

재료상변태

Phase Transformation of Materials

2008.10.09.

박은수

서울대학교 재료공학부

Contents for previous class

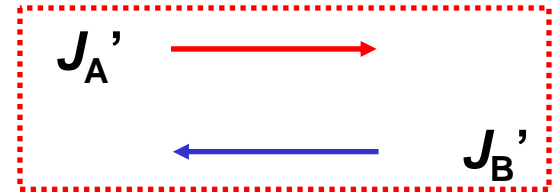
- **Diffusion in substitutional alloys**
 - 1) Interdiffusion
 - 2) Velocity of the movement of the lattice plane
 - 3) Fick's 2nd law for substitutional alloys
 - 4) Diffusion in dilute substitutional alloys
- **Atomic mobility:** Relationship between M_B and D_B

- Diffusion in substitutional alloys

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

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

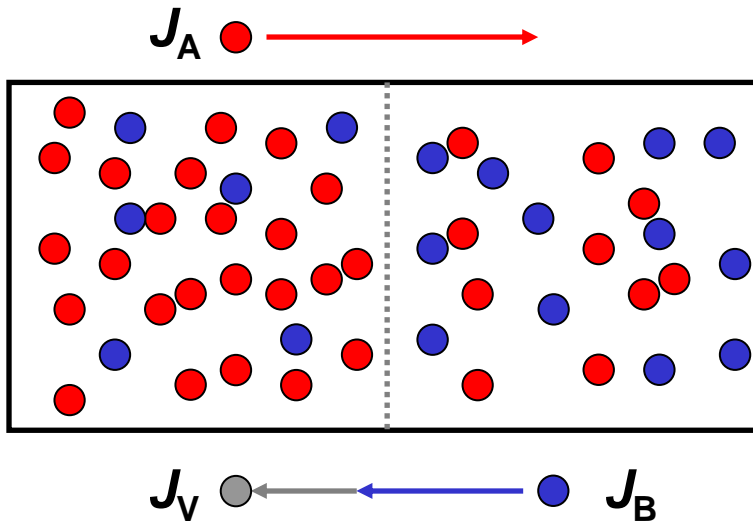
$$J'_A = J_A + J_A^v = -\tilde{D} \frac{\partial C_A}{\partial x}$$



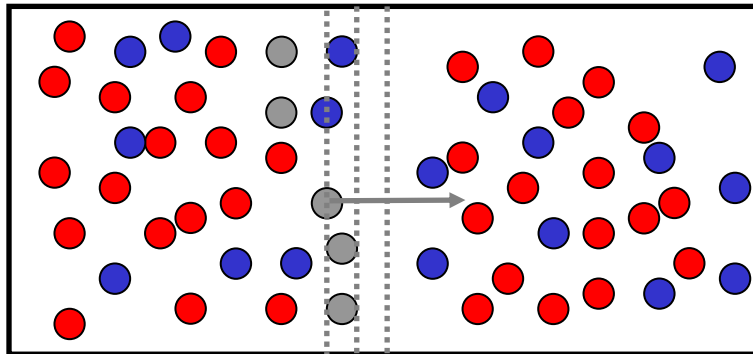
$$J'_B = J_B + J_B^v = -\tilde{D} \frac{\partial C_B}{\partial x}$$

$$\therefore J'_B = -J'_A$$

At $t = 0$,



At $t = t_1$,



Atomic mobility

- 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**: diffusion occurs down the slope of the chemical potential.

$$J_B = v_B c_B$$

A **diffusion flux** is a combined quantity of a drift velocity and random jumping motion.

$$v_B = -M_B \frac{\partial \mu_B}{\partial x}$$

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

M_B : mobility of B atoms



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

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

Relationship between M_B and D_B

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

$$\begin{aligned} \therefore J_B &= -M_B \frac{X_B}{V_m} \frac{RT}{X_B} \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}\right) \frac{\partial X_B}{\partial x} \\ &= -M_B RT F \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x} \end{aligned}$$

$$D_B = M_B RT F$$

For ideal or dilute solutions,
near $X_B \approx 0$, $\gamma_B = \text{const.}$ with respect to X_B

$$\therefore F = 1 \quad D_B = M_B RT$$

$$\mu_B = G_B + RT \ln a_B = G_B + RT \ln \gamma_B X_B$$

$$\begin{aligned} \frac{\partial \mu_B}{\partial x} &= \frac{\partial}{\partial x} (G_B^0 + RT \ln \gamma_B X_B) \\ &= RT \left(\frac{\partial \ln \gamma_B}{\partial x} + \frac{\partial \ln X_B}{\partial x} \right) \\ &= RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \frac{\partial \ln X_B}{\partial x} \end{aligned}$$

$$C_B = \frac{n_B}{V} = \frac{n_B}{(n_A + n_B)V_m} = \frac{X_B}{V_m}$$

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

For non-ideal concentrated solutions,
thermodynamic factor must be included.

