2009 fall

Phase Transformation of Materials

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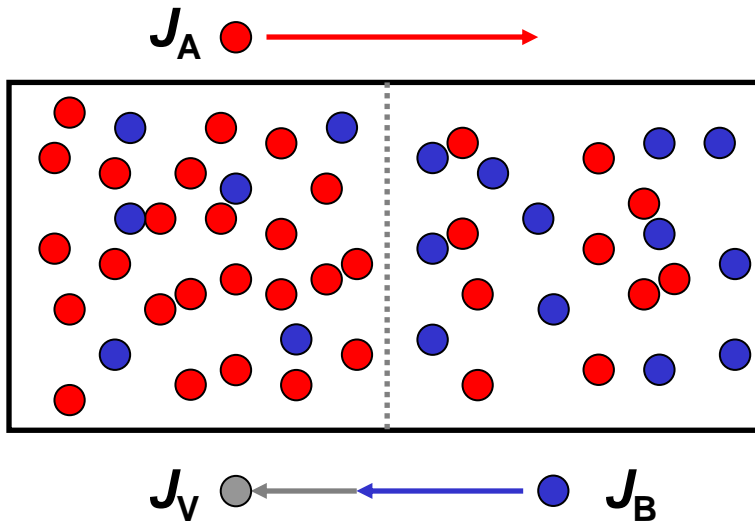
Contents for previous class

- **Interstitial Diffusion / Substitution Diffusion**

  1. Self diffusion in pure material

  2. Vacancy diffusion

  3. **Diffusion in substitutional alloys**

- **Atomic Mobility**

- **Tracer Diffusion in Binary Alloys**

- **High-Diffusivity Paths**

  1. Diffusion along Grain Boundaries and Free Surface

  2. Diffusion Along Dislocation

- **Diffusion in Multiphase Binary Systems**
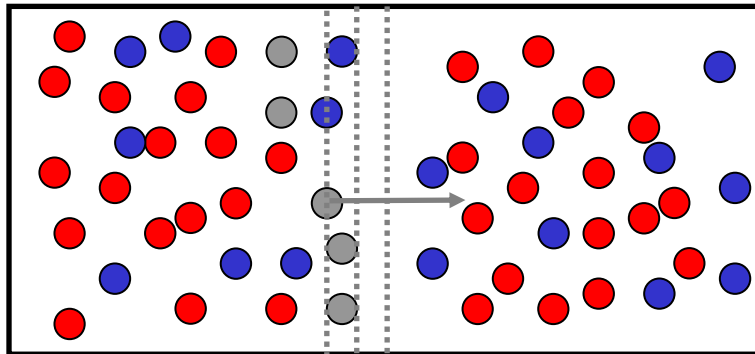
- **Diffusion in substitutional alloys**

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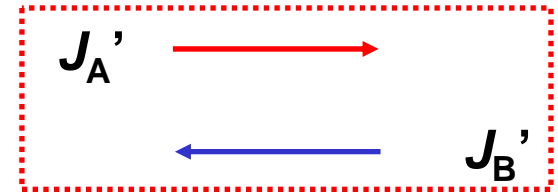
J_A

At t = 0,

J_V J_B

At t = t_1,

농도 구배에 의한 속도 **+** 격자면 이동에 의한 속도

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

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

J_A

J_V^A

J_A'

J_B'

J_V^B

J_B

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

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

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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.**

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

$-\dfrac{\partial \mu_B}{\partial x}$: 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

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

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

$$= -M_B RTF \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x}$$

$$D_B = M_B RTF$$

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

$$\frac{\partial \mu_B}{\partial x} = \frac{\partial}{\partial x}(G_B^0 + RT \ln \gamma_B X_B)$$

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

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

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

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

For ideal or dilute solutions,
near $X_B \approx 0$, γ_B = const. with respect to X_B

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

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

$\longrightarrow$ **Related to the curvature of the molar free energy-composition curve.**

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Contents for today's class

- **Interstitial Diffusion / Substitution Diffusion**

- **Atomic Mobility**

- **Tracer Diffusion in Binary Alloys**

- **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


(a)

(b)

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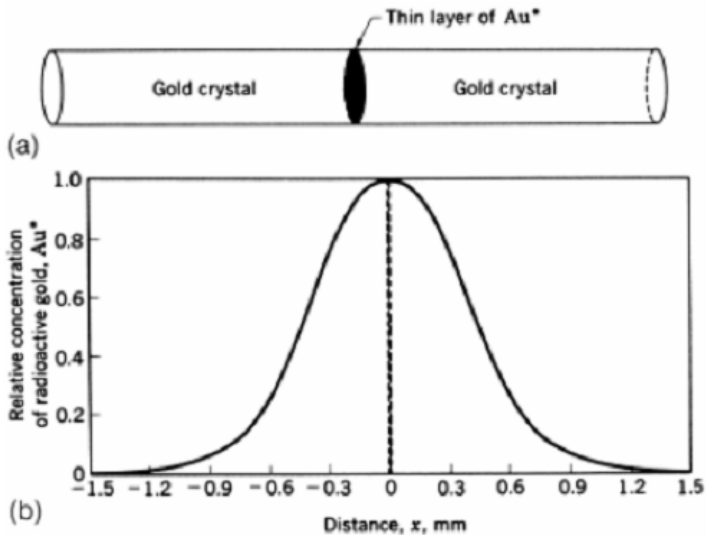
It is possible to use radioactive tracers (D^*_{Au}) to determine the intrinsic diffusion coefficients (D_{Au}) of the components in an alloy .

