

Class-5 / 5th SEM

2.3.1 Solidification of Metals

Melting and solidification are primary metalworking phenomena that allow for mixing of various elements to form an alloy that can then be solidified, or cast, into a form that will be used as an as-cast part or subsequently thermomechanically processed into other useful shapes (bar, plate, pipe, etc.). These phenomena are also the basis of the fusion welding processes, and a general knowledge of the solidification of metals is required to understand the metallurgical nature of a fusion weld.

There are several requirements for solidification. First, it is necessary to nucleate, or form, solid species within the liquid phase. Once the initial solid forms and the liquid-to-solid transformation proceeds, it is required that heat of fusion generated by the transformation be removed or dissipated. This normally occurs by conduction through the solid away from the solidification front. During the solidification of an alloy, it is also necessary to redistribute solute between liquid and solid, since the composition of the liquid and solid in contact at the solidification front changes continuously as the temperature decreases within the solidification range. This redistribution will result in local variation in composition in the solidified structure if the solid does not have time to reach its equilibrium composition, which is common in most casting and welding processes.

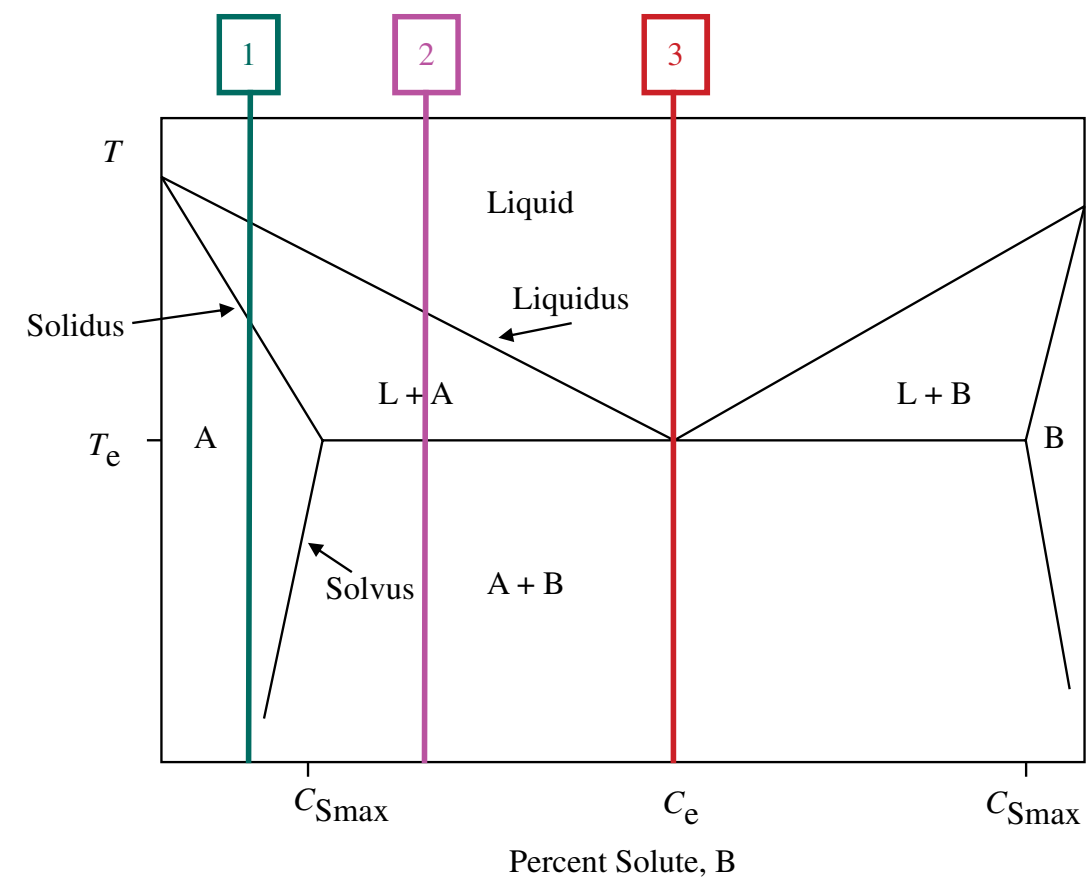
Most pure metals and alloys undergo a negative volume change when they solidify. This “shrinkage” phenomenon requires special precautions during casting to prevent shrinkage voids from forming. Solidification shrinkage also imparts stresses upon the as-solidified structure that may lead to solidification cracking. This shrinkage also contributes to the residual stress that is associated with fusion welds.

