10.2 Solidification of Metals

After molten metal is poured into a **mold**, a sequence of events takes place during solidification and cooling of the metal to ambient temperature. These events greatly influence the size, shape, uniformity, and chemical composition of the grains formed throughout the casting, which, in turn, influence the overall properties of the casting. The significant factors affecting these events are the type of metal cast, the thermal properties of both the metal and the mold, the geometric relationship between volume and surface area of the casting, and the shape of the mold.

10.2.1 Pure Metals

Because a pure metal has a clearly defined melting, or freezing, point, it solidifies at a constant temperature, as shown in Fig. 10.1. Pure aluminum, for example, solidifies at 660°C, iron at 1537°C, and tungsten at 3410°C. (See also Table 3.1.) After the temperature of the molten metal drops to its freezing point, its temperature remains constant while the *latent heat of fusion* is given off. The *solidification front* (the solid–liquid interface) moves through the molten metal from the mold walls in toward the center. The solidified metal, called the *casting*, is then removed from the mold and allowed to cool to ambient temperature.

As shown in Fig. 10.1b and described in greater detail in Section 10.5.2, metals shrink while cooling and, generally, also shrink when they solidify. This is an

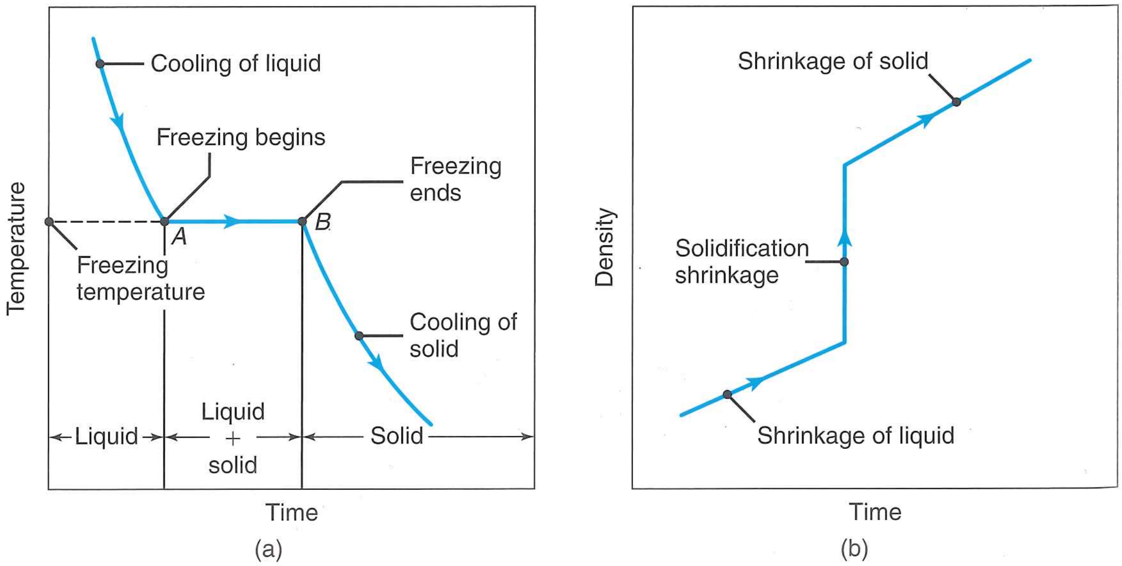

FIGURE 10.1 (a) Temperature as a function of time for the solidification of pure metals; note that freezing takes place at a constant temperature. (b) Density as a function of time.

important consideration, because shrinkage can lead to microcracking and the associated porosity, which can adversely affect the mechanical properties of the casting.

As an example of the grain structure that develops in a casting, Fig. 10.2a shows a cross-section of a box-shaped mold. At the mold walls, which are at ambient temperature at first, or typically are much cooler than the molten metal, the metal cools rapidly, producing a solidified **skin**, or *shell*, of fine equiaxed grains. The grains generally grow in a direction opposite to that of the heat transfer out through the mold.