$$D^*_{Au} = D_{Au} \ (\textit{self diffusivity})$$

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.
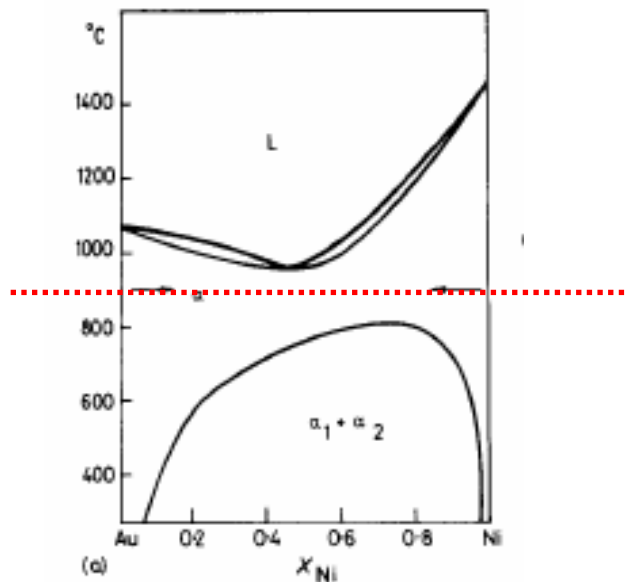
If concentration gradient exhibit,

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

the rate of homogenization will there fore be slower.

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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.

$$D^*_B = M^*_B RT = M_B RT \qquad \Longleftarrow \qquad D_B = M_B RT \left\{ 1 + \frac{d\ln\gamma_B}{d\ln X_B} \right\} = F M_B RT$$

$$D_A = F D^*_A$$

F : Thermodynamic Factor

$$D_B = F D^*_B \qquad \Longrightarrow \qquad \tilde{D} = X_B D_A + X_A D_B = F\left(X_B D^*_A + X_A D^*_B \right)$$

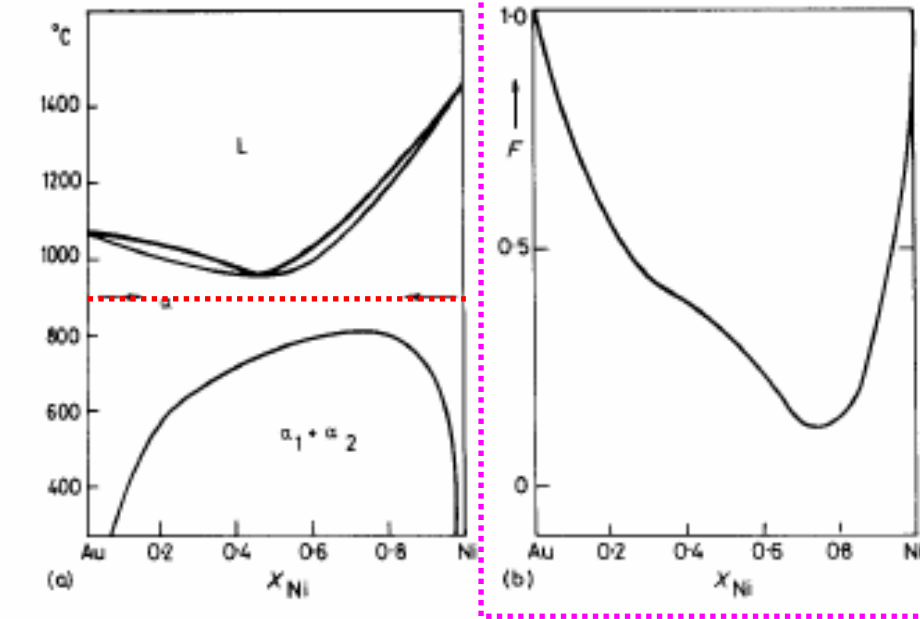**Additional Thermodynamic Relationships for Binary Solution:**
Variation of chemical potential (dμ) by change of alloy compositions (dX)
Eq.(1.71)

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

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

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2.5 Tracer diffusion in binary alloys

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

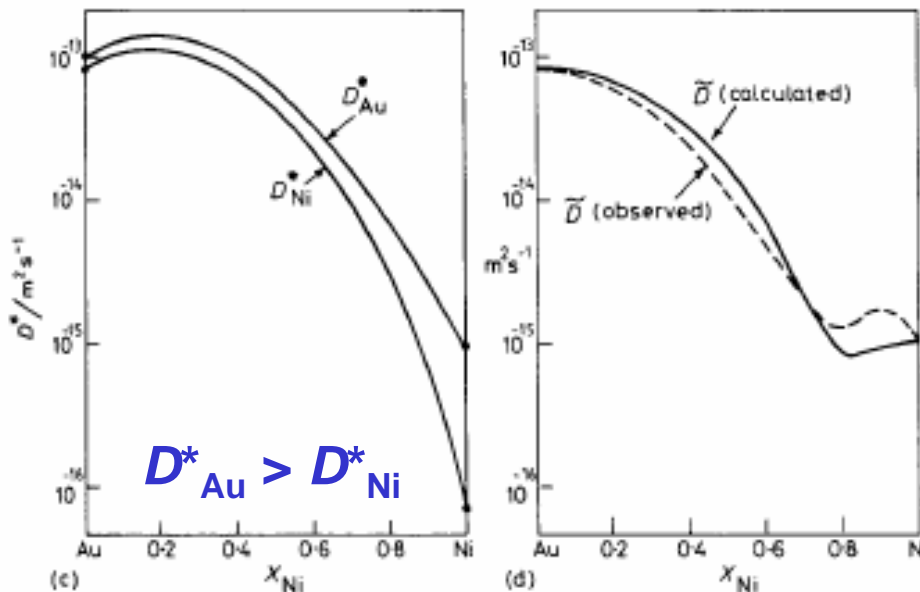$$\tilde{D} = F\left(X_B D_A^* + X_A D_B^* \right)$$

$$D^*_{Au} > D^*_{Ni}$$

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.)

