APPENDIX **B**

Fundamentals of Solidification

ALMOST ALL METALS AND ALLOYS are produced from liquids by solidification. Sometimes, the liquid metal is poured in a mold with a shape that is close to the desired final shape, a process called casting. The cast part then requires little or no final machining prior to use. On the other hand, simple castings called ingots are initially cast and then shaped by combinations of hot and cold working into wrought product forms, such as plate, sheet, or bar stock. For both castings and wrought products, the solidification process has a major influence on both the microstructure and mechanical properties of the final product.

B.1 The Liquid State

The liquid state is intermediate between a gas and a crystalline solid. Liquids possess neither the long-range order of solids nor the complete disorder of gases. Liquids do, however, possess short-range order. In fact, the structure of liquid metals is very close to the solid that freezes from it. For close-packed metals with the face-centered cubic (fcc) and hexagonal close-packed (hcp) crystalline structures, melting causes a volume decrease of only 3.5 to 6% and even less in the more loosely packed body-centered cubic (bcc) metals, which usually exhibit a volume decrease of only 1 to 3% on freezing. Some elements with even looser atomic packing, such as silicon, actually expand on freezing. In addition, the latent heat of fusion is only approximately 3 to 4% of the corresponding latent heat of vaporization. The small amount of volume change and the relatively small latent heats of fusion are evidence that the atomic bonding in liquids and solids is very similar.

X-ray diffraction studies of liquid metals indicate that the atoms in liquids are arranged in an orderly manner over short distances, but lack long-range order. This is probably due to the presence of increased amounts of defects

such as vacancies, interstitials, and dislocations. This large population of defects is believed to be responsible for the much higher rates of diffusion in liquid metals. The higher diffusion rates leads to a picture of liquid metals in which the structure is continuously changing. Atoms form clusters with a high degree of short-range order that may exist for a moment and then fall apart to appear again in another location. As the liquid is cooled towards its freezing point, the degree of short-range order increases and the ordered clusters become larger and more stable.

B.2 Solidification Interfaces

The solidifying solid-liquid interface can exhibit one of three types of interfacial growth in the liquid: planar, cellular, or dendritic. As shown in Fig. B.1, the type of growth is controlled by the manner in which heat is removed from the system. When the liquid ahead of the solid-liquid interface has a positive temperature gradient, heat is removed from the liquid by conduction through the growing solid. Because the temperature gradient is linear and uniform perpendicular to the interface, a smooth interface is maintained and the growth is planar into the liquid (Fig. B.1a). When there is a temperature inversion and the temperature decreases ahead of the solid-liquid interface, then either cellular or dendritic growth will occur (Fig. B.1b, c). The difference between the two is a matter of degree; small undercoolings will tend to produce cellular growth, while large undercoolings will tend to produce dendritic growth. In pure metals, undercooling can result from thermal supercooling, while in alloys, it can result from a combination of thermal and constitutional supercooling.

Thermal supercooling. Cellular growth, as illustrated in Fig. B.2, occurs when the advancing planar solid-liquid interface becomes unstable, and a small spike appears on the interface that then grows into a cellular-type structure. The planar surface becomes unstable because any part of the interface that grows ahead of the remainder enters a region in the liquid that is at a lower temperature. The initial spikes that form remain isolated at first, because as they grow by solidification, they release their latent heat of fusion into the adjacent liquid, causing a localized increase in the temperature. Consequently, parallel spikes of almost equal spacing advance into the liquid.

Dendritic growth is a further manifestation of cellular growth in which the spikes develop side protrusions. At still higher undercooling and higher growth velocities, the cells grow into rapidly advancing projections, sometimes of complex geometry. Their treelike forms (Fig. B.3) have given them the name dendrites, after the Greek word *dendros* for tree. The secondary arms of dendrites develop perpendicular to the primary arms because, as the primary arm solidifies and gives off its latent heat of reaction, the
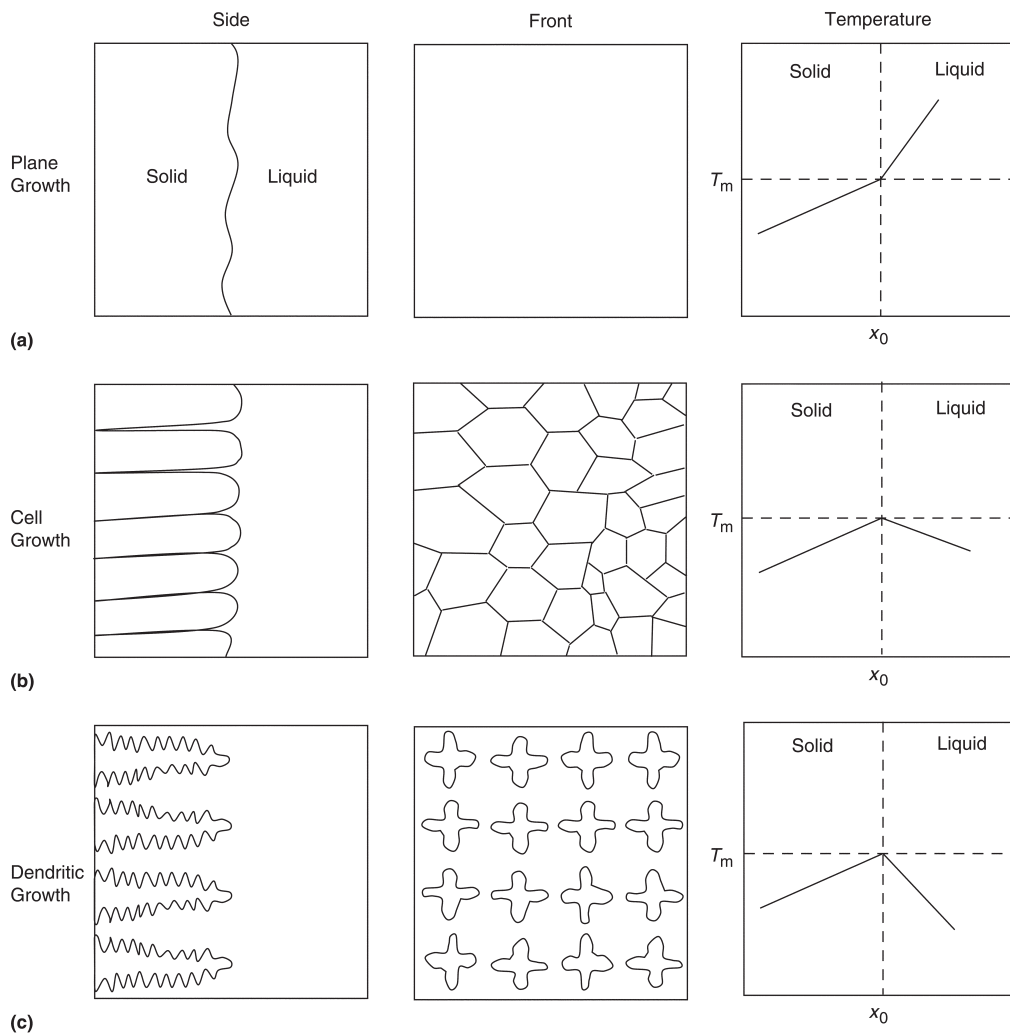
Fig. B.1   Effects of undercooling on solidification structures. Source: Ref B.1 as published in Ref B.2

