Phase Transformation of Materials

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Source or Sink for Vacancy

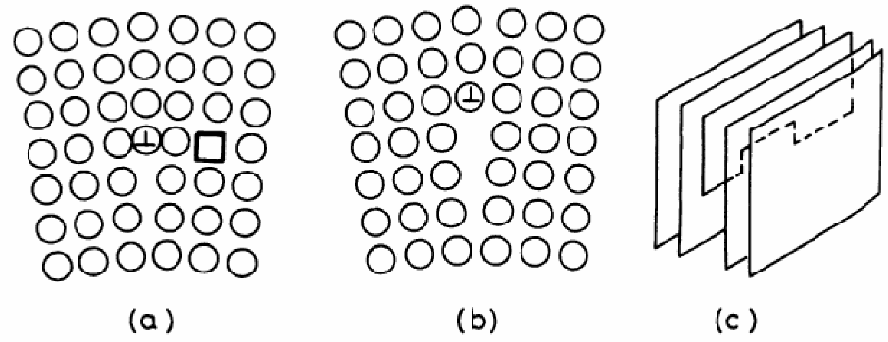


Fig. 2.17 (a) before, (b) after: a vacancy is absorbed at a jog on an edge dislocation (positive climb). (b) before, (a) after: a vacancy is created by negative limb of an edge dislocation. (c) Perspective drawing of a jogged edge dislocation.

If dislocation climbs continue to occur, what would happen?

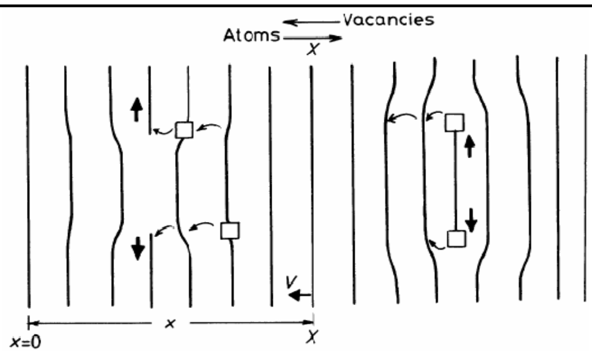


Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.

How is the velocity of the movement of the lattice plane related to the flux of vacancies crossing it? **v: marker velocity**

$A \cdot v \cdot \delta t$
$\rightarrow$ volume swept by plane during δt

$$A \cdot v \cdot \delta t \cdot C_o = J_v \cdot A \cdot \delta t \qquad J_v = C_o v$$

$$J_v = ? \qquad J_{v,(A,B)} = -J_A - J_B \qquad J_v = (D_A - D_B)\frac{\partial C_A}{\partial x}$$

$$v = \frac{1}{C_o}(D_A - D_B)\frac{\partial C_A}{\partial x} \quad = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

X_A : Mole fraction of A atoms

In practice, internal movement of lattice planes are usually not directly of interest. More practical questions concern how long homogenization of an alloy takes, or how rapidly the composition will change at a fixed position relative to the ends of a specimen.

For this purpose, what would be the appropriate diffusivity for substitutional alloys?
Can you derive it?

→ Fick's 2nd Law for Substitutional Alloys

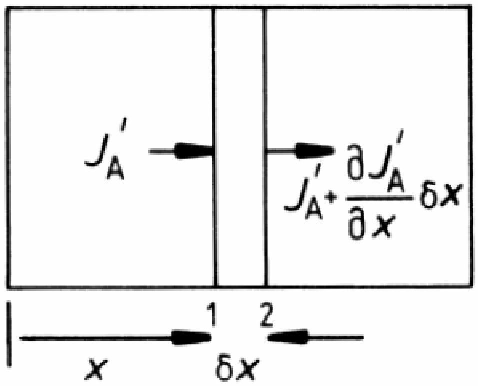


Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J'_A}{\partial x} \qquad J'_A = ? \qquad J'_A = J_A + vC_A \qquad v = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

- J'_A : the total flux of A atoms entering this slice across plane 1
- J_A : a diffusive flux due to diffusion relative to the lattice
- $v \cdot C_A$: a flux due to the velocity of the lattice in which diffusion is occurring

$$\begin{aligned} J'_A &= J_A + vC_A \\ &= -D_A \frac{\partial C_A}{\partial x} + vC_A \\ &= -(X_B D_A + X_A D_B)\frac{\partial C_A}{\partial x} \\ &= -\tilde{D}\frac{\partial C_A}{\partial x} \end{aligned}$$

$$\begin{aligned} vC_A &= (D_A - D_B)\frac{\partial X_A}{\partial x} C_A \\ &= (D_A - D_B)\frac{\partial C_A}{\partial x}\frac{C_A}{C_o} \\ &= (D_A - D_B)\frac{\partial C_A}{\partial x} X_A \end{aligned}$$

$\tilde{D} = X_B D_A + X_A D_B$

Interdiffusion Coefficient

$$J'_A = -\tilde{D}\frac{\partial C_A}{\partial x} \quad \text{(Fick's 1}^{st}\text{ law)}$$

$$\text{and } J'_B = -\tilde{D}\frac{\partial C_B}{\partial x} = \tilde{D}\frac{\partial C_A}{\partial x}$$

and also

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)$$

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

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

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

Finally, it is obtained that

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right) \quad \text{(Fick's 2nd law for substitutional alloy)}$$

$$\tilde{D} = X_B D_A + X_A D_B$$

For Dilute Substitutional Alloys if $X_A \approx 1, \quad \tilde{D} = D_B$

The interdiffusion coefficient $(\tilde{D})$ can be experimentally measured by determining the variation of X_A and X_B after annealing a diffusion couple.