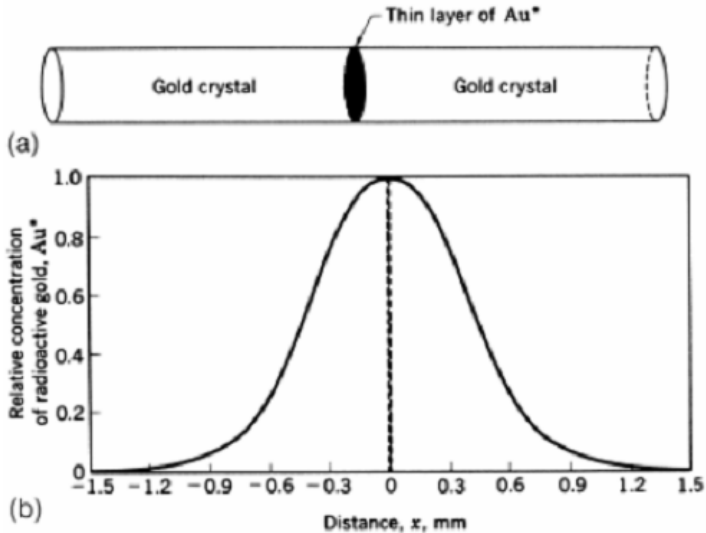
→ Related to the curvature of the molar
free energy-composition curve.

Contents for today's class

- **Tracer Diffusion in Binary Alloys**
- **Diffusion in Ternary Alloy**
- **High-Diffusivity Paths**
 - 1) **Diffusion along Grain Boundaries and Free Surface**
 - 2) **Diffusion Along Dislocation**
- **Diffusion in Multiphase Binary Systems**

2.5 Tracer diffusion in binary alloys

1) Au* in Au



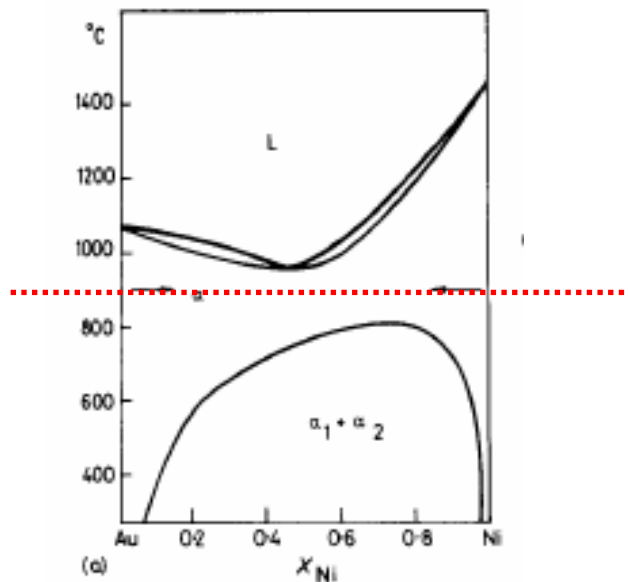
It is possible to use radioactive tracers (D_{Au}^*) to determine the intrinsic diffusion coefficients (D_{Au}) of the components in an alloy .

$$D_{Au}^* = D_{Au} \text{ (self diffusivity)}$$

How does D_{Au}^* differ from D_{Au} ?

D_{Au}^* gives the rate at which Au* (or Au) atoms diffuse in a **chemically homogeneous** alloy, whereas D_{Au} gives the diffusion rate of Au when **concentration gradient** is present.

2) Au* in Au-Ni



If concentration gradient exhibit,

$$\Delta H_{mix} > 0 \rightarrow D_{Au} < D_{Au}^*, D_{Ni} < D_{Ni}^*$$

obtained by marker's movement

Since the **chemical potential gradient** is the driving force for diffusion in both types of experiment it is reasonable to suppose that **the atomic mobility** are not affected by the concentration gradient.

What would be the relation between the intrinsic chemical diffusivities D_B and tracer diffusivities D_B^* ?

In the tracer diffusion experiment the tracer essentially forms a dilute solution in the alloy.

$$D_B^* = M_B^* RT = M_B RT \quad \leftarrow \quad D_B = M_B RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} = F M_B RT$$

$$\begin{aligned} D_A &= F D_A^* \\ D_B &= F D_B^* \end{aligned} \quad \rightarrow \quad \tilde{D} = X_B D_A + X_A D_B = F (X_B D_A^* + X_A D_B^*)$$

F : Thermodynamic Factor

Additional Thermodynamic Relationships for Binary Solution:

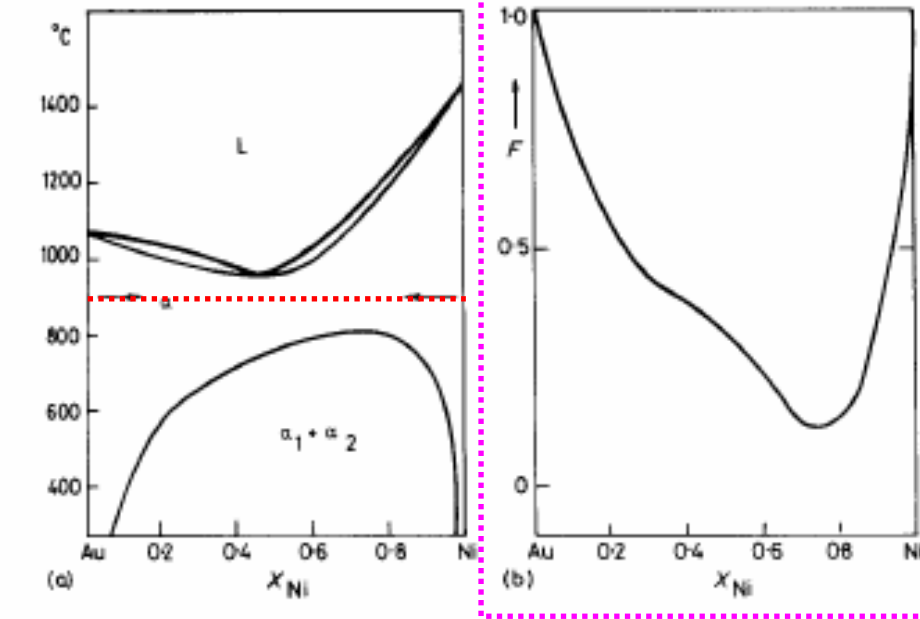
Variation of chemical potential ($d\mu$) by change of alloy compositions (dX)

Eq.(1.71)