temperature immediately adjacent to the primary arm increases. This creates another temperature inversion in the liquid between the primary arms, so secondary arms shoot out in that direction. A similar argument can be made for the formation of the tertiary arms. The spacing of the secondary arms is proportional to the rate at which heat is removed from the casting during solidification, with faster cooling rates producing smaller dendrite arm spacings. Dendrites start as long thin crystals that grow into the liquid and thicken. The change in interface morphology of a succinonitrile-4% acetone solution with increasing solidification velocity (Fig. B.4) demonstrates the evolution of a dendritic structure.
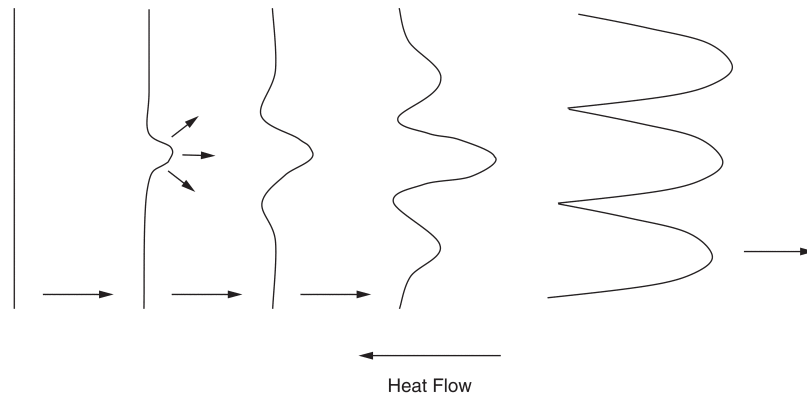
Heat Flow

Fig. B.2 Transition from planar to cellular growth. Source: Ref B.2
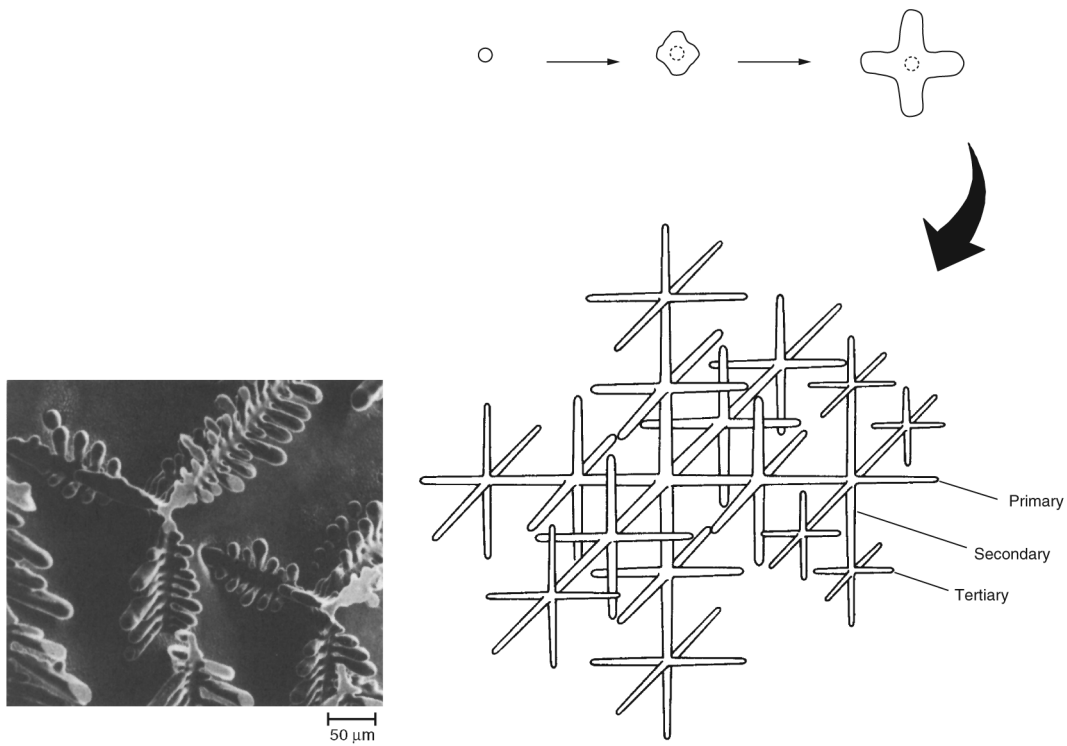

