Structural instability due to chemical free energy

2.1 Instability due to non-uniform solute distribution

The simplest instability in a metallic microstructure is that produced by a non-uniform distribution of solute in an otherwise stable single phase. Such a distribution always raises the free energy of the alloy and so it will decay to a uniform distribution at a rate determined by the thermodynamics and kinetics of diffusion. The kinetics of diffusion and its relationship to the concentration and mobility of point defects is one of the best-established topics in materials science, see, for example, Shewmon (1989), and so these topics need not be repeated here. However, the thermodynamics of diffusion is less widely discussed and is described below. Some new ideas on diffusion in alloys showing different rates of atomic motion in binary alloys as indicated by the Kirkendall effect are also described.

2.1.1 Thermodynamics of diffusion

Fig. 2.1 shows the free energy–composition diagram for a binary alloy. In stable regions of the system, where the second differential of the free energy with composition, $\partial^2 G/\partial C^2$, is less than zero, the free energy of composition C_3 is increased from G_3 to G_3' if it exists as a mixture of C_3' and C_3'' rather than as a single uniform composition. The rise in G caused by any non-uniform solute distribution in stable regions of any phase provides the driving 'force' for the diffusion that homogenises the distribution. Inside the 'spinodal' region where $\partial^2 G_A/\partial C^2 < 0$, the free energy *falls* from G_4 to G_4' if the composition changes from
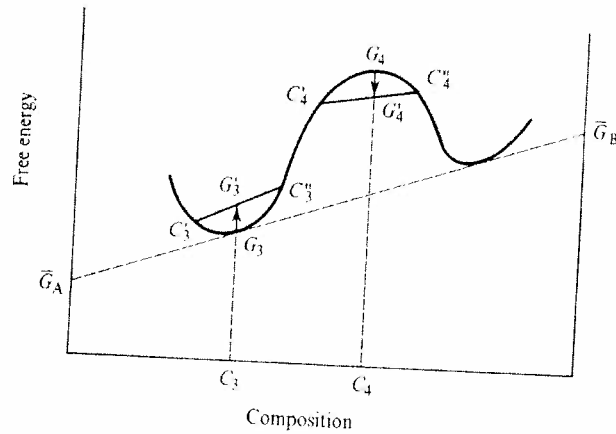
Figure 2.1 Free energy compositional relationship for a conventional nucleation and growth process.

the constant value of C'_4 to a mixture of C'_4 and C''_4. Within the spinodal 'uphill' diffusion can then occur. This is discussed later in this section and more fully in §2.2.1.

In either an ideal or a dilute solution there is no change in energy and/or enthalpy (H) on changing the composition of the alloy. In an ideal solution there is no change of enthalpy on mixing, see, for example, Gaskell (1983), and in a dilute non-ideal solution the minority solute atoms are in contact only with solvent atoms so there is no change of atomic bonding, and thus enthalpy, as the concentration changes in this dilute solution range. However, there is a change in the 'configurational' entropy – the entropy due to atomic positional order. For these situations the usually quoted *statistical* derivation of the laws of diffusion is valid. In this derivation, illustrated in fig. 2.2, there is a variation in the concentration of C_A, given in atoms of A per unit volume, in the x direction so that:

$$C_A = \text{function of } x$$

Therefore the concentration of A atoms on a plane, $C_{A_{(2)}}$, is given in terms of that on the preceding plane, $C_{A_{(1)}}$, by the Taylor expansion as:

$$C_{A_{(2)}} = C_{A_{(1)}} + (\partial C_A / \partial x)_1 b + (\partial^2 C_A / \partial x^2)_1 (b^2/2!) + \ldots$$

The spacing between adjacent atomic planes, 1 and 2, is b and, with the concentration given as atoms per unit volume, the number of A atoms on unit area of a plane is then $C_A b$. If the energy of an atom is independent of the concentration, the jump frequency, f_A, of A atoms from both planes will be the same. Under these circumstances it is readily seen that, for most concentration profiles where terms higher than $\partial C_A / \partial x$ in the Taylor expansion can be neglected, we obtain the following relationship for the net flux of A atoms in the x direction:
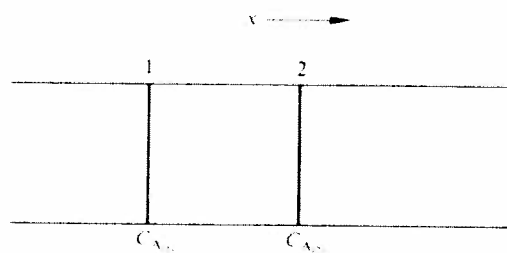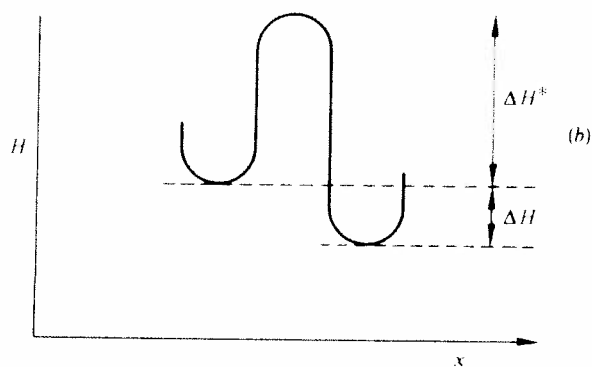
$x \longrightarrow$

(a)

Figure 2.2 (a) Variation of the concentration of A. (b) For non-ideal solution, the variation in enthalpy H between adjacent planes (much exaggerated).