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

① **Si raises the μ_C in solution.**
   (chemical potential of carbon)

② **M_{Si} (sub.) $\ll M_C$ (int.),**
   (M : mobility)
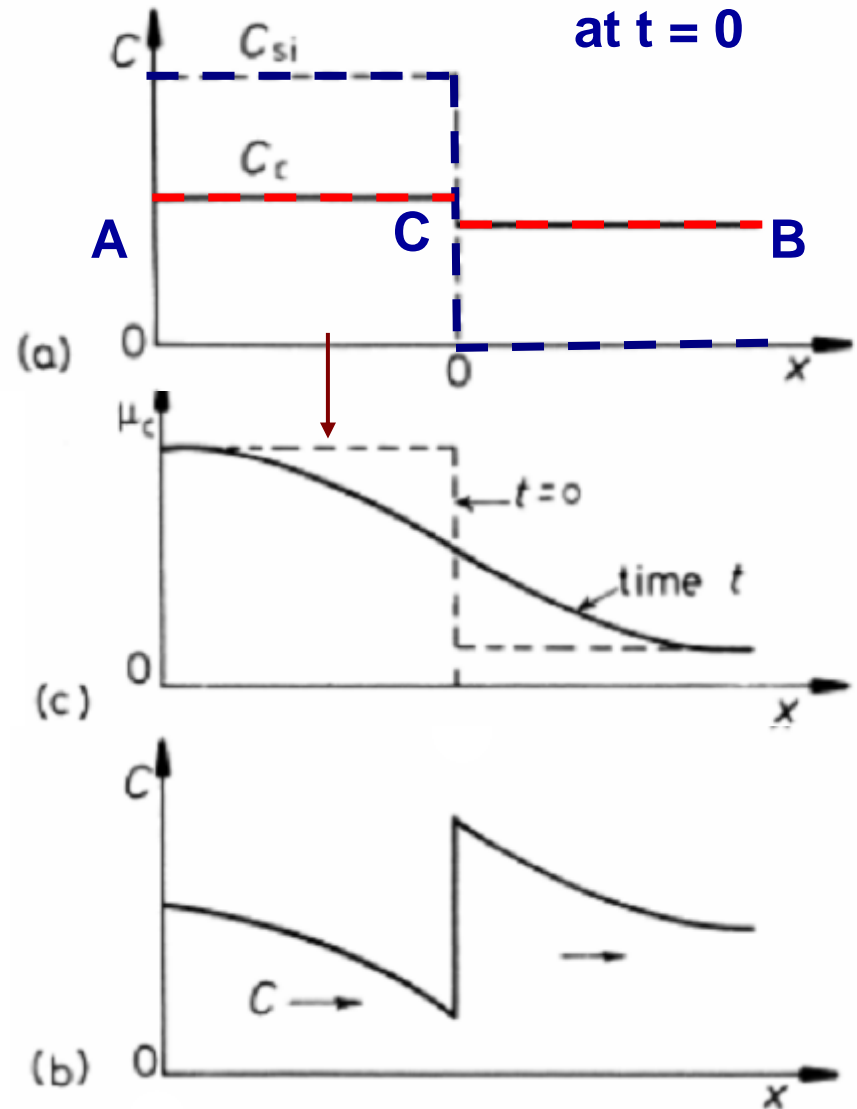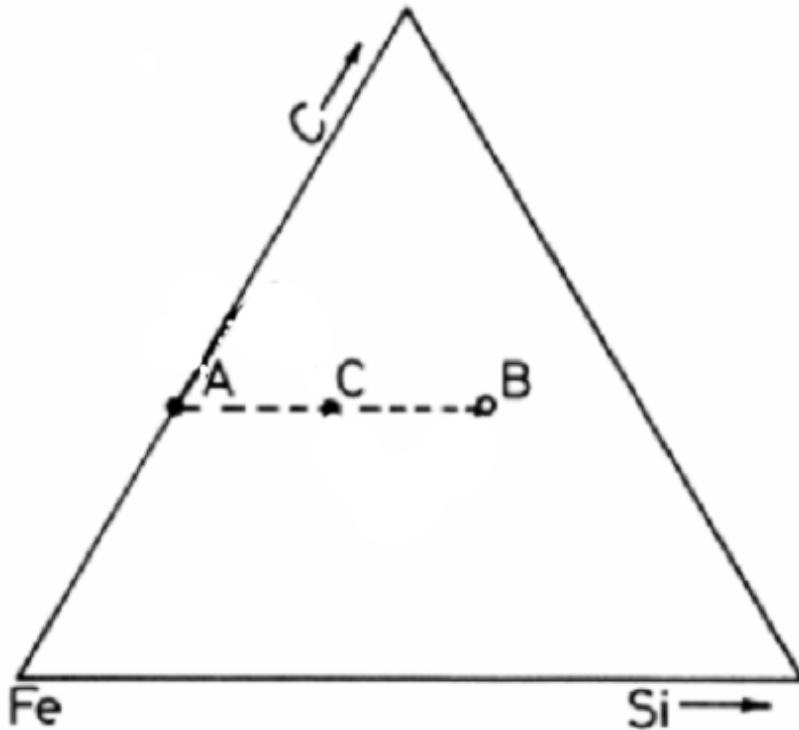
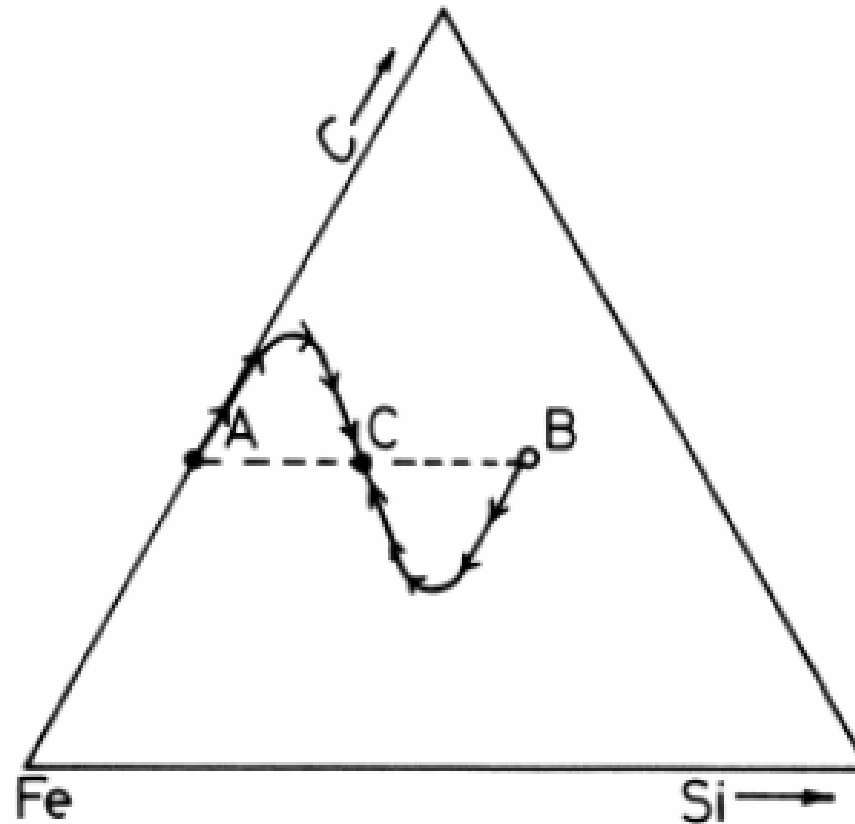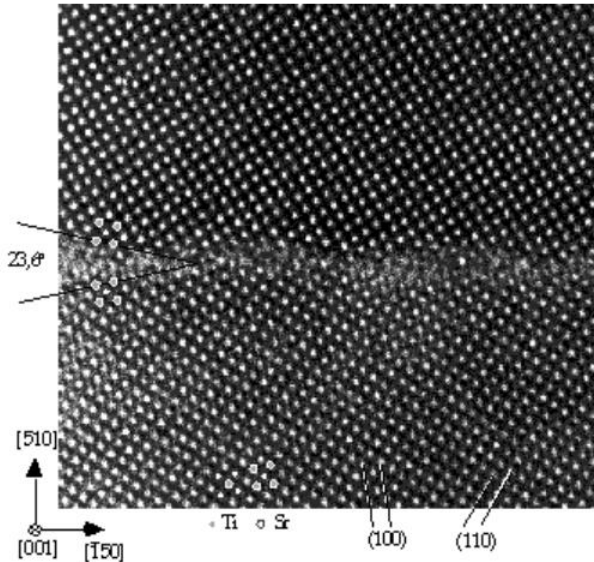# How do the compositions of A and B change with time?

