

Homework #7

Due March 25, 2008

11.4 (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 11.6 is used to compute the critical radius. The melting temperature for nickel, found inside the front cover 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 1.1 is 319°C (or 319 K). Thus, from Equation 11.6 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 11.7 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 nucleus 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

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

11.5 (a) For this part of the problem we are asked to calculate the critical radius for the solidification of nickel (per Problem 11.4), for 200 K and 300 K degrees of supercooling, and assuming that there are 10^6 nuclei per meter cubed for homogeneous nucleation. In order to calculate the critical radii, we replace the $T_m - T$ term in Equation 11.6 by the degree of supercooling (denoted as ΔT) cited in the problem.

For 200 K supercooling,

$$\begin{aligned} r_{200}^* &= \left(-\frac{2\gamma T_m}{\Delta H_f} \right) \left(\frac{1}{\Delta T} \right) \\ &= \left[-\frac{(2)(0.255 \text{ J/m}^2)(1455 + 273 \text{ K})}{-2.53 \times 10^9 \text{ J/m}^3} \right] \left(\frac{1}{200 \text{ K}} \right) \\ &= 1.74 \times 10^{-9} \text{ m} = 1.74 \text{ nm} \end{aligned}$$

For 300 K supercooling,

$$\begin{aligned} r_{300}^* &= \left[-\frac{(2)(0.255 \text{ J/m}^2)(1455 + 273 \text{ K})}{-2.53 \times 10^9 \text{ J/m}^3} \right] \left(\frac{1}{300 \text{ K}} \right) \\ &= 1.16 \times 10^{-9} \text{ m} = 1.16 \text{ nm} \end{aligned}$$

In order to compute the number of stable nuclei that exist at 200 K and 300 K degrees of supercooling, it is necessary to use Equation 11.8. However, we must first determine the value of K_1 in Equation 11.8, which in turn requires that we calculate ΔG^* at the homogeneous nucleation temperature using Equation 11.7; this was done in Problem 11.4, and yielded a value of $\Delta G^* = 1.27 \times 10^{-18} \text{ J}$. Now for the computation of K_1 , using the value of n^* for at the homogenous nucleation temperature (10^6 nuclei/m^3):

$$\begin{aligned} K_1 &= \frac{n^*}{\exp\left(-\frac{\Delta G^*}{kT}\right)} \\ &= \frac{10^6 \text{ nuclei/m}^3}{\exp\left[-\frac{1.27 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1455 \text{ K} - 319 \text{ K})}\right]} \\ &= 1.52 \times 10^{41} \text{ nuclei/m}^3 \end{aligned}$$

Now for 200 K supercooling, it is first necessary to recalculate the value ΔG^* of using Equation 11.7, where, again, the $T_m - T$ term is replaced by the number of degrees of supercooling, denoted as ΔT , which in this case is 200 K.

Thus

$$\Delta G_{200}^* = \left(\frac{16\pi \gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(\Delta T)^2}$$

$$= \left[\frac{(16)(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 \text{ K})^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2} \right] \left[\frac{1}{(200 \text{ K})^2} \right]$$

$$= 3.24 \times 10^{-18} \text{ J}$$

And, from Equation 11.8, the value of n^* is

$$n_{200}^* = K_1 \exp\left(-\frac{\Delta G_{200}^*}{kT}\right)$$

$$= (1.52 \times 10^{41} \text{ nuclei/m}^3) \exp\left[-\frac{3.24 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1455 \text{ K} - 200 \text{ K})}\right]$$

$$= 8.60 \times 10^{-41} \text{ stable nuclei}$$

Now, for 300 K supercooling the value of ΔG^* is equal to

$$\Delta G_{300}^* = \left[\frac{(16)(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 \text{ K})^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2} \right] \left[\frac{1}{(300 \text{ K})^2} \right]$$

$$= 1.44 \times 10^{-18} \text{ J}$$

from which we compute the number of stable nuclei at 300 K of supercooling as

$$n_{300}^* = K_1 \exp\left(-\frac{\Delta G_{300}^*}{kT}\right)$$

$$n^* = (1.52 \times 10^{41} \text{ nuclei/m}^3) \exp\left[-\frac{1.44 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1455 \text{ K} - 300 \text{ K})}\right]$$

$$= 88 \text{ stable nuclei}$$

(b) Relative to critical radius, r^* for 300 K supercooling is slightly smaller than that for 200 K (1.16 nm versus 1.74 nm). [From Problem 11.4, the value of r^* at the homogeneous nucleation temperature (319 K) was 1.09 nm.] More significant, however, are the values of n^* at these two degrees of supercooling, which are dramatically different— 8.60×10^{-41} stable nuclei at $\Delta T = 200 \text{ K}$, versus 88 stable nuclei at $\Delta T = 300 \text{ K}$!