(b)

$$\text{Flux } J_A = -D_A(\partial C_A/\partial x)_1 \tag{2.1}$$

The diffusion coefficient of A atoms is given by:

$$\text{Diffusion coefficient } D_A = 0.5b^2 f_A \tag{2.2}$$

The average number of atoms of A, S_A, in unit area of length, Δx, is:

$$S_A = \Delta x C_A \tag{2.3}$$

The rate of change of S_A with time is then:

$$\partial S_A/\partial t = (\partial C_A/\partial t)\Delta x + [\partial(\Delta x)/\partial t]C_A \tag{2.3a}$$

In the usual coordinate system, that of the specimen, when the length of each region remains constant so that $\partial(\Delta x)/\partial t = 0$, the rate of change of solute becomes:

$$\partial S_A/\partial t = (\partial C_A/\partial t)\Delta x = J_A(+) - J_A(-) = -(\partial J_A/\partial x)\Delta x \tag{2.3b}$$

The flux of solute into a region of fixed length Δx is $J_A(+)$ and that out of each region is $J_A(-)$. Substitution of eq. (2.1) then yields the usual form of the diffusion equation, given by

$$(\partial C_A/\partial t)_x = -(\partial J_A/\partial x) = [\partial(D_A \partial C_A/\partial x)/\partial x]_t = D_A(\partial^2 C_A/\partial x^2)_t \qquad (2.4)$$

The simplification of the final part of eq. (2.4) comes when the diffusion coefficient, D_A, does not vary with composition, C_A, and thus with distance, x.

In an alloy, which is neither ideal nor dilute, there can be an enthalpy difference, ΔH, between atoms on adjacent planes with different solute contents (fig. 2.2) so that the atomic jump frequency from 1 to 2, f_{12}, is different from the jump frequency in the reverse direction, f_{21}. (ΔH can be either <0 or >0.)

$$f_{12} = \nu \exp[-(\Delta H^*/kT)]$$

$$f_{21} = \nu \exp[-(\Delta H^* + \Delta H)/kT)]$$

Here ν is the vibration frequency of the A atoms, and ΔH^* the activation energy.

The resulting variation of jump frequency will affect the value and even the sign of the diffusion coefficient. The usual way of discussing this problem is by means of the partial molar free energy, $\bar{G}_A$, also known as the chemical potential μ_A.

$$G_A = (\partial G/\partial n_A)_{T.P.C_A}$$

where n_A is the number of gram moles of component A. The values of $\bar{G}_A$ and $\bar{G}_B$ can be found, as shown in fig. 2.1, by extrapolating the tangent to the free energy–composition curve at C_A to the pure components A and B.

Darken (1948) suggested that the drift velocity of a diffusing A atom will be proportional to the gradient of the partial molal free energy of A:

$$v_A = -\beta_A(\partial \bar{G}_A/\partial x)$$

The proportionality constant, β_A, is the inherently positive atomic mobility of the A atoms. This is the exact equivalent of Ohm's law of conductivity where the drift velocity of an electron is given by the product of the electron mobility, μ_e, and the electric field — the gradient of electrical potential:

$$v_e = -\mu_e(\partial V/\partial x)$$

The flux of A atoms is then given by the product of the mean drift velocity and the concentration of A atoms:

$$J_A = v_A C_A = -C_A \beta_A(\partial \bar{G}_A/\partial x) \qquad (2.5)$$

Comparison of eq. (2.1) and eq. (2.5) shows that the diffusion coefficient is given by:

$$D_A = -C_A \beta_A (\partial \bar{G}_A / \partial C_A) = \beta_A (\partial G_A / \partial \ln C_A) = \beta_A (\partial \bar{G}_A / \partial \ln N_A) \tag{2.6}$$

Here N_A is the molar or atomic fraction of A – given by C_A/C, where C is the total number of atoms per unit volume so that $C = 1/V_m$; V_m is the molar volume that, for simplicity, is usually assumed to be constant.