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

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

2.5 Tracer diffusion in binary alloys



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

$$\tilde{D} = F(X_B D_A^* + X_A D_B^*)$$

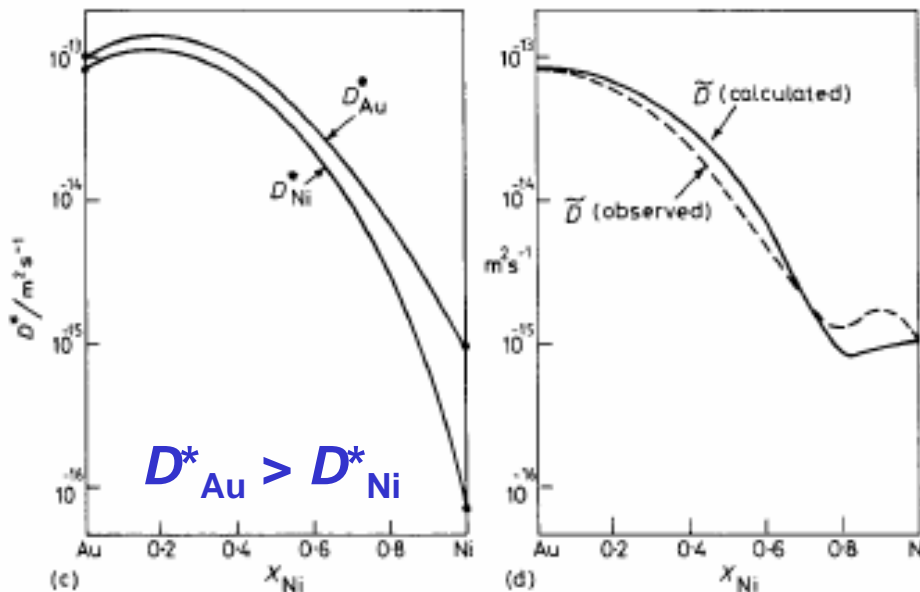
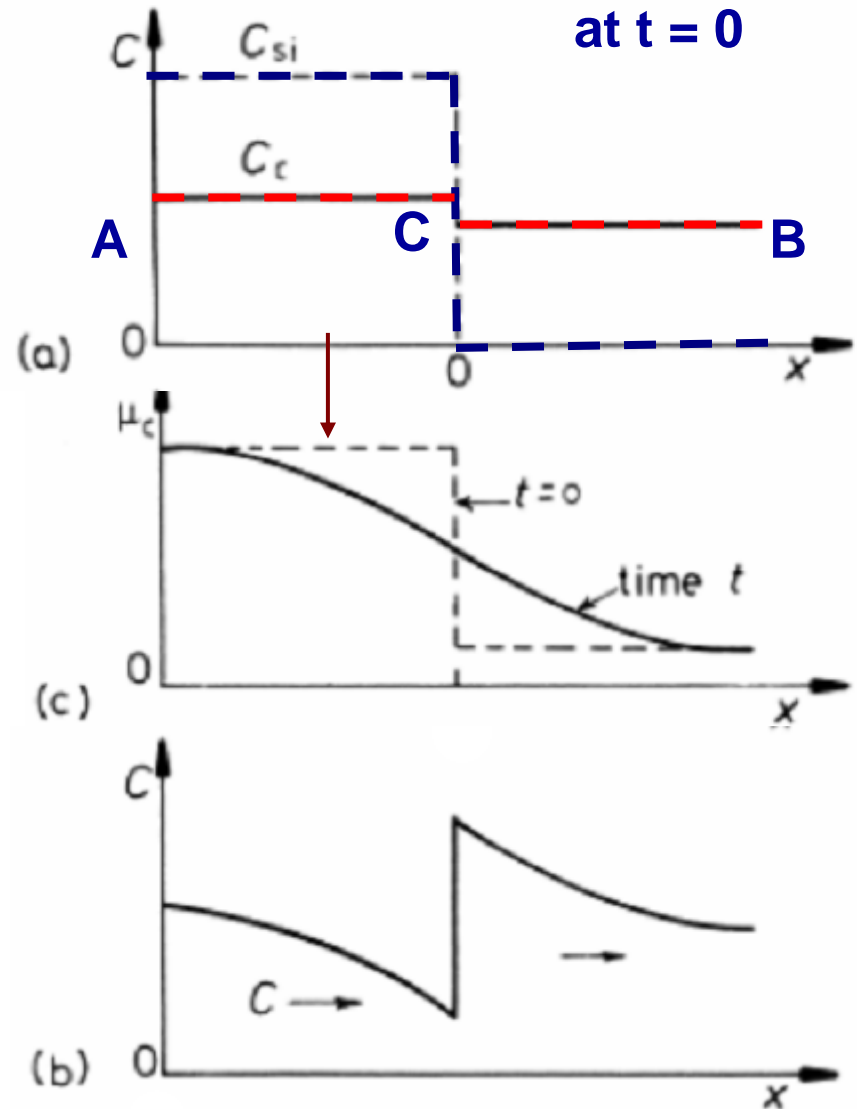
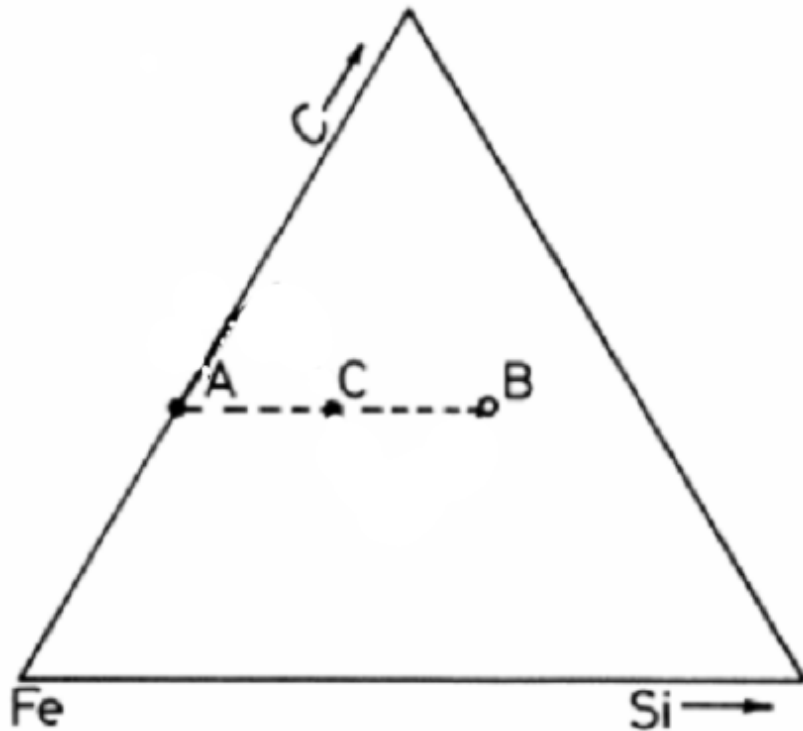


Fig. 2.22 Interdiffusion in Au-Ni alloys at 900°C (a) Au-Ni phase diagram, (b) the thermodynamic factor, F , at 900°C, (c) experimentally measured tracer diffusivities at 900°C, (d) experimentally measured interdiffusion coefficients compared with values calculated from (b) and (c). (From J.E. Reynolds,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

2.6 Diffusion in ternary alloys: Additional Effects

Example) Fe-Si-C system (Fe-3.8%Si-0.48%C) vs. (Fe-0.44%C) at 1050°C

- ① Si raises the μ_C in solution.
(chemical potential of carbon)
- ② $M_{Si} \text{ (sub.)} \ll M_C \text{ (int.)}$,
(M : mobility)



How do the compositions of A and B change with time?

