Lectures 7
Solidification
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Principles of Solidification

- Of all the processing techniques used in the manufacturing of materials, solidification is probably the most important. Like water freezes to ice, molten materials solidify as they cool below their freezing temperature. During the solidification of materials that **crystallize, the atomic arrangement changes from a short-range order (SRO) to a long-range order (LRO).** The solidification of crystalline materials requires two steps. In the first step, **ultra-fine crystallites, known as the nuclei of a solid phase, form from the liquid**. In the second step, which can overlap with the first, **the ultra-fine solid crystallites begin to grow as atoms from the liquid are attached to the nuclei until no liquid remains.**

Nucleation

- In the context of solidification, the term **nucleation refers to the formation of the first** nanocrystallites from molten material. For example, as water begins to freeze, nanocrystals, known as **nuclei, form first. In a broader sense, the term nucleation refers to the initial** stage of formation of one phase from another phase. When a vapor condenses into liquid, the nanoscale sized drops of liquid that appear when the condensation begins are referred to as nuclei. We expect a material to solidify when the liquid cools to just below its freezing (or melting) temperature, because the energy associated with the crystalline structure of the solid is then less than the energy of the liquid. This energy difference between the liquid and the solid is the free energy per unit volume *Gv and is the driving force for* solidification. When the solid forms, however, a solid-liquid interface is created (Figure 9-1(a)). A surface free energy *sl is associated with this interface. Thus, the total change in energy G, shown in Figure 9-1(b), is*

$$\Delta G = \tfrac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma_{sl} \qquad\qquad (9\text{-}1)$$

where $\tfrac{4}{3}\pi r^3$ is the volume of a spherical solid of radius r, $4\pi r^2$ is the surface area of a spherical solid, σ_{sl} is the surface free energy of the solid-liquid interface (in this case), and ΔG_v is the free energy change per unit volume, which is negative since the phase transformation is assumed to be thermodynamically feasible. Note that σ_{sl} is not a strong function of r and is assumed constant. It has units of energy per unit area. ΔG_v also does not depend on r.

An **embryo** is a tiny particle of solid that forms from the liquid as atoms cluster together. The embryo is unstable and may either grow into a stable nucleus or redissolve.

In Figure 9-1(b), the top curve shows the parabolic variation of the total surface energy $(4\pi r^2 \cdot \sigma_{sl})$. The bottom most curve shows the total volume free energy change term $\left(\tfrac{4}{3}\pi r^3 \cdot \Delta G_v\right)$. The curve in the middle shows the variation of ΔG. It represents the
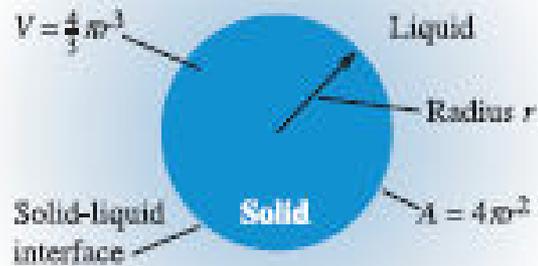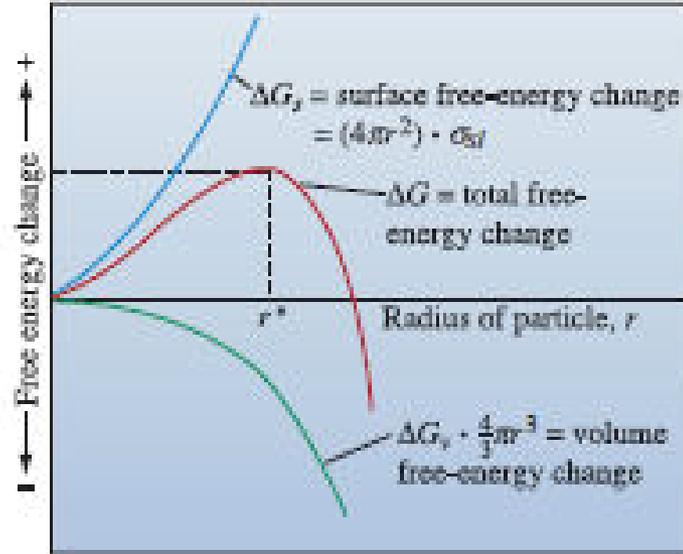
Figure 9-1 (a) An interface is created when a solid forms from the liquid. (b) The total free energy of the solid-liquid system changes with the size of the solid. The solid is an embryo if its radius is less than the critical radius and is a nucleus if its radius is greater than the critical radius.