As discussed in any account of solution thermodynamics, for example, Gaskell (1983), the partial molar free energy of A is related to the activity of A, a_A, and thus the activity coefficient of A, γ_A, by the equation:

$$\bar{G}_A - G_A^{\circ} = RT \ln a_A = RT \ln N_A + RT \ln \gamma_A \tag{2.7}$$

G_A° is the constant molar free energy of A in its standard state – usually that of pure A. So:

$$\partial \bar{G}_A / \partial \ln N_A = RT (1 + \partial \ln \gamma_A / \partial \ln N_A)$$

and therefore:

$$D_A = \beta_A RT (1 + \partial \ln \gamma_A / \partial \ln N_A) \tag{2.6a}$$

The intrinsic diffusion coefficient of A, D_A^*, in a chemically homogeneous alloy of composition C_A can be measured by the diffusion of a radioactive isotope of component A.

$$D_A^* = \beta_A^* RT (1 + \partial \ln \gamma_A^* / \partial \ln N_A^*)$$

All the terms marked with an asterisk refer to the radioisotope.

Since isotopes of an element are chemically identical their solutions are ideal, so that even in the *chemically* non-ideal alloy the term in brackets above will be unity in a homogeneous alloy in which D_A^* is determined. The mobility terms, β_A^* and β_A, will also be the same, so:

$$D_A^* = \beta_A^* RT = \beta_A RT$$

and therefore, as first shown by Darken (1948):

$$D_A = D_A^* (1 + \partial \ln \gamma_A^* / \partial \ln N_A^*) \tag{2.8}$$

In a binary alloy where $N_A + N_B = 1$ and $C_A + C_B$ is constant, the concentration gradients of the two components are related by:

$$\partial C_A / \partial x = -\partial C_B / \partial x$$

The flux of each type of atom will then occur in opposite directions but both of the fluxes contribute to the change of composition with time in the inhomogeneous alloy. In alloy systems where the thermodynamic effects are significant then the appropriate form of the diffusion equation is that given by Darken (1948), that is:

$$(\partial C_A/\partial t)_x = [\partial(\mathbf{D}\partial C_A/\partial x)/\partial x]_t \tag{2.4a}$$

The interdiffusion coefficient $\mathbf{D}$ is then given by:

$$\mathbf{D} = N_A D_B + N_B D_A \tag{2.9}$$

and therefore

$$\mathbf{D} = (N_A D_B^* + N_B D_A^*)(1 + \partial\ln \gamma_A/\partial\ln N_A) \tag{2.9a}$$

This result comes from one of the standard equations of solution thermodynamics, the Gibbs–Duhem equation (see Gaskell (1983)):

$$N_A\partial\ln G_A + N_B \partial\ln G_B = 0 \tag{2.10}$$

The Gibbs–Duhem equation can be manipulated, using the definition of the partial molar free energy, eq. (2.7), and that $N_A + N_B = 1$, to give:

$$N_A\partial\ln \gamma_A + N_B \partial\ln \gamma_B = 0 \tag{2.10a}$$

and

$$\partial\ln \gamma_A/\partial\ln N_A = \partial\ln \gamma_B/\partial\ln N_B \tag{2.10b}$$

Cahn (1968) in his review of spinodal decomposition where both $\partial^2 G/\partial C_A^2 < 0$ and $\partial^2 G/\partial N_A^2 < 0$, pointed out that the sign of $\partial^2 G/\partial N_A^2$ determines the sign of the interdiffusion coefficient $\mathbf{D}$. This is readily seen since the free energy per mole of solution, G, is given by:

$$G = N_A \bar{G}_A + N_B \bar{G}_B$$

$$G = N_A(G_A^\circ + RT\ln a_A) + (1 - N_A)(G_B^\circ + RT\ln a_B)$$

Differentiation of this twice with respect to N_A using eq. (2.10a) gives:

$$\partial^2 G/\partial N_A^2 = RT(1/N_A + 1/N_B)(1 + \partial\ln \gamma_A/\partial\ln N_A) \tag{2.11}$$

So, inside the spinodal where $\partial^2 G/\partial N_A^2 < 0$, the Darken thermodynamic factor $(1 + \partial\ln \gamma_A/\partial\ln N_A)$ is also less than 0 and so by eq. (2.9a) is the interdiffusion coefficient **D**.

Eqs.(2.6) and (2.8) show that diffusion in condensed phases is controlled by two factors. The first is the intrinsic atomic mobility, β_A or D_A^*, which for a solid is usually determined by the concentration and mobility of point defects. The second factor is the thermodynamics of the solid solution commonly given by the Darken factor $(1 + \partial\ln \gamma_A/\partial\ln N_A)$. The thermodynamic effect can accelerate diffusion when there is a negative deviation from ideality such that γ_A is less than 1 but increasing to $\gamma_A = 1$ as $N_A \to 1$, so that both $\partial\gamma_A/\partial N_A > 0$ and $\partial\ln\gamma_A/\partial\ln N_A > 0$. The thermodynamic term, where there is a positive deviation from ideality and γ_A is then more than 1, can equivalently retard diffusion and in the limit when $\partial^2 G/\partial N_A^2 < 0$ and $\partial\ln \gamma_A/\partial\ln N_A < -1$, leads to a negative diffusion and unmixing of unstable solid solutions.

