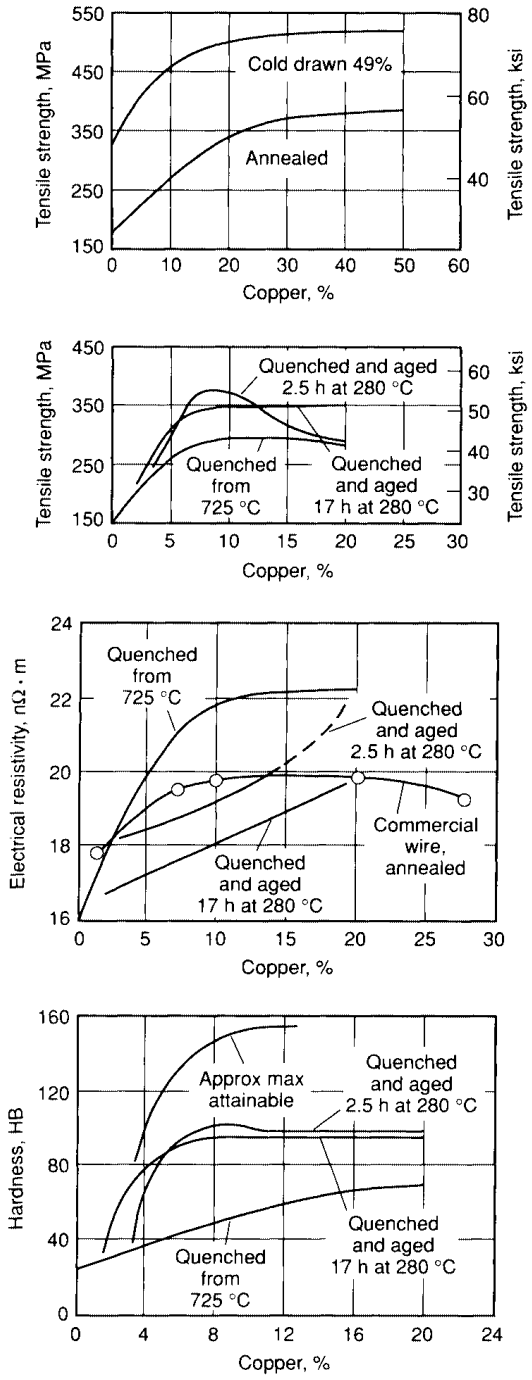


Fig. 1 Effect of copper content on properties of silver-copper alloys

however, apply only to the silver-tin alloy particles and liquid mercury used in preparing the amalgam. These are American National Standards Institute (ANSI)-MD 156.1 and International Organization for Standardization (ISO) R1559 for the silver-tin alloy, and ANSI-MD 1556.6 and ISO R1560 for the mercury. Composition limits for the alloy particles are 65% Ag minimum, 29% Sn maximum, 6% Cu maximum, 3% Hg maximum, 2% Zn maximum. These limits may be exceeded or other elements added, but if so, the manufacturer must submit the composition and the results of adequate biological and clinical tests to show that the resulting amalgam is safe and effective for use in the mouth, as directed by the manufacturer. Alloys having higher copper content, for example, have been shown to produce improved creep resistance, corrosion resistance, and durability, without producing undesirable biological reactions.

Gold and Gold Alloys

Gold is a metal with a bright, pleasing yellow color that can be substantially modified by alloy addition. It has very high malleability, thermal and electrical conductivity, and excellent corrosion resistance, including resistance to oxidation and sulfidation (i.e., to tarnish). This combination of properties has given gold and its alloys traditional applications in the jewelry and dental fields as well as a number of important industrial uses.

Jewelry Alloys. Gold and its alloys are the most popular of the jewelry metals, as they have been for thousands of years. Jewelry alloys are classified by their karat ratings and described by their colors. The most widely used alloys are 18 k gold (75% Au), 14 k gold (58% Au), and 10 k gold (42% Au). The elements that make up the balance of these alloys are silver and the base metals copper, zinc, and nickel. Each alloying element has a different effect on the color of gold:

- *Silver*: As the proportion of silver increases, gold changes in hue from yellow to greenish-yellow to white.
- *Copper*: As copper content increases, gold becomes redder in appearance.
- *Nickel*: Nickel has the effect of whitening gold. The so-called white golds substitute nickel for silver.
- *Zinc*: Zinc is considered a decolorizer.

At the 18 k level, the green golds are gold-silver alloys (e.g., UNS P00280) and red golds are gold-copper alloys (UNS P00285), while the Ag-Au-Cu alloys are yellow (UNS P00250, P00255, P00260). The red 18 k gold alloy is difficult to work because it undergoes an ordering transformation in the solid state that increases its strength and lowers its ductility.

The 10 k and 14 k gold alloys are based on the Ag-Au-Cu system (e.g., 14 k yellow golds UNS P00180, P00190, P00200, P00220); the properties of these alloys are dependent mainly on the ratios of silver to copper and not on the gold contents. The white golds are either Ag-Au-Cu alloys to which 5 to 12% Zn is added (e.g., 10 k alloy UNS P00125) or else alloys in the Au-Ni-Cu system, also containing zinc (e.g., 14 k alloys UNS P00150, P00160). The Au-Ni-Cu white golds are harder, but are susceptible to cracking when annealed after light working ("firecracking").

Electrical Contact Alloys. Gold-base alloys used for electrical contact purposes include fine gold (99.9% Au), used in dry circuit connectors and relays to improve reliability, and alloys of gold with silver, nickel, platinum, and copper. These alloys are described in the article "Electrical Contact Alloys."

Dental Alloys. A variety of gold-base alloys are available for dental applications. For example, gold-base alloys for hard inlays and crown and bridge restorations contain silver and copper as principal alloying elements, with smaller amounts of palladium, platinum, zinc, indium, and other noble metals such as ruthenium and iridium as grain refiners. Gold-base alloys for porcelain fused to alloy restorations are divided into gold-platinum-palladium, gold-palladium-silver, and gold-palladium types. Gold-base alloys for soft inlays are gold-silver-palladium types. Gold content in dental alloys generally ranges between approximately 50 and 88%.

Gold brazing alloys are used for joining jet and rocket engine components made from nickel-or cobalt-base superalloys or stainless steel. Here, joint ductility is high because alloying with the base metal is minimized. They are also used for joining hermetically sealed vacuum tube components where the low vapor pressure is advantageous. As listed in Table 3, the common brazing alloys include gold-copper alloys such as BAu-1 (UNS P00375 with 38% Au, 62% Cu), BAu-2 (UNS P00800 with 80% Au and 20% Cu), and BAu-3 (UNS P00350 with 35% Au, 62% Cu and 3% Ni),

Table 3 Nominal composition and solidification temperatures of gold-base brazing filler metals

		Composition, wt%					Solidification temperatures					
							Solidus		Liquidus		Brazing temperature range	
AWS designation(a)	UNS No.	Au	Cu	Pd	Ni	Other elements, total(b)	°C	°F	°C	°F	°C	°F
BAu-1	P00375	37.0–38.0	bal	…	…	0.15	991	1815	1016	1860	1016–1093	1860–2000
BAu-2	P00800	79.5–80.5	bal	…	…	0.15	891	1635	891	1635	891–1010	1635–1850
BAu-3	P00350	34.5–35.5	bal	…	2.5–3.5	0.15	974	1785	1029	1885	1029–1091	1885–1995
BAu-4	P00820	81.5–82.5	…	…	bal	0.15	949	1740	949	1740	949–1004	1740–1840
BAu-5	P00300	29.5–30.5	…	33.5–34.5	35.5–36.5	0.15	1135	2075	1166	2130	1166–1232	2130–2250
BAu-6	P00700	69.5–70.5	…	7.5–8.5	21.5–22.5	0.15	1007	1845	1046	1915	1046–1121	1915–2050

(a) AWS, American Welding Society. (b) The brazing filler metal will be analyzed for those specific elements for which values are shown in this table. If the presence of other elements is indicated in the course of this work, the amount of those elements will be determined to ensure that their total does not exceed the limit specified.

gold-nickel alloys like BAu-4 (UNS P00820 with 82% Au, 18% Ni), and Au-Ni-Pd alloys like BAu-5 (UNS P00300 with 30% Au, 36% Ni and 34% Pd) and BAu-6 (UNS P00700 with 70% Au, 22% Ni and 8% Pd). As in the case of silver-base brazing alloys, gold brazing alloys with modified composition requirements have also been developed for vacuum brazing applications.

Platinum-Group Metals

All six platinum-group metals are closely related and commonly occur together in nature. Their most distinctive trait in metallic form is their exceptional resistance to corrosion.

Platinum and Platinum Alloys

Platinum is the most abundant of the platinum-group metals, and it is also the most widely used. Applications are based on the corrosion resistance, high melting point, ductility, electronic properties, and overall appearance. Platinum remains bright when heated in air at all temperatures up to the melting point and is soluble only in acids that generate free chlorine, such as aqua regia.

The most common application for platinum and its alloys is as a catalyst. Platinum is an outstanding catalyst for oxidation, as in the production of H_2SO_4 and HNO_3; for hydrogenation as in the production of vitamins and other chemicals; and in the petroleum reforming process, as in the production of high-octane gasolines.

Figures 2 and 3 show the effects of alloying on the hardness and resistivity of platinum. Additional information on the effects of alloying additions on the mechanical, physical, and corrosion properties of platinum is presented in the paragraphs that follow.

Platinum-palladium alloys are used for jewelry, catalysts, insoluble anodes in seawater, and electrical contacts. The effects of palladium additions on the strength, hardness, and resistivity of platinum-palladium alloys are shown in Fig. 4 to 6.

Platinum-iridium alloys containing up to 30% Ir are used for laboratory ware, jewelry, electrical contacts, and insoluble anodes for production of persulfates and perchlorates. The effects of iridium additions on the strength, hardness, and resistivity of platinum-iridium alloys are shown in Fig. 7 to 9.

Platinum-rhodium alloys (up to 40% Rh, with 10% Rh being the most popular) are used for applications at high temperatures in oxidizing

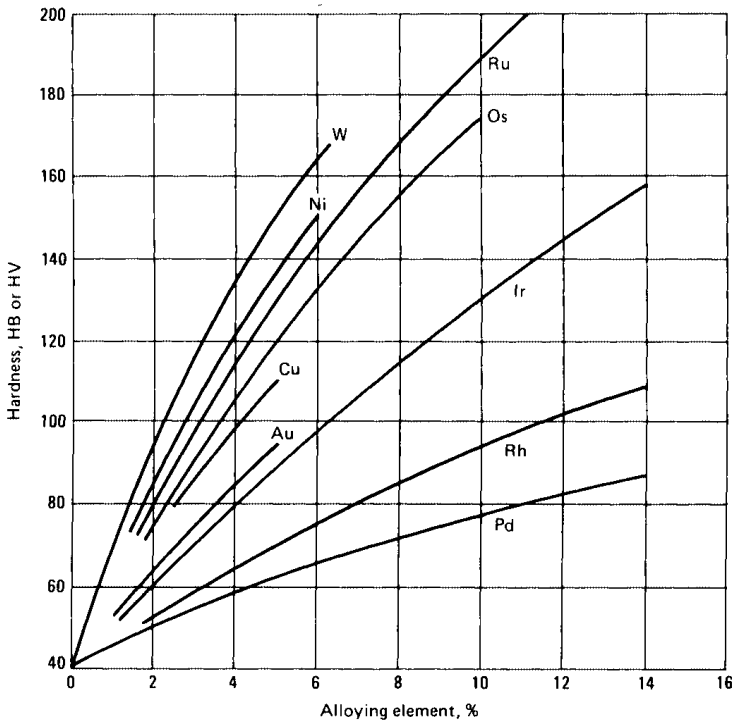


Fig. 2 Effect of various alloying additions on the hardness of annealed platinum

conditions, in addition to being used as a catalyst, as a furnace element material (at 10%, 20%, or 40% Rh), and as standard thermocouple alloys (at 10%, 13%, and 30% Rh). Platinum-rhodium alloys are also used for

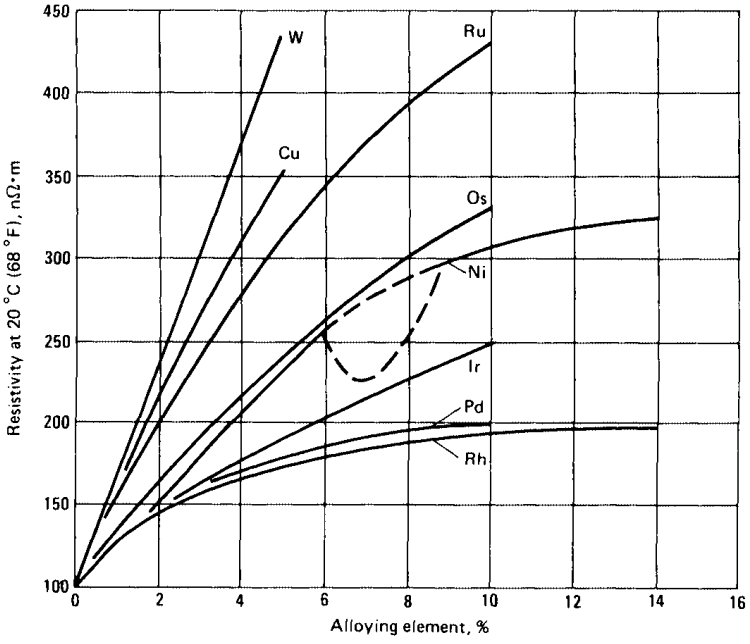


Fig. 3 Effect of various alloying additions on the electrical resistivity of platinum

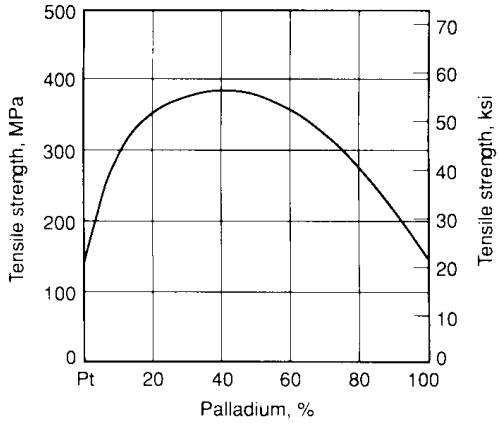


Fig. 4 Tensile strength of annealed platinum-palladium alloys as a function of palladium content

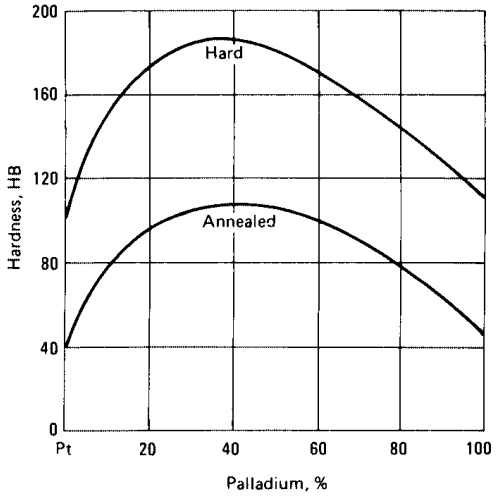


Fig. 5 Hardness of platinum-palladium alloys as a function of palladium content

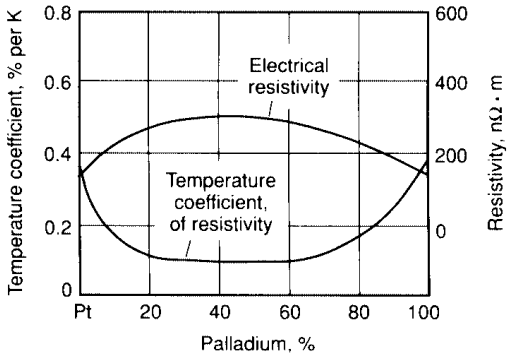


Fig. 6 Electrical resistivity of platinum-palladium alloys as a function of palladium content

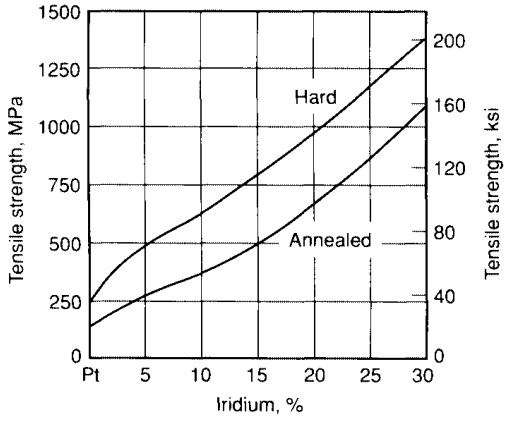


Fig. 7 Tensile strength of platinum-iridium alloys as a function of iridium content

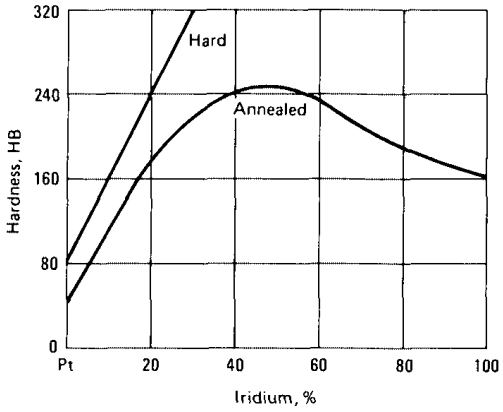


Fig. 8 Hardness of platinum-iridium alloys as a function of iridium content

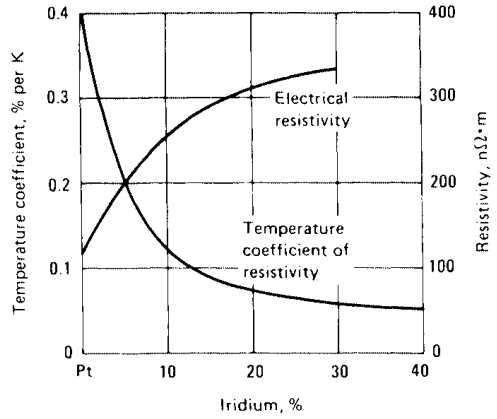


Fig. 9 Electrical resistivity of platinum-iridium alloys as a function of iridium content

Table 4 Typical properties of platinum-rhodium alloys

% rhodium and temper	Tensile strength MPa	ksi	Elongation(a), %	Hardness, HB	Density g/cm³	lb/in.³	Electrical resistivity(b), nΩ · m	Temperature coefficient(c), per °C
3.5% annealed	170	25	35	60	20.90	0.755	166	0.0022
3.5% hard(d)	415	60	…	120	20.90	0.755	166	0.0022
5.0% annealed	205	30	35	70	20.65	0.746	175	0.0020
5.0% hard(d)	485	70	…	130	20.65	0.746	175	0.0020
10% annealed	310	45	35	90	19.97	0.722	192	0.0017
10% hard(d)	620	90	2	165	19.97	0.722	192	0.0017
20% annealed	485	70	33	120	18.74	0.677	208	0.0014
20% hard(d)	895	130	2	210	18.74	0.677	208	0.0014
30% annealed	540	78	30	132	17.62	0.637	194	0.0013
30% hard(d)	1060	154	0.5	238	17.62	0.637	194	0.0013
40% annealed	565	82	30	150	16.63	0.601	175	0.0014
40% hard(d)	1255	182	0.5	290	16.63	0.601	175	0.0014

(a) In 50 mm (2 in.). (b) At 20 °C (68 °F). (c) Of electrical resistivity at 20 to 100 °C (68 to 212 °F). (d) Hard, as cold worked, 75% reduction

crucibles and dies in the glass industry, and as spinnerettes for synthetic fibers and bushings in the extrusion of fiberglass. Table 4 shows the effects of rhodium additions on the mechanical and physical properties of platinum-rhodium alloys.

Platinum-ruthenium alloys (5 to 11% Ru) are used for electrical contacts, jewelry, hypodermic needles, and as spark plug electrodes for aircraft. Figures 10 and 11 show the effects of ruthenium additions on the strength and resistivity of platinum-ruthenium alloys.

Platinum-tungsten alloys containing 8% W are used in wire form in many applications including wire-wound electrical instruments. Pt-8%W is used widely in electrical, electronic, and biochemical applications. The

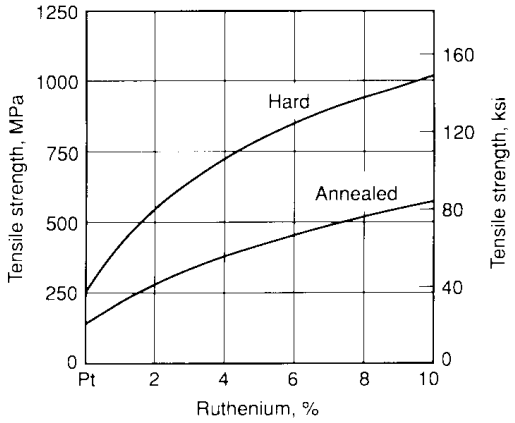


Fig. 10 Tensile strength of platinum-ruthenium alloys as a function of ruthenium content. Initially reduced by 75%, then annealed 15 min

effects of tungsten additions on the mechanical properties and resistivity of platinum-tungsten alloys are shown in Fig. 12 and 13.

Platinum-nickel alloys containing up to 20% Ni have outstanding strength at elevated temperatures. Taut band strips for electrical meters are made from 10% Ni-Pt alloys. The effects of nickel additions on the strength, hardness, and resistivity of platinum-nickel alloys are shown in Fig. 14 to 16.

Dispersion-Strengthened Platinum and Platinum Alloys. Platinum is most commonly strengthened by alloying with rhodium, but the benefit of such solid-solution strengthening becomes less marked at very high temperatures; grain coarsening occurs and the platinum-rhodium alloys fail due to

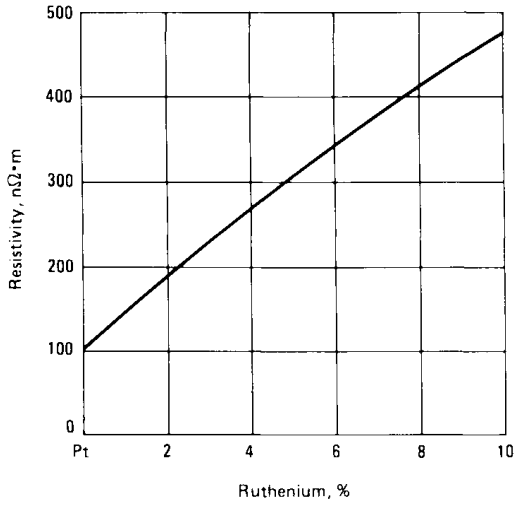


Fig. 11 Electrical resistance of platinum-ruthenium alloys as a function of ruthenium content

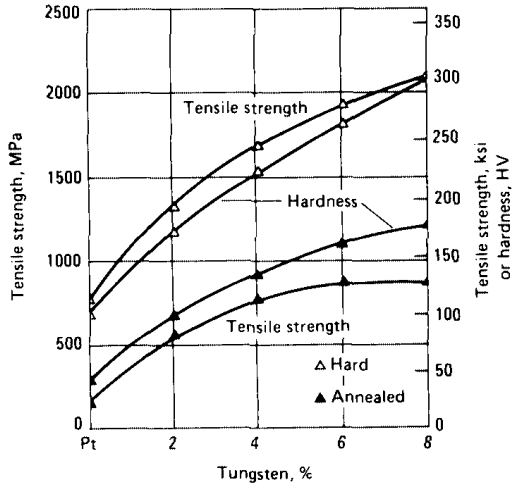


Fig. 12 Mechanical properties of platinum-tungsten alloys as a function of tungsten content

grain-boundary sliding. To remedy this situation, dispersion-strengthened platinum and platinum alloys were developed. Zirconia-grain-stabilized (ZGS) platinum materials incorporate a fine, insoluble oxide phase dispersed uniformly throughout the platinum or platinum alloy matrix.

Table 5 shows the typical properties of ZGS platinum and its alloys at room temperature, and compares the tensile strength of ZGS materials at various temperatures with conventional platinum and its alloys. Figure 17 illustrates the improvement in high-temperature life achieved by grain stabilization.