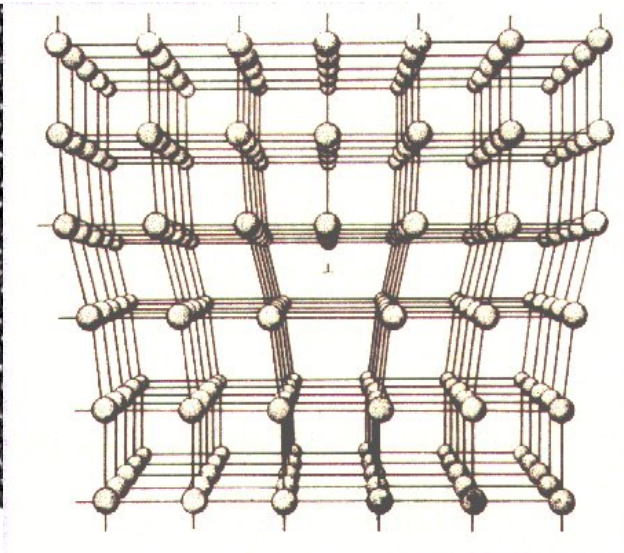Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B)

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2.7.1 High-diffusivity paths
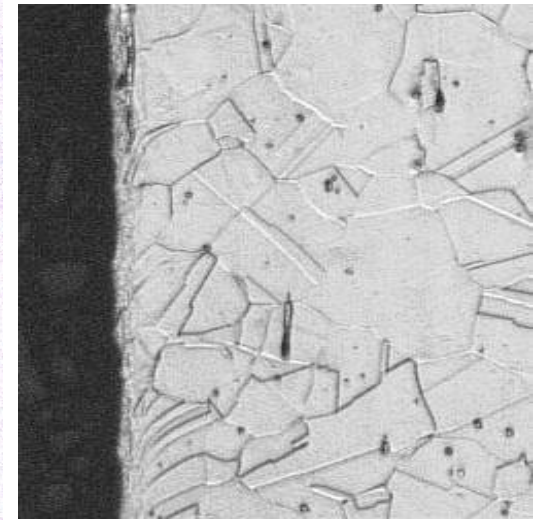
Real materials contain <u>**defects**</u>.