sum of the other two curves as given by Equation 9-1. At the temperature at which the solid and liquid phases are predicted to be in thermodynamic equilibrium (i.e., at the freezing temperature), the free energy of the solid phase and that of the liquid phase are equal (*ΔGv = 0), so the total free energy change (ΔG) will be positive. When the solid is* very small with a radius less than the **critical radius for nucleation (r*) (Figure 9-1(b)), further growth causes the total free energy to increase. The critical radius (r*) is the minimum** size of a crystal that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow. The formation of embryos is a statistical process. Many embryos form and redissolve. If by chance, an embryo forms with a radius that is larger than *r*, further growth* causes the total free energy to decrease. The new solid is then stable and sustainable since nucleation has occurred, and growth of the solid particle—which is now called a nucleus—begins. At the thermodynamic melting or freezing temperatures, the probability of forming stable, sustainable nuclei is extremely small. Therefore, solidification does not begin at the thermodynamic melting or freezing temperature. If the temperature continues to decrease below the equilibrium freezing temperature, the liquid phase that should have transformed into a solid becomes thermodynamically increasingly unstable. Because the temperature of the liquid is below the equilibrium freezing temperature, the liquid is considered undercooled.

The **undercooling (ΔT) is the difference between the** equilibrium freezing temperature and the actual temperature of the liquid. As the extent of undercooling increases, the thermodynamic driving force for the formation of a solid phase from the liquid overtakes the resistance to create a solid-liquid interface. This phenomenon can be seen in many other phase transformations. When one solid phase (α) transforms into another solid phase (ß), the system has to be cooled to a temperature that is below the thermodynamic phase transformation temperature (at which the energies of the α and ß phases are equal). When a liquid is transformed into a vapor (i.e., boiling water), a bubble of vapor is created in the liquid. In order to create the transformation though, we need to **superheat the liquid above its boiling temperature!**

Homogeneous Nucleation

As liquid cools to temperatures below the equilibrium freezing temperature, two factors combine to favor nucleation. First, since atoms are losing their thermal energy, the probability of forming clusters to form larger embryos increases. Second, the larger volume free energy difference between the liquid and the solid reduces the critical size (*r*) of the nucleus.* ***Homogeneous nucleation occurs*** when the undercooling becomes large enough to cause the formation of a stable nucleus. The size of the critical radius *r* for homogeneous nucleation is given by*

$$r* = \frac{2\sigma_{sl}T_m}{\Delta H_f \Delta T} \qquad\qquad (9\text{-}2)$$

where *Hf is the latent heat of fusion per unit volume, Tm is the equilibrium solidification* temperature in kelvin, and *T = (Tm - T) is the undercooling when the liquid temperature* is *T. The latent heat of fusion represents the heat given up during the liquid-to-solid transformation.* As the undercooling increases, the critical radius required for nucleation decerease.

Example 9-1   *Calculation of Critical Radius for the Solidification of Copper*

Calculate the size of the critical radius and the number of atoms in the critical nucleus when solid copper forms by homogeneous nucleation. Comment on the size of the nucleus and assumptions we made while deriving the equation for the radius of the nucleus.

SOLUTION

From Table 9-1 for Cu:

$$\Delta T = 236°C \qquad T_m = 1085 + 273 = 1358 \text{ K}$$
$$\Delta H_f = 1628 \text{ J/cm}^3$$
$$\sigma_{sl} = 177 \times 10^{-7} \text{ J/cm}^2$$

Thus, r^* is given by

$$r^* = \frac{2\sigma_{sl}T_m}{\Delta H_f \Delta T} = \frac{(2)(177 \times 10^{-7})(1358)}{(1628)(236)} = 12.51 \times 10^{-8} \text{ cm}$$

Note that a temperature difference of 1°C is equal to a temperature change of 1 K, or $\Delta T = 236°C = 236$ K.

The lattice parameter for FCC copper is $a_0 = 0.3615$ nm $= 3.615 \times 10^{-8}$ cm. Thus, the unit cell volume is given by

$$V_{\text{unit cell}} = (a_0)^3 = (3.615 \times 10^{-8})^3 = 47.24 \times 10^{-24} \text{ cm}^3$$

The volume of the critical radius is given by

$$V_{r^*} = \tfrac{4}{3}\pi r^3 = \left(\tfrac{4}{3}\pi\right)(12.51 \times 10^{-8})^3 = 8200 \times 10^{-24} \text{ cm}^3$$

The number of unit cells in the critical nucleus is

$$\frac{V_{\text{unit cell}}}{V_{r*}} = \frac{8200 \times 10^{-24}}{47.24 \times 10^{-24}} = 174 \text{ unit cells}$$