11.7 This problem asks that we compute the rate of some reaction given the values of n and k in Equation 11.17. Since the reaction rate is defined by Equation 11.18, it is first necessary to determine $t_{0.5}$, or the time necessary for the reaction to reach $y = 0.5$. We must first manipulate Equation 11.17 such that t is the dependent variable. We first rearrange Equation 11.17 as

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

and then take natural logarithms of both sides:

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

which may be rearranged so as to read

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

Now, solving for t from this expression leads to

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

For $t_{0.5}$ this equation takes the form

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{k} \right]^{1/n}$$

And, incorporation of values for n and k given in the problem statement (2.0 and 5×10^{-4} , respectively), then

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{5 \times 10^{-4}} \right]^{1/2} = 37.23 \text{ s}$$

Now, the rate is computed using Equation 11.18 as

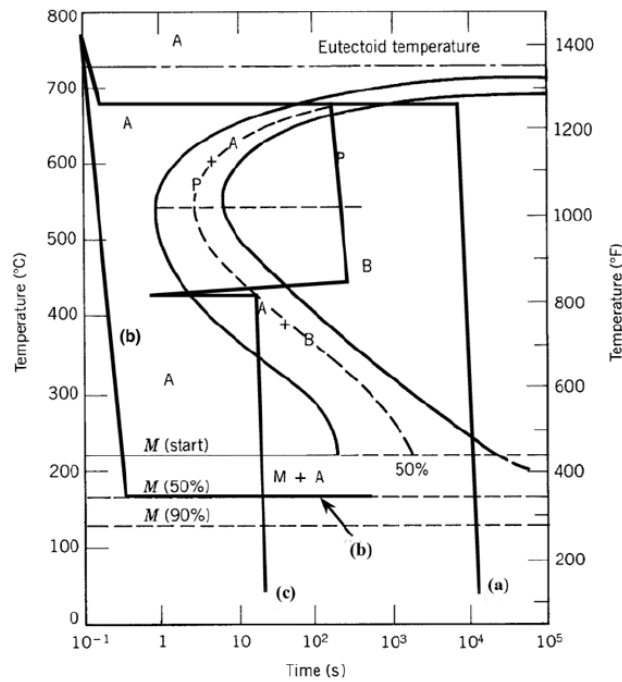
$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{37.23 \text{ s}} = 2.69 \times 10^{-2} \text{ (s)}^{-1}$$

11A. Transformation rate is a combination of growth rate (which occurs by diffusion) and nucleation rate. Growth rate is higher at higher temperatures because it is diffusion controlled and diffusion increases at higher temperatures. Nucleation rate is low at high temperatures because the critical radius size is very large and such large embryos do not form easily. Nucleation rate is also low at low temperatures because diffusion is slow, and even though the size of the critical embryo is small, the addition of atoms to the embryo (which is required to form a stable nucleus) is slow. Thus, at some intermediate temperature, nucleation and growth combine to form the maximum transformation rate.

11.18 This problem asks us to determine the nature of the final microstructure of an iron-carbon alloy of eutectoid composition, that has been subjected to various isothermal heat treatments. Figure 11.23 is used in these determinations.

- (a) 50% coarse pearlite and 50% martensite
- (b) 100% spheroidite
- (c) 50% fine pearlite, 25% bainite, and 25% martensite
- (d) 100% martensite
- (e) 40% bainite and 60% martensite
- (f) 100% bainite
- (g) 100% fine pearlite
- (h) 100% tempered martensite

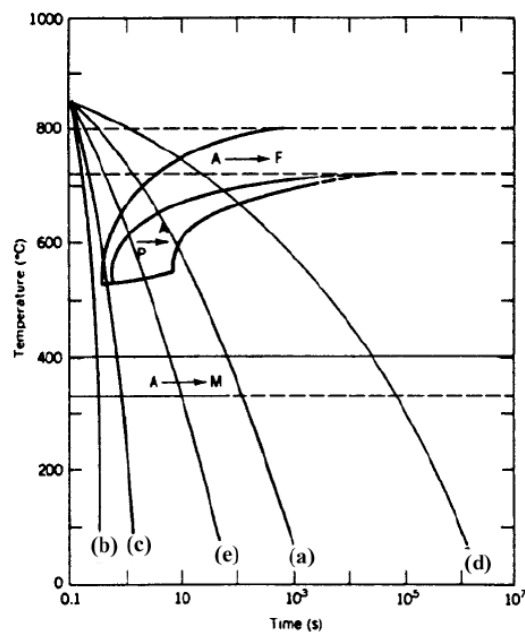
11.19 Below is shown the isothermal transformation diagram for a eutectoid iron-carbon alloy, with time-temperature paths that will yield (a) 100% coarse pearlite; (b) 50% martensite and 50% austenite; and (c) 50% coarse pearlite, 25% bainite, and 25% martensite.