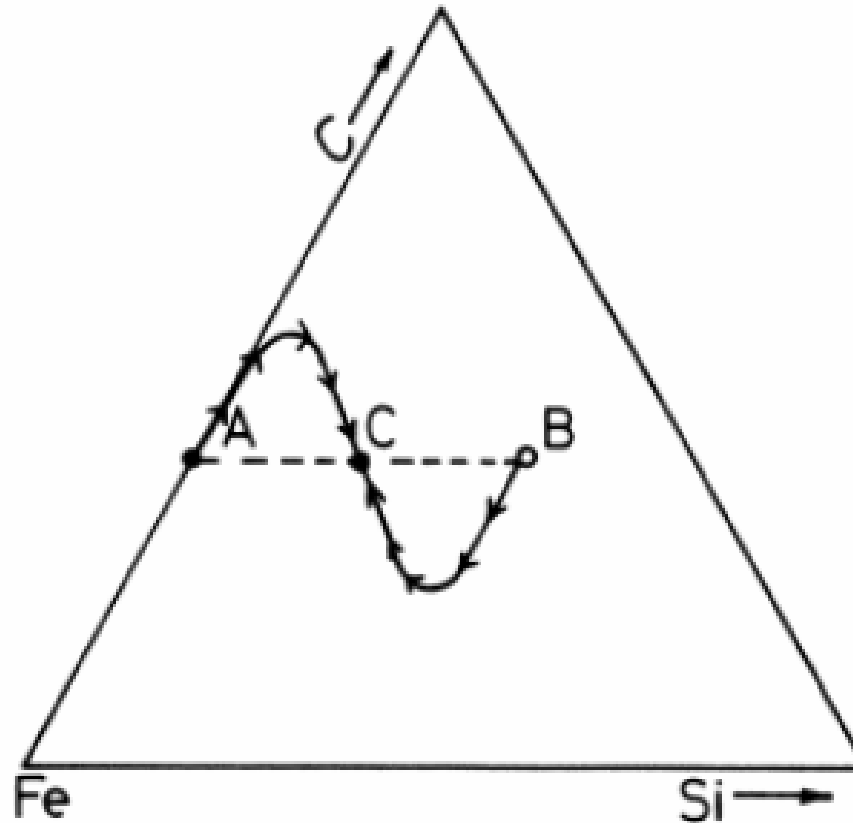
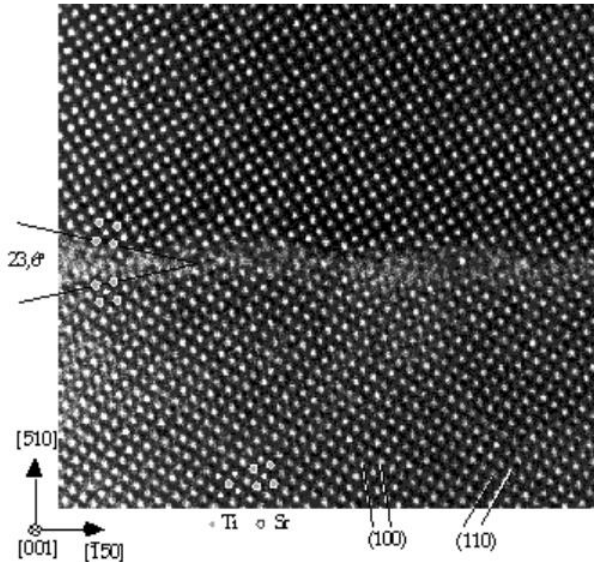


Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B)

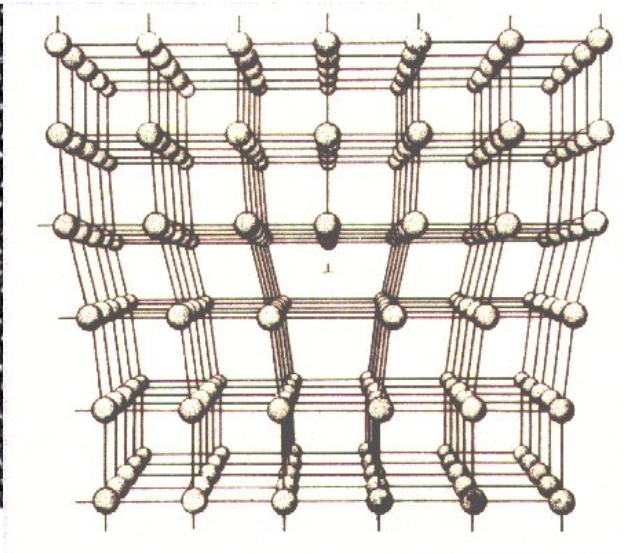
2.7.1 High-diffusivity paths

Real materials contain **defects**.