In an investigation of homogenisation of microsegregated Al–Zn, in alloys whose range of compositions included 37 at% Zn (Ciach, Dukiet-Zawadzka and Ciach 1978), it was found, exactly as expected from the discussion above, that the rate of homogenisation was very much slower than would have been expected from the atomic mobility of the aluminium and zinc atoms at the homogenisation temperature. The reduction in the rate of homogenisation arises since, as the temperature falls below a critical temperature, $T_c = 351.5$ °C, the alloy system undergoes phase separation, $\alpha \to \alpha' + \alpha''$. Below T_c, $\partial^2 G_A/\partial C^2$ and the Darken thermodynamic term $(1 + \partial\ln \gamma_{Zn}/\partial\ln N_{Zn})$ are both *negative* leading to the spinodal decomposition reaction discussed in §2.2.1. At the critical unmixing temperature, the thermodynamic term, in the absence of effects due to elastic strain (§2.2.1) is 0. At the investigated homogenisation temperature of 360 °C, the Darken term was reported to be only 0.02 at the composition of $N_{Zn} = 0.37$. The interdiffusion coefficient, **D** (eq. (2.10a)), was found at 360 °C to be only 6×10^{-16} m^2 s^{-1}, smaller by the Darken factor of 0.02 than the intrinsic atomic mobility, $N_A D_B^* + N_B D_A^*$, which was estimated to be somewhat less than 10^{-13} m^2 s^{-1} at the same temperature. Ciach *et al.* found that on annealing as-cast Al–60 wt% Zn the non-equilibrium zinc eutectic phase, η, dissolved at 360 °C. This is as expected since the zinc rich solid solution, at $N_{Zn} = 0.6$, in equilibrium with η, has a much larger value of the thermodynamic term at 360 °C, than the value of only 0.02 found at $N_{Zn} = 0.37$. Continued annealing at 360 °C for 50 h did not, however, completely remove the non-uniform zinc distribution in the resulting solid solution that included the critical composition.

The authors suggested that a well-designed homogenisation process would be one involving a preliminary low temperature initial anneal at 360 °C to remove the low melting zinc phase followed by final homogenisation at higher temperatures such as 450 °C where, due to the rise in the thermodynamic term as well as in the mobility, the value of the interdiffusion coefficient, **D**, increased by two

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orders of magnitude to $6 \times 10^{-14}\ \mathrm{m^2\,s^{-1}}$. The purpose of the low temperature first step is to remove the low temperature melting zinc inclusions before annealing at a temperature above the melting point of the non-equilibrium eutectic inclusions. Doherty (1979a), on the basis of the ideas presented above, pointed out that equivalent homogenisation difficulties are to be expected in any alloy system that undergoes, at lower temperatures, spinodal decomposition.

2.1.2 Modified diffusion equation in the presence of a Kirkendall effect

Doherty (1993) has explored, by numerical simulation, the diffusional processes occurring in a system, Cu–Ni, that was nearly ideal but in which the two diffusion coefficients, D_{Cu} and D_{Ni}, were significantly different; $D_{Cu} = 3D_{Ni}$. This means that significant Kirkendall shifts are expected (Smigelskas and Kirkendall 1947) and are found on interdiffusing pure copper and nickel (da Silva and Mehl 1951). Numerical study revealed, as first shown by Darken (1948), that the diffusion analysis will be significantly different if is carried out in the moving lattice coordinate system rather than in the stationary specimen coordinate system. In one-dimensional diffusion in the *specimen* coordinate system, a small volume element at a distance x from the end of the specimen will have, by definition, a constant length, Δx, a fixed cross-sectional area and so a constant volume. Under these circumstances, eq. (2.4a) is the correct diffusion equation to use in the specimen coordinate system and, as shown by Darken, the interdiffusion coefficient **D** of eq. (2.8) is the correct coefficient to use. If, however, the analysis or simulation is to be carried out in the *lattice* coordinate system (x') then as shown below the full form of eq. (2.3a) must be used and this gives a modified diffusion equation.