Using a simple phase diagram (Fig. 2.6), the equilibrium solidification behavior of a two-component alloy can be reviewed. For Alloy 1, solidification to solid A begins when the liquid temperature drops below the liquidus and ends when the alloy cools below the solidus. Within the solidification temperature range, the composition of liquid and solid in contact with each other at the solidification front is dictated by the isothermal tie line connecting the liquidus and solidus at a given temperature. At the end of solidification, Alloy 1 is 100% A.

For Alloy 2, solidification proceeds as described earlier until the alloy reaches the eutectic temperature (T_e). At this point, the remaining liquid, which is of eutectic composition, undergoes a eutectic reaction ($L \rightarrow A + B$). The final structure will then be a mixture of A and eutectic (A+B). The relative proportions can be determined using the lever rule.

For Alloy 3, solidification will not proceed until the system reaches the eutectic temperature. At this temperature, the liquid will completely transform to a eutectic structure with the composition of the A and B phase determined by the maximum solid solubility (C_{Smax}) of B in A and A in B at T_e .

2.3.1.1 Solidification Parameters A number of parameters are useful in describing microstructure development and solute redistribution during solidification. These are defined as follows:



Type 1 (single phase)



Type 2 (single phase plus eutectic)



Type 3 (eutectic)



FIGURE 2.6 Examples of different solidification paths in a simple eutectic system.

- Partition coefficient: $k = C_s/C_L$
- Liquid temperature gradient: $G_L = dT_L/dx$
- Solidification rate: $R = dx/dt$
- Cooling rate: $G_L \cdot R = dT/dt$

The partition coefficient, k , sometimes called the solute redistribution coefficient, is simply the ratio of the solid and liquid composition in contact with each other at a given temperature within the solidification range. For most alloy systems, k is not a constant and varies as a function of temperature. It can only be constant in systems where the liquidus and solidus lines are straight, which is uncommon. When considering solute segregation during solidification, it is typical to assume an average value of k . When the value of k is less than 1, solute will partition to the liquid. When k is greater than one, solute will be depleted in the liquid. As the value of k approaches 1, solute redistribution during solidification is reduced.

The temperature gradient in the liquid (G_L) is also an important parameter since it dictates the nature of the temperature field in advance of the solid–liquid (S–L) interface. In situations where some undercooling of the liquid has occurred prior to solidification, this gradient will be negative. This would be the typical situation for the solidification of a casting. During weld solidification, however, this gradient is normally positive since the weld pool is superheated by the welding heat source.

Solidification growth rate (R) is dictated by how fast the S–L interface is moving during the solidification process. When coupled with the temperature gradient in the liquid, the local cooling rate at the S–L interface can be determined. This latter value ($G_L \cdot R$) will have an influence on the dimensions of the solidification substructure, such as dendrite arm spacing.

2.3.1.2 Solidification Nucleation In order for the solidification process to begin, it is necessary to nucleate solid within the liquid phase. This can occur either homogeneously or heterogeneously when a nucleating particle or solid substrate is present. Homogeneous nucleation requires that solid of a critical, or threshold, size form within the liquid. The size of this spherical nucleant can be defined by a critical radius size, r^* , where

