

John E. Gruzleski

Microstructure Development During Metalcasting





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ACKNOWLEDGEMENTS

This book has its origins in the course notes that I developed over many years of teaching subjects such as casting, solidification and microstructure-property relationships. To all of the hundreds, perhaps thousands, of students who have taken these courses, I owe a deep debt of gratitude. You have provided a marvelous critique of my work with your probing questions and your demands for clarification, which so often have caused me to rethink my ideas and to recast the manner in which the material is presented. In addition, I must thank all of those companies to whom I have provided advice and services. Your problems have, indeed, been challenging, and have provided the inspiration for a book aimed at the industrial sector and dealing with the basics of microstructure development in cast metals.

Finally, I would like to acknowledge the hospitality of Dr. Mahi Sahoo and all of the staff of CANMET, Department of Natural Resources, Ottawa, Canada. They provided me with an office and stimulating conversation during the long and cold winter of 1997, in which I was able to write much of the manuscript.

JOHN E. GRUZLESKI

FOREWORD

Despite the fact that the mechanical, as well as many of the physical, properties of a casting are determined by its structure at the microscopic level, the principles that govern the development of this structure often are poorly understood by those whose task it is to produce the castings. This is not particularly surprising when you consider that foundries often hire engineers and technologists whose backgrounds are in some field other than metallurgy. Formal training in disciplines such as mechanical or chemical technology usually does not include instruction in the details of solidification science, or the development of microstructures during phase transformations.

The objective of this book is to address this problem by presenting the various facets of microstructure formation in cast metal alloys in a simple, and, hopefully, interesting way. Microstructure is interpreted broadly and includes not only the usual features viewed under a microscope, such as grain size, but also inclusions, porosity and chemical variations. This book is aimed specifically at engineers and technologists working in the metalcasting industry, but it should prove useful to all who wish to understand a little better the multitude of microscopic processes that take place when liquid metal is poured into a mold and solidifies. Much of the material is taken from courses I have conducted at McGill University over an almost 30-year period, making the book suitable as an undergraduate text in metallurgical or foundry engineering.

In writing this book, I have concentrated on the phenomenological processes of solidification in order to provide the reader a real “feel” for what goes on when a casting freezes. The text is not metal specific, but, rather, I have made an effort to choose examples from a variety of cast metals, both ferrous and nonferrous. If a certain bias toward examples from the aluminum industry is obvious, it is only because of my own particular professional interests.

In all cases, I have tried to confine the discussion to basics. By using the material presented here, it is hoped that the reader will be better equipped to understand the ever growing number of technical papers and presentations found at various conferences and in technical journals dealing with foundry and cast metal science.

The rapidly expanding knowledge base, coupled with electronic access to technical information on the Internet, limits the useful lifetime of extensive bibliographic referencing in books such as this. So, in keeping with the philosophy of dealing only with the basics, I have decided to supply only a short list of “Further Reading” at the end of each chapter. These usually are easily obtainable books and might form part of a small technical library in a foundry. The suggestions are meant to supplement and enhance the material presented, with a view toward developing a deeper understanding.

It is my sincere wish that this book will help all those who make castings to better understand how the structure of those castings comes about and, therefore, to improve the quality of their product.

JOHN E. GRUZLESKI

MONTREAL, JUNE 1999

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chapter 1

INTRODUCTION

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

Solidification, or what we know more commonly as the freezing process, is a basic phenomenon of nature. The frozen form of water, ice, is used in our drinks or to cool food, to skate on, or for those of us who live in northern latitudes, to create the unhappy experience of skidding on wintry roads. In each of these examples, water has solidified, forming ice. While this phenomenon is familiar to most of us, the process of solidification extends far beyond that of the freezing of water. It is, indeed, a basic process in the wide field of metals and materials engineering.

Virtually all commonly used metals are manufactured using a variety of processes that yield a liquid metal product in tonnage quantities, e.g. steelmaking, the aluminum reduction process or copper smelting. This liquid metal is caused to solidify, or be cast, in a simple geometric form known as an ingot. Ingots may be of round, square or rectangular cross section, and they may weigh up to several metric tons. Ingots, by themselves, have no practical use for most of us. Rather, they are shipped to various fabricators who transform them, by some forming process, into the useful, finished products of modern life: automobile bodies, pots, pans, electrical wiring, aircraft parts, computer frames, etc.

The fabrication processes used to produce these various articles are not transparent to the multitude of microscopic and macroscopic processes that occur during solidification of the initial ingot. Cracks in the ingot may carry over as defects in the finished product, as may pieces of included metal oxide, commonly referred to as inclusions. Such defects have been known to cause premature failure of structural parts under certain conditions of normal loading or in fatigue situations. Macroscopic chemical differences within the ingot (macrosegregation) may result in parts with varying chemical composition and properties. In addition, the size and distribution of intermetallic phase particles formed during ingot solidification can exert a profound effect on the quality of painted, anodized or plated surfaces. Metal ingot production is a major industrial activity as indicated in the statistics of Table 1.1, which summarizes some recent ingot tonnage for common industrial metals.

Table 1.1.
Metal Ingot Production, Approximate Values, 1994

BASE METAL	PRODUCTION (IN METRIC TONS)
aluminum	14,500,000
refined copper	11,150,000
magnesium	266,000
zinc	7,100,000
continuously cast steel	523,100,00
stainless steel	13,750,000

SOURCE: METAL BULLETIN'S PRICES AND DATA, 1996
METAL BULLETIN BOOKS LTD.
ED.: RICHARD SERJEANTSON

Not all metal produced as ingots finds its way into fabrication processes that operate in the solid state. Much of the metal produced is remelted and alloyed to produce castings. A wide variety of casting processes exist and these will be dealt with in more detail in Chapter 3.

Most of these casting processes have many features in common. Metal is melted and introduced into a mold cavity, which has the shape of the final object to be manufactured. The solid object is formed by solidification of the liquid alloy, with the resultant quality greatly dependent upon the freezing process of the alloy. Liquid metals contract on solidification, and this shrinkage must somehow be compensated for during solidification. If this is not done, the casting may contain voids, or may not be the correct shape.

Gases dissolved in the liquid metal may be evolved during freezing. These gases can interact with the natural contraction of the alloy as it freezes, producing microstructural porosity such as that shown in Fig. 1.1. Such severe porosity can deteriorate the mechanical properties, or cause the casting to leak. Certain applications require a casting to be pressure tight, and “leakers” can be cause for rejection in parts that are required to hold pressure, such as automobile cylinder heads. Clearly, the solidification process is essential to casting production, and a good understanding of the basics of solidification is necessary for all concerned with the technical aspects of casting or ingot production.

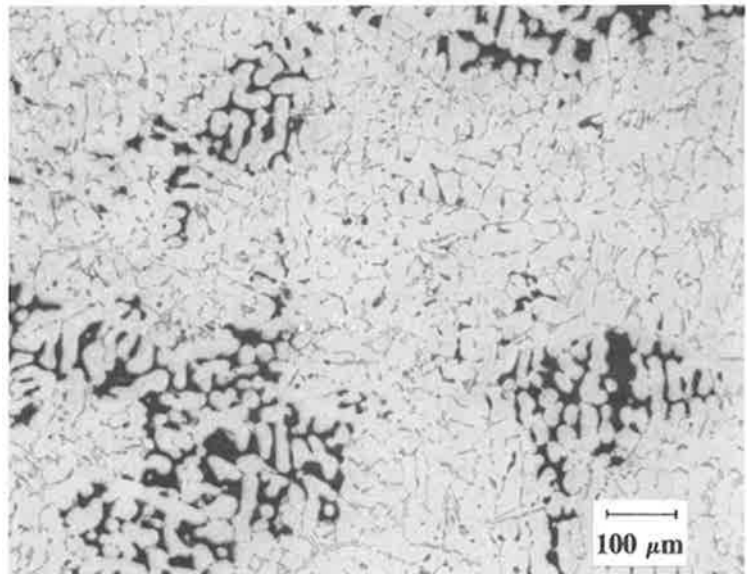


Fig. 1.1. Pores in an aluminum casting are often caused by the interaction of gas evolution on freezing and the solidification contraction of the alloy. The example shown is from a cast 319 alloy (Al-Si-Cu).

Casting production statistics summarized in Table 1.2 give only a glimpse of the importance of the metalcasting industry to overall production in net shape manufacturing. Metalcasting is the only manufacturing technique capable of producing complex shapes in one single operation. And, as the control of metalcasting processes improves, the complexity of shapes that can be produced by casting increases, and the reliability of those castings is enhanced in a very measurable way.

Consider, for example, the cylinder head of an automobile engine Fig. 1.2. This is a complex part made up of sections of varying thickness and a variety of holes and passages. To forge such a part would require a complex series of operations involving many dies. Also, it could be manufactured by bolting together a number of small parts, separated by gaskets. Such an operation would require that these smaller parts be produced individually, each with its own

Table 1.2.
World Casting Production, 1994

METAL	PRODUCTION (IN METRIC TONS)
gray cast iron	38,905,800
ductile cast iron	11,468,100
malleable cast iron	2,000,000
steel (all types)	6,159,000
copper-base alloys	1,150,000
aluminum	5,127,000
magnesium	80,100
zinc	1,428,000
TOTAL	66,318,000

SOURCE: 29TH CENSUS OF WORLD CASTING PRODUCTION, 1994
MODERN CASTING, DECEMBER, 1995

manufacturing difficulty, and the final piece would always be subject to leaking as the gaskets became worn during normal operation.

Metalcasting, on the other hand, allows the cylinder head to be created in one simple operation—pouring metal into a mold and allowing the metal to solidify. Of course, the mold itself must be made, but this is no more of a complex operation than the manufacture of dies for forging, and only one mold is required compared to many dies.

Solid state manufacturing techniques, such as rolling, extrusion or forging, are often limited with respect to the materials that may be fabricated by such methods. For example, high hot ductility is a basic requirement of such processes, and not all metals possess properties that allow them to be fabricated by these operations. By contrast,

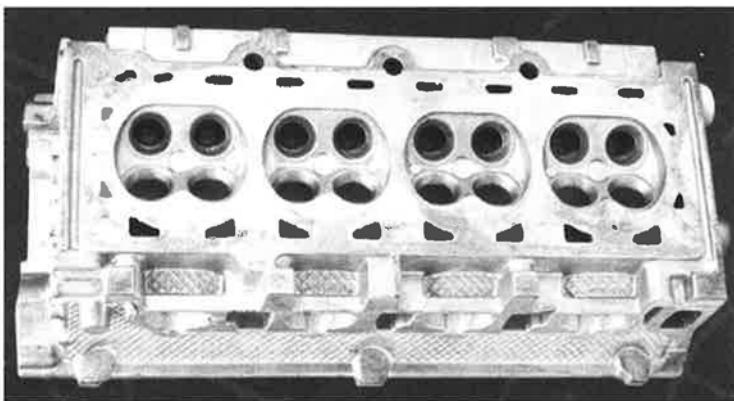


Fig. 1.2. An example of a complex shape casting is shown. The cylinder head cast in an Al-Si-Cu alloy contains sections of varying thickness as well as many holes and passages. (Photo courtesy of NEMAK S.A.)

the only basic requirement for a metal to be cast is that it be capable of being melted. There are, certainly, a few very high melting point metals for which this does pose a difficulty, but the commercially important metals, which are used for 98% of all castings, are readily melted by simple existing techniques. These include electric resistance or induction melting, used for ferrous materials as well as aluminum, copper and magnesium-base alloys, and fossil fuel melting, which

is suitable for the common nonferrous metals and alloys.

While ingot and casting production account for the major situations, on a tonnage basis, when solidification phenomena play a critical role, there are other specialized processes in which solidification plays an important part. These are high value-added processes, such as fusion welding and single crystal growth.

Fusion welding is a common joining process in which a high energy heat source, such as an electric arc or oxyacetylene flame, is used to melt filler metal into the junction between two pieces of metal. The parts to be joined are permanently fused when the filler metal solidifies. In many ways, a fusion weld solidifies like a small ingot or casting in which heat is extracted into the parent material or lost into the atmosphere above the weld. Many defects that occur during the freezing of ingots weighing many tons can also occur in small fusion welds. Figure 1.3, for example, illustrates a weld containing a centerline crack caused by solidification shrinkage.

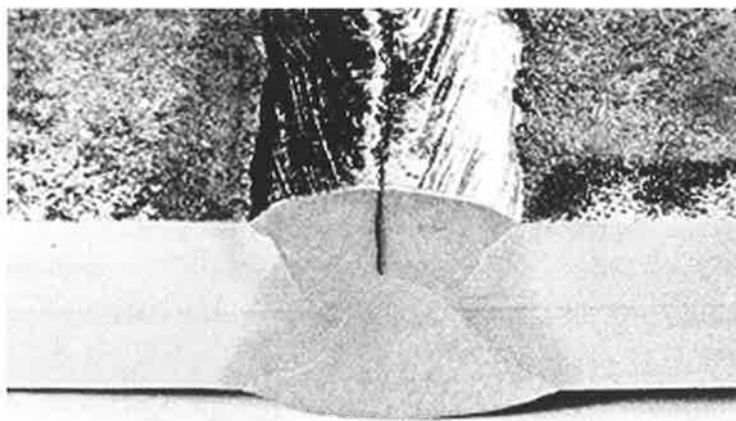


Fig. 1.3. Centerline cracking in a weld is caused by contraction of the liquid metal on freezing, coupled with thermal stresses generated during the cooling process.

Single crystal growth for specialized applications is, perhaps, the most controlled of the solidification processes. Later in this book you will learn that most cast metals are polycrystalline, and that it is often the goal to produce as many grains (or crystals) as possible during freezing. An exception to this is single crystal growth where the freezing process must be so controlled that only one grain is allowed to grow and all others are excluded. Single crystals have special properties with respect to their polycrystalline counterparts, and are prepared for electrical, optical and high temperature strength purposes.

A common example of a mass produced, single crystal product is the turbine blade shown in Fig. 1.4. These blades, which are required to operate under high stress at high temperatures, exhibit superior creep resistance compared to the same blade made from the same material in polycrystalline form.

With this background, you can readily appreciate the importance of the solidification process in metals and materials

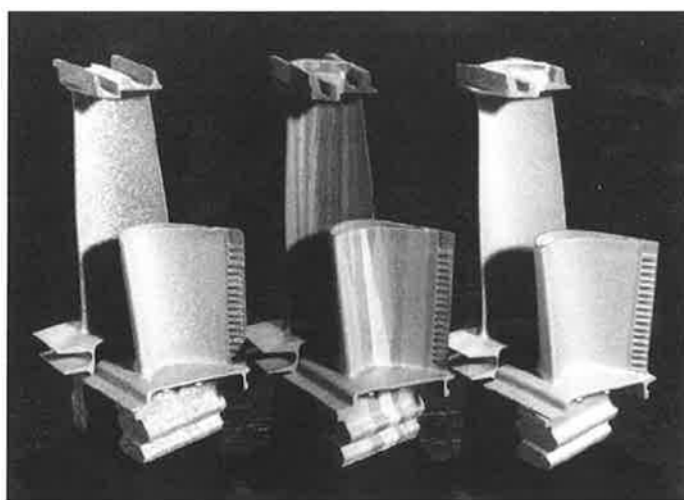


Fig. 1.4. Cast turbine blades are shown. The blade on the left is of a fine polycrystalline structure; center, a coarse polycrystalline grain structure produced by directional freezing; right, a single crystal. (Photo courtesy of Howmet Research Corp.)

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

manufacture, certainly in terms of the quantity of material undergoing solidification each year. In large part, the secret of successful casting production depends on control of the casting structure on a microscopic scale. It is this microstructure that is a determining factor in the mechanical, and many of the physical, properties of the cast metal. The concept of microstructure will become clearer as the solidification story unfolds in this book.

For the moment, you need only appreciate that it refers to the manner in which various microscopic constituents in the solidified metal are arranged with respect to each other. Microstructure control is a prime preoccupation of anyone working in metalcasting, because one alloy may form a variety of microstructures depending on the solidification conditions and the presence or absence of various impurities or chemical additives. Mechanical and physical properties are so dependent on microstructure that seemingly small differences in microstructure may result in significant changes in properties.

The purpose of this book is to present the fundamentals of the liquid to solid transformation with an emphasis of the impact of the fundamental processes on industrial solidification. This emphasis is on the mechanisms that operate to form the microstructure of the solidified product. The approach taken will be such that the book can be understood and found useful by engineers working with processes involving metal solidification, as well as by undergraduate students in engineering programs.

Before proceeding, it is useful to have a general appreciation of the solidification process itself, which can be divided into four basic steps:

- melting
- nucleation/inoculation
- growth/solidification
- final solid.

MELTING

Melting results in creation of liquid metal, which eventually solidifies. Starting materials for the melting process are numerous, and may include primary ingot and/or scrap in casting production, or exotic ultra-high purity materials used in crystal growth applications. Melting is the most energy consumptive aspect of solidification processing, consuming large quantities of electrical energy or fossil fuels.

Quality of the liquid metal that results from melting is one of the most important, and often overlooked, aspects of the entire solidification process because many features of liquid metal quality impact on the final solidified material. For example, inclusions of oxide formed during melting may become entrapped in the solid, or, certain highly volatile or easily oxidized elements may be removed from the liquid resulting in changes in overall melt chemistry. During melting, the liquid also may dissolve various gases evolved during subsequent freezing and result in micro- or macroporosity in the solid product.

NUCLEATION/INOCULATION

During nucleation, the first microscopic particles of solid begin to form in the liquid phase. As a general rule, one nucleus will eventually lead to one grain in the solid state. The nucleation stage is, therefore, of importance because it is at this point that the grain size of the eventual solid is largely determined. Many nuclei lead to a fine grain structure while only a few will result in coarse grains. An extreme example of nucleation control is single crystal growth where various mechanisms (often tricks) are employed to ensure that only one nucleus remains active.

A fine grain structure, resulting from the presence of many nuclei, often is desired in industrial solidification. Special alloy additions, known as inoculants, are added in order to promote nucleation.

GROWTH/SOLIDIFICATION

During the growth stage, heat is extracted and the solid consumes the liquid as the microscopic nuclei expand into larger three-dimensional grains. In addition, important substructures develop within the grains. It is at this stage that the cast microstructure is developed. Since both the physical and mechanical properties of the solid are influenced strongly by this microstructure, the growth stage is one of the most important in the whole solidification process. Thus, much of this book is dedicated to an explanation of the growth process and its relationship to the solidified structure.

FINAL SOLID

Strictly speaking, the freezing process ends when the final solid is completely formed. Nevertheless, mention of the final solid is included here because it is important to realize that certain operations performed on solidified solids are done as a direct result of events occurring during solidification. One of the most common examples is the homogenization heat treatment given many cast metals in order to reduce, or even eliminate, some chemical composition differences generated by the freezing process. These differences are the result of a phenomenon known as segregation, and they may occur over distances as small as a few micrometers, or as large as several centimeters.

Specialized processes have been developed to eliminate some of the defects generated in the solid during solidification. Internal porosity is a common feature of many cast metals. In high quality castings, it is eliminated through a process known as HIPING (hot isostatic pressing) in which the solidified castings are subjected to a compressive isostatic stress at high temperatures. The conditions are sufficient to cause the internal pores to collapse and to weld to seamless metal.

chapter 2

**PHASE DIAGRAMS:
WHAT THEY ARE
AND
HOW TO USE THEM**

Of all the tools available in an understanding of solidification theory and mechanisms, the phase diagram is undoubtedly the most important. Several excellent publications exist on this subject and, for an in-depth treatment, you are referred to Further Reading at the end of this chapter. Here, we will present only the basics of phase diagrams, particularly as they apply to the liquid-solid reaction.

WHAT IS A PHASE?

The first question often asked about a phase diagram is, “What is a phase?” Most of us were taught in elementary school that ice, water and water vapor (steam) represent the solid, liquid and gaseous phases, respectively, of the material we know as water. Certainly, ice, water and water vapor have very different characteristics, but what makes them separate phases?

The easiest way to distinguish a phase is to ask if it can, at least in principle, be separated physically from its surroundings in the rest of the system. In the case of the three phases of water, they most certainly can. The ice and water can be filtered and the water vapor will naturally separate from the other two because of its low density. In this example, the concept of physical separation is easy to comprehend and to bring about in fact. In most materials systems, however, the physical separation of the phases, while possible, in principle is not usually realistic. But, by using the definition of a phase as part of a system that can be separated from the rest of the system, we are readily able to tell one phase from the other.

Engineering alloys usually contain more than one solid phase. Figure 2.1 is two photomicrographs of a gray cast iron of the type that might be used to manufacture an automobile engine block. Two areas are evident in the micrographs: the black wavy flakes are the graphite phase, and the white background is the iron phase. In principle, these two solid phases could be separated. One might conceive of grinding the material into very fine pieces and then separating the iron phase from the graphite phase by magnetic means. In practice, this would be difficult if not impossible to achieve, but the concept of separation, “in principle,” allows us to identify the two types of areas as two different solid phases.

PHASES OF SOLIDIFICATION

It is obvious that freezing reactions must involve at least two phases: a liquid and a solid. Metallic liquids usually are completely miscible, and it is uncommon in metal systems to find more than one liquid phase. On the other hand, it is relatively rare to find engineering alloy systems containing only one solid phase. Solid phases that form are of two types: solid solutions and compounds.

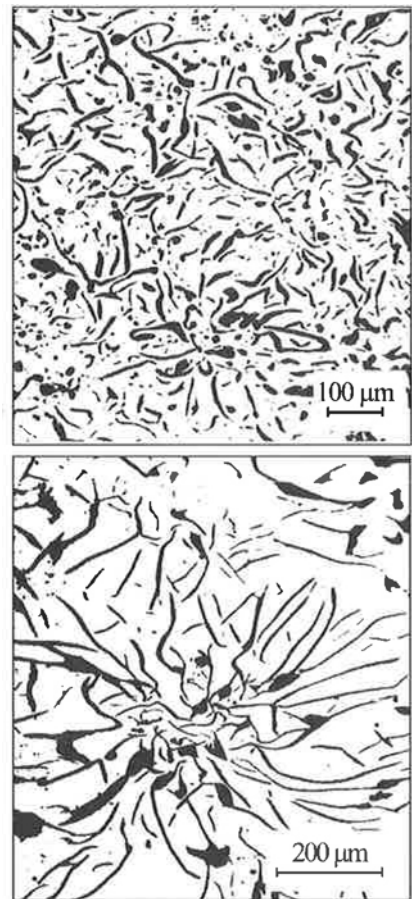


Fig. 2.1. Both graphite (black wavy flakes) and iron (white background) phases are easily seen in the microstructure of a common gray cast iron.

Solid solutions resemble the more familiar liquid solutions in many ways, except, of course, for the fact that they are solid and the atoms are arranged on a characteristic crystal lattice. This crystal lattice is that of the element present in major amounts. The atoms in most metals used in engineering applications are arranged in one of three common crystal lattices: face centered cubic (FCC), body centered cubic (BCC) or hexagonal close-packed (HCP) (Fig. 2.2 a,b,c).

In a substitutional solid solution, atoms of the element present in minor amounts (the solute) are arranged randomly on the normal crystal lattice of the element present in major amounts (the solvent). Figure 2.2d illustrates the atomic arrangement in such a solid solution. The crystal structure of solids is such that spaces exist between many of the atoms, and solute atoms may locate in these spaces if the size arrangements are correct. When this occurs, an interstitial solid solution forms, the most important example of which is the solution of carbon in iron that forms the basis of steel. A schematic diagram of the atom arrangement in an interstitial solid solution is shown in Fig. 2.2e.

Not all elements will dissolve in other elements to the same extent, and quite often one element will exhibit no tendency for solid solubility in another. While many factors may contribute to the ability of one element to dissolve in another in the solid state, the most important single consideration is one of simple geometry. Substitutional solid solutions are favored if the solute and solvent atom sizes are similar. The closer the better, but a difference of $\pm 15\%$ usually is taken as the maximum allowable for any appreciable solid solubility. For example, the sizes of the atoms of copper (Cu) and zinc (Zn) differ by only about 2%, and it is possible to dissolve an unlimited amount of zinc in copper. On the other hand, Cu and lead (Pb) atoms differ by about 37% in size, with the result that lead is virtually insoluble in solid copper.

The second most important consideration is a similarity of crystal lattice types. Indeed, for complete mutual solid solubility, the crystal structures of solute and solvent must be identical. Minor considerations are electronegativity and valency, but atom size similarity and crystal lattice geometry remain the most important. In the case of interstitial solid solutions, the solute atoms must be able to fit into the interstitial sites in the solvent material. Interstitial solid solutions are favored in situations where the solute atom is small with respect to the solvent, for example, carbon (C), hydrogen (H) and nitrogen (N) in metals.

As is the case with aqueous solutions, there usually are limits to the extent of solid solubility, dependent on the specific solvent and solute elements as well as temperature. When the solubility limits are exceeded, an intermetallic compound may be formed. While a solid solution may exist over a range of compositions, a compound has a fixed or very limited compositional range, and may be represented by a formula of the type A_xB_y where x and y are the number of atoms of elements A and B, respectively.

For example, the intermetallic compound Al_2Cu is a common feature of the microstructure of Al-Cu alloys. While the properties of a solid solution usually resemble those of the solvent material, the properties of a compound are often very different from those of any of the individual elements that make up the compound. Pure metals tend to be soft and ductile while intermetallic compounds are usually hard and brittle.

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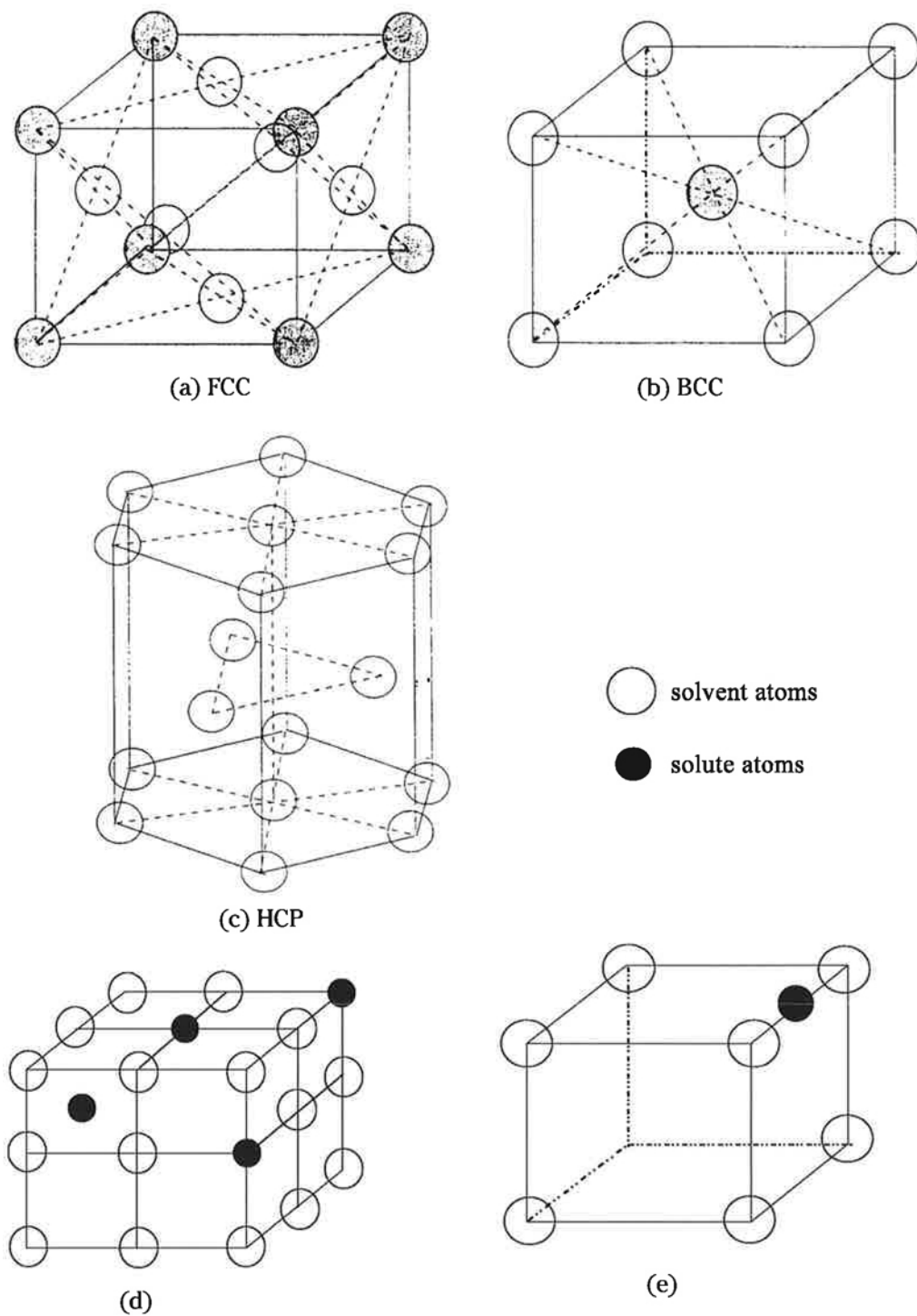


Fig. 2.2. Atomic arrangements are illustrated in (a),(b) and (c) the common crystal lattices found in metal systems; (d) a random substitutional solid solution; (e) an interstitial solid solution.

WHAT IS A PHASE DIAGRAM?

The phases found in a material depend on its composition, temperature and the pressure exerted on it. A basic rule governing phase diagrams, the “phase rule” was discovered by Gibbs and relates these parameters as follows:

$$P+F = C+2 \quad (2.1)$$

where

- P is the number of phases that may coexist;
- F is the acting number of degrees of freedom, these being temperature, composition and pressure; and
- C is the number of chemical components. The simplest way to think of this is as the number of pure elements that make up the alloy system.

Gibbs’ phase rule is a general rule made to apply to any situation. Solidification almost always takes place at normal atmospheric pressure, or at least at pressures which are not highly elevated above atmospheric. Pressure can, therefore, be considered a constant, and one degree of freedom subtracted from the left side of the phase rule to yield, for condensed systems (no vapor phase):

$$P+F = C+1 \quad (2.2)$$

For example, in a binary system ($C=2$), if three phases are present ($P=3$), the number of allowable degrees of freedom is zero ($F=0$), meaning that it is not possible to change either the temperature or the composition without changing the number of phases. Such a condition is known as an invariant condition. We will see later that the commonly found eutectic reaction corresponds to such a situation.

When two or more pure materials are mixed to form an alloy, several important features of the alloy become functions of composition and temperature. Two of these are the melting point and the number and type of phases that form in the solid state. In order to work with alloys and to predict their structure in the solid, it is essential that we know how the melting point and the solid phases change with alloy composition and temperature. The phase diagram is the tool that gives us this information in a graphic form. In a simple binary alloy system (two chemical components), the diagram is in the form of an x-y plot with temperature along the y axis and composition along the x axis. The body of the diagram consists of areas denoting which phases, or combinations of phases, are stable at any temperature-composition combination.

If enough is known about the thermodynamics of the alloy system, it is possible to calculate

the phase diagram. This is a rapidly developing method used for determination of phase diagrams, and several excellent software packages exist for this calculation. More often than not, however, such complete thermodynamic data is not available, and experimental techniques must be called into play to determine the diagram. A detailed discussion of these is beyond the scope of this book, and you are referred to Further Reading for additional information.

Methods used to experimentally determine phase diagrams include: normal and differential thermal analysis; X-ray diffraction; metallography; room temperature and high temperature electron microscopy; and electrical resistivity. Thermal analysis is most often used to establish the solidification phases of alloys, while the other techniques allow for the solid state phase structures to be established.

Before we examine some typical phase diagrams, it is necessary to point out an important limitation of these diagrams as they are applied to real industrial situations. Phase diagrams are determined under conditions that are as close to equilibrium as possible. This implies that all phase changes, such as solidification, take place quite slowly. Indeed, the diagrams often are called equilibrium diagrams, and as a result, care must be exerted in applying the predictions gleaned from phase diagrams to real situations where heating and cooling rates are high.

Consider the case of the small casting, which cools from 750 to 200C (1382 to 392F) in several minutes. This is most definitely not equilibrium cooling. In later chapters, we will return to this point and see examples of the limitations of phase diagrams when applied to real solidification conditions. That being said, they do remain a very valuable tool.

We will now consider some examples of typical phase diagrams and see how they can be used. The discussion will begin with the simpler binary diagrams, and proceed to the more complex ternary systems.

THE ISOMORPHOUS SYSTEM

Figure 2.3a presents the phase diagram for the Cu and nickel (Ni) alloy system. This isomorphous system is the simplest type of

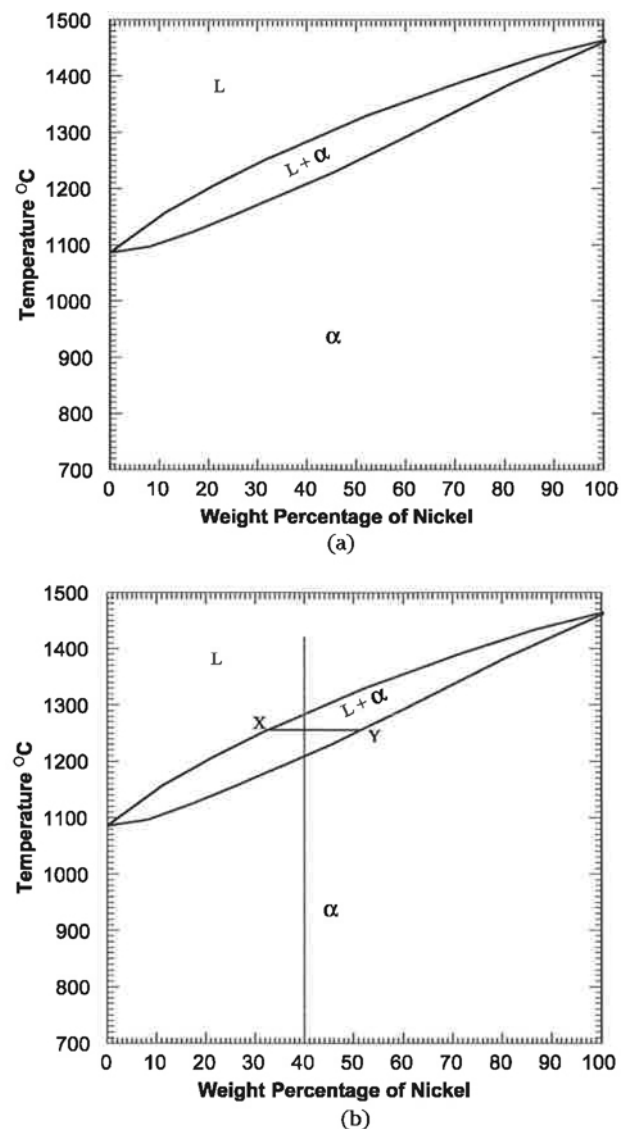


Fig. 2.3. (a) Phase diagram for the Cu-Ni alloy system is given. (b) Use of the phase diagram to determine the phases present and their compositions is shown for an alloy of composition 40%Ni-60%Cu.

PHASE DIAGRAMS: WHAT THEY ARE AND HOW TO USE THEM

binary alloy phase diagram found because only one solid phase exists for all alloys between pure nickel and pure copper. Both elements exhibit a complete mutual solid solubility because of the similarity of their atom sizes and because they each form face centered cubic crystal structures.

The diagram itself is a graph with temperature plotted vertically and composition, horizontally. The pure elements, Cu and Ni, form the extremities of the x axis, which is labeled in terms of percent by weight of nickel. Three areas are evident on the diagram and denote the following phases: liquid (L), a mixture of liquid and solid (L+ α) and solid (α). These areas are separated by two lines. The upper line is called the liquidus line, above which only liquid is present. The lower line, the solidus, is defined as the line below which only solid is present. These are general definitions and apply to all phase diagrams no matter how complicated. Thus, at temperatures above the liquidus, the alloy has melted completely, while at temperatures below the solidus, it has frozen completely.

Three pieces of information can be obtained easily from any binary phase diagram. They are:

- equilibrium phases present at any temperature and composition;
- equilibrium composition of these phases;
- relative amounts of these phases.

We will take an alloy of 40%Ni-60%Cu in Fig. 2.3b as an example of how phase diagrams can be used. At a temperature of 1400C (2552F), we see that the alloy is completely molten; the coordinates of the temperature and composition lie in the liquid region. At 1100C (2012F), the alloy is completely solid, while at 1260C (2300F), it is only partially solid, consisting of a liquid-solid mixture much like slush. Clearly, if only one phase is present, the composition of that phase must equal the overall alloy composition and 100% of the system must consist of that phase. Thus, the composition of the liquid at 1400C (2552F), or of the solid at 1100C (2012F), is 40%Ni-60%Cu.

When two or more phases coexist, the situation is more complicated because both phase compositions and their relative amounts in the system depend on the temperature. To obtain this information for our alloy example at 1260C (2300F), it is necessary to first draw a horizontal tie line across the two-phase region, as shown in Fig. 2.3b. Tie lines are an important feature of all phase diagrams. They are isotherms (horizontal lines) which join the boundaries of the two-phase region. In the present example, the two-phase region of interest is a liquid-solid region, but tie lines can be drawn in any two-phase area of a binary diagram, liquid-solid, solid-solid or even liquid-liquid.

The ends of the tie line give the compositions of the two phases: the liquid contains x% of Ni (35%), while the solid contains y% (52%). In addition to having different compositions, the solid and liquid will be present in different relative amounts, depending on the temperature. Consider that the alloy is completely liquid above its liquidus temperature (1280C, 2336F), and completely solid below its solidus temperature (1200C, 2192F). The freezing reaction, therefore, takes place in the 80°C (144°F) interval between these two temperatures, and as the temperature drops in this range, the amount of solid must increase as the amount of liquid decreases.

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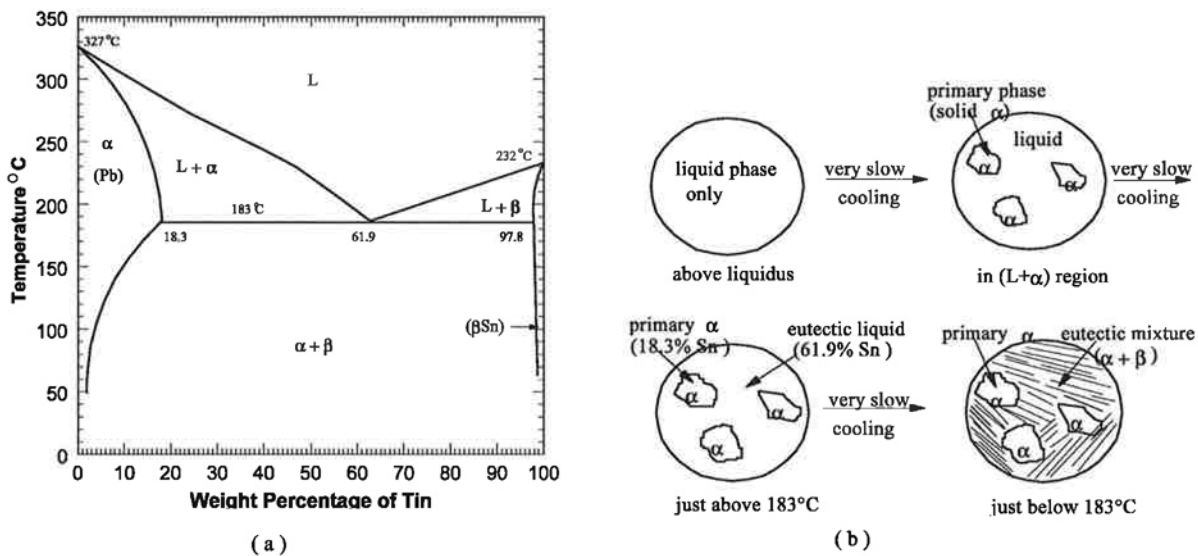


Fig. 2.4. (a) Phase diagram for the Pb-Sn alloy system is shown. (b) A diagrammatic representation of the solidification sequence in a hypoeutectic alloy is illustrated.

A basic rule of phase diagrams, called the lever rule, can be used to determine the relative amounts of the two phases present in any two-phase region. The lever rule is a graphical technique to perform a simple mass balance on the alloy system at a given temperature. For our example, the lever rule says that, at 1260C (2300F):

$$\text{wt. \% liquid} = \frac{y-z}{Y-x} \times 100\%$$

$$\text{wt. \% solid} = \frac{z-x}{Y-x} \times 100\%$$

where

z represents the alloy composition, 40%Ni: in this case

Inserting the appropriate values for x, y and z (35%, 52%, 40%) yields the following: wt. % liquid = 71% and wt. % solid = 29%. Similar calculations can be done for any temperature in the two-phase region, and they will show that, as the temperature falls, the amount of solid increases and the amount of liquid decreases, i.e., the alloy is freezing.

Note that even though the chemical compositions of the solid and liquid change with temperature during solidification, the phase diagram predicts that the final solid will be uniform in composition at 40%Ni-60%Cu. To achieve this, it is necessary that the composition of each phase be able to adjust almost instantaneously to new equilibrium compositions. Under the near equilibrium conditions used for phase diagram determination, this is possible, but it is rarely achieved in real practice. Nevertheless, it is obvious that the phase diagram is a useful guide to what occurs with the liquid and solid during solidification.

EUTECTIC SYSTEMS

When only partial solid solubility exists between two elements, a eutectic system may be formed. Common in metalcasting, many commercial alloys form these eutectic systems, the example being used here the Pb-Sn (tin) system, shown in Fig. 2.4a. This system is the basis for common solder. Eutectic systems are characterized by a lowering of the liquidus temperatures when each pure component is added to the other so that a minimum liquidus point is reached. This eutectic point (from the Greek, eutectikos, meaning lowest melting) occurs at 61.9%Sn-38.1%Pb and 183C (361.4F) in the Pb-Sn alloy system. Many casting alloys are centered around a eutectic composition to take advantage of the low melting point of eutectics. In general, cooling a liquid of the exact eutectic composition through the eutectic temperature yields the reaction:



Another important feature of eutectic systems, stemming from the limited solid solubility of their components, is the existence of two solid phases over much of the composition range. These are shown as α and β in Fig. 2.4a, where α is a substitutional solid solution of Sn in Pb and β is a substitutional solid solution of Pb in Sn.

Three types of compositions become important in eutectic alloy systems: those with the exact eutectic composition, and those having either less than (hypoeutectic) or more than (hypereutectic) this composition. Alloys with the exact eutectic composition usually freeze as a fine dispersion of the eutectic phases. Drawing a tie line immediately below the eutectic temperature allows determination of the compositions and relative amounts of the two phases present in the eutectic alloy. In our Pb-Sn example, this yields:

$$\alpha = 18.3\% \text{Sn} - 81.7\% \text{Pb}$$

$$\beta = 97.8\% \text{Sn} - 2.2\% \text{Pb}$$

and

$$\begin{aligned} \% \alpha &= \frac{97.8 - 61.9}{97.8 - 18.3} \times 100\% \\ &= 45\% \end{aligned}$$

$$\begin{aligned} \% \beta &= \frac{61.9 - 18.3}{97.8 - 18.3} \times 100\% \\ &= 55\%. \end{aligned}$$

Hypo- or hypereutectic alloys freeze first by the formation of a so-called primary phase, which forms in the liquid-solid region above the eutectic temperature. Primary freezing is followed by eutectic freezing and the final solid usually contains a relatively coarse primary phase surrounded by the fine eutectic mixture. To illustrate, consider

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a hypoeutectic alloy of composition 40%Sn-60%Pb. Primary solidification begins at the liquidus temperature of 240C (464F) and continues down to the eutectic temperature of 183C (361.4F). The maximum primary phase formation occurs just before eutectic solidification, and drawing a tie line in the liquid-solid area at 183C yields the following calculation for the amount of primary phase:

$$\begin{aligned}\% \text{ primary} &= \frac{61.9 - 40}{61.9 - 18.3} \times 100\% \\ &= 50.2\%\end{aligned}$$

The remaining 49.8% at this temperature is liquid of eutectic composition. The resultant solidified solid will contain 50.2% by weight of primary phase and 49.8% of the fine ($\alpha + \beta$) eutectic mixture.

Alloys that contain less than the limit of solid solubility (in Pb-Sn this is 18.3%Sn in the α phase and 2.2%Pb in the β phase) do not contain any eutectic because their solidification path never crosses the eutectic horizontal. Again, it must always be remembered that these remarks and calculations apply only to near equilibrium conditions of very slow cooling.

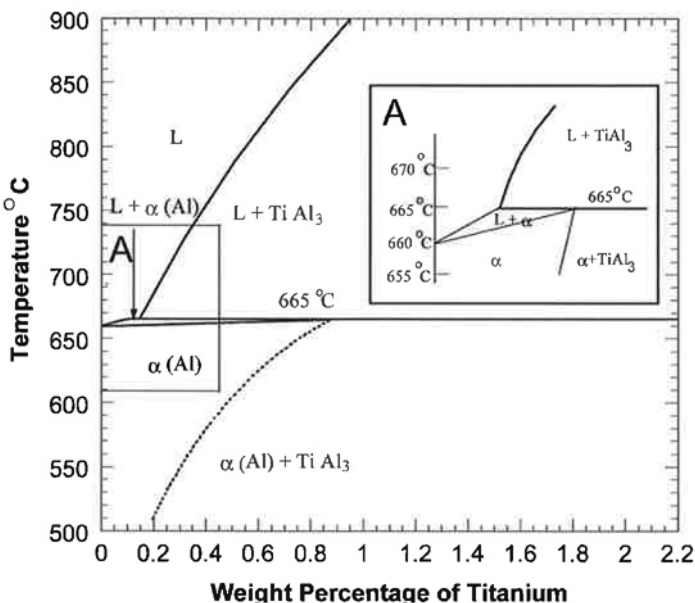


Fig. 2.5. The aluminum-rich end of the Al-Ti phase diagram contains a peritectic reaction.

PERITECTIC SYSTEMS

The peritectic, less common than the eutectic, is still a major feature on many phase diagrams in which incomplete solid solubility occurs. As an example, we will consider the aluminum-rich end of the Al-Ti (aluminum-titanium) diagram (Fig. 2.5). In Chapter 4, this diagram and the peritectic reaction will be shown to be of great importance in aluminum casting technology. In a peritectic reaction, two phases (solid and liquid) react together to form a second solid phase. Thus,



In the Al-Ti diagram, the peritectic composition is 0.9%Ti and the peritectic temperature is 665C (1229F). At this point, the reaction that occurs is:



where

TiAl_3 is a compound of composition 38%Ti; and

$\alpha (\text{Al})$ is a substitutional solid solution of Ti in Al.

Alloy compositions may be hypoperitectic or hyperperitectic, and lever rule calculations

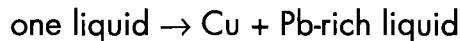
are done in the usual way. Of all the phase reactions encountered in solidification, the peritectic is the least likely to proceed in an equilibrium way. This aspect of peritectic reactions will be dealt with in Chapter 12.

MONOTECTIC REACTIONS

Monotectic reactions are not common in metallurgical systems. This reaction arises from the rare situation in which metallic liquids are immiscible, the classic metallurgical example being the Cu-Pb system (Fig. 2.6) in which two liquids, one Pb-rich and one Cu-rich, coexist between 36%Pb and 87%Pb. Monotectic solidification leads to the reaction:



In the case of the Cu-Pb system, the reaction is:



Monotectic construction on a phase diagram resembles a eutectic in many ways. In the Cu-Pb diagram, the exact monotectic composition is 36%Pb and the monotectic temperature is 955°C (1751°F). Again, hypo- and hypermonotectic compositions are possible, and because two liquid phases are involved in which diffusion rates are relatively rapid, we find that monotectic solidification proceeds fairly close to equilibrium.

SOLID STATE PHASE REACTIONS

Solidification does not directly involve solid state reactions, but the more common ones are summarized here since they will appear on most phase diagrams used for industrial solidification. Readers unfamiliar with these, or wanting further details, should consult the references listed at the end of this chapter. Sketches of the appearance of each of these solid state reactions on a phase diagram are given in Fig. 2.7.

EUTECTOID

This is the solid state version of the eutectic reaction. It has the same geometric form on the dia-

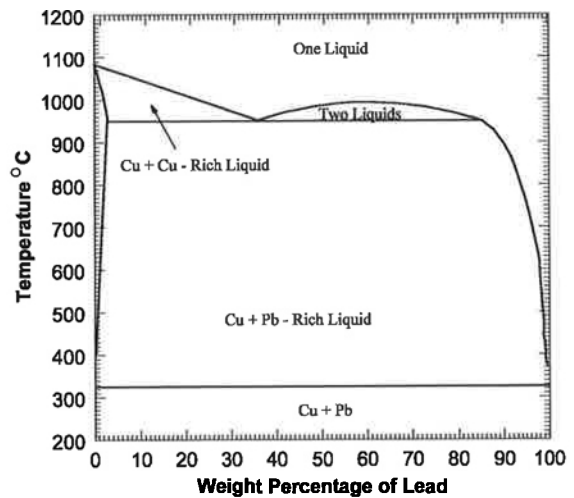


Fig. 2.6. The Cu-Pb alloy system contains a monotectic reaction.

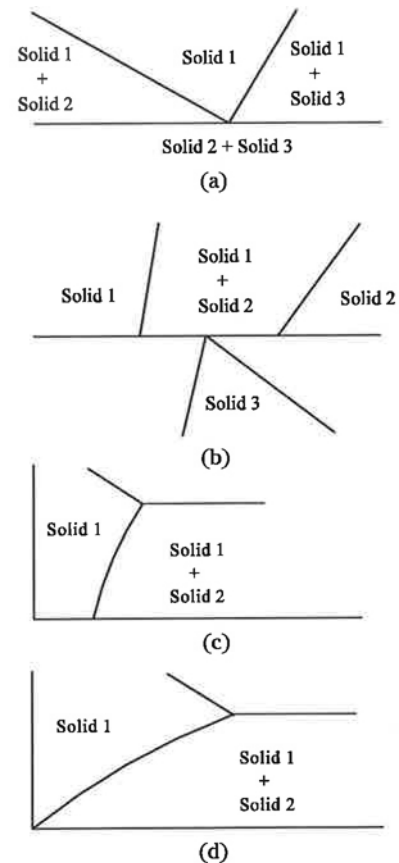


Fig. 2.7. The appearance of solid state reactions on phase diagrams is illustrated: (a) eutectoid; (b) peritectoid; (c) solvus line with a steep slope, resulting in only a small dependence of solid solubility on temperature; (d) solvus line with a shallow slope, resulting in a high temperature dependence of solid solubility.

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gram as does the eutectic, and is characterized by the reaction:



The most well known eutectoid reaction is the decomposition of austenite in carbon steels to produce pearlite.

PERITECTOID

The solid state equivalent of the peritectic, this reaction involves two solids combining to form a third as follows:



SOLID STATE PRECIPITATION

When the solid solubility of one element in the other is exceeded, a precipitation process will occur in which a second phase is formed in order to restore the equilibrium solubility conditions. This situation arises when the temperature of a solid solution phase drops, and the solubility decreases with temperature. It is the solvus line on the phase diagram that describes the relationship between solid solubility and temperature. Solvus lines that have a steep slope lead to only a small temperature dependence of solid solubility, whereas those with a shallow slope show a high temperature dependence of solubility and result in considerable solid state precipitation as the temperature falls. These cases are illustrated in Fig. 2.7c and d

COMPLEX BINARY PHASE DIAGRAMS

Most phase diagrams contain more than one of these various reactions, and some are quite complex, such as the Cu-Sn diagram used for many common bronzes and shown in Fig. 2.8. A glance at this phase diagram reveals peritectics, a eutectic, various eutectoids, a peritectoid and several changes in solid solubility. At first, such complex diagrams appear bewildering, but they are simple to use if you restrict yourself to only the area of immediate interest.

Consider an alloy of 30%Sn-70%Zn. This alloy passes successively through the following areas on the diagram as it cools from the completely liquid state: liquid + β , liquid + γ , γ , $\gamma + \delta$, $\delta + (\text{Cu})$, $(\text{Cu}) + \epsilon$.

At any of these stages when two phases are present, tie lines can be drawn to determine the phase compositions, and

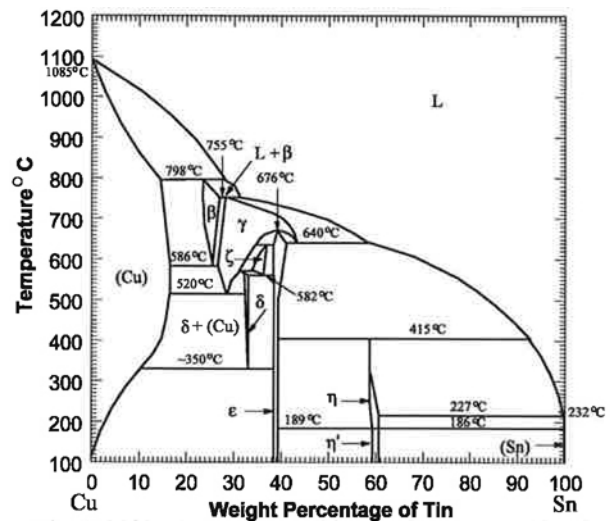


Fig. 2.8. The Cu-Sn phase diagram is an example of a complex binary phase diagram containing many phase reactions and a variety of different solid phases.

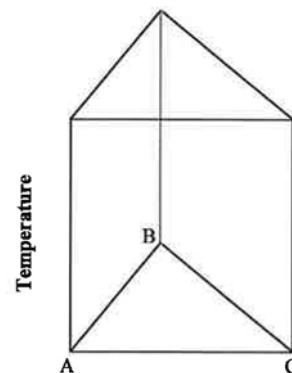


Fig. 2.9. Representation of phase relationships in a ternary system is done on a triangular prism.

PHASE DIAGRAMS: WHAT THEY ARE AND HOW TO USE THEM

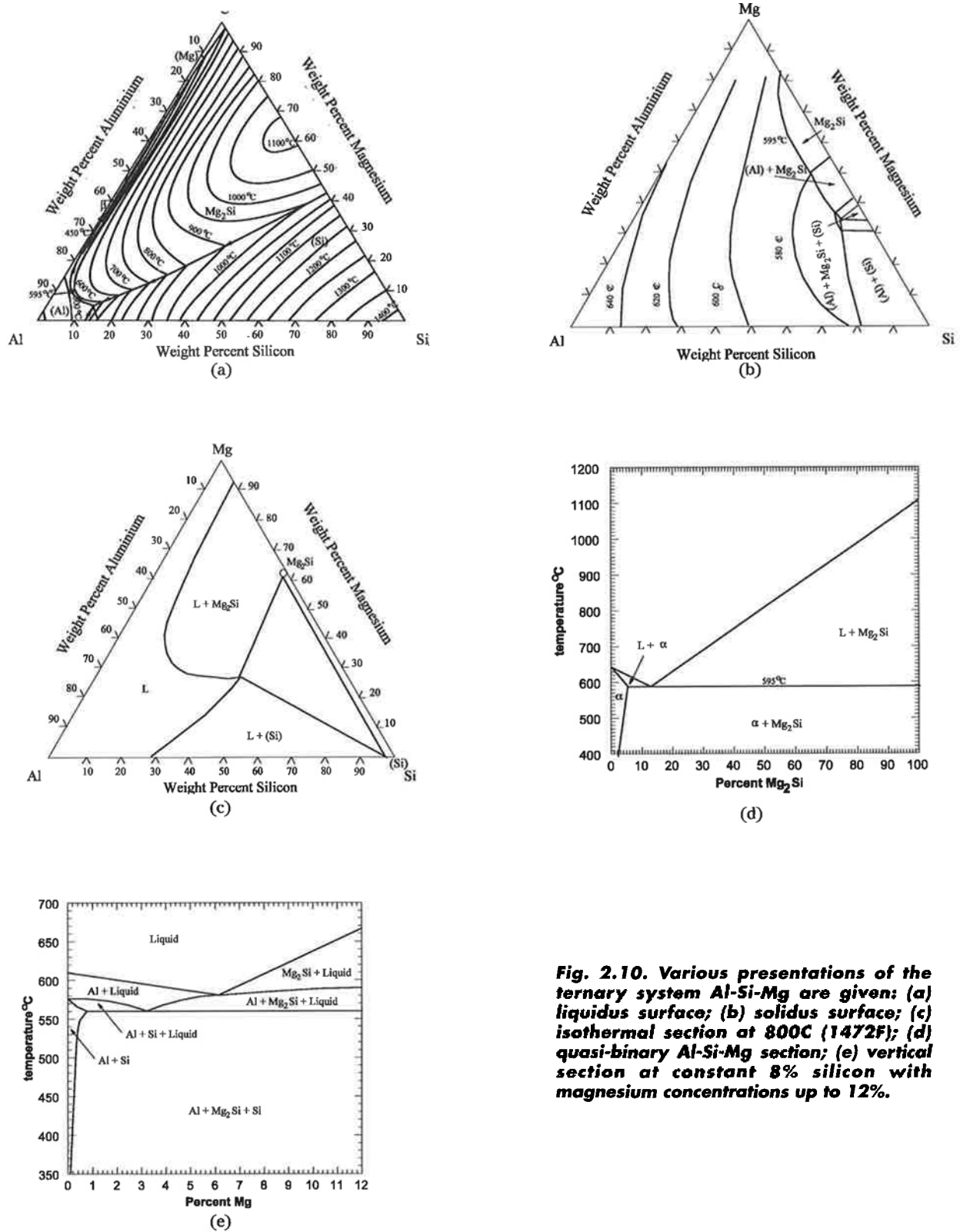


Fig. 2.10. Various presentations of the ternary system Al-Si-Mg are given: (a) liquidus surface; (b) solidus surface; (c) isothermal section at 800C (1472F); (d) quasi-binary Al-Si-Mg section; (e) vertical section at constant 8% silicon with magnesium concentrations up to 12%.

lever rule calculations will yield the relative amounts of the two phases. The trick in dealing with complex phase diagrams is simply to confine your interest and ignore parts of the diagram that are not pertinent to the composition at hand.

TERNARY PHASE DIAGRAMS

The addition of a third chemical component to an alloy system significantly complicates the presentation of phase relation data. The two-dimensional x-y plot is no longer sufficient for complete representation of the temperature-composition-phase situation. Instead, a triangular prism is used with temperature plotted vertically and the pure components located at the vertices of the triangle, as illustrated in Fig. 2.9 for the hypothetical system, A-B-C.

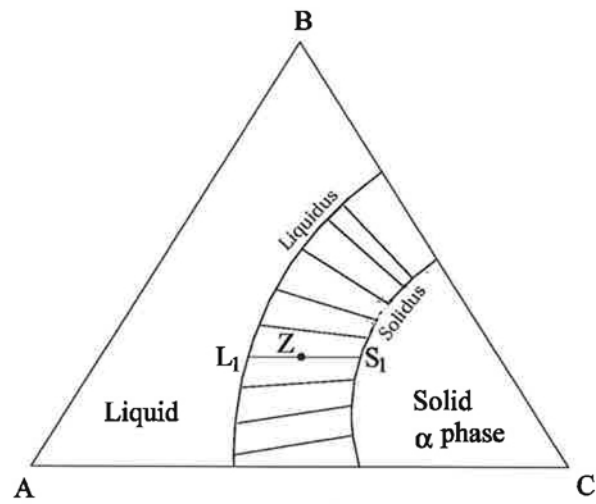


Fig. 2.11. Using experimentally determined tie lines in a ternary system is illustrated.

Phase data for ternary systems is often incomplete, and it is not usually helpful to present all of the data in a three-dimensional structure, such as that of Fig. 2.9, on a two-dimensional, printed page. In the absence of 3-D models, it is usual to present ternary phase diagrams as: horizontal sections at a fixed temperature (isothermal sections); contour maps of the liquidus or solidus surfaces (projections); 2-D vertical sections taken at a fixed composition of one of the components (pseudo-binary section); or as sections taken through one corner and a congruently melting binary compound which appears on the opposite face (quasi-binary section). Quasi-binary sections can be read like any other binary phase diagram, but the same is not true for the other methods of presentation.

Isothermal sections are triangular with the composition axes along each side of the triangle. Vertical sections have temperature plotted vertically and composition horizontally, much like a binary phase diagram.

Some examples of these various presentations are given in Fig. 2.10 for ternary system Al-Si-Mg. Figure 2.10a presents the liquidus projection of the system. Isotherm contours on the liquidus surface are shown, and the diagram is read much like a geologic contour map. The dark lines represent valleys leading to ternary eutectics or peritectics and the arrows in these valleys indicate the direction of decreasing temperature. The solidus projection is given in Fig. 2.10b and an isothermal section at 800C (1472F) in Fig. 2.10c, showing regions of liquid and solid phases. Figure 2.10d illustrates the quasi-binary section taken from the compound Mg_2Si (magnesium, silicon) to pure aluminum. This section is of particular significance because Mg_2Si is an important compound formed during the heat treatment of Al-Si-Mg alloys. Finally, Fig. 2.10e presents a vertical section taken at constant 8% silicon. Such sections are helpful in understanding the solidification of many Al-Si-Mg casting alloys that contain silicon concentrations in the area of 8 wt. %.

PHASE DIAGRAMS: WHAT THEY ARE AND HOW TO USE THEM

It is much more difficult to extract quantitative information from ternary phase diagrams than it is from binary diagrams. Tie lines must be determined experimentally, and because of this, only a few diagrams have actual tie lines. Figure 2.11 illustrates an isothermal section containing liquid, solid and liquid plus solid regions. Compositions and relative amounts can be determined from the tie line passing through the composition point of interest.

For example, the compositions of the liquid and solid phases of alloy Z are L_1 and S_1 respectively, and the relative amounts of phases are given as:

$$\% \text{ solid} = ZL_1 / S_1L_1 \cdot 100\%$$

$$\% \text{ liquid} = ZS_1 / S_1L_1 \cdot 100\%$$

If the tie lines have not been determined, they often can be approximated by knowing these general rules:

- (1) Direction of the lines varies gradually from one side of the phase region to the other and the lines do not cross.
- (2) Tie lines join two single-phase regions.
- (3) Tie lines are not necessarily oriented toward the vertices of the triangle except for the two bounding lines if they happen to coincide with the sides of the triangle.

Vertical sections are not useful for determining phase compositions or amounts because the tie lines usually lie at some angle to the plane of the vertical section. Drawing a horizontal tie line, as in a binary diagram, will yield incorrect values of composition and amounts. Instead, vertical sections are useful only for determining the phase present at a given temperature and composition.

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FURTHER READING

- "Alloy Phase Diagrams," *ASM Handbook*, vol 3, ASM International, Materials Park, OH (1992).
- Hillert, M., "Principles of Phase Diagrams," *International Metals Review*, vol 30, pp 45-67 (1985).
- "Phase Diagrams," *Materials Science and Technology*, vols 1-3, ed. Allen M. Alper, Academic Press, Inc., NY (1970).
- Prince, A., *Alloy Phase Equilibria*, Elsevier Publishing Co., Amsterdam (1966).

chapter 3

How CASTINGS ARE MADE

INTRODUCTION

Cast metal products are usually of two types: castings and ingots. Castings are objects manufactured close to their final shape and designed for use with that shape. A good example is an automobile engine block—a casting made with spaces for cylinders and passages for coolants and lubricants, all at very specific locations as dictated by the designer. Finishing operations on castings are often minimal and may include some machining, tapping, drilling, etc., but by and large the as-cast shape is the final shape of the object when it is put into use.

Ingots, on the other hand, are usually large cast shapes of simple geometry produced for the specific purpose of further processing in the solid state by rolling, extrusion, forging, etc. Thus, a rolling ingot is likely to be rectangular in cross section and several meters in length. Ingots for extrusion have circular cross sections so that they may be cut into appropriate lengths and fit into the chambers of extrusion presses. Ingots made for wire or rod production are usually square in section and of a size that may readily be rolled into rod of the desired diameter.

While many of the aspects of the solidification of castings and ingots are similar, there also are important differences. Size is one. Most ingots are very large compared to the majority of castings, with the result that their solidification time is relatively long. This feature of ingot freezing can lead to certain solidification defects, common only to ingots. Chapter 9 deals with some of these. Many features of the solidification structure of ingots are destroyed during subsequent hot or cold working, and the structure of the final product often is determined more by the deformation processes than by the ingot solidification. Such is not the case for castings where the solidification structure almost always governs the properties of the casting when it is in service.

This chapter will describe, in a simple way, the most common industrial processes for the manufacture of castings and ingots. Castings are described first, followed by a look at ingot processes. The specialized topic of single crystal growth is dealt with at the end. Technology in casting and ingot production is vast, and you are referred to publications listed in Further Reading at the end of this chapter for more detailed descriptions of the various processes.

A GENERIC VIEW OF CASTING PROCESSES

Much is made of the differences between the various processes for casting manufacture, but they all require a:

- mold that contains a cavity of the shape of the object to be made;
- means of introducing a liquid metal into that cavity; and
- means of removing the solidified casting from the mold.

The differences between the processes lie in the material from which the mold is made and in the method used to introduce the liquid into the mold cavity. The mold material dictates the method of extracting the casting. In the following discussion, casting processes have been grouped according to whether or not the mold is expendable.

CASTING PROCESSES USING A DISPOSABLE MOLD

SANDCASTING

As the name implies, sand is the mold material used in this process. An important consideration is the softening temperature of the sand in relation to the pouring temperature of the metal. Thus, silica sand (SiO_2) is used for aluminum castings while sands with higher softening temperatures, such as olivine sands ($2\text{MgO} \cdot \text{SiO}_2$ or $2\text{FeO} \cdot \text{SiO}_2$) or zircon sands ($\text{ZrO}_2 \cdot \text{SiO}_2$), are often used in the manufacture of heavy section steel castings.

Some type of binder is necessary to cause the sand grains to stick together and to make the sand moldable. The binder may be a naturally occurring clay to which a small amount of water is added, or one of a wide variety of chemical binders. These are thermosetting resins that harden with the application of heat or products that polymerize with time at room temperature, and, in so doing, bind the sand grains together. In any case, good mixing of the sand and binder is necessary.

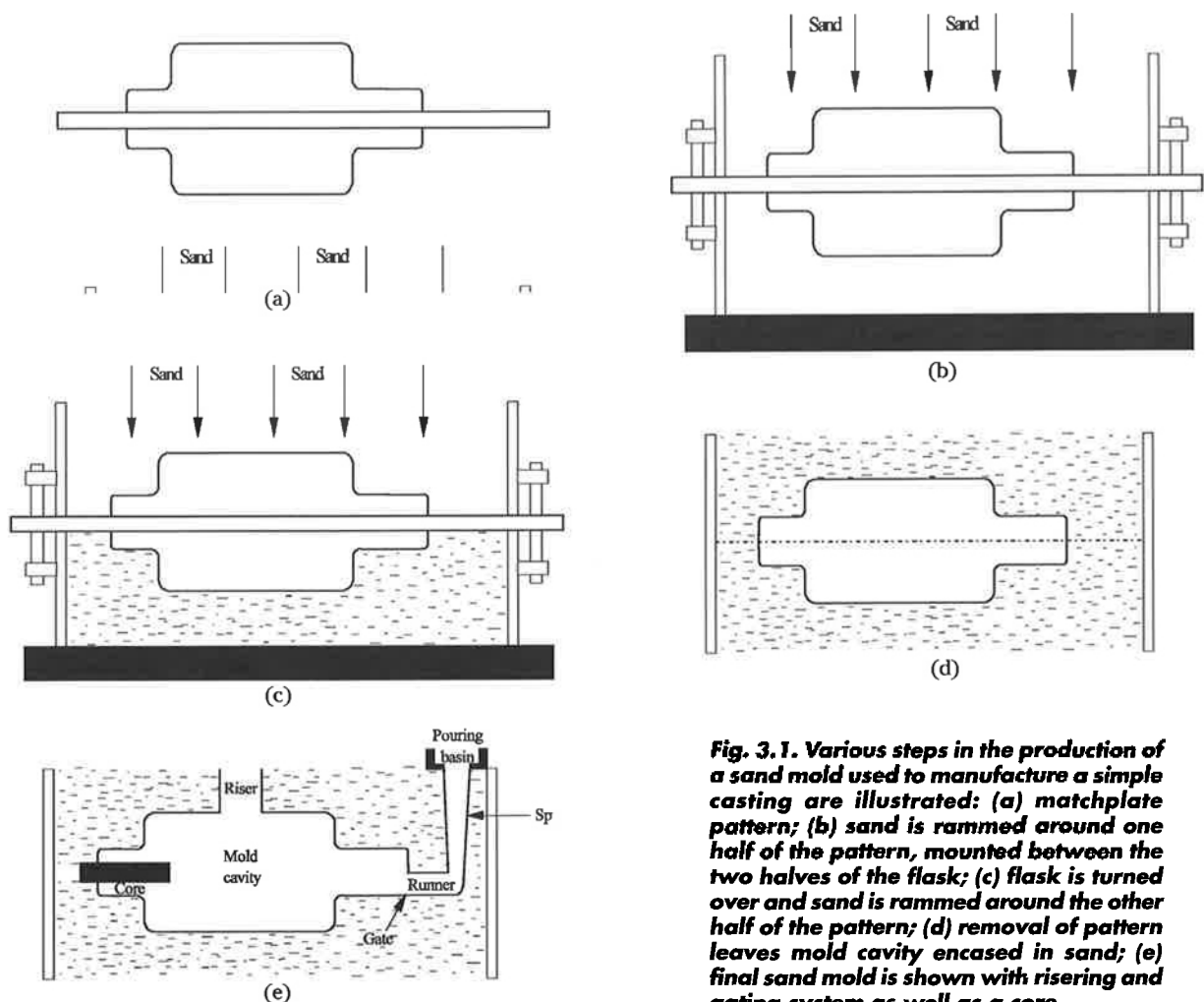


Fig. 3.1. Various steps in the production of a sand mold used to manufacture a simple casting are illustrated: (a) matchplate pattern; (b) sand is rammed around one half of the pattern, mounted between the two halves of the flask; (c) flask is turned over and sand is rammed around the other half of the pattern; (d) removal of pattern leaves mold cavity encased in sand; (e) final sand mold is shown with risering and gating system as well as a core.

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A pattern having the desired shape of the final casting must be made. This pattern may be of wood, plastic or metal, depending on its proposed lifetime. In order to facilitate the molding process, the pattern often is mounted on a matchplate. Objects of simple geometry are cut along an appropriate plane of symmetry, and each half is mounted on a side of the matchplate (Fig. 3.1a).

The actual molding of the sand around the pattern is done in a two part metal box called a flask, with the matchplate mounted between the two halves of the flask (Fig. 3.1b). A sand-binder mixture is rammed around the pattern on one half of the flask, then turned over so that the other half may be rammed (Fig. 3.1c). The sand ramming process is done under conditions of controlled pressure by automated equipment, but it also may be done by hand, using simple tools as, for example, in the manufacture of prototype castings. When both halves of the flask have been filled with sand, the halves are separated in order to remove the wooden pattern. When reassembled, the mold contains a cavity of the desired shape (Fig. 3.1d). It is now necessary to provide a way to introduce the liquid metal into the cavity.

A system of gates and runners allows the mold cavity to be filled. In effect, it is sort of a plumbing system that must be molded into the sand to allow liquid metal to flow into the cavity. In its simplest form, this system consists of the following parts:

- a pouring basin cut into the top free surface of the sand and into which the metal is poured;
- a vertical channel, called the sprue, running from the pouring basin down to the mid-plane of the flask. This mid-plane is called the parting line;
- horizontal channels, called runners, along the parting line, which allow the liquid to flow toward the mold cavity; and
- entrances (gates) connecting the runners to the mold cavity.

The liquid flows from the pouring basin down the sprue, along the runners and through the gates into the mold cavity. Figure 3.1e shows these various parts of the gating and running system. Determination of the correct size and location for all parts of the liquid flow system is an important aspect in the production of good quality castings. Gates and runners are usually molded along with the pattern itself by mounting appropriate shapes on the matchplate. The sprue may be cut into the sand or molded around a separate pattern that is pulled from the sand before the flask is separated.

If hollow sections are a part of the casting design, it is necessary to fill such sections with sand in order to prevent the metal from occupying that particular volume. This is accomplished by placing separately molded sand cores in the appropriate positions in the mold before it is closed. Coremaking is a specialized operation using sand binders that are similar to the thermosetting resins used for the mold itself. Extra strength is required in cores because they must be handled, either manually or automatically, in order to place them in the correct position in the mold. A core is shown in position in Fig. 3.1e.

Most liquid metals shrink on solidification, and if this shrinkage is not compensated for, it may result in internal or external holes in the casting. In sand castings, a riser is used to

compensate for the solidification shrinkage. The riser is a reservoir of liquid designed to freeze after the casting itself. As the liquid metal in the mold cavity solidifies and shrinks, liquid is drawn from the riser to compensate for the shrinkage.

Riser placement and design is critical to the production of defect-free castings. Risers may be cut or molded separately from the main part of the casting. Figure 3.1e shows the riser placement in the final sand mold for this shape. Removal of the solidified casting from the sand mold necessitates breaking of the mold. The sand may be recycled, although various processes may be necessary to remove or to add more binder.

Sandcasting is an extremely versatile process amenable to the production of castings of all sizes, from a few grams to several metric tons. Proper choice of the sand-binder mixture allows virtually any metal to be cast by this method. The process can be used to make prototypes or one-off art castings, or it can be adapted to the modern computer-controlled, robotized foundry, producing thousands of castings per day. On the negative side, its major disadvantage lies in a lack of precise dimensional control. Machining must be done on those parts of a sandcasting where dimensional control is critical. Nevertheless, this, the oldest of casting processes, remains the most important player in today's foundry industry.

LOST FOAM PROCESS

This casting process, also known as the EP or expanded polystyrene process, was developed originally at the School of Art at the Massachusetts Institute of Technology. In recent years, it has been adopted by several manufacturers of automotive parts for the production of cylinder heads and brake parts.

The process uses a pattern made by injection molding of expanded polystyrene into a permanent metal die. Polystyrene is an inexpensive polymer commonly used as a packaging material. In its expanded version, it is mixed with air to produce a material of very low density, composed of more than 90% air. The pattern, with expanded polystyrene gates, runners and risers attached, is coated with a light refractory and placed in a one piece flask which may be as simple as an oil drum. The pattern is then surrounded by loose, dry sand that is usually vibrated to achieve some degree of compaction.

Liquid metal poured directly onto the pattern through the sprue and runners causes

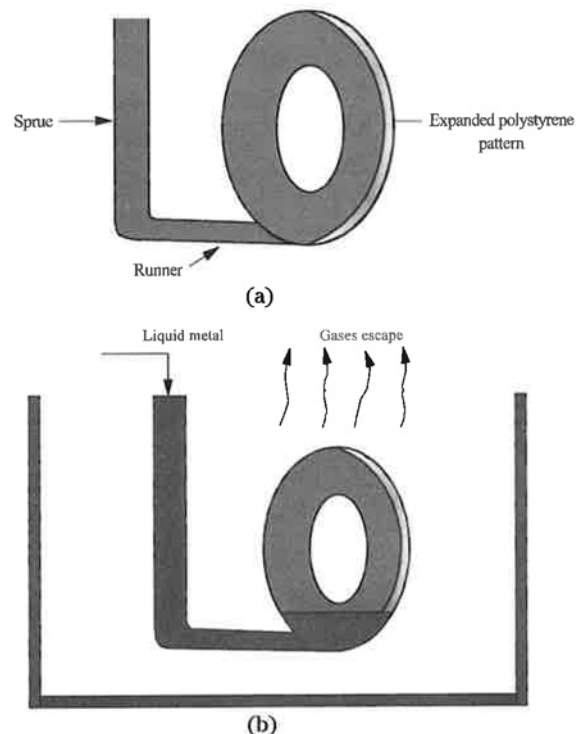


Fig. 3.2. Principles of the lost foam process are shown: (a) an expanded polystyrene pattern with attached sprue and runner; (b) liquid metal, which is poured directly onto the pattern, causes the pattern to decompose and liquid occupies the resulting cavity.

the expanded polystyrene to decompose into various gaseous hydrocarbon products. Collapse of the surrounding sand into the resulting cavity is prevented by a combination of gas expansion and the ceramic coat. Gases generated by decomposition of the polystyrene escape through the relatively porous sand. A schematic illustration of the process is given in Fig. 3.2.

The lost foam process is the only casting process in which liquid metal actually contacts the pattern and consumes it. As a process, it is particularly attractive for the manufacture of prototypes, because the pattern can be cut by hand from a block of polystyrene. It also allows the manufacture of very intricate castings, and does not require individual cores to make hollow sections.

On an industrial scale, however, there are several drawbacks associated with the lost foam process. One, most foundries do not have facilities for the manufacture of the patterns. They must be made elsewhere and transported to the foundry. Two, gases formed by decomposition of the polystyrene must be collected and treated before they can be released into the atmosphere. Three, loose sand has a relatively low thermal conductivity leading to a slow solidification rate for castings made in this way. The resulting coarse microstructure often is not the best in terms of final casting properties. Despite these shortcomings, the lost foam process remains a versatile process adaptable to any commercial metal and capable of producing complex castings over a wide size range.

INVESTMENT CASTING

This technology for the manufacture of high quality precision castings is also known as the lost wax process or precision casting. It is an ancient process developed originally by the Chinese to make art and religious castings. Many excellent Chinese bronzes found in museums around the world were made by investment casting. Then, interestingly, the process seems to have disappeared for centuries until it was rediscovered, or redeveloped, in Germany shortly before World War II.

Two versions of the process are in use today. Steps in the most common of these, the ceramic shell process, are illustrated in Fig. 3.3. The first step is the creation in wax of an exact replica of the object to be manufactured. Usually, this is done by injecting wax into a steel or aluminum die, but if a prototype is being made, the wax may be shaped by hand. In small castings, such as jewelry, several wax patterns may be connected to a common sprue (also of wax) to form a “tree.”

Next, the pattern, or assembly of patterns, is coated with a refractory layer built up by successive operations of dipping into a water-based ceramic slurry, then sifting “stuccoing” fine refractory grains onto the surface. The coating thickness is determined by the number of times the dipping and stuccoing process is repeated.

When a layer of sufficient thickness has been established, the wax is removed from the ceramic shell by heating in a furnace. When melted, most of the wax runs out of the shell, and any remaining is simply vaporized. Mechanical strength is imparted to the shell by firing it at an

HOW CASTINGS ARE MADE

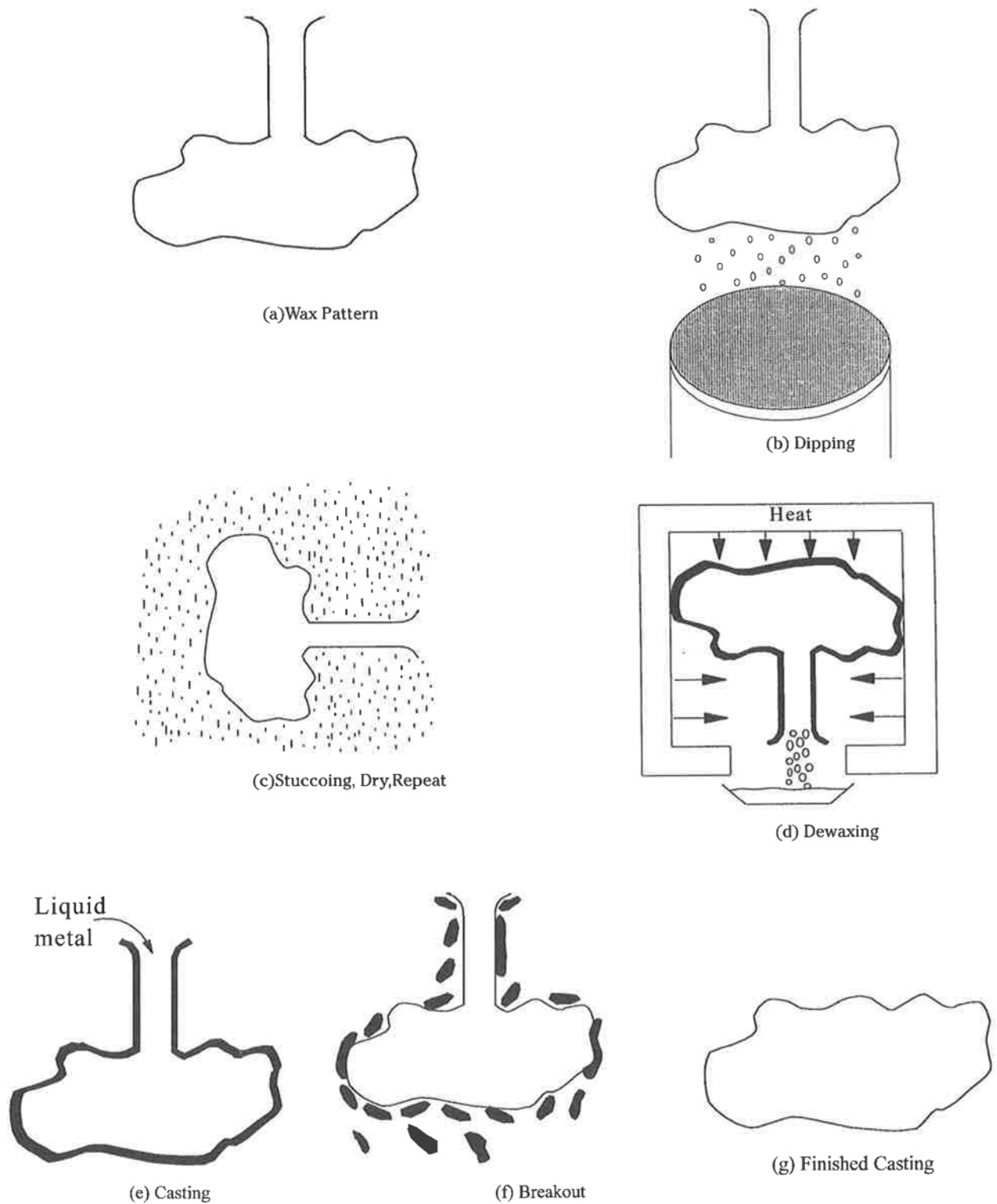


Fig. 3.3. Various steps in the production of a casting using the ceramic shell process (investment casting) are illustrated.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

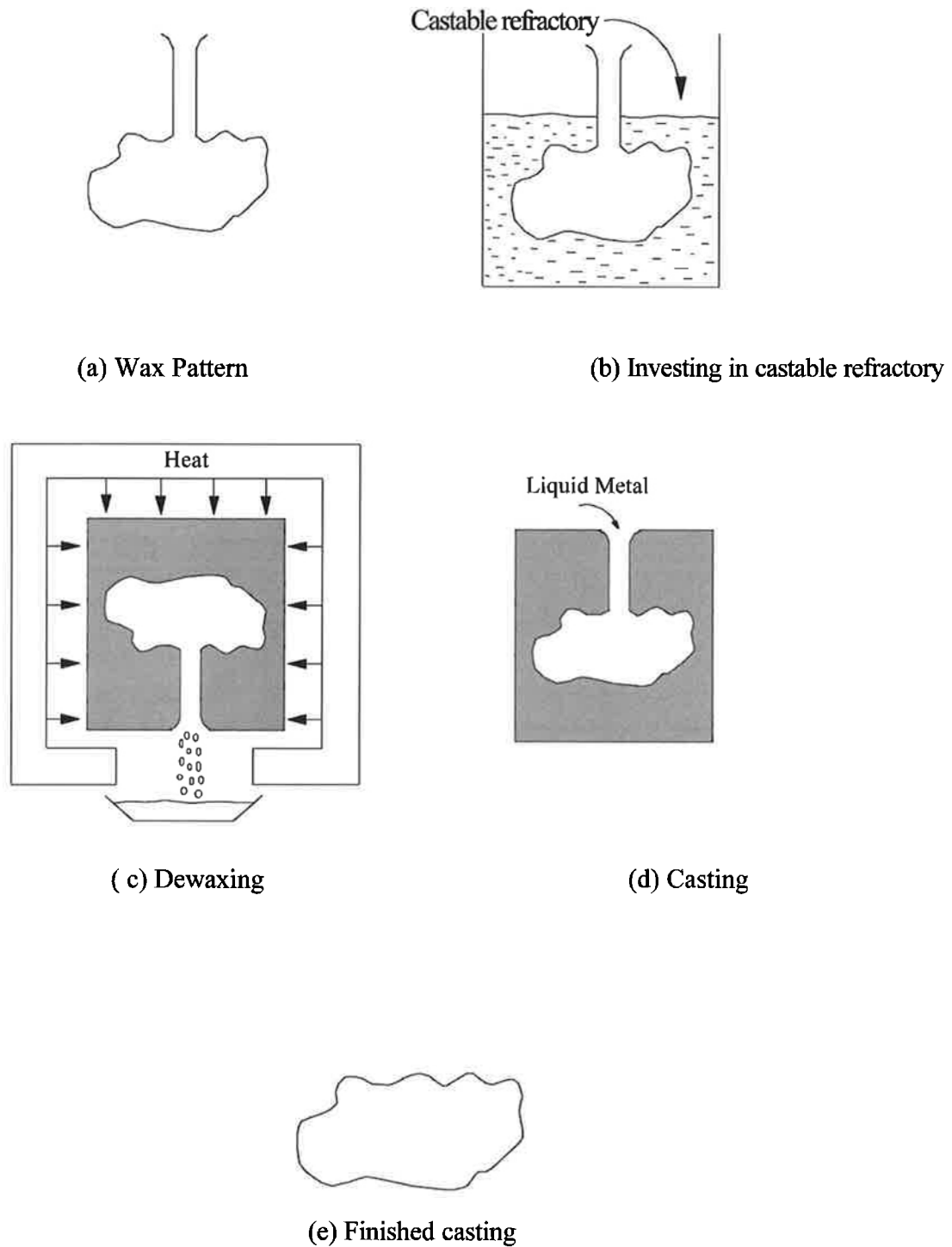


Fig. 3.4. Steps in the production of a casting using the solid mold investment process are shown.

appropriate temperature to cause sintering of the refractory grains. The shell is now ready to have liquid metal cast into it. Because the process is used to manufacture castings requiring great precision and detail reproduction, casting is sometimes accompanied by centrifuging or the application of air pressure. Both of these help to force the liquid into the fine details of the mold. After the metal has solidified, the ceramic shell must be broken to remove the casting, which is subsequently cut from the sprue and finished.