The lattice coordinate system, x', is one measured from a set, or sets, of inert markers placed in the lattice and as shown by the Kirkendall effect these markers move with a local velocity v'. Darken (1948) noted that the flux of A atoms in the *lattice* coordinate system, x', is given by the usual form of the first law, given by:

$$J_A(x') = -D_A \partial C_A / \partial x' \tag{2.1a}$$

In the *specimen* coordinate system, there is an additional contribution to the flux due to the Kirkendall velocity of the lattice plane. So the flux, measured in the specimen coordinate system, x, at the same position as in eq. (2.1a) ($x = x'$) is that given by:

$$J_A(x') = -D_A \partial C_A / \partial x' + v' C_A \tag{2.1b}$$

Darken's clear analogy was the difference between the flux of moving objects in a river as measured by an observer in a boat on the river and the same flux as seen by a stationary observer on the river bank opposite the observer in the boat. The observer on the river bank sees both the movement due to diffusion and that due to the velocity, v', of the river. Darken showed from eqs. (2.1a) and (2.1b) that the Kirkendahl velocity v' is given by:

$$v' = (D_A - D_B)(dN_A/dx') \tag{2.12}$$

This velocity is the velocity of the lattice planes relative to the end of the specimen. The lattice planes at the ends of the specimen are, by eq. (2.12), stationary since at the ends of the sample the concentration gradients are zero. This condition occurs when the length of the sample is much greater than the distance over which diffusion occurs, $(Dt)^{0.5}$. The integration of the changing velocity, given by (eq. 2.12), over the whole diffusion run for the lattice plane *at the original interface* gives the observed Kirkendall shift of inert interface markers. Such shifts were first described by Smigelskas and Kirkendall (1947). From eq. (2.12), Darken derived the correct interdiffusion coefficient, **D**, eq. (2.9), for use in the usual experimental coordinate system – that of the specimen.

In order to simulate the Kirkendall shifts in the Cu–Ni system, Doherty (1993) used the lattice coordinate system. In the lattice system the change of solute content is dependent on both terms in eq. (2.3):

$$\partial S_A/\partial t = (\delta C_A/\partial t)\Delta x' + [\partial(\Delta x')/\partial t]C_A \tag{2.3a}$$

So

$$\partial S_A/\partial t = (\delta C_A/\partial t)\Delta x' + [\partial(\Delta x')/\partial t]C_A = -\Delta x'(\partial J_A/\partial x') \tag{2.3c}$$

In the lattice coordinate system with a finite and variable Kirkendall velocity, v', the element lengths, $\Delta x'$, must change, so then the diffusion equation derived from eqs. (2.1) and (2.3c) becomes:
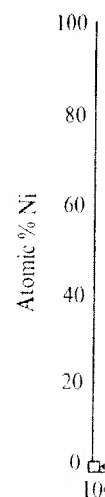
$$(\partial C_A/\partial t)_{v'} = [\partial(D_A \, \partial C_A/\partial x')/\partial x']_t - (\partial \ln \Delta x'/\partial t)_x C_A \tag{2.4b}$$

Note that in the one-dimensional diffusional analysis here the area of the sample is assumed constant, at $A = 1$, so that the length $\Delta x'$ is actually the volume, $\Delta V'$, of the region. So a more general form for the diffusion equation is given by:

$$(\partial C_A/\partial t)_{v'} = [\partial(D_A \, \partial C_A/\partial x')/\partial x']_t - (\partial \ln \Delta V'/\partial t)_x C_A \tag{2.4c}$$

This form of the diffusion equation includes the additional contribution to the change of concentration, $\partial C_A/\partial t$ (C_A is the number of B atoms per unit volume), arising from the change of the local volume of the region.

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The local volume, $\Delta x'$ or $\Delta V'$, changes by virtue of creation or destruction of vacancies, when $D_A \neq D_B$ in substitutional diffusion. So in a system such as Ni–Cu, where $D_{Cu} > D_{Ni}$, there is a reduction of the local lengths in the copper rich regions due to the net loss of atoms or, more accurately, atom sites. The net loss of atom sites results in negative values of $d(\Delta x')/dt$ so producing an *increase* in the solute composition, eq. (2.4b). Figs. 2.3–2.5 show the results of two numerical simulations of Ni–Cu interdiffusion at 1323 K for 312 h, a situation previously studied experimentally by da Silva and Mehl (1951). In fig. 2.3 the interdiffusion had been simulated both using the standard equation, eq. (2.4a), with the Darken form of the interdiffusion coefficient, D, eq. (2.10), and also using the modified (lattice) diffusion equation, eq. (2.4b), but with the individual diffusion coefficients, D_{Cu} or D_{Ni}, for profiles calculated for either element as the solute A. It is clear that both simulations give identical profiles and these profiles were found to be almost identical to the experimental profile. Fig. 2.4 gives the simulated Kirkendall marker shifts for markers placed at the initial interface – these markers move into copper with a displacement that scales with the square root of time with a constant composition as seen experimentally. The magnitude of both the shift and the local composition at the interface markers also matched the experimental values reported by da Silva and Mehl (1951). Movement of
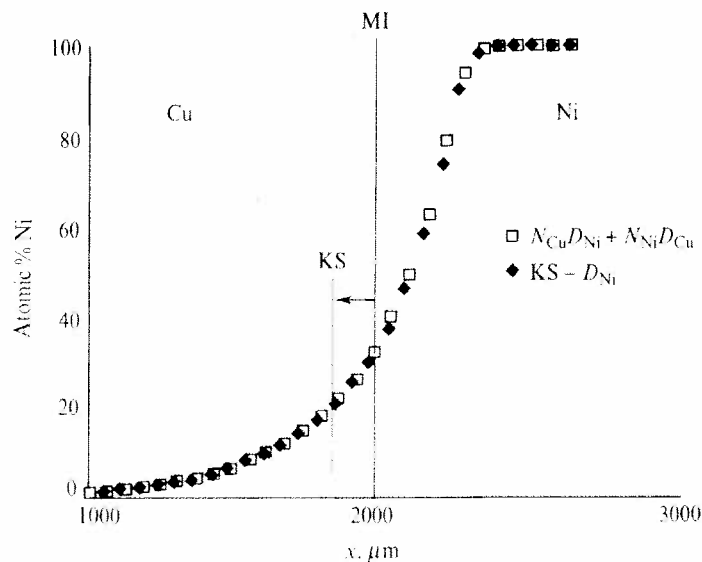

