

STEEL CASTING METALLURGY



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PREFACE

The seven lectures published in this book were presented at the 39th Annual Technical and Operating Conference of the Steel Founders' Society of America on November 12-13, 1984 in Chicago, Illinois. The lecture series was presented in university style format as a comprehensive course covering cast steel metallurgy. In excess of a full day was devoted to the presentation and discussion of the papers.

Many operating and technical personnel in the steel casting industry work in operations concerned with the metallurgy of cast steel, be it carbon, low alloy, or high alloy. However, the fundamental knowledge of the subject often escapes them since these basic principles are not generally all covered in a single source. It was the intention of the Technical and Operating Committee to provide a basic textbook of cast steel metallurgy that is readily understandable to all. While serving as an excellent guide an introduction to younger men entering the industry, these lectures also constitute an ideal refresher for metallurgical engineers in general.

The lectures have been prepared and presented by authorities on the subject cast steel metallurgy. Each lecturer was chosen because of his full understanding of the subject and his ability to impart his knowledge to those who are not necessarily too familiar with the technical terminology involved. The Society was indeed fortunate to be able to secure and present such a fine group of able speakers. A short biographical sketch of each lecturer is presented.

Technical and Operating Conferences are annual events under the direction of the Technical and Operating Committee, for the benefit of the technical and operating personnel of the member companies of the Steel Founders' Society of America. The lecture series was initiated at the 1958 T & O Conference and was designed to cover topics of prime interest in the operation of a steel foundry.

The 1984 Conference was under the direction of Mr. H. J. Emmerichs, Chairman of the Technical and Operating Committee, and Vice President-Operations, Pacific Steel Casting Company. Other members of the Committee are as follows: C. T Brandt, Missouri Steel Casting

Co.; W. Clark, Empire Steel Castings, Inc.; W. P. Donovan, American Steel Foundries; J. Dziedzic, Pelton Casteel, Inc.; R. MacDonald, Metalloy Steel Foundry, Inc.; D. MacGowan, Atlas Foundry & Machine Co.; J. Moore, Dofasco, Inc.; G. Nesbitt, Electric Steel Castings Co.; M. Rauguth, Maynard Steel Casting Co.; J. Larson, Ingersoll-Rand Co.; J. C. Farlow, ACIPCO Steel Products.

November 1984

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Dr. Carl R. Loper; Jr.
Professor of Metallurgy
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A native of Milwaukee, Wisconsin, Dr. Loper attended the University of Wisconsin at Madison, receiving Degrees of BS, MS, and PhD in Metallurgical Engineering in 1955, 1958 and 1961 respectively. While studying at the University he was named the Foundry Education Fellow, Wheelabrator Fellow, and a Ford Foundation Fellow.

His indoctrination into the foundry industry was as a metallurgical engineer for Pelton Steel Casting Company in 1955. In 1956 he returned to the Campus of the University of Wisconsin serving as an Instructor, Research Project Assistant, Assistant Professor and Professor in Metallurgical Engineering. He is also engaged as a consultant and as a failure analysis expert in legal claim cases.

Dr. Loper has published more than seventy technical papers and delivered talks to numerous technical organizations including AFS Chapters and Regional Conferences. He has served as advisor to the Wisconsin Student Chapter of AFS, as co-author of the textbook "Principles of Metal Casting", author of several chapters in the Gray and Ductile Iron Casting Handbooks, plus several other engineering handbooks. He was recipient of the AFS Howard F. Taylor Best Paper Award in 1967 and has received AFS Divisional awards. Dr. Loper served as a member of the AFS Ferrous Group Executive Committee, Chairman of the National AFS Ductile Iron Division, Past Chairman of the National Related Interests Division and a Chapter Director of the AFS Wisconsin Chapter.



Dr. Robert Voigt

Assistant Professor of Mechanical Engineering
University of Kansas

Robert Voigt is currently Assistant Professor of Mechanical Engineering at the University of Kansas, Lawrence, KS. He received his B.S. in Mechanical Engineering, and his M.S. and Ph.D. degrees in Metallurgical Engineering from the University of Wisconsin. In addition to a university research background in applied superconductivity and cast iron metallurgy Dr. Voigt has worked for Giddings & Lewis Machine Tool Company in engineering research, Norsk Hydro (Norway) working in the development of adaptive control for aluminum reduction cells, and researched the mechanical metallurgy of nickel-base superalloys at NASA Lewis Research Labs. Dr. Voigt is currently conducting research at the University of Kansas in the areas of austempering of cast irons and cast steels, and intercritical heat treatment of cast steel and cast irons and has authored 14 technical papers. He is a recipient of the 1983 SAE Ralph R. Teetor Educational Award. Dr. Voigt is a member of ASM, AFS, ASME, SME, AIME, SAE, and AWS.



Raymond W Monroe

Research Manager
Steel Founders' Society of America

Raymond W. Monroe was named SFSA Research Manager in May of 1982. Prior to this he did contract research in metallurgy, failure analysis and castings processes at the Southern Research Institute in Birmingham, Alabama for a period of six years.

Raymond holds a B.S. in Chemical Engineering from Auburn University, and received his M.S. in Engineering Science from the University of Alabama (Birmingham) in 1980. He is active in the American Society for Testing and Materials, the American Foundrymen's Society, on several Metals Properties Council (MPC) committees, and was recently selected to head the U.S. Technical Advisory Group for the ISO/TC 17/SC 11 — subcommittee on steel castings. He is presently pursuing his Ph.D in Metallurgical Engineering at the Illinois Institute of Technology.

His prior publications include several papers on metal combustion in oxygen and casting technology. The work in castings has been concerned with mold-metal reactions, quenching, heat treating, gas defects, and cast iron properties. Raymond has authored and co-authored many technical papers and publications but the best of which are his comprehensive review of steel casting process called *Making Quality Steel Castings: A Review of 20 Years of SFSA Literature*, and his paper for AFS, "Mold Binder Composition" which was selected as the outstanding paper in the Molding Methods and Materials Division in 1981.



Dr. John Svoboda
Technical & Research Director
Steel Founders' Society of America

Prior to joining the SFSA Staff, Dr. Svoboda spent several years as a technical consultant to the foundry industry with clients in the United States, Canada, Mexico, and Brazil. As a consultant, he specialized in the area of quality control, including sand control, gating and risering, melting and metallurgy. Before becoming a consultant, Dr. Svoboda was Director of Education for the AFS Cast Metals Institute. In that position, he developed a sixty-course educational program, prepared text and programmed learning courses, and designed and developed laboratory facilities. Earlier, Dr. Svoboda, who held the rank of Captain in the U.S. Army Corps of Engineers, served ten years as Project Metallurgist

and Supervisor Foundry Process Evaluation and Control for the Falk Corporation. He received B.S., M.S., and Ph.D. degrees in metallurgical engineering from the University of Wisconsin, and is an active member of the American Foundryman's Society, Iron and Steel Society—AIME, American Society of Association Executives, American Society for Metals, American Society for Testing and Materials and has been elected to Membership in the British Iron and Steel Institute. In 1982, Svoboda presented an exchange lecture to the Steel Castings Research and Trade Association in England. He is also active in the Metals Properties Council and is a Fellow of the Institution of Diagnostic Engineers.

Dr. Gordon H. Geiger
Director of Technology
North Star Steel Company



Dr. Geiger received his bachelor's degree in metallurgy from Yale University in 1959 and his master's and doctorate degrees from Northwestern University in 1961 and 1964, respectively.

He has done full-time and consulting work for several major steel firms, manufacturers, and government agencies, including Jones & Laughlin Steel Corporation, U.S. Steel Corporation, General Telephone and Electronics, and the U.S. Environmental Protection Agency.

He taught metallurgical engineering for 15 years at the Universities of Wisconsin, Illinois, and Arizona. At Arizona, he was a full professor and Head of the Metallurgical Engineering Department. Over that time, he published more than 60 technical papers and co-authored several textbooks.

In 1972 Dr. Geiger received the Bradley Stoughton Award for Young Teachers of Metallurgy from ASM. He was named an ASM Fellow in 1982.



Dr. Carl D. Lundin
Magnavox Professor of Engineering
The University of Tennessee

Dr. Carl D. Lundin is the Magnavox Professor of Engineering in Metallurgical Engineering, College of Engineering of the University of Tennessee, Knoxville, Tennessee, and is also Director of the Welding Research and Engineering Group at UTK. Dr. Lundin came to the University of Tennessee from Rensselaer Polytechnic Institute, Troy, New York, in 1968.

Dr. Lundin obtained his Bachelor of Metallurgical Engineering degree from RPI in 1957. After receiving his bachelor's degree, Dr. Lundin served for three years in the U.S. Navy in both engineering and operations capacities.

In 1960 he was appointed as Research Assistant in the Metallurgy Department, and in 1962 he was appointed as an instructor and also became Supervisor of Welding Research. He obtained his Ph.D. in 1966 from RPI. He was appointed as Assistant Professor in the Materials Division in 1966, and continued as Supervisor of Welding Research.

Dr. Lundin is a member of several Pressure Vessel Research committees and Welding Research Council committees. He currently is Project Director for the Weld Metal and Welding Procedures Subcommittee and the Significance of Discontinuities Subcommittee.

Dr. Lundin has been active at both the local and national level of the American Welding Society. He is also active in membership to the American Society for Metals, Chairman of the Welding Research Council, a member of the Pressure Vessel Research Committee, the International Institute of Welding, ASM Academy and the AWS Academy.

In the research area, Dr. Lundin has authored or co-authored over 26 technical articles and many research reports. Since 1962, Dr. Lundin

has been a consultant to the industry on welding, failure analysis and materials behavior problems.

He has been awarded such distinguished awards as the Adams Memorial Membership, the AWS Williams Spraragen Award, the AWS McKay-Helm Award, and the AWS District Meritorious Award, and was named "Tennessee Tomorrow Professor" by the University of Tennessee in April 1980.

Dr. Martin Prager
Associate Director
The Metal Properties Council, Inc.



As Associate Director of MPC, Martin Prager is responsible for organizing and managing a range of programs dealing with pressure vessel steels, weldments, turbine rotors, castings, hydrogen effects, bolting, stress-rupture testing, fracture toughness and parametric analysis to name a few. Prior to his affiliation with MPC, he maintained a consulting practice mainly serving the marine, power and aerospace industries. He has authored numerous papers on mechanical properties, welding of high alloys, the performance of large propeller castings and environmental effects. His papers have won awards from IEEE and AWS. He formerly worked for The Copper Development Association and the Rocketdyne Division of Rockwell International. He received B. Chem. Eng. and M. Met. Eng. degrees from Cornell University and a Ph.D from UCLA. He is an active member of AWS, AIME, ASM, ASTM, NACE.

Lecture I

Microstructure and Phase Relationships in Cast Steels

By Dr. Carl R. Loper, Jr.

INTRODUCTION

Perhaps the most significant concept to be addressed in any study of steel casting metallurgy is that the mechanical properties obtained are dependant upon the microstructure and macrostructure produced in the steel casting. By controlling the structure of the casting, the mechanical properties can be controlled. It is, therefore, necessary to understand those parameters that comprise the structure of cast steels and to consider the means by which these structural features might be altered or assured to achieve desired mechanical properties.

The structure of cast steel, like that of other metallic materials, is developed from specific arrangements of the atoms present. This discussion will briefly review the development of structures in metallic materials, and consider the formation of cast steel structures under conditions of equilibrium, or near equilibrium.

ATOMIC ARRANGEMENT

The atomic arrangement present in a given material plays an important role in determining the microstructure and properties. In metals, some arrangements permit exceptional strength to be obtained while other arrangements yield exceptional ductility. In crystalline materials (such as metals) atoms are arranged in a geometric pattern called a unit cell. The unit cell may be repeated in space to form a crystal in the same manner as one might stack building blocks. The individual crystals combine to form polycrystalline aggregates which may be observed in the microstructure of these materials.

A few examples of these arrangements of atoms in unit cells are pre-

sented in Figure 1. The simple cubic cell consists of an atom located at each corner of the cell. This arrangement of atoms may be repeated in three dimensions to generate a crystal of large size, Figure 2. The simple cubic cell, however, is infrequently encountered in metallic systems where the unit cells are observed to have slightly more complex arrangements.

The body centered cubic cell is typical of that found in iron at room temperature (ferrite) and is also observed, for example, in chromium and tungsten. In this case an atom is located in the center of the unit cell in addition to those atoms located at the corners. The body centered cubic cell (B.C.C.) reflects a somewhat more dense packing of the atoms than is present in the simple cubic cell.

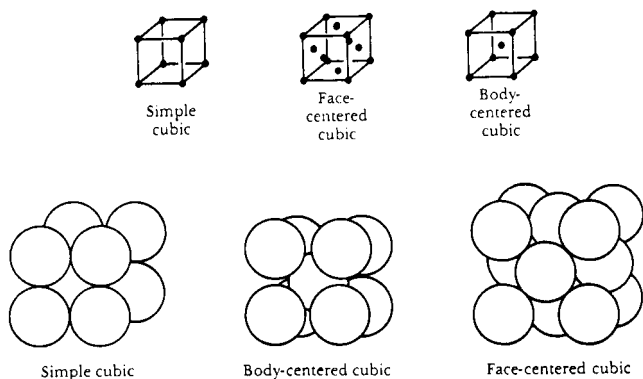


Figure 1. Simple cubic, body centered cubic (B.C.C.) and face centered cubic (F.C.C.) unit cells.

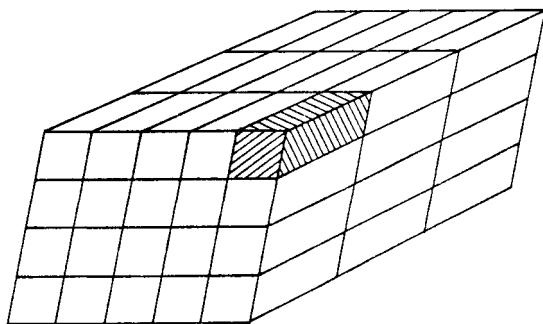


Figure 2. The repetition of the unit cell (cross hatched) in three dimensions generates a crystal.

A more common arrangement of atoms in metallic systems is the face centered cubic cell (F.C.C.). In addition to an atom at each corner of the cell, there is one present in the center of each face. This packing arrangement is even more dense than that of the B.C.C. pattern, and is found in iron at elevated temperatures (austenite), copper, aluminum, lead, silver and nickel.

These cellular arrangements of atoms develop, for example, during the solidification of a metal. Atoms in the liquid state are randomly distributed, or nearly so, and possess no regular structure. As a result, liquids flow freely and must be contained. Consider a pure metal cooled to a temperature corresponding to the freezing point or slightly below, Figure 3a. At this point crystallization has begun at a number of centers (or

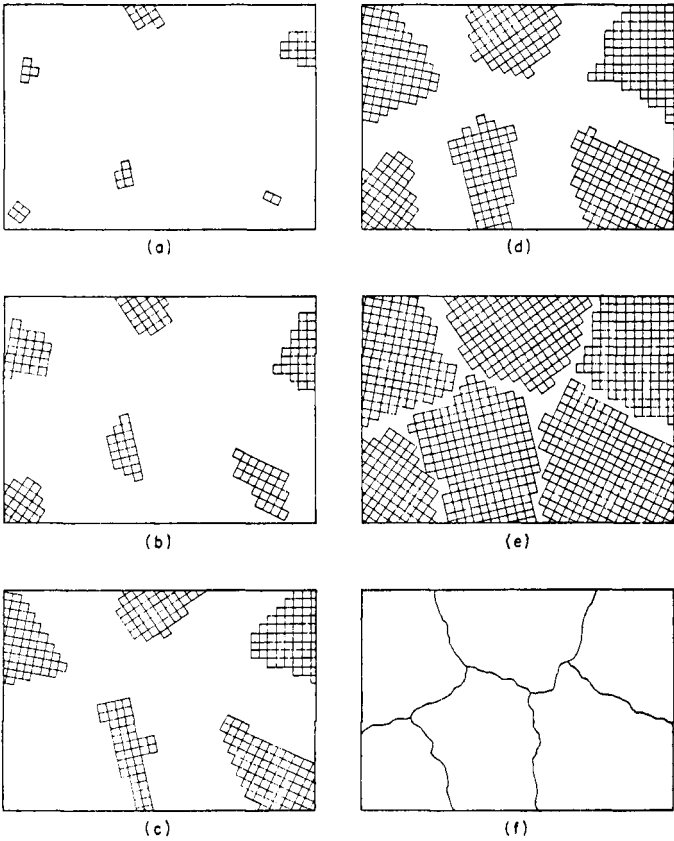


Figure 3. Stages in the process of solidification of a metal (after Rosenhain).

nuclei) by the development of unit cells to form space lattices. These lattices grow by the aggregation of more unit cells at the expense of the liquid. The lattice structures expand in the directions of the axes of the lattice until development is stopped by interference through contact with the vessel containing the liquid or by contact with an adjacent growing lattice. The resulting structure is made up of grains in which the size and shape of the grain is determined by the solidification conditions. Each of these grains is an individual single crystal, separated from each other by grain boundaries where the orientation of the adjacent lattices mismatch, Figures 3f and 4. The interference encountered at these grain boundaries causes them to be revealed when a piece of metal is polished and etched. An illustration of these is evident in Figure 5 where the grain structure of iron is shown.

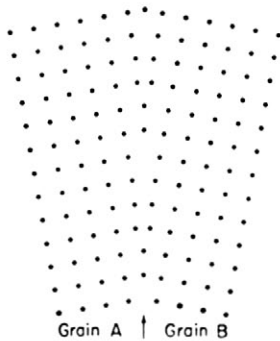


Figure 4. Grain boundary formation between space lattices.

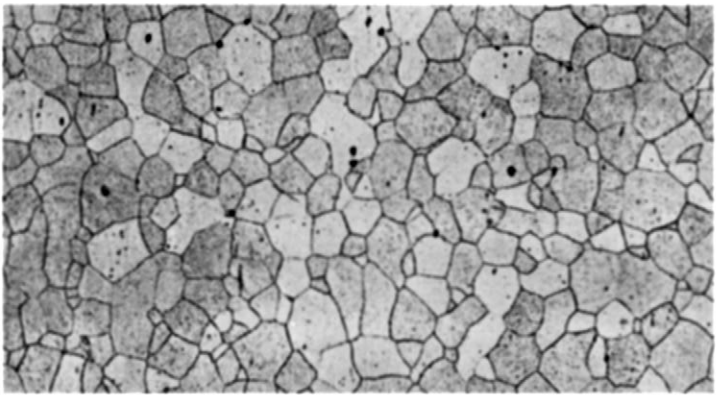


Figure 5. Grain structure of iron. 100X.

PHASES

In the previous example, the liquid and solid can be considered to be separate phases of a given metal. A phase is defined as having the following characteristics:

- A phase has the same structure or atomic arrangement throughout.
- A phase has essentially the same composition and properties throughout.
- A definite interface exists between the phase and its surroundings, or an adjoining phase.

Some examples of phases are illustrated in Figure 6. If a piece of pure

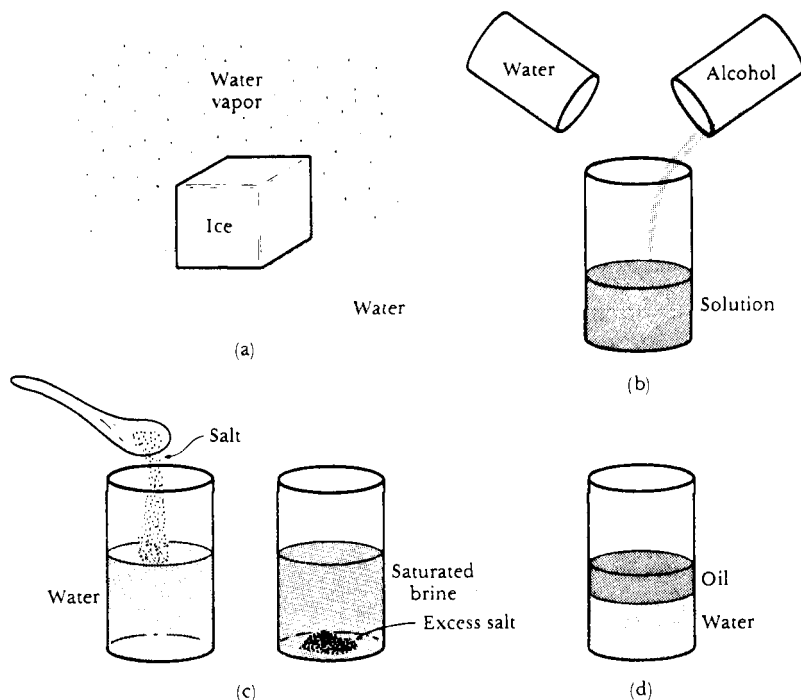


Figure 6. Illustration of phases and solubility.
a. The three forms of water (solid, liquid and gas).
b. Unlimited solubility of water and alcohol.
c. Limited solubility of water and salt.
d. Insolubility of oil and water.

ice were enclosed in a vacuum chamber at a suitable reduced pressure and temperature, the ice would begin to melt and some of the water would vaporize. Under these conditions, three phases would coexist: solid water, liquid water and gaseous water. Each phase would possess a unique atomic arrangement, have different properties, and a well defined boundary would exist between them. Three phases would be present within this system even though all phases had the same composition.

A phase, however, does not have to be a pure material (such as water), and several phases may combine to form a single phase. Consider one container of water and another of alcohol. These two components are soluble in each other, and exhibit unlimited solubility. If the water and alcohol are combined only one phase results, regardless of the amount of water and/or alcohol introduced.

A similar situation may exist in metals. Copper and nickel exhibit unlimited solubility in the liquid state, so that only one liquid phase results from alloying these two elements, regardless of the relative amounts. Furthermore, after an alloy of copper and nickel solidifies only one solid phase results, ie., no interface exists between the nickel and copper atoms, only one solid phase is formed, and copper and nickel exhibit unlimited solid solubility (often referred to as solid solution).

When a small amount of salt is added to water it also enters into solution forming a single phase. However, as the amount of salt is increased salt is observed to collect at the bottom of the container and two phases are present-brine and excess salt. In this case salt has limited solubility in water.

Copper and zinc (brass) exhibit unlimited solubility when liquid, but only a limited amount of zinc can be dissolved in the crystal structure of copper. Excess zinc (over about 40%) is present in the microstructure as a copper-zinc compound, and two solid phases exist together.

In some cases virtually no solubility may occur, such as with oil and water. Attempts to mix these two liquids may break up the material into smaller units, but the two phases remain distinctly separate from each other. A similar condition is experienced in trying to mix molten copper and molten lead. In these cases, the components are immiscible.

EQUILIBRIUM DIAGRAMS

The study of the interrelation of phases in an alloy system at different temperatures and for different alloy compositions is important in understanding the characteristics of alloys. Since it would be difficult and cumbersome to tabulate the interrelation and composition of coexisting phases at all temperatures in an alloy, this information is presented in the form of a diagram. This diagram is a plot designating which phases are present in a given alloy at a given temperature, and is referred to as an equilibrium diagram (or phase diagram, or constitution diagram). The diagram also shows the composition of all phases that are in equilibrium at all temperatures. (Equilibrium may be defined as a condition realized when the total amounts of the various phases remains constant.)

Cooling Curves

One method of determining the temperature at which a phase change occurs in an alloy system is to follow the temperature as a function of time as different alloys in the system are cooled very slowly. This procedure results in a cooling curve which exhibits changes in the slope of the curve as a function of phase changes occurring.

For example, consider using this technique to determine the phase diagram of the antimony-bismuth system. A series of alloys of varying compositions would be prepared, each alloy would be heated until molten and uniform in composition, and the alloy would then be cooled very slowly

Pure antimony, Figure 7a, exhibits an arrest in the cooling curve begin-

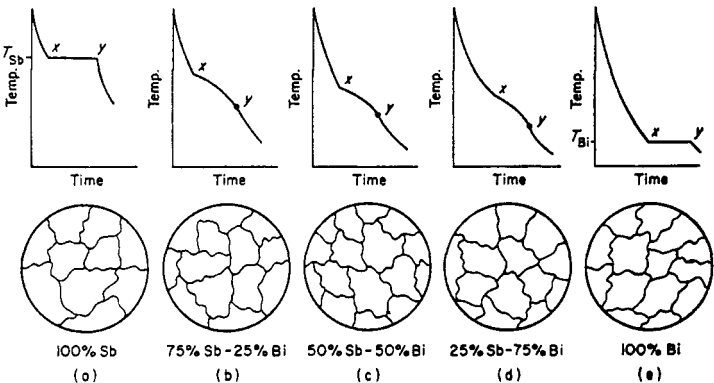


Figure 7. Cooling curves for the antimony-bismuth system.

ning at x and ending at y. Examination of the metal in the crucible would indicate that solidification begins at the time corresponding to point x and is completed at the time corresponding to point y. Solidification occurs at a constant temperature (1167°F) because of the liberation of the heat of fusion.

An alloy of 25% bismuth and 75% antimony exhibits a cooling curve shown in Figure 7b. In this case, the cooling continues in a uniform manner until the temperature reaches 1095°F at which a break in the curve is encountered, where solidification begins. Another break in the cooling curve is observed at 800°F, where solidification is completed. Examination of the structure developed during solidification reveals that a single solid phase has formed, a solid solution of bismuth and antimony.

In a similar manner other alloys in this system are evaluated, and the results obtained from the cooling curves may be plotted in a diagram called an equilibrium, or phase, diagram (Figure 8). The temperature at which solidification begins (connecting all points x from the cooling curves) forms the liquidus curve, and the solidus curve is formed from the temperature at which solidification is complete (points y).

Actually, the liquidus curve is a plot of the composition of liquid that will be in equilibrium with solid at any given temperature, and the solidus curve indicates the composition of solid that will be in equilibrium with liquid at any given temperature. For example, the phase diagram shows that for an alloy of 50% bismuth at a temperature of T_i , two phases will be present. These phases will be liquid and solid. The composition of the liquid is given by the point n, where the isothermal tie line intersects the liquidus curve. And the composition of the solid is given by the point m at the intersection of the solidus curve. Similarly, any antimony-bismuth alloy existing at a temperature such that two phases are present can be evaluated to determine the composition of those two phases.

During the course of solidification the composition of the liquid and solid phases formed changes. Note that at a temperature above T_x this 50% bismuth alloy is completely liquid, i.e., single phase. But when cooled to just below T_x it enters the two phase (liquid plus solid) region forming solid of a composition given by the point a. As the temperature drops, the composition of the solid changes along the solidus curve from point a, to point m, to point y while the liquid composition changes along the liquidus curve from point x, to point n and finally to a liquid of the compo-

sition of point c. This change in composition during the course of solidification is typical for most alloys.

Lever Arm Principle

The equilibrium diagram indicates the composition of phases that will be in equilibrium at any particular temperature. The diagram also makes it possible to determine the amount of the phases present at any given temperature. This is the lever arm principle and can be applied anywhere in the phase diagram where two phases coexist.

Consider the alloy containing 50% bismuth at temperature T_i in Figure 8. It has already been noted that this alloy is composed of solid of composition m and liquid of composition n. By considering the concentration of bismuth present in the solid phase, the liquid phase and in the alloy as a whole, it can be shown that the amount of solid solution and the amount of liquid will be inversely proportional to the distances from the point representing the composition of the alloy to the point representing the composition of the phase in question. For example, the fraction of the total mass that is liquid is given by the relation mi/mn . The fraction of the total mass that is solid is given by the relation in/mn . The percentages of each phase present can be obtained by multiplying those fractions by 100.

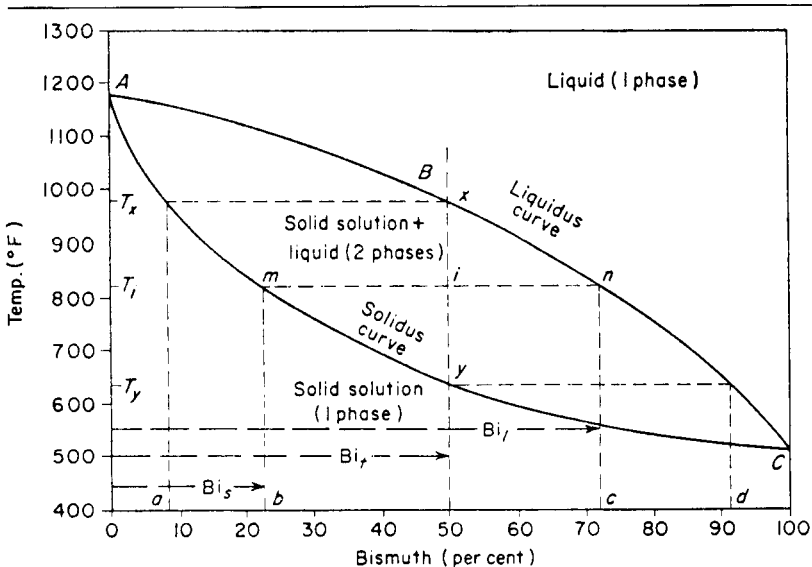


Figure 8. Equilibrium diagram for the antimony-bismuth system.

Once again, it should be noted that below the solidus temperature, all alloys in this system are single phase. The homogeneous solid solution type of system is also referred to as an isomorphous system.

Components Completely Soluble in the Liquid and Insoluble in the Solid

A system in which the components are completely soluble in the liquid state but insoluble in the solid state is illustrated by alloys of bismuth and cadmium. Cooling curves for alloys in this system are presented in Figure 9. The solidification of pure bismuth is the same as discussed previously (Figure 7). An alloy of 20% cadmium exhibits a break in the cooling curve at point x, where solidification starts. The cooling curve then continues at a lower rate of cooling until point y is reached, where there is an arrest which continues until point z is reached, and solidification is completed. It may be observed that the structure of this alloy consists of large grains of pure bismuth formed during cooling from x to y and an intimate mixture of bismuth and cadmium formed during the arrest between points y and z.

An alloy of 40% cadmium exhibits a cooling curve which is unique in that only an arrest is obtained. The structure of this alloy is entirely an intimate mixture of bismuth and cadmium, referred to as a eutectic. A fully eutectic structure formed during the solidification of this alloy, so that the alloy is called an eutectic alloy.

The phase diagram for the bismuth-cadmium system is obtained by

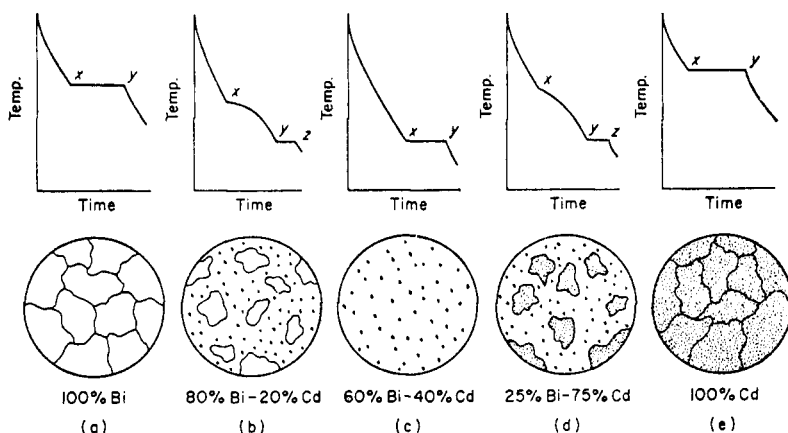


Figure 9. Cooling curves for the bismuth-cadmium system.

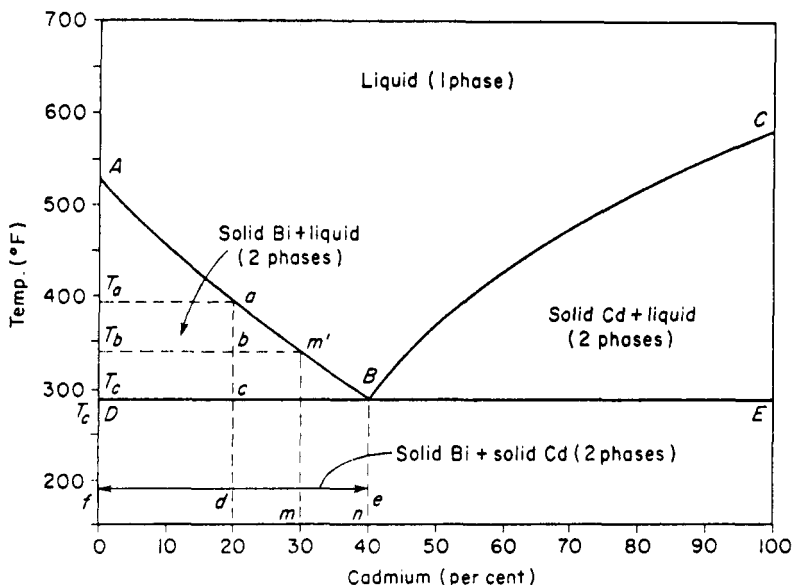


Figure 10. Equilibrium diagram for the bismuth-cadmium system.

plotting the points from the cooling curves, Figure 10. The phase regions of this system are as follows:

Above curve ABC—homogeneous liquid solution (one phase).

Area ABD—solid bismuth plus liquid (two phases).

Area BCE—solid cadmium plus liquid (two phases).

Below DBE—solid bismuth plus solid cadmium (two phases).

At composition B the structure of the alloy is 100% eutectic. Alloys having greater amounts of bismuth (to the left of the eutectic composition) are called hypoeutectic alloys. Alloys having great amounts of cadmium (to the right of the eutectic composition) are called hypereutectic alloys.

Components Completely Soluble in the Liquid and Partially Soluble in the Solid

Actually, there are few alloy systems where there is complete insolubility in the solid state as just discussed. The most common type of alloy system is that where there is partial solubility in the solid state. Consider the hypothetical alloy system A-B, the cooling curves for which are presented in Figure 11. A number of alloys have been selected covering this system, and it may be noted that some of the alloys solidify in a

manner identical to the solid solution alloys discussed using Figure 7 (Cooling curves a, b, c, g, h and i). Also several of the alloys solidify in a manner identical to the eutectic system discussed using Figure 10 (Cooling curves d, e and f).

A plot of the points x, y and z from these cooling curves establishes the phase diagram for components A and B, Figure 12. Note that this diagram is in reality a combination of features of the two systems previously discussed. The single phase solid to the left of the diagram is referred to as α , and is a solid solution of component B in component A (a maximum solubility of 20% B). The single phase solid to the right of the diagram is referred to as B, and is a solid solution of component A in component B (a maximum solubility of 30% A). The phase regions of this system are as follows:

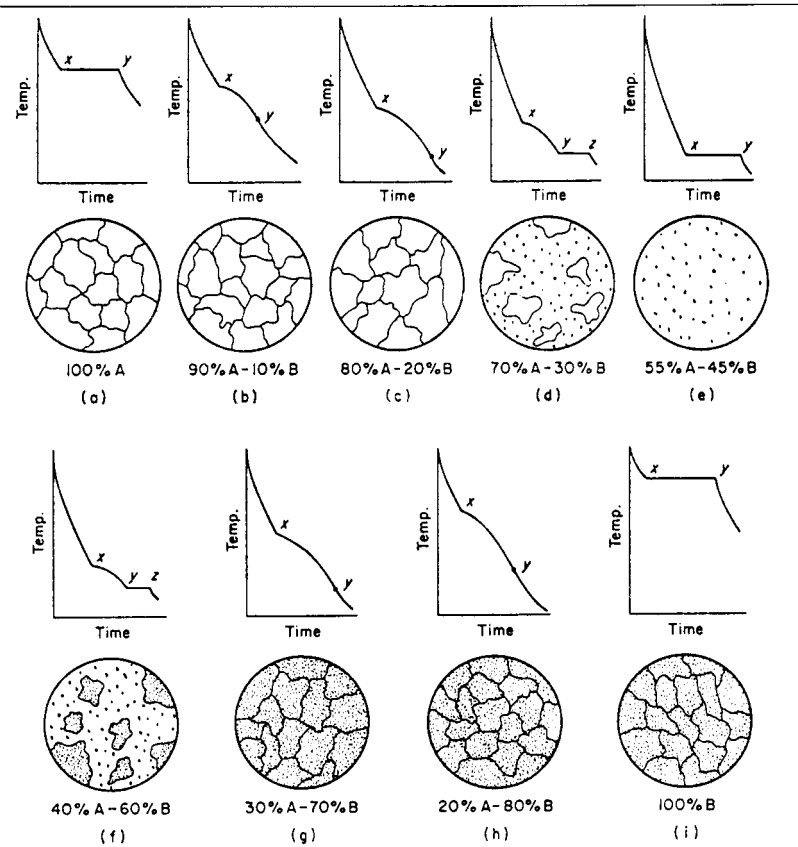


Figure 11. Cooling curves for the A-B system.

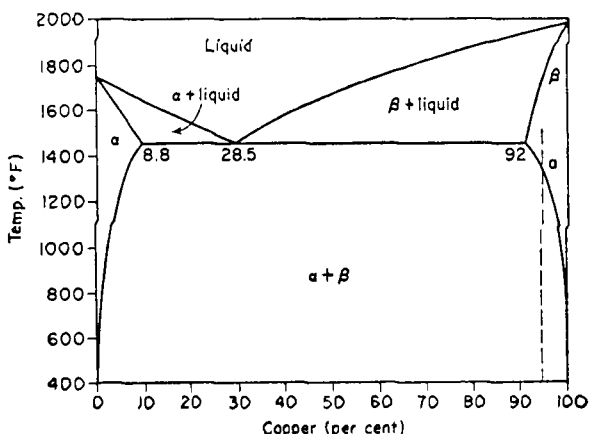


Figure 13. Equilibrium diagram for the silver-copper system.

some cases, act as the components discussed previously. But in other cases, the compounds may dissociate during heating before melting occurs. In addition, the compounds may exhibit solid solubility with other phases, while some show very limited solid solubility.

Another phase reaction (the first was the eutectic reaction) is the peritectic reaction which is essentially an inverse of the eutectic reaction. In the eutectic reaction there is a transformation from one phase (liquid) to two phases (alpha and beta solid phases) on cooling. In the peritectic reaction there is a transformation from two phases (e.g., liquid plus solid) to one phase (another solid) on cooling. These reactions are generally quite slow because the formation of the second solid phase rapidly envelopes the first solid phase making it difficult for the reaction to proceed at equilibrium. An example of the peritectic reaction is presented in Figure 14 from the iron-carbon system. In this case an alloy containing 0.18% carbon slowly cools from the liquid state forming a delta solid solution. At 2715°F there is a reaction between the liquid (of composition 0.50% carbon) and the delta solid solution (of composition 0.10% carbon) to form a second solid phase, a gamma solid solution (of composition 0.78 % carbon). The relative proportions of the phases present before and after the peritectic reaction occurs may be determined by the use of the lever arm principle.

In many more complex alloy systems occurring in metals, transformations may result entirely within the solid state. An example of this is presented in the simplified iron-carbon diagram of figure 15. (Note that this

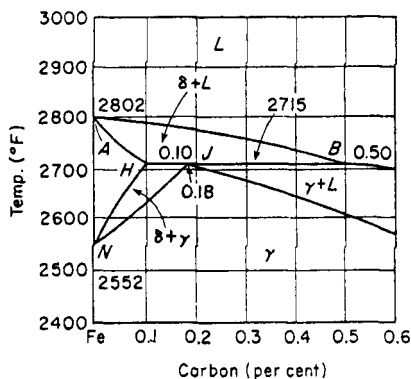


Figure 14. Iron rich portion of the iron-carbon equilibrium diagram illustrating the peritectic reaction.

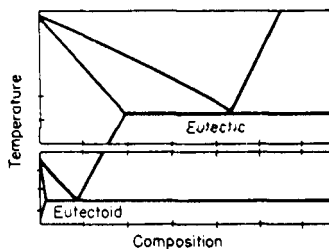
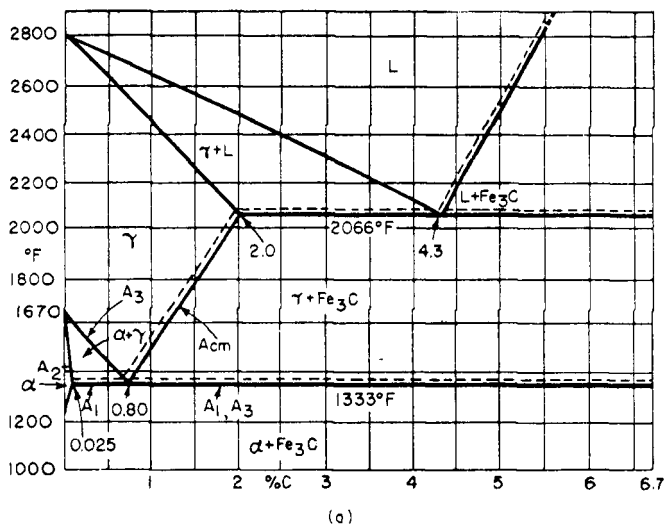


Figure 15. Simplified iron-iron carbide phase diagram.

diagram does not present the peritectic reaction shown in Figure 14.) This system exhibits a eutectic reaction (eutectic at 4.3% carbon) and a similar reaction in the solid state, called a eutectoid reaction (eutectoid at 0.8% carbon). The transformation in the solid state (from gamma solid solution to alpha solid solution plus Fe₃C) occurs just as described previously for eutectic reactions. Because of its occurrence completely in the solid state, however, the eutectoid reaction is somewhat more sluggish than eutectic reactions.

Ternary Phase Diagrams

When alloys are composed of three components the phase diagrams resulting are substantially more complex than those already discussed. In the discussion to follow, references made to these systems will be made using diagrams which reflect modifications to binary systems caused by the introduction of a third component rather than introducing the complexities of ternary phase diagrams.

PRINCIPLES OF THE IRON-CARBON PHASE DIAGRAM

To enable an understanding of the microstructure and phase relationships in cast steels, it is necessary that the iron-carbon phase diagram be considered. This phase diagram is a plot of the phases present at any temperature for a given iron-carbon alloy. From the phase diagram the composition of the phases can be determined, and the amount of phases coexisting can be calculated (lever arm principle). The iron-carbon equilibrium diagram is presented in Figure 16 for compositions up to 5% carbon.

It may be noted that this diagram actually represents two different equilibrium systems: iron-graphite (the stable system) and iron-iron carbide (the metastable system). These two phase equilibrium systems are superimposed to yield the diagram of Figure 16.

There are a number of features of this phase diagram which bear attention. Pure iron exists at room temperature in a solid form referred to as alpha in which the atomic arrangement is body centered cubic (B.C.C.). When this pure iron is heated to 910°C (1670°F) the alpha phase transforms to the gamma phase which is face centered cubic (F.C.C.). Because the F.C.C. atomic structure is more densely packed than the B.C.C. structure, there is a volumetric decrease (or contraction) when this reaction occurs (and a corresponding expansion when the reaction is encountered on cooling). Continued heating of the F.C.C. gamma

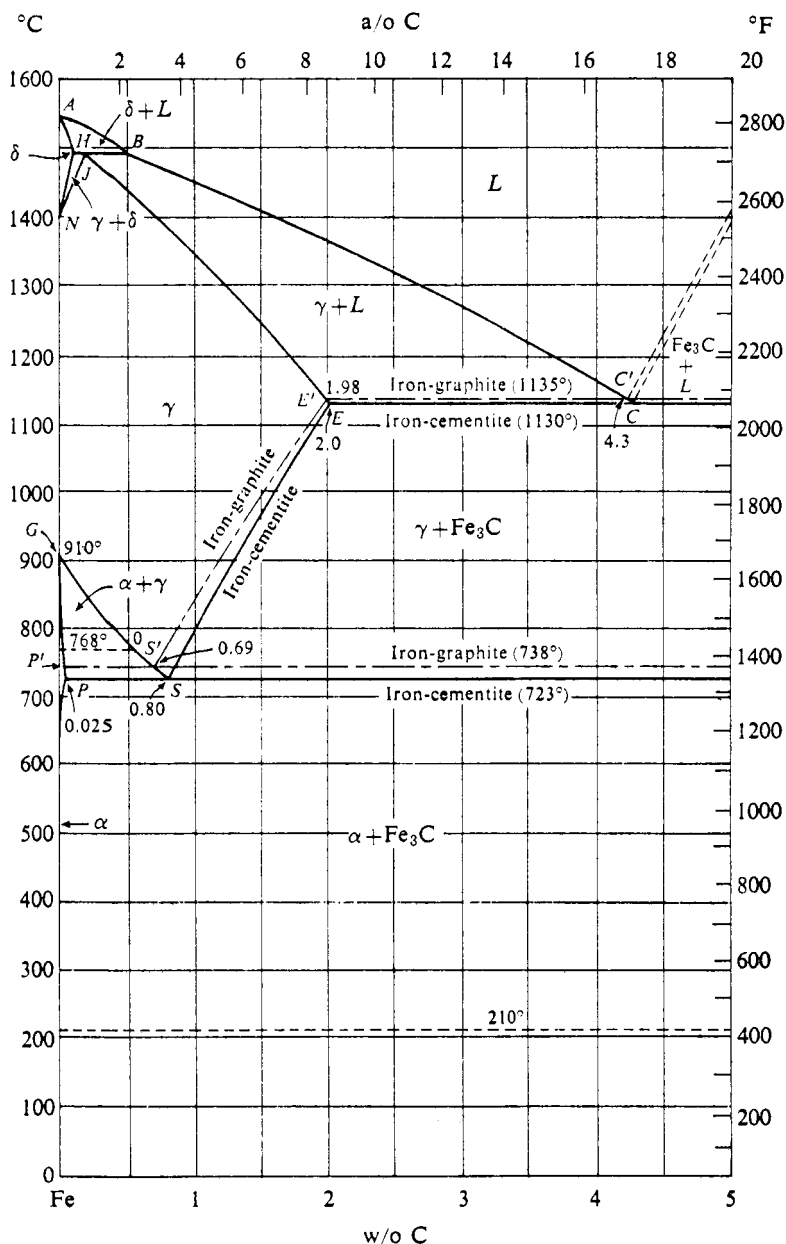


Figure 16. Iron-carbon phase diagram. The metastable iron-iron carbide system is represented by solid lines. The stable iron-graphite system is represented by broken lines. (American Society for Metals)

structure results in a transformation back to the B.C.C. structure (the delta phase) at 1390°C (2534°F). This delta phase melts when heated to 1528°C (2782°F). Thus, pure iron can exist in three solid forms (determined by the temperature), a phenomenon called allotropy.

It may also be noted that there is limited solubility of carbon in these solid phases. The maximum solubility of carbon in alpha (B.C.C.) iron occurs at 723°C (1333°F) and is only 0.025%. This alpha iron is often referred to as ferrite, or alpha ferrite. (A somewhat lower solubility exists if the carbon is in the form of graphite in the microstructure than when present as iron carbide.) The higher temperature B.C.C. structure, delta ferrite, can contain about 0.10% carbon. A substantially greater amount of carbon can be dissolved in gamma iron (also called austenite). Up to 2.0% carbon is soluble in austenite at a temperature of 1130°C (2066°F). Note, however, that the solubility limit decreases to the eutectoid composition (0.80% carbon) at 723°C (1333°F).

Three phase reactions occur in this system:

- a. Peritectic: $\delta (0.10\% \text{ C}) + \text{liquid} (0.50\% \text{ C}) = \gamma (0.18\% \text{ C})$
- b. Eutectic: $\text{liquid} (4.3\% \text{ C}) = \gamma (2.0\% \text{ C}) + \text{iron carbide} (6.67\% \text{ C})$
- c. Eutectoid: $\gamma (0.8\% \text{ C}) = \alpha (0.025\% \text{ C}) + \text{iron carbide} (6.67\% \text{ C})$

The above reactions reflect metastable equilibrium, i.e., the presence of carbon in the form of iron carbide. Note that if carbon is present as graphite, the eutectic and eutectoid reactions occur at higher temperatures and the solubility of carbon in the solid phases is somewhat lower.

The phase diagram presented in Figure 16 also contains a dashed line [at 768°C (1414°F)] across the alpha plus gamma two phase region and the alpha region. The alpha ferrite phase present in these iron-carbon alloys is non-magnetic at temperatures above this line, the gamma austenite phase is also non-magnetic. This is referred to as the Curie temperature for iron-carbon alloys.

Transformations of Austenite on Slow Cooling

The most important reactions in steels involve the decomposition of austenite (the gamma phase) on cooling. Consideration should first be

given to those reactions occurring at slow cooling rates (furnace cooling, or annealing) which simulate equilibrium transformations.

Consider a eutectoid steel (0.8%C) initially at some temperature above 723°C(1333°F) in the region of single phase austenite (F.C.C.). On cooling, at 723°C(1333°F) the entire alloy transforms from austenite (0.8% C) to alpha ferrite (0.025% C) plus iron carbide (6.67% C). (The iron carbide phase is also called cementite.) The eutectoid structure which forms under these conditions is called pearlite because it resembles mother-of-pearl when observed metallographically. A photomicrograph of this structure is presented in Figure 17.

Pearlite consists of alternate plates or lamellae of alpha ferrite and cementite which form from the austenite in patches or nodules. The amount of ferrite and cementite in the pearlite can be calculated using the lever arm principle:

$$\text{Fraction ferrite} = (6.67 - 0.80) / (6.67 - 0.025) = 0.88$$

$$\text{Fraction cementite} = (0.80 - 0.025) / (6.67 - 0.025) = 0.12$$

Or, there is about seven times as much ferrite as there is cementite, and the thickness of the ferrite lamellae is about seven times that of the cementite lamellae.

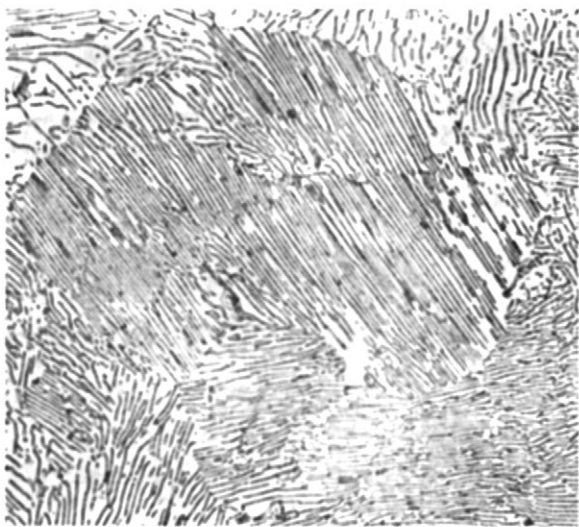


Figure 17. Structure of eutectoid steel, pearlite. 1000X.

Hypoeutectoid steels contain less than 0.80% carbon, and it is noted from the phase diagram that when these steels are cooled from the austenite region they encounter the alpha plus gamma two phase region wherein alpha ferrite forms. As an example, consider a steel of 0.30% C heated to a temperature where the structure will be fully austenite. At this temperature, the structure of the steel will consist of austenite grains, Figure 18. When cooling slowly from the austenite region, primary ferrite begins to form within the austenite grain boundaries at about 800°C (1472°F). As the temperature drops to just above the eutectoid temperature, 723°C (1333°F), the amount of ferrite increases until it consists of primary ferrite (0.025% C) and austenite (0.08% C). The fraction of phases present can be calculated:

$$\text{Fraction austenite} = (0.80 - 0.30) / (0.80 - 0.025) = 0.65$$

$$\text{Fraction ferrite} = (0.30 - 0.025) / (0.80 - 0.025) = 0.35$$

When cooling to a temperature just below the eutectoid temperature the austenite transforms to pearlite (ferrite and cementite lamellae) and the final structure contains 35% primary ferrite and 65% pearlite. An example of this microstructure is presented in Figure 19. Note the blocky ferrite (white) and the lamellar pearlite which has formed.

The transformation of a hypereutectoid steel is similar except that the primary phase forming from austenite is cementite. An example of this transformation is depicted in Figure 20 for an alloy of 1.7% C. As this alloy is cooled from a fully austenitic structure, cementite starts to form at, and within, the austenite grain boundaries and continues to develop to a temperature just above the eutectoid temperature, 723°C

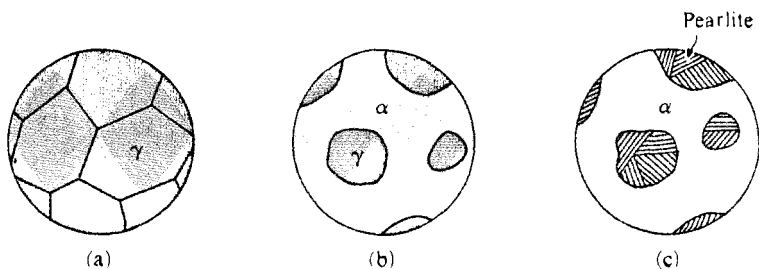


Figure 18. Development of microstructure in a hypoeutectoid steel.

- Temperature within the austenite region.
- Temperature just above the eutectoid isotherm.
- Temperature below the eutectoid isotherm.

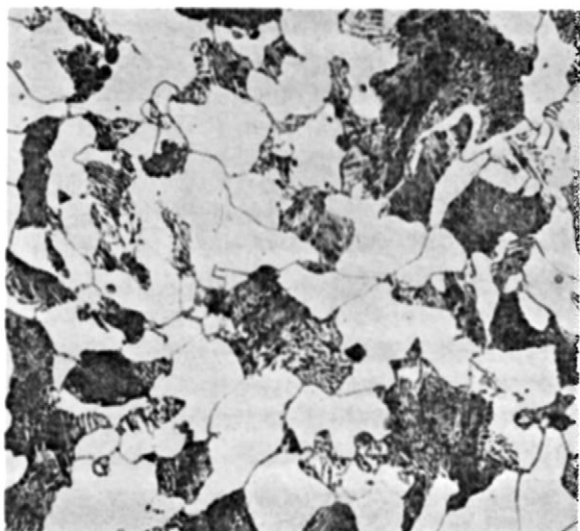


Figure 19. Structure of hypoeutectoid steel, ferrite plus pearlite. 1000X.

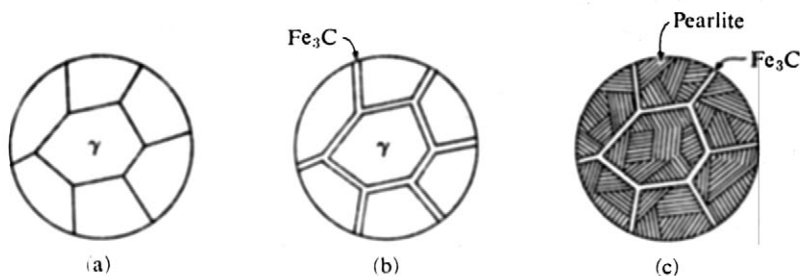


Figure 20. Development of microstructure in a hypereutectoid steel.

- Temperature within the austenite region.
- Temperature just above the eutectoid isotherm.
- Temperature below the eutectoid isotherm.

(1333°F). At this temperature the austenite composition is 0.80% C and the composition of the cementite is 6.67% C. The amount of these phases can be calculated:

$$\text{Fraction austenite} = (6.67 - 1.70) / (6.67 - 0.025) = 0.75$$

$$\text{Fraction cementite} = (1.70 - 0.025) / (6.67 - 0.025) = 0.25$$

On cooling below the eutectoid temperature the austenite transforms to pearlite so that the final structure consists of 25% primary cementite

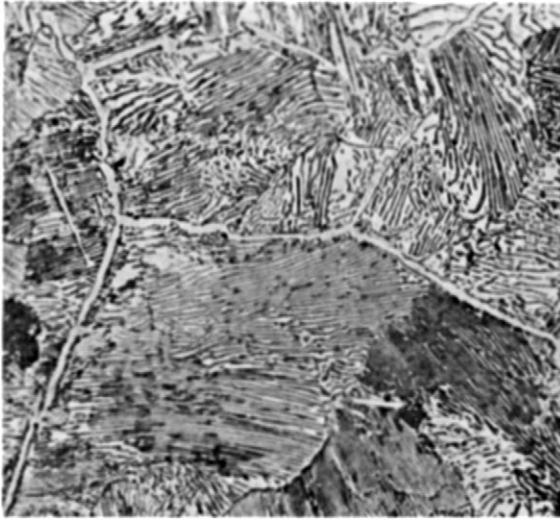


Figure 21. Structure of hypereutectoid steel, cementite plus pearlite. 1000X.

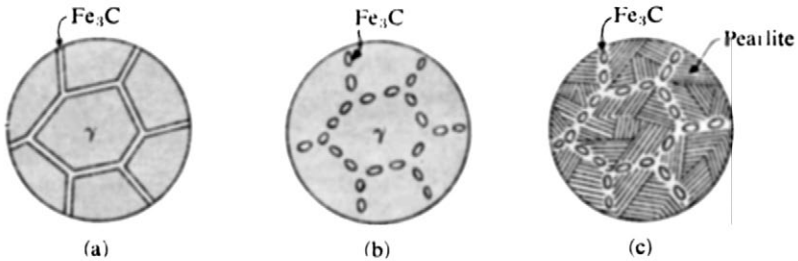


Figure 22. Spheroidization of hypereutectoid steel.

- a. Initial microstructure.
- b. After prolonged heating at a temperature just above the eutectoid isotherm.
- c. Temperature below the eutectoid isotherm.

and 75% pearlite. An example of this structure is presented in Figure 21.

The brittle cementite network formed in the prior austenite grain boundaries is often undesirable in hypereutectoid alloys. This network structure can be modified by reheating the alloy into the two phase austenite plus cementite region and holding for a prolonged period of time. The result of this treatment is shown in Figure 22 where the amounts of primary cementite and pearlite are the same as calculated previously.

Another factor to be considered in discussing the transformation of austenite on slow cooling concerns the effect of prior reheating on this transformation. As an example, refer to the sketch of Figure 23 illustrating the changes in grain structure during the heating and cooling of a 0.25% carbon steel.

Initially, at room temperature, this microstructure consists of ferrite and pearlite. On heating to a temperature above the eutectoid temperature, 723°C (1333°F), the pearlite transforms to austenite. The actual temperature at which this transformation occurs depends upon the specific heating rate employed, being somewhat higher as the heating rate is increased. Austenite begins to form at the numerous lamellae boundaries in the pearlite resulting in a large number of fine austenite grains. On further heating through the ferrite plus austenite two phase field the amount of ferrite diminishes until the structure is composed of 100% austenite. This structure is fine grained, and on further heating into the austenite region the austenite grains grow in size.

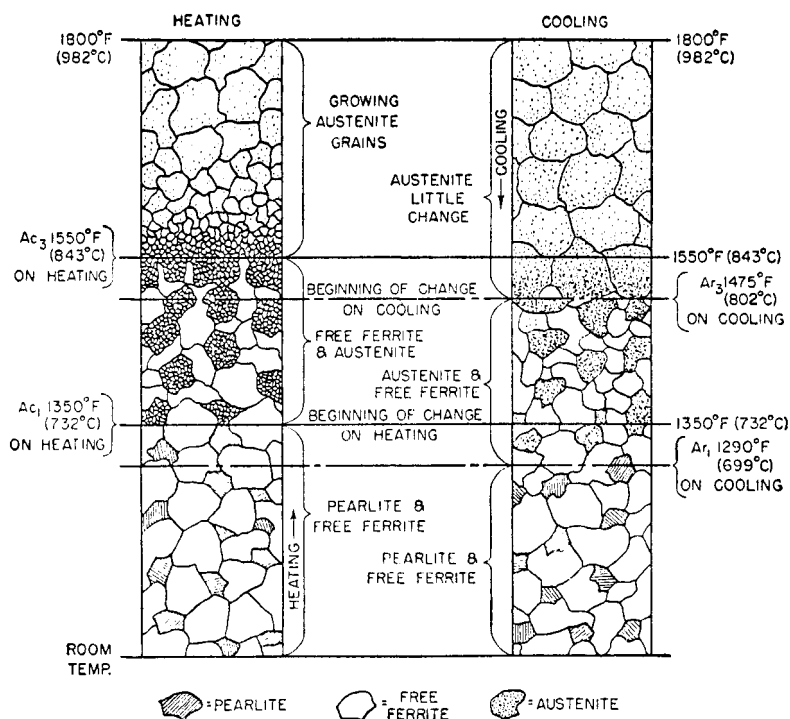


Figure 23. Changes in grain structure during the heating and cooling of a 0.25% C steel.

Unless certain grain refining agents (such as aluminum, titanium, etc.) are present the grain growth occurring in the austenite will continue as the temperature increases or as a sample is held at a given temperature. The presence of aluminum in the structure restricts the growth of these austenite grains until temperatures in excess of 1850°F are attained.