Fig. B.3 Dendrite formation. Source: Ref B.3 as published in Ref B.2

Constitutional Supercooling. While dendrites can form to a limited extent in pure metals due to temperature inversions, they are more prevalent in alloys because of the additional undercooling due to constitutional supercooling. Constitutional supercooling arises because of the
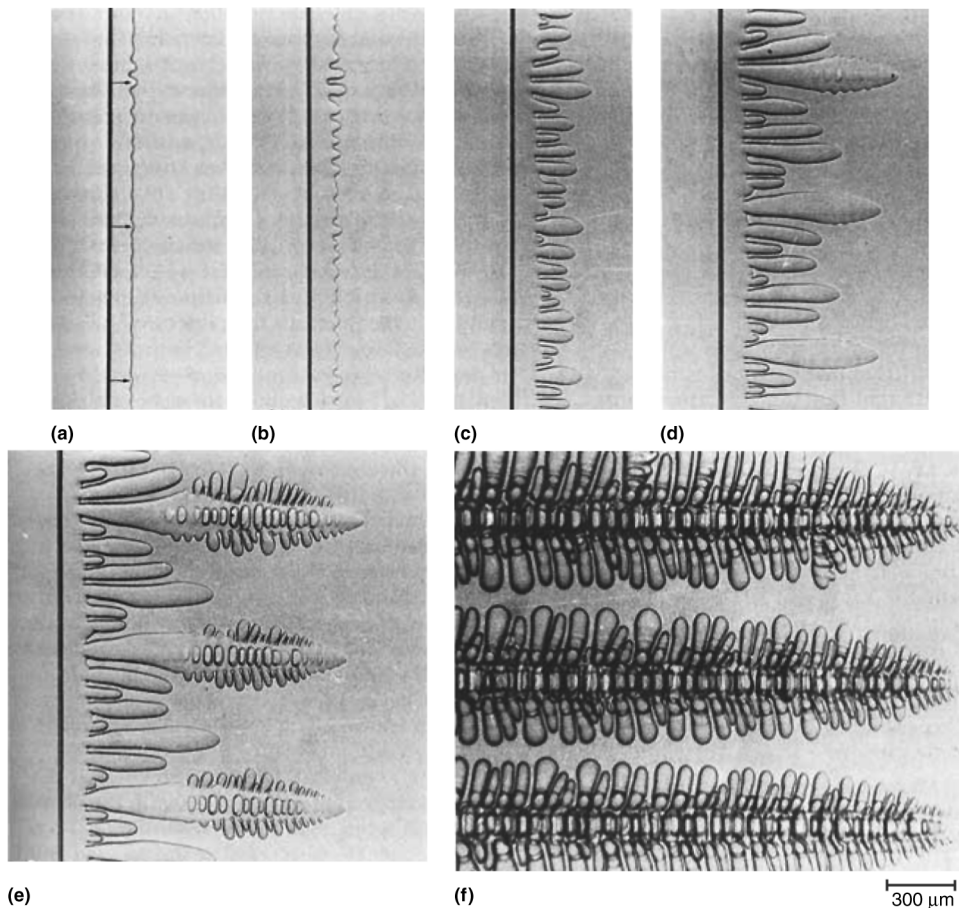
Fig. B.4 Dendrite formation in succiononitrile-4% acetone solution. Source: Ref B.3 as published in Ref B.2

segregation of alloying elements ahead of the solid-liquid front. The extra concentration of alloying elements reduces the melting point of the liquid. If this reduction is sufficient to reduce the melting point to below the actual temperature at that point, then the liquid is said to be locally constitutionally supercooled; that is, it is effectively undercooled because of a change in the constitution of the liquid.

B.3 Solidification Structures

A metal cast into a mold can have up to two or three distinct zones: a chill zone, a zone containing columnar grains, and a center-equiaxed grain zone (Fig. B.5). It should be noted that all three zones do not always occur. For example, pure metals can exhibit a chill zone and a columnar zone but do not contain a center-equiaxed zone.
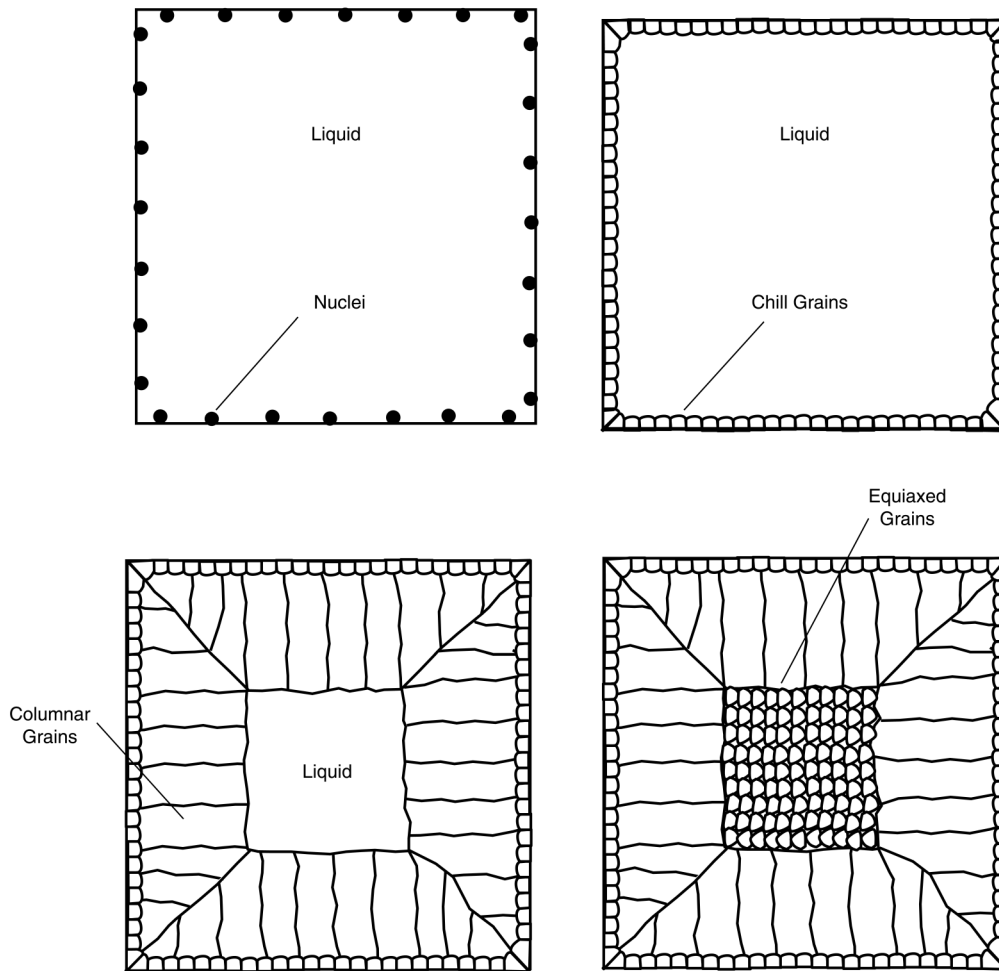
Fig. B.5 Freezing sequence for an alloy casting. Source: Ref B.3 as published in Ref B.2

Chill Zone. Because the mold is cooler than the metal, nucleation will occur over the interior surface of the mold. Because the mold wall is much cooler than the liquid metal, the nucleation rate is high and thus the average grain size is small. Each nucleation event produces an individual crystal, or grain, that grows dendritically in a direction roughly perpendicular to the mold wall until it impinges on other grains. As a large amount of latent heat of fusion is released from the solidifying grains, and as the superheat of the liquid is dissipated, the rate of growth decreases. The chill zone grains are oriented randomly with respect to the mold; that is, the major axis of each grain is randomly oriented.