Figure 2.3 Composition profile of nickel in the interdiffusion at 1323 K for 312 h of pure copper initially at $x \leq 1995$ μm. and pure nickel. at $x \geq 1995$ μm. simulated (i) by the individual diffusion coefficient. D_{Ni} in the Kirkendall shift modified diffusion equation. eqs. (2.4b) as 'KS' D_{Ni} and (ii) by use of Darken's expression for the interdiffusion coefficient. eq. (2.10) in the standard diffusion equation. eq. (2.4a). as $N_{Cu}D_{Ni} + N_{Ni}D_{Cu}$. The Matano interface. found at the initial interface at 1995 μm. is shown as the vertical line and the shift of the interface markers is indicated by the arrow marked KS. The two profiles are identical. Doherty (1993).
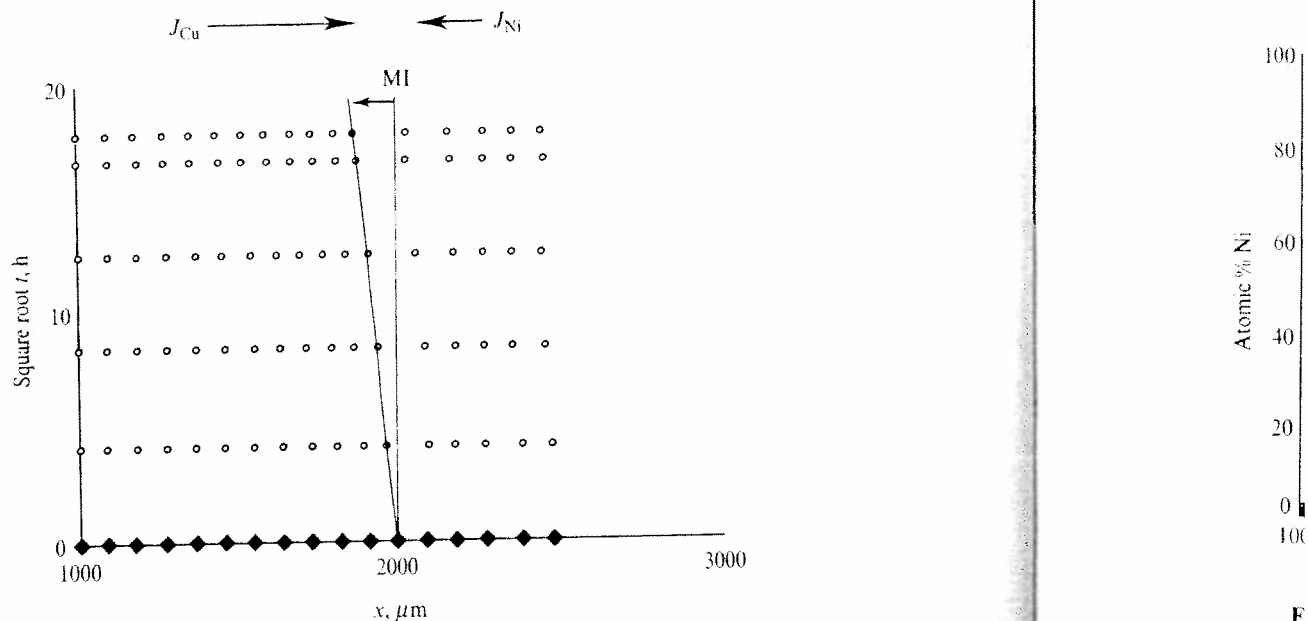
Figure 2.4 Positions of initially equally spaced markers at different values of the square root of the diffusion time, in hours, simulated by use of the modified diffusion equation during interdiffusion of Cu–Ni at 1323 K for times up to 312 h. The initial, Matano interface (MI) is shown by the vertical line while the displacements of interface markers are indicated by the sloping line. The marker spacings in copper are reduced while those in nickel are expanded. The interface markers are correctly predicted to displace, into the faster diffusing copper, linearly with $(t)^{0.5}$. Doherty (1993).