Those grains that have favorable orientation grow preferentially, and are called **columnar grains** (Fig. 10.3). Those grains that have substantially different orientations are blocked from further growth. As the driving force of the heat transfer decreases away from the mold walls, the grains become equiaxed and coarse. This sequence of grain development is known as **homogenous nucleation**, meaning that the grains (crystals) grow upon themselves, starting at the mold wall.

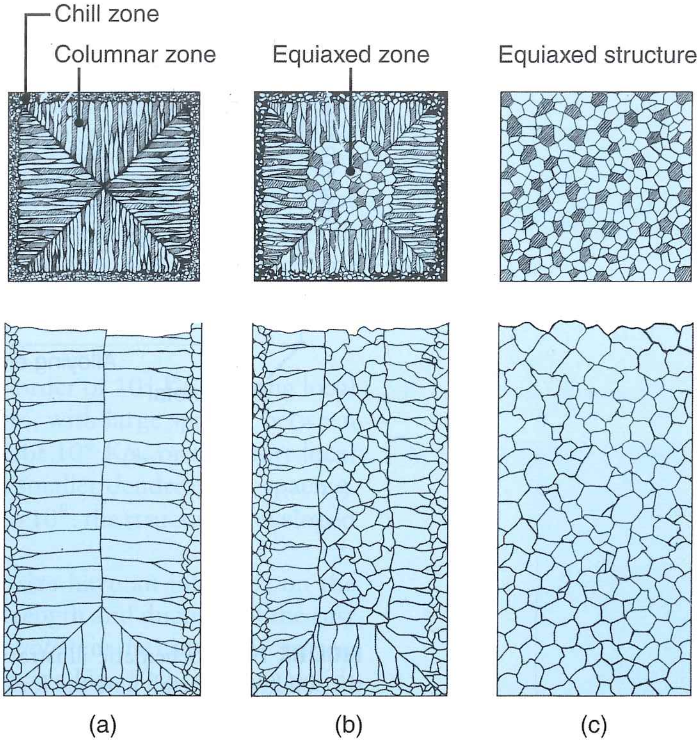

FIGURE 10.2 Schematic illustration of three cast structures of metals solidified in a square mold: (a) pure metals; (b) solid–solution alloys; and (c) structure obtained by using nucleating agents. *Source:* After G.W. Form, J.F. Wallace, J.L. Walker, and A. Cibula.

10.2.2 Alloys

Solidification in alloys begins when the temperature drops below the *liquidus*, T_L, and is complete when it reaches the *solidus*, T_S (Fig. 10.4). Within this temperature range, the alloy is in a *mushy* or *pasty* state, consisting of **columnar dendrites** (from the Greek *dendron*, meaning "akin to," and *drys*, meaning "tree"). Note the presence of liquid metal between the dendrite *arms*.

Dendrites have three-dimensional arms and branches (*secondary arms*), which eventually interlock, as can be seen in Fig. 10.5. The study of dendritic structures, although complex, is important, because such structures can contribute to detrimental factors, such as compositional variations, segregation, and microporosity within a cast part.

The width of the **mushy zone**, where both liquid and solid phases are present, is an important factor during solidification. This zone is described in terms of a temperature difference, known as the **freezing range**, as

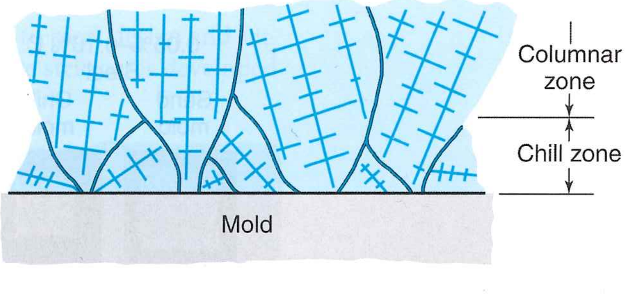

FIGURE 10.3 Development of a preferred texture at a cool mold wall; note that only favorably oriented grains grow away from the surface of the mold surface.

