

**FIG. 15.26** Variation of the distribution of the  $\theta$  precipitate particles with time at the solution temperature 540°C in an aluminum-4 percent copper alloy. (From Batz, D.L., Tanzilli, R.A., and Heckel, R.W., *Met. Trans.*, **1** 1651 [1970] With kind permission from Springer Science and Business Media.)

Aaron,<sup>19</sup> using an analysis similar to that of Zener in Sec. 15.6, has shown that the thickness of a precipitate should vary as

$$x(t) = x_0 - k\sqrt{Dt} \tag{15.60}$$

where  $x(t)$  is the thickness of the planar precipitate at any time  $t$ ,  $x_0$  is its original thickness,  $k$  is a constant, and  $D$  is the diffusion coefficient of the solute.

In the case of a spherical precipitate, the growth and dissolution kinetics are not generally so simply related. This subject is beyond the scope of this book, and for further information, one is referred to the review paper by Aaron and Kotler.<sup>20</sup>

## PROBLEMS

**15.1** The surface energy of a pure metal liquid,  $\gamma$ , is 600 dynes/cm<sup>2</sup>; the volume of an atom of this metal in the liquid is  $2.7 \times 10^{-25}$  cm<sup>3</sup>; and the free-energy difference between an atom in the vapor and liquid,  $\Delta g^{vl}$ , is  $-2.37$  J. Under these conditions, what would be the critical radius of a droplet,  $r_0^*$ , in nm and the free energy of the droplet,  $\Delta G_{r_0^*}$ , in J?

**15.2** The following data concern liquid magnesium at a temperature close to its boiling point of 1380 K: the surface energy of the liquid-vapor interface is 0.440 J/m<sup>2</sup>; the density of the liquid phase is  $1.50 \times 10^3$  kg/m<sup>3</sup>; and the atomic weight is 0.02432 kg/mol.

**(a)** First determine  $v_l$ , the volume of the liquid per atom. To do this, use the density and the atomic weight.

**(b)** Now compute the number of embryos in the vapor at a temperature just above the boiling point, that contain 10 magnesium atoms.

**15.3** Derive Eq. 15.20 of the text, starting with Eqs. 15.17 and 15.19.

**15.4** The following data are relative to the freezing of the pure metal copper: the melting point of copper is 1356 K; its latent heat of fusion is  $2.117 \times 10^5$  J/kg; its atomic weight is 0.06355 kg/mol; the surface energy of

the liquid-solid interface is 0.177 J/m<sup>2</sup>; and the density is 8.35 kg/m<sup>3</sup>.

- (a) Compute  $\Delta h^{ls}$ , the heat of fusion per atom, in J.
- (b) Evaluate the coefficients of both  $n$  and  $n^{2/3}$  in Eq. 15.15.
- (c) Determine the number of atoms in a critical nucleus when the supercooling is 5, 50, and 200 degrees.

**15.5** At this point use the data from Prob. 15.3 to evaluate the constant,  $A$ , in Eq. 15.20, where  $A = 4\eta^3\gamma_{ls}^3T_0^2/27(\Delta h^{ls})^2$ . Use Eq. 15.18 in the next two problems.

**15.6 (a)** Calculate the free energy,  $\Delta H_{nc}$ , needed to create a critical nucleus in copper when the amount of supercooling is 5 degrees.

- (b) How many times larger than  $kT$  is  $\Delta G_{nc}$ ?
- (c) Do the answers in parts (a) and (b) of this question imply that homogeneous nucleation is probable just below the melting point?

**15.7 (a)** Determine the free energy,  $\Delta G_{nc}$ , associated with a critical nucleus at 1256 K, where 1256 K corresponds to 100 degrees of supercooling.

- (b) Now compute  $\Delta G_{nc}$  if the supercooling is increased to 264 degrees, which by Table 14.1 corresponds to the maximum amount of supercooling that has been observed in copper.
- (c) Now discuss the results obtained in parts (a) and (b) of this question with respect to the probability of observing homogeneous nucleation.

**15.8** Consider the nucleation rate,  $I$ , on freezing. It is normally assumed that the vibration rate of the atoms in solids is about 10<sup>13</sup> Hertz. Assume that in the case of copper, the energy barrier,  $\Delta g_a$ , that an atom passes over in going from a liquid to the solid is about  $4.8 \times 10^{-20}$  J.