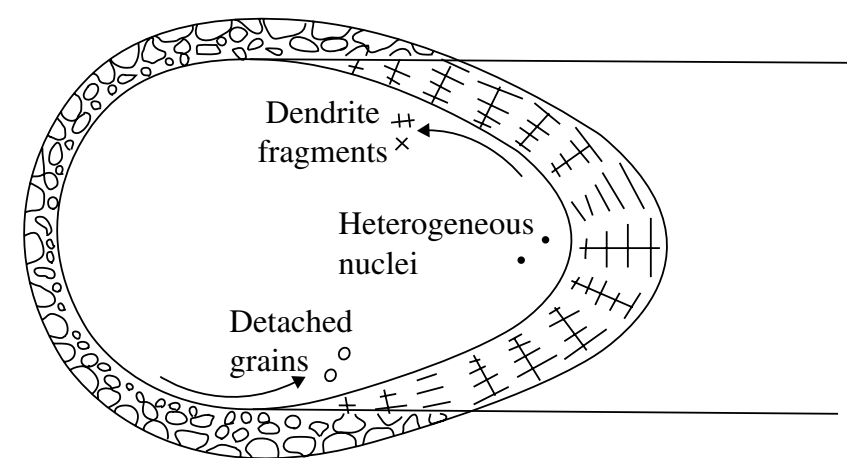
$$r^* = 2\gamma_{SL} \frac{T_m}{\Delta H_M \Delta T}$$

γ_{SL} is the S–L interfacial energy, T_m is the melting temperature, ΔH_M is the latent heat of melting, and ΔT is the amount of liquid undercooling. Note that as the amount of undercooling increases, the critical radius size decreases. Solid spheres less than r^* will simply remelt, while those exceeding r^* will grow.

In many solidification processes, heterogeneous nucleation may accompany homogeneous nucleation, or completely dominate it (as in the case of welding). Heterogeneous nucleation occurs from a foreign particle (such as an oxide, nitride, sulfide, etc.) or an existing solid substrate. Since these heterogeneous sites are stable at or above the melting temperature of the alloy, little or no undercooling is required for nucleation to occur. For example, single-crystal Ni-base turbine blades are manufactured using a “seed” crystal of a given orientation as a heterogeneous nucleation site.

In fusion welds, a number of heterogeneous nucleation events are possible, as illustrated schematically in Figure 2.7 [1]. Convective fluid flow during solidification can result in the tips of dendrites at the solidification front or grains in the surrounding solid metal to detach and be swept into the liquid. Depending on the liquid undercooling and size of the detached solid species, this solid can act as a nucleation site. In some casting operations, the casting mold walls are vibrated to induce dendrite fragmentation and subsequent refinement of the solidification structure. These heterogeneous nucleation events are only possible if the adjacent liquid is undercooled (negative G_L). In the case where the liquid is superheated (positive G_L), these nucleants will remelt. This is generally the case with weld solidification, and thus, this form of heterogeneous nucleation is generally not possible during fusion welding.

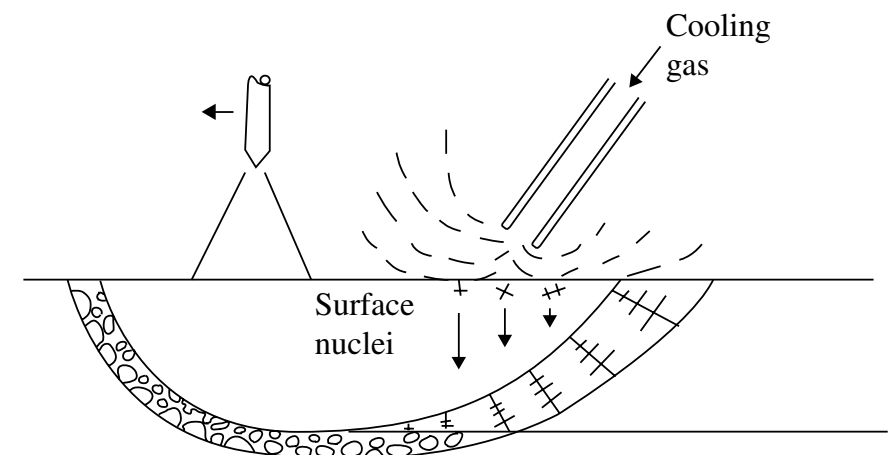
Higher melting point particles added to or formed within the liquid can also serve as nucleation sites. Sometimes called inoculants, these particles can substitute for



Mechanism 1: Dendrite fragmentation

Mechanism 2: Grain detachment

Mechanism 3: Heterogeneous nucleation



Mechanism 4: Surface nucleation

FIGURE 2.7 Various forms of heterogeneous nucleation associated with a molten weld pool (From Ref. [1]).

the homogeneous nuclei described previously. This type of nucleation can occur on the surface of the liquid, particularly if an oxide surface layer forms. In some cases, it may be possible to add nucleants directly to the molten pool, but this is usually not practical.