$$\text{Freezing range} = T_L - T_S. \qquad (10.1)$$

It can be seen in Fig. 10.4 that pure metals have a freezing range that approaches zero, and that the solidification front moves as a plane without developing a mushy zone. Eutectics (Section 4.3) solidify in a similar manner, with an essentially plane

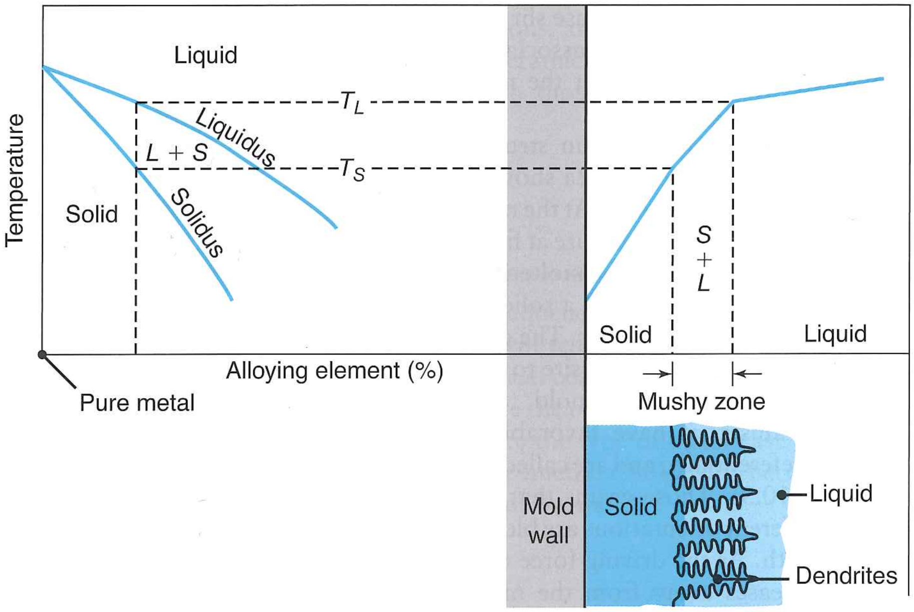

FIGURE 10.4 Schematic illustration of alloy solidification and temperature distribution in the solidifying metal; note the formation of dendrites in the mushy zone.

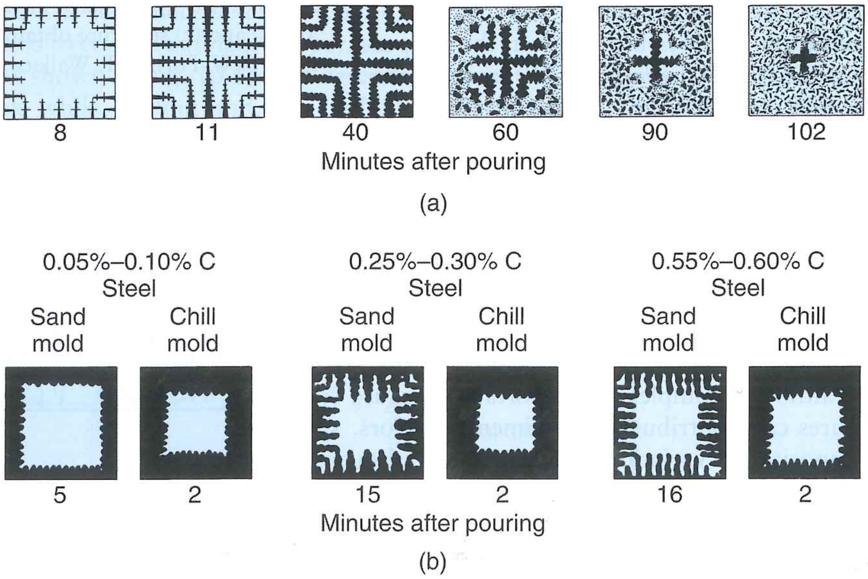

FIGURE 10.5 (a) Solidification patterns for gray cast iron in a 180-mm square casting. Note that after 11 min of cooling, dendrites reach each other, but the casting is still mushy throughout; it takes about 2 h for this casting to solidify completely. (b) Solidification of carbon steels in sand and chill (metal) molds; note the difference in solidification patterns as the carbon content increases. *Source:* After H.F. Bishop and W.S. Pellini.