= more open structure ➡ **fast diffusion path.**

Grain boundary

dislocation

surface

Diff. along lattice

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

$$\boxed{D_s > D_b > D_l}$$

Diff. along grain boundary

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

Diff. along free surface

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

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.
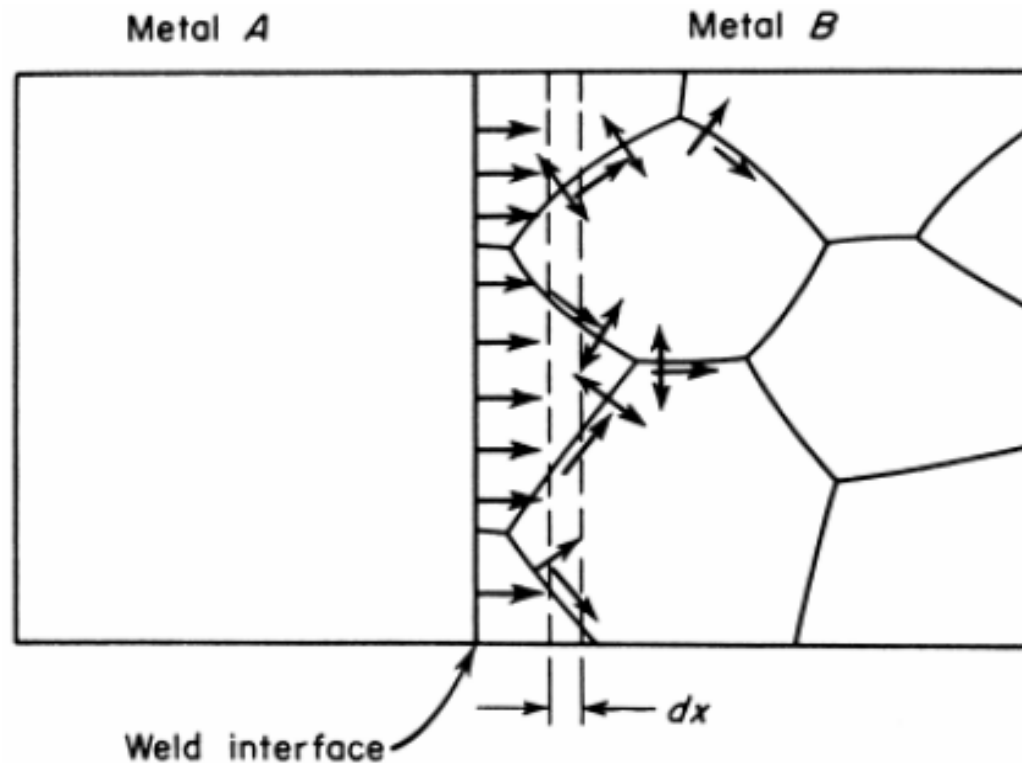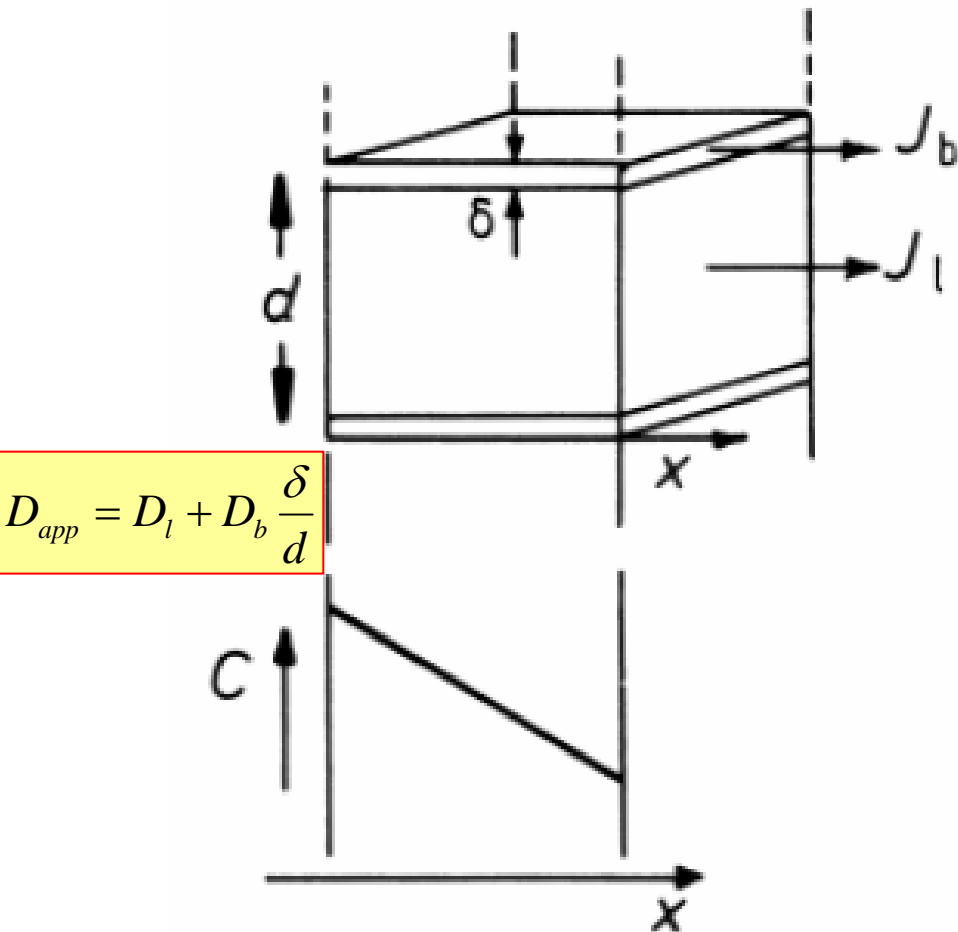