Typical applications for dispersion-strengthened platinum alloys include furnace windings, heater tapes and ignition coils, glass processing

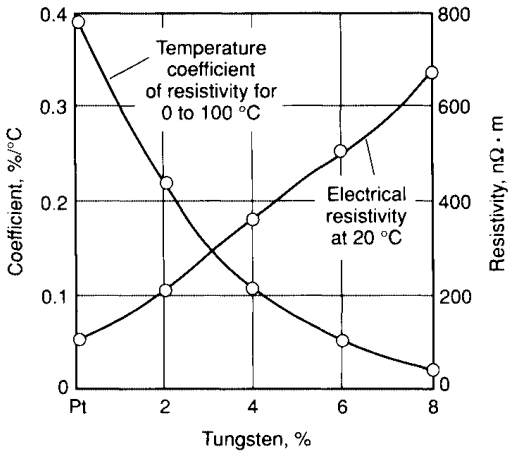


Fig. 13 Electrical resistivity of platinum-tungsten alloys as a function of tungsten content

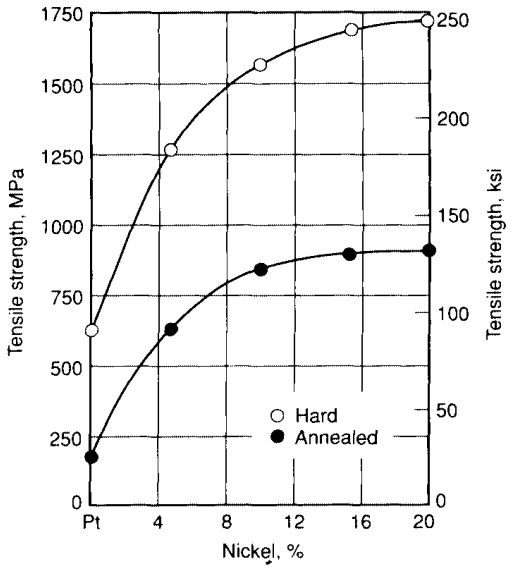


Fig. 14 Tensile strength of platinum-nickel alloys as a function of nickel content

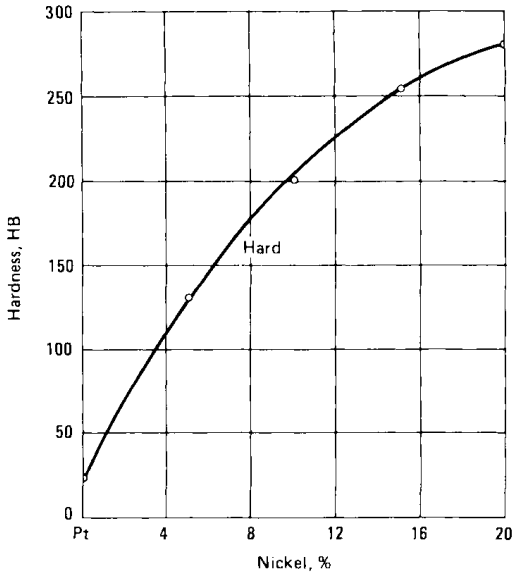


Fig. 15 Hardness of platinum-nickel alloys as a function of nickel content

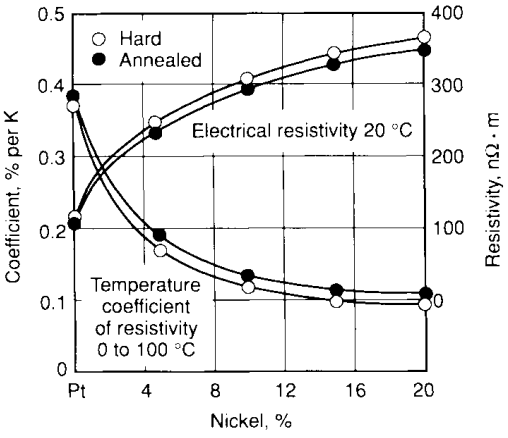


Fig. 16 Electrical resistivity of platinum-nickel alloys as a function of nickel content

Table 5 Mechanical and electrical properties of zirconia-grain-stabilized (ZGS) platinum alloys compared with conventional platinum and platinum alloys

						Ultimate tensile strength at elevated temperatures													
	Density		Specific resistance,	Temperature coefficient of resistance,	Hardness,	20 °C (70 °F) annealed		1000 °C (1830 °F)		1100 °C (2010 °F)		1200 °C (2090 °F)		1300 °C (2370 °F)		1400 °C (2550 °F)		1500 °C (2730 °F)	
Alloy	g/cm³	lb/in.³	μΩ · cm	per °C	HV	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi
100% Pt	21.4	0.773	10.6	0.0039	40	124	18.0	23	3.4	17	2.4	12.8	1.85	7.86	1.14	3.9	0.57	…	
Pt-10Rh	20.0	0.723	18.4	0.0017	90	331	48.0	82.0	11.9	61	8.8	47	6.8	38	5.5	30	4.4	23	3.4
Pt-20Rh	18.8	0.679	20.0	0.0017	115	483	70.0	230	33.4	162	23.5	99.3	14.4	68.6	9.95	49	7.1	38	5.5
ZGS Pt	21.4	0.773	11.12	0.0031	60	183	26.5	51.0	7.4	45	6.5	37	5.4	35	5.1	28	4.1	23	3.4
ZGS Pt-10 Rh	19.8	0.715	21.2	0.0016	110	355	51.5	163	23.7	140	20.3	125	18.2	92.4	13.4	83.4	12.1	70.3	10.2

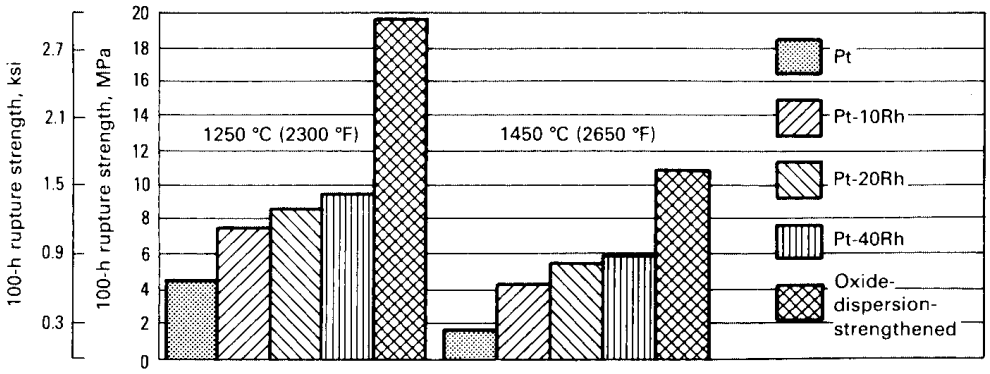


Fig. 17 Comparison of rupture strength of dispersion-strengthened platinum with platinum and platinum-rhodium alloys. Sheet thickness: 1 mm (0.04 in.) in air

equipment, and crucibles for holding molten minerals and ceramics. A particularly important industrial application is for bushings or rotors used in the manufacture of glass fibers. Typically, the equipment in these operations is expected to run continuously at temperatures above 1000 °C (1830 °F) for periods greater than 1 year.

Effects of Alloying on Corrosion Resistance. Alloys containing up to 25% Pd have essentially the same corrosion resistance as platinum and are not discolored by heating in air. The addition of palladium up to 25% raises the annealed hardness and tensile strength of platinum.

The corrosion resistance of the entire binary series of rhodium-platinum alloys is excellent, with corrosion resistance tending to improve with higher rhodium contents. For example, a 10% addition of rhodium to platinum reduces the corrosion rate in 36% hydrochloric acid (HCl) at 100 °C (212 °F) from 0.2 mm/yr (50 mils/yr) to 0 and the attack of 100 g/L ferric chloride ($FeCl_3$) at 100 °C (212 °F) from 16.7 to 0.2 mm/yr (660 to 50 mils/yr). Alloys containing less than about 20% Rh can be hot or cold worked, while those containing between 20 to 40% Rh must be hot worked prior to cold working. The practical limit for workability is about 40% Rh.

Iridium and ruthenium additions to platinum result in corrosion resistance similar to that obtained through rhodium additions. However, the ranges for working are slightly more restrictive for iridium and much more limiting for ruthenium. All the alloys of the gold-platinum binary system remain quite corrosion resistant. Alloys containing more than 60% Ag are rapidly attacked by HNO_3 and $FeCl_3$ and are tarnished by exposures to industrial atmospheres.

Nickel additions rapidly harden platinum and gradually reduce the nobility of platinum. Up to 50% Cu can be added to platinum while still retaining its resistance to HNO_3.

Dispersion-strengthened platinum and its alloys are similar to pure platinum and its alloys in their corrosion-resistant characteristics.

Palladium and Palladium Alloys

Palladium is similar to platinum in its appearance, ductility, and strength, but it is lower in melting point and in corrosion/tarnish resistance and much lower in density. Overall, it is the second-most widely used of the platinum group elements with wide applications as a material for electrical contacts. In the automotive industry, palladium is employed as a component of catalyst alloys, and palladium alloy catalysts also have applications in the chemical and pharmaceutical industries. Other uses of palladium alloys are found in medical and dental materials, in jewelry, and in brazing alloys. It can be electroplated, electroformed, and deposited by electroless methods.

Common Alloys and Applications. Figures 18 and 19 show the effects of alloying additions on the hardness and resistivity of palladium. Of the alloying elements listed in these figures, the most commonly employed

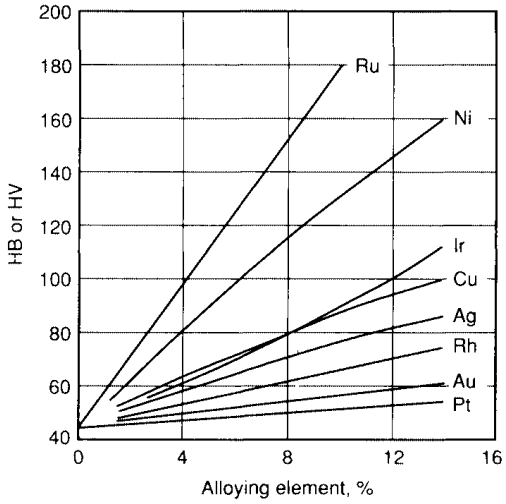


Fig. 18 Effect of various alloying additions on the hardness of annealed palladium

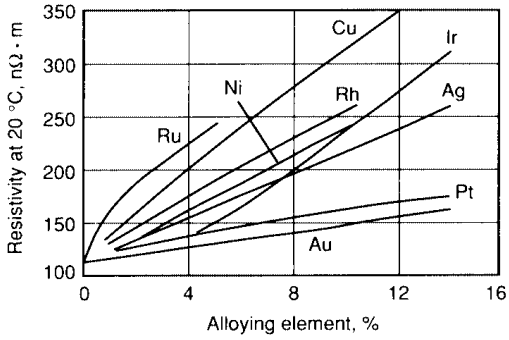


Fig. 19 Effect of various alloying additions on the electrical resistivity of palladium

are silver, copper, gold, and ruthenium. Examples of alloys containing these elements are listed subsequently.

Palladium-silver alloys find applications as electrical contact materials, and the Pd-40% Ag alloy is used as well for precision resistance wires and as a diffusion membrane for separation of hydrogen from other gases. Figures 20 to 22 show the effects of silver additions on the strength, hardness, and resistivity of palladium-silver alloys. Electrical contacts are also made from palladium-copper (40% Cu) alloy and from Pd-Ag-Cu alloys such as UNS P03440 (38% Ag, 16% Cu, 1% Pt) and UNS P03350 (30% Ag, 14% Cu, 10% Pt, 10% Au). The latter alloys can be precipitation

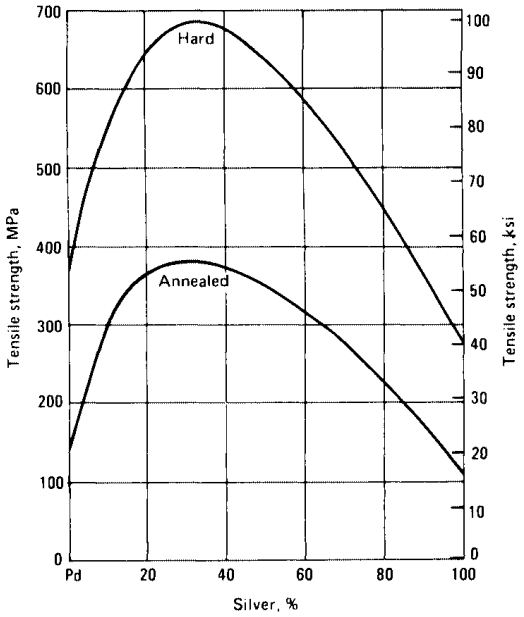


Fig. 20 Tensile strength of palladium-silver alloys as a function of silver content

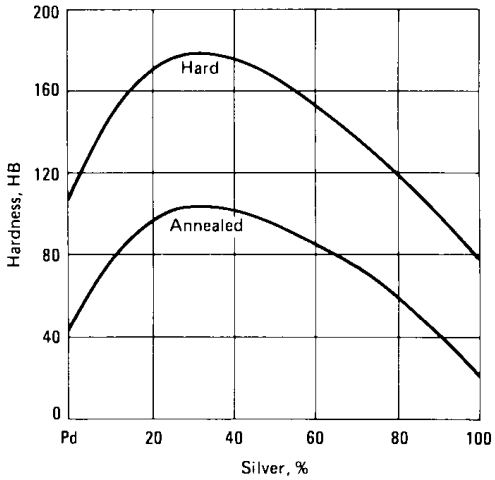


Fig. 21 Hardness of palladium-silver alloys as a function of silver content

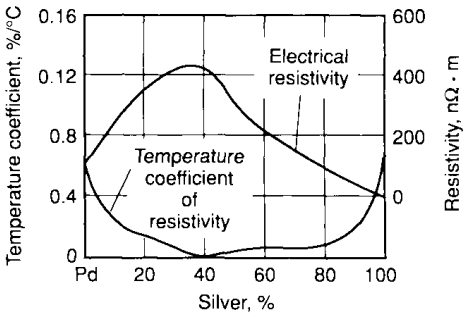


Fig. 22 Electrical resistivity of palladium-silver alloys as a function of silver content

hardened, making them useful in contact applications where sliding-wear resistance or spring properties are required. Some Pd-Ag-Au alloys are solution strengthened, but there are others that are precipitation hardened by additions of small amounts of other metals, such as copper. These are used in dental applications and in the form of cladding for severe corrosion service, particularly in halogen acids. Alloys used for brazing include palladium-cobalt alloys, such as the vacuum brazing alloy BVPd-1 (UNS P03657 with 65% Pd-35% Co). Pd-4.5% Ru is a standard jewelry alloy, in both cast and wrought forms, and palladium-ruthenium alloys up to 12% Ru are also used for electrical contacts.

Effects of Alloying on Corrosion Resistance. The additions of 2% Pt to palladium makes the alloy resistant to the jewelers' HNO_3 drop test used to determine equivalency with gold alloys, and the addition of 10% Pt to palladium makes it completely resistant to HNO_3. In $FeCl_3$ solution (100 g/L), 10% Pt decreases the room-temperature corrosion rate of palladium from 11.9 to 8.6 mm/yr (469 to 339 mils/yr). A 30% Pt addition further decreases the corrosion rate to 1.8 mm/yr (71 mils/yr).

Both iridium and rhodium are quite effective in improving the corrosion and tarnish resistance of palladium. Palladium alloys with 2% Ir or Rh are resistant to the HNO_3 drop test, and alloys with 10% of either element are untarnished by industrial sulfur-bearing atmospheres. The addition of up to 10% Ru only slightly improves the corrosion resistance of palladium. Alloys containing more than 10% Au are resistant to tarnish by industrial sulfur-bearing environments, and those with more than 20% Au are resistant to HNO_3 and HCl.

The corrosion resistance of binary palladium-nickel or cobalt alloys is intermediate between that of the component metals and can be raised to levels above those of gold alloys by the addition of platinum, rhodium, or iridium in quantities of from 5 to 20%. Small additions of palladium (0.15 to 0.20%) to titanium may have been found to be effective in improving its corrosion resistance. In such corrosive media as boiling HCl, an almost hundredfold increase in corrosion resistance is obtained. Similar effects in chromium have also been observed.

The Remaining Platinum-Group Metals

Rhodium, iridium, ruthenium, and osmium are all hard white metals that have limited ductility at room temperature. They are used primarily as alloying elements in other noble metals.

Rhodium is occasionally fabricated in the unalloyed form, but it is more commonly used as an alloying element with platinum and to a lesser extent, with palladium. It is also used as a plating on jewelry metals for whiteness and wear resistance. Rhodium is the whitest of the platinum-group metals.

Iridium, in unalloyed form, is fabricated into large crucibles that are used in the production of single crystals of yttrium-aluminum-garnet and gadolinium-gallium-garnet, which are substrates for bubble memory devices. Iridium crucibles are also used for melting nonmetallic materials up to 2100 °C (3800 °F). Iridium, which has the highest density of any metal and is the only metal that can be used for short periods at 2000 °C (3650 °F), is also used as an alloying element for platinum and rhodium.

Ruthenium is mainly used as an alloying element for platinum and palladium. When alloyed with platinum or palladium, rhodium, iridium, and ruthenium (in order of increasing effectiveness) act as hardening agents. Small amounts (~ 0.10%) of ruthenium are also added to commercially pure grades of titanium to improve their corrosion resistance.

Osmium, which is the rarest of the platinum-group metals, forms a toxic oxide at fairly low temperatures and is therefore a difficult metal to use. It is used as an alloying element to provide other precious metals with extreme hardness and resistance to corrosion.

SELECTED REFERENCES

- A.A. Johnson and J.A. von Fraunhofer, Precious Metals, *Metals Handbook Desk Edition,* American Society for Metals, 1984, p. 13-1 to 13-6
- Precious Metals in Dentistry, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 695–698
- Properties of Precious Metals, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 699–719
- E. Savitsky, V. Polyakova, N. Gorina, and N. Roshan, *The Physical Metallurgy of the Platinum Metals,* M.I.R. Publishers, 1975 (Translated by I.V. Sarin and published by Pergamon Press in 1978)
- G.D. Smith and E. Zysk, Corrosion of the Noble Metals, *Corrosion,* Vol 13, *ASM Handbook,* ASM International, 1987, p 793–807

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J.R. Davis, p573-586
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Cemented Carbides and Cermets

Introduction and Overview

Cemented carbides belong to a class of hard, wear-resistant, refractory materials in which the hard carbide particles are bound together, or cemented, by a ductile metal binder (usually cobalt). These materials were first developed in Germany in the early 1920s in response to demands for a die material having sufficient wear resistance for drawing tungsten incandescent filament wires to replace the expensive diamond dies then in use. The first cemented carbide to be produced was tungsten carbide (WC) with a cobalt binder (WC-Co). Although the term cemented carbide is widely used in the United States, these materials are better known internationally as hardmetals.

Over the years, the basic WC-Co material has been modified to produce a variety of cemented carbides containing tungsten carbide, titanium carbide, and cobalt (WC-TiC-Co), and more complex tungsten carbide-cobalt alloys containing titanium carbide, tantalum carbide, and niobium carbide (WC-TiC-(Ta,Nb)C-Co) as well as other solid-solution cubic carbides. Nickel can also be used as a binder material for improved corrosion resistance, although its use (less than 10% of total production) is considerably lower than cobalt-containing carbides. In addition, chromium carbide (Cr_3C_2) is added to both WC-Co and WC-Ni grades for further improvements in corrosion and oxidation resistance. Both unalloyed, or straight grades (WC-Co), and the more highly alloyed complex grades are used in a wide variety of applications including metal cutting, mining, construction, rock drilling, metalforming, structural components, and wear parts. Cemented carbides for machining applications are often coated with hard ceramic coatings for enhanced tooling performance.

Cermets. The term *cermet* refers to a composite of a ceramic material with a metallic binder. As defined in the literature of the cutting tool industry, the ceramic phase includes the carbides, nitrides, and carbonitrides of titanium, molybdenum, tungsten, tantalum, niobium, vanadium, aluminum, and their solid solutions. The metallic binder phase consists of nickel, cobalt, and molybdenum, or combinations thereof. By this definition, the following materials fall into the group of cermets:

- WC-Co
- WC-TiC-Co
- WC-TiC/TaC/NbC-Co
- TiC-Ni
- Ti(C,N)-Ni/Mo (titanium carbonitride + nickel and molybdenum)

However, the cutting tool industry considers only the TiC- and Ti(C,N)-base materials to be cermets, whereas the WC-base materials are referred to as cemented carbides.

For nonmachining applications, the definition of a cermet is much broader and includes carbide-, carbonitride-, nitride-, oxide-, and boride-base cermets. Despite the fact that many cermet systems have been studied, only steel-bonded TiCs used for forming tools and other wear components have achieved commercial success for nonmachining applications.

Processing. All cemented carbide and cermet components are manufactured by powder metallurgy (P/M) processing. The important steps include:

- Powder processing
- Powder treatment (e.g., mixing and milling of the various powders and the addition of a lubricant to facilitate consolidation)
- Powder consolidation (e.g., cold static pressing or cold isostatic pressing)
- Sintering or sintering plus hot isostatic pressing
- Finishing (e.g., grinding, electrical discharge machining, honing, and lapping)

A more detailed account of the processing of cemented carbides and cermets can be found in Ref 1 and 2.

Cemented Carbides for Machining Applications

The performance of cemented carbides as a cutting tool lies between that of tool steel and cermets. Compared to tool steels, cemented carbides are harder and more wear resistant, but also exhibit lower fracture resistance and thermal conductivities than tool steels. Cermets, on the other hand, are more wear resistant than cemented carbides, but may not be as tough. The performance of either carbide or cermet cutting tools is strongly

dependent on composition and microstructure, and the properties of cemented carbide tools depend not only on the type and amount of carbide, but also on the carbide grain size and the amount of binder metal.

Tungsten Carbide-Cobalt Alloys. The first commercially available cemented carbides consisted of WC particles bonded with cobalt. These are commonly referred to as straight grades. These alloys exhibit excellent resistance to simple abrasive wear and thus have many applications in metal cutting. Table 1 lists the representative properties of several straight WC-Co alloys.

The commercially significant alloys contain cobalt in the range of 3 to 25 wt%. For machining purposes, alloys with 3 to 12% Co and carbide grain sizes from 0.5 to more than 5 μm are commonly used.

The ideal microstructure of WC-Co alloys should exhibit only two phases: angular WC grains and cobalt binder phase. Representative microstructures of several straight WC-Co alloys are shown in Fig. 1. The carbon content must be controlled within narrow limits. Too high a carbon content results in the presence of free and finely divided graphite (C-type porosity), which in small amounts has no adverse effects in machining applications. Deficiency in carbon, however, results in the formation of a series of double carbides (for example, Co_3W_3C or Co_6W_6C), commonly known as η·phase, which causes severe embrittlement.

Submicron Tungsten Carbide-Cobalt Alloys. In recent years, WC-Co alloys with submicron carbide grain sizes have been developed for applications requiring more toughness or edge strength. Typical applications include indexable inserts and a wide variety of solid carbide drilling and milling tools. Grain refinement in these alloys is obtained by small additions (0.25 to 3.0 wt%) of TaC, NbC, VC, or CrC. Additions can be made before carburization of the tungsten or later in the powder blend.

Table 1 Nominal compositions and properties of representative cobalt-bonded cemented carbides

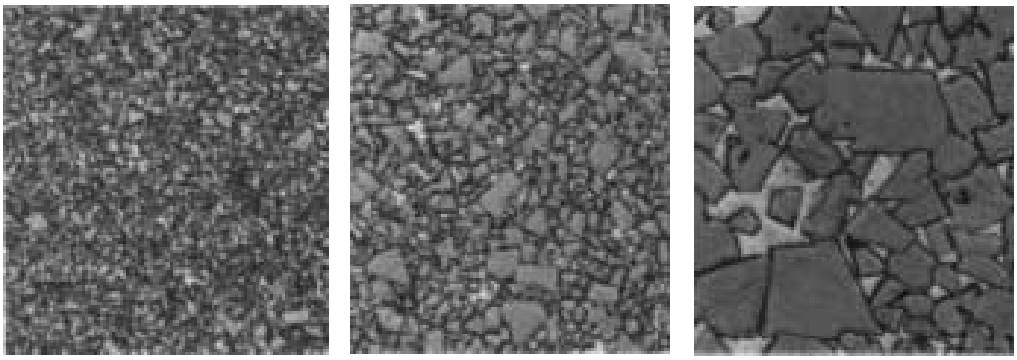
Nominal composition	Grain size	Hardness, HRA	Density		Transverse strength		Compressive strength		Modulus of elasticity		Relative abrasion resistance(a)	Coefficient of thermal expansion, μm · K		Thermal conductivity, W/m · K
			g/cm³	oz/in.³	MPa	ksi	MPa	ksi	GPa	10⁶ psi		at 200 °C (390 °F)	at 1000 °C (1830 °F)	
97WC-3Co	Medium	92.5–93.2	15.3	8.85	1590	230	5860	850	641	93	100	4.0	…	121
97WC-6Co	Fine	92.5–93.1	15.0	8.67	1790	260	5930	860	614	89	100	4.3	5.9	…
	Medium	91.7–92.2	15.0	8.67	2000	290	5450	790	648	94	58	4.3	5.4	100
	Coarse	90.5–91.5	15.0	8.67	2210	320	5170	750	641	93	25	4.3	5.6	121
90WC-10Co	Fine	90.7–91.3	14.6	8.44	3100	450	5170	750	620	90	22	…	…	…
	Coarse	87.4–88.2	14.5	8.38	2760	400	4000	580	552	80	7	5.2	…	112
84WC-16Co	Fine	89	13.9	8.04	3380	490	4070	590	524	76	5	…	…	…
	Coarse	86.0–87.5	13.9	8.04	2900	420	3860	560	524	76	5	5.8	7.0	88
75WC-25Co	Medium	83–85	13.0	7.52	2550	370	3100	450	483	70	3	6.3	…	71
71WC-12.5TiC-12TaC-4.5Co	Medium	92.1–92.8	12.0	6.94	1380	200	5790	840	565	82	11	5.2	6.5	35
72WC-8TiC-11.5 TaC-8.5Co	Medium	90.7–91.5	12.6	7.29	1720	250	5170	750	558	81	13	5.8	6.8	50

(a) Based on a value of 100 for the most abrasion-resistant material

Alloys Containing Tungsten Carbide, Titanium Carbide, and Cobalt. The WC-Co alloys, developed in the early 1920s, were successful in the machining of cast iron and nonferrous alloys at much higher speeds than were possible with high-speed steel tools, but were subject to chemical attack or diffusion wear when cutting steel. As a result, the tools failed rapidly at speeds not much higher than those used with high-speed steel. This led to the development of WC-TiC-Co alloys.

Tungsten carbide diffuses readily into the steel chip surface, but the solid solution of WC and TiC resists this type of chemical attack. Unfortunately, TiC and WC-TiC solid solutions are more brittle and less abrasion resistant than WC. The amount of TiC added to WC-Co alloys is therefore kept to a minimum, typically no greater than 15 wt%. The carbon content is less critical in WC-TiC-Co alloys than in WC-Co alloys, and the η phase does not appear in the microstructure unless carbon is grossly inadequate. In addition, free graphite rarely occurs in these alloys.

Complex Grades. The WC-TiC-Co alloys have given way to alloys of WC, cobalt, TiC, TaC, and NbC. The WC-Co alloys containing TiC, TaC, and NbC are called complex grades, multigrades, or steel-cutting grades. Adding TaC to WC-TiC-Co alloys partially overcomes the deleterious effect of TiC on the strength of WC-Co alloys. Tantalum carbide also resists cratering and improves thermal shock resistance. The latter property is particularly useful in applications involving interrupted cuts. Tantalum carbide is often added as (Ta,Nb)C because the chemical similarity between TaC and NbC makes their separation expensive. Fortunately, NbC has an effect similar to TaC in most cases. Unlike the WC-Co alloys, the microstructure of WC-TiC-(Ta,Nb)C-Co alloys shows three phases: angular WC grains, rounded WC-TiC-(Ta,Nb)C solid-solution grains, and cobalt binder (Fig. 2). The size and distribution of the phases vary widely, depending on the amounts and grain sizes of the raw materials employed and on the method of manufacture. Similarly, the properties of these complex alloys also vary widely, as indicated in Table 1 for representative steel-cutting grades.