A second version of the investment casting process has the wax pattern invested in a castable refractory to form a solid mold (Fig. 3.4). A variety of castable refractory materials are available. They are mixed with water and cast around the wax pattern in a permanent flask that may be made of metal or refractory. Dewaxing is done in a furnace, as with the ceramic shell process, and the metal is cast directly into the mold cavity after the refractory has cured and hardened. Removal of the solid casting requires that the refractory be broken from the casting.

Investment casting is a labor-intensive process, and as a result, is among the most costly of casting processes. It is, however, capable of very fine detail reproduction, and allows features to be cast to shape without subsequent machining. Its major use is in the manufacture of high quality items where cost is secondary to quality and performance. Some common applications for investment castings are in the fields of aerospace, medical and dental casting, custom jewelry and armaments.

PERMANENT MOLD CASTING PROCESSES

The advantages of using a permanent mold to produce castings are that mold (die) manufacture takes place only once, and hundreds or thousands of castings may be made from that mold. Permanent mold processes are, however, limited to long production runs of nonferrous alloys because of the high initial capital investment associated with machining the die, which may be made of cast iron, alloy steel or copper.

Removal of the casting from the permanent mold is accomplished by disassembly of the mold. Simple symmetrical castings may be made in a two-part split mold, but more complex castings require multi-part permanent molds that may also incorporate permanent metal cores to produce hollowed out sections. In some applications, sand cores may be used in conjunction with a permanent mold in what is known as a semi-permanent mold process.

Liquid metals may react with the mold material to cause sticking or welding of parts of the casting in the mold. If this occurs, removal of the casting becomes difficult, and damage to the mold itself may result. Mold coatings are used to facilitate casting removal. These are refractory slurries, sprayed or painted onto the mold surfaces to form a fairly

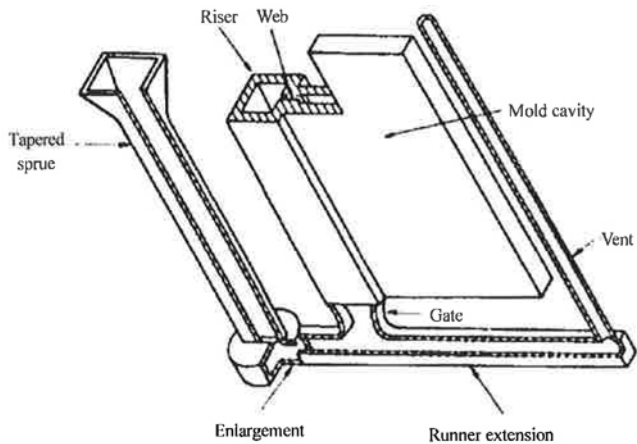


Fig. 3.5. A simple two part permanent mold is illustrated.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

adherent coat when dried. Mold coatings also may be used to control the rate of solidification in certain parts of the casting. The freezing rate may be slowed by using a low thermal conductivity coating, such as alumina, or accelerated by using a high thermal conductivity material, such as graphite.

Permanent mold processes differ mainly in the manner in which the liquid metal is introduced into the mold cavity. Three classes of the process may be identified:

- gravity permanent mold casting, which uses gravity and the metal head to force liquid into the mold;
- low pressure permanent mold casting in which air or an inert gas is used to fill the mold cavity at pressures slightly above atmospheric; and
- High-pressure diecasting processes in which the liquid is forced mechanically into the mold at very high pressures, in the range of several thousands of pounds per square inch.

GRAVITY PERMANENT MOLD CASTING

A simple die for the gravity permanent mold process is illustrated in Fig. 3.5. This two-part mold incorporates all parts of the feeding and risering system. Liquid metal is simply ladled into the sprue, the system filled and, after solidification is complete, the two parts of the die are separated to remove the casting.

Figure. 3.6 illustrates how permanent metal cores may be used in conjunction with a permanent mold. Here, five cores are used. They must be assembled and disassembled in a certain order, consistent with the geometry of the die. In the example shown, disassembly would be done by first removing the pin cores, then the center core, followed by one side core and, finally, the remaining side core. When all cores have been removed, you can open the mold and remove the casting.

Gravity permanent mold (or semi-permanent mold) processes are quite amenable to automation. Several molds may be placed on a horizontal rotating wheel located next to the pouring station. Castings are poured and solidify as the wheel rotates. In the time required for one revolution, a given mold will be filled, the casting will freeze and be removed from the mold, so that the mold is ready to receive liquid metal when it gets back to the pouring station.

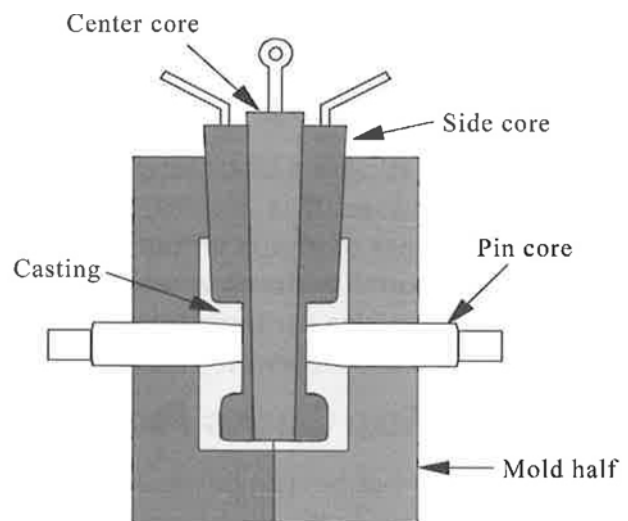


Fig. 3.6. A coring configuration is shown in a permanent mold.

LOW PRESSURE PERMANENT MOLD CASTING

Molds to be used in the gravity permanent mold process must incorporate risers, much as in sandcasting. The low pressure permanent mold process (LPPM), which is widely used in aluminum casting, eliminates the need for risers and, consequently, increases the efficiency of metal usage.

The principle of the process is illustrated in Fig. 3.7. Metal is melted and held in a crucible furnace, which may be electric or fossil fuel fired. The two-part die is supported on a platform located above the furnace. A ceramic or metal feed tube connects the liquid bath with the lower fixed part of the die. With the die closed, air or inert gas pressure is applied to the melt surface at up to 6 atmospheres gauge pressure. This pressure is sufficient to force the liquid up the feed tube and into the die. Pressure is maintained until the casting is solid, or almost so.

When the pressure is released, the metal remaining in the feed tube flows back to the crucible. The die may then be opened, and the casting ejected using an assembly of ejector pins. Efficiency of the process comes from the fact that the metal in the feed tube acts as the riser during solidification, and any excess metal remains liquid and is allowed to return to the bath when the pressure is released.

HIGH PRESSURE DIECASTING

In high pressure diecasting, a hydraulic cylinder forces liquid metal at high velocity and pressure into a water-cooled metal mold. Pressures used vary with the metal being cast and the size of the casting, but they are in the range of 3000 to 30,000 psi. These pressures, coupled with the mold cooling, ensure rapid solidification of the casting and an excellent surface finish and reproduction of

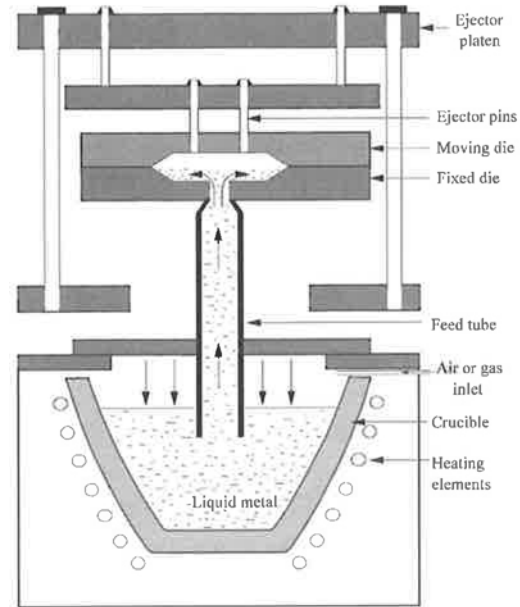


Fig. 3.7. A schematic drawing of a typical low pressure permanent mold casting machine is shown. The arrows indicate direction of applied pressure on the melt surface and the resulting liquid metal flow.

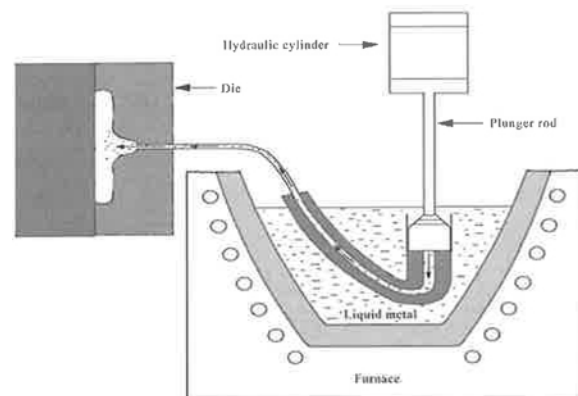


Fig. 3.8. Operation of a hot chamber diecasting machine is shown. The arrows indicate direction of liquid metal flow from the pressure chamber into the die.

detail. Many high pressure die castings require little or no finishing, although their internal structure is often quite porous due to air entrapment during the liquid injection.

High pressure diecasting machines are sophisticated, highly automated devices, often capable of producing thousands of castings per hour. The high pressures required limit the process to small castings. High pressure diecasting is used to manufacture a large number of common household items and automotive parts in the lower melting industrial metals, mainly aluminum, magnesium and zinc. The high capital cost of tooling and purchasing the casting machine limits the process to very long production runs.

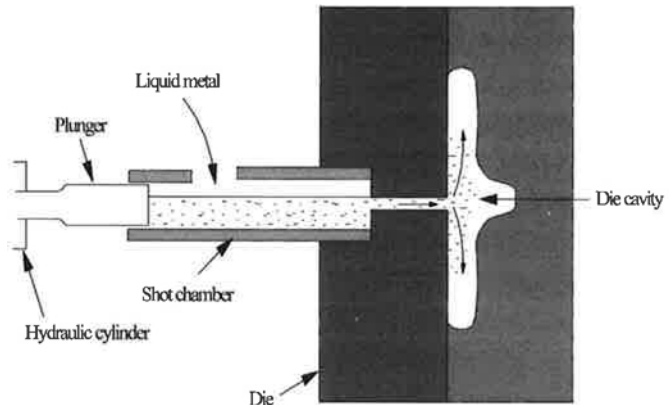


Fig. 3.9. Operation of a typical cold chamber diecasting machine is illustrated. Direction of metal flow from the shot chamber into the die is indicated by the arrows.

Two types of high pressure equipment are found. The hot chamber diecasting machine, illustrated schematically in Fig. 3.8, has the plunger submerged in the molten metal. This type of machine is used mainly for magnesium and zinc alloys as these materials are compatible with the steel from which the plunger is constructed. Cold chamber diecasting is used for aluminum. The liquid is ladled automatically into the shot sleeve and is then injected into the die cavity by a hydraulically operated plunger rod. The operation of a cold chamber machine is shown in Fig. 3.9.

SQUEEZE CASTING

Squeeze casting is a specialized permanent mold process in which pressure is applied by a hydraulically operated ram during the freezing stage of casting. The process is relatively new, with most of its development since the early 1960s. Virtually all industrially used metals can be squeeze cast successfully at pressures of several hundreds of megapascals ($1 \text{ Mpa} = 145 \text{ psi}$). Today, many automotive components are squeeze cast, with aluminum wheels being one of the largest products of this process.

The main advantage of squeeze casting is the substantial reduction of porosity, a common feature of other casting methods. In addition, the application of pressure ensures a fine and homogeneous microstructure. Thus, the tensile properties of squeeze cast metals are similar to those of forged materials with the added benefit of being isotropic. Pressure that is applied throughout the entire freezing process also gives squeeze castings an excellent surface finish and reproduction of fine details in design is possible.

Most other casting processes require that the liquid flows freely into the mold cavity, and only those liquids with a high degree of fluidity can be so cast. The use of pressure during squeeze casting limits this difficulty and serves to expand the range of alloys that can be fabricated using this process. As with high pressure diecasting, squeeze casting

requires a large initial capital investment in the casting machine itself. In addition, dies often are complex and relatively expensive to produce.

Squeeze casting has proven to be an effective way to form metal matrix composites consisting of a ceramic preform into which liquid metal is infiltrated. Figure 3.10 illustrates, in a simple way, how the squeeze casting process operates to produce a composite material. A preform, which typically might be made of short ceramic fibers, e.g. alumina fibers, is placed in the die. Molten metal is poured over the preform, and the punch, which applies pressure throughout the freezing, forces the liquid metal to fill the spaces between the fibers. The result is a solid metal matrix composite casting.

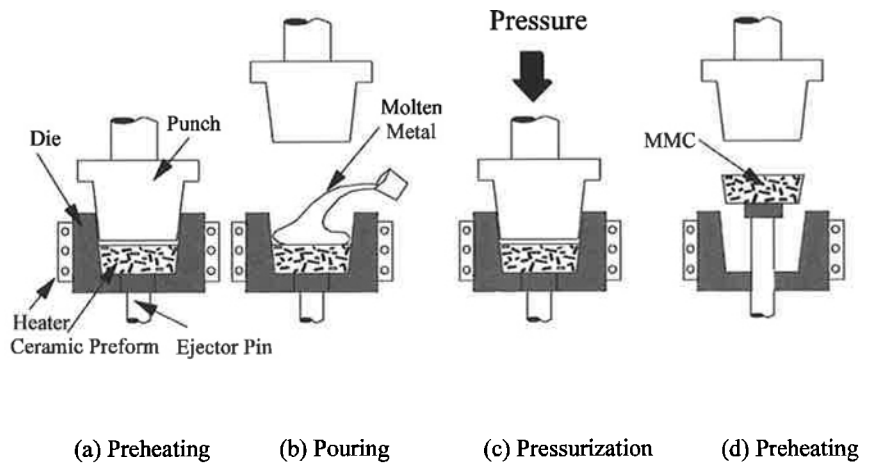


Fig. 3.10. The stages of squeeze casting to manufacture a metal matrix composite are illustrated schematically.

A variation of squeeze casting is *thixocasting* in which shaping of the alloy takes place in the semi-solid state. Slugs of the alloy are melted to a defined temperature within the liquid-solid region of the alloy composition. This liquid-solid mixture is then squeezed into a die to shape the final product. The combination of pressure and the low latent heat evolution associated with a liquid-solid mixture yields castings of low porosity and fine structure. Thixocasting is used mainly for aluminum- and magnesium-base alloys, but it is adaptable to a wide range of other alloys.

INGOT CASTING

Ingots differ from castings in both shape and size. Most ingots weigh in the tons and have simple geometric shapes to facilitate further working in the solid state. In general, castings are relatively small, compared to ingots, and are of a geometric complexity which is dictated by their final use. Among the major considerations in ingot casting is the processing of large quantities of liquid metal in short time periods to produce ingots free of surface and internal defects.

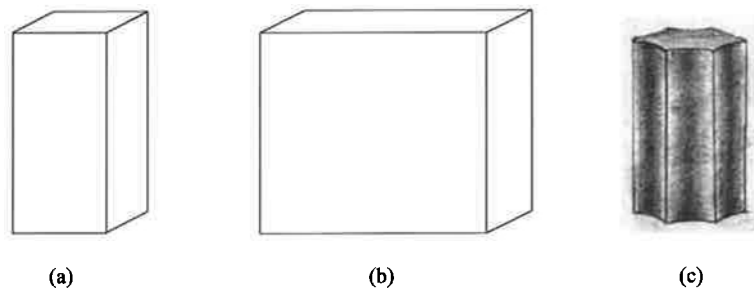


Fig. 3.11. Typical shapes of permanent mold cast ingots are illustrated: (a) square; (b) rectangular; (c) fluted.

PERMANENT MOLD INGOT CASTING

Throughout the 19th century and first half of the 20th, metal ingots were produced by pouring liquid metal into large permanent molds made of cast iron. Upon solidification, the ingot was stripped from the mold by upturning the mold. Ingots weighing many tons were made this way with a variety of cross-sectional shapes, some of which are illustrated in Fig. 3.11. Rectangular sections were amenable to rolling; small square section ingots could be used for rod or wire production; and fluted ingots were destined for forging. Surface cracking and sticking in the mold are particular problems associated with permanent mold ingot casting but surface fluting reduces the incidence of cracking defects.

Permanent mold ingot casting requires a large inventory of ingot molds, the lifetime of which is often remarkably short; 30 or even fewer casts are sometimes obtained from one mold. The process itself has never been very controllable because each ingot could exhibit differences in solidification behavior, and the very nature of the process makes it labor intensive and slow. Because of these disadvantages, permanent mold ingot casting is, today, confined to small quantities of specialty metals and alloys, such as some tool steels and precious metals. Virtually all ingot production is cast in some variation of a continuous casting process.

BULK CONTINUOUS CASTING

Bulk continuous casting is used to cast regular sections for rolling, extrusion, rod and wire drawing in all commercial metals produced in tonnage quantities. The process is conceptually the same for all metals, although there are important differences from one metal to the next. Figure 3.12 illustrates the basic idea.

Liquid metal is poured into a water-cooled, open-ended mold. At the beginning of a cast, this mold is closed at its lower end by a “dummy” or “starter” block. After the mold is filled initially and a solid shell has formed, the block is withdrawn downward, and the casting process commences. Sufficient solidification takes place within the mold to create a solid shell that is strong enough to support the head of liquid metal at the point where the ingot exits the mold and becomes unsupported.

Cooling is applied to the sub-mold region by water sprays, and final freezing takes place at some distance below the exit point of the mold. Location of the final freezing point is

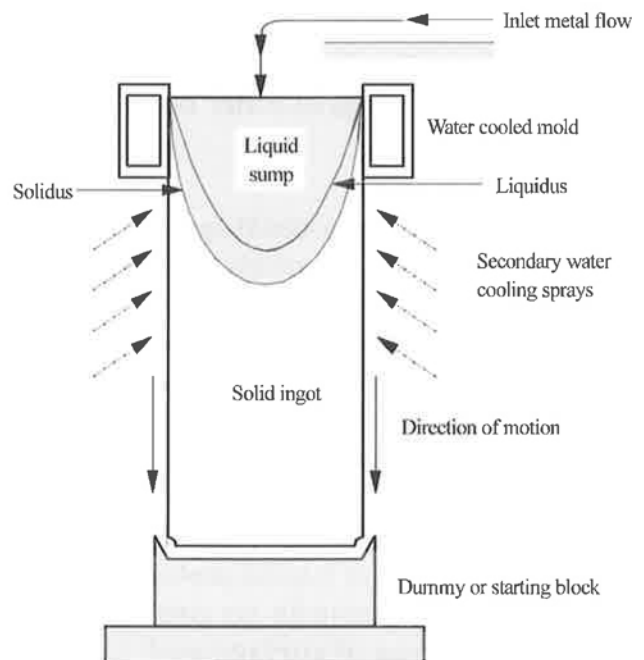


Fig. 3.12. Illustration shows the principles of continuous casting.

governed, largely, by the thermal conductivity of the metal being cast. Continuously cast aluminum may possess a sump depth of less than a meter (3.2 ft), while in steel, the sump extends many meters below the mold exit.

Mold size and design differ from metal to metal. Quite short molds, e.g., 30 cm (11.8 in.) or less, are used in the direct chill casting (DC process) of aluminum, while molds of about one meter in length are needed for steel. Lubricants added to the melt surface reduce friction between the solid shell of the ingot and the mold, and help to eliminate sticking, which could lead to surface cracking of the ingot. Canola oil is used in aluminum continuous casting, and various slag compositions provide lubrication during the continuous casting of steel. In continuously cast steel, sticking is a problem, and molds are made to oscillate vertically during casting to break any welds that do form.

An attraction of the continuous casting process is that it can, at least in principle, operate without interruption, and the cast ingot can be fed directly into a hot rolling mill. Integration of the casting and rolling operations is done in many plants, but the casting portion is usually limited by the melting capacity of the plant.

The metallurgical structure of continuously cast ingots, particularly steel, is influenced strongly by the casting process. Chapter 9 provides a more detailed discussion of steel continuous casting and structure development in ingots of this material.

WIRE BAR CASTING

Copper and aluminum destined for electrical conductors are cast by a continuous process known as the Properzi Process. The wire bar product is approximately semi-circular in cross section and forms the feed stock for the subsequent rolling and drawing operations that lead to wire.

Figure 3.13a shows the main features of the process. The mold itself is in the form of a wheel with the mold cavity lying in the wheel circumference. Liquid metal is introduced into the mold cavity at a point near the top of the wheel. This liquid is retained in the mold as the wheel rotates by a steel belt that forms the top of the mold. Heat extraction is accomplished by means of water sprays and solidification takes place as the wheel rotates. The solid wire bar is removed after slightly more than 180° of rotation. A more detailed sketch of the mold assembly is provided in Fig. 3.13b.

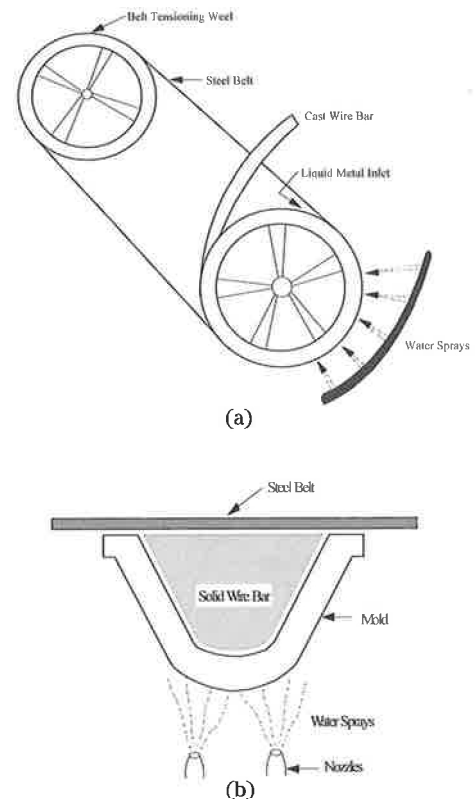


Fig. 3.13. Drawings represent: (a) a Properzi wire bar casting machine; (b) details of the wire bar mold and cooling system.

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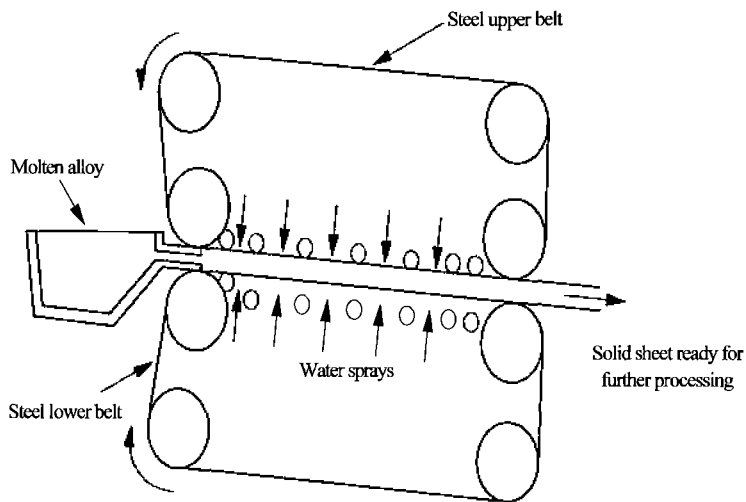


Fig. 3.14. Schematic illustration shows a belt casting machine, used in the aluminum and copper industries.

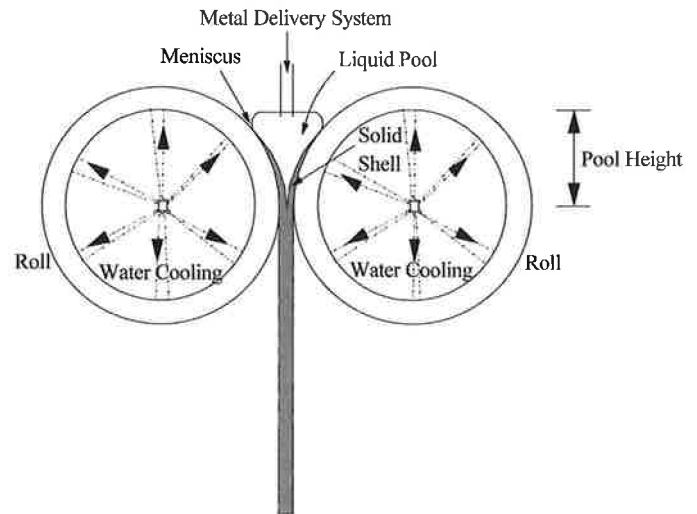


Fig. 3.15. Operating principles of a twin roll caster are illustrated.

STRIP CASTING

Conventional ingots for flat rolled products are produced in thicknesses that far exceed even the maximum desired thickness of the rolled products. As a result, large reductions with the associated expenditures of energy are necessary to reduce these ingots to the final thickness. There has always been interest in casting thin-strip ingots requiring little, or no, further reduction. Strip casting is performed routinely on many aluminum and copper alloys. Some success has been achieved with steel, and there is, currently, an intense effort in the area of continuous strip casting development.

Two common designs for strip casters are illustrated in Figs. 3.14 and 3.15. The belt casting machine (Fig. 3.14) finds application in the aluminum and copper industries. Molten metal flows between two water-cooled steel belts with freezing occurring as the metal progresses on its path between the belts. A steel chain moving in the same direction as the strip forms the sides of the mold cavity and prevents the liquid from running out of the sides of the casting machine. Various dressings are applied to the belt and chain surfaces to prevent interaction between the liquid metal and steel.

Strip thickness is determined by the spacing between the two belts, and is commonly in the range of 0.5 to 1.5 inches. The process is used worldwide and, in some plants, the strip is fed directly into a rolling mill so that flat rolled product is manufactured in one continuous step, starting with the liquid metal.

Twin roll casting (Fig. 3.15) is an old idea, first proposed by Bessemer in the 19th century, but is generating new interest, particularly in the steel industry. Liquid flows from a tundish into the space between two water-cooled steel rolls. Solidification takes place as the ingot passes through the roll gap, and once again this ingot may be fed

directly into a rolling mill. Strip casting is a rapidly developing field with many potential benefits. It is likely that new strip casting processes, as well as significant improvements to existing ones, will make their appearance in the years to come.

SINGLE CRYSTAL GROWTH

Single crystal growth is not usually regarded as a casting process, but it is an important application of controlled solidification aimed at developing a very particular and specialized structure. Melt-grown single crystals are used extensively in the field of electronics and in certain structural applications. The best known of these is the single crystal turbine blade, an example of which is shown in Fig. 1.4 (right side) .

A single crystal is a single grain of the material in question. The trick in single crystal growth is to limit the freezing process to the growth of only one grain. A common way to achieve this is to use a mold that contains a constriction, and to cause directional freezing in this mold by withdrawing heat only along the long axis of the mold. A drawing of a commonly used, simple setup for single crystal growth, known as the Bridgeman method, is presented in Fig. 3.16. Solidification occurs when the furnace surrounding the mold is moved vertically upward. Alternatively, the mold may be lowered vertically from the hot zone of the furnace into cooler regions.

Normally, several grains will form in the lower end of the mold when the liquid temperature falls to a low enough value that nucleation of the solid takes place. The mold constriction allows only one correctly oriented grain to grow through it, resulting in one single crystal being formed in the upper part of the mold. The example shown yields a crystal of simple geometry, e.g., round or rectangular cross section, but more complex shapes also may be made in this way.

Large single crystals of a specific orientation can be produced from small seed crystals by crystal pulling from the melt. This technique, known as the Czochralski method, is illustrated schematically in Fig. 3.17. The seed crystal is held on the end of a rod and placed in a bath of the liquid alloy. Growth of the seed takes place as the rod is rotated and slowly with-

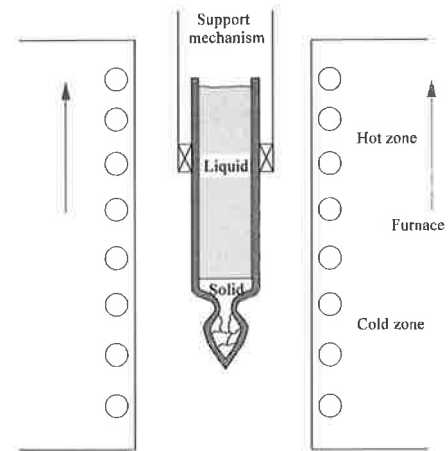


Fig. 3.16. This process of single crystal growth by restriction of nuclei is commonly known as the Bridgeman method.

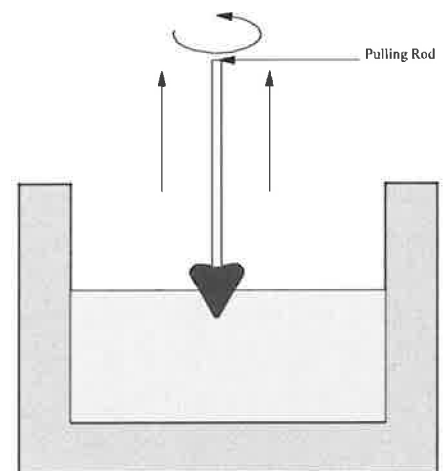


Fig. 3.17. The Czochralski method of growing large round crystals from the melt is illustrated. This method is also known as crystal pulling.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

drawn vertically from the melt. The rotating motion ensures that a crystal, which is round in cross section, is grown. This motion tends to even out any variations in heat transfer that might be present around the circumference of the crystal. Czochralski-grown single crystals of silicon are commonly used in the semiconductor industry.

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chapter 4

NUCLEATION AND GRAIN REFINEMENT

Nucleation is the first step in transformation of liquid to solid, on cooling. It is obvious that for the liquid to solid transformation to proceed, there must at some point appear a minute solid, which is capable of further growth into a bulk solid grain. This initial solid is termed a nucleus. Each individual grain in a polycrystalline material is a more or less perfect single crystal having, at its origin, one unique nucleus. The number of nuclei to act during freezing is, therefore, an important quantity. Each nucleus gives rise to one grain and the number of nuclei determine the number of grains in the final solid.

Substantial nucleation leads to a fine grain size while limited nucleation results in a coarse grain material. In the extreme, a macroscopic single crystal may result if only one nucleus acts. Much effort is expended during industrial solidification to control the number of nuclei because many properties of the solid are a direct function of the as-solidified grain size. In general, finer grain sizes are preferred, but there are special applications where coarse grains, or even single crystals, are desired.

WHY CONTROL GRAIN SIZE?

The promotion of nucleation leads to a marked change in the mechanism of freezing, as illustrated in Fig. 4.1 for the solidification of a long cylindrical shape where heat is lost primarily in a radial direction. In the presence of only limited nucleation (Fig. 4.1a), a few large grains freeze from the outer walls of the cylinder toward the center along the heat flow direction. This situation results in the formation of a long, thin liquid channel along the centerline as freezing nears completion. Such a channel creates a plane of weakness along which centerline cracking may occur because of thermally generated stresses. This is a common feature of DC cast aluminum ingots, which freeze with coarse grains. Most of the solidification shrinkage due to the volume change on freezing also may appear in this liquid region, resulting in a long narrow pipe running along the thermal center of the solid.

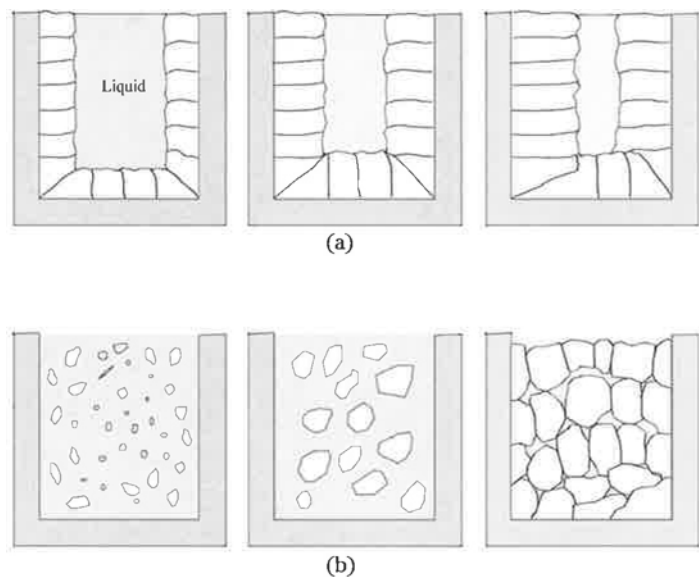


Fig. 4.1. The mechanism of solidification depends strongly on the extent of nucleation: (a) coarse grains resulting from limited nucleation at the mold walls; (b) fine grains resulting from general nucleation throughout the liquid phase.

Many alloy systems contain brittle compounds that often form along the grain boundaries. In a coarse grain material, the grain boundary area is small and these compounds may form a continuous film if their volume fraction in the alloy is sufficiently large (Fig. 4.2a). The same volume of this compound will form only isolated particles in a fine grain material

because of the larger boundary area available (Fig. 4.2b).

Coarse grains that grow from the casting walls in the heat flow direction very often exhibit a preferred crystallographic orientation or texture, with respect to ingot geometry. Deformation in the solid state varies with crystal orientation, and a preferred orientation within an ingot may lead to undesirable deformation properties during subsequent fabrication operations. Characteristics of coarse grain materials include, then, a

tendency to centerline cracking, shrinkage and segregation, coupled with texture development and an unfavorable distribution of compound phases.

When many nuclei are present, nucleation and subsequent grain growth occur throughout the bulk liquid as illustrated in Fig. 4.1b. Isolated pockets of liquid are found between the grains in this mushy type of solidification. It is within these pockets that segregation and solidification shrinkage eventually manifest themselves with the result that these effects become dispersed more or less uniformly throughout the solid, and the tendency for centerline phenomena is reduced significantly. Crystallographic randomness is assured by the presence of a large number of randomly oriented grains, and cast fine grain materials rarely exhibit any sort of texture. These effects, coupled with the more favorable

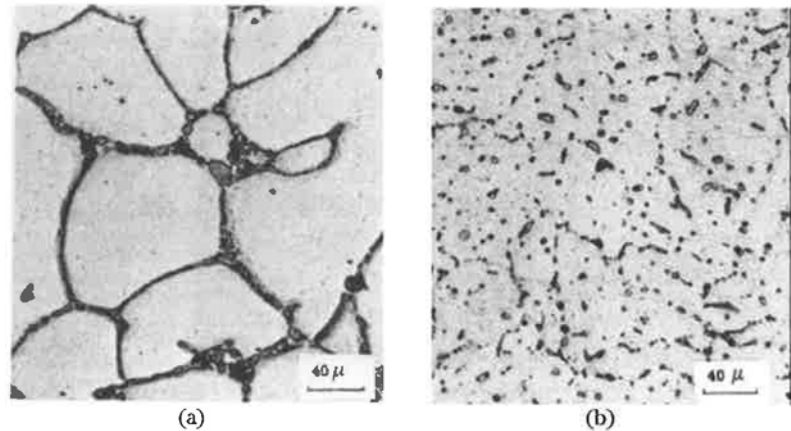


Fig. 4.2. The distribution of intermetallic phases in this aluminum-bearing alloy depends on the grain size: (a) large grain size; (b) fine grain size. [Reprinted, with permission, from *Grain Refinement in Castings and Welds*, edited by G.J. Abaschian and S.A. David, The Minerals, Metals & Materials Society, 420 Commonwealth Dr., Warrendale, PA.]

Table 4.1.
Relative Merits of Fine and Coarse Grain Sizes

FEATURE OR PROPERTY	FINE GRAIN SIZE	COARSE GRAIN SIZE
room temperature strength	high	reduced
creep resistance	poor	improved
tendency to centerline cracking	greatly reduced	high
tendency to centerline segregation	low	high
shrinkage porosity	fine, dispersed	concentrated
brittle phase distribution	fine, dispersed	may be continuous along grain boundaries
tendency to preferred grain orientation	none	significant

compound distribution pattern (Fig. 4.2b), all combine to make fine grain solidified solids more uniform in quality and properties.

An added benefit to fine grains is to be found in their inherent strength when compared to the same material with a coarser grain size. Grain boundaries block the slip process, which occurs when the yield strength of the material is reached. A larger grain boundary area found with a smaller grain size will effectively increase the yield strength of a material (Fig. 4.3). Strength considerations are of particular concern in casting manufacture where no subsequent working processes are available to change the mechanical properties.

While the preceding discussion has demonstrated that fine grain size in a cast metal is usually preferable to a coarse one, it must be kept in mind that there are a few special situations where the opposite is true. Two of the most obvious are single crystal growth and the production of castings for high temperature applications. Clearly, single crystal production requires that only one nucleus be allowed to survive. When materials are used at temperatures exceeding about 40% of their melting point, the grain boundaries that give strength at room temperature become weak and contribute to the process known as creep. Under these conditions, a coarse grain or even a single crystal is desirable. Figure 4.4 contrasts the creep behavior of fine grains, coarse grains and a single crystal of the same material. The single crystal not only lasts the longest, but also is able to resist the highest stress at temperature.

The relative benefits of fine and coarse grain sizes in cast materials are compared in Table 4.1.

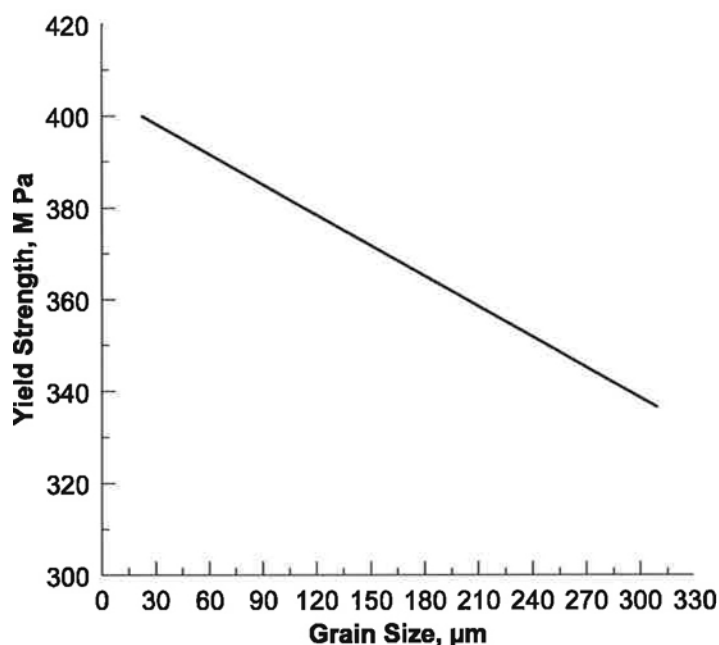


Fig. 4.3. Yield strength of aluminum 201 alloy increases as the grain size decreases. [Data taken from S. Kennerknecht, *Advanced Casting Technology*, AGARD Conference Proceedings No. 325.]

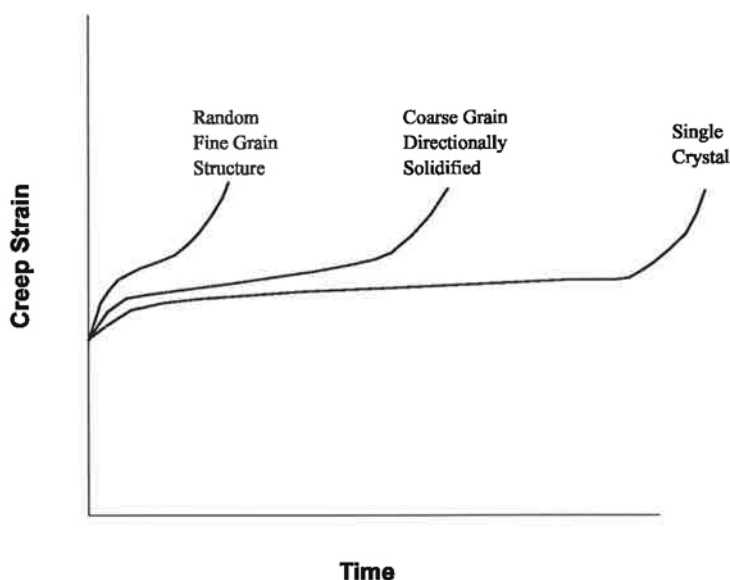


Fig. 4.4. The creep behavior is shown schematically for fine grain sizes, coarse grain sizes and a single crystal of the same material.

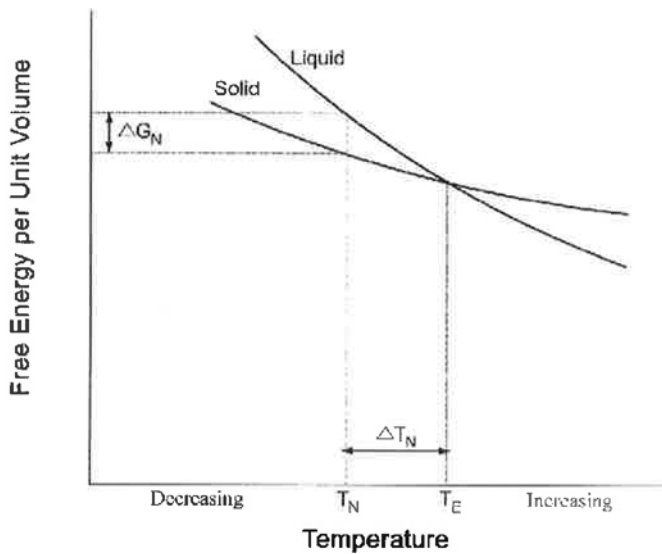


Fig. 4.5. A schematic relationship between the free energies of the solid and liquid phases is shown.

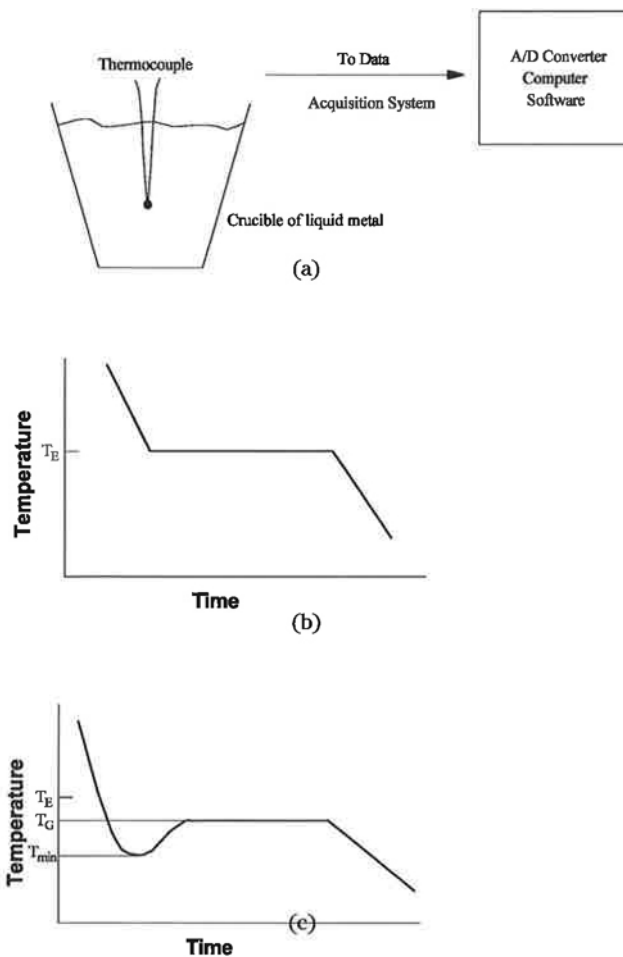


Fig. 4.6. The principles of thermal analysis are illustrated: (a) equipment for thermal analysis; (b) equilibrium cooling curve of a pure material; (c) real cooling curve of a pure metal.

NUCLEATION THEORY

THE NONEQUILIBRIUM NATURE OF SOLIDIFICATION

An understanding of how grain size can be controlled in solidification processing requires an appreciation of the simple theory of nucleation.¹ Solidification is a nonequilibrium process. It is dissipative in nature, meaning that, from an energy point of view, the process runs downhill—energy is dissipated as we begin with a hot liquid and end with a cold solid.

Figure 4.5 shows a schematic relationship between the free energies of the two phases involved in solidification, the solid and the liquid. Remembering that the phase with the lower free energy is the one that is thermodynamically stable, we note that at temperatures above the equilibrium freezing temperature, T_E , the liquid phase is stable, below T_E , the solid phase is stable and at T_E , both are in equilibrium and coexist with the same free energy. If solidification were an equilibrium process, it would occur exactly and always at the equilibrium freezing temperature. A simple experiment can be performed to illustrate that this is not the case.

Cooling curves, or thermal analysis, are often used to determine the liquidus and solidus lines on phase diagrams. A schematic of a common cooling curve setup is given in Fig. 4.6a, in which a thermocouple is placed in a small crucible of liquid and the liquid is allowed to solidify while the thermocouple records the temperature variation with time. The plot of temperature versus time is called the cooling curve. It is a thermal fingerprint of the material as it freezes, and properly interpreted can yield considerable information about the freezing process.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

Suppose we take the cooling curve of a pure material, and assume that it freezes exactly at equilibrium. The expected curve is that of Fig. 4.6b in which a plateau is evident at the equilibrium freezing temperature of T_E . It is the latent heat of fusion that maintains the temperature constant at T_E from the beginning to the end of solidification. Freezing takes place exactly at T_E , as predicted from equilibrium thermodynamics.

Equilibrium solidification as just described does not happen in reality. A more realistic result of our cooling curve experiment appears in Fig. 4.6c, where two departures from the ideal situation can be found:

- the liquid cools below T_E to some minimum temperature, T_{min} , and then rebounds to a temperature T_G
- the plateau that represents the actual solidification of the thermal analysis sample lies below T_E at T_G

These observations tell us two important facts about the freezing process. First, solidification does not begin at T_E , but, rather, the liquid undercools to some temperature, T_N , at which nucleation occurs. Latent heat evolution follows nucleation and the liquid heats up to the growth temperature, T_G , at which most of the freezing occurs. This reheating to growth temperature is called recalescence.

There is an undercooling, or departure from equilibrium, equal to $(T_E - T_N)$ necessary to cause the first solid to form. We will call this the undercooling for nucleation, ΔT_N , i.e.,

$$\Delta T_N = (T_E - T_N) \quad (4.1)$$

T_N is not necessarily at the minimum on the cooling curve. The minimum is simply the point at which the latent heat evolution exceeds heat loss to the surroundings and the system begins to exhibit recalescence. Determination of the exact value of T_N can be difficult and the minimum is often taken as equal to the nucleation temperature.

From Fig. 4.5, it is evident that the existence of ΔT_N implies a finite free energy difference, ΔG_N , required for nucleation. A thermodynamic driving force is necessary to cause nucleation.

Similarly, the growth of the solid does not take place exactly at T_E , but at some lower temperature, T_G . An undercooling for growth is necessary, equal to:

$$\Delta T_G = (T_E - T_G) \quad (4.2)$$

Again, this represents a thermodynamic driving force for the growth process. As stated earlier, solidification is most definitely not an equilibrium process. Neither nucleation nor growth takes place at the equilibrium temperature. We will return to the question of growth undercooling in the next chapter. For the moment, let us concentrate our efforts on the nucleation process.

NUCLEATION PROCESSES

Nucleation theory recognizes two types of nucleation: homogeneous and heterogeneous. Homogeneous nucleation is a process in which the nucleus arises from the bulk of the liquid itself. Liquids are known to be not completely random as far as their atomic structure is concerned, but to consist of ordered regions of a few too many thousands of atoms. These regions are in a constant state of flux, forming and dissociating with time. They become both larger and more numerous as the temperature approaches the melting point, and certainly as the temperature falls below the melting point.

While the atomic ordering present in such nanocrystalline regions may not be exactly that of the bulk solid, it is sufficiently close to allow them to act as nuclei under the right conditions. In the case of heterogeneous nucleation, the nucleus is a foreign particle present in the liquid.

Homogeneous nucleation rarely, if ever, occurs in industrial solidification, but it is easier to treat from a theoretical viewpoint. An examination of homogeneous nucleation theory serves to illustrate the important factors in nucleation while providing a convenient starting point for discussion of the more common and complex heterogeneous process.

HOMOGENEOUS NUCLEATION

The simple approach to homogeneous nucleation involves a consideration of the energies required to form a minute solid particle in a liquid bath. The particle is spherical and of the same composition as the bath. It has a radius, r , and grows at a temperature, T , which is less than the equilibrium freezing temperature, T_E . There are two energies that must be considered for such a particle:

- change in bulk free energy, ΔG_V , as the liquid transforms to the solid; and
- energy contained in the surface of the particle.

It is the surface energy that distinguishes nucleation phenomena from bulk phase transformation processes. Of necessity, nucleation involves extremely small particles having a high ratio of surface area to volume, making the surface energy an important contributor to the overall system free energy. Provision of the surface energy is the main reason for the thermodynamic driving force for nucleation.

The change in bulk free energy on formation of the spherical nucleus is given by:

$$\Delta G_V = \Delta H - T\Delta S \quad (4.3)$$

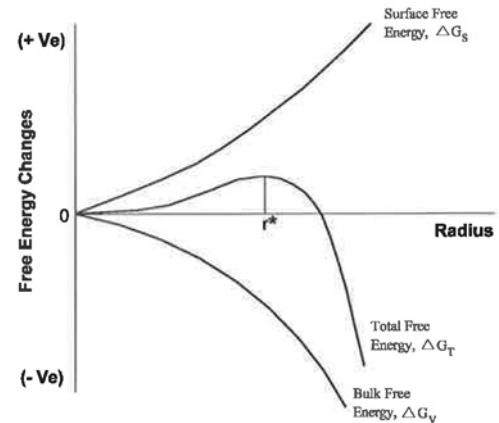


Fig. 4.7. Free energy changes involved in the formation of a particle of radius, r , are plotted versus particle size.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

The enthalpy term, ΔH , is equal to the latent heat of fusion per unit volume, L_v , while the change in entropy is L_v/T_E . Thus,

$$\Delta G_v = L_v - TL_v/T_E \quad (4.4)$$

and for the entire sphere, the bulk free energy change, ΔG_v , is:

$$\Delta G_v = (L_v - TL_v/T_E) \times 4/3 \pi r^3 \quad (4.5)$$

and when simplified, this becomes:

$$\Delta G_v = (L_v \Delta T/T_E) \times 4/3 \pi r^3 \quad (4.6)$$

This quantity is always negative at $T < T_E$, implying that the bulk liquid-solid transformation is spontaneous if the temperature is below the equilibrium freezing temperature. ΔG_v is plotted on Fig. 4.7.

The other acting energy term is the surface energy, ΔG_s . This term is positive, as it is always necessary to invest energy to create a surface.

$$\Delta G_s = 4\pi r^2 \gamma \quad (4.7)$$

where γ is the solid-liquid surface energy.

Total energy change for the particle as a whole will be the sum of the bulk and surface terms:

$$\Delta G_T = -(L_v \Delta T/T_E) \times 4/3 \pi r^3 + 4\pi r^2 \gamma \quad (4.8)$$

As seen in Fig. 4.7, the total free energy change, ΔG_T , is a strong function of particle size, r . ΔG_T is positive over a range of small particle sizes, and then rapidly becomes negative as the particle size increases. Of particular importance is the maximum on the curve, which occurs at a radius value of r^* . This is known as the critical radius. Particles of a size less than r^* will not survive in the melt, while particles larger than r^* are able to grow.

Growth involves, naturally, an increase in the value of r . If $r < r^*$, growth implies a positive change in free energy, or a thermodynamically unfavorable situation. Particles of a size

less than the critical radius will actually melt or disappear, thereby achieving their lowest free energy state. Growth is highly favored if $r > r^*$ as the ΔG_T curve rapidly becomes more negative as the particle size increases. This simple thermodynamic approach predicts that a particle must have a critical size ($r > r^*$) in order to act as a nucleus for the solidification process.

It is intuitive that nucleation should be facilitated as the temperature drops. The main reason for this is that the change in bulk free energy, ΔG_v , falls increasingly sharply as the temperature of the liquid is lowered (ΔT is increased). The change in surface energy, ΔG_s , on the other hand, is only weakly dependent on temperature and can be considered constant over modest intervals of temperature.

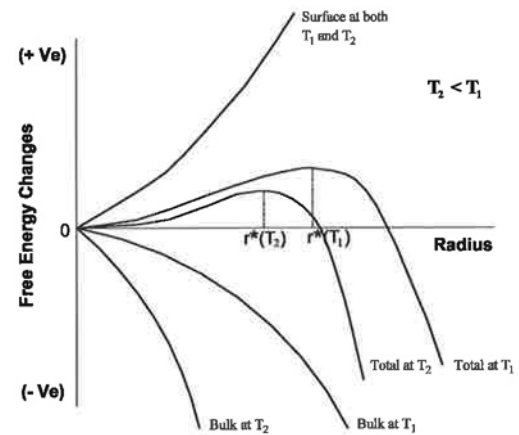


Fig. 4.8. Graph shows the variation in critical radius size as the temperature is lowered.

Figure 4.8 illustrates that the critical radius at a lower temperature (T_2) is less than at a higher temperature (T_1). Since the particles of which we are speaking arise from the liquid structure itself, chances of finding a smaller ordered region within the liquid are greater, and nucleation is more likely to occur at the lower temperature. There is, therefore, an element of chance in the nucleation process. There must be a finite probability of occurrence of the critical radius within the liquid. If this does not happen within a reasonable period of time, nucleation will simply not proceed.

The critical radius corresponds to the maximum on the ΔG_T vs. r curve. Differentiation of the expression for ΔG_T with respect to r , and setting this equal to zero, yields the following expression for r^* :

$$r^* = 2\gamma T_E / L_v \Delta T \quad (4.9)$$

If values for the undercooling necessary for homogeneous nucleation were available, it would be possible to calculate size of the critical radius. Homogeneous nucleation temperatures are not easy to obtain, but careful experimentation has resulted in some values that are reasonable.

EXPERIMENTAL VALUES OF HOMOGENEOUS NUCLEATION UNDERCOOLING

Experimental study of homogeneous nucleation in metals is hampered by the presence of foreign particles, such as oxides, which are found in all commercial melts. These particles cause nucleation to be of the heterogeneous type. In order to measure the temperatures at which homogeneous nucleation occurs, it is necessary to somehow eliminate completely all of these particles. One trick is to divide a bulk liquid into small droplets thereby isolating the foreign particles in only some of the droplets while the remainder stay completely clean.

Figure 4.9 illustrates the general idea. A volume of liquid containing three foreign particles is divided into a number of small drops represented by the squares. Only three of the drops contain a foreign particle. Measurement of the undercooling for nucleation of each individual drop will then yield two families of values—one large and the other relatively small. Large undercoolings will be found in the drops that are free of foreign particles and which nucleate homogeneously, while small undercoolings will be measured in the three drops containing a foreign particle and which cause heterogeneous nucleation. Some values from these so-called small drop experiments are given in Table 4.2 for common metals.

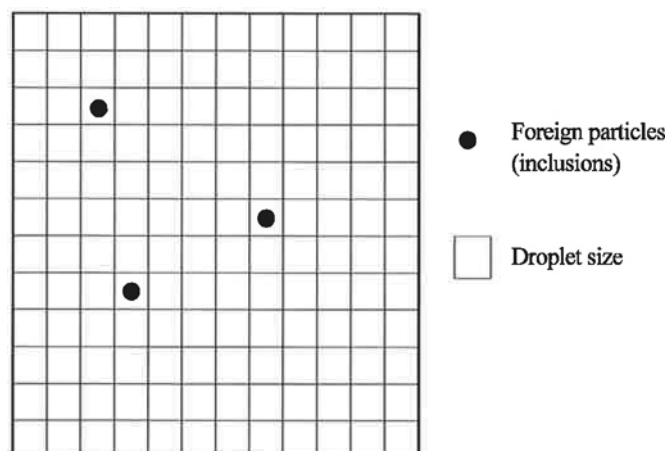


Fig. 4.9. Dividing a bulk melt containing inclusions into small drops results in most drops being free of inclusions. This technique can be used to measure the homogeneous nucleation temperature of liquid metals.

Whether or not these represent true homogeneous nucleation undercoolings is debatable, but it is obvious that the undercooling for homogeneous nucleation of pure metals is around a few hundred degrees Celsius. If appropriate values are used in equation 4.9, the size of a typical critical nucleus can be estimated at about 10^{-7} cm. Depending on the degree of atom packing in the nucleus, this spherical nucleus should contain roughly 100 atoms.

The assumptions involved in this discussion of homogeneous nucleation are very great. Bulk equilibrium thermodynamic concepts are applied to a submicroscopic system that is far from equilibrium, and it is proposed that a spherical particle will form under conditions where anisotropy of surface energy must be significant. Despite these shortcomings, the analysis has allowed us to ascertain the important features of homogeneous nucleation and set the stage for a discussion of the more important heterogeneous nucleation.

Table 4.2.
Values of Nucleation Undercooling from Small Drop Experiments²

METAL	UNDERCOOLING, °C (°F)
tin	118 (244)
copper	236 (457)
lead	80 (176)
iron	295 (563)
nickel	319 (606)
cobalt	330 (626)

HETEROGENEOUS NUCLEATION

In reality, the undercoolings measured for the nucleation of bulk metals never approach those found when homogeneous nucleation takes place. Instead of several hundred degrees, measurements range from a few tenths of a degree to perhaps 10°C (18°F). Nucleation in bulk systems is catalyzed by various foreign substrates present in commercial metals and casting systems. Among these are:

- metal oxide inclusions;
- other inclusion types, such as nitrides and carbides;
- mold wall;
- melt surface; and
- special additives (grain refiners) that promote nucleation.

In the simplest view of heterogeneous nucleation, it is assumed that a nucleus of critical radius is formed on the substrate in the shape of a spherical cap, as illustrated in Fig. 4.10a. For simplicity, the cap is treated as spherical, but in reality it probably contains various facets due to variations in the surface energy between different atomic planes of the crystalline solid and the liquid phase. An essential explanation for the relative ease of heterogeneous over homogeneous nucleation centers on the fact that a given critical radius of curvature can be formed with fewer atoms if the nucleus is only part of a sphere rather than a complete sphere.

The spherical cap of Fig. 4.10a may have the same critical radius, r^* , as the spherical nucleus (Fig. 4.10b) necessary for homogeneous nucleation, but the number of atoms required to come together to form this cap can be considerably fewer. Since the ordered arrangement of atoms

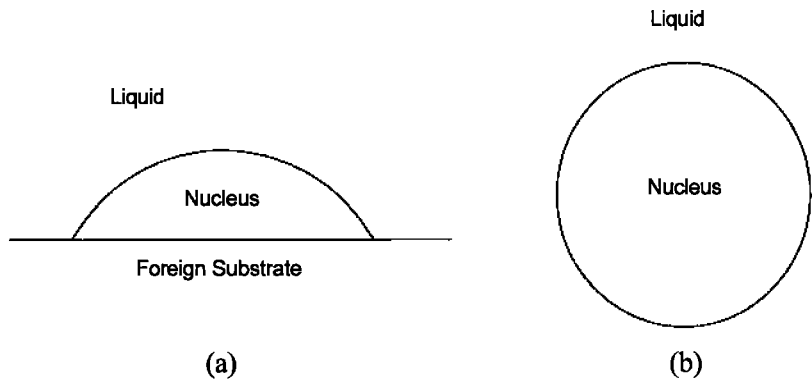


Fig. 4.10. Simple geometries for heterogeneous (a) and homogeneous (b) nucleation are illustrated.

Table 4.3.
Comparison of Cap Volume to Sphere Volume (V_c/V_s) for Various Ratios of h/r ³

h/r	V_c/V_s
1	0.5
0.8	0.35
0.5	0.16
0.3	0.06
0.1	0.007
0.01	0.00007
0.001	0.000007

in the liquid is a statistical process with smaller groupings more likely than larger ones, heterogeneous nucleation is more feasible than is homogeneous. In thermodynamic terms, this means that a smaller driving force is necessary, resulting in a lower undercooling.

The explanation is, therefore, purely geometric, depending on the height of the cap. Table 4.3 gives the ratio of the volume of a spherical cap of height, h , to the volume of the sphere, with radius, r . Very small caps of the same radius of curvature as the sphere can be formed with the expenditure of a minute fraction of the atoms required to construct the entire sphere.

To illustrate, consider a spherical cap the height of which is equal to 10% of its radius ($h/r = 0.1$). Volume of this cap is only 0.007 that of a sphere of the same radius. The number of atoms needed to form a cap with a critical radius, r^* , is, therefore, only 0.7% of the number needed to generate the same critical radius in the form of a complete sphere. Presence of the substrate has reduced the number of atoms needed to form a nucleus from the few hundred required for homogeneous nucleation to only a few. The probability of occurrence of a nucleus with only a few atoms is so much greater than that of a nucleus with several hundred atoms that heterogeneous nucleation is a far more feasible process than is homogeneous nucleation.

Size of the spherical cap can be described best in terms of the contact angle, Fig. 4.11, which is determined by the relative magnitudes of the surface energies acting at the point of nucleus, substrate, liquid contact. When the cap is geometrically stable:

$$\gamma_{LS} = \gamma_{SN} + \gamma_{NL} \cos\theta \quad (4.10)$$

and

$$\cos\theta = \frac{\gamma_{LS} - \gamma_{SN}}{\gamma_{NL}} \quad (4.11)$$

The most favorable scenario for heterogeneous nucleation occurs when the largest radius of curvature is created with the fewest number of atoms. As indicated in Fig. 4.12, this occurs when $\theta \rightarrow 0^\circ$, $\cos\theta \rightarrow 1$ and $r \rightarrow \infty$. This state is described as one of

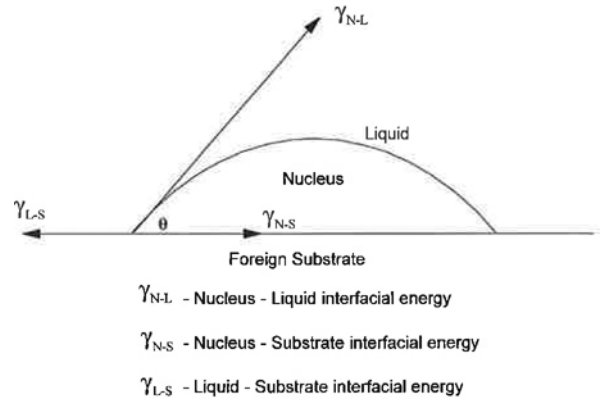


Fig. 4.11. Magnitude of the contact angle (θ) is determined by the interplay of three surface energies.

complete wetting. Contact angles that exceed 0° result in ever decreasing states of partial wetting, until $\theta = 180^\circ$, when the situation has reverted to one of homogeneous nucleation.

Achievement of complete wetting, or a zero degree contact angle, depends on relative values of the interfacial energies in the equation given above. Liquid-solid interfacial energies are all of approximately the same magnitude, being a reflection of the degree of atomic mismatch across the interface. If we say that $\gamma_{L-S} \approx \gamma_{N-L}$, then we can see that if, somehow, γ_{S-N} can be made to approach zero, or at least be very small, then $\cos \theta \rightarrow 1$ and $\theta \rightarrow 0^\circ$, i.e., complete wetting will occur.

Many features contribute to the value of an interfacial energy, but the most important is the degree of atomic matching across the interface. If the atoms on one side of the interface match well with those on the other, one phase will usually have a fixed crystallographic or epitaxial relationship with the other, and a very low energy interface will be formed. Epitaxial relationships are found when the atomic arrangement on at least one atom plane in each material is almost the same.

This usually occurs when each phase has the same crystal structure with very close lattice parameters. As the degree of atomic similarity across the interface decreases (crystal types and lattice parameters differ), the interfacial energy will increase progressively. The very good wetting and low contact angles that promote heterogeneous nucleation will, therefore, be found when substrates closely matching the material to be nucleated, in terms of crystal structure and lattice parameter, are present in the melt. This is the principle behind the development of chemical grain refiners for the promotion of nucleation in industrial melts.

GRAIN REFINEMENT

Grain refinement during solidification can be accomplished by either rapid cooling (chilling)

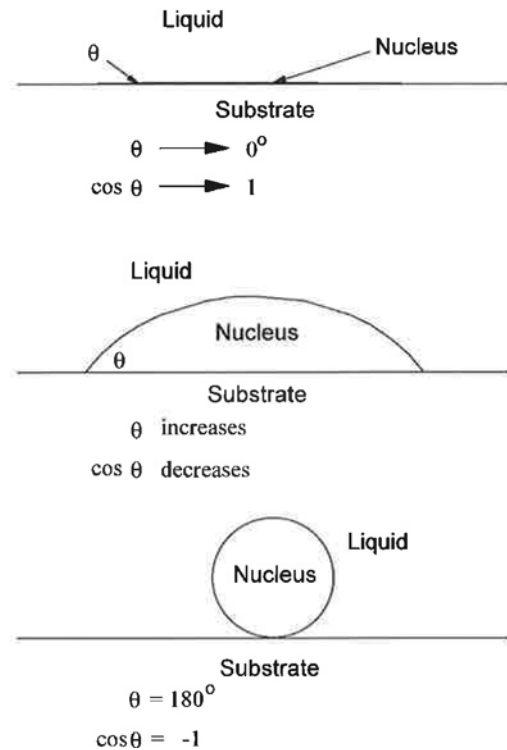


Fig. 4.12. The radius of curvature of a spherical cap depends on the contact angle, θ .

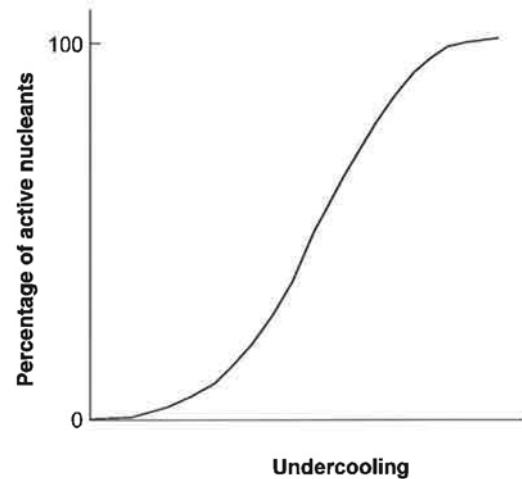


Fig. 4.13. A hypothetical spectrum of the number of nucleants that become active at various undercoolings is shown. The undercooling here is the difference between the equilibrium freezing temperature of the metal and the temperature to which the liquid cools before it begins to freeze. Larger undercoolings imply lower liquid temperatures before freezing begins.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

of the liquid, or by the addition of certain elements to the melt for the express purpose of promoting nucleation (chemical grain refinement).

CHILLING

Many casting processes are designed so that heat is removed rapidly from the liquid, e.g., pressure diecasting or the permanent mold casting of thin sections. Such chilling of the liquid promotes significant heterogeneous nucleation and, as a result, rapidly solidified castings have a fine grain size. Liquid metals contain a wide variety of potential nucleants, in the form of foreign particles, which become active at various degrees of undercooling depending on the nature of the particle (Fig. 4.13).

On slow cooling, the liquid is caused to undercool, by only a small amount, below its equilibrium freezing temperature. A small fraction of the potential nuclei are active and a coarse grain structure results. If, however, heat is extracted rapidly from the liquid phase, the temperature of the liquid can be caused to fall significantly below the liquidus temperature, thus achieving a high undercooling. Most, if not all, of the potential nuclei are able to act and a fine grain size results.

CHEMICAL GRAIN REFINEMENT

The rapid heat removal necessary to achieve significant grain refinement by chilling is possible only for certain casting processes. Medium to large size castings and ingots are not amenable to significant refinement by means of chilling, and other forms of grain refinement must be used.

Chemical grain refinement involves adding to the melt either substrates, which in themselves act as nuclei, or elements that react in the liquid phase, with the solvent or major alloying elements, to produce solid nucleant particles. Chemical grain refinement of the nonferrous metals, aluminum, magnesium and copper, is the most common industrial example. Some details of the refinement of each of these metals will be discussed, but before doing that, we should consider some of the general desirable characteristics of grain refiners.

Theory indicates that grain refiners should have a crystal structure similar to the material to be nucleated. Also, they must be stable in the melt and not undergo some other reaction that would destroy the active substrate. In order to preserve the properties of the alloy being cast, grain refiners must be effective in small amounts (we do not want to create a new alloy composition), and they should not impart any deleterious properties to the alloy being refined.

ALUMINUM AND ITS ALLOYS

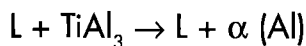
Of the three major nonferrous metals, the chemical grain refinement of aluminum and its alloys is the most developed and best understood. Great effort has been expended in this area largely because of benefits to the quality of direct chill (DC) cast ingots where cracking and segregation can be reduced substantially by proper grain refinement.

Titanium and boron are the elements usually added to aluminum just before casting to cause

chemical grain refinement. Titanium alone is effective in amounts greater than 0.15%. When boron and titanium are added together, it is possible to achieve excellent refinement at lower titanium levels. Typically, 0.05%Ti and 0.01%B are used, but the Ti/B ratio must be greater than 2.22. Titanium and boron react together to form solid particles of TiB_2 at liquid aluminum temperatures. A Ti/B ratio exceeding 2.22 implies that the melt must contain free titanium for grain refinement to be effective. Both elements are added as master alloys (often called hardener alloys) which contain titanium and boron in diluted form. Many are available from a number of suppliers. Some typical compositions include: Al-10%Ti or Al-5%Ti-1%B.

While the technology of grain refinement is reasonably well advanced, our understanding of the underlying mechanisms remains relatively poor. The difficulty is that heterogeneous nucleation is a process relying on the surface characteristics of minute particles suspended in metallic liquids at many hundreds of degrees Celsius. Direct observation of these particles is not possible, nor is a study of the nature of their surface in contact with the liquid. Explanations of the mechanisms of chemical grain refinement must, of necessity, rely on indirect, "after the fact," experimental observation. While literature on the subject is voluminous, certain facts that aid in an explanation of aluminum grain refining mechanisms are becoming better established.

The peritectic reaction found in the Al-Ti system and evident on the phase diagram of Fig. 4.14a is critical to the refinement of pure aluminum and wrought alloys. The reaction,



which proceeds at titanium levels in excess of 0.15%, results in the formation of $\alpha (Al)$, in all probability coating unreacted $TiAl_3$ (Fig. 4.14b). The $\alpha (Al)$ phase is a dilute solid solution of titanium in aluminum. It has a face centered cubic (FCC) crystal structure, a lattice parameter close to that of pure aluminum and, therefore, is an ideal heterogeneous nucleant.

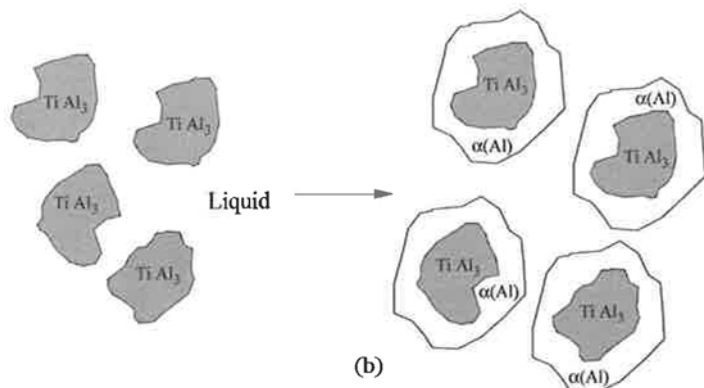
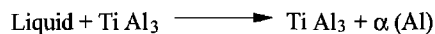
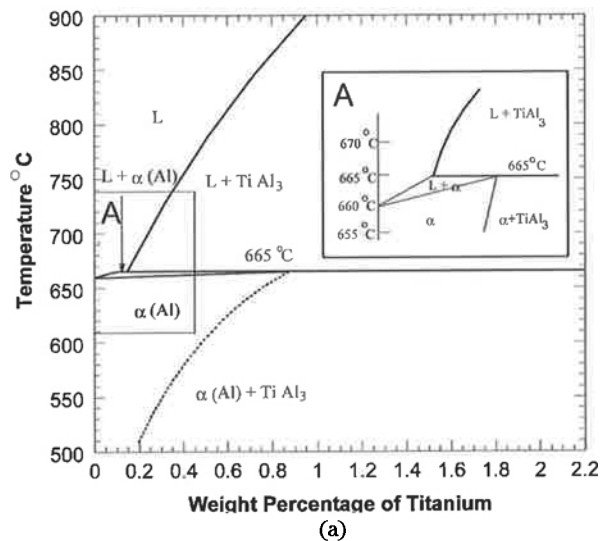


Fig. 4.14. The mechanisms of titanium grain refinement of aluminum is illustrated; (a) Al rich end of the Al-Ti phase diagram; (b) formation of $\alpha (Al)$ rings on unreacted particles of $TiAl_3$.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

This peritectic mechanism explains several of the observations associated with chemical refinement by Ti and B. In the presence of Ti alone, it is not possible for the reaction to occur unless %Ti > 0.15%. Grain refiners are known to “fade,” i.e., their effectiveness decreases with time. Fading can be caused either by the settling of TiAl_3 particles in the melt, or by their gradual dissolution after they are released from the higher titanium-containing master alloy. Peritectic reactions occurring at a low concentration of the solute element would appear to provide a general mechanism for grain refinement in which a suitable substrate is produced in a melt by a phase reaction.

The role of boron in the Ti-B combination is less clear. It has been suggested that boron in the Al-Ti-B ternary system acts to shift the peritectic to lower titanium levels, making titanium more effective as a refiner.⁴ Alternatively, TiB_2 has been proposed as the effective nucleant, but in the absence of excess Ti, the TiB_2 particles are pushed to the grain boundaries and are not found in the grain centers where nuclei would be expected. A third hypothesis proposes that a titanium-rich

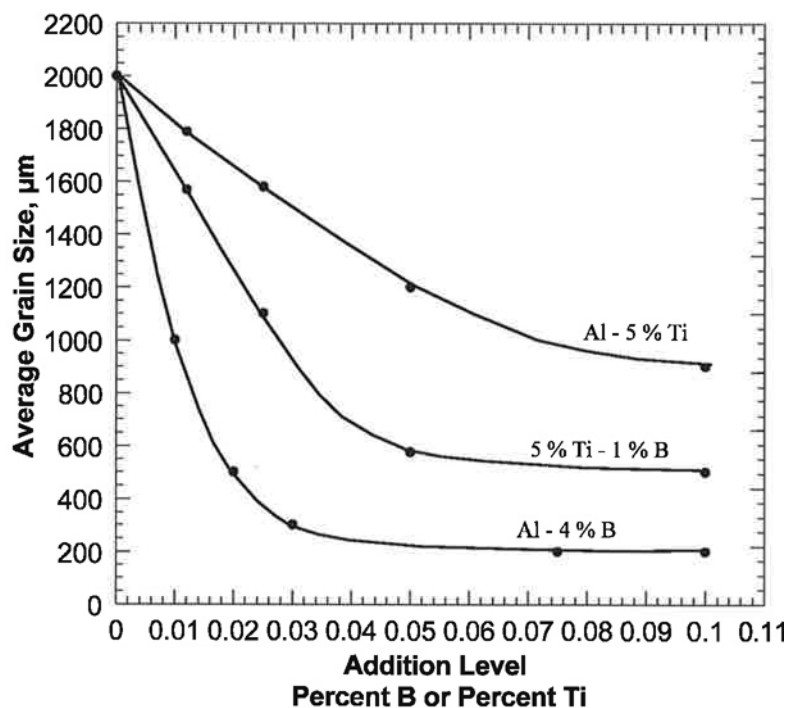


Fig. 4.15. The change in grain size of a cast 356 (Al-7%Si-0.3%Mg) alloy is shown with different grain refiner additions. [G.K. Sigworth and M.M. Guzowski, *AFS Transactions*, vol 93, pp 907-912, (1985).]

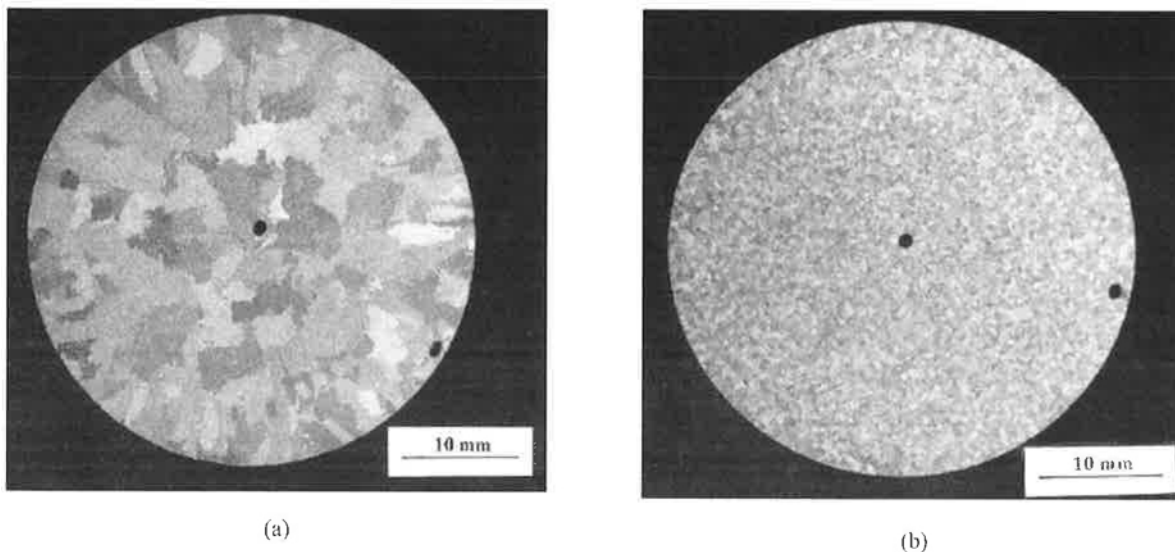


Fig. 4.16. The effect of grain refinement on an aluminum 319 foundry alloy is illustrated: (a) non-grain refined; (b) grain refined with 100 ppm Ti and 5 ppm B. Each sample was solidified at the same cooling rate. The black spots correspond to the location of thermocouples used to measure the cooling rate. [Photograph courtesy of Dr. David Gloria.]

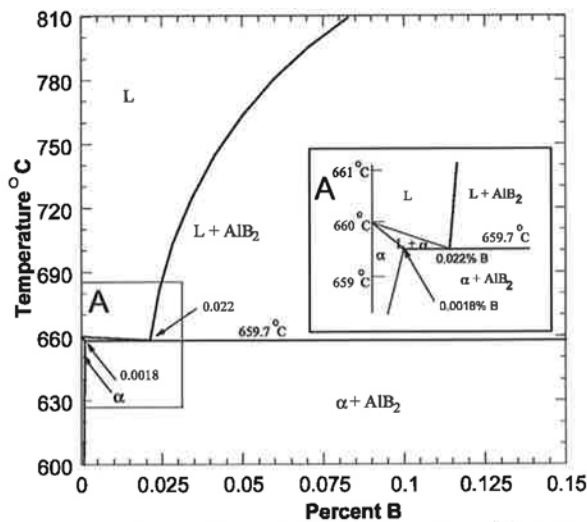


Fig. 4.17. The Al rich end of the Al-B phase diagram is illustrated.

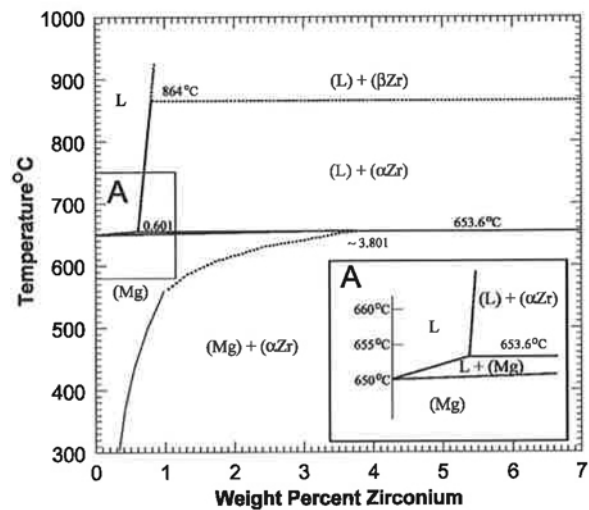
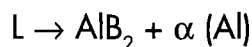


Fig. 4.18. The Mg rich end of the Mg-Zr phase diagram is illustrated.

layer forms at the TiB_2 interface. Eventually, this layer transforms to TiAl_3 , subsequently undergoing the peritectic reaction described previously. In effect, the TiB_2 has nucleated the TiAl_3 necessary for the refinement.⁵

For many years, grain refinement of aluminum foundry alloys of the Al-Si type relied on technology borrowed from the primary aluminum industry. This situation is now changing with the demonstration that boron is a more effective refiner for these alloys than are either titanium or titanium-boron combinations. Illustration of this is provided in the graph of Fig. 4.15 showing the change in grain size of a 356 alloy (Al-7%Si-0.3%Mg) with either titanium or boron content. New master alloys based on the Al-B system have been developed specifically for the grain refinement of Al-Si foundry alloys. An example of the grain refinement of an aluminum foundry alloy is shown in Fig. 4.16b.

Interestingly, it has been shown that boron, by itself, is quite ineffective in the refinement of pure aluminum. The reasons for this have not been definitely established, but it is proposed that the eutectic reaction,

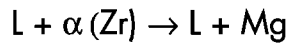


which occurs in the Al-B system (Fig. 4.17), leads to the formation of the α (Al) product as an active nucleus for the aluminum phase in Al-Si alloys. The eutectic reaction itself likely requires a few degrees of undercooling, resulting in the α (Al) formation at a temperature below the equilibrium freezing temperature of pure aluminum (660.6C, 1221.1F). The reaction will not be able to nucleate pure aluminum because the nuclei will be produced at too low a temperature. Liquidus temperatures of Al-Si alloys are much lower, in the range of 620C (1148F). At this temperature, the α (Al) can exist as a solid substrate and be effective for nucleation.⁶

MAGNESIUM AND ITS ALLOYS

Many alloys of magnesium contain aluminum in levels up to 10%. These alloys can be grain refined by adding carbon as graphite powder or as hexachloroethane tablets (C_2Cl_6). Aluminum in the alloy reacts with the carbon to form aluminum carbide, Al_4C_3 , which, like magnesium, has a hexagonal crystal structure. On the basal plane, the lattice parameters are very similar: $a = 0.321\text{nm}$ in Al_4C_3 and $a = 0.333\text{nm}$ in Mg. The basic requirements of crystallographic similarity are met.

Magnesium alloys containing no aluminum are grain refined by adding about 0.7% of zirconium (Zr). This appears to be another example of a peritectic reaction leading to grain refinement (Fig. 4.18). The reaction



forms a solid solution based on magnesium that is the effective nucleant.

COPPER AND ITS ALLOYS

Cast copper-base alloys, such as the various brasses and bronzes, are less frequently grain refined than are aluminum and magnesium alloys. Grain refinement actually has been found to be detrimental to some of the long freezing range bronzes and red brasses. When grain refined, their normally well dispersed microporosity becomes concentrated as macroscopic layer porosity, which creates large defects in the cast product.

Grain refiners for alloys that are refined include zirconium in amounts of about 0.5% and iron (Fe) at the 1% level. In alloys requiring a low iron concentration, such as aluminum bronzes and beta brasses, mixtures of 0.03%Zr with 0.02%B provide good grain refinement. Master alloys, fluxes or zirconium sponge can be used as additives.