Since there are four atoms in each FCC unit cell, the number of atoms in the critical nucleus must be

$$(4 \text{ atoms/cell})(174 \text{ cells/nucleus}) = 696 \text{ atoms/nucleus}$$

In these types of calculations, we assume that a nucleus that is made from only a few hundred atoms still exhibits properties similar to those of bulk materials. This is not strictly correct and as such is a weakness of the classical theory of nucleation.
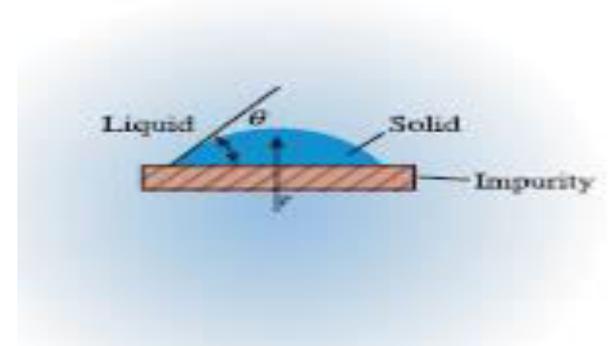
Heterogeneous Nucleation

Water will not solidify into ice via homogeneous nucleation until we reach a temperature of -40°C (undercooling of 40°C)! Except in controlled laboratory experiments, homogeneous nucleation never occurs in liquids. Instead, impurities in contact with the liquid, either suspended in the liquid or on the walls of the container that holds the liquid, provide a surface on which the solid can form (Figure 9-2). Now, a radius of curvature greater than the critical radius is achieved with very little total surface between the solid and liquid. Relatively few atoms must cluster together to produce a solid particle that has the required radius of curvature. Much less undercooling is required to achieve the critical size, so nucleation occurs more readily. Nucleation on preexisting surfaces is known as

heterogeneous nucleation. This process is dependent on the contact angle (θ) for the nucleating phase and the surface on which nucleation occurs. The same type of phenomenon occurs in solid-state transformations.

- **Rate of Nucleation** The *rate of nucleation (the number of nuclei formed* per unit time) is a function of temperature. Prior to solidification, of course, there is no nucleation and, at temperatures above the freezing point, the rate of nucleation is zero. As the temperature drops, the driving force for nucleation increases; however, as the temperature decreases, atomic diffusion becomes slower, hence slowing the nucleation process.
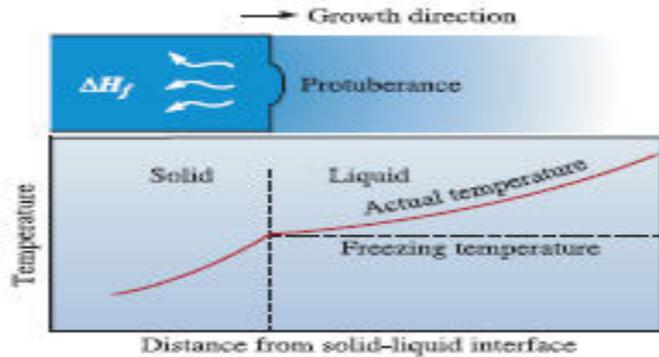
Figure 9-2
A solid forming on an impurity can assume the critical radius with a smaller increase in the surface energy. Thus, heterogeneous nucleation can occur with relatively low undercoolings.

Thus, a typical rate of nucleation reaches a maximum at some temperature below the transformation temperature. In heterogeneous nucleation, the rate of nucleation is dictated by the concentration of the nucleating agents. By considering the rates of nucleation and growth, we can predict the overall rate of a phase transformation.

Growth Mechanisms

Once the solid nuclei of a phase form (in a liquid or another solid phase), growth begins to occur as more atoms become attached to the solid surface. In this discussion, we will concentrate on the nucleation and growth of crystals from a liquid. The nature of the growth of the solid nuclei depends on how heat is removed from the molten material. Let's consider casting a molten metal in a mold, for example. We assume we have a nearly pure metal and not an alloy (as solidification of alloys is different in that in most cases, it occurs over a range of temperatures). In the solidification process, two types of heat must be removed: the specific heat of the liquid and the latent heat of fusion. The specific heat is the heat required to change the temperature of a unit weight of the material by one degree. The specific heat must be removed first, either by radiation into the surrounding atmosphere or by conduction into the surrounding mold, until the liquid cools to its freezing temperature. This is simply a cooling of the liquid from one temperature to a temperature at which nucleation begins. We know that to melt a solid we need to supply heat. Therefore, when solid crystals form from a liquid, heat is generated! This type of heat is called the latent heat of fusion (ΔHf). *The latent heat of fusion must be removed from the solid-liquid interface* before solidification is completed. The manner in which we remove the latent heat of fusion determines the material's growth mechanism and final structure of a casting.