Heterogeneous nucleation off a solid substrate is called epitaxial nucleation, coming from the Greek word *epitaxis*, which means “to grow from.” As noted earlier, the use of “seed crystals” in some casting or crystal growth applications is a form of epitaxial nucleation. Epitaxial nucleation is the dominant form of heterogeneous nucleation during weld solidification.

Epitaxial nucleation requires essentially no undercooling or other driving forces. As a result, solidification begins immediately upon cooling below the liquidus temperature. When the compositions of the base metal substrate and liquid are similar, the solidification front that grows from a given grain on that substrate will retain the same crystallographic orientation. Since grain orientation of the substrate is generally random, this results in a continuation of the crystallographic misorientation of the

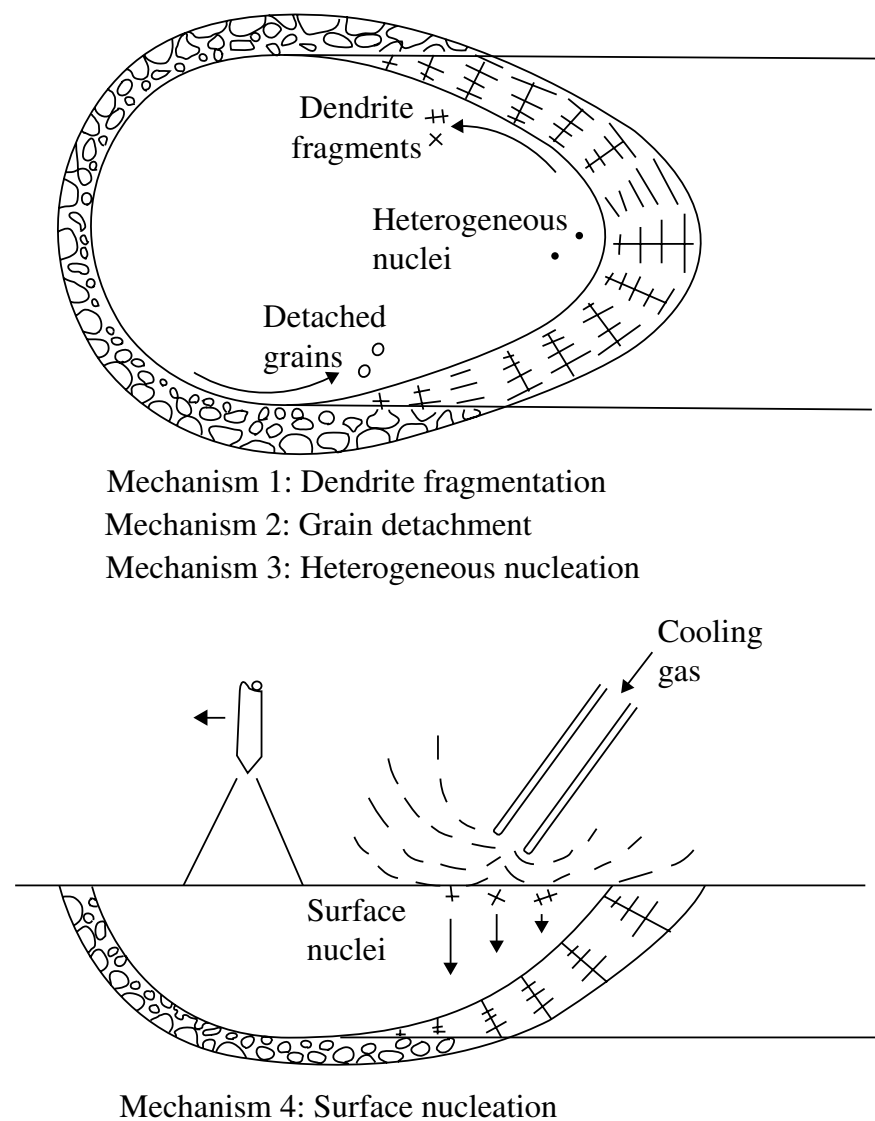


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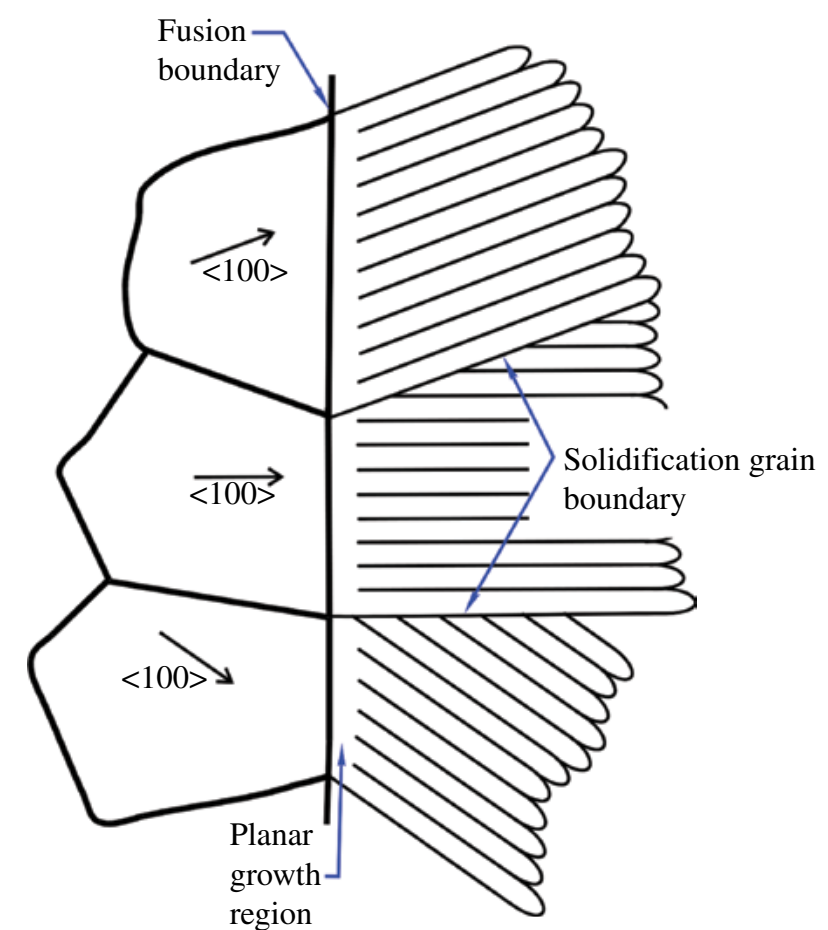


FIGURE 2.8 Schematic illustration of epitaxial nucleation.

base metal grains across the fusion boundary into the solidifying solid, as illustrated in Figure 2.8. That is to say, grain boundaries are continuous across the original fusion boundary where epitaxial nucleation occurred.

In fcc and bcc metals, solidification growth occurs preferentially along the cube edge, or $\langle 100 \rangle$ crystallographic directions. These are sometimes called “easy growth” directions, since solidification is most efficient in this crystallographic orientation. In hcp metals, growth occurs parallel to the basal plane in the $\langle 10\bar{1}0 \rangle$ direction. Growth is most favorable when these easy growth directions are parallel to the heat flow vector through the S–L interface. This results in growth that is roughly perpendicular to the S–L interface.

2.3.1.3 Solidification Modes Multiple solidification modes can occur in metals. These modes describe the different morphological forms that can exist at the S–L interface and in many cases are still apparent when cooled to room temperature. Under conditions of low solidification rates, steep temperature gradients, or both, plane front solidification can occur. In most practical cases, the plane front breaks down into other modes described by either cellular or dendritic morphologies. The solidification mode that is most stable is dictated by the combined effect of composition, temperature gradient, and solidification rate.