Columnar Zone. Inside of the chill zone, there are a series of columnar, or column-shaped, grains that are oriented almost parallel to the heat flow direction. Because each metal grows more favorably in one principal crystallographic direction, only those grains favorably oriented with their growth direction most perpendicular to the mold wall will grow into the center of the casting. The axes of the columnar grains are parallel to the direction of heat flow and they grow along specific crystalline planes. As they grow, the more perfectly oriented grains grow ahead of the less perfectly oriented grains and crowd them out (Fig. B.6). The fact that the grains most favorably oriented to the mold wall grow the fastest means that the final shape of the grains in a pure metal casting is columnar, with the parallel columns growing progressively from the mold wall into the center of the casting. The final columnar structure results from parallel growth of different colonies of dendrites and the gradual lateral growth, or thickening, between them.

Center-Equiaxed Zone. A third region at the center of some alloy castings consists of smaller grains that are randomly oriented and nearly equiaxed. As freezing progresses, the thermal gradient decreases, and this causes the dendrites to become very long. Breakdown of columnar growth may occur as a result of fracturing of the very long dendrite grains by convection currents in the melt. These broken arms (Fig. B.7) can then serve as nuclei for new grains. Another possibility is that new grains nucleate as a result of a low thermal gradient and segregation that is occurring during freezing. At low casting temperatures, the entire the casting may solidify with an equiaxed structure.
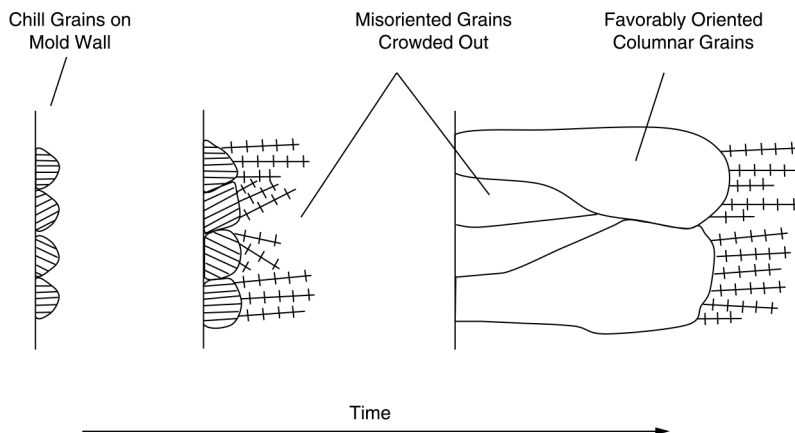

Chill Grains on Mold Wall

Misoriented Grains Crowded Out

Favorably Oriented Columnar Grains

Time

Fig. B.6 Dendritic growth from mold wall. Source: Ref B.1 as published in Ref B.2
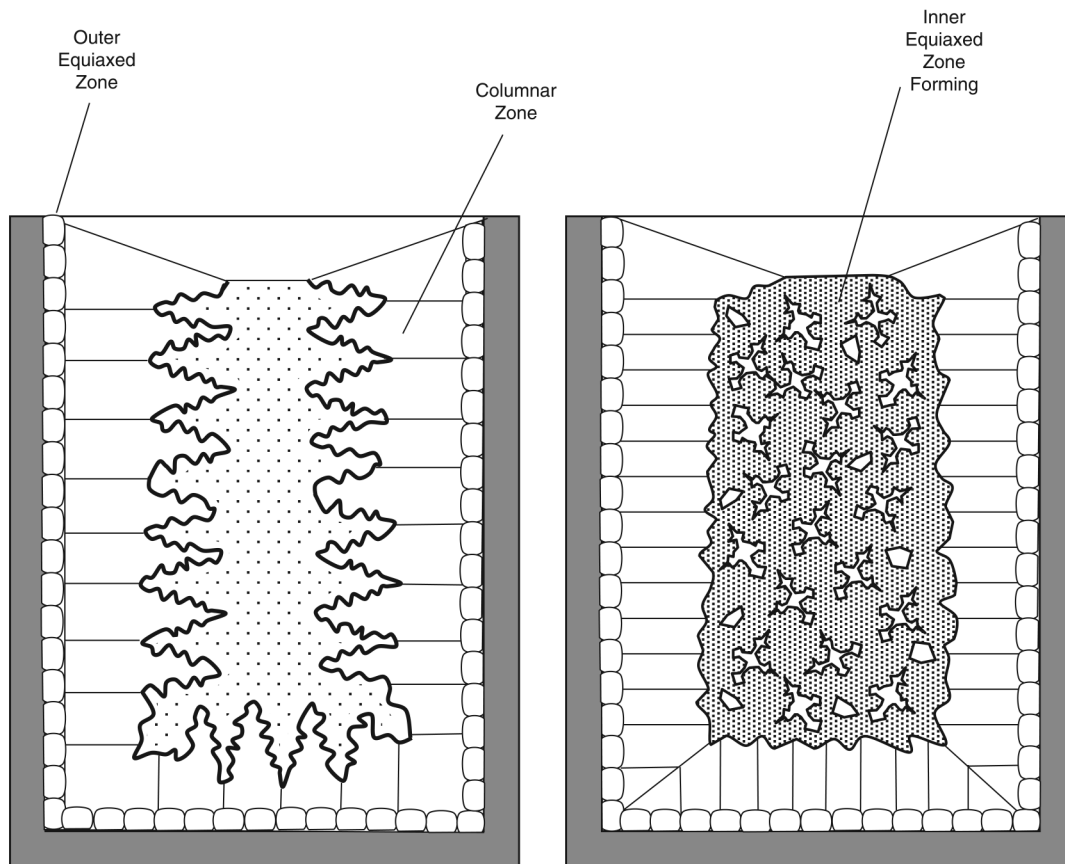
Fig. B.7 Formation of equiaxed zone in alloy casting. Source: Ref B.4 as published in Ref B.2

The amount of the final cast structure that is columnar or equiaxed depends on the alloy composition and on the thermal gradient at the liquid-solid interface during solidification. A thermal gradient is most easily controlled by controlling the rate of heat extraction from the casting, or the cooling rate. Alloys that have a wide spread between the liquidus and the solidus temperatures solidify with a mostly equiaxed grain structure at normal cooling rates, whereas alloys with small differences in solidus and liquidus temperatures solidify with a mostly columnar structure. High cooling rates encourage columnar solidification because they establish high thermal gradients at the liquid-solid interface. Low thermal gradients encourage equiaxed solidification.