- (a) What is the nucleation rate per mole of copper when the supercooling is 264 degrees?
- (b) Discuss the significance of the answer to part (a) of this question.

**15.9** In the case of pure silver, according to Table 14.1, the maximum supercooling that has been observed is 227 degrees. Determine the homogeneous nucleation rate in silver at this degree of supercooling using the following data. Note, to determine  $v_s$ , use the volume of the unit cell of silver divided by the number of atoms per unit cell in this metal. In the following table the lattice parameter,  $a$ , is given for 1233 K.

$$a = 4.17 \times 10^{-10} \text{ m}$$

$$\begin{aligned} T_m &= 1234.9 \text{ K} & \nu &= 10^{13} \text{ Hz} \\ \gamma_{ls} &= 0.123 \text{ J/m}^2 & N_0 &= 6.023 \times 10^{23} \text{ atoms/mol} \\ \Delta H_{ls} &= 11,960 \text{ J/mol} & \Delta g_a &= 6.4 \times 10^{-20} \text{ J} \end{aligned}$$

**15.10** The accompanying diagram is for a hypothetical embryo of silver growing against an arbitrary mold wall. With the aid of this diagram,

- (a) Compute the angle of contact,  $\Theta$ , of the embryo with the mold wall.
- (b) Determine the magnitude of the factor that may be used to convert the homogeneous free energy needed to obtain a nucleus into that of the corresponding heterogeneous free energy.

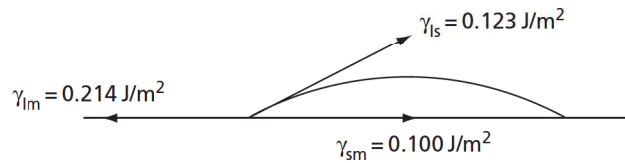


Fig. for Prob. 15.10

**15.11** Under the conditions of Prob. 8:

- (a) First determine the homogeneous nucleation rate when silver is supercooled by 20 degrees.
- (b) Next determine the heterogeneous nucleation rate when silver is supercooled 20 degrees. Use the data in Prob. 8 to determine  $I$  in nuclei per m<sup>2</sup> per second; that is, express  $N^m$  in terms of atoms per m<sup>2</sup>.
- (c) Discuss the difference between the heterogeneous and the homogeneous nucleation rates in terms of freezing at 20 degrees of supercooling.

Note that the assumed angle of contact,  $\Theta$ , from Problem 15.10 is relatively large and of the order 20°.

**15.12** Although the growth rate equations in Sec. 15.6 ignore several important factors, such as the strain energy and the surface energy, it is interesting to apply this simple theory to an analysis of the growth of the alpha phase from the gamma phase in pure iron. For this purpose, take the data given in the following table and make the indicated computations. Assume that  $\lambda = a$  and that  $\Delta g_a$  is independent of the temperature.

$$\begin{aligned} a &= 2.866 \times 10^{-10} \text{ m} \\ \nu &= 10^{13} \text{ Hz} \end{aligned}$$

Transformation temperature,  $T_0 = 1184.5 \text{ K}$

$$\Delta H^{\gamma\alpha} = 900 \text{ J/mol}$$

$$\Delta g_a = 2.08 \times 10^{-19} \text{ J}$$

(a) First take Eq. 15.35 and evaluate all the parameters in this equation so that it becomes a simplified relation between  $v$  and  $\Delta T$  and  $T$ . Next write a simple computer program to evaluate  $v$  between 1184.5 and 884.5 K in steps of 10 degrees.

(b) Plot the results from part (a) to show the variation of  $v$  with  $T$ . Express  $v$  in units of m/s.

**15.13 (a)** Suppose that an iron specimen containing 0.09 atomic percent carbon is equilibrated at 720°C (993 K) and then rapidly quenched to 300°C (573 K). Determine the length of the time needed for one side of a plate-shaped carbide precipitate to grow out by  $10^3$  nm.

(b) How wide a layer of the matrix next to a plate would have its carbon concentration lowered from 0.09 percent carbon to that corresponding to  $n_a^e$  to form a layer of cementite  $10^3$  nm thick?

(c) How long would it take to increase one side of the plate by 10 nm?

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