front. The structure developed upon solidification depends on the composition of the eutectic. In alloys with a nearly symmetrical phase diagram (see Fig. 4.4), the structure is generally lamellar, with two or more solid phases present, depending on the alloy system. When the volume fraction of the minor phase of the alloy is less than about 25%, the structure generally becomes fibrous. These conditions are particularly significant for cast irons.

For alloys, a *short freezing range* generally involves a temperature difference of less than 50°C, and for a *long freezing range*, more than 110°C. Ferrous castings generally have narrow mushy zones, whereas aluminum and magnesium alloys have wide mushy zones. Consequently, these alloys are in a mushy state throughout most of their solidification process.

Effects of Cooling Rates. Slow cooling rates, on the order of 10^2 K/s, or long local solidification times, result in *coarse* dendritic structures, with large spacing between dendrite arms. For higher cooling rates, on the order of 10^4 K/s, or for short local solidification times, the structure becomes *finer*, with smaller dendrite arm spacing. For still higher cooling rates, on the order of from 10^6 to 10^8, the structures developed are *amorphous*, as described in Section 6.14.

The structures developed and the resulting grain size have an influence on the properties of the casting. As grain size decreases, the strength and ductility of the cast alloy increase, microporosity (*interdendritic shrinkage voids*) in the casting decreases, and the tendency for the casting to crack (*hot tearing*, see Fig. 10.12) during solidification decreases. Lack of uniformity in grain size and grain distribution result in castings that have *anisotropic properties*.

A criterion describing the kinetics of the liquid–solid interface is the ratio G/R, where G is the *thermal gradient* and R is the *rate* at which the interface moves. Typical values for G range from 10^2 to 10^3 K/m, and for R the range is from 10^{-3} to 10^{-4} m/s. Dendritic-type structures (Figs. 10.6a and b) typically have a G/R ratio in the range from 10^5 to 10^7, whereas ratios of 10^{10} to 10^{12} produce a plane front, nondendritic liquid–solid interface (Fig. 10.7).

10.2.3 Structure–property Relationships

Because all castings are expected to possess certain properties to meet design and service requirements, the relationships between properties and the structures developed

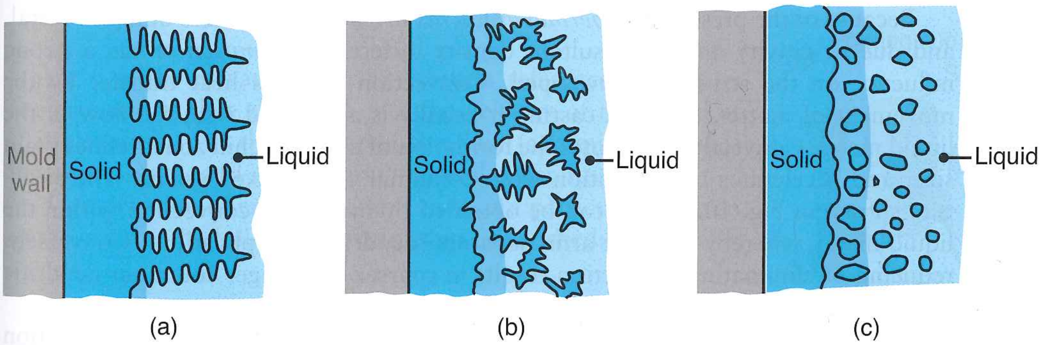

FIGURE 10.6 Schematic illustration of three basic types of cast structures: (a) columnar dendritic; (b) equiaxed dendritic; and (c) equiaxed nondendritic. *Source:* Courtesy of D. Apelian.