B.4 Segregation

Segregation may be defined as any departure from a uniform distribution of the chemical elements in the alloy. Because of the way in which alloys

partition on freezing, it follows that all castings are segregated to different degrees. Alloys can exhibit several types of segregation, and more than one type can be present in any given casting.

Normal Segregation. Normal segregation is the result of rejection of the alloy solute at an advancing interface because it is more soluble in the liquid than the solid. As freezing progresses, there is a buildup of the solute in the liquid that freezes last, such as at the center of the casting. Such long range variations in composition are called macrosegregation. Normal segregation frequently occurs when the direction of growth is inward, as in columnar growth.

An examination of the relevant portion of a phase diagram (Fig. B.8) can be used to show the effects of segregation during freezing. The original melt of composition C_o starts to freeze at the liquidus temperature, T_L. The first solid to appear has the composition $k\,C_o$, where k is known as the partition coefficient. The partition coefficient usually has a value less than 1. For example, for $k = 0.5$, the first solid has only 50% of the concentration of alloying element compared to the original melt; the first metal to appear is therefore usually rather pure. In general, k defines how the solute alloy partitions between the solid and liquid phases. Thus:

$$k = C_S/C_L \qquad\qquad\qquad \text{(Eq B.1)}$$

where C_S is the solute fraction by weight in solid and C_L is the solute fraction by weight in liquid.

For solidus and liquidus lines that are straight, k is constant for all compositions. However, even where they are curved, the relative matching of the curvatures often means that k is still reasonably constant over wide ranges of composition. When k is close to 1, the close spacing of the liquidus and solidus lines indicates little tendency toward segregation. When k is small, then the wide spacing of the liquidus and solidus lines indicates a strongly partitioning alloying element and a tendency to segregate on solidification.

On forming the solid that contains only $k\,C_o$ amount of alloying element, the alloying element remaining in the liquid has to be rejected ahead of the advancing front. Thus, although the liquid ahead of the front was initially of composition C_o, after an advance of approximately a millimeter or so, the composition ahead of the front builds up to a peak value of C_o/k.

Gravity Segregation. Gravity segregation is another type of macrosegregation that occurs due to differences in density in the liquid melt. Denser constituents tend to sink toward the bottom, while lighter ones float toward the top.

Microsegregation. As the dendrite grows into the melt, and as secondary arms spread from the main dendrite stem, solute is rejected, effectively

Temp.

T_L

T_S

kC_o C_o C_o/k

Composition

Temp.

Freezing Point
of Melt

Actual Temp.
of Melt

Effective Undercooled Region

Composition

C_o/k

Solute-rich zone built up ahead
of advancing front as a result of
solute rejection ($k<1$) on solidification