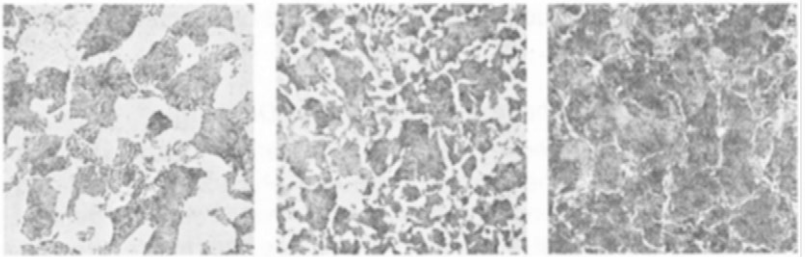
On cooling there is little change in the austenite, and the austenite grain size established during the heating cycle is retained. Some undercooling occurs before ferrite starts to form at the austenite grain boundaries. The number of sites where ferrite may form is, of course, a function of the austenite grain size since a finer grain size presents a greater number of grain boundaries in the structure. This transformation to ferrite continues as discussed previously, with some undercooling occurring prior to the formation of pearlite. Note that the fineness or coarseness of the final structure is directly affected by the grain size of the austenite prior to the transformation.

Moderate Departures from Equilibrium

As just discussed, moderate departures from equilibrium transformation result in some undercooling prior to the onset of the transformation. In effect this results in a suppression of the α - γ plus α boundary line and in the eutectoid transformation temperature. For example, cooling faster results in a depression of the temperatures of ferrite precipitation and pearlite formation in hypoeutectoid steels.

The reduction in the amount of proeutectoid constituent with increased cooling rates is due to the fact that the time permitted for the adjustment of the composition to enable the proeutectoid phase to form has been reduced. Ferrite formation requires that the carbon content be greatly reduced (since the maximum solubility of carbon in ferrite is only 0.025%), and a reduction in the time for this composition adjustment results in a reduction in the amount of ferrite that can form prior to the time that the structure cools to the start of eutectoid transformation. The net effect is that with increased cooling rates the amount of proeutectoid constituent formed is decreased, and the resultant structure approaches that of a eutectoid steel (fully pearlitic).

In addition, regardless of composition, the pearlite laminations become finer with faster cooling rates. This increased fineness of the pearlite causes an increase in hardness and tensile strength and a reduction in elongation.



a. Furnace cooled.

b. Cooled in air blast.

c. Cooled in oil.

Figure 24. Effect of various cooling rates on the microstructure of an SAE 1045 steel.

An example of this effect is shown in Figure 24 for a 0.45% C steel. The annealed (slow cooled, approaching equilibrium) structure of this steel is characteristic of the amount of ferrite and pearlite that could be calculated from the phase diagram. Increasing the cooling rate (normalizing) reduces the amount of ferrite present, delineates that ferrite is the austenite grain boundaries, and refines the pearlite. This effect is even more evident when the cooling rate is increased further by oil quenching.

Reducing the time for ferrite to form may also result in the formation of a Widmanstatten structure, Figure 25. In this case, the ferrite has been forced to develop within the prior austenite grains along preferential planes within the crystal lattice. The rapid cooling rates associated with welding also encourage this type of structure.

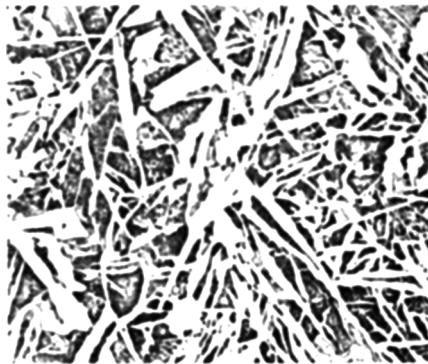


Figure 25. ASTM A27 steel, grade 70-36 (0.25% C, 0.71% Mn), 1 in. cube, normalized by austenitizing at 2200F for 1/2 hr. and air cooling. Widmanstatten pattern of proeutectoid ferrite in a matrix of ferrite and pearlite.

Departures from equilibrium in the transformation, and its effect on the structures and properties of cast steels, will be considered in a subsequent presentation.

Alloying Effects on the Iron-Carbon Phase Diagram

Metallic elements added in moderately small amounts to medium carbon steels do not generally introduce new phases into the system. These elements are generally soluble in austenite at elevated temperatures. Below the critical (eutectoid) temperature, they may exist in solution in the ferrite, in the carbide phase or be distributed in both. The distribution of alloying elements in annealed steels is depicted in Table I.

Table I Distribution of Alloying Elements in the Microstructure of Annealed steels. (Bain)

In ferrite	In carbide	Inclusions
Cu		
P		
Ni		
Si		SiO ₂
Al		Al ₂ O ₃
Zr		ZrO
Mn (strong)	Mn (weak)	MnO, MnS
Cr (mod.)	Cr (mod.)	Cr ₂ O ₃
W (weak)	W (mod.strong)	
Mo (weak)	Mo (strong)	
V (very weak)	V (very strong)	V ₄ O ₇
Ti (very weak)	Ti (very strong)	Ti ₂ O ₃

The effect of alloying elements on the critical temperature and eutectoid transformation must be realized. Figure 26 indicates that the carbon content of the eutectoid is reduced by the presence of alloying elements in the steel. This, in turn, results in an increase in the pearlite content of hypoeutectoid steels of a given carbon content. It is also apparent that alloying elements can raise or lower the eutectoid temperature, an important consideration in austenite formation as well as its transformation.

As a general rule, alloying elements added to iron have been divided into two major classes. Some of the elements behave as austenite stabilizers, that is, they cause an expansion of the temperature range over which austenite exists. The gamma to delta transformation temperature is raised while the gamma to alpha transformation is lowered. With

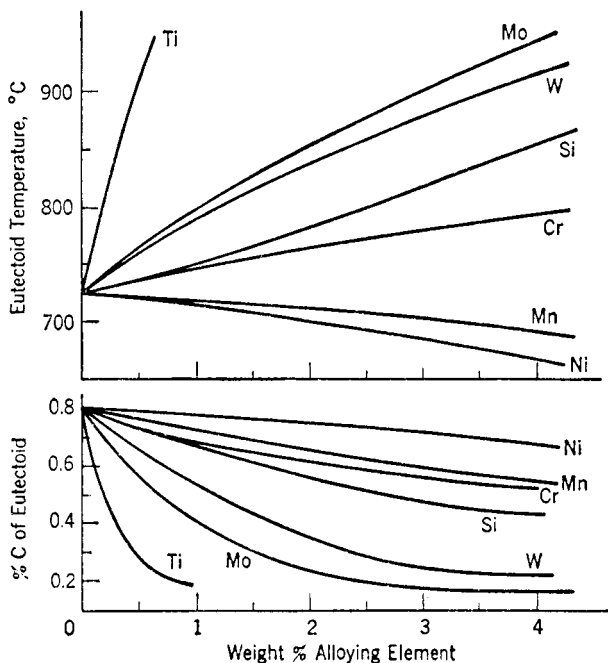


Figure 26. Effect of some common alloying elements on the eutectoid temperature and eutectoid composition. (Bain)

sufficient amounts of these alloying elements the gamma to alpha transformation temperature can be reduced to below room temperature enabling the austenitic structure to be maintained. Examples of alloysystems of this type are depicted in Figures 27a (Mn, Ni, Co) and 27b (C, N, Cu, Zn, Au).

Ferrite stabilizers include alloy elements which reduce the temperature range over which austenite is stable. Examples of this effect are depicted in Figures 27c (Cr, W, Mo, Si, Al, V, Ti, P, Be, Sn, Sb, As) and 27d (S, B, Ta, Ce, Zr). It must be appreciated that these diagrams represent binary alloys, and that the effects noted are modified by the presence of carbon.

As an example, refer to the iron-chromium phase diagram in Figure 28. The effect of chromium is to restrict the austenite phase field. It is also seen that chromium causes the alpha and delta phase fields to merge into a single region of the phase diagram. This is reasonable since both delta and alpha ferrite exhibit a B.C.C. structure.

When carbon is present, the effect of chromium on the austenite region of the iron-carbon phase diagram must be considered, Figure 29. As shown previously, the effect of chromium is to reduce the carbon content of the eutectoid and to increase the eutectoid temperature. However, note that the size of the austenite region is greatly reduced as the chromium content increases.

A convenient means of reviewing the effect of alloying elements on the microstructures attained is found in the Schaeffler diagram, an example of which is presented in Figure 30. This diagram illustrates the structures to be expected from various combinations of alloying elements grouped as “nickel equivalent” and as “chromium equivalent”. For example, a steel of the following chemical analysis is located by the point x on this diagram:

- | | |
|------------------|-----------------|
| 0.07% carbon | 1.55% manganese |
| 0.57% silicon | 18.02% chromium |
| 2.16% molybdenum | 11.87% nickel |
| 0.80% columbium | |

It is estimated that this steel will exhibit a microstructure which is austenitic with 0-5% ferrite present.

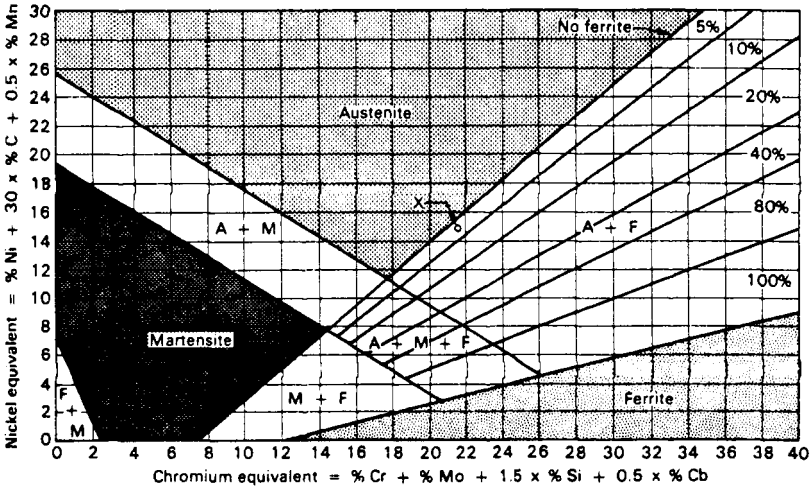


Figure 30. Schaeffler diagram for estimating ferrite content from composition of stainless steels.

SEGREGATION IN CAST STEELS

One of the most problematic aspects of the microstructure of cast steels concerns the segregation of alloying elements accompanying the solidification of these alloys. As a general rule steel castings solidify by the formation of dendrites, Figures 31 and 32. The core of these dendrites is composed of the first solid to form during solidification, i.e., that having a lower solute content, while the interdendritic regions are rich in solute, i.e., they contain a preponderance of the alloying elements. In wrought alloys, this segregation pattern is broken up by subsequent mechanical deformation, but in cast steels the segregation effects remain and can only be partially reduced by heat treatment.

The degree of segregation developed in a casting is affected by the rate of cooling from the melt. Usually slow cooling, as in a sand casting or large section, results in a strong dendritic structure. Rapid cooling of thin sections or where chills are employed, results in a fine structure where the dendritic pattern may be microscopic in nature.

Most of the alloying elements used in steel castings segregate positively, i.e., toward the interdendritic regions. This effect results in a non-homogeneous distribution of alloying elements, causing non-uniform microstructures to develop, non-uniform response to heat treatment, and the formation of phases in the interdendritic regions due to a high concentration of alloying elements.

Increased solidification cooling rates reduce the dendrite arm spacing so that the extent of alloy segregation is lessened. In this condition heat treatments can be devised to obtain a more uniform alloy distribution throughout the casting.

CLOSING REMARKS

The development of microstructures in steels under conditions of equilibrium, or near equilibrium, has been reviewed in an attempt to better understand the factors affecting the development of mechanical properties in cast steels. It should be apparent that the mechanical properties depend upon the microstructure and macrostructures produced in steel castings, and that the lack of control of these structures will be reflected in erratic and unreliable mechanical properties.

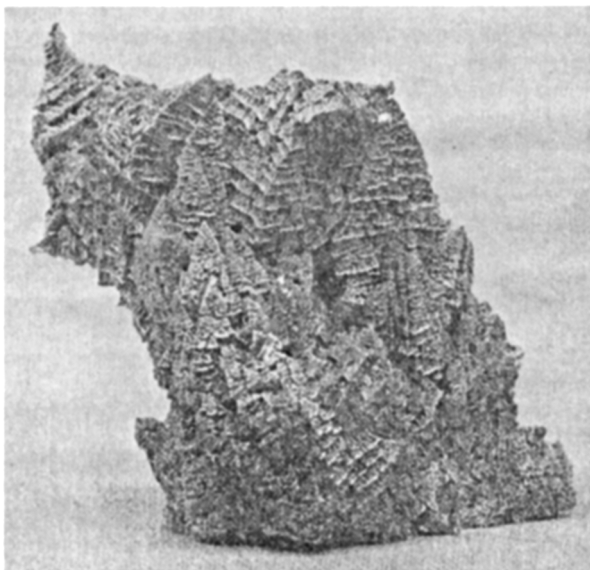


Figure 31. Dendrite formation in magnesium.



Figure 32. Dendrite structure in a steel casting.

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Microstructures and Transformations in Cast Steels

by Robert C. Voigt

INTRODUCTION

A basic understanding of the phase transformations occurring in cast steels is essential to understanding the wide variety of microstructures observed and mechanical properties obtained in these materials. Important solid state transformations occur when cooling a solidified casting and during heat treatment that dramatically affect the microstructure and therefore the properties of steel castings. By controlling both the chemical composition and the phase transformations that occur during cooling or heat treatment, specific microstructures with specific mechanical properties can be assured.

In this brief survey of microstructures and transformations in cast steel, equilibrium microstructures and transformations governed by the Fe-Fe₃C phase diagram will first be discussed followed by a more detailed description of transformation diagrams needed to understand non equilibrium conditions and microstructures obtained through heat treatment. Because it is impossible to separate these changes in microstructure from changes in mechanical properties, the interrelationship between structure and properties will be discussed throughout. Structure/property relationships will not be presented in detail but selected mechanical property data will be included only to highlight the significance of transformation reactions. Even though there are significant differences between cast and wrought steels in terms of chemical composition, microstructure, and properties, the basic transformation characteristics are the same. Information from both the cast and wrought steel literature will be used to illustrate important concepts. Transformation characteristics of high alloy cast steels will not be discussed. Supplementary topics including transformations occurring during in-

tercritical heat treatment, austempering, and transformations in microalloyed steels will be briefly introduced.

A number of introductory textbooks on metallurgy (1, 2, 3) and numerous texts on physical metallurgy (4,5,6) and heat treatment (7,8,9) contain both general and detailed information on microstructures and phase transformations in cast and wrought steels that may be useful to supplement the information in this paper.

EQUILIBRIUM CONDITIONS

A characteristic Fe-Fe₃C phase diagram is shown in Figure 1. The eutectoid reaction of austenite (γ) transforming to ferrite (α) and carbide (Fe₃C), which occurs at 727°C (1340°F) in the lower left corner of the phase diagram, is the transformation that dictates the final room temperature microstructure of a steel that has been cooled slowly or given an annealing heat treatment. As shown in Figure 2 for annealed structures, as the carbon content of a steel increases the amount of the car-

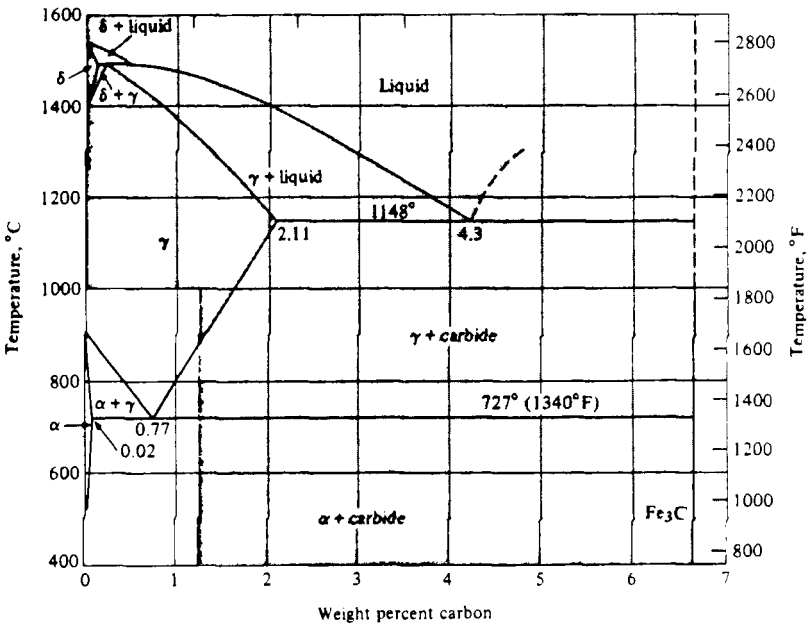


Figure 1. Fe-Fe₃C equilibrium phase diagram (3).

bon-rich Fe_3C phase increases, which results in increasing amounts of pearlite (a fine mixture of $\alpha + \text{Fe}_3\text{C}$) in the microstructure until the eutectoid composition of 0.77% C is reached. A distinction should be made between the phases present, as indicated in the phase diagram, and equilibrium microstructural constituents observed under the microscope as follows:

designation	carbon range	phases present	microstructure
hypoeutectoid	0.02 to ~ 0.77% C	$\alpha + \text{Fe}_3\text{C}$	ferrite + pearlite
hypereutectoid	~ 0.77 to 2.0% C	$\alpha + \text{Fe}_3\text{C}$	pearlite + carbide

These phase relationships have been discussed in more detail in the previous lecture.

Although alloys other than carbon are present in steels, it is the carbon that primarily controls the equilibrium microstructure and properties and shown in Figure 3. Increasing the carbon content of a steel increases its strength and hardness substantially at the expense of decreasing ductility and toughness. Other alloying elements have a much less significant effect on the equilibrium microstructure and properties. Although they do strengthen the ferrite somewhat (6) and lower the carbon content of the eutectoid (7) their presence cannot typically be detected in the microstructure. The important function of alloying elements other than carbon, namely to promote hardenability, will be discussed later.

Unfortunately the effects of carbon content on microstructure and properties are not that simple. (If it was there would probably be little need for metallurgists in steel foundries.) For a given steel with a given carbon and alloy content it is possible to significantly modify the microstructure by controlling the transformation characteristics and thereby modify and improve the mechanical properties. The phase diagram provides only limited information about a steel. It indicates only the amounts of ferrite and carbide that may be present in the equilibrium microstructure but it does not give any information about the phase distribution for either equilibrium or non-equilibrium cooling conditions. For example, it is the different segregation patterns in wrought and cast steels that result in distinctive distributions of ferrite and pearlite that are characteristic of each of these materials. By varying the “thermal history” of the steel the size, shape, and distribution of the carbide phase can be significantly altered to improve mechanical properties.

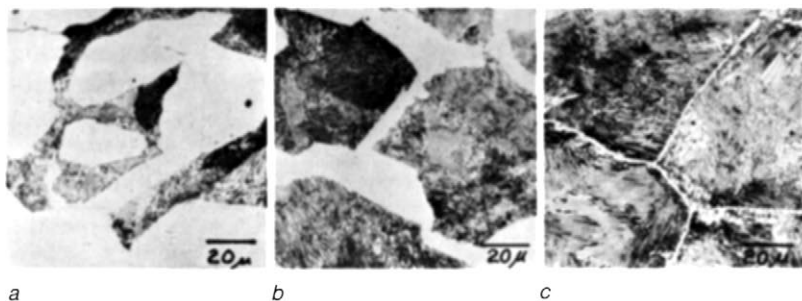


Figure 2. The effects of carbon content on the microstructure of annealed steels. (3)
 a) 0.20% C with grains of ferrite and pearlite
 b) 0.50% C with grains of ferrite and increasing amounts of pearlite
 c) 1.2% C with grains of pearlite surrounded by Fe_3C

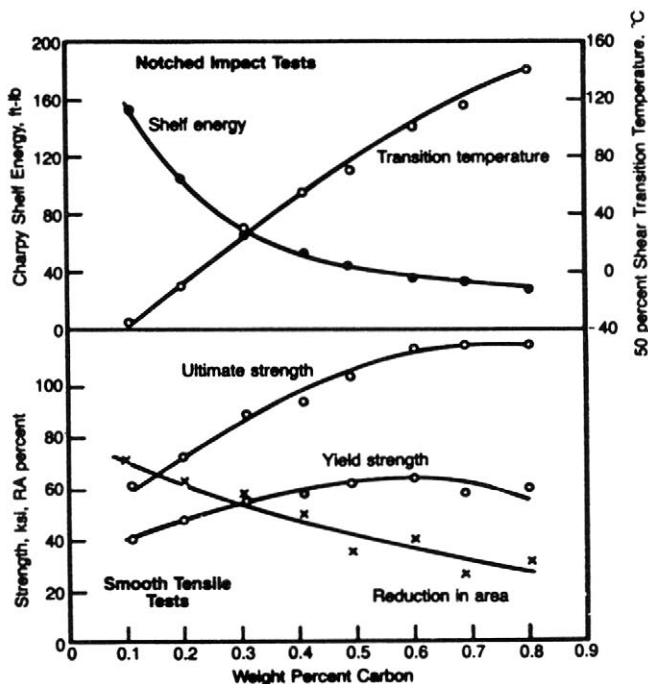


Figure 3. Mechanical properties of ferrite-pearlite microstructures as a function of carbon content (10).

NON-EQUILIBRIUM STRUCTURES AND PROPERTIES

Both the chemical composition of a steel and its “thermal history” must be known in order to identify the microstructure and mechanical properties obtainable. It is this great flexibility in controlling the structure and properties of steels that makes steel such a useful and versatile material. Because the thermal history of different castings may vary and even the thermal history of differing section sizes within a casting may vary, different transformations, microstructures, and mechanical prop-

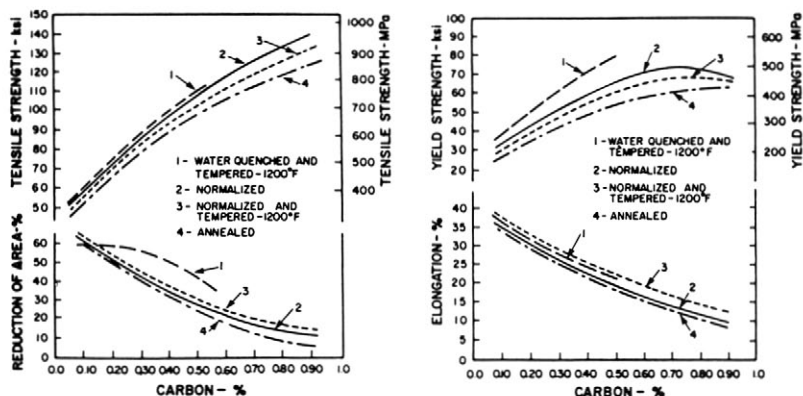
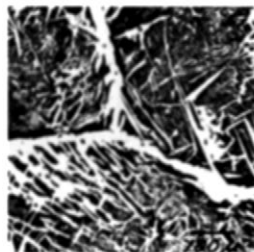
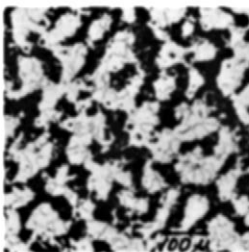


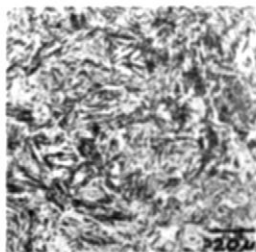
Figure 4. Tensile properties vs. carbon content for cast steels given various heat treatments. (11)



a) as - cast



b) annealed



c) quenched and tempered

Figure 5. Microstructure of a 0.23% C cast steel given different heat treatments (12).

erties can be expected for a given alloy. Figure 4 illustrates the effects of various heat treatments on the mechanical properties of cast steels with various carbon contents. Microstructure differences are illustrated in Figure 5 for a 0.23% C cast steel given various heat treatments. In each case the phases present in the microstructure are the same ($\alpha + \text{Fe}_3\text{C}$), but the distribution and shape of the phases are very different resulting in very different mechanical properties.

Heat treatments to produce the different microstructures in Figure 5 all begin in the austenite region of the phase diagram with all of the carbon distributed uniformly in solid solution in the austenite phase. A high temperature photomicrograph of a steel heated into the austenite phase region would show featureless grains of austenite with little or no evidence of the prior $\alpha + \text{Fe}_3\text{C}$ structure that was present at room temperature. This steel is now at the "starting line" waiting for phase transformations to occur upon cooling to transform the single phase austenite structure to any one of a variety of room temperature microstructures, depending on cooling conditions.

The effects of cooling rates from the austenite phase region on the phase transformations that occur are shown schematically for the extreme cases of very rapid and very slow cooling in Figure 6. Slow or equilibrium cooling at the eutectoid transformation temperature results

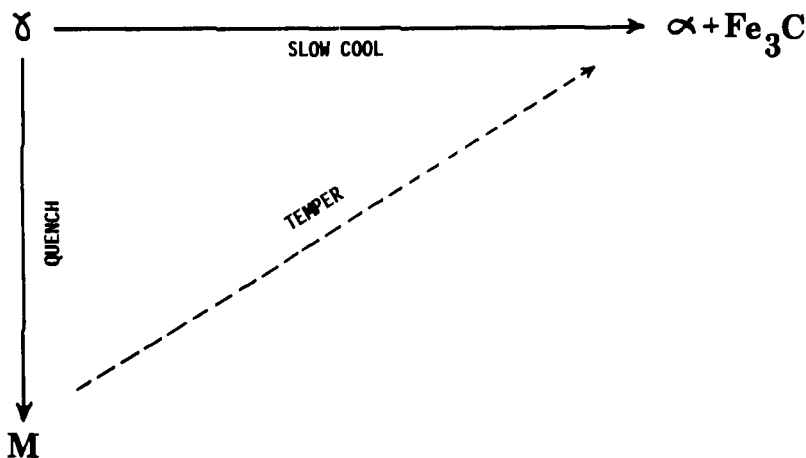


Figure 6. Schematic representation of austenite transformation in steels.

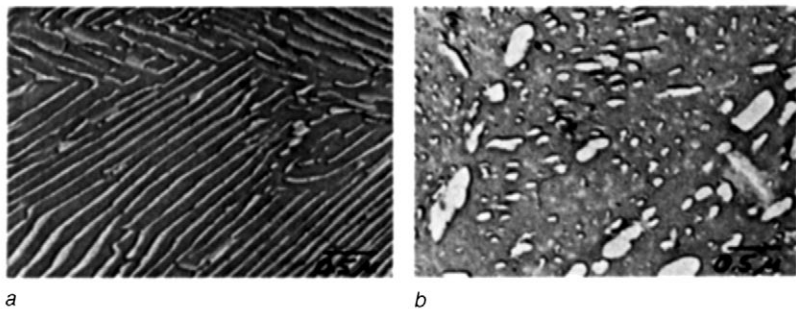


Figure 7. Alpha plus Fe_3C structures in steel at high magnification. (12)

a) pearlite

b) tempered martensite, tempered at 1100°F .

in ferrite and carbide phases forming from austenite as can be calculated from the phase diagram. The microstructure obtained would consist of grains of ferrite (α) and grains of pearlite (a fine two phase mixture of α and Fe_3C). However rapid cooling or quenching from the austenite phase region can prevent the formation of ferrite and carbide and can result in the formation of a new non-equilibrium phase, not on the phase diagram, namely martensite. Most are familiar with the mechanical properties of this hard, brittle phase formed when a steel is quenched rapidly. Much is known about the physical characteristics the martensite phase and its crystallographic relationship to the other phases of steel (4,5,6,7) but this discussion is beyond the scope of this paper. Furthermore, if the martensite phase is given a low temperature tempering heat treatment (in the $\alpha + \text{Fe}_3\text{C}$ region of the phase diagram at temperatures less than 1340°F), it will also transform forming a very fine uniform distribution of phases α and Fe_3C commonly known as tempered martensite. In most cases tempered martensite has a superior combination of strength and toughness for a given steel compared to other $\alpha + \text{Fe}_3\text{C}$ structures such as pearlite. High magnification views of pearlite formed from slow or equilibrium cooling and tempered martensite formed from quenching and tempering are shown in Figure 7. These details cannot be seen in conventional optical photomicrographs as in Figure 5. Although pearlite and tempered martensite have different properties and were formed from different transformation reactions, both are distributions of the phases ferrite and carbide and are thus very similar. (Bainite is also an intermediate phase mixture of ferrite and carbide that can be considered as a transition structure between pearlite and tempered martensite (6, 7). Because bainite is not of

much commercial importance to the steel casting industry it will not be discussed in any detail.)

At this point it is important to clarify terminology to note that not all quench and temper heat treatments result in the formation of tempered martensite microstructures. If cooling from the austenite phase region is not rapid enough upon quenching (for example, at the center of a thick casting) a fine structure of ferrite and pearlite will form instead of martensite. Tempering will not substantially change the structure of this fine ferrite and pearlite. Although the properties of pearlitic structures obtained from quenching and tempering will not be as desirable as for tempered martensite structures, the properties will be substantially better than for coarse ferrite and pearlite obtained from slower cooling. Heat treaters use the terms quench and temper to refer to the physical processing of the casting which may or may not produce tempered martensite. Metallurgists are more restrictive and assume by definition that cooling rates during quenching are rapid enough to form martensite that can subsequently be tempered to form tempered martensite.

It is clear that neither the phase diagram nor the simple diagram in Figure 6 is adequate to completely describe transformation behavior. Questions such as "How slow does slow cooling have to be to get pearlite?" or "What cooling rates are required to form martensite?" need to be answered in quantitative ways. To answer these questions austenite transformation diagrams known as time, temperature transformation diagrams (TTT diagrams) and continuous cooling transformation diagrams (CCT diagrams) need to be understood. Just as the phase diagram is the "road map" for understanding the direction of equilibrium transformations, TTT and CCT diagrams are the road maps for understanding the time and temperature transformation response under non-equilibrium conditions that go beyond the phase diagram. These transformations will first be discussed in a classical way and then discussed in a more practical way as it relates to developing microstructures and mechanical properties upon heat treatment of cast steels.

AUSTENITE TRANSFORMATION

Most heat treatments begin at high temperatures in the austenite region of the phase diagram. During austenitization the initial structure of the steel, whether as-cast or already heat treated, is "erased" and replaced by a uniform austenite solid solution. The details of the transformation of initial structures to austenite are of some interest because

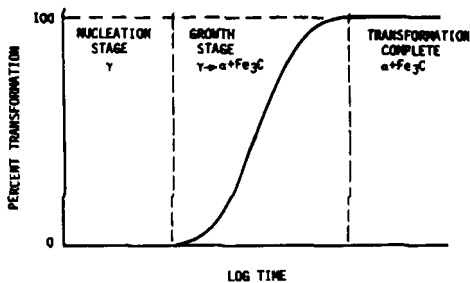
this transformation rate dictates the necessary time to fully austenitize a casting and dissolve all of the carbide phase. Recent SFSA research has indicated that standard austenitizing heat treatment practice may be overconservative and that shorter heat treatment cycles than have been used in the past may be adequate to fully austenitize steel castings (11).

However; it is the transformation of austenite upon cooling that must be studied in detail to understand the wide variety of microstructures and resultant mechanical properties that can be obtained upon cooling. The phase diagram indicates that under equilibrium conditions it is not possible to have austenite present at temperatures below 727°C (1340°F). But when austenite is cooled to below the transformation temperature it can take a considerable amount of time before ferrite and carbide form. It is this time delay that allows austenite to be commonly cooled substantially below 727°C (1340°F) and to transform at various temperatures even though the phase diagram does not indicate that this is possible. It is the temperature or temperatures at which this transformation takes place that determines the final microstructure.

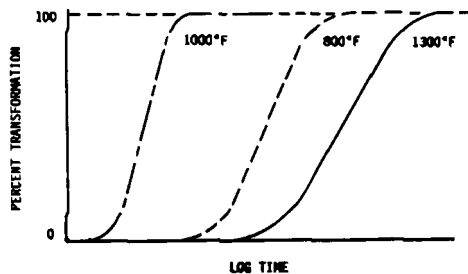
Two basic parameters determine the speed of the transformation from undercooled austenite in steel: the nucleation rate and the growth rate of the newly forming phase(s). The term nucleation rate refers to the rate of initiation of a phase transformation at discrete sites in the microstructure. In practical terms, the nucleation rate is determined by the amount of undercooling (more undercooling favors nucleation) and by the rate of diffusion of the atoms participating in the transformation.

Substantial diffusion of carbon is required during transformation because austenite typically with 0.2 to 0.6% C must form ferrite (0.02% C) and carbide (6.7% C). The growth rate of a new phase, once nucleation has occurred, is determined primarily by the transformation temperature which determines the mobility of the atoms. Much more detailed descriptions of nucleation and growth concepts can be found in numerous physical metallurgy textbooks including reference (4).

Characteristic isothermal transformation from austenite to ferrite and carbide at a temperature below 727°C (1340°F) is shown schematically as a function of time in Figure 8a and shown in somewhat more detail in Figure 8b for the transformation of a eutectoid steel (0.77% C) at selected transformation temperatures. These transformation curves can be observed experimentally using a number of techniques includ-



a) details of a nucleation and growth transformation reaction



b) austenite transformation at selected temperatures

Figure 8. Schematic representation of the transformation of austenite to ferrite + carbide.

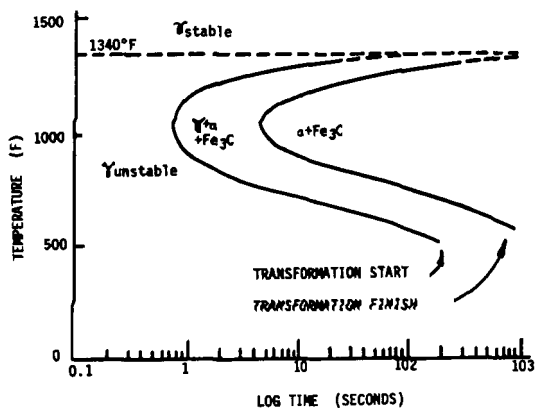


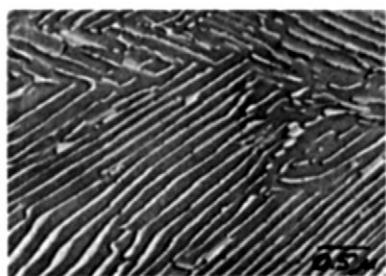
Figure 9. Isothermal transformation of austenite to ferrite + carbide for a steel of eutectoid composition (1).

ing dilatometry or electrical resistivity measurements (8). The “S” shape of these curves is characteristic for all nucleation and growth type reactions. Note that in Figure 8b, nucleation occurs most rapidly at the intermediate transformation temperature of 1000°F and more slowly at 800°F or 1300°F.

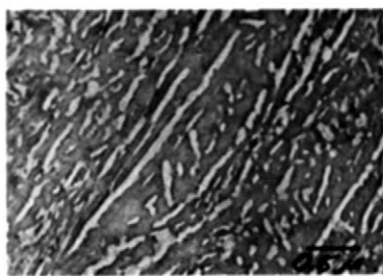
A much more common way of representing austenite transformation characteristics upon cooling is shown in Figure 9 where the austenite transformation response of a eutectoid steel is shown as a function of time and temperature with characteristic “C” shaped curves on a temperature vs. log time plot. Nucleation of ferrite and carbide from the original austenite (transformation start) occurs most rapidly at intermediate transformation temperatures where both high nucleation driving force and relatively high atom mobility favor rapid transformation.

The distribution of the ferrite and carbide phases formed isothermally from austenite at the various transformation temperatures is much different even though the phases themselves and their relative amounts are the same, as shown at very high magnification in Figure 10. As the transformation temperature decreases the $\alpha + \text{Fe}_3\text{C}$ phase distribution formed gets finer and finer and a gradual microstructural change from coarse pearlite to fine pearlite to upper bainite to finally to lower bainite is observed. (The terminology is complex, but the $\alpha + \text{Fe}_3\text{C}$ phases formed are the same in all cases.) As the $\alpha + \text{Fe}_3\text{C}$ structure becomes finer and finer at lower transformation temperatures the hardness and strength of the steel increase. Therefore it is not only the amount of the Fe_3C phase present (as determined by a steel's carbon content) but the distribution and fineness of the Fe_3C phase (as determined by the transformation conditions) that determines the strength and hardness of a steel. Figure 10 is not a complete isothermal transformation diagram (TTT diagram) for this eutectoid steel because the transformation of austenite to martensite is not shown on the diagram.

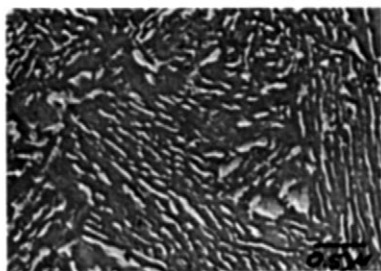
The transformation of austenite to form ferrite and carbide can be avoided if a steel is cooled rapidly enough to suppress the nucleation and subsequent growth of ferrite and carbide as either pearlite or bainite. The martensite phase that forms when cooling austenite very rapidly and the resultant martensitic transformation is substantially different from the $\alpha + \text{Fe}_3\text{C}$ nucleation and growth transformations just described. Martensite forms by a diffusionless shear transformation from austenite and has the same carbon content as the parent austenite. The intricacies of the martensitic reaction and the properties of



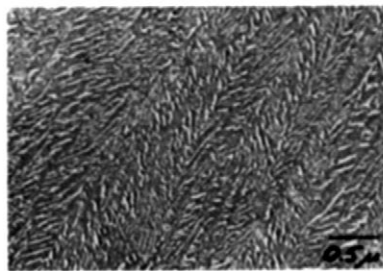
a) 1100°F, pearlite



b) 850°F, upper bainite



c) 700°F, lower bainite



d) 500°F, lower bainite

Figure 10. Ferrite + Carbide microstructures formed at different isothermal transformation temperatures. (13)

this hard, brittle carbon supersaturated phase are complex but are described elsewhere (4-8). The amount of martensite formed upon quenching a steel that has been austenitized is a function only of the quenching temperature. Austenite transforms instantaneously to martensite at any transformation temperature below the martensite start temperature (M_s temperature).

A complete TTT diagram for a 0.45% carbon steel is shown in Figure 11 along with the corresponding portion of the phase diagram for this steel. An additional region of transformation from austenite to ferrite is observed in the upper portion of the diagram. This region occurs only for hypoeutectoid steels and corresponds to the formation of some ferrite prior to the formation of pearlite at high transformation temperatures. If austenite is quenched rapidly enough to avoid the formation of $\alpha + \text{Fe}_3\text{C}$, it will transform to martensite as indicated in the lower portion of the diagram. Quenching to the martensite finish temperature (M_f temperature) or below will result in the transformation of all of the austenite to martensite. Quenching to temperature between the M_s and M_f

temperatures will result in structures with retained austenite present along with martensite. The amount of retained austenite remaining in the microstructure after quenching is of practical importance particularly for alloyed high-carbon steels where the M_f temperature may be considerably below room temperature. In general significant amounts of retained austenite are not desirable.

It is important to use and understand these transformation diagrams correctly. TTT diagrams indicate only the transformation of austenite to ferrite, pearlite, bainite, martensite, or combinations of these structures. Non-austenite microstructures that form do not further transform if cooling passes through another region on the TTT diagram. For example pearlite, once formed from austenite, cannot transform to bainite or martensite.

CONTINUOUS COOLING TRANSFORMATION

Of considerably more practical use than TTT diagrams are continuous cooling transformation diagrams (CCT diagrams) which describe the transformation response of austenite under continuous cooling conditions more characteristic of common heat treatment practice. A CCT diagram for a given steel can be directly used to predict the microstructure

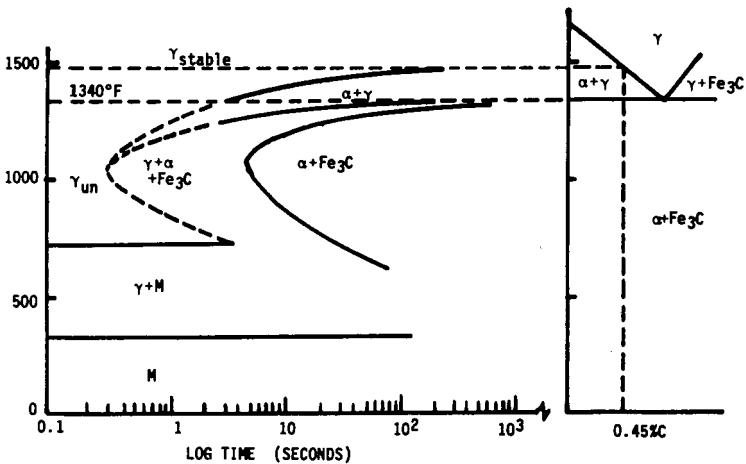


Figure 11. TTT diagram for a 0.45% C steel [the corresponding region of the Fe-Fe₃C phase diagram is shown on the right as well]. (14)

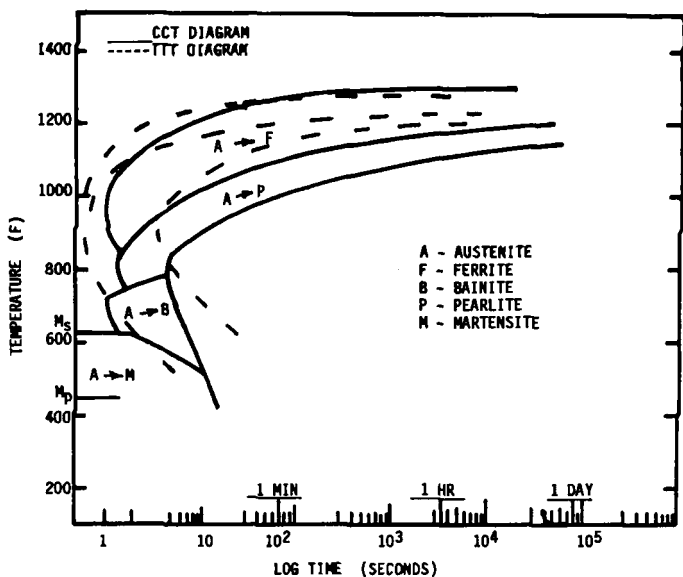


Figure 12. Continuous cooling transformation diagram (CCT diagram) for a 0.4% C steel. The TTT diagram for the same steel is indicated in dotted lines. (2)

ture of a continuously cooled steel part. Compared to a steel's TTT diagram its CCT diagram looks similar but is shifted somewhat to longer transformation times and lower transformation temperatures. A characteristic CCT diagram for a 0.40% C steel is shown in Figure 12 along with the corresponding TTT diagram indicated with dashed lines. By superimposing various cooling rate curves on this CCT diagram the effects of cooling rate on microstructure can be predicted.

The austenite cooling rate that is just rapid enough to avoid transformation to any form of ferrite and carbide is known as the critical cooling rate. This is the minimum cooling rate at which 100% martensitic structures can be formed upon cooling to low temperatures. Since the origin of the remarkably high hardness and strength of steels lies in the formation of martensite, heat treatments demanding optimum properties rely on quenching faster than the critical cooling to form martensite as an initial step in the heat treatment. (This is followed by tempering to transform the martensite to a fine distribution of ferrite + carbide that has an optimum combination of strength and toughness.)

The effects of cooling rate on the microstructure of a 0.3 %C cast steel

are shown schematically in Figure 13 where microstructures, cooling rates, and the continuous cooling transformation curves are all shown. More rapid cooling rates result in finer and finer ferrite/pearlite structures until the critical cooling rate is reached and martensite is formed. Cooling at rates faster than the critical cooling rate has no effect on the structure martensite formed or on the mechanical properties developed.

ALLOY EFFECTS

Up to this point nothing has been said about the effects of alloying elements, other than carbon, in cast steel. Indeed other alloying elements do not significantly affect the structure or properties of low alloy steels directly but they do dramatically affect the austenite transformation response and therefore are often essential to the development of good mechanical properties upon heat treatment. The potent effects of alloying elements on the speed of the austenite transformation are illustrated in Figure 14 where CCT diagrams for an alloyed and unalloyed 0.4% C steel are shown. All commonly used alloying elements, includ-

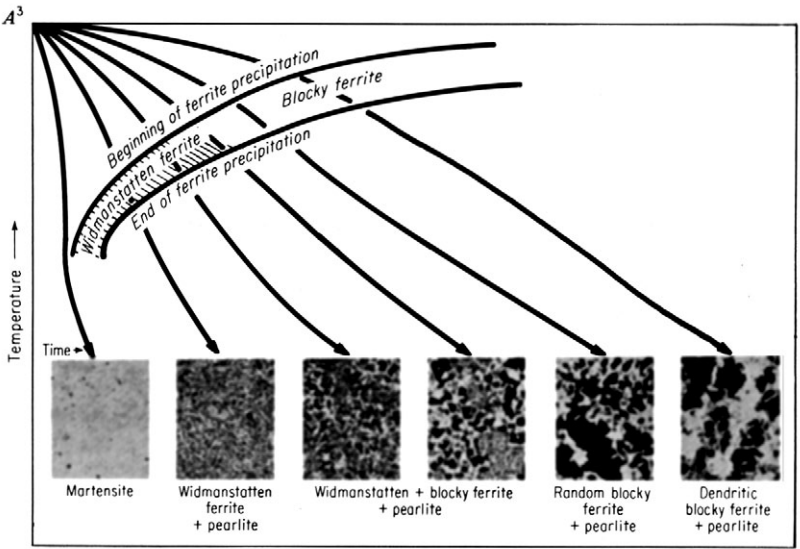


Figure 13. Schematic diagram showing the effects of cooling rate on microstructure for a 0.3%C cast steel (SFSA).

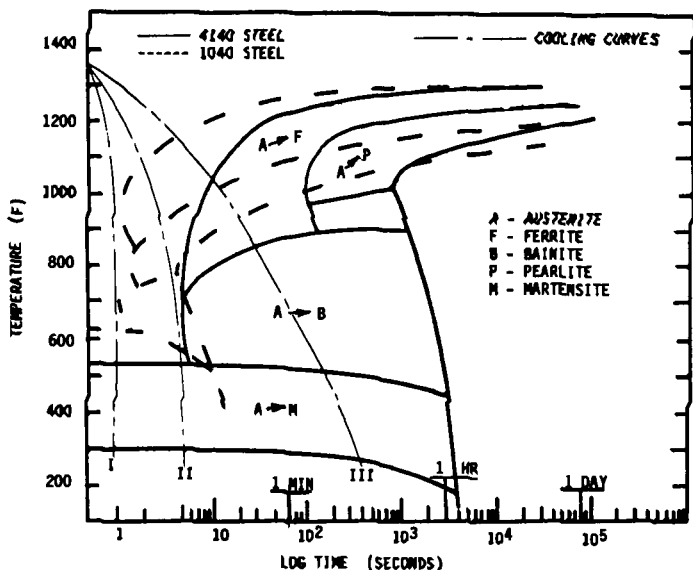


Figure 14. The effects of alloying elements on the CCT diagram of a 0.4% C steel (dashed lines: 0.4% C, 0.5% Mn, 0.2% Si) (Solid lines: 0.4% C, 0.8% Mn, 0.3% Si, 1.0% Cr, 0.2% Mo).

ing carbon, delay the transformation of austenite to $\alpha + \text{Fe}_3\text{C}$ as evidenced by a shifting of the CCT curve to the right on the log time axis. This significant effect can be illustrated by examining the cooling curves superimposed on the CCT diagrams in Figure 14. Cooling rate (1) is rapid enough to result in the formation of martensitic structures for both the 1040 and 4140 steels. If the 1040 steel is cooled at rate (2) it will have a microstructure consisting of ferrite and pearlite; however, the 4140 cooled at rate (2) will have a fully martensitic structure. If the cooling rate is further decreased to cooling rate (3) both the 1040 and 4140 steels will have structures of ferrite and pearlite although there will be somewhat more pearlite and finer pearlite in the 4140 steel because it transformed at somewhat lower temperatures than the 1040 steel.

Alloys play a primary role in heat treated steels by reducing the cooling rate necessary to produce martensitic structures upon quenching. Another way of saying this is to say that alloying elements effectively delay the nucleation of ferrite and carbide formed from austenite upon cooling. This allows the engineer to have great flexibility in designing a

proper alloy/heat treatment combinations for a given casting configuration. These concepts can be discussed in more practical terms by considering the hardenability characteristics of steels.

HARDENABILITY

Hardenability by definition refers to the relative ability of a steel to form martensite when quenched from the austenite phase region. A steel with high hardenability can be easily quenched to form martensite which means that it will transform to martensite even at low cooling rates. Conversely, a steel with low hardenability must be cooled extremely rapidly to form martensite and avoid transformation to ferrite and carbide. Hardenability is therefore directly related to the CCT behavior of a steel. A steel with high hardenability has its CCT diagram shifted to the right on the time axis allowing martensite to be formed at lower cooling rates.

The various alloying elements can be classified as to the contribution that they make to the hardenability of a steel. Certain alloying elements such as Mo and Cr are very effective in shifting the CCT diagram of a steel to longer times and are thus potent hardenability agents. Other alloys such as Cu and Ni do shift CCT curves to longer times but not as dramatically as Mo and Cr. Because the effects of alloying elements on hardenability and transformation behavior have been well studied and are well known, the hardenability behavior of a given steel can be accurately predicted from its chemical composition alone. A detailed discussion of the effects of alloying elements on hardenability is contained in many references (7, 8, 16).

Many factors affect the cooling rate that a particular portion of a casting sees during quenching as well, including the quenchant used, the section size, and whether or not this portion is in the interior or on the surface of a given section. Therefore each portion of a casting may experience a different cooling rate and may transform at different temperatures resulting in different microstructures and properties. This can be illustrated in Figure 14 where the various cooling rates (1), (2), and (3) could be caused either by different quenchants (with (1) being the most severe), or could be caused by different casting section sizes (with (1) being the thinnest section size), or could be caused by depth from surface for a given section size (with (1) being nearest the surface). Clearly experiments to accurately determine the CCT diagram for even one particular steel would require many separate cooling rate experiments

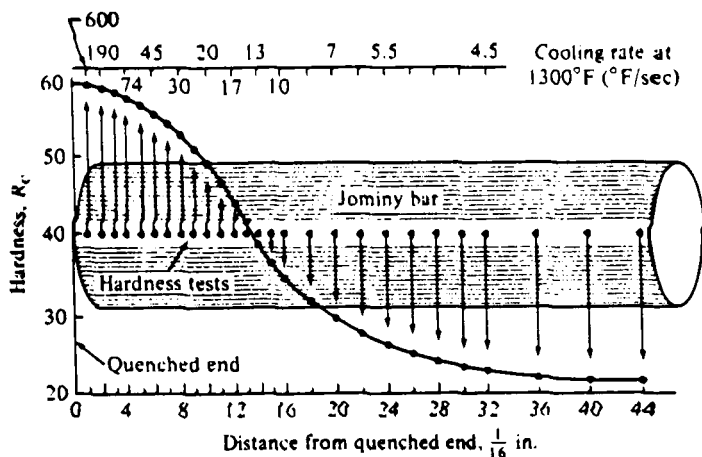


Figure 15. Typical Jominy end quench test results showing equivalent cooling rates for distances along the length of the bar. (15)

followed by detailed metallographic examination to determine the transformed structures at each of the cooling rates of interest.

Fortunately both the cooling efficiencies of various quenchants and the effect of section size on cooling rate are well known and predictable. This allows a standard quenchant to be used on a standard size bar to determine the hardenability of a given steel which can then be used to predict the transformation behavior of that steel for a wide variety of cooling conditions. This standard, hardenability test is known as the Jominy end quench test. As a 1 inch diameter, 4 inch long Jominy specimen is rapidly quenched from one end only, each portion of the bar away from the quenched end experiences its own unique cooling rate depending on position. The results of a Jominy end quench test are shown schematically in Figure 15 where hardness is plotted as a function of distance from the quenched end. The drop in hardness that occurs as transformation cooling rate decreases (i.e. as distance from the quenched end increases) corresponds to the formation of soft non-martensitic structures. The location of this transition from hard martensitic structures at the quenched end to soft martensitic structures at lower cooling rates depends critical cooling rate as discussed previously for CCT diagrams. The practical use of the Jominy end quench test, along with the selection of a proper quenchant for a given heat treatment application is discussed in many textbooks and handbooks on heat treatment (7, 8,13).

Care must be taken when using hardenability information obtained from wrought steels to predict the hardenability of cast steels. Segregation of alloying elements in cast steels can dramatically affect their hardenability as can heat treat procedures, Figure 16.

PRACTICAL ASPECTS OF AUSTENITE TRANSFORMATION

Although the transformation reactions that occur during the heat treatment of steel are complex, a basic understanding is sufficient to understand the resultant microstructures and mechanical properties that can be typically obtained in steel castings. The Appendix contains a series of photomicrographs along with accompanying descriptions that illustrate many of the important effects of alloying, section size, and heat treatment on the microstructure of cast steels.

In summary, from a practical standpoint it is important to separate the effects of carbon content and alloy content as it relates to the development of hardness (strength) and hardenability. The hardness or strength potential of a steel is determined solely by its carbon content; to increase the strength potential of a steel increases its carbon content. However, sufficient hardenability is necessary to allow a given steel to be cooled rapidly enough to form martensite so that its strength potential can be achieved. This hardenability is determined by a steel's alloy content. Hardness and hardenability are separate but complimentary.

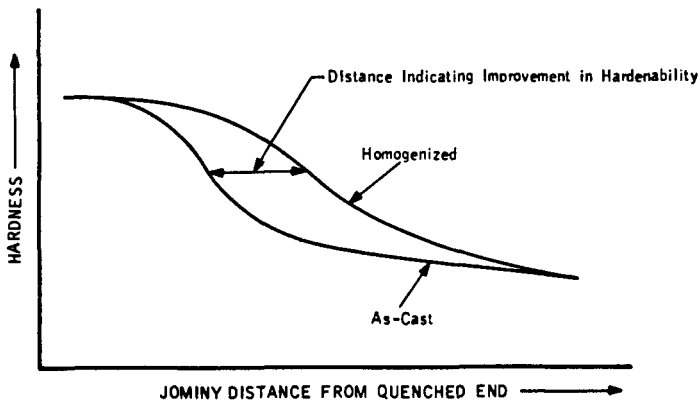


Figure 16. Schematic effect of a homogenizing heat treatment on the hardenability of cast steel as illustrated with Jominy curves. (19)

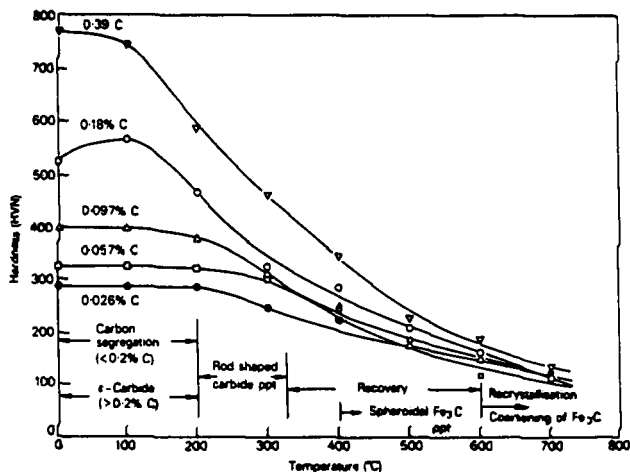


Figure 17. Transformations and softening occurring upon tempering martensites of various hardness levels. (17)

For a given heat treatment application both the necessary hardness and the necessary hardenability must be chosen (by selecting carbon content and alloy content) to get the desired heat treatment response and mechanical properties after heat treatment.

TEMPERING

Tempering is a heat treatment performed in the $\alpha + \text{Fe}_3\text{C}$ region of the phase diagram which follows quenching and sometimes follows normalizing. Tempering of quenched structures transforms the martensite phase to the $\alpha + \text{Fe}_3\text{C}$ structure of tempered martensite, while tempering of normalized $\alpha + \text{Fe}_3\text{C}$ structures softens the structure without any phase change occurring. Practically speaking, the choice of the proper tempering time and temperature allows the heat treater to accurately adjust the strength, hardness, and other mechanical properties to specified levels. Although the transformations that occur during the tempering of martensite are complex (especially during the initial stages of tempering) from a practical standpoint tempering can be thought of as a simple growth of Fe_3C upon continued time at temperature.

Details of the tempering of martensite are shown in Figure 17. At low tempering temperatures very distinct microstructural changes can be

observed including the formation of transition carbides, decomposition of retained austenite, and finally the formation of Fe_3C (5, 6, 7, 17). At higher, more typical tempering temperatures these early stages of tempering occur very early and the entire tempering process can be thought of as the diffusian-controlled growth of spheres of Fe_3C . It is the size and spacing between the Fe_3C particles that essentially changes during tempering and controls properties, Figure 18. The effects of tempering time and temperature on the hardness of a high carbon content quenched steel is shown in Figure 19. Simple carbon diffusion models can be used to explain this predictable and characteristic hardness response upon tempering (4, 5).

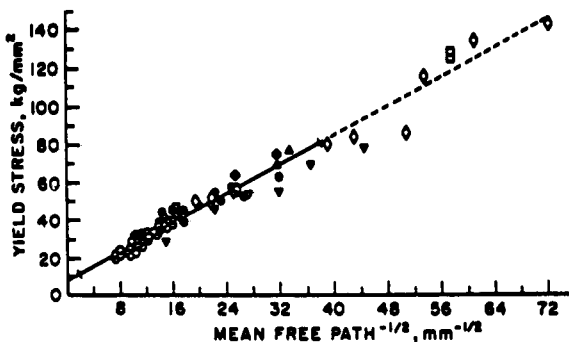


Figure 18. Relationship between the yield strength and average spacing between carbides in spheroidized or tempered steels. (20)

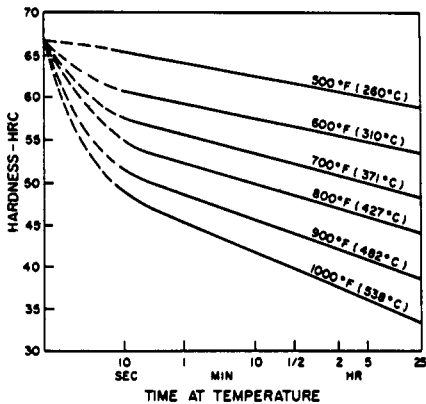
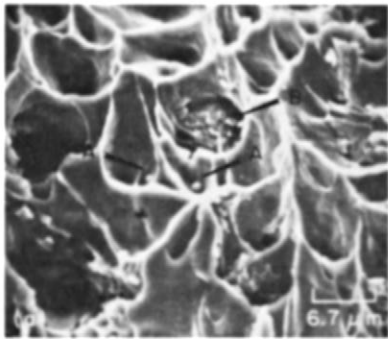
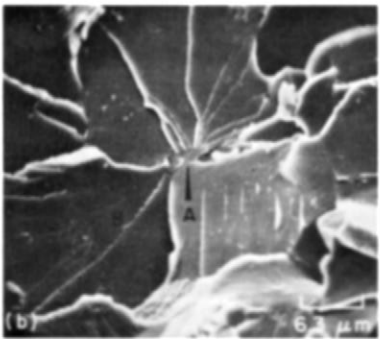


Figure 19. Effect of tempering time and temperature on the hardness of quenched steels (SFSA).

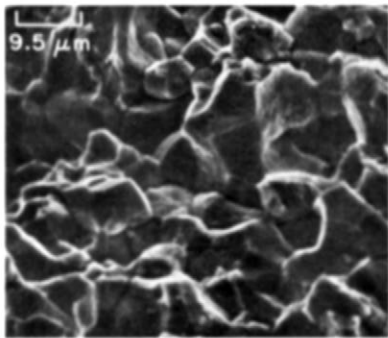
Alloys, whose primary affect is to impart hardenability, also affect the tempering response of steels by slowing down the rate of softening (7, 8). Several mathematical relationships have been developed to predict the hardness change during the tempering of wrought steels as a function of tempering time and temperature based on the chemical composition of the steel and its grain size. The Jaffe and Gordon correlation (19) has been developed for predicting the hardness change during tempering of martensite only, while the Crafts and Lamont correlation (20) can be used to predict hardness changes during tempering of any starting microstructure. Care must be taken during tempering to avoid tempered martensite embrittlement or temper embrittlement, as will be described in the next section.



a) ductile fracture with a dimpled rupture fracture mode



b) brittle cleavage fracture (transgranular)



c) brittle intergranular fracture caused by embrittlement

Figure 20. SEM fractographs indicating various fracture modes.

SUPPLEMENTARY TOPICS

Transformations occurring during heat treatment of cast steel have been discussed including the important topics of austenite transformation and tempering. Various other related transformation reactions, and variations of the transformation reactions already discussed, will now be briefly described to give a more complete picture of the relationship between transformations, microstructure and properties. These topics include a discussion of embrittlement phenomena, surface treatments, intercritical heat treatment, austempering, and micro-alloyed steels. In addition selected photographs from other microstructural analysis tools such as the scanning electron microscope (SEM) and the transmission electron microscope (TEM) will be presented to illustrate their use and capabilities. Because these supplementary topics will be only briefly discussed, selected references are indicated which contain more detailed descriptions of each topic.

