where n_B^b and n_B^a are the compositions (number of B atoms per unit volume) of the two phases at the boundary, dn_B^a/dx and dn_B^b/dx are the concentration gradients in the alpha and beta phases at the boundary, and D_α and D_β are the corresponding diffusion coefficients. The left-hand side of this equation corresponds to the number of B atoms required to move the boundary through a distance $dx_{\alpha\beta}$, while the right-hand side represents the net flux that will give this number. As will be discussed in Sec. 15.7, the boundary is assumed to move only as the result of carbon atoms diffusing into cementite. In this case one has to consider both the flux of B atoms up to the interface in the β phase, as well as the flux of B atoms away from the interface in the α phase. The Eq. 12.57 may be simplified to

$$\frac{dx_{\alpha\beta}}{dt} = \frac{1}{(n_B^b - n_B^a)}\left[D_\alpha\left(\frac{dn_B^a}{dx}\right) - D_\beta\left(\frac{dn_B^b}{dx}\right)\right] \qquad \textbf{12.58}$$

and a corresponding growth velocity expression written for the β to γ interface,

$$\frac{dx_{\gamma\beta}}{dt} = \frac{1}{(n_B^c - n_B^d)}\left[D_\gamma\left(\frac{dn_B^c}{dx}\right) - D_\beta\left(\frac{dn_B^d}{dx}\right)\right] \qquad \textbf{12.59}$$

Note that the growth velocities of the two interfaces of the β phase depend on a number of parameters. These include the concentrations of the phases at the boundaries, the diffusion coefficients, and the concentration gradients. Since the diffusion coefficients are normally functions of the composition, the solution of layer-growth problems is usually very difficult. Also, it is quite possible to conceive of growth conditions that will not allow a phase to develop a layer of visible thickness. In fact, by suitable choices of diffusion coefficients, it is possible to make either boundary move in either direction.

The above analysis has assumed a condition of dynamic equilibrium and implies a diffusion couple of such a size that its outer layers do not change their compositions. In a diffusion couple of a finite size, the situation can be quite different. Thus, if in the above example the copper and zinc layers were very thin and present in a ratio of 48 percent zinc to 52 percent copper, a sufficiently long anneal should result in a specimen containing only a single phase. This would be the β' phase, or the phase corresponding to the average composition.

A word should be said about some practical examples of layered structures. A typical example is furnished by galvanized iron. When steel is dipped in molten zinc, the zinc diffuses into the iron and a layered structure is formed that contains four phases in addition to the base metal (steel). The outermost of these phases is a liquid. On cooling, this liquid passes through an eutectic point so that the outermost layer is basically an eutectic. Hot-dipped tin plate also has a layered alloy structure. In fact, in most cases where one metal is plated on another under conditions where diffusion can occur, it will be found that layered structures tend to develop.

PROBLEMS

12.1 (a) What is the number of atoms in a cubic meter of copper? The gram-atomic weight of copper is 63.54 grams per mole and the atomic volume of copper is 7.09 cm^3 per gram-atom.

(b) Next, compute the number of copper atoms per m^3 given that the lattice constant, a, of copper is 0.36153 nm and that there are 4 atoms per unit cell in a face-centered cubic crystal.

12.2 A diffusion couple, made by welding a thin one-centimeter square slab of pure metal A to a similar slab of pure metal B, was given a diffusion anneal at an elevated

temperature and then cooled to room temperature. On chemically analyzing successive layers of the specimen, cut parallel to the weld interface, it was observed that, at one position, over a distance of 5000 nm, the atom fraction of metal A, N_A, changed from 0.30 to 0.35. Assume that the number of atoms per m^3 of both pure metals is 9×10^{28}. First determine the concentration gradient dn_A/dx. Then if the diffusion coefficient, at the point in question and annealing temperature, was 2×10^{-14} m^2/s, determine the number of A atoms per second that would pass through this cross-section at the annealing temperature.

