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

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

where _*Hf* is the latent heat of fusion per unit volume, *Tm* is the equilibrium solidification temperature in kelvin, and $\Delta T = (Tm - T)$ 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 decreases. Table 9-1 presents values for σ*sl*, Δ*Hf*, and typical undercooling's observed experimentally for homogeneous nucleation. The following example shows how we can calculate the critical radius of the nucleus for the solidification of copper.

TABLE 9-1 ■ *Values for freezing temperature, latent heat of fusion, surface energy, and maximum undercooling for selected materials*

Material	Freezing Temperature (T_m) (°C)	Heat of Fusion (ΔH_f) (J/cm^3)	Solid-Liquid Interfacial Energy (σ_{sl}) (J/cm^2)	Typical Undercooling for Homogeneous Nucleation (ΔT) (°C)
Ga	30	488	56×10^{-7}	76
Bi	271	543	54×10^{-7}	90
Pb	327	237	33×10^{-7}	80
Ag	962	965	126×10^{-7}	250
Cu	1085	1628	177×10^{-7}	236
Ni	1453	2756	255×10^{-7}	480
Fe	1538	1737	204×10^{-7}	420
NaCl	801			169
CsCl	645			152
H_2O	0			40

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 or $\Delta T = 236°C = 236$ K.

The lattice parameter for FCC copper is $a_0 = 0.3615$ nm $= 3.615 \times 1$

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

From Table 9-1, we can see that 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

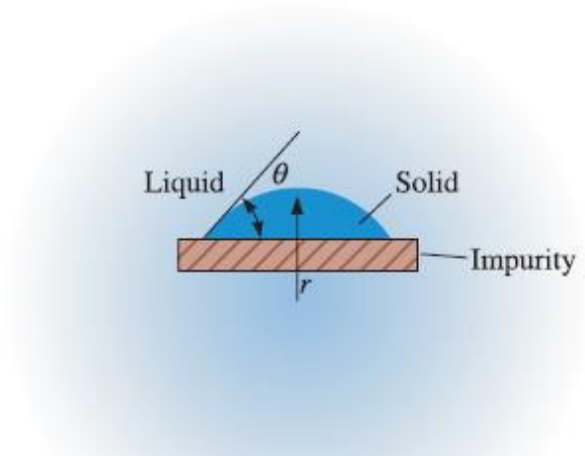

Figure 9-2
A solid forming on an impurity can assume the critical radius with a smaller increase in the surface energy. Thus, heterogeneous nucleation can occur with relatively low undercoolings.

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.

Applications of Controlled Nucleation

Grain Size Strengthening

When a metal casting freezes, impurities in the melt and the walls of the mold in which solidification occurs serve as heterogeneous nucleation sites. Sometimes we intentionally introduce nucleating particles into the

liquid. Such practices are called **grain refinement** or **inoculation**. Chemicals added to molten metals to promote nucleation and, hence, a finer grain size, are known as grain refiners or **inoculants**. For example, a combination of 0.03% titanium (Ti) and 0.01% boron (B) is added to many liquid-aluminum alloys. Tiny particles of an aluminum titanium compound (Al_3Ti) or titanium diboride (TiB_2) form and serve as sites for heterogeneous nucleation.

Grain refinement or inoculation produces a large number of grains, each beginning to grow from one nucleus. The greater grain boundary area provides grain size strengthening in metallic materials. This was discussed using the Hall-Petch equation.

Second-Phase Strengthening

In Chapters 4 and 5, we learned that in metallic materials, dislocation motion can be resisted by grain boundaries or the formation of ultra-fine precipitates of a second phase. Strengthening materials using ultra-fine precipitates are known as **dispersion strengthening** or **second-phase strengthening**; it is used extensively in enhancing the mechanical properties of many alloys. This process involves **solid-state phase transformations** (i.e., one solid transforming into another). The grain boundaries as well as atomic level defects within the grains of the parent phase (α) often serve as nucleation sites for heterogeneous nucleation of the new phase (β). This nucleation phenomenon plays a critical role in strengthening mechanisms.

Glasses

For rapid cooling rates and or high viscosity melts, there may be insufficient time for nuclei to form and grow. When this happens, the liquid structure is locked into place and an amorphous—or glassy—solid forms. The complex crystal structure of many ceramic and polymeric materials prevents nucleation of a solid crystalline structure even at slow cooling rates. Some alloys with special compositions have sufficiently complex crystal structures, so they may form amorphous materials if cooled rapidly from the melt. These materials are known as metallic glasses. Typically, good metallic glass formers are multi-component alloys, often with large differences in the atomic sizes of the elemental constituents. This complexity limits the solid solubility of the elements in the crystalline phases, thus requiring large chemical fluctuations to form the critical-sized crystalline nuclei. Metallic glasses were initially produced via **rapid solidification processing** in which cooling rates of 106°C-1 were attained by forming continuous, thin metallic ribbons about 0.0015 in. thick. (Heat can be extracted quickly from ribbons with a large surface area to volume ratio.)

Bulk metallic glasses with diameters greater than 1 in. are now produced using a variety of processing techniques for compositions that require cooling rates on the order of only tens of degrees per second. Many bulk metallic glass compositions have been discovered, including $Pd_{40}Ni_{40}P_{20}$ and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$. Many metallic glasses have strengths in excess of 250,000 psi while retaining fracture toughness's of more than 10,000 psi Excellent corrosion resistance, magnetic properties, and other physical properties make these materials attractive for a wide variety of applications.

Other examples of materials that make use of controlled nucleation are colored glass and **photochromic glass** (glass that can change color or tint upon exposure to sunlight). In these otherwise amorphous materials, Nano crystallites of different materials are deliberately nucleated. The crystals are small and, hence, do not make the glass opaque. They do have special optical properties that make the glass brightly colored or photochromic.

Many materials formed from a vapor phase can be cooled quickly so that they do not crystallize and, therefore, are amorphous (i.e., amorphous silicon), illustrating that amorphous or non-crystalline materials do *not* always have to be formed from melts.