Figure 9-3
When the temperature of the liquid is above the freezing temperature, a protuberance on the solid-liquid interface will not grow, leading to maintenance of a planar interface.
Latent heat is removed from the interface through the solid.

Planar Growth : When a well-inoculated liquid (i.e., a liquid containing nucleating agents) cools under equilibrium conditions, there is no need for undercooling since heterogeneous nucleation can occur. Therefore, the temperature of the liquid ahead of the solidification front (i.e., solid-liquid interface) is greater than the freezing temperature. The temperature of the solid is at or below the freezing temperature. During solidification, the latent heat of fusion is removed by conduction from the solid liquid interface. Any small protuberance that begins to grow on the interface is surrounded by liquid above the freezing temperature (Figure 9-3). The growth of the protuberance then stops until the remainder of the interface catches up. This growth mechanism, known as planar growth, occurs by the movement of a smooth solid-liquid interface into the liquid.

Dendritic Growth   When the liquid is not inoculated and the nucleation is poor, the liquid has to be undercooled before the solid forms (Figure 9-4). Under these conditions, a small solid protuberance called a dendrite, which forms at the interface, is encouraged to grow since the liquid ahead of the solidification front is undercooled. The word dendrite comes from the Greek word *dendron that means tree. As the solid dendrite* grows, the latent heat of fusion is conducted into the undercooled liquid, raising the temperature of the liquid toward the freezing temperature. Secondary and tertiary dendrite arms can also form on the primary stalks to speed the evolution of the latent heat. Dendritic growth continues until the undercooled liquid warms to the freezing temperature. Any remaining liquid then solidifies by planar growth. The difference between planar and dendritic growth arises because of the different sinks for the latent heat of fusion. The container or mold must absorb the heat in planar growth, but the undercooled liquid absorbs the heat in dendritic growth. In pure metals, dendritic growth normally represents only a small fraction of the total growth and is given by

$$\text{Dendritic fraction} = f = \frac{c\Delta T}{\Delta H_f} \qquad\qquad (9\text{-}3)$$

where *c is the specific heat of the liquid. The numerator represents the heat that the* undercooled liquid can absorb, and the latent heat in the denominator represents the total heat that must be given up during solidification. As the undercooling Δ*T increases,*
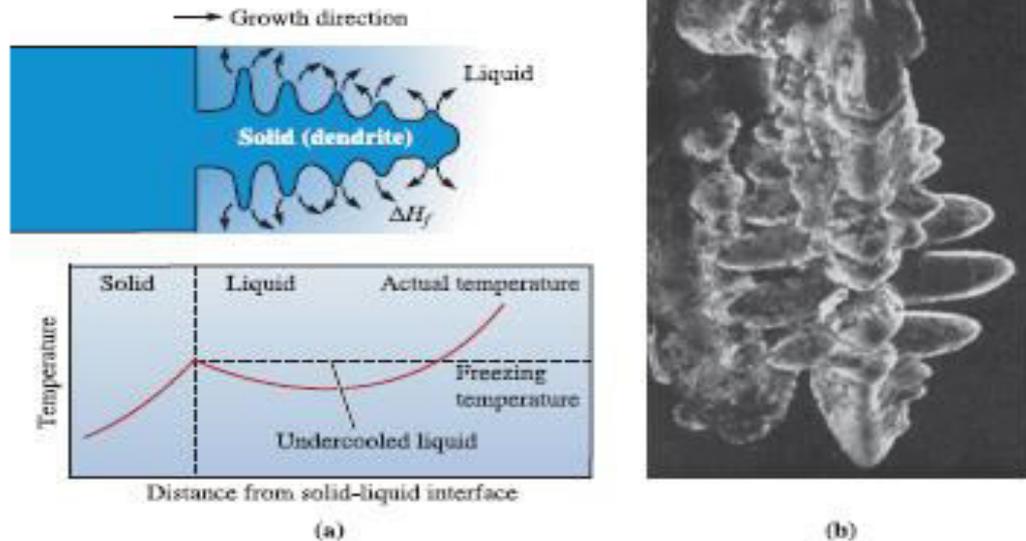
Figure 9-4 (a) If the liquid is undercooled, a protuberance on the solid-liquid interface can grow rapidly as a dendrite. The latent heat of fusion is removed by raising the temperature of the liquid back to the freezing temperature. (b) Scanning electron micrograph of dendrites in steel (* 15). (Reprinted courtesy of Don Askeland.)

more dendritic growth occurs. If the liquid is well-inoculated, undercooling is almost zero and growth would be mainly via the planar front solidification mechanism.