C_o
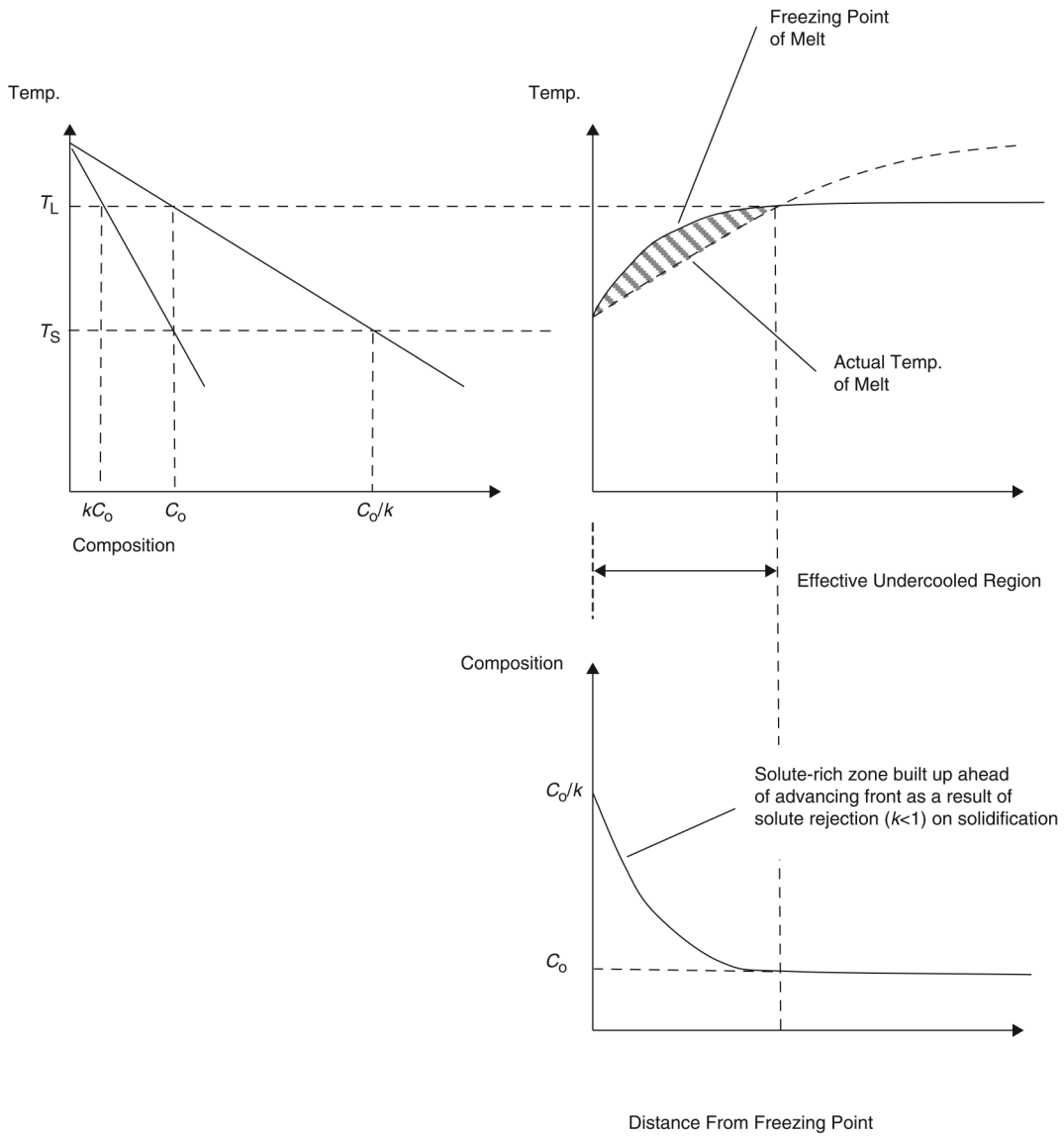
Distance From Freezing Point

Fig. B.8 Constitutional supercooling. Source: Ref B.1 as published in Ref B.2

being pushed aside to concentrate in the tiny regions enclosed by the sec-
ondary dendrite arms. This gradation of composition from the inside to
the outside of the dendrite is called coring, because on etching a polished
section of such dendrites, the progressive change in composition appears
as onionlike layers around a central core.

Inverse Segregation. Inverse segregation occurs when the solute content at, or near, the surface is higher than it is at the center—exactly opposite of what is expected. Under certain conditions, channels form between the dendrites that are growing toward the center of the casting, forming a path in which the last-to-freeze solute-enriched liquid can flow back from the center to the outside. This reverse flow path could be caused by differential contraction between the mold and the ingot creating a suction effect that pulls the solute-enriched liquid toward the surface. Another possible mechanism is that a large amount of gas evolving at the end of solidification pushes the solute-enriched liquid through the dendritic channels toward the surface.

It should be recognized that this discussion on segregation is rather cursory. An examination of the segregation patterns in the aluminum-killed steel ingot of Fig. B.9 shows the complexity of segregation that can be observed in real castings. While ingot homogenization treatments can be effective in smoothing out microsegregation, they are not very effective
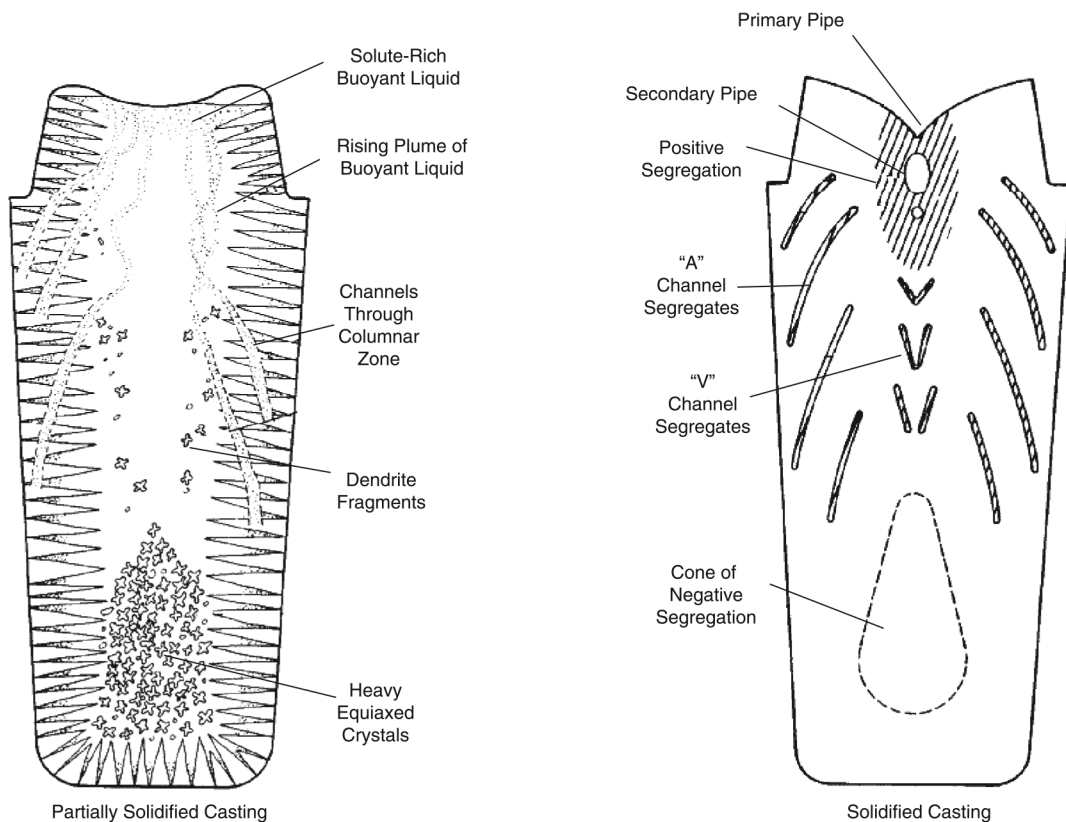

Fig. B.9 Segregation in killed steel ingot. Source: Ref B.1 as published in Ref B.2

for macrosegregation. Because macrosegregation occurs over distances ranging from 1 to 100 cm (0.4 to 40 in.), the diffusion lengths are just too long and the times required are prohibitive. Segregation is one of the prime reasons that wrought products are often preferred over castings. The severe plastic deformation that occurs during hot working will heal internal porosity and help break up and eliminate segregated areas.

B.5 Grain Refinement and Secondary Dendrite Arm Spacing

Rapid solidification rates are usually desirable because they tend to produce finer grain sizes and finer dendrites. Grain size control for castings is important because fine grain sizes result in higher strengths and greater ductility. Because the size of porosity in a casting often corresponds somewhat with grain size, finer porosity also goes with finer grain sizes. In addition, shrinkage and hot cracking are more prevalent in castings with a coarse grain size. Grain size is a function of pouring temperature, solidification rate, and the presence or absence of a grain-refining agent. Low pouring temperatures, faster solidification rates, and grain refiners, such as titanium and boron in aluminum, all produce finer grain sizes.