markers placed at different distances from the initial interface was simulated and the results also plotted in fig. 2.4. Movement of markers away from the initial interface seems, however, never to have been studied experimentally or at least not reported. Fig. 2.4 clearly shows that the 'mesh' lengths, $\Delta x'$, in the copper rich regions of the interface markers all *decrease* while those on the nickel rich side all grow larger. This means that according to the modified diffusion equation, eq. (2.4a), the solute content will be increased by this effect on the copper rich regions and decreased in the nickel rich regions. Fig. 2.5 demonstrates this result. The figure shows the results of running two simulations – both using D_{Ni} for the diffusion coefficient. For the simulation based on the modified lattice diffusion equation, eq. (2.4b), we obtain the same profile as was given in fig. 2.3, but calculated in two ways. The incorrect use of D_{Ni} rather than the Darken **D** in the standard diffusion equation, eq. (2.4a), is seen to underestimate significantly the change of composition *on both sides of the diffusion profile*. In the copper rich region the incorrect use of D_{Ni} in eq. (2.4a) leads to an *underestimate* of the content of the solute, A = Ni. The additional flux of copper atoms out of the
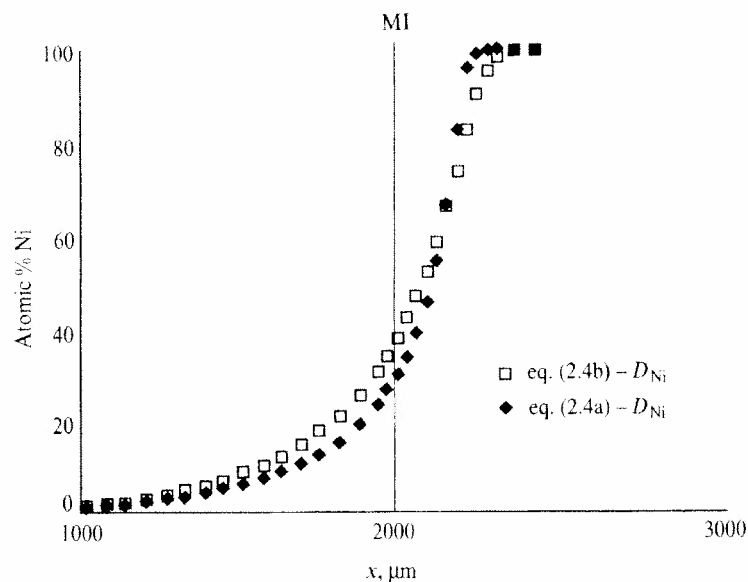
Figure 2.5 Simulated composition profiles of Ni during interdiffusion of Cu–Ni at 1323 K for 312 h: (i) correctly predicted using D_{N_i} in the KS modified diffusion equation, eq. (2.4b) (this is the same profile as in fig. 2.3) and (ii) incorrectly, by use of D_{N_i} in eq. (2.4a). The incorrect equation here underpredicts the changes in composition. The full vertical line indicates, for both profiles, the initial position of the interface which is also the Matano interface (MI). Doherty (1993).

copper region, neglected by the use of D_{N_i} in eq. (2.4a), leads to the observed *increase* in solute content on the low nickel (copper rich) side of the diffusion couple. An analogy is the increased concentration of the salt content of a salt solution by evaporation of the solvent water. The equivalent extra flux of copper atoms into the nickel rich side of the interface leads to the observed decrease in solute (nickel) contents in the nickel rich regions. The fall of solute (nickel) content comes from the further dilution of the alloy by the additional flux of the solvent — copper. These pairs of simulations thus serve to illustrate the *physical* reason behind the increase of effective diffusion coefficient from D_{N_i} to $\mathbf{D}$ required mathematically by Darken's analysis leading to $\mathbf{D} = N_{N_i} D_{Cu} + N_{Cu} D_{N_i}$ (eq. (2.10)) (noting that $D_{N_i} = 0.3 D_{Cu}$).