(a) (b) (c)

Fig. 1 Microstructures of 90WC-10Co cemented carbide (straight grade). The light constituent is the cobalt binder. (a) Fine grain size. (b) Medium grain size. (c) Coarse grain size. All at 1500×

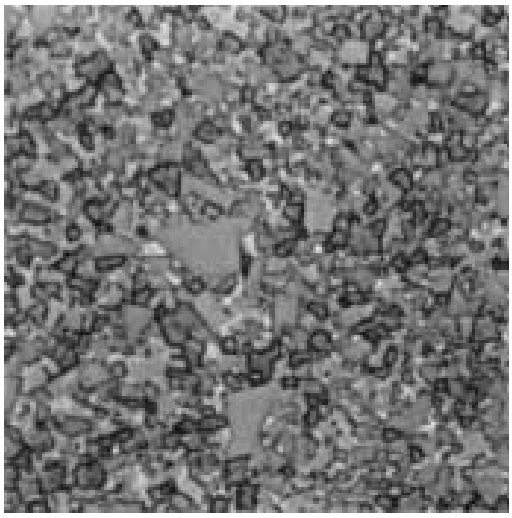


Fig. 2 Microstructure of 85WC-9(Ta,Ti,Nb)C-6Co steel-cutting grade of cemented carbide, medium grain size. The gray angular particles are WC, and the dark gray, rounded particles are solid-solution carbides. The white areas are cobalt binder. 1500×

Cemented Carbides for Nonmachining Applications

Almost 50% of the total production of cemented carbides is now used for nonmetal cutting applications such as metalforming dies, punches, and rolls, transportation and construction, mining, oil and gas drilling, forestry tools, and fluid-handling components. The majority of cemented carbides used for nonmachining applications are uncoated, straight WC-Co grades. Alloyed (complex) grades are used in only specialized applications.

In general, cobalt contents vary from 5 to 30 wt% and WC grain sizes range from <1 to >8 μm and sometimes even up to 30 μm. The selection of a proper grade for a given application depends on an understanding of the complete process and the dominant failure mechanisms observed in the tool material. Examples of typical applications are shown in Table 2.

Table 2 Properties of representative cemented carbides used for nonmachining applications

Typical application	Binder content, wt%	Grain size	Hardness, HRA
Heavy blanking punches and dies, cold heading dies	20–30	Medium	85
Heading dies (severe impact), hot-forming dies, swaging dies	11–25	Medium to coarse	84
Back extrusion punches, hot-forming punches	11–15	Medium	88
Back extrusion punches, blanking punches, and dies for high shear strength steel	10–12	Fine to medium	89
Powder compacting dies, Sendzimir rolls, strip-flattening rolls, wire-flattening rolls	6	Fine	92
Extrusion dies (low impact), light blanking dies	10–12	Fine to medium	90
Extrusion dies (medium impact), blanking dies, slitters	12–16	Medium	88
Corrosion-resistant grades, valves and nozzles, rotary seals, bearings	6–12	Fine to medium	92
Corrosion-resistant grade with good impact resistance for valves and nozzles, rotary seals, and bearings	6–10Ni	Medium	90
Deep draw dies (nongalling), tube sizing mandrels	10 Co with TiC and TaC	Medium	91

Influence of Composition, Grain Size, and Binder Content on the Properties of Cemented Carbides

Specific properties of individual grades of cemented carbides depend not only on the composition of the carbide, but also on its grain size and on the amount and type of binder.

The compositions and properties of nine straight grades and two complex grades of cobalt-bonded carbide are given in Table 1. Because properties are influenced by both composition and structure, both characteristics must be specified to define a specific grade.

For straight WCs of comparable WC grain size, increasing cobalt content increases transverse strength and toughness, but decreases hardness, compressive strength, elastic modulus, and abrasion resistance. If, for example, medium-grain carbides having 3, 7, and 25% Co are compared, 3% Co grade is found to have the greatest hardness and abrasion resistance—properties that make it well suited for wiredrawing dies and for cutting tools used in machining of cast iron and other abrasive or gummy materials. The 6% Co grade has moderate values for all properties and is a good general-purpose carbide material. The 25% Co grade has the greatest toughness and is used for applications involving heavy impact. Because of its relatively low hardness and abrasion resistance, it is not used for cutting tools. Similar parallels in properties and uses can be drawn both for the fine-grain grades and for the coarse-grain grades containing 6, 10, and 16% Co. Figures 3 and 4 show the relationship of cobalt content and grain size on the properties of straight WC-Co grades.

Another set of comparisons can be drawn for the grades containing 6% Co. All three grades—fine, medium, and coarse—are used for cutting tools, but the applications to which they are applied involve different machining conditions and different work materials. The fine-grain material is used for finish to medium-rough machining of ductile, gray, and chilled irons and of austenitic stainless steels, high-temperature alloys, and nonmetallic materials; the medium-grain material for light to heavy machining of these same wrought work materials; and the coarse-grain grade for heavy to extremely heavy rough machining of such materials. The medium-grain material is widely employed for general-purpose machining because its properties have been found to offer a good practical balance between hardness and toughness. The coarse-grain grade, which has the lowest hardness and abrasion resistance and the best toughness of the three grades, is used where a combination of moderate hardness and high toughness is needed. Similar comparisons can be made for the grades that contain 10 and 16% Co. In general, decreasing grain size improves abrasion resistance and makes it easier to retain the edge on a cutting tool; increasing grain size improves toughness and makes the cemented carbide more suitable for die applications.

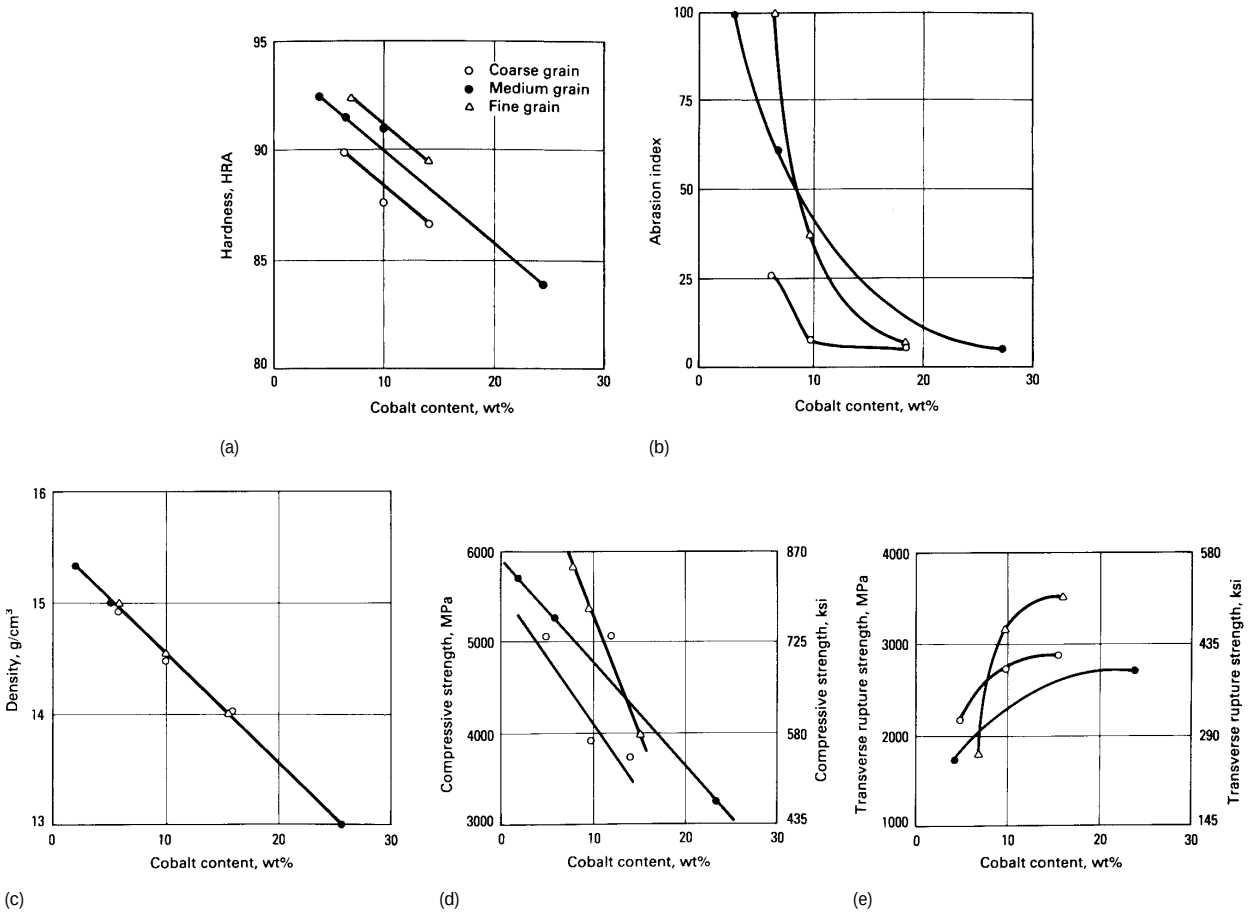


Fig. 3 Variation in properties with cobalt content and grain size for straight WC-Co alloys. (a) Variation in hardness. (b) Variation in abrasion resistance. (c) Variation in density. (d) Variation in compressive strength. (e) Variation in transverse rupture strength

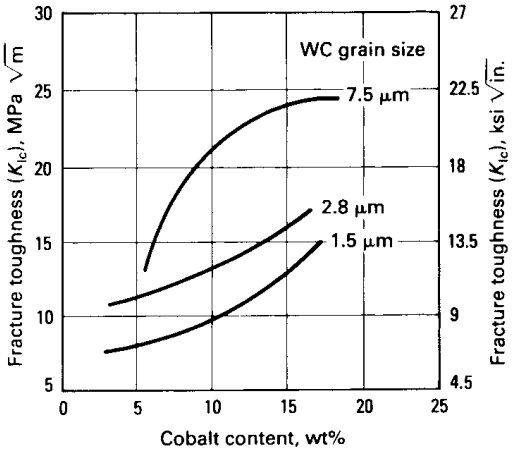


Fig. 4 Variation in fracture toughness (K_{Ic}) with cobalt content for WC-Co alloys with different tungsten carbide grain sizes

For complex grades, comparisons similar to those drawn for the straight grades are not as readily made. Variations in carbide type, as well as in binder content, affect properties, which in turn influence suitability for specific types of service.

The two complex grades listed in Table 1 contain about the same amount of WC, but one contains about twice as much binder. The lower-cobalt grade is used for lighter-duty cutting. The complex grade high in TiC is relatively low in transverse strength and high in resistance to abrasion and cratering. It is used extensively for high-speed, light-duty finishing. The complex grade highest in cobalt content and in TaC is preferred for hot-work tools, in both cutting and shaping of metals.

Thermal conductivity of WC-Co alloys is important in machining applications because the ability of the tool to conduct heat away from the tool/workpiece interface has a definite effect on tool performance. In non-machining applications, such as a rotary mechanical-pump seal, the tungsten carbide seal ring must have high thermal conductivity to ensure heat flow away from the rotary seal/stationary seal interface. Thermal conductivity decreases with increasing cobalt content and is unaffected by tungsten carbide grain size, as illustrated in Fig. 5(b). The addition of titanium carbide reduces the thermal conductivity significantly.

Coefficients of thermal expansion are an important design consideration when using WC-Co materials. The linear coefficient of thermal expansion of WC-Co increases with increasing cobalt content (Fig. 5c) and is independent of grain size. Typical low-carbon steels, tool steels, and stainless steels have thermal expansion coefficients two to three times greater than those of carbides. In metalforming applications at elevated temperatures, such as warm forming or extrusion, this difference must be

taken into consideration when designing steel/carbide assemblies. This expansion coefficient mismatch also complicates brazing operations when joining cemented carbides to metals.

Corrosion resistance is not typically thought of as a requirement for carbides, and in terms of straight corrosion resistance, there are commercially available materials that are clearly superior. However, when a combination of corrosion resistance, wear resistance, stiffness, toughness, and thermal conductivity is required, cemented carbides are the material of choice.

The corrosion resistance of carbides is limited by the susceptibility of the cobalt binder to chemical attack, although there are some corrosive media that attack tungsten carbide. The corrosive media typically dissolve the cobalt binder from the matrix, leaving behind a weak, unsupported skeleton of tungsten carbide grains, which are easily abraded away. The corrosion resistance of straight WC-Co alloys is, in general, inversely related to that of the binder content. The straight substitution of nickel binder for cobalt does provide limited improvement in both corrosion and oxidation resistance. There are several grades available that utilize

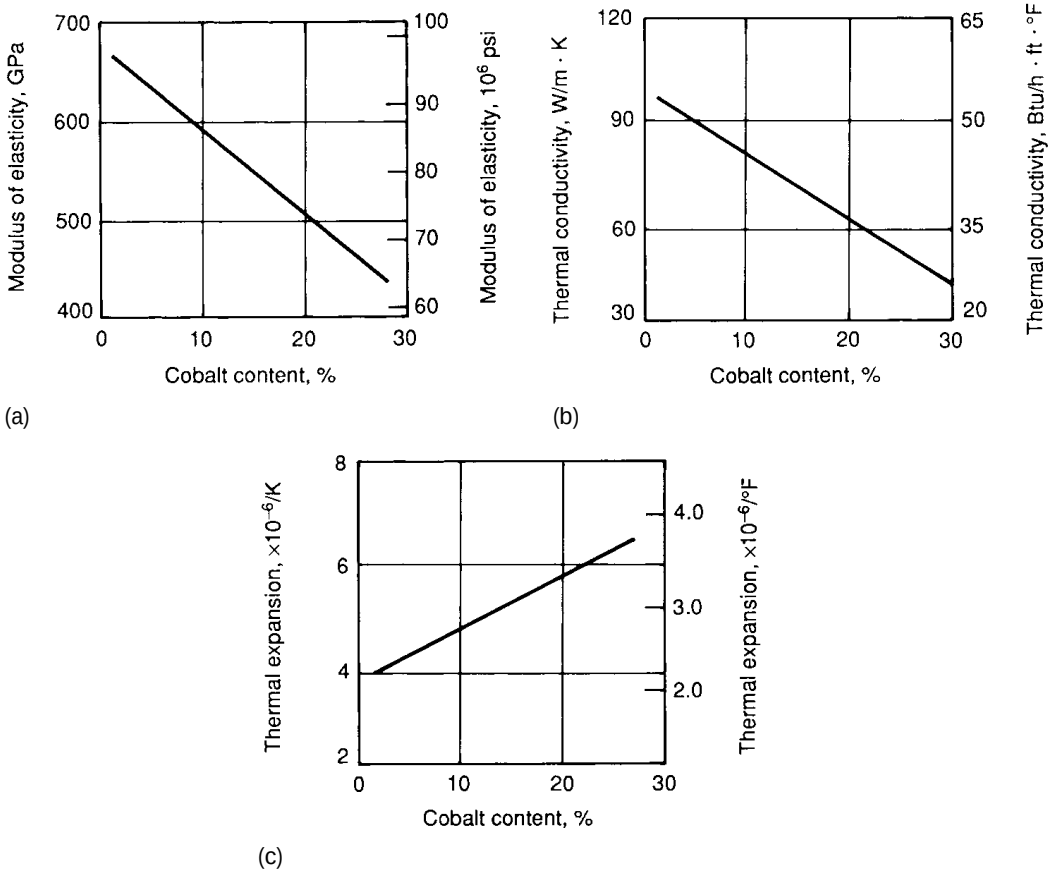


Fig. 5 Variation in properties with cobalt content for straight WC-Co alloys. (a) Variation in modulus of elasticity. (b) Variation in thermal conductivity. (c) Variation in thermal expansion

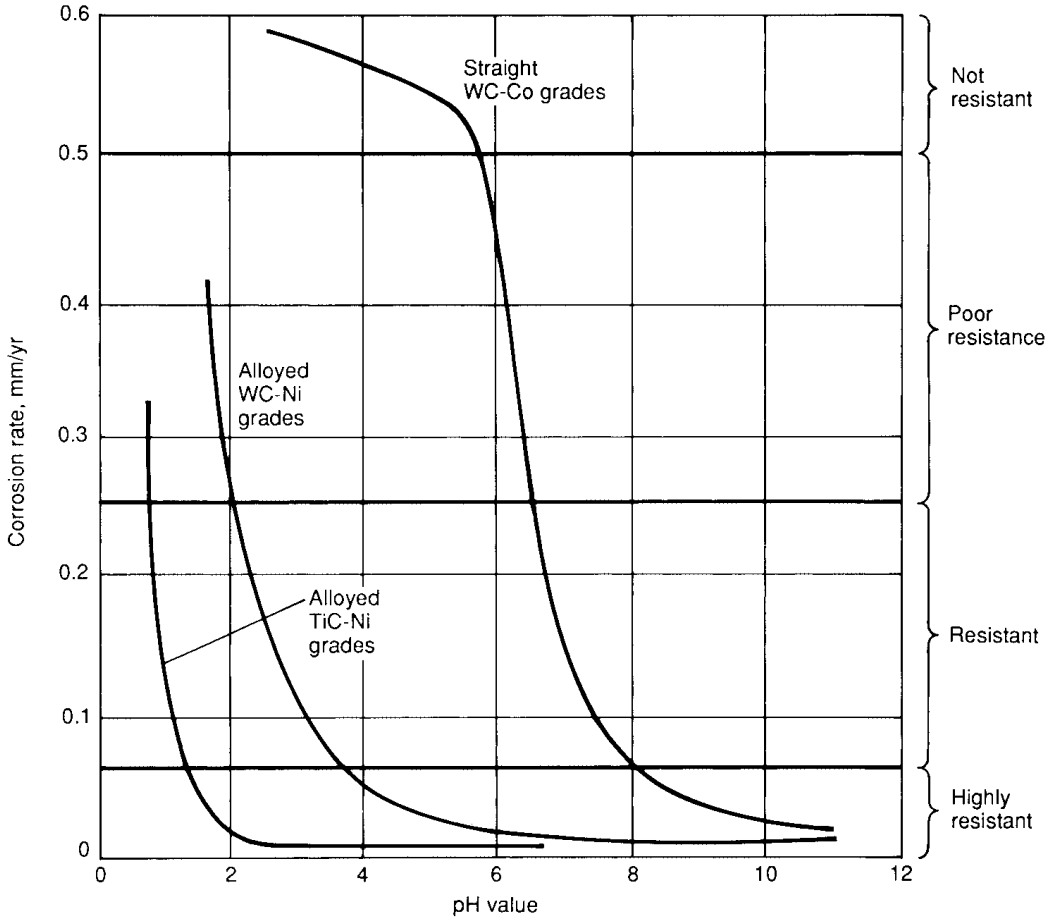


Fig. 6 Corrosion resistance of cemented carbides and cermets

chromium additions to the cobalt binder to improve corrosion resistance. Chromium, however, promotes the formation of the carbon-deficient η-phase with a resultant decrease in toughness and strength. The development of nickel binder grades alloyed with chromium, molybdenum, and other elements has resulted in a significant improvement in corrosion resistance with little sacrifice in strength or toughness. Figure 6 shows corrosion resistance versus pH for three different types of materials: WC-Co, alloyed WC-Ni, and TiC-Ni cermets. Although titanium-carbide-base cermets exhibit superior corrosion resistance, their use has been severely limited due to their inferior strength and lower thermal conductivity.

Cermets for Machining Applications

Cermets used for machining applications include TiCs and Ti(C,N)s with nickel or nickel-molybdenum binders. The manufacture of TiC/Ti(C,N)

cermets is carried out with P/M methods, including liquid-phase sintering, similar to those applied for conventional carbides. As with cemented carbides, the cermet microstructures show hard, wear-resistant particles embedded in a ductile binder phase. Although the hardness at room and elevated temperatures of these materials are comparable to those of cemented carbides, their density, strength, and toughness are somewhat lower than conventional cemented carbides. Properties vary with the proportion of binder in the overall composition (Fig. 7). In general, the corrosion resistance of TiC- and Ti(C,N)-base cermets is superior to WC-base carbides (Fig. 6). Cermets have clearly superior oxidation resistance when compared to cemented carbides and can be used at temperatures up to 900 °C (1650 °F).

The first cutting tool in the cermet family, a TiC-Ni alloy, was commercialized as early as the 1930s, but it could not compete with the inherently stronger WC-Co-base tools. Additions of molybdenum to TiC alloys in 1960 brought cermets closer in performance to WC-Co-base tools in finish machining of steels.

Titanium carbonitride cermets based on Ti(C,N)-Ni-Mo were introduced in 1970, followed by (TiMo)(C,N)-base compositions that provided a balance of wear resistance and toughness due to their finer microstructures. Continued development in this area has now resulted in complex cermets having a variety of additives, such as Mo_2C, TaC, NbC, ZrC, HfC, WC, VC, Cr_3C_2, and aluminum. Various mixes of these additives impart different combinations of wear resistance, thermal shock resistance, and toughness, and they allow tools to be tailored for a wide range of machining applications. The newer cermets are used in semifinishing and finishing of carbon and alloy steels, stainless steels, ductile irons, free-machining aluminum and other nonferrous alloys, and some high-temperature alloys. The metal removal operations may include turning, boring, milling, threading, and grooving.

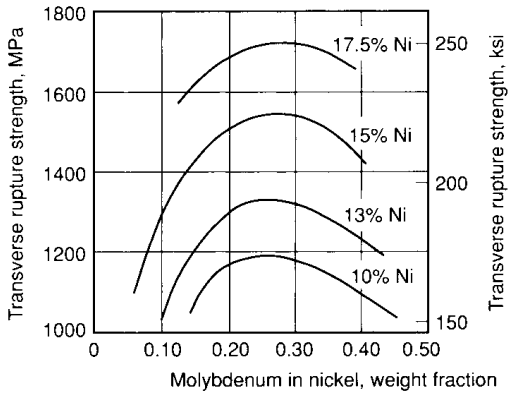


Fig. 7 Effect of binder metal composition on the transverse rupture strength of a titanium carbonitride cermet

Steel-Bonded Carbides

Steel-bonded carbides are P/M materials that are intermediate in wear resistance between tool steels and cemented carbides based on WC-Co. They consist of 25 to 45 vol% TiC homogeneously dispersed in a steel matrix.

TiC Cermets with Various Steel Binder Compositions. The wetting and solubility characteristics of TiC make it compatible with a great many alloy steels for formulating steel-bonded carbide cermets. From the many possible combinations, a few significant ones have been developed into actual cermet grades. Table 3 gives the compositions, properties, and heat

Table 3 Properties of steel-bonded titanium carbide cermets

Grade	Carbide content, vol %	Matrix alloy type	Heat-treating cycle, °C (°F)/h	Tempering cycle, °C (°F)/h	Hardness, HRC		Relative machinability(a)	Maximum working temperature		Density	
					Annealed	Hardened		°C	°F	g/cm^3	lb/in.^{3}
C	45	Medium-alloy tool steel	955 (1750)/1	190 (375)/1	44	70	1	190	375	6.60	0.239
CM	45	High-chromium tool steel	1080 (1975)/1	525 (975)/1 + 510 (950)/1	48	69	2	525	975	6.45	0.233
CM-25	25	High-chromium tool steel	1080 (1975)/1	485 (900)/1 + 470 (875)/1	32	66	2	540	1000	7.00	0.253
CHW-45	45	Tool steel	1040 (1900)/1	540 (1000)/1 + 540 (1000)/1	45	64	2	540	1000	6.45	0.233
CHW-25	25	Tool steel	985 (1800)/1	540 (1000)/1 + 525 (975)/1	30	61	2	540	1000	7.00	0.253
SK	35	Impact-resistant tool steel	1025 (1875)/1	425 (800)/1 + 425 (800)/1	38	62	1	540	1000	6.80	0.246
CS-40	45	Martensitic stainless steel	1060 (1940)/1	150 (300)/1	50	68	3	370	700	6.45	0.233
PK	42	Maraging steel	485 (900)/3	…	50	61	3	450	840	6.60	0.239
MS-5A	41	Age-hardening martensitic stainless steel	485 (900)/10	…	48	61	1	450	840	6.55	0.237

Grade	Carbide content, vol %	Matrix alloy type	Expansion test range, from 20 °C (70 °F) to:		Expansion coefficient		Transverse rupture strength		Compressive strength		Impact strength(b)		Thermal shock, number of cycles(c)	Linear size change through heat treatment, %
			°C	°F	μm/m · °C	μ in./in.·°F	MPa	ksi	MPa	ksi	J/cm^2	in. · lb/in.^{2}		
C	45	Medium-alloy tool steel	190	375	3.53	1.96	1490	216	3585	520	5.66	323	5	+0.048
CM	45	High-chromium tool steel	525	975	5.54	3.08	1275	185	3323	482	3.69	211	2	–0.011
CM-25	25	High-chromium tool steel	540	1000	10.13	5.63	1744	253	3226	468	6.58	376	103	+0.058
CHW-45	45	Tool steel	540	1000	5.72	3.18	1165	169	2206	320	3.14	179	6	+0.019
CHW-25	25	Tool steel	540	1000	6.71	3.73	1979	287	2813	408	6.27	358	106(d)	+0.039
SK	35	Impact-resistant tool steel	540	1000	9.47	5.26	1551	225	2627	381	7.39	422	100	+0.034
CS-40	45	Martensitic stainless steel	370	700	4.41	2.45	1027	149	3123	453	2.59	148	1	+0.016
PK	42	Maraging steel	450	840	3.80	2.11	1379	200	2875	417	7.37	421	84	–0.029
MS-5A	41	Age-hardening martensitic stainless steel	450	840	3.55	1.97	1765	256	2861	415	6.00	343	9	–0.009

(a) A rating of 1 indicates the greatest ease of machining. (b) Unnotched specimen. (c) Tested by heating the specimen to 1000 °C (1830 °F) and oil quenching; the cycle is repeated until a crack appears. (d) Specimen did not fail. Source: Alloy Technology International

Table 4 Characteristics and applications of steel-bonded carbides

See Table 3 for carbide content and matrix steel type.