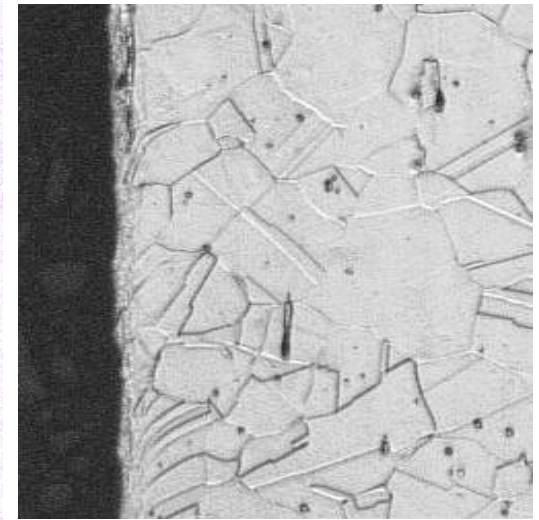
= more open structure → fast diffusion path.



Grain boundary



dislocation



surface

Diff. along lattice

$$D_l = D_{lo} \exp\left(-\frac{Q_l}{RT}\right)$$

Diff. along grain boundary

$$D_b = D_{bo} \exp\left(-\frac{Q_b}{RT}\right)$$

Diff. along free surface

$$D_s = D_{so} \exp\left(-\frac{Q_s}{RT}\right)$$

$$D_s > D_b > D_l$$

But area fraction → **lattice** > **grain boundary** > **surface**

Diffusion along grain boundaries

Atoms diffusing along the boundary will be able to **penetrate much deeper** than atoms which only diffuse through the lattice.

In addition, as the concentration of solute builds up in the boundaries, atoms will also **diffuse from the boundary into the lattice**.

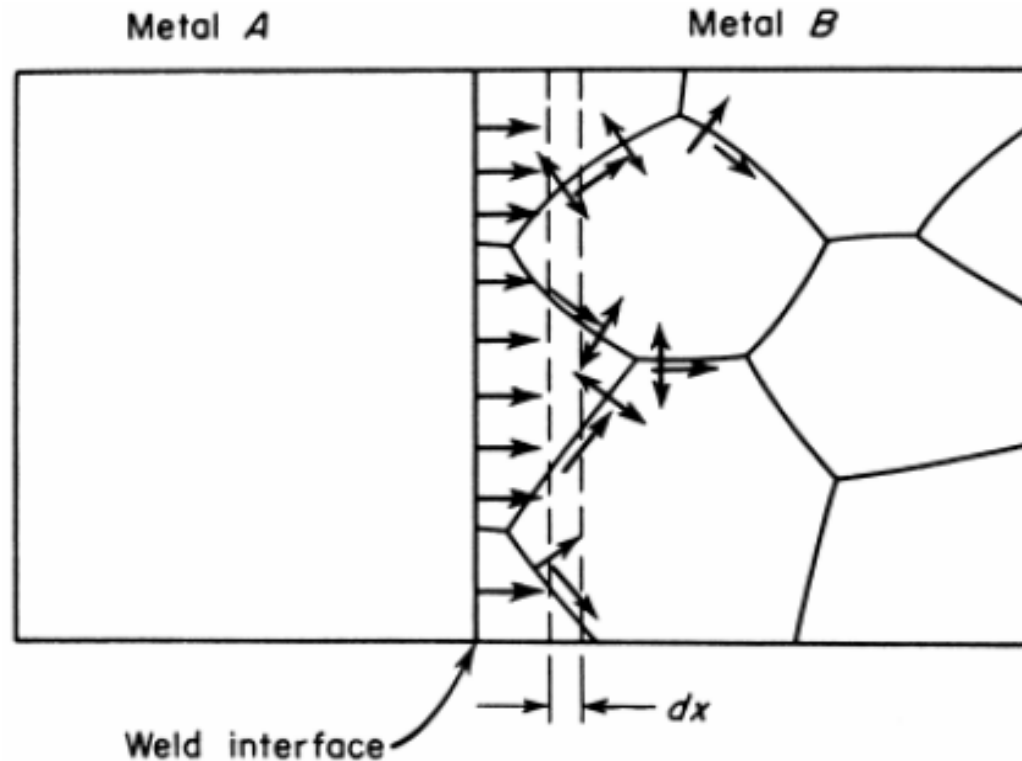
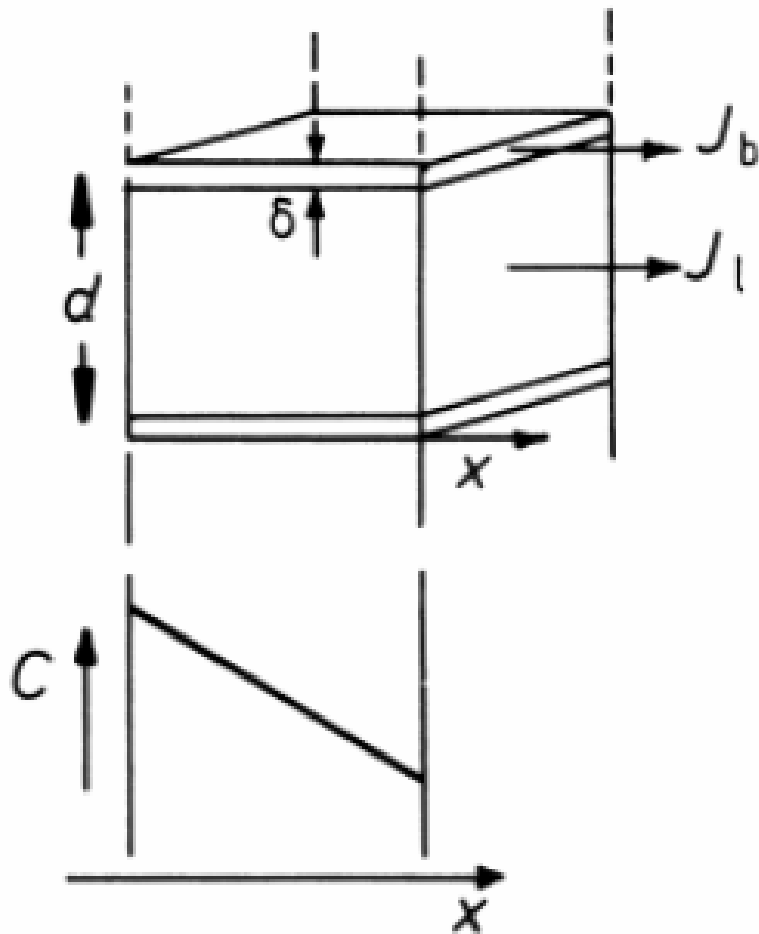