2.1.3 The origin of non-uniform solid solutions – coring or interdendritic segregation

The most usual cause of an inhomogeneous solid solution is the coring that results from solidification. Any alloy that freezes over a range of temperature forms a solid with a range of composition. The name of *coring* for this phenom-
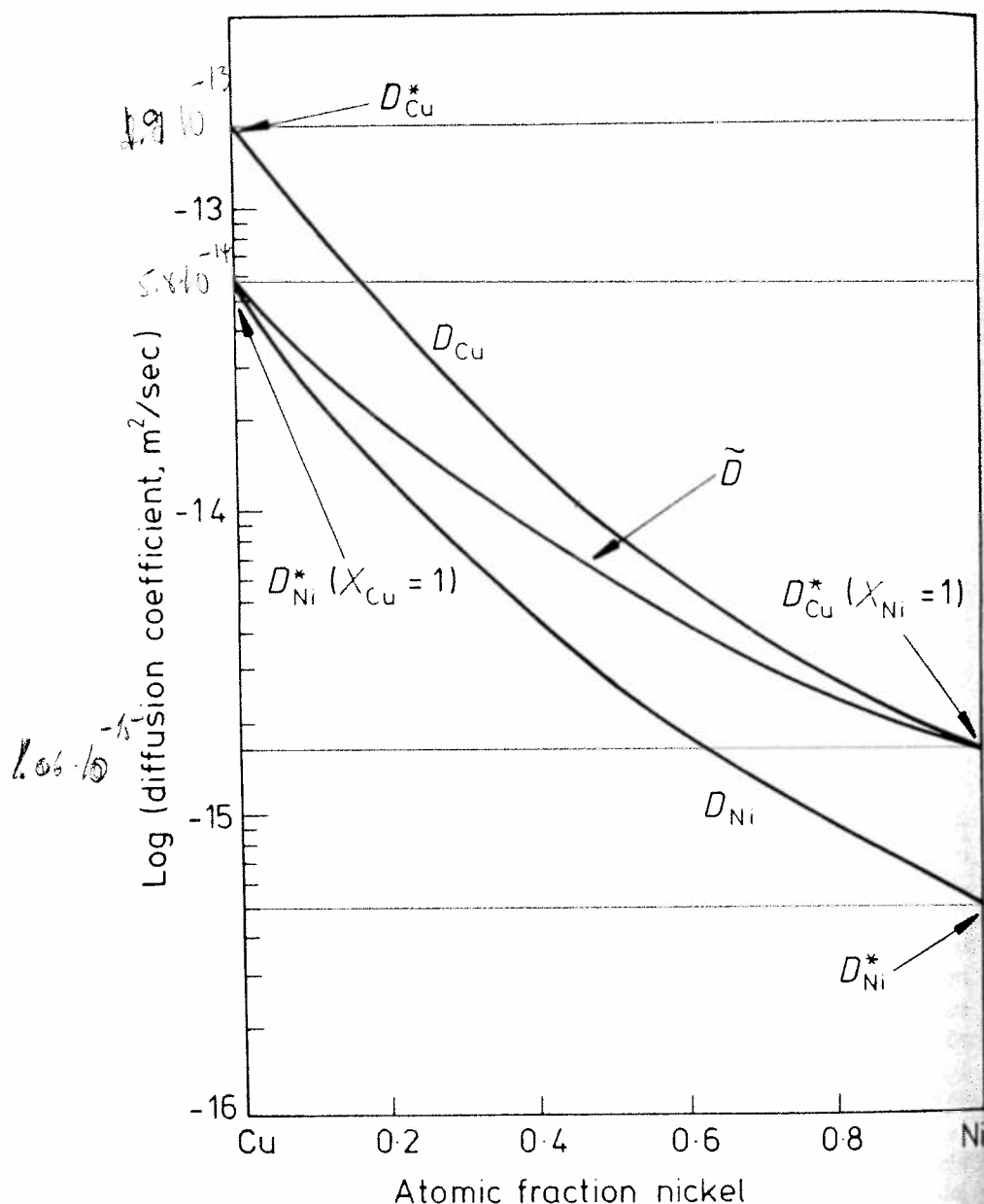
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Fig. 2.21 The relationship between the various diffusion coefficients in the Cu–Ni system at 1000 °C (After A.G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1971.)

other diffusivities, so that

$$\tilde{D} = \tilde{D}_0 \exp \frac{-Q}{RT}$$

$$D_A = D_{A0} \exp \frac{-Q_A}{RT}$$

$$D_B = D_{B0} \exp \frac{-Q_B}{RT}$$

However the factors that determi
there is no simple atomistic mod
   The variation of $\tilde{D}$ with compo
not been measured, by utilizing

1. For a given crystal structure
   Therefore if adding B to A
   at a given temperature, and

2. For a given solvent and tem
   diffusion are more rapid in
   example, for the diffusion c
   850 °C the self-diffusior
   $D_{Fe}^{\alpha}/D_{Fe}^{\gamma} \sim 100$. The reaso
   bcc structure is more open a
   distortion.

2.3.4 Diffusion in Dilute Subst

Another special situation arises
and $X_A \sim 1$, Equation 2.51 bec

$$\tilde{D} = D_B$$

This is reasonable since it mear
alloys is controlled by how fast t
only way homogenization can be
into the solute-depleted regions.
the impurity diffusion coefficier
interdiffusion data in concentra
fusion coefficients can be measu
   It is often found that D_B in a
The reason for this is that the so
is *more* than a random probabili
with the result that they can d
between a solute atom and a vac
the solvent atoms or if it has higl
the vacancy will be unable to'e:
solute–vacancy pair can diffuse