Grade	Characteristics/applications
C	Excellent vibration dampening in the annealed condition. Excellent cryogenic properties. Applications include lamination dies, progressive dies, lancing and piercing punches, shell punches, and trimming dies. Replaces A2 tool steel. Highly magnetic
CM	For warm metalworking, drawing, and forming. Also used successfully for screws, barrel liners, and extrusion molding components in the plastics industry. Available as thermal spray powder. Replaces D2 tool steel. Magnetic
CM-25	Provides improved thermal shock resistance and impact strength over CM. Highly magnetic
CHW-45	For hot metalworking and forming. Used to replace H13 tool steel. Magnetic
CHW-25	For severe thermal shock applications. Used to replace H13 for hot extrusion. Highly magnetic
SK	Excellent impact strength. Increased wear resistance over CM-25 and CHW-25. Used in tooling applications where impact is encountered, or in hot-working applications where thermal cycling between contact with the work and cooling with a lubricant is repeated thousands of times. Specific applications include cold and hot heading dies, swaging dies, mandrels, hot-work rolls, etc. Also used as a pelletizer knife material in the plastics industry. Magnetic
CS-40	High hardness with corrosion resistance of 400-series stainless steels. Also available as thermal spray powder. Ideally suited for applications such as mechanical seal rings or tooling and equipment parts for the food processing and chemical industries. Magnetic
PK	Combination of excellent transverse rupture strength, impact strength, and corrosion resistance. Good thermal shock resistance. Magnetic
MS-5A	Excellent corrosion resistance. Excellent size stability at elevated temperatures. Replaces 17-4 PH stainless. Slightly magnetic

treatments of several quench- and precipitation-hardening steel-bonded carbide grades.

Grade C is a general-purpose cermet with a low-chromium, low-molybdenum binder steel composition and 45 vol% TiC. It is comparatively tough and readily machinable in the annealed condition, and it quench hardens to a level of 70 HRC. It is well suited for tool and wear applications in which operating temperatures do not exceed 190 °C (375 °F). Above this temperature, the alloy steel binder will overtemper, with a resulting loss of hardness and wear resistance.

Grade CM has a high-chromium, low-molybdenum steel binder composition and contains 45 vol% TiC. This cermet is more heat resistant than grade C and has slightly lower toughness, good machinability, and reliable hardenability from 1080 °C (1975 °F). It will withstand maximum working temperatures of 525 °C (975 °F).

Other steel-bonded carbide grades have lower TiC contents in order to enhance their toughness and thermal shock resistance. Some grades with age-hardening characteristics allow for higher maximum operating temperatures and greater resistance to oxidation and corrosion.

Applications Table 4 gives a list of applications and characteristics for steel-bonded carbides.

REFERENCES

1. A.T. Santhanam, P. Tierney, and J.L. Hunt, Cemented Carbides, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose*

Materials, Vol 2, *ASM Handbook,* ASM International, 1990, p 950–977

2. J.L. Ellis and C.G. Goetzel, Cermets, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 978–1007

SELECTED REFERENCES

- K.J.A. Brookes, *World Directory and Handbook of Hard-metals,* 5th ed., International Carbide Data, 1992
- J.R. Davis, Ed., *ASM Specialty Handbook*: *Tool Materials,* ASM International, 1995

Alloying: Understanding the Basics
J.R. Davis, p587-595
DOI:10.1361/autb2001p587
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Low-Expansion Alloys

Introduction and Overview

One of the best examples of alloying to influence physical properties is iron alloyed with nickel in the range of 30 to 60% in order to tailor coefficients of thermal expansion to requirements. Low-expansion alloys, which also include several iron-nickel-base ternary systems and some specialized alloys, are used in application such as the following:

- Rods and tapes for geodetic surveying
- Compensating pendulums and balance wheels for clocks and watches
- Moving parts that require control of expansion, such as pistons for some internal-combustion engines
- Bimetal strip
- Glass-to-metal seals
- Thermostatic strip
- Vessels and piping for storage and transportation of liquefied natural gas
- Superconducting systems in power transmissions
- Integrated-circuit lead frames
- Components for radios and other electronic devices
- Structural components in optical and laser measuring systems

Low-expansion alloys are also used with high-expansion alloys (65%Fe-27%Ni-5%Mo, or 53%Fe-42%Ni-5%Mo) to produce movements in thermoswitches and other temperature-regulating devices.

Iron-Nickel (Invar) Alloys

Alloys of iron and nickel have coefficients of linear expansion ranging from a small negative value (–0.5 ppm/°C) to a large positive (20 ppm/°C) value. Figure 1 shows the effect of nickel content on the linear expansion of iron-nickel alloys at room temperature. In the range of 30 to 60% Ni, it

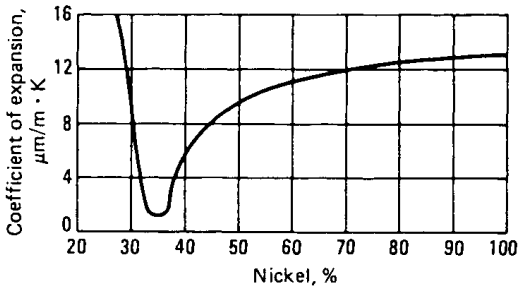


Fig. 1 Coefficient of linear expansion at 20 °C versus Ni content for Fe-Ni alloys containing 0.4% Mn and 0.1% C

is possible to select alloys with appropriate expansion characteristics. The alloy containing 36% nickel (with small quantities of manganese, silicon, and carbon amounting to a total of less than 1%) has a coefficient of expansion so low that its length is almost invariable for ordinary changes in temperature. This alloy is known as *Invar,* meaning invariable.

Effects of Alloying on Expansion Coefficient of Invar. The effect of variation in nickel content on linear expansivity is shown in Fig. 1. Minimum expansivity occurs at about 36% Ni, and small additions of other metals have considerable influences on the position of this minimum. Because further additions of nickel raise the temperature at which the inherent magnetism of the alloy disappears, the inflection temperature in the expansion curve (Fig. 2) also rises with increasing nickel content.

The addition of third and fourth elements to Fe-Ni provides useful changes of desired properties (mechanical and physical), but significantly changes thermal expansion characteristics. Minimum expansivity shifts toward higher nickel contents when manganese or chromium is added, and toward lower nickel contents when copper, cobalt, or carbon is added. Except for the ternary alloys with nickel-iron-cobalt compositions (Super-Invars), the value of the minimum expansivity for any of these ternary alloys is, in general, greater than that of a typical Invar alloy.

The effects of additions of manganese, chromium, copper, and carbon are shown in Fig. 3. Additions of silicon, tungsten, and molybdenum produce effects similar to those caused by additions of manganese and chromium; the composition of minimum expansivity shifts towards higher contents of nickel. Addition of carbon is said to produce instability in Invar, which is attributed to the changing solubility of carbon in the austenitic matrix during heat treatment.

Effects of Nickel Content on Magnetic Properties of Invar. Invar and all similar iron-nickel alloys are ferromagnetic at room temperature and become paramagnetic at higher temperatures. Because additions in nickel contents raise the temperature at which the inherent magnetism of the alloy disappears, the inflection temperature in the expansion curve rises with increasing nickel content. The loss of magnetism in a well-annealed sample of a true Invar begins at 162 °C (324 °F) and ends at

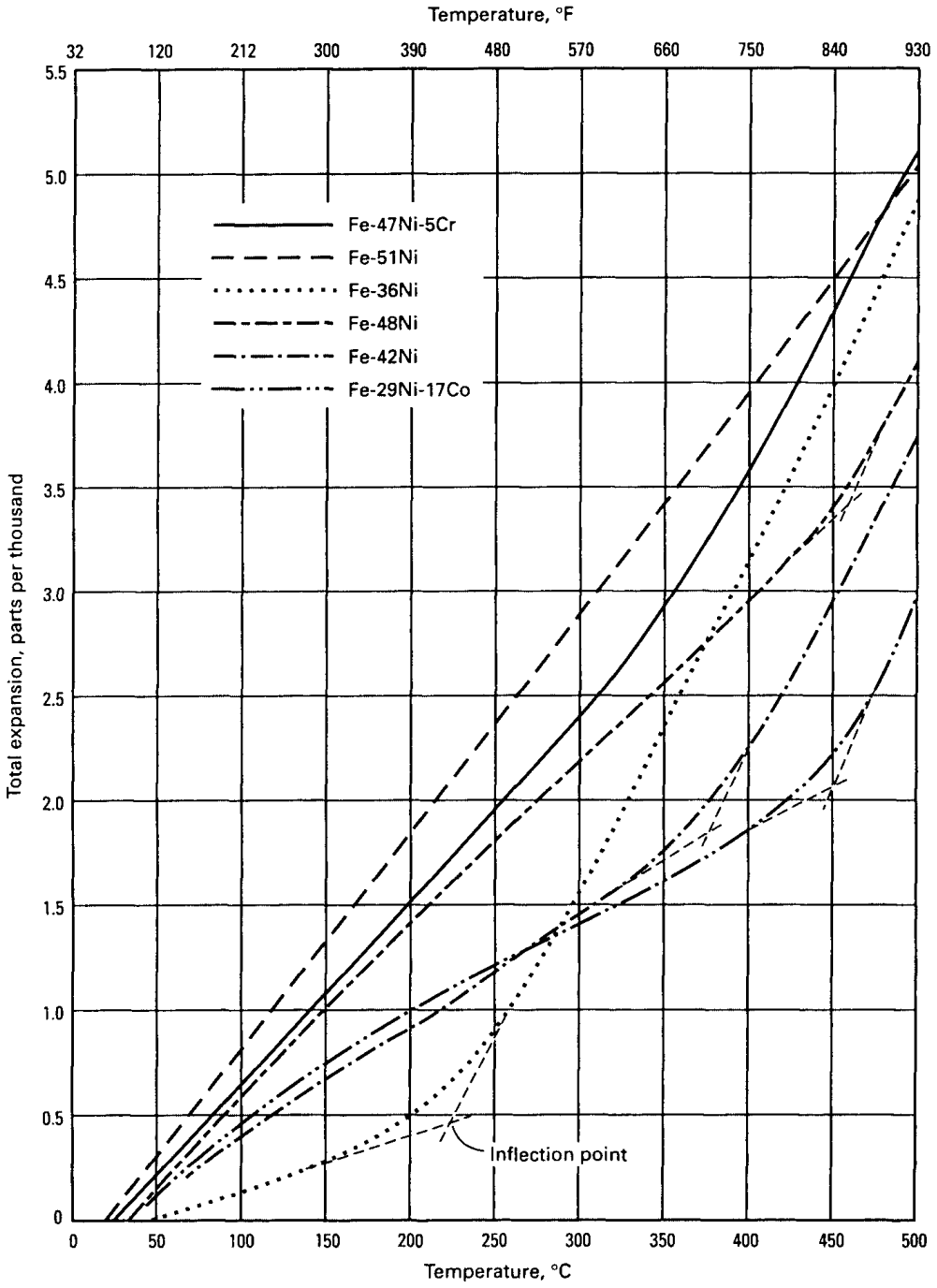


Fig. 2 Total thermal expansion of iron-nickel alloys showing the effect of nickel content and third elements

271 °C (520 °F). In a quenched sample, the loss begins at 205 °C (400 °F) and ends at 271 °C (520 °F). Figure 4 shows how the Curie temperature changes with nickel content in iron.

Effects of Nickel Content on the Thermoelastic Coefficient of Invar. The thermoelastic coefficient, which describes the changes in the modulus of elasticity as a function of temperature, varies according to the

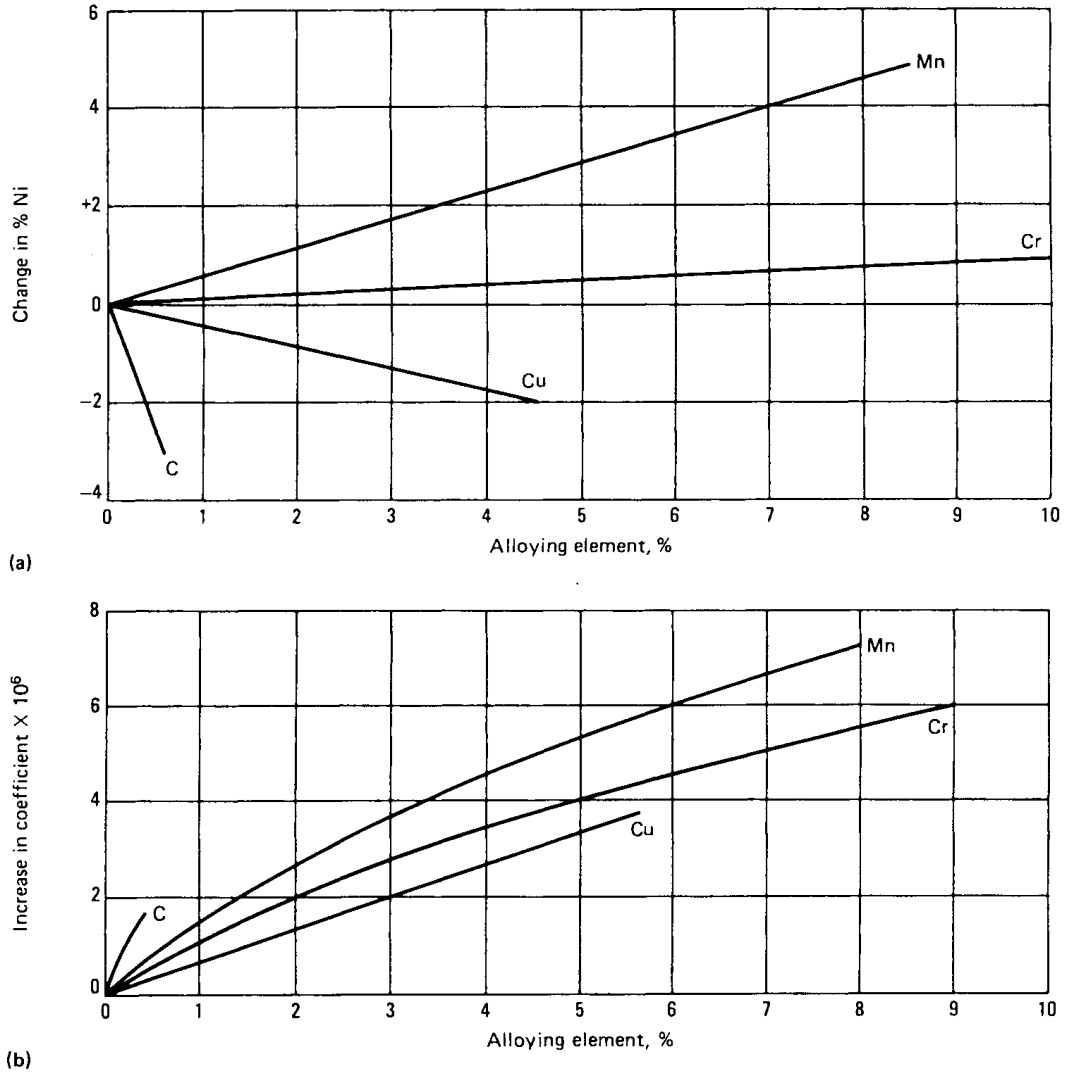


Fig. 3 Effect of alloying elements on expansion characteristics of Fe-Ni alloys. (a) Displacement of nickel content caused by additions of manganese, chromium, copper, and carbon to alloy of minimum expansivity. (b) Change in value of minimum coefficient of expansion caused by additions of manganese, chromium, copper, and carbon

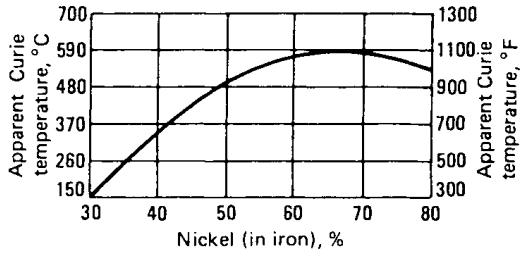


Fig. 4 Effect of nickel content on the Curie temperature of iron-nickel alloys

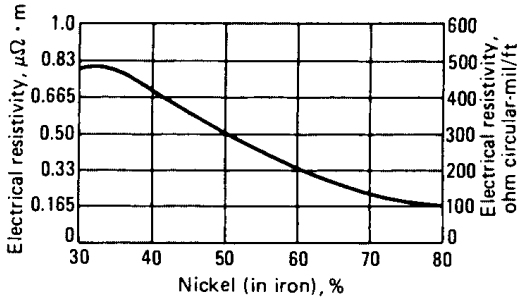


Fig. 5 Effect of nickel content on electrical resistivity of nickel-iron alloys

nickel content of iron-nickel low-expansion alloys. Invar has the highest thermoelastic coefficient of all low-expansion iron-nickel alloys, while two alloys with 29 and 45% nickel have a zero thermoelastic coefficient (that is, the modulus of elasticity does not change with temperature). However, because small variations in nickel content produce large variations in the thermoelastic coefficient, commercial application of these two iron-nickel alloys with a zero thermoelastic coefficient is not practical. The iron-nickel-chromium Elinvar alloy described later in this article provides a practical way of achieving a zero thermoelastic coefficient.

Effects of Nickel Content on the Electrical Resistivity of Invar. The electrical resistivity of 36Ni-Fe Invar is between 750 and 850 nΩ · m at ordinary temperatures. The temperature coefficient of electrical resistivity is about 1.2 mΩ/Ω · K over the range of low expansivity. As nickel content increases above 36%, the electrical resistivity decreases to ~165 nΩ · m at ~80% NiFe. This is illustrated in Fig. 5.

Iron-Nickel Alloys Other Than Invar

Although iron-nickel alloys other than Invar have higher coefficients of thermal expansion, there are applications where it is advantageous to have nickel contents above or below the 36% level of Invar. The alloy containing 39% Ni, for example, has a coefficient of expansion corresponding to that of low-expansion glasses.

Alloys that contain less than 36% Ni have much higher coefficients of expansion than alloys with a higher percentage. Alloys containing less than 36% Ni include temperature-compensator alloys (30 to 34% Ni). These exhibit linear changes in magnetic characteristics with temperature change. They are used as compensating shunts in metering devices and speedometers.

Iron-nickel alloys that have nickel contents higher than that of Invar retain to some extent the expansion characteristics of Invar. Because further additions of nickel raise the temperature at which the inherent magnetism of the alloy disappears, the inflection temperature in the expansion curve

Table 1 Composition and typical thermal expansion coefficients for common iron-nickel low-expansion alloys

Alloy	ASTM specification	Composition (a), % C(max)	Mn(max)	Si(max)	Ni(nom)
42 Ni-Iron	F 30	0.02	0.5	0.25	41
46 Ni-Iron	F 30	0.02	0.5	0.25	46
48 Ni-Iron	F 30	0.02	0.5	0.25	48
52 Ni-Iron	F 30	0.02	0.5	0.25	51
42 Ni-Iron (Dumet)	F 29	0.05	1.0	0.25	42
42 Ni-Iron (Thermostat)	B 753	0.10	0.4	0.25	42

Alloy	Typical thermal expansion coefficients from room temperature to: 300 °C (570 °F) ppm/°C	ppm/°F	400 °C (750 °F) ppm/°C	ppm/°F	500 °C (930 °F) ppm/°C	ppm/°F
42 Ni-Iron	4.4	2.4	6.0	3.3	7.9	4.4
46 Ni-Iron	7.5	4.2	7.5	4.2	8.5	4.7
48 Ni-Iron	8.8	4.9	8.7	4.8	9.4	5.2
52 Ni-Iron	10.1	5.6	9.9	5.5	9.9	5.5
42 Ni-Iron (Dumet)	…	…	6.6	3.7	…	…
42 Ni-Iron (Thermostat)	5.8(b)	3.2(b)	5.6(c)	3.1(c)	5.7(d)	3.15(d)

(a) Balance of iron with residual impurity limits of 0.25% max Si, 0.015% max P, 0.01% max S, 0.25% max Cr, and 0.5% max Co. (b) From room temperature to 90 °C (200 °F). (c) From room temperature to 150 °C (300 °F). (d) From room temperature to 370 °C (700 °F)

(Fig. 2) rises with increasing nickel content. Although this increase in range is an advantage in some circumstances, it is accompanied by an increase in coefficient of expansion.

Of significant commercial interest are those alloys containing approximately 40% to 50% nickel-iron alloys. Typical compositions and thermal expansions for some of these alloys are given in Table 1. The 42% Ni-irons listed in Table 1 are widely used in applications for their low-expansion characteristics. These include semiconductor packaging components, thermostat bimetals, incandescent light bulb glass seal leads (copper clad), and seal beam lamps. The 43 to 48% Ni-iron alloys listed in Table 1 are commonly used for glass seal leads, grommets, and filament supports.

Iron-Nickel-Chromium Alloys

Elinvar is a low-expansion iron-nickel-chromium alloy with a thermoelastic coefficient of zero over a wide temperature range. It is more practical than the straight iron-nickel alloys with a zero thermoelastic coefficient, because its thermoelastic coefficient is less susceptible to variations in nickel content expected in commercial melting.

Elinvar is used for such articles as hair-springs and balance wheels for clocks and watches and for tuning forks used in radio synchronization. Particularly beneficial where an invariable modulus of elasticity is required, it has the further advantage of being comparatively rustproof.

The composition of Elinvar has been modified somewhat from its original specification of 36% Ni and 12% Cr. The limits now used are 33 to 35 Ni, 61 to 53 Fe; 4 to 5 Cr, 1 to 3 W, 0.5 to 2 Mn, 0.5 to 2 Si, and 0.5 to 2 C.

Table 2 Type, composition, and typical thermal expansion for some iron-nickel-chromium glass-seal alloys

Alloy type	ASTM specifications	Composition(a), % Mn(max)	Si(max)	Cr(nom)	Ni(nom)
42-6	F 31	0.25	0.25	5.75	42.5
45-5	…	0.25	0.30	6.00	45.0
48-5	…	0.30	0.20	6.00	47.5

Alloy type	Average thermal expansion coefficients from room temperature to: 200 °C (390 °F) ppm/°C	ppm/°F	300 °C (570 °F) ppm/°C	ppm/°F	400 °C (750 °F) ppm/°C	ppm/°F	500 °C (930 °F) ppm/°C	ppm/°F
42-6	7.1	3.9	8.3	4.6	10.0	5.55	11.5	6.4
45-5	8.2	4.55	8.7	4.8	10.0	5.55	11.2	6.2
48-5	…	…	9.4	5.2	10.3	5.7	…	…

(a) Balance of iron with 0.05% max C, 0.015% max P, 0.015% max S, and 0.50% max Co

Other iron-nickel-chromium alloys with 40 to 48% Ni and 2 to 8% Cr are useful as glass-sealing alloys because the chromium promotes improved glass-to-metal bonding as a result of its oxide-forming characteristics. The most common of these contain approximately 42 to 48% nickel with chromium of 4 to 6%. Although chromium additions increase the minimum thermal expansion and lower inflection points (Curie temperature), they have a beneficial effect on the glass-sealing behavior of these alloys. The chromium promotes formation of a surface chromium oxide that improves wetting at the metal/glass interface. Some of this metal oxide is absorbed by the glass during the actual glass seal and promotes a higher-strength metal/glass bond (graded seals). Compositions and thermal expansions for some Fe-Ni-Cr alloys are shown in Table 2.

Iron-Nickel-Cobalt Alloys

Super-Invar. Substitution of ~ 5% Co for some of the nickel content in the 36% Ni (Invar) alloy provides an alloy with an expansion coefficient even lower than Invar. A Super-Invar alloy with a nominal 32% Ni and 4 to 5% Co will exhibit a thermal expansion coefficient close to zero, over a relatively narrow temperature range. Figure 6 compares thermal expansion for 32% Ni-5% Co Super-Invar with that of an Invar alloy.

Cobalt has been added to other Fe-Ni alloys in amounts as high as 40%. Such additions increase the coefficient of expansion at room temperature. However, because they also raise the inflection temperature, they produce an alloy with a moderately low coefficient of expansion over a wider range of temperature.

Kovar is a nominal 29%Ni-17%Co-54%Fe alloy that is a well-known glass-sealing alloy suitable for sealing to hard (borosilicate) glasses. Kovar has a nominal expansion coefficient of approximately 5 ppm/°C and, as shown in Fig. 2, an inflection temperature of ~ 450 °C (840 °F).

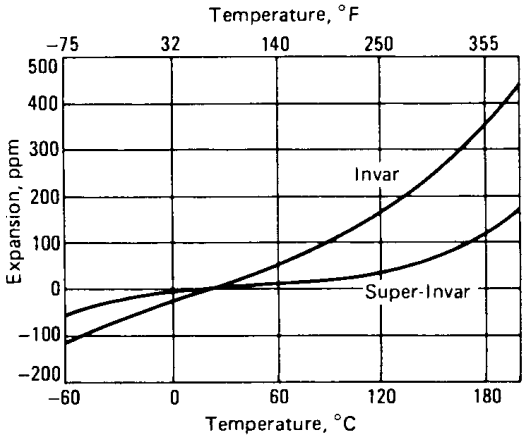


Fig. 6 Comparison of thermal expansion for Super-Invar (63% Fe, 32% Ni, 5% Co) and Invar (64% Fe, 36% Ni) alloys

Special Alloys

Iron-Cobalt-Chromium Low-Expansion Alloys. An alloy containing 36.5 to 37% Fe, 53 to 54.5% Co, and 9 to 10% Cr has an exceedingly low, and at times, negative (over the range from 0 to 100 °C, or 32 to 212 °F) coefficient of expansion. This alloy has good corrosion resistance compared to low-expansion alloys without chromium. Consequently, it has been referred to as "Stainless Invar." A similar alloy containing 37% Fe, 30% Ni, 25% Co, and 8% Cr has been used for seal-in wires for electronic components sealed in special glasses.

Hardenable Low-Expansion Alloys. Alloys that have low coefficients of expansion, and alloys with constant modulus of elasticity, can be made age hardenable by adding titanium. In low-expansion alloys, nickel content must be increased when titanium is added. The higher nickel content is required because any titanium that has not combined with the carbon in the alloy will neutralize more than twice its own weight in nickel by forming an intermetallic compound during the hardening operation.