Grain refinement of copper-base alloys has not been studied to any great extent at the scientific level, and the mechanisms involved are not at all clear. The Cu-Fe system contains a peritectic reaction at about 3%Fe, which could account for the grain refining ability of iron. Both the Cu-Zr and Cu-B systems exhibit eutectic reactions, producing a copper solid solution at temperatures above the liquidus of some commercial alloys. A mechanism similar to that proposed for the boron refinement of Al-Si alloys may operate here, but more research is necessary to substantiate any proposed mechanism.

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chapter 5

GROWTH OF PURE MATERIALS

AT THE SOLID-LIQUID INTERFACE

Metallurgical microstructures found in castings and ingots are a result of the growth stage in the freezing process. Growth of the solid from the liquid occurs by transfer of individual atoms or molecules from the liquid phase to the solid, where they are incorporated into the crystal structure of the solid. Pure metals are among the simplest of materials, and their growth takes place by the transfer of single atoms from one phase to the other. More crystallographically complex materials, such as polymers, grow by the transfer of molecules from the liquid to the solid. This atom by atom (or molecule by molecule) process is complicated and involves several steps, any one of which may be slow enough to control the rate of the process. These steps are:

- transport of the atomic species through the liquid to the solid-liquid interface, with diffusion being the transport mechanism;
- attachment of the atom or molecule to the solid-liquid interface with an associated release of energy; and
- movement of the atom or molecule by surface diffusion to a location on the liquid-solid interface that is consistent with the crystal structure of the solid. This final step is important because crystalline solids have a well-defined crystal structure that must be respected during the freezing process.

On an industrial scale, the metals cast are virtually always alloys. Their solidification is more complex than that of a pure metal because more than one atom type is present. Our objective is to understand some of the basics of the freezing process, and we begin by examining how pure metals freeze. The more complicated behavior of alloys will be discussed in Chapter 6.

One of the simplest and most useful approaches taken for an understanding of what is involved in solidification is that described by Chalmers¹ in his 1964 book on this subject. Solidification is treated as a chemical reaction involving an activated state. Two atomic processes are possible at the interface. Atoms may leave the solid and enter the liquid (melting), or they may leave the liquid to enter the solid (freezing). In either case, they must pass through some higher energy-activated state. Relative energies of the liquid, solid and activated state are indicated schematically in Fig. 5.1.

Atoms in the liquid are at a higher energy than those in the solid, the difference being the latent heat that is given out on freezing. The activation energy for melting is greater than that for freezing by an

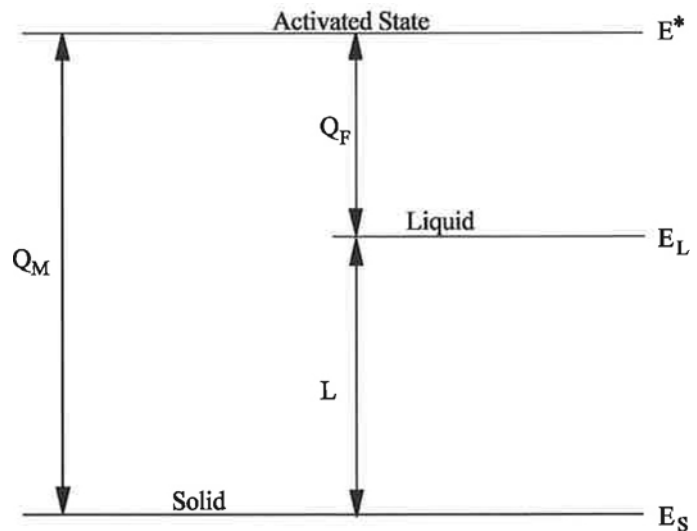


Fig. 5.1. Relative energies of the solid, liquid and activated states are shown.

amount equal to the latent heat. As with all classical activation energy approaches to reactions, the nature of the so-called activated state is not very clear. Perhaps the easiest way to visualize the physical significance of Q_F , the activation energy for freezing, is to regard it as being due partly to diffusion in the liquid to bring the atom into contact with the interface, and partly as the energy necessary to place the atom in the correct location with respect to the crystallography of the solid.

The solid-liquid interface is a location of intense atomic activity with atoms both leaving and entering the interface. The number of atoms leaving (rate of melting, R_M) per unit time is:

$$R_M = N_s V_s A_m G_m \exp(-Q_M/RT) \quad (5.1)$$

and the number entering (rate of freezing, R_F) is:

$$R_F = N_l V_l A_f G_f \exp(-Q_F/RT) \quad (5.2)$$

where

N_s, N_l are the number of atoms per unit area in the solid and liquid, respectively, at the solid-liquid interface;

V_s, V_l are the vibrational frequencies of atoms in the solid and liquid, respectively (the Debye frequency). It is assumed that atoms will move from one phase to the other only if they vibrate in the correct direction so as to be released from their parent phase;

G_m, G_f are geometric factors in the solid and liquid, respectively, which express the geometric difficulty for an atom to leave that phase. They represent a type of escape angle;

A_m, A_f are, again, geometric factors (Chalmers calls them accommodation factors) that describe the geometric difficulty for an atom or molecule to enter the liquid or solid phase, respectively;

R is the gas constant; and

T is the absolute temperature.

RATE OF SOLIDIFICATION

When temperature equals exactly the equilibrium freezing temperature, T_E , the melting and freezing processes occur at the same rate but in opposite directions so that:

$$R_M = R_F \quad (5.3)$$

There is no net motion of the solid-liquid interface even though there is intense atomic or molecular activity there. This is, of course, the definition of equilibrium.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

In order to cause the system to freeze, this equilibrium must be disrupted so that the rate of freezing exceeds the rate of melting and there is a net addition to the solid. When this occurs, the solid phase will grow at the expense of the liquid. The only way to cause this to happen is to allow the temperature to fall below the equilibrium freezing temperature to one we will call the growth temperature, T_g . A departure from equilibrium, or an undercooling for growth, ΔT_g , is necessary to cause solidification to occur. The presence of this undercooling was illustrated on the simple cooling curve described in Chapter 4. Hence:

$$\Delta T_g = (T_E - T_g) \quad (5.4)$$

At the growth temperature, $R_F > R_M$ and the net rate of freezing is given by:

$$R = (R_F - R_M) = N_l V_l A_l G_f (\exp - Q_F/RT) - N_s V_s A_s G_m (\exp - Q_M/RT) \quad (5.5)$$

Unfortunately, many of the terms in this equation are virtually impossible to determine with any degree of confidence, and the best that is possible is to plot a result that is at least functionally correct after estimating values of Q_M and Q_F from the activation energies for viscous flow. From the typical plot given in Fig. 5.2, we can deduce the important fact that the rate of freezing depends on the magnitude of undercooling for growth, i.e.:

$$R_F = f(\Delta T_g) \quad (5.6)$$

At temperatures above T_E , growth is negative—the system melts rather than freezes. As the temperature falls below T_E and the growth undercooling increases, the freezing rate also increases to a maximum value, R_{max} . With a further lowering of the temperature, we see a decrease in the freezing rate until, at some point, the rate becomes zero and solidification ceases. At these low temperatures, the thermodynamic driving force for solidification is great, but the transport of atoms from the liquid to the solid-liquid interface becomes increasingly difficult because of the slower rate of diffusion in the liquid. The regular atomic arrangement characteristic of a crystalline solid cannot

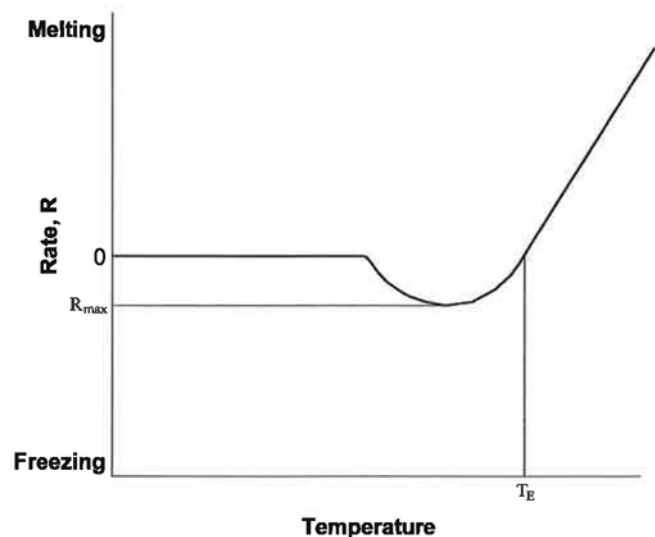


Fig. 5.2. Schematic shows the rate of freezing versus temperature.

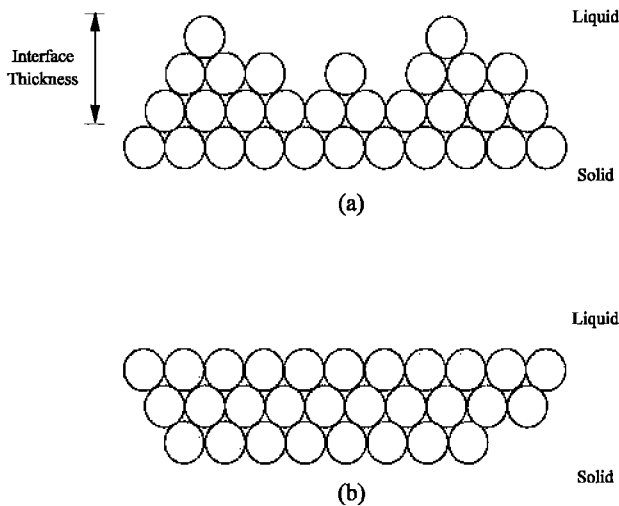


Fig. 5.3. Atomic arrangements for the two types of solid-liquid interface are shown in (a) atomically rough interface and (b) atomically smooth interface.

form. Instead, the solid adopts the atomic structure of the liquid, and forms a glass.

For many materials, such as metals, it is extremely difficult to reach a growth undercooling sufficiently large to create a glassy structure. Certainly for castings and ingots, this is never even a remote possibility. Nonmetals, such as slag and polymers, with their complex liquid structures, have diffusion coefficients that decrease rapidly with temperature, and in these materials, glassy phases are a real possibility.

The exact form of equation 5.6 depends on the actual atomistic mechanism of growth which, in turn, depends on the atomic nature of the solid-liquid interface. Two extremes of

interface structure are illustrated in Fig. 5.3. Atomically rough solid-liquid interfaces are often called diffuse interfaces. They have an atomic thickness that is at least several atom layers and are characterized by atomic hills and valleys. It is not possible to ascribe a particular atomic plane to a rough interface, because, as shown in Fig. 5.3a, different areas on the interface can be associated locally with different crystallographic planes.

Atomically smooth (Fig. 5.3b) or faceted interfaces form the other extreme. A distinct transition occurs over one atom layer from the solid to the liquid phase, and the interface is easily and unambiguously determined to be a specific crystallographic plane of the material. Materials with rough or smooth interfaces behave differently when they freeze. We will see later how it is possible to predict the atomic nature of the interface for a specific material. For the moment, let us concentrate on the kinetics of freezing and how that changes with the atomic nature of the interface.

KINETICS OF SOLIDIFICATION

The functional relationship between the driving force for freezing (growth undercooling) and the resultant rate of solidification is called the kinetics of solidification. Several kinetic laws can be identified, depending on the atomic structure of the solid-liquid interface.

NORMAL OR CONTINUOUS GROWTH

If the interface is atomically rough, there are no preferred locations for atom attachment; in other words, all of the atom sites are equivalent. Atomic attachment is completely random and the rough nature of the interface is preserved as growth proceeds, although the details of the atomic hills and valleys will fluctuate with time. If one could observe the atom addition process, it would resemble atomic rain falling onto the interface with the raindrops (in reality, the atoms) adhering at whatever location they happen to fall. This continuous growth can be described by the relation:

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

$$R = C(D_L/D_{LM})\Delta T_g \quad (5.7)$$

where

R is the linear rate of growth;

C is a constant;

D_L is the diffusion coefficient of atoms in liquid at the growth temperature;

D_{LM} is the diffusion coefficient of atoms in liquid at the melting temperature; and

ΔT_g is the undercooling required for growth, $(T_E - T_g)$.

We will not dwell on the value of the constant, C . It contains a plethora of terms, many of which are very difficult, if not impossible, to quantify with any degree of certainty. Instead, let us concentrate on the form of equation 5.7. If the growth undercooling is small, T_E is approximately equal to T_g , with the result that $D_L \cong D_{LM}$, and the equation becomes:

$$R = C\Delta T_g \quad (5.8)$$

indicating that the freezing rate varies linearly with undercooling (Fig. 5.4a). This situation exists with simple metals, where growth undercoolings are typically in the range of 10^{-2} to 10^{-4} °C (10^{-2} to 10^{-4} °F).

It is interesting to note that if considerable growth undercoolings can be developed so that $T_g \ll T_E$, then the temperature dependence of the diffusion coefficients will lead to an ever decreasing value of D_L , and the freezing rate will decrease progressively after some maximum value has been reached. If the temperature can be lowered sufficiently before complete solidification takes place, a glassy structure may be produced when the freezing rate becomes zero (Fig. 5.4b).

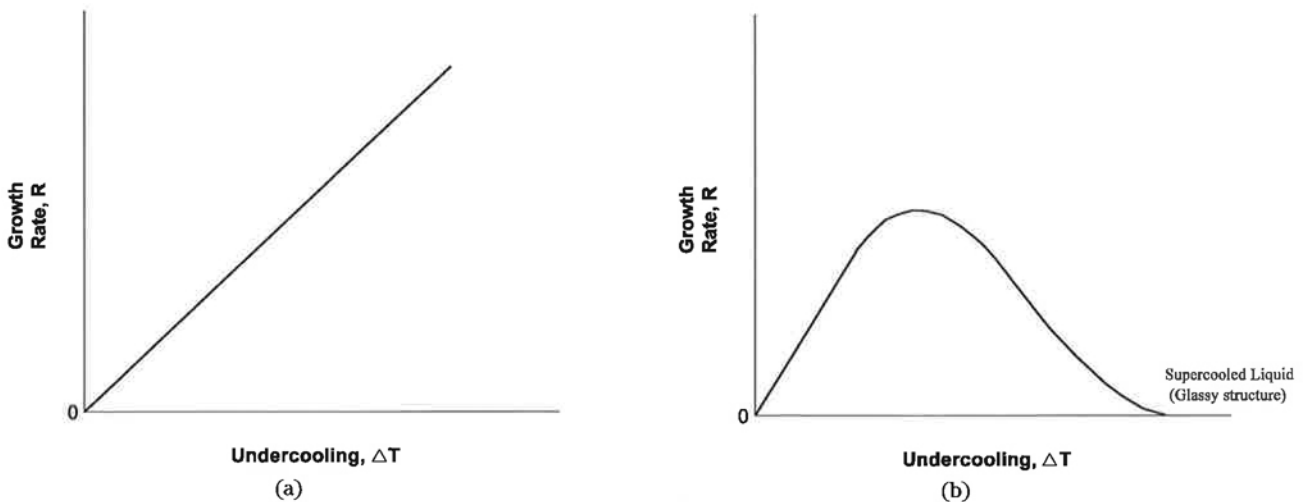


Fig. 5.4. A growth rate undercooling curve is given for a material exhibiting normal or continuous solidification kinetics: (a) simple linear kinetics; (b) linear growth kinetics that reach a maximum and then decrease to zero at a low temperature.

TWO DIMENSIONAL NUCLEATION AND GROWTH

While atoms can be added easily to an atomically rough interface, the opposite is true of an atomically smooth interface. A single atom located on a smooth interface has little opportunity to form bonds with adjacent atoms because of the lack of atoms in the interface plane. The only possible bonding will be with those atoms directly below it on the smooth interfacial plane. If the interface were a close-packed plane, a maximum of three nearest atoms would exist. Large undercoolings become necessary under such conditions to ensure that the atoms stay bonded to the solid.

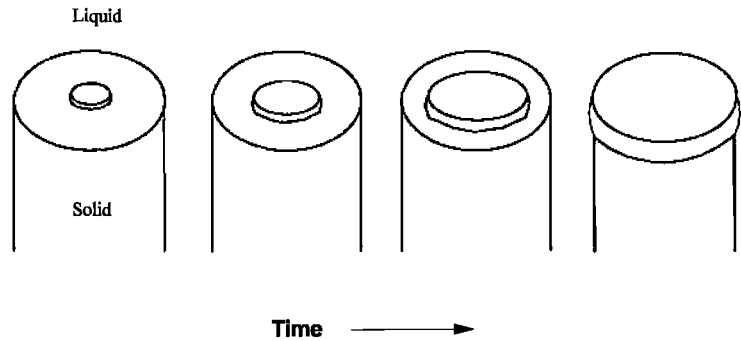


Fig. 5.5. Layer growth involving nucleation and sideways growth of a platelet on the interface is shown.

Solidification on an atomically smooth interface can be made somewhat more favorable if a plate-like surface nucleus is formed on the interface. This nucleus provides a step at which further growth can more easily occur due to the possibility of bonding not only with atoms on the smooth interface plane, but also with atoms along the edge of the surface nucleus. The nucleus will expand in a sideways direction parallel to the interface until it has completely covered the interface. Layer growth occurs as illustrated in Fig. 5.5, and a new surface nucleation event becomes necessary after completion of each layer. Growth is discontinuous and follows the kinetic law:

$$R = C_2(D_L/D_M) \exp(-C_3/\Delta T_g) \quad (5.9)$$

where

C_2 and C_3 are constants and the other terms are as defined previously.

The graph of Fig. 5.6 depicts this kinetic law. A typical nucleation behavior is exhibited as a result of a finite range of undercoolings over which no growth can occur because the undercooling is insufficient to allow surface nucleation. Once nucleation does take place, growth is very rapid until the layer has completely covered the interface. The process then begins again with the nucleation of another atomic layer and its subsequent growth. Viewed at the atomic level, freezing consists of multiple nucleation and growth cycles.

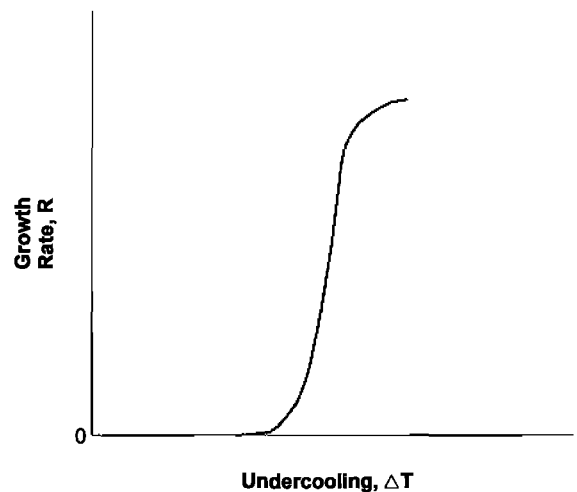


Fig. 5.6. The variation in growth rate with undercooling is shown for a 2D nucleation and growth mechanism.

DISLOCATION-AIDED GROWTH

Crystallographic defects can play important roles in solidification phenomena. One of the best examples of this is dislocation-aided growth in a material with an atomically smooth interface. The benefits of a ledge or step on the interface were outlined previously. A good example of how a crystallographic defect can aid in the freezing process is seen when a screw dislocation intersects the solid-liquid interface. A self-perpetuating step, at which atom attachment can occur, is formed at the point of intersection.

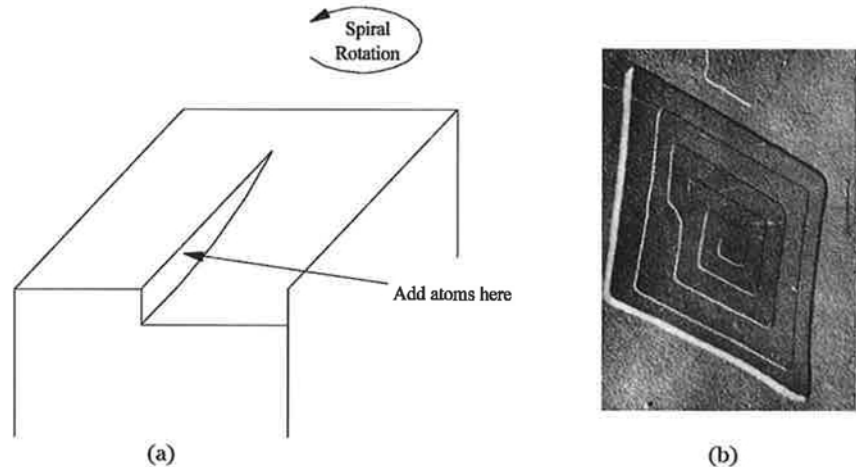


Fig. 5.7. (a) A self-perpetuating step is produced at the point where a screw dislocation intersects the interface; (b) Pyramidal steps on the surface of a crystal of paraffin crystallized from petroleum ether result from screw dislocation growth. [Reproduced from F.C. Frank, *Advances in Physics*, vol 1, p 91, (1952).]

The freezing mechanism on the atomic scale is shown schematically in Fig. 5.7a. As atoms are added at the step to take advantage of the extra bonding possible, the step rotates in a counter-clockwise direction and the solid-liquid interface advances. Unlike the previous case, the step is never destroyed and no new nucleation events are necessary. Pyramidal steps resulting from screw dislocation growth can sometimes be observed on the free surfaces of materials in which this growth mechanism is important. An example is shown in Fig. 5.7b.

Analysis of screw dislocation growth yields the following relationship, illustrated graphically in Fig. 5.8.

$$R = C_4(D_L/D_{LM}) \Delta T_g^2 \quad (5.10)$$

SUMMARY OF KINETIC LAWS

Experimental verification of the various kinetic relationships is difficult because of the often small undercoolings at the interface, which cannot be accurately measured. If the undercooling is increased with a view to making its measurement easier, the rates of freezing often become so large that they, too, present measurement difficulties. This is particularly true of metals, but data has been obtained from other systems, verifying at least the general functional relationship. An example is given in Fig. 5.9.

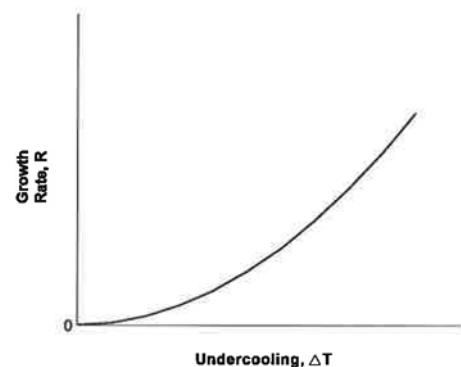


Fig. 5.8. The growth rate/undercooling relationship for screw dislocation growth is illustrated.

Theory predicts that at high undercoolings, all materials should solidify by normal or continuous growth. The driving force for the phase change is so great that atoms are forced onto the interface, and the site discrimination characteristic of atomically smooth interfaces is lost. Figure 5.10 summarizes the various relationships. Note that metals exhibiting normal growth kinetics solidify the fastest at any undercooling, and at small undercoolings, they freeze significantly faster than materials transforming by either of the other two mechanisms.

PREDICTION OF INTERFACE TYPE

The preceding discussion of various kinetic laws governing solidification makes it clear that the atomic nature—rough or smooth—of the solid-liquid interface is an important consideration in determining how materials freeze. One of the cornerstones of solidification theory was laid in 1958 when K.A. Jackson developed a simple method to determine the atomic nature of the interface. His analysis is a thermodynamic one in which he calculates the change in free energy of an initially smooth interface as atoms are added to it. Several criticisms can be levied against details of the analysis, but it has remained viable and allows us to make certain important predictions about solidification. (See Jackson's original paper for the details of development of the analysis.)²

What concerns us here is the final result, shown in Fig. 5.11 as a plot of the relative free energy change of the interface as atoms are added to fill all available addition sites. Thus, in the Figure, $N_A/N = 0$ corresponds to the initial interface configuration with no atoms added; $N_A/N = 0.5$ means that half the sites are occupied; and $N_A/N = 1.0$ implies that all sites are occupied and the addition process could begin again.

What we see in Fig. 5.11 is a family of curves distinguished by a parameter:

$$\alpha = \frac{L}{kT_E} \left(\frac{\eta}{v} \right) \quad (5.11)$$

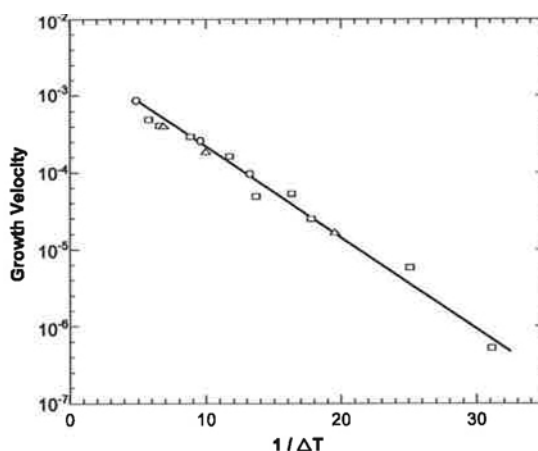


Fig. 5.9. Experimental values used to determine the linear growth kinetics of ice crystals are shown. [Data taken from W.B. Hillig, *Growth and Perfection of Crystals*, ed. R.H. Doremus et al., pp 350-360, John Wiley, (1958).]

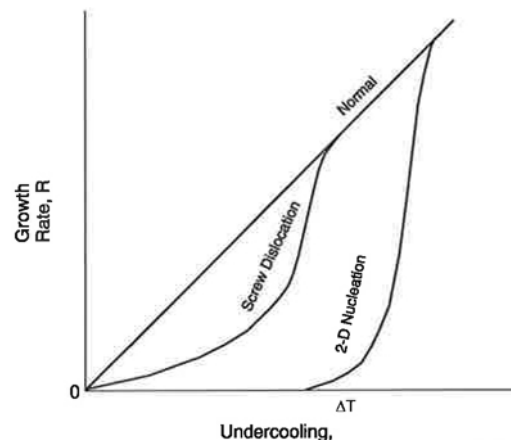


Fig. 5.10. Graph illustrates a summary of the various kinetic relationships.

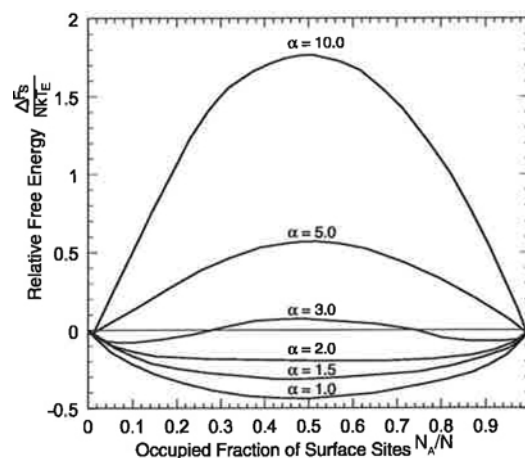


Fig. 5.11. Plot illustrates the relative free energy change of a solid-liquid interface as atoms are added to it.

where:

L is the latent heat of fusion;

k is Boltzman's constant;

T_E is the equilibrium freezing temperature;

η is the number of nearest "neighbors" an atom has in the interface plane; and

v is the number of nearest "neighbors" in the bulk solid.

This factor has become known simply as the α factor.

Now, if we accept that the solid-liquid interface will arrange itself so that it is always at the state of lowest free energy change during solidification, we can see that two types of behavior are typified by Fig. 5.11, and that the behavior depends on the value of the α factor. At high values of α (e.g., $\alpha = 10$), the state of minimum free energy change occurs when $N_A/N = 0$ or 1.0 , implying that the interface normally should consist of completed atom layers or, in other words, be an atomically smooth interface. Screw dislocation or 2D nucleation and growth kinetics should prevail.

On the other hand, when α is small, (e.g., $\alpha = 1.0$), the minimum free energy occurs at $N_A/N = 0.5$. The physical interpretation of this result is that the interface is atomically rough—at any time, only about half of the possible atom sites are occupied. Normal growth kinetics should be operative. The transition point between the two classes of behavior is usually taken as $\alpha = 2$, but the transition is not abrupt and materials with an α factor of about 2.0 may exhibit different types of interfaces on different atomic planes. We will return to this point later.

The terms in equation 5.11 are all well known material parameters allowing the α factor to be calculated with confidence, and at least a general statement made about the type of growth kinetics likely to occur. Equation 5.11 can be simplified somewhat by realizing that L/T_E is the entropy of fusion, ΔS_f , of the material. Thus:

$$\alpha = \frac{\Delta S_f}{k} \left(\frac{\eta}{v} \right) \quad (5.12)$$

High entropy of fusion materials, $\alpha > 2$, will have atomically smooth interfaces freezing by a screw dislocation or 2D nucleation and growth mechanism. Low entropy of fusion materials, $\alpha < 2$, will solidify by continuous growth on an atomically rough interface.

It is apparent that the entropy of fusion is an important consideration. Entropy changes are related to the change in order that occurs during a phase transformation. Since liquid structures all have more or less the same degree of order (or disorder), the major factor in setting the value of the entropy change is the degree of order present in the solid phase. Thus, solids having complex crystal structures will, as a general rule, have large values of the entropy of fusion; crystallographically simpler solids will have lower entropy of fusion values.

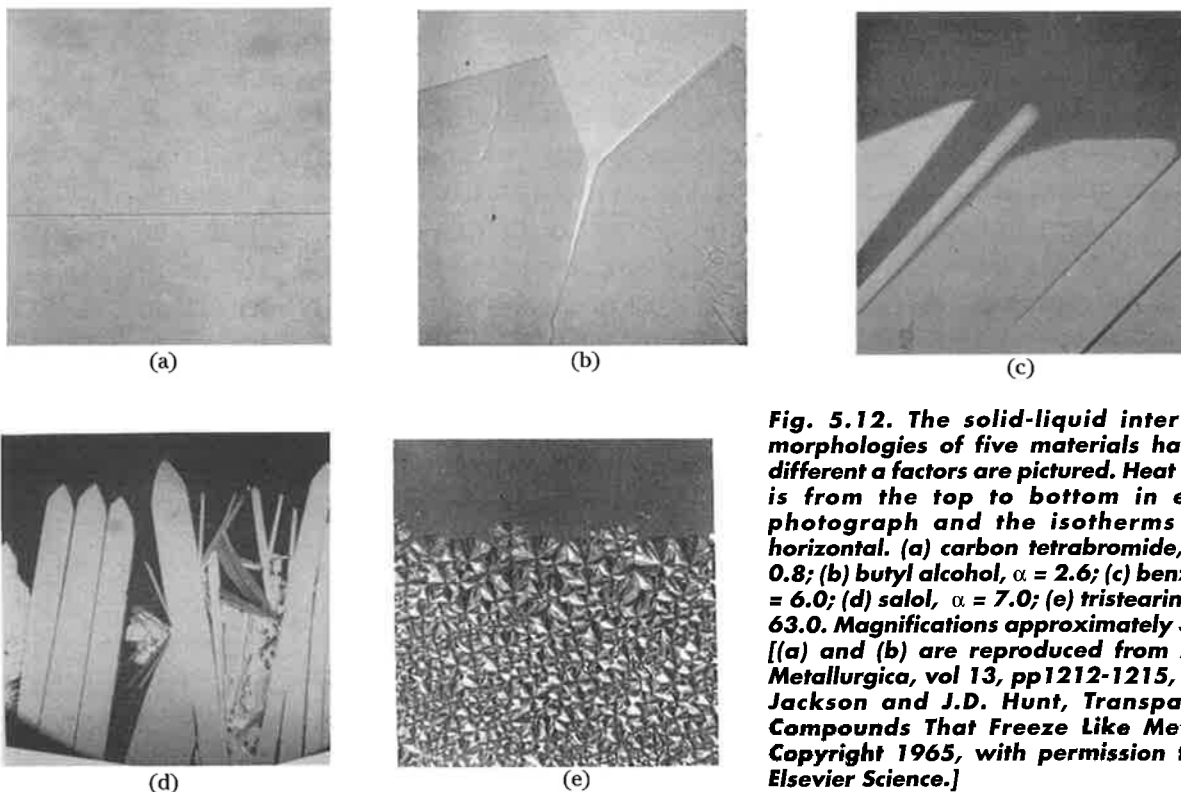


Fig. 5.12. The solid-liquid interface morphologies of five materials having different α factors are pictured. Heat flow is from the top to bottom in each photograph and the isotherms are horizontal. (a) carbon tetrabromide, $\alpha = 0.8$; (b) butyl alcohol, $\alpha = 2.6$; (c) benzil, $\alpha = 6.0$; (d) salol, $\alpha = 7.0$; (e) tristearin, $\alpha = 63.0$. Magnifications approximately 35X. [(a) and (b) are reproduced from *Acta Metallurgica*, vol 13, pp1212-1215, K.A. Jackson and J.D. Hunt, *Transparent Compounds That Freeze Like Metals*, Copyright 1965, with permission from Elsevier Science.]

This simple approach leads to the conclusion that solids with complex crystal structures will likely have atomically smooth interfaces in contact with their liquid phase, while those solids with simple crystal structures will freeze with atomically rough interfaces. Examples of solids having what might be considered complex crystal structures are: polymers, minerals and many intermetallic compounds. The most important class of materials with simple crystal structures includes the common industrial metals, which usually crystallize in the cubic or hexagonal systems.

The distinction between smooth and rough interfaces is important not only from the viewpoint of solidification kinetics, but also because of other significant differences in solidification characteristics. One of the most significant practical differences lies in the relative importance of heat flow and crystallography in the freezing process.

In the freezing of low α factor materials, such as metals, the heat flow conditions are usually more important than crystallography. This means that the simple normal growth kinetics of these materials allows their freezing to follow the heat transfer direction with ease, and chills and mold design can be used to force the solidification path into any desired direction. High α factor materials, on the other hand, tend to freeze in very definite crystallographic directions, often paying scant attention to the heat flow direction. Crystallographic considerations simply override thermal considerations.

Solid-liquid interface morphologies of several materials with different α factor values are illustrated in Fig. 5.12. These examples are chosen from optically transparent materials having a variety of crystal structures ranging from simple (carbon tetrabromide, FCC, Fig. 5.12a) to a complex polymer. The photographs were taken under conditions of directional heat flow, from top to bottom in each. The isotherms, therefore, run in the horizontal direction. Note that the interface of the lowest α factor material follows the isotherm exactly. This is the manner in which a simple industrial metal, such as iron, copper or aluminum, would freeze. A bending of the isotherm by, for example, chill insertion, would also bend the interface into exact conformity with the isotherm. Heat flow dominates.

The other four interfaces illustrated exhibit the effect of increasing the α factor or the entropy of fusion. Growth becomes more highly crystallographic and deviates from the heat flow (vertical) direction. The solid-liquid interface exists over a wide temperature range even though the material is pure and has a unique freezing temperature.

The fact is evident that different crystal planes solidify at different temperatures, or alternatively, require different undercoolings for growth. The most crystallographically complex material shown is the polymer, tristearin (Fig. 5.12e). Undercoolings at the interface are so great that nucleation and some growth occur in the liquid phase ahead of the general interface. The growth mode here is spherulitic, and bears almost no relation to the overall heat flow direction.

Table 5.1.
Solidification Characteristics of High and Low α Factor Materials

FEATURE	HIGH α	LOW α
solidification kinetics	2D nucleation and growth screw dislocation	normal (continuous)
growth undercoolings	large ($> 0.5^{\circ}\text{C}$)	very small ($< 0.1^{\circ}\text{C}$)
importance of heat flow	limited	growth in heat flow direction
importance of crystallography	high; interface is very faceted	small; interface is not faceted

The major differences in the solidification of high and low α factor materials are summarized in Table 5.1.

No mention has yet been made of the term (η/v) in equations 5.11 and 5.12. This term represents the fraction of atomic nearest neighbors possible in the bulk solid and actually present on the interface plane. For example, if the close-packed plane in a FCC material is chosen, $\eta = 6$ and $v = 12$, or $(\eta/v) = 0.5$. The α factor is, therefore, a function of the crystal plane making up the interface. In many cases, this term will have no effect on whether the plane is faceted or not, but it can be significant in materials the α factor of which is about 2. Depending on the plane in question, it may be rough or smooth, and it is quite possible to have different freezing kinetics on different planes because of variations in the quantity (η/v) . The most important class of materials that falls into this category is the semi-metals (e.g., silicon (Si), germanium (Ge), selenium

(Se), bismuth (Bi)), which have both metallic and nonmetallic qualities.

Adaptations to Jackson's original analysis have been made to account for such effects as alloying. Further mention of these will be made in Chapter 12, Polyphase Solidification, because, in some instances, the presence of alloy elements can change conclusions made from the simple Jackson analysis presented here. Nevertheless, this simple analysis does allow us to understand many of the features of the freezing of pure materials, be they metals or nonmetals.

SOLID - LIQUID INTERFACE MORPHOLOGY OF PURE METALS

Many features of the solidification structure are determined by the morphology of the solid-liquid interface. In the case of pure materials, the microscopic morphology depends on the atomic nature of the interface (rough or smooth) as well as the temperature distribution in the liquid. Highly faceted materials usually freeze with interfaces that are not planar because of the dominant effect of crystallography on the process. When the interface is atomically rough, however, the micromorphology may be either flat or highly corrugated, depending on thermal conditions present in the liquid.

Normally the bulk liquid is hotter than the solid with heat flowing from liquid to solid and then to the surrounding atmosphere. This gives rise to a positive temperature gradient in the liquid, as shown in Fig. 5.13a. If the solid-liquid interface is atomically rough ($\alpha < 2$), as for example with a simple metal, the interface will be isothermal and will be planar. That a planar geometry is stabilized by a positive temperature gradient is demonstrated in Fig. 5.13b. If a perturbation forms on the interface to disrupt the planar geometry, the tip of the perturbation will be located in a hotter region, and the growth undercooling will be reduced. Since the growth rate varies as the undercooling, the perturbation will slow allowing the rest

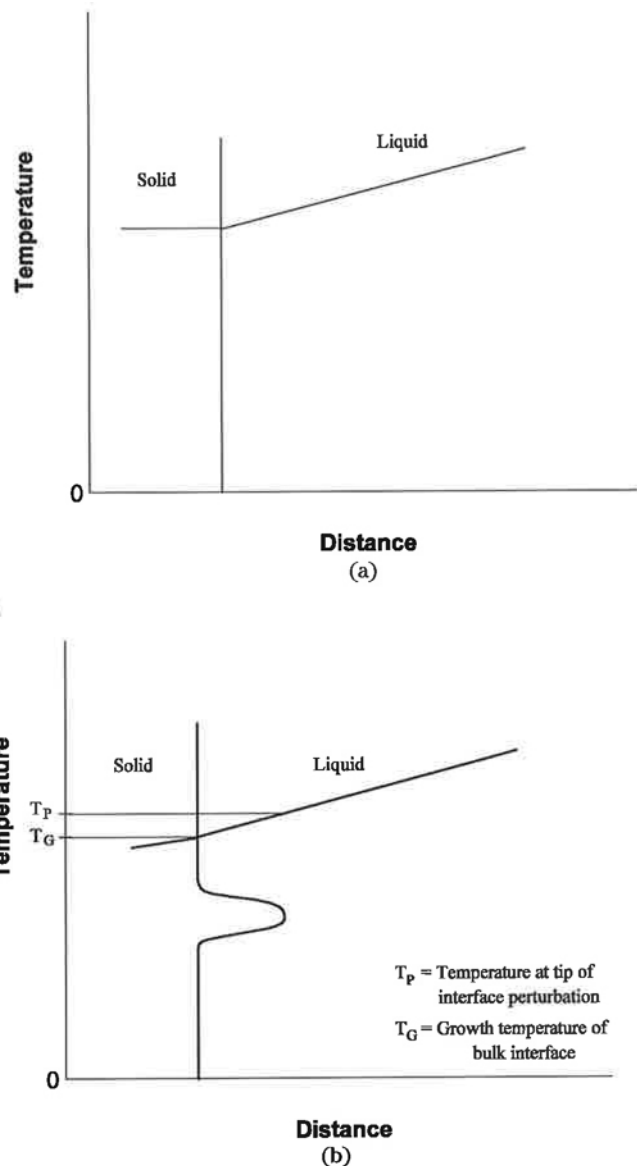


Fig. 5.13. (a) A positive temperature gradient in the liquid usually occurs in industrial solidification. (b) A planar interface geometry is stabilized in the presence of a positive temperature gradient.

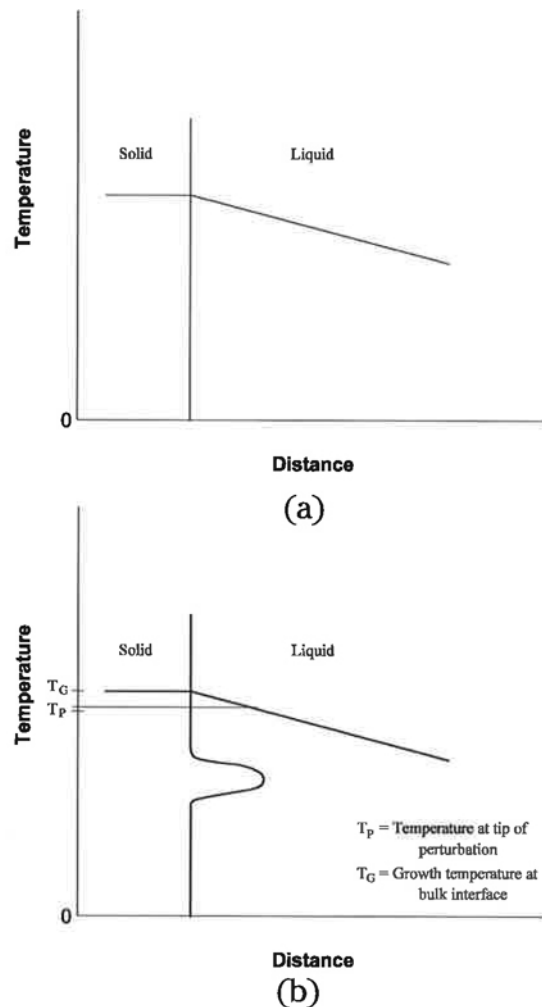


Fig. 5.14. (a) A negative temperature gradient in the liquid is illustrated. (b) Negative temperature gradients in the liquid may give rise to dendritic solidification of metals.

ing will cause the perturbation to accelerate and form a spike. Side branches may result from similar perturbations located along the edges of the spike. The tree-like result of this process is called a dendrite. Eventually latent heat evolution into the liquid will heat it so that the negative temperature gradient will be destroyed. All subsequent solidification will occur by passage of a planar interface between the dendrites as heat is now extracted through the solid. The amount of dendritic growth that can occur in this way depends on the degree of thermal undercooling and the latent heat of the material, but in practical terms, the dendritic growth of pure metals can never be more than a small percentage of the total volume.

The growth morphology of a high α factor material solidifying into a negative temperature gradient is less easy to predict. These materials have high solid-liquid surface

of the interface to catch up, restoring the original planar geometry.

Should the interface be atomically smooth ($\alpha > 2$), then, as shown in Fig. 5.12, solidification may occur over a temperature range as the growth undercooling varies from one crystallographic plane to another. The magnitude of the liquid temperature gradient will determine the width of the region over which growth takes place. Higher gradients will compress the thickness, while lower gradients will elongate it.

Negative temperature gradients in the liquid are possible (Fig. 5.14a), at least in principle, but to extract heat through the liquid for any sustained period of time requires special design of the solidification system. In practice, this situation may arise for short transient periods when pouring into a cold mold. Chilling of a layer of liquid in contact with the mold wall can take place, and for a period of time this liquid layer may be at a temperature below its freezing temperature and will be thermally undercooled. When a pure metal liquid becomes thermally undercooled, the planar interface is no longer stable and will change its morphology to adapt to the situation.

Again, we can use a simple perturbation to see what occurs (Fig. 5.14b). The tip of the perturbation is now at a lower temperature than the base, and the enhanced growth undercooling

energies and their growth morphologies are governed by crystallography. The high surface energies will tend to stabilize the growth morphology although the negative temperature gradient will certainly allow the physical distance over which liquid and solid coexist to become greater.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

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chapter 6

SOLIDIFICATION OF ALLOYS



In solidification processing, the most distinguishing characteristic of an alloy compared to a pure element is that an alloy contains more than one chemical species. Solidification rarely results in a solid in which the alloying elements are distributed uniformly. In general, a redistribution of that solute takes place during freezing, resulting in a solid that is inhomogeneous on the microscale, the macroscale or both. This chapter deals with the question of solute redistribution and looks at its underlying problem.

SOLUTE REDISTRIBUTION - THE BASIC PROBLEM

The simple isomorphous Cu-Ni system described in Chapter 2 will serve as an example. Consider the solidification of an alloy of 20%Ni-80%Cu, shown on the phase diagram in Fig. 6.1. The chemically homogeneous liquid phase separates into solid and liquid fractions as the temperature falls below the liquidus temperature of 1195°C (2183°F). At 1180°C (2158°F), the solid should be a uniform composition of 32%Ni-68%Cu and the liquid should contain 15%Ni-85%Cu. The phase diagram predicts that as the temperature falls, the solid and liquid compositions change so that at 1150°C (2102°F), for example, the solid composition is 26%Ni-74%Cu and the liquid is 10%Ni-90%Cu. Finally, when the temperature falls below the solidus temperature of 1130°C (2066°F), the solid phase is predicted to be uniform in composition at 20%Ni-80%Cu.

As the temperature falls, freezing of an alloy through a two-phase region is characterized by a constantly changing chemistry of the two phases involved. The mechanisms acting here are heat transfer processes, such as conduction, convection and radiation, which drive the temperature change, and liquid stirring, liquid diffusion and solid state diffusion, which bring about the required compositional changes.

The inhomogeneous solute distributions associated with solidified alloys stem from a discrepancy in the rates at which these two mechanisms can occur. Heat transfer in solidification processing is a relatively rapid process, very responsive to change. For example, air or water cooling in a

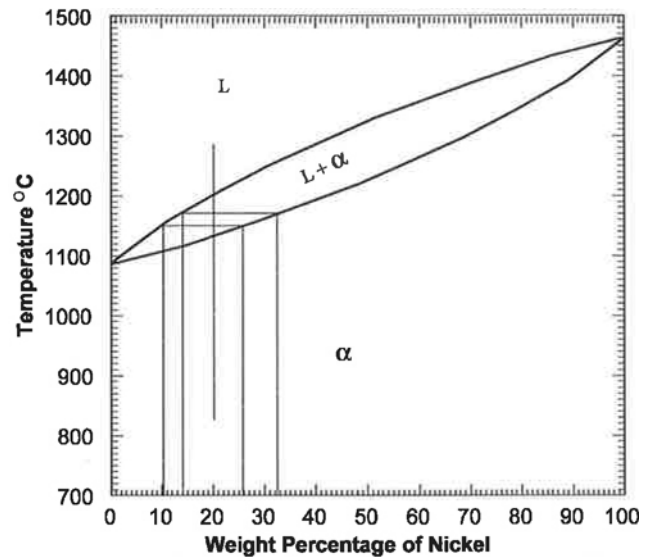


Fig. 6.1 The Cu-Ni phase diagram is shown with tie lines for an alloy of 20%Ni -80%Cu.

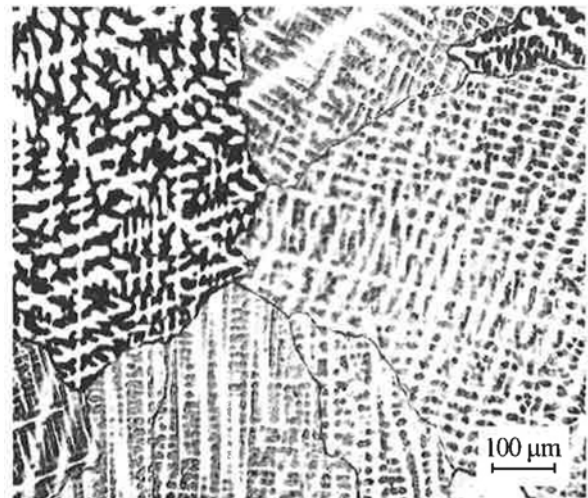


Fig. 6.2. Microscopic inhomogeneities (microsegregation) are generated within the solid grains during the solidification of a brass of composition 70%Cu-30%Zn. [Photo courtesy of the Copper Development Association.]

permanent mold can exert a profound and rapid effect on heat transfer rates, as can chills placed in a sand mold. Solid state diffusion, on the other hand, is relatively slow and difficult, and becomes slower and more difficult as the temperature falls and the diffusion coefficient decreases. Thus, while the temperature in a solidifying system can be made to decrease rapidly, the slowness of solid state diffusion limits the ability for compositional change in the available time.

Chemical changes dictated by the phase diagram are unable to respond to the rapidly changing temperature imposed by the heat flow. As a result, temperature and chemical composition become uncoupled and the phase diagram is no longer strictly obeyed.

One of the common results of this decoupling is the generation of chemical inhomogeneities on the microscale. The photomicrograph of Fig. 6.2 shows a cast brass (70%Cu-30%Zn) that has been etched to reveal compositional differences. The white regions froze at a higher temperature and are richer in copper than the darker areas, which froze later and contain more zinc. While the Cu-Zn phase diagram predicts a uniform 70%Cu-30%Zn composition, the reality of the situation is quite different.

EQUILIBRIUM DISTRIBUTION COEFFICIENT

The phase diagram provides useful information about solute redistribution during solidification. With alloys, the solid and liquid are usually of different chemical compositions. The equilibrium distribution coefficient quantifies this difference. The addition of a solute to a solvent can have only two effects on the melting point of the resultant alloy: it may be lowered (Fig. 6.3), or it may be raised (Fig. 6.4). In either case, the compositions of the solid and the liquid are different at any temperature. The equilibrium distribution coefficient is defined as:

$$k_0 = C_s / C_l \quad (6.1)$$

where

C_s and C_l are the equilibrium solute concentrations in the solid and the liquid.

Inspection of a phase diagram will show that the equilibrium distribution coefficient is just the ratio of the ends of the tie line at the temperature of interest for the alloy composition under consideration. The value of k_0 is not a constant over wide temperature ranges, but often it does not vary too greatly and average values can be used over the composition

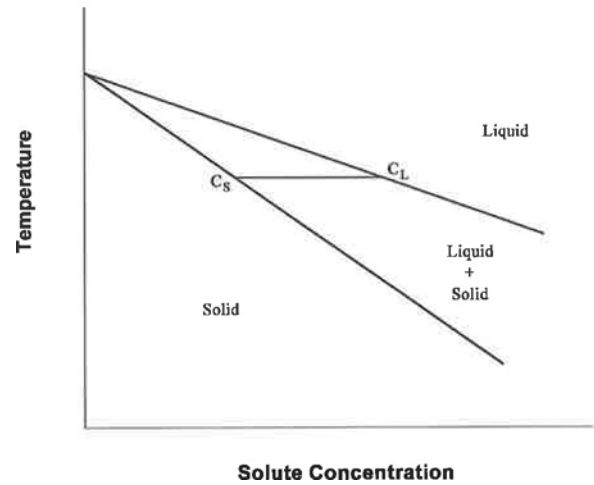


Fig. 6.3. If the melting point of a solvent is lowered by addition of a solute, the equilibrium distribution coefficient $k_0 < 1$.

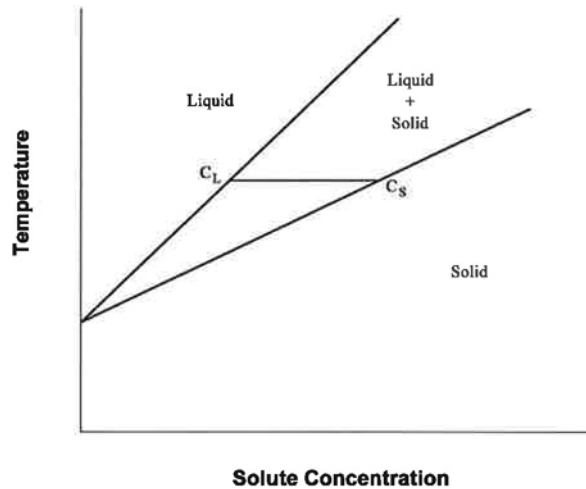


Fig. 6.4. If the melting point of a solvent is raised by addition of a solute, the equilibrium distribution coefficient $k_0 > 1$.

of 0.05 grams of B. The initial 5 grams of liquid from which this solid formed contained 0.5 grams of element B and, on freezing, 0.45 grams of B have gone into the remaining liquid. It is said that solute is rejected into the liquid; more properly, it is just “left behind” as the liquid freezes because of the different solubilities in the solid and liquid phases. If $k_0 < 1$, solute becomes concentrated in the liquid; if $k_0 > 1$, it is the solvent that becomes concentrated. Note that in each case, the concentration moves toward a lower freezing point as solidification continues.

MECHANISMS OF SOLUTE REDISTRIBUTION

The extent of solute mixing in the solid and liquid is an important factor in determining the resultant solute distribution in solidified solids. The following text will present several examples of the types of solute distribution expected with different mixing conditions, but first it is worth cataloging the various ways in which solute atoms may be moved about in solids and liquids.

Solute mixing in the solid state is the most restrictive, with diffusion being the only active mechanism. Metallic solutes generally experience vacancy diffusion because of their larger atom sizes. This is a slow process that is extremely temperature dependent. Smaller solutes, such as the gases (C, H, N, etc.), diffuse by the more rapid interstitial mechanism, which is 100 to 1000 times

range of interest. Alternatively, it is possible to derive a function describing the exact variation of k_0 with composition.

If the melting point is raised by the addition of solute, $C_S > C_L$ and $k_0 > 1$. Alternatively, a lowering of the melting point on solute addition implies that $C_S < C_L$ and $k_0 < 1$. Deviation of the value of k_0 from unity leads to the rejection of either solute or solvent into the liquid during solidification with a resultant concentration of that species. A simple example serves to illustrate the rejection process.

Suppose we freeze half of a 10 gram (0.357 ounce) liquid sample containing 10% alloying element, B. If $k_0 = 0.1$, the resulting 5 grams of solid will have a concentration of 1%B, or a mass

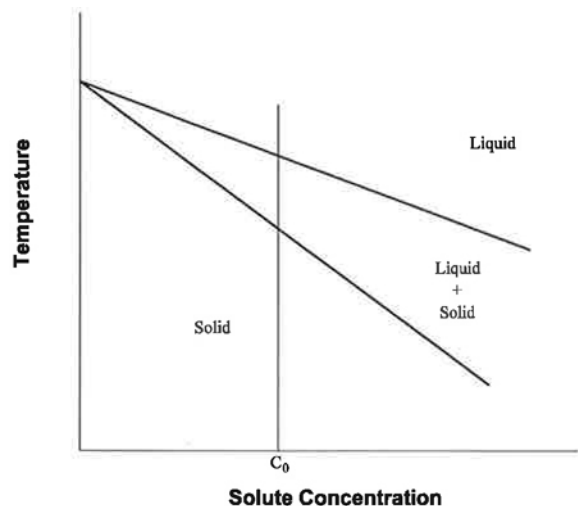


Fig. 6.5. A portion of a simple $k_0 < 1$ solid-solution system is illustrated.

faster than vacancy diffusion at the same temperature.

The nonrigid nature of liquids allows for a greater variety of mixing mechanisms. Liquid state diffusion is 10 to 1000 times more rapid than solid state, and liquids are able to mix by convection, as well. This may be natural convection in response to density differences resulting from temperature gradients, or it may be externally generated convection, such as mechanical or electromagnetic stirring.

EXAMPLES OF SOLUTE DISTRIBUTION PROFILES

The classical approach to understanding solute redistribution is to consider the directional solidification of a simple bar of material, and the effects of various solute mixing combinations on the resultant distribution. While a bar's geometry may seem an excessive oversimplification when compared to a complex casting, it is a useful simple shape. In addition to being relatively easy to visualize, the unidirectionally freezing bar can represent a narrow slice of many cast shapes that freeze from the mold wall inward by heat transfer through the mold.

Four cases of mixing will be considered with emphasis on $k_0 < 1$ alloy systems solidifying by the phase diagram shown in Fig. 6.5. The overall alloy composition in each case will be C_0 .

Case 1—Equilibrium solidification by complete and instantaneous mixing of solute in both the solid and the liquid, (Fig. 6.6).

The first solid to form will have a solute concentration of $k_0 C_0$, as given by the tie line at the liquidus temperature. Solute will be rejected into the remaining liquid because of the difference in composition of the solid just formed from the initial liquid (Fig. 6.6a). Solute rejection occurs at the solid-liquid interface and will tend to generate a solute gradient within the liquid. This gradient will, however, be eliminated instantaneously by the liquid state mixing, which may be diffusion, convection or some combination of the two. The increased liquid concentration will result in an increased solute concentration in the solid, which also will tend to generate a concentration gradient.

In a similar manner, this gradient will also be eliminated by the instantaneous solid state mixing (diffusion). Solidification will follow the phase diagram exactly with the bulk solid

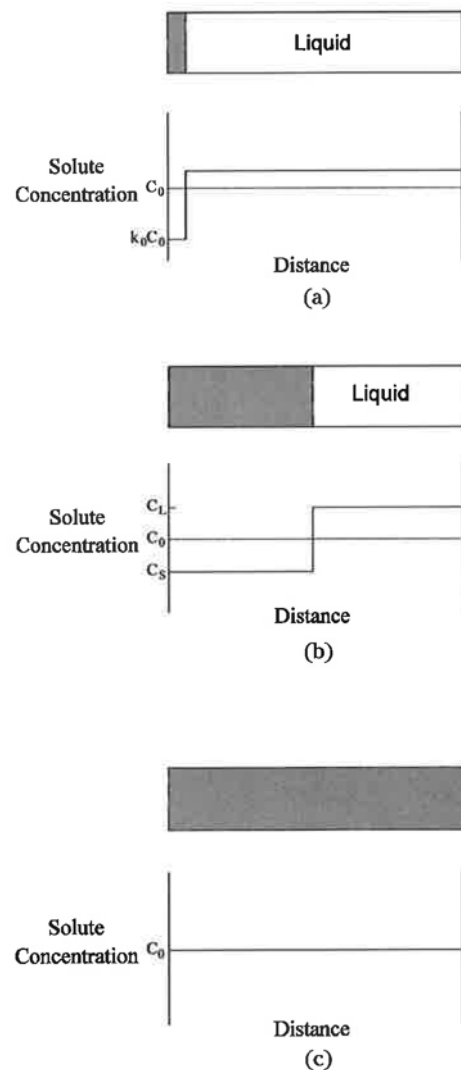


Fig. 6.6. The evolution of the solute profile along a directionally frozen bar is shown where complete and instantaneous mixing of solute occurs in both the solid and liquid phases: (a) beginning of freezing; (b) approximately half has frozen; and (c) final solute distribution.

of uniform concentration, C_s , in equilibrium with bulk liquid of uniform concentration, C_L , (Fig. 6.6b). Solid and liquid compositions will change as the temperature falls, but no concentration gradients will develop.

Final solidification will take place at the solidus temperature of the alloy, and will lead to a bar of uniform composition, C_0 (Fig. 6.6c). Note that even though a tendency to generate solute gradients persists throughout the process, the mixing conditions effectively eliminate them. If $k_0 > 1$, the final solute distribution will once again be uniform and at the bulk alloy concentration, exactly as predicted from the phase diagram.

Freezing under these conditions is exactly the equilibrium solidification described in Chapter 2. Equilibrium freezing in metal systems is rare because of the relatively low values of diffusion coefficients. It may occur in microsystems where the diffusion distance is small. Diffusion distance can be approximated by:

$$x^2 = Dt \quad (6.2)$$

where

x is the distance a species may diffuse in time, t , if the diffusion coefficient is D .

Equilibrium solidification is also known to occur in some geological systems where bodies of magma freeze over very long periods of time. The one metallurgical example in which equilibrium freezing is a possibility occurs when the solute atoms are nonmetals diffusing by an interstitial mechanism. Possibilities include carbon in steel or gases, such as nitrogen or hydrogen, which may be found dissolved in iron or aluminum.

Case 2—No diffusion in the solid state; complete mixing in the liquid, (Fig. 6.7).

The absence of diffusion in the solid makes this case much more realistic than Case 1. Again, the initial solid contains $k_0 C_0$ of solute, and solute is rejected into the liquid. Complete mixing in the liquid eliminates all concentration gradients there (Fig. 6.7a);

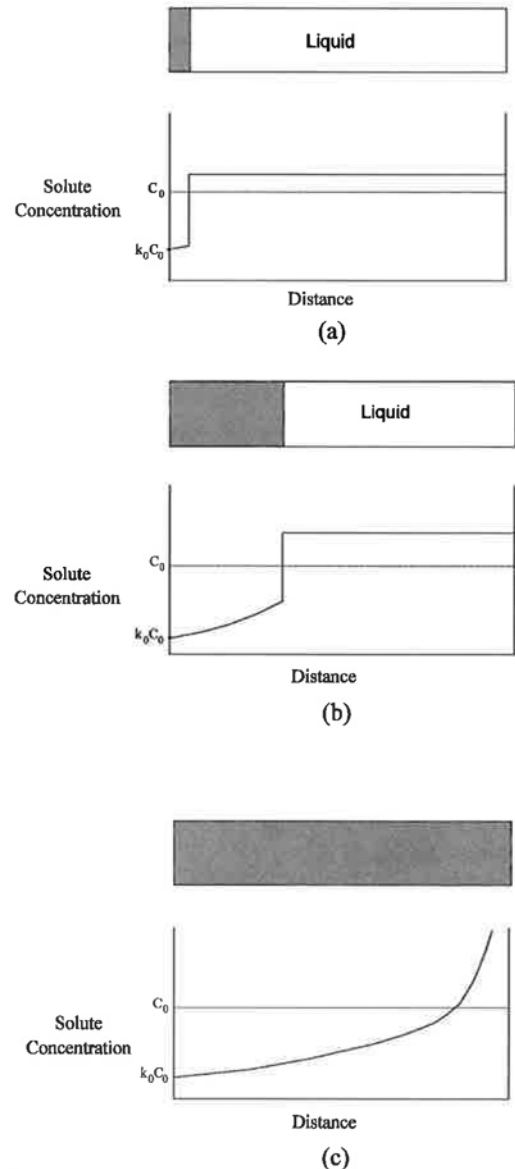


Fig. 6.7. Development of the solute profile along a directionally frozen bar is shown under conditions of complete liquid phase mixing and no diffusion in the solid: (a) beginning of freezing; (b) quarter point; and (c) final solute distribution.

however, as the liquid concentration rises, so does that of the solid. The lack of effective mixing in the solid results in the establishment of a concentration gradient as the solid forms from liquid of ever increasing solute concentration (Fig. 6.7b). Eventually, the solid concentration will surpass the overall alloy composition, C_0 , and will continue to rise until the solubility limit is reached (Fig. 6.7c).

The Scheil equation describing the resultant solute profile is one of the best known in solidification theory and is as follows:

$$C_s = k_0 C_0 (1 - f_s)^{k_0 - 1} \quad (6.3)$$

or, alternatively,

$$C_s = k_0 C_0 f_l^{k_0 - 1} \quad (6.4)$$

where

- C_s = solute concentration in the solid;
- k_0 = equilibrium distribution coefficient;
- C_0 = overall alloy composition;
- f_s = fraction solid; and
- f_l = fraction liquid.

Changing the nature of the distribution coefficient from $k_0 < 1$ to $k_0 > 1$ implies that it is the solvent that is rejected. The first solid to form will be solute-rich, while the last will be solute-poor. The final result is a solute distribution that will be the mirror image of that for a solute of $k_0 < 1$ (Fig. 6.8). It can be seen in Fig. 6.8 that solute becomes concentrated in the first part to solidify if $k_0 > 1$, and that the last portions of the system to freeze are solute depleted. This is exactly the opposite of what occurs if $k_0 < 1$. The Scheil equation is widely employed in calculations of solute profiles because its basic assumptions usually reflect real solidification conditions quite well.

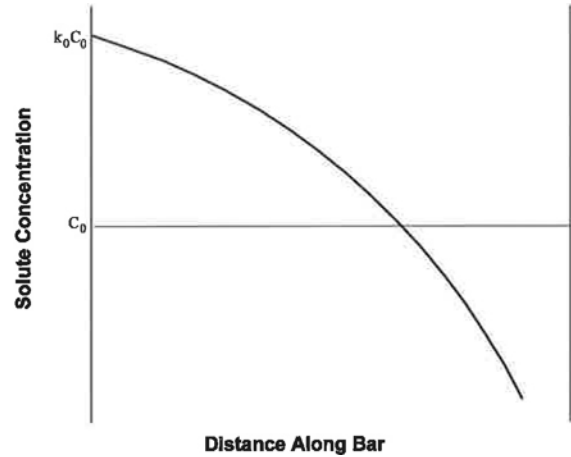


Fig. 6.8 The final solute profile for an alloy in which $k_0 > 1$ is shown when the alloy freezes with complete liquid mixing but no solid state diffusion.

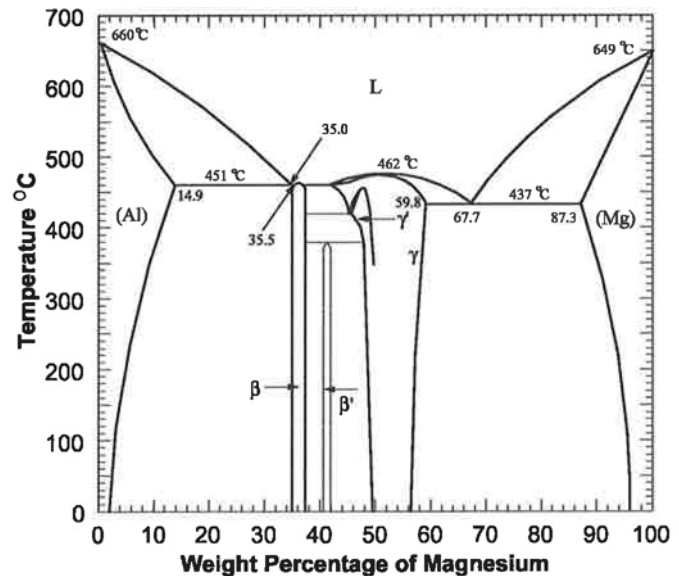


Fig. 6.9. Al-Mg phase diagram is shown.

A change in the mixing conditions from those of Case 1 to Case 2 results in a very marked change in the solute distribution. The following example of the solidification of an Al-10%Mg alloy (Fig. 6.9) illustrates this change. Under equilibrium conditions, this alloy should contain no eutectic since its composition is less than the maximum solid solubility of magnesium in aluminum (14.9%). If, however, we eliminate solid state diffusion and apply the Scheil equation using an average value of $k_0 = 0.3$, we obtain the solute distribution of Fig. 6.10.

The magnesium concentration rises continuously from its initial value of $k_0 C_0$, (3%), until it reaches the solubility limit of 14.9% at a fraction solid of 0.9. At this point, the remaining liquid, which comprises 10% by weight, has the eutectic composition (65%Al-35%Mg). The eutectic is an invariant point (zero degrees of freedom) and any further drop in temperature causes the liquid to freeze with a uniform composition of 35%Mg. Changing the mixing conditions has resulted in a drastic change in solute distribution. Most real metal systems freeze with little or no diffusion in the solid, resulting in solute distributions that are not predicted by the phase diagram. This is one of the limitations of the phase diagram when applied to real phase transformations, as pointed out in Chapter 2.

When using the Scheil equation, care must be paid to the units of f_s and f_l . These are weight fractions when the concentrations C_s and C_L are expressed in weight percentages. Conversion to volume fractions, which often is a more useful unit when dealing with metallographic structures, requires that they be divided by the densities of the appropriate phases.

Case 3—No solid state diffusion; mixing in the liquid by diffusion only, (Fig. 6.11)

Like the previous situation, this too is often a realistic approximation to actual solidification conditions. While diffusion in liquids is certainly more rapid than in solids, it is still relatively slow compared to most freezing rates encountered in practice. Solute rejected at the solid-liquid interface accumulates there and only slowly diffuses ahead of the interface into the bulk liquid. Solidification under these conditions is characterized by the presence of a solute-enriched boundary layer in the liquid at the solid-liquid interface.

Figures 6.11a-c illustrate the development of this solute-enriched layer. After an initial solute concentration in the solid of $k_0 C_0$, rejection at the interface leads to an increasing solute-enriched boundary layer. As solute builds at the interface, the concentration in the

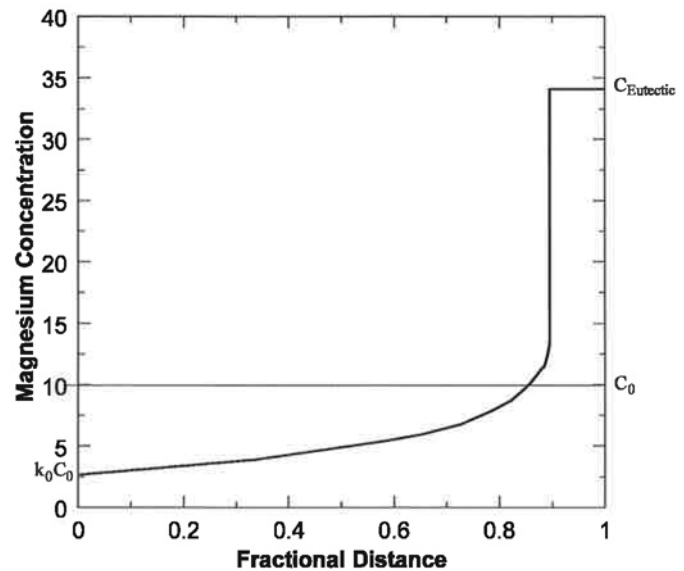


Fig. 6.10. The calculated Mg distribution along a unidirectionally frozen bar of Al-10%Mg alloy is given. It is assumed that solidification takes place according to the Scheil equation with an average $k_0 = 0.3$.

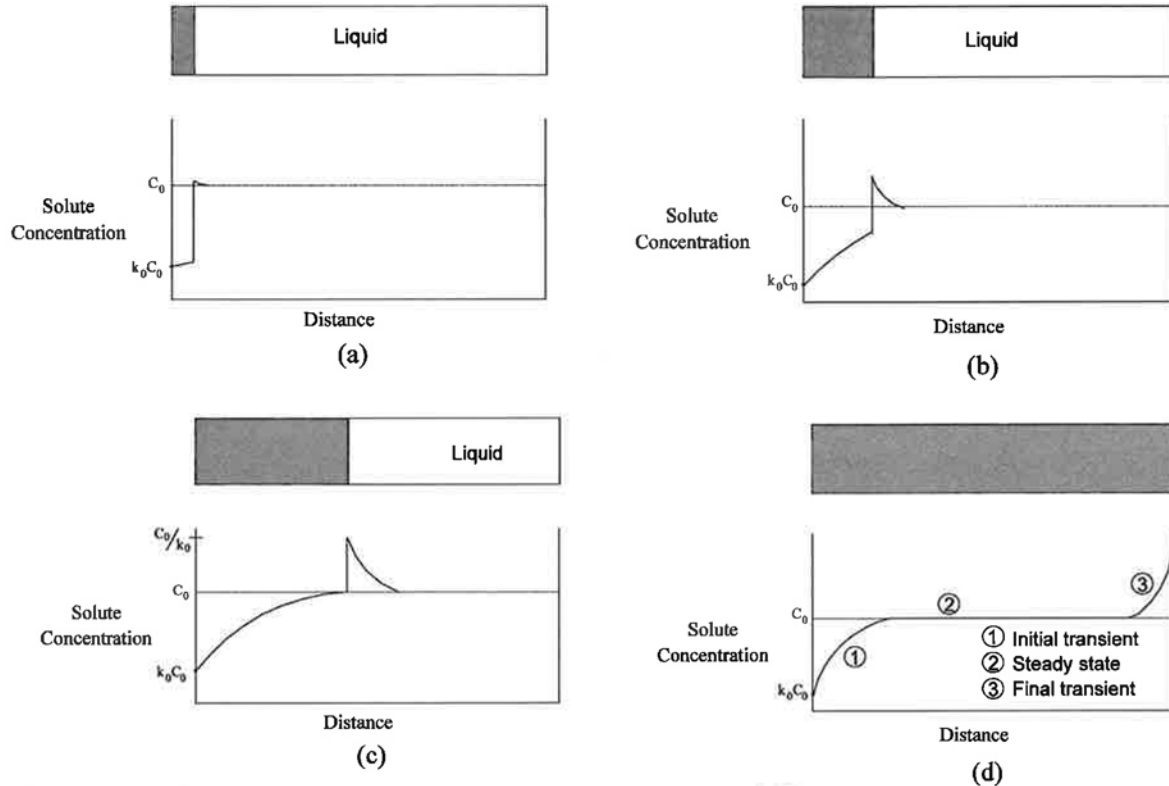


Fig. 6.11. The evolution of the solute distribution along a directionally solidified bar of alloy is shown when there is no solid state diffusion and mixing occurs in the liquid by diffusion only: (a) beginning of freezing; (b) as the solute boundary layer develops; (c) during steady state solidification; and (d) final solute distribution showing the initial transient, steady state and final transient regions.

solid rises and the lack of solid state diffusion ensures the establishment of a concentration gradient. In metal systems exhibiting small values of kinetic undercooling, temperatures of the liquid and solid at the interface contact point are virtually the same. Local equilibrium exists at this point, and the solid and liquid compositions at the interface are related by the equilibrium distribution coefficient. Thus:

$$C_{S \text{ (interface)}} = k_0 C_{L \text{ (interface)}}$$

Local equilibrium will not be possible if the kinetic undercoolings are large, for example, in high α factor materials where differences of many degrees, or even tens of degrees, may exist between the solid and liquid temperatures at the interface. It is a significant feature of metal solidification that local equilibrium may be present at the interface while the system as a whole is not in equilibrium because of insufficient mixing in the bulk phases.

Further freezing results in the accumulation of ever more solute in the boundary layer until, eventually, a steady state amount is reached. At steady state, the amount of solute rejected into the boundary per unit of time by the freezing process equals exactly the amount which diffuses into the bulk liquid ahead of the interface. The concentration of solute in the liquid at the interface, C_L^1 , will equal:

$$C_l^I = C_0/k_0 \quad (6.5)$$

and the resultant solid concentration, C_s , will be:

$$C_s = C_0 \quad (6.6)$$

As long as there are no changes in the freezing conditions, this steady state will persist until very near the end of solidification, and the steady state boundary layer is thought to be “pushed” ahead of the interface. In reality, it moves by diffusion into the bulk liquid. Steady state conditions will continue until the physical limit of the container holding the system is reached. With no further space into which solute can diffuse, there is a sharp rise in concentration at the end of freezing (Fig. 6.11d).

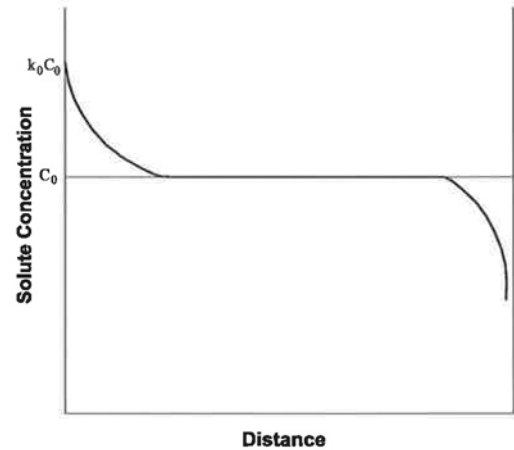


Fig. 6.12. The final solute distribution for a $k_0 < 1$ solute is shown when solidification occurs with no solid state diffusion and mixing in the liquid is by diffusion only.

Solidification under these mixing conditions leads to a solid with three distinct compositional regions:

- an initial transient during which the solute concentration rises from an initial value of $k_0 C_0$ to C_0 , and a steady state solute boundary layer is established;
- a steady state comprising most of the solidification when $C_s = C_0$; and
- a small final high solute concentration transient resulting from the compression of the solute boundary layer into an ever decreasing volume of liquid at the end of solidification.

If $k_0 > 1$, the initial transient is solute-rich (solvent-poor), while the final transient is solute-poor (solvent-rich), and the entire solute distribution is the mirror image of Fig. 6.11d as shown in Fig. 6.12.

Alloy solidification phenomena are largely governed by events at the solid-liquid interface or, in other words, all the “action” is at the interface. Solute distributions are greatly dependent on the extent and form of solute boundary layers at the interface. Equations have been developed to describe the shape of the steady state boundary layer for the mixing conditions considered here. At steady state, the amount of solute in this layer is a constant and can be described by:

$$D_l(d^2C_l/dx^2) + R(dC_l/dx) = 0 \quad (6.7)$$

where

D_l = diffusion coefficient of the solute species in the liquid;

C_L = solute concentration in the liquid at a distance, x , from the interface; and
 R = linear rate of freezing.

The appropriate boundary conditions are:

$$C_L = C_0/k_0 \text{ at } x = 0$$

$$C_L = C_0 \text{ at } x = \infty$$

and the solution is:

$$C_L = C_0 \{1 + (1-k_0/k_0) \exp \{-R/D_L\}x\} \quad (6.8)$$

The solute boundary layer in steady state is, therefore, exponential in form, as expected for a diffusion controlled process, and it has a “characteristic distance” of (D_L/R) . This value may be thought of as an approximate thickness. A typical value for the diffusion coefficient in liquid metals is $6 \times 10^{-5} \text{ cm}^2/\text{sec}$, and linear freezing rates, R , in casting processes fall roughly in the range 10^{-2} to 10^{-1} cm/sec . Thus, the solute boundary layer ranges in approximate thickness from $6 \times 10^{-3} \text{ cm}$ to $6 \times 10^{-4} \text{ cm}$ (0.06 to 0.006 mm). This is, most definitely, a microscopic feature of alloy freezing and has important macroscopic consequences.

The final transient will have a thickness roughly equal to the boundary layer thickness as it originates from compression of the layer. Very high concentrations can be reached here with the maximum composition usually limited by the phase diagram as eutectics or other phases form.

Equations have been developed for the initial transient, which is longer than the final, with a characteristic distance, x_i , of:

$$x_i = D/k_0 R \quad (6.9)$$

Equilibrium distribution coefficients in metal alloys range from 0.8 to 0.01, approximately. If the value of k_0 is at the low end of this range, the initial transient may be up to 100 times longer than the final, a reflection of the increased solidification length necessary to reach the steady state interface concentration of (C_0/k_0) . While this may seem like a large length, values of (D/R) are so small compared to the size of macroscopic solidification systems, that the physical sizes of the initial and final transients are almost insignificant.

BANDING

Equation 6.8 predicts that the steepness of the solute boundary layer should change if the

freezing rate, R , also changes. At high values of R , steepness would be greater and at slower freezing rates, more shallow, as indicated in Fig. 6.13 where $R_2 > R_1$. If the freezing rate changes because of heat flow conditions, the boundary layer profile will gradually adjust by diffusion from that characteristic of the initial rate to that of the final rate. Diffusion, however, is relatively slow compared to heat transfer, and the adjustment process will require some time, leading to a transient behavior during the transition.

Consider a rate increase from R_1 to R_2 . More solute is rejected per unit of time at the interface, and this solute must diffuse down the shallow concentration gradient established at R_1 (remember that the driving force for diffusion is the gradient of concentration). Solute is not effectively removed from the interface, and the concentration there rises above (C_0/k_0) , resulting in a higher concentration frozen into the solid. With time, the solute profile readjusts by diffusion to that proper for the new rate, R_2 , the interface concentration falls back to (C_0/k_0) and steady state freezing is re-established with solid of composition, C_0 , freezing. The net result of this rate change is, however, a high solute band frozen into the solid (Fig. 6.14a).

A rate decrease from R_2 to R_1 has the opposite effect. Less solute rejection per unit time and diffusion down the steep gradient formed at R_2 leads to a drop in the interface concentration to a value lower than (C_0/k_0) . The result is a low solute band (Fig. 6.14b), existing until the boundary layer profiles adjust to the new conditions.

Undesirable high and low solute bands are common features of "controlled" solidification processes, such as alloy crystal growth. Very stringent control of the thermal conditions is necessary to avoid this effect, with growth in temperature-controlled environments often being the only way to avoid banding. Considerations of solute conservation dictate that the

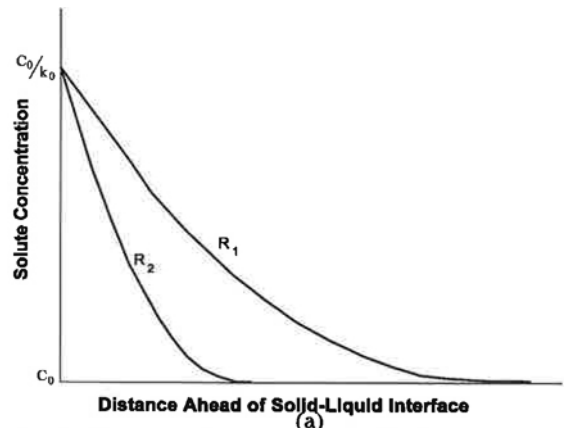


Fig. 6.13. Two solute profiles in the liquid ahead of the solid-liquid interface are illustrated for freezing rates R_1 and R_2 , where $R_2 > R_1$.

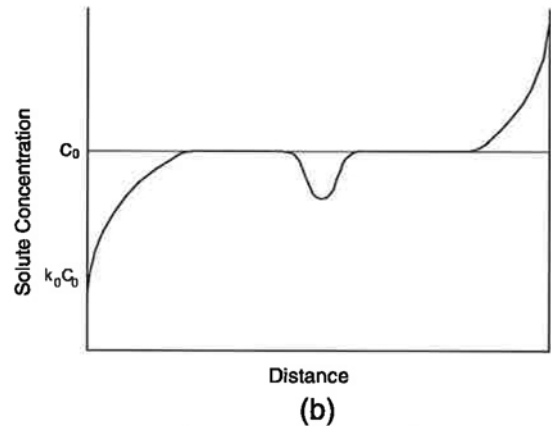
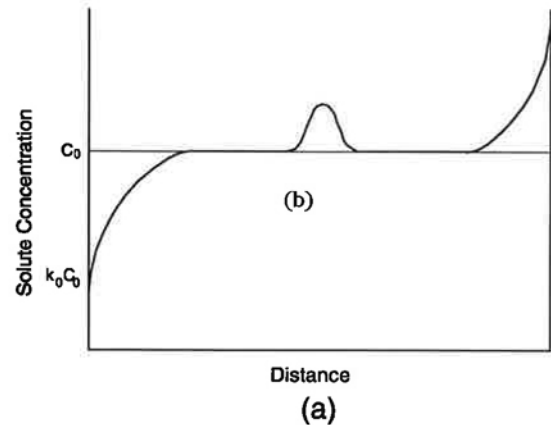


Fig. 6.14. Banding, as a result of freezing rate changes, is illustrated for a: (a) high solute band caused by a rate increase; and (b) low solute band caused by a rate decrease.

presence of high or low solute bands will ultimately influence the amount of solute finding its way into the final transient. A high solute band will reduce the final transient, and vice versa.

Case 4—No diffusion in the solid and limited liquid mixing.

This is the most realistic solute redistribution model for industrial solidification, where some degree of convection is almost always present. Very often, the extent of this convection is insufficient to remove completely the solute boundary layer at the interface. A modified boundary layer is present with convection leading to complete liquid mixing up to a distance, δ , in front of the interface. Solute transport within the stagnant boundary layer, δ , is by diffusion only, in a direction perpendicular to the interface.

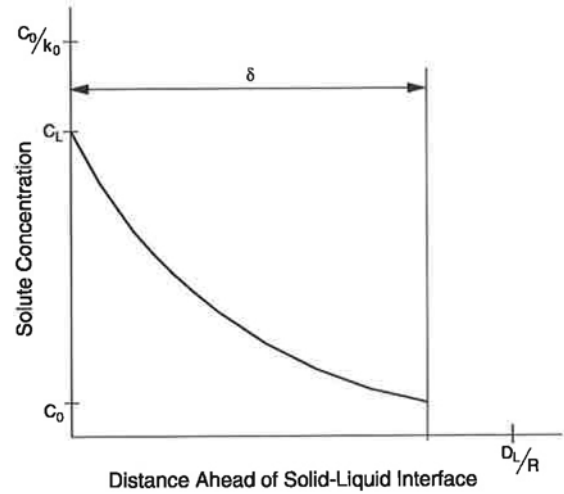


Fig. 6.15. A modified solute boundary layer of thickness, δ , exists ahead of a solid-liquid interface in the presence of partial liquid mixing.