The solidification rate also affects the size of the dendrites that form during freezing. The dendrite size is normally measured as the distance between the secondary dendrite arms, referred to as the secondary dendrite arm spacing (SDAS). As shown in Fig. B.10, faster solidification rates produce smaller SDAS. The SDAS is related to the solidification time, t, by:

$$SDAS = kt^n \tag{Eq B.2}$$

where k and n are constants that depend on the composition of the metal. Small secondary dendrite arm spacings are associated with higher strengths and improved ductility (Fig. B.11). Homogenization heat treatments are also dependent on the time, t, required to diffuse a solute over a given average distance, x. If the coefficient of diffusion in the solid is D, then the relationship between time and distance is approximately:

$$x = \sqrt{Dt} \tag{Eq B.3}$$

Thus, finer SDAS results in shorter homogenization times, or better homogenization in similar times.

B.6 Porosity and Shrinkage

Porosity is the presence of pores in the casting. These pores may be connected to the surface, or they may be wholly internal. While mild porosity
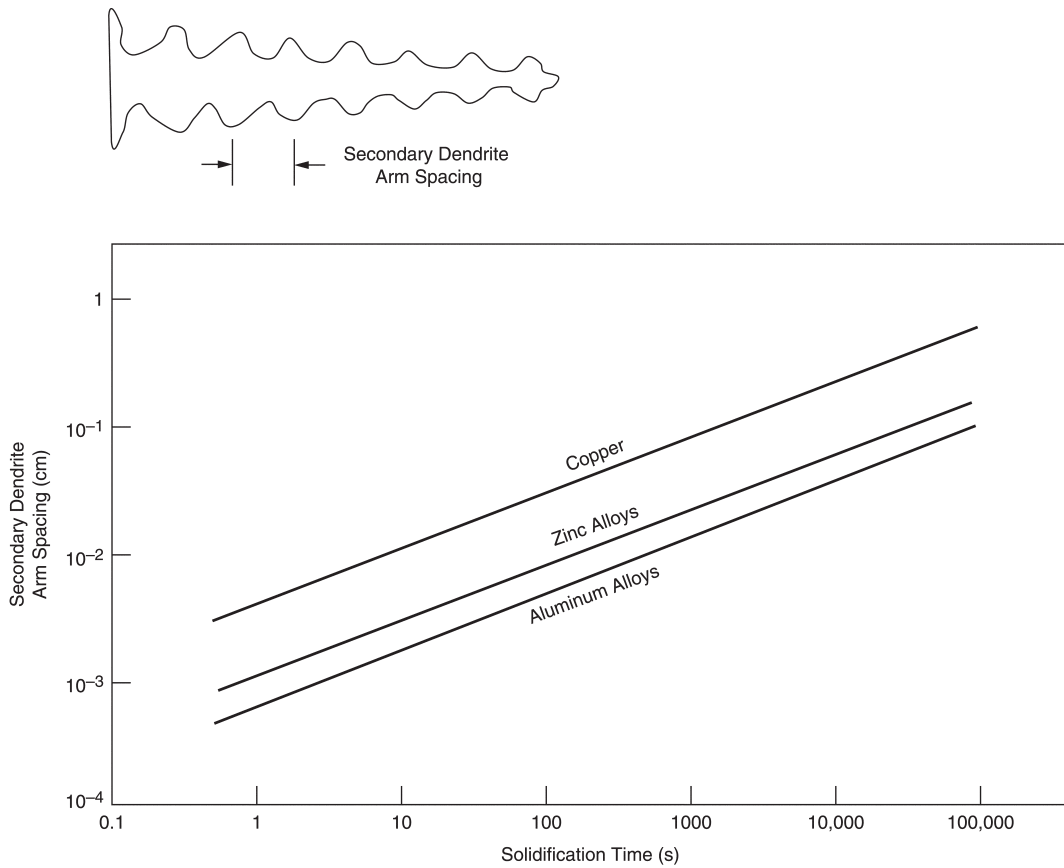
Fig. B.10   Effect of solidification time on secondary dendrite arm spacing. Source: Ref B.5 as published in Ref B.2
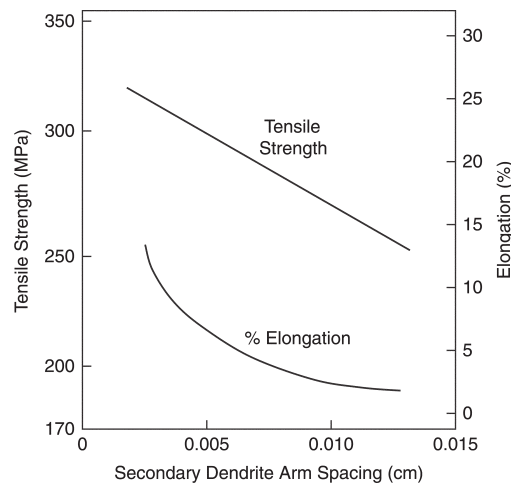

Fig. B.11   Effect of secondary dendrite arm spacing on properties of aluminum casting alloy. Source: Ref B.5 as published in Ref B.2

does not normally degrade static properties, such as tensile strength, it can severely impact dynamic properties, such as fatigue strength. However, a reduction in static properties can occur if the porosity is extensive enough to significantly reduce the cross-sectional area or if it has sharp corners that produce stress concentrations. If the surfaces of small porosity in ingots are not oxidized, they will generally be welded shut during hot working such as rolling or forging. Small porosity in finished castings must either be accepted or healed by processes such as hot isostatic pressing, where the metal is subjected to significant heat and pressure. Porosity that is open to the surface in finished castings is sometimes ground out and weld repaired. Both gas evolution and metal shrinkage during casting can produce porosity.

Gas porosity is caused by the absorption of gases in the liquid metal prior to casting. The most troublesome gas is hydrogen, which usually comes from either moisture in the air or from burning fossil fuels for heating and melting. Moisture and liquid metal can react to form molecular hydrogen according to:

$$x\mathrm{M} + y\mathrm{H_2O} \rightarrow \mathrm{M}_x\mathrm{O}_y + y\mathrm{H_2} \tag{Eq B.4}$$

where M is the metal, and x and y are stoichiometric coefficients balancing the equation. At the high temperatures in the liquid melt, molecular hydrogen decomposes into atomic hydrogen that dissolves in the metal. The solubility of hydrogen in liquid metals increases sharply with temperature, as shown in Fig. B.12 for nickel and iron. If the hydrogen is not removed prior to solidification, the large decrease in solubility during freezing results in the formation of porosity. One problem with gas porosity is the formation of blisters during subsequent processing such as heat treating or annealing. The equilibrium gas concentration in a liquid metal can be determined by Sievert's law:

$$G = k\sqrt{p_g} \tag{Eq B.5}$$

where G is the equilibrium gas solubility, k is the equilibrium constant, and p_g is the partial pressure of gas at the metal surface.