Embrittlement Phenomena

Both cast and wrought steels are susceptible to a number of different types of embrittlement. They are all characterized by significant reductions in toughness and a brittle, intergranular fracture mode easily identified by the scanning electron microscope (SEM). Figure 20 illustrates the most common fracture modes that can be observed for cast steel and other metals at high magnification. Dimpled rupture, Figure 20a, is a high energy fracture mode characterized by localized ductility and tearing on the microscopic scale. Cleavage fracture, Figure 20b, is a brittle, low energy, transgranular fracture mode which is common when fracture occurs at temperatures below the ductile-to-brittle transition temperature. Brittle intergranular fracture, Figure 2C, is characterized by brittle fracture at the grain boundaries that can occur even at high temperatures.

The various embrittlement phenomena observed in cast steel are also the result of phase transformations; submicroscopic precipitation of phases typically at grain boundaries. Optical microscopy generally gives no indication whether or not the material is embrittled. Four basic types of embrittlement will be briefly described: tempered martensite embrittlement, temper embrittlement, aluminum nitride embrittlement, and hydrogen embrittlement. Although heat treatment and processing guidelines for avoiding these various types of embrittlement have been developed for many years, the mechanisms causing these phenomena have only been recently understood and must be studied using sophisticated analytical tools such as auger electron spectroscopy.

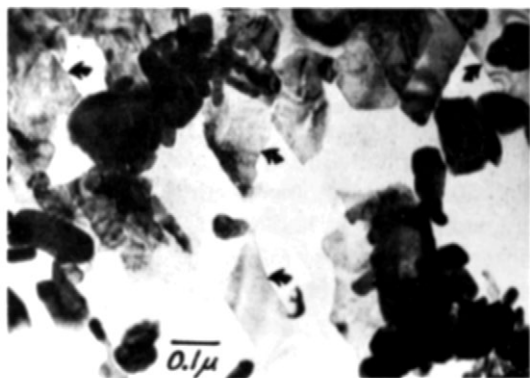


Figure 21. TEM photomicrograph of extracted aluminum nitride particles contributing to "rock candy" fracture. (7)

Tempered martensite embrittlement, commonly known as "blue brittleness," "500°F embrittlement," or "350°C embrittlement" occurs when tempering is in the temperature range of 500-700°F (260-370°C). It is caused by the formation of submicroscopic carbides at prior austenite grain boundaries (5, 6, 7) and is enhanced by the presence of phosphorous and other tramp elements such as Sn, Sb, and As.

Temper embrittlement is a long-standing metallurgical problem that has only recently begun to be understood. This type of embrittlement occurs when tempering alloy steels at temperatures are heated in or cooled through a temperature range of approximately 700-1100°F (370-590°C). Temper embrittlement can be avoided by rapid cooling from high temperature tempering. The interaction and co-segregation among the alloying elements Ni, Mn, and Cr and the impurity atoms P, Sb, Sn and As result in easy grain boundary decohesion resulting in brittle fracture (5, 6, 7, 21). Mo is particularly effective in delaying the onset of embrittlement during long time elevated temperature service in the temper embrittlement temperature range.

Another type of intergranular embrittlement sometimes encountered in cast steels is aluminum nitride embrittlement. The coarse "rock-candy" fracture that occurs, particularly for heavy section quenched and tempered cast steels, is caused by the formation of sheet-like aluminum nitrides, and sometimes borides or borocarbides, at prior austenite grain boundaries and sub-boundaries (7, 22). Preventing aluminum nitride

embrittlement involves keeping the nitrogen content of the steel low by using good melting practice or by denitriding with Zr and Ti, and limiting the Al and B addition levels (22). Figure 21 illustrates a TEM photomicrograph of extracted aluminum nitride particles at very high magnification.

The presence of hydrogen in steels, particularly for high strength steels, often leads to brittle intergranular fracture that can act in conjunction with temper embrittlement. While much hydrogen escapes from steel during solidification and heat treatment, some can remain and precipitate at carbide-matrix interfaces or other internal surfaces and form microcracks (6). Hydrogen embrittlement is not sensitive to composition as is observed for the other embrittlement phenomena but is sensitive to the strength level of the steel. Hydrogen absorption must be minimized during melting, welding, heat treatment, or service to avoid hydrogen induced brittle fracture at low stress levels.

Surface Treatments

For many cast steel applications such as gearing both a wear-resistant surface and tough ductile core properties are desired. A number of processes can be used to impart wear-resistance to the surface either by transformation hardening (quench hardening) or by diffusing hardening elements such as carbon or nitrogen into the surface which can be followed by transformation hardening. Table I briefly categorizes selected surface treatments.

Table I Summary of Surface Hardening Techniques

Process	Process Description	Processing Techniques
Case Hardening	A) Transformation hardening of the surface, only caused by rapid surface austenitization and quenching.	1) flame hardening 2) induction hardening 3) laser hardening
Carburizing	A) Diffusion of carbon into the surface of a low carbon steel at > 1600F B) Quench to form high carbon surface martensite; center remains soft.	1) gas carburizing 2) pack carburizing
Nitriding	A) Diffusion of nitrogen into the surface of a steel to form a hard brittle iron nitride phase	1) nitriding 2) carbonitriding (diffusion of C & N)

The transformations that can occur during surface hardening are identical to the transformations that occur during through-section heat treatment. By locally heating just the surface of a casting into the austenite temperature region, surface transformation to austenite will occur. Rapid quenching, either with water or by self quenching (as in laser heat treatment) results in transformation to martensite at the surface. Similarly by introducing carbon into the surface of a low carbon steel casting from a carbon-rich atmosphere during an austenitizing heat treatment, the surface can be carbon enriched and strengthened and then subsequently transformed to high carbon content martensite while the center transforms to tough low-carbon content martensite or remains ferrite + pearlite, Figure 22. In the nitriding process, nitrogen is introduced into the surface of a casting at approximately 950°F (510°C) forming a thin, hard, brittle iron nitride layer at the surface. Carbonitriding introduces both carbon and nitrogen into the surface of a steel casting to enhance surface properties. Detailed discussions of the various surface hardening techniques can be found in a number of references (5,7,21).

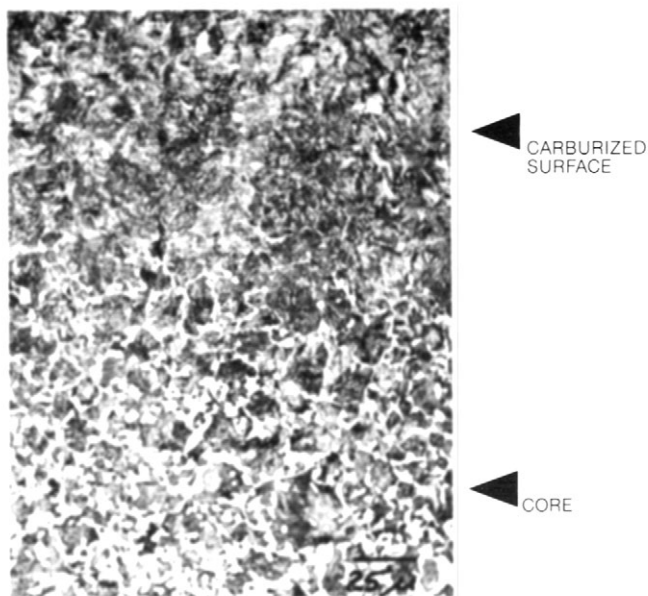


Figure 22. Carburized surface of a 0.2% carbon steel after quenching from the carburizing temperature. (courtesy, K. E. Rose, University of Kansas)

Intercritical Heat Treatment

A new approach to developing good combinations of strength, ductility, and toughness in steels consists of intercritically annealing steels rather than fully annealing prior to quenching. By heating between the upper and lower critical temperatures in the $\alpha + \gamma$ region of the phase diagram, Figure 23, fine structures of ferrite and martensite can be developed upon quenching. These heat treatments have made great inroads in the automotive industry, where intercritically heat treated, "dual-phase" wrought steel sheet products exhibit both high strength and excellent formability (7,23). Initial studies on intercritical heat treatment of cast steel have indicated that these heat treatments, when applied after full austenization and quenching but before the final tempering step can improve toughness, reduce the ductile to brittle impact transition temperature, and possibly eliminate temper embrittlement (24).

At the intercritical temperature the microstructure is transformed to a two phase mixture of ferrite and austenite. Properties are controlled by the amount and carbon content of the austenite phase which are a strong function of the intercritical temperature chosen as can be dem-

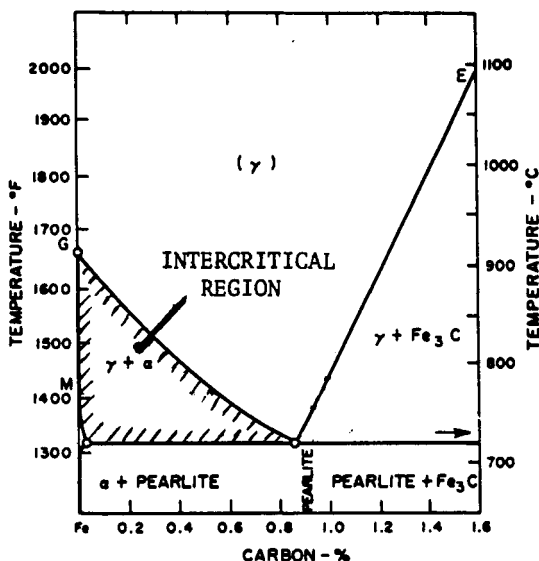


Figure 23. Eutectoid region of a Fe-Fe₃C phase diagram indicating the intercritical temperature range.

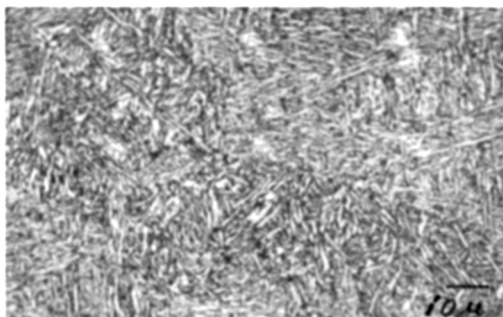


Figure 24. Microstructure of a 0.3% carbon cast steel intercritically heat treated at 1380°F, followed by quenching and tempering. Structure consists of ferrite and tempered martensite.

onstrated with simple phase diagram lever law calculations. The distribution of the ferrite and austenite phases formed at the intercritical temperature also controls final properties and is a strong function of the microstructure formed prior to intercritical heat treatment. It is primarily the grain refinement associated with intercritical heat treatment that improves the toughness of the material. Upon quenching the ferrite portion of the microstructure remains unchanged but the austenite transforms to pearlite, bainite, or martensite just as for any fully austenitized steels. A typical microstructure for a 0.3% cast steel given an intercritical heat treatment followed by tempering is shown in Figure 24. The potential benefits of intercritical heat treatments on the properties of steel castings have yet to be fully explored.

Austempering

Austempering heat treatments traditionally result in the formation of bainitic structures of ferrite + carbide. Because similar properties can be achieved upon quenching and tempering (a less costly heat treatment) austempering is rarely performed on cast steels. However, laboratory results have shown that if high-carbon, silicon-alloyed cast steels are austempered, unique carbide-free structures of ferrite and stable austenite are formed with exceptional combinations of strength, toughness, and wear resistance (25). Work is continuing at the University of Kansas in conjunction with AMAX Laboratories to investigate the microstructure, transformation kinetics, and properties of this new family of materials. Ten years of research on austempered ductile cast iron has resulted in the development of ductile irons with vastly superior strength, toughness and wear resistance (26). Because of the chemical

composition similarities of high-carbon, silicon-alloyed cast steel to ductile iron it is expected that similar high strength, high toughness cast steels can be developed upon austempering. Initial results by Sandvik and Nevalainen (25) in Finland have shown that the following properties can be obtained

steel composition:	0.8% C, 2.4% Si, 0.5% Mn, 0.8% Cr
austempering temperature:	320°C (610°F)
tensile strength:	250,000 psi
yield strength:	200,000 psi
tensile elongation:	23%
room temperature charpy impact toughness:	32 ft-lbs

Micro-alloyed Steels

Micro-alloyed or high strength low alloy (HSLA) cast steels are beginning to receive more attention in the United States because of the combination of high strength and toughness along with good weldability and low alloy cost of these alloys. Substantial work in the last 15 years on wrought HSLA steels and some European work on cast HSLA steels (27) has demonstrated the properties obtainable and the complexity of the metallurgical reactions taking place. Conventional cast steels use carbon as the primary strengthening agent. However, micro-alloyed steels with low carbon contents ($\sim 0.1\%$ C) take advantage of ferrite strengthening, ferrite grain refinement, and precipitation hardening schemes enhanced by small amounts of the alloying elements N, V, and Nb in addition to strengthening from carbon. A recent review by Bechet and Rohrig has summarized structure/property/processing relationships for HSLA cast steels (27).

In brief, exceptional mechanical properties are the result of a number of transformation reactions going on simultaneously during the heat treatment of HSLA steels. The austenitizing treatment normally used as a first step in the heat treatment of steels also acts as a solution heat treatment* for putting niobium and vanadium carbonitrides into solid

*A solution heat treatment is a common first step in the heat treatment of age-hardenable non-ferrous metals.

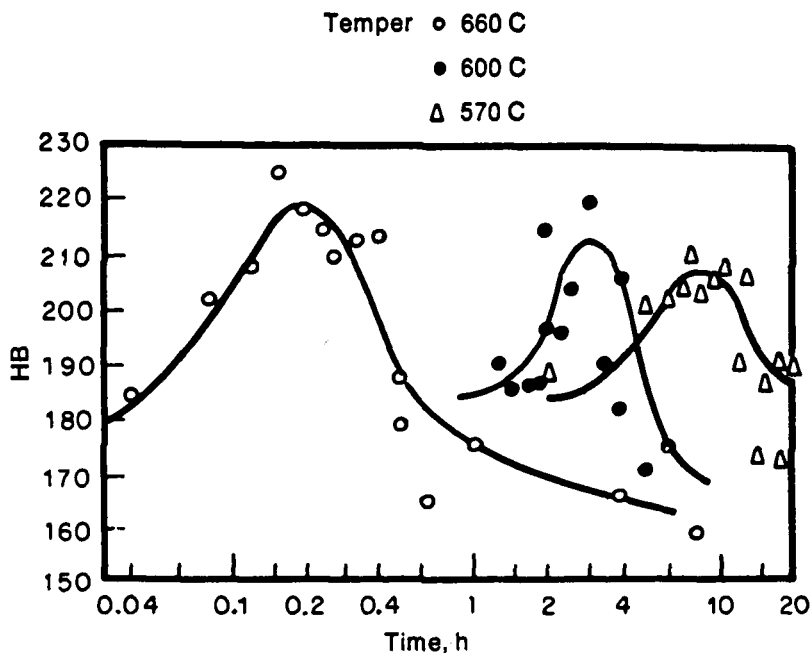


Figure 25. Effect of tempering time and temperature on the hardness of a niobium-vanadium HSLA cast steel. (27)

solution in the austenite. Quenching transforms the austenite to martensite and prevents the carbonitrides from forming initially. The subsequent tempering process not only transforms the martensite to ferrite and carbide (a softening reaction) but also causes a precipitation reaction resulting in an increase in hardness caused by the formation of a distribution of fine, submicroscopic, carbonitride precipitates that effectively strengthen the steel as it tempers, Figure 25.

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APPENDIX

The concepts of transformation reactions in cast steel have been briefly presented in a theoretical way using CCT diagrams. An understanding of these diagrams and a knowledge of the cooling conditions of a particular steel casting provides a direct link to the resultant microstructure and mechanical properties of that casting. In this appendix, a series of representative photomicrographs are shown that illustrate the effects of heat treatment cooling rate, casting section size, and alloy content

on the development of room temperature microstructures, Figures A1 through A6 (28). Additional photomicrographs further illustrating these same concepts can be found in references (11) and (28).



Figure A1 WCA steel, 1 in. thick, as-cast
ASTM A216 steel, grade WCA (0.2% C,
0.6% Mn, 0.5% Si) 1 inch thick section
Microstructure consists of pearlite,
blocky ferrite, and widmanstatten
platelets of ferrite.
As-cast structure

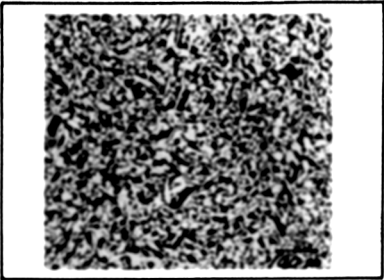


Figure A2 WCA steel, 1 in. thick,
normalized
Same steel as in A1, normalized
Microstructure consists of fine pearlite in
a matrix of ferrite.
As-cast structure is refined during heat
treatment. Air cooling produces ferrite
and pearlite.



Figure A3 WCA steel, 1 in. thick Q & T
Same steel as in A1, quenched and
tempered
Microstructure consists of extremely fine
pearlite with some ferrite, (note
magnification difference).
Rapid cooling rate, but not rapid enough
to form martensite upon quenching.

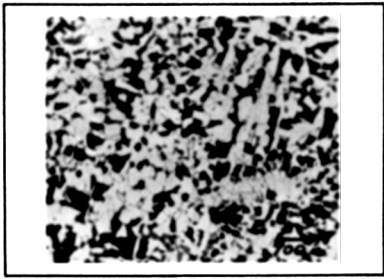
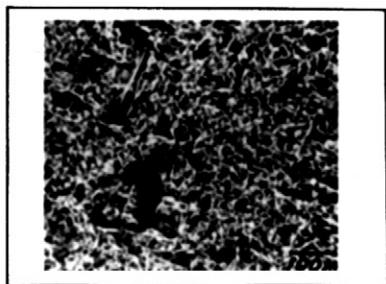
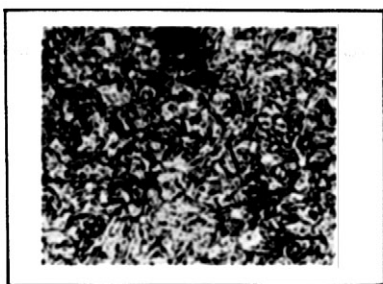


Figure A4 WCA steel, 6 in. thick,
normalized
Same steel as in A1, normalized as in A2,
from a 6 in. thick section.
Microstructure consists of fine pearlite in
a mixture of blocky ferrite.
Cooling rate is slower than in A2 resulting
in a coarse ferrite/pearlite structure.



*Figure A5 WCA steel, 6 in. thick, Q & T
Same steel as in A1, quenched and
tempered as in A3 from a 6 in. thick
section*

*Microstructure consists of fine-grain
ferrite with some platelets of
Widmanstatten ferrite and fine pearlite.
Cooling not as rapid as in A3 resulting in
fine ferrite and pearlite. Structure
indicates that the cooling rate was similar
to that of A2*



*Figure A6 LC3 steel, 6 in. thick, Q & T
ASTM A352 steel, grade LC3 (0.2% C,
0.6% Mn, 0.5% Si, 4.2% Ni) quenched
and tempered as in A5 from a 6 in. thick
section.*

*Microstructure consists of tempered
martensite. (Note magnification
difference.)*

*Higher hardenability of this alloyed steel
results in martensite upon quenching
even though the cooling rate was the
same as in A2 and A5.*

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Alloying Effects in Cast Steels

by Raymond W. Monroe

Steel castings are made of atoms of various elements arranged in more or less regular orders. The way the atoms group together to form crystals determines the microstructure and properties of the steel casting. The composition of the casting is the elements or kinds of atoms that make up the casting and is controlled by the charge make up, melting practice, alloy additions and deoxidation. The microstructure is the arrangement of atoms and is controlled by solidification conditions and subsequent heat treatments. The interaction between composition and processing is of fundamental importance in the production of steel castings. The understanding of these interactions allows appropriate selection and control of the composition and processing.

PROCESSING AND COMPOSITION

Processing in a steel foundry includes melting, pouring, heat treatment and welding. Each processing step interacts with the steel casting to change the composition or structure. The process and composition should work together to achieve the appropriate structure and properties for the service and design of the casting produced.

Melting

The single most determinative factor in the composition of steel castings is the charge make up. Atoms are not destroyed in an electric furnace. What is put into the furnace, is what comes out. In melting, some composition modification of the charge is possible by use of metal-slag interactions. What goes in, comes out; either in the metal composition or as slag.

After charging, including any furnace heel as part of the charge, metal/slag interactions, metallgas interactions, late or ladle alloying additions, and deoxidation are the only composition modifications.

The most influential melting practice that modifies the composition combines metal/slag and metal/gas interactions and is the oxygen blow. In earlier melting practices, oxygen was added to the heat as mill scale or iron ore and the reaction between oxygen and carbon to form carbon monoxide caused a bubbling reaction that was known as a car-

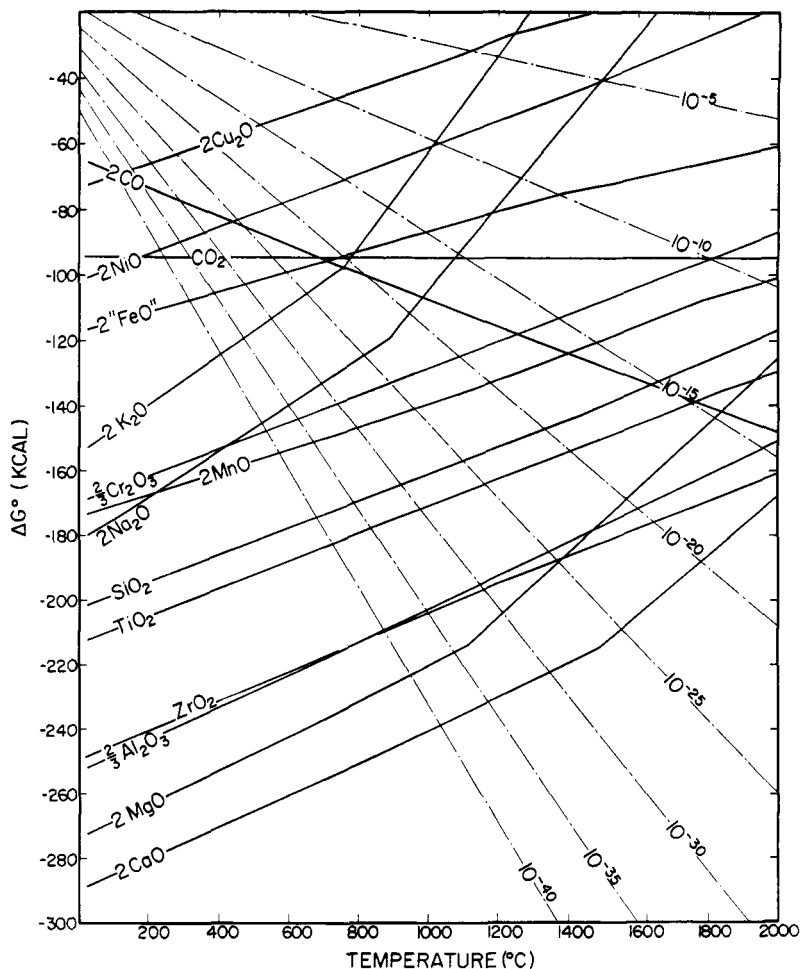


Figure 1. Solid curves showing standard free energies of formation of various oxides from the elements as a function of temperature, based mainly on data summarized by Coughlin⁽³⁾ and by Elliott and Gleiser.⁽⁴⁾ The curve for SiO_2 has been drawn on the basis of new data presented by Chipman.⁽⁵⁾ Light dash-dot curves are lines of equal oxygen pressures (atm) of the gas phase, as labeled on each curve.

bon boil. Now oxygen is injected into the melted heat to cause a much more vigorous stirring action. This oxidation period lowers the gas content of the heat and oxidizes into the slag elements which are more oxidizable than carbon. The gas contents of hydrogen and nitrogen, are reduced by combining with an existing bubble and floating out of the heat. The bubbles that are formed are primarily carbon monoxide. Any element in the heat that likes oxygen more than carbon reacts with the bubble to form an oxide and floats into the slag.

How much an element likes oxygen is measured by the thermodynamic stability of the oxide which is illustrated in Figure 1. The higher negative numbers show a greater oxide stability. Any element below another element likes oxygen better and will take it from the element above. At molten steel temperatures, about 2900°F (1600°C) any element below the $2C + O_2 = 2CO$ line will be completely oxidized out, including calcium, aluminum, magnesium and titanium. Elements which at 2900°F (1600°C) that are between the $2C + O_2 = 2CO$ line and the $2Fe + O_2 = 2FeO$ line will be partially oxidized during the oxidizing period. The closer to the $2C + O_2 = 2CO$ line the element is, the more oxidized it becomes. Silicon is essentially removed while chromium and manganese are only partially oxidized. Elements above the $2Fe + O_2 = 2FeO$ line at 2900°F (1600°C) do not oxidize and ride through the melting process unchanged. Elements that are not reduced include nickel, copper, cobalt, and tin. A summary of the effect of refining on composition is given in Table I.

Table 1. Effect of refining operations on materials present in the charge. (10)

Completely Recovered	Partially Recovered	Practically Eliminated
Copper	Sulfur	Zinc
Nickel	Phosphorus	Silicon
Cobalt	Manganese	Aluminum
Tin	Chromium	Titanium
Antimony	Carbon	Zirconium
Arsenic	Nitrogen	Magnesium
Tungsten	Hydrogen	Calcium
Molybdenum	Lead	
	Vanadium	

Lead and zinc are not oxidized out but have a low vapor pressure and are reduced in the heat by boiling them off. This is not particularly desir-

able from an overall viewpoint since the lead and zinc end up as oxides in the baghouse dust. Lead fumes can create a health problem in the foundry work environment especially around the furnace and also render the baghouse dust a toxic waste. Lead and zinc can be eliminated during melting but should be avoided in the charge.

Sulfur and phosphorus can be reduced in the heat through the metal/slag interactions. Melting practice can be basic, acid or neutral depending on the melting slag with:

$$\text{Basic Slag } \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2} > 1.2$$

$$\text{an Acid Slag } \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2} < 0.8 \text{ and}$$

$$\text{a Neutral Slag } 1.2 > \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2} > 0.8$$

Therefore, basic melting implies a slag with CaO greater than 50% normally with:

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2} = 2 \quad \text{to} \quad 3.$$

Basic practice is more expensive than acid but does allow removal of some sulfur and phosphorus. Double slag basic practice allows better removal, especially phosphorus, but increases the heat time and refining period and is prone to gas pick up. Inverse basic slag practice allows the reduction of gas content by having an oxidizing period after refining, but this increases heat time even more.

When the slag is reduced, i.e. low in oxygen, then the oxidized elements in the slag tend to return to the metal, e.g. chromium, manganese and phosphorous.

Pouring

Pouring includes deoxidation, late alloy additions, and solidification. The composition and cooling rate affect the as-cast structure that is the composition distribution that must be subsequently processed.

The role of deoxidation is to prevent pinholes due to carbon monoxide formation during solidification. Oxygen content should be less than 100 ppm to prevent porosity. Silicon and manganese are mild deoxidizers

and are added to stop the carbon boil and adjust the chemistry. Manganese and silicon additions are limited by other alloy effects and are normally inadequate to prevent pinholes.

Aluminum is the most used supplemental deoxidizer to prevent pinholes. As little as 0.01% aluminum will prevent pinholes. This is normally supplemented at the pour ladle with additional deoxidation, which could be more aluminum or calcium, barium, silicon, manganese, rare earths, titanium or zirconium as alloy combinations. More than the minimum amount of deoxidizer than is needed to prevent porosity, is needed to maintain sulfide shape control—but excessive amounts can cause intergranular failures or dirty metal. Nonmetallic inclusions that form during solidification depend on the oxygen and sulfur content of the casting. Deoxidation decreases the amount of nonmetallic inclusions by reducing the oxides and affects the type of sulfide inclusions. High levels of oxygen, greater than 0.012% in the metal, form FeO which decreases the solubility of FeMn-sulfides and the sulfides freeze early in solidification as globules. The use of silicon deoxidation alone normally causes the formation of globular sulfides, Type I as shown in Figure 2c. Decreasing the oxygen, between 0.008% and 0.012% in the metal, through the use of aluminum, titanium or zirconium, increases the solubility of the FeMn-sulfide so that they solidify last as grain boundary films as shown in Figure 2a. These grain boundary sulfide films, also

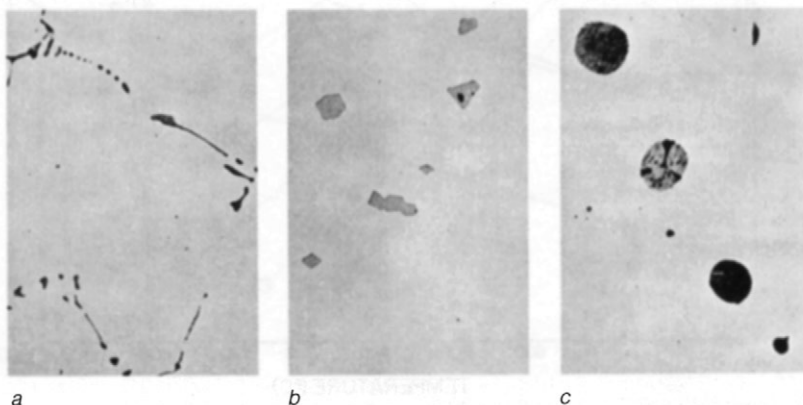


Figure 2. Sulfide inclusions in 0.35 percent carbon, 0.74 percent manganese, 0.39 percent silicon steel, (a) Type II, 0.009 percent aluminum residual content after deoxidation, (b) Type III, 0.030 percent aluminum residual content after deoxidation, and (c) Type I, silicon killed, 500X. (26)

known as Type II, have a very detrimental effect on the ductility and toughness of the steel. If the oxygen is very low, less than 0.008% in the metal, then the deoxidizer forms a complex sulfide that is crystalline and forms early in solidification. This crystallized sulfide, Type III, is less harmful than Type II but more harmful than Type I.

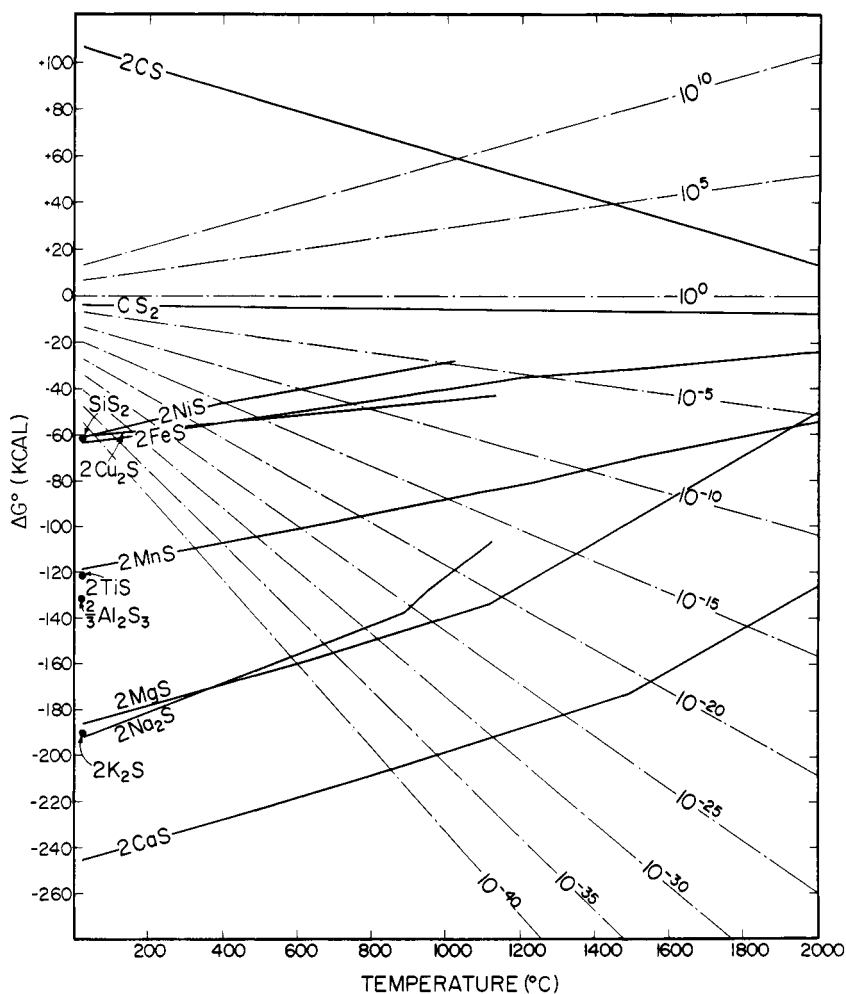


Figure 3. Solid curves showing standard free energies of formation of various sulfides from the elements as a function of temperature, based on data tabulated by Coughlin⁽³⁾ and by Elliott and Gleiser.⁽⁴⁾ Light dash-dot curves are lines of equal sulfur pressures (atm) of the gas phase, as labeled on each curve.

If a high level of rare earth metals ($Re/S > 1.5$) are added, then galaxies of sulfides form, Type IV but these are only for rare earth additions.

The relative stability of sulfides is shown in Figure 3. Manganese is added to all steels to form manganese sulfides or oxysulfides. Therefore, all the elements above the $2Mn + S_2 = 2MnS$ do not affect the sulfides formed. Aluminum would rather form an oxide and is close to manganese in desire for sulfur at room temperature and probably is above manganese at 2900°F (1600°C). Calcium is insoluble in iron and is strongly attracted to sulfur and therefore forms Type I sulfides, rare earths, like cerium, also form Type I.

Aluminum, titanium, boron and zirconium affect the sulfide form by their action on the oxygen content of the melt. As can be seen in Figure 4, the actual sulfide shape depends on the type and amount of deoxidizer. There are complex interactions, so care must be taken to avoid porosity and Type I sulfides.

Intergranular fracture, also known as chonchoidal or rock candy fracture, is normally caused by grain boundary films of aluminum nitride. Boron can also form grain boundary boronitrides or borocarbonitrides that can induce this type of fracture. Boron should probably not exceed 0.003% to avoid boron related intergranular fracture. Aluminum content should probably not exceed 0.06% to avoid aluminum nitride intergranular fracture.

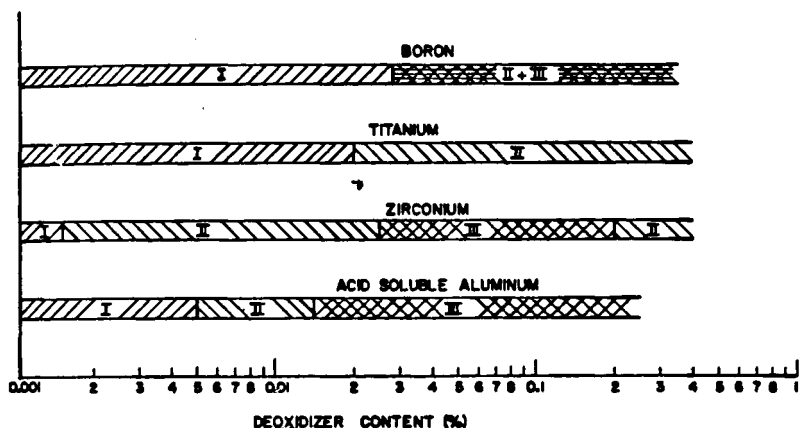


Figure 4. Effect of varying amounts of Al, Zr, Ti, and B on the type of sulfide inclusions in medium carbon steel (0.3 C, 0.6 Mn, 0.35 Si, 0.03 S, 0.013 P).

Aluminum nitride formation is most affected by the aluminum and nitrogen contents of the melt and by the cooling rate of the section as shown in Figure 5. Therefore, the problem becomes more significant the larger the casting section becomes. Heavy section casting deoxidation practice avoids the use of aluminum.

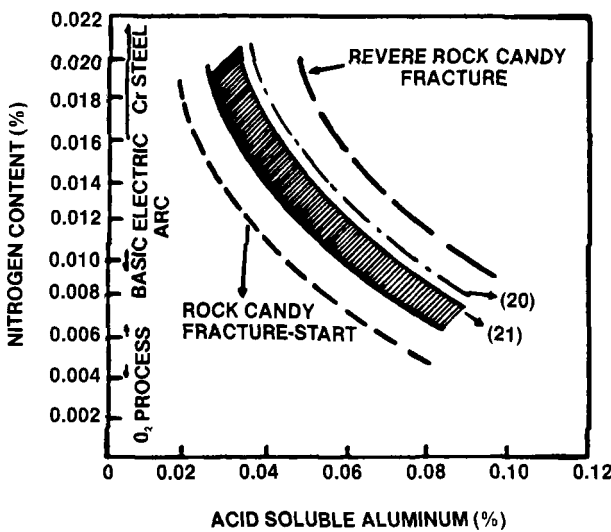


Figure 5. The relation of nitrogen content to the effect of acid soluble aluminum content on the incidence of rock candy fracture from aluminum nitride formation. (20)

The stability of various nitrides is shown in Figure 6. Zirconium and titanium are used in conjunction with aluminum because they like nitrogen better and can prevent aluminum nitride formation.

Therefore, deoxidation can be seen to substantially influence precipitation in the as-cast microstructures of oxides, sulfides and nitrides. These phases are not particularly affected by subsequent heat treatment so that care must be taken in melting and pouring to minimize their effect.

Other elements segregate such as carbon, manganese and phosphorus during solidification and the segregation is worse in larger castings. The largest concentrations of the segregated species are in the cast metal to solidify. This is hopefully in the riser but in a closely risered casting the segregation can occur at the riser contact and will greatly aggravate under riser cracking problems.

Heat Treatment

The as-cast steel casting may be the proper shape and composition but the coarse and segregated microstructure is unsuitable for most service conditions. The as-cast properties are relatively soft, low in ductility and toughness. Heat treatment can dramatically increase strength,

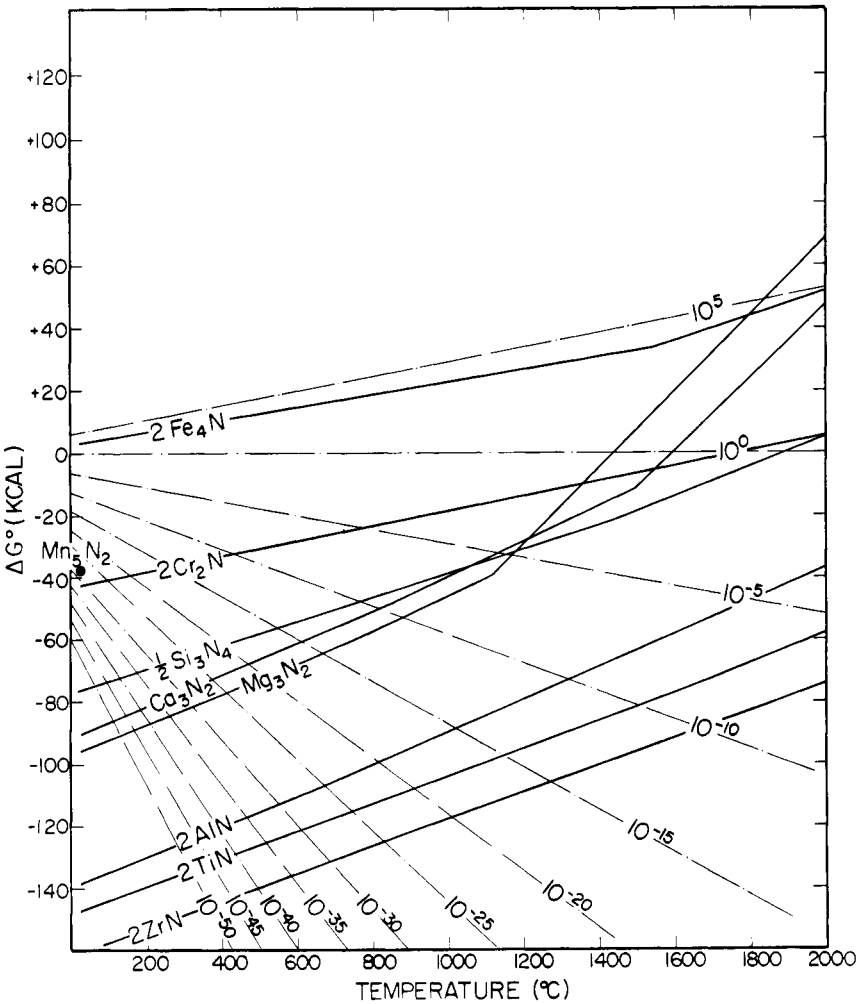


Figure 6. Solid curves showing standard free energies of formation of various nitrides from the elements as a function of temperature, based on data tabulated by Coughlin⁽³⁾ and by Elliott and Gleiser.⁽⁴⁾ Light dash-dot curves are lines of equal nitrogen pressures (atm) of the gas phase, as labeled on each curve.

ductility and toughness. Heat treatment of steel castings consists primarily of either normalizing or quenching followed by tempering. The composition chosen for the particular casting is generally chosen to give the properties desired based on the heat treatment and casting shape. Composition is then tied to properties obtainable by heat treatment in particular, strength and toughness.

Normalizing is intended to overcome the wide variety of microstructures resulting from mold and shakeout cooling. It is the most basic treatment and serves to bring the casting to a more constant condition. In plain carbon and low alloy steels, the predominant normalized structure is pearlite with variable amounts of ferrite. Fine pearlite sometimes provides the strength and ductility required for general duty and therefore, many castings are used in the normalized condition. The elevated

Table II Diffusivities of elements in γ - and α -iron

Solvent	Solute	Activation energy, Q (kJ mol ⁻¹)	Frequency factor, D_0 (cm ² s ⁻¹)	Diffusion coefficient, $D_{910^\circ\text{C}}$ (cm ² s ⁻¹)	Temperature range (°C)
γ -iron	C	135	0.15	1.5×10^{-7}	900-1050
	Fe	269	0.18	2.2×10^{-13}	1060-1390
	Co	364	3.0×10^2	24.0×10^{-12} (at 1050°C)	1050-1250
	Cr	405	1.8×10^4	58.0×10^{-12} (at 1050°C)	1050-1250
	Cu	253	3.0	15.0×10^{-11}	800-1200
	Ni	280	0.77	7.7×10^{-13}	930-1050
	P	293	28.3	3.6×10^{-12}	1280-1350
	S	202	1.35	1.5×10^{-9}	1200-1350
	W	376	1.0×10^3	12.0×10^{-12} (at 1050°C)	1050-1250
α -iron	C	80	6.2×10^{-3}	1.8×10^{-6}	
	N	76	3.0×10^{-3}	1.3×10^{-6}	
	Fe	240	0.5		700-750
	Co	226	0.2	2.1×10^{-11}	700-790
	Cr	343	3.0×10^4		
	Ni	258	9.7	3.7×10^{-11}	700-900
	P	230	2.9	2.0×10^{-10}	860-900
	W	293	3.8×10^{-2}		

Data from Askill, J., *Tracer Diffusion Data for Metals, Alloys and Simple Oxides*, IFI/Plenum, 1970; Wohlbier, F. H., *Diffusion and Defect Data*, Materials Review Series, Vol. 12, Nos. 1-4, Trans Tech Publications, 1976; Krishtal, M. A., *Diffusion Processes in Iron Alloys*, translated from Russian by A. Wald, ed. J. J. Becker, Israel Program for Scientific Translations, Jerusalem, 1970.

temperature properties of castings are also maximized by normalizing rather than quenching and tempering.

Normalizing is often seen as a homogenizing treatment. The diffusivities of various elements in austenite and ferrite are shown in Table II. As can be seen in Figures 7, and 8, very little diffusion or homogenization actually takes place at normalizing times and temperatures. Carbon and nitrogen diffuse 6 or 7 orders of magnitude faster than chromium or nickel so that relatively short times can homogenize the carbon and nitrogen content while impractically long times would be necessary to relieve any segregation of the chromium or nickel.

Longer normalizing times can benefit the toughness of heavy section castings. This does not occur by homogenization but through subtle modifications of second phase particles i.e., carbides, nitrides, sulfides and oxides. During long normalizing cycles small second phase parti-

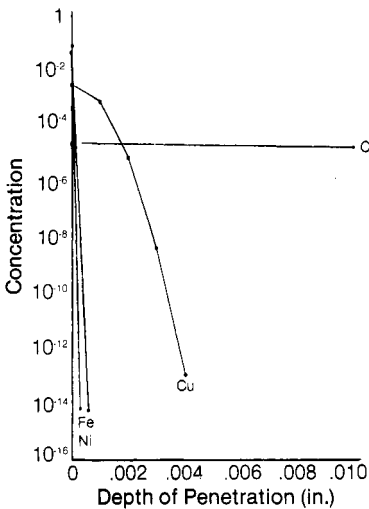


Figure 7. Depth of homogenization of various elements during a 910°C, normalize for 2 hours.

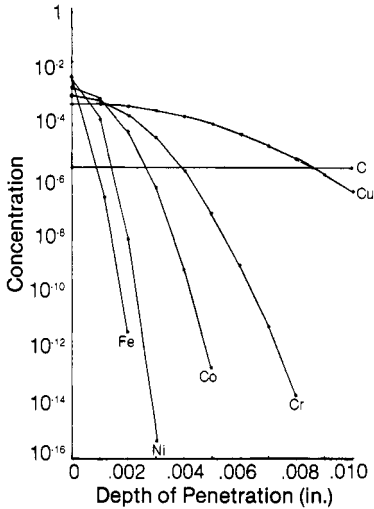


Figure 8. Depth of homogenization of various elements during a 1050°C, normalize for 20 hours.

cles are incorporated into the larger particles and the radius of any sharp edges on second phase particles is increased causing increases in toughness and ductility.

The strength of a normalized steel is based on the amount of carbides, the fineness of the carbides, the grain size and the solid solution strengthening of any alloying elements. Increasing the carbon content increases the amount of the carbides and is the single biggest contributor to strength of carbon and low alloy steels as seen in the hardness plot in Figure 9. This increase in strength is accompanied by an equally dramatic fall in ductility, toughness and weldability. Toughness and weldability are often more important properties than strength. The decrease in toughness with increasing carbon content is shown in Figure 10.

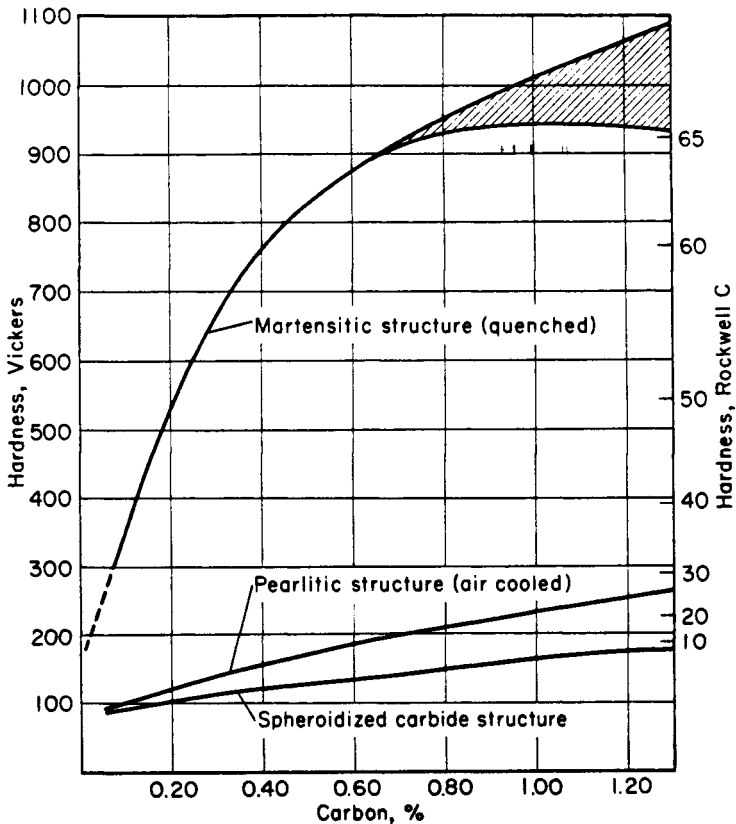


Figure 9. Approximate hardness of carbon steels in three microstructural conditions as a function of carbon content. (Top curve) Fully hardened martensite; (middle curve) lamellar structure (with proeutectoid constituents) as formed in normal cooling after rolling; (bottom curve) carbide coarsely spheroidized—minimum hardness commercially obtainable.

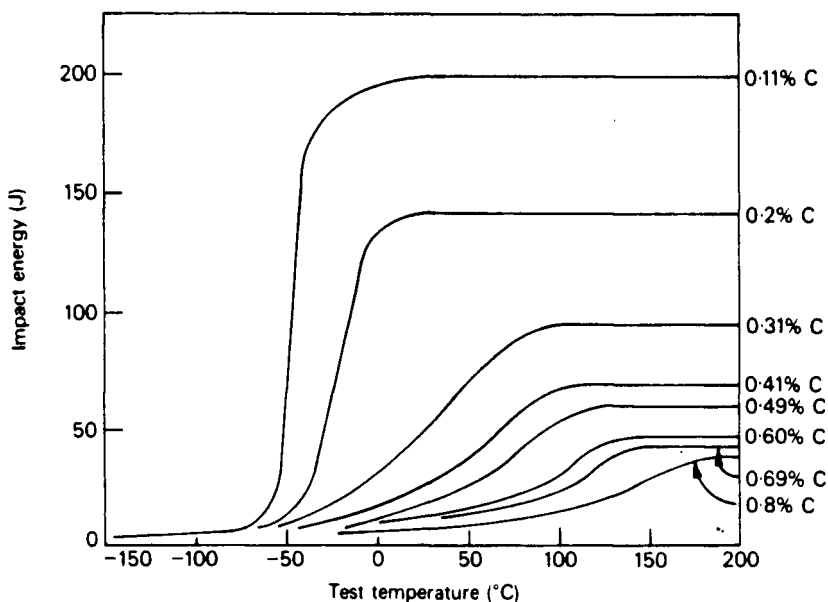


Figure 10. Effect of carbon content on the impact transition temperature curves of ferrite/pearlite steels (Pickering, In: Micro-alloying 75, Union Carbide Corporation, 1975).

Quenching is used to develop higher mechanical properties than attainable with normalizing, say above 140,000 psi tensile strength. Quenching also improves the toughness of low alloy steels at any strength level, and benefits even plain carbon steels not amenable to martensitic hardening, by producing finer pearlite.

Quenched and tempered materials provide a very useful mixture of toughness and strength. Alloying elements are primarily used to render alloys susceptible to heat treatment to form martensite or bainite.

The determination of composition is generally done in three steps. First, the strength and hardness requirements are used to pick a suitable carbon content based on the maximum hardness possible from Figure 9 less the amount of hardness to be lost tempering. Secondly, section size and quenching practice is decided which gives the hardenability needed in the steel. Finally, alloy elements are selected based on hardenability, cost, toughness, etc.

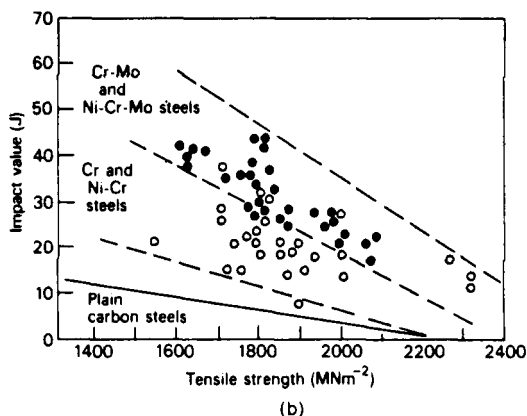
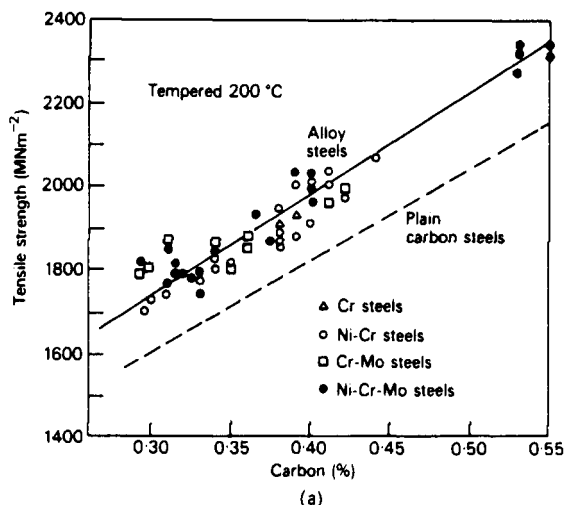


Figure 11. Comparison of mechanical properties of plain carbon and alloy steels tempered at 200 °C (Irving and Pickering, JISI, 1960, 194, 137): a; effect of C on tensile strength; b; relation between tensile strength and impact value. Note beneficial effect of Mo.

The influence of carbon on strength and toughness can be seen in Figure 11. As the strength and carbon increases, the toughness and weldability decreases. The heat treating effectiveness of the element is measured by its DI factor-the higher the factor is, the more effective the element is at preventing ferrite/pearlite and promoting bainite/martensite. In Table III, and Figure 12 are the alloy DI factors. Carbon is the

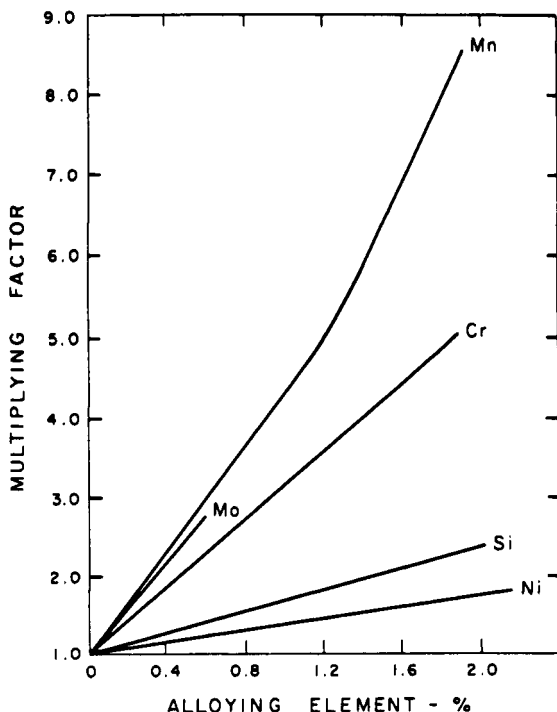


Figure 12. The effect of alloying elements on the hardenability index D for cast steel (2).

Table III Elemental Multiplying Factors

CARBON/GRAIN SIZE 7

Up To 0.40% Incl	MF = 0.54 (%C)
Over 0.40% To 0.55% Incl	= 0.171 + .001 (%C) + 0.265 (%C) ²
Over 0.55% To 0.65% Incl	= 0.115 + .268 (%C) - 0.038 (%C) ²
Over 0.65% To 0.75% Incl	= 0.143 + 0.2 (%C)
Over 0.75% To 0.90% Incl	= 0.062 + .409 (%C) - 0.135 (%C) ²

MANGANESE

Up To 1.20% Incl	= 3.3333 (%Mn) + 1.00
Over 1.20% To 1.95% Incl	= 5.10 (%Mn) - 1.12

SILICON

$$= 1.00 + 0.7 (\%Si)$$

NICKEL

$$= 1.00 + .333 (\%Ni) + .066 (\%Ni)^2 - .055 (\%Ni)^3 + .018 (\%Ni)^4$$

CHROMIUM

$$= 1.00 + 2.16 (\%Cr)$$

MOLYBDENUM

$$= 1.00 + 3.00 (\%Mo)$$

COPPER

$$= 1.00 + 0.365 (\%Cu)$$

VANADIUM

$$= 1.00 + 1.73 (\%V)$$

most effective element. Manganese, molybdenum, and chromium are especially effective in increasing hardenability. Copper and nickel do not provide very effective hardenability increases. Small additions of nitrogen, niobium and vanadium greatly increase the hardenability as shown in Figure 13. These small additions form the basis of microalloys.

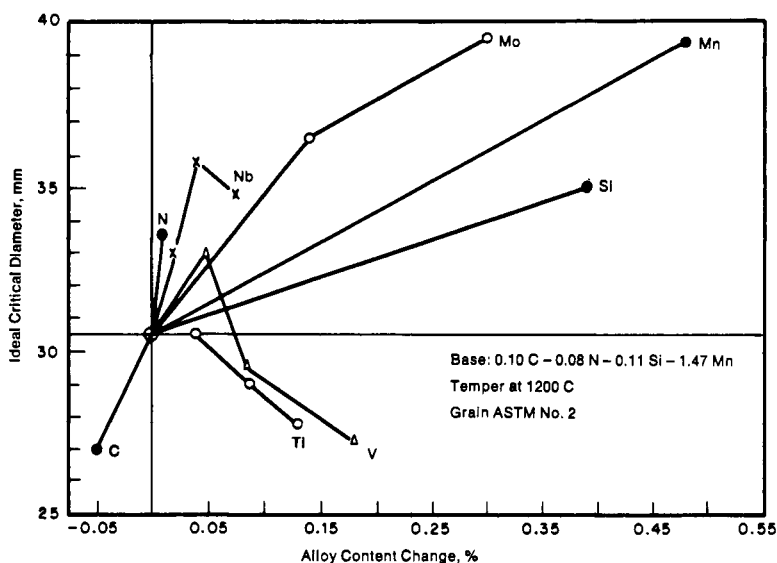


Figure 13. Effects of individual alloying elements on the hardenability of a carbon-manganese steel (43).

Tempering follows hardening and involves the decomposition of martensite into microstructures of fine carbide dispersions. Tempering heat treatments are commonly conducted to improve toughness. However, tempering in the range 500-1050°F generally does not benefit toughness even though strength is decreased. Tempering is also done after normalizing to improve toughness. Both the time and temperature of the temper is important to the properties developed.

The effect of tempering temperature is shown in Figure 14. Below 400°F (200°C) has little effect on the hardness or properties. Between 400-600°F (200-310°C), some softening begins to occur. Above 1100°F (600°C), softening occurs very rapidly. Carbon content, temperature and time are the main influences on the tempering response. Some elements inhibit the uniform softening response, like chromium or molybdenum shown in Figures 15 and 16.

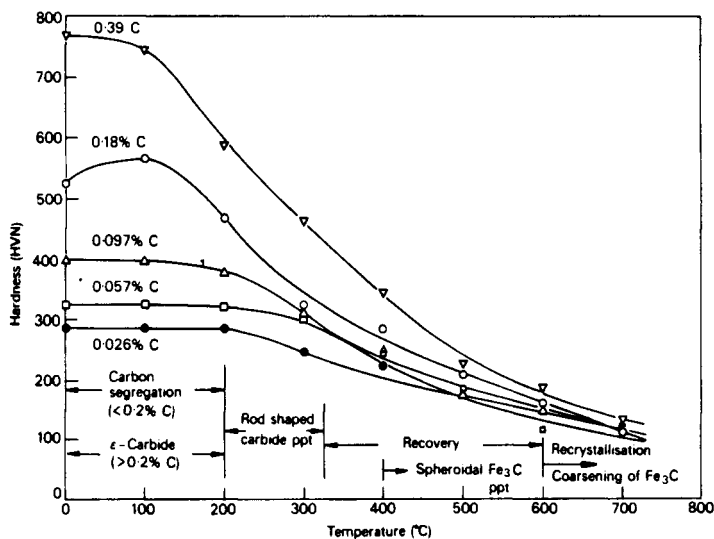


Figure 14. Hardness of iron-carbon martensites tempered 1h at 100-700 C (Speich. Trans. Met. Soc. AIME, 1969, 245, 2553).

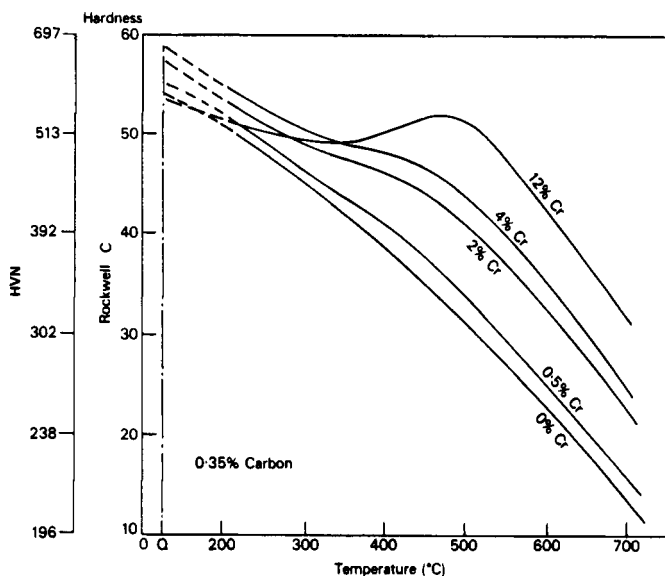


Figure 15. The effect of chromium on the tempering of a 0.35C steel (Bain and Paxton, The Alloying Elements in Steel, 2nd edition, ASM, 1961).