The local distribution, as illustrated in Fig. 6.15, leads to a solute concentration in the liquid at the interface of $C_L < C_0/k_0$ and a solid concentration that increases as solidification proceeds, and the liquid becomes progressively richer in solute. Note that the concentration in the solid will not increase as quickly as in complete liquid mixing (Case 2) since a partial solute boundary layer still remains at the interface.

Equation 6.7 can also be used to describe the solute boundary layer, but with the boundary conditions:

$$C_L = C_L \text{ at } x = 0$$

$$C_L = C_0 \text{ at } x = \delta$$

If we now define an effective distribution coefficient, k' , given by:

$$k' = C_s / C_{L(\text{bulk})} \quad (6.10)$$

and substitute this value of k' into the solution for equation 6.7, with the boundary conditions given above, we obtain:

$$k' = k_0/k_0 + (1-k_0) \exp -(R\delta/D_L) \quad (6.11)$$

This approach allows us to use the familiar Scheil equation to describe the solute distribution with the value of k_0 now replaced by k' , i.e.:

$$C_s = k' C_0 (1-f_s)^{k'-1} \quad (6.12)$$

or, alternatively,

$$C_s = k' C_0 f_l^{k'-1} \quad (6.13)$$

Figure 6.16 presents a schematic representation of the solute distributions for various values of k' .

An examination of equation 6.11 reveals that the value of the effective distribution coefficient depends on the linear rate of freezing, R . Two extremes are possible: if $R \rightarrow 0$, $k' \rightarrow k_0$; if $R \rightarrow \infty$, $k' \rightarrow 1$. Substituting these limiting values for k' into equation 6.12 yields the following results:

- at very slow freezing rates ($R \rightarrow 0$), equation 6.12 becomes $C_s = k_0 C_0 (1-f_s)^{k_0-1}$, which is the Scheil equation;
- at very rapid rates ($R \rightarrow \infty$), equation 6.12 becomes $C_s = C_0$, which describes the steady state when liquid mixing is diffusion controlled.

We can conclude that at very slow rates of solidification, a state of complete mixing prevails in the liquid and the Scheil equation applies. In physical terms, the diffusion distance possible (equal, approximately, to (D_L/R) , at very low rates of freezing, greatly exceeds the thickness of the stagnant or laminar flow layer, δ , with the result that virtually all solute rejected at the interface becomes mixed into the bulk liquid.

At very high freezing rates, the opposite occurs. The allowable diffusion distance is small and lies completely within the laminar flow layer, δ . Liquid convection is unable to interact with the solute boundary layer, and the concentration of the solid equals the overall alloy composition, C_0 . Even in the presence of liquid convection, a solid of uniform composition, except for the initial and final transients, may be produced, as described in Case 3.

Freezing rates intermediate between very slow ($R \rightarrow 0$) and very rapid ($R \rightarrow \infty$) will yield solute distributions intermediate between those predicted by the Scheil equation, on the one hand, and uniform with $C_s = C_0$, on the other hand. Figure 6.17 summarizes the types of distribution that may be expected for different mixing conditions in alloys containing $k_0 < 1$ and $k_0 > 1$ solutes. Note that the initial transient is not shown in the figure.

PRACTICAL IMPLICATIONS

A few practical implications of solute redistribution are presented here. The next two chapters will deal in greater detail with other consequences of solute redistribution.

A study of Cases 1 to 4 shows that the greatest redistribution of solute occurs when the

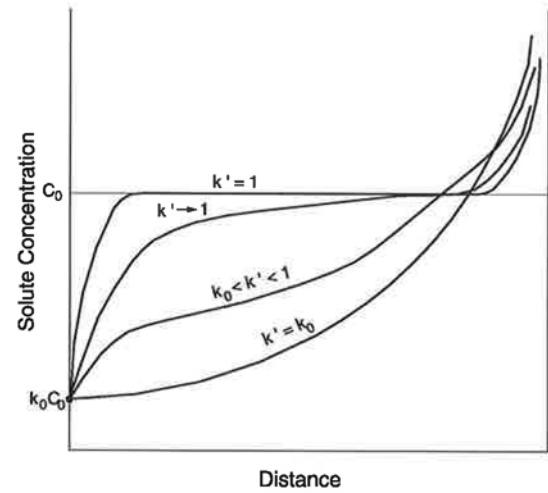


Fig. 6.16. A schematic representation is given of the solute distributions for various values of k' , the effective distribution coefficient.

liquid is completely mixed or when the freezing rate is very low with some convection present. These conditions prevail in large castings and ingots, and so it may be expected that they will exhibit the most severe long-range solute redistribution. Small, rapidly solidified castings, such as pressure die castings, are likely to be much more homogeneous, at least on a macroscale.

Alloy single crystal growth aims to produce crystals of uniform longitudinal composition. Since complete equilibrium is a virtual impossibility, an environment must be promoted in which liquid mixing occurs only by diffusion, and the initial and final transient regions must be cropped off. In addition, the freezing rate must be kept constant to avoid banding.

A common example for the beneficial use of solute redistribution is in the process of zone refining, used to manufacture ultra-high purity materials. Pfann discusses zone refining in great detail in his book (see Further Reading). Only the rudiments will be given here by way of illustrating the usefulness of solute redistribution.

Zone refining aims to purify a solvent material by controlling solidification in such a manner that all impurity elements are redistributed to either the first or last regions to solidify. In its simplest form, a heater is passed along a bar of the material to melt a zone, as illustrated in Fig. 6.18. When the heater reaches the end of the bar, it is returned to the beginning automatically and the zone passes again along the bar.

Solutes with $k_0 < 1$ become concentrated in the liquid zone and slowly move to the end of the bar. Solutes with $k_0 > 1$ are concentrated in the first solid to freeze and gradually move to the front end of the bar. The net result is an increase in overall solute redistribution as a function of the number of zone passes, as illustrated in Fig. 6.19. At the end of refinement, the front and trailing ends of the bar are cut off, and the pure central region is retained for use.

The discussion of solute redistribution given in this chapter allows us to make some recommendations about the operation of the zone refining process to

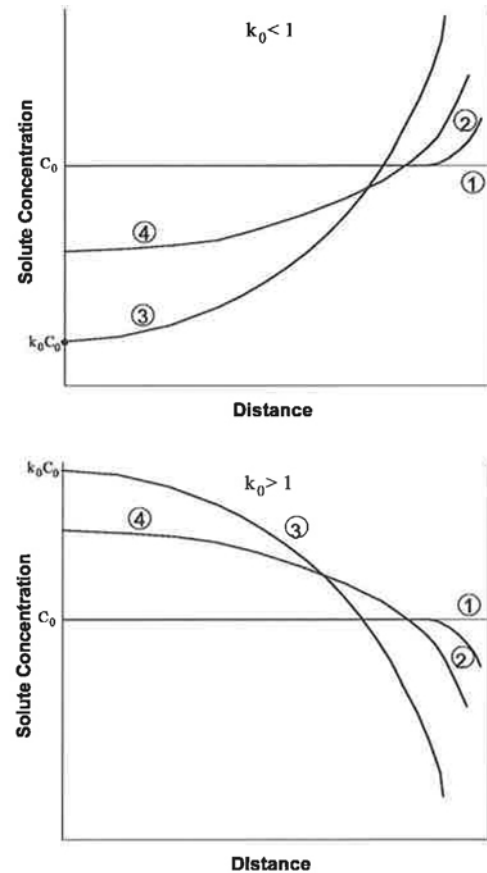


Fig. 6.17. Graphical summaries show the various solute distributions that can be expected for different mixing conditions. Note that the initial transients are not shown. Numbers on the graphs indicate: 1) complete equilibrium; 2) no solid state diffusion, mixing in the liquid only by diffusion; 3) no solid state diffusion, complete mixing in the liquid; and 4) no solid state diffusion, partial mixing in the liquid.

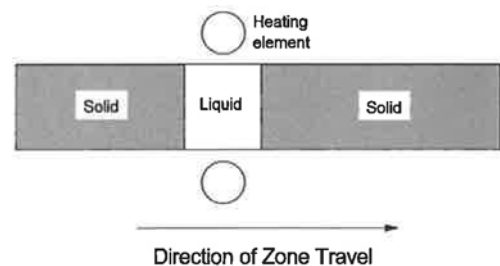


Fig. 6.18. Zone refining is conducted by passing a molten zone along a bar of material that contains impurity elements.

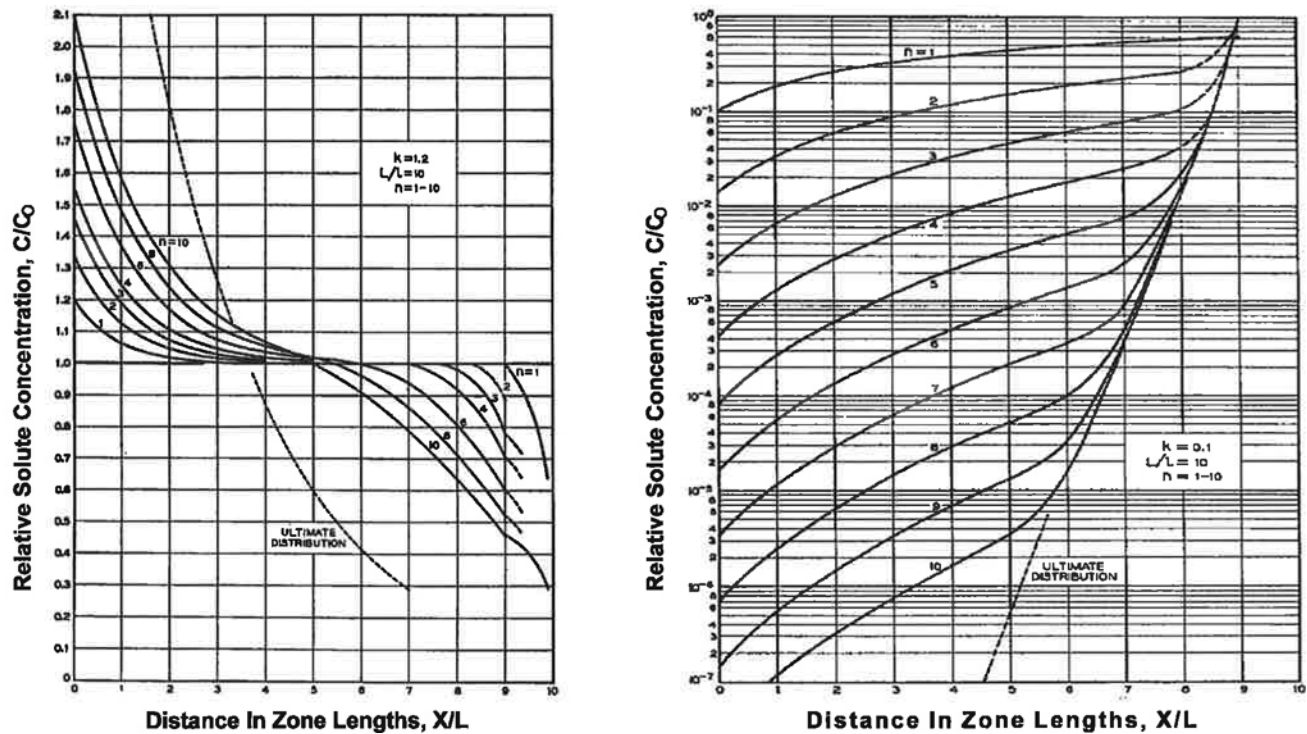


Fig. 6.19. The change in solute distribution during zone refining is shown as a function of the number of zone passes. In these figures, the relative solute concentration is given as a function of the distance in zone lengths from the beginning of a bar that is being refined. X is the length of the molten zone and L is the total length of the bar. The number of passes of the molten zone is denoted by n . (a) For a solute of $k_0 = 1.2$; (b) For a solute of $k_0 = 0.1$. [Reproduced from W.G. Pfann, *Zone Melting*, 2nd edition, John Wiley & Sons Inc. 1966, Copyright, 1966, Lucent Technologies.

achieve optimum solute movement. The zone in the first pass should be as long as possible and, ideally, should equal the entire length of the bar. Slow freezing, with maximum convection achieved by induction stirring or a high thermal gradient, will encourage complete liquid mixing and the maximum longitudinal solute redistribution according to the Scheil equation and Fig. 6.7. After the first pass, the zone should be kept as short as possible to avoid melting-in of the high solute material at either the front or trailing ends.

In order to achieve the greatest efficiency of solute partitioning within the zone, solute boundary layers at the interface must be avoided. These conditions can be reached by slow solidification, with maximum liquid convection produced again by some form of external stirring or by a high temperature gradient in the liquid to maximize density differences and thermal convection.

FURTHER READING

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chapter 7

CONSTITUTIONAL UNDERCOOLING

Constitutional undercooling is the most important single concept in solidification theory for it allows us to explain many details of cast alloy microstructure. As the name implies, constitutional undercooling is a departure from equilibrium because of compositional factors. It can, therefore, occur only in alloys.

This chapter will describe the phenomenon in a general, qualitative way in order to demonstrate the main acting solidification variables. A quantitative approach will then lead us to an equation that predicts the onset of constitutional undercooling and, finally, the effects of constitutional undercooling on cast microstructure will be discussed.

QUALITATIVE DESCRIPTION

As noted in Chapter 6, solute or solvent rejection during freezing can lead to the establishment of a concentration gradient in front of the solid-liquid interface. This gradient results in a progressive variation in equilibrium freezing temperature (liquidus temperature), with distance ahead of the interface, and the exact form of the variation depends on the shape of the liquidus line linking composition and temperature.

The relation between composition and equilibrium freezing temperature for a case of diffusion control in the liquid is shown in Fig. 7.1 for $k_0 < 1$ and in Fig. 7.2 for $k_0 > 1$. In each case, the solute concentration at the interface is C_0/k_0 , and the equilibrium freezing temperature is lowest at the interface, rising continuously to reach the liquidus temperature of the alloy in the bulk liquid.

We can conclude, therefore, that whenever solute, or solvent, rejection occurs, there is a gradient of equilibrium freezing temperature in front of the interface and extending some distance into the liquid phase. This distance will be the thickness of the solute boundary layer in front of the interface, as discussed in the preceding chapter. It may approach zero at one extreme and (D_L/R) at the other.

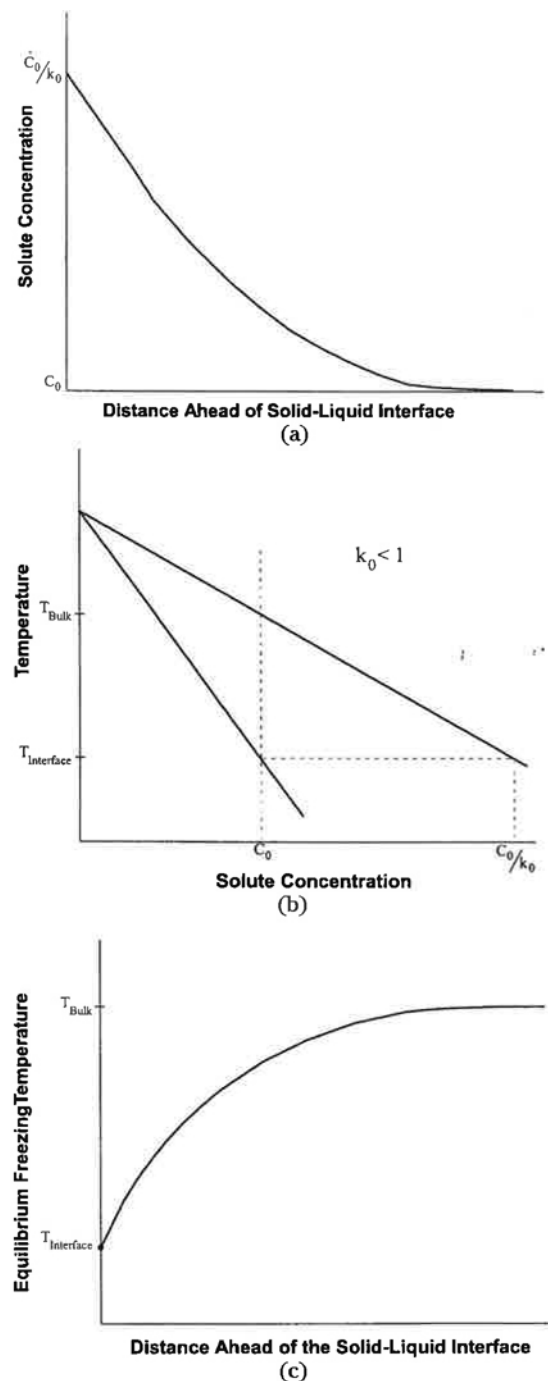


Fig. 7.1. Relationship between solute concentration ahead of a solid-liquid interface and equilibrium freezing temperature is shown for an alloy phase diagram in which $k_0 < 1$: (a) solute profile in front of the interface; (b) liquidus and solidus line of the phase diagram; and (c) liquidus line in (b) can be used to determine the equilibrium freezing temperature variation resulting from the solute profile in (a).

In addition to a distribution of both alloy element concentration and equilibrium freezing temperature, there also exists a distribution of actual, or real, temperature in front of the interface. This variation of temperature with distance is the temperature gradient in the liquid. It is usually positive, with temperature increasing into the liquid away from the growing solid, but on some occasions it may become negative, resulting in liquid actually being cooler away from the interface. Temperature gradients in the liquid phase can be measured by inserting thermocouples into the liquid. The gradient in bulk liquids often is close to zero due to thermal convection, but it can become significant close to the solid-liquid interface where fluid flow is laminar.

This actual temperature gradient is, primarily, a function of heat flow while the gradient of equilibrium freezing temperature depends mainly on the alloy system (value of k_0), freezing rate and extent of liquid mixing. The gradients of equilibrium freezing temperature and actual temperature are, to some extent, independent of each other; one may be greater or less than the other or they may both be equal. The magnitude of these two gradients at the interface determines whether or not constitutional undercooling is present.

Figure 7.3 illustrates two possibilities. The temperature distribution shown in Fig. 7.3a describes a situation in which the actual liquid temperature is greater than the equilibrium freezing temperature everywhere, or in other words, the liquid is superheated. The distribution of Fig. 7.3b shows a case in which the liquid, for a certain distance ahead of the interface, is at a temperature lower than the equilibrium freezing temperature. This liquid is undercooled, and

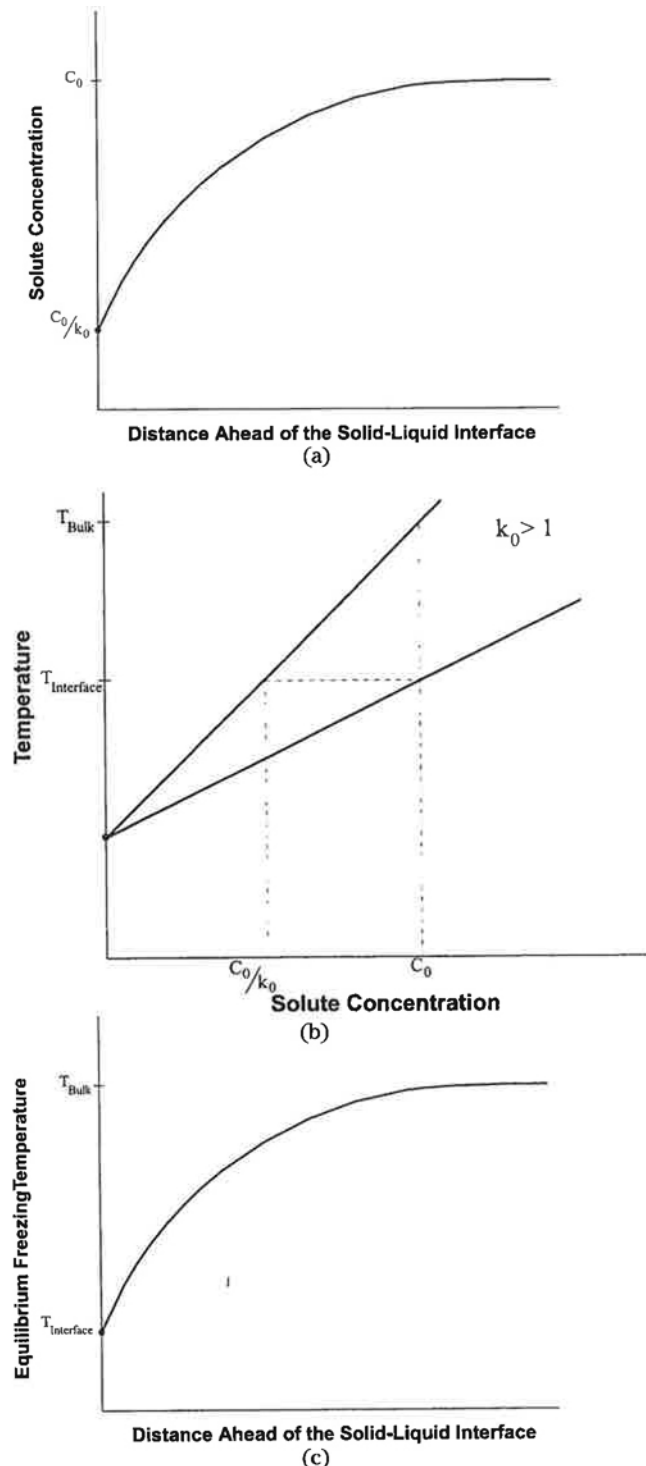


Fig. 7.2. Relationship between solute concentration ahead of a solid-liquid interface and equilibrium freezing temperature is shown for an alloy phase diagram in which $k_0 > 1$: (a) solute profile in front of the interface; (b) liquidus and solidus lines of the phase diagram; and (c) liquidus line in (b) can be used to determine the equilibrium freezing temperature variation resulting from the solute profile in (a).

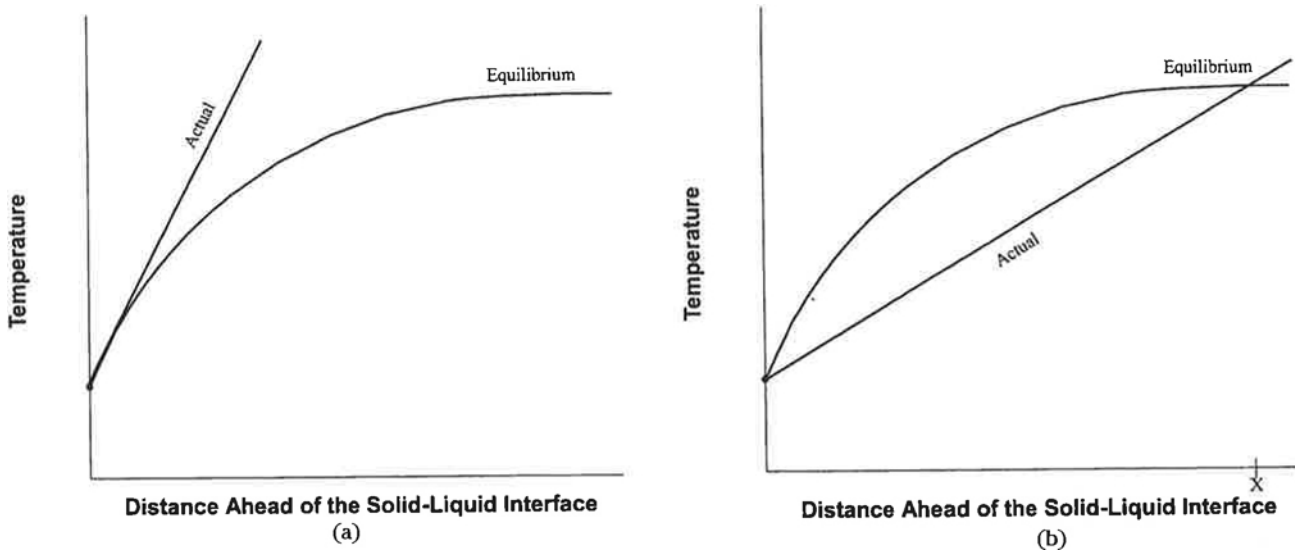


Fig. 7.3. (a) In this graph of temperature versus distance ahead of the interface, the actual temperature is greater than the equilibrium temperature everywhere. (b) In this graph of temperature versus distance ahead of the interface, the actual temperature is less than the equilibrium temperature for a certain distance ahead of the interface.

since the undercooling results from the presence of a solute-enriched boundary layer at the interface, we call this constitutional undercooling.

Constitutional undercooling is expressed as units of temperature, the one in question being the temperature difference between the two curves of Fig. 7.3. It can be seen that there is a gradient of constitutional undercooling present. Exactly at the interface, the amount of constitutional undercooling is zero. The only undercooling to be found here is the normal kinetic undercooling associated with the atomic attachment process. Constitutional undercooling then increases to reach a maximum and subsequently decreases to become zero at point X, beyond which the liquid is superheated.

Figure 7.3 demonstrates that one of the important variables determining the extent of constitutional undercooling is the temperature gradient in the liquid ahead of the interface. Remember that the temperature gradient is the variation of temperature with distance, or the slope of the actual temperature distributions shown in Fig. 7.3. Low gradients promote constitutional undercooling while high gradients will eliminate it.

If we disallow negative temperature gradients in the liquid as being unrealistic for real solidification phenomena, we see that the maximum amount of constitutional undercooling occurs with a zero temperature gradient (Fig. 7.4), and equals the difference between the liquidus temperature of the bulk alloy and the solid-liquid interface temperature. This difference is simply the freezing range of the alloy—the difference between the liquidus and solidus temperatures.

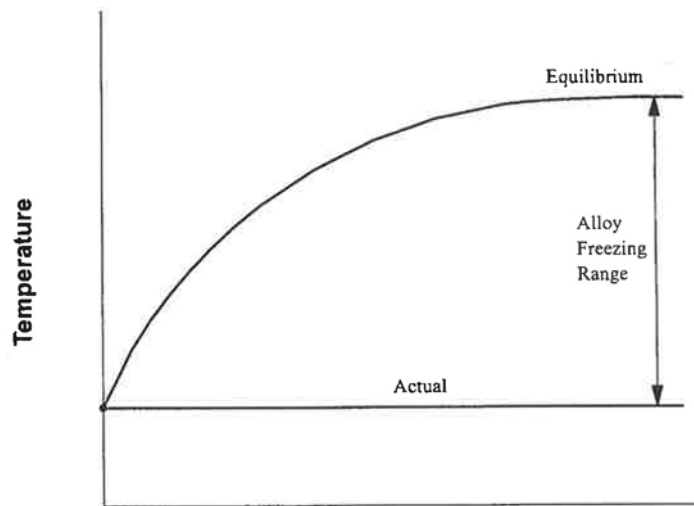
A second significant variable is the shape of the distribution of equilibrium liquidus temperature in front of the interface. If this temperature rises sharply at the interface, constitutional undercooling will be promoted; if it changes slowly with distance in front of the interface, the undercooling may be avoided. These two cases are illustrated in Fig. 7.5 for a fixed gradient of actual temperature.

In Chapter 6 it was shown that the shape of the solute profile in front of the interface depends mainly on the freezing rate. High freezing rates lead to steep concentration gradients while low rates result in more shallow gradients. The slope of the equilibrium liquidus curve in front of the interface is related directly to the slope of the concentration profile at the interface.

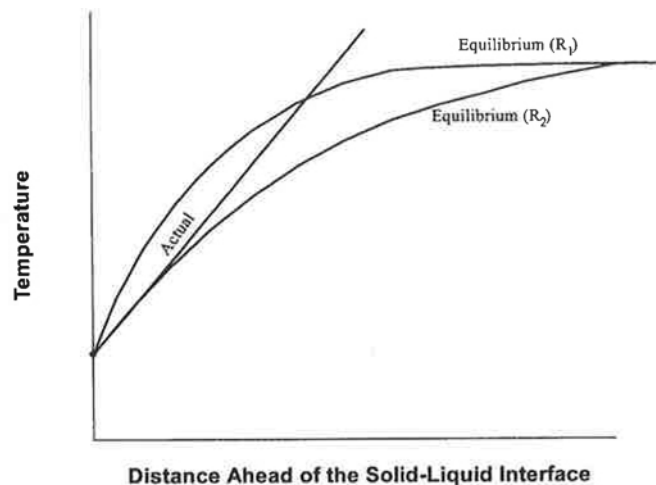
We conclude, therefore, that fast freezing rates resulting in steep concentration profiles also result in sharply rising liquidus temperature profiles at the interface with a consequent tendency to generate constitutional undercooling. Slow freezing rates, which yield shallow concentration gradients and liquidus temperature profiles, may eliminate constitutional undercooling provided that a sufficiently high temperature gradient can be maintained in the liquid. Unfortunately, this is difficult to achieve in real casting situations since slow cooling causes both the freezing rate and the temperature gradient in the liquid to decrease.

Actual liquid temperature gradients and freezing rate are the two solidification variables affecting the degree of constitutional undercooling. Other significant considerations relate to alloy composition, the phase diagram and the extent of liquid convection. Since the maximum possible solute concentration at the interface is (C_0/k_0) , it is clear that both the amount of alloy, or impurity elements, as well as the value of the distribution coefficient are important. Higher solute element concentrations lead to more constitutional undercooling, all else being equal.

Similarly, the larger the deviation of the value of k_0 from unity, the greater will be the tendency to generate constitutional undercooling. Liquid convection enters the picture because it is obvious that the origin of the undercooling lies in the solute-enriched layer at the interface. A decrease in the extent of this layer by enhanced liquid convection will diminish the amount of constitutional undercooling.



Distance Ahead of the Solid-Liquid Interface
Fig. 7.4. The maximum amount of constitutional undercooling occurs if the actual liquid temperature gradient is zero.



Distance Ahead of the Solid-Liquid Interface
Fig. 7.5. The amount of constitutional undercooling depends on the shape of the equilibrium freezing temperature variation in front of the interface. In this example, freezing rate R_1 is greater than R_2 .

During casting or ingot solidification, many of these variables are, to some extent, interdependent and it usually is not possible to vary one without changing others. For example, enhanced liquid convection also lowers temperature gradients in the liquid and improves heat transfer thus influencing the freezing rate. With the exception of specialized processes such as controlled crystal growth or zone refining, it usually is not possible to control the amount of constitutional undercooling, and industrial casting processes operate under conditions in which significant amounts of this undercooling are present.

The qualitative description presented here has concentrated on alloy systems in which $k_0 < 1$, but constitutional undercooling is also found in $k_0 > 1$ systems, where solvent rejection at the interface leads to a lowering of the equilibrium temperature there, as illustrated in Fig. 7.2. While the large majority of commercial alloy systems are of the $k_0 < 1$ type, there are some important systems in which $k_0 > 1$, for example Cu-Ni alloys in which Ni is the solvent.

An important difference between $k_0 < 1$ and $k_0 > 1$ systems lies in the range of distribution coefficients found in practice. Distribution coefficients greater than about 3 are uncommon but they may vary over at least two orders of magnitude down to about 0.01 if $k_0 < 1$. The amount of constitutional undercooling possible in $k_0 > 1$ systems is, therefore, significantly less than in $k_0 < 1$ systems.

QUANTITATIVE DESCRIPTION

We shall assume a system solidifying with a planar solid-liquid interface and some steady state solute distribution in front of that interface. Solute rejection per unit time and per unit area of interface is:

$$R(C_L^* - C_S^*)$$

where:

R is the linear freezing rate;

C_L^* is the concentration of solute in the liquid at the interface; and

C_S^* is the concentration of solute in the solid at the interface.

This solute rejection can also be expressed as:

$$RC_L^*(1-k_0)$$

Solute rejected at the interface diffuses down the concentration gradient at the interface according to the laws of diffusion. Thus,

$$J = -D_L(dC_L/dx)_{x=0}$$

where:

J is the diffusion flux;

D_L is the diffusion coefficient of solute in the liquid; and

$(dC_L/dx)_{x=0}$ is the gradient of solute concentration at the interface.

The definition of steady state requires that the rate of solute rejection at the interface equal the diffusion flux ahead of the interface. Thus:

$$RC_L^*(1-k_0) = -D_L(dC_L/dx)_{x=0}$$

and

$$(dC_L/dx)_{x=0} = -RC_L^*(1-k_0)/D_L$$

Now the gradient of equilibrium liquidus temperature in front of the interface is related to C_L by m , which is the slope of the liquidus line on the alloy phase diagram, and:

$$(dT_E/dx)_{x=0} = m(dC_L/dx)_{x=0}$$

From the earlier qualitative discussion of the origins of constitutional undercooling, it is apparent that the undercooling will occur only if the actual liquid temperature gradient at the interface is less than the slope of the equilibrium freezing temperature curve at the interface. Mathematically:

$$G_L < (dT_E/dx)_{x=0}$$

where

G_L is the actual temperature gradient, (dT/dx) , in the liquid phase.

The condition for the onset of constitutional undercooling is, then:

$$G_L \leq -mRC_L^*(1-k_0)/D_L$$

or, since $C_L^* = C_s^*/k_0$

$$G_L \leq -mRC_s^*(1-k_0)/k_0D_L \quad (7.1)$$

C_s^* is the solute concentration in the solid at the interface. The value of this quantity will depend on the mixing conditions that apply during solidification, as described in

the previous chapter. In its most general form, equation 7.1 can be written as:

$$G_L \leq -mR(1-k_0)k'C_0f_L^{k-1}/k_0D_L \quad (7.2)$$

where the appropriate value for the effective distribution coefficient is used. A common form of equation 7.2 is found when mixing in the liquid is by diffusion only and diffusion is absent in the solid. Then:

$$G_L \leq -mRC_0(1-k_0)/k_0D_L \quad (7.3)$$

CONSEQUENCES OF CONSTITUTIONAL UNDERCOOLING

Like any undercooling, the constitutional variety represents a departure from equilibrium. In the presence of a zero liquid temperature gradient, an amount of constitutional undercooling equal to the freezing range of the alloy is possible. Depending on the particular alloy system, the freezing range may extend up to 100°C (180°F) or even greater. Such large departures from an equilibrium state are virtually impossible to sustain, and the freezing system will somehow adapt in such a way that the cause of the nonequilibrium is removed.

When an alloy solidifies under conditions such that a planar solid-liquid interface would experience constitutional undercooling according to equation 7.1 or 7.2, the interface morphology changes from planar to a form where the undercooling is eliminated. Many morphologies are possible, but one of the simplest is the two dimensional cell shown schematically in

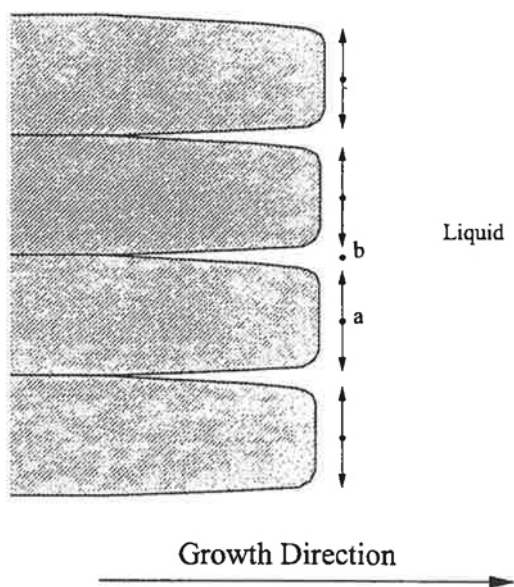


Fig. 7.6. Schematic illustrates a two-dimensional cellular structure. The directions of lateral solute diffusion are shown.

Fig. 7.6. Let us examine how the morphological change from a planar to a cellular interface is able to eliminate constitutional undercooling. The reasoning presented is developed for a $k_0 < 1$ solute because this is the most common solute type found in commercial alloys, but it should be noted that the same conclusions apply for a $k_0 > 1$ system.

Diffusion of solute at a planar interface can occur in one direction only—perpendicular to that interface into the bulk liquid. No lateral diffusion is possible because no lateral (parallel to the interface) solute gradients are present. If the interface now adopts a nonplanar morphology, lateral solute gradients are developed, and diffusion of solute parallel to the interface becomes possible.

Consider the two points a and b in Fig. 7.6. They lie on a line normal to the growth direction or the heat flow direction. Point b is farther from the local interface than

point a because of the nonplanar nature of the interface. Therefore, point b will experience a lower solute concentration than point a, and a driving force then exists for solute diffusion laterally from a to b.

The solute-enriched boundary layer in front of the cell centers will be minimized by this diffusion, which serves to locate solute in the cell boundaries. This depresses the local freezing temperature and causes solidification of the boundaries to occur at a lower temperature, well behind the main interface. The overall effect of the lateral diffusion is a local redistribution of solute from in front of the main solidifying interface to boundaries between the cells. Constitutional undercooling is eliminated, but local chemical inhomogeneities are produced.

CELLULAR SOLIDIFICATION

Cellular solidification takes place if the alloy and growth conditions are such that only small degrees of constitutional undercooling are present, as predicted by equations 7.1 and 7.3. Considerable research has been conducted into the formation of cells during solidification and it has been established that a gradual transition takes place from the planar interface to well developed hexagonal cells.

The various stages in this transition are shown in Fig. 7.7 in different views of “decanted” solid-liquid interfaces produced by rapid separation of solid from liquid during growth. When no constitutional undercooling is present, the interface is featureless except for a few grain boundaries. At very small amounts of the undercooling, one-dimensional solute-rich cells, which resemble pipes, form in the interface leading to the node structure.

As growth conditions are changed to favor the development of more constitutional

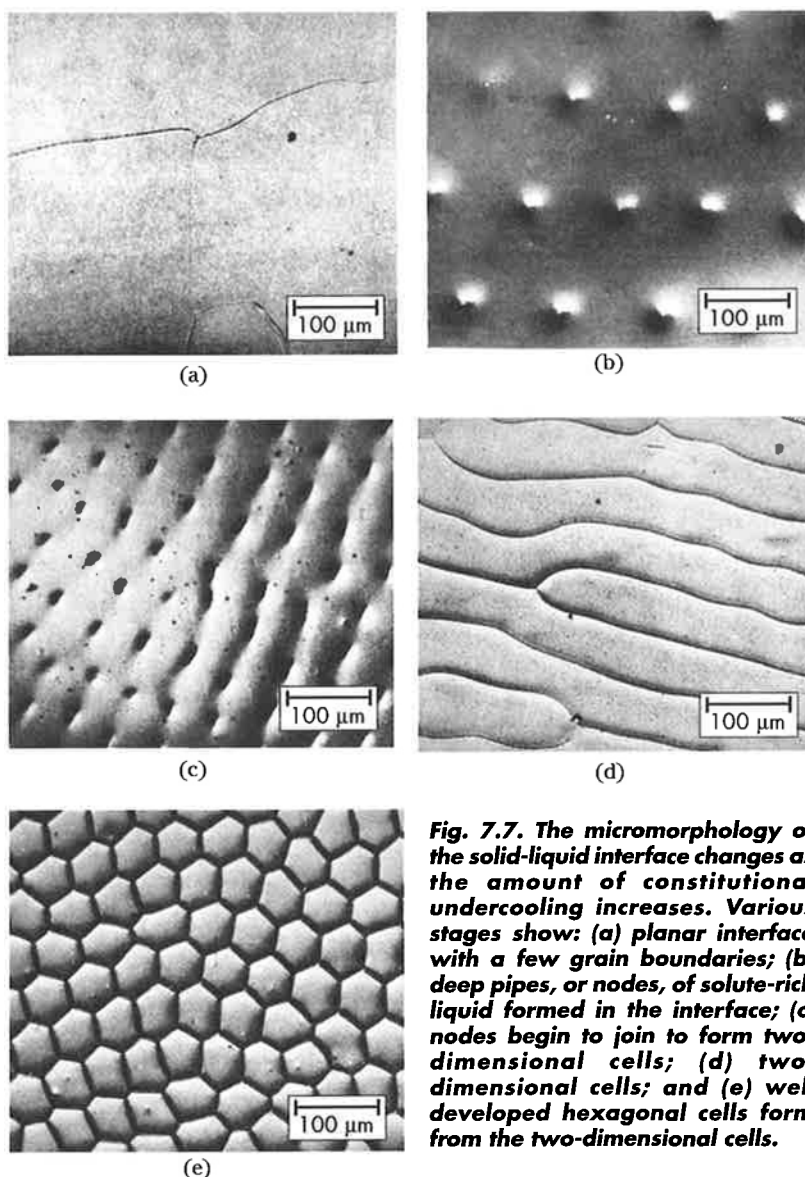


Fig. 7.7. The micromorphology of the solid-liquid interface changes as the amount of constitutional undercooling increases. Various stages show: (a) planar interface with a few grain boundaries; (b) deep pipes, or nodes, of solute-rich liquid formed in the interface; (c) nodes begin to join to form two-dimensional cells; (d) two-dimensional cells; and (e) well developed hexagonal cells form from the two-dimensional cells.

undercooling, for example by increasing the freezing rate or lowering the liquid temperature gradient, valleys form between the nodes and are eventually joined to yield a two-dimensional cellular structure. Further encouragement of constitutional undercooling results in a segmenting of the two-dimensional cells with eventual formation of hexagonal cells arranged in close-packed arrays. Note that as the freezing conditions change to produce increasing amounts of constitutional undercooling, the morphology responds by providing a structure capable of redistributing increasing amounts of solute into a larger and larger cell boundary area.

The association of the cellular structure with the presence of constitutional undercooling was demonstrated in the early days of solidification research through controlled freezing experiments in which liquid mixing was by diffusion only. Solidification parameters were varied, as was alloy composition, and the growth morphology was studied.

Some typical results taken from this early literature are plotted in Fig. 7.8, showing a linear transition line from planar to cellular growth when morphology is plotted as a function of solute concentration (C_0) and ratio of temperature gradient to growth rate (G_L/R). This is precisely what would be expected on the basis of equation 7.3, and is generally accepted as verification of the dependence of the growth morphology on the presence of constitutional undercooling.

Equations 7.1 to 7.3 predict the thermodynamic state of the liquid ahead of the interface. It has been pointed out by Mullins and Sekerka¹ that the transition from a planar to a cellular interface should also involve surface energy because there is a considerable solid surface area increase when cells are formed.

The authors developed an elegant criterion for instability of the solid-liquid interface considering whether or not a change in shape is dynamically possible rather than just thermodynamically possible. Their analysis predicts the same conclusions as does the simpler thermodynamic one for normal growth conditions. Differences are predicted for materials, such as those with high α -factors, possessing a high latent heat or for metals freezing at rapid rates. Unfortunately, the assumptions of the analysis break down

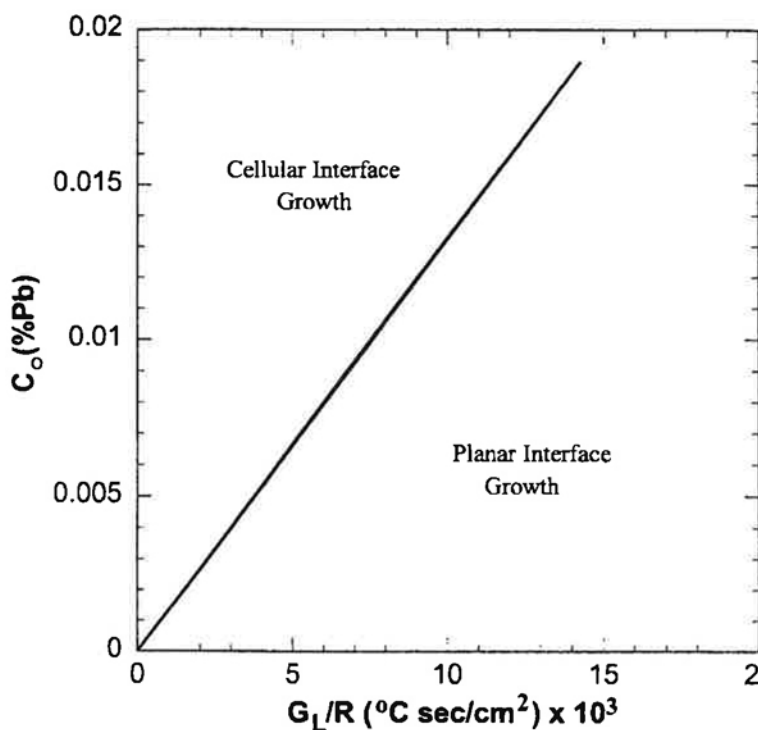


Fig. 7.8. Experimental data show a linear transition from a planar to a cellular interface when C_0 is plotted versus (G_L/R) . [From D. Walton et al., *Trans. AIME*, vol 203, pp 1023-1031 (1955)].

under these conditions making verification difficult. The simpler thermodynamic criteria are the ones generally accepted for prediction of a planar to a cellular transition.

DENDRITIC GROWTH

The freezing of industrial castings and ingots takes place under conditions that generate amounts of constitutional undercooling far in excess of what can be eliminated by simple cellular solidification. This difficulty is handled by generating a highly branched three-dimensional structure known as a dendrite (Fig. 7.9). Solute is displaced by lateral diffusion to the spaces between adjacent dendrites and to spaces between the various dendrite arms. This tree-like structure is a very efficient means of solute redistribution and, hence, of constitutional undercooling elimination.

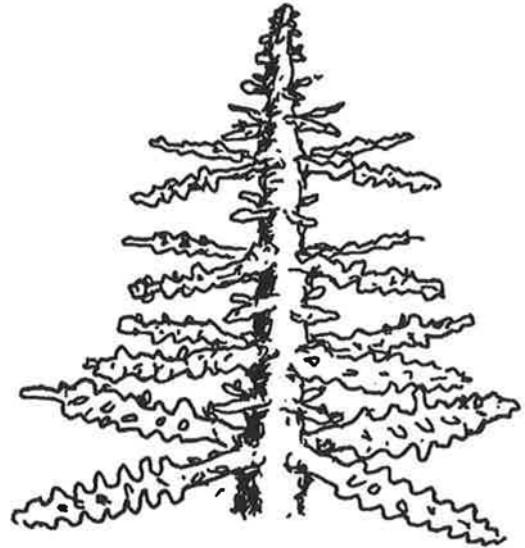
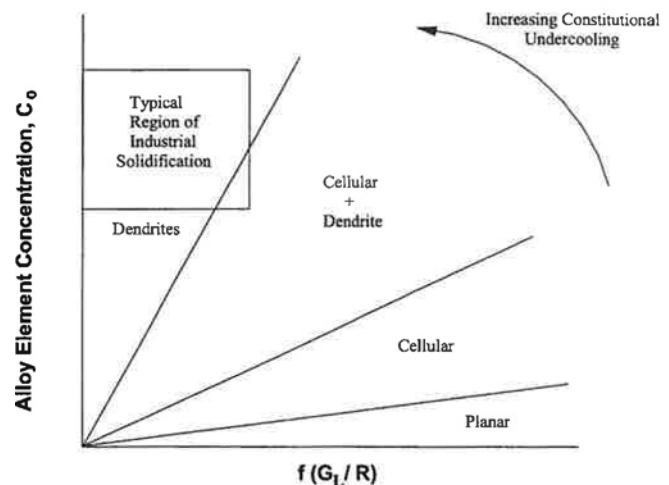


Fig. 7.9. Schematic presents an interpretation of a three-dimensional dendrite.

As a result, it is the basic solidification morphology encountered in practice. It should also be acknowledged that the dendrite is a basic morphological form in nature, commonly found in trees, foliage and various coral formations. The book by D'Arcy Thompson, listed in Further Reading at the end of this chapter contains an interesting discussion of the dendritic form.

Figure 7.10 presents a schematic view of the change in solidification morphology as the amount of constitutional undercooling increases. A planar interface is present under solidification and alloy composition conditions at which no constitutional undercooling exists. These conditions are rarely met in practice, except in some single crystal growth processes. Then, as conditions change so that the alloy level increases or the ratio (G_L/R) decreases, the micromorphology becomes progressively cellular, a mixture of cells and dendrites and, finally, fully dendritic. As indicated, industrial solidification is fully dendritic with just a possibility of some cell formation under special conditions.



Dendrites in metal alloys are usually seen on two-dimensional metallographic sections where they can have many appearances. They also can be viewed by scanning

Fig. 7.10. Solidification morphology changes as the amount of constitutional undercooling is increased by either increasing the amount of alloying element (C_0) or decreasing the ratio of G_L to R . Note that the precise (G_L/R) function is not specified. This function is different for each transition and is not necessarily linear.

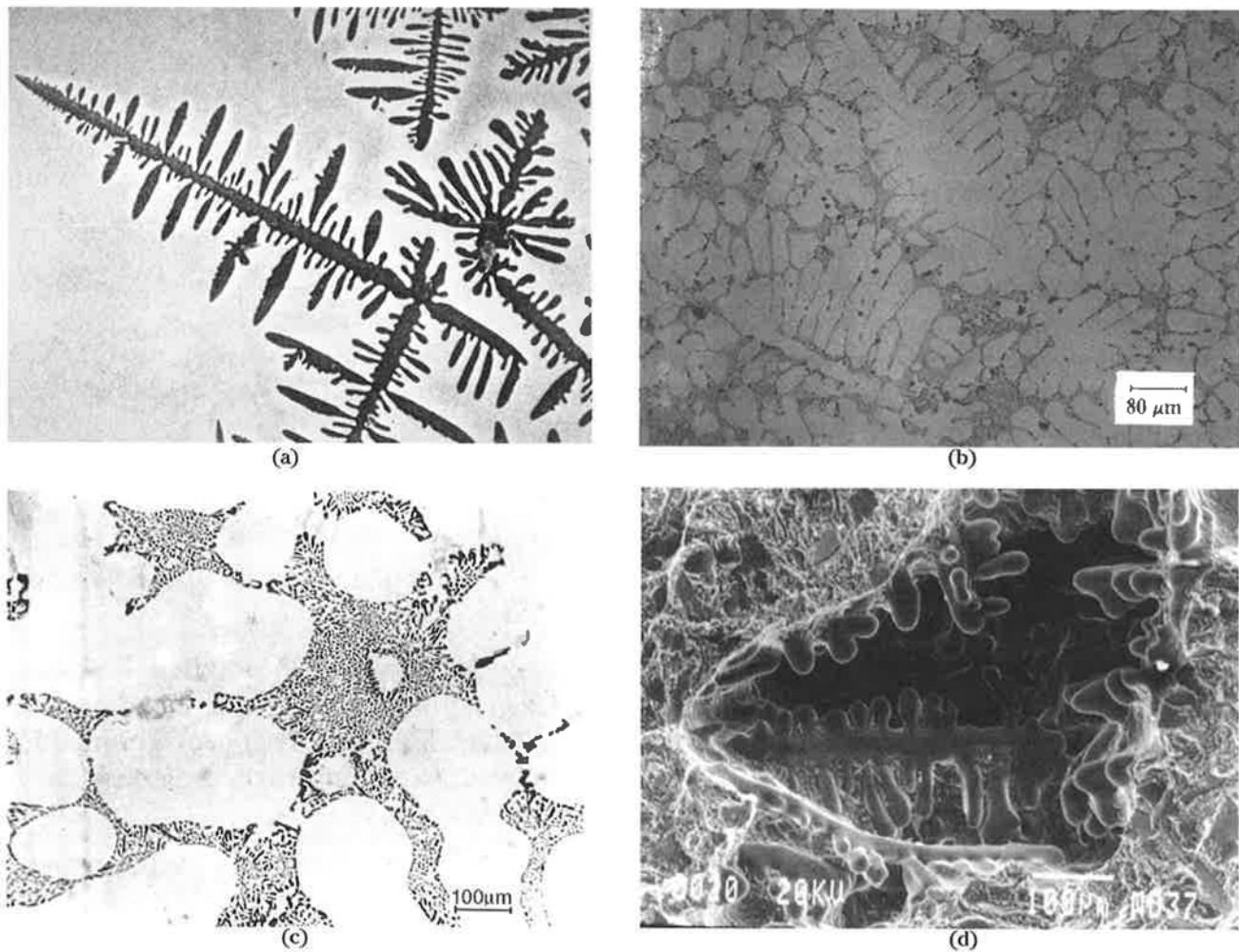


Fig. 7.11. (a) A partially solidified dendrite of hexachloroethane is shown; (b) An aluminum dendrite in an Al-Si casting alloy is sectioned along its primary stalk. (c) Random sectioning reveals dendrite arms as disconnected primary phase particles (white phase). (d) Free surface of growing dendrite arms can be seen inside a pore.

electron microscopy on the inner surface of gas or shrinkage pores in castings. Figure 7.11 shows various dendritic structures as they may appear to the observer.

A partially solidified dendrite of hexachloroethane is seen in Fig. 7.11a and aluminum dendrites on a metallographic section are shown in b and c. Sectioning a dendrite along its primary stalk reveals the typical branched structure where secondary, and sometimes even tertiary, arms can be seen (Fig. 7.11b), but most often the random sectioning associated with metallographic preparation reveals dendrites as randomly placed particles of primary phase (Fig. 7.11c). If removal of the matrix material between these primary phase structures were possible, for example by deep etching, it would be seen that the primary phase was interconnected within a dendritic morphology. The free surface of dendrite arms is seen clearly inside the shrinkage pore of Fig. 7.11d.

The appearance of metal dendrites on a metallographic specimen depends strongly

on the level of alloying elements present. Since the function of the dendrite is to displace solute away from the solidifying interface and, hence, to relieve constitutional undercooling, it is apparent that the space between dendrite arms must increase to accommodate increasing amounts of solute elements. The higher the alloy element concentration, the more filamentary is the dendrite, or alternatively, dendrites at low alloy concentrations are more bulbous in appearance. The influence of alloy element level is illustrated very well in Fig. 7.12, showing dendrites of lead formed in a lead-antimony alloy. The increasingly filamentary nature of the dendrites with higher solute concentrations is a result of the greater volume of interarm solute-rich material.

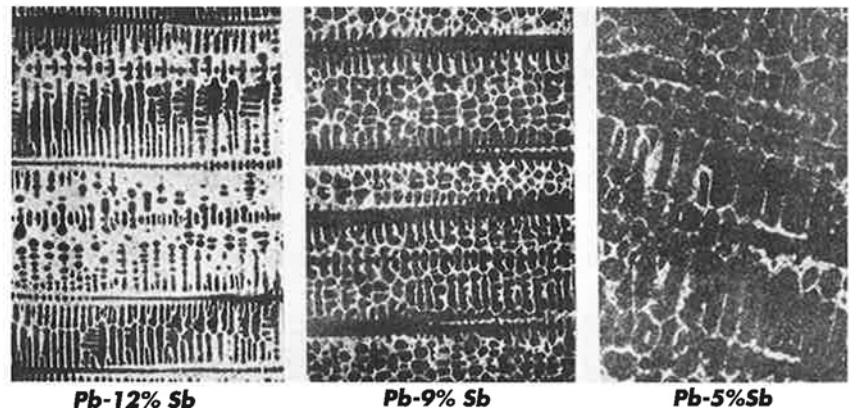


Fig. 7.12. The metallographic appearance of dendrites depends on the alloying level as seen in this Pb-Sb example.

The photographs of Fig. 7.11a and b, in particular, demonstrate that the branching is regular and follows definite directions. Branching in cubic materials is along the $\langle 100 \rangle$ directions giving these dendrites a four-fold symmetry. Hexagonal materials solidify with dendrites having a six-fold symmetry (e.g., a snowflake) with branching along the $\langle 10\bar{1}0 \rangle$ directions. Dendrites in commercial castings are almost always well developed and very distinct because of the high solute concentrations present in commercial alloys. Various intermediate stages in dendrite development may occur at lower degrees of constitutional undercooling. These are sketched in Fig. 7.13, which shows dendrite development from a circular cell in a cubic material.

By far, the most important practical aspect of the dendritic structure is the secondary dendrite arm spacing. This quantity, usually referred to as the DAS, is significant because it has been shown that many mechanical properties can be related to it (Fig. 7.14), with the

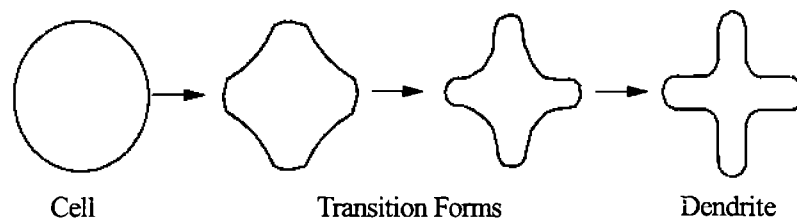


Fig. 7.13. A schematic interpretation of the cell to dendrite transition is presented.

best properties always associated with the smallest DAS. In many ways, DAS is just a measure of the overall fineness of the cast microstructure. A small value of DAS implies that the structure is fine, with all of the associated benefits including smaller grains, finer intermetallics, better microhomogeneity and less as well as better distributed porosity. All of these desirable features of the cast structure are responsible for the good mechanical properties associated with small DAS.

For many alloys, an empirical relationship exists between DAS and the local freezing time. An example, for a commonly used aluminum foundry alloy, is given in Fig. 7.15. The general relationship is:

$$\text{DAS} = at_f^n$$

where:

- a is a constant, the value of which depends on the alloy;
- n is a constant with a value between 0.3 and 0.5; and
- t_f is the local solidification time.

Local solidification time is defined as the time it takes a given location to pass from the liquidus to the solidus temperature. Thus:

$$t_f = F/GR$$

where:

- F is the alloy freezing range;
- G is the local temperature gradient; and
- R is the linear rate of freezing.

The value of F applied in this equation is the nonequilibrium freezing range that is the temperature difference between the

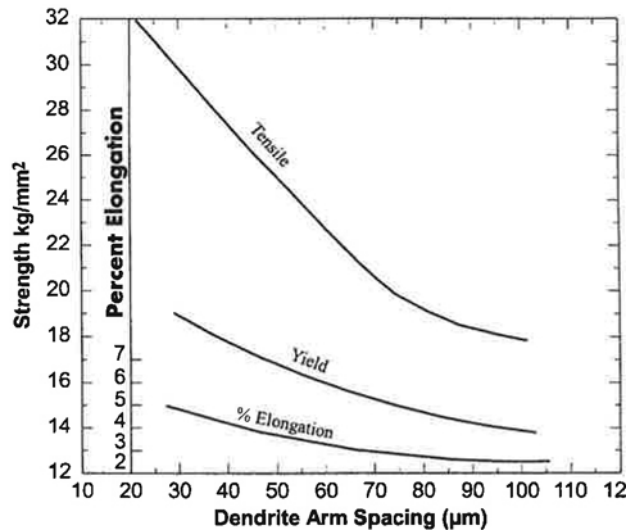


Fig. 7.14. Some mechanical properties can be related to the dendrite arm spacing. The example presented is for a 356 aluminum alloy. [Data replotted from K. Rodhakrishna et al., *AFS Transactions*, vol 88, pp 695-702 (1980)].

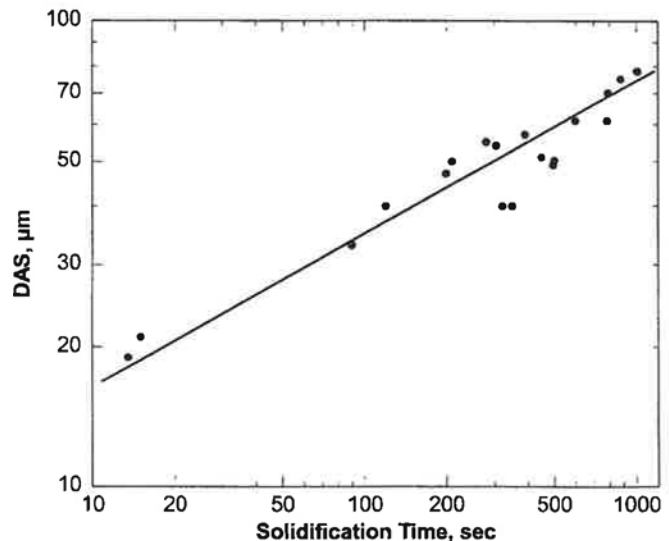


Fig. 7.15. The relationship between DAS and local freezing time is given for a 356 aluminum alloy. [Data replotted from Q.S. Hamid and R. Elliott, *Cast Metals*, vol 6, pp 42-46 (1993).]

liquidus and the freezing point of the lowest melting segregate. In a eutectic system, the freezing range would be the temperature difference between the liquidus and the eutectic temperatures.

Local solidification times are usually measured from cooling curves obtained by placing thermocouples in appropriate locations within the casting. They may also be determined by thermal modeling. Measurement of DAS is painstaking and requires measurement of the average spacing on dendrites that have been sectioned along their primary stalk (Fig. 7.16). Sufficient measurements must be taken to ensure statistical reliability. One of the main uses of reliable DAS-local freezing time data, such as that shown in Fig. 7.15, is to calculate local freezing times from metallographically-obtained measurements of DAS. Local solidification times so obtained are reasonably reliable and require neither thermal modeling nor insertion of thermocouples into the cast alloy.

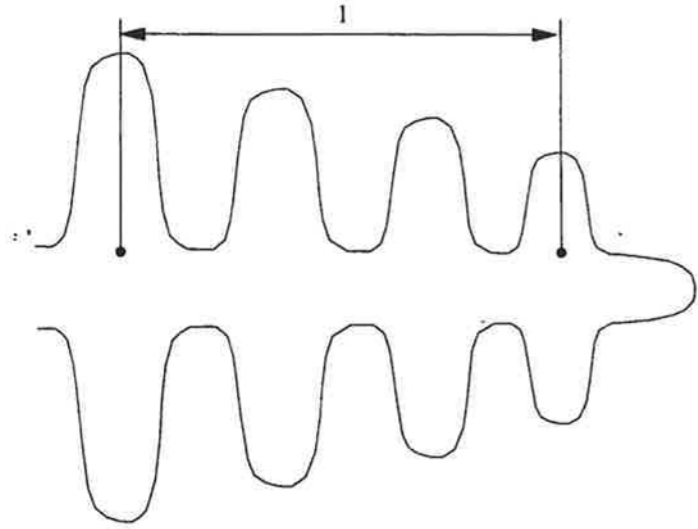


Fig. 7.16. A methodology for measurement of DAS is illustrated.

The dependence of DAS on local freezing time is an interesting example of the general phenomenon of coarsening, or Ostwald Ripening, which is common when dealing with microscopic features having a small radius of curvature. Coarsening was first studied in the 19th century when photographic emulsions were found to coarsen with time leading to graininess in the image. The phenomenon is based on a relationship first developed by Gibbs, which states that the equilibrium temperature of a phase change depends on the radius of curvature of the particles taking part in the reaction. Normal equilibrium reaction temperatures pertain to flat particles (infinite radius of curvature). These temperatures will be increased or decreased if the radius of curvature is finite according to the relation:

$$\Delta T_r = 2\gamma T_{E(\infty)} / rL$$

where:

- ΔT_r is the difference in reaction temperature between a flat particle and one with curvature. (In our case, we are speaking of solidification and this quantity represents a depression or an elevation of the freezing point with respect to a flat solid-liquid interface.);
- r is the radius of curvature;
- γ is the solid-liquid surface energy;
- $T_{E(\infty)}$ is the melting point for a flat interface with infinite radius of curvature; and
- L is the latent heat of fusion.

The freezing point is lowered if the solid particle is convex into the liquid. Conversely, it is raised if the interface is concave into the liquid. These effects may be rationalized in a qualitative way by regarding atoms at a highly convex interface as having somewhat fewer nearest neighbors than if the interface were flat. As a result, they are less firmly bound into the solid and can leave the solid for the liquid at a lower temperature. The reverse also is true. Atoms at a concave interface have effectively more nearest neighbors, are bound more tightly and require a higher temperature to give them the energy to escape from the solid and enter the liquid. While any deviation from a planar interface will generate some effect on the melting point, this is negligible unless one is dealing with very small radii of curvature, as is the case with dendritic growth.

Melting point dependence on radius of curvature implies that the location of the liquidus line on the phase diagram also should depend on the radius of curvature. Consider two adjacent dendrite arms, as illustrated in Fig. 7.17, having different radii of curvature at their tips such that $r_b < r_a$. A depression of the liquidus below the normal liquidus for $r = \infty$ occurs with the depression being greater for the arm with the smaller radius of curvature (arm b), (Fig. 7.18). Now the dendrites coexist within a few micrometers of each other and are, therefore, isothermal. A tie line on the phase diagram indicates that the liquid composition in contact with each arm is different, with the smaller arm having less solute, or alternatively, more solvent. A composition gradient, then, exists between the two arms such that solute diffuses from the larger to the smaller arm, depressing the freezing point and causing the smaller arm to melt. Perhaps more importantly, solvent diffuses from the smaller to the larger arm. Since the dendrites are solvent-rich structures, the smaller arm will disappear. The overall effect is a disappearance of small radii of curvature arms and a growth of those arms with large radii of curvature. High temperature and liquid phase diffusion facilitate the process, which can only occur at significant rates while the alloy is within the liquid plus solid, or mushy, region of solidification. The time spent in this region, which is the local freezing time, therefore determines the ultimate dendrite arm spacing seen in a cast material.

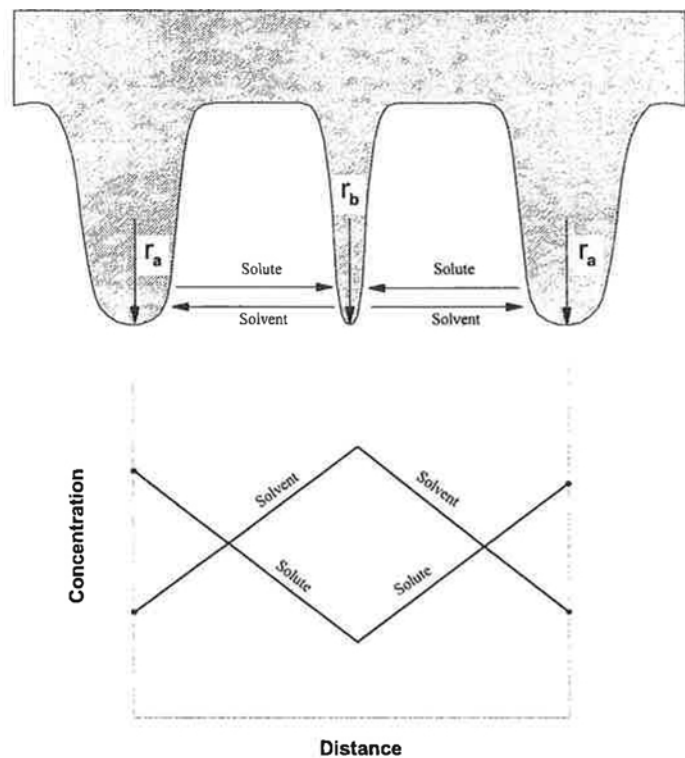


Fig. 7.17. Two adjacent dendrite arms having different tip radii of curvature are shown, as is the concentration gradient of solute and solvent between them. The arm with the smaller radius of curvature contains more solvent but less solute than the neighboring arms. The smaller radius of curvature arm eventually disappears as solvent atoms diffuse away from it and solute atoms diffuse toward it.

In the example just presented, diffusion acts to cause the arm to disappear completely. Dendrite arms are often observed to melt away from the main stalk to form free-floating pieces of solid. Close examination of the dendrite in Fig. 7.11a will show that the secondary arms are attached weakly to the main stalk by only a thin solid connection of the type sketched in Fig. 7.19. Growth through the solute boundary layer at the primary stalk-liquid interface is slow because of the relatively low solvent concentration here.

Once through the boundary layer, the arm grows more rapidly in all directions, resulting in the observed “onion” shape. The radius of curvature at the base of the arm is less than that on the adjacent primary stalk or on the rest of the arm. Matter transport occurs as described previously and the connection with the stalk melts, allowing the remainder of the arm to float free. We will see later that these bits of solid can be effective nucleation sites for further growth, particularly in ingot solidification.

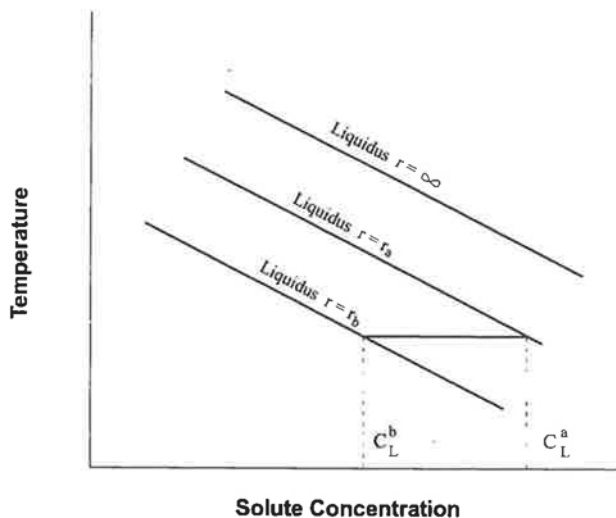


Fig. 7.18. The liquidus line positions for an infinite radius of curvature (flat) interface and for the dendrite radii of Fig. 7.17 are shown.

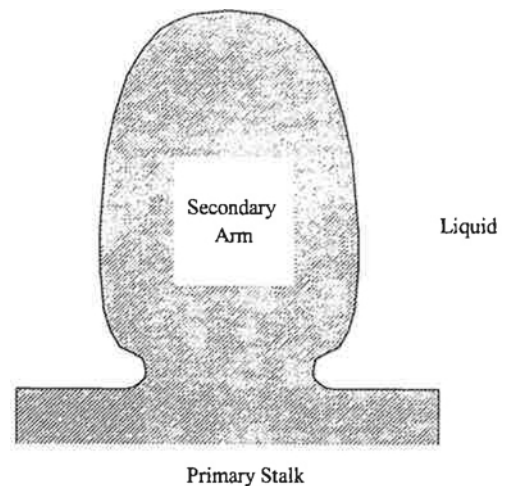


Fig. 7.19 A schematic representation of the primary stalk/secondary arm junction is given.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

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chapter8

SEGREGATION PHENOMENA

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

Segregation is the practical consequence of the solute redistribution phenomena discussed in Chapter 6. The term refers to the inhomogeneous distribution of solute elements on either the microscale (microsegregation) or the macroscale (macrosegregation). Segregation of either variety is one of the major difficulties associated with the production of cast materials, ingots or castings, although the problem generally is more severe in ingot solidification because of the thicker sections and longer freezing times associated with ingots.

MICROSEGREGATION

Segregation on the microscale usually refers to inhomogeneities associated with the dendritic structure at the size scale of dendrites, i.e., from a few micrometers to a few hundred micrometers. Cellular solidification also results in inhomogeneities because of solute accumulation in the cell boundaries ($k_0 < 1$) or in the cell centers ($k_0 > 1$), but this type of microsegregation is of little practical concern because industrial solidification almost always proceeds by a dendritic growth mechanism.

Two examples of interdendritic microsegregation, as it appears on metallographic sections, are given in Fig. 8.1. The microstructure shown in Fig. 8.1a is that of a leaded gunmetal (85%Cu-5%Sn-5%Zn-5%Pb). Lead is virtually insoluble in copper and segregates to the interdendritic spaces. It is evident as the black phase appearing between the arms of the primary copper dendrites. Figure 8.1b shows the microstructure of a 90%Cu-10%Sn phosphor bronze. The interdendritic eutectoid is formed as a result of tin segregation during solidification. Under equilibrium conditions, this alloy should freeze as a single phase solid solution.

Because of the general importance of dendritic solidification, the remainder of this discussion will focus on interdendritic segregation.

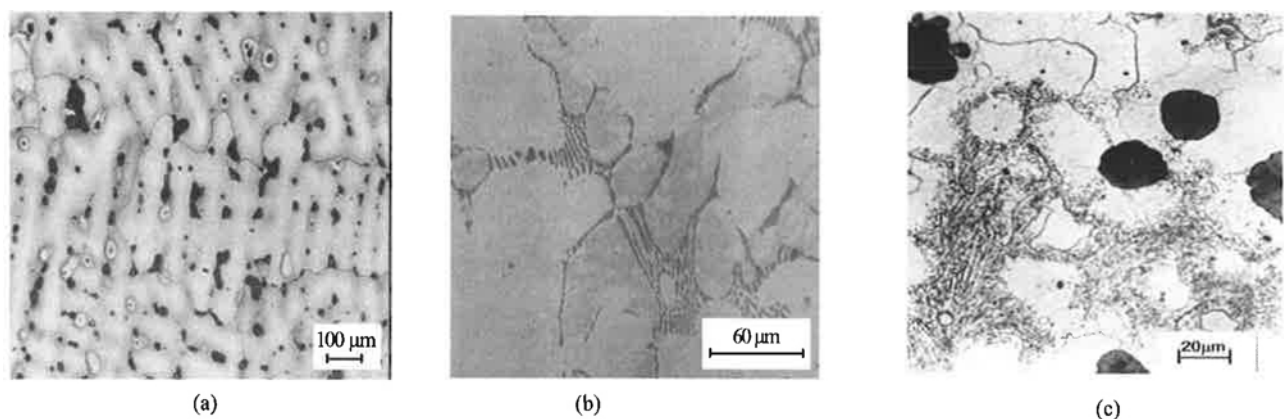


Fig. 8.1 Examples of microsegregation are shown. The microstructures are: (a) leaded gunmetal (85%Cu-5%Sn-5%Zn-5%Pb); (b) 90%Cu-10%Sn phosphor bronze; (c) steadite formation in a nital etched ductile cast iron. [Photographs (a) and (b) courtesy of the Copper Development Association.]

Interdendritic segregation can be quantified by measuring solute concentrations within the microstructure by either electron microprobe analysis or energy dispersive analysis. The segregation ratio, defined as

$$S = C_{\text{MAX}}/C_{\text{MIN}}$$

is often used to indicate the extent of microsegregation, where the appropriate concentrations are measured by the techniques indicated above.

The solute distributions and their metallographic appearance, arising from microsegregation, depend on the form of the phase diagram. Alloy systems in which extensive solid solubility is possible usually will exhibit continuous variations in solute concentration from one dendrite to the next, or from one dendrite arm to the next. The brass sample shown in Fig. 6.2 is an excellent example, with the color variations showing the continuously changing zinc concentrations.

The general form of the solute distribution from the center of one dendrite to the center of its adjacent neighbor is shown in Fig. 8.2 for a simple isomorphous system such as Cu-Ni. Note that in the absence of solid state diffusion, composition in the center of the dendrite should be $k_0 C_0$, the composition of the first solid to form in any freezing process.

If the alloy system contains a eutectic reaction, as is so often the case in industrial alloys, segregation to the eutectic composition usually will occur between dendrite arms and between the dendrites themselves, even though no eutectic formation is predicted from the phase diagram. A solute gradient is found within the primary phase, and some amount of the two-phase eutectic structure will form between dendrite arms and between dendrites. A schematic variation of the Mg concentration is shown in Fig. 8.3 for the Al-10%Mg alloy referred to in Chapter 6.

CALCULATION OF MICROSEGREGATION

The composition gradients resulting from microsegregation can be estimated relatively well using the Scheil equation. It will be recalled that the assumptions behind this equation are a lack of

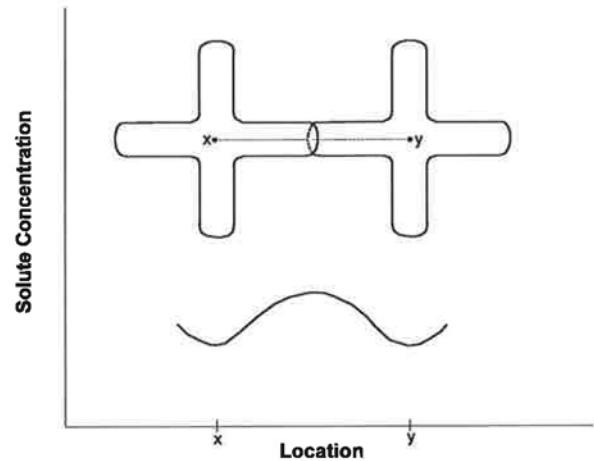


Fig. 8.2. In an isomorphous system ($k_0 < 1$), solute distribution varies continuously from the center of one dendrite to the center of the next.

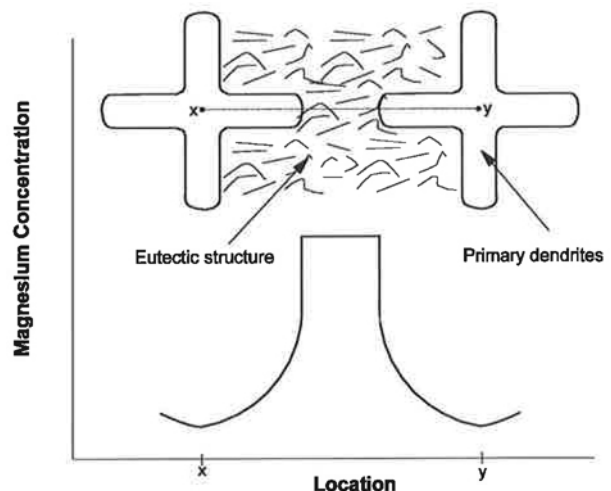


Fig. 8.3. In a eutectic system, such as Al-Mg, the solute concentration varies continuously within the primary phase, and some eutectic is found within the interdendritic region.

diffusion in the solid and a state of complete mixing in the liquid. The assumption of no diffusion in the solid is usually quite valid for small castings; in larger castings and ingots, it is less valid, but can be corrected for, as we shall see later. The small volume of liquid existing in the interdendritic spaces assures a state of complete liquid mixing, due not so much to convection, but to diffusion which can be effective over the short distances involved within the solidification times available.

The results of a Scheil calculation for interdendritic segregation in the Al-10%Mg alloy of Fig. 8.3 are illustrated in Fig. 8.4. It is easiest to consider that the two dendrite arms grow toward each other with the resultant solute distribution symmetrical about the center of the interarm space. The magnesium concentration rises continuously from 3%Mg in the arm center to the 15%Mg limit of solid solubility when 90% of the interarm liquid has frozen. Beyond that point, the eutectic solidifies, resulting in 10% by weight of the interarm material being of eutectic composition. Conversion to volumetric percentages is possible by dividing by the densities of the phases involved.

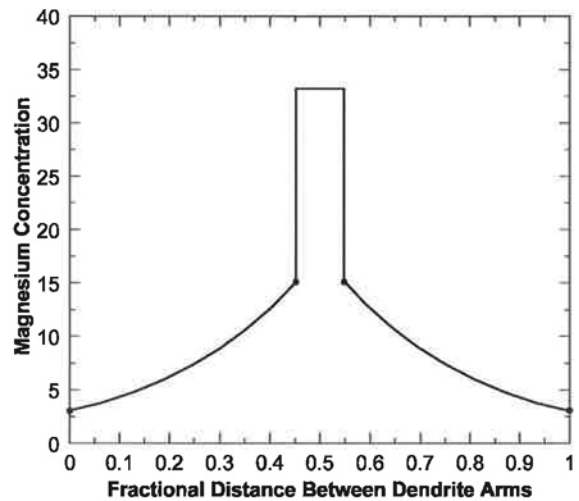


Fig. 8.4. Illustration shows the calculated magnesium distribution between two adjacent dendrites in an Al-10%Mg alloy.

Diffusion in the solid state, if present in any significant quantity, will act to reduce the concentration gradients, somewhat, by increasing the solute concentration in the center (for $k_0 < 1$) and decreasing the amount of eutectic that forms. Nevertheless, a simple Scheil calculation often gives an excellent first approximation to the extent of interdendritic segregation. If substantial solid state diffusion is present, a modified version of the Scheil equation may be employed:

$$C_s = k_0 C_0 (1 - f_s / \beta k_0)^{k_0 - 1}$$

where

$$\beta = 4D_s t_f / DAS^2$$

D_s = solute solid state diffusion coefficient

t_f = local freezing time and

DAS = dendrite arm spacing.

The quantity, β , is relatively independent of freezing rate which determines the local freezing time and, thus, the DAS as outlined in Chapter 7. Dendrite arm spacing usually varies as the square root of the local solidification time. An increase in the value of t_f will increase the DAS by the same amount, and β will remain constant. Even when the DAS does not vary exactly as $t_f^{0.5}$, the deviation from this relationship is usually small. We can conclude, therefore, that the extent of microsegregation is approximately constant over a wide range of casting processes.

Note that here we are considering only the compositional variations in microsegregation as measured by the segregation ratio. The coarseness or size of the segregated regions is another matter, and is strongly dependent on the local cooling rate and, consequently, on the exact casting process used. Rapid cooling, by permanent mold casting for example, will produce smaller volumes of segregation than will the slower cooling typical of sandcasting. The reason for this, of course, is the dependence of DAS on cooling rate, and the fact that the segregated regions lie between the dendrite arms.

Of all the solidification and alloy variables that contribute to solute redistribution, it is the distribution coefficient, k_0 , that is the most important since the greater the deviation of k_0 from unity, the greater the amount of solute rejection at the solid-liquid interface. The segregation ratio, thus, increases as k_0 decreases. One of the practical difficulties involved in trying to calculate exactly the amount of microsegregation lies in knowing the value of k_0 in complex alloys. Values taken from binary or ternary phase diagrams usually are used, but caution must be exerted as the addition of even small amounts of elements may cause the value of k_0 to change markedly.

INTERGRANULAR SEGREGATION

There is a lot of information available pertaining to the occurrence of intergranular segregation during solidification. It is supposed that two grains grow toward each other and the terminal transients of solute overlap to form a solute-rich (if $k_0 < 1$) grain boundary area. In fact, this phenomenon almost never occurs in actual alloy solidification because the solid-liquid interface is never planar and has no appreciable solute-enriched layer in front of it. All of the solute lies between, or within, the dendritic structures and the segregation is totally interdendritic.

Alloy grains consist of a family of dendrites originating from a common nucleus. The microsegregation, therefore, is found within the grain, but not along the grain boundary. It is probable that the concept of grain boundary segregation arose from wrought alloys, where indeed it can be found as a result of preferential precipitation in the solid state of certain phases at the grain boundary.

CONSEQUENCES OF MICROSEGREGATION

Microsegregation may result in totally unexpected alloy behavior, especially when the equilibrium phase diagram is used as the basis for prediction of alloy microstructure. Some examples are given below.

Case 1—Occurrence of unexpected phases.

As alloying elements concentrate in the interdendritic areas, phases that are not predicted from the bulk alloy composition may form in these locations. Such phases are usually equilibrium phases in the system concerned and normally would be found at higher alloying levels. Very often, these are intermetallic phases which, because of their morphology or properties, act to determine the overall properties of the material.

The microstructure of Fig. 8.1b is an example. The eutectoid phase would be absent if it were not for the interdendritic segregation of tin. Another example of the occurrence of unexpected phases is seen in the microstructure of Fig. 8.5a showing a cast 355 aluminum alloy. This alloy contains 5%Si, 1.4%Cu, and 0.2%Fe. Three intermetallic phases are seen in the structure, each of which arises from interdendritic segregation. Had the alloy solidified in an equilibrium fashion, none of these intermetallic phases would form.

The various cast irons provide many examples of unexpected phases resulting from microsegregation. These alloys are among the most chemically complex cast metals. They can contain a variety of impurities, as well as alloying elements added to control the graphite type, the matrix structure or to facilitate heat treatment. The iron-iron phosphide eutectic (steadite) is a common segregate that can occur at phosphorus (P) levels as low as 0.08%, even though the Fe-Fe₃P eutectic composition itself is found at 10.2%P.

Steadite (Fig. 8.1c) is detrimental to the mechanical properties and cannot be removed by heat treatment. Another significant problem in cast iron solidification is the strong tendency of molybdenum to segregate interdendritically. This element is added to allow effective austempering of heavy section ductile iron castings. Molybdenum tends to segregate heavily to the interdendritic spaces, resulting in the formation of various molybdenum carbides. If sufficient molybdenum is combined in this form, a successful austempering may not be possible.

Case 2—Formation of low melting eutectics.