As shown in Table 3, addition of titanium raises the lowest attainable rate of expansion and raises the nickel content at which the minimum expansion occurs. Titanium also lowers the inflection temperature.

In alloys of the constant-modulus type containing chromium, addition of titanium allows the thermoelastic coefficients to be varied by adjustment of heat-treating schedules. The alloys in Table 4 are the three most

Table 3 Minimum coefficient of expansion in low-expansion Fe-Ni alloys containing titanium

Ti, %	Optimum Ni, %	Minimum coefficient of expansion, μm/m · K
0	36.5	1.4
2	40.0	2.9
3	42.5	3.6

Table 4 Thermoelastic coefficients of constant modulus Fe-Ni-Cr-Ti alloys

Composition, %				Thermoelastic coefficient, annealed condition, μm/m · K	Range of possible coefficients(a), μm/m · K
Ni	Cr	C	Ti		
42	5.4	0.06	2.4	0	18 to −23
42	6.0	0.06	2.4	36	54 to 13
42	6.3	0.06	2.4	−36	−18 to −60

(a) Any value in this range can be obtained by varying the heat treatment.

Table 5 Composition and thermal expansion coefficients of high-strength controlled-expansion alloys

		Coefficient of thermal expansion, from room temperature to:						Inflection temperature	
		260 °C (500 °F)		370 °C (700 °F)		415 °C (780 °F)			
Alloy designation	Composition, %	ppm/°C	ppm/°F	ppm/°C	ppm/°F	ppm/°C	ppm/°F	°C	°F
Incoloy 903 and Pyromet CTX-1	0.03 C, 0.20 Si, 37.7 Ni, 16.0 Co, 1.75 Ti, 3.0 (Nb + Ta), 1.0 Al, 0.0075 B, bal Fe	7.51	4.17	7.47	4.15	7.45	4.14	440	820
Incoloy 907 and Pyromet CTX-3	0.06 C max, 0.5 Si, 38.0 Ni, 13.0 Co, 1.5 Ti, 4.8 (Nb + Ta), 0.35 Al max, 0.012 B max, bal Fe	7.65	4.25	7.50	4.15	7.55	4.20	415	780
Incoloy 909 and Pyromet CTX-909	0.06 C max, 0.40 Si, 38.0 Ni, 14.0 Co, 1.6 Ti, 4.9 (Nb + Ta), 0.15 Al max, 0.012 B max, bal Fe	7.75	4.30	7.55	4.20	7.75	4.30	415	780

widely used compositions. The recommended solution treatment for the alloys that contain 2.4% Ti is 950 to 1000 °C (1740 to 1830 °F) for 20 to 90 min., depending on section size. Recommended duration of aging varies from 48 h at 600 °C (1110 °F) to 3 h at 730 °C (1345 °F) for solution-treated material.

High-Strength, Controlled-Expansion Alloys. There is a family of Fe-Ni-Co alloys strengthened by the addition of niobium and titanium that show the strength of precipitation-hardened superalloys while maintaining low coefficients of thermal expansion typical of certain alloys from the Fe-Ni-Co system. Compositions and expansion coefficients of these alloys are shown in Table 5. The combination of exceptional strength and low coefficient of expansion makes this family useful for applications requiring close operating tolerances over a range of temperatures. Several components for gas turbine engines are produced from these alloys.

SELECTED REFERENCES

- E.L. Frantz, Low-Expansion Alloys, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 889–896
- K.C. Russel and D. Smith, Ed., *Physical Metallurgy of Controlled Expansion Invar-Type Alloys,* The Metallurgical Society of AIME, 1989

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Electrical Contact Alloys

Introduction and Overview

Electrical contacts are metallic devices that make and break electrical circuits. Contacts are made of either elemental metals or alloys made by the melt-cast method or composites manufactured by powder metallurgy (P/M) processes. Powder metallurgy facilitates combinations of metals that ordinarily cannot be achieved by conventional alloying.

Contact Material Requirements. If an ideal electrical contact material could be found, it would have high electrical conductivity to minimize the heat generated during passage of current; high thermal conductivity to dissipate both the resistive and arc heat developed; high reaction resistance to all environments in which it was to be used to avoid formation of insulating oxides, sulfides, and other compounds; and immunity to arcing damage on the making and breaking of electrical contact. The force required to close a contact made of this material would be low, as would the electrical resistance between mating members. The melting point of the material would be high enough to limit arc erosion, metal transfer, and welding or sticking, but it would also be low enough to increase resistance to reignition in switching. (When the melting point is high, contacts continue to heat gas in the contact gap after the current drops to zero, thus facilitating reignition.) The vapor pressure would be low to minimize arc erosion and metal transfer. Hardness would be high to provide good wear resistance, and yet ductility would be high enough to ensure ease of fabrication. Purity of the material would be maintainable at a level that ensures consistent performance. Neither the material nor any process step necessary to fabricate it would present an environmental hazard. Finally, the material would be available at low cost in any desired form.

Because no metal has all the desired properties, a wide variety of contact materials is required to accomplish the objectives of different contact applications. The economic choice of materials is usually a compromise

between the various processing variables and the application requirements. Load conditions, service requirements, and ambient conditions present during the life of the unit must be considered in the selection of contact materials. The contact materials discussed in this article are alloys or P/M composites based on silver, copper, gold, platinum, palladium, tungsten, or molybdenum. Emphasis has been placed on silver-base contact materials, because these are the most widely used.

Silver Contact Alloys

Silver, which has the highest electrical and thermal conductivities of all metals, is the most widely used material in pure or alloyed form for a considerable range of arcing contacts (1 to 600 A). Because of its electrical and thermal conductivity, silver is widely used in contacts that remain closed for long periods of time and, in the form of electroplate, as a coating for connection plugs and sockets. It is also used on contacts subject to occasional sliding, such as in rotary switches, and to a limited extent for low-resistance sliding contacts, such as slip rings.

The various types of silver-base contact alloys include:

- Binary, ternary, and multicomponent silver alloys such as silver-cadmium, silver-copper, silver-copper-nickel, or silver-cadmium-nickel contact materials
- Composite silver-base materials with refractory constituents such as cadmium oxide, zinc oxide, tin oxide, graphite, tungsten, tungsten carbide, or molybdenum

The composite silver-bases are often made using P/M processes, which allow the combination of constituents that ordinarily cannot be alloyed. However, some silver-base composites with cadmium oxide can also be made by preparing binary alloys of silver and cadmium, then converting the cadmium into an oxide by internal oxidation. Contact materials with refractory or oxide constituents are described in the section "Composite Materials" in this article.

This section describes the effects of specific alloying elements on the properties and performance of silver contact materials. Mechanical properties and hardness of pure silver are improved by alloying, but its thermal and electrical conductivities are adversely affected. Figure 1 shows the effect of different alloying elements on the hardness and electrical resistivity of silver. Nominal compositions and properties of the principal silver metals used for electrical contacts are given in Table 1.

Silver-Copper Alloys. Copper additions improve the hardness of silver appreciably and slightly decrease its conductivity. However, copper

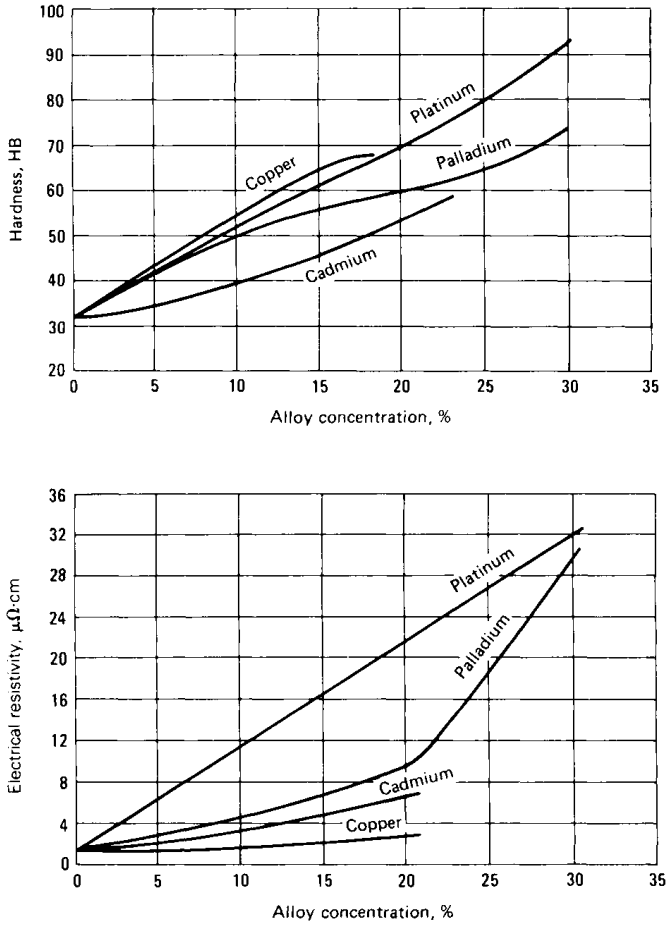


Fig. 1 Hardness and electrical resistivity versus alloy content for silver alloy contacts

Table 1 Nominal compositions and properties of silver metals used for electrical contacts

Alloy	Solidus temperature °C	Solidus temperature °F	Electrical conductivity, % IACS	Hardness, HR15T Annealed	Hardness, HR15T Cold worked	Tensile strength Annealed MPa	Tensile strength Annealed ksi	Tensile strength Cold worked MPa	Tensile strength Cold worked ksi	Density, g/cm³	Elongation in 50 mm or 2 in., % Annealed	Elongation in 50 mm or 2 in., % Cold worked
99.9Ag	960	1760	104	30	75	170	25	310	45	10.51	55	5
99.55Ag-0.25Mg-0.2Ni	…	…	70	61	77	207	30	345	50	10.34	35	6
99.47Ag-0.18Mg-0.2Ni-0.15Cu	…	…	75	64	84	…	…	…	…	10.38	…	…
99Ag-1Pd	…	…	79	44	76	180	26	324	47	10.14	42	3
97Ag-3Pd	977	1790	58	45	77	186	27	331	48	10.53	37	3
97Ag-3Pt	982	1800	45	45	77	172	25	324	47	10.17	37	3
92.5Ag-7.5Cu	821	1510	88	65	81	269	39	455	66	10.34	35	5
90Ag-10Au	971	1780	40	57	76	200	29	317	46	11.03	28	3
90Ag-10Cu	775	1430	85	70	83	276	40	517	75	10.31	32	4
90Ag-10Pd	1000	1830	27	63	80	234	34	365	53	10.57	31	3
86.8Ag-5.5Cd-0.2Ni-7.5Cu	…	…	43	72	85	276	40	517	75	10.10	43	3
85Ag-15Cd	877	1610	35	51	83	193	28	400	58	10.17	55	5
77Ag-22.6Cd-0.4Ni	…	…	31	50	85	241	35	469	68	10.31	55	4
75Ag-24.5Cu-0.5Ni	…	…	75	78	85	310	45	552	80	10.00	32	4
72Ag-28Cu	775	1430	84	79	85	365	53	552	80	9.95	20	5
60Ag-23Pd-12Cu-5Ni	…	…	11	86	93	517	78	758	110	10.51	22	3

decreases the tarnish resistance of silver; hence, the oxidized film increases contact resistance. Switching devices that have silver-copper contacts should have a high closing force and large wiping action to break down the oxide films.

Silver-copper alloys are used in place of fine silver (99.9% Ag) where electrical, mechanical, and atmospheric conditions are compatible. For the same application, silver-copper alloys usually cost less than fine silver.

Addition of a small amount of nickel to a silver-copper alloy (as in Ag-24.5Cu-0.5Ni, for example) makes the oxide film brittle, so that switching devices can use less closing force.

Silver-Cadmium Alloys. Cadmium improves the arc-quenching ability of silver, and also increases its resistivity and mechanical strength. Silver-cadmium alloys are more resistant to arc erosion and welding than fine silver and silver-copper alloys.

Ag-22.6Cd-0.4Ni Alloy. Because of the nickel addition, the oxidation film of this alloy is also brittle. Ag-22.6Cd-0.4Ni is used in electrical gages and automotive voltage regulators, where the closing force is light and where a stable resistance and low transfer rate are required. It is also used to make positive contact and retard material transfer when paired with Ag-3Pd alloy in polarized low-voltage circuits.

Ag-15Cd alloy, which typically undergoes internal oxidation to form a Ag-CdO composite, is a widely used composition. The Ag-CdO composite (discussed in the section "Composite Materials" in this article) exhibits low welding tendencies at the contact interface and is the material most commonly used to switch light or medium current in alternating current (ac) or direct current (dc) circuits such as line starters, solenoid relays for automotive starters, and other devices subjected to high-surge current.

Ag-5.5Cd-0.2Ni-7.5Cu alloy, has excellent resistance to corrosion and good spring properties. It is used to make current-carrying spring contacts in television tuners, collector rings, and radio frequency switches.

Silver-Platinum Alloys. A small addition of platinum increases the hardness, wear resistance, and corrosion resistance of silver, but concurrently decreases its electrical conductivity. Silver-platinum alloys are used in switching devices having low closing force, where cost is not the main concern.

Silver-Palladium Alloys. Palladium improves the wear resistance of silver, but also decreases its conductivity. Silver-palladium alloys are less susceptible to oxidation than fine silver. Ag-3Pd alloy is used as the negative contact paired with Ag-22.6Cd-0.4Ni in low-voltage dc circuits. Silver and palladium form a complete solid solution, and their alloys have very good fabricability.

Silver-Gold Alloys. Gold increases hardness and improves oxidation resistance of silver. The tarnish films on contact surfaces are more stable than those of any other alloy. Ag-10Au is primarily used in ac and dc relays with current capacities less than 0.5 A where high reliability is essential. This alloy is very ductile and can be fabricated in the same manner as fine silver.

Multicomponent Alloys. Ag-0.25Mg-0.20Ni and Ag-0.18Mg-0.20Ni-0.15Cu have similar properties. In low-current dc applications (voltage regulators, thermal gages, and relays), these materials provide low transfer characteristics. Mechanical properties can be improved by internally oxidizing the alloying elements into oxides.

Ag-23Pd-12Cu-5Ni has high hardness (good resistance to wear), better tarnish resistance, and a higher melting point than fine silver. It is limited to light current applications. Because of its high hardness, the alloy is used as brush contacts in potentiometers and other sliding applications. This alloy is also made into disks for composite rivets.

Copper Contact Alloys

High electrical and thermal conductivities, low cost, and ease of fabrication account for the wide use of copper alloys in electrical contacts. The main disadvantage of copper contacts is low resistance to oxidation and corrosion. In many applications, the voltage drop resulting from the film developed by normal oxidation and corrosion is acceptable. In some circuit breaker applications, the contacts are immersed in oil to prevent oxidation. In other applications, such as in drum controllers, sufficient wiping

Table 2 Nominal compositions and properties of copper metals used for electrical contacts

UNS number	Solidus temperature °C	Solidus temperature °F	Electrical conductivity, % IACS	Hardness OS035 temper	Hardness H02 temper	Tensile strength OS035 temper MPa	Tensile strength OS035 temper ksi	Tensile strength H02 temper MPa	Tensile strength H02 temper ksi
C11000 (99.95 Cu-0.04 O)	1065	1950	100	40 HRF	40 HRB	220	32	290	42
C16200 (99 Cu-1 Cd)	1030	1886	90	54 HRF	64 HRB(a)	240	35	415(a)	60(a)
C17200 (98 Cu-1.7 Be-0.20 Co)	865	1590	15–33(b)	60 HRB(c)	93 HRB(d)	495(c)	72(c)	655(d)	95(d)
C23000 (85 Cu-15 Zn)	990	1810	37	63 HRF	65 HRB	285	41	395	57
C24000 (80 Cu-20 Zn)	965	1770	32	66 HRF	70 HRB	315	46	420	61
C27000 (65 Cu-35 Zn)	905	1660	27	68 HRF	70 HRB	340	49	420	61
C50500 (98.7 Cu-1.3 Sn)	1035	1900	48	60 HRF	59 HRB	276	40	365	53
C51000 (94.8 Cu-5 Sn-0.2 P)	975	1785	20	28 HRB	78 HRB	340	49	470	68
C52100 (92 Cu-8 Sn)	880	1620	13	80 HRF	84 HRB	400	58	525	76

(a) H04 temper. (b) Depends on heat treatment. (c) TB00 temper. (d) TD02 temper

occurs to maintain fairly clean surfaces, thus providing a circuit of low resistance. In some applications, such as knife switches, plugs, and bolted connectors, contact surfaces are protected with grease or coatings of silver, nickel, or tin. In power circuits, where oxidation of copper is troublesome, contacts frequently are coated with silver. Vacuum-sealed circuit breakers use oxygen-free copper contacts (wrought or powder metal) for optimal electrical properties.

In air, copper does not provide high resistance to arcing, welding, or sticking. Where these characteristics are important, copper-tungsten or copper-graphite mixtures made by P/M processing are used. However, when used in a helium atmosphere, a Cu-CdO contact performs similarly to an Ag-CdO contact. Copper alloys are used for high currents in vacuum interrupters.

Pure copper is relatively soft, anneals at low temperatures, and lacks the spring properties sometimes desired. Some copper alloys, harder than pure copper and having much better spring properties, are listed in Table 2. The annealing temperature and the elevated-temperature properties of copper can be increased by additions of 0.25% Zn, 0.5% Cr, 0.03 to 0.06% Ag (10 to 20 oz per ton) or small amounts of finely dispersed metal oxides, such as Al_2O_3, with little loss of conductivity. On the other hand, improved mechanical properties are obtained only at the expense of electrical conductivity. Precipitation-hardened alloys, dispersion-hardened alloys, and powder metal mixtures can provide a wide range of mechanical and electrical properties.

Gold Contact Alloys

Pure gold has unsurpassed resistance to oxidation and sulfidation, but a low melting point and susceptibility to erosion limit its use in electrical contacts to situations where the current is not more than 0.5 A. Although oxide and sulfide films do not form on gold, a carbonaceous deposit is sometimes formed when a gold contact is operated in the presence of

organic vapors (this is referred to as polymer formation). The resistance of this film may be several ohms.

When gold is used in contact with palladium or rhodium, very low contact resistances have been reported.

The low hardness of gold can be increased by alloying with copper, silver, palladium, and platinum, but use is necessarily restricted to low-current applications because of the low melting point.

Properties of gold and its alloys are listed in Table 3. If low tarnish rates and low contact resistance are to be preserved, the gold content should not be less than about 70%.

Au-26.2Ag-1.8Ni and Au-27Ag-3Ni Alloys. Silver and nickel increase the hardness of gold, thereby increasing resistance to mechanical wear and deformation. Au-26.2Ag-1.8Ni resists welding and transfer better than pure gold and is used in devices that carry less than 0.5 A current where high reliability is required. The alloy is ductile and has good fabricability. Alloy Au-27Ag-3Ni is more widely used than Au-26.2Ag-1.8Ni.

Au-25Ag-6Pt. Both silver and platinum increase the hardness of gold. Au-25Ag-6Pt is employed in low-current and low-closing-force relays such as those used in telecommunication systems, where high reliability is required. Under conditions of erosion, contacts have long life if the current is limited to 0.4 A. The alloy is also highly satisfactory for use in sliding contacts, such as in rotary switches or low-pressure slip rings, because it has good wear resistance and maintains low contact resistance. It is less susceptible to polymer formation than palladium and, where this is important, its greater cost may be justified.

Au-25Ag and Au-50 Ag. Silver increases the hardness of gold, but decreases its tarnish resistance. Gold-silver alloys are used where a higher degree of reliability is required than can be obtained with silver-base alloys.

Au-5Ag-9Pt-15Cu provides good tarnish resistance as well as high hardness and strength. It is used as a contact where a large wipe is

Table 3 Nominal compositions and properties of gold metals used for electrical contacts

Alloy	Solidus temperature °C	Solidus temperature °F	Electrical conductivity, % IACS	Hardness, HR15T: Annealed	Hardness, HR15T: Cold worked	Tensile strength: Annealed MPa	Tensile strength: Annealed ksi	Tensile strength: Cold worked MPa	Tensile strength: Cold worked ksi	Density, g/cm³
99Au	1085	1985	74	40	65	…	…	…	…	19.36
90Au-10Cu	932	1710	16	76	91	400	58	705	102	17.18
75Au-25Ag	1029	1885	17	50	77	…	…	…	…	15.96
71.5Au-14.5Cu-8.5Pt-4Ag-1Zn	925	1700	11	88	96	…	…	…	…	15.9
72.5Au-14Cu-8.5Pt-4Ag-1Zn	954	1750	10	88	96	…	…	…	…	16.11
72Au-26.2Ag-1.8Ni	…	…	14	61	81	230	33	345	50	15.56
71Au-5Ag-9Pt-15Cu	…	…	8	88.5	75(a)	700	101	1170	170	16.02
69Au-25Ag-6Pt	1029	1885	10	70	84	275	40	415	60	15.92
50Au-50Ag	…	…	…	…	…	…	…	…	…	13.59

(a) Rockwell 15N

required. It is also used as brush contacts against slip rings made of Au-26.2Ag-1.8Ni.

Au-10Cu. Copper increases the hardness of gold with only a small sacrifice in corrosion resistance. Au-10Cu is used in low-voltage dc devices such as alternators or voltage regulators, and as a positive contact paired with a platinum-iridium negative contact. Under light closing forces, this combination provides a low transfer rate and good antiwelding characteristics.

Au-14.5Cu-8.5Pt-4.5Ag-1Zn. This multiple-component alloy is age hardenable. Compared to other high-gold-content alloys, it can be two to three times harder. The high gold, silver, and copper content make it a low producer of frictional polymers; thus, an excellent material for applications with voltages too low to electrically puncture these films. The combined strength and nobility of this alloy make it the ideal material for sliding contacts, slip rings, and resistance wire. This alloy is the preferred mating material for Pd-30Ag-14Cu-10Au-10Pt-1Zn alloy. Applications also include self-contained cantilever beam contacts.

Platinum and Palladium Contact Alloys

Platinum and palladium are the two most important metals of the platinum group. These metals have a high resistance to tarnishing, and therefore provide reliable contact closure for relays and other devices having contact forces of less than 490 mN (0.110 lbf). Their high melting points, low vapor pressure, and resistance to arcing make them suitable for contacts that close and open the load, particularly in the range up to 1 A. The low electrical and thermal conductivities of these metals, as well as their cost, generally exclude them from use at currents above about 5 A.

Palladium has an arcing limit only slightly less than that of platinum and gives comparable performance in relays for telephones and similar services handling 1 A or less. Palladium is a satisfactory substitute for platinum in these applications.

Platinum Alloys

Nominal compositions and properties of platinum and its alloys are listed in Table 4. The effect of alloying on the hardness and electrical resistivity of platinum is shown in Fig. 2.

Platinum-Iridium Alloys. Platinum and iridium form a complete solid solution. The physical properties, melting point, hardness, and mechanical strength of platinum-iridium alloys increase almost linearly with the

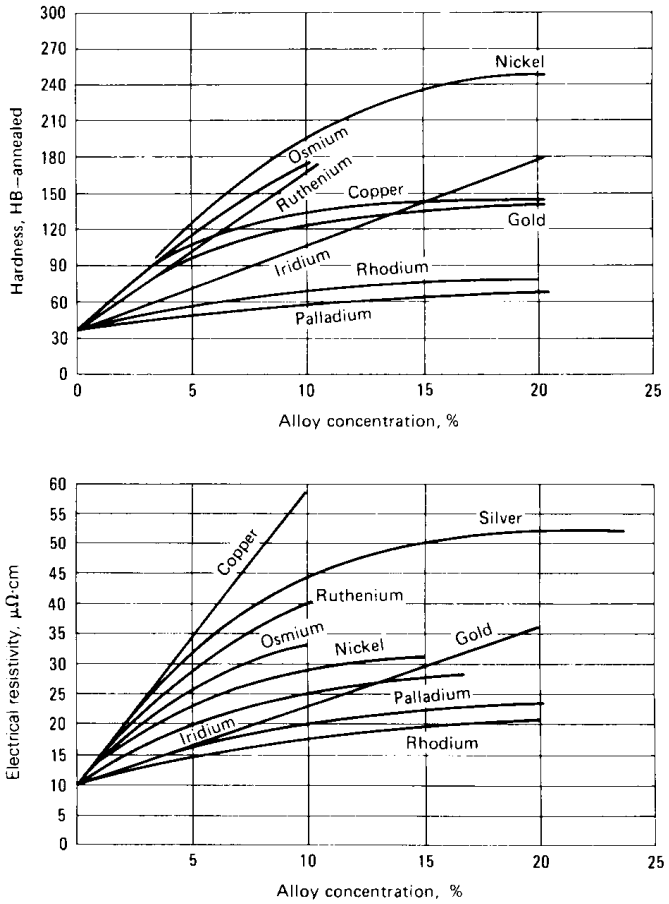


Fig. 2 Hardness and electrical resistivity versus alloy content for platinum contacts

Table 4 Nominal compositions and properties of platinum and palladium metals used for electrical contacts

Alloy	Solidus temperature °C	Solidus temperature °F	Electrical conductivity(a), % IACS	Hardness, HR15T Annealed	Hardness, HR15T Cold worked	Tensile strength Annealed MPa	Tensile strength Annealed ksi	Tensile strength Cold worked MPa	Tensile strength Cold worked ksi	Density, g/cm³	Elongation(a) in 50 mm (2 in.), %
99.9Pt	1770	3220	15	60	73	138	20	241	35	21.45	35
95Pt-5Ru	1775	3230	5	84	89	414	60	793	115	20.57	18
92Pt-8Ru	…	…	4	86	91	483	70	896	130	20.27	15
90Pt-10Ir	1780	3240	7	87	92	379	55	620	90	21.52	12
89Pt-11Ru	1815	3300	4	91	96	586	85	1034	150	19.96	12
86Pt-14Ru	1843	3350	3	93	99	655	95	1172	170	19.06	10
85Pt-15Ir	1787	3250	6	90	95	517	75	827	120	21.52	12
80Pt-20Ir	1810	3290	5	93	97	689	100	1000	145	21.63	12
75Pt-25Ir	1819	3310	5	95	98	862	125	1172	170	21.68	10
73.4Pt-18.4Pd-8.2Ru	…	…	4	90	92	517	75	862	125	17.77	12
65Pt-35Ir	1899	3450	4	97	99	965	140	1344	195	21.80	8
99.9Pd	1554	2830	16	62	78	193	28	324	47	12.17	28
95Pd-5Ru	1593	2900	8	79	89	372	54	517	75	12.00	15
89Pd-11Ru	1650	3000	6	85	92	483	70	689	100	12.03	13
72Pd-26Ag-2Ni	1382	2520	4	82	90	469	68	689	100	11.52	13
60Pd-40Ag	1338	2440	4	65	91	372	54	689	100	11.30	28
60Pd-40Cu	1200	2190	8	82	92	565	82	1331	193	10.67	20
35Pd-9.5Pt-9Au-14Cu-32.5Ag	1085	1985	5	90	94	689	100	1034	150	11.63	18
35Pd-10Pt-10Au-14Cu-30Ag	1015	1860	5	90	98	827	120	1240	180	11.8	20
44Pd-38Ag-16Cu-1Pt-1Zn	1032	1890	7	91	96	758	110	1205	175	10.8	15

(a) For material in annealed condition

amount of iridium in platinum, without affecting the corrosion resistance of the latter. This group of alloys is used in low-current ac and dc circuits when the mechanical forces are high and high wear resistance and strength are required.