Tempering, especially for maximum toughness, should avoid two forms of embrittlement, one associated with 500°F also known as blue brittleness or temper martensite embrittlement (TME) and the other associated with 900°F also known as temper embrittlement (TE). TME is caused by the precipitation of carbides and is avoided by having enough alloy and carbon to avoid tempering in the 400-600°F range. TME is irreversible and only affects martensite structures.

TE is reversible and happens in the range of 800-1100°F. TE is caused

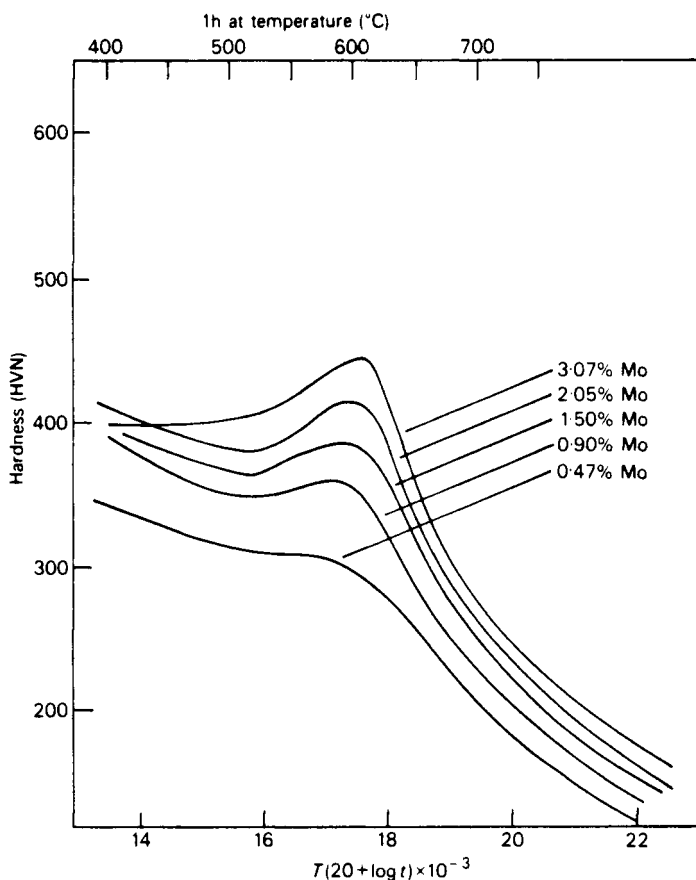


Figure 16. The effect of molybdenum on the tempering of quenched 0.1C steels (Irving and Pickering, JISI, 1960, 194, 137).

by a segregation of solute atoms to grain boundaries. Antimony, phosphorus, arsenic, tin and manganese all increase the susceptibility of an alloy to TE. Molybdenum decreases the susceptibility to TE. The effect of elements on TE is given in Table IV: TE is worst in martensite but can occur with bainite or even pearlite-ferrite materials. Tempering above 1100°F reverses the TE.

Table IV Effect of various impurity elements on embrittlement. (5)

Element	Specific Contribution to Embrittlement	Interaction with Other Elements	Effect of Interaction on Embrittlement
P	very strong	Mn Si Ni Cr Ni + Cr	— strong strong very strong
S	weak		
Si	weak (amount > 0.3%)	Mn	strong
Sb	strong	Cr Ni Mn Cr + Ni	strong strong very strong
As	weak	Cr Ni	weak weak
Sn	strong	Ni Cr Mn	strong strong
V	moderate		
W	moderate		
Rare earth elements	null	null	null
Zr, Te	null	null	null
Ni	weak	Cr Cr + P Cr + Sb Sn Ni Ni + Sn Ni + Sb	strong very strong very strong strong strong very strong very strong
Cr	weak		
Mo	beneficial	V	beneficial
Mn	strong	Sn As Sb Cr Ni	very strong strong very strong strong strong
C		unresolved	unresolved

Welding

Weld cracks are a result of the interaction of microstructure, hydrogen and stress. Preheat is used to reduce shrinkage stresses, slow cooling rate to form a softer microstructure and to slow cooling to allow the hydrogen a chance to escape from the weld area. The need to preheat is generally expressed as a function of metal chemistry such as:

$$CE = C + Mn/6 + Ni/15 + Mo/4 + Cr/4 + Cu/13$$

If CE is less than .45% then no preheat is required. If CE is between .45% and .60% then 200-400°F preheat is required. If CE exceeds .60% then 400 to 700°F preheat is required. Section size and geometry are also important.

COMPOSITION NOMENCLATURE

AISI/SAE has designations for major alloy groups for carbon and alloy steels. These steels have been identified in the AISI classification by a numerical index system that is partially descriptive of the composition. The first digit indicates the type to which the steel belongs; thus "1" indicates a carbon steel; "2" indicates a nickel steel; "3" indicates a nickel-chromium steel. In the case of the simple alloy steels, the second number usually indicates the percentage of the predominating alloying element. Usually the last two or three digits indicate the average carbon content in "points," or hundredths of a per cent. Thus, "2340" indicates a nickel steel of approximately 3 per cent nickel (3.25 to 3.75) and 0.40 per cent carbon (0.35 to 0.45).

Series Designation	Types
10xx	Carbon steel grades
11xx	Resulfurized carbon steel grades
12xx	Rephosphorized and resulfurized carbon steel grades
13xx	Manganese 1.75 percent
15xx	Manganese over 1.00 to 1.65
23xx	Nickel 3.50 percent
25xx	Nickel 5.00 percent
31xx	Nickel 1.25 percent—Chromium 0.65 percent
33xx	Nickel 3.50 percent—Chromium 1.55 percent
40xx	Molybdenum 0.25 percent
41xx	Chromium 0.50 or 0.95 percent—Molybdenum 0.12 or 0.20 percent
43xx	Nickel 1.80 percent—Chromium 0.50 to 0.80

	percent—Molybdenum 0.25 percent
44xx	Molybdenum 0.40 or 0.53
46xx	Nickel 1.55 or 1.80 percent—Molybdenum 0.20 or 0.25 percent
47xx	Nickel 1.05 percent—Chromium 0.45 percent—Molybdenum 0.20 percent
48xx	Nickel 3.50 percent—Molybdenum 0.25 percent
50xx	Chromium 0.28 or 0.40 percent
51xx	Chromium 0.80, 0.90, 0.95, 1.00 or 1.05 percent
5xxx	Carbon 1.00 percent—Chromium 0.50, 1.00 or 1.45 percent
61xx	Chromium 0.80 or 0.95 percent—Vanadium 0.10 percent or 0.15 percent min.
81xx	Nickel 0.30—Chromium 0.40—Molybdenum 0.12
86xx	Nickel 0.55 percent—Chromium 0.50 or 0.65 percent—Molybdenum 0.20 percent
87xx	Nickel 0.55 percent—Chromium 0.50 percent—Molybdenum 0.25 percent
88xx	Nickel 0.55—Chromium 0.50—Molybdenum 0.35
92xx	Manganese 0.85 percent—Silicon 2.00 percent
93xx	Nickel 3.25 percent—Chromium 1.20 percent—Molybdenum 0.12 percent
B	denotes Boron Steel, as in 51B60 and others.
BV	denotes Boron Vanadium Steel, as in TS 43BV12 and TS 43BV14.
L	denotes leaded steel, as in 10L18.

Many people order steel castings using these wrought designations. Most steel castings specifications allow the foundry to choose composition but many customers desire a specific steel that they have had good experience with. A real need exists for a comparable cast specification nomenclature to allow this freedom to order a cast composition equivalence with appropriate silicon and manganese.

A number of cast compositions are frequently used for specific service conditions. Some of these materials are listed in Table V. For general use, carbon steels or carbon manganese steels are weldable, reasonably tough and ductile. Increasing alloy elements allows quenching to form martensite which increases strength and toughness. As the section size increases, the alloy content must increase to assure through-hardening and good properties. Generally chromium, nickel and molybdenum are added to maintain hardenability, toughness and resistance to TE.

Table V Some Possible Materials For Selected Services

Use	MATERIAL		UTS	PROPERTIES		
	Spec.	Grade		YS	EL	RA
General	A27	60-30	60	30	22	30
	A27	70-40	70	40	22	30
NTor	A148	90-60	90	60	20	40
QT	A148	150-135*	150	135	7	18
	*Cast 8630					
Low Temp.	A352	LCA	60-85	30	13	-25
		LCC	70-95	40	13	-50
		CL2	70-95	40	15	-100
		LC2-1	105-130	80	30	-100
	ST -	A743 CF-8	70	30	50	-100
Elevated Temp. NT	A216	WCA	60-85	30	24	35
		WCC	70-95	40	22	35
		WC6	70-95	40	20	35
		WC9	70-95	40	20	35
		CA-15	90-115	65	18	30
	ST -	A351 CF3	70	30	35	—

Table V (continued)

		COMPOSITION			
C	MN	Ni	Cr	Mo	Others
.30	.60	—	—	—	—
.25	1.20	—	—	—	—
.30	1.25	—	—	—	—
.30	.7-.9	.4-.7	.4-.6	.15-.25	—
.25	.70	—	—	—	—
.25	1.20	—	—	—	—
.25	.50-.80	2-3	—	—	—
.22	.55-.75	2.5-3.5	1.4-1.8	.3-.6	—
.08	.5-.7	8-11	18-21	—	—
.25	.70	—	—	—	—
.25	1.20	—	—	—	—
.20	.5-.8	—	1.1-1.5	.45-.65	—
.18	.4-.7	—	2.0-2.75	.9-1.2	—
.15	1.0	—	11.5-14	—	—
.03	1.5	8-12	17-21	—	—

For low temperature service, nickel is added to increase the toughness as seen in Figure 17. Carbon, phosphorus and sulfur, content must be kept at a minimum. Quench and tempering produces the toughest material. If alloy steels are inadequate then the austenitic steels, high alloy, are used.

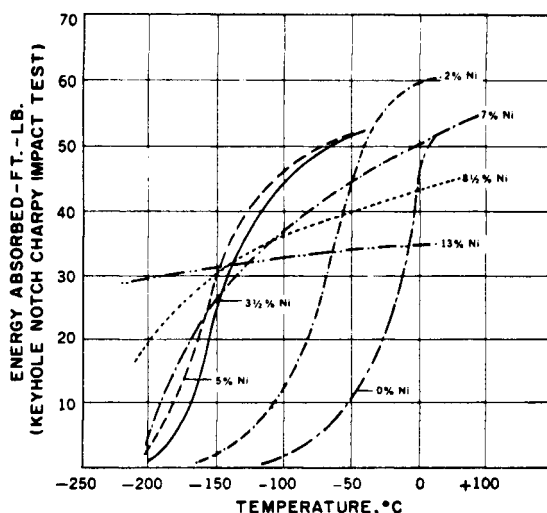


Figure 17. Effect of nickel on notch toughness of steel as a function of temperature. (Courtesy, International Nickel Company, Inc.)

For elevated temperature service, chromium and molybdenum are added to resist creep and to provide oxidation resistance as seen in Figures 18 and 19. Normalizing and tempering is used to provide optimum creep resistance. If alloy steels are inadequate then the austenitic steels, high alloy, are used.

ELEMENTAL COMPOSITIONAL EFFECTS

In order to understand the effects of each element on the final steel casting it is necessary to know its effects on each of the areas of interest including melting, pouring, heat treatment and welding. The element interacts physically with the iron structure based on its own crystal structure and atomic radius summarized in Table VI. If the crystal structure is different and the radius is more than 15% different then the element will have only limited solubility in the iron. Also included is the normal range to be expected in cast steels.

Table VI Elements Present in Cast Steels

Element	Symbol	Crystal	Ionic Radius	Solubility		Normal Range
				Austenite	Ferrite	
Aluminum	Al	FCC	1.43	1.1	36	.01-.08
Boron	B	Hex	.98	.021	.008	< .005
Calcium	Ca	FCC	1.97	~ 0	~ 0	< 0.10 added
Carbon	C	Hex	.91	1.8	.05	.1-.5
Cerium	Ce	FCC	1.81	~ 12	~ 12	< 0.10 added
Chromium	Cr	BCC	1.27	∞	13	< .2
Cobalt	Co	Hex	1.25	∞	75	< 8
Copper	Cu	FCC	1.28	8.5	1.4	< 1.5
Iron	Fe	BCC	1.26	—	—	—
Hydrogen	H	—	—	.0008	.0005	< .0005
Lead	Pb	FCC	1.75	~ 0	~ 0	< .01
Manganese	Mn	Cubic	1.26	∞	3	.3-2
Molybdenum	Mo	BCC	1.39	8	3.75	< 2
Nickel	Ni	FCC	1.24	∞	10	< 5
Niobium	Nb	BCC	1.46	2	.35	< .1
Nitrogen	N	—	—	.026	.001	.004-.010
Oxygen	O	—	—	~ .010	~ .010	.002-.010
Phosphorus	P	Cubic	1.28	.5	2.8	.010-.040
Silicon	Si	Diamond	1.32	9	18.5	.5-1
Sulfur	S	Cubic	1.27	~ .025	~ .025	.002-.040
Tantalum	Ta	BCC	1.46	6.5	0.02	< .1
Tin	Sn	Tetra.	1.62	~ 12	~ 12	< .02
Titanium	Ti	Hex	1.47	.75	6	< .02
Tungsten	W	BCC	1.39	6	4.2	< .10
Vandium	V	BCC	1.34	4	∞	< .10
Zirconium	Zr	Hex	1.60	.7	.3	< .20

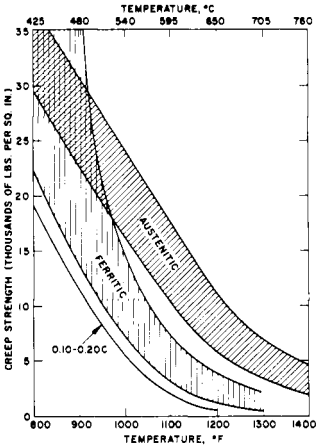


Figure 18. Creep strength of various steels between 800 and 1400°F

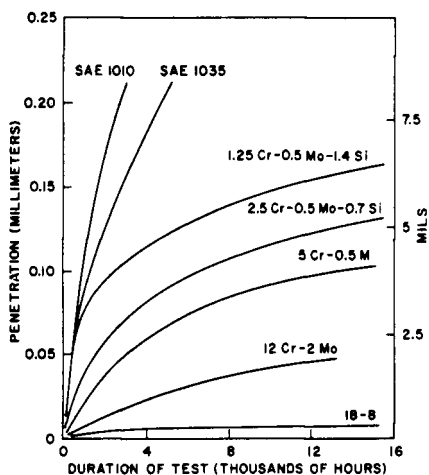


Figure 19. Effect of long-time exposure to steam at 595°C (1100°F) on steel bars. (After Rohrig, et al: see bibliography.)

Aluminum

Melting—Residual aluminum is essentially eliminated during the oxidation stage of melting.

Pouring—Aluminum is widely used to prevent the porosity that would be a result of only silicon-manganese deoxidation practice. Aluminum must only be greater than 0.01% to prevent porosity, but also must be over 0.02% to prevent Type II sulfides and under 0.06% (or lower in larger section sizes) to prevent rock candy fracture. Aluminum recovery ranges from 30-50% and about 2 lbs./ton at tap is normally added. Final deoxidation at the pouring ladle can be 1--1-1/2 lbs/ton of aluminum but some other element is often used. Excessive aluminum deoxidation also decreases the fluidity of the metal, causes difficult to machine alumina particles (optimum content 0.02%) to form just below the cope surface, and causes the formation of mixtures of Type I and II inclusions. The optimum range appears to be 0.02-0.05% aluminum.

Heat Treatment—Aluminum as aluminum oxides or nitrides are used to prevent grain growth during austenitization in wrought steels. In cast steels, the absence of cold work prevents the breakup of the aluminum nitride network formed on solidification that causes embrittlement. Higher aluminum contents do cause grain refinement in cast steels but care must be taken to avoid excess. Aluminum contributes very little to the hardenability of an alloy. Higher aluminum contents degrade creep resistance.

Aluminum is also added to form wrought steels susceptible to surface nitriding. The high aluminum requirements, 0.4-1.5%, prevent this kind of material from being cast.

Boron

Melting—Boron is eliminated by oxidation during melting.

Pouring—Boron reacts strongly with oxygen or nitrogen and must be protected to insure appropriate addition. Boron additions are made in conjunction with other deoxidizers to try to maintain consistent results. Inconsistent recovery and difficulty of analysis along with unacceptable brittleness at high boron levels, prevents more utilization of boron as an alloying element. External refining techniques may renew interest in boron.

Heat Treatment—Boron is added to steels because of the large increase in hardenability for a small amount. Boron must be in excess of .0003% for an effect on hardenability but should be less than .005% to avoid intergranular fracture from borocarbides or borocarbon nitrides.

The effect of boron on hardenability depends on the composition and base hardenability of the alloy. Low-carbon, low-hardenability steels show the most effect with high carbon, high hardenability steels can show almost no effect. Heat treatment conditions also has an effect on the boron influence. The optimum boron range for hardenability is 0.0003 to 0.0030%. Boron does not retard tempering.

Calcium

Melting—Calcium is eliminated by oxidation during melting.

Pouring—Calcium is used to desulfurize in external processes and to control sulfide shape. Calcium is insoluble in steel and has a low boiling point which makes it somewhat difficult to add and control in pouring practices. Addition of .05 to .1 % calcium tends to control sulfide shape to Type I. Addition of calcium is also reported to improve the machinability of cast steel by softening the cope side nonmetallic inclusions. High levels of calcium tend to cause formation of a granular nonmetallic in the nozzle of bottom pour ladles which reduces pouring rates and can lead to leaking ladles.

Heat Treatment—Calcium is insoluble in iron and does not affect the heat treated properties. Calcium does improve ductility and toughness but only because of the sulfide shape control.

Carbon

Melting—Carbon combines with oxygen to form carbon monoxide which provides the boiling action during the oxygen blow. Carbon should be .30 to .50% higher than the desired final composition at melt in to provide sufficient carbon to boil. Boil should reduce carbon content to the desired final compositional level.

Pouring—Final adjustment of carbon can be accomplished through a ladle addition. Carbon level does affect the oxygen level and therefore the effectiveness of other deoxidizers.

Heat Treatment—Carbon is the single biggest determinant of steel properties. Carbon level sets the hardness and tensile strength that can be achieved as well as the ductility and toughness. Carbon increases susceptibility to weld cracks and quench cracks particularly above 0.30%. For this reason steel castings are generally made at or below this level. High toughness materials require even lower carbon levels of .15% or less. Higher carbon levels than 0.30% are common but suffer from increased cracking and decreased ductility and toughness. However, higher carbon levels do increase strength and hardness which may be the dominant factor in some applications such as wear.

Other alloys are always studied in conjunction with carbon content. Carbon content does not retard tempering.

Cerium

Melting—Cerium is eliminated by oxidation during melting.

Pouring—Cerium and rare earth (RE) mixture have many technical merits to recommend their use as deoxidizers and sulfide shape controllers. RE combines with sulfur to form Type I sulfides except at high RE levels, $RE/S > 5$, where Type IV sulfides are formed. Cerium and RE are very expensive and must be protected from oxygen to be effective. RE has not been used very much in the steel foundry industry.

Heat Treatment—Like calcium, RE metals do not affect heat treat response but do improve toughness and ductility through sulfide shape control.

Chromium

Melting—Chromium is partially lost from oxidation in melting. Deoxidation of the furnace slag in basic or AOD practice can recover a great deal of the chromium that was lost to the slag.

Pouring—Chromium containing steels are more susceptible to gas pickup so that the time from the oxidation/boil till pouring should be minimized and exposure to humidity or air should also be minimized. Chromium as an alloy addition can be made effectively to the ladle after deoxidation with little loss.

Heat Treatment—Chromium enhances the properties of steel in a number of ways. Chromium is not an effective solid solution strengthener but does refine the pearlite structure and retard pearlite/ferrite formation allowing increased through-hardening. Chromium is primarily added to increase the hardenability. Chromium increases corrosion resistance markedly and also improves heat and creep resistance. Chromium does not generally reduce ductility or toughness any more than the increase in strength would indicate. Improved toughness is generally gained by the use of nickel with chromium.

Chromium does retard tempering and increased chromium increases tempering resistance. Chromium also increases susceptibility to temper embrittlement so that molybdenum is often used with chromium to prevent this.

Cobalt

Melting—Cobalt level is relatively unaffected by the melting process. Cobalt is not reduced in melting or refining.

Pouring—Cobalt is not added to cast steels.

Heat Treatment—Cobalt is not used as an alloy in cast steels but may be permitted up to 0.20%. It increases tensile strength but decreases hardenability and hardness during tempering. It does improve corrosion and wear resistance.

Copper

Melting—Copper does not oxidize during melting.

Pouring—Copper has no effect on pouring. Copper along with nickel has been implicated in surface craze cracks especially in mold systems catalyzed with sulfur containing acids. It has also been implicated as contributing to hot tear formation.

Heat Treating—Copper has a relatively small effect of increasing hardenability. Precipitation hardening is possible in copper containing steels with copper contents more than 0.6%. This requires a solution treatment that can be normalizing or quenching with a subsequent aging treatment at 850°F (450°C). Copper is commonly added to improve corrosion resistance in the atmosphere especially from .15 to .75%. With more than 8% copper, the steel is brittle forming a grain boundary copper rich phase.

Hydrogen

Melting—Hydrogen can be introduced during melting from the charge, water of hydration in the refractories or exposure to humid air. The hydrogen level is reduced during the oxidation/boil period but begins to increase immediately afterwards.

Pouring—External refining techniques that employ bubbling with inert gas can reduce hydrogen. Gas that has a high dew point used to bubble and agitation cause excessive exposure of metal to the atmosphere, can increase hydrogen pickup. Hydrogen in the metal plus that picked up in the pouring and from the mold can result in pinholes if the local hydrogen exceeds .0008%. No element forms a stable compound with hydrogen so that no deoxidation practice can eliminate its effects.

Heat Treatment—Excessive hydrogen, above .0004% can cause poor ductility, although it will have little effect on toughness. Hydrogen can be reduced by thermal treatment, for example, 12 hours at 400°F with moderate section sizes. Increased section sizes require more time, higher temperatures or both.

Lead

Melting—Lead can be eliminated from the heat.

Pouring—Lead is insoluble and was added to some steel for machinability but is toxic and is no longer used.

Heat Treatment—Lead has the effect of slightly decreasing hardenability.

Manganese

Melting—Manganese is eliminated by oxidation during melting. Some manganese is recovered from the slag in basic practice after deoxidation. Manganese, along with silicon, is added to stop or block the carbon boil.

Pouring—Manganese is a weak deoxidizer. Its main function in solidification is to combine with sulfur to prevent grain boundary iron sulfide. The manganese should be at least 20 times the sulfur content. Manganese above 2% causes segregation to increase significantly.

Heat Treatment—Manganese is a strong solid solution strengthener, a carbide former and a strong factor in increasing hardenability. Manganese and carbon are balanced to obtain the tensile strength, ductility and toughness required in carbon or carbon-manganese steels. Maximum toughness occurs when the ratio of manganese to carbon is 6 to 8 but more commonly used around 3 to 4. Manganese above 2% causes increased brittleness, grain growth, quench cracking, and decreases weldability.

Manganese increases susceptibility to temper embrittlement. To avoid this, molybdenum is added forming the manganese-molybdenum steel grades.

Molybdenum

Melting—Molybdenum does not oxidize during melting.

Pouring—Molybdenum does not affect pouring. It can be added to the ladle.

Heat Treatment—Molybdenum has a marked effect on the heat treatment response of steels. Molybdenum is very powerful in increasing the hardenability of an alloy, even stronger than chromium and like chro-

mium it retards the tempering of steels. Chromium and molybdenum are used together to produce alloys with good elevated temperature properties including creep strength.

Molybdenum is also used to retard temper embrittlement, e.g., manganese-molybdenum or chromium-nickel-molybdenum steels.

Nickel

Melting—Nickel does not oxidize during the melting.

Pouring—Nickel has no effect on pouring. It has been implicated in shallow surface cracks especially in mold systems catalyzed with sulfur containing acids.

Heat Treatment—Nickel is primarily used to increase the toughness of steels especially for low temperature service. It does not increase the hardenability of steel markedly, but does act as a solid solution strengthener increasing strength and hardness without decreasing ductility or toughness. Above 5% nickel, steel becomes too brittle for normal usage. Low carbon steels containing nickel, .1%C, 3%Ni, has a charpy v-notch value of 40-50 ft/lbs. at -75°C while without nickel the value would be about 10 ft/lbs.

Nickel does increase the atmospheric corrosion resistance of a steel. More than 1% nickel decreases the stress corrosion cracking resistance of low alloy steels in hydrogen sulfide and is therefore, excluded from use in sour gas service.

Niobium or Columbium

Melting—Niobium is eliminated by oxidation during melting.

Pouring—Niobium is not generally added during pouring, but if desired should be added after deoxidation.

Heat Treatment—Niobium is used with vanadium and nitrogen to create microalloyed steels. Niobium is used up to 0.10% but more typically about 0.05% to precipitate as a complex niobium carbonitride and strengthens the steel by precipitation hardening. Niobium increases the

creep resistance of steels. Niobium has the effect of slightly decreasing the hardenability of steels.

Nitrogen

Melting—Nitrogen can come from the charge but also from the disassociated nitrogen from the arc. Molecular nitrogen in the air must disassociate to dissolve in molten steel. It is removed from the heat during the oxidation stage.

Pouring—Nitrogen content must be kept below 0.01 % to avoid gas holes in casting. Some sand binders contain nitrogen that can dissolve in the metal and also form gas holes. Nitrogen generally precipitates during solidification. Aluminum nitride can form a continuous brittle network at grain boundaries leading to "rock candy" or intergranular failure. Titanium or zirconium will react with dissolved nitrogen to form particles and are used alone or with aluminum to avoid gas holes or intergranular failure from nitrogen.

Heat Treatment—Nitrogen is used with niobium and vanadium to strengthen microalloyed steels. The precipitation strengthening of these alloys depends on niobium and vanadium carbonitrides. Aluminum nitrides help avoid grain growth during heat treatment.

Oxygen

Melting—Oxygen is added to the molten steel bath during the carbon boil to rapidly accomplish the reduction of carbon to the desired level, reduce other soluble gases to acceptable levels, and eliminate undesirable oxidizable elements.

Pouring—To avoid gas holes and poor sulfide shape the oxygen content must be reduced before pouring the steel casting. This is accomplished by the addition of a deoxidizer such as aluminum, silicon, manganese, titanium, vanadium, calcium or complex mixtures of these and other elements. The oxygen content should be reduced below 0.01%.

Heat Treatment—Oxygen apparently has no effect on heat treatment but proper nonmetallic shape along with low levels insures the optimum ductility and toughness.

Phosphorus

Melting — Phosphorus can be reduced by basic practice especially using the double slag practice.

Pouring — Phosphorus segregates during solidification and can contribute to underlayer cracking.

Heat Treatment — Phosphorus increases strength and hardenability of steels. It is avoided in steel production since it reduces toughness and ductility of steels. Phosphorus has been identified as a major contributor to temper embrittlement.

Silicon

Melting — Silicon is oxidized during the melting procedures. Silicon along with manganese is used to block the heat, i.e., to stop the carbon boil.

Pouring — Silicon helps deoxidation. It is primarily used to enhance fluidity and generally is used at about 0.50%.

Heat Treatment — Silicon increases hardenability and strength but decreases ductility and toughness. Silicon increases the susceptibility to temper embrittlement.

Silicon increases resistance to corrosion especially in oxidizing hot environments.

Sulfur

Melting — Sulfur can be removed by basic practice or during external refining such as AOD or ladle desulfurization.

Pouring — Deoxidization practice determines sulfide shape and care must be exercised to avoid grain boundary films which have a detrimental effect on toughness and ductility. Manganese is added to ensure better sulfide shapes.

Heat Treatment — Sulfur is detrimental to the toughness and ductility of the steel and is generally kept as low as possible.

Tantalum

Melting — Tantalum is eliminated by oxidation during melting.

Pouring — Tantalum would have to be added with deoxidation to ensure recovery.

Heat Treatment — Tantalum is similar to niobium in increasing creep resistance, decreasing grain size and increasing strength.

Tin

Melting — Tin is not oxidized or reduced during melting.

Pouring — Tin has no effect on pouring or solidification.

Heat Treatment — Tin increases strength and hardenability but is not used due to the loss of ductility. Temper embrittlement is greatly increased by tin and molybdenum does not counteract it in this case. Therefore, tin is very undesirable.

Titanium

Melting — Titanium is eliminated by oxidation during melting.

Pouring — Titanium is used to deoxidize steel and is effective at combining with nitrogen. It must be used less than 0.02% to avoid intergranular sulfides.

Heat Treatment — Titanium helps control grain size and can be used with aluminum. It can contribute to hardenability if dissolved into the steel but the steel must be heated above 1800°F: Below this temperature the titanium carbide is not dissolved and decreases hardenability. The amount of titanium allowed in steel castings is low and does not appreciably affect heat treated properties.

Tungsten

Melting — Tungsten is partially oxidized during melting and is not generally present in the charge.

Pouring — Tungsten has no effect on pouring or solidification.

Heat Treatment-Tungsten forms strong stable carbides that require a long time at high temperatures to dissolve. If dissolved, tungsten increases the hardenability but if not dissolved, tungsten carbides decrease the hardenability. Tungsten is not generally used in cast steels due to cost. Tungsten retards tempering.

Vanadium

Melting—Vanadium is eliminated by oxidation during the melting.

Pouring—Vanadium can be added with or after deoxidation as an alloy element.

Heat Treatment-Vanadium significantly increases hardenability at relatively low levels of addition. Vanadium retards tempering. Vanadium is used to give additional creep resistance to chromium and chromium-molybdenum steels.

Zirconium

Melting—Zirconium is lost by oxidation during melting.

Pouring-Zirconium can be added after aluminum to prevent "rock candy" or by itself as a deoxidizer.

Heat Treatment-Zirconium promotes grain refinement and hardenability. Zirconium can help creep resistance in conjunction with nitrogen.

CONCLUSION

In Creation, God commanded Adam to subdue the earth and have dominion over it. When we use our knowledge and labor to control the composition, shape, and processing to make high quality steel castings that are suitable in service, we are subduing and exercising dominion over the earth.

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Melting and Deoxidation of Cast Steels

by Dr. John M. Svoboda*

INTRODUCTION

The steel melting process as performed by the foundry is basically a re-melt process and consists of two separate operations. First is the conversion of raw materials to molten metal, while the second is the refining of the molten metal to meet certain chemical analysis and other quality specifications. The aim of any steelmelting process is to produce a heat of material with the desired engineering properties at the lowest cost. These properties depend on the control of many parameters, among the more important being:

1. Carbon
2. Silicon
3. Manganese
4. Sulfur & Phosphorus
5. Other Alloying Elements
6. Temperature

Let us begin with a review of the main steps in the process of producing a heat of steel.

The first step in the process is to introduce the charge materials into the furnace. This usually consists of purchased scrap and foundry returns, since few foundries have a source of "hot metal" from a blast furnace.

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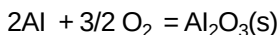
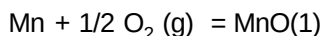
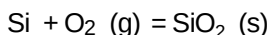
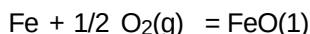
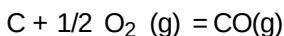
The main types of furnaces used in foundries are either the direct arc (acid and basic) and coreless induction. In addition, alloy additions are introduced in some cases and flux and slag forming materials are also introduced.

Next the charge is melted and various oxidizing reactions occur during this period. Gases may be absorbed by the molten metal, and various reactions occur between the metal and the slag which is forming during this period.

Following melt-down, we go into the refining period. It is during this stage that the carbon content is reduced by reaction with oxygen . . . usually in gaseous form. Hydrogen and nitrogen are removed (to a degree) by this carbon-oxygen reaction called the carbon boil. Other reactions occur between the metal and slag which may remove sulfur and phosphorus in basic practice. At the end of the refining period, final alloy additions may be made and chemical analysis and temperature adjusted to the desired level.

The heat is tapped and deoxidation additions introduced. Since cast steel receives no mechanical work following solidification, it is essential that the metal be “dead killed.” This is a basic difference from steel production for ingot use, and will be discussed in more detail in the body of this lecture.

The principal reactions which take place during these stages of the steelmaking operation are as follows:



In addition, it is becoming popular to employ an external refining process such as AOD (argon/oxygen/decarburization) or ladle refining to improve properties. These techniques also will be discussed further.

This lecture has been divided into two parts for convenience. The body of the paper will discuss the step-by-step procedures important to the production of quality cast steel. Appendix A covers the metallurgical

chemistry involved and is included for the reader who wishes to pursue the topic in more depth. Each of the major processes will now be considered.

ACID MELTING PRACTICE

The purpose of this section is to consider the acid practice for steel melting with regard to the operations involved and controls required. The term acid practice implies that the bath is contained by acid refractories (silica) and that the slag developed is acid in chemical behavior. As stated previously, sulfur and phosphorus cannot be removed to any significant degree in the acid practice, and this results in the need for careful control of the sulfur and phosphorus levels in the charge and slag making materials.

The Charge

The acid electric furnace charge usually consists of foundry returns, such as gates; risers, and scrapped castings, and purchased scrap. The purchased scrap may be forgings, springs, rails, stampings, and other such materials.

It is essential that the scrap be low in sulfur and phosphorus content, and should be purchased on this basis. Basic electric and BOF steels are excellent charge materials.

The amount of foundry returns charged is usually 30-40%¹ of the charge. Up to 100% foundry returns may be used if the chemical analysis is carefully controlled.

The scrap should be below 0.05% for both sulfur and phosphorus because many steel specifications set maximum limits of 0.05 % and oxidation losses tend to concentrate the sulfur and phosphorus to a slight degree. In addition, other residual elements should be controlled in order to prevent complications during heat treating or welding. The principal residuals and their sources are in Table I.

The residuals which are contained in the charge may be picked up by the slag, absorbed by both metal and slag, picked up by the metal, or vaporized. The various residuals exhibit the behavior shown in Table II.

Since most steel foundries produce a large number of alloy types and grades, a good identification system is required for foundry returns.

Table I Sources of Residual Elements²

- a. Sulfur
 - 1. Free machining steels
 - 2. Boiler tubes
 - 3. Rubber
 - 4. Cutting oil
 - b. Phosphorus
 - 1. Cast iron
 - 2. Pig iron
 - 3. Motor blocks
 - c. Copper & Tin
 - 1. Electrical equipment
 - 2. Bearings—Bushings
 - 3. Unprepared auto scrap
 - 4. Non-ferrous materials
 - d. Chromium, Nickel, Molybdenum, Tungsten, Cobalt
 - 1. Stainless steel
 - 2. Alloy steels
 - 3. Auto bumpers
 - 4. High-temperature alloys
 - 5. Tool steels
-

Table II Behavior of Residuals²

- | | |
|--------------------------------|------------|
| 1. Picked up by the slag: | |
| Calcium | Titanium |
| Magnesium | Zirconium |
| Boron | Silicon |
| Lanthanum | Vanadium |
| 2. Absorbed by slag and metal: | |
| Manganese | Tantalum |
| Selenium | Vanadium |
| Columbium | Beryllium |
| 3. Retained in the metal: | |
| Copper | Tin |
| Molybdenum | Arsenic |
| Cobalt | Silver |
| Tungsten | Antimony |
| Sulfur | Phosphorus |
| 4. Vaporized: | |
| Cadmium | Bismuth |
| Zinc | Lead |
-

Many scrapped heats have been produced because the wrong type of foundry returns were charged.

The size and physical condition of the scrap should also be carefully controlled. Popp² makes the following comments concerning visual scrap inspection. (1) Oversize scrap can cause furnace damage and delays, (2) Excessive rust can cause low metallic yield and a low melt-down carbon, (3) Excessive oil is a source of hydrogen and creates air pollution, (4) Sealed containers are a potential explosive hazard, possibly resulting in equipment damage and/or personal injuries, (5) Suspicious scrap should be unhesitatingly put aside since it can be the cause of contaminated heats, broken electrodes, and refractory problems, and (6) Siliceous material will increase slag volume.

Some foundries add 2 or 3 percent pig iron to the charge to insure a vigorous carbon boil after meltdown. This is usually done when the charge averages only 0.25-0.30% carbon. A low phosphorus grade of pig iron is available for this purpose.

The placement of the charge materials in the bucket also has an effect on furnace operations. A recommended makeup is illustrated in Figure 1. The bottom of the charge is made up of borings, turnings, and light scrap which acts as a cushion when the charge is dropped into the furnace. Next heavy scrap is placed in the electrode triangle which prevents the heavy scrap from falling against the electrodes. Above this are placed bundles and medium scrap which absorb heat and protect the sidewall. The top of the charge consists of borings, turnings, and light scrap which allow easy and fast electrode penetration which protects the roof and sidewalls from arc glare. A typical charge consists of

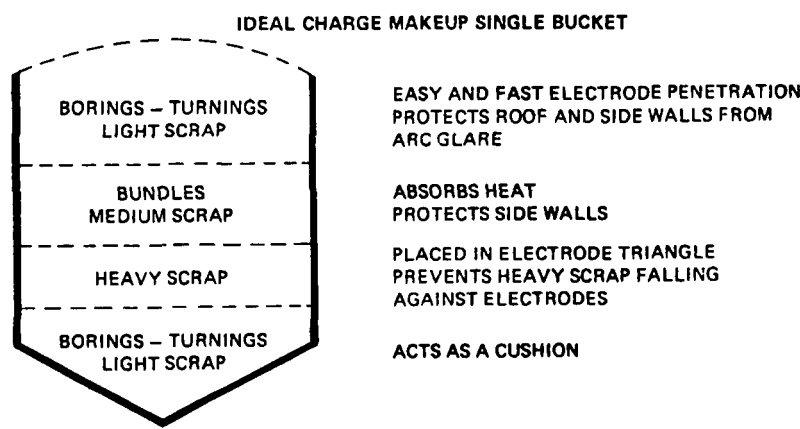


Figure 1. Ideal Charge Makeup of Single Bucket Charge.

35% heavy scrap (270-300 lb/cu ft), 40% medium scrap (100-150 lb/cu ft), and 25% light scrap (20-50 lb/cu ft).

Usually the entire charge is introduced at one time. However, if the available scrap is not dense enough, it may be necessary to add the second bucket (backcharge) after 60-70% of the first charge is melted.

It is common to aim for a melt down carbon 0.25-0.35 above the finish carbon level. Many foundries add carbon containing materials to the charge in order to obtain the carbon content after meltdown. Some carbon sources are pig iron, Sorel metal, coke, cast iron, broken electrodes, and commercial carbon raisers. The carbon content of any ferro alloy additions must also be considered.

Melting and Refining

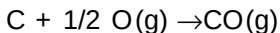
While other melting processes have been used over the years, the complete oxidation process is almost universally used at the present time, and will be the process discussed in this section. The complete oxidation process involves a vigorous carbon boil to remove hydrogen and nitrogen in order to meet metal specifications.

After the charge is introduced, melting begins at high voltages (tap settings). Some operators prefer to start melting at a moderate tap setting until the electrodes have bored into the charge, and then switch to a higher tap setting. The purpose of this procedure is to minimize sidewall exposure to arc flare. Slag-forming materials, other than sand adhering to gates and risers, are generally not added to the charge. After the charge is melted, the voltage is reduced and the refining period begins.

The melt-down carbon will range from 0.18-0.40 percent depending on the carbon in the charge. A recommended melt-down carbon is 0.30-0.35 percent greater than the desired finish carbon level, which is the carbon specification for the grade involved less the amount of carbon contained in deoxidizing and final alloy additions. The manganese content at melt-down will be 0.25-0.35 percent, and the silicon content will be 0.13-0.20 percent. If iron ore is added with the charge, the manganese and silicon contents will be lower depending on the degree of oxidation. They also will be more variable and difficult to control.

The carbon boil is next produced by introducing oxygen into the bath. The generally accepted practice is the injection of gaseous oxygen through a submerged lance inserted through the furnace door. The prin-

cipal reaction during the carbon boil is the oxidation of carbon to carbon monoxide:



The CO bubbles rising through the bath produce a vigorous bubbling action, which is called the “carbon boil.” As the bubbles rise through the bath, hydrogen and nitrogen dissolved in the bath diffuse into the CO bubbles and are removed. This is the only practical method of reducing dissolved hydrogen and nitrogen other than vacuum or AOD processing. The vigorous bubbling also provides a stirring action which helps produce a more uniform chemical composition and temperature distribution in the bath. Hydrogen and nitrogen will be discussed in detail later in the paper.

During the carbon boil, manganese and silicon will also be removed from the bath. Silicon content after the carbon boil will vary from about 0.02 to 0.10 percent, and manganese from 0.07 to 0.15 percent. Recommended aims at this stage are 0.08 percent silicon and 0.15 percent manganese. Manganese contents greater than 0.15 percent tend to inhibit gas removal because the manganese causes the boil to be less vigorous.

Normal practice is to reduce the carbon content 0.30-0.35 percent. For efficient hydrogen and nitrogen removal, the boil must be vigorous. This is a function of both temperature and blowing rate. Oxygen is blown through a mild steel pipe that is inserted through the furnace door and submerged below the slag-metal interface. It is important to control pressure and use the proper size pipe to insure standardized operation. Some of the factors which are important for a good oxygen blowing practice are:

1. Adequate pressure at the end of the hose for the heat size.
2. Proper size pipe.
3. Adequate oxygen supply system.
4. Continuous blowing.
5. Lance held at about 45° angle.
6. Lance tip in metal or at slag-metal interface.
7. Determination of volume of oxygen required.

Benefits obtained from a good oxygen blowing practice include?

1. Vigorous boil.
2. Optimum decarburization rate.
3. Optimum oxygen efficiency.
4. Increased metallic yield.
5. Increased refractory life.
6. Lower hydrogen and nitrogen content.

Many studies have been conducted on the optimum blowing rate. Barnsley and Thornton³ have derived an empirical formula for the optimum rate as follows:

$$\text{Max Blowing Rate (cu. ft./min.)} = 50 \times \text{Lance I.D. (in.)} \\ \times [6 + \text{bath wt. (tons)}]$$

The amount of oxygen required to remove various elements is given in Table III.

Table III Oxygen Requirements

Cu. Ft. per 0.01 % per Ton Steel	
Silicon	— 2.8
Manganese	— 0.70
Carbon	— 3.2
Chrome	— 0.74
Iron	— 0.69

As the carbon content drops, the efficiency of the oxygen blow also drops. Above a carbon content of 0.25 percent, oxygen efficiency is assumed to be 100 percent. As the bath carbon drops below this level, the oxygen blow efficiency drops as shown in Table IV

During the oxidation period (oxygen blow) silicon and manganese are oxidized as well as carbon. The oxidation of silicon occurs first, followed by manganese and then carbon as the temperature increases. The silica (SiO_2) and MnO rise to the top of the bath and join the slag. At this point, additional slag forming materials may be added, and the slag adjusted for composition. There is a wide variation in slag materials used

Table IV Oxygen Needed to Remove 0.01 % Carbon Per Ton of Melt

Bath Carbon	Above 0.25 % C, O ₂ Efficiency Assumed to be 100%	
	O ₂ , (Cu. Ft.)	Efficiency (%)
Above 0.25 %	3.2	100
0.25 %	4.0	80
0.20 %	4.7	68
0.15 %	6.5	49
0.10 %	10.0	32
0.075 %	15.0	21
0.05 %	24.0	13
0.04 %	32.0	10
0.03 %	57.0	6

by different foundries. Some add no slag-forming materials at all. It is generally felt that slag volume should be no more than about 6 % of the bath volume. Sand additions may vary between 0.2 and 2.0 percent. If limestone is used, the amount should produce a CaO content of the slag of about 6-8 percent. In some cases fluorspar is added to increase the fluidity of the slag.

Slag Control

Slag materials in the acid electric process are silicon dioxide, iron oxide and manganese oxide plus oxides of calcium and aluminum. The silicon dioxide (SiO₂) content of the slag comes from the erosion of the bottom, silica sand shoveled into the furnace and a small amount from the reaction of iron oxide and silicon to form SiO₂.

The calcium oxide (CaO) comes from the addition of lime or limestone. The manganese oxide (MnO) content of the slag is the product of the reaction of manganese and iron oxide. The percentage of MnO will depend on the percentage of manganese in the charge. The iron oxide content of the slag comes from the rust on the scrap and the oxidation while the steel is being melted. There are other elements in the slag such as aluminum oxide (Al₂O₃) and magnesium oxide (MgO). The latter elements are usually in small percentages, and are therefore of no concern to the makers of acid electric steel.

The use of the Herty viscosimeter is a practical way to measure slag fluidity. At the melt down, when the iron oxide content is approximately 40 to 45%, a slag test poured into the viscosimeter will run its full length.

During the boil, the FeO of the slag enters the metal to oxidize silicon, manganese and carbon. As these reactions occur, the percentage of iron oxide in the slag will decrease. The iron oxide will be reduced and left in the steel as iron, and the oxygen will combine with the silicon, manganese and carbon to form the corresponding oxides. The amount of FeO loss in the slag will depend largely on the amount of oxidation required to bring these elements down to the required chemical analysis. The slag begins to thicken as the SiO_2 content increases and the iron oxide content decreases. The addition of lime (CaO) to the slag results in the lime replacing some of the iron oxide without a loss of fluidity.

In summing up the effects of the constituents on slag fluidity, it can be stated that the higher the total percentage of basic materials in the slag, the higher the fluidity will be, and the higher the percentage of SiO_2 in the slag, the more viscous the slag.

It is very important in making steel in the acid electric furnace that the furnace operator knows the approximate analysis of the slag. If the heat melts down with a high SiO_2 content, it becomes very sluggish and instead of oxidizing a small part of the silicon, manganese and carbon on the meltdown, the melt will actually pick up silicon from the reduction of SiO_2 to Si.

In a heat of this type, it is very hard to get a vigorous boil. On the other hand, if the heat melts with an extremely high FeO content in the slag, over oxidation has taken place during the meltdown.

Some melters attempt to estimate the FeO content of the slag by pouring a slag cake test and observing the color of the skin and the fracture after breaking.

Slags containing more than 40% FeO exhibit a dull black color on both the surface skin and in the fracture. As the FeO content decreases to 30% the fracture has a grayish black color with a dull black surface.

Slag with 20 to 30% FeO has a dark green fracture and a dull black surface. As the iron oxide content falls under 20%, the fracture becomes a light green or a gray-green with the surface changing to a shiny black or a shiny dark chocolate brown. Slag colors change considerably depending on the MnO and the CaO content of the slag. The density of the slag-cake fracture is considered a better way to estimate the FeO content of the slag.

Additions

At this point, the alloy additions are made and allowed to dissolve in the bath. A "block," or partial deoxidation addition is usually added to stop the boil and prepare the heat for tapping.

The following procedure may be used to calculate the amount of alloy additions. The following information must be known in order to calculate the additions.

- A. Percent of alloy in ferro-alloy.
- B. Percent recovery expected.
- C. Amount of alloy (%) addition required.
- D. Weight of melted metal in furnace.

An example will be given for a chromium addition to a 10,000 lb. charge of Ni - Cr - Mo steel with a desired chromium aim of 0.70%. The analysis of the ferrochrome is 70% Cr. A recovery of 85% has been observed. If we assume a melting loss in the furnace of 3%, then the amount of molten metal in the furnace at the time of addition is 97% of 10,000 lb. or 9700 lb.

Then:

$$\text{Weight of addition} = \frac{D \times C}{A \times B} \times 100$$

$$\frac{9700 \times 0.70}{70 \times 85} \times 100 = 114 \text{ lb.}$$

By similar calculations, the weights of the other additions would be as follows:

Carbon as pig iron	263 lbs.
Manganese as 50% Ferrosilicon	107 lbs.
Silicon as 50% Ferrosilicon	69 lbs.
Nickel as 100% Nickel	133 lbs.
Molybdenum as Ferro-Molybdenum (62%)	40 lbs.

The total additions amount to 612 lbs. giving a total bath weight of 9700 + 612 = 10,312 lbs. Since this is significantly more than the 9700 lbs.

used for the original calculation, the additions must be recalculated on the new weight. For chromium, the calculation would be as follows:

$$\text{Weight of chromium addition} = \frac{10,312 \times 0.70}{70 \times 85} \times 100 = 122\text{lb.}$$

Deoxidizing and Tapping

After the addition of deoxidizers (block) and other additions the heat is ready for tapping. Final slag and temperature adjustments are made at this time. After the block is dissolved, the heat should be tapped as soon as possible as a deoxidized heat will pick up hydrogen and nitrogen. The elapsed time from the silicon addition to tapping should be a maximum of eight minutes, and preferably 5-6 minutes. Tapping is accomplished by rapidly tilting the furnace which allows the steel to be poured into the ladle. Rapid tilting allows the slag to be held back and the steel flows into the ladle first.

Alloys and final deoxidizers are added to the base of the metal stream in the ladle. Good tapping practice insures a compact metal stream, uniform tapping times, and slag-metal separation. This results in minimum re-oxidation of the metal, minimum nitrogen pickup, more uniform and higher alloy recoveries, simplified alloy addition practice, and agitation of metal in the ladle.

In order to obtain uniform alloy recovery, temperature control and chemical control, Popp² recommends:

1. Add ferroalloys in stream or base of stream.
2. Make proper sequence of additions:
 - A. Carbon.
 - B. Manganese and Silicon.
 - C. Calcium alloys.
3. Add all additions by the time the ladle is 75% full.
4. Minimize ladle additions.
5. Weigh additions accurately.
6. Use proper alloy sizing for heat size.

Control

Throughout the production of a heat various control tests are required. Slag is normally controlled by use of a Herty viscosimeter and/or slag pancake test. Chemistry is controlled with wet chemical analyses, air

and vacuum spectrometers, or direct reading instruments for carbon, silicon, sulfur, hydrogen, nitrogen, and total oxygen. Temperature is preferably measured with immersion thermocouples (Pt-Pt 10% Rh or Pt-Pt 13% Rh).

Summary

To summarize the process of producing a heat, a heat log of a Cr-Ni-Mo steel is illustrated in Figure 2. Although many variations to the procedures discussed do exist, they represent a normal practice as used by the majority of steel foundries.

MELTERS' REPORT ABC STEEL CASTING CO.								
Chemical Analysis								
Preliminary: C = .35					Mn = .20			
	C	Mn	Si	P	S	Cr	Ni	Mo
Aim	.40	.70	.45	.045	.045	.70	1.35	.25
Specified	.35/.45	.60/.90	.40/.50	.050 max.	.050 max.	.60/.90	1.25/1.50	.20/.30
Made	.39	.68	.47	.035	.042	.69	1.39	.23
METALS CHARGED				Power				
			Pounds					
Scrap - Foreign			6,025	Meter at End	56,580			
Scrap - Own			5,475	Meter at Start	53,760			
Iron Ore			150	Total KW Hours	2,820			
Total			11,650	KW Hours per Ton	512			
				Highest Demand	2,112			
Additions to Furnace			Time	Time Readings				
Ferromanganese	1:45 PM		131	Charging Time	10 Min			
Ferrosilicon	1:40 PM		84	Power on	12:05 PM			
Iron Ore	1:00 PM		200	Power off	1:50 PM			
Pig Iron	1:35 PM		327	Time of Heat	1 Hr. 45 Min			
Ferrochromium (6%C)	1:45 PM		141	Refractory Data				
Nickel	1:20 PM		162	No. of Heats from present lining	982			
Molybdenum	1:20 PM		49	No. of Heats from present roof	296			
Aluminum			16	No. of Heats from ladle No.	14			
Total Charge			12,760	Delays				
Material Used Other Than Metal			Pounds	Temperature 3170°F				
Carbon in charge			14	at 1:39 PM				
Lime or Limestone			40					
HEAT NO.			DATE	MELTER				

Figure 2. Log Sheet of a Chromium-Nickel-Molybdenum Heat Made in the Acid Electric Furnace.

BASIC MELTING PRACTICE

The basic electric melting process will be discussed in terms of operating practices and controls. Since many aspects of the basic practice are the same as those in the acid practice, only the differences will be pointed out and discussed. The term "basic practice" implies that the bath is contained in a basic refractory hearth, and that the slags used are generally basic in chemical characteristics. The principal reason for the use of the basic practice, rather than the acid practice, is that sulfur and phosphorus may be removed from the steel. This is required for the production of steels to specifications requiring low sulfur and phosphorus for improved impact properties. In some cases, the basic practice can be more economical for plain carbon grades where lower quality scrap may be upgraded. The basic practice is almost universally used for high alloy and stainless steels as well as manganese steel.

The Charge

The comments concerning charging practices in the acid furnace given previously also pertain to the basic operation. The charge generally consists of 20 to 50 percent foundry returns. The charge is generally limited to 0.10 percent phosphorus and 0.08 percent sulfur; and frequently will run at lower levels. If the charge is low in carbon, pig iron may be added to give a sufficient melt down carbon. Limestone or lime may be added to assist in the formation of a basic slag. A typical charge may consist of:

Foundry return scrap	30-50%
Purchased scrap	30-50%
Basic pig iron	5-15%
Limestone	6%

The choice of the use of limestone or lime is subject to many considerations. Popp² describes the advantages and disadvantages of the two materials as follows:

Lime

1. Accurate CaO content
2. Low SiO₂ content
3. Absorbs water

4. Tends to build up bottom
5. Tends to float in slag
6. Does not have to be calcined
7. Not considered source of oxygen

Limestone

1. CaO content varies
2. High, variable SiO_2 content
3. Does not absorb water
4. Does not build up bottom
5. Not likely to float in slag
6. Power needed for calcination
7. Source of oxygen with oxidizing power 2/3 of iron ore

The foundry returns (gates, risers, rejected castings) should be free of excess sand, since adhering sand will lower the slag basicity and reduce the dephosphorizing ability of the slag. All materials in the charge, and all additions, should be free from moisture to prevent hydrogen absorption by the melt. Some operators preheat all these materials before placing them in the furnace.

Melting & Oxidation

Meltdown is accomplished in the same manner as with the acid practice. The voltage is systematically reduced as the meltdown nears completion, and the lime or limestone added to give a CaO content equal to about 2.5 percent of the charge. If the meltdown carbon is too low, carbon should be added to insure a minimum of 0.30 percent above the finish carbon, or perhaps even 0.40 percent for high grade alloy steels.

The oxygen blow and resulting carbon boil occur in the same manner as in acid practice. Plain carbon steels are usually blown in one increment, while alloy steels are blown in two increments, thus allowing time for an interim chemical analysis. Often fluorspar additions are made during the blow to control the foaming of the slag and to provide slag fluidity. Addition of burnt lime is usually found necessary toward the end of the oxidizing period to maintain a highly basic slag. Popp² lists the function

of a basic slag as follows:

1. Removes phosphorus and sulfur
2. Prevents surface oxidation of the liquid metal
3. Protects refractories
4. Removes oxidizable elements
5. Assists in maintaining a stable arc

The oxidizing slag which develops during the carbon boil will usually be high in manganese and iron oxides. It will appear black and brittle when cold, and will be reasonably fluid. A slag which appears to be excessively fluid usually contains excessive amounts of silicates and insufficient calcium oxide. Burnt lime should be added to control the slag viscosity.

Refining — Single Slag Practice

Two common methods are used in the refining operation . . . the single slag practice, and the double slag practice. The double slag practice allows substantial sulfur removal, while the single slag practice allows only minor sulfur removal. However, the single slag practice produces steel with better fluidity and takes less time.

In the single slag practice the oxidizing slag developed during the boil is allowed to remain on the bath and powdered limestone or calcined lime are added to adjust the lime-silica ratio (V-ratio) in the slag. The amount to add is best determined through practice with the desired aim being a CaO content of 55-60 percent or a lime-silica ratio of approximately 3:1.

The phosphorus is oxidized and is transferred to the oxidizing slag. Factors which effect phosphorus removal are² (1) Low metal temperature, which is promoted by maintaining temperature control, (2) Highly basic slag with a minimum 3:1 lime/silica ratio, (3) High FeO in the slag attained by addition of mill scale or iron ore, (4) Low SiO₂ in slag attained by slagging off and adding lime, (5) An active bath caused by a good carbon boil, (6) A fluid slag and (7) Lime in solution, both promoted by increasing slag temperature and the addition of fluorspar.

It is good practice to bring the heat to finishing temperature gradually rather than have the temperature fall at the end of the refining period. This permits a light carbon boil to exist throughout the heat which prevents gas pickup at the end of the heat.

After the heat has reached the proper carbon level, and the temperature and chemistry are adjusted, the heat is ready for partial deoxidation or "block." Most heats are blocked with 0.10% silicon added as ferrosilicon or silicomanganese. Chromium and nickel additions are made shortly after the block. There is usually some slight reversion of phosphorus at the end of the heat, but the final phosphorus content should be less than 50 percent of the phosphorus content of the charge.

Ferromanganese is added and the heat tapped within 1.5-2 minutes. Final additions are made to the ladle, and the heat deoxidized with aluminum, calcium-silicon alloys, or other deoxidizers. Frequently, limestone is added to the slag in the ladle to chill the slag, and inhibit phosphorus reversion.

Refining-Double Slag Practice

The double slag process, as the name implies, utilizes two slags, one to remove phosphorus and the second to remove sulfur. The first oxidizing slag is completely removed after dephosphorization to prevent reversion of phosphorus during the reducing conditions present during desulfurizing.

The carbon boil proceeds in the same manner as in the single slag practice. As soon as the carbon content has reached the desired level, and the boil has begun to slow down, the oxidizing slag is completely removed from the bath. The electrodes are raised for this operation and rakes used to remove all traces of the slag. The slag removal may be facilitated by adding burnt lime to thicken and agglomerate fluid slag near the banks.

After slag-off, the oxygen content of the bath should be substantially reduced before applying the reducing slag. This reduction of the oxygen content (Initial blocking) is accomplished by adding lump ferrosilicon, ferromanganese, or both to the bath. The usual practice is to add about one-half of the total ferrosilicon and ferromanganese required for the heat at this stage.

The reducing slag is generally premixed and consists of lime, fluorspar, and powdered carbon. The ratio of lime to spar is two or three to one, and the carbon amount is 15-20 percent of the lime addition. An amount of slag making materials equal to about three percent of the bath weight is added to the furnace. If these materials are not premixed, the lime and spar are added first, and the slag dusted with the powdered carbon.

The slag should be stirred (rabbled) to insure good slag-metal content.

The voltage should be reduced when the reducing slag is in place to prevent overheating of the metal and undue fluxing of the roof and lining. The slag, when cooled to room temperature, will be black during the first part of the reducing period. As this refining period progresses, the color will change to dark brown, then through light brown, brownish white, to white or gray which indicates the formation of excess stable calcium carbide.

The continual addition of powdered carbon to the slag allows the reactions to proceed and refining to continue. The factors which effect sulfur removal are:²(1) Low SiO_2 in the slag which is attained by slagging-off and adding lime, (2) A hot fluid slag and (3) Lime in solution, both of which are promoted by increasing slag temperature and adding fluor-spar, (4) A highly basic slag obtained by adding lime, (5) Low FeO in the slag from dusting with powdered carbon, and (6) Good slag-metal contact obtained by rabbling the slag.

Once the slag reaches the white or gray stage, final deoxidizers and alloy additions should be made and the heat tapped.

The final additions of manganese, silicon, and chromium may be made through the white slag. Recarburizing, if necessary, is best done by adding low phosphorus, low sulfur pig iron, or by carbon injection with an inert carrier gas. About ten minutes after the alloys are added, the heat is ready for tapping. Bath temperature is adjusted for tapping, usually in the 2950-3050°F range. Tapping and final deoxidation are carried out as with the single slag practice.

Alloy Steel

The melting practice for low-alloy steels is essentially the same as for plain-carbon steels. In the case of alloys containing nickel, copper, and molybdenum, these are generally added with the charge as they are not readily oxidized. Alloys such as chromium and manganese are not added until a carbide slag is obtained since they are readily oxidized.

In cases of large alloy additions, care should be taken not to chill the bath too abruptly and time allowed to insure complete melting. Thorough rabbling will insure complete mixing.

Stainless steel is seldom, if ever, melted with a carbide slag. Instead,

powdered ferrosilicon is added to the slag to produce reducing conditions, or an alumina slag is employed. If stainless steel scrap is used, the single slag practice is generally employed.

High-manganese steel (12-14 percent) is always produced with the basic practice using a sintered magnesite furnace bottom. The single slag practice is used with lime being added during the melting period. The analysis aim after meltdown is approximately 1.0 percent carbon, 11.0 percent manganese, and 0.3 percent silicon. A good basic slag is maintained with a composition of approximately 50 percent CaO; 20 percent SiO₂; 3 percent FeO; and 10-15 percent MnO.