If the alloy phase diagram contains a eutectic reaction, microsegregation likely will proceed to the point where isolated regions of this low melting structure are formed. These may melt during subsequent heat treatment, for example, during a homogenization treatment, if the treatment temperature is determined simply as the equilibrium solidus temperature of the alloy. Melting also may occur during service if there is exposure to high temperatures. Such “burning” of the alloy will cause an embrittlement and may result

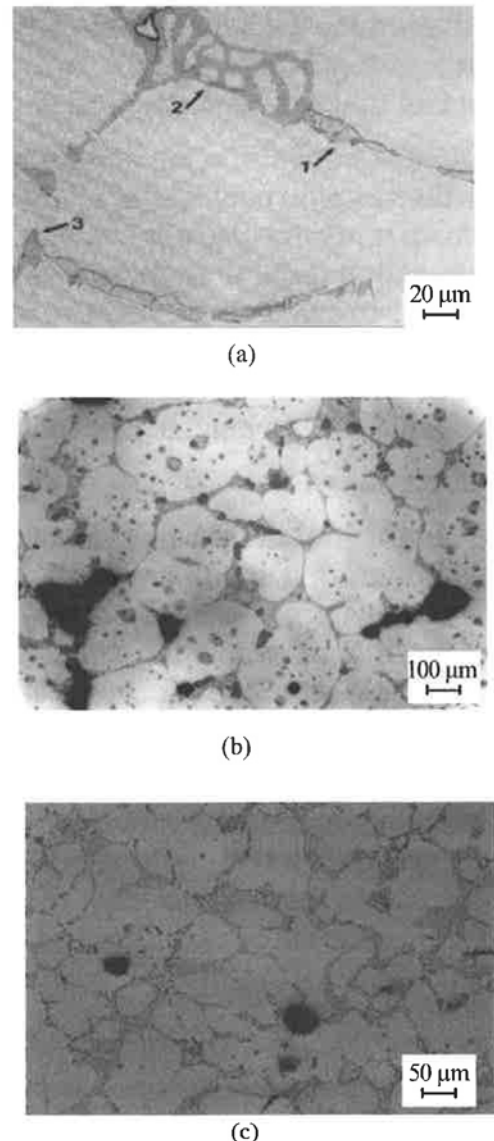


Fig. 8.5. (a) The microstructure of a cast 355 Al alloy is shown. In addition to the aluminum solid solution, the structure contains three intermetallic phases: (1) CuAl_2 ; (2) $\text{Al}_3\text{Mg}_2\text{FeSi}_6$; and (3) $\text{Al}_3\text{Mg}_2\text{Cu}_2\text{Si}_6$. (b) “Burning,” or partial melting, in a 319 aluminum alloy (Al-Si-Cu), resulting from heat treatment at an improper temperature, is shown. [Photo courtesy of A. Lakshmanan.] (c) Gas pores, resulting from hydrogen segregation coupled with shrinkage, form during the solidification of aluminum alloys.

in shape changes due to slumping while at temperature. Figure 8.5b shows the microstructure of an overheated or burned 319 aluminum alloy that was heat treated above the eutectic temperature in the Al-Si-Cu system.

Case 3—Gas porosity.

Many liquids readily dissolve gases, and in some cases the gas solubility in the solid is significantly lower than in the liquid. Atomically dissolved gases act exactly as do metallic solutes, and if $k_0 < 1$, they will become concentrated in the interdendritic spaces during solidification. At sufficiently high concentrations, a gas pore may be nucleated, often with the aid of shrinkage (Fig. 8.5c). Porosity can cause a drop in ductility of the material as well as a casting that may leak if subjected to high internal pressures of gases or liquids.

Case 4—Need to heat treat.

Cast alloys are heat treated for a variety of reasons, and the subject is a whole study in itself, but one of the important reasons for heat treatment is to attempt to remove some of the effects of microsegregation. Homogenization anneal is a heat treatment at a temperature sufficiently high that diffusion rates are rapid enough to bring about significant lowering of the concentration gradients resulting from microsegregation. To avoid “burning,” temperatures must be chosen with the melting points of possible segregates kept in mind.

Heat treatment is a large consumer of energy, and lengthy treatment times are often required to eliminate certain undesirable features of the microstructure. While concentration gradients within a solid solution phase are relatively easy to lower, the dissolution or structural modification of some intermetallic phases requires extended treatment times. An example is in 6061 aluminum alloy where the solution treatment at 575C (1067F) has two purposes:

- to place all Mg into solid solution as the first step in the age hardening process;
- to cause the brittle $\beta\text{-Al}_5\text{FeSi}$ phase to change to the more desirable $\alpha\text{-AlFeSi}$.

Typical heat treatment times extend to six hours. Dissolution of the Mg is complete within 30 minutes, but conversion of the iron-containing phases is kinetically slow and serves to lengthen the heat treatment times by 4-5 hours more.

CONTROL OF MICROSEGREGATION

Prevention of interdendritic segregation is a virtual impossibility in industrial solidification because it would require that freezing take place with a planar solid-liquid interface. As we have seen in Chapter 7, this is not the case. Planar interface freezing requires controlled growth conditions, which are outside the possibility of large scale solidification processing.

The best that can be done is to ensure that freezing takes place as quickly as possible in order to produce as fine a dispersion of segregates as possible. In this way, the deleterious

effects of some of the aspects of microsegregation, such as the production of brittle intermetallics, will be minimized by making these microstructural features small and uniformly distributed. For example, thin section permanent mold castings are generally superior to thick sand cast sections as far as their mechanical properties are concerned, all else being equal.

MACROSEGREGATION

Macrosegregation refers to compositional variations extending to distances of the order of half the casting or ingot dimensions. This was first observed by Vannoccio Biringuccio¹ in 1540 while casting large bronze ingots for cannon manufacture and is one of the oldest recorded metallurgical observations. He found that the outer surface of the ingot was covered with small metallic drops, which appeared to exude from the interior of the ingot. These drops were later shown to consist of almost pure tin, and the phenomenon became known as tin sweat, an example of a type of macrosegregation known as inverse segregation.

Macrosegregation arises because of the operation of certain long-range transport processes during solidification. The highly stylized, partially solidified, simple ingot shown in Fig. 8.6 illustrates the possibilities for matter transport. Several regions having different solute concentrations can be identified. If $k_0 < 1$, these are:

- dendrite stalks that are low in solute concentration;
- interdendritic liquid that is high in solute concentration; and
- liquid in the center at, or close to, the bulk alloy concentration.

Segregation occurs when solute from one or more of these areas is transported to a location where it would not normally be found. The main transport processes that can operate during freezing are outlined below.

TURBULENT LIQUID CONVECTION

This transport process, caused by density differences or thermal gradients, is a common feature of most industrial freezing processes. Liquid convection can remove solute progressively from in front of the interface and from the interdendritic regions near the dendrite tips. This solute is then mixed into the remaining bulk liquid, which is constantly solute-enriched. The dimensionless Rayleigh number, (Ra), given below, predicts that turbulent flow that occurs when $Ra > 10^8$ can be present at very small temperature gradients typical of those found in industrial solidification.

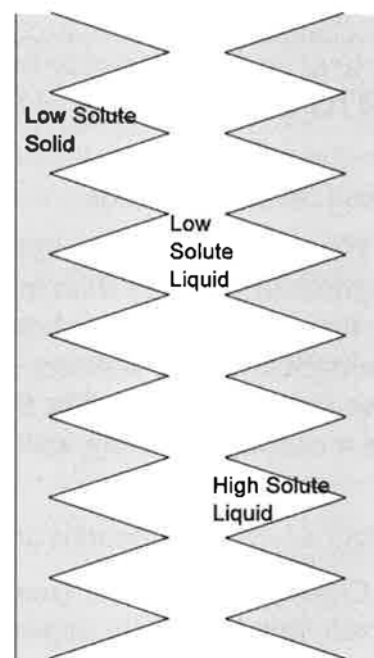


Fig. 8.6. A schematic representation of a partially solidified ingot shape shows the general areas of different solute concentration. If $k_0 < 1$, the dendrite stalks are solute-poor, while the interdendritic liquid is solute-rich. Liquid in the center is relatively low in solute concentration compared to the interdendritic liquid.

$$Ra = g\beta'R_L^3\Delta T/\alpha_L\nu$$

where

g is the acceleration due to gravity;

β' is the volume coefficient of thermal expansion;

R_L is the radius of the free liquid region;

ΔT is the temperature difference in the liquid between the liquid center and the solid liquid interface;

α_L is the thermal diffusivity of the liquid; and

ν is the kinematic viscosity of the liquid.

In addition to thermally induced liquid convection, some casting processes, such as continuous casting, subject the liquid to intense forced convection caused by the momentum of the liquid flow into the sump.

FLOATING OR SETTLING OF SOLID GRAINS

Solid grains formed early in solidification will float or settle if there is a substantial density difference between the solid and liquid phase.

LIQUID MOVEMENT IN THE INTERDENDRITIC SPACES

This movement may take place in response to density changes resulting from solidification at the base of the dendrite. If compositional changes within the interdendritic liquid are such that the density increases because of microsegregation, the interdendritic liquid will move slowly toward the outside of the solidifying shape, i.e., toward the mold wall. Compositional changes resulting in a density decrease will lead to liquid movement toward the center of the freezing system.

Similarly, volumetric changes due to solidification at the base of the dendrite can result in liquid movement. If the density increases on freezing, there will occur a net contraction at the base of the dendrite, and liquid will move toward the outside. Density decreases on freezing have the opposite effect, causing liquid to move in the interdendritic spaces toward the remaining bulk liquid in the center. These various possibilities are illustrated in Fig. 8.7.

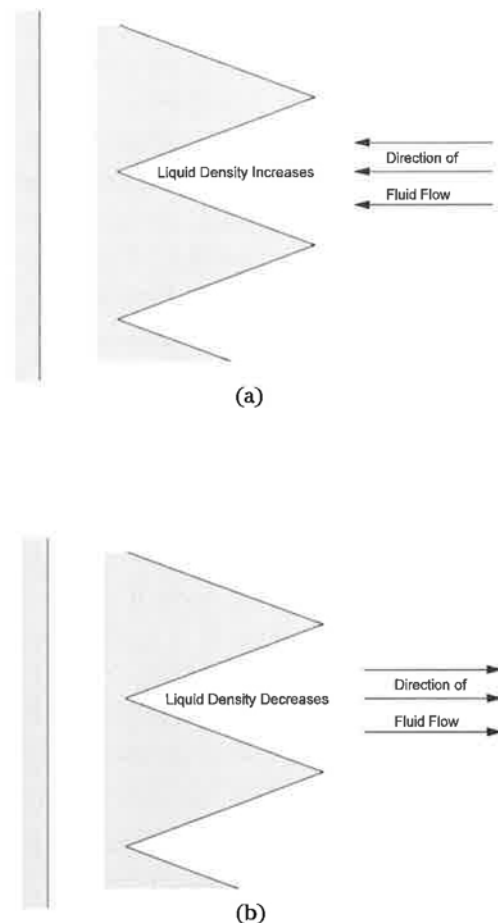


Fig. 8.7. Liquid movement within the interdendritic spaces is illustrated.

NORMAL SEGREGATION

Normal, or positive, segregation results in a general solute enrichment in the center of the solidified piece if $k_0 < 1$ (Fig. 8.8a), or a solvent enrichment if $k_0 > 1$ (Fig. 8.8b). Concentration gradients are gradual and segregation may be caused by both bulk liquid convection and by the motion of interdendritic liquid toward the central regions. Time is an important variable, with increased segregation occurring at longer solidification times. Normal segregation is, therefore, more pronounced in larger solidified shapes, such as heavy section castings and ingots. Rapidly frozen castings, such as pressure die castings, do not usually exhibit any significant normal segregation.

The mechanisms leading to this segregation rely on the presence of a distinct liquid region during freezing, similar to the configuration shown in Fig. 8.6. Anything that disrupts this distinct liquid will act to minimize normal segregation. Grain refinement is very effective in this regard since it promotes a mushy solid-liquid mixture throughout the entire solidifying body. Similarly, rapid chilling will promote overall nucleation and growth and will limit the time available for the solute transport processes to act, thus reducing the total segregation.

INVERSE SEGREGATION

As the name implies, inverse segregation is the opposite of what is expected on the basis of value of the distribution coefficient. Thus, in inverse segregation, $k_0 < 1$ solutes appear on the outside of the casting or ingot, and $k_0 > 1$ solutes are in the central area. It has been established that inverse segregation results from movement of interdendritic liquid toward the outside. If $k_0 < 1$, this process leads to a general enrichment of solute near the external surfaces; if $k_0 > 1$, the outer regions become solvent-rich and the inner ones, solute-rich.

Several features of the alloy contribute to inverse segregation. Substantial interdendritic flow requires that a long dendritic zone form. This will happen in alloys with a long freezing range, most notably many aluminum and copper-base alloys.

The driving forces for interdendritic flow toward the outside must also be present. These include significant solute rejection, large solidification shrinkage and density increases

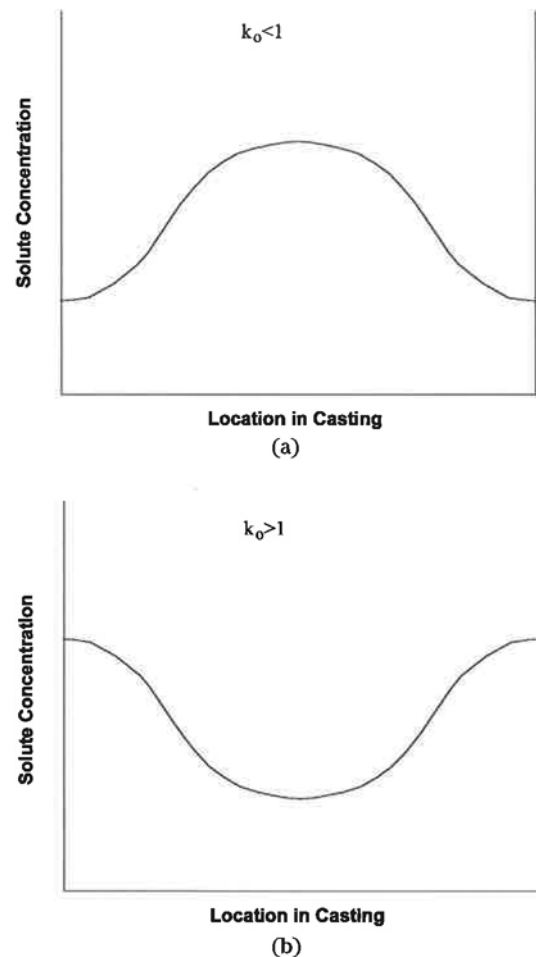


Fig. 8.8. Solute distributions resulting from normal segregation are sketched for (a) $k_0 < 1$ and (b) $k_0 > 1$ alloy systems. The macroscopic distributions shown are those expected to be found across a section of a casting cut through its thermal center.

due to interdendritic segregation. The latter are promoted in alloys based on a low density solvent, but containing denser alloying elements. Aluminum alloys in which the alloy elements are Cu, Fe, Cr (chromium) and Mn (manganese) very often show severe inverse segregation for this reason. Small values of the distribution coefficient of these elements in aluminum, coupled with the large volumetric shrinkage of aluminum, contribute substantially to the segregation.

Computation of exact solute profiles as a result of inverse segregation is difficult, but some simple equations have been developed. Flemings² has described inverse segregation against a chill plate with a modified Scheil equation:

$$C_L = C_0 f_L^{-(1-k')/(1-\beta)}$$

where

C_L is the solute concentration in the liquid at the chill;

C_0 is the overall alloy composition;

f_L is the liquid fraction;

k' is the effective distribution coefficient; and

β is the coefficient of volumetric solidification shrinkage.

Note that if $\beta = 0$, this equation becomes the Scheil equation.

A particularly severe form of inverse segregation occurs if the outer solidified shell cracks, because of thermal stresses, or melts, partially because of the temperature rise associated with air gap formation at the casting-mold wall interface. If this occurs, high solute interdendritic liquid may exude onto the free surface and, subsequently, solidify. The result is a rough surface marked by frozen droplets of high solute liquid. Tin sweat in bronzes (Fig. 8.9) was the inverse segregation reported originally by Biringuccio and mentioned earlier. Such exudation is also found in DC cast aluminum alloys prone to inverse segregation.

The mechanisms operative in inverse segregation all rely on the presence of a long and well developed mushy dendritic zone. The segregation can be minimized by destroying this zone through grain refinement or by electrical means, described in the next chapter. As with all types of macrosegregation, time accentuates the segregation. Small solidified volumes and rapid cooling aid in minimizing inverse segregation.

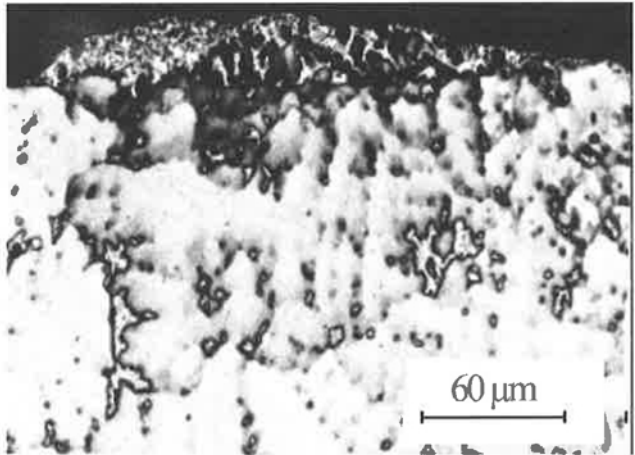


Fig. 8.9. Tin sweat on the bottom surface of a horizontally cast strip of bronze (5%Sn) is shown. [From A. Cibula, *Review of Metallurgical Factors Influencing the Quality of Copper and Copper Alloy Castings*, Proceedings of an International Conference on the Control of the Composition and Quality of Copper and Copper Alloy Castings for Fabrication, Dusseldorf, 30-31, October, 1967, sponsored by The British Non-Ferrous Research Association.]

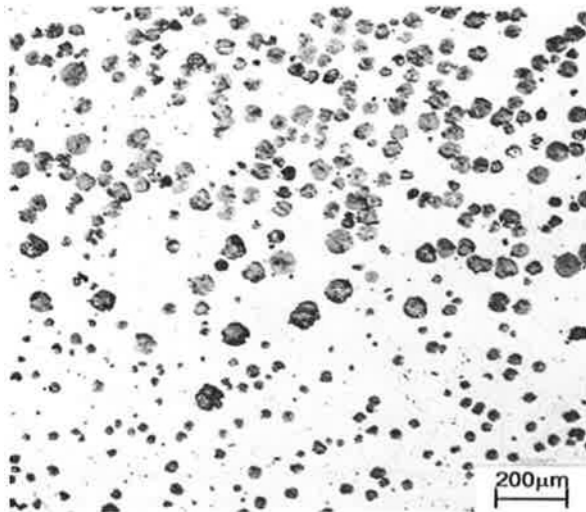


Fig. 8.10. Micrograph shows carbon flotation in a ductile iron casting. A concentration of larger graphite nodules is found in the cope area. [Microstructure of Ductile Iron, American Foundrymen's Society (1965).]

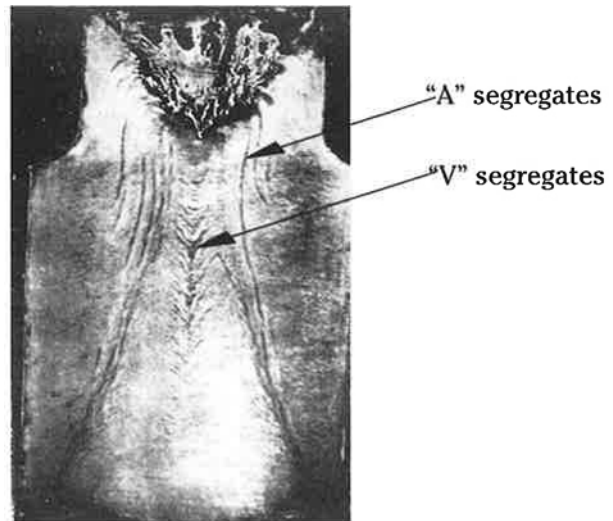


Fig. 8.11. "A" and "V" segregates in a steel ingot are shown.

GRAVITY SEGREGATION

If significant density differences are present between solid and liquid phases during solidification, these phases may separate under the force of gravity. Gravity segregation is usually a problem only when density differences are large, for example in lead alloys or in cast irons in which primary graphite is formed. In hypereutectic cast irons, carbon flotation, in which the primary phase, being lighter, floats to the upper (cope) surface of a casting, is a problem of gravity segregation (see Fig. 8.10).

Short of changing the alloy composition, gravity segregation can be controlled only by minimizing the time available for phase separation, or by stirring the liquid-solid mixture during freezing. Stirring is usually difficult, if not impossible, to do, but minimization of the time can be accomplished by chilling and by reducing the size of castings manufactured with gravity-segregation prone alloys.

"A" AND "V" SEGREGATION

These are special segregates of light elements, C, P and S (sulfur), found in large steel ingots. Their names are derived from their shapes. As seen in Fig. 8.11, "A" segregates are pipe shaped, solute-rich areas inclined to the axis of the ingot and extending from near the outer surface toward the center. "V" segregates lie along the thermal center of the ingot and point toward the base. The origin of each type is slightly different, and they will be treated in turn.

"A" segregates arise from liquid motion within the mushy zone due to gravitational effects. Figure 8.12 illustrates the process whereby these segregates form. C-, P- and S-rich interdendritic liquid tends to rise because of its lower density as compared to liquid iron. The ability of this iron-saturated liquid to rise in a purely vertical direction

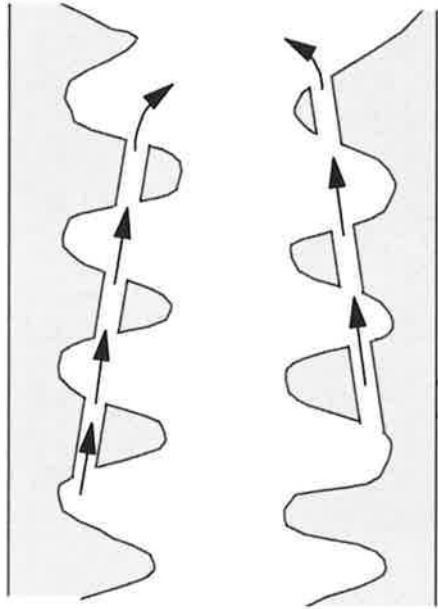


Fig. 8.12. "A" segregates form from channels of slowly flowing liquid rich in C, P and S. These channels form in the mushy zone of large ingots and lead to a slow upward motion of the lighter liquid.

is greatly constrained by the presence of the surrounding iron dendrites. If, however, the liquid moves toward the ingot center, it is heated, and becoming unsaturated with respect to iron, is able to dissolve some of the surrounding iron dendrites while rising. The net result is that, given sufficient time, the C-, P, S-rich liquid dissolves a channel having both a vertical and a horizontal component. A slow flow of the less dense solute-enriched liquid occurs within this channel which, when finally frozen, appears as a pencil of high solute material in the ingot structure.

The formation of "V" segregates is less well understood, but appears to proceed by the mechanism illustrated in Fig. 8.13. Iron-rich grains formed in the upper regions of the ingot slowly sink to the bottom, forming an inverted cone as a result of restraining effects of the mushy zone. When the repose angle of this pile of grains is exceeded, fissures form as aggregates of grains slide downward to restore the stable repose angle. Further segregation of C, P and S into the fissures takes place, and they become the last areas to freeze. Subsequent sectioning along the ingot centerline will reveal sections of the inverted cone in the observed "V" shape.

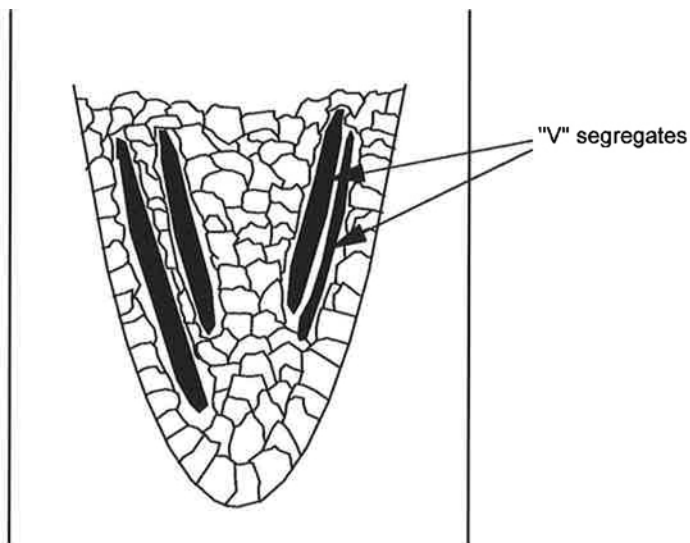


Fig. 8.13. Fissures formed between grains in the ingot center result in "V" segregates.

In steel ingots, macrosegregation of these types can lead to banding within the microstructure of steel hot worked from the segregated ingots. Alternating bands of pearlite and ferrite in Fig. 8.14 result from the forging of a steel in which macrosegregation of manganese has occurred. Pearlite is stabilized in the high manganese regions, while ferrite forms in those areas having a low manganese content. Macrosegregation of sulfur can result in the formation of the Fe-FeS eutectic, which melts at 988C (1810F). This temperature is within the hot working range of many steels, and the eutectic, if present, will melt during rolling, resulting in ingot cracking.

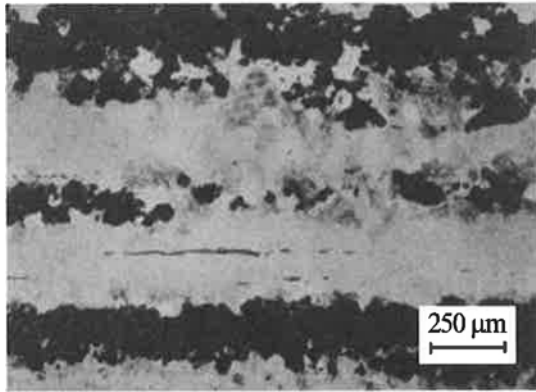


Fig. 8.14. Alternate bands of pearlite and ferrite in a forged carbon steel result from segregation of manganese during ingot solidification. [Reproduced with permission of The Minerals, Metals and Materials Society from G.S. Cole, *Transactions of the AIME*, vol 2, pp 357-370 (1971).]

While “A” segregates are, in practice, found only in carbon steels, they may, in principle, occur in any alloy system in which interdendritic segregation of very light alloying elements takes place. Their formation does require time, with the result that they will form only if the mass of material being solidified is large, hence, their occurrence only in ingots.

Destruction of the long mushy zone and enhanced rates of freezing will serve to avoid these types of segregation. Electromagnetic stirring, as described in the next chapter, has been used to advantage in the elimination of “A” and “V” segregation.

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chapter 9

THE GRAIN STRUCTURE OF INGOTS

GRAIN TYPES

From a solidification process, two basic grain geometries may result. These are the equiaxed grain (Fig. 9.1a), characterized by roughly equal dimensions in all directions, and the columnar grain (Fig. 9.1b), which is elongated in one direction. Equiaxed grains are the result of copious nucleation throughout the body of the liquid, followed by free growth of the individual grains until that growth is halted by grain impingement (Fig. 9.2). The free growth mechanism yields a structure composed of randomly oriented equiaxed grains. Equiaxed structures usually have isotropic properties as a result of the random grain orientation.

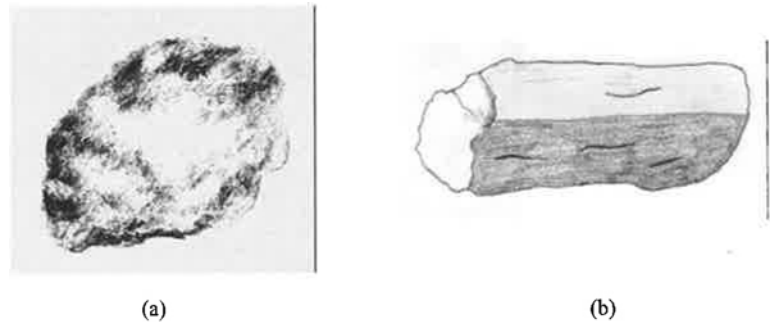


Fig. 9.1. Schematic interpretations of an equiaxed grain (a) and a columnar grain (b) are shown.

Columnar grains are the result of a competitive growth process beginning with random nucleation of several grains. Certain nuclei are more favorably oriented for growth, and these survive at the expense of less favorably oriented grains. Favorable orientations are usually relative to the heat flow direction leading to columnar grain growth along the direction of heat transfer. In most casting situations, this direction is approximately perpendicular to the mold wall.

Since columnar grains form in preferential directions, a columnar structure is usually anisotropic in nature. In some instances, crystallographic defects play an important role in columnar growth. For instance, the twinned columnar grains (TCG) found in certain aluminum alloys are aided in their growth by the presence of a crystallographic twin running along the centerline of the grain (Fig. 9.3).

CASTINGS VERSUS INGOTS

The present chapter deals with the grain structure of ingots as opposed to castings. This doesn't mean that controlling grain size and geometry is not a concern in casting production; it most certainly is, but it is more easily controlled than in ingot production, and wide variations in grain type occur less often in castings than in ingots. It is also true that the properties of castings are often determined by factors other than grain size or type, e.g., the presence of nonmetallic or intermetallic phases, porosity or state of heat treatment. The further processing of ingots, on the other hand,

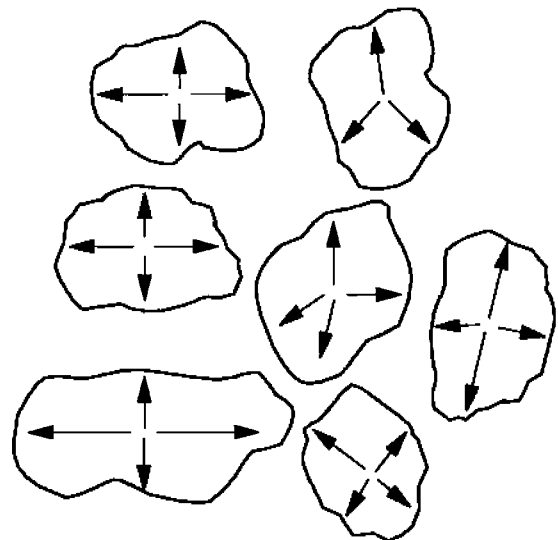


Fig. 9.2. Equiaxed grains grow almost equally in all directions and growth is halted when grain impingement takes place.

usually by hot deformation, is very sensitive to the size and shape of the as-solidified grains, and considerable effort is expended in ingot casting to control grain structure.

The limited scope for a wide variation in grain size and shape within a casting compared to an ingot is largely a matter of the differences in size between the two. With few exceptions, castings are smaller than ingots. They freeze more quickly and usually with a high degree of mushy (solid plus liquid) solidification due to their level of alloying elements. Using a suitable grain refiner under these conditions may be enough to yield a fine equiaxed grain structure. This is particularly true in the casting of aluminum and aluminum alloy ingots, but grain refinement is more difficult when producing steel ingots.

Ingots, being significantly larger than castings, have the potential for distinct zones of liquid and solid during freezing. Interaction of these zones can determine the resultant grain type. The large majority of alloys cast in ingot form have much lower alloy element contents than do the usual casting alloys. Their chemistry, therefore, often serves to reduce the extent of mushy solidification, making the liquid and solid zones yet more distinct. Finally, it is important to remember that the fluid flow conditions present during casting solidification are very different from those found during the freezing of a continuously cast ingot.

Casting processes are designed to ensure tranquil metal flow into the mold in a batch process. When mold filling is complete, the only forces causing fluid flow are a result of thermal convection or constitutional factors, as described in the previous chapter. In continuous ingot casting, however, liquid is continuously introduced into the mold, generating turbulent flow in at least a part of the system throughout the whole of the casting process. This turbulent flow may play an important role in determination of grain size and shape.

STRUCTURE OF PERMANENT MOLD CAST INGOTS

In the discussion of casting processes presented in Chapter 3, it was indicated that permanent mold casting of ingots is confined to small specialty materials, while some form of continuous or semi-continuous casting is used for the common metals and alloys. Grain formation in permanent mold casting is, however, somewhat simpler; we will begin, therefore, by considering how grains form in this case and what the important physical mechanisms controlling their formation are.

The grain structure of an ingot cast from a pure metal is noticeably different than that of an alloy ingot. Definitions of purity vary, but for our purposes we will define a pure metal as one that freezes with either a planar or a cellular interface under the lowest liquid temperature gradient/growth rate ratio (i.e., G_L/R in equation 7.2,) present. It is to be noted

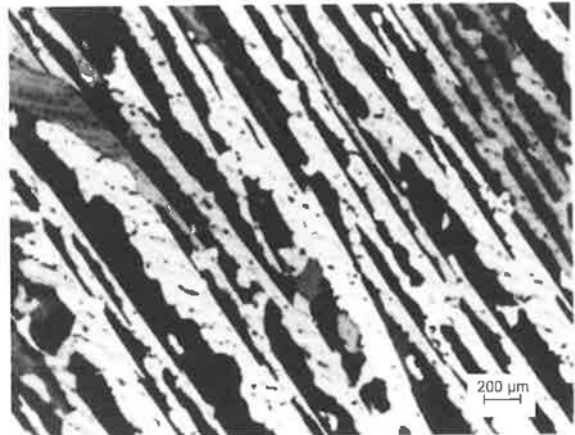


Fig. 9.3. Twinned columnar grains in an aluminum alloy are shown. [Photo courtesy of L.Zhang.]

that these conditions are such that no dendritic growth is allowed. Later, it will be seen that dendrites are a critical factor in the determination of ingot grain structure.

PURE METAL INGOTS

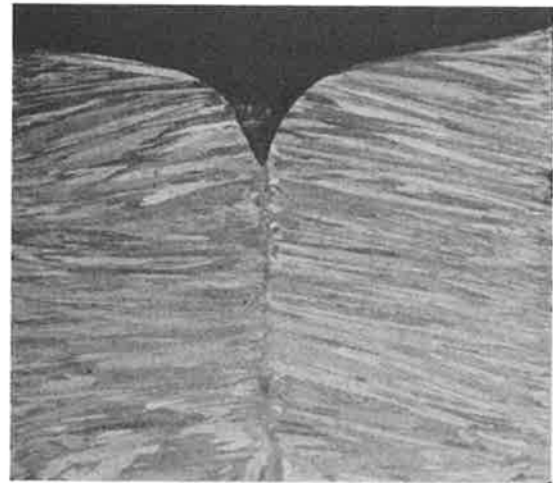
The grain structure of an ingot of pure metal is shown in Fig. 9.4. The photograph gives the impression that the structure consists entirely of columnar grains from mold wall to ingot center. Closer microscopic examination would reveal a thin layer of very fine equiaxed grains around the outer surface, as indicated in the sketch. Pure metal ingots cast into a permanent mold, then, contain two distinct grain zones:

- an outer layer of fine equiaxed grains; and
- a columnar zone extending to the ingot center.

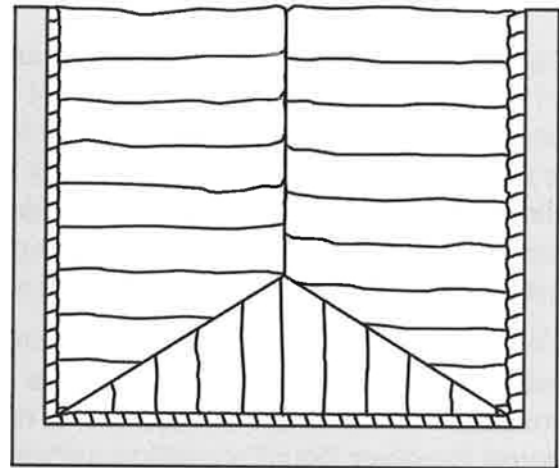
The outer layer of equiaxed grains, called the chill zone, forms by random heterogeneous nucleation, on the mold wall, of liquid that is rapidly cooled by the mold. The columnar grains are formed by preferential growth of selected chill zone grains.

In a pure material, certain specific atom planes form the lowest energy solid-liquid interface, and growth will take place in a direction perpendicular to this lowest energy interface. The preferred atomic interface planes in FCC metals such as Al or Cu, are the close-packed (111) planes and the preferred growth direction is $\langle 111 \rangle$. Chill zone grains oriented such that their $\langle 111 \rangle$ directions are parallel to the heat flow direction (usually perpendicular to the mold wall) will predominate over grains with other orientations.

The mechanism of grain selection leading to columnar zone development is explained in Fig. 9.5. Three grains are illustrated; grains A and B have their $\langle 111 \rangle$ directions normal to the mold wall and in the heat flow direction, while the third grain, C, has $\langle 111 \rangle$ at an angle θ to the heat flow. Within a given time period, each grain will grow the same distance, d , in $\langle 111 \rangle$, but because of the different orientations, the component of growth in the heat flow toward the ingot center will only be, $d \cos \theta$, for the unfavorably oriented middle grain and it will equal d for the other two grains.



(a)



(b)

Fig. 9.4. The grain structure of a permanent mold cast pure metal ingot is shown: (a) ingot of tin, magnification 1.5X [Reproduced with permission from G.S. Cole and G.F. Bolling, *Transactions of the AIME*, vol 239, pp 1824-1835, (1967)]; (b) schematic illustrating the two zones of grains.

On the left, growth of grain C will be impeded physically by grain A, while grain B, on its right, will extend itself sideways and always grow ahead of grain C. The net result, as indicated, is that growth of grain C will be stopped, and only the two favorably oriented grains will be allowed to continue growth. The columnar zone of a pure FCC metal will have a preferred crystallographic orientation with the $\langle 111 \rangle$ directions of all grains lying in the heat flow direction. In the example shown, this occurs after a total growth equal to the distance z .

If the liquid is perfectly quiescent, columnar growth will be exactly normal to the mold wall, but often it is observed that the grains are inclined slightly upward. This inclination is the result of thermal convection cells that cause denser and cooler liquid to fall over the solid-liquid interface. Growth into cooler liquid occurs naturally, resulting in the upward inclination. Natural thermal convection during solidification in a simple ingot geometry is illustrated in Fig. 9.6.

ALLOY METAL INGOTS

Alloy ingots differ from pure metal ingots, as far as grain structure is concerned, by exhibiting a third grain region in the form of a central equiaxed zone. Both an idealized sketch and a photograph of a typical alloy ingot cast into a permanent mold are shown in Fig. 9.7. Of course, another important difference between pure metal and alloy ingots is that the latter freeze with a dendritic micromorphology, which plays an important role in determining the ingot grain structure.

CHILL ZONE GRAINS

Structure of the chill zone grains is determined by the heat extracting ability of the mold, as well as the degree of turbulent flow at the mold wall. If the thermal conductivity of the mold is low and the melt superheat high, dendritic chill zone grains nucleate and are fragmented by the fluid flow. Fragments that do not remelt may act as nuclei elsewhere. Such grain multiplication is common in alloy ingot solidification, particularly when the chill zone

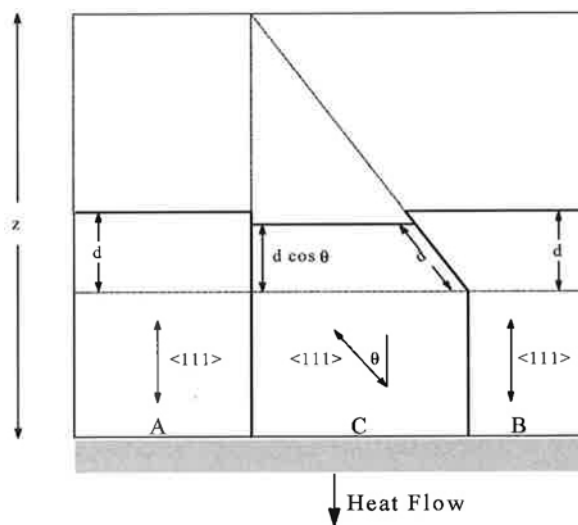


Fig. 9.5. The mechanism of grain selection during growth from the chill zone is illustrated.

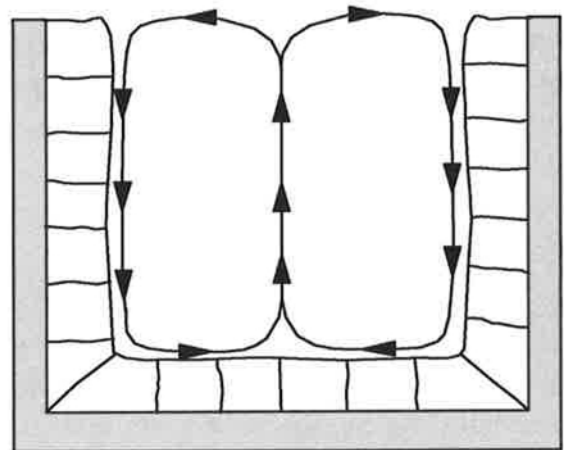


Fig. 9.6. The flow pattern generated by natural thermal convection during solidification in a simple permanent mold is shown.

is being formed and considerable turbulence is present from the initial pouring operation.

When the mold material possesses a high thermal conductivity and the melt superheat is low, chill zone grains may form by a solidification process so rapid that there is insufficient time for diffusion of the alloying elements to take place. If this occurs, a two-dimensional platelet with composition equal to the bulk alloy composition, C_0 , is formed. As latent heat evolves, growth of the platelet slows and diffusion begins to be effective. The composition falls to $k_0 C_0$ and then slowly rises to C_0 exactly as predicted by the solute redistribution theory discussed in Chapter 6. As solute is redistributed and the solute layer builds at the interface, constitutional undercooling comes into play and the solidification morphology changes progressively from planar to cellular to dendritic, as in Fig. 9.8.

COLUMNAR ZONE GRAINS

Grains in the columnar zone of an alloy ingot are dendritic in nature and, like their pure metal counterparts, develop by a selective process from the chill zone to yield grains with a preferred orientation. Dendritic growth now dictates that the preferred growth direction is the dendrite growth direction, $\langle 100 \rangle$ for cubic metals and $\langle 10\bar{1}0 \rangle$ for hexagonal. With exception of the preferred growth direction, the selection process operates in exactly the same way as in pure metal ingots, according to the mechanism of Fig. 9.5.

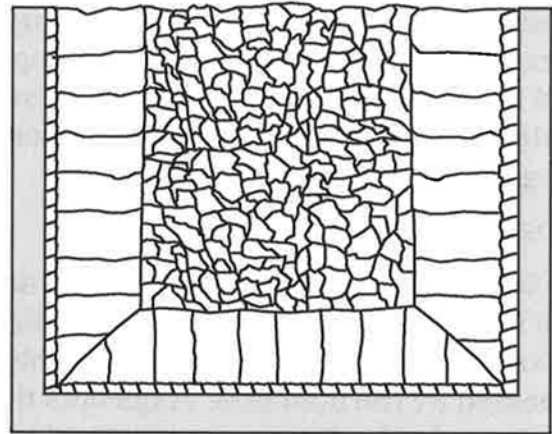
CENTRAL EQUIAXED GRAINS

Grains in the central equiaxed zone are formed in a melt of high solute ($k_0 < 1$) concentration, if normal segregation occurs, and in the presence of a small temperature gradient. As a result of their growth conditions, they are composed of coarse and highly filamentary dendrites. Perhaps the most significant feature of the columnar and equiaxed zones in alloy ingots is that the relative proportions of these two grain types can be varied by changes in the casting conditions such that ingots may consist entirely of an equiaxed grain structure or a columnar grain structure.

Three variables are most significant in altering the columnar/equiaxed ratio: alloying



(a)



(b)

Fig. 9.7. The grain structure of a permanent mold cast alloy ingot is given: (a) ingot of Sn-3%Zn alloy, magnification 1.5X [Reproduced with permission from G.S. Cole and G.F. Bolling, Transactions of the AIME, vol 239, pp 1824-1835, (1967)]; (b) schematic illustrating the three zones of grains.

element level, pouring superheat and degree of liquid turbulence present throughout solidification. Alloy level is fixed by the alloy composition, and usually cannot be varied, but within a given alloy system, the tendency to form equiaxed grains will increase as the total concentration of alloying elements increases (Fig. 9.9a). One extreme of behavior discussed earlier is the pure solvent that solidifies in a completely columnar structure.

Increases in pouring superheat tend to reduce the size of the central equiaxed zone yielding a completely columnar structure at high superheats (Fig. 9.9b). Alternatively, if casting is done only a few degrees above the liquidus, completely equiaxed ingot structures are formed. The influence of liquid turbulence will be dealt with at length through much of the remainder of this chapter; for the moment, it is sufficient to say that any increase in movement of the liquid during freezing serves to accentuate the development of an equiaxed grain structure.

The possibility of different equiaxed/columnar ratios raises the question of which type of structure is desired in ingot solidification. As a general rule, the case can be made for as much equiaxed grain as possible. Equiaxed structures possess more evenly distributed segregation and microporosity, with a reduced tendency to crack during casting and subsequent processing. In addition, texture formation on working is reduced as a result of the random orientations of the equiaxed grains, and fabrication operations generally are easier to perform because of the lack of anisotropy in the cast ingot.

ORIGINS OF THE CENTRAL EQUIAXED ZONE

The solidification literature is replete with research aimed at explaining the origins of grains found in the central equiaxed zone and the transition from columnar to equiaxed growth. Fortunately, the various theories and hypotheses can be reduced to a few simple concepts that explain the industrial observations very well.

The prevailing picture of the columnar-to-equiaxed transition is one of gradual change. It is not a rapid transition occurring at one point in time, but rather a slow impediment of columnar growth by equiaxed grains growing in the central liquid, perhaps even from some early time in the solidification history of the ingot. Grains originate from nuclei, and an

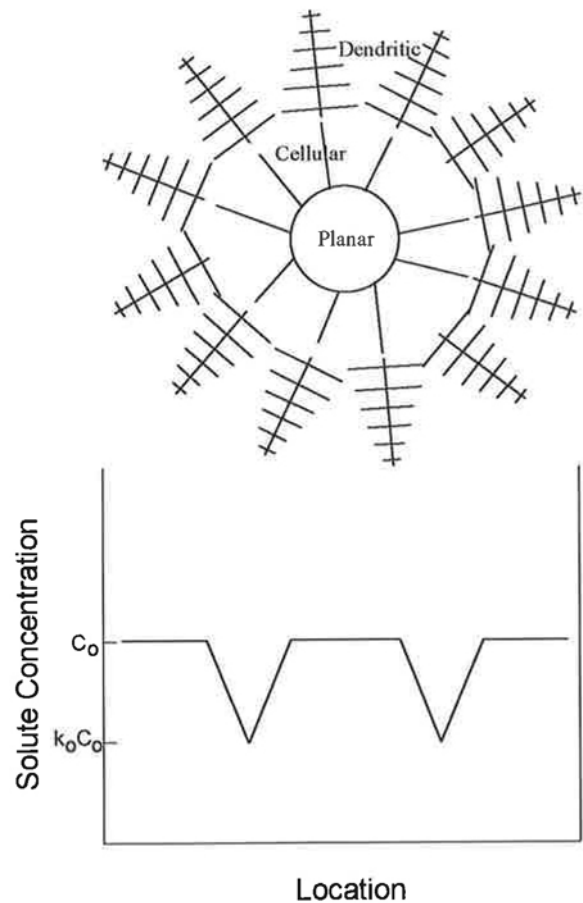


Fig. 9.8. Rapid solidification in the chill zone may lead to a diffusionless transformation and a growth morphology that changes from planar to cellular to dendritic.

understanding of the origin of the central equiaxed grains must be based on the origins of their nuclei. Several possibilities exist.

Case 1—Nuclei are formed on the initial chill.

Hot liquid is rapidly chilled by the cold mold wall in the first few seconds of mold filling. Many nuclei are formed, some of which adhere to the mold wall and give rise to the outer equiaxed zone. Others are swept into the bulk liquid or are produced by fragmentation of dendrites in the outer equiaxed zone. As long as these various nuclei and dendrite bits are not melted by the remaining superheat, they are able to grow into mature grains in the central liquid. This mechanism will become more important as the melt superheat is decreased and the possibility for nuclei melting is reduced.

Case 2—Nuclei are formed at the free surface.

Radiation and convection often result in the free surface of an ingot cooling at a faster rate than other locations. This is the reason for using various hot tops to retard surface solidification. In the absence of a hot top, nucleation of grains may occur at the free surface, aided by oxide film substrates. As solids generally are more dense than the liquids from which they form, these surface nucleated grains can sink into the bulk liquid to contribute to central equiaxed growth.

Case 3—Nuclei arise from fragmented columnar zone dendrites.

The filamentary dendrite is a fragile structure of secondary and tertiary arms, weakly connected to a central stalk (see Fig. 7.11a, for example). These weak structures are easily broken by the mechanical forces of liquid in movement due to thermal and forced convection. Melting of the arm/primary stalk junction also is possible. This junction is richer in solute than other parts of the partially solidified dendrite, and fluctuations of up to 10°C (18°F) because of thermal convection are certainly sufficient to cause melting and release of dendrite bits into the bulk liquid. Whether formed by mechanical or thermal fragmentation, these bits are excellent nuclei for the equiaxed grains.

A COMMON DENOMINATOR

The three mechanisms of nuclei generation just described will not all be active at the same time. Casting at a low superheat will promote the formation of nuclei at the initial

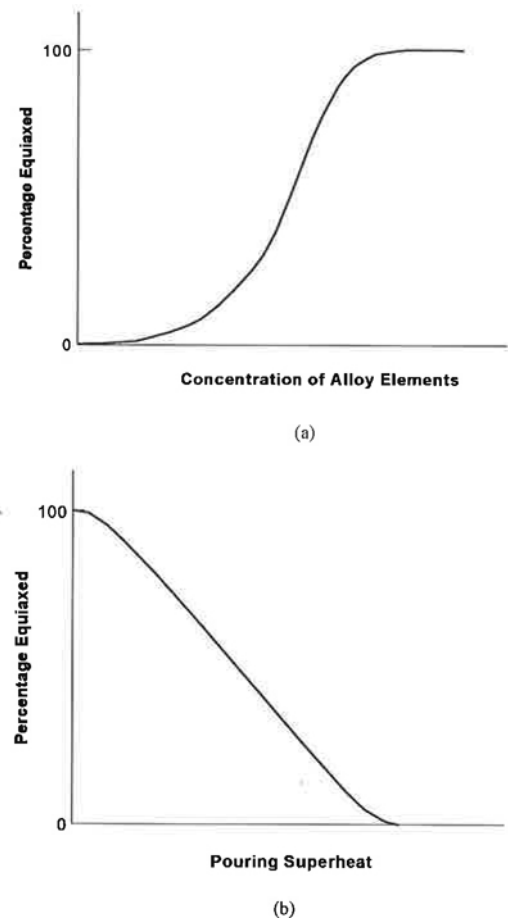


Fig. 9.9. Effects of increases in alloy content on the amount of equiaxed grains are shown in (a); effect on casting from increasing the superheat is shown in (b).

chill. Geometries favorable to surface cooling will aid in nucleation there, and casting systems designed to produce substantial liquid motion will favor fragmentation of columnar zone dendrites. Despite these differences, there is one feature common to each of these mechanisms: liquid state convection.

Convection is necessary to rapidly deplete the casting superheat through enhanced heat transfer, and to both fragment and transport broken dendrites and nuclei from the initial chill into the central liquid zone. Convective currents move liquid across the top of the solidifying ingot (Fig. 9.6), causing fragmentation of any solid surface layer that may have formed. Thermal fluctuations resulting from convecting liquid may remelt portions of the columnar zone dendrites, thus forming dendrite bits which are able to nucleate central equiaxed grains.

Convection of the liquid during ingot solidification is obviously a very important feature of the entire grain formation process. Controlling convective flow should allow the regulation of relative amounts of columnar and equiaxed grains that ultimately form. So, let's take a look at how convection may be controlled in a solidifying system, and the effect such control has on the final grain structure of the solid.

CONTROL OF CONVECTION

The motion of a liquid resulting from thermal or forced convection, or some combination of the two, imparts to that liquid a momentum having a value proportional to the velocity of movement and the liquid density. If the motion is to be stopped, it is necessary to apply an external force of equal and opposite magnitude to the convective forces. Alternatively, it is possible to enhance the motion by supplementing it with an external force.

Four approaches are taken to control convection during solidification. They are:

- directional heat flow
- solidification in zero gravity
- application of a Coriolis force
- application of an electromagnetic field.

Following is a discussion of some aspects of each.

Directional heat flow involves configuring the freezing system so that the colder and denser liquid is always on the bottom. Thus, directional solidification in an upward direction (Fig. 9.10a) yields minimum convection and will promote a columnar structure because the mechanisms for nucleus formation have been eliminated. Note that it is possible to sustain high temperature gradients in the liquid with this configuration. Any nuclei present will melt if the temperature gradient is sufficient. Vertical upward solidification is used in the production of turbine blades where a single crystal or a coarse columnar structure is desired.

Maximum convection is assured by freezing in a vertical downward direction (Fig. 9.10b). Colder and denser liquid in contact with the solid will fall, producing significant currents. Fragmentation of dendrites at the interface will result in equiaxed grain formation, which will be stabilized by the convection reduced temperature gradients.

Solidification in a horizontal mode (Fig. 9.10c) presents an intermediate example. Colder and denser liquid flows parallel to the solid-liquid interface producing dendrite fragmentation and nuclei. Survival and growth of these nuclei depends on the level of temperature gradient sustained in the liquid. Low gradients allow equiaxed growth, but if higher gradients can be supported, some of the nuclei will melt and columnar growth will be favored.

It is possible to control the direction of heat flow in some specialized processes, such as crystal growth, but it is not a practical method for control of cast ingot structures where heat flow is governed by the overall design of the casting system.

Solidification in zero gravity removes density differences that are responsible for thermal convection in the presence of gravity. Zero gravity solidification is the preferred tool for the researcher with access to a space shuttle. At present, however, it is not suited to the processing of large quantities of material, but it does hold interesting prospects for small, specialized applications.

Application of a Coriolis force requires rotation of the solidifying system about a vertical axis to eliminate convection. The simple description of thermal convection given in Fig. 9.6 shows that fluid motion has both horizontal and vertical components. A sufficiently rapid rotation about the vertical axis is capable of generating a centrifugal force that suppresses vertical motion and, as a result, stops the convection. The principle is well demonstrated by the midway rides in which a car or a platform is rapidly spun about its axis. Anyone who has experienced such a ride will agree that freedom of motion is severely limited by the centrifugal force.

Ingot rotation is not very practical given the masses involved and the required rotation rates—on the order of 100 rpm—but laboratory experiments have verified that such rotations will suppress equiaxed growth and yield a completely columnar structure. While constant rotation prevents nuclei formation, a reversing rotation, such as occurs in a washing machine, enhances nuclei formation by generating a shear at the solid-liquid interface to fragment the dendritic structure. Fine equiaxed structures such as those appearing in Fig. 9.11 can be produced by this method, but the associated mechanical difficulties make it impractical for all but the smallest ingots. The effectiveness of grain refinement by this method is, nevertheless,

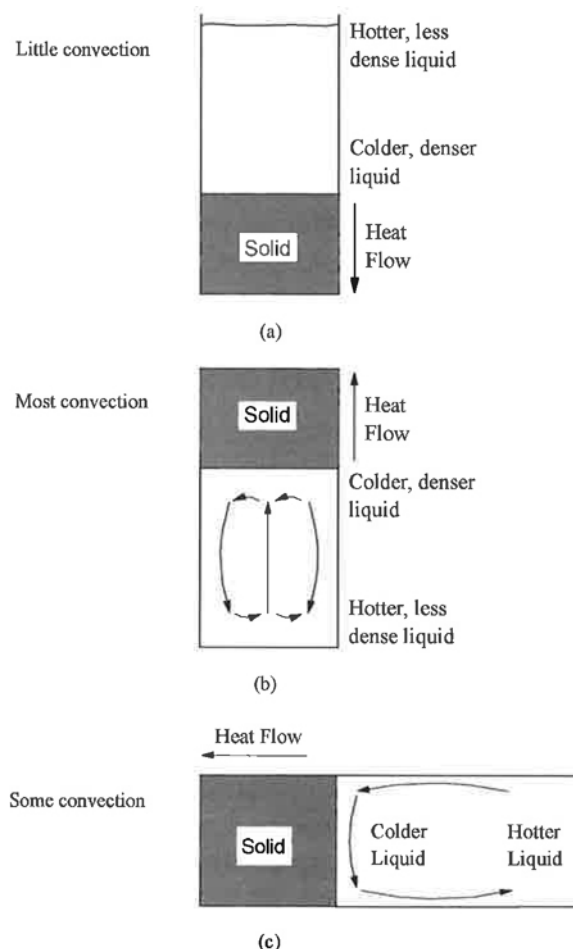


Fig. 9.10. The amount of natural thermal convection is determined by the direction of solidification.

spectacular, as can be seen by comparing the grain structures seen in Figs. 9.11 and 9.7a.

Application of an electromagnetic field is the one means of grain structure control that is amenable to the practical processing of large quantities of solidifying metal. The principle is based on Lenz's Law, which states that an electrical conductor moving in a magnetic field will experience a force such that the movement is stopped. Convecting liquid metals are moving conductors, and if a magnetic field is applied across the metal, the convective motion will be arrested. The force, F , generated is proportional to the metal velocity, v , and the square of the magnetic field strength, B .

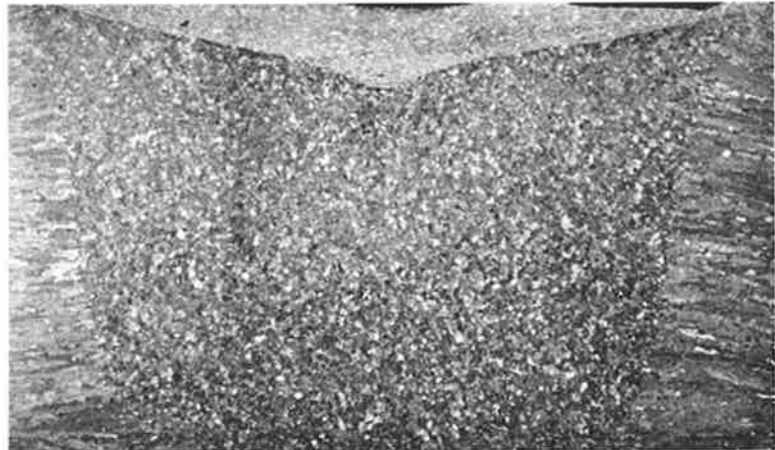


Fig. 9.11. A very fine equiaxed structure can be generated by a reversing rotation imparted to the interface during solidification. This Sn-3%Zn ingot was oscillated at 72 rpm. Shown at 75% of original size. [Reproduced with permission from G.S. Cole and G.F. Bolling, *Transactions of the AIME*, vol 239, pp 1824-1835, (1967).]

The simple statement of Lenz's Law is, therefore:

$$F \propto B^2v$$

Experiments have shown that it is possible to produce columnar grain structures by this means, but of more interest is using magnetic fields to generate fine equiaxed structures. This is accomplished by application of an alternating magnetic field achieved either through rotation of the magnet about the solidifying ingot or by constant changing of the field polarity. Force directions in the liquid are in continuous change, enhanced fluid motion results and all of the mechanisms necessary to produce equiaxed grain nuclei become operative. Benefits of fluid flow enhancement through electromagnetic stirring during the continuous casting of steel are detailed in the following sections.

CONTINUOUS CASTING OF STEEL

The principles of continuous casting are dealt with in a general way in Chapter 3, but specific attention to some features of steel continuous casting is necessary to appreciate the benefits of grain control through application of electromagnetic fields. These particular features are shell formation in the mold and segregation and porosity formation.

SHELL FORMATION

The solid shell that forms in the mold serves to contain the liquid steel until a sufficiently thick solid layer is established to prevent liquid breakouts. Shells of 2-3 cm (just under one inch to just over) in thickness form by a complex heat transfer process

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

involving the following steps:

- conduction through the shell;
- conduction through the mold lubricant;
- conduction and radiation across the air gap between the ingot and mold wall;
- conduction through the mold; and
- convection at the mold/cooling water interface.

Heat transfer across the air gap between the shell and the mold is the limiting step and accounts for 80-85% of the total thermal resistance. The shell is rarely uniform in thickness and has the shape in transverse section shown in Fig. 9.12. Ferrostatic pressure is sufficient to cause the shell to bulge outward at the centers of the four faces of the ingot. Such bulging creates better ingot-wall contact, increasing heat transfer and leading to a thicker shell at the face centers. Heat transfer is poorer at the corners, which are thinner, and it is here that cracking and breakouts are likely to occur.

SEGREGATION AND POROSITY

The relatively low thermal conductivity of solid steel, coupled with the high casting speeds associated with economic production, lead to very long and narrow liquid sumps during the solidification of continuously cast steel. In some cases, liquid may extend up to 30 m (98 ft) below the mold. This very particular solidification geometry leads to several specific features of concast steel ingots.

Equiaxed grains form by nucleation in the mold or submold regions, usually by dendrite fragmentation from the columnar zone, and slowly sink in the sump to pile up at the base

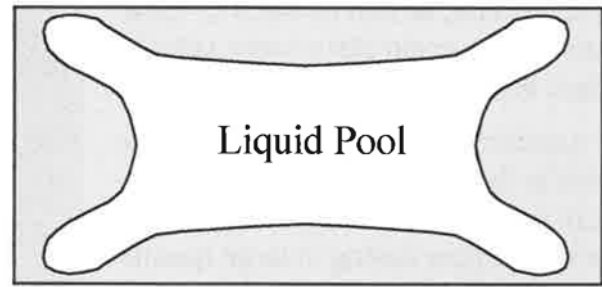


Fig. 9.12. A transverse section of the solid shell formed in the mold during the continuous casting of steel is shown.

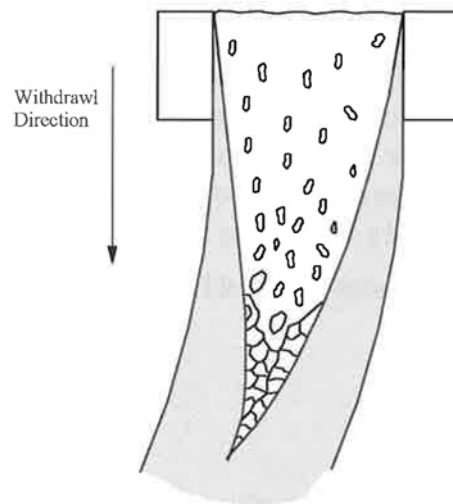


Fig. 9.13. Equiaxed grains originate in the upper parts of the solidifying ingot and sink to the bottom the sump.

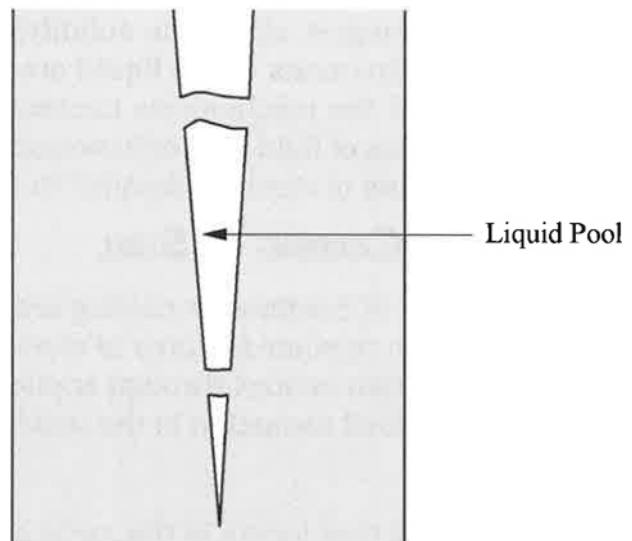


Fig. 9.14. Bridging across the narrow sump leads to isolation of liquid.

(Fig. 9.13). This is the usual situation for "V" segregation, which is common in concast steel. In addition, the narrowness of the sump near its base, coupled with local nonuniformities in heat transfer, can lead to solid bridging across the sump and isolation of a volume of liquid (Fig. 9.14). Solidification of this liquid results in a centerline shrinkage pore since liquid feeding from higher in the ingot is now impossible.

Centerline shrinkage is often associated with an area of high positive segregation caused by the sucking of solute-rich interdendritic liquid from surrounding areas into the low pressure region generated by the unfed solidification. Figure 9.15 shows schematically the main undesirable microstructural features to be found along the centerline of a continuously cast steel ingot. Reflection on the origin of these features will show that they are the result of the long narrow sump, which is related to the relatively poor heat transfer conditions prevailing in the submold region of the ingot. Improvement of heat transfer would lead to a shortening and broadening of the sump with a related decrease in the incidence of "V" and centerline segregation, as well as porosity. The poor heat transfer conditions are due, in large part, to the lack of fluid flow in the sump liquid.

Fluid flow conditions during the continuous casting of steel are illustrated in Fig. 9.16. The momentum of the input stream flowing through a nozzle from the tundish creates rapid turbulent flow in the mold. Dendrite fragmentation is extensive here and many of the equiaxed grains appearing farther down in the sump are nucleated at this point in the casting operation.

The viscous forces present in the liquid quickly dissipate turbulence generated by the input stream, and fluid flow below the mold is primarily the result of thermal convection and solidification shrinkage. This flow is slow and, as seen in Fig. 9.16, it follows a definite pattern sweeping downward across the solidifying interfaces and rising up the center of the sump. The heat flow

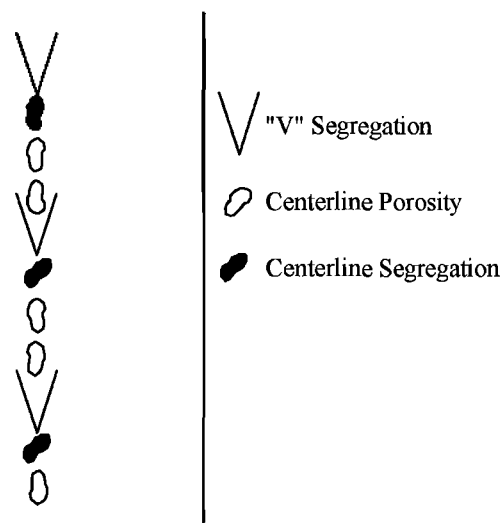


Fig. 9.15. Schematic shows the main undesirable microstructural features formed along the centerline of a steel ingot.

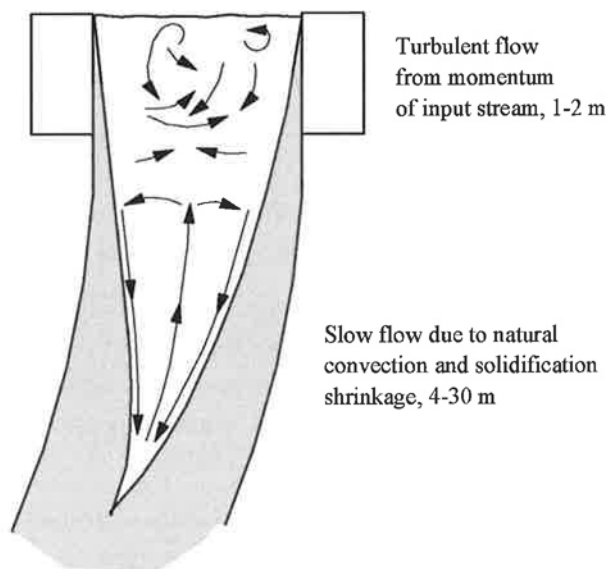


Fig. 9.16. Illustration shows the fluid flow patterns in a solidifying ingot of continuously cast steel.

accompanying this slow fluid flow is also relatively slow and contributes to the deep and narrow nature of the sump.

ELECTROMAGNETIC STIRRING

Stirring of the liquid steel in the sump accelerates heat transfer and changes the sump geometry such that beneficial results accrue to the ingot structure. Electromagnetic stirring (EMS) is the only practical way to enhance fluid flow during

continuous casting, and is the only fluid flow control used extensively to improve solidification structures. The principle of EMS is to use electromagnetic fields to stir either part or all of the liquid pool with the primary aim of creating equiaxed grains. Many types of stirrers have been patented, but two find general application:

- AC coils placed around the mold or submold region. The coils act as the stator of an electric motor while the liquid steel becomes the rotor and rotates. Low frequencies (1 to 20 Hz) are necessary to achieve penetration of the field through the mold and the solid steel shell;
- permanent magnets rotated about the mold or submold regions by a motor.

Permanent magnetic stirrers affect only localized rotary stirring (Fig. 9.17a), which has a limited effect on structure. AC coils may be placed along the length of the ingot and arranged to fire in succession leading to an up and down stirring effect that is considerably more successful in structure control (Fig. 9.17b).

The metallurgical effects of electromagnetic stirring are threefold and arise from the enhanced dendrite fragmentation and heat transfer associated with the stirring of liquid steel. Figures 9.18, 9.19 and 9.20 summarize these effects graphically. Only general trends are shown, as specific values will depend on the exact casting and stirring conditions.

As expected, electromagnetic stirring results in enhanced equiaxed grain growth at the expense of columnar (Fig. 9.18). The percentage of equiaxed grains present in the structure becomes relatively insensitive to casting superheat if electromagnetic stirring is used. In its absence, however, an almost completely columnar structure forms when the superheat exceeds a certain value.

Maximization of equiaxed grain growth at the expense of columnar, coupled with enhanced heat transfer in the lower sump area, shortens the depth of the sump and eliminates the long narrow liquid channel shown in Fig. 9.13. Strong centerline segregation and porosity are both associated with this sump geometry and are

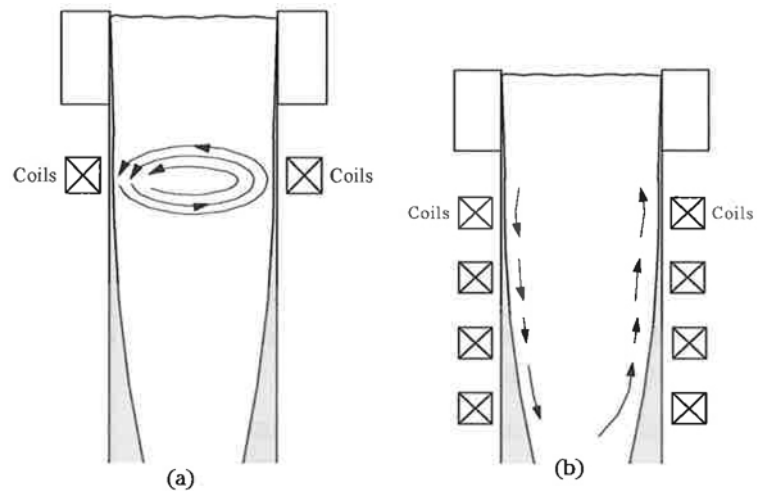


Fig. 9.17. Localized rotary stirring (a) and up and down stirring (b) are illustrated.

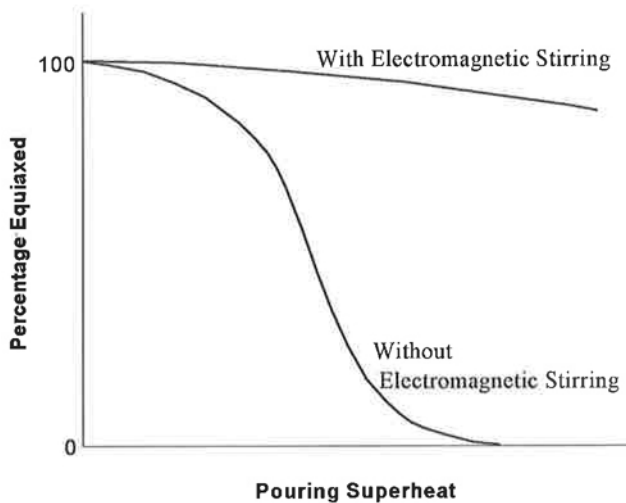


Fig. 9.18. Diagram shows the relative amount of equiaxed grain formation with and without electromagnetic stirring.

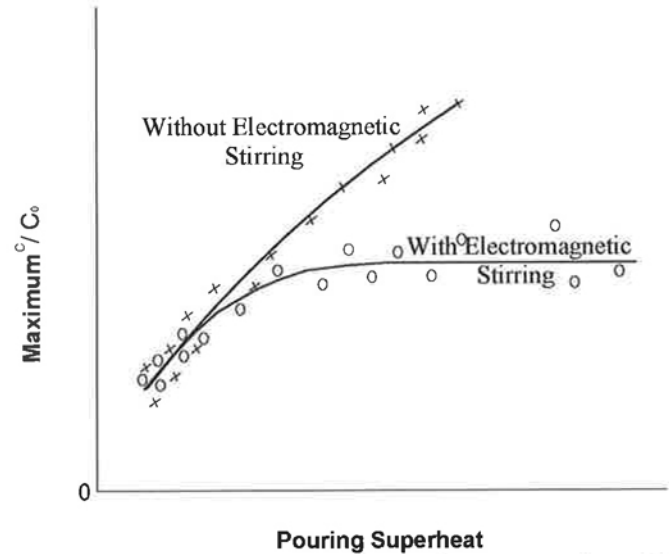


Fig. 9.19. The amount of centerline segregation with and without electromagnetic stirring is shown. [Data replotted from J.J. Moore, *Continuous Casting*, vol 3, Iron and Steel Society of AIME, (1984).]

reduced by electromagnetic stirring.

Figure 9.19 shows a typical variation of the enhancement of solute concentration, resulting from centerline segregation, as a function of melt superheat. In the absence of electromagnetic stirring this value increases strongly with superheat as the sump deepens and becomes narrower. When EMS is applied, the dependence on superheat is significantly less as sump geometry is changed. Note that at very low superheats there is no effect of electromagnetic stirring. At these low casting temperatures, solidification is largely equiaxed in nature and the sump geometry is such that, even in the absence of EMS, centerline segregation is minimized.

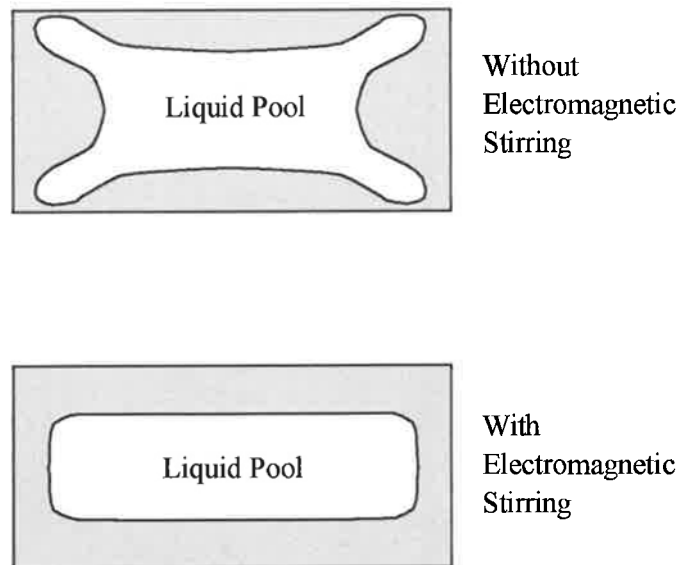


Fig. 9.20. Electromagnetic stirring in the mold results in a more uniform shell thickness.

Benefits of EMS are also found when stirring is applied in the mold itself. Accelerated heat transfer yields a shell that is of more uniform thickness than in the absence of stirring (Fig. 9.20), reducing the incidence of breakouts.

Overall, fluid flow control in continuous casting of steel serves to make the final ingot structure less sensitive to the casting conditions and, as a result, imparts a greater degree of control to the whole process.

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chapter 10

GASES IN LIQUID METALS

INTRODUCTION

Liquid metals are in contact with various gases throughout the entire processing sequence leading to an ingot or a casting. Depending on the specific metal or alloy and the gas type, various reactions may take place that later will influence the properties of the solidified metal. Several gases that may contact liquid metals and the possible origins of these gases should be considered.

The most significant source of gas comes from the atmosphere covering the melt during the melting, melt treatment or pouring sequences. If this atmosphere is simply air, the metal may interact with oxygen, nitrogen or water vapor. The relative amounts of oxygen and nitrogen are fixed in air, but the amount of water vapor depends on the relative humidity. Melting through combustion of fossil fuels generates CO, CO₂, SO₂ and H₂O, all of which can also react with the liquid. Other sources of gas are numerous and include:

- fluxes, which are often hygroscopic and contain chemically attached water;
- solid additives, such as scrap, grain refiners or even virgin ingot. All of these may contain adsorbed moisture or entrapped gases originating in a prior processing operation; and
- tools, crucibles, furnace linings and mold materials which, if not preheated, may contain moisture. In certain cases, chemical reaction between the furnace lining and crucible may change the melt composition in such a way that increased gas solubility occurs.

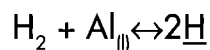
MELT-GAS REACTIONS

At room temperature, common gases are molecular in nature, consisting of covalently bonded atoms of the same or different species. When these gases contact liquid metals at the elevated temperatures characteristic of industrial processing, the molecule dissociates into its atomic components, and it is these atoms that react with the liquid.

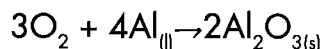
These reactions may cause the gas to dissolve in atomic form in the liquid or it may react to form a solid product. The solid product can remain on the surface of the melt as, for example, when an oxide dross layer covers the surface, or it may become a solid particle within the liquid. In this case, an inclusion is formed. Inclusions will be dealt with in greater detail in the following chapter.

One of several possible reactions will result, depending on the gas and metal concerned. Some common examples follow.

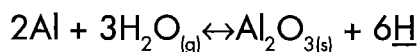
A gas composed of a single atomic species dissolves in the liquid. The best known example of this is the dissolution of hydrogen in aluminum by the reaction:



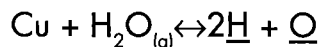
A gas composed of a single atomic species reacts with the liquid to form a solid reaction product. The oxidation of aluminum is a good example:



A compound gas reacts to form both a solid product and an atomically dissolved species. The important reaction of aluminum with water vapor falls into this category:



A compound gas dissociates to yield two atomic species in solution. The familiar reaction of copper with water vapor results in the dissolution of both oxygen and hydrogen according to the following reaction:



Solubilities of diatomic gases in liquid metals are expressed through Sievert's Law which states that:

$$\text{solubility} = K_s \sqrt{P_{\text{GAS}}}$$

where

K_s is Sievert's constant and

P_{GAS} is the partial pressure of the gas in the atmosphere above the melt.

Sievert's Law is based on a state of equilibrium between the gas content of the liquid metal and gas in the atmosphere above the melt. Equilibrium conditions are rarely met in practice and strict application of Sievert's Law is not all that useful. Nevertheless, the law does illustrate some important points related to gas pick-up by liquid metals. Solubility is decreased by lowering the partial pressure of the gas in the atmosphere above the melt, but this solubility is decreased only by the square root of the change in partial pressure. Thus, a lowering of the partial pressure by 25 times results in only a fivefold solubility decrease.

Gas solubility in liquid metals may either increase or decrease with temperature. If the dissolution reaction is endothermic, solubility increases; if the dissolution reaction is exothermic, solubility decreases with increasing temperature. Both cases are met. For example,

hydrogen solubility increases with temperature in Al, Mg, Cu and Fe, but decreases in Ti, Zr, Pd (palladium) and Ce (cerium).

The question of increasing or decreasing solubility with temperature is important when viewed from the aspect of casting and ultimate solidification of the metal. If the solubility increases as the temperature rises, large quantities of gas may be dissolved at liquid processing temperatures. Upon casting, this gas will come out of solution as the temperature falls and solubility decreases. Gas pores may be nucleated which, as we shall see later, can have a negative effect on casting quality. If, however, solubility decreases as the temperature rises, then a cooling liquid will simply be able to dissolve more gas, and no tendency to gas bubble formation will be apparent when the liquid is cast.

Unfortunately, the gases found most commonly all exhibit increasing solubility with temperature in the common industrial metals and alloys. Hydrogen dissolution in aluminum and its alloys is the classic case, as seen in the solubility/temperature curves of Fig. 10.1. Three features of the solubility are shown here:

- solubility in the solid is low and not very temperature dependent;
- there is a large solubility increase when the liquid is formed. The distribution coefficient, given as the ratio of the solid to liquid compositions at the melting point, is about 0.01. This is a very small value, indicating that most of the hydrogen is rejected into the liquid on freezing; and
- temperature dependence of solubility in the liquid is much higher than in the solid. The solubility roughly doubles if the melt is superheated by 140°C (252°F) above its melting point.

Once again, it must be emphasized that the curves of Fig. 10.1 represent an equilibrium situation not usually reached in practice. Nevertheless, most of the hydrogen dissolved in liquid aluminum will tend to come out of solution as that liquid is cast, cooled and, ultimately, freezes.

Compound gases are somewhat more complex in their behavior since the solubility of

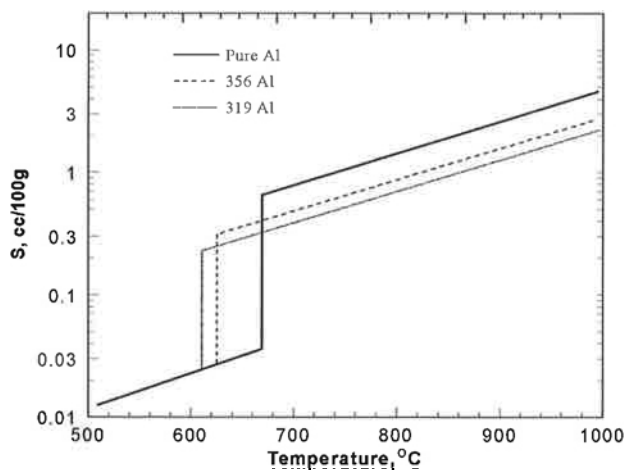


Fig. 10.1. The solubility of hydrogen in aluminum and some common foundry alloys is shown.

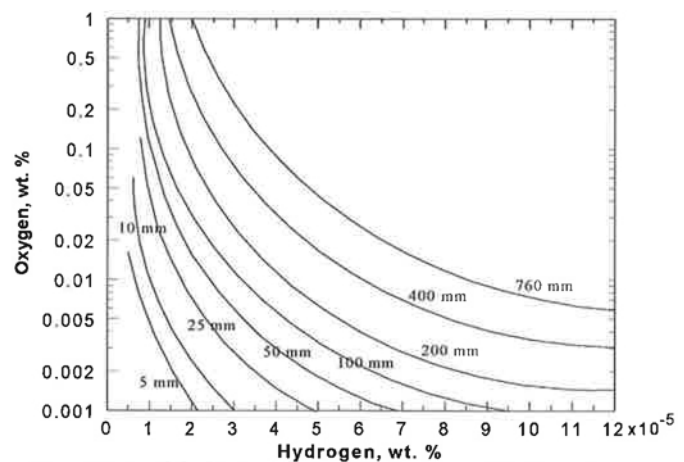


Fig. 10.2. The hydrogen-oxygen equilibrium in pure copper is shown for various partial pressures of water vapor over the melt.

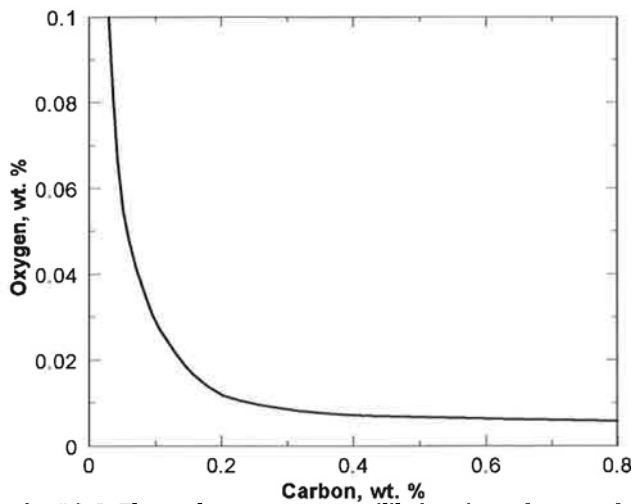


Fig. 10.3. The carbon-oxygen equilibrium in carbon steels is shown.

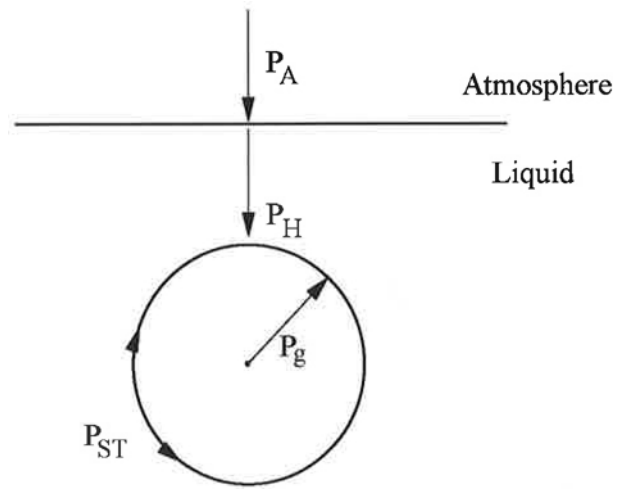


Fig. 10.4. Forces acting on a bubble in a molten metal are illustrated.

one atomic constituent depends on the concentration of the other constituent in the liquid. The case of hydrogen and oxygen in pure copper is shown in Fig. 10.2 where the equilibrium concentrations of each are given for various partial pressures of H_2O over the melt. It is seen that a low hydrogen concentration results in high oxygen, and vice versa. This fact is used to control dissolved gas contents in some copper alloys. Oxidizing atmospheres are used in melting, and little hydrogen is dissolved, while the oxygen can be removed later by a relatively simple treatment.

Carbon monoxide (CO) gas is evolved during solidification of steels when oxygen is dissolved during steelmaking. The C-O equilibrium is shown in Fig. 10.3. Low carbon allows significant oxygen dissolution and CO evolution during subsequent solidification. Gas evolution may, therefore, pose a problem during casting of low carbon steels. High carbon alloys, such as the cast irons, have a lessened tendency for CO evolution because it is not possible to dissolve large quantities of oxygen in the liquid. There is, however, a slight increase in the oxygen solubility as the carbon content moves into the cast iron range.