Fabrication of platinum-iridium alloys becomes difficult when the iridium content is high. These alloys are usually used in the form of disks to make composite rivet faces.

Platinum-Ruthenium Alloys. Ruthenium forms a solid solution with platinum up to 79% Ru. Ruthenium increases the hardness, strength, and wear resistance of platinum, but high ruthenium content makes the alloy brittle. To ensure good fabricability, the ruthenium content should not exceed 15%.

Platinum-ruthenium alloys have good tarnish resistance and cost less than platinum-iridium alloys. Platinum-ruthenium alloys are used as positive contacts in low-voltage dc circuits, almost always paired with negative contacts made of tungsten. Platinum-ruthenium alloys can be made into rivets or disks for composite rivets.

Pt-18.4Pd-8.2Ru. This ternary alloy has properties similar to those of platinum-ruthenium and platinum-iridium alloys, but costs less. It is used in low-voltage dc circuits as the positive contact and paired with tungsten as the negative contact. This alloy has poor fabricability and can be used in the form of disks for composite rivets.

Palladium Alloys

Table 4 gives properties of palladium metals. Figure 3 shows the effect of alloying elements on palladium.

Palladium-Ruthenium Alloys. Palladium forms only a limited solid solution with ruthenium. Ruthenium increases the hardness of palladium without sacrificing its corrosion resistance. Palladium-ruthenium alloys are used in low-current relays where closing forces are high. These alloys are used mostly as positive contacts paired with tungsten in dc circuits. In some applications, they are used to replace platinum-ruthenium alloys when cost is important. Practically all of the palladium-ruthenium alloys are used in the form of rivets, because of their poor fabricability.

Pd-40Cu. Corrosion resistance of Pd-40Cu is good, but it is inferior to that of other noble metals. The alloy has high hardness and is used primarily as brush contacts and in instruments and gages. Because of its very poor headability, it can be used only in disk form to make composite rivets.

Pd-40Ag. Silver improves the hardness of palladium. Pd-40Ag costs less than fine palladium, but has the same corrosion resistance against a sulfiding atmosphere. It is used in high-closing-force contacts with less than 1 A current. It has a fair headability, but is used mostly in disk form for composite rivets.

The Pd-40Ag alloy is often clad to base metals for electronic connector applications for increased wear resistance compared to gold alloys. A particular structure of gold diffused into the Pd-40Ag alloy has been found to offer superior properties for electronic connectors used in telecommunications. When clad to copper-base metals, this system offers corrosion resistance and wear resistance at lowest cost.

Multiple-Component Alloys. Table 4 lists multiple-component alloys that are designed to increase mechanical properties and decrease cost, with some sacrifice of corrosion resistance.

Pd-9.5Pt-9.0Au-32.5Ag alloy is used for brushes and slide contacts. It has a modulus of elasticity of 115 GPa (17×10^6 psi) and a proportional limit of 930 MPa (135 ksi), which are the highest for precious-metal contacts.

Pd-26Ag-2Ni is used in ac or dc contact devices where operation frequency is high, such as in business machines and computers. In dc circuits, it is also used as a positive contact paired with tungsten.

Pd-30Ag-14Cu-10Au-10Pt-1Zn has one of the highest strength and nobility combinations of all other precious-metal contact materials. This alloy has excellent ductility in the annealed condition, which makes it

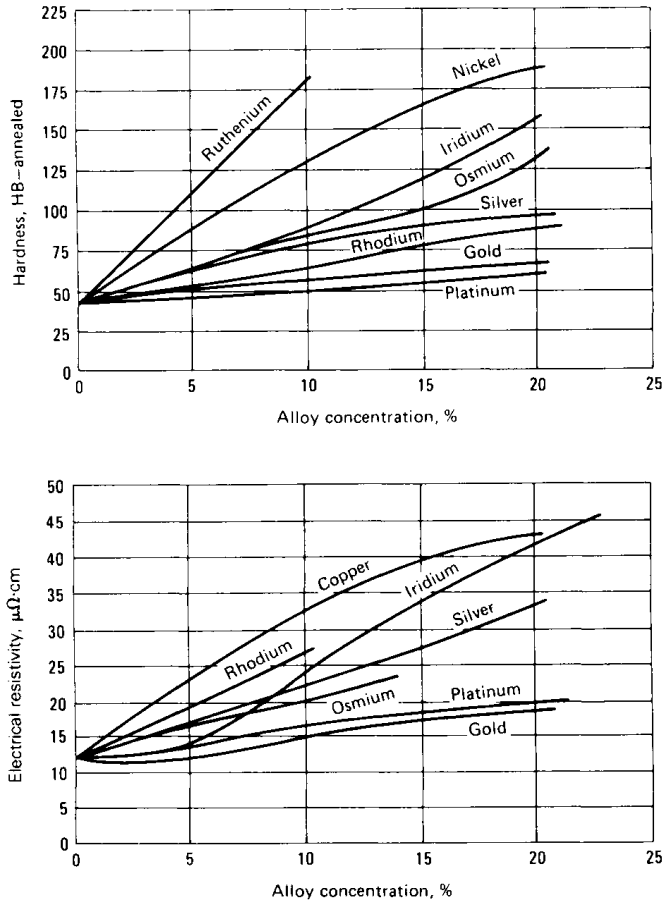


Fig. 3 Hardness and electrical resistivity versus alloy content for palladium contacts

extremely well suited for forming, drawing, and other deformation processes. After the forming operation, the material is age hardened to achieve desired mechanical properties.

Because this alloy is age hardenable, the mechanical properties can be altered to provide the maximum flexibility to the designer. The age-hardening characteristics also provide resistance to stress relaxation at elevated temperatures, which allows for the use of very low contact forces at elevated temperatures without loss of contact pressure. Before hardening, this alloy has good workability, owing to its ductility in the annealed condition. After hardening, it also has superior wear properties as a result of hardness values that approach 400 HV. Applications include potentiometers, brushes, make-break contacts, spring arms, and probes for integrated and printed circuits.

Pd-38Ag-16Cu-1Pt-1Zn is another age-hardenable alloy. It is more economical than Pd-30Ag-14Cu-10Au-10Pt-1Zn because it does not have gold and has less platinum. It has high strength and hardness in the age-hardened condition, providing wear resistance and making it ideal for self-contained cantilever beam contacts. The combined 45% noble and 38% seminoble content gives this alloy good resistance to tarnish and corrosion.

Composite Materials

The composite materials described in this section contain immiscible individual constituents and are produced by P/M processing or internal oxidation, or combinations of P/M and internal oxidation. They include three categories of materials:

- Those that contain refractory constituents such as tungsten or molybdenum carbide
- Those that contain semirefractory constituents such as cadmium oxide, zinc oxide, and tin oxide
- Those that contain elements (such as silver and nickel) that do not conventionally alloy but which are formed by P/M processes to produce contact materials with unique properties

The various types of composite contact materials generally have a base material of silver, copper, or refractory metals and their carbides. The refractory-base and silver-base contacts are used in switching devices operated in air. Copper-base composite contacts are used in vacuum and oil switching devices.

Table 5 presents the compositions and properties of various composite contact materials. Because manufacturing methods affect the properties of materials with the same composition, the manufacturing methods are also given in Table 5.

Table 5 Properties of selected composite electrical contact materials

Nominal composition, %	Manufacturing method(a)	Density, g/cm^3	Electrical conductivity, % IACS	Hardness	Tensile strength	
					MPa	ksi
Molybdenum-silver						
90Ag-10Mo	PSR	10.38	65–68	35–40 HRB	…	…
65Ag-35Mo	PSR	10.30	55–64	49–55 HRB	…	…
35Ag-65Mo	INF	10.00–10.08	40–45	82–92 HRB	…	…
10Ag-90Mo	INF	10.13	27–30	97–102 HRB	…	…
Silver/cadmium oxide						
85Ag-15CdO	PSR	8.60–9.58	55–75	35 HRF(b)	83(b)	12(b)
	PSE	9.90–10.06	55–75	57 HRF(b)	193(b)	28(b)
				80 HRF(c)	241(b)	35(c)
	IO	10.06	65	50 HRF(b)	207(b)	30(b)
				85 HRF(c)	269(c)	39(c)
	PPSE	10.06	72	70 HRF(b)	276(b)	40(b)
				90 HRF(c)	331(c)	48(c)
Silver-graphite						
99Ag-1C	PSR	9.40–10.12	87–99	24–36 HRF(b)	162(b)	23.5(b)
				68–69 HRF(c)	241(c)	35(c)
95Ag-5C	PSR	8.30–8.68	55–62	25 HRF(d)	…	…
	PSE	8.84	75	40 HRF(d)	…	…
90Ag-10C	PSR	6.30–7.20	43–53	13 HRF(b)	…	…
				30 HRF(c)	…	…
Silver-nickel						
90Ag-10Ni	PSR	9.70–10.32	75–90	35 HRF(b)	172(c)	25(c)
				89 HRF(c)	…	…
60Ag-40Ni	PSR	8.90–9.60	44–47	40 HR30T(b)	241(b)	35(b)
				92 HR30T(b)	414(c)	60(c)
	PSE	9.60	60	46 HR30T(b)	…	…
40Ag-60Ni	PSR	8.80	32	35 HR30T(b)	…	…
				97 HR(c)	…	…
	PSE	9.30	40	68 HR30T(b)	…	…
20Ag-80Ni	PSR	8.00	21	35 HR30T(b)	…	…
Silver/tin oxide						
92Ag-8SnO_2	PSE	10.00	88	58 HV(b)	205–230	30–33.5
				92 HV(c)	…	…
90Ag-10SnO_2	PSE	9.97	82	64 HV(b)	215(b)	31(b)
				98 HV(c)	…	…
88Ag-12SnO_2	PSE	9.68	72	72 HV(b)	…	…
				105 HV(c)	…	…
Tungsten carbide-silver						
65Ag-35WC	INF	11.53–11.85	55–60	50–65 HRB	272	39.5
	PSR	11.10–11.80	50–60	50–62 HRB	…	…
50Ag-50WC	INF	12.12–12.50	43–52	75–85 HRB	276	40
35Ag-65WC	INF	12.90–13.18	30–37	95–105 HRB	…	…
Tungsten-silver						
90Ag-10W	PSR	10.30–11.20	90–95	20–33 HRB	…	…
65Ag-35W	PSR	12.1	68	80 HV(b)	…	…
				90 HV(c)	…	…
35Ag-65W	INF	14.20–14.77	45–53	80–93 HRB	…	…
	PS	13.90–14.20	47–50	85–87 HRB	…	…
	PSR	14.65–14.74	47–50	55–65 HRB(c)	…	…
10Ag-90W	PSR	17.25	29–35	95–105 HRB	379	55

(continued)

(a) PSR, press-sinter-repress; INF, press-sinter-infiltrate; PS, press-sinter; PSE, press-sinter-extrude; IO, internal oxidation; PPSE, preoxidize-press-sinter-extrude. (b) Annealed. (c) Cold worked

Table 5 Properties of selected composite electrical contact materials (continued)

Nominal composition, %	Manufacturing method(a)	Density, g/cm³	Electrical conductivity, % IACS	Hardness	Tensile strength	
					MPa	ksi
Tungsten carbide-copper						
50Cu	INF	11.00–11.27	42–47	90–100 HRF	…	…
30Cu	INF	12.65	30	38 HRC	…	…
Tungsten-copper						
75Cu-25W	PSR	9.45–10.00	50–79	35–60 HRB	…	…
50Cu-50W	INF	11.90–11.96	45–63	60–81 HRB	…	…
35Cu-65W	INF	13.35	54	83–93 HRB	…	…
20Cu-80W	INF	15.20	30–40	95–105 HRB	758	110
Tungsten-graphite-silver						
46Ag-53W-1C	PSR	12.85	55	85 HRB	…	…
45Ag-50W-5C	PSR	10.60	37–43	45–55 HRB	…	…

(a) PSR, press-sinter-repress; INF, press-sinter-infiltrate; PS, press-sinter; PSE, press-sinter-extrude; IO, internal oxidation; PPSE, preoxidize-press-sinter-extrude. (b) Annealed. (c) Cold worked

Refractory Metal and Carbide-Base Composites

Refractory metals and their carbides are distinguished by high melting and boiling points, and high hardness, but poor electrical and thermal conductivities and poor oxidation resistance. In pure elemental form, refractory metals perform well only under low-current conditions.

Forming a composite can compensate for these drawbacks. For example, the development of composite contact materials involving silver or copper with tungsten or molybdenum or their carbides has resulted in materials that can withstand higher currents and more arcing than other contact materials, without experiencing sticking or rapid erosion. The refractory metal content may vary from 10 to 90%, although 40 to 80% usually is used in air- and oil-immersed circuit breaker devices. Refractory metals offer good mechanical wear resistance and resistance to arcing. The silver and copper provide the good electrical and thermal conductivities.

Because silver or copper does not alloy with tungsten, molybdenum, or their carbides, P/M processes are required in fabrication. Depending on the composition, refractory metals containing silver or copper contact materials are made either by pressing and sintering or by the press-sinter-infiltrate method. When infiltration is used, either all refractory metal powder is compacted to shape, or a small amount of silver or copper powder is blended with the refractory metal, compacted, and sintered in a reducing atmosphere. The sintered compact is then returned to the furnace; silver or copper is added to act as the infiltrant.

Most infiltrated composite contacts use silver as the infiltrant because of its excellent thermal and electrical conductivities, as well as its superb oxidation resistance. Copper infiltrant, which costs less but has very poor corrosion resistance, is used for composites that operate in noncorrosive environments, such as oil, vacuum, or inert atmospheres.

In a material made by infiltration, the function of the infiltrant (silver or copper) is twofold. First, because silver or copper does not alloy with tungsten, molybdenum, or carbides, the conductivity of the composite depends strictly on the volume percentage of infiltrant. Second, during arcing, the high temperature melts the infiltrant; consequently, the heat of fusion absorbs (quenches) a portion of the heat generated by the arc. Theoretically, the skeleton, which is made of a high-melting element, will not begin to melt until all the low-melting component evaporates. The refractory skeleton also prevents molten infiltrant from flowing by capillary action. Because of this erosion loss of the contact is low. Properties of the contact vary with the composition of the composite. A composite with high skeletal composition has high hardness and better wear resistance, but lower current-carrying capacity. On the other hand, a high-silver composite possesses high electrical and thermal conductivities, and undergoes lower temperature rise, but is softer.

Silver-Base Composites

The main advantage of a silver composite over a silver alloy is that the bulk conductivity of a silver composite depends generally on the percentage of silver by volume. An alloying element in solution greatly decreases the conductivity of silver. For instance, the volume of silver in Ag-15CdO composite is less than that in Ag-15Cd alloy, yet the electrical conductivity of the former (65% IACS) is much greater than that of the latter (35% IACS).

In silver composites, the second phase forms discrete particles that are dispersed in the silver matrix. The dispersed phase improves the matrix in two ways. First, it increases the hardness of the composite material in a manner similar to dispersion hardening. Second, in the region where two mating contacts touch upon closure, the second-phase particles reduce the surface area of silver-to-silver contact. This greatly reduces the tendency to stick or weld. In cases where the contacts do weld, the second-phase oxide particles (which are weaker and more brittle than silver) behave as slag inclusions and reduce the strength of the weld, allowing the device contact-separating force to pull the contacts apart.

Silver-base composites can be divided into two types: type 1 uses a pure element or carbide as the dispersed phase; type 2 uses oxides as the dispersed phase. In both types, the hardness increases and the conductivities decrease as the volume fraction of dispersed phase increases, and vice versa.

Silver-Base Composites with a Pure Element or Graphite. In type 1, the dispersed phase functions as a hardener and improves the mechanical properties of the silver matrix. The dispersed phase also promotes improved electrical performance such as antiwelding properties. Examples of type 1 silver-base composites include:

- Silver-tungsten and silver-molybdenum composites containing from 10 to 90% Ag
- Silver-nickel composites (60Ag-40Ni and 85Ag-15Ni being the most widely used)
- Silver-graphite composites (95Ag-5C being the most frequently used composition)

Silver-Base Composites with Dispersed Oxides. Type 2 silver-base composites use semirefractory oxides as the dispersed phase. These contact materials are produced by P/M processing, internal oxidation, or consolidation of preoxidized powders.

The semirefractory component of type 2 silver-base composites includes metal oxides such as cadmium oxide (CdO), tin oxide (SnO_2), and zinc oxide (ZnO). Of these, silver-cadmium oxide is the most widely used of all the semirefractory contact materials. Silver-cadmium oxide compositions are used for medium- to high-current-carrying contacts that convey 30 to 1500 A and 120 V. These contacts are used in make-and-break switches, in which arcing reduces the contact life. Cadmium oxide contents in such contacts range from 2.5 to 25%, with Ag-15CdO the most widely used composition.

Cadmium oxide particles confer anti-welding characteristics by distributing the arc over the contact surface; when molten silver forms on the contact, the oxides agglomerate at the solid-liquid interface to embrittle any welds that form. Cadmium oxide also retards contact erosion in two ways. When an arc forms between two contacts, the cadmium oxide endothermically decomposes to cool the surrounding matrix and quench the arc. Secondly, the high cadmium oxide surface tension retains molten silver on the contact surface and prevents it from being blown away by the arc (Fig. 4).

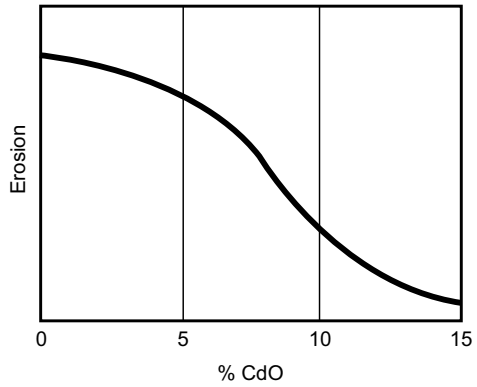


Fig. 4 Effect of cadmium oxide content on the arc erosion of Ag-CdO composite contact materials

SELECTED REFERENCES

- Y.-S. Shen et al., Electrical Contact Materials, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 840–868
- J.E. Synk, Dispersion-Strengthened Silver, *Powder Metallurgy,* Vol 7, *Metals Handbook,* American Society for Metals, 1984, p 716–720

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Magnetic Alloys

Introduction and Overview

Magnetic metals and alloys are broadly classified into two groups with either hard or soft magnetic characteristics. Hard magnetic materials are characterized by the tendency to retain a large amount of residual magnetism after exposure to a strong magnetic field. These materials have coercive force, H_c, values of several hundred to several thousand oersteds (Oe) and are considered to be *permanent magnets*. The coercive force is a measure of the magnetizing force required to reduce the magnetic induction to zero after the material has been magnetized. In contrast, soft (or temporary) magnetic materials become magnetized by relatively low-strength magnetic fields, and when the applied field is removed, they return to a state of relatively low residual magnetism. Soft magnetic materials typically exhibit coercive force values of approximately 400 $A \cdot m^{-1}$ (5 Oe) to as low as 0.16 $A \cdot m^{-1}$ (0.002 Oe).

Magnetically Soft Metals and Alloys

As described previously, magnetically soft metals and alloys are ferromagnetic materials that have little or no retentivity—that is, if they are magnetized in a magnetic field and then are removed from that field, they lose most, if not all, of the magnetism they exhibited while in the field. The most important characteristics of magnetically soft alloys are as follows:

- Low hysteresis loss (easy domain movement during magnetization)
- Low eddy-current loss from electric currents induced by flux changes
- High magnetic permeability and sometimes constant permeability at low field strengths
- High magnetic saturation induction
- Minimum or definite change in permeability with temperature in special applications

Cost, availability, strength, corrosion resistance, and ease of processing are several other factors that influence the final selection of a soft magnetic material.

Magnetic metals and alloys produced in large quantities include high-purity and commercial purity irons, phosphorus irons, low-carbon steels, silicon (electrical) steels, nickel-iron alloys, iron-cobalt alloys, and ferritic stainless steels. (Large quantities of soft magnetic ceramic materials, i.e., ferrites, are also produced but will not be addressed in this article.) Soft magnetic materials are used in any application involving changing electromagnetic induction, such as solenoids, relays, motors, generators, transformers, magnetic shielding, and so on.

Ferromagnetic Properties

Only three elements and their respective alloys are truly magnetic: iron, nickel, and cobalt. The ferromagnetic and electrical properties of these materials can be divided into two general categories: those that are structure sensitive and those that are structure insensitive. Structure insensitive refers to those properties not markedly affected by small changes in gross composition, small amounts of certain impurities, heat treatment, or plastic deformation. Several generally accepted structure-insensitive properties are the saturation induction (B_s), resistivity (ρ), and Curie temperature (T_c). These properties are largely dependent upon the composition of the alloy selected and are not changed substantially in the process of manufacturing a component from the alloy.

Structure-sensitive properties are those drastically affected by impurities, residual stresses, and grain size. Permeability (μ), coercive force (H_c), hysteresis losses (W_h), residual induction (B_r), and magnetic stability are all considered to be structure sensitive. A means of controlling structure-sensitive properties is through manufacturing processing of the alloy and/or by the proper use of a final annealing heat treatment.

The remainder of this section will examine how impurities or alloying additions influence the properties of soft magnetic metals and alloys. Information on the effects of processing, and in particular heat treating, on soft magnetic properties can be found in Ref 1.

Effect of Impurities on Magnetic Properties

Elements such as carbon, oxygen, nitrogen, and sulfur are commonly found as impurities in all alloys. Even in very low concentrations, these elements tend to locate at interstitial sites in the crystalline lattice; thus, the lattice can be severely strained. Very minor concentrations may interfere with the easy movement of magnetic domains and impair soft magnetic properties. Figure 1 shows the approximate relationship between carbon content and the hysteresis loss of iron. Hysteresis losses are

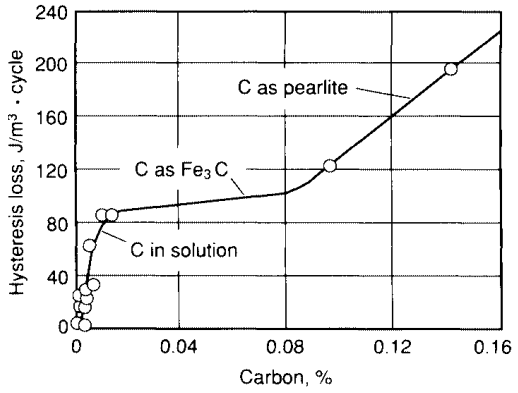


Fig. 1 Relationship between carbon content and hysteresis loss for unalloyed iron. Induction B = 1 T (10 kG).

similarly related to sulfur and oxygen content. Furthermore, if carbon and/or nitrogen remains in the alloy uncombined, or if these elements exceed their respective solubility limits near room temperature, they may migrate in time and precipitate in a form of fine particles that can pin the magnetic domain walls. This causes a hardening of the magnetic properties known as aging.

Steel producers utilize raw materials and melting methods that provide impurity levels for those alloys guaranteed to provide a certain level of magnetic performance. In certain cases, particularly with fully processed silicon steels, the producer then utilizes a decarburization heat treatment to further reduce the carbon content of the as-supplied strip product. This process is not economically or physically possible for all soft magnetic alloys and for heavier strip or bar product forms. Thus, it is often desirable and necessary that the consumer anneal the parts in a strongly reducing, nonoxidizing atmosphere as part of the component manufacturing process. Annealing of the final part further reduces impurities, particularly carbon and sulfur, below the levels that can be achieved by melting control alone. In iron alloys and silicon steels, the content of the finished part should be less than 0.003% C to optimize soft magnetic properties and minimize aging.

Effect of Alloying Additions on Magnetic Properties

The major constituents of most soft magnetic alloys are one or more of the common ferromagnetic elements: iron, nickel, or cobalt. Most useful combinations of these elements and the typical additional alloying additions made to soft magnetic alloys are fully substitutional. They contribute to the control of crystalline lattice structure to promote high permeability, low coercive force, and low hysteresis loss.

Certain alloying additions may also increase electrical resistivity that helps to reduce eddy-current losses in alternating current (ac) devices. For example, pure iron can exhibit good soft magnetic properties and has a

high saturation induction. It is used extensively in direct current (dc) applications and small fractional horsepower motors; however, its low electrical resistivity results in high eddy-current losses in ac applications. Figure 2 shows the changes in resistivity that result from additions of various elements to iron.

Silicon raises the electrical resistivity of iron. As a result, iron alloys containing 1 to 4% silicon are commonly used in ac applications. Well-annealed pure iron is very soft, typically ranging from 20 to 40 HRB. The addition of silicon also strengthens the annealed alloy. Iron containing ~2.5% Si exhibits an annealed hardness of ~90 HRB.

Silicon additions greater than approximately 2.5% to pure iron can eliminate the transformation from α to γ phase found in pure iron. Consequently, higher silicon-content alloys can be annealed to promote grain growth at high temperatures without passing through a phase transformation. The lack of a phase transformation also facilitates the development of preferentially oriented (cube on edge) grain structure in silicon steels. The oriented silicon steels typically contain 3.15% Si.