11.20 We are asked to determine which microconstituents are present in a 1.13 wt% C iron-carbon alloy that has been subjected to various isothermal heat treatments. These microconstituents are as follows:

- (a) Martensite
 - (b) Proeutectoid cementite and martensite
 - (c) Bainite
 - (d) Spheroidite
 - (e) Cementite, medium pearlite, bainite, and martensite
 - (f) Bainite and martensite
 - (g) Proeutectoid cementite, pearlite, and martensite
 - (h) Proeutectoid cementite and fine pearlite
-

11.24 Below is shown a continuous cooling transformation diagram for a 0.35 wt% C iron-carbon alloy, with continuous cooling paths that will produce (a) fine pearlite and proeutectoid ferrite; (b) martensite; (c) martensite and proeutectoid ferrite; (d) coarse pearlite and proeutectoid ferrite; and (e) martensite, fine pearlite, and proeutectoid ferrite.



11.34 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 11.28 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 spheroidite to martensite, austenitize at a temperature of about 760°C, then quench to room temperature at a rate greater than about 140°C/s (according to Figure 11.28).

(c) 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 11.28).

(d) For pearlite to bainite, first austenitize at a temperature of about 760°C, rapidly cool to a temperature between about 220°C and 540°C, and hold at this temperature for the time necessary to complete the bainite transformation (according to Figure 11.23).

(e) For spheroidite to pearlite, same as (c) above.

(f) For pearlite to spheroidite, heat at about 700°C for approximately 20 h.

(g) 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 11.28).

(h) For bainite to spheroidite, simply heat at about 700°C for approximately 20 h.

11.34 Bainite to martensite: From 100% bainite, increase temperature to above the eutectoid temperature to create a solid solution of austenite. Cool rapidly to room temperature to form a martensite structure.

11.41 This problem asks us to compare various aspects of precipitation hardening, and the quenching and tempering of steel.

(a) With regard to the total heat treatment procedure, the steps for the *hardening of steel* are as follows:

- (1) Austenitize above the upper critical temperature.
- (2) Quench to a relatively low temperature.
- (3) Temper at a temperature below the eutectoid.
- (4) Cool to room temperature.

With regard to *precipitation hardening*, the steps are as follows:

- (1) Solution heat treat by heating into the solid solution phase region.

- (2) Quench to a relatively low temperature.
- (3) Precipitation harden by heating to a temperature that is within the solid two-phase region.
- (4) Cool to room temperature.

(b) For the *hardening of steel*, the microstructures that form at the various heat treating stages in part (a) are:

- (1) Austenite
- (2) Martensite
- (3) Tempered martensite
- (4) Tempered martensite

For *precipitation hardening*, the microstructures that form at the various heat treating stages in part (a) are:

- (1) Single phase
- (2) Single phase--supersaturated
- (3) Small plate-like particles of a new phase within a matrix of the original phase.
- (4) Same as (3)

11.B Precipitation hardening is only possible when it is possible to create a supersaturated solid solution. Thus, in an isomorphous solid solution (where there is complete solid solubility) precipitation hardening is not possible.

Figure 11.23

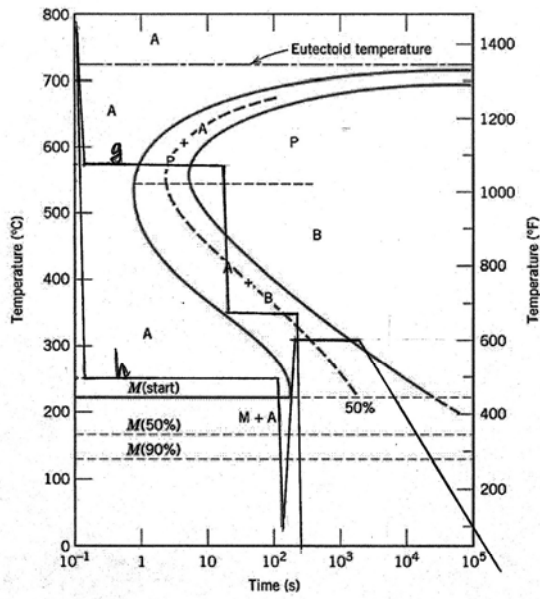
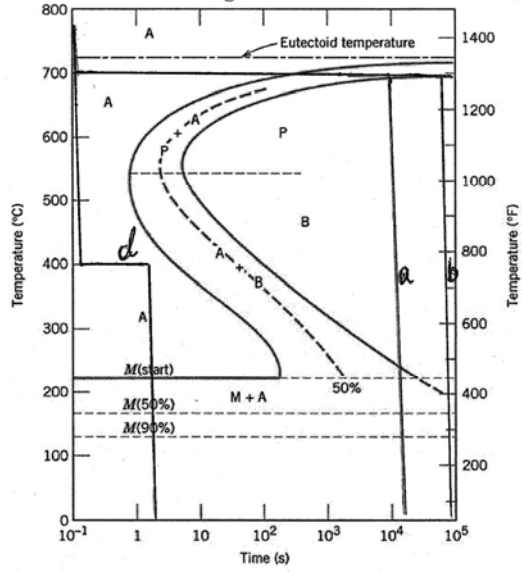


Figure 11.47