Cooling Curves

A cooling curve shows how the temperature of a material (in this case, a pure metal) decreases with time [Figure 9-8 (a) and (b)]. The liquid is poured into a mold at the pouring temperature, point *A. The difference between the pouring temperature and the freezing temperature is* the superheat. The specific heat is extracted by the mold until the liquid reaches the freezing temperature (point *B). If the liquid is not well-inoculated, it must be undercooled*
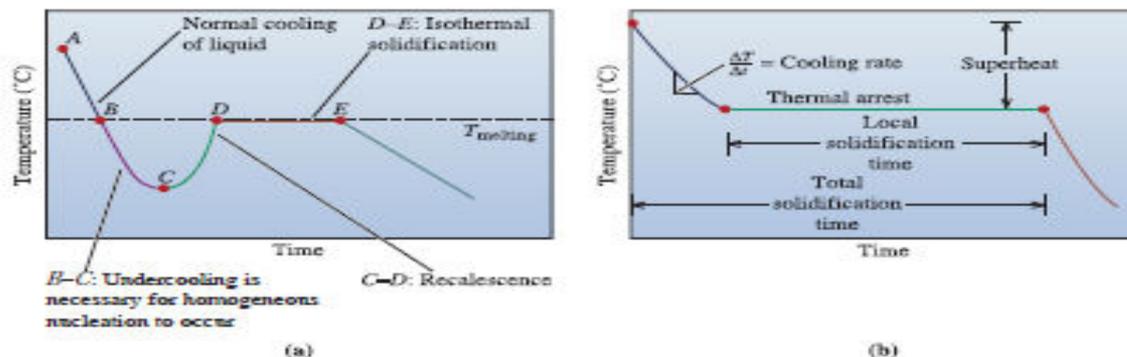

Figure 9-8 (a) Cooling curve for a pure metal that has not been well-inoculated. The liquid cools as specific heat is removed (between points A and B). Undercooling is thus necessary (between points B and C). As the nucleation begins (point C), latent heat of fusion is released causing an increase in the temperature of the liquid. This process is known as recalescence (point C to point D). The metal continues to solidify at a constant temperature (Tmelting). At point E, solidification is complete. The solid casting continues to cool from this point. (b) Cooling curve for a well-inoculated, but otherwise pure, metal. No undercooling is needed. Recalescence is not observed. Solidification begins at the melting temperature.

(point *B* to *C*). The slope of the cooling curve before solidification begins is the cooling rate $\frac{\Delta T}{\Delta t}$. As nucleation begins (point *C*), latent heat of fusion is given off, and the tem-

perature rises. This increase in temperature of the undercooled liquid as a result of nucleation is known as recalescence (point *C to D*). *Solidification proceeds isothermally at the* melting temperature (point *D to E*) *as the latent heat given off from continued solidification* is balanced by the heat lost by cooling. This region between points *D and E, where* the temperature is constant, is known as the thermal arrest. A thermal arrest, or plateau, is produced because the evolution of the latent heat of fusion balances the heat being lost because of cooling. At point *E, solidification is complete, and the solid casting cools from* point *E to room temperature.* If the liquid is well-inoculated, the extent of undercooling and recalescence is usually very small and can be observed in cooling curves only by very careful measurements. If effective heterogeneous nuclei are present in the liquid, solidification begins at the freezing temperature [Figure 9-8 (b)]. The latent heat keeps the remaining liquid at the freezing temperature until all of the liquid has solidified and no more heat can be evolved. Growth under these conditions is planar. The total solidification time of the casting is the time required to remove both the specific heat of the liquid and the latent heat of fusion. Measured from the time of pouring until solidification is complete, this time is given by Chvorinov's rule. The local solidification time is the time required to remove only the latent heat of fusion at a particular location in the casting; it is measured from when solidification begins until solidification is completed. The local solidification times (and the total solidification times) for liquids solidified via undercooled and inoculated liquids will be slightly different. We often use the terms "melting temperature" and "freezing temperature" while discussing solidification. It would be more accurate to use the term "melting temperature" to describe when a solid turns completely into a liquid. For pure metals and compounds, this happens at a fixed temperature (assuming fixed pressure) and without superheating. "Freezing temperature" or "freezing point" can be defined as the temperature at which solidification of a material is complete.