After meltdown, the slag is deoxidized with pulverized coke and fluor-spar added to adjust slag viscosity. The heat is blocked with ferrosilicon. A desirable finishing slag will contain approximately 59 percent CaO; 24 percent SiO₂; 9 percent FeO; and 1 percent MnO.

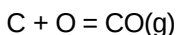
DEOXIDATION AND CONTROL OF GASES

Oxygen

The deoxidation process is of vital importance to the production of steel castings free from defects, and consequently has been the topic of numerous books and technical papers. The basic principles of deoxidation will be discussed here, and references will be provided.

Steel produced for castings *must* be "dead-killed," that is, completely deoxidized. The reason for this is, that the carbon-oxygen reaction equilibrium value drops with temperature and the "boil reaction" will start again with the formation of CO bubbles. This leads to blow holes, porosity, and pin holes. Castings poured in green sand molds are more prone to this problem than castings poured in dry sand molds.

The reaction of concern is as follows:



The ΔG° value for this reaction is given by:

$$\Delta G^\circ = - 5.35 - 9.48T$$

For a CO partial pressure of one atmosphere we find the following values:

Temperature °C	1500	1600	1700	1800	1900
[%C] [%O]	.00186	.00200	.00218	.00232	.00245

If the external CO pressure is reduced, the equilibrium value of [%C][%O] decreases in direct proportion to the CO pressure. As an example, if the pressure is reduced to 0.01 atmosphere, then [%C][%O] at 1600°C becomes 0.00002, which gives a value of %O of 0.00001 at a 0.2% carbon level. This is the reason that carbon is an effective deoxidizer in vacuum degassing operations.

The usual method of reducing the oxygen content is to add an element which has a greater affinity for oxygen than carbon, and which forms a solid or liquid oxide product. Common elements which are suitable for this purpose are aluminum, manganese, silicon, calcium, zirconium, and titanium. The relative deoxidizing power of these elements is illustrated in Figure 3. These elements are often used in combination, and the deoxidizing power of these combinations is also shown in Figure 3.

In the steel castings industry, aluminum is almost universally used as the final deoxidizer. The deoxidation products are alumina (Al_2O_3) and hercynite ($\text{FeO-Al}_2\text{O}_3$), both of which are solid at steelmaking temperatures. As can be seen from Figure 3, the deoxidation effect of aluminum in combination with silicon and manganese is much more

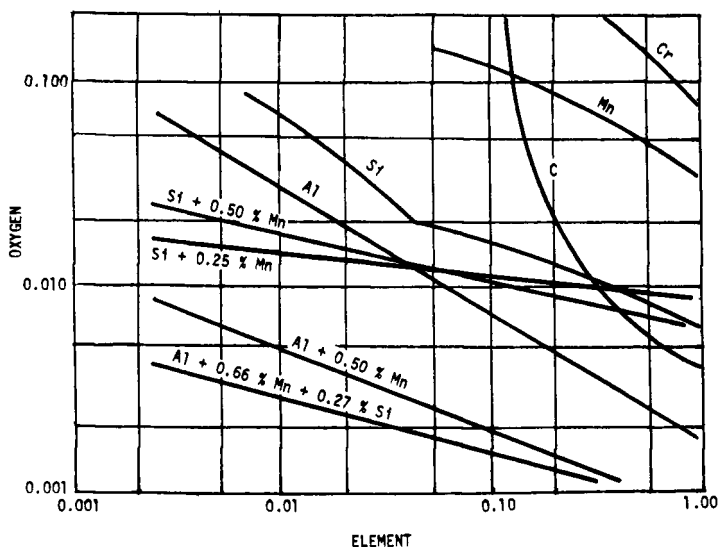


Figure 3. Relationship Between Deoxidizing Elements and Oxygen Content at 2912°F.

powerful than when used alone. The amount of the aluminum addition has been shown to be critical²² because of its effect on physical properties due to its effect on the type of inclusions formed. In melts with no aluminum, a globular Type I inclusion was formed due to the presence of oxygen. A small aluminum addition, 0.04 to 0.05 percent resulted in eutectic MnS films in the grain boundaries.

These steels were characterized by low ductility. A larger aluminum addition, 0.10 percent or more, resulted in larger, more scattered and irregularly shaped Type III inclusions with restored ductility. It was felt that this improvement was due to the excess aluminum, forming aluminum sulfide Al_2S_3 which is less soluble than MnS and FeS, and is precipitated at a higher temperature, causing the inclusions to be large and scattered.⁶ The strong deoxidizers, silicon, manganese, and vanadium gave Type I inclusions.

Castings produced in green sand require extra deoxidation protection because of the water vapor formed at the interface which results in oxygen and hydrogen being dissolved into the steel. This is particularly true for high carbon steels because the C x O equilibrium is easily exceeded.²³

The effect of rate of cooling on inclusion type has also been studied²⁴ and it was found that Type II inclusions could be eliminated from rapidly cooled sections by the addition of 3 lb. per ton of calcium/silicon/manganese along with the aluminum. Considerable additional work has been done on the effect of calcium and barium on inclusion formation and is discussed in references 25-26.

Nitrogen

Nitrogen may be absorbed in the steel from the slag making materials or from reaction of CaO in the slag with the carbon of the electrodes. Nitrogen is also absorbed directly from the furnace atmosphere, particularly in the high temperature area around the arcs. The solubility of nitrogen is related to the partial pressure of nitrogen in the atmosphere as follows:

$$\text{wt. \%N} = 0.045 \sqrt{pN_2}$$

Under a partial pressure of one atmosphere nitrogen, the solubility in pure iron is 0.045%. At the freezing point, however, the solubility drops to 0.013%. If these values are exceeded gas is evolved forming poros-

ity. Fortunately these values are seldom reached and porosity due to nitrogen alone is uncommon. Due to the flushing action of the carbon boil, nitrogen values usually run about 0.002 percent.

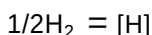
Another problem is that of "rock candy" fracture. This brittle type of failure is due to the formation of aluminum nitride in critical concentrations. Critical nitrogen levels above which "rock candy" fracture can occur appear to be 0.004 percent for plain carbon steel, and 0.002 percent for low alloy steel. The nitrogen can be fixed by the addition of zirconium or titanium. With the use of titanium, however, aluminum must still be added to prevent Type II inclusions. Cooling rate also has a pronounced effect on formation of aluminum nitrides.

Hydrogen

Hydrogen is generally present to some extent but is always unwanted in commercial steels. It can cause porosity and hair line cracks, particularly in large steel castings. Prolonged heat treatment over several weeks could be required to decrease the hydrogen by solid state diffusion to an acceptable level. This is expensive and thus where steel is required with low hydrogen contents, every attempt should be made to minimize hydrogen absorption during processing of liquid steel.

The solubility limit of hydrogen in solid iron at its melting point is about 0.001 percent (i.e. 10 ppm). The abbreviation ppm means parts-per-million. If the hydrogen content of the liquid exceeds this amount, it will be rejected during freezing and this leads to pin-hole formation and porosity.

The reaction between H_2 and liquid iron can be written:



$$\text{and, } [\text{wt \% H}] = K (pH_2)^{1/2}$$

The effect of temperature on the equilibrium constant is given by:

$$\log K = -1670/T - 1.68$$

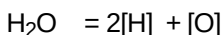
For a partial pressure of one atmosphere equation, the above equations give the solubility of hydrogen in pure iron at 2912°F (1873°K) as 0.0027 wt. percent (27 ppm). If the pressure is reduced to 10^{-3} atmospheres as in vacuum degassing, the equilibrium content would be about one ppm.

As in the case of nitrogen, interaction parameters are available which

describe the effect of various alloying elements on the solubility of hydrogen in alloy steels.

Absorption of hydrogen by molten steel can take place from moisture or hydrocarbons in the furnace atmosphere, from limestone, ore, mill-scale, scrap or alloy additions during refining, from the atmosphere during tapping and pouring, from damp refractories in the ladle, or from hydrocarbons contained in mold coatings or binders.

The dissolution of hydrogen in molten steel from water vapor may be expressed as:



$$K = [\text{a}_\text{H}]^2[\text{a}_\text{O}]/\text{pH}_2\text{O}$$

$$\text{and } \log K = -10390/T + 7.81$$

Expanding this equation

$$\log [\text{a}_\text{H}] = 1/2 \log K + 1/2 \log \text{pH}_2\text{O} - 1/2 \log \text{a}_\text{O}$$

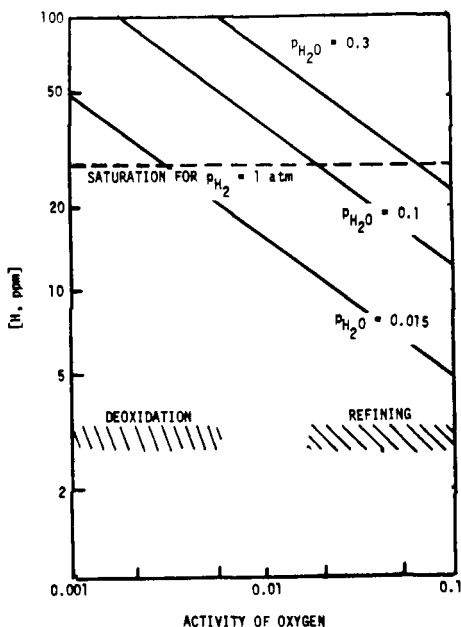


Figure 4. Relationship Between Hydrogen Content and Oxygen Content at 2912°F.

This relationship between hydrogen and oxygen in liquid iron at 2912°F is shown in Figure 4 for a range of water vapor pressures from that typical for an arc furnace (0.015) to that for an open hearth (0.3). From this diagram it can be seen that the hydrogen content increases as the oxygen content decreases. At low oxygen levels typical of killed steels, or at the higher water vapor pressures, the equilibrium hydrogen content actually exceeds that which would be in equilibrium with pure hydrogen at one atmosphere pressure. Fortunately these equilibrium values are well in excess of those normally encountered in practice (i.e. about 2-6 ppm), due mainly to the continuous removal of hydrogen during refining by the rinsing action of carbon monoxide bubbles. Further removal of hydrogen can be accomplished by argon rinsing in the ladle or vacuum processing to give hydrogen levels below 2-3 ppm.

In summary, hydrogen absorption can be decreased by:

- (a) Preheating scrap and other furnace additives.
- (b) Maintaining a good carbon boil.
- (c) Minimizing the time deoxidized metal is exposed to the atmosphere.
- (d) Ensuring the ladle refractories are properly dried.

Further information on hydrogen and nitrogen are given in the references.

INDUCTION MELTING

Induction furnaces are used to melt all of the common grades and alloys encountered in the steel foundry industry. The size and type of furnace is dictated by the economics of the specific application; refractories are a limiting factor in many cases. The requirement for air pollution abatement equipment is also a governing factor.

One of the main advantages claimed for induction furnaces is the small amount of alloy material that is lost in the melting operation. For all practical purposes, what goes in—goes out. This allows for good composition control through careful weighing of alloy additions. If the composition of the charge materials is accurately known, precise metallurgical control is rather easily realized. This is quite important where expensive alloying additions are used.

On the other hand, refining is rather limited such as is used in arc melting operations. Lower grade scrap cannot be used because it cannot be refined in the conventional manner. No distinct slag layer is developed due to the stirring action in an induction furnace, and the slag volume/metal volume ratio is not high enough to permit normal refining.

One of the advantages of induction melting is the strong stirring action which is developed. This gives the metal bath exceptional uniformity of both chemical composition and temperature, and allows more predictable results.

The conventional steel melting/refining process employing a carbon boil is not used in the induction furnace. This is principally due to the differences in the slag volume and interface area relationships between induction furnaces and direct arc furnaces. However, a limited amount of melting/refining operations are being carried out, and will be discussed later in this section.

Most induction melted steel is melted in medium to high frequency coreless furnaces. This is an excellent processing method for high alloy steels. The process is essentially a "dead-melting" operation, that is, the oxidation level of the bath is intentionally kept as low as possible and no carbon boil is induced. The process consists of charging the furnace, melting the charge, making the required alloy additions to adjust chemistry, adjusting the temperature, and tapping the heat.

Because the scrap used is generally clean, and melting is rapid, the oxidation losses are low and accurately predictable. Alloy additions may be made as ferroalloys or commercially pure metallic additions. The following formula is used to calculate the amount of addition required:⁴

$$\text{weight of ferroalloy} = \frac{(\text{final analysis} - \text{charge analysis}) \times (\text{bath weight})}{(\% \text{recovery}) \times (\% \text{alloy in addition})}$$

Recoveries average approximately 95% but do vary somewhat and should be determined for each operation.

As mentioned previously, usually no attempt is made to refine the steel. Sulfur and phosphorous levels should be maintained by careful charge material selection.

The pronounced stirring action of the coreless furnace is an important

advantage, particularly with highly alloyed steels, insuring homogeneity of the melt. Since the heat is generated within the charge itself by the electromagnetic field, there is no possibility of carbon pickup from electrodes as in a direct arc furnace, or from combustion gases in an open hearth furnace.

It is, however, possible to do limited refining in the coreless furnace. If a carbon boil is desired, it may be initiated by introducing iron ore, nickel oxide, or gaseous oxygen to the bath. Taconite pellets are frequently used. Temperature must be carefully controlled in order to control the rate of carbon boil.

It is also possible to desulfurize and dephosphorize by using slags composed of lime, alumina, silica, and fluorspar. This type of refining slag, however, is destructive to $\text{MgO-Al}_2\text{O}_3$ linings.

Steel melting in the line frequency coreless induction furnace is not as common as the higher frequency operations. This is primarily due to the traditional use of silica linings in these furnaces. The silica lining is not as refractory as some of the other materials used for linings, and erosion of the lining occurs faster. Also, active aluminum, calcium, magnesium, carbon, and titanium attack the silica lining if added in large quantities or early in the melt cycle.³⁵

The replacement of the silica lining with other refractories allows oxidation of silicon and manganese at lower temperatures and carbon at higher temperatures.³⁶ Providing that adequate provisions are made for slag handling, the refining reactions are the same as with other steel making processes. The ease of control of temperature, and the good mixing action, favor this process.

AOD REFINING

In 1967 at Joslyn Steel the first commercial heat of steel was produced by using the Linde AOD process. By the end of 1977, just ten years later, approximately 75 to 80% of U.S. stainless production will be made using this process. Most of this production will be wrought products, of course, but it has been found that the AOD method can be economically successful in the foundry as well.

Before going too deeply into the use of the vessel, AOD should be described. AOD stands for argon/oxygen/decarburization which basi-

cally describes the process. It is the decarburization of metal through the use of oxygen with argon or some other inert gas. The refining process is carried out in vessels similar to Bessemer converters by blowing the oxygen-inert gas mixture into the molten bath through submerged tuyeres located in the lower sides of the vessel. While the main charge that goes into the vessel must be melted in some other furnace before processing in the AOD up to 30% cold charge can be added to the vessel without significantly changing the refining efficiency.

The process is based upon the thermodynamic equation for the oxidation of carbon in the presence of chromium:

$$\text{Cr}_3\text{O}_4 + 4\text{C} = 3\text{Cr} + 4\text{CO(g)}$$

$$K = \frac{(a_{\text{Cr}})^3 \cdot (\text{PCO})^4}{(a_{\text{Cr}_3\text{O}_4}) \cdot (a_{\text{C}})^4}$$

This formula shows that for any given temperature, the partial pressure of CO must be reduced in order to maximize the Cr to C ratio. Lowering the PCO can be done by mixing a gas that is preferably inert with the CO. This is what is done in the AOD. In the arc furnace this injection of an inert gas to lower the partial pressure of CO is not possible due to the shape of the bath and the economics of injection through a submerged tuyere which is necessary. Therefore, in the arc furnace in order to reduce carbon to very low levels, it is necessary to have low levels of chromium. After decarburization the chromium must be built up using low carbon chromium at a premium price.

The following procedure is used by many AOD operators.

The heat is melted down in an electric furnace and the chemistry is adjusted somewhat. The heat is tapped into a ladle, sampled, slagged, and then transferred into the vessel. A slag is built in the vessel and a temperature is taken. Oxygen is then injected along with argon to get the temperature to about 3100 F. A temperature and sample are taken at the end of this cycle. Oxygen and argon are then injected at a lower oxygen to argon ratio for a length of time determined by the carbon of the sample taken at the end of the first period. A still lower oxygen to argon blowing cycle is often used at the end to reach the final aim carbon. The last cycle is sometimes not used when high tap temperatures are needed because of the temperature loss during this blow. The reduction mix is calculated from the beginning analysis and the total amount of oxygen injected and added at the end of the last oxygen injection period. A temperature is taken and is adjusted by blowing argon

to cool or oxidizing silicon to heat up if it is needed. When the final chemistry adjustments have been made and the temperature is correct then the heat is tapped. Generally, it is a pretty simple operation, and control is so good that often it is not necessary to wait for a final analysis. Figure 5 gives a summary of the basic stainless AOD process.

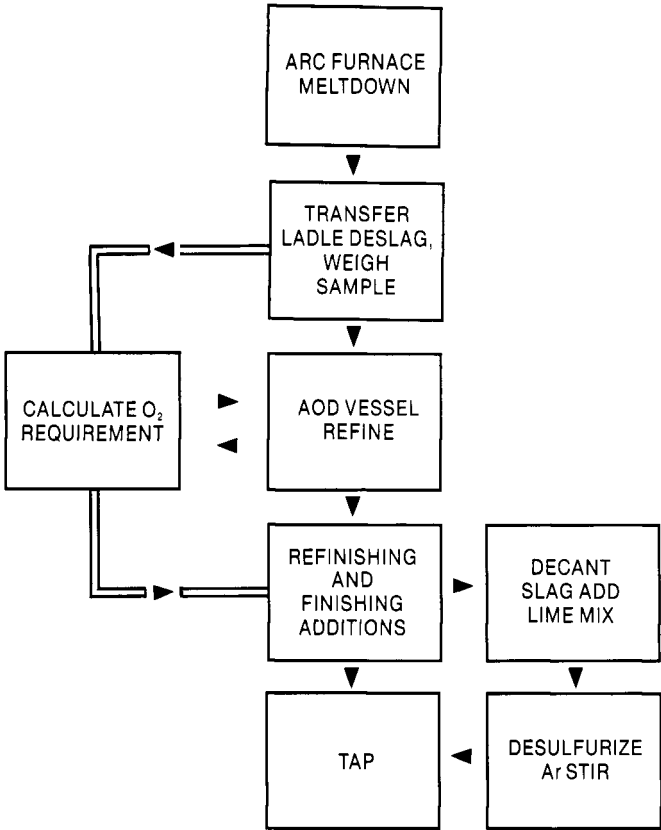


Figure 5. AOD process flow charts.

Casting quality often is improved by virtue of some of the inherent properties produced by the AOD process. One of the items is the way sulfur is reduced without special steps. (Sulfurs commonly run between 0.001 and 0.007).

The AOD also naturally reduces other interstitials and traps elements. Lead and bismuth are reduced to less than 0.001. Union Carbide claims that most vessels run with 60 to 90 ppm finishing oxygens.

Summary of Advantages of AOD

1. Can use lower cost chromium
2. Improved chromium recovery
3. Reduces use of silicon
4. Improves total metal yield compared to an arc furnace
5. Produces lower sulfurs
6. Lowers gas contents in final product
7. Simplifies production of ELC grades of stainless steel
8. Increases production capacity
9. Improved metal quality

Summary of Disadvantages of AOD

1. High refractory cost somewhat offset by reduced arc furnace cost
2. Cost of argon

The above summary shows that AOD can be a useful tool in the foundry industry. The advantages far outweigh the disadvantages. With some work even the high cost of refractory may be reduced.

LADLE DESULFURIZATION

Ladle processes can be utilized to desulfurize acid melted steels. However before ladle desulfurization can be utilized in the steel foundry, several limitations related to foundry melting must be overcome.

First, because of the relatively small ladle size in the foundry, heat-temperature losses during ladle desulfurization processes will be high relative to large steel mill size ladles. Measures such as added super heat and better ladle preheat must be exercised to produce the proper pouring temperatures after the completion of the desulfurization operation.

Second, for acid melting, efficient means must be developed to prevent furnace slag from entering the ladle. If this is not accomplished, efficient desulfurization will not occur.

Aluminum losses and altered recovery rates of other oxidizable elements must be established as a function of the desulfurization variables employed for foundry-size heats.

Ladle Slag Processes

The thermodynamic principles of ladle slag processes are the same as those for furnace slag processes. The ladle slag technique consists of pouring deoxidized liquid steel into a ladle in which a high basicity slag has been added. Some of the ladle slag processes require premelting of the slag — this is not common. In most processes, dry slag additions are made to the ladle while the liquid metal is being tapped into the ladle. The energy of the liquid metal stream entering the ladle serves as the mixing force. The dry slag mixtures normally employed for this process generally consist of lime, spar, silica, alumina, deoxidizers such as aluminum and silicon, and fluidizers such as sodium and potassium compounds. Fig. 6 shows results for such a ladle slag operation. The actual results obtained in the foundry will depend on the energy of the tap stream as well as the ladle refractory. Extremely low levels of sulfur can be obtained by the ladle slag technique if the steel and slag are mixed by external forces such as gas bubbling or magnetic stirring. If such forces are applied, the sulfur reduction obtained will approach the Lime Theoretical line shown in Figure 6.

The ladle slag process can be used to desulfurize acid melted steel. Care must be taken to exclude the acid furnace slag from the ladle. Acid or basic lined ladles can be used for the ladle slag process. Wear of the lining will be greater for acid lined ladles however. Also, the efficiency of sulfur removal will be less for acid lined ladles.

Because ladle slag desulfurization processes can be used for treating acid melted steels, they have great interest to the steel founder.

Powder Injection/Wire Injection

injection of reactive metals (Ca, Mg, or rare earths) into liquid steel for desulfurization has come to the forefront of technology in the past decade. Ultra low levels of sulfur can be obtained by this technique (less than 0.005%).

The basis of reactive metal injection desulfurization is the chemical combination of the reactive metal with sulfur dissolved in the liquid

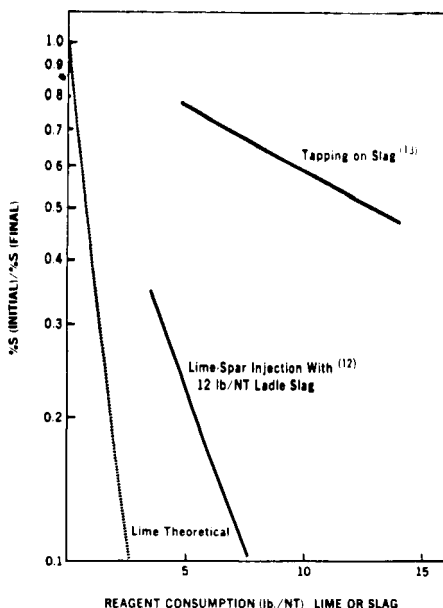


Figure 6. Lime consumption in steel desulfurization.

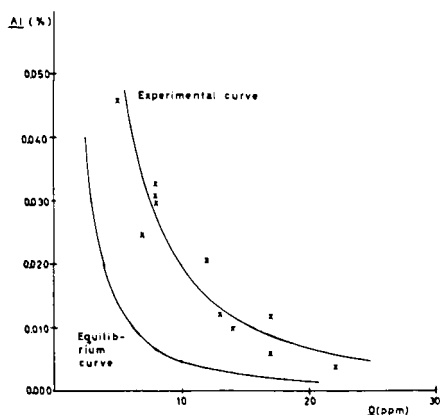


Figure 7. Experimental and equilibrium oxygen level as a function of Al level.

steel. Because the reactive metals are strong deoxidizers, it is necessary to have a low oxygen level in the liquid steel before the start of the injection process. Otherwise, the reactive metal would combine with the dissolved oxygen and not the dissolved sulfur. Aluminum is used as the deoxidizer to obtain the necessary low oxygen levels. Figure 7 shows the aluminum oxygen relationship in liquid steel.

It is also necessary to have a slag present which will hold the sulfur removed by the reactive metal. If such a slag is not present, the metal sulfide will be oxidized and the sulfur will return to the liquid metal.

SFSA Project

The Steel Founders' Society has recently completed Research Project No. 123 which examined the use of the various ladle desulfurization techniques for acid melted steel. A process has been developed which allows simple and economical desulfurization approaching AOD levels.

Details are contained in Research Report No. 97.

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APPENDIX—METALLURGICAL CHEMISTRY

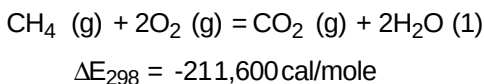
The purpose of this appendix is to provide the interested reader with a basic understanding of the metallurgical chemistry involved in the production of steel for foundry applications. The step-by-step procedures of steel production have been covered in the body of the paper, and while an understanding of metallurgical chemistry is not essential for production purposes, the author feels strongly that understanding what is happening in the furnace is useful in diagnosing the causes when problems occur.

For purposes of this discussion, the term metallurgical chemistry encompasses the disciplines of thermodynamics, kinetics, and transport phenomena.

Introduction

All matter possesses a certain amount of energy which is divided between bond energies between the atoms or molecules, and atomic or molecular vibrations. We have no way to measure the absolute amount of energy in the material, however, we can determine the change in energy from one state to another. The units of energy can be either calories, or British Thermal Units (BTU's). All chemical reactions either absorb or liberate heat. If they liberate heat, they are called exothermic. If, on the other hand, they absorb heat, they are called endothermic. The energy change, . . . written ΔE . . . is positive if heat must be added, and negative if heat is given off.

For example:



This means that 211,600 calories are given off when one molecular weight of methane reacts with oxygen at 298°K to form carbon dioxide and water.

This also implies the consumption of the following amounts of materials:

16.04 lbs. of Methane (one lb. molecular weight)

64.00 lbs. of Oxygen (two lbs. molecular weight)

and the formation of:

44.01 lbs. of carbon dioxide (one lb. molecular weight)

36.03 lbs. of water (two lbs. molecular weight)

Heat and Enthalpy

Heat is a measurement of the energy in the system. The symbol used is H and the relationship with the pressure and volume of the system is:

$$H = E + p v$$

Again—since we cannot measure absolute quantities of H, we use values of H relative to some reference temperature such as 25°C (298°K) which are known and tabulated in the literature. Examples are given in Table A-I. Thus -

$$\Delta H = \Delta E + \Delta(pv)$$

For example:

$$\text{for iron } (H_{1800^{\circ}\text{K}} - H_{298^{\circ}\text{K}}) =$$

13,910 cal. for solid

17,610 cal. for liquid

This is the quantity of heat required to raise one mole (55.85 grams) from 298°K to 1800°K. The difference (17,610 – 13,910 = 3700 cal.) is the amount of heat required to melt the iron at its melting temperature at constant temperature . . . i.e., the latent heat of fusion. In other words, it takes 13,910 cal. to raise the iron to its melting temperature, and another 3700 cal. to melt it.

Heat Capacity

The amount of heat required to raise one gram mole of the material one degree C is called the heat capacity, Cp. Heat Capacity usually in-

Table A-I Heat of Formation and Entropies

Substance	$-H^\circ_{298}$ kcal	S°_{298}
Al	0	6.77
Al ₂ O ₃	400.4	12.24
AlN	76.47	6.84
C	0	1.37
CO(g)	26.42	47.30
CO ₂ (g)	96.05	51.06
Ca	0	9.95
CaF ₂	290.3	16.45
CaO	151.8	9.63
Ca ₃ (PO ₄) ₂	160.5	57.6
CaS	114.3	13.66
CaCO ₃	42.5	22.2
Cr	0	5.68
Cr ₂ O ₃	272.7	19.46
Fe	0	6.49
FeO	63.5	13.73
Fe ₃ O ₄	266.8	35.0
Fe ₂ O ₃	196.2	21.41
FeS	22.4	16.37
Fe ₂ SiO ₄	8.2	34.7
H ₂ (g)	0	31.21
H ₂ O	57.80	45.11
H ₂ S	4.8	49.1
Mg	0	7.81
MgO	143.8	6.42
Mn	0	7.65
MnO	92.05	14.37
Mn ₃ O ₄	331.4	35.5
MnS	48.75	18.57
Mo	0	6.83
MoO ₂	140.8	11.06
N ₂ (g)	0	45.77
Ni	0	7.14
NiO	57.3	9.2
NiS	21.68	12.93
O ₂ (g)	0	49.00
S	0	7.62
S(g)	-56.9	40.09
S ₂ (g)	-30.84	54.51
SO(g)	0.1	53.07
SO ₂ (g)	70.86	59.25
Si	0	4.53
SiO ₂	217.3	10.26
SiC	13.0	3.89
Ti	0	7.33
TiO ₂	225.75	12.06
TiN	80.47	7.23
Zr	0	9.29
ZrO ₂	261.5	12.17
ZrN	87.3	9.3

creases with increasing temperature so that, for example, it requires more heat to go from 500° to 510° than from 100° to 110°. A convenient method to record this information is in the form:

$$C_p = a + bT - cT^{-2}$$

where T = absolute temperature

$a, b, c,$ = constants for a given material

Therefore, to raise an amount of material from a temperature of T_1 , to a temperature of T_2 a quantity of heat (Q) is required as follows:

$$Q = H_2 - H_1 = C_p(T_2 - T_1)$$

This holds true only if C_p is constant between T_1 and T_2 . If C_p is not constant, it becomes necessary to integrate the expression between T_1 and T_2 :

$$Q = H_2 - H_1 = \int_{T_1}^{T_2} C_p dT = a (T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) + C \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Generally it is easier to use tabulated data, such as presented in Table A-11.

Heat of Reaction

It was stated earlier that the energy (heat) representing the state of the material may be stated as follows:

$$\Delta H = \Delta E + \Delta(pv)$$

For most metallurgical processes, the change in the pressure-volume term, $\Delta(pv)$ is negligibly small and may be disregarded. This is *not* true, of course, for reactions involving gases where:

$$(pv) = nRT$$

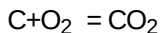
where n = number of moles of gas

R = Universal Gas Constant

T = Absolute Temperature

The "Heat of Formation" (H) is the heat absorbed or evolved in the formation of one mole of the substance from its elements. If heat is evolved, H is negative.

For example:



$$\Delta H = -94,052 \text{ cal/mole}$$

Heats of reaction may be easily calculated from the heats of formation

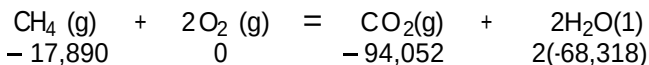
Table A-II Typical Values of Molar Enthalpy

Substance	$H_{1,800}^{\circ} - H_{298}^{\circ}(\text{kcal})$
Al	12.93
Al ₂ O ₃	43.22
C	7.33
CO(g)	11.84
CO ₂ (g)	18.99
Ca	49.60
CaF ₂	42.05
CaO	18.78
Ca ₃ (PO ₄) ₂	123.30
Cr	11.98
Cr ₂ O ₃	45.18
Fe	13.91
FeO	28.14
Fe ₃ O ₄	73.75
Fe ₂ O ₃	51.88
FeSiO ₄	91.55
H ₂ (g)	11.03
H ₂ O	14.97
H ₂ S	16.34
Mg	43.06
MgO	17.61
Mn	18.58
MnO	19.35
Mn ₃ O ₄	72.75
MnS	19.97
Mo	10.38
N ₂ (g)	11.71
Ni	16.23
NiO	20.26
O ₂ (g)	12.36
S (g)	13.12
S ₂ (g)	43.96
SO ₂ (g)	19.04
Si	21.36
SiO ₂	24.53
SiC	16.88
Ti	12.13
TiO ₂	26.34
TiN	18.51

of the products and reactants.

$$\Delta H_{\text{RXN}} = \Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}$$

Example:



$$\Delta H = \{(-94,052) + 2(-68,318)\} - \{(-17,890) + (0)\}$$

$$\Delta = -212,798 \text{ calories}$$

Often we wish to know the heat of reaction at some high temperature when we know it at some lower temperature. We can correct for the temperature difference by applying the correction factor of $C_p \Delta T$. Thus:

$$\Delta H_2 = \Delta H_1 + C_p (T_2 - T_1)$$

Entropy

Remember that as the temperature of a material increases, more energy is tied up in molecular motion and is not available for doing useful work. This thermal or bound energy is determined by two quantities . . . temperature (T) and Entropy (S). The bound energy = TS or TΔS. The units are cal/deg/mole. ΔS quantities are also tabulated in the literature. (Table A-1)

For phase transformations (*not* chemical reactions) such as melting—

$$\Delta S = \frac{Q_{\text{rev}}}{T} \text{ where } Q = \text{heat of fusion, etc.}$$

Free Energy

When the "bound" energy discussed above is subtracted from the total energy, the balance is called the "free energy." Again . . . only energy changes are known, so:

$$\Delta G = \Delta H - T \Delta S$$

(Δ G is sometimes written as Δ F)

The free energy is the driving force for the reaction to occur in the direction it is written. When ΔG is negative the tendency is for the reaction to

occur, and the larger the numerical value of ΔG , the greater the tendency to occur.

For example:



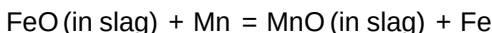
$$\text{at } 77^\circ\text{F } \Delta G = +31,260 \text{ cal. at } 1 \text{ atm CO}_2$$

The reaction does not occur. However at 1830°F ; $\Delta G = -4,000 \text{ cal.}$, and the reaction does occur.

Equilibrium

Equilibrium is defined as the condition where $\Delta G = 0$ and there is no tendency to go either way with the reaction. Stated another way, when the free energies of the reactants equal the free energies of the products, we are at a state of equilibrium.

For example:



$$\Delta G = (G_{\text{MnO}} + G_{\text{Fe}} - (G_{\text{FeO}} + G_{\text{Mn}})) = 0 \text{ at equilibrium}$$

Rate of Reaction

The rate of reaction depends on the amounts of materials on both sides.

$$k_1 \{ (\text{FeO}) \times (\text{Mn}) \} = k_2 \{ (\text{MnO}) \times (\text{Fe}) \}$$

$$\frac{(\text{FeO})(\text{Mn})}{(\text{MnO})(\text{Fe})} = \frac{k_2}{k_1} = K \text{ (equilibrium constant)}$$

The amount of material shown is the chemical activity of the material. Essentially pure materials have an activity of unity. When the chemical activity is equal to its percentage or mole fraction or pressure, then these values can be substituted for activity.

Thus:

$$K = \frac{(A_{\text{MnO}} \times (A_{\text{Fe}})^1)}{A_{\text{FeO}} \times A_{\text{Mn}}}$$

$$K = \frac{(\% \text{ MnO})}{(\% \text{ FeO} \times (\% \text{ Mn}))}$$

Temperature effects the free energy change as follows:

$$\Delta G = -RT \ln K$$

Where: R = Universal Gas Constant

T = Absolute Temperature

K = Equilibrium Constant

Up to this point we have been talking about the free energy change at equilibrium, the "standard free energy change" G° . When we apply a correction for temperature, we get:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where ΔG = "actual free energy change."

Q has the same form as K, but describes actual conditions. Thus, at equilibrium $Q = K$ and $\Delta G = \Delta G^\circ = 0$.

Data for calculating ΔG° are given in Table A-III and Figure A-1.

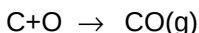
Oxidizing Reactions

As discussed in previous sections, we find that the oxidation of the silicon, manganese, and carbon is governed by the free energy at the temperature of interest.

Silicon is oxidized first at lower temperatures and is essentially completely removed. Manganese is also removed and levels off at low value. As temperature increases, the carbon oxidation reaction is favored and carbon is removed as carbon monoxide.

Carbon Boil

The carbon boil is essential to the proper control of carbon content and removal of hydrogen and nitrogen in the direct arc processes. We intentionally supply oxygen to produce the reaction:



The carbon monoxide bubbles out of the bath, and hydrogen and nitrogen diffuse to the CO bubbles and are removed.

Oxygen is introduced as gaseous oxygen, usually through a submerged lance.

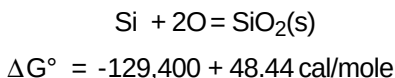
There are two types of bubble nucleation . . . homogeneous and heterogeneous. Homogeneous nucleation, or spontaneous nucleation, requires that the partial pressure of CO_2 be equal to the atmospheric pressure *plus* the ferrostatic pressure *plus* the energy of formation of the bubble. Usually this value is too high to overcome and we do not get homogeneous nucleation.

Heterogeneous nucleation refers to nucleation at a small crack in the refractory. These conditions favor bubble formation due to the lower energy which must be overcome.

A classic experiment illustrates this point. When iron was melted in a completely glazed crucible, and was supersaturated with carbon and oxygen, no carbon boil occurred. However, when the side of the crucible was scratched to give a site for bubble nucleation, a violent boil occurred.

Mn & Si Reactions

As discussed previously, both manganese and silicon are lost during the oxygen blow with a subsequent evolution of heat. Silicon is preferentially oxidized in the early stages of refining when temperature is lower and carbon content higher. This reaction may be written as follows:



$$K = \frac{Q_{\text{SiO}_2}}{(\text{Si})(\text{O})^2}$$

$$\text{at } 1600^\circ\text{C-K} = 30,000$$

$$\text{thus -if } (\text{O}) = 0.015\% (0.40\%\text{C})$$

$$\text{then } (\text{Si}) = 0.15\%$$

Manganese also oxidizes and distributes between metal and slag in a ratio approximately proportional to:

$$\frac{(\%\text{MnO})(\text{Slag})}{(\%\text{FeO})(\text{Slag})} \quad (\text{When slag V ratio is above 2.2})$$

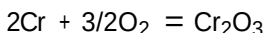
Thus, an increase in (FeO) causes an increase in (MnO) in the slag, and a subsequent reduction of residual manganese in the bath. As the tem-

perature increases, the equilibrium shifts to cause some reversion of manganese back into the metal toward the end of the heat

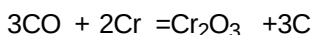
We are principally concerned with manganese and silicon as deoxidizing materials. This will be covered later in the text.

Chromium Reactions

Chromium is oxidized according to the reaction



During the blow, we observe the reactions



Equilibrium ($\Delta G^\circ = 0$) occurs at 1220°C (2228°F)

$$\text{and } K = \frac{Q_{\text{Cr}_2\text{O}_3} \times Q_{\text{C}}^3}{Q_{\text{Cr}}^2 \times P_{\text{C}}^3 \text{O}} = 1$$

To conserve chrome (that is to avoid oxidation) we must operate under conditions such that K is much less than 1. We do this by operating at temperatures much greater than 1220°C (2228°F). We also wish to use a high blow rate to minimize chromium loss. The rise in temperature depends on the rate of oxidation and the rate of heat loss.

Other Elements

Many other elements are found in the bath occurring because of either intentional addition or as tramp elements in the scrap. Some of these are detrimental to engineering properties and scrap must be carefully controlled. Some are very difficult to remove because they are not readily oxidized. Examples are nickel, cobalt, molybdenum and copper.

Copper for example

at 1600°C



while at 1600°C ,



thus the oxidation of iron occurs

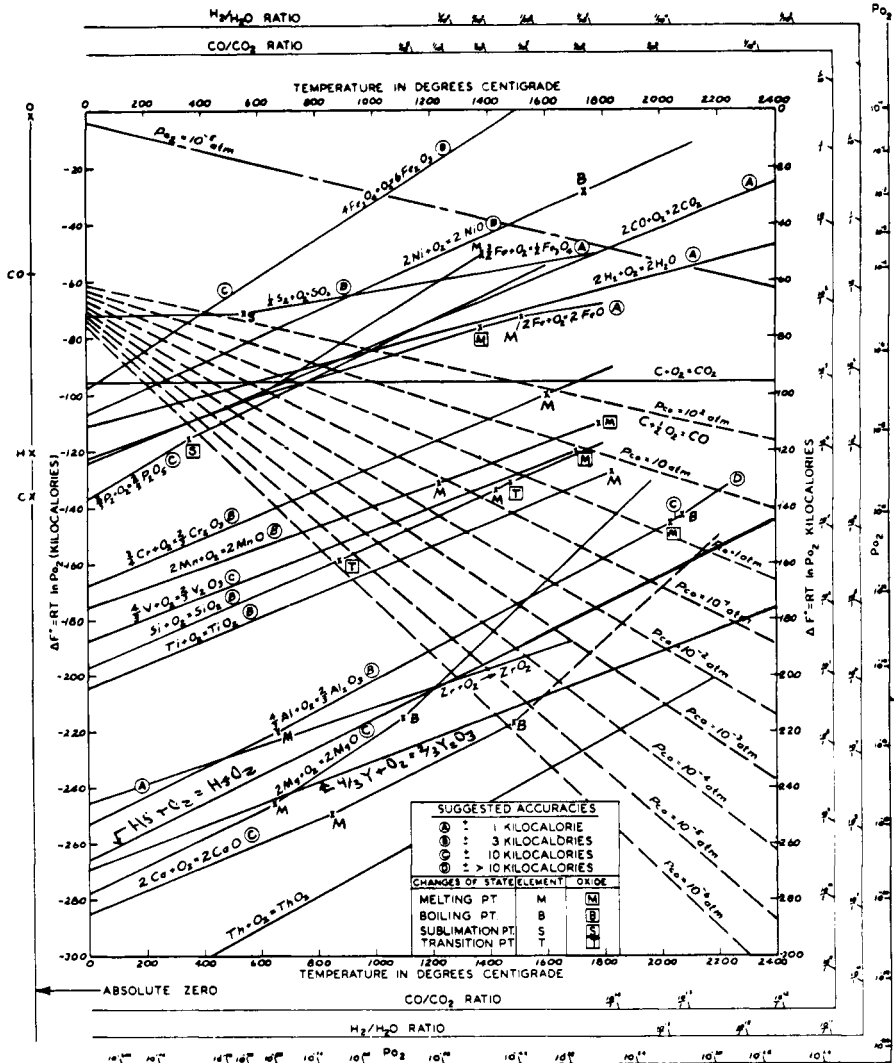


Figure A-1. Standard Free Energies of Formation of Oxides of Interest in Steel Melting as a Function of Temperature.

Carbon is removed in accordance with the carbon-oxygen equilibrium relationship. At 1600°C:

$$C \times O \approx 2.0 \times 10^{-3}$$

In actual practice, we only approach equilibrium, and the observed oxygen values are somewhat higher. The limiting factor is a mass transport process. For the reaction to proceed, a bubble must be nucleated and then grow.

Table A-III Standard Free Energy Data**A. Standard Free Energy of Solution of Various Elements in Liquid Iron.**

M (pure) = M (1 % Solution)

Element	ΔG°		
Al (1)	-10,300	-7.71	T
C	5,100	-10.00	T
Cr (s)	5,000	-11.31	T
Cu	8,000	-9.40	T
Hydrogen			T
($1/2\text{H}_2(\text{g}) = \text{H}$)	7,640	-10.62	T
Mn (1)		-9.11	T
Mo (s)	5,800	-13.3	T
Ni (1)	-5,000	-7.42	T
Nitrogen			
($1/2\text{N}_2(\text{g}) = \text{N}$)	860	+5.71	T
Oxygen			
($1/2\text{O}_2(\text{g}) = \text{O}$)	-28,000	-0.69	T
$\text{FeO}(1) = \text{O} + \text{Fe}(1)$	28,900	-12.51	T
Si (1)	-28,500	-6.09	T
Zr (s)	-12,800	-12.02	T

B. Free Energies of Formation of Compounds

(1) Elements dissolved in Liquid Iron

Reaction	ΔG°		
$\text{CO}_2(\text{g}) + \text{C}(\text{g}) = 2\text{CO}(\text{g})$	38,400	+40.40	T
$\text{CO}_2(\text{g}) + \text{C} = 2\text{CO}(\text{g})$	33,300	-30.40	T
$\text{CO}(\text{g}) + \text{O} = \text{CO}_2(\text{g})$	-38,700	+20.9	T
$\text{C} + \text{O} = \text{CO}(\text{g})$	-5,350	-9.48	T
$\text{H}_2\text{O}(\text{g}) - 2\text{H} + \text{O}$	47,480	-35.87	T
$\text{Fe}(1) + 1/2\text{O}_2(\text{g}) = \text{FeO}(1)$	-56,900	+11.82	T
$\text{MnO}(1) = \text{Mn} + \text{O}$	58,400	-25.98	T
$\text{SiO}_2(\text{s}) = \text{Si} + 2\text{O}$	142,000	-55.0	T

(2) Oxides

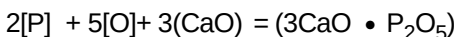
$2\text{Al}(1) + 3/2\text{O}_2(\text{g}) = \text{Al}_2\text{O}_3$	-401,500	+76.91	T
$\text{Ca}(1) + 1/2\text{O}_2(\text{g}) = \text{CaO}(\text{s})$	-152,850	+25.78	T
$\text{C}(\text{s}) + 1/2\text{O}_2(\text{g}) = \text{CO}(\text{g})$	-28,200	-20.16	T
$\text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	94,755	+0.02	T
$2\text{Cr}(\text{s}) + 3/2\text{O}_2(\text{g}) = \text{Cr}_2\text{O}_3(\text{s})$	-270,550	+61.35	T
$\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g})$	-60,200	+13.94	T
$\text{Fe}(1) + 1/2\text{O}_2(\text{g}) = \text{FeO}(1)$	-56,900	+11.82	T
$2\text{Fe}(\text{s}) + 3/2\text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3$	-190,950	+57.46	T
$3\text{Fe}(\text{s}) + 2\text{O}_2(\text{g}) = \text{Fe}_3\text{O}_4$	-259,550	+70.91	T
$\text{Mg}(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{MgO}(\text{s})$	-174,750	+49.09	T
$\text{Mn}(1) + 1/2\text{O}_2(\text{g}) = \text{MnO}(\text{s})$	-97,550	+21.22	T
$\text{Ni}(1) + 1/2\text{O}_2(\text{g}) = \text{NiO}(\text{s})$	-60,350	+22.61	T
$\text{Si}(1) + \text{O}_2(\text{g}) = \text{SiO}_2$	-223,800	+46.08	T

(3) Sulfides

$\text{Ca}(1) + 1/2\text{S}_2(\text{g}) = \text{CaS}(\text{s})$	-132,060	+25.91	T
$\text{H}_2(\text{g}) + 1/2\text{S}_2(\text{g}) = \text{H}_2\text{S}(\text{g})$	-21,540	+11.73	T
$\text{Fe}(1) + 1/2\text{S}_2(\text{g}) = \text{FeS}(1)$	-29,970	+7.90	T
$\text{Mn}(1) + 1/2\text{S}_2(\text{g}) = \text{MnS}(1)$	-63,100	+15.77	T
$1/2\text{S}_2(\text{g}) + \text{O}_2(\text{g}) = \text{SO}_2(\text{g})$	-86,130	+17.24	T
$1/2\text{S}_2(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{SO}(\text{g})$	-15,360	-1.24	T

BEHAVIOR OF PHOSPHORUS

Phosphorus in general is undesirable in steel but its removal is complicated because of the similarity in affinity of P and Fe for oxygen (Figure A-2). P transfer from the metal to the slag during refining can be considered as follows:



To prevent excessive iron loss by oxidation a highly basic slag is required. During refining with a basic slag, the P_2O_5 line in Figure A-2 shifts downwards to a more stable location below the FeO line, thus favoring the oxidation of P rather than Fe. It can also be seen from Figure A-2 that the oxide stability increases with decreasing temperature and thus lower temperatures will favor dephosphorization.

The equilibrium constant for reaction is given by

$$K = \frac{(a_{3\text{CaO}} \cdot \text{P}_2\text{O}_5)}{[a_P]^2 [a_O]^5 [a_{\text{CaO}}]^3}$$

i.e. $\frac{(a_{3\text{CaO}} \cdot \text{P}_2\text{O}_5)}{[a_P]^2} = K [a_O]^5 (a_{\text{CaO}})^3$

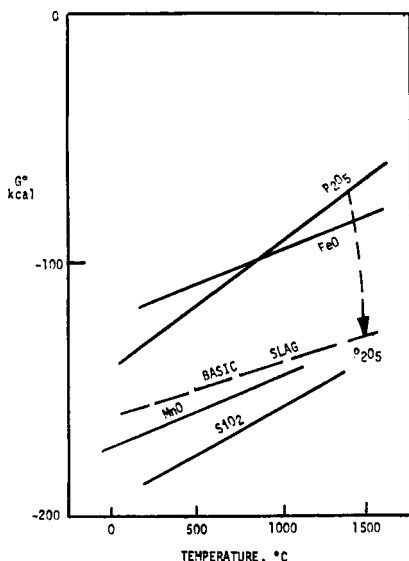


Figure A-2. Free Energies of Formation of FeO , P_2O_5 , MnO , and SiO_2 as a Function of Temperature.

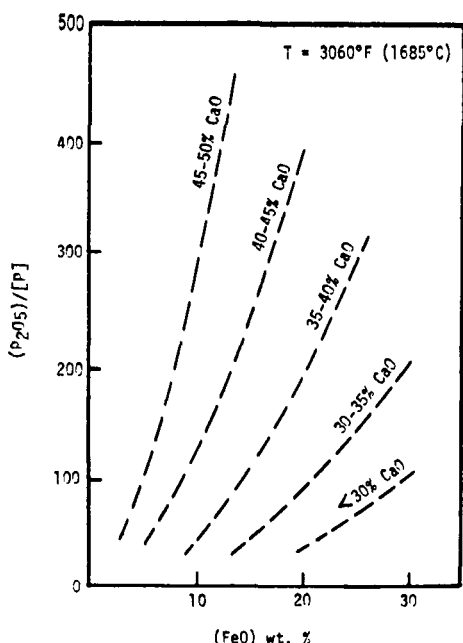


Figure A-3. Relationship Between Phosphorus Distribution and % FeO at Different CaO Levels.

Consideration of this expression indicates that dephosphorization is favored by:

- (i) An increase in K , i.e. lower temperatures
- (ii) An increase in activity of the oxygen in the metal, i.e. more oxidizing conditions and this is related to the FeO content of the slag.
- (iii) An increase in (a_{CaO}) i.e. greater slag basicity, and this is related to high CaO/SiO₂ ratios.

Factors (ii) and (iii) are inter-related and this is illustrated by Figures A-3 and A-4. For a given slag bulk there is a limitation to the total amount of (FeO + CaO) which the slag can contain. Thus when the % FeO is high, the % CaO is low and when the % CaO is high, the % FeO is low. Expressing the slag basicity in terms of the CaO/SiO₂ ratio, and plotting the slag/metal P ratio as a function of wt % FeO in the slag, it can be seen that there is an optimum FeO content of about 15%.

For FeO contents below 15%, conditions are not sufficiently reducing, i.e. the activity of the oxygen in the metal is too low.

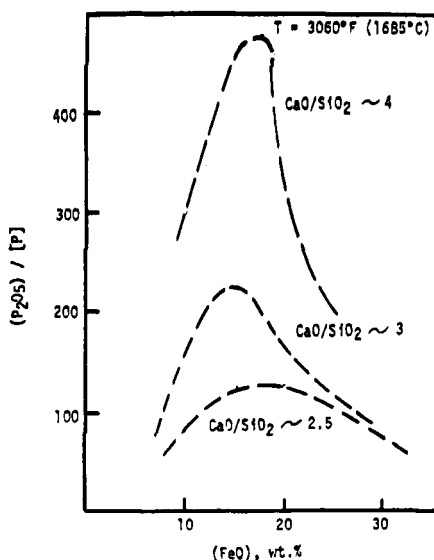


Figure A-4. Relationship Between Phosphorus Distribution and % FeO at Different CaO/SiO₂ Ratios.

For FeO contents above 15%, the amount of lime present becomes too small for effective dephosphorization.

In refining, high P charges, (above about 0.2% P), may require the use of two or more slags involving lime injection, the addition of fluorspar (CaF₂), bauxite (Al₂O₃), or other fluxes to promote early slag formation. Under these conditions the first slag formed will be rich in CaO and P₂O₅ but low in FeO, (about 5%). The final slag, however, will be high in FeO and this may be retained in the furnace to form the basis for the first slag during the next heat.

Rephosphorization or Phosphorus Reversion

Consideration of the expressions shown previously indicate that P may return to the metal from the slag under two conditions:

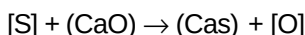
- (i) When the activity of the oxygen in the metal is reduced by de-oxidation, and
- (ii) When the activity of the CaO in the ladle slag is reduced by pick-up of SiO₂ from the refractories (Figure A-4).

In such instances the P content of the metal in the ladle can increase during the casting process and the P concentration in the last metal to be poured could exceed specification. For this reason there should be sufficient free lime present in the ladle slag to counteract the increase in SiO_2 . It has been found that P reversion does not occur when ladles are lined with basic refractories.

The Sulfur Problem

With a few exceptions sulfur is considered undesirable in steel and there is an increasing demand for steels with lower and lower sulfur levels. Problems associated with sulfur are due mainly to the harmful effect of sulfide inclusions. For many steel grades the maximum sulfur level is now 0.02 or even 0.01 %.

Sulfur transfer from the metal to the slag may be represented by the reaction:



for which,

$$k = \frac{(a_{\text{CaS}})}{[a_{\text{S}}]} \cdot \frac{[a_{\text{O}}]}{(a_{\text{CaO}})}$$

$$\text{i.e.} \quad \frac{(a_{\text{CaS}})}{[a_{\text{S}}]} = \frac{K(a_{\text{CaO}})}{[a_{\text{CaO}}]}$$

$$\text{i.e.} \quad \frac{(N_{\text{CaS}})}{[\text{wt \%S}]} = \frac{K(\gamma_{\text{CaO}}) \cdot (N_{\text{CaO}})}{(\gamma_{\text{CaS}}) \cdot (\text{wt \%O})}$$

Consideration of expression (S-2) indicates that desulfurization is favored by:

- (i) An increase in γ_{CaO} and/or N_{CaO} , i.e. an increased basicity.
- (ii) An increase in a_{S} , (Figure A-5). In hot metal containing about 4%C and 1%Si, a_{S} is about 5. During refining as C and Si are gradually removed, a_{S} decreases to about unity. This means that sulfur is about five times more active in hot metal than it would be in steel at the end of refining.
- (iii) A decrease in γ_{CaS} . This is achieved with a basic slag which has a greater capacity for sulfur absorption than an acid slag.

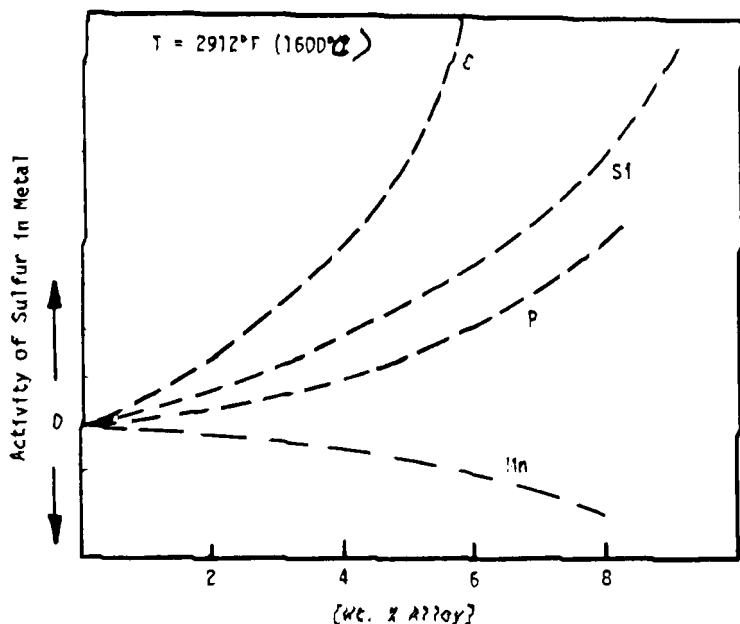


Figure A-5. Effect of Alloying Element on the Activity of Sulfur in the Metal.

- (iv) A decrease in a_{O} . In hot metal a_{O} is less than 0.01 whereas at the end of refining when the steel is highly oxidized, a_{O} is close to unity.
- (v) A decrease in [wt %O] in contrast to P, S transfer to the slag is favored by a low (FeO) content. It is for this reason that low S levels are obtained with steels made under reducing conditions in the electric arc furnace.

The effects of slag basicity and the strong influence of iron oxide on the S distribution ratio are shown in Figure A-6. From this diagram it is clear that desulfurization is most readily accomplished either in the blast furnace or between the blast furnace and the steelmaking unit, (external desulfurization), while the C and Si are still high and the FeO content of the slag is still low. In the arc furnaces S transfer is favored during the early stages of refining by a fluid, basic slag, low in FeO

Sulfur Reversion

Consideration of reaction (S-1) indicates that S may transfer back to the metal phase towards the end of a heat when the oxygen content of the

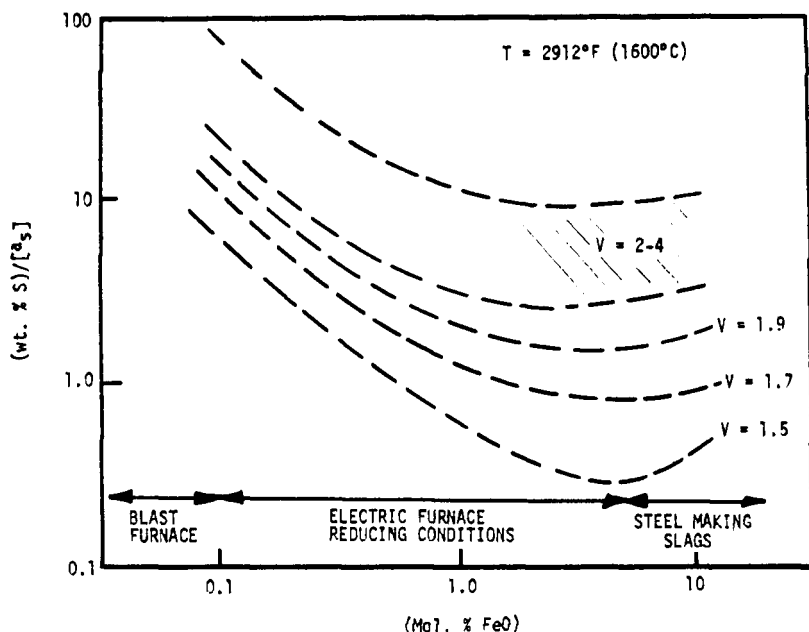


Figure A-6. Effects of Slag Basicity and Iron Oxide on Sulfur Distribution Ratio.

metal, and also the slag, is increasing. Where particularly low sulfurs are required, less than 0.01, a two-slag practice may be necessary in the steelmaking unit.

Summary

This brief introduction has presented some of the basic concepts of metallurgical chemistry. The practical applications of these concepts will be presented in the following chapters.

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Heat Treatment of Steel Castings

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ABSTRACT

The properties of steel castings are attained by the interaction of casting shape, composition and heat treatment. Heat treatment can be effectively used to obtain a wide variation of desired properties using approximately the same composition. The flexibility available in heat treatment can also lead to unacceptably wide variations. Therefore, process control is very necessary to give reproducibly good properties.

Heat treatment, when used effectively and marketed correctly, can be used to give castings excellent properties. Foundries should see heat treatment as an opportunity to meet customer and service demands by uniform good properties. Quality Assurance could make this area a place for serious improvement in the foundry process.

HEAT TREATING PROCESSES

A number of heat treating processes are used in the treatment of steel castings including some recently developed methods. Normally applied to carbon and low alloy steels are normalizing, quenching, and tempering. Also used in special situations are annealing, intercritical heat treatment, martempering, austempering, aging or carburizing. Nitriding is not generally applied to cast steel parts. Stainless alloys have special

heat treatment cycles, primarily solution treating. Also used are aging and stabilization treatments.

Normalizing consists of austenitizing followed by air cooling and is intended to overcome the wide variety of microstructures affected by mold and shakeout cooling. In plain carbon and low alloy steels, the predominant normalized structure is pearlite with variable amounts of ferrite. Fine pearlite provides the strength and ductility required for many applications and therefore, many castings are used in the normalized condition. A normalize followed by tempering is used to give good elevated temperature properties, i.e., creep resistance and is used for the Cr-Mo steel types. Normalizing is also used as a term for heat treating martensitic stainless steels such as CA15 or CA6NM even though a martensitic structure is obtained.