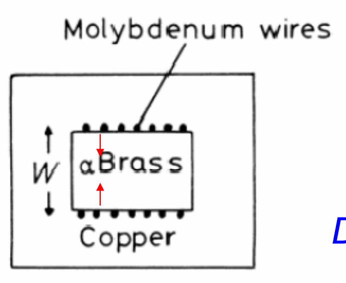
How can we determine D_A and D_B?

$$v = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

When the velocity of a lattice (v) and interdiffusion coefficient $(\tilde{D})$ are known D_A and D_B for the composition at the markers can be calculated.

How can we determine the velocity of a lattice (v)?

The displacement of wires during diffusion was first observed by Smigelskas and Kirkendall in1947 and is usually know as the Kirkendall effect.



$D_{Zn} > D_{Cu}$

Fig. 2.20 An experimental arrangement to show the Kirkendall effect.

After annealing at a high temperature it was found that the separation of the markers (w) had decreased.

In concentrated alloys the experimentally determined values of $\tilde{D}$, D_A and D_B are also found to show the same form of temperature dependence.

Variation of $\tilde{D}$ with composition:

For a given crystal structure, $\tilde{D}$ at T_m is roughly constant. Therefore if a solute decreases T_m of the solvent, then $\tilde{D}$ decreases also, and vice versa.

For both interstitial and substitutional alloys , diffusion is more rapid in bcc than in a close-packed lattice.

$$ex)\ for\ Fe\ at\ 910^oC,\ D_C^{\alpha}/D_C^{\gamma} \sim 100$$

$$at\ 850^oC,\ D_{Fe}^{\alpha}/D_{Fe}^{\gamma} \sim 100$$

Phase Transformations in Metals and Alloys NRL of Charged Nanoparticles

Diffusion in dilute substitutional alloy

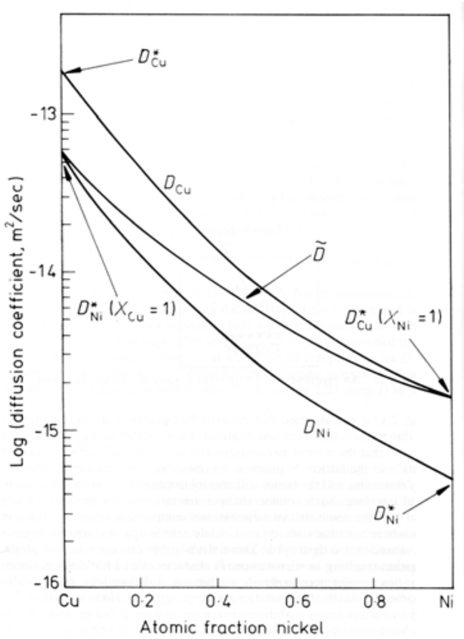
$X_B \approx 0(\text{solute})$ $X_A \approx 1(\text{solvent})$ $\tilde{D} = ?$ $\tilde{D} = D_B$

In this case, D_B is called **'impurity diffusion coefficient'.**

Often, $D_B > D_A$ in a dilute solution. **Why?**

The reason for this is that the solute atoms can attract vacancies so that there is more than a random probability of finding a vacancy next to a solute atom with the result that they can diffuse faster than solvent.

This is caused by the larger size or higher valency of the B atoms compared to those of A atoms. If the binding energy is very large, the vacancy will be unable to escape' from the solute atom.



Atomic mobility

Fick's law alone is insufficient to describe how the concentration will vary with distance and time.

The problem of atom migration can be solved by considering the thermodynamic condition for equilibrium; namely that the chemical potential of an atom must be the same everywhere. In general the flux of atoms at any point in the lattice is proportional to the chemical potential gradient.

$$J_B = v_B C_B \qquad \left\{ \begin{array}{l} J \text{ : a diffusive flux} \\ v \text{ : a net drift velocity} \end{array} \right\}$$

Since atoms always migrate so as to remove differences in chemical potential, the drift velocity is proportional to the local chemical potential gradient.

$$v_B = -M_B \frac{\partial \mu_B}{\partial x} \quad (M_B\text{: Mobility of B atoms})$$

$$-\frac{\partial \mu_B}{\partial x} \text{: Chemical force causing atom to migrate}$$

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

How the mobility of an atom is related to its diffusion coefficient?