Fig. 2.25. The effect of grain boundary diffusion combined with volume diffusion. (After R.E. Reed-Hill, *Physical Metallurgy Principles, 2nd edn.*, Van Nostrand, New York, 1973.)

Combined diffusion of grain boundary and lattice?

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

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

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

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

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

δ : grain boundary thickness ≈ 0.5nm
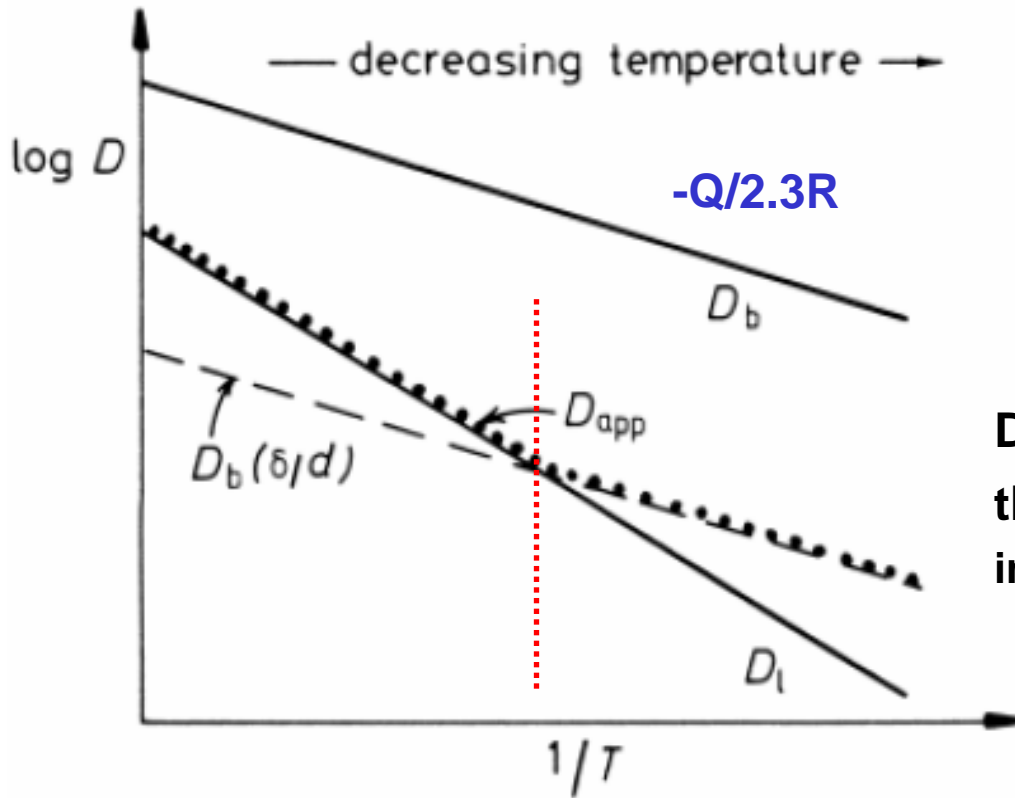
d : grain size

D_{app} : apparant diffusivity

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

Thus, grain boundary diffusion makes a significant contribution only when $D_b\delta > D_l d$.

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

Fig. 2.27 Diffusion in a polycrystalline metal.

$D_b > D_l$ 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 lnD versus 1/T.

➡ **Therefore, the grain boundary diffusion becomes predominant at temperatures lower than the crossing temperature.**