The important factors influencing strength in the cast ferritic-pearlitic steels that are normalized are grain size, carbon content, i.e. pearlite amount, pearlite spacing and solid solution strengthening, i.e. alloy content. Figure 1 shows the relative contributions of carbon content, grain size, and solid solution strengthening in a carbon steel. Increasing the carbon increases the amount of pearlite, approximately .01% carbon increases pearlite 1%. Manganese increases the strength of C-Mn steels by solid solution strengthening. Toughness in normalized and tempered materials is attained by low carbon steels strengthened by fine grain size and solid solution strengthening. As the strength of the

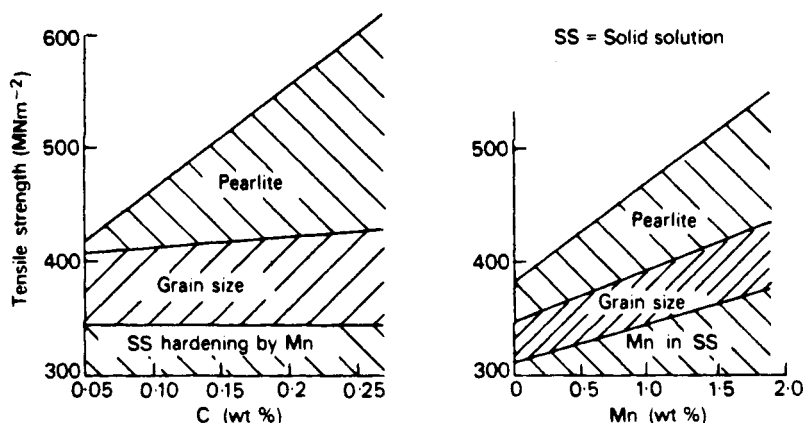


Figure 1 Factors contributing to the strength of C-Mn steels.

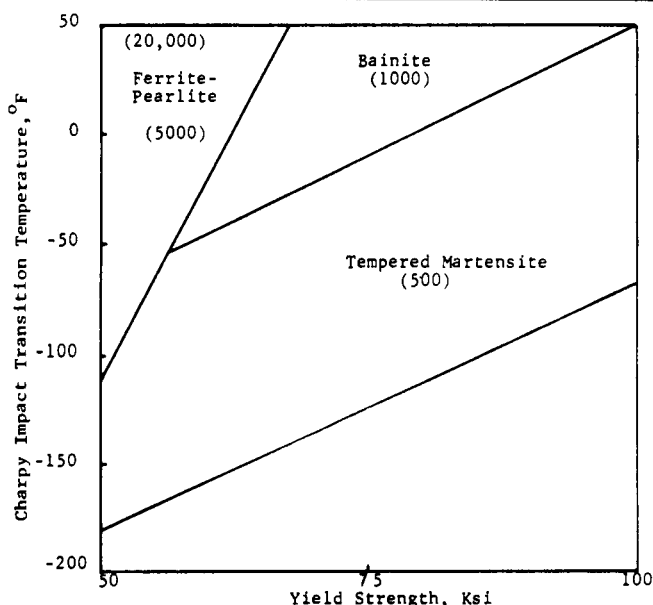


Figure 2 Generalized relation between mechanical properties, heat treated microstructure, and carbide spacing (mean free ferrite path, A).

normalized or normalized and tempered steels increase the ductility and toughness decrease, as shown in Figure 2. Each 1% pearlite increase, increases the transition temperature 3.5°F:

Normalizing at high temperatures or for long times does not seem to increase or improve properties. Normalizing prior to quench and temper does not seem to improve properties but may improve toughness, especially in heavy sections. Long time normalizing has also been called homogenizing but carbon and nitrogen are the only elements that are substantially redistributed during the procedure.

Alloy elements do effect the temperature required for normalizing which is usually done 100 to 150°F over the A_{c3} temperature. Table I lists A_{c1} and A_{c3} for various cast carbon and low alloy steels. They can also be estimated from the chemistry with the regression equations:

$$A_{c3}(^{\circ}\text{C}) = 910 - 203 \sqrt{\text{C}} - 15.2 \text{ Ni} + 44.7 \text{ Si} + 104 \text{ V} + 31.5 \text{ Mo} + 13.1 \text{ W} \quad (1)$$

$$A_{c1}(^{\circ}\text{C}) = 723 - 20.7 \text{ Mn} - 16.9 \text{ Ni} + 29.1 \text{ Si} + 16.9 \text{ Cr} + 290 \text{ As} + 6.38 \text{ W} \quad (2)$$

Table I Critical temperatures of cast carbon and low alloy steels

Alloy Type	Composition—%									Ac ₁		Ac ₂	
	C	Si	Mn	S	P	Al	Ni	Cr	Mo	F	C	F	C
C Steel	.22	.39	.83	.009	.014	.035	.20	.09	.03	1346	730	1580	860
	.34	.43	.95	.013	.010	.058	.06	.03	<.01	1382	750	1517	825
C-Mo	.21	.40	.75	.024	.020	.076	.16	.10	.63	1409	765	1634	890
Ni	.18	.38	.66	.005	.006	.035	2.68	.070	.03	1256	680	1508	820
	.12	.35	.89	.016	.010	.075	4.00	.030	.01	1247	675	1454	790
Mn	.20	.38	1.35	.014	.010	.068	.06	.03	.01	1375	745	1580	860
Mn-Mo	.34	.47	1.45	.015	.010	.060	.06	.03	.39	1382	750	1508	820
	.125	.36	1.28	.018	.016	.078	.09	.07	.35	1382	750	1643	895
Cr-Mo	.27	.42	.79	.022	.015	.065	.16	.99	.25	1409	765	1553	845
Ni-Cr-Mo	.25	.43	.66	.009	.010	.024	.57	.47	.52	1346	730	1580	860
	.29	.40	.68	.007	.005	.011	2.30	2.55	1.02	1436	780	1652	900
	.20	.37	.79	.009	.018	.015	3.35	1.10	1.00	1409	765	1688	920
	.165	.37	.91	.016	.010	.080	.25	.49	.40	1382	750	1544	840
	.184	.36	1.0	.016	.010	.075	.34	1.02	.52	1328	720	1481	805
	.14	.37	.64	.018	.023	.068	.26	1.50	.42	1211	655	1553	845

The temperature of 1650 to 1750°F is generally used for normalizing cast steel materials. If the normalizing temperature is low, close to the Ac₃, then it takes a long time to dissolve carbides and allow diffusion to minimize carbon segregation. If the normalizing temperature is too high, then the grain size of the austenite will grow which will decrease strength, toughness and ductility. Aluminum deoxidation prevents grain growth so that temperatures above 1850°F are needed to cause excessive grain growth in aluminum deoxidized steels.

Normalizing is completed by air cooling the parts to form a fine grain size with a fine pearlite spacing for good strength and ductility. Sometimes forced air cooling is supplied in order to attain the properties required.

Quenching is used to develop higher mechanical properties than attainable with normalizing, above 100,000 psi tensile strength. Quenching also improves the toughness of low alloy steels at any strength level, and benefits even plain carbon steels by producing finer pearlite. Severe quenching of nonhardenable alloys is used to produce a surface compressive layer and is used by some industrial equipment manufacturers to increase the fatigue life of components. However, tempered martensite is the microstructure generally sought for combined strength and toughness, and it is attained with various combinations of

alloy content and cooling rate. Quenching consists of austenitizing followed by a rapid cooling to form martensite. Through-hardening is a function of section size, quenching and composition. Understanding the relationships between these three factors is essential to the proper heat treatment of cast steels.

Hardenability is a measure of the effectiveness of a steel composition to avoid forming pearlite, ferrite, or bainite and form martensite instead. Hardness is the resistance to penetration, and is measured by a Brinell or Rockwell test. Carbon content is the single most determining factor limiting the hardness of a carbon or low alloy steel. Carbon content of an alloy must be adequate to allow sufficient strength and hardness after tempering as shown in Figures 3 and 4 and Table II.

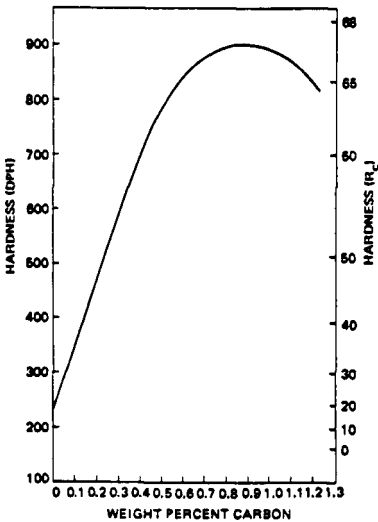


Figure 3 Hardness of martensite as a function of carbon content in Fe-C alloys.

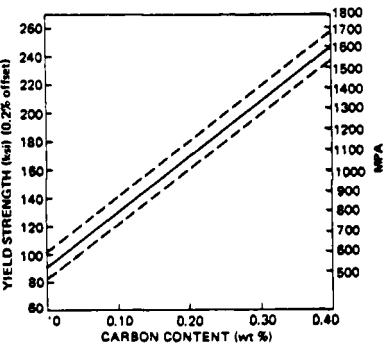


Figure 4 The effect of carbon content on the yield strength of untempered martensites.

Table II Carbon-Hardness Factors at 99.9% Martensite

Carbon %	Maximum hardness HRC	Carbon %	Maximum hardness HRC	Carbon %	Maximum hardness HRC	Carbon %	Maximum hardness HRC
0.10	38	0.23	46	0.36	54	0.49	60
0.11	39	0.24	46	0.37	55	0.50	60
0.12	40	0.25	47	0.38	55	0.51	60
0.13	40	0.26	48	0.39	56	0.52	61
0.14	41	0.27	49	0.40	56	0.53	61
0.15	41	0.28	49	0.41	57	0.54	61
0.16	42	0.29	50	0.42	57	0.55	61
0.17	42	0.30	50	0.43	58	0.56	61
0.18	43	0.31	51	0.44	58	0.57	62
0.19	44	0.32	51	0.45	58	0.58	62
0.20	44	0.33	52	0.46	59	0.59	62
0.21	45	0.34	53	0.47	59	0.60	62

All of the other alloy elements make it easier to form martensite, especially in heavier sections. The largest section bar that can be through-hardened by the fastest theoretical cooling rate is given by:

$$DI = (\text{Carbon-grain size}) * F_{MN} * F_{Si} * F_{Ni} * F_{Cr} * F_{Mo} \dots$$

The factors for the various alloying elements are given in Table III. Increasing the hardenability will allow heavier sections to be through-hardened or a slower cooling rate to be used.

The Jominy test is used to measure the hardenability of a given steel and is a standard test ASTM A255. In this test, a one inch bar is austenitized and then one end is quenched. This results in a wide variety of

Equations for Table III Elemental Multiplying Factors

Carbon/Grain Size 7

Up to 0.40 % Incl.	MF = 0.54 (%C)
Over 0.40% to 0.55% Incl.	= 0.171 + .001 (%C) + 0.265 (%C) ²
Over 0.55% to 0.65% Incl.	= 0.115 + .268 (%C) - 0.038 (%C) ²
Over 0.65% to 0.75% Incl.	= 0.143 + 0.2 (%C)
Over 0.75% to 0.90% Incl.	= 0.062 + .409 (%C) - 0.135 (%C) ²

Manganese

Up to 1.20% Incl.	= 3.3333 (%Mn) + 1.00
Over 1.20% to 1.95% Incl.	= 5.10 (%Mn) - 1.12

Silicon	= 1.00 + 0.7 (%Si)
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Nickel	= 1.00 + .333 (%Ni) + .066 (%Ni) ² - .055 (%Ni) ³ + .018 (%Ni) ⁴
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Chromium	= 1.00 + 2.16 (%Cr)
----------	---------------------

Molybdenum	= 1.00 + 3.00 (%Mo)
------------	---------------------

Copper	= 1.00 + 0.365 (%Cu)
--------	----------------------

Vanadium	= 1.00 + 1.73 (%V)
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quench rates from the high rate at the quenched end to a slow cooling rate at the other end. After quenching, a flat is carefully ground on one side and the hardness measured in 1/16" intervals. Typical results are shown in Figure 5. Any particular hardness is associated with a cooling rate. The further from the quenched end the steel retains the high hardness, the higher is the hardenability. Hardness refers to the actual hardness measurement, but hardenability is the ability to attain the high hardness at slower cooling rates. The Jominy curve can be estimated from the equations in Table IV.

The hardness at $J = 1$ is equal to the maximum hardness for the carbon content of interest. This hardness is divided by DF to obtain the remainder of the estimated Jominy curve. The Jominy test is only valid for DI less than 6.6 inches. If the DI is greater than that, the one inch bar will air harden and no meaningful Jominy curve will be found.

Very hardenable alloys must use something other than DI or Jominy curves to express their transformation characteristics. A continuous cooling transformation, (CCT) diagram allows the prediction of hardenability of large pieces made with high hardenability materials. A CCT

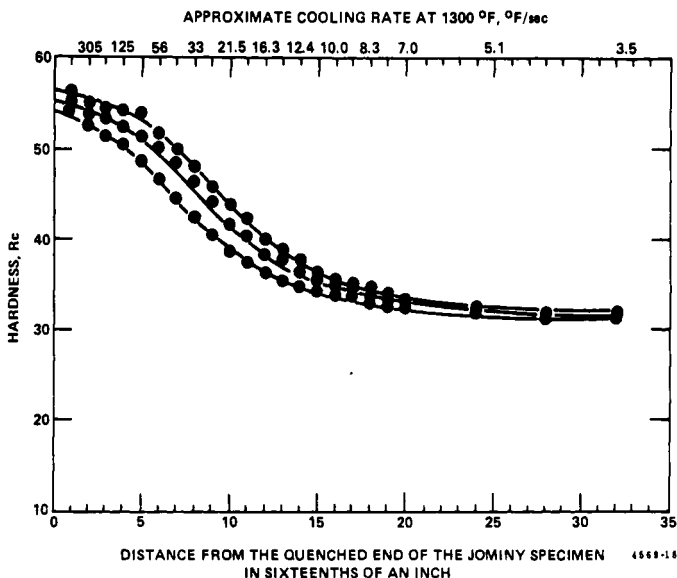


Figure 5 Jominy hardenability band of AISI 4140 used in quench facility evaluations.

diagram for a material similar to CA15 is shown in Figure 6. Cooling rates for the formation of various microstructures can also be estimated from:

$$\text{Log (Cooling rate @ 700°C in °C/h)} \geq 9.81 - (4.62C + 1.05 \text{ Mn} + .5\text{Cr} + .66 \text{ Mo} + .54 \text{ Ni}) \text{ for martensite}$$

$$\text{Log (Cooling Rate)} \geq 10.17 - (3.80C + 1.07 \text{ Mn} + .57 \text{ Cr} + 1.58 \text{ Mo} + 0.70 \text{ Ni}) \text{ for bainite}$$

$$\text{Log (Cooling Rate)} \leq 6.36 - (.43C + .49 \text{ Mn} + .26\text{Cr} + .38 \text{ Mo} + 2 \sqrt{\text{Mo}} + .78 \text{ Ni}) \text{ for pearlite}$$

Cooling time from the A_{c3} to 500°C to form various microstructures can be estimated from:

$$\text{Log (CT; seconds)} \leq 3.274C + .046\text{Si} + .626 \text{ Mn} + .706 \text{ Cr} + .520 \text{ Mo} + .026 \text{ Ni} + .675 \text{ Cu} - 1.818 \text{ for martensite}$$

$$\text{Log (CT)} \leq 3.288C - .168\text{Si} + 1.068 \text{ Mn} + 1.266 \text{ Cr} + 2.087 \text{ Mo} + .300 \text{ Ni} + .626 \text{ Cu} - 1.931 \text{ for bainite}$$

$$\text{Log (CT)} \geq .597C + .100 \text{ Si} + 1.395 \text{ Mo} + 1.295 \text{ Cr} + 3.730 \text{ Mo} + .395 \text{ Ni} + .398 \text{ Cu} + .869 \text{ for pearlite}$$

Table IV Equations for Dividing Factors

"J" Distance (1/16 Inch)	DI	Dividing Factor*
2	To 2.1 Incl	DF = $4.94793 - 11.91710 \times + 15.09047 \times^2 - 9.65814 \times^3 + 3.07316 \times^4 - 0.38650 \times^5$
	Over 2.1	DF = 1.00
3	To 3.1 Incl	DF = $2.41626 - .47878 \times - 1.20932 \times^2 + 1.04741 \times^3 - .30684 \times^4 + .03085 \times^5$
	Over 3.1	DF = 1.00
4	To 4.1 Incl	DF = $5.67889 - 6.17426 \times + 3.55534 \times^2 - 1.07232 \times^3 + .16561 \times^4 - .01037 \times^5$
	Over 4.1	DF = 1.00
5	To 4.4 Incl	DF = $4.54393 - 2.94391 \times + 1.02014 \times^2 - .17808 \times^3 + .01506 \times^4 - .00049 \times^5$
	Over 4.4	DF = 1.00
6	To 5.0 Incl	DF = $4.37760 - 2.12231 \times + .52764 \times^2 - .06852 \times^3 + .00600 \times^4 - .00036 \times^5$
	Over 5.0	DF = 1.00
7	To 5.3 Incl	DF = $4.16512 - 1.45563 \times + .01827 \times^2 + .10757 \times^3 - .02285 \times^4 + .00145 \times^5$
	Over 5.3	DF = 1.00
8	To 5.6 Incl	DF = $4.40495 - 1.70370 \times + .17598 \times^2 + .05995 \times^3 - .01645 \times^4 + .00114 \times^5$
	Over 5.6	DF = 1.00
9	To 5.8 Incl	DF = $4.97077 - 2.47031 \times + .65700 \times^2 - .08883 \times^3 + .00560 \times^4 - .00011 \times^5$
	Over 5.8	DF = 1.00
10	To 6.1 Incl	DF = $5.31768 - 2.81301 \times + .84426 \times^2 - .14262 \times^3 + .01315 \times^4 - .00052 \times^5$
	Over 6.1	DF = 1.00
12	To 6.6 Incl	DF = $5.58137 - 2.78420 \times + .82634 \times^2 - .14823 \times^3 - .01513 \times^4 - .00066 \times^5$
	Over 6.6	DF = 1.00
14		DF = $5.83176 - 2.99646 \times + .94088 \times^2 - .17734 \times^3 + .01839 \times^4 - .00079 \times^5$
16		DF = $6.06952 - 3.15198 \times + .99297 \times^2 - .18010 \times^3 + .01720 \times^4 - .00066 \times^5$
18		DF = $7.32018 - 4.60605 \times + 1.68442 \times^2 - .33844 \times^3 + .03451 \times^4 - .00139 \times^5$
20		DF = $7.81382 - 5.10022 \times + 1.92141 \times^2 - .39459 \times^3 + .04078 \times^4 - .00165 \times^5$
24		DF = $9.18138 - 6.69048 \times + 2.75891 \times^2 - .61161 \times^3 + .06772 \times^4 - .00293 \times^5$
28		DF = $9.27904 - 6.21461 \times + 2.33158 \times^2 - .46972 \times^3 + .04727 \times^4 - .00186 \times^5$
32		DF = $8.62857 - 5.16125 \times + 1.81214 \times^2 - .35489 \times^3 + .03569 \times^4 - .00143 \times^5$

*Where $\times$ = DI

13 Cr (51410)

AUSTENITISED AT 980 C

PREVIOUS TREATMENT ROLLED, SOFTENED 650 C 1 h

ANALYSIS Wt % (See note on page 8)

C	Si	Mn	P	S	Cr	Mo	Ni	Al	Nb	V
0.12	0.40	0.50	0.020	0.010	12.5	—	0.20	—	—	—

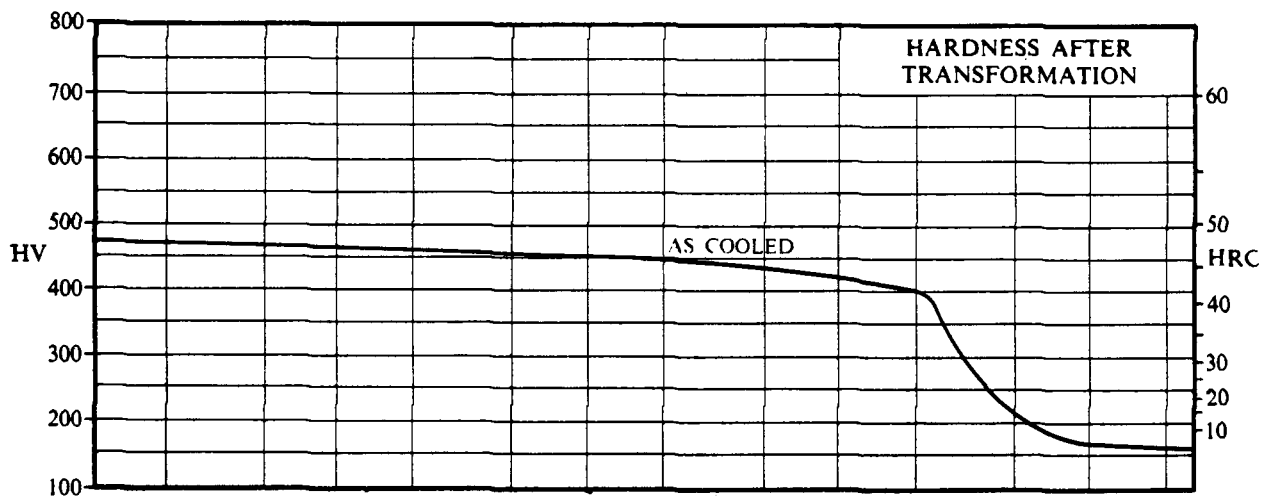
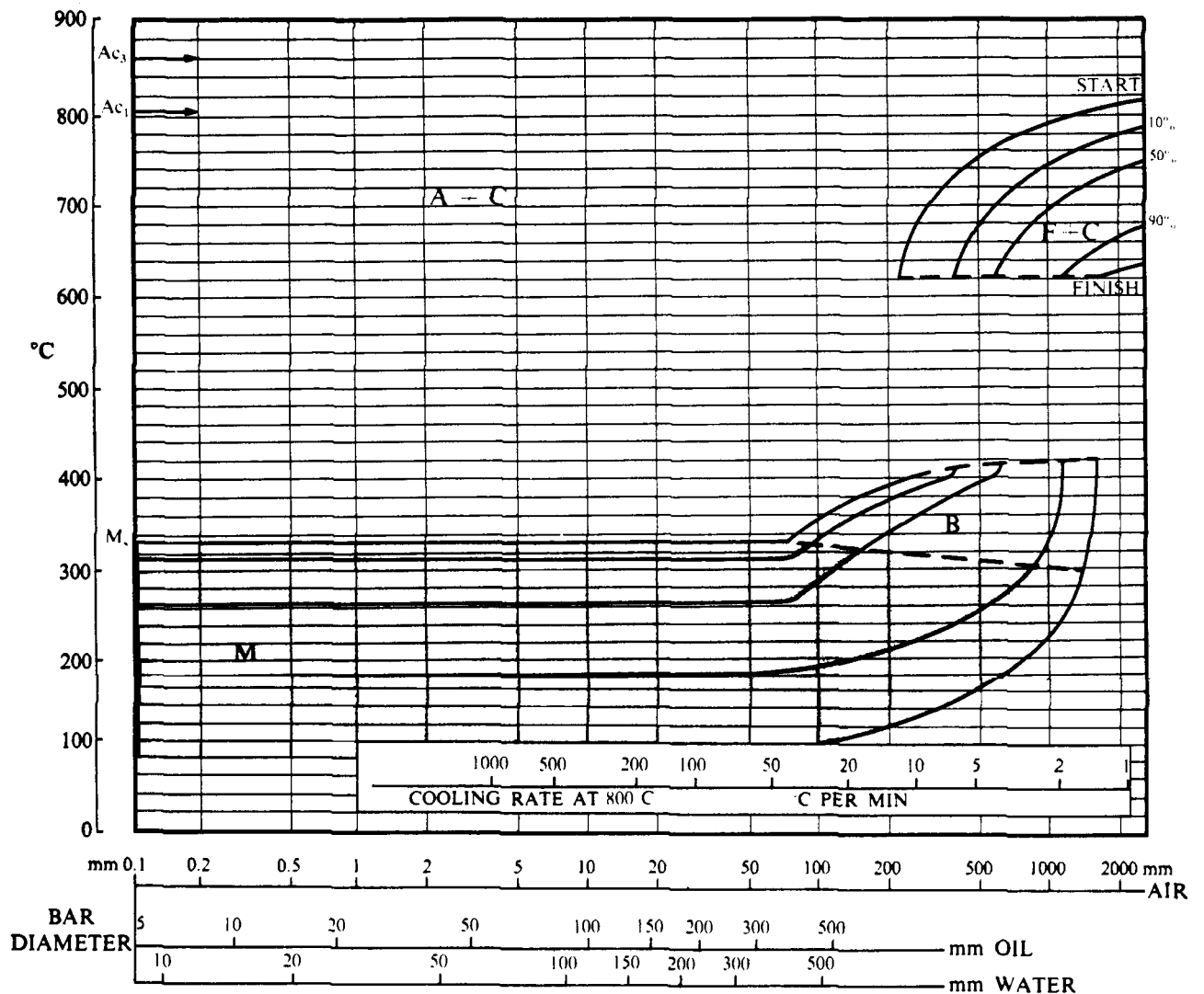


Figure 6 CCT Diagram of a 13 Chromium Steel.

Alloy compositions are selected to minimize cost while still meeting properties and higher alloy contents are needed as the cooling rate in a part decreases.

The cooling rate depends on the type of quenchant, quenchant temperature, and quenchant agitation interacting with part shape. In furnace cooling the quenchant is hot air, which forms coarse pearlite and is called annealing. Cooling in air forms fine pearlite and is called normalizing. Liquid cooling, using water; oil, etc., can form martensite and is known as quenching.

The section size and cooling media are the determining factors in the cooling rate achieved. The quenchant and section size of a quenched part are expressed as an equivalent Jominy Distance in Table V: The Quench Severity "H" is a measure of the quench bath performance. The information from this table can be extended to other shapes using Figure 7.

For a given part, the type of quenchant is the single biggest determining factor for cooling rate. Quenchants include saltwater; water, polymer-water, and oil, ranked from the fastest to the slowest. Salt-water is corrosive and is not generally used. Water is the fastest commonly used quenchant. Polymer-water solutions have become increasingly popular because they are slower than water, avoiding cracks and warpage, and faster than oil, allowing greater hardening without smoke or the possibility of fire. Polymer-water solutions require the greatest process control to operate properly. Oil quenching gives slow uniform rates with little problem from cracking. However, the slow cooling rate when quenching in oil requires more alloy in the steel to get through-hardening. Oil also smokes and can catch fire.

The quenchant bath temperature is another important variable in quenching performance. In water, but especially in polymer-water, the bath must be maintained below 110°F or the cooling rate will become much slower—even slower than oil in some cases. With oil the bath temperature does not affect the cooling rate much but the bath must be kept at least 150°F below the flash point to avoid a fire.

The quenchant bath agitation also has an effect on cooling rate. All quenchants should be agitated to get the best performance. Agitation also helps to get uniformity in the hardness profiles of all the parts. This uniformity also reduces the tendency to warp or crack parts.

Table V End-Quench Distance vs. Bar Diameter (30)

When the end-quench hardness curve of a steel has been found, this table enables one to estimate the hardnesses that would be obtained at the centers of quenched round bars of different diameters, when the same steel is quenched with various severities of quench.

For each successive 1/16" position, the hardness obtained in the end-quench test would be found at the center of the bar size shown.

Distance from End in End- Quench Test		Equivalent Bar Diameter When Quenched					
		Still Oil	Circulated Oil	Still Water	Circulated Water	Still Brine	Infinite or Idealized Quench
		H = 0.25	H = 0.45	H = 1.0	H = 1.5	H = 2.0	H = ∞
Inches							
1/16		0.1	0.15	0.3	0.35	0.4	0.7
2/16	1/8	0.2	0.3	0.5	0.65	0.75	1.15
3/16		0.35	0.55	0.85	1.0	1.25	1.6
4/16	1/4	0.5	0.80	1.15	1.3	1.5	1.9
5/16		0.6	0.95	1.4	1.6	1.75	2.2
6/16	3/8	0.8	1.2	1.6	1.8	2.0	2.4
7/16		1.0	1.4	1.8	2.0	2.3	2.7
8/16	1/2	1.1	1.5	2.1	2.3	2.5	2.9
9/16		1.3	1.7	2.3	2.5	2.7	3.2
10/16	5/8	1.4	1.9	2.5	2.7	2.9	3.4
11/16		1.6	2.1	2.8	3.0	3.2	3.6
12/16	3/4	1.7	2.2	3.0	3.2	3.4	3.8
13/16		1.9	2.4	3.2	3.4	3.5	4.0
14/16	7/8	2.0	2.5	3.3	3.5	3.7	4.2
15/16		2.1	2.7	3.5	3.7	3.9	4.4
16/16	1	2.3	2.8	3.7	3.9	4.1	4.6
17/16		2.4	3.0	3.9	4.1	4.2	4.7
18/16	1 1/8	2.5	3.1	4.0	4.2	4.4	4.9
19/16		2.6	3.3	4.1	4.4	4.5	5.0
20/16	1 1/4	2.7	3.4	4.3	4.5	4.7	5.1
21/16		2.8	3.5	4.4	4.7	4.8	5.3
22/16	1 3/8	2.9	3.6	4.5	4.8	4.9	5.4
23/16		3.0	3.7	4.7	5.0	5.1	5.5
24/16	1 1/2	3.1	3.8	4.8	5.1	5.2	5.6
25/16		3.2	4.0	4.9	5.2	5.3	5.8
26/16	1 5/8	3.3	4.0	5.0	5.3	5.4	5.9
27/16		3.4	4.1	5.1	5.4	5.5	6.0
28/16	1 3/4	3.5	4.2	5.2	5.5	5.6	6.1
29/16		3.6	4.3	5.3	5.6	5.6	6.2
30/16	1 7/8	3.6	4.4	5.4	5.7	5.7	6.2
31/16		3.7	4.5	5.5	5.8	5.8	6.3
32/16	2	3.8	4.5	5.5	5.8	5.9	6.4

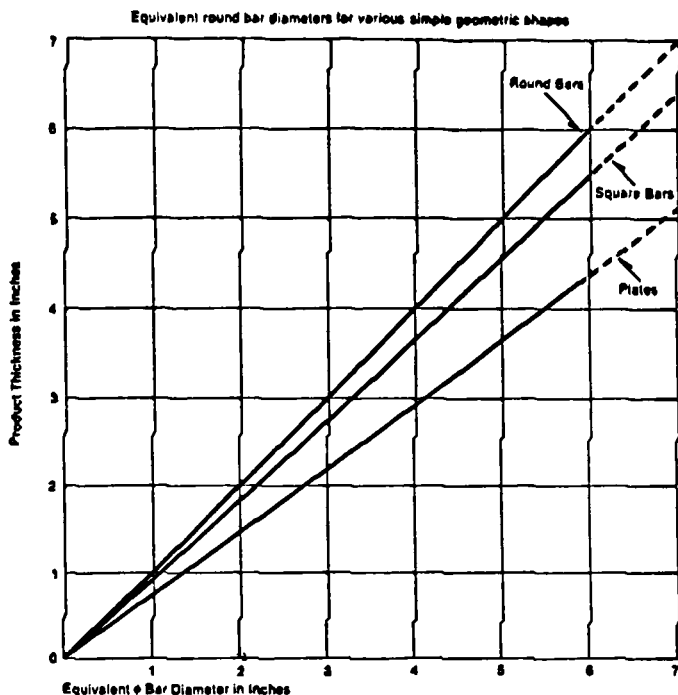


Figure 7 Relationship between the through-quenched bar diameter and the through-quenched thickness of other shapes.

Tempering follows quenching and involves the decomposition of martensite into subtle microstructures of fine carbide dispersions. Tempering heat treatments are commonly conducted to improve toughness. However, tempering in the range 500-1050°F generally does not benefit toughness even though strength is decreased. Tempering is also done after normalizing to improve toughness.

Both the time and temperature of the temper is important to the properties developed. Short tempering times (15-30 minutes) can generally give the same properties at the same hardness as longer times at lower tempering temperatures. Tempering is done at 400°F to give the maximum hardness and strength and above 1050°F to give the maximum toughness and ductility. The effect of tempering on hardness is illustrated in Figure 8. Chromium and molybdenum retard the tempering of cast steels and require longer times or higher temperatures. The effect of alloying elements on final tempering hardness is shown in Figure 9 and 10.

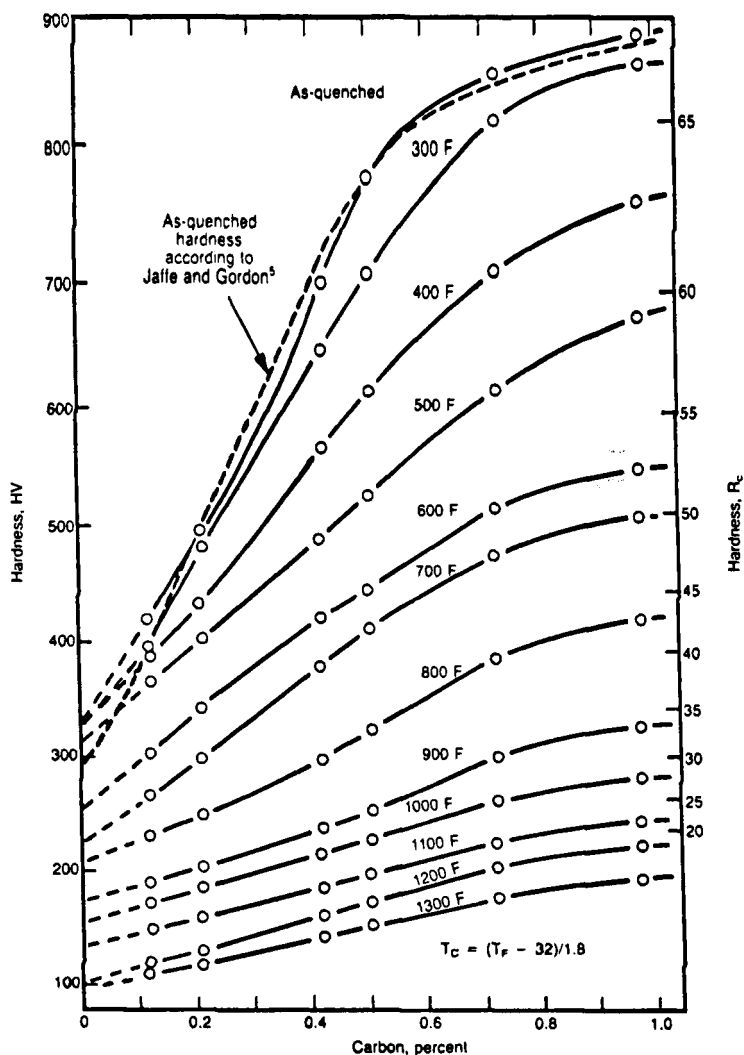


Figure 8 Hardness as a function of carbon content of martensite in Fe-C alloys tempered at various temperatures. (Ref 8.5)

Tempering, especially for maximum toughness, should avoid two forms of embrittlement, one associated with 500°F also known as blue brittleness or temper martensite embrittlement (TME) and the other associated with 900°F also known as temper embrittlement (TE). TME is caused by the precipitation of carbides and is avoided by having enough alloy and carbon to avoid tempering in the 400-600°F range. TME is irreversible and only affects martensite structures.

TE is reversible and happens in the range of 800-1100°F: TE is caused by a segregation of solute atoms to grain boundaries. Antimony, phosphorus, arsenic, tin and manganese all increase the susceptibility of an alloy to TE. Molybdenum decreases the susceptibility to TE. TE is worst in martensite but can occur with bainite or even pearlite-ferrite mater-

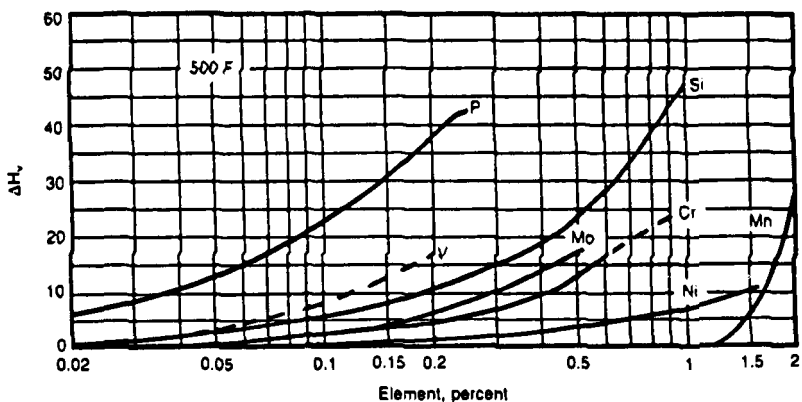


Figure 9 Effect of alloying elements on the retardation of softening during tempering at 260°C (500°F) relative to Fe-C alloys. (Ref 8.5)

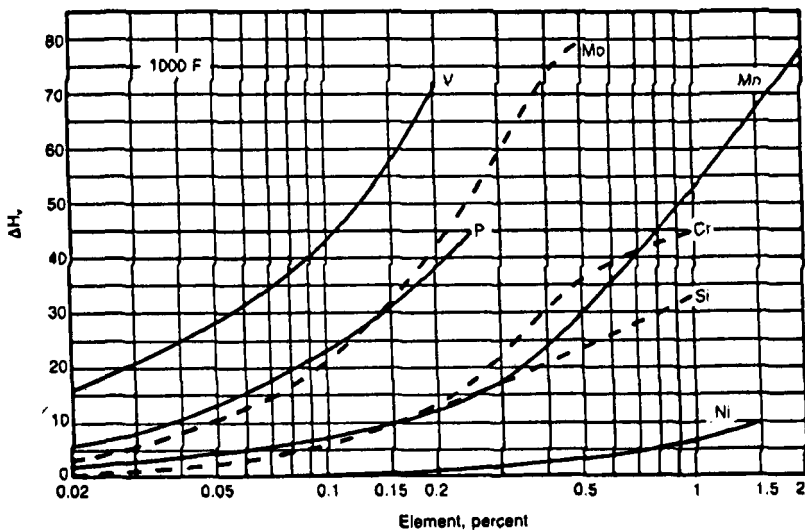


Figure 10 Effect of alloying elements on the retardation of softening during tempering at 540°C (1000°F) relative to Fe-C alloys. (Ref. 8.5)

ials. Tempering above 100°F reverses the TE. TE is commonly known as 885° embrittlement and causes problems in any steel with a ferritic or martensitic structure exposed in the susceptible range including the martensitic or ferritic stainless steels or the ferrite of the duplex austenitic-ferritic stainless steels. Heavy section parts tempered above 885°F should be quenched from the temper or forced air cooled to avoid embrittlement.

Annealing is intended to soften steel for machining or cold working. Various cycles are used from slow cooling from above the Ac_3 (full annealing) to prolonged tempering just below the Ac_1 , (sub-critical annealing). Structurally, one seeks a relatively coarse dispersion of carbides in a ferrite matrix. This structure produces minimum hardness and maximum ductility, but does not necessarily lead to best toughness.

It should be noted that whereas alloying elements are beneficial to hardening, they are a decided handicap in annealing.

Intercritical Heat Treatment (ICHT) is used to improve the toughness of low alloy steels made in large section sizes. The ICHT is performed after quenching to achieve the most benefit. The part is heated to between the Ac_1 and Ac_3 . This causes about half the microstructure to convert back from martensite to austenite. This treatment is followed by a quench and a final temper. ICHT is reported to refine the grain size and reduce TE.

Martempering is to avoid warping and quench cracking often associated with standard heat treating practices. In martempering, the steel is quenched to avoid forming pearlite or ferrite but is held above the M_s temperature to allow the part to regain a uniform temperature. Then the steel is slowly cooled to form martensite and immediately tempered. This procedure is not often used on steel castings.

Austempering is a term used for quenching a steel to avoid ferrite and pearlite and then isothermally transforming to produce bainite. Bainite has good strength, better ductility and poorer toughness than martensite. This procedure is not often used.

Renewed interest in austempering has been generated by the ductile iron industry. A high silicon, high carbon steel, when austempered, forms bainitic ferrite, then metastable austenite which finally decomposes to ferrite and carbides. If cooled during the stage when ferrite and austenite are present, then a unique combination of properties in-

cluding good strength, toughness and ductility have resulted. This process could be applied to steel castings and might have potential for toughness or wear resistant parts.

Aging is a treatment to cause a fine precipitate to form. It is similar to a temper cycle. Copper containing steel can be aged to achieve maximum strength. CD-4MCu and CB-7Cu both can be aged as well as copper bearing alloy steels. Cracking and welding problems have discouraged the wide spread use of the copper bearing alloy steels. The high alloy copper bearing steels are generally supplied in the unaged condition.

Carburizing is the addition of carbon to the surface of a part to increase the hardness and strength of the surface while leaving the center tough and ductile. The carbon is added by adjustment of the furnace atmosphere using methane, carbon monoxide and carbon dioxide. This operation is not often applied to castings by the foundry.

Solution Treating is used in stainless steels to dissolve the carbides and allow the chromium to give the maximum corrosion resistance. The formation of chrome carbides with the loss of chromium at the grain boundaries is called sensitization and occurs at 950-1450°F. The high alloy steels are heat treated for corrosion resistance, not to attain the necessary mechanical properties. It is also used to eliminate molybdenum segregation especially in the nickel based materials. In general, solution treating is done by heating the cast material above 1900°F followed by quenching. If molybdenum is present then the treatment temperature must be higher to minimize segregation, about 2050° or higher.

Stabilizing is used with the columbium containing stainless alloys. The columbium forms a stable carbide that denies the carbon to the chromium. It is used to maintain corrosion resistance in alloys that are used at elevated temperatures in the sensitizing area. The stabilizing treatment is applied after solution treating and is done at about 1600°F to ensure corrosion resistance. This does not eliminate the need for post weld heat treatment since part of the heat affected zone loses its corrosion resistance during welding.

The ultimate choice of heat treatment must be selected for the properties required, service conditions considered, composition appropriate and shape known. This will allow good engineering procedures to give

the highest quality product. To heat treat requires procedures that have been certified to give the desired results.

HEAT TREATMENT PROCEDURES

Heat treatment of any material for any purpose has several elements in common. Each cycle has a heating rate, holding time, holding temperature and cooling rate. The selection of these variables determines the effectiveness at heat treatment.

Heating Rate is normally rapid to maximize production, minimize heating costs. The heating rate is limited by the equipment capabilities but generally rapid heating does not cause problems. Warpage and cracking have been attributed to rapid heating. However, most warpage and cracking occur during cooling not during heating. Additionally warpage and cracking normally happen due to nonuniformity not actual rate. Heating a long casting on one side can lead to warpage. Castings must also be supported during heating in order not to warp. Indiscriminate stacking up large heavy castings can lead to substantial warpage in the bottom castings. Fixturing and tray loading are important in the prevention of distortion. Cracking during heat up is rare but extremely brittle materials are an exception and may require a reduced rate of heating or a more uniform heating to prevent cracking. The problems of distortion and cracking must be attributed to heating or cooling rates or else long uneconomical heat up cycles can evolve which do not prevent the problem but cost money long after the problem has been solved in other ways.

Holding Time depends on the operation. The historical rule of thumb was 1 hr/inch of cross section for normalizing or quenching and 2 hr/inch for tempering once the furnace was at temperature. These rules are old and were used when furnaces were not uniform in heating and it was difficult to know when the whole furnace load was at temperature. If the furnace is well designed giving uniformity of temperature, and the temperature of the castings is monitored, then shorter times are sufficient.

Holding times are designed to insure that all the castings are at temperature, including those in the center of the stack and that sufficient time is allowed for dissolving the carbides.

Knowing the furnace load is at temperature requires that the furnace be

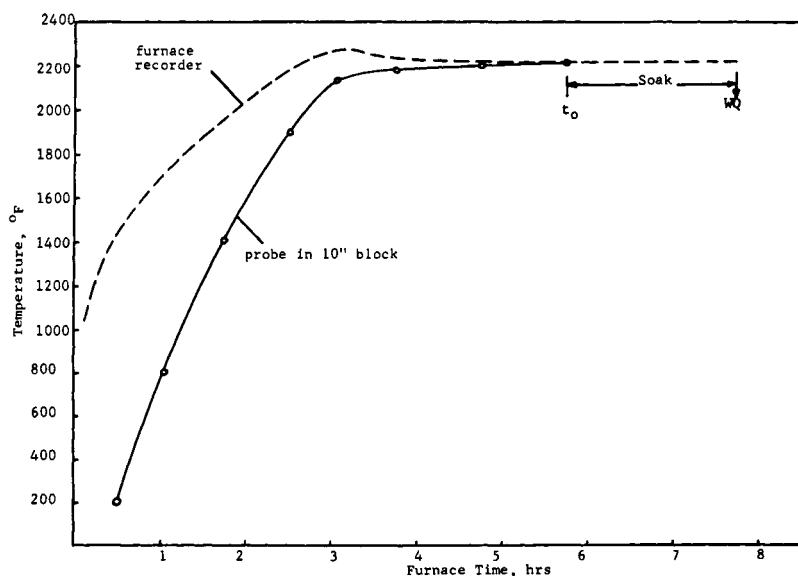


Figure 11 Solution treating alloy 27 (CW-12M) gas turbine rings (72" dia.) at 2250°F.

checked with thermocouples inbedded in castings throughout the load. This is a direct test which assures uniformity and gives a measurement of lag time between the furnace temperature and the casting temperature. The lag time in austenitizing or normalizing tends to be small as shown in Figure 11 and the lag between the surface and center of the casting is small as shown in Figure 12. Lower temperature operations, such as tempering, have longer lag times and require longer holding times. After the castings are at temperature in normalizing and quenching, the part should be austenitized for 1 hour for sections up to 2 inches thick plus 15 min/in. of cross section over 2 inches. Tempering should be done for 2 hours for sections up to 2 inches thick plus 15 min/in. of cross section over 2 inches.

Once a tray loading-furnace combination has been documented then subsequent holding times can be based on experiences with additional time added. Each heat treatment load should be evaluated by hardness testing to insure adequate treatment. Critical items should always have attached thermo-couples.

Holding Temperature is varied according to the type of heat treatment

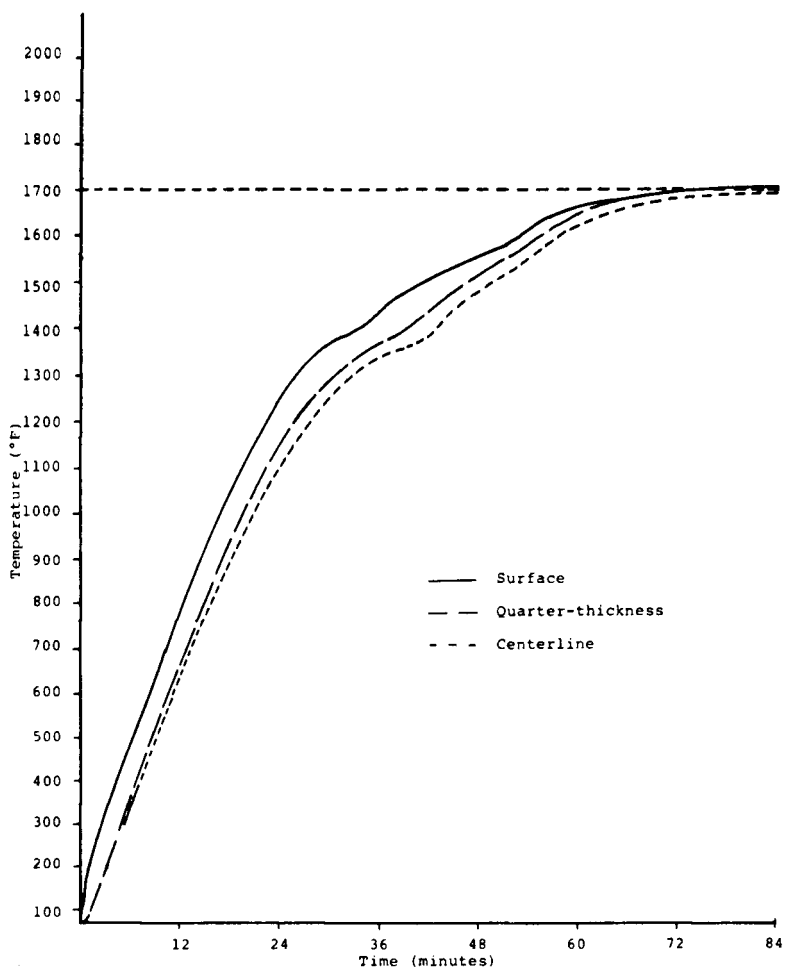


Figure 12 Heating rate at the surface, quarter thickness and center of a 5-in. thick plate casting placed into a furnace at 1700°F.

used. The highest heat treating temperatures used are over 2200°F to try and dissolve aluminum nitride and eliminate "rock candy" from a casting. This excessive temperature is ineffective and builds heavy oxidation scale and can lead to corners melting. Aluminum nitride embrittled castings are generally scrapped and remade since heat treating rarely works. The next highest temperatures used are over 2050°F in the molybdenum bearing stainless steels to eliminate micro segregation. Most high temperature heat treatments are used to dissolve carbides, in the stainless steels for corrosion resistance and in the carbon

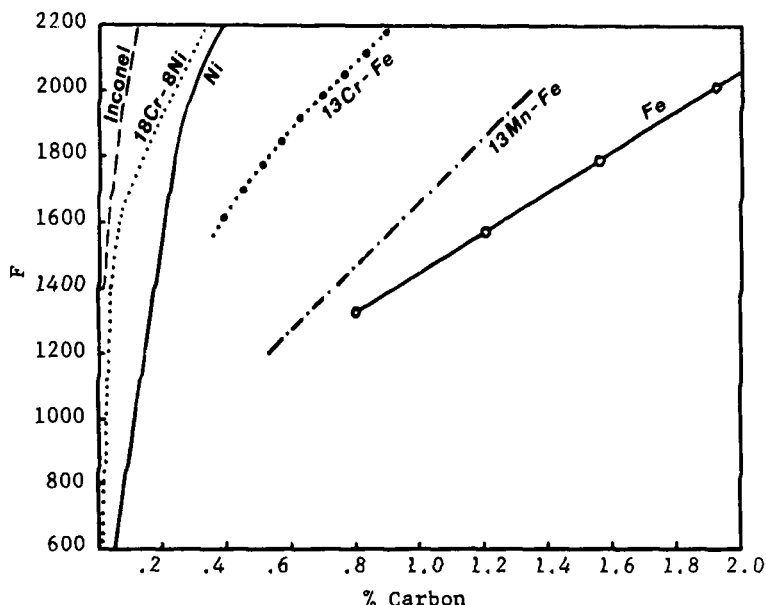


Figure 13 Comparison of carbide solubilities.

and alloy steels to permit subsequent hardening. The temperatures required are illustrated in Figure 13. Temperatures in excess of the minimum needed shortens the holding time needed by increasing the diffusion and insures that all carbides are dissolved. Figure 14 shows the effect of time and temperature necessary for the complete dissolution of carbides in various alloys. Cast materials are generally treated at 100-200°F above the A_{c3} and 50°F above the similar wrought composition. In carbon and low alloy steels it is important to stay under 1850°F to prevent excessive grain growth. Solution treating is normally done at 1950-2150°F, austenitizing for normalizing or quenching is done at 1550-1750°F. Intercritical heat treatment is done between the A_{c1} and A_{c3} temperatures, normally in the middle of this range at about 1450°F; but this depends on the steel composition. Tempering is done from 400-1200°F, but should avoid 400-600°F temper martensite embrittlement and 800-1000°F temper embrittlement.

Cooling Rate depends on the operation and properties desired. Annealing requires a slow cooling from the austenitizing temperature. In old brick lined furnaces this is easily accomplished by furnace cooling but in fiber lined furnaces it sometimes requires a cool down burner cycle

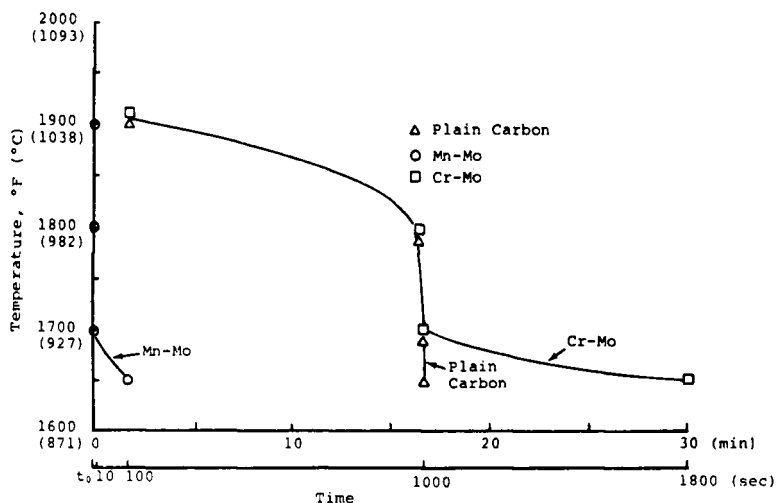


Figure 14 Effect of temperature on time for complete austenitization of three steels.

to slow the cooling rate down. Normalizing is done by cooling in still air. Sometimes forced air is used to achieve the necessary properties, but air cooling is an insensitive process. Tempering is also normally air cooled although additional toughness can be gained from quenching a high temperature temper, above 1050°F, to avoid temper embrittlement. Intercritical heat treatment requires quenching to maximize the toughness. Quenching is also used to through-harden parts for the best toughness and strength.

In quenching there are three stages of heat extraction, referred to as A, B, and C Stages, associated with quenching in liquids. A temperature-time curve obtained with a thermocouple embedded in a steel probe illustrating these stages is shown in Figure 15. Relatively slow cooling occurs in an A Stage because a quenchant vapor blanket develops around the part.

The highest cooling rates occur in Stage B. During this period the vapor blanket collapses and high heat extraction rates are achieved associated with nucleate boiling on the part surface. The final C Stage of cooling is associated with conductive and convective heat transfer into the quenchant and is slower than B Stage cooling.

In general, more violent quenchant agitation accelerates heat removal by limiting the duration of the vapor blanket in Stage A and improving

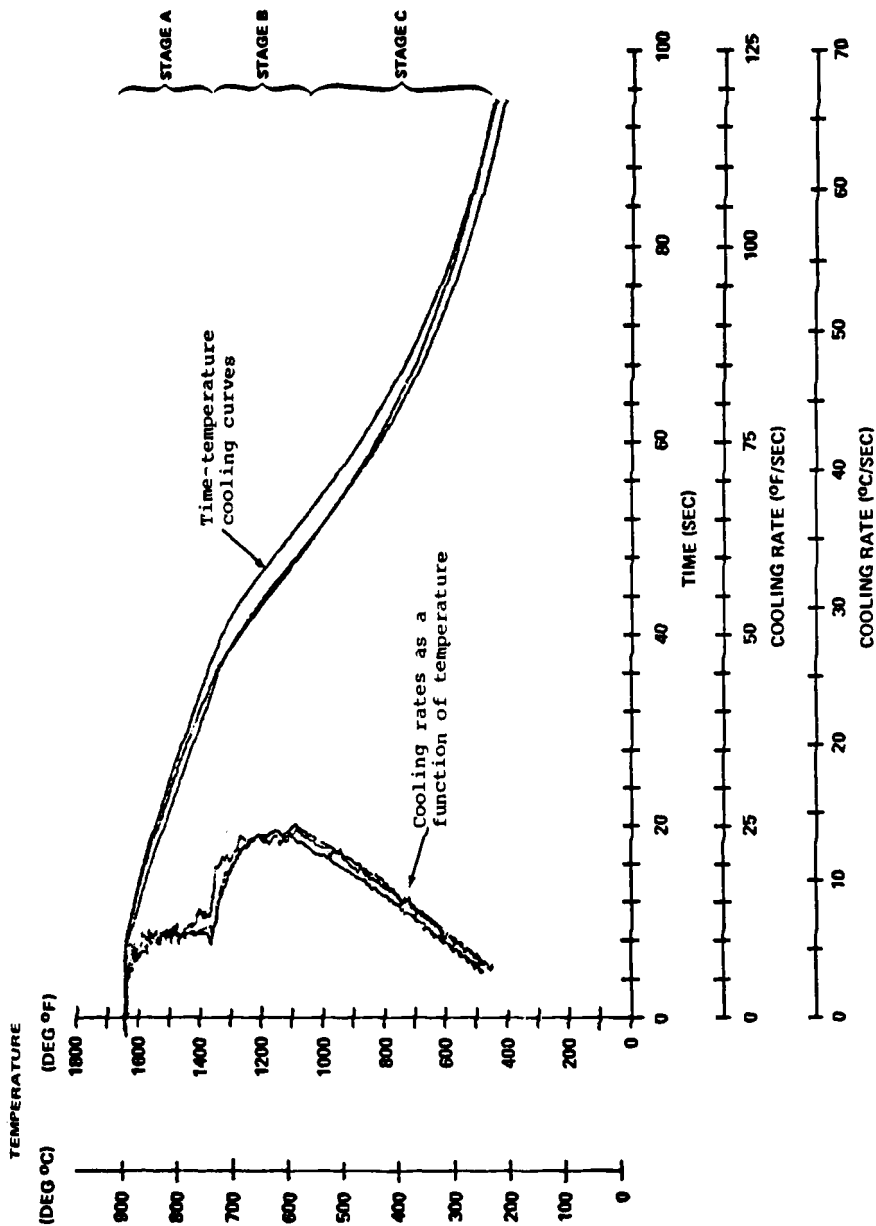


Figure 15 Triplicate temperature-time curves and cooling rate curves at center of 2" diameter probe quenched in fast oil at 85°F.

conductive and convective heat removal in Stages B and C. Higher quenchant temperatures generally slow the rate of heat removal by extending the duration of the vapor blanket.

The actual cooling rates and temperature ranges associated with the stages of cooling vary with the type of quenchant and the mass of the parts being quenched. The highest overall cooling rates are obtained with brine solutions, generally followed by water, synthetic quenchants, oils, and air. There are, of course, variations in the attainable cooling rates within particular classes of quenchants depending on the formulation and viscosity.

The actual cooling rate that can be achieved in a part is a function of the thickness and geometry of the part, the quenchant, and the characteristics of the quenching facility especially the bath temperature range and extent of agitation. Once the quench severity has been estimated the cooling rate or cooling time needed to estimate quench rate are given in Figures 16 and 17 and in Table VI.

Water is one of the most commonly used quenchants. It has several advantages because it is readily available, cheap, not considered hazardous, and can be used to produce high cooling rates. However, its ability to rapidly extract heat in thin sections and form a steam vapor blanket around thicker, hotter areas can produce differential stresses that can cause cracking. Water quenching is prone to cracking parts with significant differences in cross-sectional area and parts containing holes and grooves. Contamination of the quench water with sludge, oils, and scale generally reduces the cooling rate, and contamination with salt tends to increase the cooling rate.

Water-based polymer quenchants consist of high molecular weight organic compounds added to water to retard the rate of heat extraction and reduce cracking and distortion. The advantage of polymers is that they generally reduce the cracking tendency compared to water while providing deeper hardening and reduce smoke and fume compared to oil. The purchase cost of polymer quenchants is higher than oil on a per gallon basis, but polymers are usually concentrates that are diluted with water. Water-based polymers do require more process control over temperature and concentration than either water or oil quenchants.

Oils can be formulated to provide a range of cooling rates, but generally lower than those produced by water. Oils are considerably more expen-

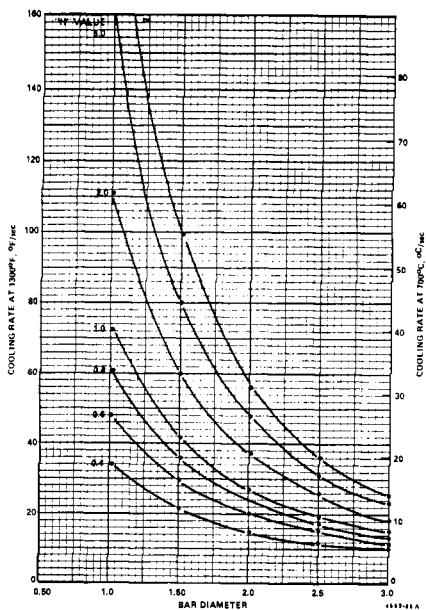


Figure 16 Theoretical centerline cooling rates at 1300°F at the center of bars quenched under conditions producing different quench severity factors (H).

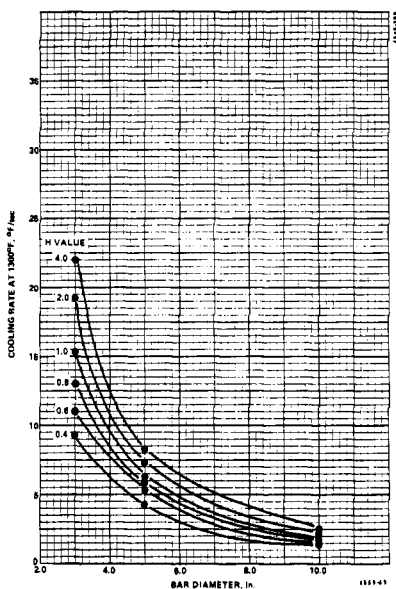


Figure 17 Theoretical centerline cooling rates at 1300°F at the center of bars quenched under conditions producing different quench severity factors (H).