Cast Structure

In manufacturing components by casting, molten metals are often poured into molds and permitted to solidify. The mold produces a finished shape, known as a *casting. In other* cases, the mold produces a simple shape called an ingot. An ingot usually requires extensive plastic deformation before a finished product is created. A *macrostructure sometimes* referred to as the ingot structure, consists of as many as three regions (Figure 9-9).

Chill Zone :

The chill zone is a narrow band of randomly oriented grains at the surface of the casting. The metal at the mold wall is the first to cool to the freezing temperature. The mold wall also provides many surfaces at which heterogeneous nucleation takes place.

Columnar Zone

The columnar zone contains elongated grains oriented in a particular crystallographic direction. As heat is removed from the casting by the mold material, the grains in the chill zone flow, or from the coldest toward the hottest areas of the casting. This tendency usually means that the grains grow perpendicular to the mold wall. Grains grow fastest in certain crystallographic directions. In metals with a cubic crystal structure, grains in the chill zone that have a 81009 direction perpendicular to the mold wall grow faster than other less favorably oriented grains (Figure 9-10). Eventually, the grains in the columnar zone have 81009 directions that are parallel to one another, giving the columnar zone anisotropic properties. This formation of the columnar zone is influenced primarily by growth—rather than nucleation—phenomena. The grains may be composed of many dendrites if the liquid is originally undercooled. The solidification may proceed by planar growth of the columnar grains if no undercooling occurs.

Figure 9-9

Development of the ingot structure of a casting during solidification: (a) nucleation begins, (b) the chill zone forms, (c) preferred growth produces the columnar zone, and (d) additional nucleation creates the equlaxed zone.
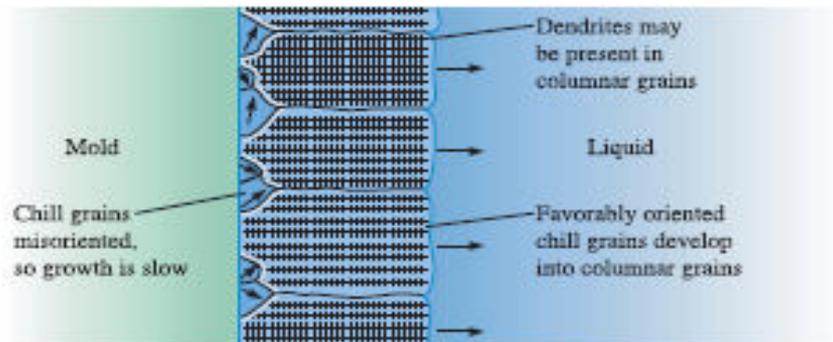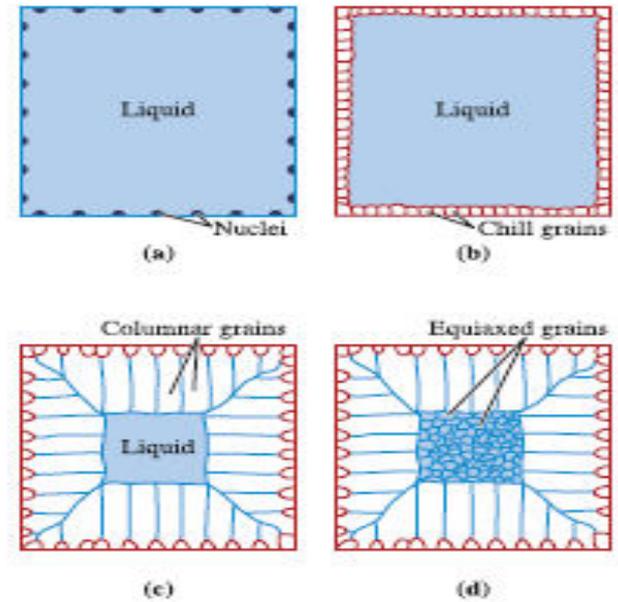

Figure 9-10 Competitive growth of the grains in the chill zone results in only those grains with favorable orientations developing into columnar grains.

• Equiaxed Zone

Although the solid may continue to grow in a columnar manner until all of the liquid has solidified, an equiaxed zone frequently forms in the center of the casting or ingot. The equiaxed zone contains new, randomly oriented grains, often caused by a low pouring temperature, alloying elements, or grain refining or inoculating agents. Small grains or dendrites in the chill zone may also be torn off by strong convection currents that are set up as the casting begins to freeze. These also provide heterogeneous nucleation sites for what ultimately become equiaxed grains. These grains grow as relatively round, or equiaxed, grains with a random orientation, and they stop the growth of the columnar grains. The formation of the equiaxed zone is a nucleation-controlled process and causes that portion of the casting to display isotropic behavior.

