

10.1 (a) Rewrite the expression for the total free energy change for nucleation (Equation 10.1) for the case of a cubic nucleus of edge length a (instead of a sphere of radius r). Now differentiate this expression with respect to a (per Equation 10.2) and solve for both the critical cube edge length, a^* , and ΔG^* .

(b) Is ΔG^* greater for a cube or a sphere? Why?

Solution

(a) This problem first asks that we rewrite the expression for the total free energy change for nucleation (analogous to Equation 10.1) for the case of a cubic nucleus of edge length a . The volume of such a cubic nucleus is a^3 , whereas the total surface area is $6a^2$ (since there are six faces each of which has an area of a^2). Thus, the expression for ΔG is as follows:

$$\Delta G = a^3 \Delta G_v + 6a^2 \gamma$$

Differentiation of this expression with respect to a is as

$$\begin{aligned} \frac{d \Delta G}{da} &= \frac{d(a^3 \Delta G_v)}{da} + \frac{d(6a^2 \gamma)}{da} \\ &= 3a^2 \Delta G_v + 12a \gamma \end{aligned}$$

If we set this expression equal to zero as

$$3a^2 \Delta G_v + 12a \gamma = 0$$

and then solve for a ($= a^*$), which gives

$$a^* = - \frac{4\gamma}{\Delta G_v}$$

Substitution of this expression for a in the above expression for ΔG yields an equation for ΔG^* as

$$\begin{aligned} \Delta G^* &= (a^*)^3 \Delta G_v + 6(a^*)^2 \gamma \\ &= \left(- \frac{4\gamma}{\Delta G_v} \right)^3 \Delta G_v + 6\gamma \left(- \frac{4\gamma}{\Delta G_v} \right)^2 \\ &= \frac{32\gamma^3}{(\Delta G_v)^2} \end{aligned}$$

(b) ΔG_v for a cube—i.e., $(32) \left[\frac{\gamma^3}{(\Delta G_v)^2} \right]$ —is greater than for a sphere—i.e., $\left(\frac{16\pi}{3} \right) \left[\frac{\gamma^3}{(\Delta G_v)^2} \right]$ = (16.8) $\left[\frac{\gamma^3}{(\Delta G_v)^2} \right]$. The reason for this is that surface-to-volume ratio of a cube is greater than for a sphere.

10.2 (a) For the solidification of nickel, calculate the critical radius r^* and the activation free energy ΔG^* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are $-2.53 \times 10^9 \text{ J/m}^3$ and 0.255 J/m^2 , respectively. Use the supercooling value found in Table 10.1.

(b) Now calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.360 nm for solid nickel at its melting temperature.

Solution

(a) This portion of the problem asks that we compute r^* and ΔG^* for the homogeneous nucleation of the solidification of Ni. First of all, Equation 10.6 is used to compute the critical radius. The melting temperature for nickel is 1455°C ; also values of ΔH_f ($-2.53 \times 10^9 \text{ J/m}^3$) and γ (0.255 J/m^2) are given in the problem statement, and the supercooling value found in Table 10.1 is 319°C (which is also 319 K because this value is really $T_m - T$, which is the same for Celsius and Kelvin). Thus, from Equation 10.6 we have

$$\begin{aligned} r^* &= \left(-\frac{2\gamma T_m}{\Delta H_f} \right) \left(\frac{1}{T_m - T} \right) \\ &= \left[-\frac{(2)(0.255 \text{ J/m}^2)(1455 + 273 \text{ K})}{-2.53 \times 10^9 \text{ J/m}^3} \right] \left(\frac{1}{319 \text{ K}} \right) \\ &= 1.09 \times 10^{-9} \text{ m} = 1.09 \text{ nm} \end{aligned}$$

For computation of the activation free energy, Equation 10.7 is employed. Thus

$$\begin{aligned} \Delta G^* &= \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(T_m - T)^2} \\ &= \left[\frac{(16)(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 \text{ K})^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2} \right] \left[\frac{1}{(319 \text{ K})^2} \right] \\ &= 1.27 \times 10^{-18} \text{ J} \end{aligned}$$

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius r^*), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as nickel has the FCC crystal structure, its unit cell volume is just a^3 where a is the unit cell

length (i.e., the lattice parameter); this value is 0.360 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\begin{aligned}\# \text{ unit cells/particle} &= \frac{\frac{4}{3}\pi r^3}{a^3} \\ &= \frac{\left(\frac{4}{3}\right)(\pi)(1.09 \text{ nm})^3}{(0.360 \text{ nm})^3} = 116 \text{ unit cells}\end{aligned}$$

Inasmuch as 4 atoms are associated with each FCC unit cell, the total number of atoms per critical nucleus is just

$$\begin{aligned}& (116 \text{ unit cells/critical nucleus})(4 \text{ atoms/unit cell}) \\ &= 464 \text{ atoms/critical nucleus}\end{aligned}$$

10.5 The kinetics of the austenite-to-pearlite transformation obeys the Avrami relationship. Using the fraction transformed–time data given here, determine the total time required for 95% of the austenite to transform to pearlite:

<i>Fraction Transformed</i>	<i>Time (s)</i>
0.2	280
0.6	425

Solution

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of n and k . In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp(-kt^n)$$

Now taking natural logarithms

$$\ln(1 - y) = -kt^n$$

Or

$$-\ln(1 - y) = kt^n \quad (10.17c)$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again of both sides of this equation, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. Using values cited in the problem statement, the two equations are thus

$$\ln\left\{\ln\left[\frac{1}{1 - 0.2}\right]\right\} = \ln k + n \ln(280 \text{ s})$$

$$\ln\left\{\ln\left[\frac{1}{1 - 0.6}\right]\right\} = \ln k + n \ln(425 \text{ s})$$

Solving these two expressions simultaneously for n and k yields $n = 3.385$ and $k = 1.162 \times 10^{-9}$ for time in seconds.

Now it becomes necessary to solve for the value of t at which $y = 0.95$. Equation 10.17c given above may be rewritten as follows:

$$t^n = -\frac{\ln(1-y)}{k}$$

And solving for t leads to

$$t = \left[-\frac{\ln(1-y)}{k} \right]^{1/n}$$

Now incorporating into this expression values for n and k determined above, the time required for 95% austenite transformation is equal to

$$t = \left[-\frac{\ln(1-0.95)}{1.162 \times 10^{-9}} \right]^{1/3.385} = 603 \text{ s}$$

10.22 Briefly describe the simplest heat treatment procedure that would be used in converting a 0.76 wt% C steel from one microstructure to the other, as follows:

- (a) Martensite to spheroidite
- (b) Bainite to pearlite
- (c) Spheroidite to pearlite
- (d) Tempered martensite to martensite

Answer

In this problem we are asked to describe the simplest heat treatment that would be required to convert a eutectoid steel from one microstructure to another. Figure 10.28 is used to solve the several parts of this problem.

- (a) For martensite to spheroidite, heat to a temperature in the vicinity of 700°C (but below the eutectoid temperature), for on the order of 24 h.
- (b) For bainite to pearlite, first austenitize at a temperature of about 760°C, then cool to room temperature at a rate less than about 35°C/s (according to Figure 10.28).
- (c) For spheroidite to pearlite, same as (b) above.
- (d) For tempered martensite to martensite, first austenitize at a temperature of about 760°C, and rapidly quench to room temperature at a rate greater than about 140°C/s (according to Figure 10.28).