Cobalt. Most alloying additions made to iron lower its saturation induction (B_s) as shown in Fig. 3. However, the addition of cobalt results in increased saturation induction up to approximately 2.46 T (24.6 kG) at approximately 35% Co.

Vanadium. The addition of vanadium to 50Co-50Fe alloys can improve processing by allowing quenching to obtain ductility for cold rolling of strip products.

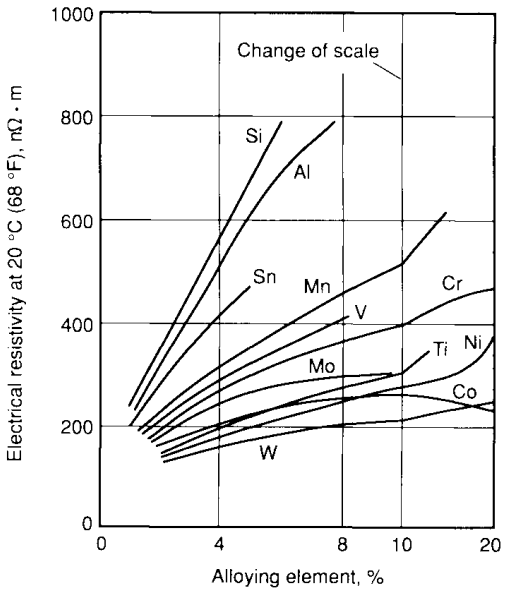


Fig. 2 Effect of alloying elements on electrical resistivity of iron

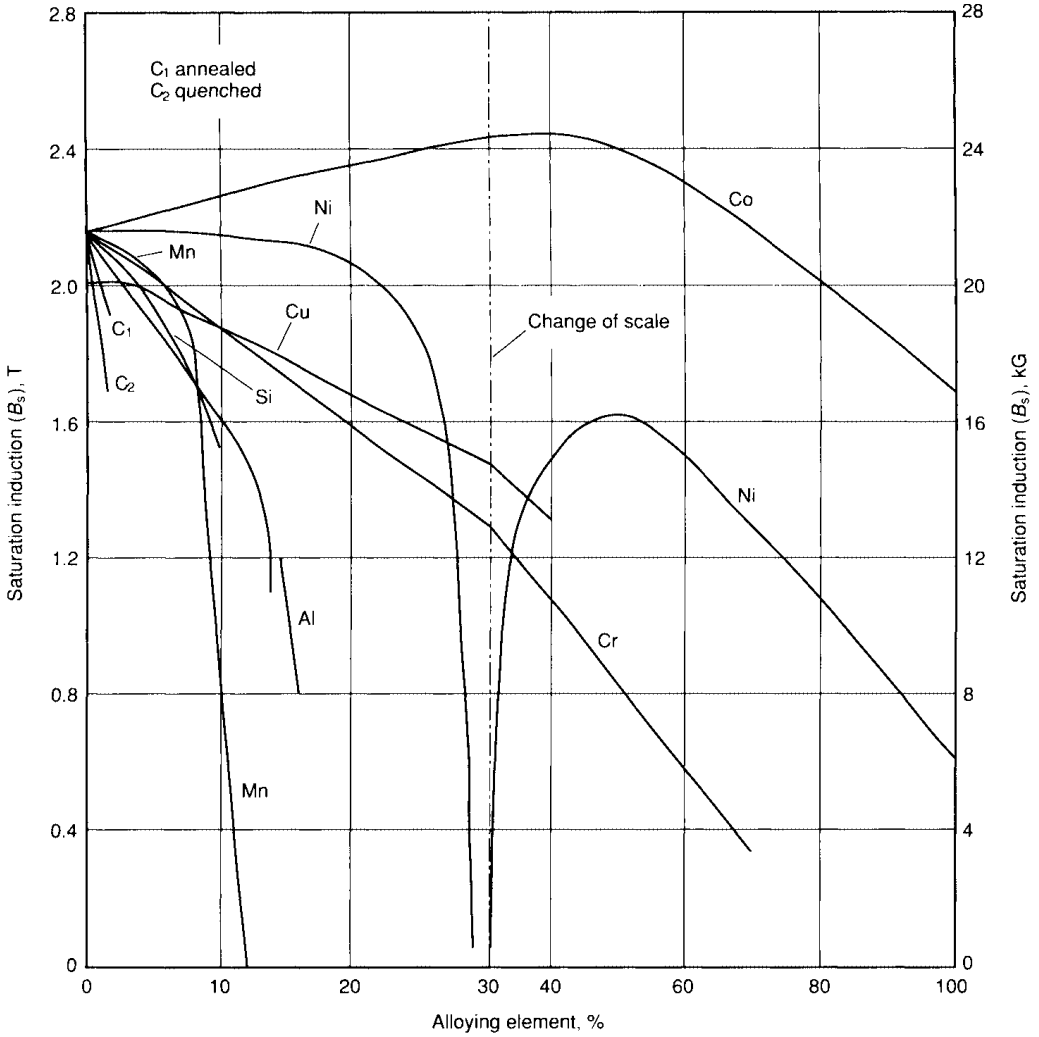


Fig. 3 Effect of alloying elements on room-temperature saturation induction of iron

Phosphorus may be added to pure irons and silicon irons to enhance stampability and machinability and to aid the sintering of powdered irons.

Chromium is added to iron to produce ferritic stainless steels with suitable soft magnetic characteristics for certain applications.

Additional Elements. Additions of molybdenum, copper, and/or chrome can be made to ~80Ni-Fe alloys to optimize crystallographic parameters to achieve very high permeability.

High-Purity and Commercially Pure Irons

High-Purity Iron. For many years, extremely high-purity iron (99.99% Fe) has been produced for researching its magnetic characteristics. Those impurities that have the strongest detrimental effect on its magnetic properties are carbon, sulfur, and nitrogen.

These elements can all be reduced to levels well below their room-temperature solubility in iron by annealing at 1300 to 1500 °C (2370 to 2730 °F) in hydrogen for several hours. It is necessary to cool slowly from the high temperature through the γ to α transformation to produce excellent soft magnetic properties.

The saturation induction of high-purity iron based upon a density of 7.878 g/cm^3 (0.2846 lb/in.^{3}) is reported as 2.158 T (21.58 kG). The electrical resistivity is 9.8 $\mu\Omega \cdot$ cm (59 $\Omega \cdot$ circ mil/ft) at 20 °C (68 °F), and the temperature coefficient of resistivity is 0.0065/°C (0.0036/°F).

Commercially pure irons with purity levels of 99.6 to 99.8 are available in a variety of shapes. These irons have a saturation induction of about 2.15 T (21.5 kG), a specific gravity of 7.86, and an electrical resistivity of approximately 13 $\mu\Omega \cdot$ cm at 20 °C (68 °F). The as-supplied carbon content of low-carbon magnetic iron is below 0.025%, typically 0.010% or less. The machinability of low-carbon iron bars is somewhat difficult, due to the physical softness of the product. A variation of this product contains approximately 0.15% P, which strengthens the ferritic structure and enhances its machinability. The phosphorus content is not detrimental to the soft magnetic capability of the iron.

Phosphorus Irons

Phosphorus irons are produced by powder metallurgy (P/M) processing. Phosphorus is normally admixed with water-atomized iron powder as ~ 10 μm Fe_2P or Fe_3P powder. These phosphorus additions improve the sinterability of the compressed iron and allow higher densities to be achieved. Higher densities in turn improve magnetic performance. Phosphorus also increases resistivity, which lowers eddy current losses. The addition of 0.45 or 0.8% wt% P does little to reduce the saturation magnetization of iron. In general, phosphorus lowers the magnetic induction by about 0.05 T (500 G), as shown in Fig. 4. Typical magnetic properties of the two Fe-P P/M alloys considered for current commercial applications are shown in Table 1.

Low-Carbon Steels

For many applications that require less than superior magnetic properties, low-carbon steels (type 1010, for example) are used. Frequently, higher-than-normal phosphorus and manganese contents are used to increase electrical resistivity. Such steels are not purchased to magnetic specifications. Although low-carbon steels exhibit power losses higher than those of silicon steels, they have better permeability at high flux density. This combination of magnetic properties, coupled with low price, makes low-carbon laminated steels especially suitable for applications such as fractional-horsepower motors, which are used intermittently.

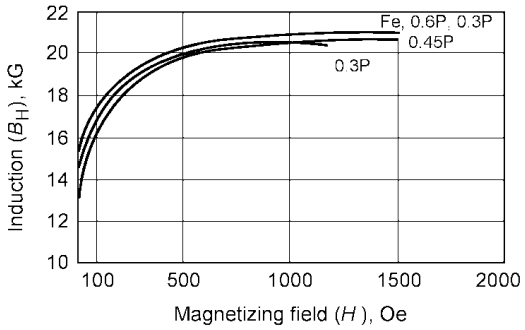


Fig. 4 Magnetization curves for hot repressed iron-phosphorus alloys

Table 1 Typical direct-current magnetic properties of phosphorus iron alloys

	Compacting pressure					
	0.45% P compacted at pressures of:			0.80% P compacted at pressures of:		
Property	410 MPa (30 tsi)	550 MPa (40 tsi)	685 MPa (50 tsi)	410 MPa (30 tsi)	550 MPa (40 tsi)	685 MPa (50 tsi)
Sintered density, g/cm^3	6.80	7.10	7.23	6.88	7.12	7.28
Induction, for a field of 1200 A/m (15 Oe), T (kg)	1.06 (10.6)	1.19 (11.9)	1.27 (12.7)	1.12 (11.2)	1.23 (12.3)	1.31 (13.1)
Residual induction, T (kG)	0.87 (8.7)	0.99 (9.9)	1.08 (10.8)	1.01 (10.1)	1.13 (11.3)	1.20 (12.0)
Maximum relative permeability	2400	2800	3100	3680	4240	4640
Coercive force, A/m (Oe)	135 (1.7)	135 (1.7)	127 (1.6)	112 (1.4)	112 (1.4)	112 (1.4)

Silicon Steels (Flat-Rolled Products)

The beneficial effects of silicon additions to iron include:

- Increase of electrical resistivity
- Suppression of the γ loop enabling desirable grain growth
- Development of preferred orientation grain structure

The addition of silicon also reduces magnetocrystalline anisotropy energy, and at ~6.5% Si content reduces the magnetostriction constants to nearly zero. High-permeability and low hysteresis losses can therefore be attained at the 6.5Si-Fe composition. On the negative side, the addition of silicon to iron lowers magnetic saturation, lowers Curie temperature, and seriously decreases mechanical ductility. At silicon levels above ~4%, the alloy becomes brittle and difficult to process by cold-rolling methods; thus, few commercial steels contain more than ~3.5% Si.

The commercial grades of grain-oriented or nonoriented silicon steel in common use are made mostly in electric or basic oxygen furnaces. Continuous casting and/or vacuum degassing (V-D) may be employed. Flat-rolled silicon-iron sheet and strip has low sulfur content, typically below 0.025%, with better grades below 0.01%. Small additions of phosphorus (0.03 to 0.15%), manganese (0.25 to 0.75), and aluminum (< 0.6%)

may also be present to increase resistivity, which subsequently lowers eddy current losses. These alloys are not generally sold on the basis of their composition, but rather are sold based upon controlled magnetic properties, particularly ac core losses. Table 2 lists maximum allowable core losses for various silicon (electrical) steels.

Table 2 Core loss values for flat-rolled electrical steels

AISI type (approximate equivalent)	Nominal (Si + Al) content, %	Thickness mm	Thickness in.	ASTM designation	Maximum core loss at 60 Hz and B = 1.5 T (15 kG) W/kg	W/lb
Nonoriented						
Semiprocessed (ASTM A 683)(a)						
M-47	1.10	0.64	0.025	64S350	7.71	3.50
	1.10	0.47	0.019	47S300	6.61	3.00
M-45	1.70	0.64	0.025	64S280	6.17	2.80
	1.70	0.47	0.019	47S250	5.51	2.50
M-43	2.00	0.64	0.025	64S260	5.73	2.60
	2.00	0.47	0.019	47S230	5.07	2.30
M-36	2.40	0.64	0.025	64S230	5.07	2.30
	2.40	0.47	0.019	47S200	4.41	2.00
M-27	2.70	0.64	0.025	64S213	4.69	2.13
	2.70	0.47	0.019	47S188	4.14	1.88
…	3.00	0.64	0.025	64S194	4.28	1.94
…	3.00	0.47	0.019	47S178	3.92	1.78
Fully processed (ASTM A 677)(b)						
…	0.50	0.64	0.025	64F600	13.22	6.00
…	0.80	0.47	0.019	47F450	9.92	4.50
M-47	1.05	0.64	0.025	64F470	10.36	4.70
	1.05	0.47	0.019	47F380	8.38	3.80
M-45	1.85	0.64	0.025	64F340	7.49	3.40
	1.85	0.47	0.019	47F290	6.39	2.90
M-43	2.35	0.64	0.025	64F270	5.95	2.70
	2.35	0.47	0.019	47F230	5.07	2.30
M-36	2.65	0.64	0.025	64F240	5.29	2.40
	2.65	0.47	0.019	47F205	4.52	2.05
	2.65	0.36	0.014	36F190	4.19	1.90
M-27	2.8	0.64	0.025	64F225	4.96	2.25
	2.8	0.47	0.019	47F190	4.19	1.90
	2.8	0.36	0.014	36F180	3.97	1.80
M-22	3.2	0.64	0.025	64F218	4.80	2.18
	3.2	0.47	0.019	47F185	4.08	1.85
	3.2	0.36	0.014	36F168	3.70	1.68
M-19	3.3	0.64	0.025	64F208	4.58	2.08
	3.3	0.47	0.019	47F174	3.83	1.74
	3.3	0.36	0.014	36F158	3.48	1.58
M-15	3.5	0.47	0.019	47F168	3.70	1.68
	3.5	0.36	0.014	36F145	3.20	1.45
Oriented						
Fully processed (ASTM A 876)(c)						
M-6	3.15	0.35	0.014	35G066	1.45	0.66
	3.15	0.35	0.014	35H094	2.07(d)	0.94
M-5	3.15	0.30	0.012	30G058	1.28	0.58
	3.15	0.30	0.012	30H083	1.83(d)	0.83
M-4	3.15	0.27	0.011	27G051	1.12	0.51
	3.15	0.27	0.011	27H074	1.63(d)	0.74
…	3.15	0.23	0.009	23G046	1.01	0.46
…	3.15	0.23	0.009	23H071	1.56(d)	0.71
…	3.15	0.27	0.011	27P066	1.45(d)	0.66
…	3.15	0.30	0.012	30P070	1.54(d)	0.70

(a) Refer to ASTM A 683-84 and companion specification A 683M-84 (metric) for detailed information. (b) Refer to ASTM A 677-84 and companion specification A 677M-83 (metric) for detailed information. (c) Refer to ASTM A 876-87 and companion specification A 876M-87 for detailed information. (d) B = 1.7 T (17 kG)

Nickel-Iron Alloys

The effect of nickel content in nickel-iron alloys on saturation induction (B_s) and on initial permeability (μ_0) after annealing are illustrated in Fig. 5 and 6. Below ~28% Ni, the crystalline structure is bcc low-carbon martensite if cooled rapidly and ferrite and austenite if cooled slowly; these alloys are not considered useful for soft magnetic applications. Above ~28% Ni, the structure is fcc austenite. The Curie temperature in this system is approximately room temperature at ~28% Ni and increases rapidly up to ~610 °C (1130 °F) at 68% Ni. Thus, these austenitic alloys are ferromagnetic. The magnetic properties are controlled by saturation magnetization and the magnetic anisotropy energies, particularly magnetocrystalline (K_1) and magnetostrictive (λ_1) anisotropies.

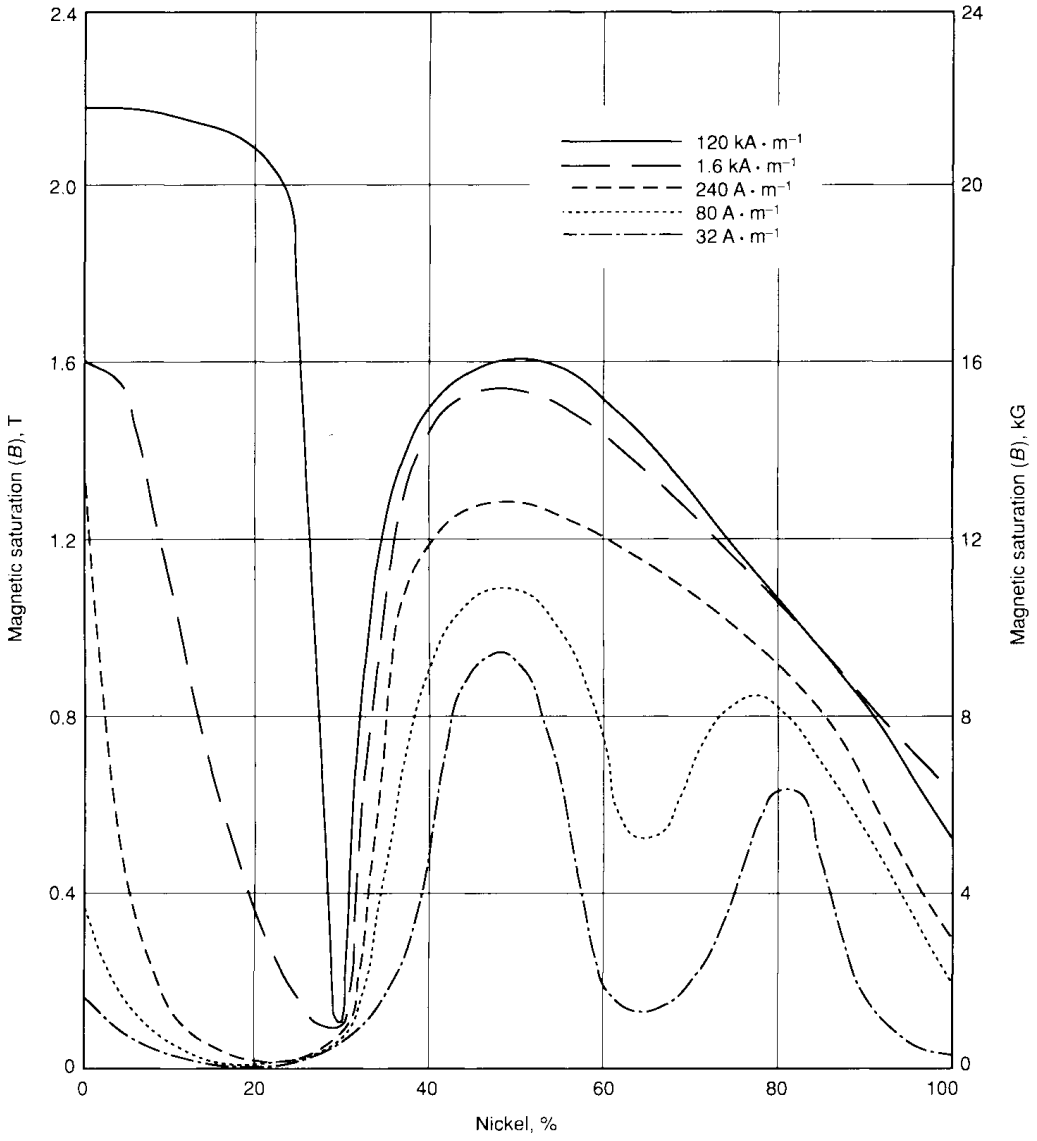


Fig. 5 Magnetic saturation of binary nickel-iron alloys at various field strengths. All samples were annealed at 1000 °C (1830 °F) and cooled in the furnace.

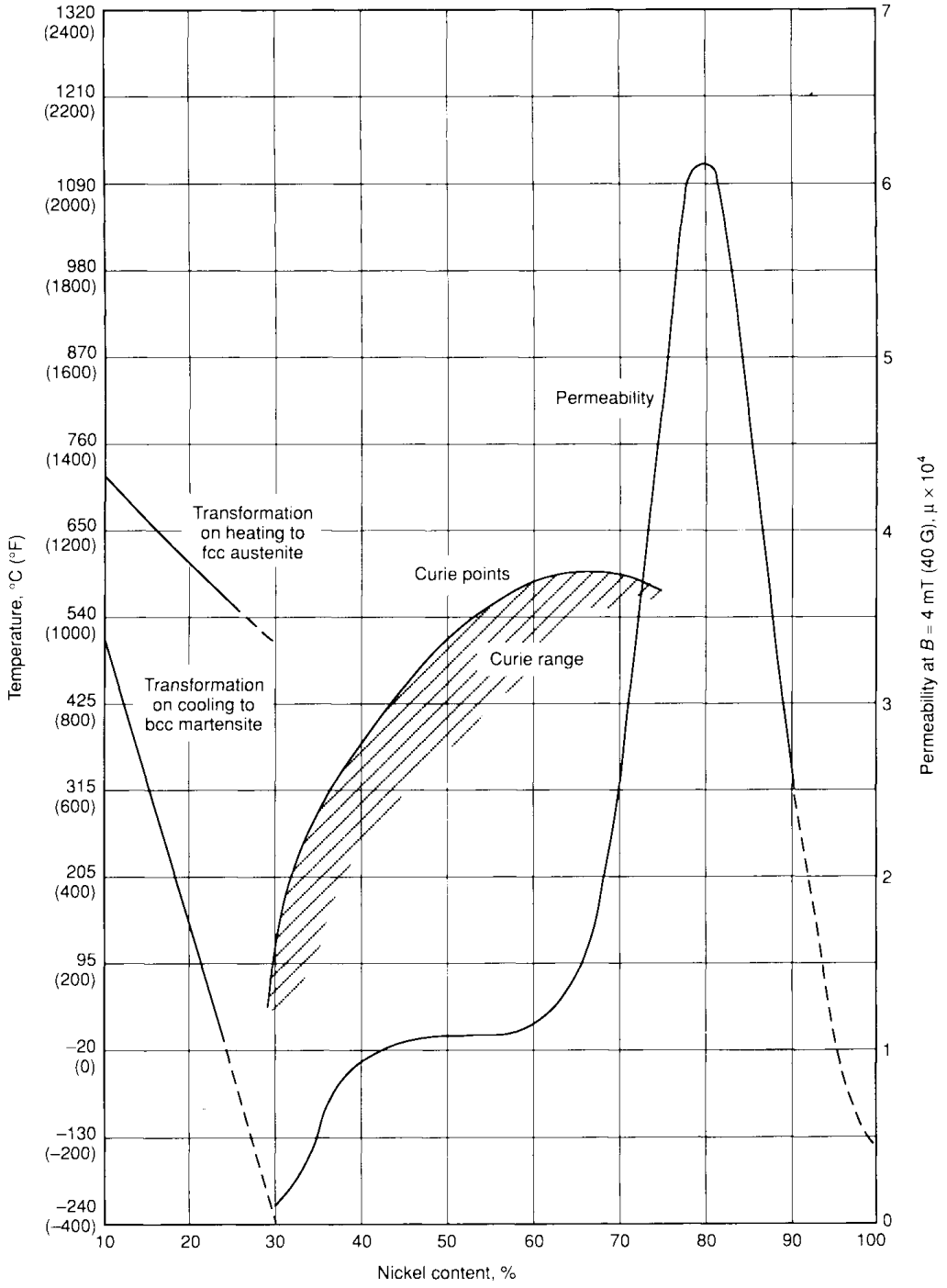


Fig. 6 Effect of nickel content on initial permeability, Curie temperature, and transformation temperature in nickel-iron alloys

Two broad classes of commercial alloys have been developed in the nickel-iron system. The high-nickel alloys (about 79% Ni) have high initial and maximum permeabilities and very low hysteresis losses, but they also have a saturation induction of only ~0.8 T (8 kG). The low-nickel alloys (about 45 to 50% Ni) are lower in initial and maximum permeability than

the 79% Ni alloys, but are still much higher than silicon irons. The low-nickel alloys have a saturation induction of about 1.5 T (15 kG). Values of initial permeability (at B of 4 mT, or 40 G) above 1.2×10^4 are typically obtained in low-nickel alloys, and values above 6.5×10^4 are obtained for 79Ni-4Mo-Fe alloys at 60 Hz using 0.36 mm (0.014 in.) thick laminations. Maximum dc permeabilities of 1.4×10^5 for low-nickel alloys and 3.75×10^5 for high-nickel alloys are routinely attained.

Figure 7 contains data from early laboratory studies to illustrate the effect of both composition and heat treatment on initial permeability. To obtain very high magnetic permeability, both the magnetocrystalline anisotropy (K_1) and the magnetostrictive anisotropy (λ_1) must be minimized. The magnetostrictive anisotropy is highly dependent upon the alloy composition. Generally, there is little that the purchaser can do to the alloy that will change this characteristic. However, in the high-nickel alloys, the magnetocrystalline anisotropy can be altered by the appropriate annealing cycle cooling rate. In these alloys, short-range atomic ordering occurs as the alloy is cooled from ~760 °C (1400 °F) to ~400 °C (750 °F). The degree of ordering has a profound effect on K_1, and, therefore, each composition will have an optimum cooling rate that minimizes the net anisotropy energies and can result in very high permeability.

Alloying additions of 4 to 5% Mo, or of copper and chromium to ~79Ni-Fe, alter the kinetics of ordering and the magnetostrictive anisotropy energy. Alloying also increases the electrical resistivity; however, saturation induction is reduced to the 0.8 T (8 kG) level. Specialty steel manufacturers produce a variety of carefully designed very high-permeability alloys that permit the use of practical commercial annealing

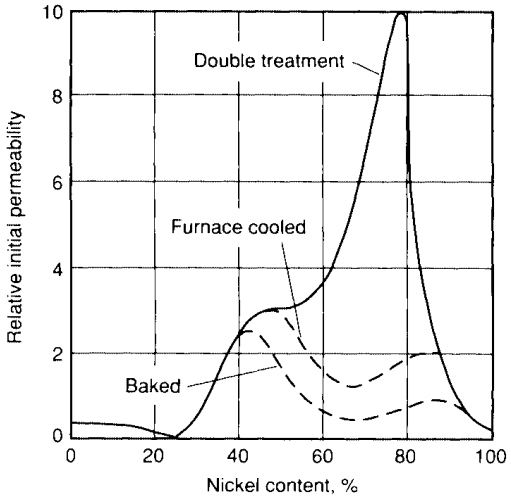


Fig. 7 Relative initial permeability at 2 mT (20 G) for Ni-Fe alloys given various heat treatments. Treatments were as follows: furnace cooled—1 h at 900 to 950 °C (1650 to 1740 °F), cooled at 100 °C/h (180 °F/h); baked—furnace cooled plus 20 h at 450 °C (840 °F); double treatment—furnace cooled plus 1 h at 600 °C (1110 °F) and cooled at 1500 °C/min (2700 °F/min).

procedures. Popular alloys include the Moly-Permalloys (typically 80Ni-4 to 5Mo-bal Fe) and MuMetals (typically 77Ni-5Cu-2Cr-bal Fe).