($T < 0.75{\sim}0.8\ T_m$)
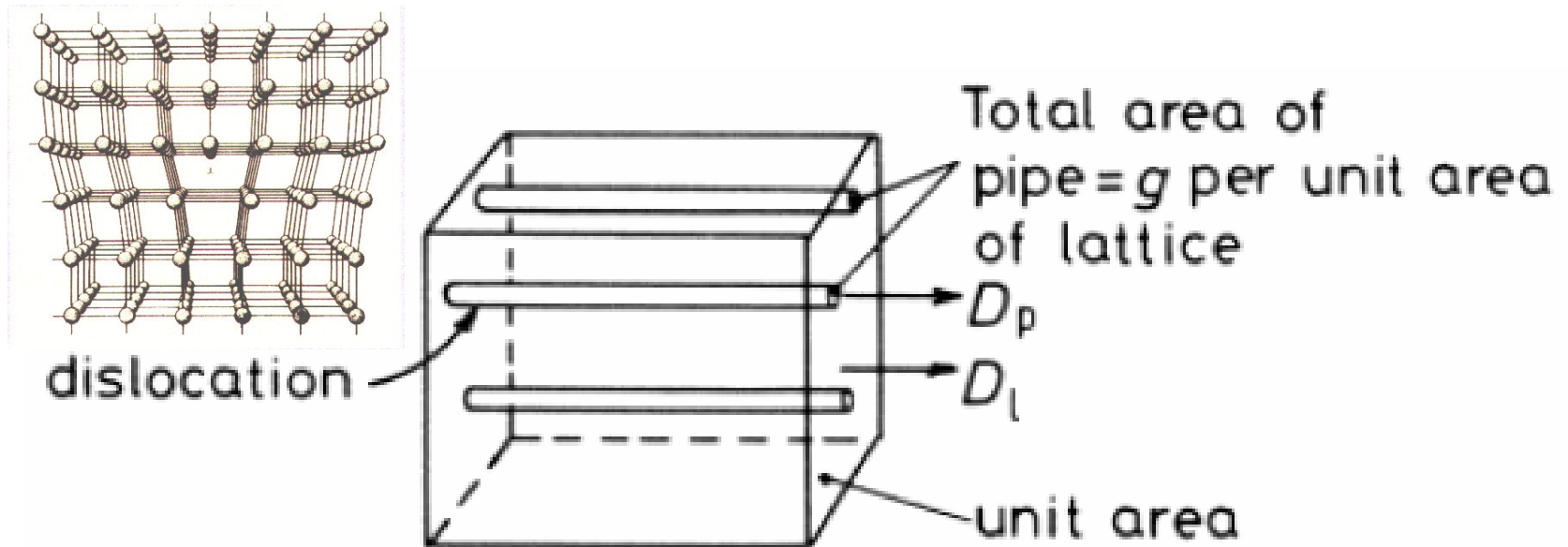
2.7.2 Diffusion along dislocations

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.**

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

ex) annealed metal $\sim 10^5$ disl/mm^2; one dislocation($\perp$) accommodates 10 atoms in the cross-section; matrix contains 10^{13} atoms/mm^2.

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

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
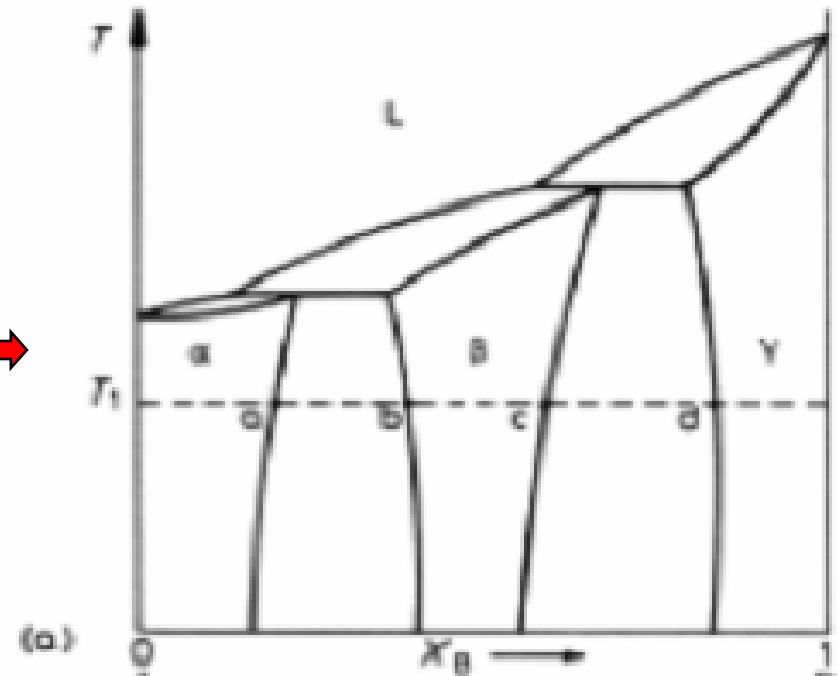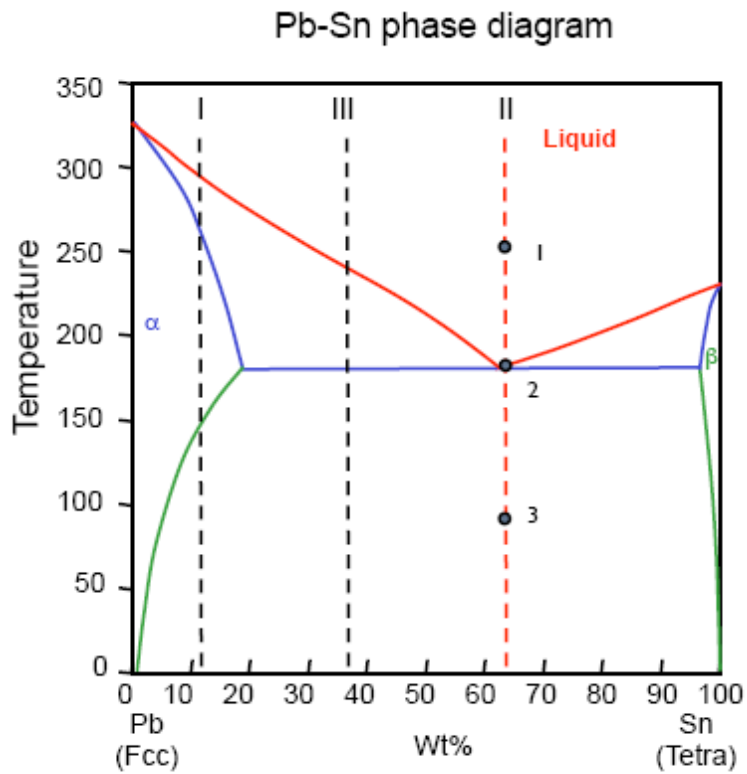so that the dislocation contribution to the total flux of atoms is very small.