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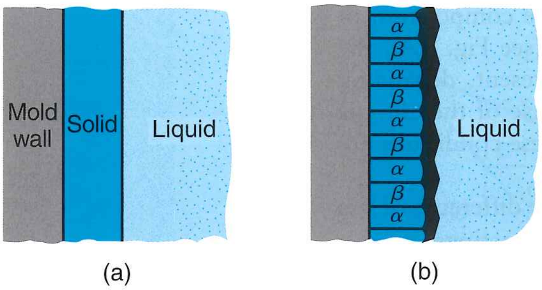

FIGURE 10.7 Schematic illustration of cast structures in (a) plane front, single phase, and (b) plane front, two phase. *Source:* Courtesy of D. Apelian.

during solidification are important aspects of casting. This section describes these relationships in terms of dendrite morphology and the concentration of alloying elements in various regions within the casting.

The compositions of dendrites and the liquid metal are given by the *phase diagram* of the particular alloy. When the alloy is cooled very slowly, each dendrite develops a uniform composition. However, under the normally higher cooling rates encountered in practice, **cored dendrites** are formed. These dendrites have a surface composition different from that at their centers, a difference referred to as *concentration gradient*. The surface of the dendrite has a higher concentration of alloying elements than at its core, due to solute rejection from the core toward the surface during solidification of the dendrite (**microsegregation**). The darker shading in the interdendritic liquid near the dendrite roots shown in Fig. 10.6 indicates that these regions have a higher solute concentration. Microsegregation in these regions is much more pronounced than in others.

There are several types of **segregation.** In contrast to microsegregation, **macrosegregation** involves differences in composition throughout the casting itself. In situations where the solidification front moves away from the surface of a casting as a plane (Fig. 10.7), lower melting-point constituents in the solidifying alloy are driven toward the center (**normal segregation**). Consequently, such a casting has a higher concentration of alloying elements at its center than at its surfaces. In dendritic structures, such as those found in solid–solution alloys (Fig. 10.2b), the opposite occurs; that is, the center of the casting has a lower concentration of alloying elements (**inverse segregation**) than does at its surface. The reason is that the liquid metal (having a higher concentration of alloying elements) enters the cavities developed from solidification shrinkage in the dendrite arms, which have solidified sooner.

Another form of segregation is due to gravity. **Gravity segregation** involves a process whereby higher-density inclusions or compounds sink while lighter elements (such as antimony in an antimony–lead alloy) float to the surface.

A typical cast structure of a solid–solution alloy, with an inner zone of equiaxed grains, is shown in Fig. 10.2b. This inner zone can be extended throughout the casting, as shown in Fig. 10.2c, by adding an **inoculant** (*nucleating agent*) to the alloy. The inoculant induces nucleation of the grains throughout the liquid metal (**heterogeneous nucleation**).

Because of the presence of *thermal gradients* in a solidifying mass of liquid metal, and due to gravity and the resultant density differences, *convection* has a strong influence on the structures developed. Convection involves heat transfer by the movement of matter, and in a casting it usually is associated with the flow of the liquid metal. Convection promotes the formation of an outer chill zone, refines grain size, and accelerates the transition from columnar to equiaxed grains. The structure shown in Fig. 10.6b also can be obtained by increasing convection within the liquid metal, whereby dendrite arms separate (**dendrite multiplication**). Conversely, reducing or eliminating convection results in coarser and longer columnar dendritic grains.

The dendrite arms are not particularly strong and can be broken up by agitation or mechanical vibration in the early stages of solidification (as in **semisolid metal forming** and **rheocasting**, described in Section 11.4.7). This process results in finer grain size, with equiaxed nondendritic grains distributed more uniformly throughout the casting (Fig. 10.6c). A side benefit is the *thixotropic* behavior of alloys (that is, the viscosity decreases when the liquid metal is agitated), leading to improved castability of the metal. Another form of semisolid metal forming is **thixotropic casting**, where a solid billet is first heated to a semisolid state and then injected into a die-casting mold (Section 11.4.5).