Table VI — The Relationship Between Bar Diameter, “H”, Cooling Time and Cooling Rate Based on the Analytical Model

Bar Diameter (In)	H-Value	Cooling Time 1350-500°F (Sec)	Cooling Rate 1300°F (F/Sec)
.25	0.40	9.1	155.
0.50	0.40	18.6	73.39
1.00	0.40	39.2	34.77
1.50	0.40	61.4	21.83
2.00	0.40	86.4	15.49
2.50	0.40	112.8	11.69
3.00	0.40	142.8	9.17
5.00	0.40	280.0	4.47
10.00	0.40	800.0	1.52
.25	0.60	6.0	230.
0.50	0.60	12.8	107.33
1.00	0.60	27.6	49.22
1.50	0.60	44.0	29.98
2.00	0.60	63.2	20.63
2.50	0.60	85.2	15.24
3.00	0.60	108.0	11.74
5.00	0.60	227.5	5.43
10.00	0.60	700.0	1.72
.25	0.80	4.6	292.8
0.50	0.80	9.8	139.86
1.00	0.80	21.6	62.33
1.50	0.80	35.6	36.82
2.00	0.80	51.2	24.75
2.50	0.80	69.6	17.89
3.00	0.80	92.4	13.63
5.00	0.80	200.0	6.07
10.00	0.80	645.0	1.84
.25	1.00	3.8	363.68
0.50	1.00	8.0	170.10
1.00	1.00	18.4	73.28
.50	1.00	30.0	42.30
2.00	1.00	44.8	28.03
2.50	1.00	62.4	20.00
3.00	1.00	81.6	15.08
5.00	1.00	185.0	6.54
10.00	1.00	615.0	1.93
.25	1.50	2.6	527.00
0.50	1.50	5.6	239.40
1.00	1.50	13.6	95.63
1.50	1.50	24.0	52.76
2.00	1.50	36.0	33.98

Table VI-continued

2.50	1.50	51.6	23.70
3.00	1.50	69.6	17.57
5.00	1.50	165.0	7.27
10.00	1.50	585.0	2.05
.25	2.00	2.0	676.
0.50	2.00	4.6	293.10
1.00	2.00	11.2	112.35
1.50	2.00	20.4	60.24
2.00	2.00	32.0	37.98
2.50	2.00	45.6	26.13
3.00	2.00	63.6	19.11
5.00	2.00	152.5	7.71
10.00	2.00	560.0	2.12
.25	3.00	1.4	955.
0.50	3.00	3.4	382.50
1.00	3.00	9.2	136.35
1.50	3.00	17.2	70.13
2.00	3.00	28.0	43.09
2.50	3.00	42.0	29.14
3.00	3.00	56.4	21.00
5.00	3.00	145.0	8.20
10.00	3.00	545.0	2.19
.25	4.00	1.2	1177.50
0.50	4.00	2.8	449.10
1.00	4.00	8.0	152.10
1.50	4.00	15.6	76.50
2.00	4.00	25.6	46.18
2.50	4.00	38.4	30.90
3.00	4.00	54.0	22.08
5.00	4.00	140.0	8.48
10.00	4.00	535.0	2.22

sive than water on a cost per gallon basis, but more forgiving and less prone to cause cracking or soft spots when excursions in quenchant temperature or local variations in velocity occur. The main objections to oil are the cost, an inability to rapidly quench parts, the surface residue left on parts and the possibility of fires. The actual effect of temperature and agitation are given in Table VII.

Water is found to require closer temperature and agitation control than oil. This can be seen in the data in Table VIII.

Water-soluble polymer quenchants are capable of providing a range of cooling rates depending on the concentration in the water, the bath temperature, and the extent of agitation. The extent of control required with

synthetics appears greater than that required for either water or oil. The concentration of synthetic quenchants must be monitored and adjusted when required.

Some general recommendations on quenching in water, oil, and polyglycol based on the laboratory results and published literature are presented in Table IX, X and XI.

Distortion and cracking during quenching limits the severity of the quenchant and equipment that may be used. A more severe quench produces martensite to a greater depth (with a steel of given hardenability), but it also increases the likelihood of distortion and cracking.

Distortion during quenching can be understood by remembering that: (1) steel has a higher strength when cold than when hot, and (2) steel shrinks while cooling and expands while hardening. Linear dimensional changes occurring during cooling and transformation are illustrated in Figure 18 for both slow cooling and fast quenching conditions. Quenching to form martensite results in an expansion of the material compared to that achieved with a slow cooled pearlitic matrix. However it is recognized that both materials contract over 1% during cooling from the austenite temperature, but martensitic materials have a lower net contraction.

Warping during non-uniform cooling of a part is schematically illustrated in Figure 19. Assume that the bar in Figure 19(a) was initially at a uniformly high temperature. If the bar were quenched on one side, as illustrated in 19(b), the more rapidly cooled side would contract earlier and at a higher rate than the opposite side. Since the rapidly cooled side becomes shorter and stronger as it cools, it causes plastic deformation in the hot side. The deformation is followed by cooling and contraction on the more slowly cooled side.

When the part has cooled to a uniform temperature, it will then be warped, as illustrated in Figure 19, with the slowly cooled side being shorter and the part being warped concave on the more slowly cooled side. The plastic deformation on the hot side results in compressive stresses on the rapidly cooled side and tensile stresses on the more slowly cooled side.

Deformation can result from non-uniform thermal contraction during quenching or the expansion associated with martensite formation or a combination of the two. Deformation resulting from non-uniform ther-

Table VII Effect of Temperature and Velocity on the Cooling Rate and Quench Factor Produced by Oil

Quenchant Temp. (F°)	Velocity (fpm)	Avg. Cooling Rate at 1300°F (F°/sec)	Cooling Time- 1350 to 500°F (sec)	Quench Severity Factor (H)
1" Diameter Probe				
85	0	28.9	20.8	0.31
85	50	30.8	20.4	0.35
85	80	22.5	22.0	0.25
85	110	38.2	20.0	0.45
85	140	41.1	18.8	0.49
120	0	18.5	25.2	0.20
120	50	22.1	21.2	0.24
120	80	25.7	19.6	0.29
120	110	46.9	18.0	0.57
120	140	42.1	17.6	0.51
160	0	19.5	24.4	0.21
160	50	38.3	20.4	0.45
160	100	46.0	19.2	0.56
160	110	54.4	17.2	0.69
		33.93		
1.5" Diameter Probe				
85	0	22.9	55.3	—
85	50	19.2	35.2	0.21
85	95	17.0	35.6	0.30
85	135	16.7	34.8	0.29
85	160	17.7	34.8	0.32
120	0	15.5	56.0	0.26
120	60	18.2	35.2	0.32
120	95	17.7	34.8	0.31
120	125	19.9	34.0	0.36
120	160	18.8	34.4	0.34
160	0	20.1	58.5	0.37
160	60	22.2	56.8	0.42
160	100	23.9	33.6	0.46
160	125	21.9	34.4	0.41
160	160	25.8	32.8	0.51
2.0" Diameter Probe				
85	0	19.8	57.4	0.61
85	70	19.8	56.2	0.61
85	110	17.4	54.2	0.50

85	150	17.3	54.8	0.51
85	195	16.6	55.5	0.47
120	0	16.9	54.2	0.48
120	70	20.9	54.5	0.62
120	110	17.5	55.7	0.51
120	150	18.1	55.1	0.53
120	195	16.7	54.9	0.47
160	0	14.1	55.4	0.36
160	70	20.3	56.4	0.63
160	100	20.1	56.5	0.62
160	150	21.3	55.8	0.68
160	195	25.4	57.2	0.88

mal contraction is illustrated in Figure 20. If a part is initially uniformly hot, as illustrated in figure 20 (a), and is rapidly quenched, the outer surface shrinks while the center is still relatively hot. This process puts the outer surface into tension and the inside into compression, causing plastic flow. As the center of the part cools down and the temperature reaches a uniformly low value, thermal contraction in the center of the bar occurs, which reverses the stress state and places the center in tension, as illustrated in Figure 20 (c).

The stress states associated with through-hardened 0.6 carbon steel, 0.025% carbon iron, and an 0.3% carbon steel are illustrated in Figure 21. The length and diameter changes are illustrated, as well as the stress profiles in 1.97" bars after water quenching from 1560°F.

In general, the distortion occurring during quenching depends on the size and shape of the part, the part composition, and the characteristics of the quenchant employed. Parts with section size ratios greater than 1 to 4; large parts with relatively thin cross sections; and parts containing slots, keyholes, drilled holes, or grooves cause problems because of the difficulty in achieving uniform cooling rates. Quench cracking is often found when water quenching parts made of steels more hardenable than AISI 1140.

Quench cracking results from the same stresses and becomes more prevalent as the ideal diameter (calculated from the chemical composition or determined using a Jominy test) increases. The danger of cracking a part is at a maximum when the martensite skin thickness is about 50-60% of the cross sectional area.

Cracking is most commonly associated with non-uniform quenching. Uniform surface compressive stresses produced by a uniform rate of

heat removal helps suppress cracks. However, as the quench severity increases, maintaining a uniform rate of heat extraction is more difficult. The uniformity of the heat extraction rate must increase exponentially if cracks are to be avoided.

HEAT TREATING CERTIFICATION

Certification implies that a procedure, that has been demonstrated to give desirable results, has been used in a consistent way to achieve a uniform product. Heat treating, like weld or nondestructive testing, leaves no visual evidence, especially after cleaning, that it has been

Table VIII Effect of Temperature and Velocity on the Cooling Rate and Quench Factor Produced by Water

Quenchant Temp. (F°)	Velocity (fpm)	Avg. Cooling Rate at 1300°F (F°/sec)	Cooling Time- 1350 to 500°F (sec)	Quench Severity Factor (H)
1" Diameter Probe				
85	0	104.3	10.8	1.79
85	30	120.3	10.4	2.34
85	50	130.2	10.4	2.75
85	80	125.0	10.0	2.53
85	110	133.2	10.0	2.93
85	140	133.4	9.6	2.93
125	0	33.7	14.8	0.40
125	30	59.7	11.6	0.78
125	50	80.2	12.4	1.16
125	80	112.2	10.4	2.04
125	115	105.7	10.8	1.83
125	140	117.3	10.0	2.23
160	0	15.4	22.4	0.17
160	30	21.0	19.6	0.24
160	50	31.7	16.8	0.37
160	80	24.4	18.4	0.28
160	110	38.2	14.8	0.46
		81.52		
1.5" Diameter Probe				
85	0	57.8	22.4	1.85
85	35	59.9	22.4	2.02
85	60	58.7	22.4	1.92
85	80	60.8	22.0	2.10
85	95	59.0	23.2	1.92

85	160	58.0	21.6	1.85
100	0	51.9	23.2	1.43
100	35	47.1	23.6	1.20
100	60	54.8	23.2	1.62
100	95	57.2	22.4	1.80
100	125	59.4	22.0	1.98
100	160	61.0	21.6	2.10
125	0	40.4	24.4	0.95
125	35	37.1	24.4	0.84
125	60	45.4	24.0	1.14
125	95	53.2	22.8	1.50
125	125	58.8	22.4	1.92
125	160	59.2	22.0	1.97
150	0	17.6	30.0	0.31
150	35	22.3	28.4	0.42
150	60	24.9	27.6	0.51
150	95	35.6	26.4	0.79
150	125	41.0	24.4	0.97
150	160	41.4	24.0	0.98
160	0	10.2	49.6	0.16
160	35	14.3	32.4	0.24
160	60	15.7	32.8	0.27
160	95	17.2	30.8	0.30
160	130	23.1	27.2	0.44
160	160	30.1	26.8	0.63

42.43

2" Diameter Probe

85	0	33.4	61.7	1.46
85	40	34.2	39.6	1.65
85	70	34.1	40.4	1.52
85	110	34.5	38.4	1.58
85	150	34.4	38.4	1.56
85	195	34.9	36.8	1.63
125	0	21.2	55.1	0.67
125	40	24.4	55.4	0.83
125	70	32.5	41.6	1.37
125	110	31.1	41.2	1.25
125	150	33.5	39.6	1.47
125	195	33.3	39.6	1.44
160	0	7.1	85.4	0.14
160	40	13.5	54.3	0.34
160	70	8.3	62.4	0.16
160	110	16.4	54.7	0.46
160	150	16.3	53.0	0.46
160	195	17.6	53.3	0.51

25.59

Table IX. General Recommendations for Water Quenching

Temperature:	<i>Maintain the bath temperature in the range of 85°-90°F</i> Quench rates tend to deteriorate with bath temperatures over 90°F and are noticeable at 100°F; substantial deterioration occurs with bath temperatures over 130°F.
Flow:	Quenchant velocities of about 100 fpm over the part surface produce consistent quenching behavior in water tanks.
Loading:	A single layer of parts on a quench grid tray provides the most uniform quench and least interaction between rates in the interior and on top of the load. Rule of thumb—separate castings by one casting thickness, allow quenchant to flow upward (circulate upward) taking advantage of the thermal rise. Do not allow castings to lie on bottom of tank. Aim at having castings at 1/3 of depth of quenchant from bottom. Control and maintain a consistent transfer time from the furnace to the quench tank.
Volume: *	Use approximately one gallon of water quenchant per pound of steel quenched. Bath temperature should not rise more than 25°F during quenching and preferably no more than 15°F.
Control of Quenchant Quality:	Monitor for salt and oil contamination.

*From literature

Table X. Recommendations for Oil Quenching

Temperature:	Oils give less variation in cooling rates over a wider range of temperatures than do water or polymers. Bath temperature throughout the quench is normally 120°-150°F and should always be at least 50°F below the flash point.
Velocity:	A velocity over 25 fpm appears adequate for uniform heat removal and minimization of hot spots. Variations in velocity have less effect than when using water or polymers.
Loading:	A single layer of castings on the tray gives the most consistent results.
Volume:	The quench tanks should contain approximately one gallon of oil for each pound of steel quenched. This may vary, depending on the specific heat of the particular oil. Check with the oil supplier.
Control of Quenchant Quality: *	Bath characteristics, including viscosity, flash point, water content, and quench rate should be checked periodically to maintain consistency.

*From literature

Table XI. Recommendations for Polymer Quenching (Polyglycol)

Temperature:	Bath temperature must be controlled according to manufacturer's recommendations. The quench rate can substantially deteriorate with bath temperatures over 100°F.
Flow:	Velocities of 50-100 fpm are recommended. Watch for air entrainment, which can substantially reduce heat transfer coefficients, especially at high velocities.
Loading:	A single layer of castings on a tray gives the most consistent quenching results.
Volume*:	Use approximately 1.5-2.0 gallons of quenchant for each pound of steel including tray weight, depending on quench cycle time and other operating conditions.
Control of Quenchant Quality:	Concentration of polymer must be carefully controlled within the specified range. Contamination, which can lead to solution deterioration, should be monitored.

*From literature

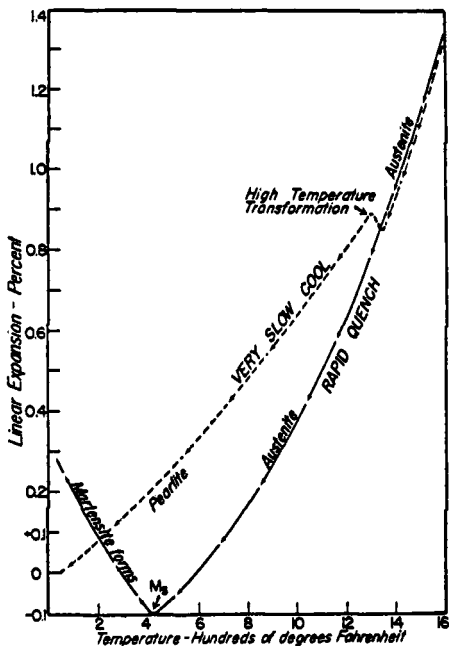


Figure 18 Dilatometric studies show that, when cooling a steel from a high temperature, it experiences reversals of its dimensional contractions which vary, depending on the quenching rate.

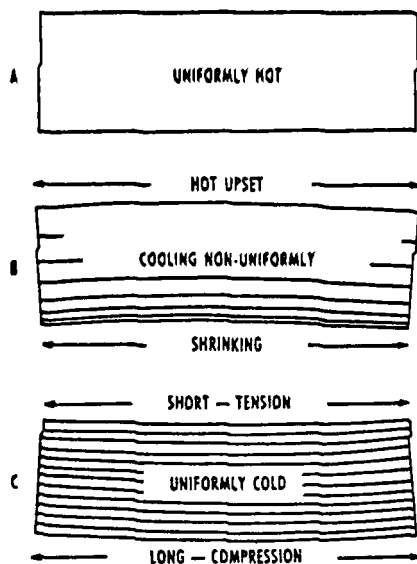


Figure 19 Warpage caused by non-uniform quenching of a 30% nickel steel block.

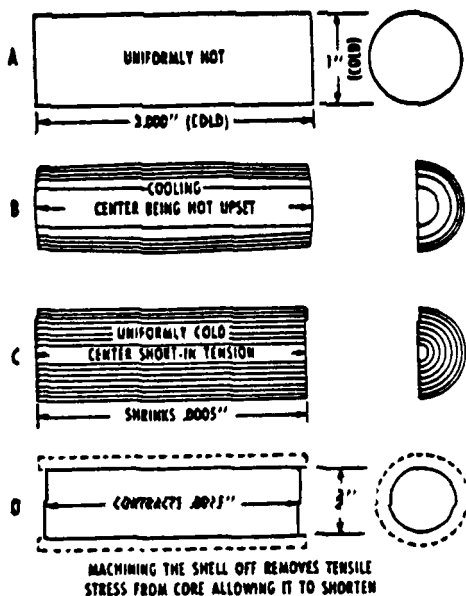


Figure 20 Effect of quenching on 30% nickel steel cylinder—water quenched from 1425°F (774°C).

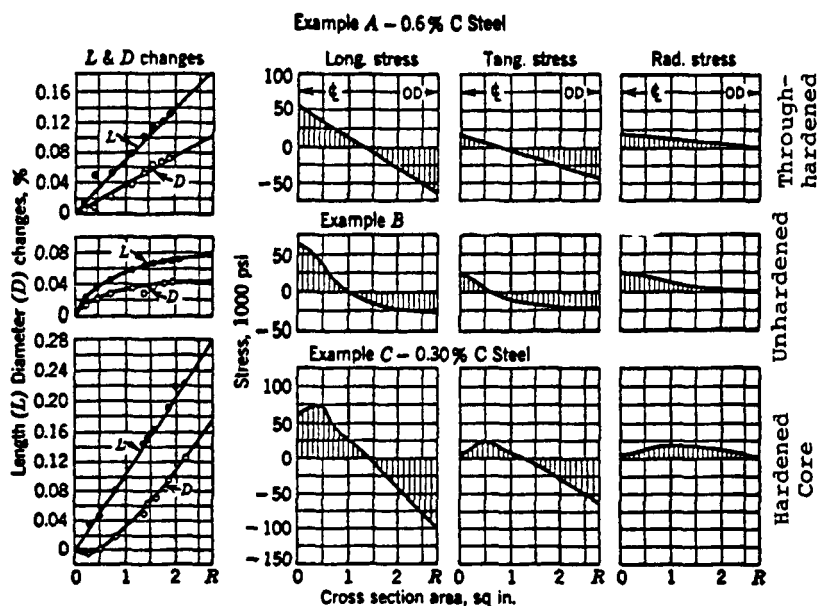


Figure 21 Residual-stress distribution in 1.97-in. diameter bars water quenched from 1560°F.

done or that it has been done properly. Therefore, it is in the interest of the foundry, to limit its liability and maintain a uniformly high quality product to use certification in heat treating. The heat treat area is generally responsible for making sure that the parts conform to the properties specification. The use of a computer to check the actual chemistry and properties against the specification can result in improvements in quality and reliability and be used to print the final certification for the customer.

For certification to be effective, procedures must be developed that result in reproducible compliance to customer requirements. There must be documentation that those procedures were followed for their castings. Finally, there should be a check or audit that the required results have been accomplished.

Procedures must be developed to achieve the desired results. Like welding procedures, similar materials and casting types can use the same procedures. The rate of heating is generally not a significant fea-

ture, but rate of heating and furnace loading combine to determine when the load reaches the desired temperature. Thermocouple demonstration of the furnace load temperature response is necessary to develop holding times. Bigger furnace loads do not necessarily save money since they require longer to achieve the desired temperature and give variable cooling rates during cooling which causes warping, cracking and inadequate hardness.

Another often overlooked variable is the time required from the furnace to the quench bath. This can account for soft surfaces and variable heat treat response. The casting load should be transported from the furnace to the quench tank in about ten seconds to achieve good uniform quenching. Longer transfer times allow exposed areas to cool slowly through the transformation range and form soft spots. As always consistent quality will improve productivity by avoiding reheat treatment.

Strict adherence to written procedures will give consistent results. This will allow the application of appropriate statistical process control. The procedures could be changed if they do not give the desired results but constant change guided by "seat of the pants" judgements will result in variations that are impossible to control.

Documentation must be generated that confirm that the applicable procedures were followed. Each batch or group of castings should have a chemical analysis available before heat treatment so that the heat treater can check the carbon content and hardenability so that the heat is within the specification limits and is suitable for heat treatment. Next, the heat treat cycles for each load must be available for the record. In the heat treat shop, there should be a furnace cycle chart, transfer time to quench bath, quench bath temperatures, quench bath concentration if using polymers, castings in each load, etc. Finally the hardness of castings and the results of mechanical properties testing should be recorded.

Audit Procedures matches the chemistry, heat treat cycles, and resulting properties against the specification requirements and internal procedures used. This is done before issuing the customer certification and safeguards the integrity of the foundry. If discrepancies are often found or rework is common then there is not a high commitment to quality in the foundry. The castings were not made right the first time. Few castings or shipments should be delayed or require rework due to this final audit. Hopefully the final audit would be used to determine areas for improvement of future quality, not a policeman to catch current violations.

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Lecture VI

Welding of Cast Steels

by Dr. Carl D. Lundin

INTRODUCTION

The title of this lecture, by its nature, signifies that “Cast Steels” exhibit different behavior with regard to welding than do “steels” in general. In fact, cast steels do not behave significantly different than wrought steels as far as the techniques and methods of welding are concerned.

Remember that wrought steels were once castings (ingots) and are now commonly continuously cast to near form. Thus, some casting related considerations must be addressed in wrought products, i.e., ingotism or banding.

There are some unique aspects of cast steels which might make one consider special treatment in welded structures, but in like manner, wrought steels must be considered in light of their characteristics for welded fabrication. Consider the case of lamellar tearing in steels, a consideration in wrought materials but not in cast. In contrast, the segregation pattern and casting discontinuities (porosity and shrinkage) possible in castings are not modified, except by heat treatment, in the cast steels and consideration must be given to these efforts.

In a rather extensive study of “The Performance of Cast and Rolled Steels in Relation to the Problem of Brittle Fracture,” Pellini et al. (1) found that cast and wrought materials are similar as far as notch toughness is concerned provided they have received similar thermal treatments. Aside from the normal range of casting discontinuities, porosity, shrinkage and small hot tears, castings would be expected to behave in a given loading situation like their counterpart wrought products.

The prime consideration in the welding of carbon steel castings and wrought steels is the concern for heat affected zone (HAZ) or weld

metal cracking due to the presence of hydrogen (Hydrogen Assisted Cracking—HAC). Hot cracking is normally not a bothersome condition unless the chemical composition is unusual or contamination from external sources occurs.

Thus, this presentation will deal with various aspects of HAC in cast and wrought materials, contrasting the behavior and discussing the procedures necessary for properly constituted weldments.

This lecture is divided into three basic parts; 1) the historical perspective of cast vs. wrought steel weldability and 2) the mechanisms of HAC in wrought and cast steels and 3) the practical and pragmatic considerations for engineering weldability.

HISTORICAL REVIEW

The use of welding in foundries came about slowly through a long period of transition from fully cast components to cast-cast and cast-wrought components. The literature available on the weldability of cast steels is relatively meager.

An early study of welded structures in cast and wrought steels was performed by Bolton and Smith (2). They grouped the cast and wrought steels tested according to their relative tendencies for martensite formation. Use of preheat prior to welding was found to give rise to coarser grains in the heat affected zone of all the steels. However, an interesting conclusion they drew from their limited tests was that their wrought steels were more susceptible to grain coarsening than their cast ones; the addition of molybdenum was found to reduce this tendency. The weldability of the steels was evaluated based on this grain coarsening tendency from which it was concluded that cast carbon steel with carbon contents up to 0.24% could be safely welded without any preheat. Preheating to temperatures greater than 600°F was not recommended because excessive grain growth could occur in the HAZ. The minimum preheat temperatures needed to avoid formation of hard structures (martensite) in the HAZ were evaluated, although no hardness values were given. Smith and Bolton (3) concluded that fears regarding the weldability of aluminum deoxidized cast steels were unwarranted, and that these steels showed as good, and in many cases better weldability than comparable wrought steels, the "weldability" being related to the tendency to form martensite in the HAZ.

Mueller et al. (4) reported that for satisfactory welding of plain carbon

steel castings having a maximum carbon content of 0.35% associated with 0.60 manganese, no preheat need by used. However,they speci-fieda subsequent stress relief of full anneal. Preheat was specified for the welding of Mn-Mo cast steel having a carbon content of 0.35 to 0.40% associated with 1.25 to 1.50% manganese and 0.20% molybdenum. To completely prevent cracking in the Mn-Mo steels a preheat ranging from 300 to 600°F together with a post weld heat treatment (PWHT) at 1200°F was specified. The maximum hardness in the HAZ for a single pass and a multipassweld is shown as a function of preheat temperature in Figure 1. The multipass weld as opposed to the single pass weld has a beneficial effect in that it partially refines and tempers preceding passes. Hence, preheats were seen not to have any major effect on the maximum hardness during multipass welding. Mueller et al. also concluded that casting stresses and segregation have no detrimental effects on weldability. It is interesting to note that no mention of hydrogen was made in connection with the cracking observed.

Williams et al. (5) at Battelle conducted an extensive weldability study of cast and wrought carbon-manganese steels. In the underbead cracking test, they observed that the cast steels were less susceptible to HAC

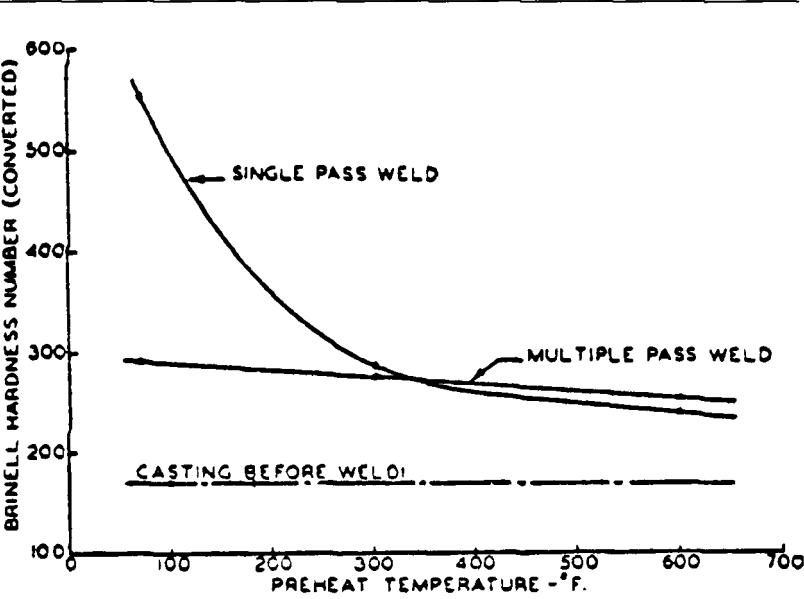


Figure 1. Effect of preheat on the maximum hardness obtained in the heat-affected zone of manganese-molybdenum steel castings.

than the rolled steels of similar composition. Typical underbead cracking test results are shown in Figure 2. From the results of their tests, which plot average underbead cracking versus carbon equivalent as given by $\%C + (\%Mn + \%Si)/4$, it is clear that the cast steels (2x, 3x, 4x) were less susceptible to cracking than wrought steels of similar carbon equivalent. This observation was made at all preheat temperatures used. The reasons for this behavior were not explained. Furthermore, cast steels unexpectedly exhibited a higher underbead hardness and a lower bend angle than wrought steels of the same carbon equivalent, thus illustrating the danger of using hardness alone to predict crack sensitivity.

The beneficial effects of preheat and postheat treatments were utilized by Bland et al. (6) in welding 2Cr-1/2 Mo alloy steel (ASTM-A157, Grade C-3A) in the shape of a tee fitting, for use with 5 in Schedule 160 piping (ASTM-A-355, Grade P36). The welding was done by using 2 1/4Cr-1 Mo

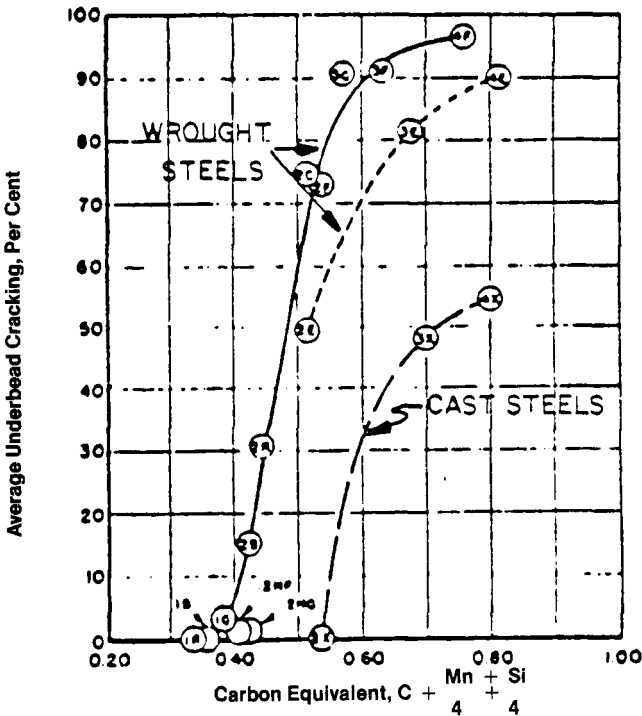


Figure 2. Underbead cracking vs. carbon equivalent (room temperature).

low hydrogen electrodes. Residual stress measurements showed that preheat was effective in reducing residual stresses in the weld deposit. Another interesting result obtained by them was that the heat affected zone hardnesses of the cast alloy materials were higher than those of similar (nominal) analysis of wrought pipe materials. This agrees with the observations made by Williams et al. (5). However, hardnesses in wrought or cast base metals were relatively unaffected by a 300°F preheat. This is because that preheat level probably had a small effect upon the cooling rate.

Ridal (6) has given results of extensive tests carried out on a plain carbon cast steel (B.S. 592GR A - C-0.2%, Si-0.33%, Mn-0.73%) and a 112 Ni-Cr-Mo steel (B.S. 1459). Though the results are mainly concerned with the mechanical properties of the welds, some useful information regarding the preheats required to weld these steels is also given. The recommended procedure for welding BS 592 GrA given by the B.S.C.R.A. specifies no preheat but a post weld heat treatment (PWHT) at 600-650°C (1100-1200°F) and with a note that this PWHT is not always essential. For B.S. 1459 a minimum preheat of 200°C (392°F) is recommended; also PWHT is specified. For certain hardened and tempered castings, the PWHT temperature is suggested to be kept low to maintain specific tensile strengths. However, Ridal informs that even without using the recommended minimum preheat temperature of 200°C (392°F) for B.S. 1459, underbead cracking was not observed in his tests. He cautions that as restraint was absent in his test, the results do not represent actual conditions. In any case, the situation where a preheat of 200°C (392°F) is recommended, although the absence of preheat in testing resulted in no cracking, indicates that welding specifications for castings are probably conservative.

The power industry has adopted significant cast weldment fabrication. Whitley (8) points out that as operating temperatures increased turbine castings changed from C-Mo steels to the 2 1/4Cr-1Mo type for service up to 565°C (1050°F). A switch then took place (in Britain) to the 1Cr-1Mo-V, as this was thought to have a superior creep strength. However, this was done at the cost of weldability and increased susceptibility to HAZ cracking during stress relief treatment after welding. The aluminum content of the steel was found to affect its stress-relief cracking tendency. This led to an aluminum restriction of 0.03% maximum soluble content.

For the 1/2-1Cr-1/2Mo-1/4V cast steel, Whitley reports the results of research aimed at studying the effect of trace elements on hot strength

and ductility of HAZ material. The results led to copper, tin and aluminum being further restricted to 0.25%, 0.20% and 0.025%, respectively. Use of zirconium and titanium as deoxidation elements was encouraged.

Walleit (9) has given typical examples of cast weldments encountered in the power industry. Details of joint preparation, preheat, post heat treatments are given for interceptor valve chests, reheat steam chest assembly, low pressure casings and astern cylinders.

Wu (10) conducted synthetic HAZ studies on centrifugally cast 5% chromium steel. He found that this steel possesses good weldability. However, charpy specimens thermally cycled using 1800 and 2000°F as peak temperatures showed low impact strength. This was attributed to the presence of retained austenite and high carbon martensite resulting from these thermal cycles. A post weld tempering treatment was suggested to improve the toughness of the martensite and to decompose the austenite.

Mellili and Biron (11) provided suggestions on postheating and stress relief of castings. They recommend that large and extensive welds in low alloy steel castings be partially welded so that an intermediate sub-critical tempering heat treatment can be employed. This would help to reduce the buildup of stresses. They also stress the importance of avoiding notches due to undercutting and overlapping prior to post weld heat treatment. The avoidance of notches is important especially when an intermediate, sub-critical tempering PWHT is employed. This type of PWHT is to be employed especially on heavy section welds of large castings which are highly restrained.

The factors which decide whether or not a casting is to be cooled from the preheat temperature prior to PWHT are:

1. Base metal heat treatment before welding;
2. Transition temperature of base metal;
3. Impact strength of base metal;
4. HAZ properties;
5. Geometry and section size of the casting;
6. Volume and extent of process welding;
7. Characteristics of the alloy steel.

Mellini and Biron identify stress relief treatments as those treatments

which are usually conducted at sub-critical temperatures to reduce residual stresses. They also alter HAZ hardness and toughness.

The removal of residual stresses is very important as far as the dimensional stability of a casting is concerned. If such an operation is not performed, stress relaxation can occur during service which may alter the dimensions of a casting. Stress relieving also improves brittle fracture characteristics for service at low temperatures.

Finally, the importance of using a qualified welding procedure should not be overlooked. As Gross (12) suggests, use of a qualification procedure which has been proven by years of experience minimizes the possibility of missing essential elements in a repair or fabrication procedure. He recommends the use of ASME Boiler and Pressure Vessel Code Section IX or other standards such as ASTM A488.

COMPARATIVE WELDABILITIES OF CAST AND WROUGHT STEELS

The earliest differences in weldability between cast and wrought steels were reported by Williams et al. (5) and have been described earlier. They found that cast steels were less susceptible to HAC than wrought steels in the underbead cracking test. Linnert (13), however, quotes that cast steels are more susceptible to cracking than wrought steels. CTS tests (14) on cast and wrought steels of low sulfur contents ($S < 0.01\%$) have shown that cast steels are more crack resistant. This has been attributed to presence of voids and interdendritic shrinkage areas in cast steels to which hydrogen can diffuse and avoid building up of high pressures. The superior resistance of cast steels to HAZ cracking has also been reported by Short (15) and Granjon (16). However, an implant test (an externally applied restraint test) result of Aymard and Nectoux (17) indicates that the weldabilities of cast and equivalent wrought steels may be the same.

In the entire extent of literature reviewed, few investigations were found to be reported which compared the relative weldabilities of cast and wrought steels. Only the work of Williams et al. (5) gave some definite results in that they found cast steels were less susceptible to cracking than equivalent wrought steels. The reasons why this difference of weldability exists may be attributed to:

1. Porosity and microshrinkage associated with cast steels may provide 'sinks' for hydrogen;
2. The transformation behavior in the heat affected zone may be af-

ected by localized variations in elemental concentration which result from segregation;

3. The globular inclusion morphology in cast steels differs from that in wrought steels in which the inclusions are elongated. The elongated inclusions could act as crack initiators.

The work of Menon and Lundin (18) has provided the answers to the differences in the HAC cracking of cast and wrought steels. They have suggested a consolidated mechanism to explain the phenomenological aspects on a fundamental basis. A condensed summary of their findings is presented to bring the information in regard to the mechanism of HAC up to date.

"Consolidated Mechanism of HAC." The most important variable with respect to the occurrence of HAC is the microstructure in the coarse grained HAZ. Among the different micro-constituents that can result in the HAZ due to a weld thermal cycle, martensite is the most susceptible to HAC. The carbon content is therefore the most important compositional variable since it has the greatest contribution to the hardenability of the steel as well as governing the hardness of the martensite. Higher carbon martensites are more susceptible to HAC than lower carbon martensites, with twinned martensitic structures having the greatest susceptibility. The increased susceptibility of as-quenched martensite to HAC can be attributed to a limited capacity for plastic deformation and a low fracture toughness. Further, the dislocation density in martensite is of the order of 10^{11} to 10^{12} per sq. cm. compared to 10^6 to 10^8 per sq. cm. for upper and lower bainite in steels of identical composition. This high dislocation density implies that martensite provides a high hydrogen trapping capacity. Cracking in martensite is known to occur in both an intergranular and transgranular manner, further, it can occur translat, interlat or intercolony. To explain these modes of cracking, one has to consider the role of hydrogen. In a typical welding situation using high hydrogen electrodes (E 6010), approximately 25-30 cc of hydrogen per 100 grams (25 - 30 ppm) are present in the weld metal. This is above the equilibrium solubility of hydrogen in liquid iron and hence the weld metal in the liquid state is saturated with hydrogen. However, as the weld metal solidifies, the solubility of hydrogen decreases sharply to approximately half the value in liquid iron. Hydrogen is therefore rejected out of the weld metal into the atmosphere as well as into the HAZ. Further rejection of hydrogen into the HAZ is aided, as the austenite, under the fast cooling rates experienced in the HAZ, transforms to martensite. The diffusivity of hydrogen in the BCT mar-

tensite is higher than in the austenite and hence it is able to diffuse easily through the lattice as well as via the grain boundaries. Hydrogen atoms close to the metal surface will be able to diffuse out in a short period of time. For hydrogen diffusing into the HAZ, trapping takes place at areas of high dislocation density (martensite, grain boundaries) or at macroscopic areas such as inclusion/matrix interfaces and voids. Though the specific nature of traps has not been defined, the term "trap" includes any discontinuity in the microstructure such as grain boundaries, precipitates, voids, dislocations and solid/solid interfaces. Trapping has been suggested to be due to the attractive interactions between the dissolved hydrogen atoms and structural imperfections. For hydrogen diffusing into the HAZ, as-quenched martensite offers a region of high dislocation density composed of dislocation tangles and a large concentration of low angle boundaries. In a typical situation for cast steels, depicted in Figure 3, in addition to areas of high dislocation density, inclusion/matrix interfaces can also be expected to be areas of high hydrogen concentration. However, Type II inclusions can be expected to be more effective in trapping hydrogen than Type I or III since Type II inclusions have a larger inclusion/matrix interface area than the Type I or III inclusions which are "rounded" in nature. Moreover, Type II inclusions are situated at the primary solidification grain boundaries which further aids hydrogen trapping. Crack initiation occurs when the hydrogen concentration reaches a critical value; the higher the stress present, the lower the critical amount of hydrogen required, and conversely the higher the amount of hydrogen, the lower is the stress required to initiate cracking. Type II inclusions can therefore be expected to render cast steels more susceptible to HAC than Type I or Type III's.

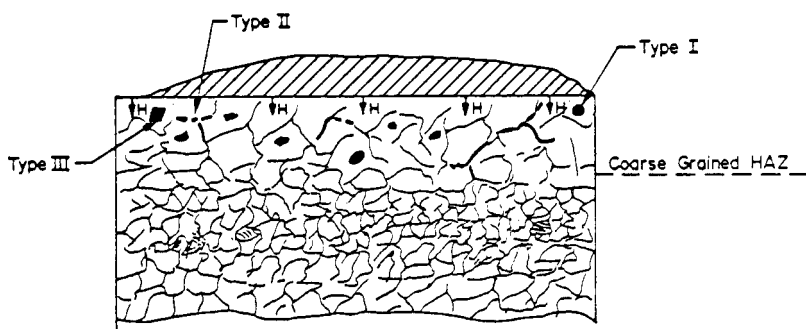


Figure 3. Schematic representation of HAZ in cast steels illustrating location of microstructure and inclusions with respect to diffusing hydrogen front (from the weld metal into the HAZ).

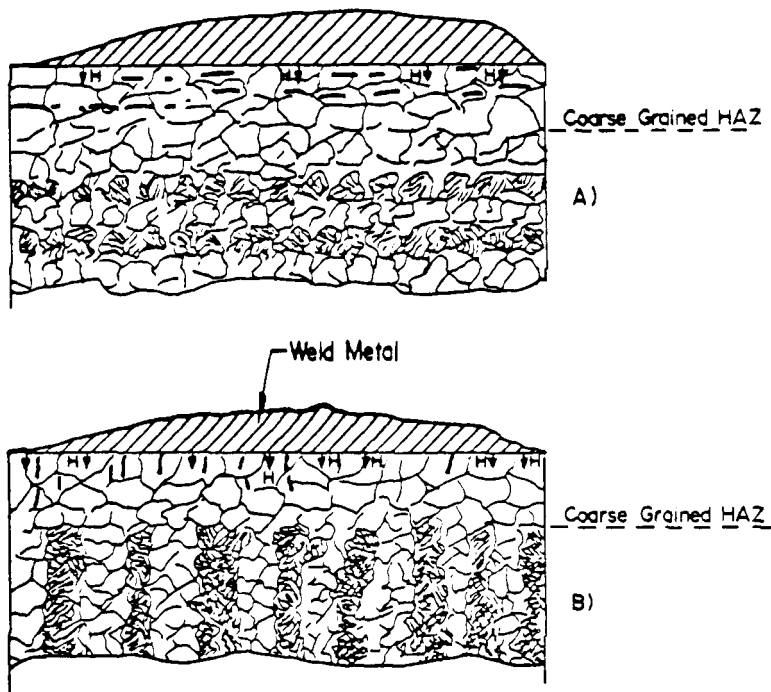


Figure 4. Schematic representation of HAZ in wrought steels showing location of microstructure and inclusions with respect to diffusing hydrogen front.
a) welded PRD, b) welded TTD.

The greater susceptibility of high carbon martensites can be understood on the basis of the high trapping potential for hydrogen and the high internal stress that exists within such microstructures. Crack propagation occurs until the concentration of hydrogen at the crack tip falls below the critical value. At this stage, the crack is arrested. Based on the above reasoning, the beneficial effect of preheating and post weld holds can be rationalized. Preheating causes the temperature of the weldment to remain higher for a longer time causing the hydrogen to diffuse ahead of the arrested crack front. The hydrogen is eventually diffused out of the weldment, thus keeping the hydrogen concentration below that required for crack initiation or propagation.

In the case of the wrought plate steels, two unique situations can be effective in altering the influence of hydrogen. When the weld is made parallel to the rolling direction in the plane of the plate, the elongated sulfide inclusions as well as banding (if present) are aligned parallel to the fusion line and perpendicular to the path of the hydrogen diffusing into the HAZ (Figure 4). The inclusion/matrix interfaces hence lie in the

correct aspect ratio to provide large interface regions for hydrogen trapping. Further, inclusion asperities form ideal stress concentrators and this enables hydrogen concentrations to be easily built up to the critical value for crack initiation. Cracking proceeds so long as the hydrogen concentration is above the critical level. In addition, chemical banding (which is not erased during a weld thermal cycle), provides a region of continuous crack propagation. The association of HAC in the HAZ with inclusions in the ferrite bands can be related to the fact that initial precipitation of the inclusions takes place in the ferrite phase during ingot solidification and during subsequent hot working these inclusions are rolled out in the ferrite.

When the welds in the wrought steels are made in the through thickness direction (TTD), the inclusions and banding are aligned perpendicular to the fusion line, traversing from hard martensitic regions in the coarse grained HAZ to softer nonmartensitic regions. Hydrogen can diffuse out of the coarse grained HAZ along inclusion matrix interfaces in a short circuiting manner. Also, chemical banding does not provide a continuous easy path for crack propagation. (See microstructures for wrought steel tested in the Battelle Test in two orientations in Figure 5. Cracking occurs in the longitudinal PRD direction only.) Evans et al. (18) have also reported lower susceptibilities in wrought steels tested TTD in implant tests.

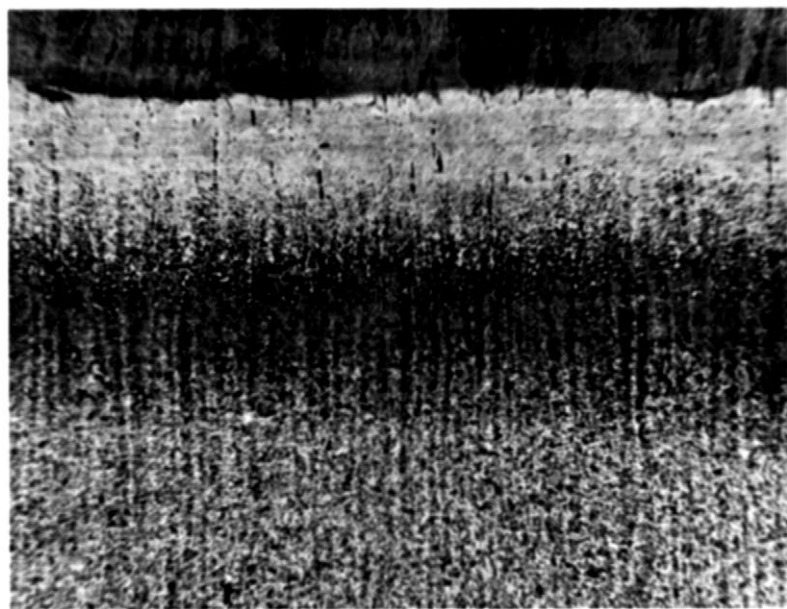
The mechanism of HAC presented above is based on an assumption that some critical concentration of hydrogen has to be reached at potential sites for crack initiation. The critical concentration depends on the nature of the potential crack site that is a hydrogen trap, its shape and location in the lattice and the state of stress at the site. Studies (20) have shown that elongated manganese sulfide inclusions initiate cracks at lower hydrogen concentrations than rounded ones and that the effect is more pronounced in bainitic-martensitic microstructures than in ferritic-pearlitic structures.

The fracture morphologies evidenced in underbead cracking can be explained using Beachem's model (21) of hydrogen-assisted cracking. The model proposes that hydrogen diffuses into the lattice just ahead of the crack tip and aids whatever deformation processes the material will allow. The deformation processes that can exist are governed by the stress intensity at the crack tip.

In summary, a unified mechanism of HAC has been proposed for cast



a)



b)

Figure 5. Cracking vs. orientation of weld fusion zone and wrought inclusion geometry.
a)PRD b) TTD

and wrought steels. It involves the concept of hydrogen accumulation of critical levels at microscopic and macroscopic sites in the HAZ causing initiation and the propagation of cracks. The fracture modes and morphologies can be explained using Beachem's (20) model of hydrogen-assisted cracking. In addition, the presence of "perfect" intergranular (IG) fracture (plane grain faces) on grain boundaries sometimes observed in the IG mode of cracking indicates that hydrogen absorption may be causing a low energy mode of cracking. These features were found to be more prevalent in the low sulfur steels (0.001%) where the absence of inclusions "forces" the hydrogen to grain boundaries thus altering the fracture morphology.

THE PRAGMATIC AND PRACTICAL ASPECTS OF WELDING CAST AND WROUGHT STEELS

As indicated earlier, cast steels and wrought steels in the equivalent heat treated condition, should behave in a similar manner. The cast steels may even offer some advantage in the form of a lessened susceptibility to HAC because of their more "rounded" inclusion morphologies and microporosity which act as low stress raising sites when hydrogen is present. However, for both wrought and cast steels preheating should be considered when welding is planned. The need for and the level of preheat necessary to prevent Hydrogen Assisted Cracking (HAC), Hydrogen Induced Cracking (HIC), Underbead Cracking, (all relatively synonymous terms) is related to microstructural stress state and hydrogen.

The principle considerations in the assessment of the potential for hydrogen assisted cracking in cast and wrought steels are:

1. Susceptibility of the microstructure resulting in the HAZ from the combined action of weld cooling rate, carbon content and hardenability is a governing factor. (The last two conditions are often assessed together as the carbon equivalent.) It is universally agreed that if the hardness of the HAZ does not exceed HRC 35 (DPH/Vickers 350) there is no concern over hydrogen since hydrogen assisted cracking will not occur. In other words, if the HAZ is unhardened no special precautions such as preheat or low hydrogen welding procedures are necessary to avoid hydrogen cracking. Thus, when welds are made in certain steels with conditions leading to HAZ hardnesses less than HRC 35, control of hydrogen level is not important since, whatever the hydrogen content of the weld, spontaneous cracking will not occur. (It is to be noted that low preheats do not significantly affect cooling rates.)

2. The hydrogen content of the weld metal, which is derived from the plate material, electrodes, shielding gas and atmosphere, is critical to hydrogen cracking in welds with HAZ hardnesses in excess of HRC 35. The greater the level of hydrogen the lower the HAZ hardness (above HRC 35) which can be tolerated before the susceptibility to hydrogen assisted cracking becomes of concern. With low hydrogen levels in the weld (0-5 ppm) HAZ hardnesses in excess of HRC 35 can be tolerated and steel welded successfully without risk of cracking. High hydrogen levels would be considered to be approximately 20-30+ ppm and would normally result from improperly dried electrodes or improperly stored and reconditioned electrodes. The sources of hydrogen most effective in increasing the weld metal hydrogen content are shown in the equations developed by the IIW (IIW Doc 929-80) in Figure 6 with an example showing that for properly stored and handled low hydrogen electrodes, the diffusible hydrogen is on the order of 3.5ppm. If moisture is condensed on a plate when welding is attempted, the partial pressure of the water in the atmosphere surrounding the vicinity of the arc should saturate. If the mean temperature of the air in the near vicinity of the arc is 30°C, the partial pressure of

DIFFUSIBLE HYDROGEN IN WELDS

$$H_D = (260A_1 + 30A_2 + 0.9B - 10)^{\frac{1}{2}} \dots \text{UNITS: PPM}$$

A_1 - CHEMICALLY COMBINED H_2O (WT.%)

A_2 - ABSORBED MOISTURE (WT.%)

B - PARTIAL PRESSURE OF H_2O IN ATM. (MM HG)

10 - SLAG FACTOR

TYPICAL VALUES

A_1 - PROPERLY DRIED ---- 0.05 WT.%

A_2 - EXPOSED TO ATMOSPHERE -- 0.4+ WT.%

B - 10 MM HG

IF PROPERLY DRIED AND STORED: $A_2 = 0$

$$H_D = (260 \times 0.05 + 0 + 0.9 \times 10 - 10)^{\frac{1}{2}}$$

$$H_D = (12)^{\frac{1}{2}} = 3.5 \text{ PPM}$$

*NOTE: IT HAS BEEN FOUND THAT 80-90% OF THE ABSORBED MOISTURE IS USUALLY DRIVEN OFF BY THE HEAT OF THE ARC AND IS NOT AVAILABLE TO THE WELD POOL.

IIW DOC. 11-929-80

Figure 6. Hydrogen pickup in welds.

water in saturated air is approximately 30 mm of Hg. The hydrogen level resulting from this increased air moisture is 13 ppm. Thus, the effectiveness of plate moisture when giving rise to higher H₂O atmosphere levels is only mildly effective in increasing weld metal diffusible hydrogen. Recent studies in the welding lab at The University of Tennessee have shown that wet, cold (32°F) C-Mn-Si steel can be welded using low hydrogen electrodes and the weld metal diffusible hydrogen level will not rise above 5ppm.

3. The weld restraint is a factor in determining the stresses in and about the weld. The local stress state is governed by the weld solidification shrinkage whereas the long range stress state is a function of the structure and its rigidity. Welding toward open ends minimizes weld stresses and minimizes the potential for hydrogen assisted cracking even under conditions giving rise to critical HAZ hardnesses and high weld metal hydrogen levels.

In the absence of any one of the above factors;

1. Critically hardened HAZ (HRC 35)
2. Hydrogen at levels greater than "low hydrogen"
3. Stress or restraint,

weld HAZ cracking is reduced to an insignificant occurrence.

The most common location to find HAC is the coarse grained region of the HAZ and the locations are illustrated schematically in Figure 7. Fig-

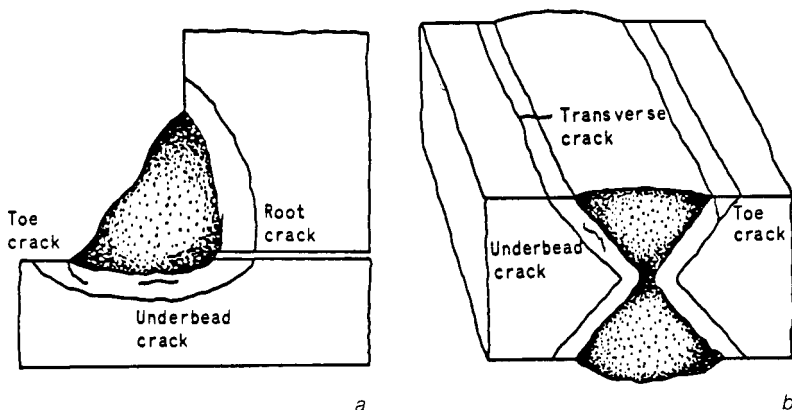


Figure 7. Schematic location of HAC cracking (after Coe²²).

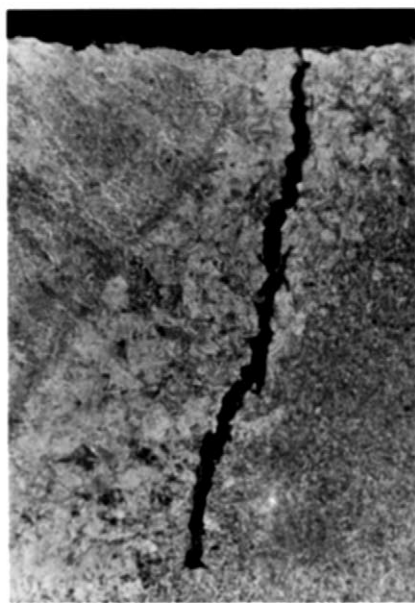


Figure 8. HAC cracking at the toe of butt weld.

ure 8 shows a typical toe crack at two magnifications. It is clearly evident that the cracking is confined to the coarse grained HAZ and in this instance the microstructure is martensitic in nature (most susceptible to HAC).

The microstructure is governed by the steel composition and cooling rate and can be assessed by jominy behavior by an emperical relationship between carbon and alloy content known as the carbon equivalent (CE) approach coupled with the effects of welding conditions such as material thickness, preheat and arc energy input.

The effect of plate thickness, energy input and preheat is shown in Figure 9. The cooling rate characteristic of a given set of welding parameters can be modified to a certain extent by a change in preheat. Thus preheat is employed as a means of altering cooling rate and modifying the microstructure of the HAZ. The relationship between microstructure and carbon equivalent (CE) or hardenability is shown in Figure 10. For three C, Mn, Si steels welded for the Battelle Underbead Cracking Test as the C.E. changes from 0.37 to 0.47 and then to 0.58 the microstructure is altered from mixed pearlite, martensite and bainite to all martensite. The hardness changes from HRC 20 to HRC 30 to HRC 42 and cracking results in the higher hardness martensitic HAZ.

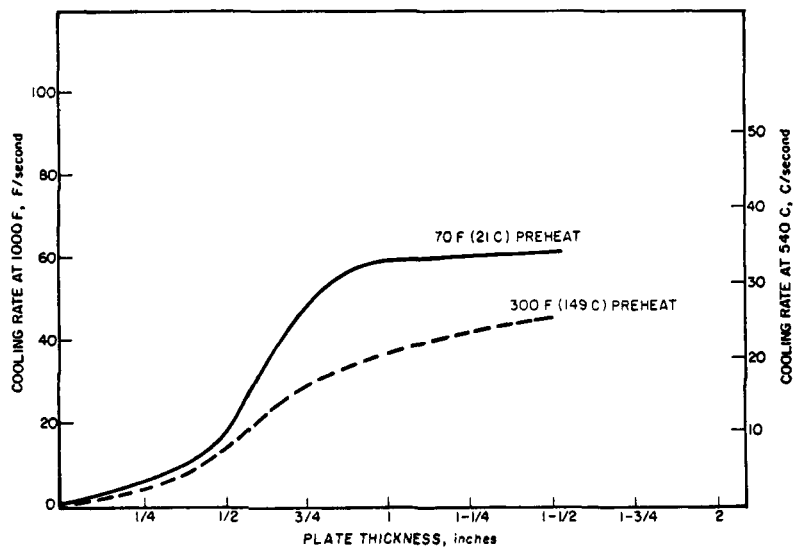
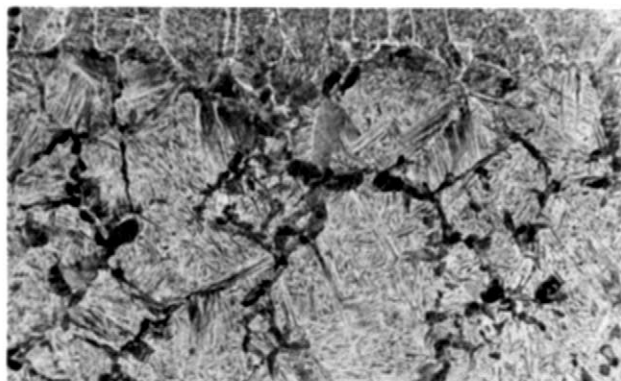
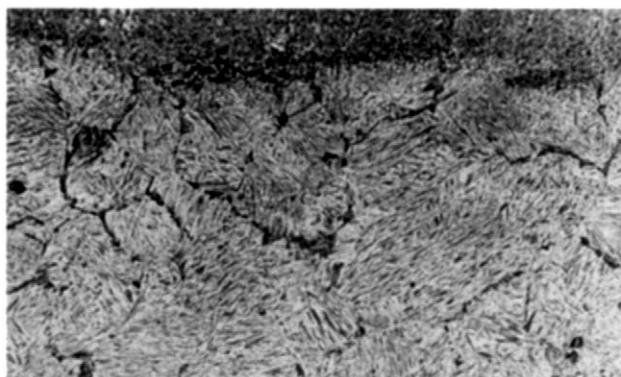


Figure 9. Effect of preheat, plate thickness and energy input on cooling rate.



a) C.E. = 0.37



b) C.E. = 0.47



c) C.E. = 0.58

Figure 10. Microstructures as function of carbon equivalent in Battelle under beack crack test samples. 200X.

Linnert (13) presents one of the commonly used C.E. formulas (Table 1) and derives preheat levels based on the CE. Note that as the CE increases the required preheat increases. The preheat influences cooling rate, reduces hardness, enhances hydrogen evolution from the weld, and lowers the potential for cracking with a given thickness material and welding energy input.

The full circle of hardenability (microstructure) cooling rate and hydrogen content must be addressed to adequately deal with HAC in cast and wrought steels.

In general, the preheat is derived based on the HAZ hardness level

Table 1. Carbon equivalent and preheats suggested.

Equivalent carbon content	=	% C	+	$\frac{\% \text{ Mn}}{6}$	+	$\frac{\% \text{ Ni}}{15}$	+	$\frac{\% \text{ Cr}}{5}$	+	$\frac{\% \text{ Cu}}{13}$	+	$\frac{\% \text{ Mo}}{4}$
The preheat temperatures suggested for several ranges of equivalent carbon content are:												
Equivalent Carbon Content				Suggested Preheat Temperature								
Up to 0.45%				Optional								
0.45 to 0.60%				200-400 F								
Above 0.60%				400-700F								
AFTER LINNERT-WELDING MET.												

which can be tolerated for crack free performance, i.e., < HRC 35. This approach has been documented by The Welding Research Council in its Bulletin #191 for both wrought and cast steels. The solutions to the complex hardenability questions were combined with the normal range of welding conditions and the level of preheat for each material was determined. The introduction to this publication indicates a conservative approach for preheat levels. It does caution about post heating as a possible additional requirement for as-cast steel castings (normalized castings behave no differently than wrought materials).

WRC Bulletin 191 states,

To the practical fabricator, the recommendations in the tables may seem conservative, sometimes excessively so. For the most part, this policy was followed deliberately, because the difficult jobs will prompt the welding engineer to consult the tables. Where

small units are being assembled, or large but simply designed structures are involved, the cautions may be eased. There is a certain amount of equivalence among factors such as high heat inputs, preheating, postheating, special welding sequences and peening. Thus submerged-arc welding or the use of special techniques or sequences with manual welding may obviate preheating in some cases. Experience with castings indicates that high preheating temperatures may be avoided, if postheating is specified. It is emphasized again that the table is intended as a guide, not as a specification of standard practice.