Fig. 2.25. The effect of grain boundary diffusion combined with volume diffusion. (After R.E. Reed-Hill, *Physical Metallurgy Principles*, 2nd edn., Van Nostrand, New York, 1973.)

Combined diffusion of grain boundary and lattice?



$$J_l = -D_l \frac{dC}{dx}$$

$$J_b = -D_b \frac{dC}{dx}$$

$$J = (J_b \delta + J_l d) / d = -D_{app} \frac{dC}{dx}$$

δ : grain boundary thickness $\approx 0.5\text{nm}$

d : grain size

D_{app} : apparant diffusivity

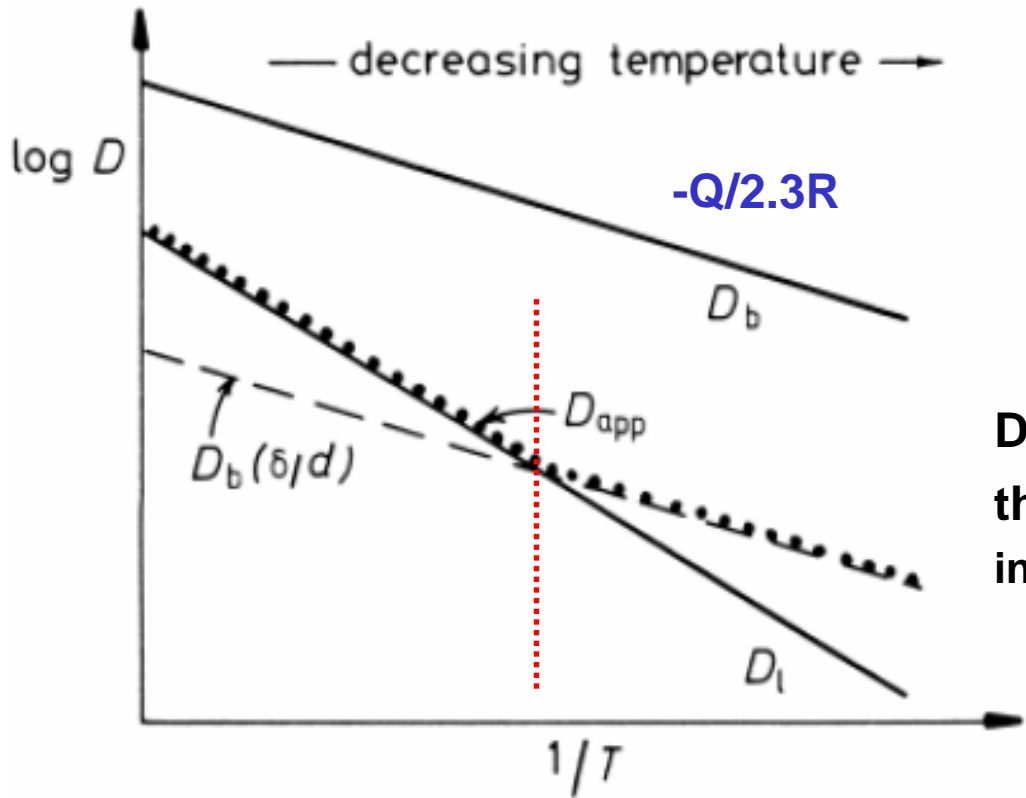
$$D_{app} = D_l + D_b \frac{\delta}{d}$$

Thus, grain boundary diffusion makes a significant contribution

only when $D_b \delta > D_l d$.