The range of solidification modes that are observed in metals are illustrated in Figure 2.9 [6]. A planar solidification front first breaks down into a cellular front and

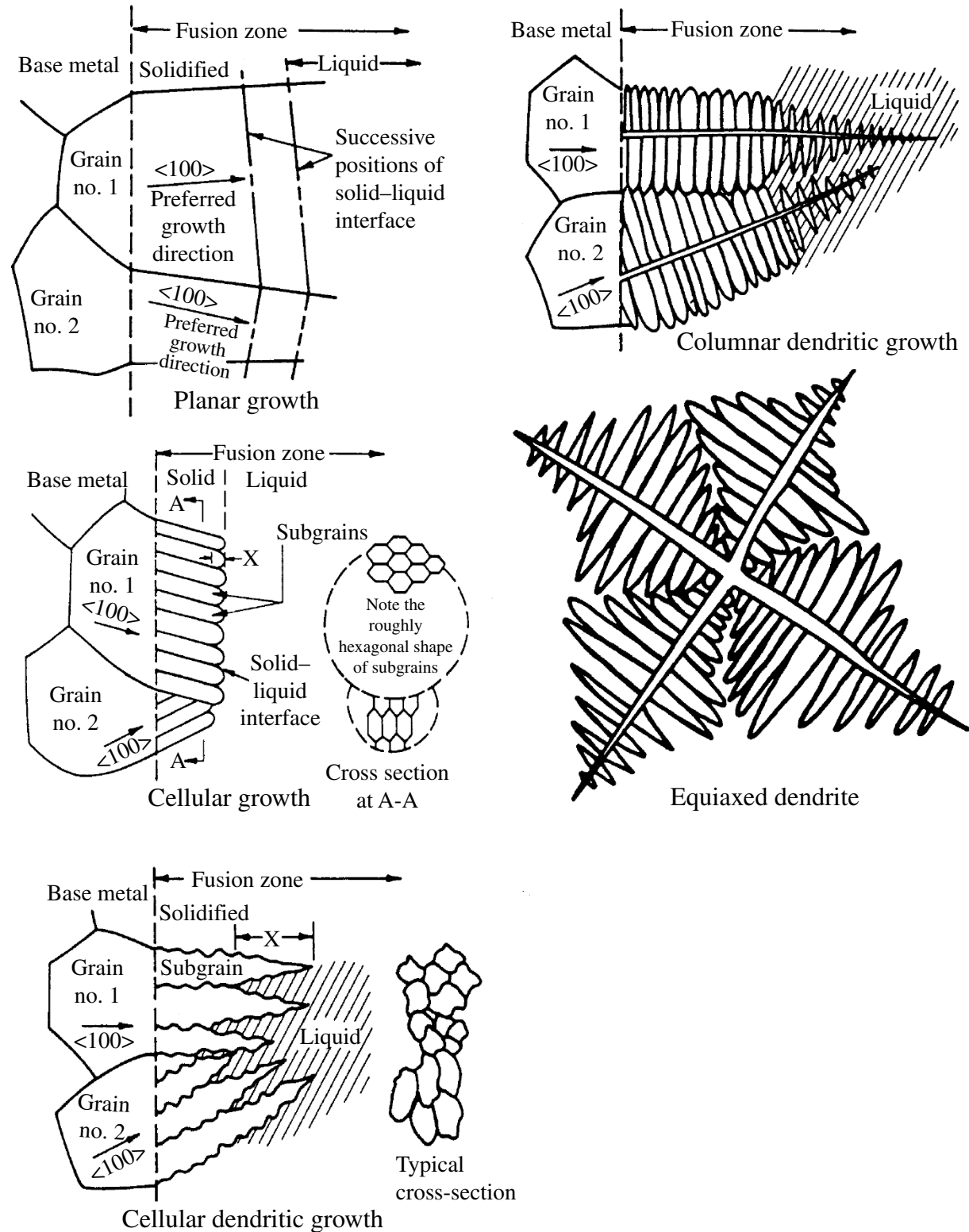


FIGURE 2.9 Solidification modes that occur in metals (From Ref. [6]. © AWS).

then into more complex dendritic morphologies, depending on solidification conditions. Most alloys solidify in either cellular, cellular dendritic, columnar dendritic modes, or a combination of these. According to Chalmers [7], the solidification mode is determined by the degree of *constitutional supercooling*, or undercooling, that exists in the liquid immediately in front of the S–L interface. As the extent of supercooling increases, more dendritic modes of solidification are favored. This concept will be described later in this chapter.