Hydrogen is often removed by vacuum degassing prior to casting. For example, premium-quality steels are commonly vacuum degassed. In addition, some metals, such as titanium, are so reactive that all melting and casting operations must be done under vacuum. In open-air casting operations, hydrogen is removed from the melt by using degassing fluxes. The removal of hydrogen is a mechanical, not chemical, process in which the hydrogen attaches itself to the fluxing gas.

The presence of nonmetallic inclusions has an effect on gas porosity formation. It has been shown that nucleation of pores is difficult in the
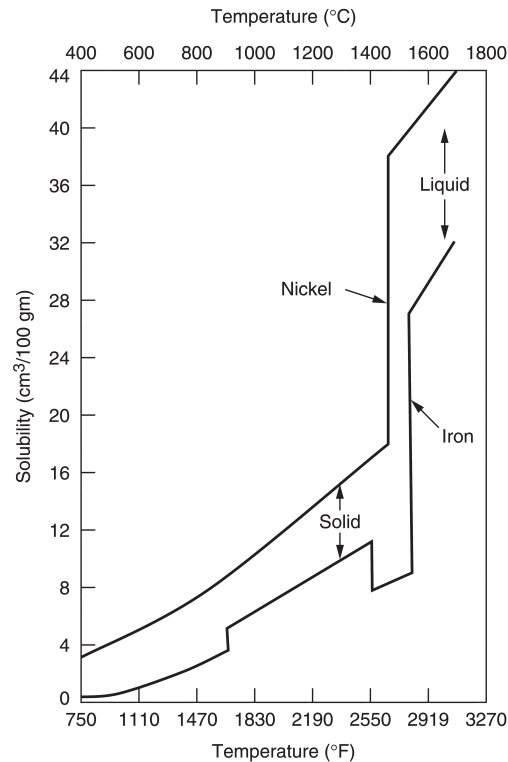
Fig. B.12 Maximum solubility of hydrogen in nickel and iron. Source: Ref B.6 as published in Ref B.2

absence of some sort of substrate, such as a nonmetallic inclusion, a grain refiner, or a second-phase particle. Investigations have shown that castings free of inclusions have less porosity than castings that contain inclusions.

As a metal casting cools and solidifies, the volume decreases, contributing to three types of shrinkage: liquid shrinkage, solidification shrinkage, and solid shrinkage. The shrinkage occurring in the liquid metal itself does not cause casting problems. The extra liquid metal required to compensate for this small reduction in volume is provided by a slight extension to the pouring time or by a slight fall in feeder level.

Solidification shrinkage occurs at the freezing point when the metal transitions from a liquid to a more highly ordered crystalline solid. The volume change on melting for a number of metals is given in Table B.1. Solidification shrinkage is usually compensated for by designing the mold with reservoirs for liquid metal, called risers, which allow liquid metal to flow in and fill the areas being vacated by the solidifying metal. Shrinkage porosity often forms in areas that the liquid metal from the risers cannot reach. For example, it is difficult to effectively feed metal into the interdendritic areas where shrinkage is occurring. Because this type of

Table B.1 Volume changes on melting

Metal	Crystal Structure(a)	Volume change on melting, %
Al	fcc	6.0
Au	fcc	5.1
Cu	fcc	4.2
Zn	hcp	4.2
Ag	fcc	3.8
Pb	fcc	3.5
Fe	bcc	3.4
Sn	bct	2.8
Nb	bcc	0.9
Sb	Rhombohedral	−0.95
Si	Diamond cubic	−12

(a) fcc, face-centered cubic; hcp, hexagonal close-packed; bcc, body-centered cubic; bct, body-centered tetragonal. Source: Ref B.2

porosity occurs late in solidification, especially in alloys with wide freezing ranges and a large mushy zone, it is particularly difficult to eliminate. A comparison of shrinkage porosity and gas porosity is shown in Fig. B.13. Shrinkage porosity tends to follow the directions of the dendritic arms and forms along the grain boundaries, while gas porosity occurs throughout the matrix.

Solid shrinkage occurs after the casting has solidified and is cooling down to room temperature. As cooling progresses, and the casting attempts to contract, it is constrained to some extent by the mold. This constraint always leads to the casting being somewhat larger than would be expected from free contraction alone. This can lead to difficulties in accurately designing the size of the pattern, because the contraction allowance is not easy to quantify. Mold constraint during cooling can also lead to problems such as hot tearing or cracking of the casting.
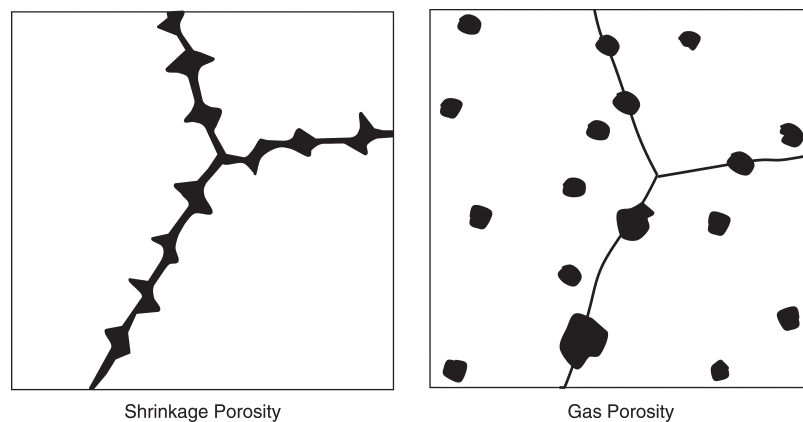

Shrinkage Porosity   Gas Porosity

Fig. B.13 Porosity in cast metals. Source: Ref B.7 as published in Ref B.2

ACKNOWLEDGMENT

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