Data typical of that appearing in WRC Bulletin 191 is shown in Table 2 for A36 wrought steel. The preheat levels are seen to be a function of thickness, carbon content and hydrogen potential of the weld atmosphere. Similar data, for cast A216/A660 is given in Table 3.

Several cast steels are compared in Table 4 in terms of preheat temperatures suggested by ASTM, WRC 191 and Battelle (UBCT) at The University of Tennessee. From this table it is clear that the WRC 191 recommendations are conservative and generally in line with the underbead cracking tests. The ASTM specifications apparently assume low hydrogen conditions always prevail and the suggested preheats are lower. A situation which is more economical but less conservative. (Low hydrogen must be maintained especially for the more highly alloyed materials.)

CLOSURE

The presentation has covered the historical, mechanistic and practical-pragmatic aspects of the weldability of cast steels. The techniques and methodologies available to provide for conservative approaches to the avoidance of HAC, the most common weldability related difficulty with both cast and wrought steels, have been briefly described. In addition, the application of practical engineering know-how has to be integrated with the foregoing to arrive at procedures applicable to each particular situation.

Table 2. Typical WRC Bulletin 191 Data.

Steel Specification	Suggested Welding Conditions					Peening May Be Necessary
	For Carbon Range, %	For Thickness Range, Inch	Minimum Preheat and Interpass Temperature, °F		Post-Weld Heat-Treatment Range, °F	
			Low-Hydrogen	Other than Low-Hydrogen		
ASTM A36-75 Structural steel	Up to 0.25, Incl.	Up to 1, Incl.	Ambient, Above 10F	Ambient, Above 10F	Optional 1100/1250	—
		Over 1 to 2, Incl.	Ambient, Above 10F	200	Optional 1100/1250	—
		Over 2 to 4, Incl.	100	300	Optional 1100/1250	Yes
	0.26-0.29, Incl.	Up to 1/2, Incl.	Ambient, Above 10F	Ambient, Above 10F	Optional 1100/1250	—
		Over 1/2 to 1, Incl.	Ambient, Above 10F	200	Optional 1100/1250	—
		Over 1 to 2, Incl.	100	300	Optional 1100/1250	Yes
		Over 2 to 4, Incl.	200	300	Optional 1100/1250	Yes

Note:

For welding and post-weld heat-treatment requirements for boilers or pressure vessels fabricated from this material refer to appropriate section of ASME Boiler & Pressure Vessel Code.

Table 3. Cast steel data WRC 191.

Steel Specification	Suggested Welding Conditions					Peening May Be Necessary
	For Carbon Range, %	For Thickness Range, Inch	Minimum Preheat and Interpass Temperature, °F		Post-Weld Heat-Treatment Range, °F	
			Low-Hydrogen	Other than Low-Hydrogen		
For Total Residual Alloys Less Than 0.50%						
ASTM A216-75 Carbon Steel Casting Suitable for Fusion Welding for High Temperature Service	Up to 0.20, Incl.	Up to 1, Incl.	Ambient, Above 10F	Ambient, Above 10F	Optional 1100/1250	—
		Over 1 to 2, Incl.	Ambient, Above 10F	100	Desirable 1100/1250	
		Over 2 to 4, Incl.	100	200	Desirable 1100/1250	Yes
	0.21-0.25, Incl.	Up to 1, Incl.	Ambient, Above 10F	Ambient, Above 10F	Optional 1100/1250	—
		Over 1 to 2, Incl.	100	200	Desirable 1100/1250	Yes
		Over 2 to 4, Incl.	200	100	Desirable 1100/1250	Yes

ASTM A660-76 Centrifugally Cast Carbon Steel Pipe for High Temperature Service	0.26-0.30, Incl.	Up to 1/2, Incl.	Ambient, Above 10F	Ambient, Above 10F	Optional 1100/1250	—
		Over 1/2 to 1, Incl.	100	200	Desirable 1100/1250	—
		Over 1 to 2, Incl.	100	100	Desirable 1100/1250	Yes
		Over 2 to 4, Incl.	200	400	Desirable 1100/1250	Yes

For Total Residual Alloys Over 0.50%

Up to 0.30, Incl.	Up to 2, Incl.	100	300	Desirable 1100/1250	Yes
	Over 2 to 4, Incl.	200	400	Desirable 1100/1250	Yes

Notes:

1. Thickness refers to that at point of welding.
2. For welding and post-weld heat-treatment requirements for boilers or pressure vessels fabricated from this material refer to appropriate section of ASME Boiler & Pressure Vessel Code.

Table 4. Comparison of preheat temperatures (°F) obtained at U.T. to avoid HAC with ASTM and WRC recommendations.

Steel-ASTM Spec		Minimum ASTM Rec. Low H ₂ 1" Thickness	WRC 191-Minimum Rec. 1" Thickness		UT-Battelle UCT's 1" Thickness Non Low H ₂
Spec.	C.E.		Low H ₂	Non Low H ₂	
A27 (Mild to Medium Strength Castings)	0.50 Max w/o Residuals	NS	100	300	150-200
A148 High Strength Castings	NS S < 0.06 P < 0.05	NS			Depending Upon Composition
A216-WCB, WCC Castings for Fusion Welding	0.56 MAX	NS	100	200	200-250
A356-Carbon & Low Alloy Castings For Steam Turbines	0.49 Max	50	100	200	100-150
A486-Highway Bridges (CL. 70)	0.53 Max	50	200	350	150-200
A487-Castings For Pressure Service	0.54 Max				
Class 1N		175	100	300	150-200
A643-Carbon & Low Alloy for Pressure Vessels	0.53 Max				
GR A		50	200	300	150-200
AISI 8630	0.60				
	Max	—	250	350	250
Cast 8630	0.54				
A487	Max				
Class 1N (Except for Higher Allowable Sl)		175	100	300	150-200

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Cast High Alloy Metallurgy

by Martin Prager

INTRODUCTION

High alloy steels go by many names. A list of the conventional terminology well defines the breadth of this family. Some commonly used descriptive terms are:

- heat resistant high alloy steels
- corrosion resistant high alloy steels
- austenitics
- ferritics
- martensitics
- duplex stainless steels
- super ferritics
- austenitic age-hardenable steels
- martensitic age-hardenable steels
- stainless steels
- stabilized stainless steels
- Hgrades

The primary components are typically iron, chromium, nickel and carbon. However, the ranges and ratios vary widely and hence the diversity of the alloys. Copper, molybdenum, or small amounts of other elements are added intentionally to tailor the alloys to specific applications. Significant improvements in strength or corrosion resistance result.

Obviously, this wide range of alloys affords the user many options with regard to heat or corrosion resistance and cost. Additionally, the ranges

Table 1 ACI Alloy Designations and Chemical Composition Ranges for Heat- and Corrosion-Resistant Castings

Cast Alloy Designation	Wrought Alloy Type (See Note A)	Composition†—percent (balance Fe)							
		C	Mn	Si	P	S	Cr	Ni	Other Elements
CA-15	410	0.15	1.00	1.50	0.04	0.04	11.5-14	1	Mo 0.5††
CA-15M	—	0.15	1.00	0.65	0.04	0.04	11.50-14.0	1.00	Mo 0.15-1.00
CA-40	420	0.20-0.40	1.00	1.50	0.04	0.04	11.5-14	1	Mo 0.5††
CA-6NM	—	0.06	1.00	1.00	0.04	0.03	11.5-14.0	3.5-4.5	Mo 0.4-1.0
CA-6N	—	0.06	0.50	1.00	0.02	0.02	10.5-12.0	6.0-8.0	
CB-30	431	0.30	1.00	1.50	0.04	0.04	18-21	2	—
CB-7Cu-1	—	0.07	0.70	1.00	0.035	0.03	14.0-15.5	4.5-5.5	Cb 0.15-0.35, N 0.05, Cu 2.5-3.2
CB-7Cu-2	—	0.07	0.70	1.00	0.035	0.03	14.0-15.5	4.5-5.5	Cb 0.15-0.35, N 0.05, Cu 2.5-3.2
CC-50	446	0.50	1.00	1.50	0.04	0.04	26-30	4 max.	
CD-4MCu	—	0.04	1.00	1.00	0.04	0.04	24.5-26.5	4.75-6.00	Mo 1.75-2.25, Cu 2.75-3.25
CE-30	—	0.30	1.50	2.00	0.04	0.04	26-30	8-11	—
CF-3	304L	0.03	1.50	2.00	0.04	0.04	17-21	8-21	—
CF-8	304	0.08	1.50	2.00	0.04	0.04	18-21	8-11	—
CF-20	302	0.20	1.50	2.00	0.04	0.04	18-21	8-11	—
CF-3M	316L	0.03	1.50	1.50	0.04	0.04	17-21	9-13	Mo 2.0-3.0
CF-8M	D319(316)	0.08	1.50	2.00	0.04	0.04	18-21	9-12	Mo 2.0-3.0
CF-8C	347	0.08	1.50	2.00	0.04	0.04	18-21	9-12	Cb 8 x Cmin., 1.0 max.
CF-16F	303	0.16	1.50	2.00	0.17	0.04	18-21	9-12	Mo 1.5, Se 0.20-0.35
CG-12	—	0.12	1.50	2.00	0.04	0.04	20-23	10-13	
CG-8M	317	0.08	1.50	1.50	0.04	0.04	18-21	9-13	Mo 3.0-4.0
CH-20	309	0.20	1.50	2.00	0.04	0.04	22-26	12-15	—
CK-20	310	0.20	2.00	2.00	0.04	0.04	23-27	19-22	—
CN-7M	—	0.07	1.50	1.50	0.04	0.04	19-22	27.5-30.5	Mo 2.0-3.0, Cu 3.0-4.0
CN-7MS	—	0.07	1.00	2.50-3.50	0.04	0.03	18-20	22-25	Mo 2.0-3.0, Cu 1.5-2.0
CW-12M	—	0.12	1.00	1.50	0.04	0.03	15.5-20	Bal.	Fe 7.5
CY-40	—	0.40	1.50	3.00	0.03	0.03	14-17	Bal.	Fe 11.0

CZ-100	—	1.00	1.50	2.00	0.03	0.03	—	Bal.	Fe 3.0, Cu 1.25
N-12M	—	0.12	1.00	1.00	0.04	0.03	1.0	Bal.	Mo 0.26-0.33, V 0.60, Co 2.50, Fe 6.0
M-35	—	0.35	1.50	2.00	0.03	0.03	—	Bal.	Cu 26-33, Fe 3.50
HA	—	0.20	0.35-0.65	1.00	0.04	0.04	8-10	—	Mo 0.90-1.20
HC	446	0.50	1.00	2.00	0.04	0.04	26-30	4 max.	Mo 0.5††
HD	327	0.50	1.50	2.00	0.04	0.04	26-30	4-7	Mo 0.5††
HE	—	0.20-0.50	2.00	2.00	0.04	0.04	26-30	8-11	Mo 0.5††
HF	302B	0.20-0.40	2.00	2.00	0.04	0.04	18-23	8-12	Mo 0.5††
HH	309	0.20-0.50	2.00	2.00	0.04	0.04	24-28	11-14	Mo 0.5†† N 0.2
HI	—	0.20-0.50	2.00	2.00	0.04	0.04	26-30	14-18	Mo 0.5††
HK	310	0.20-0.60	2.00	2.00	0.04	0.04	24-28	18-22	Mo 0.5††
HL	—	0.20-0.60	2.00	2.00	0.04	0.04	28-32	18-22	Mo 0.5††
HN	—	0.20-0.50	2.00	2.00	0.04	0.04	19-23	23-27	Mo 0.5††
HP	—	0.35-0.75	2.00	2.50	0.04	0.04	24-28	33-37	Mo 0.5††
HP-50WZ	—	0.45-0.55	2.00	2.00	0.04	0.04	24-28	33-37	W 4.0-6.0, Zr 0.2-1.0
HT	330	0.35-0.75	2.00	2.50	0.04	0.04	15-19	33-37	Mo 0.5††
HU	—	0.35-0.75	2.00	2.50	0.04	0.04	17-21	37-41	Mo 0.5††
HW	—	0.35-0.75	2.00	2.50	0.04	0.04	10-14	58-62	Mo 0.5††
HX	—	0.35-0.75	2.00	2.50	0.04	0.04	15-19	64-68	Mo 0.5††

†Maximum, unless Range is given.

††Molybdenum not intentionally added.

Designations with the initial letter "C" indicate alloys generally used to resist corrosive attack at temperatures less than 1200F. Designations with the initial letter "H" indicate alloys generally used under conditions where the metal temperature is in excess of 1200F. The second letter represents the nominal chromium-nickel type; the nickel content increasing in amount from "A" to "Z". For example, "F" stands for the 19% Cr-9% Ni, "K" for the 25% Cr-20% Ni, and "W" for the 12% Cr-60% Ni alloy types. Numerals following the letters indicate the *maximum* carbon content of the corrosion-resistant alloys; carbon content may also be designated in the heat-resistant grades by following the letters with a numeral to indicate the *midpoint* of a $\pm 0.05\%$ carbon range. If special elements are included in the composition they are indicated by the addition of a letter to the symbol. Thus, "CF-8M" is an alloy for corrosion-resistant service, of the molybdenum-containing 19% Cr-9% Ni type with a maximum carbon content of 0.08%.

Note A—Wrought alloy type numbers are listed only for the convenience of those who want to determine corresponding wrought and cast grades.

Because the cast alloy chemical composition ranges are *not the same* as the wrought composition ranges, buyers should use cast alloy designations for proper identification of castings.

Note B—Most of the standard grades listed are covered for general applications by American Society for Testing and Materials specifications A 743 and A 297. ASTM specifications A 217, A 351, A 447, A 451, A 452, A 744, and A 757 also apply to some of the grades.

Note C—For additional alloy designations consult the current SFSA Handbook Supplement on specifications.

for strength and toughness achievable with this class of materials cover almost as broad a spectrum as is possible. Subtle change in composition and heat treatment may have a profound effect on microstructure, strength, pitting resistance, toughness, weldability, magnetic properties, machinability, hardness or other engineering properties. Familiarity with the metallurgical principles is essential for optimizing the desired properties on the one hand and avoiding disastrous consequences on the other.

Many types of tests have now verified that properties achieved in cast alloys are very similar to those found with their wrought counterparts. However, whether wrought or cast material is used, the opportunity for misapplication exists. Since these alloys are relatively costly, high performance materials, they are specified for conditions of temperature, environment or stress which are potentially very destructive if proper precautions are not taken. Examples are pumps, impellers and propellers in seawater or liquid metal service, furnace tubes, chemical equipment, boiler components, refinery valves and pumps, etc.

GENERAL METALLURGY

A good starting point for understanding the metallurgy of high alloy castings is the behavior of iron or simple steels. On cooling from casting temperatures these materials solidify as (body centered cubic) "delta" ferrite, transform to (face centered cubic) austenite at temperatures on the order of 2500°F and then again transform to ferrite after cooling another 1,000°F: If cooling from the austenite field is sufficiently rapid, ferrite formation is suppressed in alloys containing carbon. Instead, they transform at low temperatures to the relatively high strength structure known as martensite. Addition of alloying elements serves to stabilize or promote the appearance of one or another of the aforementioned phases.

The principal ingredient in the high alloy family is usually chromium which, through the formation of protective oxide films, also starts these alloys on the road to the so-called "stainless," or as it used to be called, "rustless," quality. For all practical purposes, stainless behavior requires at least 12% chromium. As will be discussed later, corrosion resistance further improves with additions of chromium to at least the 30% level. As may be seen in Table I (Ref. I), nickel and lesser amounts of molybdenum and other elements are added to the iron-chrome matrix.

While chromium is a ferrite and martensite promoter, nickel is an austenite promoter. By varying the amounts and ratios of these two elements (or their equivalents) almost any desired combination of microstructure, strength or other properties may be achieved. Equally important is heat treatment. Temperature, cooling rate and time at temperature must be controlled to obtain the desired results.

CHROMIUM AND NICKEL EQUIVALENTS

It is useful to think of the compositions of high alloy steels in terms of the balance between austenite promoters and ferrite promoters. This is done on the widely used Schaeffler type diagrams as shown in Figure 1 (Ref. 2). The phases shown are those which persist after cooling to room temperature at rates normally used in fabrication.

Chromium equivalent is plotted on the abscissa. Included in the summation are all ferrite promoting elements. These are: chromium, silicon, molybdenum, vanadium, aluminum, niobium, titanium, and tungsten. They have been correlated by Schneider as follows on the basis of weight percent (Ref. 3):

$$\text{Chromium equivalent} = (\text{Cr}) + 2(\text{Si}) + 1.5(\text{Mo}) + 5(\text{V}) + 5.5(\text{Al}) + 1.5(\text{Nb}) + 1.5(\text{Ti}) + 0.75(\text{W})$$

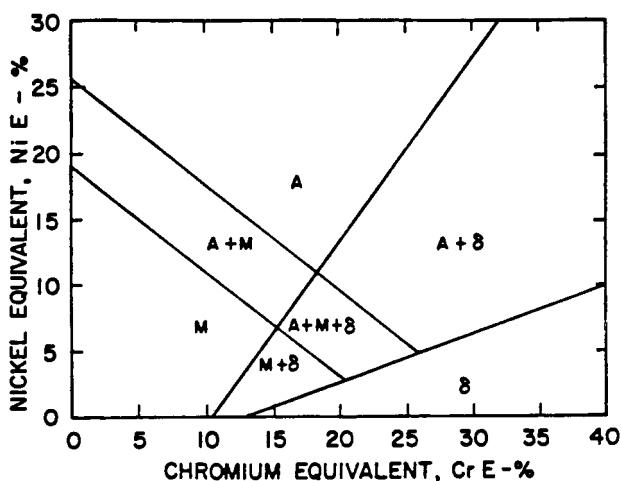


Figure 1 Schaeffler diagram indicating phases occurring at room temperature in iron-chromium alloys.

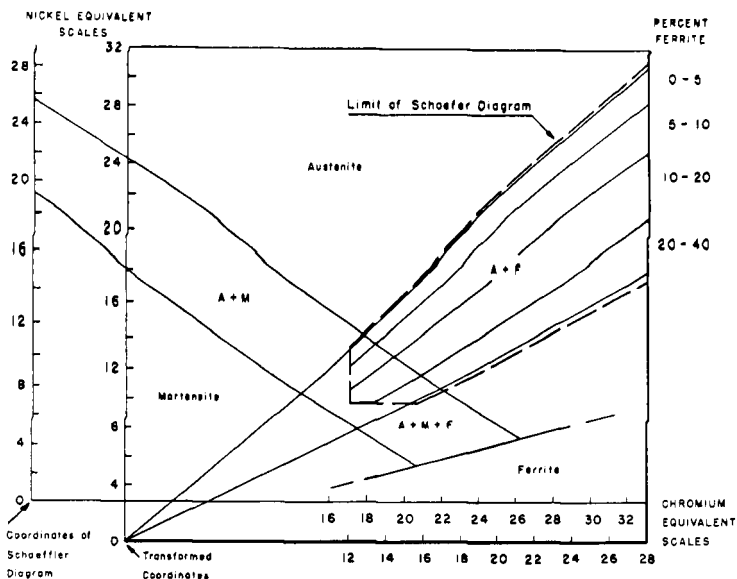


Figure 2 Relation between Schoefer and Schaeffler coordinates for computing phase relations.

Nickel equivalent is plotted on the ordinate. Other austenite promoters included in the equation are cobalt, manganese, copper, nitrogen and carbon.

$$\text{Nickel equivalent} = (\text{Ni}) + (\text{Co}) + 0.5(\text{Mn}) + 0.3(\text{Cu}) + 25(\text{N}) + 30(\text{C})$$

The above computations derived from the work of Schaeffler and Schneider are widely used, especially for predicting the behavior of weldments. The foundry industry has developed another correlation for estimating the ferrite content (in terms of a ferrite number). The equations used were developed by Schoefer (Ref. 4) and resemble those shown above but do yield different equivalent values. The relation between Schoefer's and Schaeffler's coordinates may be seen in Figure 2. Schoefer's formula only must be used in defining the composition ratio shown in Figure 3. The application of Figure 3 will be explained shortly. However, the equations developed by Schoefer are as follows:

$$\begin{aligned} \text{Chromium Equivalent} &= (\text{Cr}) + 1.5(\text{Si}) + (\text{Mo}) + (\text{Cb}) - 4.99 \\ \text{and} \\ \text{Nickel Equivalent} &= (\text{Ni}) + 30(\text{C}) + .5(\text{Mn}) + 26(\text{N} - .02) + 2.77 \end{aligned}$$

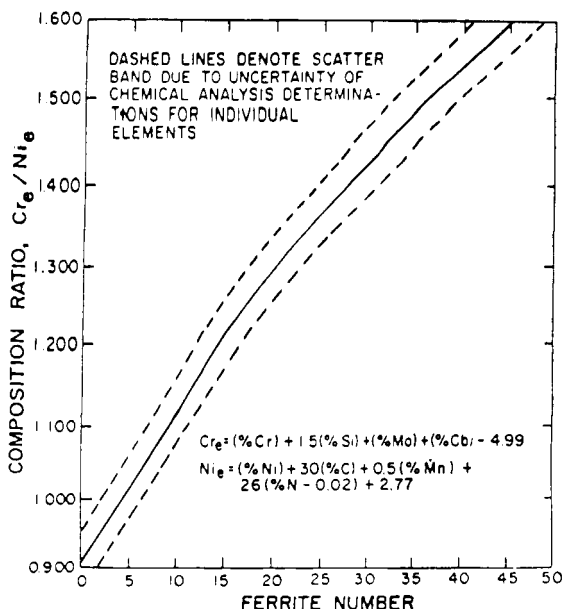


Figure 3 Diagram used for estimating ferrite number based on Schoefer's formula.

The empirical correlations depicted in Figure 1 and 2 may be understood from the following. The field designated as M or Martensite encompasses alloys such as CA-15, CA-40, CA-6NM and even CB-7Cu. These alloys contain 12 to 17% chromium with adequate nickel, molybdenum and carbon to promote high hardenability i.e., the ability to transform completely to martensite when cooled at even the moderate rates associated with air cooling heavy sections. Please note that high alloys have low thermal conductivities and cool slowly. To obtain the desired properties, a full heat treatment is required following casting. That is the casting in austenitized by heating to 1600 to 1800°F rapidly cooled to room temperature to produce the hard martensite and then tempered at 1100 to 1400°F until the desired combination of strength, toughness, ductility and resistance to corrosion or stress corrosion is obtained.

Increasing the nickel equivalent i.e., moving vertically in Figure 1 eventually results in an alloy which is fully austenitic, such as CC-20, CH-20, CK-20 or CN 7M. These alloys are extremely ductile, tough and corrosion resistant. On the other hand, as shown in Figure 4, yield and tensile strength are among the lowest of the high alloys. Because these high nickel alloys are fully austenitic, they are nonmagnetic. Heat treatment consists of a single step, water quenching from a relatively high temperature at which carbides have been taken into solution. Solution anneal-

ing may also homogenize the structure but, because no transformation occurs, there can be no grain refinement. The solutionizing step and rapid cooling assures maximum resistance to corrosion. Typically temperatures well above 2000°F are required.

Adding chromium to the lean alloys i.e., proceeding horizontally in Figure 1, stabilizes the delta ferrite which forms when the casting solidifies. This results in alloys in the field indicated by the delta, δ , Figure 2. Examples are CB-30 or CC-50. With high chromium content, these alloys have relatively good resistance to corrosion particularly in sulfur bearing atmospheres. However, being single phase, they are able and have moderate to low strength and are often used as-cast or after only a simple solutioning treatment.

Between the fields designated M, A, and δ in Figure 1 are regions indicating the possibility of two or more phases in the alloys. Commercially, by far the most important of these is the one in which austenite and ferrite coexist. Examples are CF-3, CF-8, CF-3M, CF-8M, CG-8M, and CE-30. Typically, these alloys contain from 3 to 40% ferrite in a matrix of austenite. Predicting and controlling ferrite content is vital to the successful application of these materials. Duplex alloys offer superior strength, weldability and corrosion resistance. Strength, for example, increases directly with ferrite content. Achieving specified minimums may require controlling ferrite within narrow bands. Figure 3 and Schoefer's equations noted earlier are used for this purpose. The ferrite number so determined is not the percent ferrite which would be obtained by metallographic means. It more closely approximates determinations made using a Magnegage or Severn Gage as is the conventional quality control practice.

Properly, these duplex alloys should be solution annealed and rapidly cooled prior to use to assure maximum resistance to corrosion.

The presence of ferrite is not entirely beneficial. Ferrite tends to reduce toughness, although given the extremely high toughness of the austenite matrix, this is not of great concern. However, in those applications which require exposure to elevated temperatures, usually from 600°F on up, metallurgical changes associated with the ferrite can be severe and detrimental. In the low end of the range reductions in toughness observed have been attributed to carbide precipitation or reactions associated with "885°F embrittlement." The "885 embrittlement" is caused by precipitation of an intermetallic phase with a composition

of approximately 80% chromium and 20% iron. The name derives from the fact that this embrittlement is most severe and rapid when it occurs in the vicinity of 885°F. At 1000°F and above, with extended exposure in service, the ferrite converts to a complex Fe-Cr-Ni intermetallic compound known as sigma phase which reduces toughness and creep ductility. The extent of the reduction increases with time and with temperature to about 1500°F and may persist to 1700°F. In extreme cases, Charpy V-notch energy at room temperature may be reduced 95% from its initial value.

THE EFFECTS OF ALLOY ADDITIONS

In addition to their influence on the calculated chromium and nickel equivalents, each of the other elements commonly found in high alloy castings is important from the metallurgical point of view and should be considered in drawing a picture of this family of alloys.

Molybdenum while a strong ferrite former is highly beneficial to the corrosion resistance of all types of high alloys. Molybdenum carbides increase the strength of martensites and improve the creep resistance of austenitic and duplex alloys.

Carbon stabilizes austenite and through the action of carbides, increases the high temperature strength of all alloys. To achieve the highest resistance to creep, .3 or .4% carbon is commonly added. However, because carbon may combine with elements such as molybdenum or chromium which are beneficial to corrosion resistance, its effect on that property is negative. Where aqueous corrosion resistance is not important, but high temperature strength is, the "H" grades are specified in preference to "C" types shown in Table I. These heat resistant grades are high carbon versions of the "C" alloys but also contain additions of carbide formers to enhance performance.

Where resistance to corrosion is of paramount concern, carbon content is minimized. Ultra low carbon grades may be specified for some situations. The intention is to prevent "sensitization", susceptibility to intergranular corrosion. Sensitization is caused by precipitation of chromium carbides in grain boundaries and the formation of chromium depleted zones in the adjacent areas. It occurs during service at moderate temperatures or more often during cooling after welding or heat treatment. Carbon pickup from mold materials may reduce the corrosion resistance of material near the casting surfaces. Intergranular corrosion or stress corrosion are likely consequences.

To improve strength without the detrimental effects of ferrite or carbon, nitrogen may be added to a content of over 1 thousand ppm. Since nitrogen stabilizes austenite it must be included in calculating the nickel equivalent. Nitrogen forms carbonitrides with elements such as chromium, titanium and vanadium and these are effective hardeners.

Vanadium, titanium, and columbium form carbides which are stable at high temperatures. They may impart resistance to sensitization (as in stabilized stainless steels) or improve creep strength and resistance to tempering. They are used for example in "superferritic" steels which are in the developmental stages as cast alloys. The complex carbides and carbonitrides formed are resistant to softening and overaging. The superferritics have creep strength superior to more costly; highly alloyed austenitic materials.

Copper modestly stabilizes austenite. Its major influence is in precipitation hardening the matrix. Alloys containing copper such as CB-7Cu and CD-4MCu require aging to achieve full strength. The precipitate in these alloys is actually elemental copper. The temperature required for the precipitation reaction is relatively low and may impair toughness because it is in the regime of 885°F embrittlement.

Silicon is used in heat resisting castings such as HK, HT and HU. It is beneficial to resistance to oxidation and resistance to carburization. Foundrymen know silicon improves fluidity and therefore the quality of castings. However, silicon does increase the tendency for fissuring in welds, especially in low carbon, high alloy steels.

STRENGTH AND WELDABILITY CONSIDERATIONS

Martensitic Steels:

Martensitic steels have the highest strength of the high alloy family. The alloys are fully austenitized during heat treatment and transform to martensite on cooling to room temperature. At that point the structure is too hard and brittle for use and must be tempered, at least partially, immediately. Otherwise, the casting may crack while awaiting further processing. Full tempering may be performed at a later occasion.

The same considerations apply to welding, which is in effect a very localized heat treatment. Because of the brittleness of martensite, heavy section castings must be preheated and postheated to avoid cracking from thermal stresses or hydrogen dissolved during welding.

The martensitic microstructure is extremely prone to hydrogen embrittlement. At the strength levels achieved in the as-welded condition, sensitivity to embrittlement is extremely high. It is manifested by delayed, very brittle cracking. Hydrogen is likely to be introduced by the welding operation or by corrosion of the steel by any aqueous environment, including condensing moisture.

The reaction producing martensite is a diffusionless shifting of the atoms. The atomic lattice is left highly distorted and internally stressed with carbon and carbide forming elements trapped in the supersaturated matrix. The resulting high hardness structure has very poor resistance to impact or crack propagation and extreme notch sensitivity.

During tempering, the internal strains are partially relaxed, toughness increased and carbides precipitate.

It is essential that the composition of martensitic alloys be properly balanced to obtain maximum strength and toughness in the final product. For example, addition of molybdenum and vanadium enhances strength at room and elevated temperature. However, these elements are ferrite promoters. Their addition must be balanced by carbon, nickel, manganese or copper to promote austenite during heat treatment prior to quenching. A duplex microstructure at the austenitizing temperature would quench to a martensite of lower strength and toughness. Carbon can be added only judiciously to promote austenite since it severely degrades weldability (the resulting martensite is hard and brittle and susceptible to hydrogen embrittlement and stress corrosion).

For optimum resistance to corrosion and stress corrosion, the martensitic alloys should be fully heat treated (austenitized, quenched and tempered) after welding.

Ferritic Alloys:

These nonhardenable alloys are of moderate strength, but relatively poor toughness. The high chromium content makes them suitable for very high temperature corrosion resisting applications where poor room temperature toughness is not likely to be a problem. However, high chromium alloys are susceptible to grain coarsening during heat treatment or welding. With very high carbon contents, grain boundary precipitation during heat treatment or welding may noticeably impair

ductility and resistance to corrosion. These alloys should be annealed after welding for optimum properties.

Austenitic Alloys

Fully austenitic alloys such as CH-20, CK-20, CN-7M, N-12M and M-35 and H grades HF, HH, HI, HK, HL, HN, HP, HT, HU, HW and HX are the most ductile of the cast alloys. This may be judged from Figure 4. They are suitable for applications where resistance to thermal shock is required. Generally they have the best resistance to sigma phase formation and therefore retain resistance to thermal shock even after long exposure at elevated temperatures.

Grade HF is commonly used to temperatures of 1600°F while grades HH, HI, HK to HX can be used to temperatures approaching 2150°F. These alloys owe their high creep strength to carbides dispersed in a fully austenitic alloy. Proprietary modifications of the H grades may contain tungsten, cobalt, molybdenum and columbium to enhance creep resistance. In any event it is the substantial amounts of fine and coarse carbides and other precipitated phases which account for the remarkable creep strength of the H grades relative to C grades and wrought alloys.

In the early days of the development of H grades, the alloys lacked toughness and were severely degraded by precipitation and other embrittling reactions occurring during service. This is no longer the case. Today, these compositions can retain a substantial fraction of initial toughness even after long exposure in service. However, achieving these properties requires relatively tight control of composition, purity and initial microstructure. In this way, sigma phase formation may be delayed or prevented in fully austenitic microstructures.

Silicon is beneficial to the high temperature properties of these alloys. Manganese may be added to counteract silicon's promotion of delta ferrite.

The Achilles' Heel of the austenitic alloys is their weldability. The problem is associated with liquation which occurs in the heat affected zone and hot shortness of fully austenitic weld metals. Where applications permit, duplex (austenitic-ferritic) filler metals are used. Typically filler metals with at least 3 to 5% ferrite content are employed. The austenitic materials do not require preheating or postheating as part of the welding operation since the structure is both ductile and nearly totally immune to the detrimental effects of hydrogen.

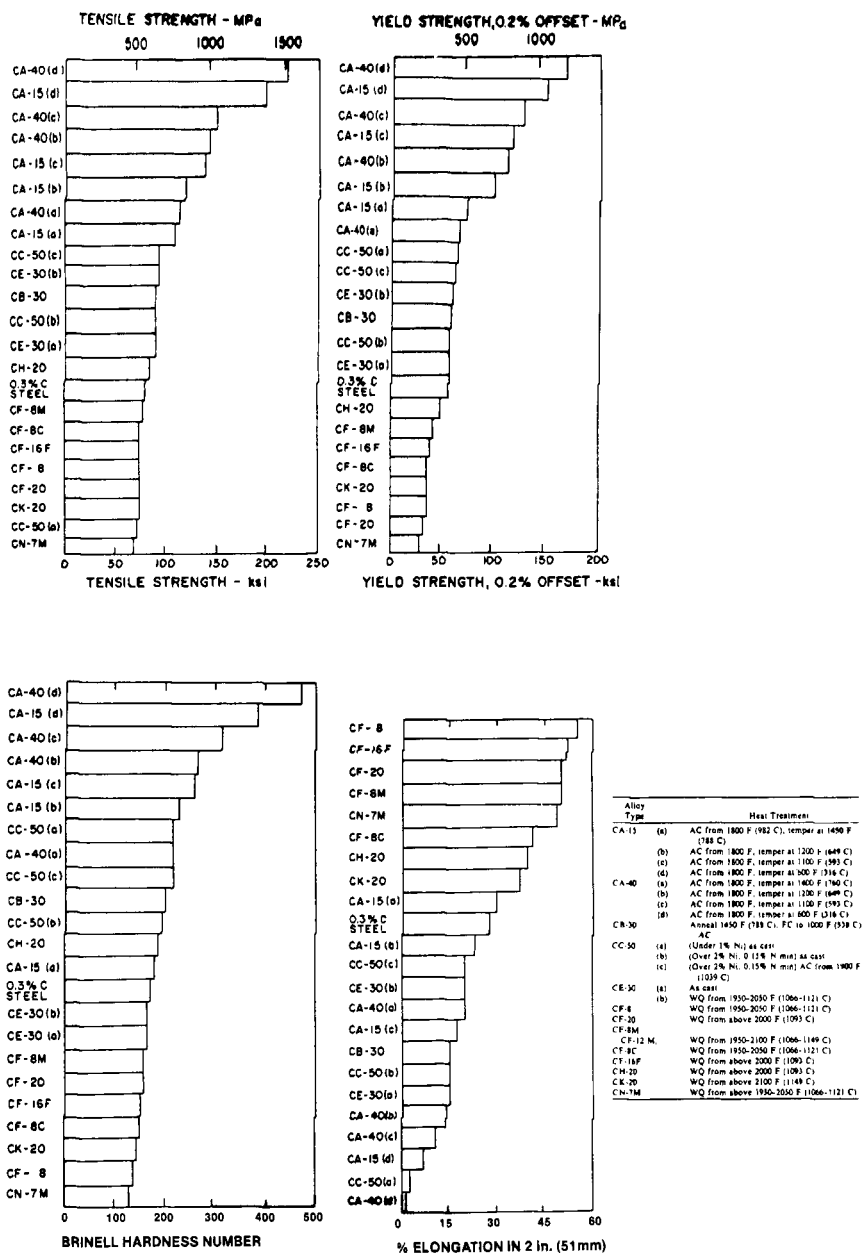


Figure 4 Comparison of mechanical properties of some cast high alloys heat treated as indicated.

The fully austenitic castings may display sensitization as a result of Cr_{23}Cr type precipitation at grain boundaries during welding. After welding it may be advisable to solution anneal the alloy and remove the attendant susceptibility to intergranular corrosion. Alternatively, exposures to temperatures of 1650°F and above will restore chromium to depleted zones and also remove the tendency for local galvanic interaction which is at the root of the sensitization problem. For applications where aqueous corrosion resistance is the primary concern, carbon contents below .03% is an effective counter to the tendency for sensitization.

The strength of austenitic alloys may be conveniently increased up to 20 ksi by nitrogen additions up to 0.2%. At higher levels, porosity becomes a significant problem. Also, the effect of nitrogen on weldability and long-term creep properties is not well understood.

Ferritic-Austenitic Alloys

The advantages of the duplex microstructure are many. Strength increases in proportion to ferrite content. As shown in Figure 5 (Ref. 5) in-

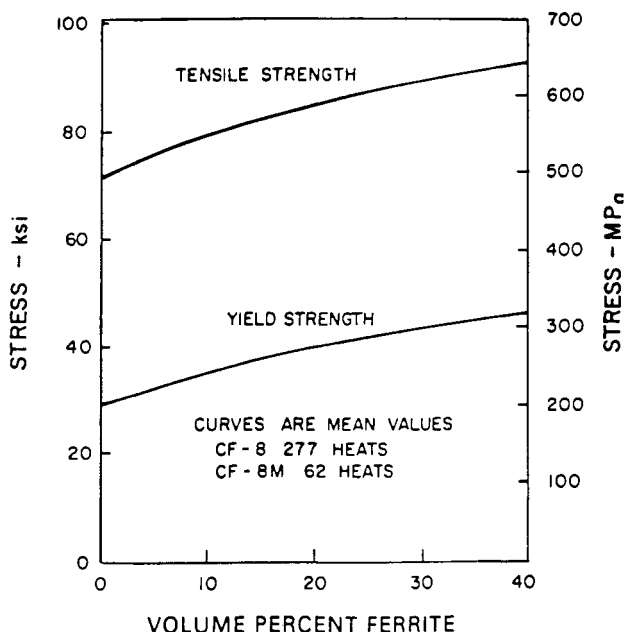


Figure 5 Yield strength and tensile strength at room temperature as a function of ferrite content of CF-8M alloys.

creasing ferrite to the twenty percent level results in roughly the same percentage increase in tensile strength. The corresponding increase in yield strength is even larger. Typically, duplex castings contain ferrite contents greater than 15%. At this level degradation of impact properties has been found to be significant at service temperatures of 800°F and above (Figure6). ASTM and ASME materials specifications and the Boiler and Pressure Vessel Code caution that because of thermal instability (sigma phase precipitation), these materials are not recommended for elevated temperature service above about 800°F.

Landerman and Bamford (Ref. 5) have reported that tensile properties and J Integral values are not nearly as severely degraded as the impact values for CF-8M (Figures 7 and 8) for exposures at 800°F to 3,000 hours. This duration was thought to duplicate at least 12 years of service at 600°F based upon the kinetics of the embrittling reaction. Those authors consider that J_{IC} values are an important indicator of the tolerance of the castings for flaws. Similarly, fatigue crack growth behavior (Figure 9) suggested no dramatic effect of aging on behavior. The width of the scatter band shown is about the same as for unaged material.

Weldability improves with increasing ferrite content. The tendency for

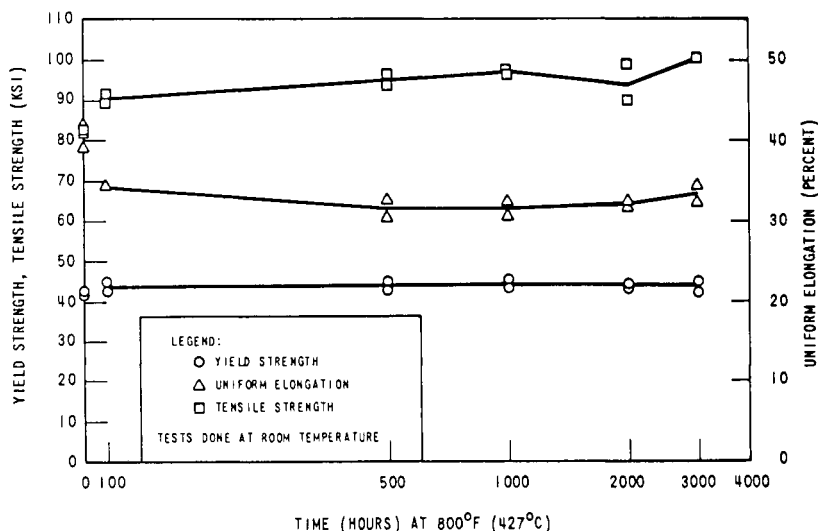


Figure 6 Effect of aging on tensile properties of a heat of CF-8M.

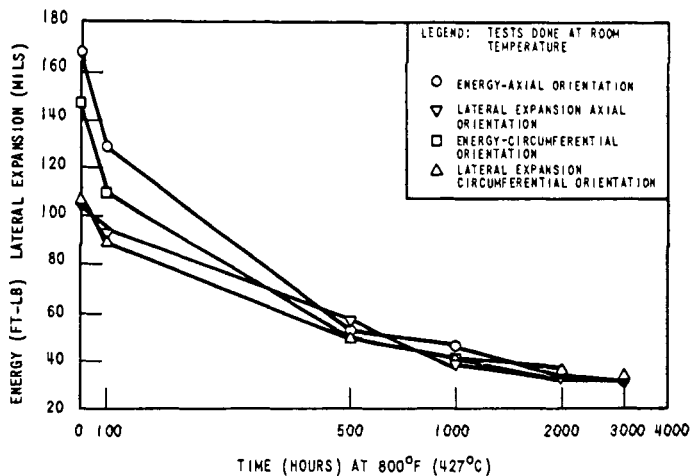


Figure 7 Effect of aging on impact properties of a heat of CF-8M.

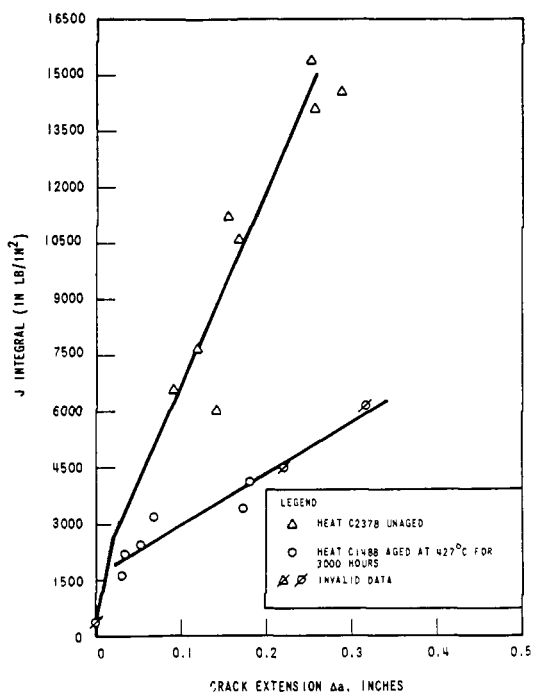


Figure 8 J-Integral behavior of two similar heats of CF-8M, one aged, one as received (solution treated).

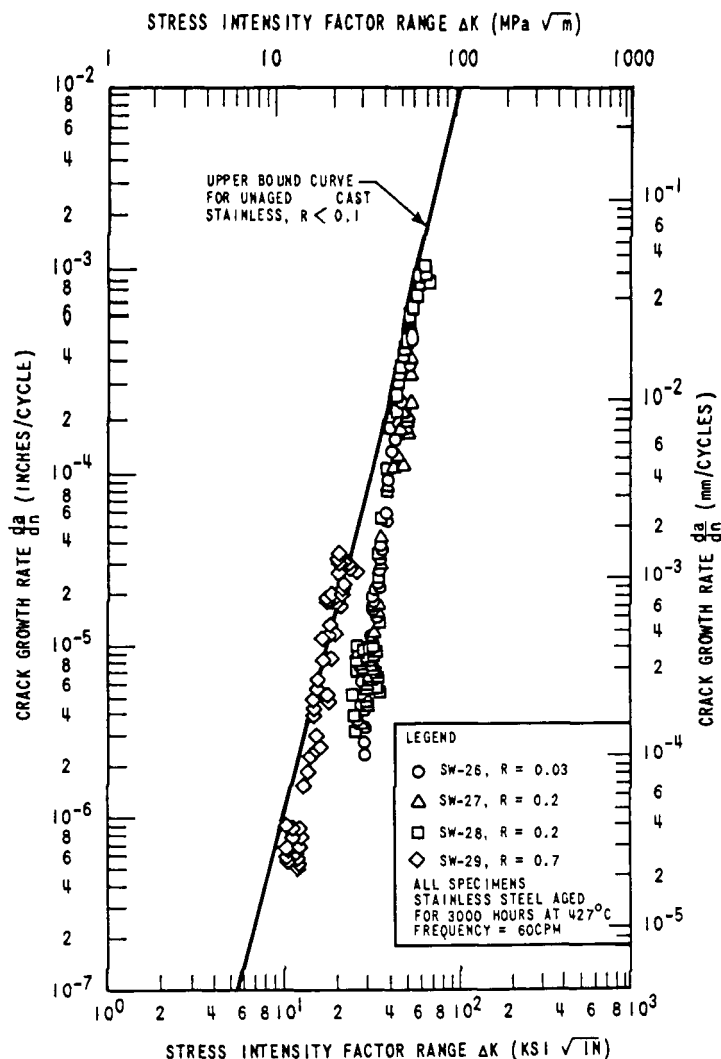


Figure 9 Fatigue crack growth behavior of aged CF-8M compared with unaged upper bound. Tests were in air.

hot cracking encountered with austenitic alloys is largely alleviated by ferrite contents in excess of 5%. This tendency is conventionally evaluated using the Varestraint test in which contraction strains in the weld zone are augmented by bending during welding. This is a very severe test representative of the most heavily restrained welds. It can be seen in Figures 10 and 11 that performance improves in direct proportion to ferrite content.

As with the austenitic castings, the duplex alloys do not require preweld and postweld heating. The solubility of austenite for hydrogen and its resistance to hydrogen embrittlement, especially at the low strength levels obtained, remove the need for any precautions in that regard when handling the duplex alloys.

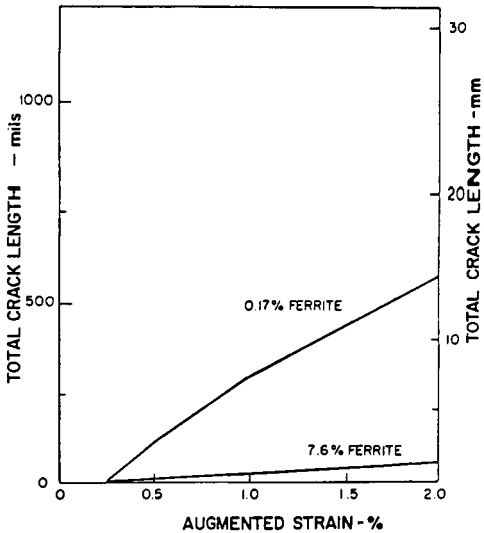


Figure 10 The influence of strain on Vareststraint test behavior at two ferrite levels.

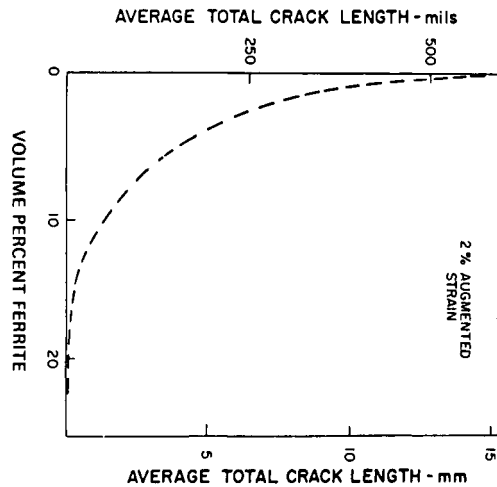


Figure 11 Vareststraint test trend on as-cast CF-8M alloy.

CORROSION BEHAVIOR

Corrosion is a broader subject that can be accommodated in a text of this type. Since high alloys must be corrosion resistant much might be said with regard to the many environments in which they regularly serve. Here, an attempt will be made to present only the general principles and important highlights as influenced by the metallurgy of these materials. Topics include:

- Oxidation
- Sulfidation
- Carburization
- General Corrosion
- Localized and Crevice Corrosion and Pitting
- Corrosion Fatigue
- Stress Corrosion

Probably the most important metallurgical factor pertaining to corrosion behavior is chromium content. Chromium imparts resistance to oxidation and sulfidation in high temperature environments. In aqueous and oxidizing acids, it offers significant protection except where crevices, deposits, or other conditions conducive to localized attack are established. Localized corrosion can be extremely aggressive and the resulting pitting may lead to corrosion fatigue or stress corrosion. More on this below.

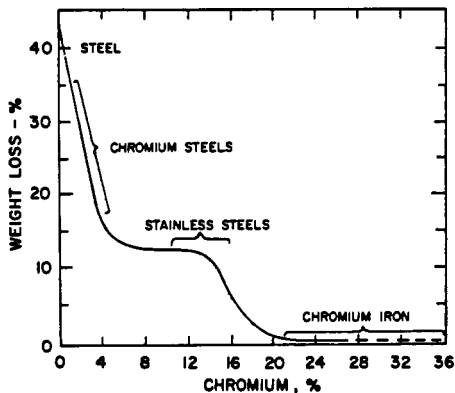


Figure 12 The effect of chromium on oxidation resistance at 1832°F (48 hour exposure, 0.5-in. cubes).

Oxidation:

Resistance to oxidation increases directly with chromium content (Figure 12). For the most severe service at temperatures above 2000°F; 25% or more chromium is required. Additions of nickel, silicon, manganese, and aluminum promote the formation of relatively impermeable oxide films which retard further scaling. Thermal cycling is extremely damaging to oxidation resistance because it leads to oxide breakdown, cracking or spalling. The best performance is obtained with austenitic alloys containing 40-50% combined nickel and chromium. Figure 13 describes the behavior of H grades.

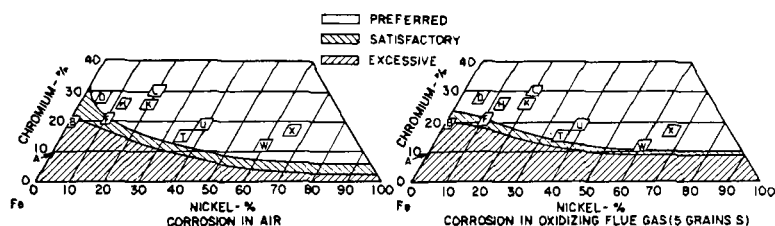


Figure 13 Corrosion behavior of H grade alloys in air and oxidizing flue gases.

Sulfidation:

Sulfidizing environments are growing in importance. Petroleum processing, coal conversion, utility and chemical applications and waste incineration have increased the need for alloys resistant to sulfidation attack in relatively weak oxidizing or reducing environments. Fortunately, high chromium and silicon contents are also beneficial with sulfur. On the other hand, nickel has been found to be detrimental in the most aggressive gases. The problem is attributable to the formation of low melting nickel-sulfur eutectics. These compositions produce highly destructive liquid phases at temperatures even below 1500°F. Once formed, the liquid may run onto adjacent surfaces and rapidly corrode other metals. The behavior of H grades in sulfidizing environments is shown in Figure 14.

Carburization:

High alloys are often used in non-oxidizing atmospheres where carbon diffusion into metal surfaces is possible. Depending on chromium content, temperature and the carburizing potential, the surface may become extremely rich in chromium carbides rendering it hard and possibly susceptible to cracking. Silicon and nickel are thought to be beneficial and enhance resistance to carburization.

General Corrosion:

Formation of nickel and chromium rich passive films on steels significantly shifts the free corrosion potential under aqueous conditions. These corrosion product films remain protective as long as they are intact or can be repaired by oxygen from the environment. Since the films are also thin and dense, they are durable and provide good protection even in moderately rapidly flowing solutions. However, if repair is impeded due to a deposit, stagnant conditions, a crevice, or material inhomogeneity (e.g., a chromium depleted zone), a large difference in potential develops between protected and non-protected zones. This

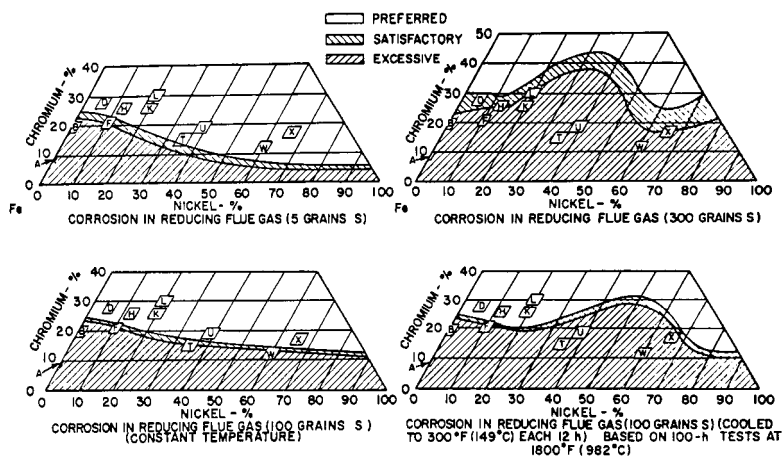


Figure 14 Corrosion behavior of H grade alloy in reducing sulfur bearing gases.

results in rapid localized attack (see below). Alloy additions are beneficial in enhancing resistance to general corrosion. Resistance to general corrosion usually increases with increasing chromium content, however there are exceptions as shown in Figure 15.

Localized Corrosion:

Austenitic and martensitic alloys display a tendency for localized corrosion. The conditions conducive to this behavior may be any situation in areas where an oxygen concentration cell may be established. Duplex alloys have been found to be less susceptible. Behavior is particularly acute in chloride and in acidic solutions as shown in Figure 16 (Ref. 9).

Increasing alloy content is beneficial. Molybdenum has long been recognized to be an effective retardant of localized corrosion, although it is not a total answer. Excellent results have been obtained with CG8M, while CF 3M or CN 7M are readily attacked.

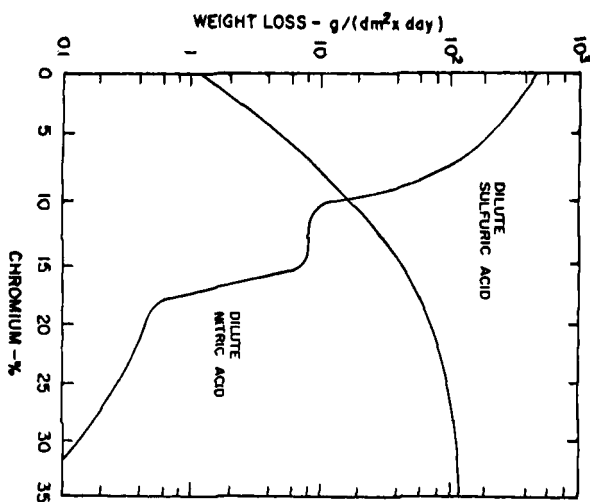


Figure 15 The effect of chromium on the corrosion rate of Fe-Cr alloys in dilute sulfuric and nitric acids.

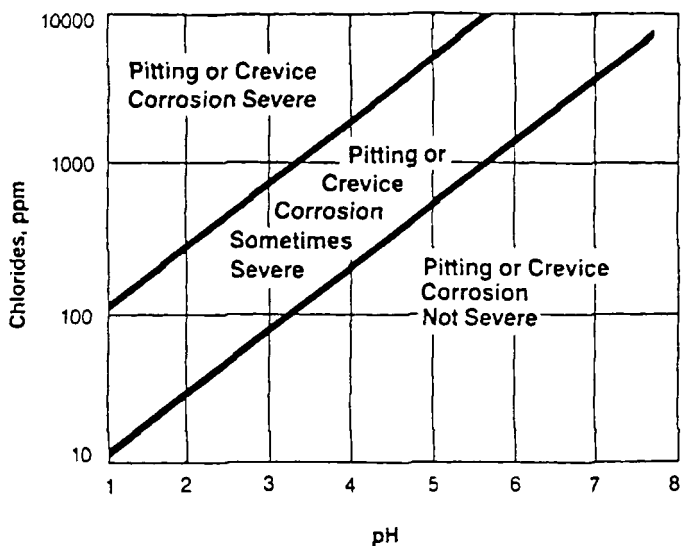


Figure 16 Effect of pH and chloride on pitting of a stainless steel.

It has been suggested that resistance to pitting is good when (%) chromium + $3.3 \times$ ([%] molybdenum) exceeds 28%. The basis for this may be seen in Figure 17 (Ref. 9) which depicts the shift in pitting potential for a number of alloys. Other parameters have also been proposed (Ref. 9).

Corrosion Fatigue:

Corrosion fatigue is one of the most destructive and unpredictable phenomena. Behavior is highly specific to the environment and alloy. The martensitic materials are degraded most, both in absolute and relative terms. Left to freely corrode in seawater they have practically no endurance limit. This is remarkable in view of their very high strength and fatigue resistance in air.

If suitable cathodic protection is applied, properties may be largely restored. However, since these materials are susceptible to hydrogen embrittlement, cathodic protection must be carefully applied. Too large a protective potential will lead to catastrophic hydrogen stress cracking.

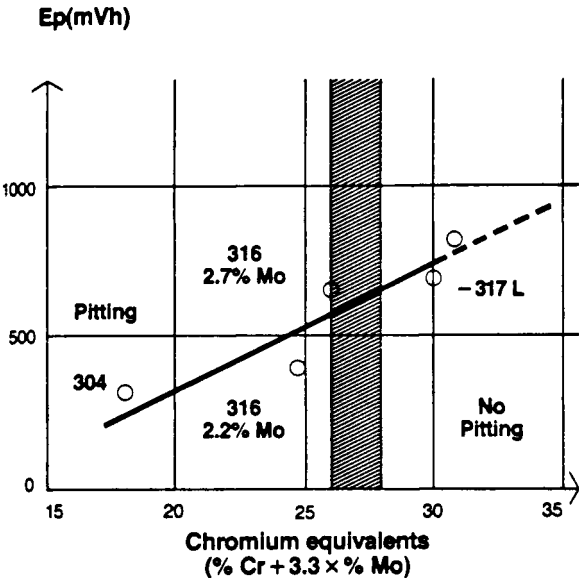


Figure 17 Pitting behavior and pitting potential for several stainless steels.

Austenitic materials are also severely degraded in corrosion fatigue strength under conditions conducive to pitting, such as in seawater. However, they are easily cathodically protected without fear of hydrogen embrittlement and perform well in fresh waters.

Duplex alloys have not been widely studied.

Stress Corrosion:

Stress corrosion susceptibility is similarly specific to the alloy, environment and conditions of exposure. As a general rule, the high strength martensitic steels have displayed sensitivity to stress corrosion as have the austenitic alloys. Duplex stainless steels are an improvement over single phase alloys.

Figure 18 indicates the relative performance of several duplex alloys. The test conditions involved a relatively short exposure to a sodium chloride solution at 400°F. While the trends suggested are complex, it is apparent that resistance generally increases with ferrite content. Large improvements appear possible through control of alloy composition.

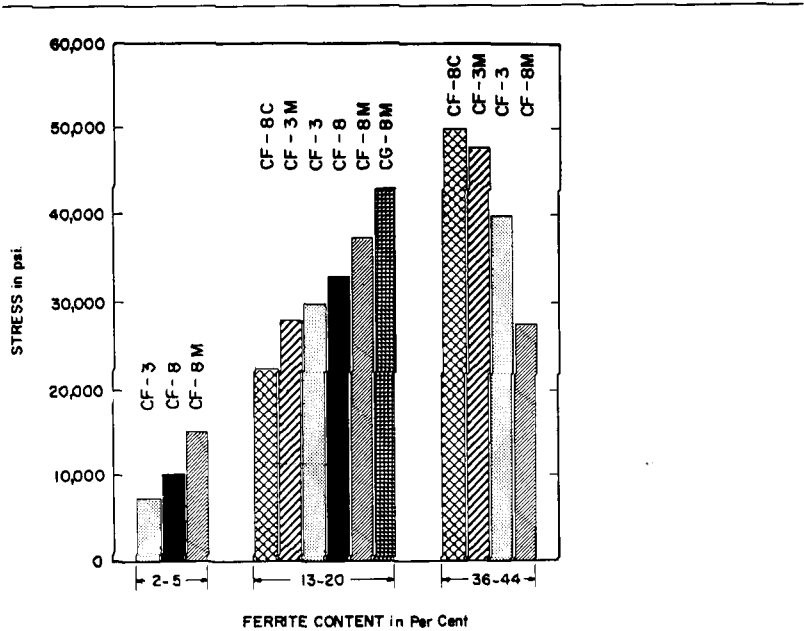


Figure 18 Stress required to produce stress corrosion cracking under a particular set of conditions for several alloys and ferrite levels.

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