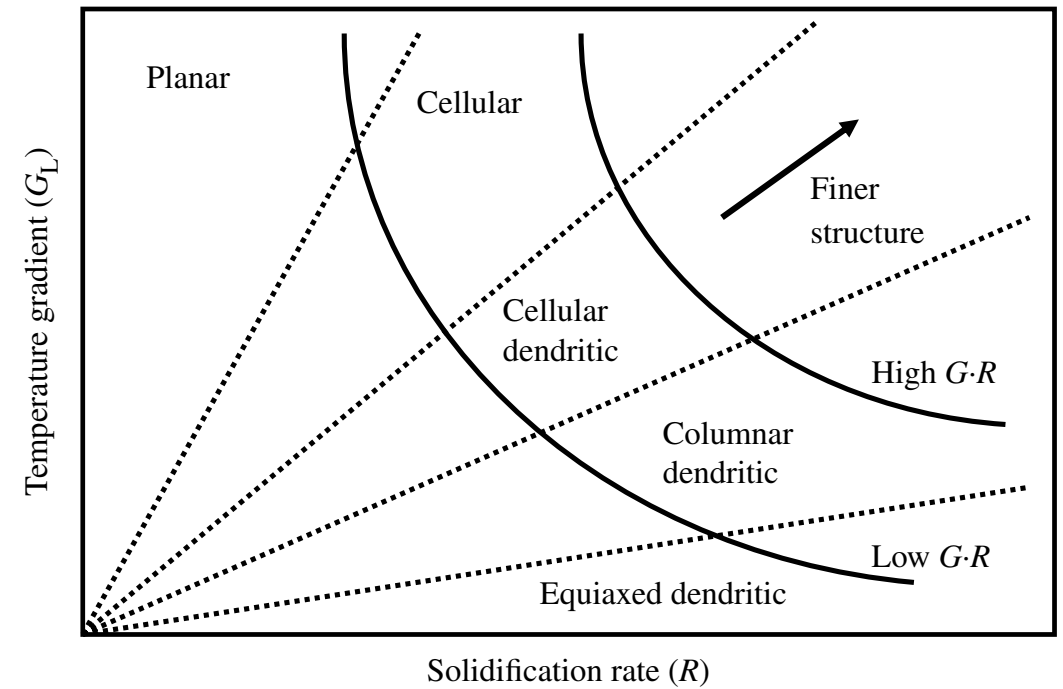


FIGURE 2.10 Effect of temperature gradient in the liquid, G_L , and solidification growth rate, R , on solidification mode.

The two most common solidification modes found in fusion welds and castings are the cellular and cellular dendritic modes. A planar solidification mode is normally not stable in actual practice. In laboratory experiments, it can be maintained at very slow growth rates in pure materials. Under normal solidification conditions, the planar interface quickly breaks down into a cellular or cellular dendritic growth front.

Equiaxed dendritic growth is also not normally observed in fusion welds due to the large constitutional supercooling required. It is sometimes observed in the terminal weld crater of fusion welds of some materials where the temperature gradient is very low due to the extinction of the arc (or other heat sources).

In metal alloys, the combination of temperature gradient, G_L , and solidification growth rate, R , influences solidification mode. As shown in Figure 2.10, a planar growth mode is favorable when the gradient is high and/or the solidification rate is very low. As solidification rate increases for all but very high temperature gradients, the solidification mode shifts to cellular and then dendritic. If the temperature gradient is extremely low, equiaxed dendritic growth is possible. As the product $G \cdot R$ increases, reflecting an increase in cooling rate, the structures that form become finer. This results in cellular or dendritic structures that are spaced much more closely relative to the distance between adjacent cell and dendrite arms.

Composition also has an effect on solidification mode. As shown in Figure 2.11, a pure metal will solidify with a planar front under most combinations of G_L and R . When solute or impurity elements are added, planar growth is only favorable when the gradient is very high, the solidification rate is very low, or a combination of these conditions. Most alloys will solidify in dendritic or cellular modes, as illustrated by the shaded region in the diagram. As described previously, equiaxed dendritic growth is only favored when the gradient is very shallow, a condition that usually does not exist in fusion welds.