Fig. 2.26 Combined lattice and boundary fluxes during steady-state diffusion through a thin slab of material.

The relative magnitudes of $D_b\delta$ and $D_l d$ are most sensitive to temperature.



$D_b > D_l$ at all temp.

Due to $Q_b < Q_l$,
the curves for D_l and $D_b\delta/d$ cross
in the coordinate system of $\ln D$ versus $1/T$.

Fig. 2.27 Diffusion in a polycrystalline metal.

➔ Therefore, the grain boundary diffusion becomes predominant at temperatures lower than the crossing temperature.
($T < 0.75 \sim 0.8 T_m$)

2.7.2 Diffusion along dislocations

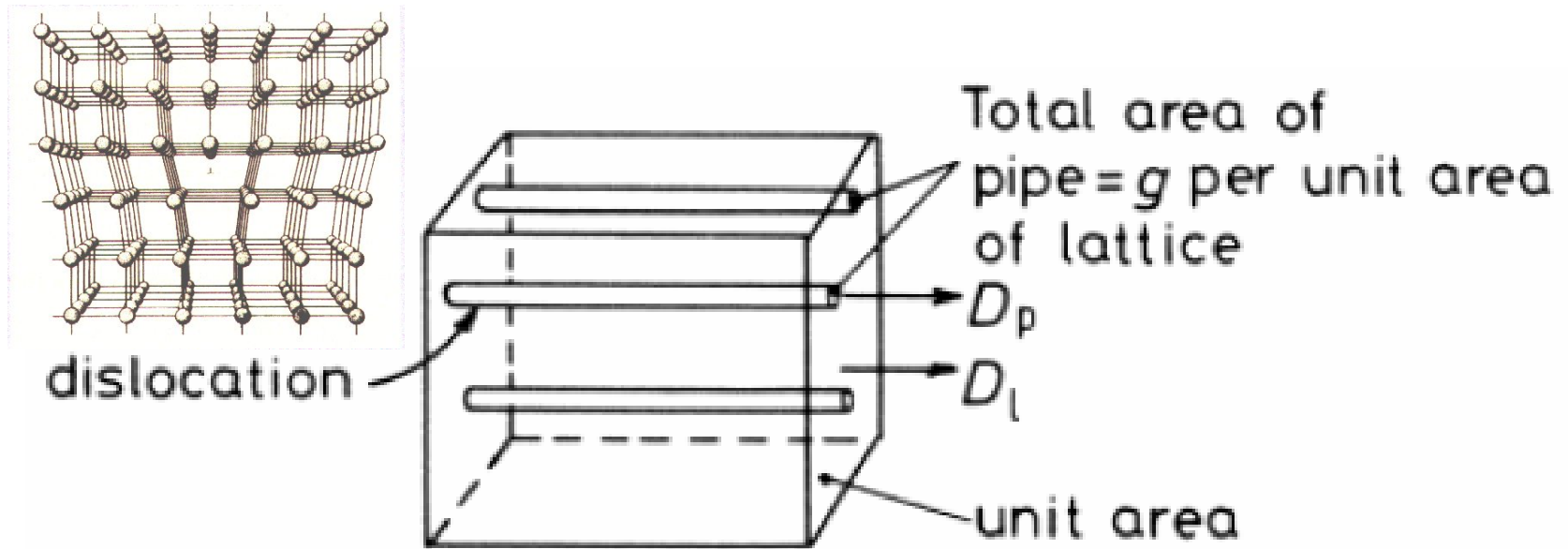


Fig. 2.28. Dislocations act as a high conductivity path through the lattice.

$D_{app} = ?$ hint) 'g' is the cross-sectional area of 'pipe' per unit area of matrix.

$$D_{app} = D_l + g \cdot D_p \quad \rightarrow \quad \frac{D_{app}}{D_l} = 1 + g \cdot \frac{D_p}{D_l}$$

ex) annealed metal $\sim 10^5$ disl/mm²; one dislocation(\perp) accommodates 10 atoms in the cross-section; matrix contains 10^{13} atoms/mm².

$$g = \frac{10^5 * 10}{10^{13}} = \frac{10^6}{10^{13}} = 10^{-7}$$

g = cross-sectional area of 'pipe' per unit area of matrix

At high temperatures,

diffusion through the lattice is rapid and gD_p/D_l is very small so that the dislocation contribution to the total flux of atoms is very small.

Due to $Q_p < Q_l$,

the curves for D_l and gD_p/D_l cross in the coordinate system of $\ln D$ versus $1/T$.

At low temperatures, ($T < \sim 0.5 T_m$)

gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.