Equilibrium curves similar to those for H-O and C-O are found for other compound gases. Careful composition control is necessary if compound gas formation is possible. For example, copper alloys melted by the burning of high sulfur fossil fuels may dissolve sulfur as well as oxygen, raising the possibility of SO_2 evolution on cooling. Low sulfur concentrations allow significant oxygen dissolution while high sulfur content results in only low oxygen. Carbon pick-up from crucibles may occur during the processing of nickel containing copper alloys. The C-O equilibrium then comes into play and CO evolution is a distinct possibility, particularly if the amount of carbon dissolved is small.

GAS SOLIDIFICATION INTERACTION

When dissolved gas is rejected on freezing, two results are possible. If the gas concentration at the solid-liquid interface (C_0/k_0) is low, the gas atoms will behave like any other

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

atomically dissolved solute. They will form a solid solution, usually interstitial, with the solvent. As the temperature of the solid falls, supersaturation may result, and eventual precipitation of a gaseous pore may occur. This secondary porosity often occurs at grain boundaries or in interdendritic areas and can lead to a weakening of the alloy.

More importantly, if the gas concentration during solidification reaches high enough levels, a pore may be nucleated during the freezing process itself, and this pore may interact with the solid-liquid interface to produce many results. Before dealing with these, some of the simple physical concepts surrounding a gas bubble immersed in a liquid will be examined.

PHYSICS OF A PORE

Consider the simple bubble of Fig. 10.4. Several forces act on this bubble, some internal and others external:

- P_g is the internal gas pressure;
- P_A is the atmospheric pressure;
- P_H is pressure from the metallostatic head above the bubble; and
- P_{ST} is the pressure due to the gas-liquid surface tension. This pressure is necessary to form the surface of the bubble in contact with the liquid.

Of these four pressures, only P_g acts to expand the bubble; the remaining three conspire to cause it to shrink and eventually disappear.

If the bubble is to be in mechanical equilibrium, i.e., to neither grow nor shrink, then the internal pressure must equal the sum of the external pressures, so that:

$$P_g = P_H + P_A + \gamma(1/r_1 + 1/r_2) \quad (10.1)$$

where

γ is the gas-liquid surface energy and

r_1 and r_2 are the principal radii of curvature of the bubble. For a spherical bubble:

$$P_g = P_H + P_A + 2\gamma/r \quad (10.2)$$

where

$$r_1 = r_2 = r$$

PORE NUCLEATION

Equation 10.2 is quite straightforward for the case of an existing bubble with a finite radius, r . The difficulty arises in trying to imagine how a bubble nucleates since the surface

tension term varies as $(1/r)$, predicting that an infinite gas pressure is necessary at nucleation when $r \rightarrow 0$. Even if application of equation 10.2, derived for a macroscopic system, to the submicroscopic world of nucleation is not completely justified, very high initial pressures must be required, especially for liquid metals exhibiting large values of surface tension, γ .

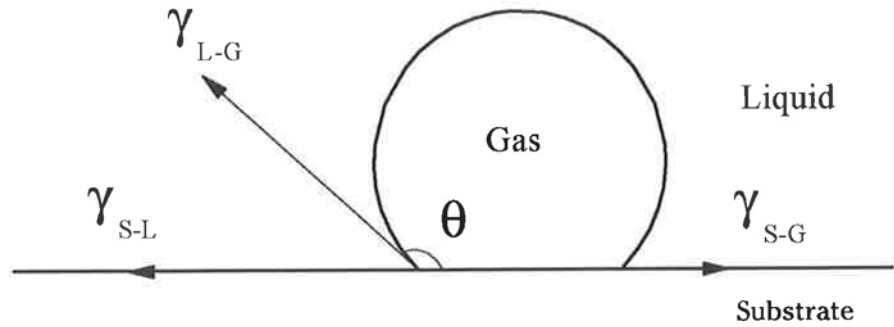


Fig. 10.5. Drawing shows a gaseous cap formed on a solid substrate, along with the various interfacial acting energies.

Estimates of the pressures necessary to homogeneously nucleate a gas pore in liquid metals are in the range of 30,000 to 50,000 atmospheres, depending on the liquid metal concerned. These are high values but they can be reduced somewhat by accumulation at the solid-liquid interface of solutes that are capable of reducing surface tension of the liquid. Oxygen, present in liquid iron, approximately halves the surface tension if in sufficient quantity, and the low value of the distribution coefficient ($k_0 = 0.05$) makes the presence of such quantities quite feasible. Despite these considerations, homogeneous nucleation of gas pores in liquid metals remains a difficult proposition and most evidence leads to the conclusion that this nucleation is heterogeneous.

As with all heterogeneous nucleation phenomena, a foreign substrate is necessary to aid the nucleation process. Gas bubble nucleation will occur where the gas concentration is highest, i.e., at or very close to the solidifying interface. Two substrates are then possible: the solid-liquid interface itself or inclusions in the vicinity of the interface. A classical heterogeneous nucleation geometry is sketched in Fig. 10.5 in which a gaseous cap forms on a solid substrate. The value of the contact angle, θ , is given by:

$$\cos\theta = (\gamma_{S-L} - \gamma_{S-G})/\gamma_{L-G} \quad (10.3)$$

where

- γ_{S-L} is the substrate liquid surface energy;
- γ_{S-G} is the substrate gas surface energy; and
- γ_{L-G} is the liquid gas surface energy.

Solid-gas surface energies are generally the largest in a solid/liquid/gas system because of the degree of disorder between gaseous and crystalline solid phases. Values of $\cos\theta$, therefore, become negative, implying that the contact angle, θ , > 90 degrees. As noted in Chapter 4, this is not a particularly favorable situation for heterogeneous nucleation, but it is more likely than homogeneous.

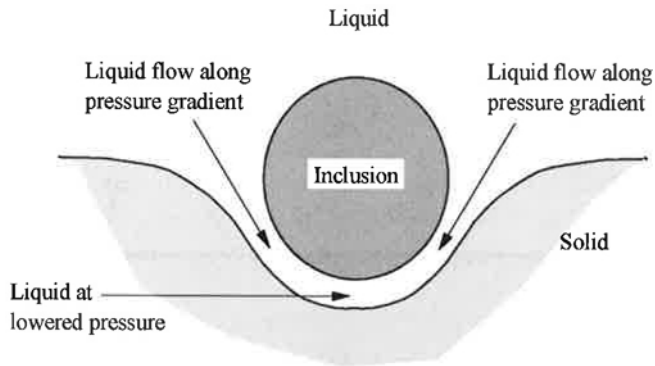


Fig. 10.6. Gas pores may be nucleated as a result of the pressure drop behind a nonwetted inclusion that is pushed ahead of the solid-liquid interface.

Let us now consider two possible solid substrates for nucleation: the solid-liquid interface itself, and inclusions of various types. Liquid melts wet their solid solidifying interfaces. In terms of equation 10.3, the γ_{SL} term will be very small, leading to a large negative value of $\cos\theta$ and making bubble nucleation on the interface itself highly unlikely. Consideration of equation 10.3 leads to the conclusion that bubble nucleation will be favored if the relative value of the liquid-sub-

strate interfacial energy, γ_{SL} , is high. In other words, solid substrates that are poorly wetted by the liquids in which they find themselves are good candidates for gas bubble nucleation.

A normal melt will contain a variety of inclusion types. Some may be effective in pore nucleation; others will not. Oxides usually are poorly wetted by the melt from which they form and, hence, may nucleate gas bubbles. Inclusions more metallic in nature, such as borides, nitrides or carbides, are better wetted. They are less effective in nucleating gas, but more effective in nucleation of the solid phase. Grain refiners, which of necessity are well wetted, nucleate the solid, but should be unable to nucleate gaseous phases.

Despite the apparent inability of the solid-liquid interface to nucleate gas, it should be noted that gas pores are found in the vicinity of the interface. There are several reasons for this. Not only is the highest gas concentration to be found at the interface, but this location also sees a concentration of nonwetted inclusions which are pushed ahead of the general interface.

The phenomenon of particle pushing by a solidifying interface has been known for a long time, but only recently has its importance to pore nucleation been appreciated. Particles are pushed ahead of the interface if the energy change associated with their remaining in the liquid is less than if they were to be incorporated into the solid. In terms of surface energies, this means that a particle may be pushed if:

$$(\gamma_{PS} - \gamma_{PL}) \text{ is positive,}$$

where

γ_{PS} is the particle solid interfacial energy; and

γ_{PL} is the particle liquid interfacial energy.

In fact, particle pushing is a very complex phenomenon involving many other variables, including particle size, interface velocity and liquid viscosity.

Mohanty et al.¹ have developed a model, shown in simple form in Fig. 10.6, to explain how

gas pores may be nucleated on a nonwetted inclusion pushed ahead of the interface. Gas atom rejection at the interface creates a high gas concentration in the vicinity of the inclusion. Solidification, and its associated shrinkage, necessitates a flow of liquid into the gap between the interface and the inclusion. The narrowness of this gap makes fluid flow extremely difficult, and a low pressure region develops in the gap. The lowered pressure in concert with the high concentration of gas atoms and the presence of a favorable substrate all combine to favor gas phase nucleation at, but not on, the solidifying interface.

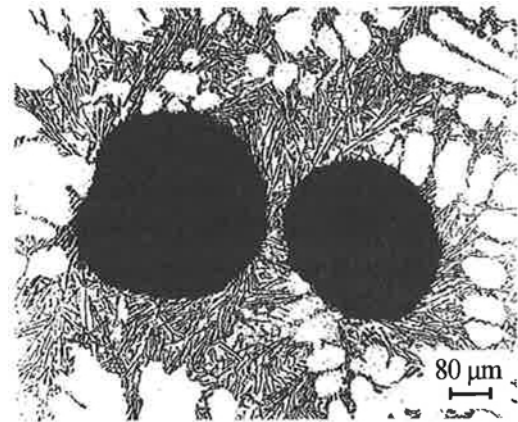
The preceding discussion has emphasized that nucleation of gas porosity is difficult during solidification processes. In some instances, nucleation is not necessary because of the presence of pre-existing bubbles. Refractories, which should not be wetted by the melts they contain, trap bubbles of air or other gases in their multitude of minute cracks and crevices. The same may be said of tools immersed into liquid metals, or of oxide films stirred into the melt during processing. The exact role of these various sources of pre-existing nuclei is not known and certainly has not been quantified, but it could be quite significant in industrial solidification, especially since effective nuclei for gas bubbles need to contain only a few gas molecules at the outset.

IMPORTANCE OF SHRINKAGE

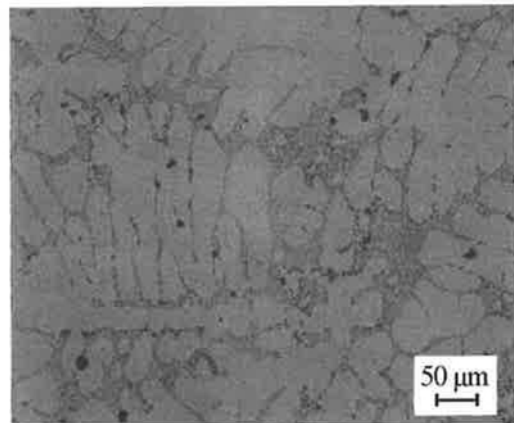
This discussion of gas nucleation indicates that while pore formation in solidifying metals is feasible, it is certainly not easy. One might suspect, therefore, that the formation of gas pores in castings and ingots is rare, and that gas porosity is not a problem. Anyone familiar with the microstructure of cast metal products knows that this is far from true. In fact, porosity formation is the largest single problem associated with casting quality. Why then are pores such a common feature of cast metal structure if they are so difficult to nucleate in the first place?

Classical nucleation theory, explained in Chapter 4, relates nucleation potential to surface energy alone. Such a concept is perfectly adequate for condensed phases, but when gas bubble nucleation is concerned, one must also consider the local pressure existing in the liquid at the point where the pore might nucleate.

During solidification, particularly dendritic



(a)



(b)

Fig. 10.7. Spherical pores form at high gas concentrations. Large pores form if the freezing rate is low (a) while small spherical pores are trapped in the solid at high freezing rates (b). These photographs were taken from a cast A356 alloy (Al-7%Si-0.3%Mg).

solidification, substantial local pressure drops may develop because of the inability of liquid metal to feed into regions where solidification (and solidification shrinkage) is taking place. Dropping pressures encourage dissolved gas to come out of solution, and nucleation is aided. This “shrinkage pressure” assists the chemical pressure resulting from gas supersaturation in the liquid, and in the presence of a suitable nucleus substrate, a pore will form.

Porosity is, therefore, often a result of the combination of dissolved gas and unfed solidification shrinkage. This is particularly true in long freezing range alloys that form wide mushy zones of dendritic solidification. Large volume contractions on solidification and high gas solubilities in the liquid compound the problem. It is for these reasons that many aluminum alloys and long freezing range brasses, in particular, are prone to porosity.

PORE GROWTH

Once nucleated, pores will grow by gas diffusion into them, and by solidification shrinkage of metal at the pore-liquid interface. Most pores found in cast metals result from both a gas and a shrinkage component, and the final pore morphology will depend on which component is predominant.

If gas concentration is high enough and/or if the alloy freezes with an almost flat interface, pores are formed when the fraction solid is low. Such pores will be spherical and will grow by diffusion of the atom species into them. Diffusion of gases in liquid metals is rapid, and if the freezing rate is low, the spherical bubble may grow to a size that causes it to be expelled from the liquid by buoyancy forces. Growth of such pores is limited by the ability of gas in the liquid to diffuse into them. If physical escape is not possible, the spherical pore will remain frozen in the solid, as shown in Fig. 10.7a. When the freezing rate is rapid, the solid-liquid interface may envelop the pore before substantial growth by diffusion can occur. In such a case, small spherical pores are found in the cast structure (Fig. 10.7b).

A special growth situation arises when the rate of diffusion of gas into the pore allows growth at about the same rate as interface advancement. As most of the pore quickly becomes surrounded by solid, the three phases—gas, solid, liquid—meet at the interface. Overgrowth of the gas phase by the solid does not occur, and the result is an elongated cylindrical pore as shown in Fig. 10.8a. The wormholes found around the edges of rimmed steel ingots are an excellent example of this type of growth (Fig. 10.8b), as are the elongated air pores extending from the outside to near the center of an ice cube.

Close inspection of the inner surface of wormholes will reveal that the surface is not smooth, but contains ridges that narrow the diameter of the pore and valleys that increase it. These surface undulations are due to fluctuations in the growth rate of the solid. If the rate increases, the solid phase tends to grow ahead of the pore, narrowing its diameter and vice versa. Fluctuations in the diameter of air pores found in ice cubes are caused by the on/off cycling of the freezer.

It should be noted that pores in which gas plays the predominant role are found only at

very high dissolved gas levels. Proper melt processing procedures will usually lead to lower gas levels. In aluminum foundry alloys, for example, true gas pores form only if the hydrogen concentration in the melt exceeds about 0.4 ml/100 g Al. Pores formed at low gas levels, particularly in long freezing range alloys, nucleate and grow late in the freezing process with their growth limited by the surrounding dendrite mesh. Such porosity appears interdendritic in nature with the dendrite arms clearly defined (see Fig. 7.11d). Very often, this type of porosity is attributed to shrinkage, but in reality both gas and shrinkage caused by inadequate feeding contribute to pore nucleation and growth.

POROSITY AND PROPERTIES

As a general rule, microporosity in castings resulting from gas-shrinkage interactions is undesirable, although there are occasions when a certain amount of gas is useful to avoid or limit macroshrinkage caused when the mold is improperly designed. Major difficulties caused by microporosity include:

- a deterioration of mechanical properties;
- leaking castings; and
- surface defects on painted, enameled or chromed finishes.

Tensile properties, in particular, are very sensitive to the presence of microporosity. Figure 10.9 presents some data relating the tensile properties of a 319 aluminum alloy to the measured porosity levels. These data were taken from castings containing a wide range of porosity amounts. Both the ultimate tensile strength and the tensile elongation are reduced by porosity. The effect on elongation is particularly significant since it implies that the material becomes more brittle as the amount of porosity increases.

The yield strength relates to the onset of plastic flow and it, too, may be decreased by the presence of porosity due to stress concentration around the pores. Microporosity is also responsible for the increased scatter in tensile test results obtained on cast

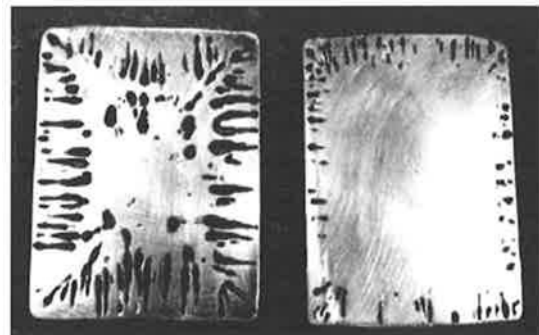
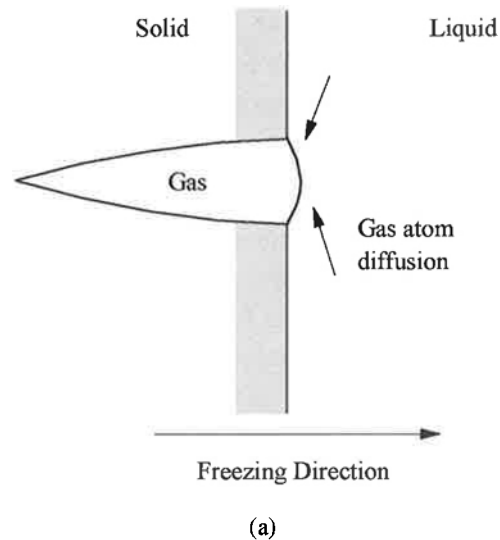


Fig. 10.8. Elongated pores form if the rate of pore growth equals, approximately, the linear rate of solidification. Fluctuations in the pore diameter are caused by growth rate fluctuation (a). An example of wormhole pores in steel is apparent in (b). The photographs are reduced approximately 73% for reproduction.

alloys, as compared to those on wrought metals. Many more tensile tests are required to obtain statistically significant results on cast than on wrought materials.

Microporosity does not affect impact strength to the same degree unless it is present in very large amounts. This property is mainly a function of the material microstructure and sample mass.

On the other hand, fatigue properties are very sensitive to the presence of porosity. Micropores can act to initiate fatigue cracks and assist in their propagation. It is for this reason that defect size and number are very strictly limited in aircraft castings, and many of these are treated by hot isostatic pressing (HIPping) to seal up the pores.

Castings that are required to hold liquids or gases under pressure may leak if microporosity is present. When viewed on a two-dimensional metallographic section, porosity appears disconnected but, in reality, the gas-shrinkage interaction that causes porosity in most castings may result in an interconnected and tortuous pore path running through the entire section of the casting. Many automotive parts, such as cylinder heads, wheels and engine blocks, cannot sustain high levels of microporosity for this reason, and pressure testing of these parts is a common quality control procedure.

Much porosity is found just below the surface of castings, and machining what appears to be a sound casting often reveals this porosity. The reason for the location is that some time and some solidification are necessary to set up the correct conditions for pore nucleation. Reactions between melt and mold also can cause gas evolution here and lead to porosity. Subsurface porosity may have no important structural effect on the casting, but it will make acceptable surface finishing impossible. Blisters usually form when a surface pore is covered by enamel or chrome, destroying the cosmetic appearance of the casting and making it unacceptable to the customer.

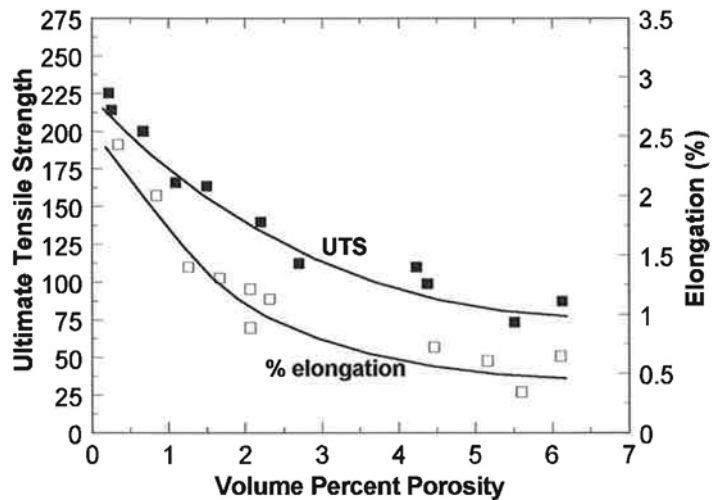
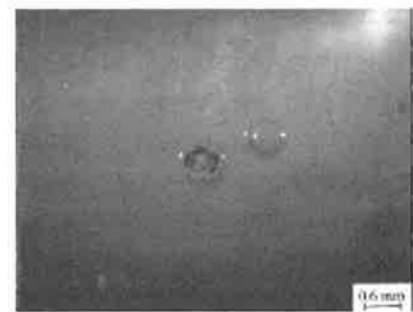


Fig. 10.9. The change in tensile properties of an aluminum alloy with porosity is shown.



(a)



(b)

Fig. 10.10. Porosity can create surface defects on finished castings as can be seen in this example of blisters formed on the surface of a zinc-magnesium alloy die casting. (a) is the casting in profile, (b) a photograph of the surface blister.

Figure 10.10 shows a porosity related blister on the surface of a zinc-magnesium alloy die casting.

Porosity in ingots is much less of a problem than it is in castings because the pore surfaces, being free of oxides, usually weld during hot working, destroying the pore. If, however, the pore has extended to the free surface of the ingot, its inner surface will have oxidized and will not weld on working. Blisters on the surface of rolled plain carbon steel sheet are caused by this effect.

There are times when a certain amount of internal microporosity is desirable in a casting. Usually this is the case when the mold and gating design are such that insufficient metal feeding takes place during solidification and macroshrinkage cavities result. Figure 10.11 shows an x-ray image of a 319 aluminum alloy plate casting made by the low pressure process. The plate dimensions and gate size are improperly designed and the gate freezes before the casting solidifies completely.

Macroporosity is seen in several locations along the centerline of the plate, due largely to shrinkage effects. When metal with a higher gas content (hydrogen in this case) is cast, these large areas of shrinkage are greatly diminished because of the generation of a finer dispersion of micropores caused by gas-shrinkage interaction. The casting is certainly not completely sound, but using the correct level of gas has eliminated the large defects.

MEASUREMENT OF GAS

The importance of the influence of dissolved gases on the freezing of castings and ingots requires actual measurement of the concentrations of these gases. Several techniques have been developed for the various gases and metals involved. It is possible to measure the amount of gas dissolved in a solid metal using mass spectrometry or a variety of patented solid state analyzers. But, knowing the amount of gas present in the solid is of little practical importance to the solidification of castings or ingots when the significant influences of the gas occur during the liquid to solid transformation.

It is the quantity of gas present in the liquid that is of interest because it is this quantity that must be controlled. Even the taking and analyzing of a solid sample is of little use because, by the time the analysis is complete, the metal would be cast or the gas level in the melt would be substantially changed. The following information details some common methods used to quantify the gas concentrations present in commercial metals and alloys before casting.

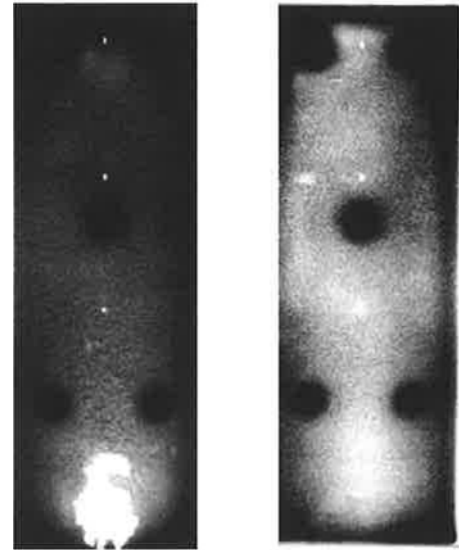


Fig. 10.11. Dispersed internal porosity can sometimes be used to compensate for shortcomings in die design that lead to macroshrinkage, as seen in this radiograph of a 319 aluminum alloy plate casting with dimensions of 11x4x1/2 in. The plate on the left was cast from metal containing a low gas concentration while that on the right is from a melt with a higher gas concentration. Areas of porosity appear white in the radiographs. Increasing the dissolved gas level has caused the large shrinkage area at the bottom of the plate on the left to disappear.

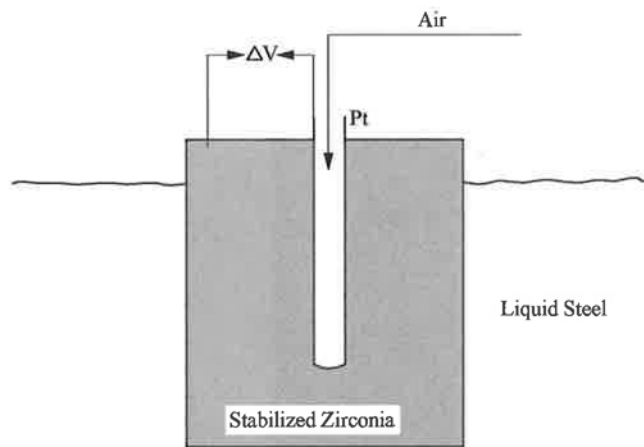


Fig. 10.12. A solid electrolyte-oxygen cell used to measure the oxygen concentration in molten steel is illustrated schematically.

Solid electrolyte-oxygen cells, first developed in the 1960s, are an effective means of measuring oxygen content in liquid steel where one of the main advantages of oxygen control is to reduce the level of solid inclusions to produce cleaner steels. These probes utilize a ceramic, such as stabilized zirconia, through which oxygen atoms may pass via cation vacancies. The workings of such a probe are shown in Fig. 10.12. When a gas of known oxygen concentration, such as air, is passed through the probe, a potential difference is established across the cell because of differing oxygen concentrations in the air and melt. Cell potentials are readily measured and can be related directly to the dissolved oxygen content of the liquid steel, providing a rapid *in situ* measurement.

In situ gas measurement in aluminum and its alloys is done using a recirculating gas principle. A fixed volume of an inert gas, such as nitrogen or argon, is circulated through a porous ceramic block. The pores in the block are not large enough to allow escape of the circulating gas into the liquid, but they are of sufficient size to allow contact of the liquid melt and inert gas at the ceramic-liquid interface (Fig. 10.13). Since the partial pressure of the dissolved gas (hydrogen) in the inert circulating gas is initially zero, diffusion of hydrogen into the circulating gas will take place.

Eventually, equilibrium will be reached between the amount of hydrogen in the liquid alloy and that in the circulating gas stream. Measurement of hydrogen content in the circulating gas is done through its thermal conductivity by means of specialized equipment. Apparently, the thermal conductivity of gases is very

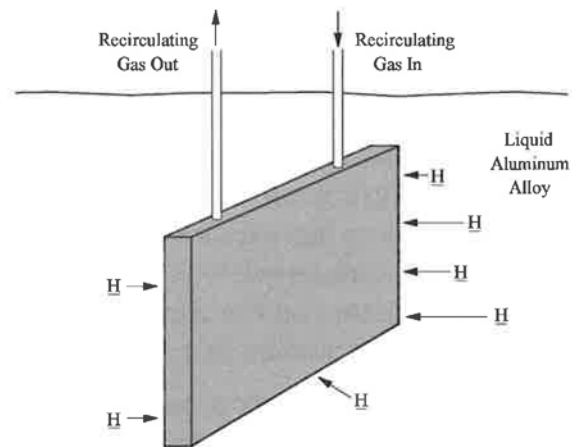


Fig. 10.13. Operation of a porous ceramic probe used to measure the dissolved hydrogen concentration in liquid aluminum is shown.

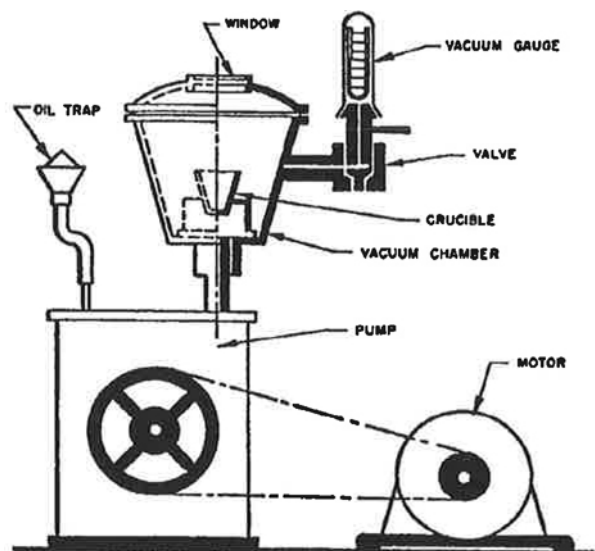


Fig. 10.14. Schematic illustrates equipment for the reduced pressure test.

sensitive to their composition. The concentration in the gas stream, then, can be related directly to that in the liquid aluminum with a total measurement time of 10 to 12 minutes.

Solidification of small samples of liquid aluminum or copper alloys under reduced pressure is the basis for a commonly used semi-quantitative method of gas measurement in these metals (Fig. 10.14). Reduction of the atmospheric pressure (P_A in equation 10.1) encourages pore growth, with the result that samples so solidified will contain an exaggerated amount of porosity, as seen in the example of Fig. 10.15. Higher levels of dissolved gas result in more porosity, and the reduced pressure test is often used semi-quantitatively in conjunction with a visual rating scale such as that shown in Fig. 10.16.

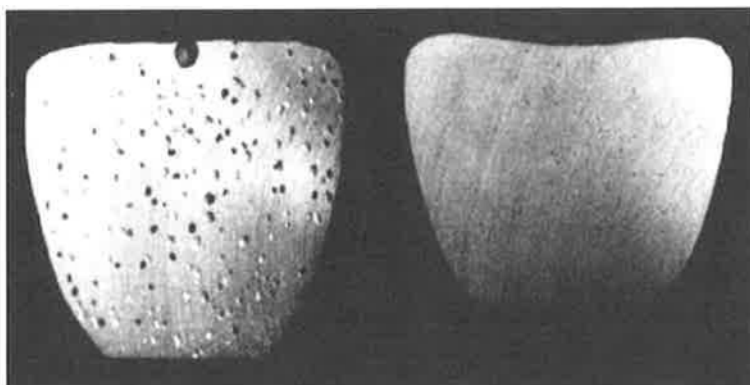


Fig. 10.15. Solidification under reduced pressure exaggerates the amount of porosity, as is evident in this example. The sample on the right was solidified at atmospheric pressure; that on the left, under reduced pressure of 0.1 atmospheres.

The density of reduced pressure samples can be measured by weighing them in air and water, according to Archimedes' Principle. Attempts have been made to use this test for quantitative determination of melt gas content by assuming that all pores were filled with gas at the solidus temperature of the alloy and at the test pressure. If this were the case, the gas content of the melt could be calculated from the following expression:

$$\text{gas content} = 100 \cdot P_2 T_1 / P_1 T_2 \{1/\rho_{th} - 1/\rho_s\}$$

where

gas content is in ml/100g of alloy;

P_1 is the value of atmospheric pressure, usually 760 mm Hg;

P_2 is the solidification pressure during the test (often 29 mm Hg);

T_1 is 273K;

T_2 is the solidus temperature of the alloy;

ρ_{th} is the theoretical density of the alloy; and

ρ_s is the measured density of the reduced pressure sample.

Gas contents determined by this method are lower than those measured by the recirculating gas technique just described. There are several reasons for this. Two of the most important are the loss of some gas into the vacuum pumping system during sample solidification, and the formation of gas bubbles at a temperature higher than the alloy solidus temperature, somewhere in the alloy mushy region.

It is possible, however, to calibrate the reduced pressure test for a specific sample geometry. This has been done using risered samples, and curves such as that shown in Fig.

10.17 can now be used to provide a quick and inexpensive measure of the dissolved hydrogen concentration in several commonly used aluminum foundry alloys.

While the reduced pressure test is used in the casting of copper-base alloys, its application is still purely qualitative. Samples solidified with an outward bulging convex surface are indicative of a high gas content; those that freeze with surface shrinkage are typical of a low gas content (Fig. 10.18). The relative lack of sophistication of the reduced pressure test applied to copper alloys in comparison to aluminum is probably because of the lack of structural applications for cast copper alloys. Such applications require that mechanical properties be controlled within narrow limits, necessitating close control of melt gas content.

GAS CONTROL

Fortunately, there are several methods available for the removal of dissolved gases from liquid metals. Applied in conjunction with some quantitative or semi-quantitative measure of gas concentration, these techniques can be very effective in controlling dissolved gas at whatever level is desired. Methods for gas control are divided into five groups as follows:

- care in melt preparation
- directional solidification
- vacuum degassing
- chemical combination
- gas purging.

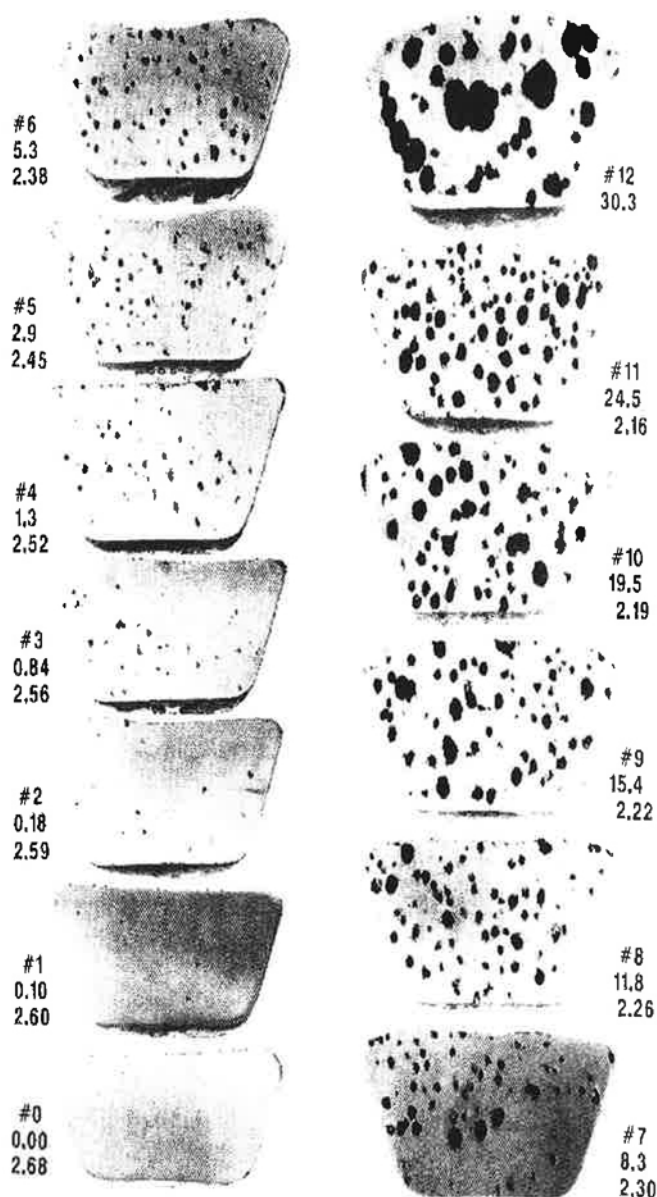


Fig. 10.16. A visual rating scale for use with the reduced pressure test is illustrated. Samples were solidified under a pressure of 100 mm Hg. The middle number beside each sample gives the percent surface area porosity, while the last number is the sample density in g/cm³. [Photo courtesy of Stahl Specialty Company.]

CARE IN MELT PREPARATION

Gases are most often dissolved during preparation of the melt, and care taken during this stage of metal processing can help to eliminate problems of gas dissolution. Tools, crucibles, alloy additions, etc., should be dried before exposure to liquid metal in order to prevent reaction with hydrogen or oxygen originating from water vapor. Gas dissolution occurs at the melt-gas interface, and any steps taken to minimize the size of this interface will be effective. Stirring, for example, should be done in such a way that splashing or excessive turbulence of the melt is avoided. The height of pours should always be minimized, and a metal stream should never be allowed to break up into droplets while pouring.

If gas dissolution is a concern, consider using a melting method that avoids combustion products. If economics permit, electric melting is preferable to melting with natural gas because no combustion gases that can dissolve in the liquid alloy are produced. Common sense used during the preparation of a liquid metal for casting will often go a long way to eliminating, or at least minimizing, a gas problem.

DIRECTIONAL SOLIDIFICATION

Directional solidification provides a free liquid path allowing gas bubbles to escape to the atmosphere instead of being trapped by the growing solid. The ability to promote directional solidification depends on design of the casting system and use of chills to direct freezing into the risers. In many cases, effective use of directional solidification to reduce the results of gas evolution during freezing may be limited by casting design.

Alloy freezing range is also important in determining the effectiveness of directional freezing. Long freezing range alloys with their extensive mushy zones may trap gas pores and allow gas-shrinkage interaction despite all the best attempts to create directional freezing. Short freezing range alloys are less likely to trap pores and more amenable to the production of sound castings by directional freezing.

Also significant is the level of gas. At high gas levels, bubbles form early in the freezing process and are more likely to escape unhindered by the growing solid. If pores form very late, as will occur if gas levels are low, their escape from the system may become impossible even if freezing is highly directional.

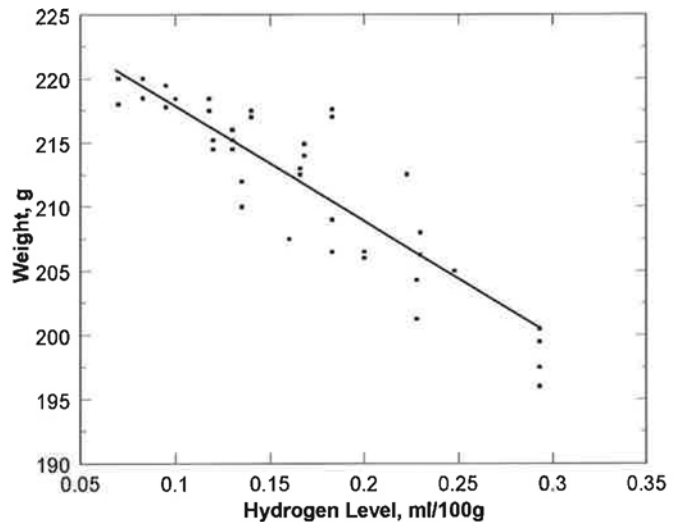


Fig. 10.17. The reduced pressure test can be made quantitative using calibration curves such as the one shown in conjunction with a specific sample cup and riser design. Using a riser allows the hydrogen level of this 357 aluminum alloy to be determined from a simple weighing of the sample rather than a density determination. [Data reproduced from *Transactions of the American Foundrymen's Society*, vol 103, pp 565-574 (1995).]

VACUUM DEGASSING

Reduction of the atmospheric pressure over a melt will encourage the formation of gas bubbles, according to equation 10.1. If formed by creation of a vacuum, these bubbles will be drawn into the pumping system, and the melt will be degassed. Gas atoms at the surface of the melt will also combine into molecular form and will be removed from the liquid. While any metal bath can, in principle, be vacuum degassed, the fact is that kinetics of the process are usually so slow that it becomes impractical. The one metal for which vacuum degassing is used extensively is steel, although there has been some limited applicability for aluminum.

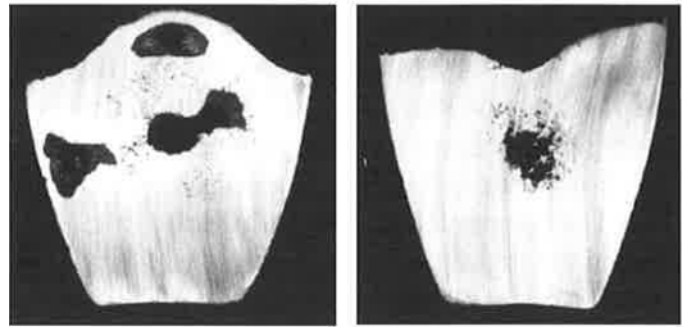
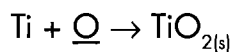
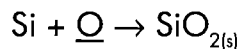
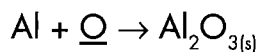


Fig. 10.18. Reduced pressure samples of copper are sectioned to show the effect of degassing on both the sample surface shape and the internal shrinkage. Sample on the left was poured from non-degassed aluminum bronze (alloy C95800) while that on the right was produced from the same metal after degassing. [Photo courtesy of Dr. Y. Fasoyinu.]

Processes for the vacuum degassing of steel are numerous, but one of the most common, illustrated in Fig. 10.19, is stream degassing. Liquid steel is tapped into a ladle seated on top of the vacuum chamber. A stopper rod is raised allowing the liquid steel to stream into the chamber. As it falls into another ladle placed in the vacuum chamber, the liquid stream breaks into small droplets in which bubbles of CO nucleate, grow rapidly and further fragment the liquid droplet. Success of this method is dependent largely on the breaking of the stream into droplets, reducing the metallostatic head term (P_H) in equation 10.1, and further encouraging gas bubble formation.

CHEMICAL COMBINATION

The principle of chemical combination is to chemically combine the dissolved gas atoms with some other element so that a solid or liquid product is formed in the melt. The best known examples of this practice are in using Al, Si or Ti to deoxidize liquid steel. The corresponding chemical reactions are:



In each case, dissolved oxygen is removed from solution and precipitation of CO gas on solidification is prevented. However, the method has the disadvantage of producing solid or liquid inclusions that can be the source of other problems with the solidified product.

Phosphorus often is used to deoxidize copper through the formation of a phosphorus oxide. Phosphorus is added as a Cu-P alloy, which dissolves readily in the melt. Internal

scrap recycling in a foundry may lead to high residual phosphorus levels in the charge material, and if proper control of the P level is not maintained, excessive deoxidation can occur with resultant high hydrogen pick-up. In copper, it is the H-O equilibrium that is important (Fig. 10.2) and, at very low dissolved oxygen concentrations, it is difficult to prevent high hydrogen absorption. Control of dissolved gas requires a thorough understanding of the physical-chemical processes occurring in the liquid.

The H-O problem in copper alloys often can be remedied by using various proprietary degassing agents which are able to combine chemically with both hydrogen and oxygen. Zirconium and titanium are often found in these agents, and both readily form oxides and hydrides, which are stable at liquid metal temperatures.

GAS PURGING

Gas purging is used extensively in the non-ferrous metals industry for gas removal. The principle is illustrated in Fig. 10.20. A bubble of some gas is introduced into the bottom of a melt. The gas may be inert or reactive with the metal concerned, but initially it must contain no atoms of the gas species to be removed from solution. Since partial pressure of the gas to be removed is initially zero in the bubble, there exists a driving force for diffusion of gas atoms from the liquid into the introduced bubble. As this bubble rises through the bath, it will pick up progressively more and more of the undesirable dissolved gas until it finally escapes from the free surface of the melt.

Chemical kinetics of the removal process are complex, and it has been shown that, to be effective in a minimum of time, it is necessary to produce a very fine dispersion of bubbles in the liquid. Considerable effort has been directed to this end with the result that most gas purging is done via a rotary impeller degasser

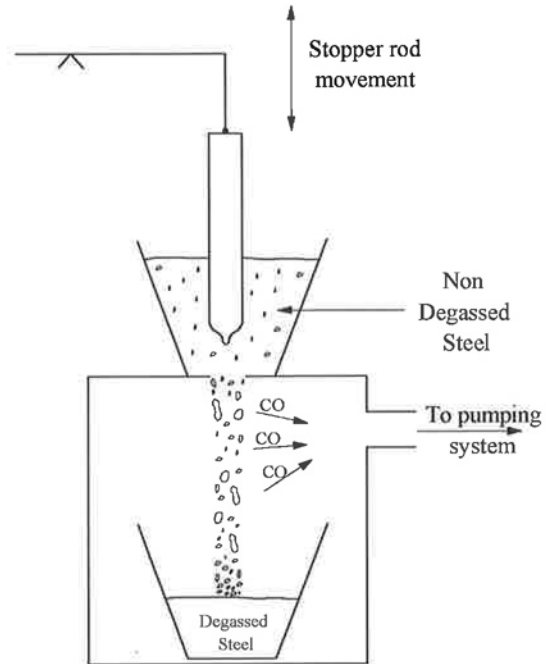


Fig. 10.19. Schematic illustrates the stream degassing of molten steel.

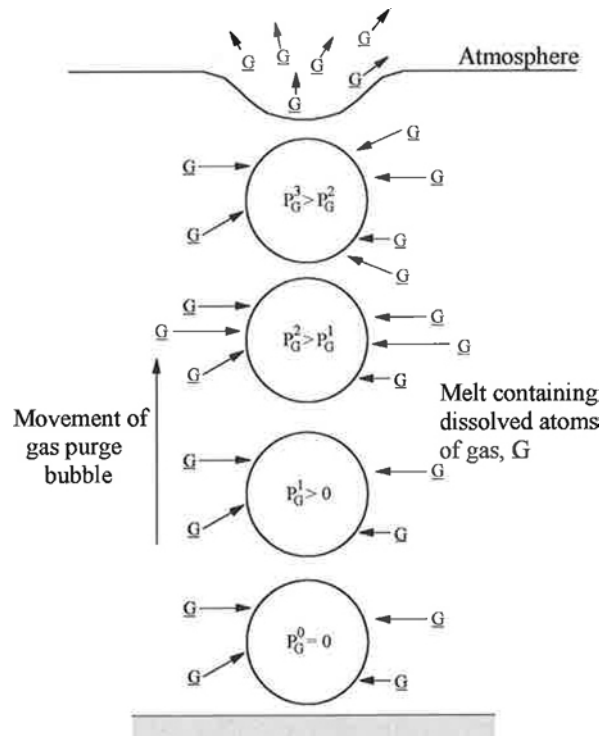
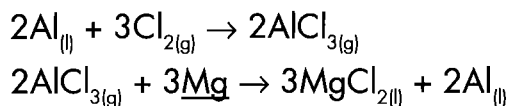


Fig. 10.20. The principle of gas purging to remove dissolved gas is shown.

(Fig. 10.21) consisting of a series of vanes which chops a gas stream into a mass of fine bubbles and then disperses them throughout the melt.

Most degassing of aluminum and its alloys is done in this way with nitrogen being the most common gas used. Argon may also be employed, but it is much more expensive, and there is no evidence to indicate that it is any more effective than nitrogen. Reactive gases, such as chlorine or sulfur hexafluoride, also are used in a form diluted with nitrogen.

There is considerable controversy over whether reactive gases actually speed the degassing process, but they do appear to assist if the process is inefficient and the bubble size relatively large. Reactive gases may remove some of the alloying elements and care must be exercised in their use. Chlorine, for example, can remove magnesium, an important alloying element, from aluminum alloy melts through the reactions:



One of the main advantages in using reactive gases is that they help to clean inclusions from the melt, as well as to degas. Melt cleaning will be dealt with in the next chapter.

The principles of gas purging apply to any liquid containing a dissolved gas. Dry nitrogen can be used to remove gas from copper-based alloys, as can dry oxygen. Using oxygen for this purpose is interesting and underlines the need for a good understanding of the chemical processes that might take place in degassing. If the initial hydrogen content is high, oxygen injection will cause it to drop according to the O-H equilibrium. However, excessive use of oxygen will serve to oxidize alloying elements, such as aluminum, and eventually the copper itself. Not only will the melt chemistry be changed dramatically, but also excessive oxide (dross) formation will occur.

While purging is usually accomplished by direct introduction of the purging gas into the melt, various solid additives are available that decompose into a gaseous form when added to the liquid metal. Hexachloroethane tablets generate chlorine gas when added to aluminum melts, and polytetrafluoroethylene creates fluorine gas when added to molten copper alloys. Use of these tablets is declining because of the generation of obnoxious fumes, and the inherent inefficiency of the process.

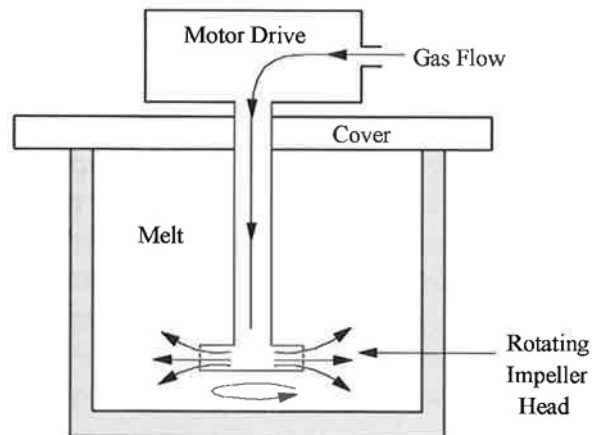


Fig. 10.21. A schematic of a rotary impeller degassing unit is shown. The rotating impeller chops the gas stream into a mass of fine bubbles that provide very efficient degassing of the melt.

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chapter 11

LIQUID METAL CLEANING

INTRODUCTION

Most of the cast microstructure is developed during the solidification of the metal phase, but one important microstructural feature is formed in the liquid even before actual solidification begins. This feature, inclusions, or “dirt” as they are often called, can have an important influence on mechanical properties of the cast material, as well as its formability and machinability, and great effort has been expended in the area of inclusion control to produce “clean” liquid metal. This chapter will trace the origin of many inclusions commonly found in the most significant metals and detail their effect on the cast material, how they can be removed from the liquid metal and how their number can be measured.

ORIGIN OF INCLUSIONS

Inclusions occur in two general classes. Exogenous inclusions originate from outside of the bulk melt. They are usually entrained refractory bits broken off from crucible or furnace linings, flux particles, or pieces of slag or dross that have become trapped in the melt. Sand castings often include sand grains picked up from the loose sand left in mold running systems and a foundry’s recycling of gates and risers may result in broken ceramic filters appearing as exogenous inclusions in castings.

Exogenous inclusions are often large and may even be visible to the naked eye. Because they do not originate from any particular characteristic of the melt chemistry, their occurrence is sporadic and difficult to predict. Very often, they can be eliminated or minimized by taking extra care with the maintenance and installation of refractories and by ensuring that molds are clean before casting. The photomicrograph in Fig. 11.1 shows a typical exogenous inclusion in a steel casting.

Indigenous inclusions originate within the melt as a result of a chemical reaction between the melt and some other chemical species that the melt contacts. This other chemical element, or elements, may be found in refractories, molds, the atmosphere above the melt or around the pouring stream, or in additions made to the melt for various reasons.

The type of indigenous inclusions that form depends very much on the melt chemistry, the type of refractories used for melt processing and the nature of the various additions made to the melt. Inclusion control requires a detailed knowledge of the chemistry of the entire liquid processing sequence. Because indigenous inclusions are so chemistry specific, it is not possible to describe them in a very general way. Instead, the formation of some common indigenous inclusions in two important industrial metals will be described. Examples are taken from steel and aluminum alloys.

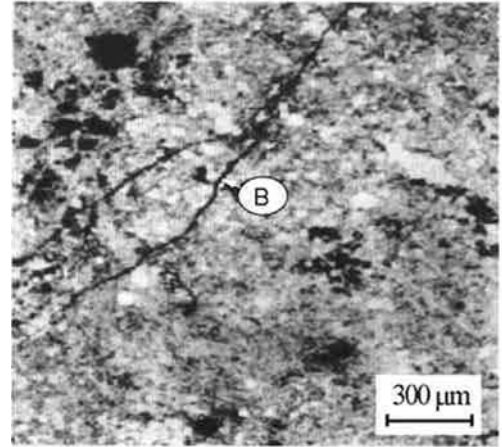
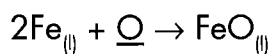


Fig. 11.1. An example of an exogenous slag inclusion (labeled B) from a high alloy steel casting is shown.

INCLUSIONS FORMED IN LIQUID STEEL

NONDEOXIDIZED STEEL

As seen in Chapter 10, liquid steel contains a certain amount of dissolved oxygen, dependent on the carbon content of the steel (Fig. 10.3). The solubility of oxygen in solid steel is virtually nil, and the oxygen will react with iron to form FeO inclusions as the liquid steel is cooled. The inclusion-forming reaction is:

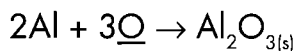


Note that the FeO is formed as a liquid phase. It appears, therefore, as a spherical inclusion in the solidified steel (Fig. 11.2).

DEOXIDATION INCLUSIONS

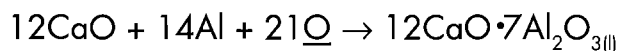
Oxygen content of liquid steel can be reduced by deoxidation with elements having a higher affinity for oxygen than iron. The usual elements used are Al, Si, Mn and Ti, sometimes alone, but often in combination with each other. No matter which element or combination of elements is used, inclusions result. They usually are small, less than 20μm in size, and often form clusters in the structure. Some examples are listed below.

- *Aluminum* is the strongest of these deoxidants and is usually used to produce killed steel, i.e., it removes virtually all of the oxygen through the reaction:



This reaction is valid if the soluble aluminum exceeds about 0.005%; otherwise, iron-manganese aluminates may form with the composition (FeO,MnO)Al₂O₃. An alumina cluster in deoxidized steel is illustrated in Fig. 11.3.

- *Aluminum mixed with lime* (CaO) is a more effective deoxidant, leaving less aluminum dissolved in the steel and producing liquid calcium aluminates by the reaction:



- *Silicon and manganese* are weaker deoxidizers than aluminum and are used to produce rimmed steels. These elements often are added together and, depending on their relative amounts, will produce either SiO₂ or MnSiO₂ as the reaction product.

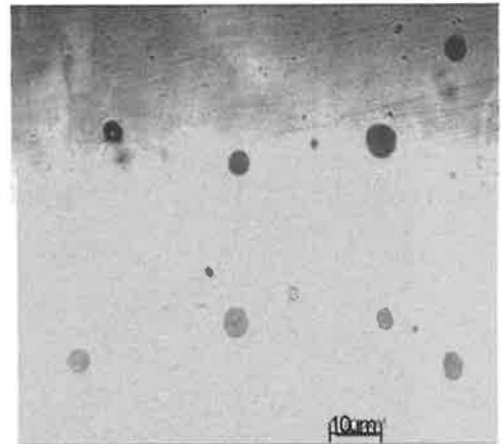


Fig. 11.2. Spherical FeO inclusions are shown in steel. [Photo courtesy of C. Tian.]

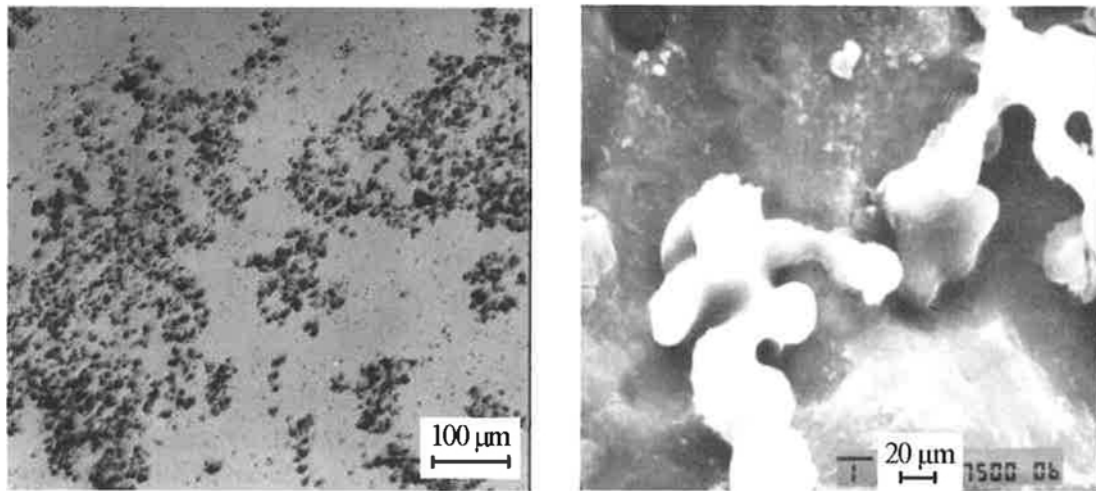


Fig. 11.3. An alumina (Al_2O_3) cluster in deoxidized steel is shown: (a) optical micrograph; (b) scanning electron micrograph of deep etched specimen. [Photos courtesy of C. Tian.]

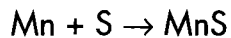
- An Al-Si-Mn mixture may be used to produce semi-killed steels and will generate inclusions of Al_2O_3 (corundum), $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite) or $\text{MnO} \cdot \text{Al}_2\text{O}_3$ (galaxite), depending on relative amounts of the three elements.

REOXIDATION INCLUSIONS

Excess primary deoxidants will react with oxygen, which continues to dissolve in the steel after the initial deoxidation reactions have ceased. Reoxidation can take place during melt holding or pouring. The products of reoxidation are a complex mixture of oxides containing Al, Mn, Si and Ti and, in a high alloy steel, some of the alloying elements. Reoxidation inclusions usually are large, several millimeters in size, and contain included metal droplets.

DESULFURIZATION INCLUSIONS

If the sulfur content of a steel is too high, the Fe-FeS eutectic may form at 988C (1810F). The presence of this eutectic can lead to cracking or hot shortness during subsequent hot working of the steel. Manganese will eliminate this hot shortness through removal of the soluble sulfur by the formation of MnS inclusions that precipitate onto other existing inclusions or form along the grain boundaries in the cast steel by the reaction:



NITROGEN-CONTAINING INCLUSIONS

Nitrogen will dissolve in liquid steel, and in the presence of dissolved oxygen will remain in atomic form. If, however, the steel is highly deoxidized, the nitrogen may react with other elements to form various nitride inclusions, the most common being AlN, TiN, ZrN and VN.

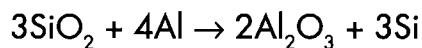
CASTINGS VERSUS INGOTS

The types of inclusions that form and are important may be quite different in steel ingots than in steel castings. During the steelmaking process, prior to ingot casting, the liquid state exists for a considerable period of time. Small Al_2O_3 inclusions formed on deoxidation have time to agglomerate into larger clusters. Pouring an ingot takes considerably longer time than pouring a casting simply because of the differences in size. Reoxidation inclusions are, therefore, likely to be found in steel ingots, but the largest inclusions found in castings tend to result from refractory erosion and sand mold erosion.

INCLUSIONS FORMED IN LIQUID ALUMINUM AND ITS ALLOYS

As in the case of steel, a number of different inclusions can form in aluminum alloys, depending on the specific alloy composition and the melt treatment procedures. Alumina (Al_2O_3) is by far the most common. It will form at any oxygen partial pressure greater than 10^{-50} atmospheres, meaning that, for all practical purposes, alumina is always present. Most Al_2O_3 forms on the melt surface where liquid-air contact is made. Liquid aluminum does not wet its oxide, resulting in a natural tendency for the oxide to remain on the melt surface. However, entrainment of oxide films can occur during pouring or melt treatment processes, such as alloying. Entrained films can become incorporated into the castings, therefore representing one of the most significant types of defects found in aluminum castings (Fig. 11.4).

Liquid aluminum is a powerful oxidant, which can reduce various refractory materials. Small alumina inclusions form through reduction of silica in refractories according to the reaction:



In order for this reaction to proceed, it is first necessary for the aluminum to wet the silica. Normally this does not happen, but wetting may be promoted when halide salt fluxes are used. Salt flux treatment is a common foundry practice used to protect the melt from oxidation, or to clean certain elements from it. Unfortunately, halide salts exert profound effects on the surface properties of liquid aluminum, and their use may promote, rather than hinder, inclusion formation.

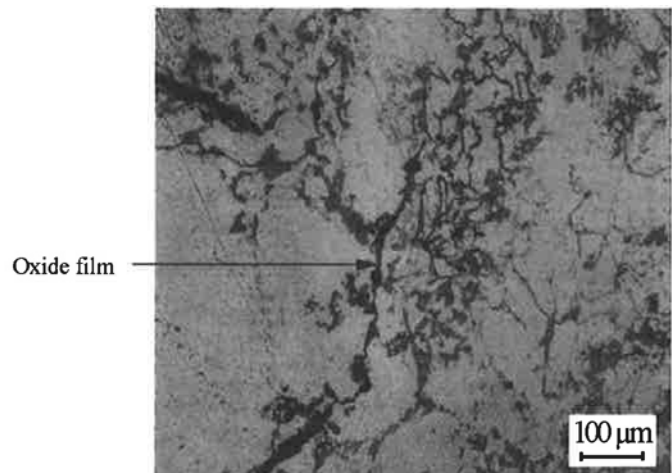
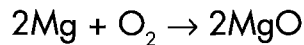


Fig. 11.4. Oxide films are one of the most serious types of inclusion defect found in cast aluminum alloys.

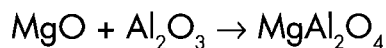
MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

Many aluminum alloys contain magnesium, which is added to age harden the alloy. The alloying process with magnesium can yield the formation of magnesia (MgO) inclusions by the reaction:



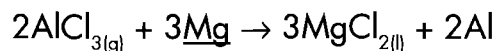
Normal magnesium levels in these alloys are so low that MgO will not form, but when magnesium in concentrated form is added in alloy manufacture, local pools of very high magnesium content form and rise to the melt surface, because of their lower density. Here, they oxidize as a white fume of MgO, some of which may become incorporated in the liquid alloy.

Spinel is a magnesium aluminate that forms by reaction between MgO and Al_2O_3 as:



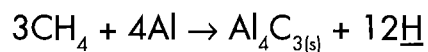
Spinel, in particular, are prone to formation in high magnesium-containing alloys and, when they do form, their growth is rapid, as the spinel, unlike alumina, is a nonprotective oxide.

Aluminum alloys subjected to halide flux treatments are often found to contain a variety of halide inclusions, depending on the flux and melt chemistry. The most commonly found are chloride inclusions of magnesium formed by reaction between magnesium and aluminum chloride gas, which is an intermediate product of the flux treatment. The inclusion forming reaction is:

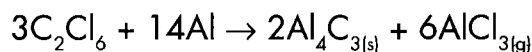


This is an example of a chemical reaction, resulting in a liquid inclusion. They are usually small and very difficult to remove from the melt by filtration.

Reactions between aluminum and carbon in various forms are common and result in aluminum carbide (Al_4C_3) inclusions. Melting by combustion of natural gas may lead to an aluminum-methane reaction, which also adds dissolved hydrogen to the melt, in addition to producing dirt. The appropriate chemical reaction is:



Hexachloroethane tablets, sometimes used for degassing purposes, decompose in the liquid aluminum according to the reaction:



The aluminum chloride gas removes hydrogen, but also reacts with any magnesium present to produce halide inclusions in addition to the carbides. Once again, the importance of the melt chemistry is obvious.

INCLUSION CONSEQUENCES IN CAST METALS

The effects of inclusions on the final product are many and varied and depend on the inclusion type formed and the size and number present. In many cases, quantitative relationships between a given property and the number of inclusions in the solid product do not exist, mainly because of the difficulties associated with the quantification of inclusion size and number.

HOT AND COLD WORKING OPERATIONS

The deformability of inclusions is a major consideration in ingot casting. If the plasticity of the inclusions is less than that of the matrix material, stresses will develop between the inclusions and the matrix during fabrication processes such as rolling or forging. These stresses may eventually result in decohesion of the inclusions, leading to cracking at the inclusion-matrix interface. The tensile properties and the ability of the metal to undergo further deformation may be adversely affected.

The fractured steel cord wire shown in Fig. 11.5 is an example of the effect inclusions can have during drawing operations. Here, size of the inclusion contained in the wire was sufficiently large to reduce the cross-sectional area of the wire to the point where tensile strength was exceeded and fracture resulted during drawing.

Inclusion plasticity depends not only on the type of inclusion, but also on the temperature at which hot deformation is conducted. Corundum and spinel are not deformable at steel or aluminum hot working temperatures and always remain as troublesome inclusions in these materials. Pure silica also is generally brittle, even at high temperatures, but its deformability will increase if it dissolves some MnO in solid solution. Sulfide inclusions in steel

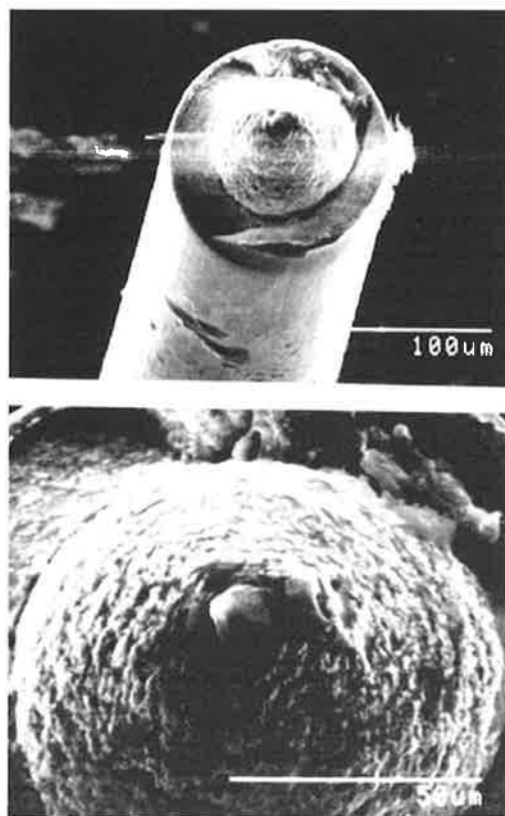


Fig. 11.5. Scanning electron micrographs show inclusions at the break in a steel cord wire. [ASM Handbook, vol 1, Properties and Selection: Irons, Steels and High-Performance Alloys, p 117, Fig. 14, ASM International, Materials Park, OH 44073-0002 (1990).]

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

are deformable over the entire temperature range for steel fabrication. Many simple calcium aluminates are hard and brittle, but if silica is present as part of their chemical make-up, they do become more plastic.

Once again, it is apparent that melt chemistry and chemical composition of all constituents present in the solidified product are critical factors in determining the behavior of that product.

MECHANICAL PROPERTIES

Tensile properties of inclusion-containing cast metals are generally lower than those of the same material containing few or no inclusions. Not only does the inclusion represent a structural discontinuity that will hasten fracture through simple stress concentration, but its presence also aids in microcrack formation in tension when decohesion of the inclusion-matrix interface occurs. Tensile elongation is reduced, and fabrication processes in which large tensile forces are involved will be more difficult to operate if the metal has a high inclusion content. The drawing break shown in Fig. 11.5 is a good example.

Further examples of these effects are shown in Fig. 11.6. In (a), the total elongation in a tensile test is plotted versus the yield strength of steel for samples containing no inclusions elongated in rolling, and for samples that do contain such inclusions. Inclusion-containing samples exhibit an almost 10% lower elongation. The practical result of the lowered elongation can be seen in fabrication processes, such as stretch forming, in which the material is stretched, an example being the manufacture of dome shaped tops on aerosol cans. A test commonly used to measure stretch forming capacity is to force a punch into a sheet of the metal and to measure the punch travel length before cracking takes place. Data for punch tests on steel sheet is presented in Fig. 11.6b, where it is obvious that the presence of inclusions serves to make the steel less deformable in tension.

SERVICE PROPERTIES

Several service properties are affected by the presence of inclusions. Large inclusions close to the surface may act as stress raisers in castings or wrought products subjected to cyclical stressing.

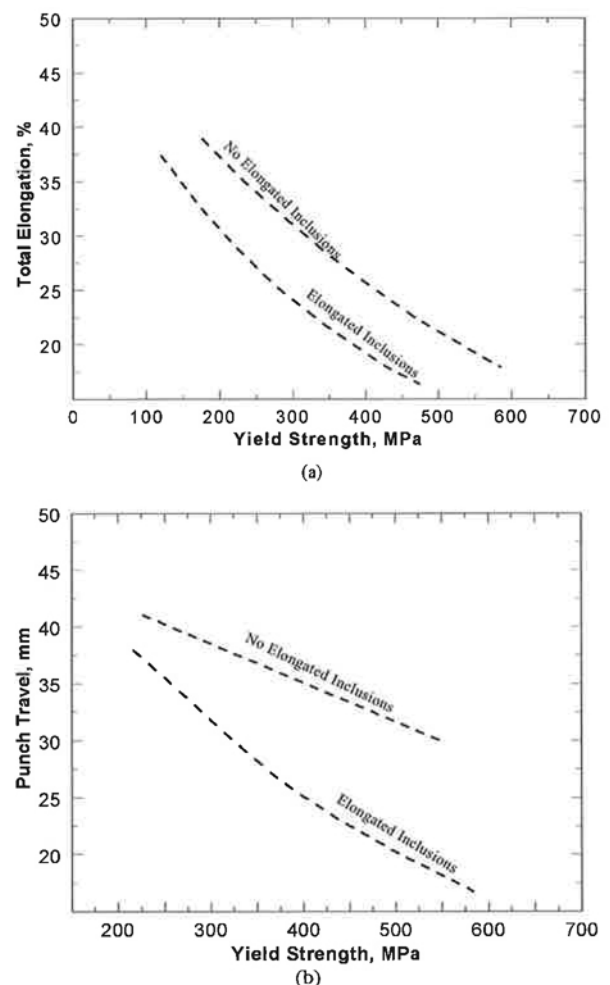


Fig. 11.6. The effect of elongated inclusions on (a) tensile properties and (b) stretch forming properties of steel is shown. [Data summarized from R.M. Hobbs, *Inclusions and Residuals in Steels*, eds. J.D. Boyd and C.S. Champion (1985).]

These sites are prime candidates for fatigue crack nucleation, which obviously will lower the fatigue strength of the material.

A strong correlation has been shown between the inclusion content of pipeline steel and its toughness (Fig. 11.7). The upper shelf energy decreases dramatically as the number of large inclusions ($> 70\mu\text{m}$) increases.

Corrosion resistance also is decreased when inclusions are present at or near the surface. Small electrochemical cells are established between the inclusion and the surrounding metal, resulting in pitting corrosion. Flux inclusions, which are sometimes found on the surface of nonferrous castings, are hygroscopic in nature and will react with moisture to give a freckled white appearance on the casting surface.

FINISHING OPERATIONS

Metal products are often finished with a painting or plating process. Each of these may be affected by inclusions at or near the surface. Thin glossy paint films highlight surface defects caused by inclusions. In the absence of paint, these defects might be only scarcely visible, if at all. Surfaces are normally buffed before plating, and subsurface inclusions revealed by the operation will show up as pits on the finished surface.

MACHINABILITY

Most inclusions in cast metals are ceramics, and as such are much harder than the surrounding metal matrix. These hard inclusions are a constant source of increased tool wear and breakage during the machining of both aluminum and steel castings. Machining remains one of the major costs associated with casting production and significant potential benefits can accrue from the reduction of inclusions in castings that must be machined.

FLUIDITY

The ability to manufacture intricate castings requires that the liquid metal possess a property commonly referred to as fluidity—the ability to flow long distances before freezing. Fluidity is one of the most complex foundry parameters, depending on alloy composition, pouring temperature, method of measurement and melt cleanliness. Melt cleanliness is important because large oxide films collect in the flow path and slow metal flow. Cleaner melts will flow further and faster if all else is equal.

As is the case with many foundry properties, quantitative data is sparse, but some idea

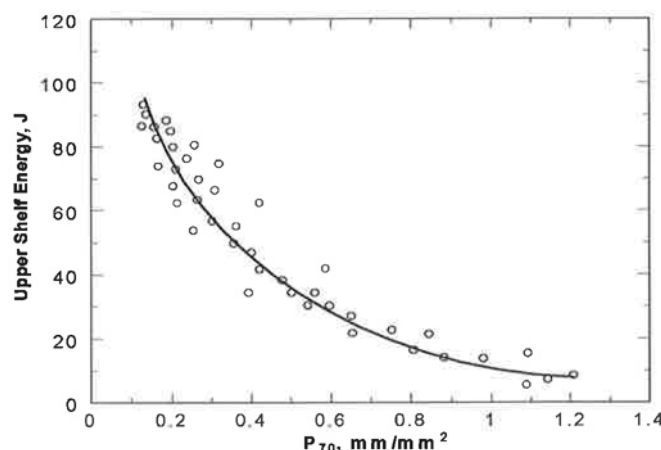


Fig. 11.7. The upper shelf energy of pipeline steel is given as a function of the number of inclusions greater than $70\mu\text{m}$ in size. The unit P_{70} refers to the total intercept distance through inclusions with a size greater than $70\mu\text{m}$ encountered in an area of one mm^2 . [Data replotted from R.M. Hobbs, *Inclusions and Residuals in Steels*, eds. J.D. Boyd and C.S. Champion (1985).]

of the significance of oxide films can be obtained from Fig. 11.8, which compares a filtered (clean) aluminum alloy with an unfiltered (contaminated) alloy of the same composition. Filtration is one of the main means of removing inclusions from liquid metal and, in this example, cleaning of the liquid allows its fluidity, as measured by inches of flow, to increase by about 70%.

POROSITY

Perhaps the most significant influence of inclusions in aluminum castings is their role in assisting porosity formation. Of course, inclusions also aid in porosity formation in ingots, but presence of the pores is less serious as they are usually eliminated during subsequent hot working. In castings, on the other hand, the pores remain (unless the castings are HIPPED) to decrease mechanical properties, cause the castings to leak and mar the surface finish.

While the mechanisms whereby inclusions assist in pore nucleation are not at all well established, the relationship between porosity and inclusions is definite. A graphic demonstration of this relationship in aluminum alloys can be seen by performing reduced pressure tests (see Chapter 10, Measurement of Gas) on samples containing the same dissolved hydrogen concentration, but different inclusion contents.

Figure 11.9 shows porosity amounts in reduced pressure samples of an Al-7%Si alloy (356 alloy) as a function of the measured inclusion content. Inclusion concentration was measured on a metallographic section of a filter through which a certain mass of liquid alloy had been passed. Thus, the units of inclusion concentration are expressed as the area of inclusions on the section per unit mass of metal passed through the filter, (see Measurement of Melt Cleanliness—Preconcentration Methods later in this chapter). The greater the number of inclusions, the higher the number of pores.

Inclusions that are not wetted by the liquid are the most effective in nucleating porosity. These include oxides of the parent metal, always abundant in liquid metal processing. A possible mechanism for pore formation in the presence of an inclusion was shown in Fig. 10.6. In addition, oxide films entrained in a melt from the surface by stirring, for example, may contain minute air bubbles trapped in their many cracks and crevices. These bubbles can easily serve as nucleants for further pore growth.

INCLUSION REMOVAL

The preceding discussion has highlighted the overall negative effects of inclusions on the structure and properties of cast metals. Without inclusions, cast metals would be stronger, more fatigue resistant, leaktight, more deformable and would possess better surface finishes.

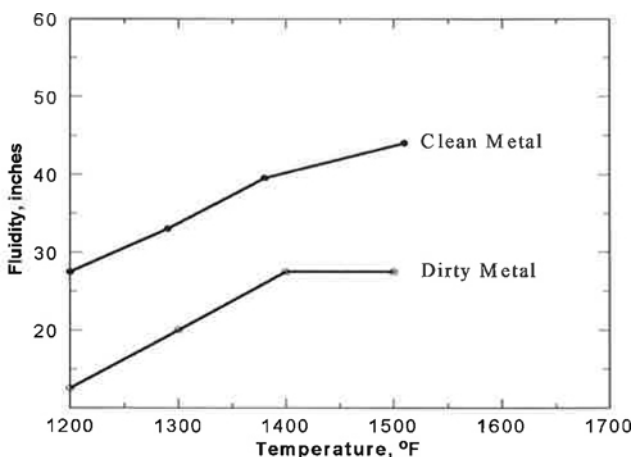


Fig. 11.8. The fluidity of a filtered (clean) and a nonfiltered (dirty) aluminum melt are compared.

It is no wonder, therefore, that so much effort has been expended in devising ways to remove inclusions from liquid metal. Discussion of some of these methods follows.

FILTRATION

Filtration remains the most successful way to remove inclusions from liquid metals. First developed for use with aluminum, filtration has been applied successfully to copper, magnesium, cast iron and steel, with some variations in filter type and material for each. The first filters used were simply screens made from woven fiberglass or stainless steel mesh. Such filters are inefficient and can remove only the largest inclusions. More sophisticated types are now used commonly.

Three basic filter configurations are used, mainly in the aluminum industry where filtration is the most highly developed. They are ceramic particulates, ceramic monoliths and ceramic foams. Alumina use is commonplace, but filters can be made from mullite or zirconia, depending on the application.

Ceramic particulate filters are formed from either ceramic balls or irregularly shaped ceramic particles, usually alumina, which are formed into thick beds. Liquid metal passing through these beds is filtered by one or more mechanisms described later. The ceramic particles are either packed together to form a packed bed filter, or they may be bonded together permanently by mixing the ceramic with a binder and firing at high temperature to sinter the mixture. In any case, this bed filtration is amenable only to large scale liquid metal processing operations and finds its main application in primary metal production.

For casting manufacture, a smaller disposable filter is necessary. These are placed in the gating system of the casting to filter the liquid as it flows into the mold cavity. Two varieties are found: ceramic monoliths and ceramic foams (Fig. 11.10). Ceramic monoliths are composed of parallel straight-through holes in a ceramic body while the foam filters consist of a series of tortuous paths through the filter. Monoliths are manufactured by extrusion, and subsequent firing, of a thick ceramic slurry through an appropriate die. Ceramic foam filters are formed by impregnation of a polymeric foam with the ceramic slurry. After drying, the polymer is burned out and the ceramic is fired to develop strength. The ceramic foam is, therefore, the negative imprint of the original polymeric foam. In all cases, different filter pore

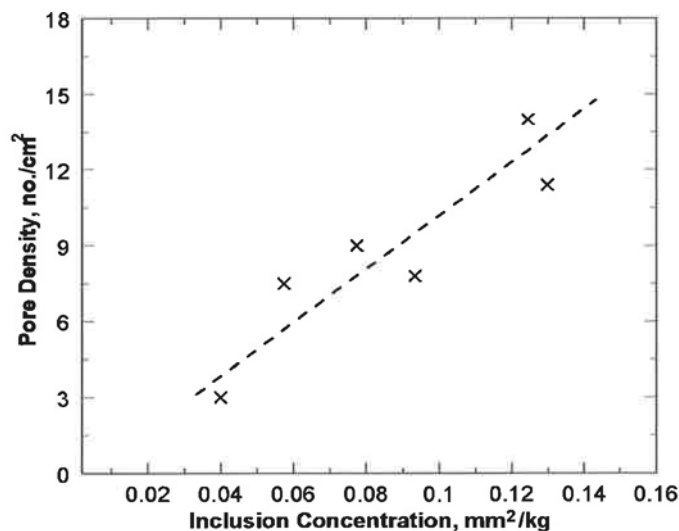


Fig. 11.9. Relationship between the amount of porosity in reduced pressure samples of an Al-7%Si alloy and the number of alumina inclusions present is shown. The dissolved hydrogen concentration is 0.22 ml/100g Al. [Data replotted from X.G. Chen and J.E. Gruzleski, *International Journal of Cast Metals Research*, vol 9, pp 17-26 (1996).]

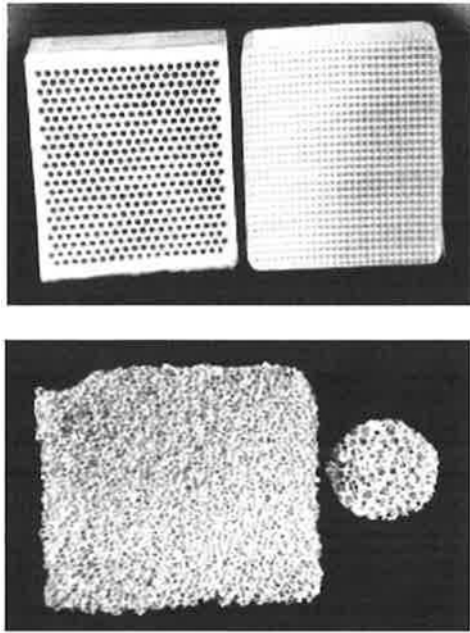


Fig. 11.10. Ceramic monolith filters (top) and ceramic foam filters (bottom) are pictured.

sizes are available. Typical ceramic foam filters are found in the 15-30 pores per inch (ppi) range.

A variation on the ceramic foam filter is the bonded particle filter manufactured by mixing ceramic particles, such as alumina or silicon carbide, with a binder and firing. Pore size variations are possible by changing the particle size distribution of the original refractory grains. These filters are more robust than the ceramic foam, and are often used in the dip-out wells of furnaces.

Placement of the filter in the casting system depends on the type of filter in use. The nature of bed filters dictates their use in primary production to filter the metal, usually just before it is ingot cast. The bed filter is found between the holding furnace and the casting machine.

In foundry operations, filtration is done in the furnace, the crucible or the mold itself, depending on

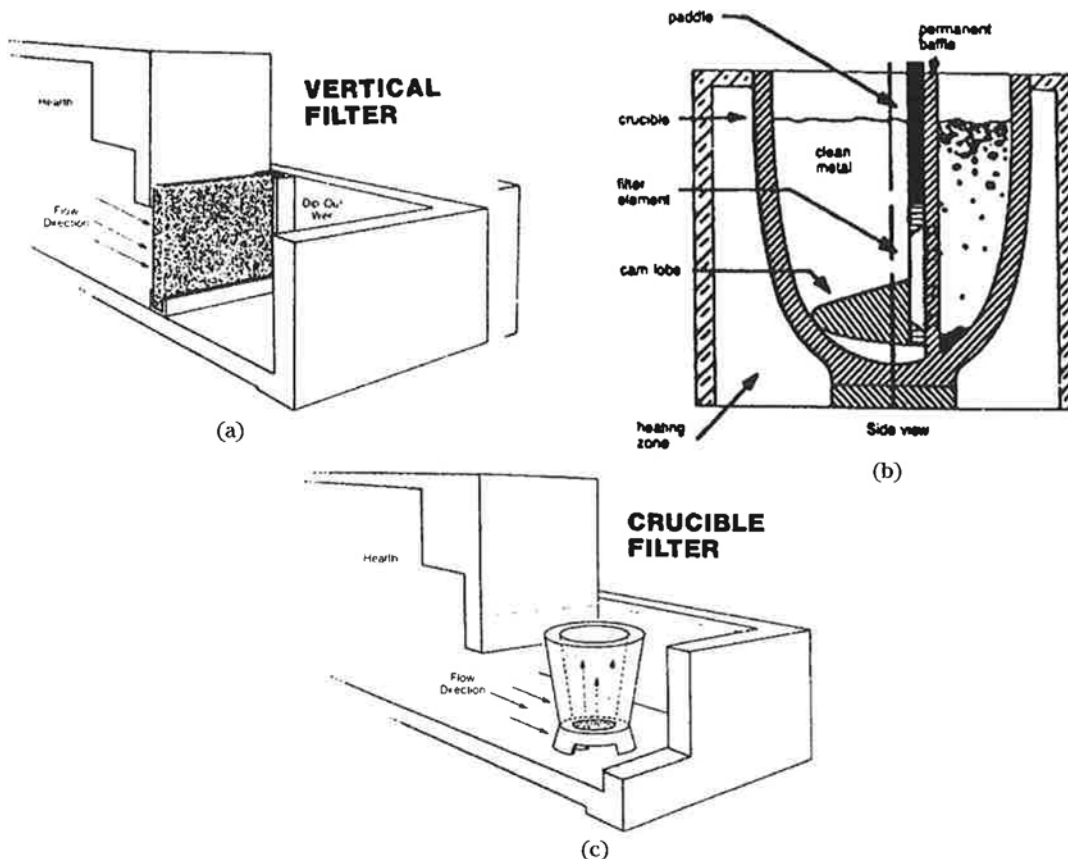


Fig. 11.11. Typical furnace and crucible filter configurations are shown.

the casting process. Some typical furnace and crucible filter configurations are shown in Fig. 11.11. These installations require a robust filter with an extended lifetime; bonded particle filters are the most suitable. The furnace filter (Fig. 11.11a) is an example of the type of filtration that might be used in a high pressure diecasting plant. The mechanics of high pressure diecasting preclude filter placement in the die itself, and so the metal, if it is to be filtered, usually is cleaned by a vertical gate filter placed in the dip-out well of the holding furnace.

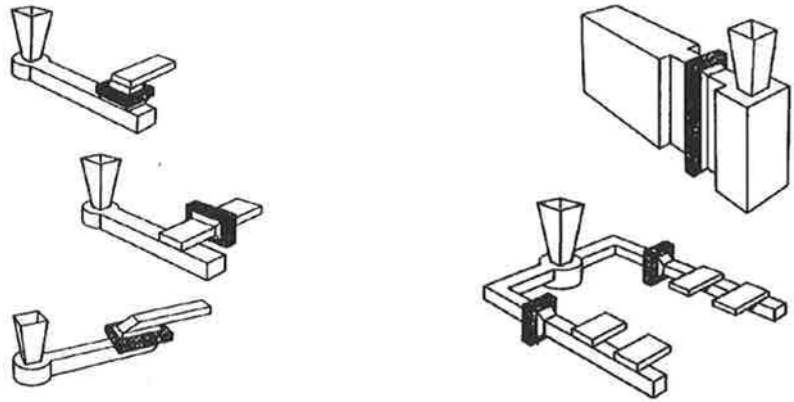


Fig. 11.12. Filters can be placed at different locations in the gating system of a casting.