Solidification Defects

Although there are many defects that potentially can be introduced during solidification, shrinkage and porosity deserve special mention. If a casting contains pores (small holes), the cast component can fail catastrophically when used for load-bearing applications (e.g., turbine blades).

Shrinkage

Almost all materials are more dense in the solid state than in the liquid state. During solidification, the material contracts, or shrinks, as much as 7% (Table 9-2). Often, the bulk of the shrinkage occurs as cavities, if solidification begins at all surfaces of the casting, or *pipes, if one surface solidifies more slowly than the others* (Figure 9-11). The presence of such pipes can pose problems. For example, if in the production of zinc ingots a shrinkage pipe remains, water vapor can condense in it. This water can lead to an explosion if the ingot gets introduced in a furnace in which zinc is being remelted for such applications as hot-dip galvanizing.

TABLE 9-2 ■ Shrinkage during solidification for selected materials

Material	Shrinkage (%)
Al	7.0
Cu	5.1
Mg	4.0
Zn	3.7
Fe	3.4
Pb	2.7
Ga	+3.2 (expansion)
H₂O	+8.3 (expansion)
Low-carbon steel	2.5–3.0
High-carbon steel	4.0
White Cast Iron	4.0–5.5
Gray Cast Iron	+1.9 (expansion)

Note: Some data from DeGarmo, E. P., Black, J. T., and Kosha, R. A. Materials and Processes in Manufacturing, Prentice Hall, 1997.
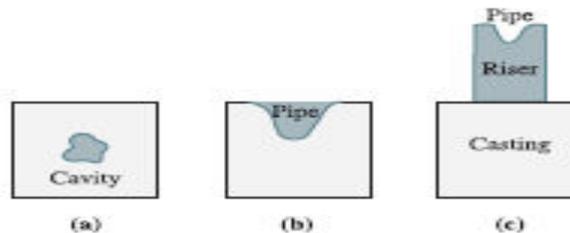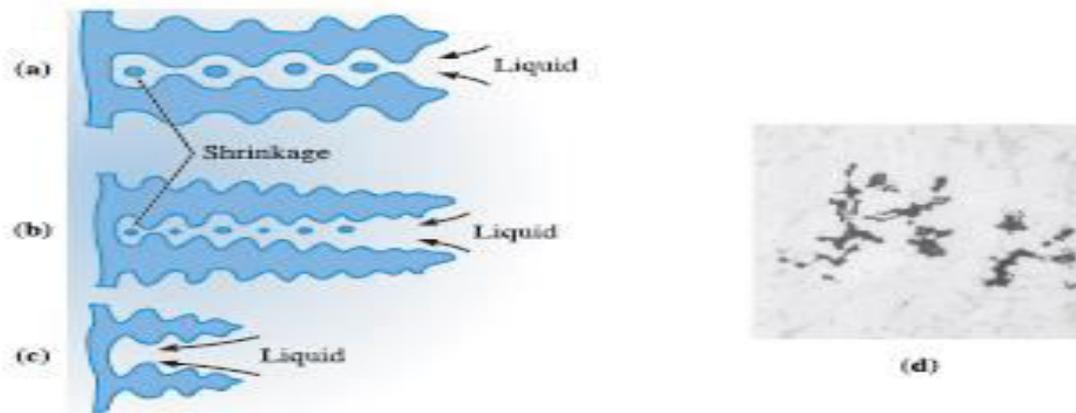

Figure 9-11
Several types of macroshrinkage can occur, including cavities and pipes. Risers can be used to help compensate for shrinkage.

A common technique for controlling cavity and pipe shrinkage is to place a riser, or an extra reservoir of metal, adjacent and connected to the casting. As the casting solidifies and shrinks, liquid metal flows from the riser into the casting to fill the shrinkage void. We need only to ensure that the riser solidifies after the casting and that there is an internal liquid channel that connects the liquid in the riser to the last liquid to solidify in the casting

Figure 9-13 (a) Shrinkage can occur between the dendrite arms. (b) Small secondary dendrite arm spacings result in smaller, more evenly distributed shrinkage porosity. (c) Short primary arms can help avoid shrinkage. (d) Interdendritic shrinkage in an aluminum alloy is shown (× 80). (Reprinted courtesy of Don Askeland.)

