Glass-ceramics

The term **glass-ceramics** refers to engineered materials that begin as amorphous glasses and end up as crystalline ceramics with an ultra-fine grain size. These materials are then nearly free from porosity, mechanically stronger, and often much more resistant to thermal shock. Nucleation does not occur easily in silicate glasses; however, we can help by introducing nucleating agents such as titania (TiO_2) and zirconia (ZrO_2). Engineered glass-ceramics take advantage of the ease with which glasses can be melted and formed. Once a glass is formed, we can heat it to deliberately form ultra-fine crystals, obtaining a material that has considerable mechanical toughness and thermal shock resistance. The crystallization of glass-ceramics continues until all of the material crystallizes (up to 99.9% crystallinity can be obtained). If the grain size is kept small (50–100 nm), glass ceramics can often be made transparent. All glasses eventually will crystallize as a result of exposure to high temperatures for long lengths of times. In order to produce a glass-ceramic however, the crystallization must be carefully controlled.

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.

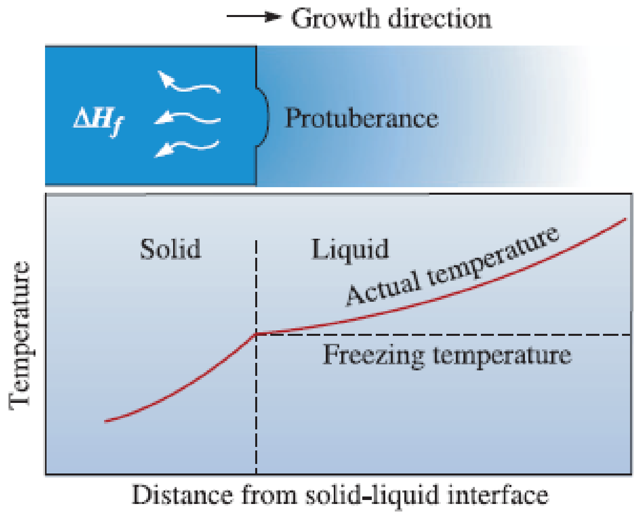


Figure 9-3 When the temperature of the liquid is above the freezing temperature, a protuberance on the solid-liquid interface will not grow, leading to maintenance of a planar interface. Latent heat is removed from the interface through the solid.

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.

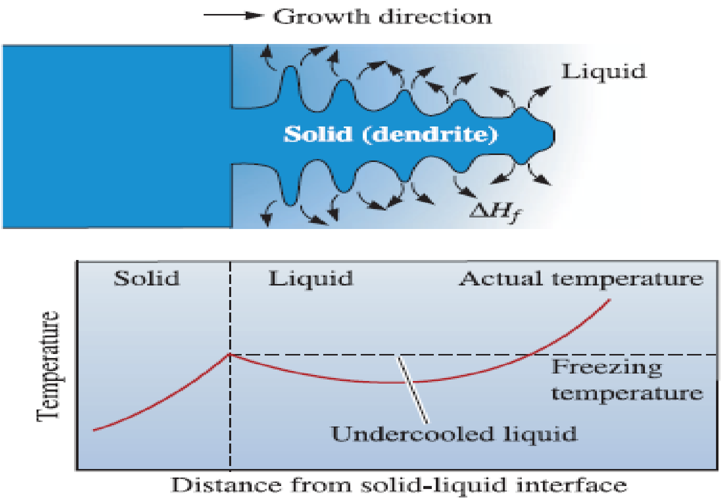
Dendritic Growth

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 (9-3)

$$\text{Dendritic fraction } = f = \frac{c\Delta T}{\Delta H_f}$$

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 ΔT increases 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.



(a)

Figure 9-4 (a) If the liquid is undercooled,

Solidification Time and Dendrite Size

The rate at which growth of the solid occurs depends on the cooling rate, or the rate of heat extraction. A higher cooling rate produces rapid solidification, or short solidification times. The time *ts* required for a simple casting to solidify completely can be calculated using **Chvorinov's rule**:

$$t_s = B\left(\frac{V}{A}\right)^n \qquad (9\text{-}4)$$

where *V* is the volume of the casting and represents the amount of heat that must be removed before freezing occurs, *A* is the surface area of the casting in contact with the mold and represents the surface from which heat can be transferred away from the casting, *n* is a constant (usually about 2), and B is the **mold constant**. The mold constant depends on the properties and initial temperatures of both the metal and the mold. This rule basically accounts for the geometry of a casting and the heat transfer conditions. The rule states that, for the same conditions, a casting with a small volume and relatively large surface area will cool more rapidly.

Example 9-2 *Redesign of a Casting for Improved Strength*

Your company currently is producing a disk-shaped brass casting 2 in. thick and 18 in. in diameter. You believe that by making the casting solidify 25% faster the improvement in the tensile properties of the casting will permit the casting to be made lighter in weight. Design the casting to permit this. Assume that the mold constant is 22 min>in.2 for this process and *n* = 2.

SOLUTION

One approach would be to use the same casting process, but reduce the thickness of the casting. The thinner casting would solidify more quickly and, because of the faster cooling, should have improved mechanical properties. Chvorinov’s rule helps us calculate the required thickness. If *d* is the diameter and *x* is the thickness of the casting, then the volume, surface area, and solidification time of the 2-in. thick casting are

$$V = (\pi/4)d^2x = (\pi/4)(18)^2(2) = 508.9 \text{ in.}^3$$

$$A = 2(\pi/4)d^2 + \pi dx = 2(\pi/4)(18)^2 + \pi(18)(2) = 622 \text{ in.}^2$$

$$t = \mathrm{B}\left(\frac{V}{A}\right)^2 = (22)\left(\frac{508.9}{622}\right)^2 = 14.73 \text{ min}$$

The solidification time *tr* of the redesigned casting should be 25% shorter than the current time:

tr = 0.75*t* = (0.75) (14.73) = 11.05 min