Sandcasting and gravity or low pressure diecasting lend themselves to filter placement in the gating system itself, as seen in Fig. 11.12. Ceramic monoliths or foams are used. Since the filter is an added flow impediment, it usually is necessary to design the gating system to allow for an added metal head pressure to force the liquid through the filter. Priming of the filter also may be a problem because, in addition to friction effects, there is an initial capillary resistance to flow caused by surface energy effects. The liquid metal, which normally does not wet the filter material, resists flow through it, and extra pressure in the form of metal head is necessary.

FILTRATION MECHANISMS

Two mechanisms for inclusion removal operate depending on the size of inclusions and condition of the filter. Mechanical entrapment of large inclusions, such as oxide films or endogenous inclusions, occurs on the surface of the filter. These large inclusions simply are unable to pass through the spaces in the filter. As the layer of large inclusions builds on the filter surface, a cake is formed that in itself acts as a filter. This is known as cake filtration. The cake thickness eventually advances to a point where flow resistance is so great that the filter becomes blocked. Primitive filters, such as stainless steel screens, operate exclusively by cake filtration.

Inclusions that are much smaller than the

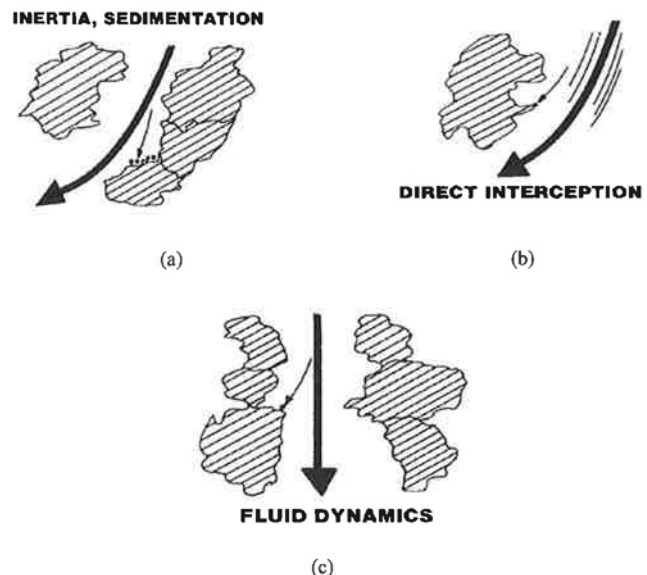


Fig. 11.13. Mechanisms whereby inclusions are trapped within the body of a filter are illustrated schematically.

openings in the filter are trapped within the body of the filter in what is known as deep bed filtration. Small inclusions contact the internal walls of the filter pores, and may then become weakly attached, or stabilized, on the walls.

Contact between small inclusions and the filter wall happens in three possible ways, illustrated schematically in Fig. 11.13. If the inclusion is much denser than the liquid, it may simply sink onto the filter wall surface (sedimentation). Direct interception occurs if the inclusion is carried by fluid flow so that it hits the wall surface directly. Contact by fluid dynamics depends on the fact that a gradient of flow velocity exists within the filter pore channel. Velocity is a maximum in the center of the channel and reduces to zero at the liquid-channel wall interface. An inclusion within the channel will be subjected to a force gradient across its diameter and, as a result, the inclusion will rotate. Rotation will be such that the inclusion tends to move toward the wall surface and eventually comes into contact with it. The larger the inclusion, the greater will be the rotation and the more readily the inclusion will become trapped.

Inclusions trapped internally within a filter are, at the best of times, only weakly bound there. Mechanical agitation of the filter can cause large numbers of inclusions to become detached and wash out in the liquid metal stream. There are, however, two effects that to some extent stabilize the inclusions within the filter body.

If the interfacial energy between the inclusion and the filter is less than that between the inclusion and the liquid metal, the inclusion will, for energetic reasons, be stabilized on the filter channel surface. Stabilization replaces a high energy interface with one of lower energy. We can conclude, therefore, that inclusions not wetted by the liquid are more easily removed than those that are. Oxides, for example, are filtered out with relative ease. Wettability depends strongly on melt chemistry and can be changed significantly by the addition of even minor quantities of some elements. Filtration effectiveness depends, therefore, on exact melt chemistry in addition to the nature of the inclusions.

Sintering between the inclusion and the filter material will also tend to bond inclusions to the filter. Mass transfer occurs between filter and inclusion by volume or surface diffusion to replace high energy interfaces with ones of lower energy. Asperities of small radius of curvature are the sites at which initial bonding takes place.

FLOTATION

Inclusions can be removed by contacting them with small gas bubbles in a process somewhat similar to mineral flotation. The method is particularly amenable to inclusion removal from nonferrous melts where gases are commonly used for degassing by a rotary impeller degasser. Degassing and melt cleaning are done simultaneously, using the same equipment in the same operation. A schematic interpretation of inclusion flotation is presented in Fig. 11.14.

Both inert and reactive gases can be used for inclusion flotation, but most evidence points to reactive gases as being more effective cleansing agents. In order to be removed

by flotation, the inclusion must contact the bubble and break through the bubble-liquid interface. Contact is assured by producing a dispersion of fine bubbles as with the standard rotary impeller degasser. The ability to actually adhere to the bubble surface depends, once again, on the wettability of the inclusion in the melt. Nonwetted inclusions, such as alumina in liquid aluminum, will experience a lowering of the interfacial energy if they become attached to

a bubble of AlCl_3 gas formed by reactive gas injection. The preferred location of the inclusion will then be in the gas bubble rather than in the liquid aluminum.

Halides and halide gases tend to cause wetting in nonferrous systems. It is probably for this reason that reactive gases are more effective flotation agents than are inert gases. Inclusions better wetted by the melt, e.g., TiB_2 , AlN and Al_4C_3 in molten aluminum, will be more difficult to remove by flotation. Inclusions so removed will be transported to the dross or oxide layer on the melt surface. They must remain trapped in this layer and not fall back into the bulk liquid if the flotation process is to be effective.

SEDIMENTATION

Inclusions will float or sink if their density is appreciably different from that of the melt. Some idea of the sedimentation velocity can be obtained by using Stokes' Law, which applies to spherical particles floating or sinking in a quiescent liquid. The terminal velocity, V_T , of such particles is given by:

$$V_T = 2R^2(\rho_l - \rho_i)g/9\eta$$

where

R is the particle (inclusion) radius;

ρ_l and ρ_i are the densities of the liquid and the inclusion, respectively;

g is the acceleration due to gravity; and

η is the viscosity of the liquid.

Stokes' Law predicts that sedimentation should be particularly effective for large inclusions since the terminal velocity varies as the square of the inclusion radius. For example, it is predicted that a $50\mu\text{m}$ alumina inclusion should have a terminal velocity of 0.17 cm/sec in

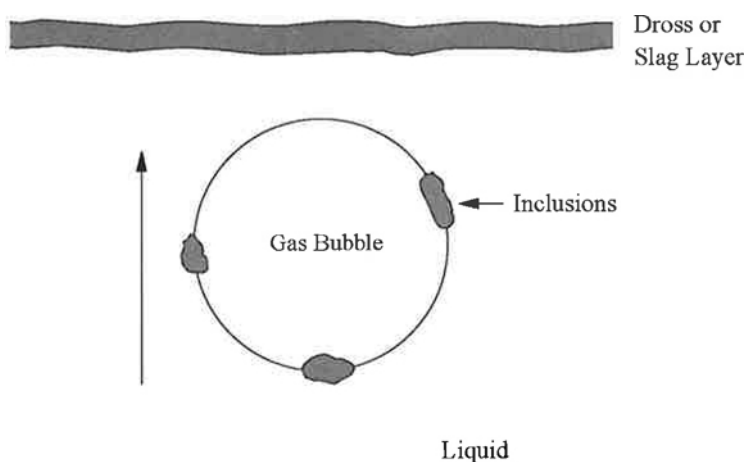


Fig. 11.14. A schematic interpretation of inclusion flotation is given.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

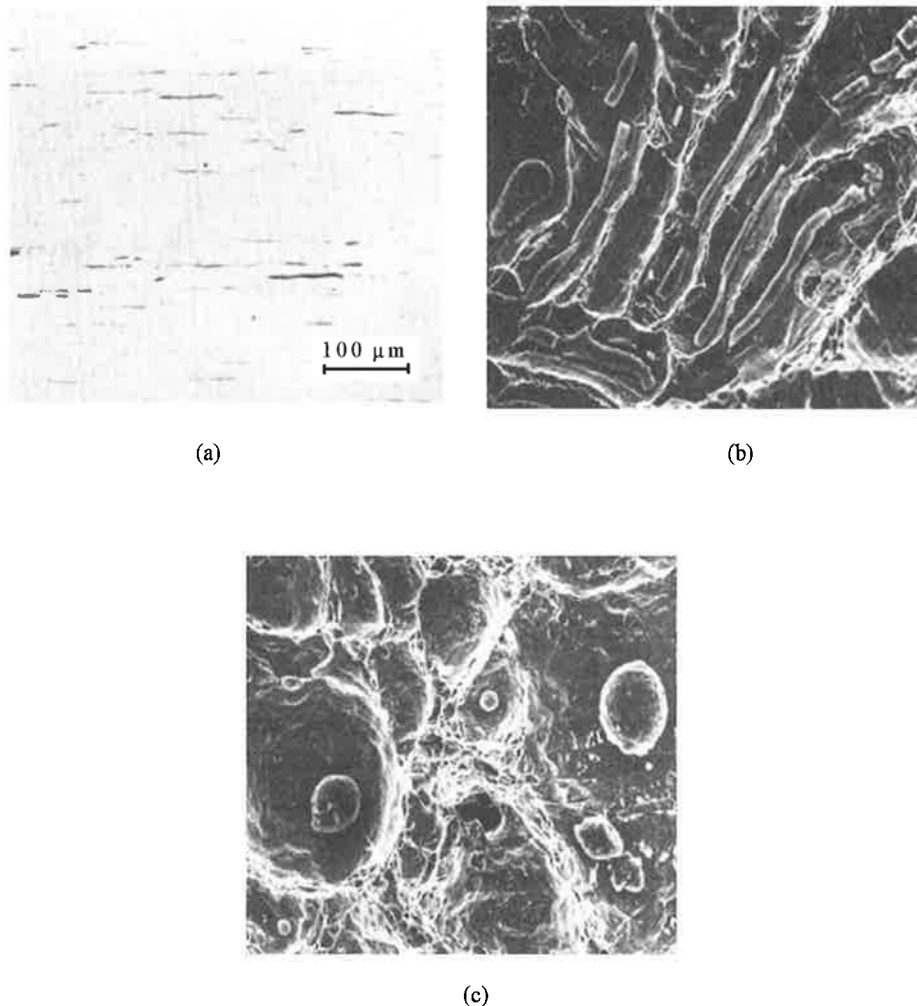


Fig. 11.15. (a) MnS inclusions form as stringers in hot rolled steel. [Photo reproduced from "Making Shaping and Treating of Steel," 9th Edition, by permission of the AISI Steel Foundation.] (b) A scanning electron micrograph of the fracture surface of a steel in which MnS stringers are found exhibits evidence of brittle fracture seen as cleavage between the stringers. (c) A scanning electron micrograph of the fracture surface of a calcium treated steel in which spherical inclusions occur reveals a ductile fracture. [(b) and (c) reproduced from ASM Handbook, vol 15, Casting, p 92, Figs. 7a and 7b, ASM International, Materials Park, OH 44073-0002 (1988).]

liquid aluminum. It should rise at a rate of 10.2 cm/min. While this appears to be a significant rate, which should allow clean aluminum melts to form in only a few minutes, sedimentation is not nearly as effective a mechanism as it first appears.

Two factors contribute to its relative ineffectiveness. Many inclusions are not spherical; for example, the alumina referred to here is most likely present as an extended film. These shapes experience greater flow resistance and will not rise or sink at rates near those predicted by Stokes' Law. A second important consideration is the ever-present liquid convection, which stirs the melt and prevents the ideal terminal velocity from ever being reached. Nevertheless, some sedimentation will take place in any melt, and large baths of liquid metal that are relatively quiescent will have higher inclusion concentrations at the top and bottom as lighter inclusions float and heavier ones sink. This type of inclusion distribution is common in large holding furnaces and ladles.

STIRRING

Inclusions brought into contact with dross, slag or a crucible wall will often stick there. Stirring of a melt can cause some cleansing to occur by forcing inclusions to these locations. Stirring by bottom porous plug gas injection into ladles has found some application in ferrous metallurgy, but has not been applied to nonferrous liquid processing where more and easier methods of melt cleaning are available.

SHAPE MODIFICATIONS OF INCLUSIONS

Removal of all inclusions from liquid metal by the methods just described is a virtual impossibility, but modifying the shape the inclusion assumes after hot working can eliminate some of the negative effects of certain inclusion types. Shape modification of inclusions is done in steel processing by adding calcium or rare earth elements. The exact amounts added depend strongly on the steel chemistry, particularly the Al, O and S contents.

MnS inclusions formed as the result of desulfurization are deformed during working so that they normally exist in the form of thin platelets, which act as internal stress raisers in the structure, and may contribute to a more brittle failure mechanism. Calcium additions change these inclusions to a spherical calcium oxysulfide that does not deform into stringers but, rather, remains more or less spherical after deformation, yielding a material with improved ductility and toughness. Figure 11.15a illustrates MnS stringers formed in hot rolled steel bars. The effect of calcium treatment is seen in (b), which illustrates the fracture surface of steel in which stringers are found, and in (c) where treatment has resulted in spherical inclusions. Evidence of brittle fracture is seen in the first instance, while ductile fracture occurs in the second.

Alumina usually forms as clusters of fine particles in liquid steel. These clusters are particularly troublesome in continuous casting as they clog nozzles during the process. Calcium additions cause liquid calcium aluminates to form instead, which separate more easily from the melt and do not lead to nozzle clogging.

MEASUREMENT OF MELT CLEANLINESS

The importance of inclusions to cast metal quality and processing, as well as the immense variety of possible inclusion types, has been pointed out. If inclusions are to be controlled, their numbers and size distributions must be measured in some way to assure that proper melt processing techniques can be applied. Several methods of quantification have been developed, some simple and some very sophisticated. In general, inclusion quantification in cast aluminum and its alloys is the most advanced because of widespread use of rolled aluminum in thin walled beverage cans and cast aluminum in aerospace castings. The relatively low melting point of aluminum makes instrumentation easier than for ferrous alloys.

CHEMICAL METHODS

Chemical methods involve analysis for elements chemically present in the inclusions. For example, oxygen analysis in steel or aluminum may be done with a view toward learning

something about the oxide contents of the cast product. In fact, such methods yield little useful information about inclusions because it is not possible to know their number or size from a simple chemical analysis. It is precisely these parameters that determine the ultimate effect of the inclusions on the cast solid.

DIRECT METALLOGRAPHIC OBSERVATION

One of the most obvious ways to assess melt cleanliness is to study a metallographic sample taken from the melt. While simple in concept, the approach does pose several difficulties. It is, first of all, an “after the fact” technique. Metallographic preparation requires time, and melt cleanliness can only be assessed after the melt has been cast. Metallographic methods are not on-line methods.

Other difficulties are centered on the number of inclusions visible per field examined and the difficulty of distinguishing these inclusions from phases normally present in the microstructure. The number of inclusions intersected by a random plane cut through the sample normally will be quite small, perhaps only one or two per field in a very clean melt. The exact number seen depends on the inclusion size and the magnification at which it is necessary to view the sample. Observation of a very large number of fields may be necessary in order to obtain statistically significant results. While modern automated image analysis equipment has minimized this problem to some extent, direct metallographic observation can still be very time consuming and expensive.

In alloys containing significant amounts of intermetallic phases, it may prove difficult to distinguish these phases from the inclusions. Aluminum-silicon casting alloys are a good example. They contain large quantities of eutectic silicon in their normal cast microstructure as well as other magnesium and copper bearing phases. Unless the dirt particles are very large, e.g., oxide films, it may be impossible to distinguish them, and color differences may be insufficient to allow identification of the inclusions alone by image analysis equipment.

Metallographic determination of inclusion levels is most successful in steel where inclusions can be seen easily on unetched polished surfaces. Counting is facilitated by the availability of several charts of representative microstructures, and exact

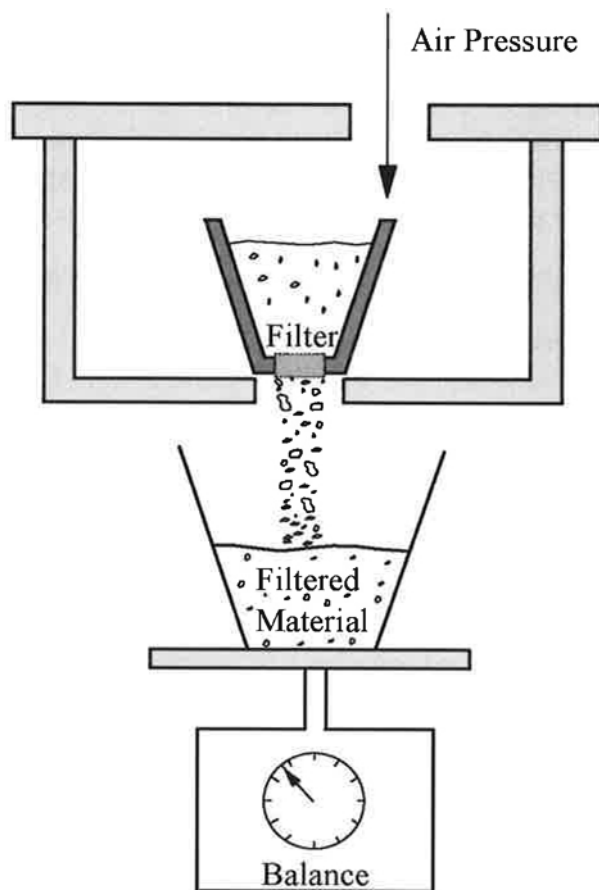


Fig. 11.16. Illustration shows a PODFA apparatus.

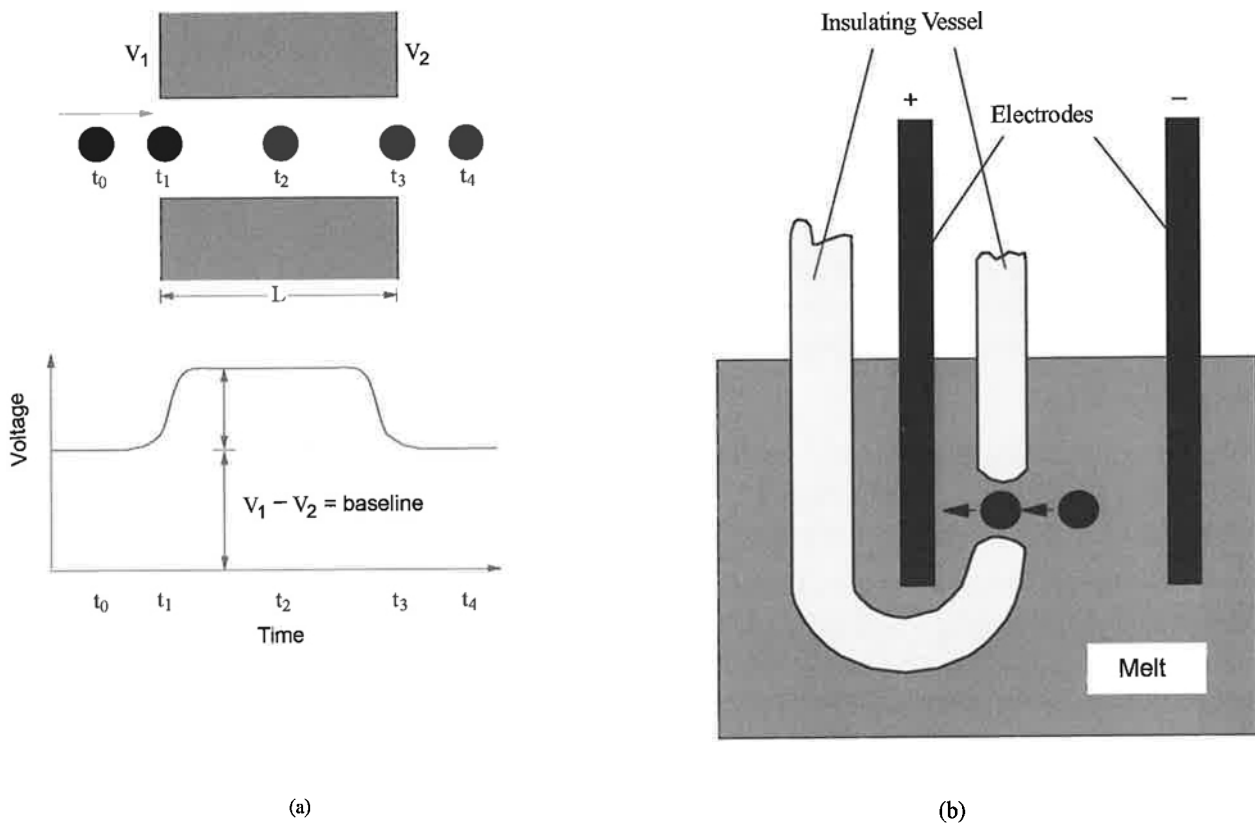


Fig. 11.17. The principle behind operation of the LIMCA apparatus for measuring the cleanliness of liquid metals is shown. In (a), the voltage change across the sensor orifice is shown as an inclusion passes through the orifice of length, L . The sensor itself is shown in (b), as is the position of the electrodes across which the potential difference is measured.

metallographic procedures have been set down, as described in ASTM standard E45.

PRECONCENTRATION METHODS

Some of the difficulties associated with simple metallographic techniques are overcome by concentrating the inclusions on a very fine filter. The most common of these preconcentration methods is the PODFA (porous disk filtration analysis), widely used in the aluminum industry (see Fig. 11.16). A known mass of liquid metal is forced through a fine bonded particle filter by air pressure applied to the melt surface. The filter cake is then examined metallographically, and the inclusions are counted, either manually or by an image analyzer. Inclusion densities are expressed as mm^2/kg of metal passed through the filter.

This unit derives from the fact that it is easiest to measure the total area occupied by the inclusions on the sample surface. It is a time consuming technique with results known only well after the melt has been cast. One of its main advantages, however, is that exact inclusion types and shapes can be determined by direct observation.

FLOW INTERRUPTION METHODS

Several on-line methods for characterizing melt cleanliness of aluminum alloys have recently appeared. They often are based on the mass of metal that can pass through a

standard filter before the filter becomes blocked. Blockage with dirty melts will occur sooner than with clean melts, and more liquid will pass through the filter in the latter case. Quantification of melt cleanliness can be done by weighing the mass of metal passed, or in terms of the fraction of some standard mold filled before flow stops.

Filter blockage takes place by the accumulation of large oxide films on the filter surface, i.e., cake formation. These techniques, therefore, provide only a rough comparative measure of the number of these large films existing in the melt. This knowledge is important, as it is large inclusions that are most deleterious in castings. Small inclusions are also of significance but these rapid on-line methods provide no information about them.

PHYSICAL METHODS

The primary aluminum industry has been instrumental in the development of two means of quantifying melt cleanliness in liquid aluminum. One is based on ultrasonics and the other on the electrical resistance of inclusion-containing liquid aluminum.

The ultrasonic technique uses a titanium probe to measure the attenuation and the discontinuity of an ultrasonic signal introduced into the liquid. Decreases in melt quality result in increases in each of these parameters. Ultrasonic methods can be used on-line. They are particularly effective for large inclusions, but are limited in their ability to detect inclusions in the 50 μm range or smaller.

Electrical resistance is the basis of the LIMCA (liquid metal cleanliness analyzer) method, the principle of which is illustrated in Fig. 11.17. The LIMCA is a high temperature adaptation of the Coulter counter used to measure fat particles in blood. Liquid aluminum is pumped through a small orifice across which there is a potential difference. When an inclusion passes through the orifice, the potential drop will change because of the change in electrical resistance introduced by the inclusion. If the inclusion is a poor conductor (this is the usual case since most inclusions are ceramics), the potential drop will increase; if the inclusion is a better conductor than liquid aluminum, the reverse will be true. Signal analysis of the potential changes across the orifice provides information on the number and size of inclusions. As with the ultrasonic method, there is a detection limit in the neighborhood of 20 μm .

LIMCA is currently used in many aluminum smelters around the world. At present, it is not used for foundry alloys, which are chemically more complex than most wrought alloys and, as a rule, much dirtier. The principle of the LIMCA can be applied to inclusion measurement in any electrical conducting liquid, and it has been used successfully in many of the lower melting point metals. At high temperatures, such as those met in steel casting, the practical limitation lies in the resistance of the probe material itself to attack from the liquid.

FURTHER READING

Engh, T. Abel, *Principles of Metal Refining*, chap 5, Oxford University Press (1992).

Gruzleski, John E. and Closset, Bernard M., *The Treatment of Liquid Aluminum-Silicon Alloys*, chap 11, American Foundrymen's Society, Inc., Des Plaines, IL (1990).

chapter 12

POLYPHASE SOLIDIFICATION

The early chapters of this book deal mainly with the solidification of a single solid phase from its liquid, either a pure material or a solid solution. A majority of the commercial materials freeze as polyphase structures from the liquid. The most important of these are alloys that undergo a eutectic or a peritectic reaction.

Of these reactions, eutectic solidification is, by far, the most significant, forming the basis for such widely used materials as the cast irons, aluminum-silicon foundry alloys and many cast magnesium- and zinc-based alloys. Eutectic reactions are characteristic in foundry alloys because eutectic compositions are associated with high liquid fluidity, facilitating the manufacture of intricate and thin walled castings. Eutectic compositions also have the lowest melting point compositions found in an alloy system.

Eutectic, or near eutectic, alloys are, therefore, relatively easy to melt and melt treatment processes, such as degassing or chemical modification, are made easier by the lower liquid processing temperatures. In addition, the polyphase eutectic mixture is often stronger than a single phase structure because of the contribution of interphase boundaries to overall alloy strength.

As with all cast materials, the solidified microstructure of the eutectic alloy is a prime factor in determining the properties of a casting containing significant proportions of eutectic phases. In this chapter, some of the basics of eutectic solidification are examined, primarily from a microstructural point of view. For simplicity, the discussion is limited to binary eutectics. These are the most commonly encountered, as well as the most studied and best understood. Peritectic solidification is of lesser importance in metalcasting, and will be dealt with briefly at the end of the chapter.

EUTECTIC SOLIDIFICATION STRUCTURES

Eutectic alloys form a variety of different microstructures, many of which can be varied significantly by changes in the solidification conditions. Some of these microstructures are extremely regular in appearance, forming beautiful and intriguing geometric patterns, while others are completely irregular and consist of nothing more than a random mix of the two eutectic phases. Typical eutectic microstructures are shown in Fig. 12.1a-e.

Virtually all eutectic solidification structures fall into one of the three following categories.

- Regular eutectics form a lamellar or plate-like structure, or freeze as rods or fibers of one phase embedded in a matrix of the other. The most regular structures are produced by controlled directional freezing, but regular lamellar or fibrous microstructures will also result when the alloy is cast into a mold in which freezing is multidirectional.
- Semi-regular microstructures contain certain areas in which regular geometric patterns form and other areas in which the eutectic phases appear completely disorganized. Eutectic alloys in which semi-regular microstructures form are those in which changes in the solidification conditions can have the greatest influence on microstructure. Structures are usually made more regular by directional freezing, and tend

to be more irregular if the alloy is just cast into a mold.

- Irregular eutectic microstructures occur when both phases of the eutectic are arranged in a completely disorganized way with respect to each other. Controlling the solidification by directional heat flow has little effect on ordering the microstructure of an irregular eutectic.

Growth of these different eutectic types from the liquid will be discussed in the following sections of this chapter, but first, important differences between single phase and two phase solidification will be considered.

COMPARISON OF SINGLE AND TWO PHASE SOLIDIFICATION

Several important differences are found between the freezing of a single phase solid solution and a two phase alloy, such as a eutectic, and it is important to note these differences before eutectic solidification is examined in greater detail.

NUCLEATION

Nucleation in the single phase case requires formation of only one type of nucleus whereas binary eutectic solidification requires that each solid phase nucleate before growth can commence. Nucleation of one of the solid phases may be completely independent of the other. One may nucleate at small undercoolings, and the other at very high undercoolings. On the other hand, one phase may act as a substrate for the other, thus facilitating the entire nucleation process. Nucleation effects are particularly important in understanding cast eutectic structures (as compared to directionally frozen). In some cases, e.g., cast irons, special inoculants are used to aid in the simultaneous nucleation of each eutectic phase.

DIFFUSION DURING GROWTH

While solidification of a single phase solid solution requires only the diffusion of rejected atomic species ahead of, or parallel to, the solid-liquid interface, eutectic freezing involves a more complicated two-way diffusion between solid phases. Consider the hypothetical simple eutectic phase diagram shown in Fig. 12.2. During eutectic solidification, both the A-rich α

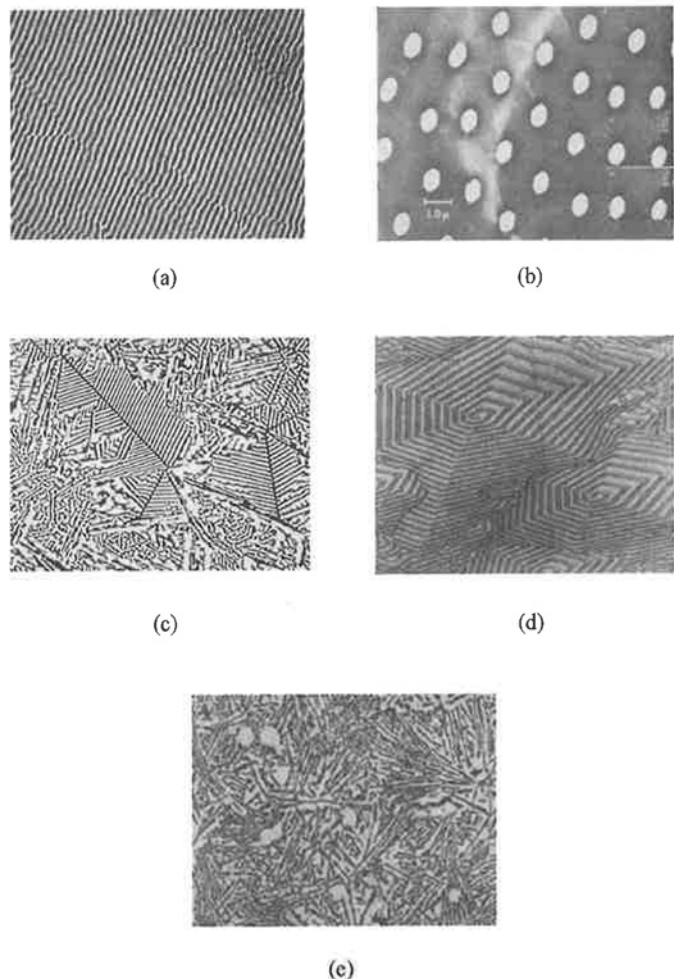


Fig. 12.1. Several typical eutectic microstructures are shown: (a) lamellar (Al-CuAl₂) 300X; (b) fibrous (Al-Al₃Ni) 5000X; (c) semi-regular (Al-Ge) 250X; (d) spiral (Zn-Mg-Zn) 350X; and (e) irregular (Al-Si) 200X.

phase and the B-rich β phase freeze simultaneously. Element B is a solute in the α phase and will be rejected by it, resulting in B-enriched liquid ahead of the α phase.

Similarly, liquid ahead of the growing β phase becomes enriched in the A component. Growth of α requires that it have access to atoms of A, the source of which is the A-rich liquid accumulated ahead of the β phase. Thus, A-rich liquid must diffuse from the vicinity of the β phase to the growing α phase while, at the same time, B-rich liquid diffuses from the neighborhood of the α phase to the growing β phase. This two-way coupled diffusion process in the liquid characterizes eutectic growth. If the process is disrupted in any way, growth of at least one of the phases will cease and the microstructure will be altered.

Diffusion during peritectic solidification can be even more complex and, as will be shown later, can involve not only liquid diffusion, but also a component of solid state diffusion limiting the extent to which the peritectic transformation can proceed.

CONCEPT OF A GRAIN

The definition of a grain in a single phase material is quite straightforward—it is a volume of material in which the unit cells of the crystal structure all have the same orientation. In eutectic alloys, however, this concept becomes blurred, because the structure consists of two phases with different crystal structures, orientations and compositions. Furthermore, the orientation of one of the phases may change during freezing while that of the other remains constant.

The question of how, exactly, to define a grain in a eutectic structure has never been satisfactorily resolved. The best way to regard a eutectic is as a structure consisting of two interpenetrating single crystals, or alternatively, as a structure made up of grains of one phase intermixed with grains of the other phase.

WHAT DETERMINES THE EUTECTIC MICROSTRUCTURE?

This question has intrigued and puzzled investigators since the beginning of metallographic science when it became known that eutectic alloys could solidify with such a variety of microstructures. The quick answer is that the structure is determined mainly by the growth kinetics of each of the solid phases. It was explained in Chapter 5 that the α -factor represents an easy way to determine the general solidification kinetics of a material, and that materials in which $\alpha < 2$ behave quite differently from those in which $\alpha > 2$. Now, in a binary eutectic, there are three possible combinations of the α factor:

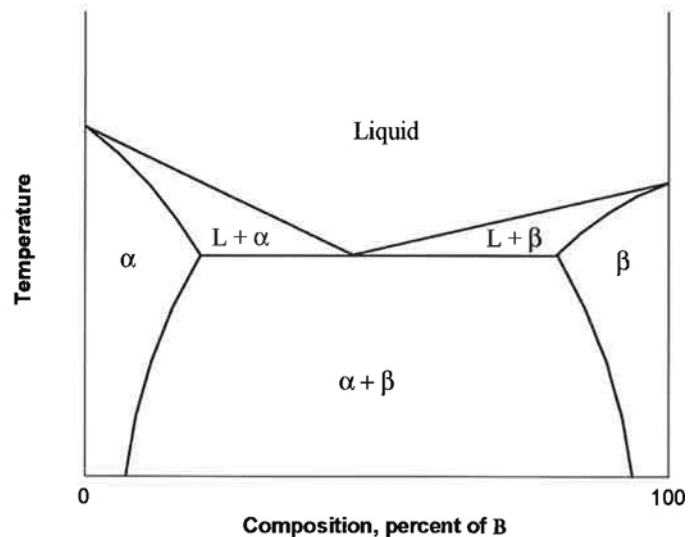


Fig. 12.2. A simple eutectic phase diagram for the hypothetical system A-B is illustrated.

- both phases possess $\alpha < 2$;
- both phases possess $\alpha > 2$; and
- one phase has $\alpha < 2$ while the other has $\alpha > 2$.

Let us examine the likely solidification pattern of a binary eutectic in each of these three circumstances.

BOTH PHASES $\alpha < 2$

If both phases have $\alpha < 2$, each is nonfaceted and is likely to be a simple metal phase, the solidification of which is controlled more by heat flow and diffusion considerations than by crystallography. The kinetic undercooling required for growth of each phase will be small, and each will solidify at a temperature that is virtually indistinguishable from the equilibrium eutectic temperature. An isothermal solid-liquid interface will result, much like that shown schematically in Fig. 12.3.

A consequence of this interface shape is that each phase grows in close and regular proximity to the other. The coupled two-way diffusion necessary to sustain growth is facilitated by the interface geometry. Eutectic growth, under these conditions, results in a highly regular and organized growth morphology of the lamellar or fibrous type.

BOTH PHASES $\alpha > 2$

When the α factor of each phase is greater than two, each phase is faceted and will be a nonmetal or, perhaps, a semi-metal. Growth of each phase is dominated by its own crystal structure rather than local heat flow or solute diffusion. These high α factor materials generally require a large kinetic undercooling to drive the atomic attachment to their complex crystal structures. Solidification of each phase will take place at a temperature far from equilibrium, and the dominant effect of crystallography leads to little, if any, cooperative growth. In effect, each phase of the eutectic grows as a separate entity, paying little attention to the other.

Some two-way diffusion is necessary to sustain growth, and each phase will reject atoms of the other at the interface. But the diffusion is uncoupled so continuous growth of each phase does not necessarily happen. If a particular phase particle is not able to receive solute from the other phase, it will cease growing, and a new particle may be nucleated elsewhere in a location more favorable for receiving the required atomic species.

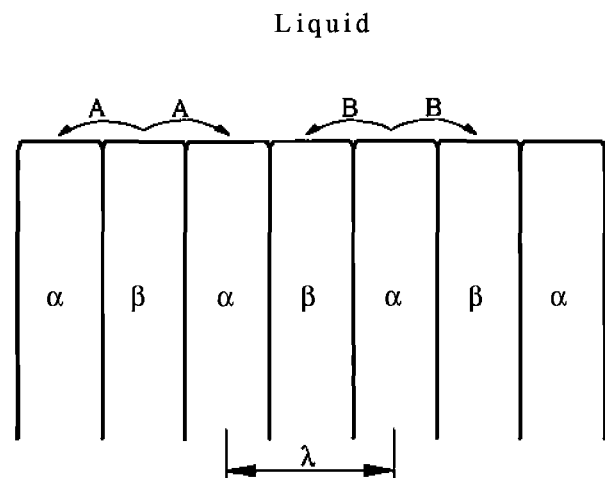


Fig. 12.3. A schematic representation of the solid-liquid interface of a growing lamellar eutectic structure is shown. Coupled diffusion of the A and B species occurs in front of the interface.

All of these considerations conspire to make eutectic freezing of two $\alpha > 2$ materials completely irregular and, generally, the greater the deviations of the α factors from two, the more irregular the structure.

ONE PHASE $\alpha < 2$, THE OTHER $\alpha > 2$

This combination of α factors is intermediate between the previous ones and, as might be expected, leads to intermediate type microstructures. Different considerations govern the freezing of each phase; heat flow and solute diffusion control the $\alpha < 2$ phase, while crystallography determines the behavior of the $\alpha > 2$ phase. Usually, the faceted phase grows ahead of the nonfaceted (Fig. 12.4a), and if the temperature gradient in the vicinity of the interface is very low, the lead of the faceted phase may be so great that any highly coupled diffusion is impossible. The faceted phase may even branch in the liquid ahead of the nonfaceted. Irregular microstructures develop, as the two phases solidify with little regard for each other.

If, however, the temperature gradient is high, the lead distance will be reduced and the two phases are forced to grow in close proximity at an almost isothermal interface (Fig. 12.4b). Coupled diffusion results and a regular microstructure may be formed. Eutectics falling into this category are those in which the structure can be altered significantly by changes in the solidification conditions, principally the temperature gradient in the liquid at the solid-liquid interface. Metal-nonmetal eutectics are of this type with the two best commercial examples being the iron-graphite and the aluminum-silicon systems, both of which will be discussed in greater detail in Chapter 13.

Some exceptions to the above classification system can be found, mainly when the α factors of one or both of the phases are in the vicinity of 2.0, but this simple approach to understanding eutectics, first addressed by J.D. Hunt and K.A. Jackson,¹ has proven exceptionally useful. The α -factors normally used are those of the pure materials calculated at their melting points. Refinements to the approach, in which the α factors are calculated for the eutectic solid solutions at

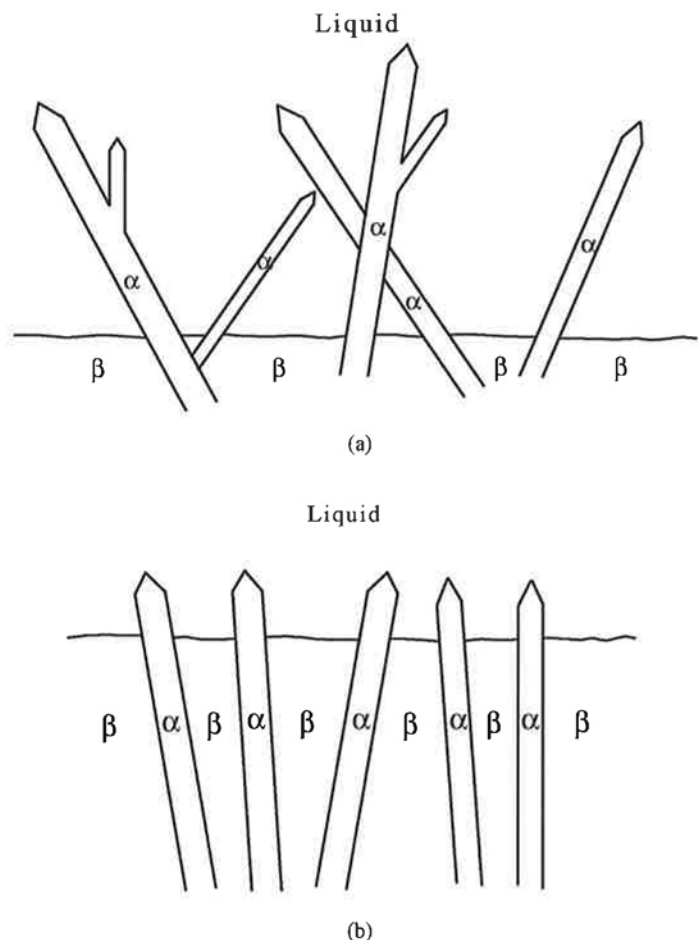


Fig. 12.4. If the α factor of one eutectic phase is greater than 2 while the other is less than 2, the faceted phase may grow ahead of the nonfaceted and may even branch if the temperature gradient is low (a). At high temperature gradients, the phases grow more cooperatively (b).

the eutectic temperature, eliminate many of the discrepancies arising from use of the α factors of pure materials.

LAMELLAR EUTECTIC GROWTH

Eutectic solidification is amenable to a detailed quantitative analysis only if a very regular microstructure forms. This is possible in the case of lamellar and fibrous eutectics, and is useful in providing insight into the complexities of polyphase solidification. Consider the freezing of the α - β eutectic in the system A-B (Fig. 12.2). The solid-liquid interface has the shape shown in Fig. 12.3 in which alternate lamellae of the α and β phases form from the liquid. Coupled diffusion of the two chemical species, A and B, occurs, as illustrated, parallel to the interface with atoms of A diffusing from β to α and vice versa.

The driving force for coupled diffusion is the presence of concentration gradients parallel to the solid-liquid interface—the liquid ahead of an α lamella is enriched in the B component while that ahead of its neighboring β lamella is depleted in B, as illustrated in Fig. 12.5. There are two consequences of this: one, the coupled diffusion pattern; and two, an undercooling ahead of each lamella. The magnitude of this undercooling, ΔT_s , due to solute accumulation is:

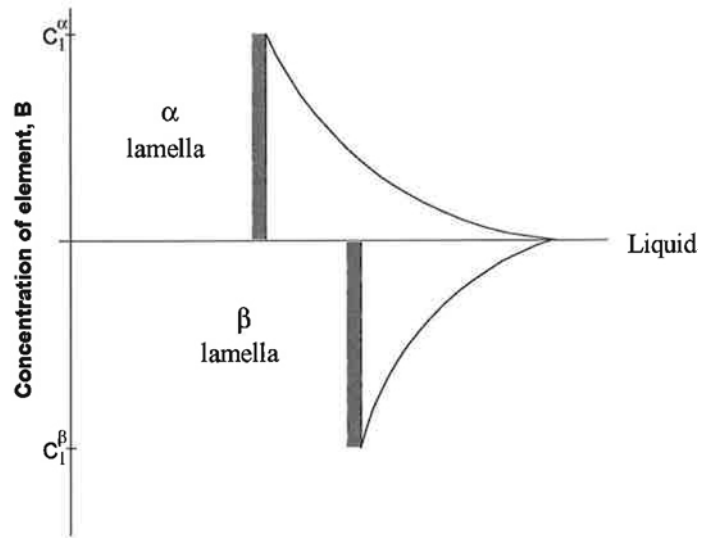


Fig. 12.5. The concentration distribution of element B in the liquid, ahead of the growing α and β lamellae, is shown.

$$\Delta T_s = \Delta C_{\alpha\beta} / m_\beta^{-1} - m_\alpha^{-1} \quad (12.1)$$

where

$\Delta C_{\alpha\beta}$ is the concentration difference between the center of an α lamella and the center of its neighboring β lamella, i.e., $(C_1^\alpha - C_1^\beta)$ in Fig. 12.5; and

m_β and m_α are the slopes of the β and α phase liquidus lines on the phase diagram.

In addition to this solute related undercooling, two other departures from equilibrium are required for lamellar growth: they are kinetic undercooling, ΔT_k , the exact form and magnitude dependent on the solidification growth kinetics. Each phase of the eutectic will have its own growth rate/undercooling relationship according to its own growth characteristics, as described in Chapter 5.

The other undercooling needed for lamellar solidification is required to form the large

number of interphase boundaries between the lamellae. Phase boundaries are higher energy regions of a microstructure, and departures from equilibrium (undercoolings) are always necessary to provide the energy investment in them. A lamellar eutectic possesses an immense number of interphase boundaries because of the fineness of the structure. For example, one cubic centimeter of eutectic having an interlamellar spacing of $10\mu\text{m}$ will contain a total interphase boundary area of 2000 cm^2 . The interlamellar spacing referred to here is the distance from the center of one lamella to the center of the next lamella of the same type. This value is indicated as λ in Fig. 12.3.

The energy, or undercooling, ΔT_B , necessary to form these boundaries is determined by:

$$\Delta T_B = 2\gamma_{\alpha\beta} T_E / \lambda L \quad (12.2)$$

where

- $\gamma_{\alpha\beta}$ is the interphase boundary energy;
- T_E is the equilibrium eutectic temperature;
- λ is the interlamellar spacing; and
- L is the latent heat of fusion of the eutectic.

Eutectic solidification will take place at an undercooling equal to the sum of that due to solute accumulation, growth kinetics and interphase boundary energy. Thus,

$$\Delta T_{\text{TOTAL}} = \Delta T_S + \Delta T_K + \Delta T_B \quad (12.3)$$

and the growth temperature, $T_G = T_E - \Delta T_{\text{TOTAL}}$.

Figure 12.6 shows the relationship between all of these temperature and undercooling values. Note that once the solute and interphase boundary undercoolings have been provided for, the lamellar eutectic structure can be thought of as formed but, in order to get it to grow into the liquid, it is necessary to provide for the kinetic undercooling.

Literature on the theory of eutectic growth is abundant, and much of it attempts to arrive at a relationship between the freezing rate of the lamellar eutectic and the interlamellar spacing λ . The interlamellar spacing is an important basic microstructural parameter describing the overall fineness of the structure, while the freezing rate is the one solidification variable most amenable to control.

When appropriate values for the various parameters are placed in equation 12.3, a relationship between ΔT_{TOTAL} and λ of the form shown in Fig. 12.7 is obtained. A minimum total undercooling is found at one unique value of interlamellar spacing. Solidification at lamellar spacings greater than this value results in an increase in the total undercooling required for growth because solute must now diffuse farther from one lamella to the next. Solute diffusion is more difficult, and ΔT_S increases. At lamellar spacings less than that

corresponding to the minimum in total undercooling, there is again an increase in the undercooling resulting from the creation of more interphase boundaries since the spacing decreases and the necessity to invest more energy in them increases. In terms of equation 12.3, the value of ΔT_B increases.

Good thermodynamic arguments can be advanced to show that solidification should occur with a minimum total undercooling, which is equivalent to saying that eutectic growth should occur as close to equilibrium as possible. When equation 12.3 is minimized with respect to the interlamellar spacing, the following relation is obtained:

$$\lambda = AR^n$$

where

- λ is the interlamellar spacing;
- A is a complex constant containing many of the physical parameters of the alloy system;
- R is the freezing rate; and
- n is a constant for a particular alloy system and lies in the range of 0.3 to 0.5.

Log-log plots of λ vs. R yield straight lines with slopes of 0.3 to 0.5 depending on the eutectic system (Fig. 12.8). Values of $n = 0.5$ are obtained if the kinetic term ΔT_K in equation 12.3 is ignored. We can presume that alloy systems in which $n = 0.5$ is obtained experimentally are ones for which the growth kinetics of each phase are so simple that they pose no particular barrier to freezing, e.g., normal growth kinetics. Many simple metal systems fall into this category, including the eutectics in Cd-Zn, Pb-Sn and Pb-Cd alloys. Experimentally determined values of the exponent n , which are less than 0.5, lead to the suspicion that the growth kinetics of one or both eutectic phases are complex enough to influence the solidification process. Such systems often contain an intermetallic compound as one of the eutectic phases, e.g., Fe-Fe₃C or Mg-Al.

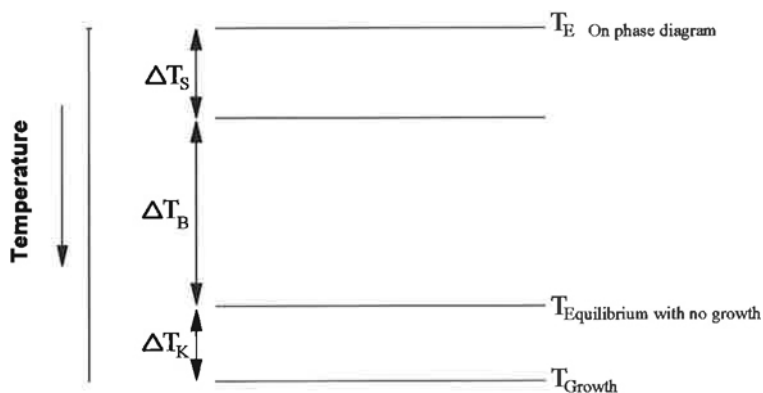


Fig. 12.6. The total undercooling for lamellar eutectic growth is the sum of the individual undercoolings. ΔT_S is the undercooling to drive the diffusion process, ΔT_B provides the energy in the interphase boundaries and ΔT_K is the kinetic undercooling.

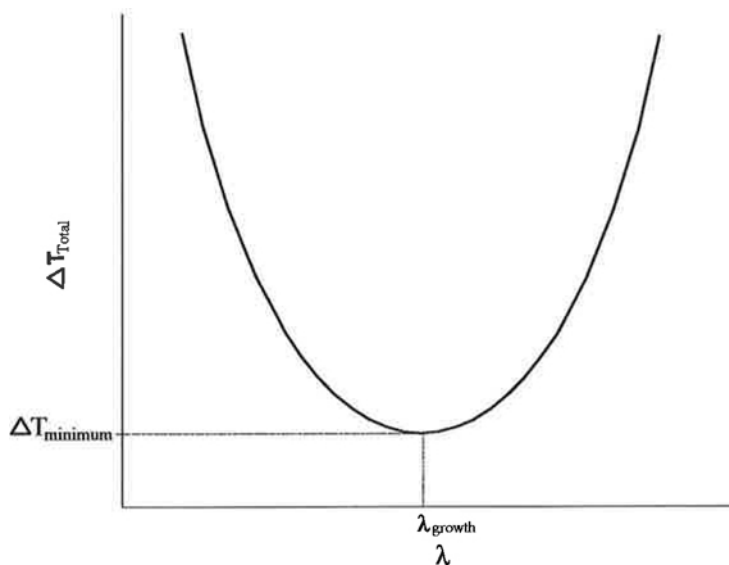


Fig. 12.7. The total undercooling for lamellar growth is shown as a function of the interlamellar spacing, λ .

LAMELLAR MICROSTRUCTURE

At first glance, the microstructure of a lamellar eutectic appears to be inherently unstable because, simply, it contains too much interphase boundary area per unit volume of eutectic. Normally, plate-like structures tend to spheroidize in order to reduce the total interphase boundary area. Yet, lamellar eutectic structures are remarkably stable even at elevated temperatures where spheroidization would be expected to proceed rapidly. This stability originates from interphase boundaries of low energy.

Detailed crystallographic studies have established that preferred crystallographic relationships exist between the eutectic phases across the interphase boundary, creating boundaries having energies similar to coherent twin boundaries with only 10-20% of the energy of high angle grain boundaries. The ability to form such stable low energy boundaries comes directly from the crystal structures of the two solid eutectic phases. Close atomic matching across the interphase interface results in an epitaxial relationship without which it is doubtful that a lamellar structure could form.

Many cast eutectics develop the radiating structure illustrated in Fig. 12.9a. These are cellular structures formed because of impurity elements that are rejected by the growing eutectic and cause general constitutional undercooling ahead of the interface. A nonplanar cellular interface results (Fig. 12.9b) which is similar to the cellular structure formed in single phase materials containing impurities.

Note that the lamellae always grow normal to the local solid-liquid interface and are forced to bend at the cell edges. Bending out of the preferred interfacial plane destroys the low energy epitaxial relationship between the two phases. Lamellae then become unstable as a result of their large ratio of surface area to volume, and they transform into the rods or fibers seen around the cell edges. A rod has a lower surface area to volume ratio than does a lamella if the volume fraction of the rod phase is less than a critical value. This will be discussed in the next section.

LAMELLAR OR FIBROUS?

Many regular microstructures are fibrous rather than lamellar (see Fig. 12.1), and very often these occur when the volume fraction of the minor (discontinuous) phase is only a few percent. Eutectic compositions highly displaced to one side of the phase diagram often yield fibrous structures. A simple calculation serves to illustrate that fibers yield a lower surface area per unit volume than do lamellae, if the volume fraction of one eutectic phase is less than a critical value. Under such conditions, fibers, not lamellae, should prevail.

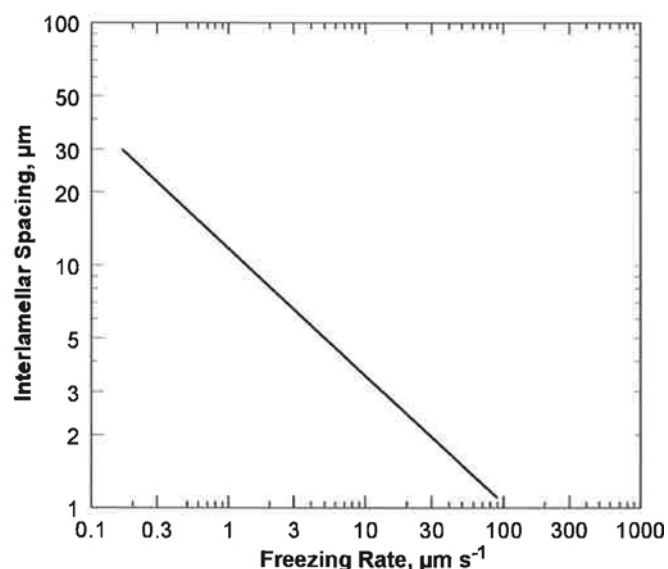


Fig. 12.8. A typical log-log plot of λ vs. R is shown for a lamellar eutectic.

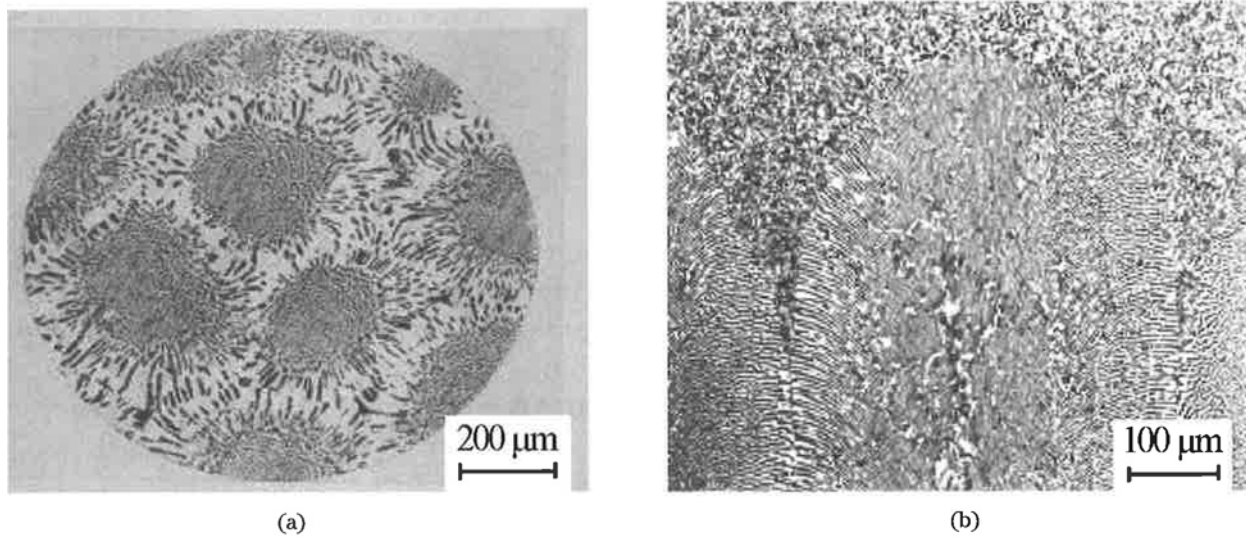


Fig. 12.9. A cellular structure caused by impurity elements in a cast Cd-Zn eutectic alloy is seen in (a) and a cellular solid-liquid interface of a lamellar eutectic (Sn-Cd) is seen in (b). This photograph was obtained by quenching the interface during directional solidification.

Consider the two eutectic microstructure cross sections illustrated in Fig. 12.10. Each section has dimensions of λ by λ and a depth of one unit. The volume of each microstructure is, therefore, λ^2 cubic units. In each structure, the interfacial area/volume of eutectic is as follows:

$$\text{lamellar structure: } 2\lambda/\lambda^2 = 2/\lambda$$

$$\text{rod structure: } 2\pi R/\lambda^2$$

where R is the rod radius

These two ratios become equal when,

$$2\pi R/\lambda^2 = 2/\lambda, \text{ or } R = \lambda/\pi$$

Now, the volume fraction, V_F , of the fibrous phase is,

$$V_F = \pi R^2/\lambda^2$$

If $R < \lambda/\pi$, the fibrous structure will possess a lower surface area per unit volume than will the lamellar. This occurs when:

$$V_f = 1/\pi = 0.32$$

This simple calculation predicts that eutectic systems in which the discontinuous phase forms 32% or less by volume of the microstructure should freeze in a fibrous rather than lamellar morphology. Isotropic interfacial surface energies are assumed here, but if preferred orientations leading to epitaxial relationships can develop, these will serve to stabilize lamellar morphologies over fibers. This often is the case and many lamellar structures are found in systems in which the volume fraction of one phase is much less than 32%. Lamellae often are stable down to volume fractions of about 18%, and an extreme example of lamellar stabilization by preferred orientations is found in the Fe-Fe₃C eutectic (white cast iron), where the volume fraction of the Fe₃C phase is only 7%.

THE COUPLED ZONE

Eutectic freezing often proceeds at undercoolings measurable using even very simple thermocouples and data acquisition systems. These relatively large undercoolings, of at least a few degrees, result from the added complexities of two phase, compared to single phase, solidification. Chief among these complexities is a two-way diffusion process, as well as the creation of significant interphase boundaries.

In many ways, the equilibrium phase diagram is inadequate to predict solidification behavior under such nonequilibrium conditions, and there are many experimental observations related to eutectic growth that simply cannot be explained using the equilibrium diagram. Among these are the following.

- It is often observed that eutectic structures form over a range of compositions around the eutectic point rather than at just the exact eutectic composition. Furthermore, under conditions of high temperature gradient freezing, as used in the directional solidification of some composites, the extent of this phenomenon increases.

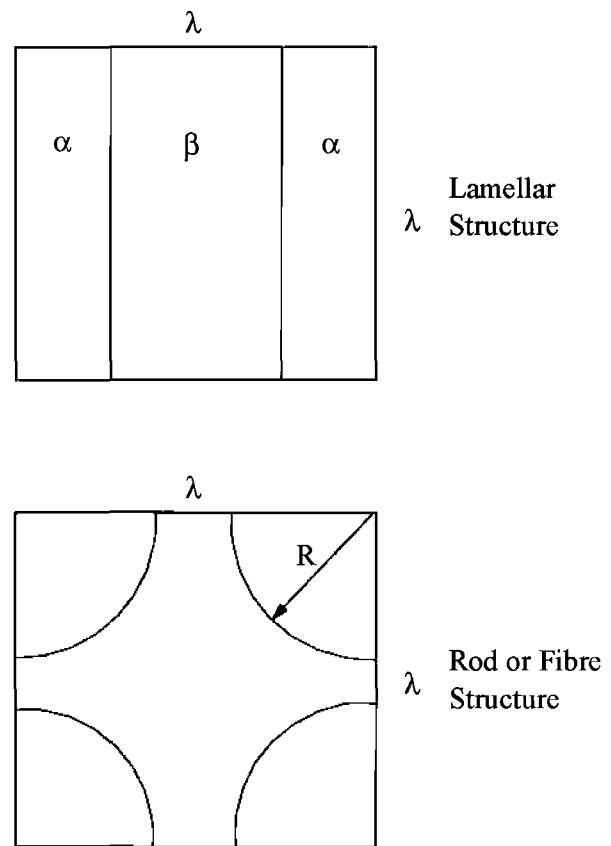


Fig. 12.10. Cross sections of equal area of a fibrous and a lamellar eutectic structure are shown.

- Cast alloys of exact eutectic composition sometimes contain primary dendrites.
- Cast alloys that are slightly hypereutectic sometimes contain primary dendrites of the hypoeutectic phase and none of the hypereutectic phase.

These interesting effects all stem from the nonequilibrium nature of eutectic solidification, and can be explained by reference to the coupled zone. The coupled zone concept proposes that there exists, below the equilibrium eutectic temperature, a composition-temperature zone in which coupled growth of the two eutectic phases can take place producing a eutectic microstructure free of primary phases. Coupled zones have actually been measured, first in some organic eutectics and then more recently in several metal-nonmetal eutectics. As will be demonstrated later, it is possible, in principle, to derive the coupled zone for a given eutectic system if you know the exact kinetic equations relating growth rate to undercooling for the coupled structure, as well as for each of the primary phases.

Coupled zones may be found in two forms, shown in Fig. 12.11. The symmetric zone (a) occurs most often if the eutectic composition is near the center of the phase diagram. The asymmetric zone (b) is found in phase diagrams in which the eutectic is highly displaced toward one side of the diagram and one of the eutectic phases is a nonmetal. The best way to appreciate the significance of the coupled zone is to follow through the rationale for it in terms of the freezing rates of primary phases and the coupled eutectic.

Figure 12.12 presents a symmetric eutectic phase diagram, as well as curves describing the freezing rates of the α and β primary phases and the coupled eutectic at each of three temperatures: the equilibrium eutectic temperature, T_E , and two temperatures below the equilibrium. Since we are dealing with nonequilibrium solidification, it is necessary to extrapolate the liquidus lines of the phase diagram into the nonequilibrium range. Such a procedure is justified if the departures from equilibrium are not too great. Now, consider what happens at each of the three temperatures, T_E , T_1 and T_2 .

At T_E , the freezing rate of the eutectic is zero; the system is at equilibrium and there is no driving force for eutectic solidification. As the composition moves away from the eutectic to either hypo- or hypereutectic compositions, the driving force for primary (α or β) solidification increases progressively, as does the freezing rate of either phase. The driving force

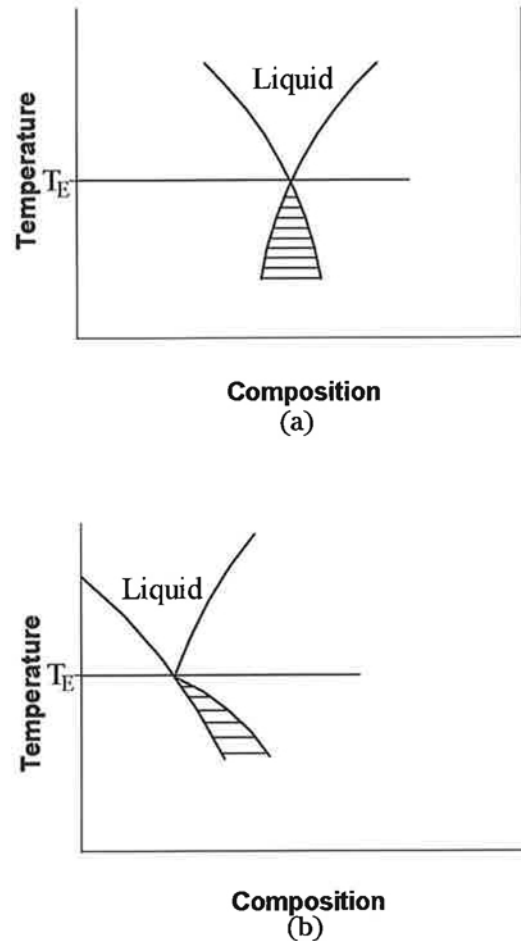


Fig. 12.11. A symmetric coupled zone is illustrated in (a) and an asymmetric coupled zone in (b).

is the degree of supersaturation of the liquid with respect to either phase, and is measured by the temperature difference between the appropriate liquidus line and the eutectic temperature.

With undercooling below T_E , as occurs if the temperature is T_1 , it is necessary to use the extended liquidus lines to determine the compositions at which the α and β primary phases begin to form. Primary α solidifies at any composition less than s , and primary β , at any composition greater than r . Once again, the growth rate of each phase rises sharply as the liquidus- T_1 temperature difference increases.

The freezing rate of the coupled two-phase eutectic also is indicated in Fig. 12.12. Between points m and n , coupled eutectic growth takes place faster than primary solidification of either phase and, as a result, it is the coupled eutectic that predominates and forms the microstructure. Compositions corresponding to m and n become the boundaries of the coupled zone at the temperature of T_1 .

Similar considerations apply when the undercooling increases further and the temperature falls to T_2 . Points q and p are the compositions at which the liquid is saturated with respect to α and β primary, respectively. Each primary phase freezes increasingly quicker as the alloy composition changes so that the driving force for solidification is increased. Coupled eutectic growth is, however, faster between compositions m' and n' and these delimit the coupled zone at a temperature of T_2 .

Shape of the coupled zone is determined by many factors. Among these are the slopes of the

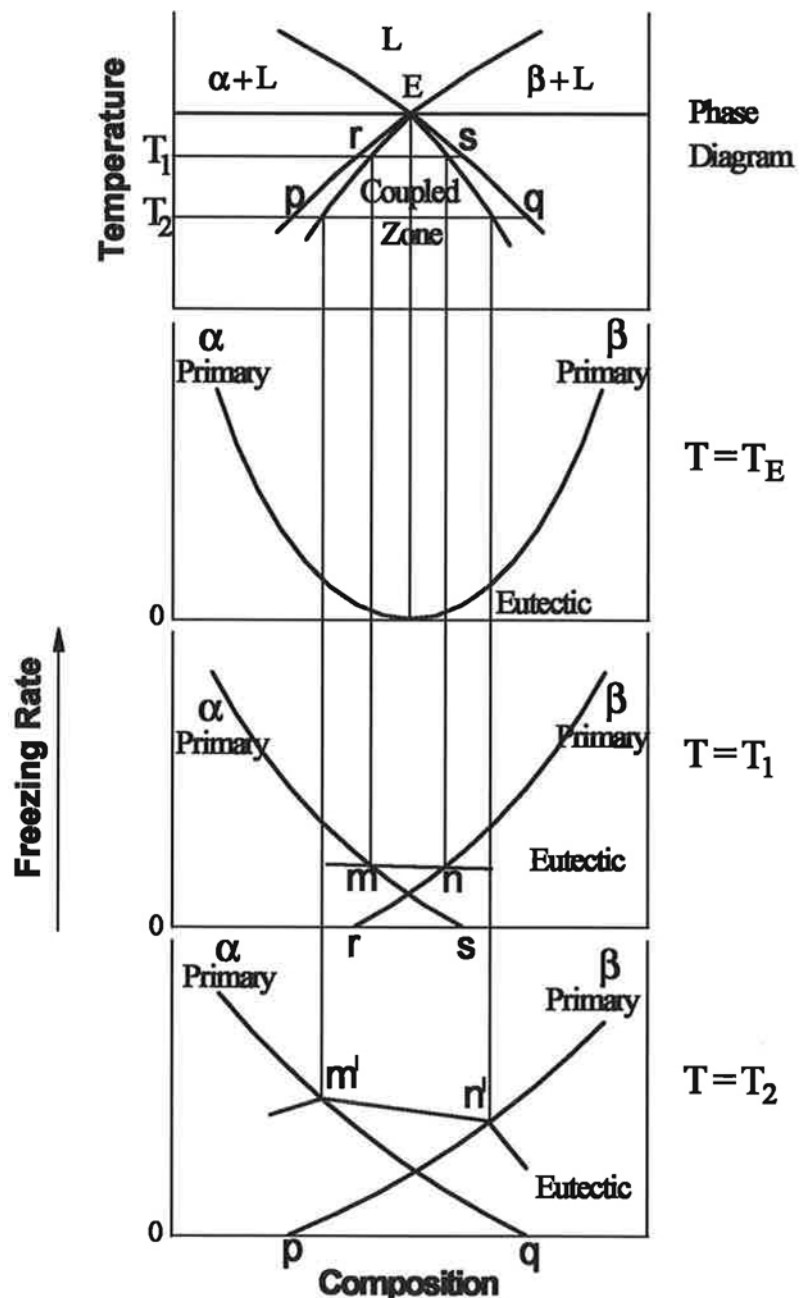


Fig. 12.12. The shape of the coupled zone is derived from the phase diagram as well as the growth rate-composition curves of the primary phase and the coupled eutectic.

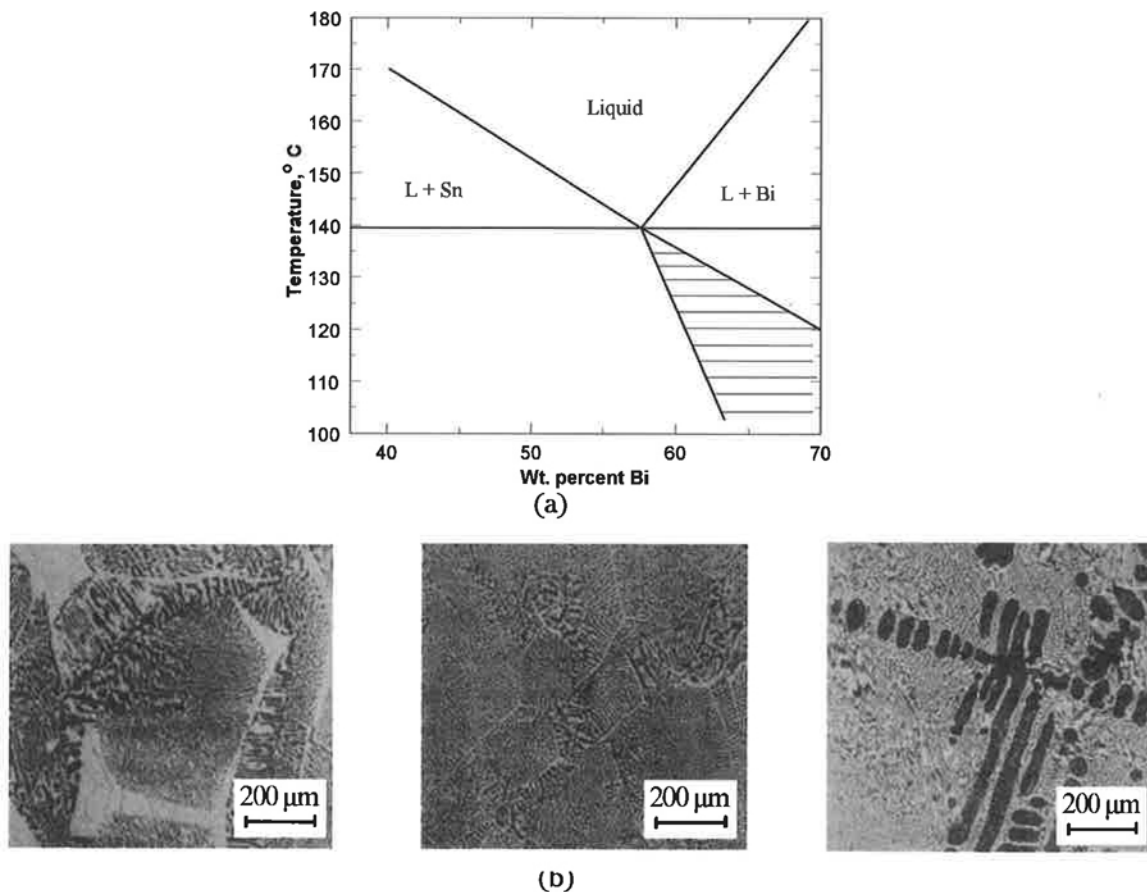


Fig. 12.13. The experimentally determined coupled zone in the Bi-Zn eutectic is shown in (a), while three cast microstructures are presented in (b). These structures were produced by casting at an undercooling of 5°C (9°F) below the eutectic temperature. Compositions are, from left to right: Sn-62%Bi, Sn-61%Bi and exact eutectic composition. Note that the eutectic microstructure is found in an alloy of hypereutectic composition, while the alloy of exact eutectic composition yields a structure of primary Sn dendrites in a eutectic matrix. [Reproduced with permission of The Minerals, Metals and Materials Society from M.F. Gigliotti et al., *Metallurgical Transactions*, vol 1, p 1038 (1970).]

freezing rate-composition curves of the primary phases which are governed not just by the individual growth kinetics, but also by the steepness of the liquidus lines on the phase diagram. A steep liquidus leads to a rapidly increasing driving force for primary growth and a corresponding steep freezing rate-composition curve. This is one of the main reasons why symmetric phase diagrams yield eutectics with symmetric coupled zones, and asymmetric diagrams such as Al-Si or Fe-C contribute to asymmetric zones, with the zone displaced toward the higher melting, nonmetallic component which has the more difficult growth kinetics.

Detailed knowledge of the growth kinetics of all phases involved would allow the coupled zone to be drawn for any eutectic system using the methodology just described. This knowledge usually is not available, but the coupled zone can be delineated experimentally, to some extent, by freezing samples with compositions in the vicinity of the eutectic and observing their microstructure. This is done best with eutectic systems in which one of the components is a nonmetal, or a semi-metal, since these eutectics do freeze with measurable undercoolings, and by changing the freezing rate, it is possible to

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

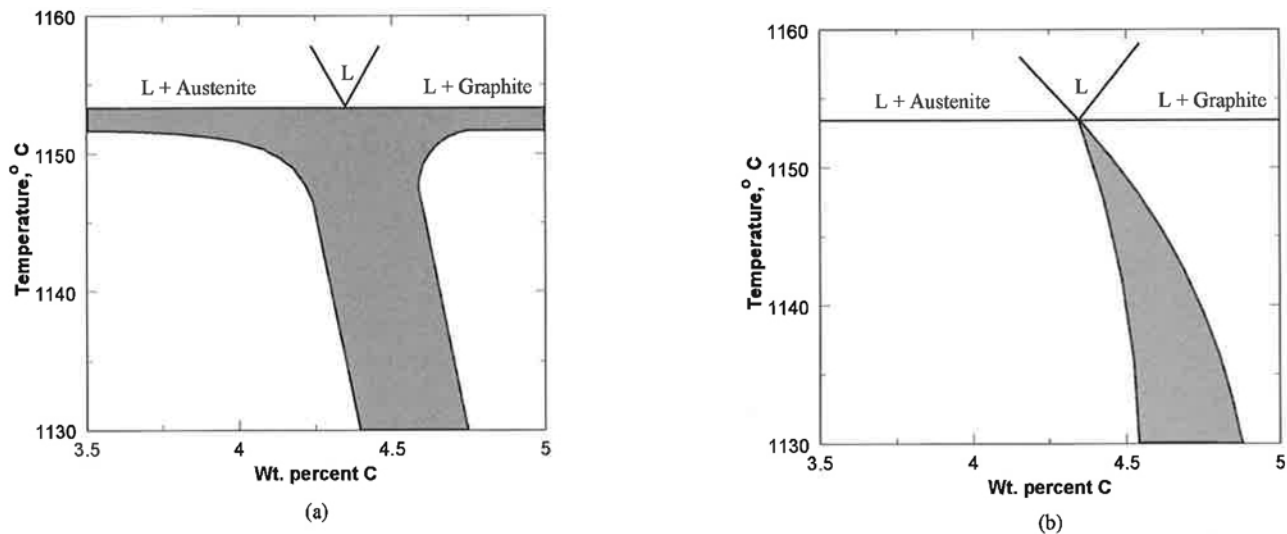


Fig. 12.14. The coupled zone in the iron-graphite eutectic at a temperature gradient of 70C/cm is shown in (a); the coupled zone at zero temperature gradient is shown in (b). [Data replotted from H. Jones and W. Kurz, *Metallurgical Transactions*, vol 11A, p 1265 (1980).]

perform the experiment at a few different undercooling values. Figure 12.13 shows the results of such experimental work on the Bi-Zn eutectic along with some typical microstructures obtained at various compositions and undercoolings.

EFFECT OF TEMPERATURE GRADIENT

Cast alloys usually freeze into liquids in which the temperature gradient is near zero as a result of the rapid dissipation of superheat in a mold. In these cases, coupled zones, such as those just described, result.

Very high temperature gradients can be developed in special solidification processes such as the directional freezing of composite materials. High temperature gradients, in the 50-150C/cm range, have the effect of widening the coupled zone, particularly at low undercoolings. It appears that the primary phase, which normally solidifies dendritically as the composition deviates from the eutectic, is forced to become part of the eutectic structure resulting in a typical eutectic microstructure with a noneutectic composition.

The coupled zone in the iron-graphite eutectic at a temperature gradient of 70C/cm is given in Fig. 12.14, along with the general shape of the zone at low or zero gradients. Of greatest interest is use of the coupled zone concept to explain the microstructure of cast eutectic alloys.

COUPLED ZONE-MICROSTRUCTURE RELATIONSHIPS IN CAST EUTECTICS

Cast eutectic alloys, when compared to directionally frozen, often exhibit quite different microstructures resulting from the different ways in which eutectic solidification proceeds in each case. When an alloy is directionally frozen, nucleation occurs at the start of growth, and the structure of the entire solid evolves from the initial nucleus into some steady state microstructure.

In a casting, however, nucleation takes place usually throughout the entire body of liquid. Nuclei grow into grains and growth ceases when these grains impinge on each other. Steady state microstructures do not have time to develop, and the cast microstructure of the eutectic is greatly influenced by the nucleation sequence and the shape of the coupled zone. The most complex situations occur if the coupled zone is asymmetric.

Consider the asymmetric coupled zone in the hypothetical alloy system A-B, (Fig. 12.15). A cast alloy of exact eutectic composition will undercool before solidification commences, and this undercooling will take the alloy out of the coupled zone. Nucleation of the α and β phases will not happen simultaneously, and one of these phases will nucleate before the other.

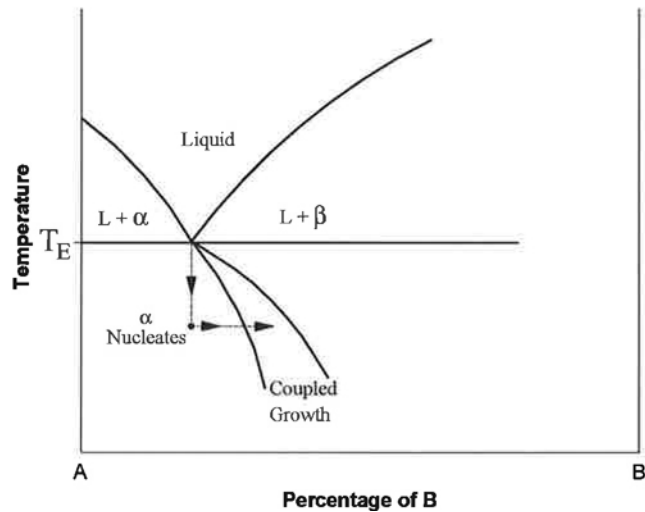


Fig. 12.15. The solidification sequence of a eutectic alloy in which the α phase is the first to nucleate is shown. The structure of this eutectic when cast will consist of primary dendrites of the α phase from which the eutectic structure grows directly.

Suppose that it is the α phase that is first to form. Growth of primary α dendrites leads to enrichment of the remaining liquid in the B component, and the liquid composition moves into the coupled zone. Sufficient B enrichment allows for nucleation of the β phase, and coupled growth of the two-phase eutectic within the coupled zone completes the solidification sequence. The cast microstructure consists of primary α dendrites from which the eutectic grows directly. Primary dendrites form even though the alloy is of exact eutectic composition, and the eutectic structure itself, if analyzed chemically, will be found to be somewhat hypereutectic.

Solidification is even more complex if the β phase is the first to nucleate (remember that primary nucleation depends on the available substrates in the liquid and the crystal structure of the primary phase). If conditions favor β nucleation first (Fig. 12.16a), the liquid becomes enriched in the A component and the liquid composition moves away from the coupled zone, while at the same time continuing to cool. Eventually, α nucleates with sufficient A component enrichment and undercooling.

The highest concentration of element A is found at the β phase liquid interface, and it is here that α nucleation occurs, forming a halo that completely envelops the primary β phase and halts its growth. Any further solidification is now by growth of the α halo, and the liquid composition, progressively enriched in the B component, moves into the coupled zone where cooperative growth of the two phases leads to establishment of the eutectic structure. Cast eutectic microstructures contain primary β dendrites surrounded by an α halo from which the coupled eutectic structure grows (Fig. 12.16b).

Sometimes it is observed that the microstructures of slightly hypereutectic alloys

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

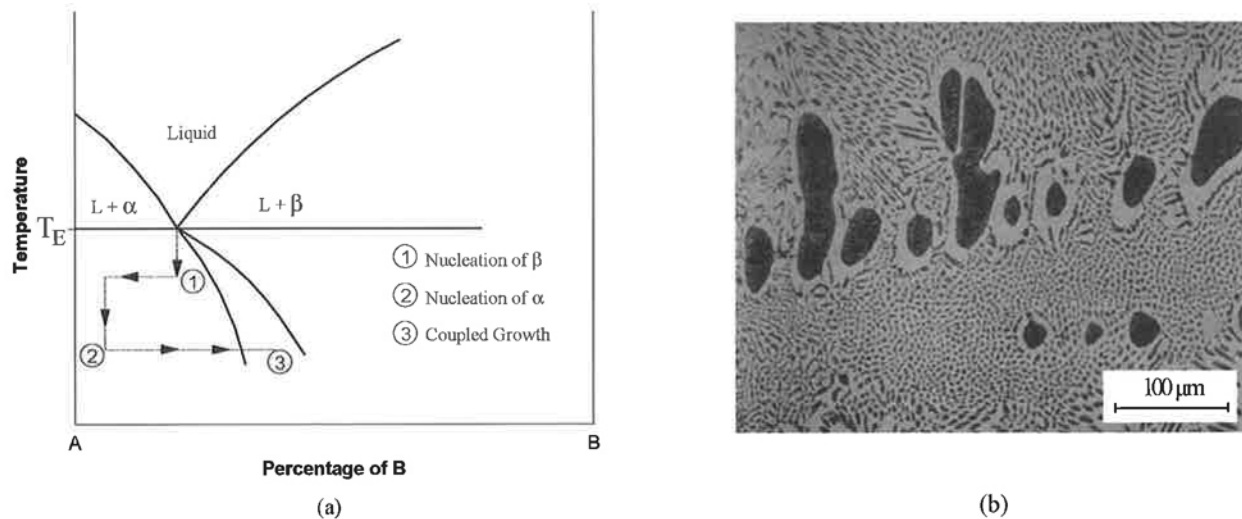


Fig. 12.16. The solidification sequence of a eutectic alloy in which the β phase is the first to nucleate is shown in (a) and a typical cast eutectic structure resulting from such a sequence is shown in (b). The cast structure shown is that occurring in the (silver-copper) Ag-Cu eutectic. Note the halo of the Ag-rich solid solution surrounding the primary Cu-rich β dendrites. The coupled eutectic structure grows from the halo into the surrounding liquid.