Interdendritic Shrinkage This consists of small shrinkage pores between dendrites (Figure 9-13). This defect, also called microshrinkage or shrinkage porosity, is difficult to prevent by the use of risers. Fast cooling rates may reduce problems with interdendritic shrinkage; the dendrites may be shorter, permitting liquid to flow through the dendritic network to the solidifying solid interface. In addition, any shrinkage that remains may be finer and more uniformly distributed.

Gas Porosity Many metals dissolve a large quantity of gas when they are molten. Aluminum, for example, dissolves hydrogen. When the aluminum solidifies, however, the solid metal retains in its crystal structure only a small fraction of the hydrogen since the solubility of the solid is remarkably lower than that of the liquid (Figure 9-14). The excess hydrogen that cannot be incorporated in the solid metal or alloy crystal structure forms bubbles that may be trapped in the solid metal, producing gas porosity. The amount of gas that can be dissolved in molten metal is given by Sievert's law:

$$\text{Percent of gas} = K\sqrt{p_{gas}} \qquad (9\text{-}7)$$

where p_{gas} *is the partial pressure of the gas in contact with the metal and K is a constant* which, for a particular metal-gas system, increases with increasing temperature. We can minimize gas porosity in castings by keeping the liquid temperature low, by adding materials to the liquid to combine with the gas and form a solid, or by ensuring that the partial pressure of the gas remains low. The latter may be achieved by placing the molten metal in a vacuum chamber or bubbling an inert gas through the metal. Because *pgas is low in the vacuum, the gas leaves the metal, enters the vacuum, and is*
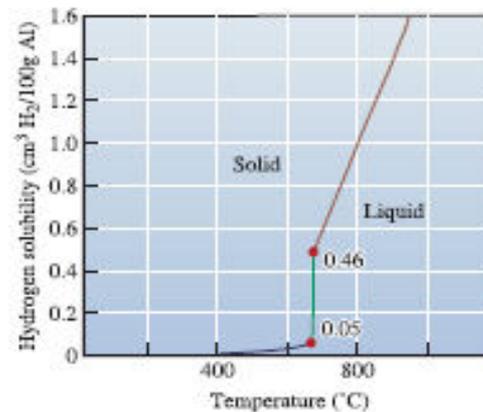

Figure 9-14
The solubility of hydrogen gas in aluminum when the partial pressure of $H_2 = 1$ atm.

carried away. Gas flushing is a process in which bubbles of a gas, inert or reactive, are injected into a molten metal to remove undesirable elements from molten metals and alloys. For example, hydrogen in aluminum can be removed using nitrogen or chlorine. The following example illustrates how a degassing process can be designed.

## Example 9-7   *Design of a Degassing Process for Copper*

After melting at atmospheric pressure, molten copper contains 0.01 weight percent oxygen. To ensure that your castings will not be subject to gas porosity, you want to reduce the weight percent to less than 0.00001% prior to pouring. Design a degassing process for the copper.

SOLUTION

We can solve this problem in several ways. In one approach, the liquid copper is placed in a vacuum chamber; the oxygen is then drawn from the liquid and carried away into the vacuum. The vacuum required can be estimated from Sievert's law:

$$\frac{\% \, O_{initial}}{\% \, O_{vacuum}} = \frac{K\sqrt{p_{initial}}}{K\sqrt{p_{vacuum}}} = \sqrt{\left(\frac{1 \text{ atm}}{p_{vacuum}}\right)}$$

$$\frac{0.01\%}{0.00001\%} = \sqrt{\left(\frac{1}{p_{vacuum}}\right)}$$

$$\frac{1 \text{ atm}}{p_{vacuum}} = (1000)^2 \quad \text{or} \quad p_{vacuum} = 10^{-6} \text{ atm}$$

Another approach would be to introduce a copper-15% phosphorous alloy. The phosphorous reacts with oxygen to produce P_2O_5, which floats out of the liquid, by the reaction:

$$5O + 2P \rightarrow P_2O_5$$
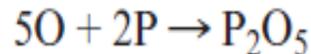
Typically, about 0.01 to 0.02% P must be added remove the oxygen.

In the manufacturing of **stainless steel**, a process known as **argon oxygen decarburization** (AOD) is used to lower the carbon content of the melt without oxidizing chromium or nickel. In this process, a mixture of argon (or nitrogen) and oxygen gases is forced into molten stainless steel. The carbon dissolved in the molten steel is oxidized by the oxygen gas via the formation of carbon monoxide (CO) gas; the CO is carried away by the inert argon (or nitrogen) gas bubbles. These processes need very careful control since some reactions (e.g., oxidation of carbon to CO) are exothermic (generate heat).