12.3 On the assumption that the self-diffusion coefficient of a simple cubic metal whose lattice constant, a, equals 0.300 nm is given by the equation

$$D = 10^{-4}e^{-200{,}000/RT},\ m^2/s,$$

determine the value of the diffusion coefficient at 1,200 K and use this to determine the mean time of stay, τ, of an atom at a lattice site.

12.4 It is determined by experiment that the Kirkendall markers placed at the interface of a diffusion couple, formed by welding a thin plate of metal A to a similar plate of metal B, move with a velocity of 4.5×10^{-12} m/s toward the A component when the concentration $N_A = 0.38$ and the concentration gradient, dn_A/dx, is 2.5×10^2 per m. The chemical diffusion coefficient $\tilde{D}$ under these conditions is 3.25×10^{-14} m^2/s. Determine the values of the intrinsic diffusivities of the two components.

12.5 This problem and the next require an error function (probability integral) table. However, it is suggested that one develop such a table using the following procedure. The error function is based upon integrating the exponential e^{-y2} between the limits $y = 0$ and $y = y$. A convenient way of doing this is to integrate the first six terms of the series expansion for e^{-y2}, which are

$$e^{-y2} = 1 - y^2 + y^4/2! - y^6/3! + y^8/4! - y^{10}/5! + \ldots.$$

This integration yields the following expression for the error function, accurate to 5 significant figures for y from 0 to 0.80.

$$\frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}\,dy = \frac{2}{\sqrt{\pi}}\left[y - \frac{y^3}{3} + \frac{y^5}{15} - \frac{y^7}{42} + \frac{y^9}{216} - \frac{y^{11}}{1320} + \cdots\right]$$

A simple computer program should now be written around this latter equation and the error function evaluated in steps of 0.01 from $y = 0$ to $y = 0.80$.

A thin plate of a binary alloy of composition $N_{A1} = 0.245$ and $N_{B1} = 0.755$ was welded to a similar plate of composition $N_{A2} = 0.255$ and $N_{B2} = 0.745$ so as to form a diffusion couple. After a diffusion anneal for 200 hours at 1300 K, the composition at a plane 2×10^{-4} m from the original weld interface, on the side whose starting composition was $N_A = 0.245$, was observed to be $N_A = 0.248$. Compute the diffusivity using the Grube method.

12.6 Using the diffusivity determined in Prob. 12.5 and the error function equation associated with this problem, write a computer program to determine the composition of the specimen as a function of the time at a point 2×10^{-4} m from the weld interface and on the side of the couple with the starting composition $N_A = 0.245$. Determine this composition by varying the time from 3 to 70 hours in 2-hour intervals. Plot your results in a curve of composition versus time. What is the significance of the composition limit that is approached at long times?

12.7 With the aid of the data available in Table 12.3 and Fig. 12.14 determine $\tilde{D}$, the interdiffusion coefficient, at the composition $N_A = 0.625$ using the following directions:

(a) Draw a tangent to the penetration curve at $N_A = 0.625$ in order to determine $\partial x/\partial N_A$ at this composition.

(b) With the aid of Simpson's Rule, graphically integrate the data in Table 12.3 from $N_A = 0$ to $N_A = 0.625$.

(c) Using the results of the above, evaluate the Matano equation for D letting the time, t, equal 50 hours. Compare your answer with Fig. 12.15.

12.8 According to Eq. 12.28 the self diffusion coefficient for a face-centered cubic metal may be expressed by the following equation: $\tilde{D} = a^2/12\tau$ where a is the lattice parameter and τ is the mean time of stay of an atom in a lattice site. Derive this relationship using a procedure similar to that in Sec. 12.1 for the case of a simple cubic lattice.

12.9 With the aid of the data in Table 12.5, determine a value for the self-diffusion coefficient of nickel at a temperature of 1173 K and compare it with the value shown in Fig. 12.18.

12.10 Determine the interdiffusion coefficient, $\tilde{D}$, for nickel in a 50 atomic percent Ni nickel-gold alloy at 1173 K using the data plotted in Figs. 12.18 and 12.19.