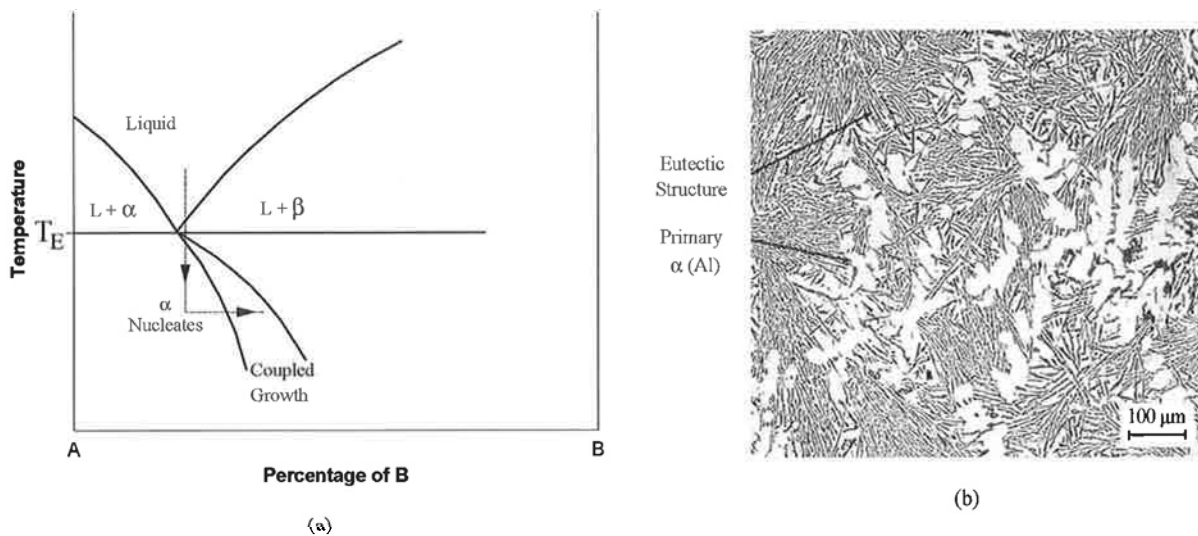


Fig. 12.17. The solidification sequence of a slightly hypereutectic alloy in which β phase nucleation is suppressed is shown in (a) and a typical cast structure resulting from such a sequence is shown in (b). The cast structure shown is that of an Al-Si alloy. Even though the alloy composition is hypereutectic, primary α (Al) dendrites are found in the microstructure.

contain no primary dendrites of the hypereutectic phase, but do contain dendrites of the hypoeutectic phase. A solidification sequence leading to this microstructure is shown in Fig. 12.17a. Nucleation of primary β does not happen due to lack of sufficient and suitable substrates. With sufficient undercooling, primary α can nucleate out of the coupled zone, and with its growth, the liquid composition moves into the coupled zone to allow a eutectic microstructure to develop. Figure 12.17b shows the microstructure of a slightly hypereutectic Al-Si alloy in which this has happened. Despite the alloy composition, primary

aluminum, not primary silicon, is visible in the structure.

If the coupled zone is symmetric, a casting of the exact eutectic composition will usually yield a microstructure similar to that obtained by directional freezing because the composition remains within the coupled zone at any, and all, undercoolings. Exceptions may result if nucleation of one of the eutectic phases is, for some reason, greatly inhibited. Growth of only one of the phases may cause the liquid composition to move out of the coupled zone until nucleation of the second phase becomes possible. The liquid composition can then move back into the zone, and eutectic solidification will proceed.

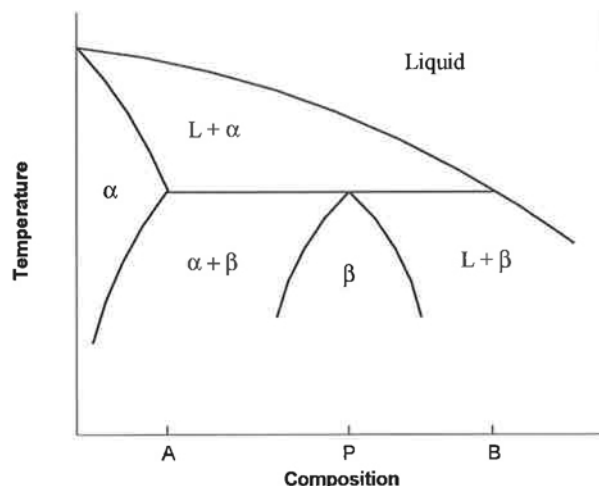


Fig. 12.18. A binary peritectic reaction as it appears on a phase diagram is illustrated.

It is clear from this discussion that interpretation of cast eutectic microstructures is much more complex than that of single phase structures. Fortunately, the coupled zone concept makes this interpretation easier, and allows some degree of microstructural prediction in these materials.

PERITECTIC REACTION

In terms of sheer numbers, there are probably more peritectic reactions appearing in metallurgical phase diagrams than there are eutectics, although the peritectic is of much lesser importance in casting and foundry alloys. Despite their number, the mechanisms of peritectic transformations have been less studied than those of eutectics, and the peritectic reaction remains relatively poorly understood.

A simple binary peritectic reaction as it appears on a phase diagram is sketched in Fig. 12.18. The exact peritectic composition is given as, P. Alloys with compositions between A and P are hypoperitectic, while those in the range P to B are hyperperitectic. The peritectic reaction proceeds by a decomposition of the properitectic α phase into the secondary β phase by the reaction:



Of all phase reactions involving solidification, the peritectic is the least likely to proceed to equilibrium and it is probably for this reason that it has not been studied extensively. The basic difficulty with the peritectic is that two reactants, the α phase and the liquid, must react to yield one product, the β phase. Since the product forms at the point where the reactants meet, there is a tendency for the secondary β phase to separate the α and liquid reactants. A so-called peritectic ring then forms and further reaction can proceed only

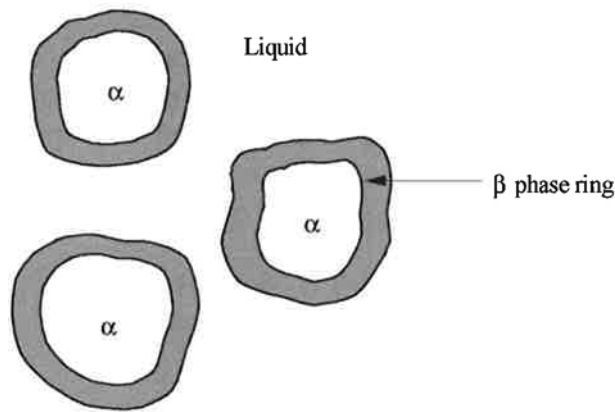


Fig. 12.19. A schematic representation of the peritectic ring is shown.

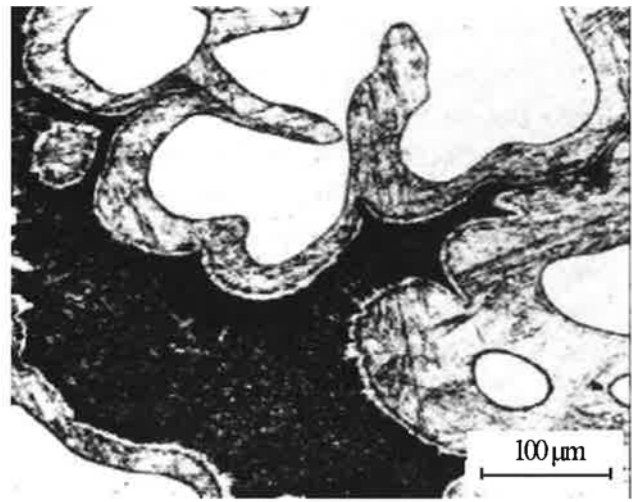


Fig. 12.20. The microstructure of a quenched Cu-20%Sn alloy is shown. The peritectic phase, β , (gray), has formed a continuous layer over the properitectic α phase (white). The very fine unresolved structure is quenched liquid. [Reproduced from ASM Handbook, vol 9, Metallography and Microstructures, p 677, Fig. 9, ASM International, Materials Park, OH 44073-0002 (1985).]

by solid state diffusion through the β phase ring. Diffusion in solids is much slower than in liquids and the transformation often ceases completely when the peritectic ring forms.

Figure 12.19 is a schematic representation of the phase distribution at this point in the reaction, while Fig. 12.20 shows a Cu-20%Sn alloy quenched during the peritectic transformation. The ring of secondary β phase formed on the properitectic α is clearly visible, as is the region of quenched liquid.

Retention of the properitectic phase at room temperature is not uncommon because of the slowness of solid state diffusion. Any factor that facilitates diffusion through the secondary phase barrier will allow the transformation of α to β to be more complete. Some of those factors are as follows:

- slower cooling rates;
- longer holding times below the peritectic temperature;
- higher holding temperatures below the peritectic temperature;
- a fine initial distribution of the properitectic phase; and
- a high rate of diffusion in the secondary phase.

This list indicates that copious nucleation of the properitectic phase yields a greater likelihood of completion of the reaction. The more numerous the properitectic particles, the finer they are, and the more easily they are transformed to the secondary phase.

Growth of the secondary phase over the properitectic phase is thought to occur by the mechanism sketched in Fig. 12.21. Partial dissolution of the α phase results by atom diffusion through the liquid near the point of α - β liquid contact. A thinning of the

properitectic phase is caused near this contact point. If the properitectic phase particles are very thin to begin with, this thinning may be sufficient to result in their complete dissolution, and to allow the reaction to go to completion.

Many of the intermetallic compounds found in wrought aluminum alloys form through peritectic reactions that often appear to go to completion, as evidenced by the lack of the properitectic phase in the microstructure. The low alloy element contents of many of these materials lead to very small volume fractions of intermetallics, and it is probable that the properitectic phase is present, initially, as very thin platelets that may be completely consumed by the reaction mechanism proposed in Fig. 12.21.

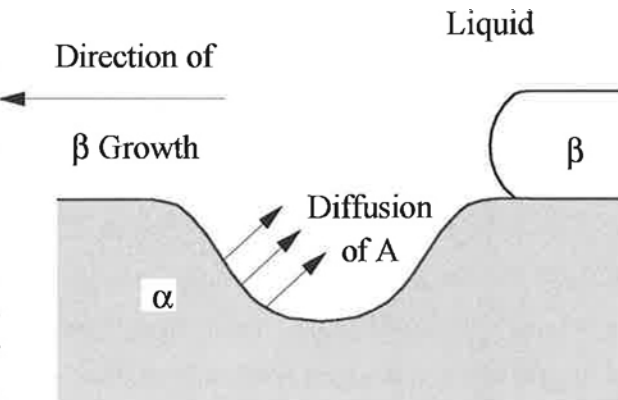


Fig. 12.21. Growth of the secondary phase over the properitectic phase involves atom diffusion in the liquid near the α - β liquid contact point and thinning of the properitectic particles.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

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chapter 13

MORPHOLOGICAL MODIFICATION IN INDUSTRIAL ALLOYS

An interesting feature in solidification and casting of several important industrial alloys is the ability to cause dramatic shape changes to one of the alloy phases. Alloys amenable to this morphological modification are those in which one of the phases is a nonmetal, or at least a semi-metal. The most important of these are the graphitic cast irons, aluminum-silicon alloys and some aluminum wrought alloys that contain iron-bearing intermetallic phases.

Small amounts of certain elements are added to the alloy in order to cause phase modification, resulting in the phase having a more desirable shape within the microstructure and the alloy having enhanced mechanical properties. These modification processes are not only of considerable commercial value. They also have led to extensive research into the solidification of some alloys in an attempt to discover the exact mechanisms whereby small amounts (usually in the ppm range) of certain elements can result in such drastic changes in solidification behavior.

Many excellent books are available dealing with the technology of morphological modification, and some of these are listed at the end of this chapter. This final chapter concentrates on the possible mechanisms that bring about morphological modification. It is generally agreed that it is the faceted nature, ($\alpha > 2$), of the nonmetallic phase that makes it amenable to shape change, but the mechanisms involved at the atomic level are very complex and there is little overall agreement as to the exact manner in which the modification is caused. The most plausible theories or hypotheses are presented, and because the alloys involved are so different, they are discussed separately with an attempt then made to find some common threads.

GRAY AND WHITE CAST IRON

The cast irons comprise those ferrous alloys that undergo eutectic solidification in the Fe-C system. Typically, these alloys contain approximately 3-4.5% C in addition to many other elements present as impurities, or added intentionally. The family of cast irons provides us with several interesting examples of morphological modification, the two most important being the transition from white to gray iron, and the change from flake to nodular graphite.

The eutectic region of the Fe-C phase diagram is shown in simplified form in Fig. 13.1. In reality, two eutectic reactions are possible in this system: the Fe-Fe₃C (cementite) eutectic and the Fe-C (graphite) eutectic. In the pure binary system, a temperature

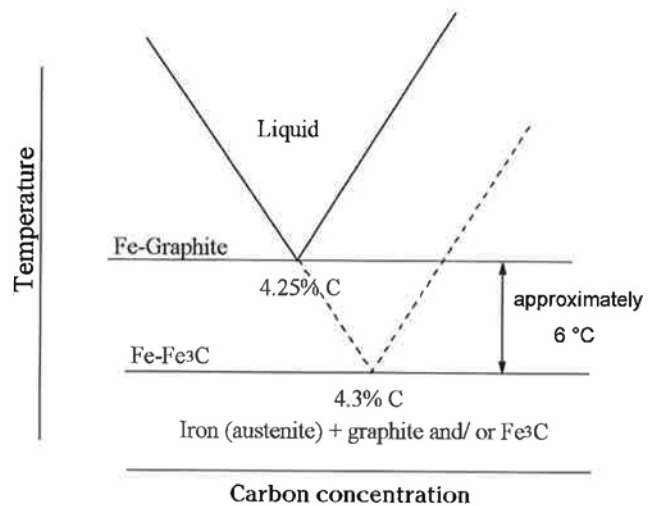


Fig. 13.1. A simplified version of the eutectic region of the Fe-C phase diagram is shown. This is the region of carbon concentration found in commercial cast irons.

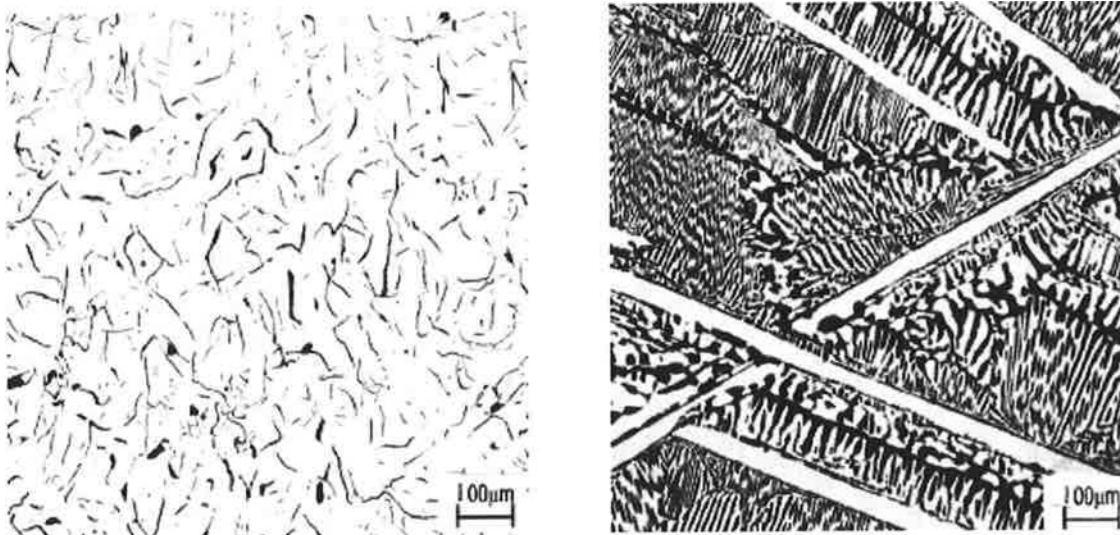


Fig. 13.2. The microstructures of common gray (left) and white (right) cast iron are shown. Picral etch.

difference of only about 6°C (10.8°F) separates the two eutectic reactions. Eutectic reactions often require considerable undercoolings before they can proceed, and the Fe-C eutectics are no exception.

Solidification may occur in the interval between the Fe-C and Fe-Fe₃C eutectic temperatures. If this happens, then only the Fe-graphite eutectic reaction can proceed, and some form of graphite will solidify along with iron (austenite). These graphitic cast irons are called gray cast irons because of their gray colored fracture surface. If, however, conditions are such that freezing takes place at a larger undercooling with the solidification temperature below that of the Fe-Fe₃C, then it is thermodynamically possible for both the Fe-graphite and the Fe-Fe₃C eutectics to form.

If this is the case, the microstructure may contain mixtures of graphite and cementite (mottled cast iron), or it may consist solely of the cementite-austenite eutectic mixture. The metallic nature of the fracture surface of this material has resulted in its being called white cast iron. The typical microstructures of a common gray and white cast iron are shown in Fig. 13.2a and b.

Graphite and cementite have very different physical properties. Graphite is soft, a good lubricant, and has a high thermal conductivity, while cementite is hard and brittle. These properties of the individual constituents are reflected in the overall properties of gray or white cast iron. Gray cast irons tend to be relatively soft, easily machined and often find application in heat exchangers where their excellent thermal conductivity can be exploited. White cast irons, on the other hand, are extremely hard and difficult to machine and they possess poor mechanical properties as a result of the brittle nature of the cementite phase. These different properties necessitate that the solidification of cast irons be controlled so that they are either completely gray or completely white, depending on the application. In general, mixtures of graphite and cementite are not desirable.

Controlling which eutectic reaction takes place is accomplished by modifying the chemistry of the liquid alloy in such a way that the temperature gap between the Fe-C and the Fe-Fe₃C eutectics is either widened or narrowed. In addition, proper additives to the melt encourage nucleation of one or the other of the phases.

When the desired result is gray cast iron, various graphite stabilizers are added. Silicon, in the form of ferrosilicon, is the most common of these. The addition of about 2%Si widens the temperature gap between the two eutectics from about 6 to 30°C (10.8 to 54°F). Since the undercoolings required for solidification of the Fe-graphite eutectic are less than 30C, only graphite will form during the eutectic reaction because the solidification temperature will not reach the Fe-Fe₃C equilibrium eutectic temperature.

At the same time, nucleation of graphite is encouraged by impurities present in the ferrosilicon. Chief among these is calcium, which forms calcium carbide, CaC₂, by reaction with carbon present in the liquid iron. Certain atom planes of calcium carbide have almost exactly the same atomic arrangement as some atom planes in the crystal structure of graphite. Consequently, calcium carbide provides an excellent substrate for the heterogeneous nucleation of graphite.

The applications for white cast iron are fewer than those for gray cast iron, but they do depend on the absence of graphite in the microstructure. A completely white structure is ensured by the addition of various carbide stabilizers, such as Mo, Zr, Cr or Ti, to the melt. These elements have two functions. They narrow the gap between the Fe-C and Fe-Fe₃C

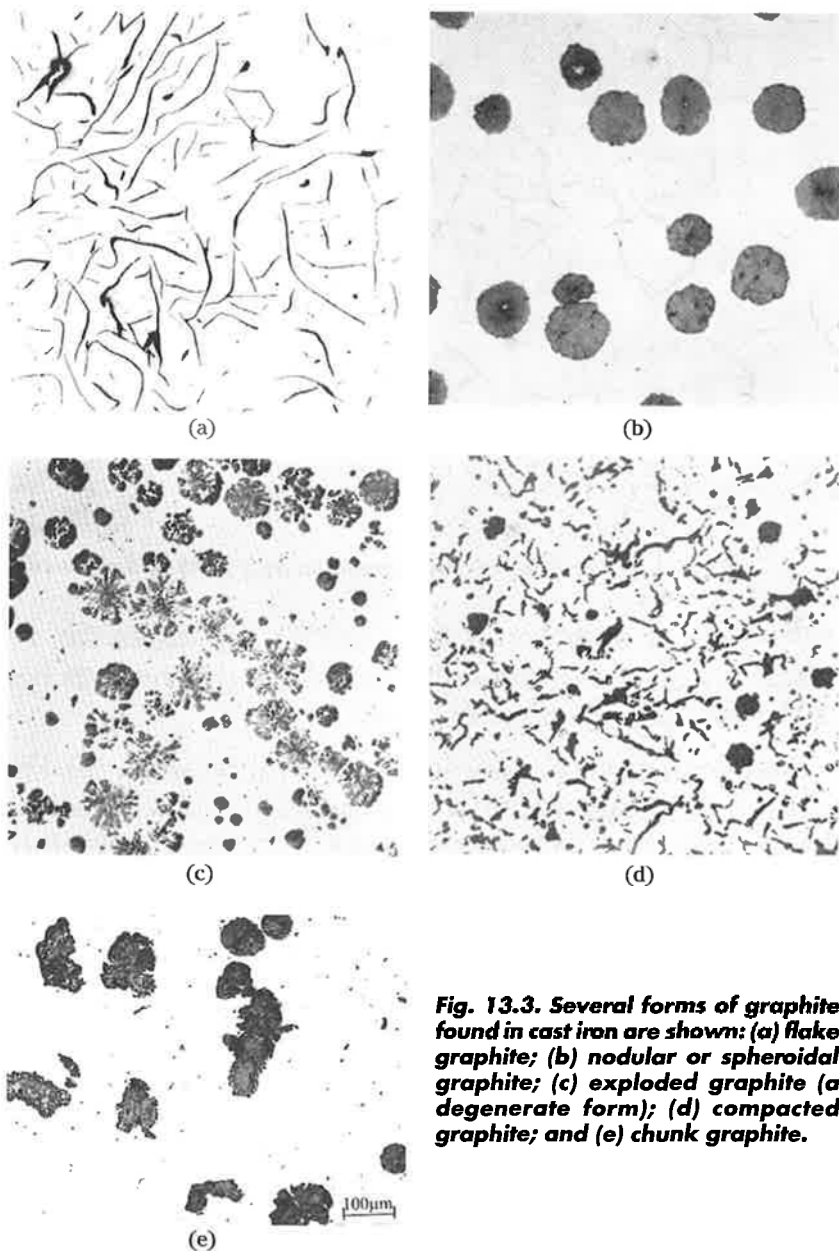


Fig. 13.3. Several forms of graphite found in cast iron are shown: (a) flake graphite; (b) nodular or spheroidal graphite; (c) exploded graphite (a degenerate form); (d) compacted graphite; and (e) chunk graphite.

eutectic temperatures, thus making the formation of graphite less likely, and they promote the nucleation of cementite. Cementite, once nucleated, freezes at a faster rate than graphite, and will, as a result, dominate the microstructure. Kinetically, cementite freezes by a more normal growth mechanism, while graphite growth depends on crystallographic defects, such as twins and dislocations. As discussed in Chapter 5, a material that freezes with normal kinetics will solidify rapidly at very small values of undercooling.

GRAPHITIC CAST IRON

A wide variety of graphite morphologies may form in graphitic cast irons, depending on the melt chemistry and the solidification conditions. Some of these are shown in Fig. 13.3 and will be discussed in the following sections. The oldest, and still most common, form of graphitic cast iron is flake graphite cast iron, which solidifies as a mixture of austenite and graphite in the form of flakes. The austenite may transform on cooling to pearlite, but the flake morphology of the graphite, as determined on solidification, generally remains unchanged as the cast iron cools to room temperature.

The flakes (Fig. 13.3a) are usually wavy in appearance, and may split or branch. Graphite flakes seen on a two dimensional micrograph are but part of a three dimensional graphite cell composed of a multitude of wavy flakes emanating from a single nucleus (Fig. 13.4). Several variations in flake size and morphology can be found, and these have been classified into different types, as shown in Fig. 13.5.

Type A graphite consists of long wavy flakes that form by the partially coupled eutectic growth of graphite and austenite. This type of graphite is favored in cast irons of approximately eutectic composition, which have relatively slow freezing rates. At higher rates of freezing, nucleation of graphite-austenite cells takes place in the bulk of the liquid, and rosettes of type B graphite form. These grow radially in three dimensions in the liquid, and a cross section of their radiating structure is seen as the familiar rosette shape.

Cast irons in which primary graphite forms exhibit type C graphite, which appears as large crystallographic flakes. These are examples of primary graphite growth in the liquid, and the faceted nature of graphite is often evident in their shape as seen on a metallographic section. Hypoeutectic cast irons will contain primary dendrites of austenite (pearlite or ferrite at room temperature) that solidify before the eutectic is reached. Type D, or undercooled graphite, is often found between these dendrites. This is a fine flake form that freezes rapidly when nucleation occurs in the pockets of liquid between the dendrites. Undercooled graphite forms in almost coupled growth with austenite, and is the morphology closest to the classic lamellar eutectic that is found in commercial cast irons.



Fig. 13.4. Schematic illustration shows a flake graphite cell.

A fifth graphite form, type E, also is identified. This type refers to undercooled graphite formed between primary dendrites having a preferred orientation due to preferential growth in the heat flow direction. The specific melt chemistry and solidification circumstances determine the flake type that forms, and the properties of the alloy vary from one flake type to another. See the books on cast iron listed at the end of this chapter for further details on flake type.

Flake graphite cast irons are relatively weak and quite brittle compared to steels, but they do possess some very desirable properties stemming from the physical properties of the graphite phase itself. For example, the high thermal conductivity of graphite makes the alloy, as a whole, an excellent heat conductor, and the chip breaking properties of graphite impart an outstanding machinability to the flake graphite cast irons. The relatively poor mechanical properties derive directly from the graphite phase. Its plate-like nature, coupled with the pointed ends of the flakes, result in its acting as an internal stress raiser within the microstructure. Under load, decohesion takes place at the graphite-metal interface and the material fails.

One way in which improved strength may be imparted to gray cast irons is by controlling the matrix structure. The matrix of a cast iron is essentially a high carbon steel and can be made to exist in many forms, depending on heat treatment and chemistry, e.g., ferrite, pearlite, mixtures of the two, bainite, tempered martensite, etc. The most common matrix structures are ferrite and pearlite in various combinations ranging from 0 to 100% of each. Ferrite imparts a ductility and softness to the cast iron at the expense of strength; cast irons with pearlitic matrices tend to be stronger and more brittle.

A highly significant development related to strength improvement of graphitic cast irons took place in 1948 with the discovery that small additions of certain elements could change the flake graphite morphology to a spheroidal form. Thus was born ductile, or nodular, cast iron (Fig. 13.3b). Many elements have been reported to cause the formation of spheroidal graphite, but the most commonly used are Mg, Ca or Ce, which is added as a rare earth mixture. Required levels vary and depend strongly on the sulfur content of the melt,

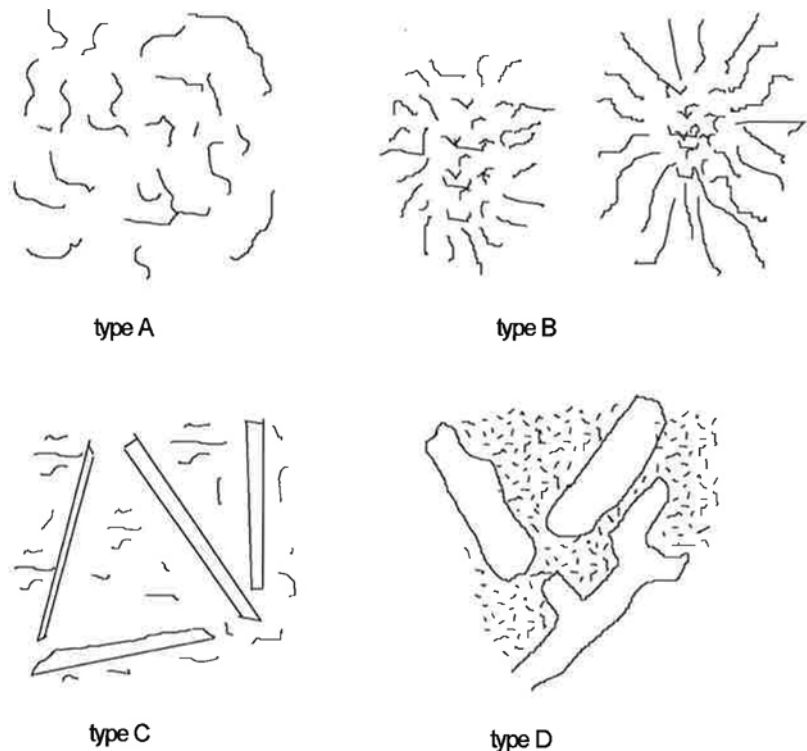


Fig. 13.5. Different forms of graphite flakes found in commercial cast irons are shown. These graphite types are commonly referred to as Type A, Type B, etc.

as well as the treatment agent used, but they are typical of morphological modification processes in general, being in the 100 to 300 ppm range.

With the discovery of nodular graphite came the realization that many intermediate or degenerate forms of graphite also are possible. Their formation can be traced to the presence of insufficient (or sometimes excess) nodularizer, or to trace impurity elements in the cast iron. The list of deleterious elements is long and includes Al, Sb, As, Bi, Cd, Pb, Se, Te, Ti, Zn and Zr. For each of these elements, there is a maximum concentration that should not be exceeded if degenerate growth forms are to be avoided.

Ductile cast iron is a true structural cast iron with mechanical properties far superior to those of gray cast iron. The shape and relative perfection of the graphite spheres eliminate much of the internal stress concentration associated with flake graphite and impart excellent strength and impact properties to the material.

The intermediate and degenerate forms of graphite, (an example of the latter is seen in Fig. 13.3c), are less desirable because they cause enhanced stress concentration under load and reduced mechanical properties. One intermediate form, compacted graphite (Fig. 13.3d), has become an accepted industrial cast iron. While its tensile properties are intermediate between those of gray and ductile iron, it does have a thermal conductivity equivalent to gray iron. Compacted graphite cast irons find application where good thermal conductivity is required, along with mechanical properties better than those of the flake graphite irons, e.g., in brake calipers or ingot molds.

Some typical properties of gray, ductile and compacted graphite cast irons, with a ferritic matrix, are presented in Table 13.1. Property variations in cast irons are extensive, depending on the specific composition, casting conditions and nature of the matrix. The lower thermal conductivity of ductile cast iron, as compared to gray or compacted iron, is a result of the complete separation of the graphite nodules from each other.

Ductile cast iron freezes as a completely divorced eutectic. Flake and compacted graphite

Table 13.1.
Typical Properties of Graphitic Cast Irons with a Ferrite Matrix¹

PROPERTY	GRAY IRON	DUCTILE IRON	COMPACTED GRAPHITE IRON
Tensile Strength (MPa)	150-200	400-450	300-350
Proof Stress (MPa)	105-140	300-350	190-210
Percent Elongation	<1	20-25	4-8
BHN	110-140	150-180	130-150
Impact (ft-lb)*	1-5	10-20	4
Thermal Conductivity (W/m.K)	45	35	42

* UNNOTCHED CHARPY

cast irons, on the other hand, are semi-regular eutectics in which the graphite phase is continuous, or nearly so, throughout the microstructure. It is this continuous path of high thermal conductivity graphite that makes these alloys such excellent conductors of heat.

The question that has puzzled metallurgists and scientists alike since the discovery of ductile cast iron is how the nodularizing element, e.g., Mg, Ca or Ce, actually acts to bring about this morphological change. Even today, the answer is not known for sure, but many good ideas have been presented and links can be found between several of them. Since graphite is the material modified, a good starting place is examination of the structure of both graphite flakes and graphite nodules.

FLAKE GRAPHITE STRUCTURE

From a solidification point of view, graphite is a faceted material, meaning that its crystal structure must play a dominant role as it crystallizes from an iron-carbon melt. Graphite is hexagonal (Fig. 13.6) and forms a layered structure. Strong covalent bonds exist between the atoms in the close-packed (0001) planes while only weak electrostatic (Van der Waals) bonding is found between the (0001) planes. This is why graphite is such a good lubricant. When subjected to a shear, the basal planes of the crystal structure readily slide over each other. The prism planes, (10 $\bar{1}$ 0), are not close-packed and are, therefore, of higher energy than the basal planes, which by virtue of their close-packed nature are the lowest energy planes in the graphite structure.

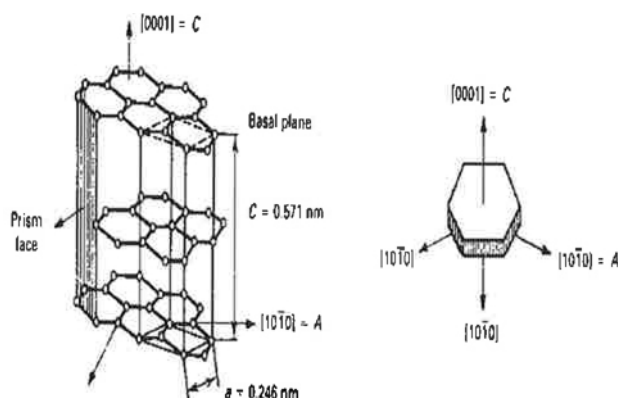


Fig. 13.6. The hexagonal crystal structure of graphite is illustrated, as are the "a" and "c" growth directions.

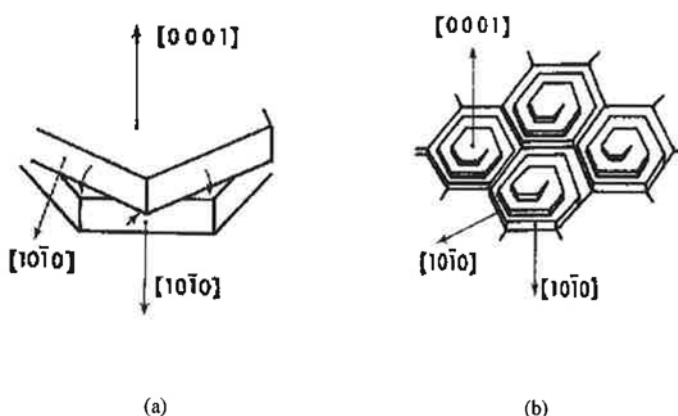


Fig. 13.7. Growth mechanisms on the prism planes, (a), and basal planes, (b), are illustrated.

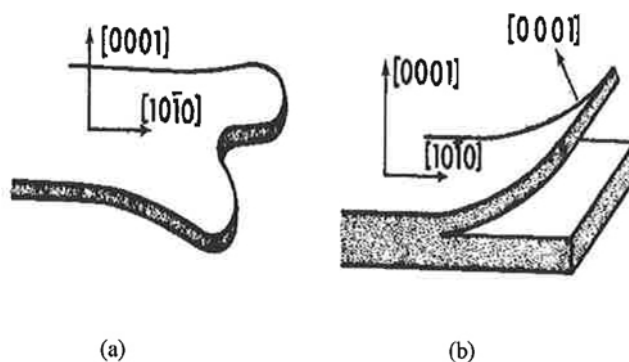


Fig. 13.8. Two methods of flake branching are shown.

For energetic reasons, the large bounding surfaces of crystals growing from a melt are the atomic planes of lowest energy in the crystal structure of the material. In the case of flake graphite, these are the basal planes. Atom addition to the graphite as it freezes from the melt must, therefore, take place on the prism planes, and growth is in the “a” direction in the graphite crystal lattice, (Fig. 13.6). Atom attachment on the prism planes leading to “a” growth is most likely to occur at ledges caused by the twisting of the basal planes about the “c” axis. Twisting of this nature is likely in view of the weak bonding between basal planes. Such ledges are illustrated in Fig. 13.7a and atom addition sites also are indicated.

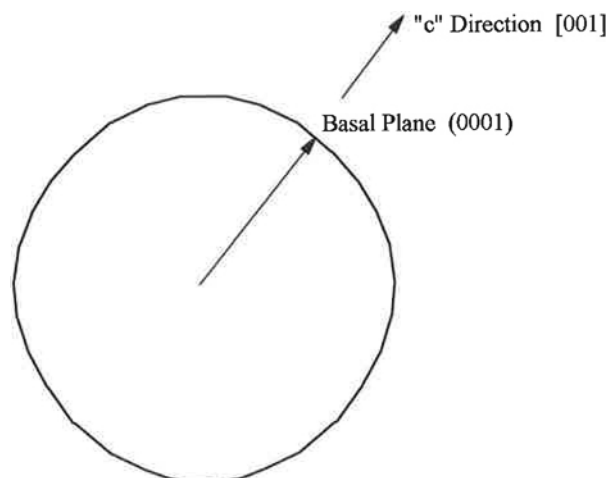


Fig. 13.9. Schematic illustration of a graphite nodule shows the location of close-packed planes.

Flake graphite is observed to have a measurable thickness implying that some “c” direction growth is also possible. This is probably screw dislocation growth taking place on the (0001) planes (Fig. 13.7b). The number of screw dislocations is limited, and screw dislocation growth kinetics, as described in Chapter 5, are sluggish resulting in only slow flake thickening.

Branching of flakes is a common occurrence that may take place by either of two methods, shown in Fig. 13.8. Growth on two (10 $\bar{1}$ 0) ledges, such as those seen in Fig. 13.7a, can lead to a separation of the type illustrated in Fig. 13.8a, where the branch forms in the “a” direction. Delamination of the basal plane (Fig. 13.8b) can result in branching in the “c” direction. These two mechanisms, arising directly from the crystal structure of the graphite, allow flake graphite to bend and branch in any direction leading to the familiar complex flake forms seen in gray cast iron.

NODULAR GRAPHITE STRUCTURE

The graphite nodule, like the flake, is bounded by the low energy, close-packed basal planes of the graphite crystal structure (Fig. 13.9). Electron microscope studies show a circumferential layer structure, as well as a radial structure. Both of these features, evident in the scanning electron micrograph of a graphite nodule shown in Fig. 13.10, have played a role

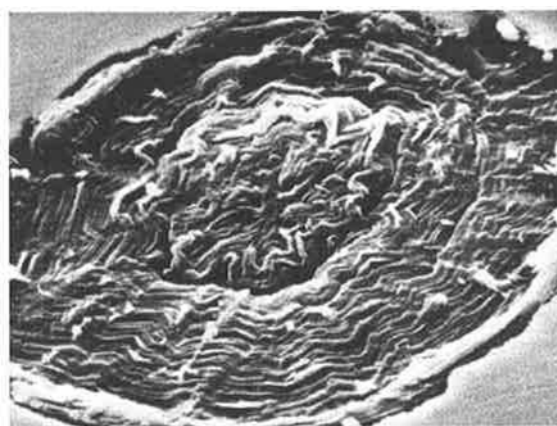


Fig. 13.10. A scanning electron micrograph of a graphite nodule is shown at 3000X. This sample has been given a cathodic vacuum etch to reveal the surface structure. [Reproduced from Ductile Iron Production, S.I. Karsay, Quebec Iron and Titanium Corp. (1976).]

in the development of one or more of the various theories for graphite growth.

It is immediately apparent that growth directions of flake and nodular graphite appear to be different. Flake graphite undergoes "a" direction growth, but if we acknowledge that a sphere grows radially, it appears that nodular graphite forms by "c" direction growth (Fig. 13.11). Any mechanism to explain the formation of graphite nodules must account for this difference.

Many theories related to the growth of nodular graphite have been proposed over the years since the discovery of ductile cast iron. It is interesting to examine each of these in order to see which stand and which fall when considered in terms of solidification theory. It is seen that some are based on very shaky theoretical grounds while others are well supported. In the final analysis, no single theory is able to account for the growth of nodular graphite, but some common threads can be drawn from several of the theories in order to develop a plausible growth mechanism.

SOLID STATE GROWTH MECHANISMS

The first investigators of ductile cast iron believed that nodular growth was a solid state phenomenon with the graphite resulting from decomposition of iron carbide. This idea originated from malleable cast iron in which rather imperfect nodules are produced by Fe_3C decomposition during lengthy heat treatment in the 900C (1652F) range. Indeed, the malleable iron structure, (Fig. 13.12), does bear many similarities to that of ductile iron, so it is not surprising that early research workers made this connection. It has, however, been definitely established that nodules grow in contact with the liquid for much of their formation time. Simple evidence for this

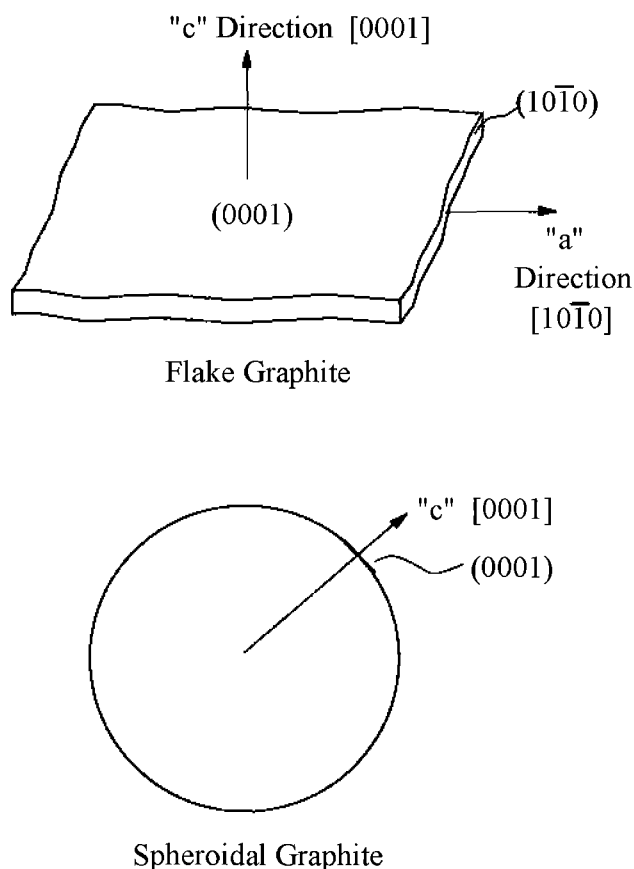


Fig. 13.11. The different growth directions of flake graphite and spheroidal graphite are indicated.

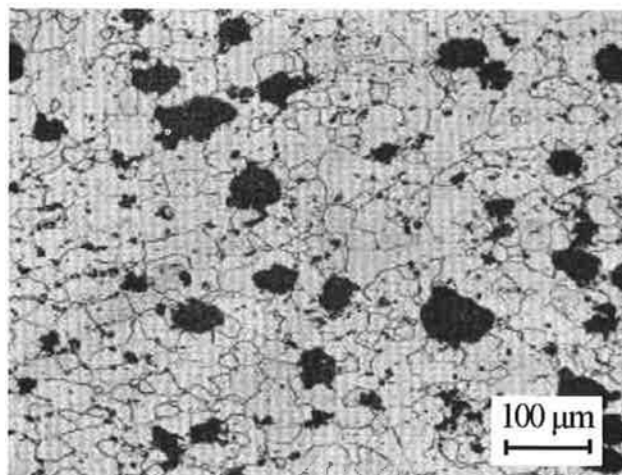


Fig. 13.12. A micrograph of a malleable cast iron is shown, illustrating graphite nodules formed by solid state decomposition of iron carbide.

is provided by graphite flotation (actually gravity segregation) to the cope surface of large ductile iron castings.

A variation on the solid state growth mechanisms is provided by the various austenite encapsulation theories. These postulate that the graphite nodule becomes encapsulated in an austenite shell and grows by solid state diffusion of carbon through this shell (Fig. 13.13). A uniform diffusion rate through the shell leads to equal growth rates in all directions, and a spheroidal shape results.

Most likely, this idea arose from the observation of carbon depleted (ferrite) rings around the nodules. These rings are, however, largely the result of diffusion in the solid state after completion of solidification. Quenching experiments have established that at least most of the nodular graphite growth takes place in direct contact with the liquid. Encapsulation by austenite at a later stage of solidification is not ruled out, but even if it does occur it does not account for the presence of spheroidal graphite in the liquid before encapsulation.

GAS BUBBLE THEORIES

Some of the early explanations for spheroidal growth were not based on any consideration of the theory of crystal growth and solidification. The gas bubble theories most definitely fall into this category. Proponents of these theories suggested that nodules grow from the outside toward their center after nucleating on the surface of gas bubbles existing in the melt. The supposed mechanism is illustrated in Fig. 13.14.

CO is the active gas produced by the reduction of SiO_2 inclusions by carbon at the gas-liquid interface. Graphite then nucleates at this interface and grows inward in the "c" direction until the bubble is more or less filled. Aside from being difficult to visualize, this

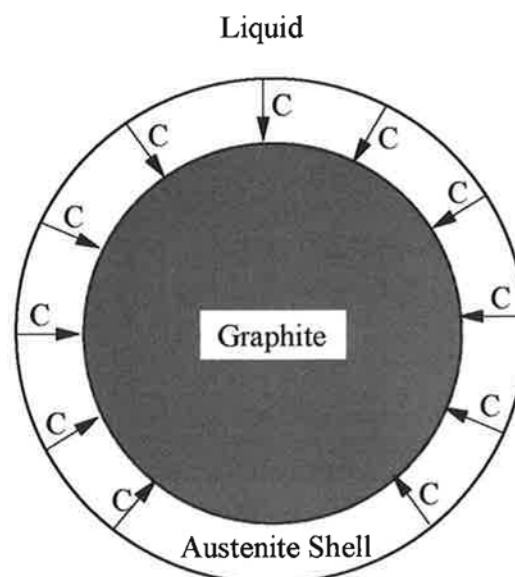


Fig. 13.13. The proposed mechanism of growth of a graphite nodule encapsulated by an austenite shell is shown.

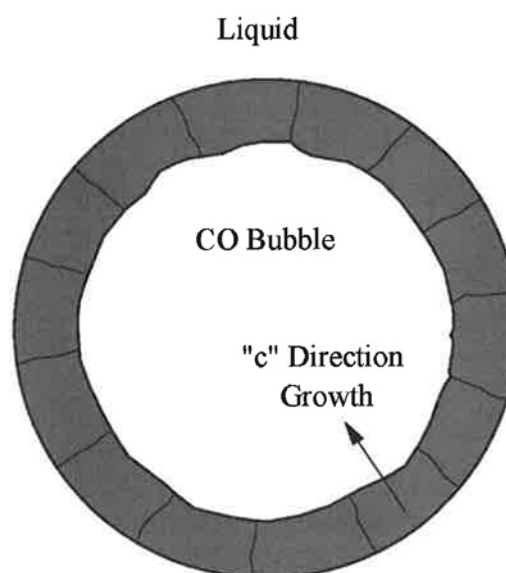


Fig. 13.14. The supposed mechanism of growth of a graphite nodule inside a CO gas bubble is illustrated.

theory suffers from two major difficulties. First, there is no evidence of the presence of large numbers of minute gas bubbles in liquid ductile iron. The mechanism requires one bubble for each nodule produced. Second, the mechanism does nothing to explain why graphite should grow in the “c” direction when under all other circumstances it grows in the “a” direction.

NUCLEATION THEORIES

Also included in the early thinking on ductile iron production were hypotheses stating that the nodularizing element produced special nuclei that led to spheroidal graphite growth. The exact nature of these nuclei was not specified, and the idea fails on two important counts. As seen in Chapter 4, the simple theory of heterogeneous nucleation predicts that nucleating ability is primarily a function of crystal structure matching across the nucleus-substrate interface. The crystal structure of graphite is the same whether it is present as a flake or as a nodule, and a particular substrate should have the same nucleation potential for either morphology.

The second objection to the nucleation hypotheses arises from difficulty in seeing how the nucleation stage of the freezing process can influence the subsequent growth stage to such a large extent. While nucleation events determine features, such as the number of graphite particles, their growth and not their nucleation mechanisms govern the morphology of these particles.

SURFACE TENSION THEORIES

These theories relate to the effect of magnesium on the surface tension of liquid cast iron (Fig. 13.15). Magnesium additions act to increase the surface tension to some maximum value, most likely the result of interactions between magnesium and dissolved atomic sulfur to form the compound MgS. It is known that dissolved sulfur decreases the surface tension of liquid iron, but sulfur can be removed through magnesium additions.

Under conditions of high surface tension, a sphere should be more stable than a flake of the same volume because of its lower total surface area. The initial surface energy theories simply drew a connection between the nodular shape and the increased surface energy in the

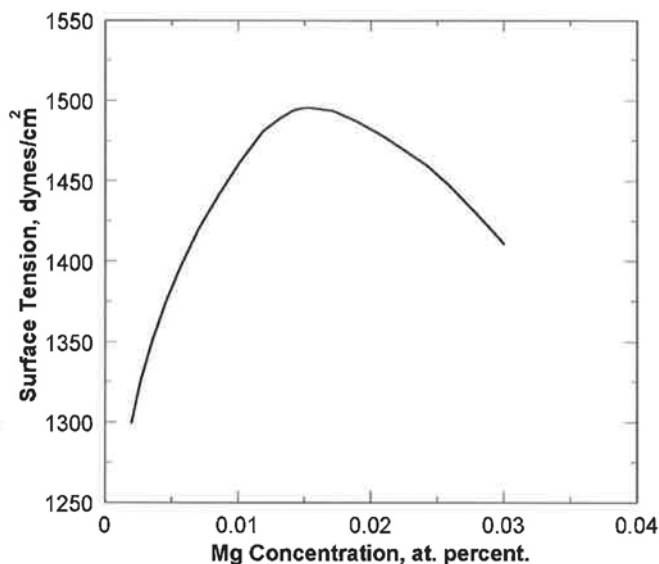


Fig. 13.15. The surface tension of liquid cast iron changes when magnesium is added.

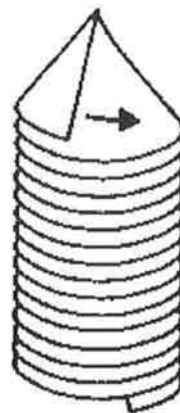


Fig. 13.16. Conical helix growth of graphite is illustrated.

presence of magnesium; however, later, more sophisticated, approaches attempt to explain how the growth mode changes from the “a” to “c” direction.

These refinements to the surface energy theories make use of the fact that graphite, like some other materials, can exhibit a phenomenon known as curved crystal growth. Crystals growing on a substrate can be made to curve as a result of stresses between the two. The most familiar example of this is the formation of large ice dendrites (frost) on window panes during the winter. These frost patterns often consist of large sweeping dendrites that gently curve across the window due to the ice-substrate stresses.

It is supposed that graphite, like ice, also can undergo curved crystal growth. Pyrolytic graphite, for example, is known to form as a conical helix (Fig. 13.16) in which growth is on the prism planes (“a” direction growth), with the basal planes forming the bounding surfaces of the helix. Two possible models for graphite nodule growth have been proposed using the principle of curved crystal growth. These are illustrated in Figs. 13.17 and 13.18.

One model, (Fig. 13.17), proposes that the nodule grows as a series of conical helices from a common nucleus, thus generating the internal structure of the spheroid shown in Fig. 13.10. The second model, (Fig. 13.18), proposes that the nodule grows much like a cabbage, with leaves of graphite curving around the circumference. Several leaves are present at any one time, and their growth results in a gradual increase in the diameter of the nodule.

On the surface, these two mechanisms appear quite different, but they are remarkably similar, because each one results in a sphere bounded by the (0001) planes of graphite, but in which growth is always in the “a” direction on the (10 $\bar{1}$ 0) prism planes. There is no conflict between the well established “a” direction growth of graphite flakes and the growth direction of the nodule. Both models imply that “a” direction growth is the normal and only growth direction for graphite, and that the essential difference between a flake and a nodule is the absence of curved crystal growth in the former.

Surface tension theories are supported by the well known observations that low sulfur content promotes good nodularization, and the best pig irons for ductile iron manufacture are the purest. Support is also offered by noting that nodular graphite can be produced

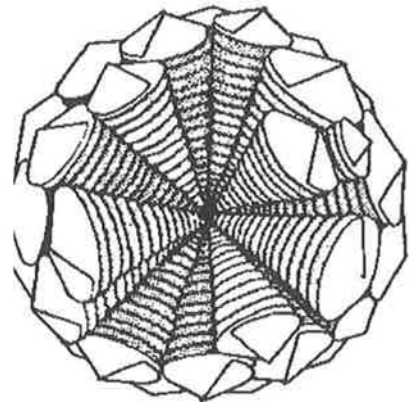


Fig. 13.17. A graphite spheroid composed of conical helices, such as that shown in Fig. 13.16, is illustrated.

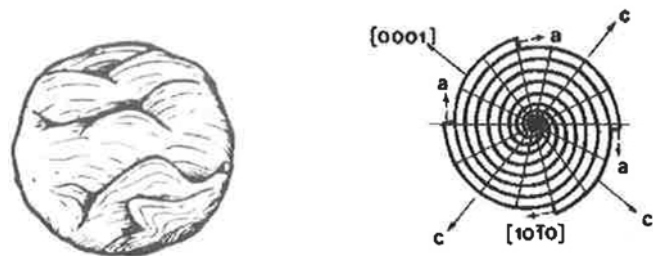


Fig. 13.18. A model of graphite spheroid growth is illustrated in which curved layers of graphite grow around the sphere circumference, much like a cabbage.

without a nodularizer if melts of very high purity are prepared in vacuum.

GROWTH POISONING THEORIES

The surface active nature of graphite implies that elements present in a cast iron melt may adsorb onto one or more of the growing crystal planes. If this happens, atomic density on these planes is altered, and significant changes in the solidification kinetics on the affected planes also can take place. For example, a normally rapid growing plane might experience a marked decrease in growth rate in the presence of surface adsorption. Since flakes and nodules appear to form by growth in different directions within the graphite crystal lattice, i.e., “a” versus “c” growth, theories explaining this difference based on poisoning of growth on the prism or basal planes are numerous.

Surface adsorption occurs preferentially on planes of lower atomic density. In the case of graphite, these are the $[10\bar{1}0]$ prism planes. Elements likely to be adsorbed are sulfur and oxygen, both of which are present in cast iron melts and are known to affect the quality of ductile cast iron. Nodularizing elements scavenge these impurities from the melt by forming stable compounds with them, e.g., MgS , and it is also possible that the nodularizing elements themselves may adsorb onto the growing graphite crystals.

Several variations of the effect of growth poisoning have been proposed. In each case, it is necessary to consider the effect of surface adsorption on the solidification kinetics of either the basal or the prism planes of the graphite. If graphite crystallizes by 2D nucleation and growth, then the growth rate will be fastest on the most densely packed plane simply because chances for nucleation of new atomic layers are greatest there. Normally, this would be the (0001) basal plane, which may explain why spheroids form in very pure melts in the absence of nodularizers.

When impurities are present, however, these will adsorb onto the less dense prism planes, thus increasing the atomic density on these planes and favoring increased 2D nucleation and subsequent growth. Flakes bounded by the basal planes would result and, indeed, flake morphology is the one commonly found in normal impure cast irons. The action of the nodularizing element then is to scavenge the impurities and allow 2D nucleation and

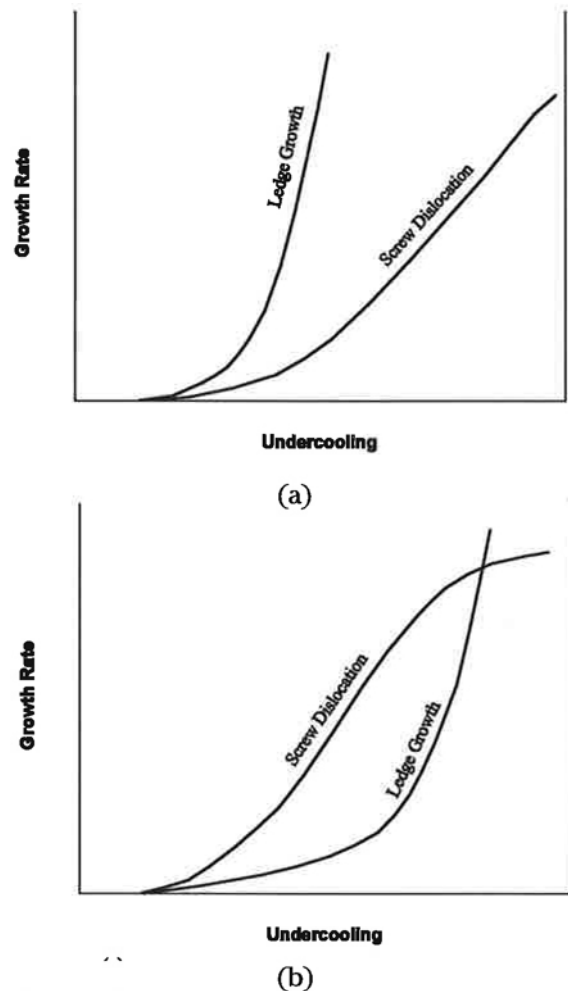


Fig. 13.19. Hypothetical growth rate/undercooling relationships are shown for growth on the prism planes by two-dimensional nucleation and growth and by screw dislocation growth on the basal planes: (a) without a nodularizing element; (b) with nodularizing element adsorption on the prism planes.

growth on the basal plane to again become predominant. In other words, the melt is purified as far as graphite growth is concerned.

It is also possible that the reactive nodularizing elements themselves adsorb onto the prism planes. If these atoms were located at the ledges caused by twisting about the “c” axis (Fig. 13.7a), growth in the “a” direction would effectively be blocked and the rate of screw dislocation growth on the basal plane might become greater than the rate of 2D nucleation and growth on the prism plane, see Fig. 13.19. This leads to growth of a polycrystalline graphite spheroid.

RATIONALIZATIONS

It is clear that our understanding of the commercially important flake to nodule transition is far less than complete. No one theory or hypothesis seems to account for all of the observations, but the most essential points appear to be:

- surface active impurity elements (S, O, etc.) are important in graphite growth;
- removal of these elements, either by using ultra pure starting materials or by scavenging with a nodularizing element, promotes spheroidal growth;
- high purity liquid cast irons have a higher surface tension than do lesser purity liquid cast irons; and
- under some circumstances, graphite can grow in a curved manner by atom addition to the prism planes.

Considering the above, it is likely that the final mechanism for the flake to nodule transition in cast iron will be based on the increased melt surface tension caused by the scavenging action of the nodularizer. Also influential would be the growth poisoning which favors curved crystal growth by atom addition onto the prism planes. The flake and the nodule may be very different in appearance, but their basic growth process is probably the same—atom addition onto the (1010) prism planes of graphite.

GROWTH OF COMPACTED AND OTHER FORMS OF GRAPHITE

With the confusion surrounding the spheroidal graphite growth mechanism, it is not surprising that little is understood about the growth of other forms. It is assumed that twin/tilt boundaries are important in the formation of compacted graphite. As illustrated in Fig. 13.20, compacted graphite grows by atom addition to the (1010) planes and these planes occasionally tilt by a twinning mechanism to produce the zigzag flake shape of the compacted structure. Twin boundaries are readily seen in compacted graphite, under polarized light, so this general mechanism seems reasonable, but the role of the various chemical elements that produce compacted graphite is not at all understood.

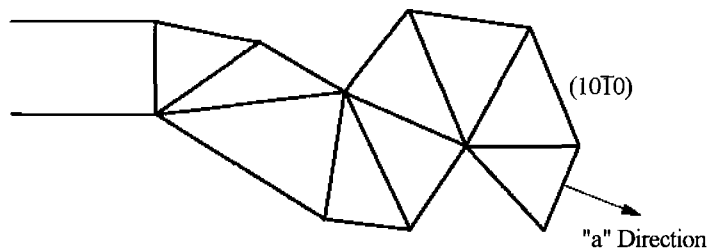


Fig. 13.20. A possible mechanism for the formation of compacted graphite by zigzag growth at twin/tilt boundaries is illustrated.

Other degenerate forms of spheroidal graphite may form by breakdown of the graphite-liquid interface. Exploded graphite could form in this way. The transition illustrated in Fig. 13.21 proposes that the interface gradually becomes cellular, and deepening of the cell walls ultimately leads to a star-like shape. The driving force for breakdown of the original spheroid is not known. It could be constitutional undercooling caused by impurity elements, but faceted materials like graphite are often so stabilized by surface energy and crystallographic considerations that constitutional undercooling has little effect on growth morphology.

Chunk graphite (Fig. 13.3e) often is found in the center of heavy section ductile iron castings. Although the mechanism of its formation is not understood, the fact that it occurs in the last part of the casting to freeze has led to an association between slow solidification rates and chunk graphite formation. In addition, segregation of subversive elements to the last regions of the casting to solidify also may contribute to formation of this degenerate form of graphite.

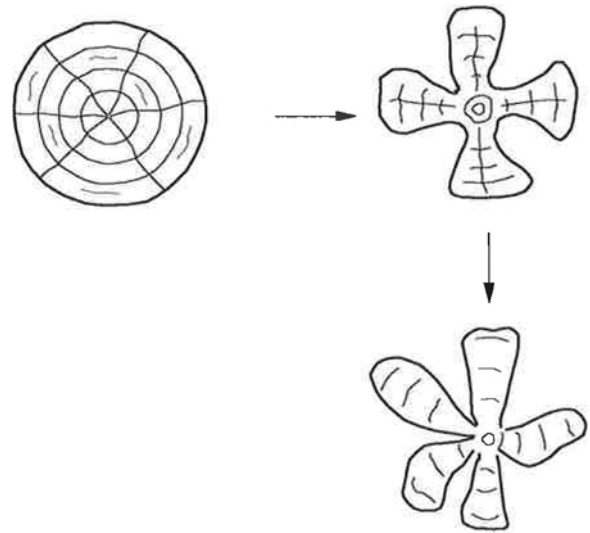


Fig. 13.21. Exploded graphite may form by breakdown of the graphite phase/liquid interface to form a series of deep cell boundaries.

MODIFICATION OF ALUMINUM-SILICON ALLOYS

Most aluminum alloys used for foundry applications are based on the Al-Si eutectic system with silicon concentrations in the 5-19% range. When cast, these alloys contain high percentages of the Al-Si eutectic structure, which tends to determine the mechanical properties of the alloy. The normal microstructure of this eutectic, seen in Fig. 13.22a, consists of coarse silicon needles embedded in a matrix of aluminum solid solution. The needles, seen on a two-dimensional metallographic section, are in reality plates, as revealed by the SEM image of the deep etched eutectic structure shown in Fig. 13.22b. These coarse platelets act as internal stress raisers causing the alloy to be relatively brittle and weak, in much the same way that graphite flakes influence the properties of gray cast iron.

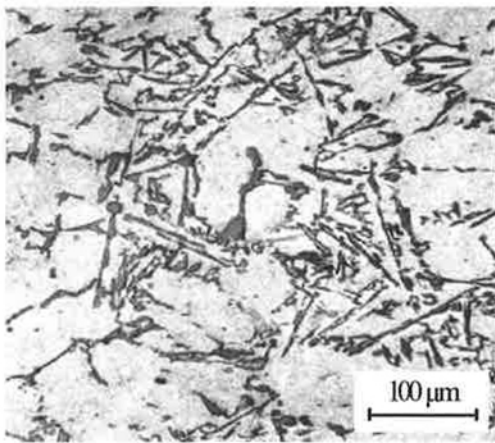
A morphological change known as eutectic modification is, however, possible. Several elements are capable of causing this modification, but the most commonly used are sodium or strontium in the 50 to 200 ppm. range. Addition of the correct amount of these elements causes the coarse acicular structure of the unmodified alloy to change to a fine fibrous one, as seen in the photomicrographs of Figs. 13.22c and d. This finer and more rounded silicon structure imparts a significant increase in both ductility and strength to the alloy. Some typical mechanical properties of as-cast modified and unmodified A413 alloy are given in Table 13.2.

In a manner similar to the production of ductile cast iron, the technology of eutectic

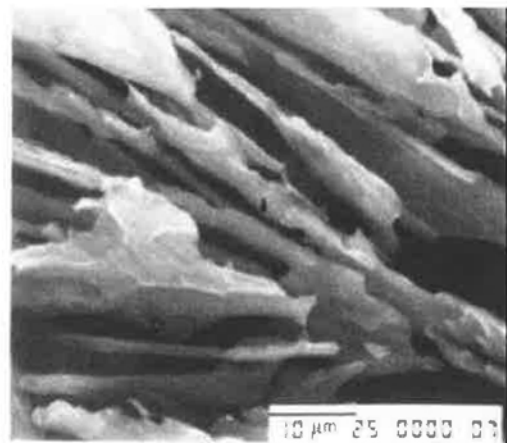
TABLE 13.2.
Typical Properties of Modified and Unmodified AS-CAST 413 Alloy

PROPERTY	UNMODIFIED	MODIFIED
Tensile strength (MPa)	148	175
Percentage elongation	2.5	13
Impact strength (J cm^{-2})*	5	39
Yield Strength (Mpa)	65	71

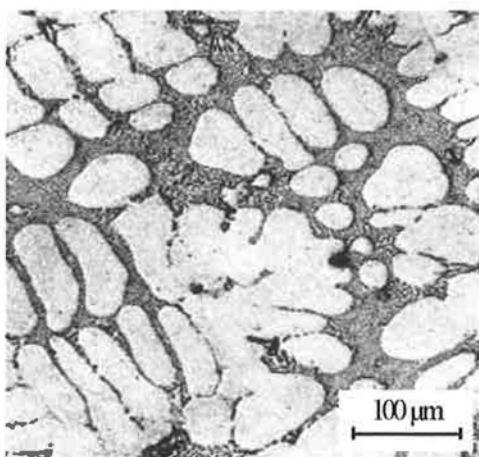
* UNNOTCHED CHARPY



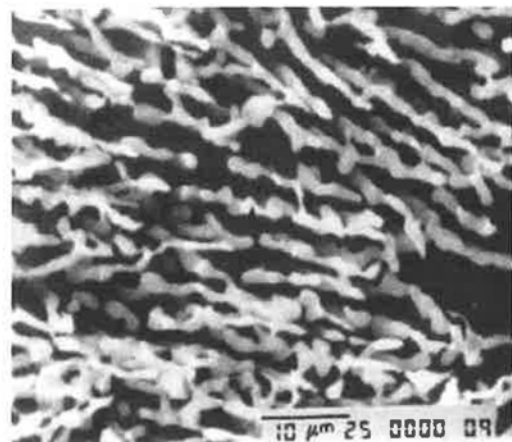
(a)



(b)



(c)



(d)

Fig. 13.22. Microstructure of the cast Al-Si eutectic is shown as: (a) an unmodified structure; (b) an unmodified structure seen on a deep etched sample by SEM; (c) a modified structure; and (d) a modified structure seen on a deep etched sample by SEM.

modification is now well established and suggested references are provided at the end of the chapter. The mechanism of the modification process, likewise, has been the subject of considerable controversy, but it is now better established than the flake-nodule transition in cast irons. Our examination of the eutectic modification process will begin with an explanation of the growth of unmodified silicon.

SILICON GROWTH FROM THE MELT

Silicon, like graphite, is a faceted material in which crystallography plays a dominant role in growth from the melt. Silicon readily forms crystallographic twins, and acicular silicon crystallizes by a 2D nucleation and growth process in which nucleation of atomic layers is aided by the presence of such twins.

This twin plane re-entrant edge (TPRE) mechanism can be understood with the help of Fig. 13.23. Intersection of the twin planes with the solid-liquid interface creates a series of grooves containing a 141° angle. Nucleation of new atomic layers takes place at the base of these grooves, because it is here that any newly added atoms have the greatest number of nearest neighbors. Growth then occurs by extension of the newly nucleated layer up the two sides of the groove and across the interface. Growth by the TPRE mechanism is highly directional, and results in the large flat crystals bounded by (111) planes evident in Fig. 13.22b.

MODIFIED SILICON GROWTH FROM THE MELT

Fibrous modified silicon differs from acicular silicon, not only in morphology, but also in terms of number of twins that are found in the silicon. Twins are easily seen by

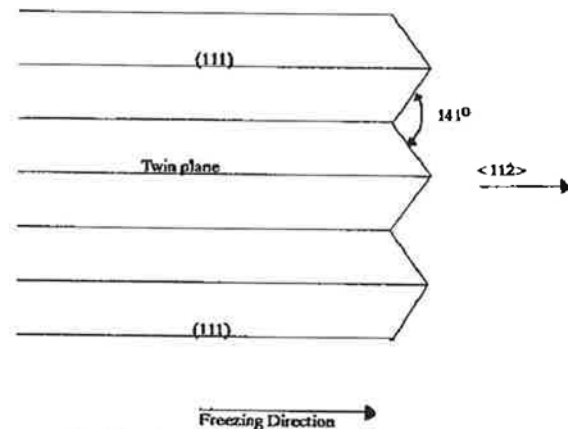


Fig. 13.23. The twin plane re-entrant edge growth mechanism (TPRE) of silicon is illustrated.

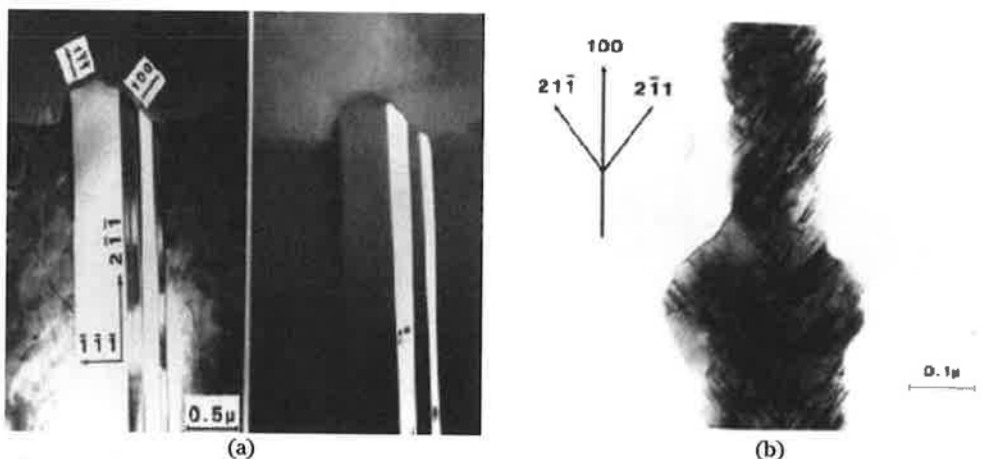


Fig. 13.24. Transmission electron micrographs of unmodified (a) and modified (b) eutectic silicon reveal large differences in their twin densities. [Reproduced with the permission of the Minerals, Metals and Materials Society from Shu-Zu Lu and A. Hellawell, *Metallurgical Transactions A*, vol 18A, pp 1721-33 (1987).]

transmission electron microscopy, which reveals significant differences between the two types of silicon (Fig. 13.24). Unmodified silicon (a) shows a very low twin density with the twins running parallel to the flat faces of the silicon crystal, as anticipated on the basis of the TPPE mechanism. Modified silicon (b), on the other hand, contains a very high twin density and a much rougher external surface than does acicular silicon.

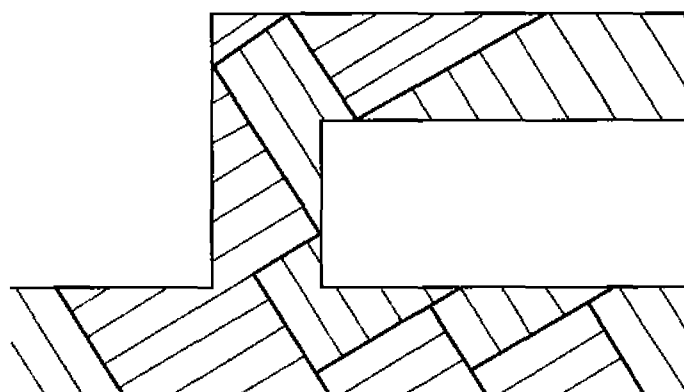


Fig. 13.25. Multiple twinning sequence leading to formation of a branched modified silicon particle is illustrated. Location of the parallel atom planes in each twin sequence is indicated.

Crystallographic studies of silicon have revealed that impurity elements of the correct size can trigger twin formation when these elements are incorporated into the crystal structure of silicon. The ideal atomic radius ratio, $r_{\text{impurity}}/r_{\text{silicon}}$, is 1.646 for maximum twin generation. Commercial modifying elements do have atomic radii that yield ratios in this range, and measurements of the twin density in modified silicon particles show that elements producing the finest modified structures, Na for example, also result in the smallest twin spacing and, hence, the greatest twin density. Some measured twin spacings are listed in Table 13.3.

Multiple twinning caused by modifier element incorporation into silicon allows the growing silicon crystal to bend and twist in a zigzag type of motion. Each twinning event causes a change in local growth direction until the next twinning event, resulting in a bent fibrous structure. A good example is given in Fig. 13.25, which shows how multiple twinning can lead to a branched silicon crystal. Short spurts of growth in one direction are followed by equally short spurts in another direction. This mechanism, based on the generation of crystallographic defects, is not dissimilar to that proposed for the growth of compacted graphite, (Fig. 13.20), and emphasizes the important role of crystal defects in the solidification of faceted materials.

Table 13.3.
Measured Twin Spacings in Eutectic Silicon²

SILICON STRUCTURE	MODIFIER	TWIN SPACING (nm)
acicular	none	400
modified	Na	5
modified	Sr	30
modified	Ba	30
modified	Ca	100
modified	Yb	50

It is interesting that, as with nodular graphite growth in cast irons, there is an element interfering significantly with the growth process. In the case of ductile cast iron, this element is sulfur; in the case of silicon modification, it is phosphorus. It is well known that high phosphorus-containing alloys are much more difficult to modify than are low phosphorus alloys. Apparently, modifiers such as Na or Sr act as scavengers to remove phosphorus from the melt in the form of phosphides. Nodularizers, such as Mg, remove sulfur in the form of sulfides.

MODIFICATION OF IRON-BEARING INTERMETALLICS IN WROUGHT ALLOYS

Wrought aluminum alloys contain a number of intermetallic phases that play an important role in determining their mechanical properties and formability. Many of these alloys contain iron and silicon, and in such alloys, two of the most important intermetallics are $\text{Al}_8\text{Fe}_2\text{Si}$ (α -AlFeSi) and Al_5FeSi (β -AlFeSi).

Of these two, β -AlFeSi is the least desirable. This phase forms highly faceted platelets on solidification which, like acicular silicon or graphite flakes, deteriorate the mechanical properties of the alloy. The interface between the platelet and the surrounding matrix is flat and strained, as seen in the transmission electron micrograph of Fig. 13.26. As a result, these particles are easily torn out of the microstructure during extrusion processes, and contribute to surface defects known as pickup.

Figure 13.27 shows the α -AlFeSi intermetallic, which forms a more rounded Chinese script morphology, resulting in a lowered stress concentration on loading and a less deleterious effect on mechanical properties. In addition, the interface between the intermetallic and the aluminum matrix is atomically rough, (Fig. 13.28), contributing to a greater stability of the intermetallic within the matrix during extrusion and a lessened tendency for pull-out and the generation of surface defects.

Several technologies exist to promote the formation of the more desirable α form. Long heat treatment processes can be used on the billets before extrusion, or additions of Mn, Cr or Co will promote formation of α -AlFeSi on ingot solidification. Transition element additions are undesirable in some applications, such as electrical conductors, because of the increase in electrical resistivity brought about by these elements. Recently, it was discovered that microadditions of strontium will promote α -AlFeSi stabilization. While

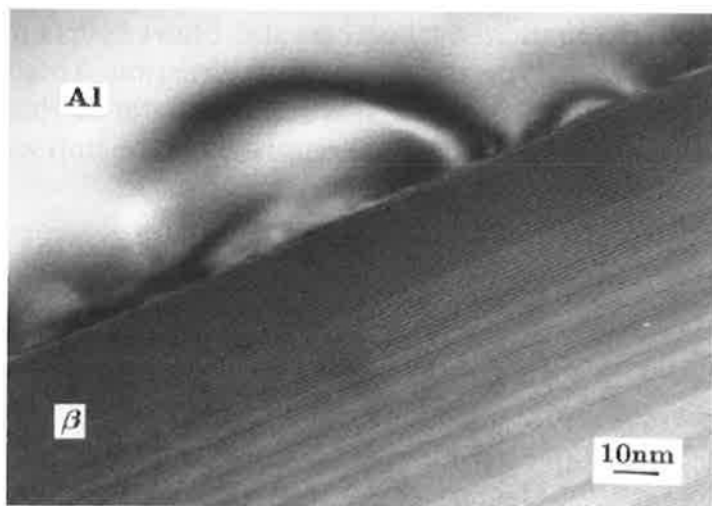


Fig. 13.26. A transmission electron micrograph of the β -AlFeSi interface with the aluminum matrix shows the faceted nature of the interface and strain contours present in the matrix at the interface. [Reproduced with permission of The Minerals, Metals and Materials Society from M.H. Mulazimoglu, A. Zaluska, J.E.Gruzleski, F. Paray, *Metallurgical and Materials Transactions A*, vol 27A, pp 929-936 (1996).]

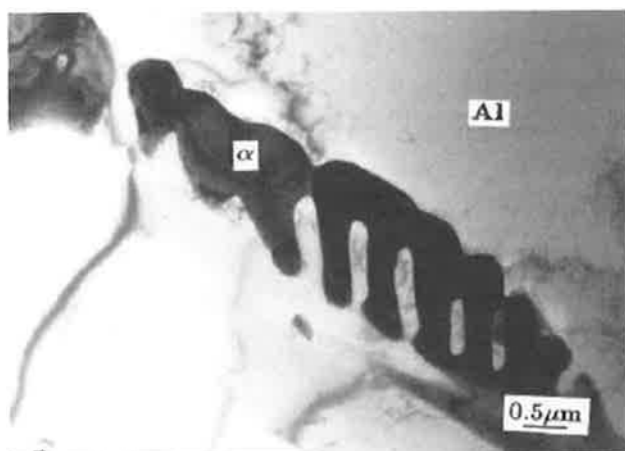


Fig. 13.27. A transmission electron micrograph of the Chinese script α -AlFeSi is shown.

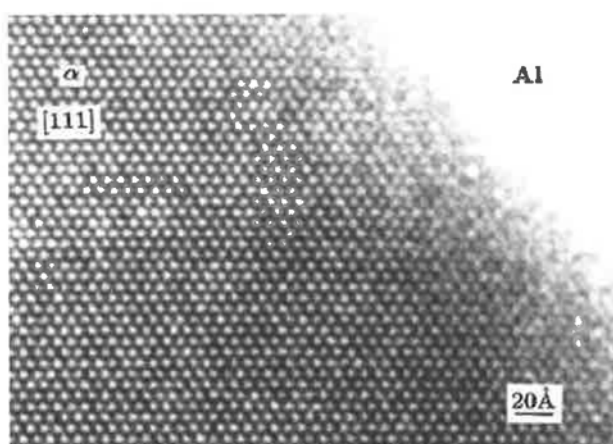


Fig. 13.28. A high resolution transmission electron micrograph of the interface between α -AlFeSi and the aluminum matrix is shown. [Reproduced with permission of The Minerals, Metals and Materials Society from M.H. Mulazimoglu, A. Zaluska, J.E. Gruzleski, F. Paray, *Metallurgical and Materials Transactions A*, vol 27A, pp 929-936 (1996).]

the mechanism is not yet completely understood, this is yet another example of morphological modification caused by a surface active element.

The effects of a 30 ppm Sr addition to the cast structure of a 6201 electrical conductor alloy are evident in Fig. 13.29b, where the needle-like β -AlFeSi has been replaced by the Chinese script α -AlFeSi in the presence of strontium. In this case, the mechanism of microstructural modification involves a blocking of the normal reaction sequence during alloy solidification. Al_5FeSi , which is the phase normally formed, is thought to be the result of the following series of reactions:

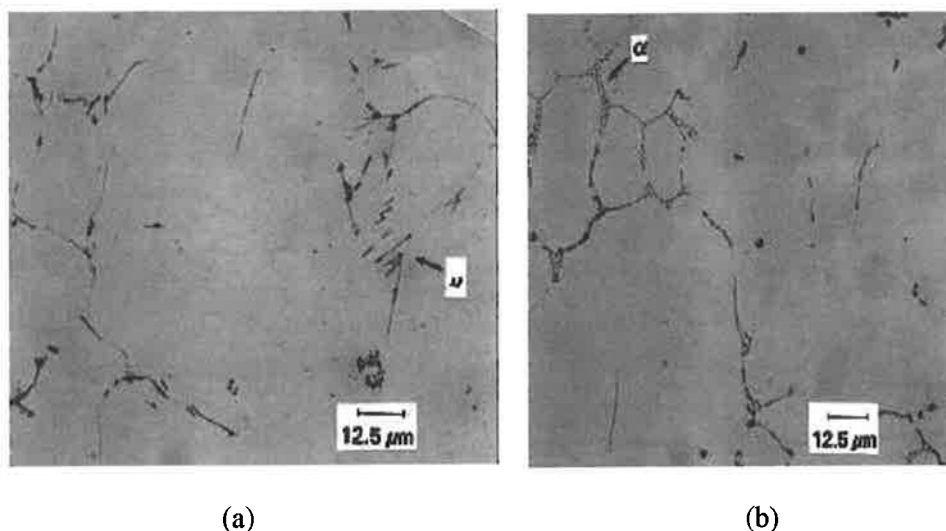


Fig. 13.29. The cast microstructure of a 6201 electrical conductor alloy is shown: (a) without strontium; and (b) containing 30 ppm of strontium. [Reproduced with permission of The Minerals, Metals and Materials Society from M.H. Mulazimoglu, A. Zaluska, J.E. Gruzleski, F. Paray, *Metallurgical and Materials Transactions A*, vol 27A, pp 929-936 (1996).]

(reaction 1)	$L \rightarrow \alpha \text{ (Al)}$ dendritic network	655C (1211F)
(reaction 2)	$L \rightarrow \alpha \text{ (Al)} + \text{Al}_8\text{Fe}_2\text{Si}$	618-615C (1144-1139F)
(reaction 3)	$L + \text{Al}_8\text{Fe}_2\text{Si} \rightarrow L + \alpha \text{ (Al)} + \text{Al}_5\text{FeSi}$	612C (1133.6F)
(reaction 4)	$L \rightarrow \alpha \text{ (Al)} + \text{Al}_5\text{FeSi} + \text{Si} + \text{Mg}_2\text{Si}$	585C (1085F)

In this sequence, the key reaction is the peritectic decomposition of $\alpha\text{-AlFeSi}$ at 612C to form the $\beta\text{-AlFeSi}$. The presence of $\alpha\text{-AlFeSi}$ in the room temperature microstructure implies that the reaction sequence ceases at reaction 2 and that the subsequent reactions are suppressed by the microadditions of strontium. The transmission electron micrograph of Fig. 13.30 provides some clues as to how this may occur.

A silicon rich layer is found to surround the unreacted $\alpha\text{-AlFeSi}$ in the presence of strontium. It is believed that strontium, being a surface active element, adsorbs onto the surface of the $\alpha\text{-AlFeSi}$ and presents a barrier to silicon diffusion into the $\alpha\text{-AlFeSi}$. Silicon diffusion is necessary for the transformation, as Al_5FeSi contains more silicon than does $\text{Al}_8\text{Fe}_2\text{Si}$. Thus, reaction 3 at 612C is prevented, and the desirable $\alpha\text{-AlFeSi}$ is retained in the microstructure.

COMMON THREADS

In this chapter we have examined three important examples of microstructural modification by ppm additions of reactive elements to the base alloy. Although the alloys and their uses are very different, there are several features they have in common, and it is quite possible that microstructural modification by microalloy additions may prove beneficial in many situations not yet identified.

Among the common threads in this phenomenon, we may list the following.

- Faceted phases are amenable to modification. In metal systems, these are intermetallics, semi-metals or nonmetals.

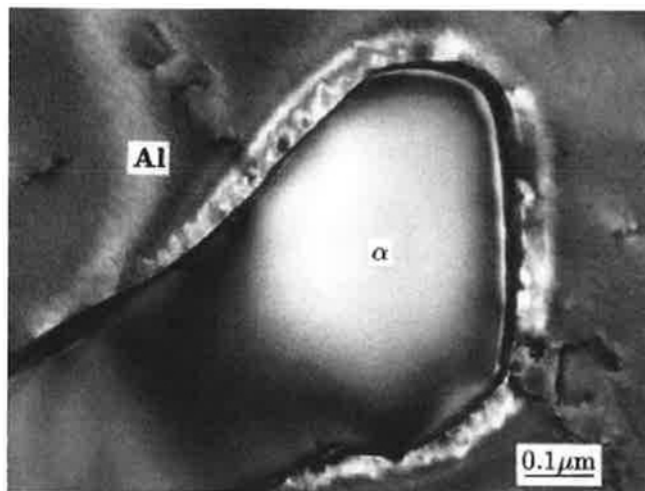


Fig. 13.30. A transmission electron micrograph of $\alpha\text{-AlFeSi}$ in a strontium treated 6201 alloy reveals a silicon layer at the boundary between the $\alpha\text{-AlFeSi}$ and the aluminum matrix. [Reproduced with permission of The Minerals, Metals and Materials Society from M.H. Mulazimoglu, A. Zaluska, J.E. Gruzleski, F. Paray, *Metallurgical and Materials Transactions A*, vol 27A, pp 929-936 (1996).]

- Defects in the crystal structure, such as twin boundaries, twist boundaries or tilt/twist boundaries, play a key role in bringing about microstructural modification. This is because of the role that crystallography always plays in the solidification of faceted materials.
- The element causing the modification is often a scavenger for surface active elements that are impurities in the alloy. For example, magnesium scavenges sulfur in cast iron, and strontium scavenges phosphorus in aluminum alloys.
- Rare earth elements and alkali metals seem to be active microstructural modifiers and would make a good starting point in the search for new applications of this facet of solidification science.

MICROSTRUCTURE DEVELOPMENT DURING METALCASTING

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