Phase Transformations in Metals and Alloys
NRL of Charged Nanoparticles

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

$$\mu_B = G_B + RT \ln a_B = G_B + RT \ln \gamma_B X_B \qquad \frac{d\mu_B}{dX_B} = ?$$

$$\frac{d\mu_B}{dX_B} = \frac{RT}{X_B}\left(\frac{X_B d\ln\gamma_B}{dX_B} + \frac{X_B d\ln X_B}{dX_B}\right) = \frac{RT}{X_B}\left(\frac{d\ln\gamma_B}{dX_B / X_B} + \frac{d\ln X_B}{dX_B / X_B}\right)$$

$$= \frac{RT}{X_B}\left(\frac{d\ln\gamma_B}{d\ln X_B} + \frac{d\ln X_B}{d\ln X_B}\right) = \frac{RT}{X_B}\left(1 + \frac{d\ln\gamma_B}{d\ln X_B}\right)$$

$$\frac{d\mu_B}{dx} = ? \qquad x : \text{distance}$$

$$d\mu_B = \frac{RT}{X_B}\left(1 + \frac{d\ln\gamma_B}{d\ln X_B}\right) dX_B \qquad \frac{d\mu_B}{dx} = \frac{RT}{X_B}\left(1 + \frac{d\ln\gamma_B}{d\ln X_B}\right)\frac{\partial X_B}{\partial x}$$

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

$$\frac{d\mu_B}{dx} = \frac{RT}{X_B}\left(1 + \frac{d\ln\gamma_B}{d\ln X_B}\right)\frac{\partial X_B}{\partial x}$$

$$J_B = -M_B C_B \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}\frac{\partial X_B}{\partial x} \qquad C_B = \frac{n_B}{V} = \frac{n_B}{(n_A + n_B)V_m} = \frac{X_B}{V_m}$$

$$J_B = -M_B \frac{X_B}{V_m}\frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}\frac{\partial X_B}{\partial x}$$

$$= -M_B RT \left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}\frac{\partial (X_B / V_m)}{\partial x} \qquad = -M_B RT \left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}\frac{\partial C_B}{\partial x}$$

Phase Transformations in Metals and Alloys
NRL of Charged Nanoparticles

$$J_B = -M_B RT \left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\} \frac{\partial C_B}{\partial x}$$

Comparison with Fick's 1st law

$$D_B = M_B RT \left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

$$F = \left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\} = \text{thermodynamic factor}$$

For ideal or dilute solutions *($X_B \to 0$) γ_B is a constant and the term in brackets is unity.*

$$D_B = M_B RT$$

For non ideal concentrated solutions the term in brackets (thermodynamic factor), must be included.

Effect of strain energy on J_B? $\mu_B = G_B + RT\ln\gamma_B X_B + E$

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x} \quad \rightarrow J_B = -M_B C_B \frac{\partial E}{\partial x} \qquad D_B = M_B RT$$

$$\Rightarrow \quad J_B = -D_B \cdot \frac{\partial C_B}{\partial x} - \frac{D_B C_B}{RT} \cdot \frac{\partial E}{\partial x}$$

The diffusive flux is also affected by the gradient of strain energy, ∂E/∂x.

Tracer diffusion in binary alloys

$D_B^* = M_B^* RT = M_B RT$

Recall that

$D_B = M_B RTF$ (F : the thermodynamic factor)

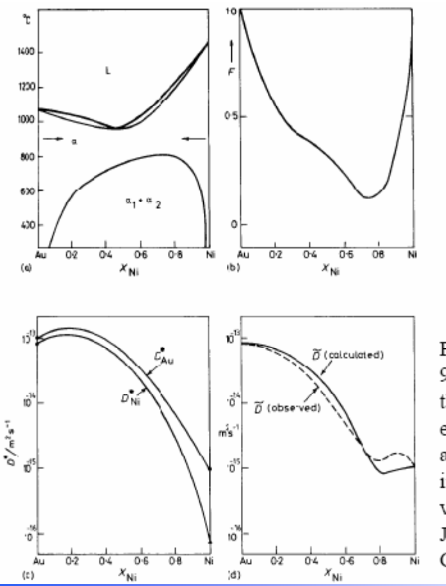
$$F = \left\{1 + \frac{d \ln \gamma_B}{d \ln X_B}\right\} = \frac{X_A X_B}{RT} \frac{d^2 G}{dX^2}$$

$$\therefore D_B = F D_B^*$$

$$\tilde{D} = X_A D_B + X_B D_A$$

$$= F\left(X_A D_B^* + X_B D_A^*\right)$$

Tracer diffusion in binary alloys



It is possible to use radioactive tracers to determine the intrinsic diffusion coefficients of the components in an alloy (Fig.2.22)

Fig. 2.22 Interdiffusion in Au-Ni alloys at 900°C (a) Au-Ni phase diagram, (b) the thermodynamic factor, F, at 900°C, (c) experimentally measured tracer diffusivities at 900°C, (d) experimentally measured interdiffusion coefficients compared with values calculated from (b) and (c). (From J.E. Reynolds, B.L. Averbach and Morris Cohen, *Acta Metallurgica*, 5 (1957) 29.)