Iron-Cobalt Alloys

Pure iron has a saturation induction of 2.158 T (21.58 kG). Higher saturation values can be achieved only in alloys of iron and cobalt. The highest known value is approximately 2.46 T (24.6 kG), which occurs at a cobalt content of ~35%.

In Fig. 8, the dc magnetic induction response at several magnetizing forces from 0.25 to 1400 kA · m^{-1} (0.003 to 17 kOe) for binary iron-cobalt

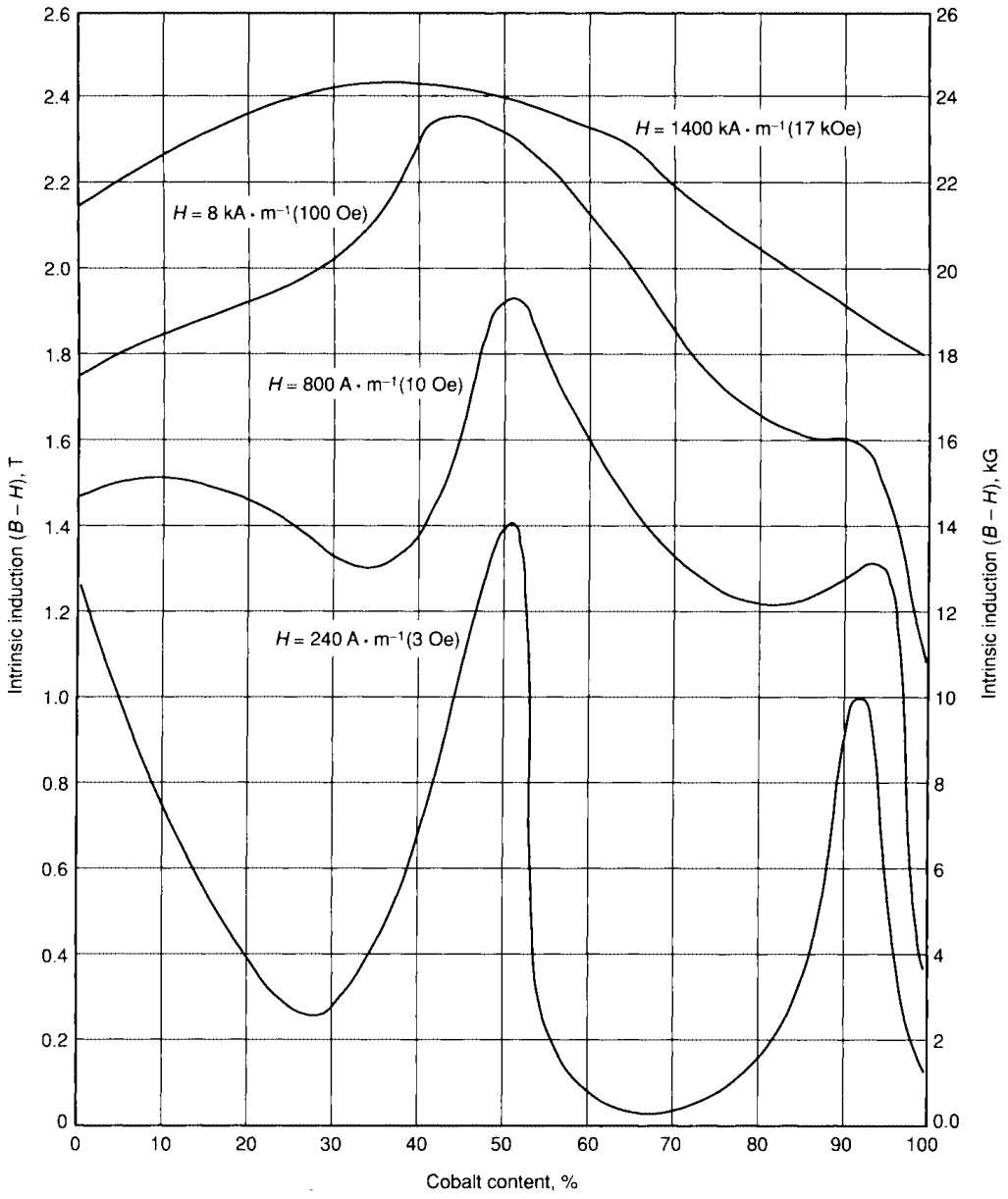


Fig. 8 Intrinsic induction of iron-cobalt alloys at various magnetizing levels

compositions is shown. The composition corresponding to ~50Co-50Fe is of particular interest due to its peaked response at low magnetizing force (that is, high permeability). The room-temperature crystallographic structure of iron-cobalt alloys containing up to approximately 70% Co is ferritic (α-Fe), except that the 50Co-50Fe compositional range orders very rapidly to α', a brittle cesium-chloride type structure, upon cooling below ~725 °C (1340 °F). The binary 50:50 alloy was never widely manufactured due to its extreme brittleness. In the 1930s, a modified alloy was developed by adding ~2% V (2V-49Co-49Fe), which slowed the embrittling reaction sufficiently so that hot-rolled strip (thickness less than 3.04 mm, or 0.120 in.) could be rapidly cooled, retaining the ductile structure. The vanadium addition also provides increased resistivity (to 43 $\mu\Omega \cdot$ cm), but does lower saturation induction slightly. Vanadium additions greater than ~2% shift the Fe-Co-V phase boundary limits, producing semihard and hard magnetic materials.

Another iron-cobalt alloy composition, containing 27Co-0.6Cr-bal Fe, is commercially available. It is primarily produced as a lamination strip product and as a bar product. The 27% Co content provides saturation levels similar to the 2V-49Co-49Fe composition, and does not require the same degree of specialized manufacturing. The addition of 0.6% Cr increases electrical resistivity to 19 $\mu\Omega \cdot$ cm. Its lower cobalt content makes the alloy less expensive, but it is not as magnetically soft as the 2V-49Co-49Fe alloy. In dc field applications (pole pieces, flux return members, and so on), energy losses due to low resistivity and relatively low permeability (hysteresis losses) may not be of concern. Therefore, the 27Co-Fe alloy may be preferred due to its high saturation and lower price. In ac applications, particularly as frequency is increased, the 2V-49Co-49Fe alloy is generally selected. Table 3 compares the magnetic properties of the 2V-49Co-49Fe and 27Co-0.6Cr-Fe alloys.

Ferritic Stainless Steels

Ferritic stainless steels are ferromagnetic and have been used as soft magnetic components in products such as solenoid housings, cores, and pole pieces. Although their magnetic properties are not generally as good as conventional soft magnetic alloys, they have been successfully used for magnetic components that must withstand corrosive environment. (The 17% Cr addition confers the corrosion resistance.) As such, they offer a cost-effective alternative to plated iron and silicon-iron components. In addition, the relatively high electrical resistivity of ferritic stainless steels has resulted in superior ac performance.

Special restricted analyses of AISI type 430F are produced for use in solenoid valve components. The ASTM A 838 specification provides typical properties for these alloys. Alloy type 1 is 430F, containing approximately 0.4% Si and exhibiting an electrical resistivity of

Table 3 Typical dc and ac magnetic properties of annealed iron-cobalt alloys in the form of 0.15 to 0.5 mm (0.006 to 0.020 in.) thick lamination strip products

Alloy nominal composition	Annealing temperature °C	°F	Thickness mm	in.	dc induction in T (kG) at indicated H (a): H = 160 A · m^{-1} (2 Oe)	H = 0.8 kA · m^{-1} (10 Oe)	H = 4 kA · m^{-1} (50 Oe)	H = 8 kA · m^{-1} (100 Oe)	H = 20 kA · m^{-1} (250 Oe)
2V-49Co-49Fe	845	1550	All	All	1.35 (13.5)	2.16 (21.6)	2.30 (23.0)	2.36 (23.6)	2.41 (24.1)
27Co-0.6Cr-Fe.....	845	1550	All	All	0.5 (5)	1.35 (13.5)	1.92 (19.2)	2.12 (21.2)	2.30 (23.0)
2V-49Co-49Fe.....	875	1610	0.51	0.020	…	…	…	…	…
			0.36	0.014	…	…	…	…	…
			0.25	0.010	…	…	…	…	…
			0.20	0.008	…	…	…	…	…
			0.15	0.006	…	…	…	…	…
			0.51	0.020	…	…	…	…	…
			0.36	0.014	…	…	…	…	…
			0.25	0.010	…	…	…	…	…
			0.20	0.008	…	…	…	…	…
			0.15	0.006	…	…	…	…	…
27Co-0.6Cr-Fe.....	845	1550	0.36	0.014	…	…	…	…	…
			0.36	0.014	…	…	…	…	…

Alloy nominal composition	Frequency Hz	ac total core loss, P_c, in W/kg (W/lb) at indicated peak induction, B (b): B = 1 T (10 kG)	B = 1.5 T (15 kG)	B = 2 T (20 kG)	Saturation induction, B: T	kG	From H = 8 kA · m^{-1} (100 Oe): H_c A · m^{-1}	Oe	B_r: T	kG
2V-49Co-49Fe.....	…	…	…	…	2.42	24.2	72	0.9	1.6	16
27Co-0.6Cr-Fe.....	…	…	…	…	2.43	24.3	130	1.6	1.4	14
2V-49Co-49Fe.....	60	1.5 (0.67)	2.89 (1.31)	4.76 (2.16)	…		…		…	
	60	1.4 (0.65)	2.69 (1.22)	4.17 (1.89)	…		…		…	
	60	1.3 (0.57)	2.31 (1.05)	3.57 (1.62)	…		…		…	
	60	1.2 (0.56)	2.29 (1.04)	3.48 (1.58)	…		…		…	
	60	1.2 (0.53)	2.1 (0.95)	3.08 (1.40)	…		…		…	
	400	21 (9.5)	53.8 (24.4)	112 (50.8)	…		…		…	
	400	17 (7.5)	36.8 (16.7)	67.4 (30.6)	…		…		…	
	400	13 (6.0)	27.3 (12.4)	46.9 (21.3)	…		…		…	
	400	12 (5.4)	23.6 (10.7)	38.3 (17.4)	…		…		…	
	400	10 (4.7)	20 (9.0)	31.5 (14.3)	…		…		…	
27Co-0.6Cr-Fe.....	60	3.13 (1.42)	5.55 (2.52)	8.00 (3.63)	…		…		…	
	400	36.8 (16.7)	73.2 (33.2)	110 (50.0)	…		…		…	

(a) Ring laminations tested per ASTM A 596 method. (b) Ring laminations tested per ASTM A 697 method

60 μΩ · cm. When fully mill annealed, it has a hardness of approximately 78 HRB. Its maximum dc permeability is approximately 2×10^3, with a coercivity of approximately 160 A · m^{-1} (2 Oe). Alloy type 2 is a higher-silicon version of 430F, with an electrical resistivity of 76 μΩ · cm and a fully annealed hardness of 82 HRB. Despite its higher hardness, alloy type 2 typically exhibits a dc permeability of 2.6×10^3 and a coercivity of 130 A · m^{-1} (1.6 Oe).

Permanent Magnet Alloys

Contrary to soft magnetic materials, permanent magnets cannot be easily demagnetized once they are magnetized. They provide a steady magnetic field and are unaffected by stray fields.

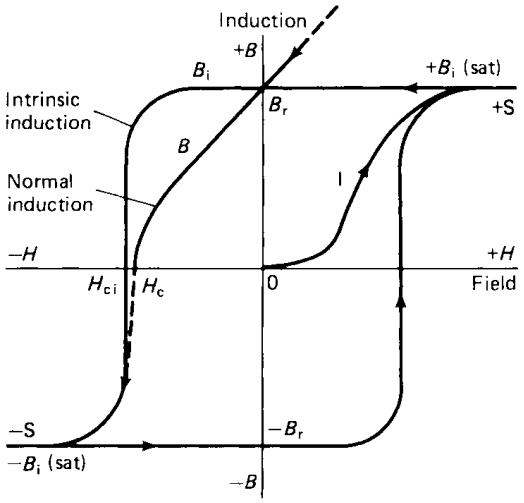


Fig. 9 Major hysteresis loop for a permanent magnet material. B_i (sat) is the saturation induction.

Permanent magnets are characterized by a high coercive force (H_c) and residual induction (B_r). These alloys are processed to provide the maximum energy product, which is the numerical value of $B_x \cdot H_x$ in the second quadrant (top left) of the hysteresis curve (Fig. 9). The energy product is measured by fitting the largest rectangle to the demagnetization curve, found in the second quadrant of the hysteresis loop (Fig. 9). It is normally expressed as the product $(B_dH_d)_{max}$ and determines the quality of the permanent magnet. A more detailed discussion on the fundamentals of permanent magnetism, including magnetic hysteresis, demagnetization, and magnetic energy, can be found in Ref 2.

Compositions, Properties, and Applications

Compositions and Properties. Permanent magnet materials include a variety of alloys, intermetallics, and ceramics, such as the following:

- High-carbon steels
- Alnicos
- Cunife (60Cu-20Ni-20Fe)
- Iron-cobalt alloys containing vanadium or chromium
- Platinum-cobalt
- Hard ferrites, including barium ferrite ($BaO \cdot 6Fe_2O_3$) and strontium ferrite ($SrO \cdot 6Fe_2O_3$)
- Cobalt-rare earth alloys
- Neodymium-iron-boron alloys

Of the metallic materials listed above, the Alnicos, cobalt-rare earths, and neodymium-iron-boron alloys are by far the most commercially important and will be discussed further in the following paragraphs.

Each type of permanent magnet materials possesses unique magnetic and mechanical properties, corrosion resistance, temperature sensitivity, fabrication limitations, and cost. These factors provide designers with a wide range of options in designing magnetic parts. Table 4 lists selected permanent magnet materials commercially available and their nominal compositions. Magnetic properties are summarized in Table 5.

Applications. Over the years, the number and range of applications utilizing permanent magnets has increased dramatically. Some of the more predominant applications include aircraft magnetos, alternators, magnetos for lawn mowers, garden tractors, and outboard motors; small and large direct current (dc) motors (including automotive motors); acoustic transducers; magnetic couplings; magnetic resonance imaging;

Table 4 Nominal compositions, Curie temperatures, and magnetic orientations of selected permanent magnet materials

Designation	Nominal composition	Approximate Curie temperature		Magnetic orientation(a)
		°C	°F	
$3\frac{1}{2}$% Cr steel	Fe-3.5Cr-1C	745	1370	No
6% W steel	Fe-6W-0.5Cr-0.7C	760	1400	No
17% Co steel	Fe-17Co-8.25W-2.5Cr-0.7C	…	…	No
36% Co steel	Fe-36Co-3.75W-5.75Cr-0.8C	890	1630	No
Cast Alnico 1	Fe-12Al-21Ni-5Co-3Cu	780	1440	No
Cast Alnico 2	Fe-10Al-19Ni-13Co-3Cu	810	1490	No
Cast Alnico 3	Fe-12Al-25Ni-3Cu	760	1400	No
Cast Alnico 4	Fe-12Al-27Ni-5Co	800	1475	No
Cast Alnico 5	Fe8.5Al-14.5Ni-24Co-3Cu	900	1650	Y, H
Cast Alnico 5DG	Fe-8.5Al-14.5Ni-24Co-3Cu	900	1650	Y, H, C
Cast Alnico 5-7	Fe-8.5Al-14.5Ni-24Co-3Cu	900	1650	Y, H, C
Cast Alnico 6	Fe-8Al-16Ni-24Co-3Cu-2Ti	860	1580	Y, H
Cast Alnico 7	Fe-8Al-18Ni-24Co-4Cu-5Ti	840	1540	Y, H
Cast Alnico 8	Fe-7Al-15Ni-35Co-4Cu-5Ti	860	1580	Y, H
Cast Alnico 9	Fe-7Al-15Ni-35Co-4Cu-5Ti	…	…	Y, H, C
Cast Alnico 12	Fe-6Al-18Ni-35Co-8Ti	…	…	No
Sintered Alnico 2	Fe-10Al-17Ni-12.5Co-6Cu	610	1490	No
Sintered Alnico 4	Fe-12Al-28Ni-5Co	800	1475	No
Sintered Alnico 5	Fe-8.5Al-14.5Ni-24Co-3Cu	900	1650	Y, H
Sintered Alnico 6	Fe-8Al-16Ni-24Co-3Cu-2Ti	860	1580	Y, H
Sintered Alnico 8	Fe-7Al-15Ni-35Co-4Cu-5Ti	860	1580	Y, H
Cunife	20Fe-20Ni-60Cu	410	770	Y, R
Bonded ferrite A	$BaO\text{-}6Fe_2O_3$ + organics	450	…	No, P
Bonded ferrite B	$BaO\text{-}6Fe_2O_3$ + organics	450	…	No
Sintered ferrite 1	$BaO\text{-}6Fe_2O_3$	450	840	No, P
Sintered ferrite 2	$BaO\text{-}6Fe_2O_3$	450	840	Y, A
Sintered ferrite 3	$BaO\text{-}6Fe_2O_3$	450	840	Y, A
Sintered ferrite 4	$SrO\text{-}6Fe_2O_3$	460	860	Yes
Sintered ferrite 5	$SrO\text{-}6Fe_2O_3$	460	860	Yes
Bonded neodymium	NdFeB + organics	…	…	Y, P, E
Hot-formed neodymium	…	…	…	Y, R
Hot-pressed neodymium	NdFeB + organics	…	…	Y, R
Sintered neodymium	NdFeB	310	590	Y, A
FeCrCo	…	640	1185	Y, R
Platinum cobalt	76.7Pt-23.3Co	480	900	No
Cobalt rare earth 1	$SmCo_5$	725	1340	Y, A
Cobalt rare earth 2	$SmCo_5$	725	1340	Y, A
Cobalt rare earth 3	$SmCo_5$	725	1340	Y, A
Cobalt rare earth 4	Sm_2Co_{17}	800	1475	Y, A
Bonded Co rare earth	…	…	…	Y, P, E

(a) Y, yes; H, orientation developed during heat treatment; C, columnar crystal structure developed; P or E, some orientation developed during pressing or extrusion; R, orientation developed by rolling or other mechanical working; A, orientation developed predominately by magnetic alignment of powder prior to compacting but alignment influenced by pressing forces also

Table 5 Nominal magnetic properties of selected permanent magnet materials

	H_c		B_r		$(BH)_{max}$	
Designation	**kA · m^{-1}**	**Oe**	**T**	**kG**	**kJ · m^{-3}**	**MG · Oe**
3½% Cr steel	5.3	66	0.95	9.5	2.3	0.29
6% W steel	5.9	74	0.95	9.5	2.6	0.33
17% Co steel	14	170	0.95	9.5	5.2	0.65
36% Co steel	19	240	0.975	9.75	7.4	0.93
Cast Alnico 1	35	440	0.71	7.1	11	1.4
Cast Alnico 2	44	550	0.725	7.25	13	1.6
Cast Alnico 3	38	470	0.70	7.0	11	1.4
Cast Alnico 4	58	730	0.535	5.35	10	1.3
Cast Alnico 5	50	620	1.25	12.5	42	5.25
Cast Alnico 5DG	52	650	1.29	12.9	49	6.1
Cast Alnico 5–7	58	730	1.32	13.2	59	7.4
Cast Alnico 6	60	750	1.05	10.5	30	3.7
Cast Alnico 7	84	1,050	0.857	8.57	30	3.7
Cast Alnico 8	130	1,600	0.83	8.3	40	5.0
Cast Alnico 9	115	1,450	1.05	10.5	68	8.5
Cast Alnico 12	76	950	0.60	6.0	14	1.7
Sintered Alnico 2	42	525	0.67	6.7	12	1.5
Sintered Alnico 4	56	700	0.52	5.2	10	1.2
Sintered Alnico 5	48	600	1.04	10.4	29	3.60
Sintered Alnico 6	61	760	0.88	8.8	22	2.75
Sintered Alnico 8	125	1,550	0.76	7.6	36	4.5
Cunife	44	550	0.54	5.4	12	1.5
Bonded ferrite A	155	1,940	0.214	2.14	8	1.0
Bonded ferrite B	92	1,150	0.14	1.4	3	0.4
Sintered ferrite 1	145	1,800	0.22	2.2	8	1.0
Sintered ferrite 2	175	2,200	0.38	3.8	27	3.4
Sintered ferrite 3	240	3,000	0.32	3.2	20	2.5
Sintered ferrite 4	175	2,200	0.40	4.0	30	3.7
Sintered ferrite 5	250	3,150	0.355	3.55	24	3.0
NdFeB (sintered)	848	10,600	1.16	11.6	255	32
Bonded NdFeB	430	5,400	0.69	6.9	76	9.5
Hot-pressed NdFeB	560	7,000	0.80	8.0	110	13.7
Hot-formed NdFeB	880	11,000	1.20	12.0	274	34.2
Platinum cobalt	355	4,450	0.645	6.45	74	9.2
Cobalt rare earth 1	720	9,000	0.92	9.2	170	21
Cobalt rare earth 2	640	8,000	0.86	8.6	145	18
Cobalt rare earth 3	535	6,700	0.80	8.0	120	15
Cobalt rare earth 4	640	8,000	1.13	11.3	240	30

For nominal compositions, see Table 4

magnetic focusing systems; ammeters and voltmeters; and watt-hour meters. Table 6 lists applications for permanent magnets in the automotive industry.

Alnicos are a family of low-cost iron-base alloys containing aluminum, nickel, and cobalt. Various other elements are often added to Alnicos. For example, to lessen the deleterious effect of carbon, carbide stabilizers such as titanium or niobium may be added. Titanium and copper increase H_c at the expense of B_r, but niobium increases H_c without decreasing B_r. Increasing the basic cobalt content by about 20% or more results in a major improvement in magnetic performance, because such large amounts of cobalt make it possible to develop a preferred orientation by heat treating the material in a magnetic field. Less striking improvements in H_c and B_r are obtained in nonoriented samples. Compositions and properties of both cast and P/M Alnico alloys are listed in Tables 4 and 5.

Table 6 Automotive applications for permanent magnets

Top usage: Currently, 20–30 per vehicle; future, 100 per vehicle

Door locks
Windows
Mirrors
Starter
Radiator fan
Idle speed
Cruise control
Air pump
Brake assist
Steering
Transmission control
Antilock
Suspension
Fuel pump
Seat base
Seat recline
Seat supports
Heater blower
Water pump
Oil pump
Air conditioning
Electric braking
Differential control
Wipers
Spoilers/aerodynamics
Headlight wipers
Headlight direction
Entertainment
Sunroof
Traction control

Cobalt-Rare Earth Alloys. Permanent magnet materials based on $SmCo_5$ and Sm_2Co_{17} are the materials of choice for most small, high-performance devices operating between 175 and 350 °C (345 to 660 °F). The role of the samarium in these materials is to lock in the magnetic moments of the cobalt and to prevent them from rotating in an applied magnetic field. Properties of cobalt-samarium alloys are listed in Tables 4 and 5.

An alloy need not contain only a single rare earth metal; mixtures are often used. For example, some samarium may be replaced with praseodymium or heavy rare earths, such as gadolinium or holmium. Likewise, a portion of the cobalt can be replaced with copper and iron to obtain desired magnetic characteristics. In some alloys containing copper and iron, some of the samarium is replaced with cerium for cost savings. These are of the $(RE)_2(TM)_{17}$ type, where RE is rare earth and TM is mostly cobalt with some substitution of iron and copper, as mentioned.

In precipitation-hardened $Sm(Co, Cu)_{7.5}$, copper is substituted for some of the cobalt. This produces a fine, coherent precipitate (~10 nm) when aged at 400 to 500 °C (750 to 930 °F). The coherent precipitates pin domain walls at the fine-precipitated particles. A magnetic field can be employed in conjunction with the compacting cycle to align the magnetic field with the applied field. Additions of small amounts of iron and zirconium can further increase the coercivity.

Neodymium-iron-boron alloys are manufactured by consolidating rapidly solidified materials. An alloy close to the composition of $Nd_{15}Fe_{77}B_8$ is produced. The role of neodymium, which is also a rare earth element, is to lock in the magnetic moments of the iron and to prevent them from rotating in an applied field. In some of these alloys, praseodymium has been substituted for neodymium with favorable results. Likewise, additions of aluminum, dysprosium (see below), gallium and other elements are made to obtain desired magnetic characteristics.

The Nd-Fe-B alloys have a higher magnetic energy product than the Sm-Co alloys, but the major advantage of the former is that neodymium and iron are cheaper than the samarium and cobalt, respectively. The main disadvantage of the $Nd_2Fe_{14}B$ compound is its low Curie temperature (~ 300 °C, or 570 °F), which limits use for high-temperature (> 100 °C) applications. However, the Curie point can be improved by the substitution of cobalt for iron and dysprosium for neodymium. Dysprosium additions also substantially increase the intrinsic coercivity and reduce the reversible temperature coefficient and remanence. Properties of Nd-Fe-B alloys are listed in Tables 4 and 5.

REFERENCES

1. D.W. Dietrich, Magnetically Soft Materials, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 761–781
2. J.W. Fiepke, Permanent Magnet Materials, *Properties and Selection*: *Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 782–803

SELECTED REFERENCES

- K.H. Moyer, Magnetic Materials and Properties for Part Applications, *Powder Metal Technologies and Applications,* Vol 7, *ASM Handbook,* ASM International, 1998, p 1006–1020
- R.A. Schmucker, Jr., Cast Alnico Alloys, *Casting,* Vol 15, *ASM Handbook,* ASM International, 1988, p 736–739

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Alloying: Understanding the Basics (#06117G)

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