Due to $Q_p < Q_l$,
the curves for D_l and gD_p/D_l cross in the coordinate system of lnD versus 1/T.

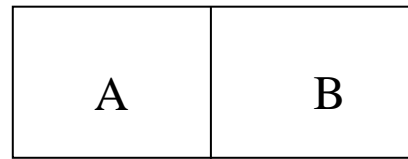At low temperatures, **($T < \sim 0.5\ T_m$)**
gD_p/D_l can become so large that the apparent diffusivity is entirely
due to diffusion along dislocation.
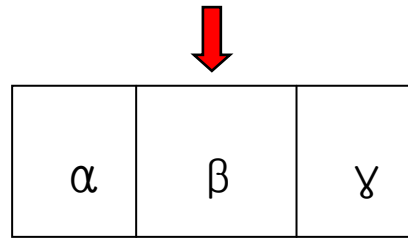
2.8 Diffusion in multiple binary system

Pb-Sn phase diagram

2.8 Diffusion in multiple binary system

A diffusion couple made by welding together pure A and pure B

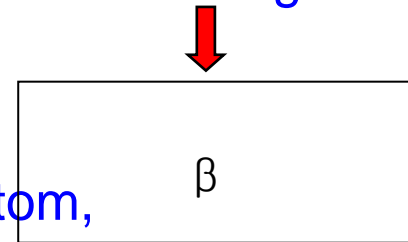| A	B

α	β	ɣ

What would be the microstructure evolved after annealing at T_1 ?

→ **a layered structure**

   containing α, β & ɣ.

Draw a phase distribution and composition profile in the plot of distance vs. X_B after annealing at T_1.
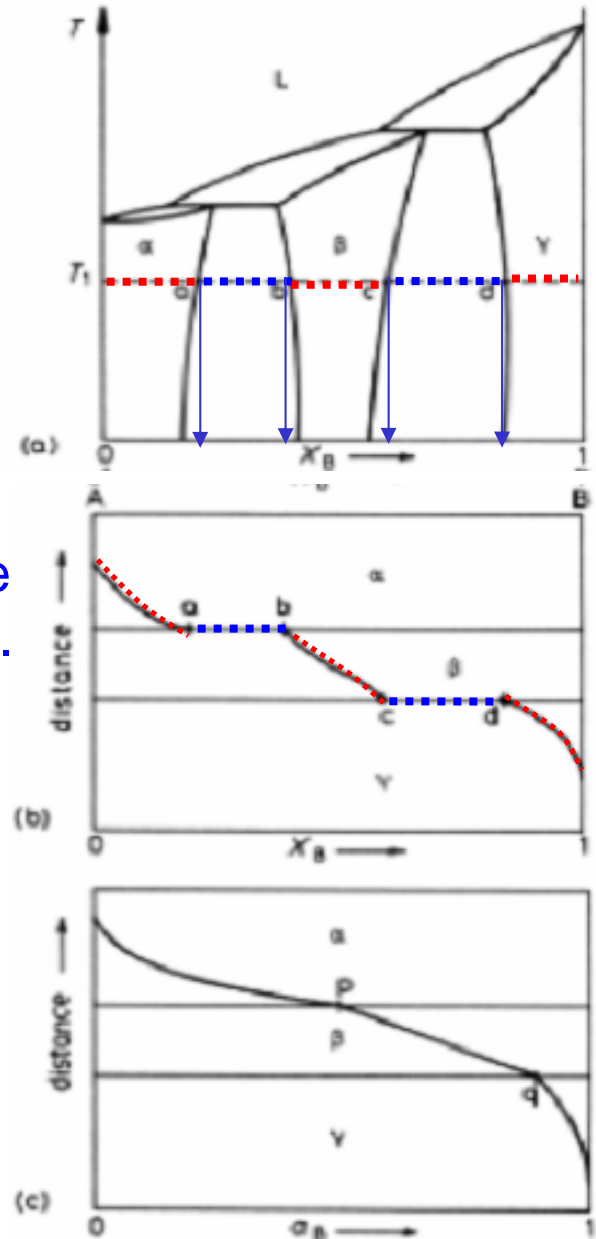
β

Draw a profile of activity of B atom, in the plot of distance vs. a_B after annealing at T_1.

A or B atom → easy to jump interface (local equil.)

$$\rightarrow \mu_A^{\alpha} = \mu_A^{\beta}, \ \mu_A^{\beta} = \mu_A^{\gamma} \text{ at interface}$$

$$(a_A^{\alpha} = a_A^{\beta}, \ a_A^{\beta} = a_A^{\gamma})$$

How can we formulate the interface (α/β, β/γ) velocity?

If unit area of the interface moves a distance dx,
a volume (dx·1) will be converted
from α containing C_B^α atoms/m³
to β containing C_B^β atoms/m³.

$$\left(C_B^\beta - C_B^\alpha\right)dx \rightarrow shaded\ area$$

$\alpha \rightarrow \beta$

$\left(C_B^\beta - C_B^\alpha\right)dx$ equal to
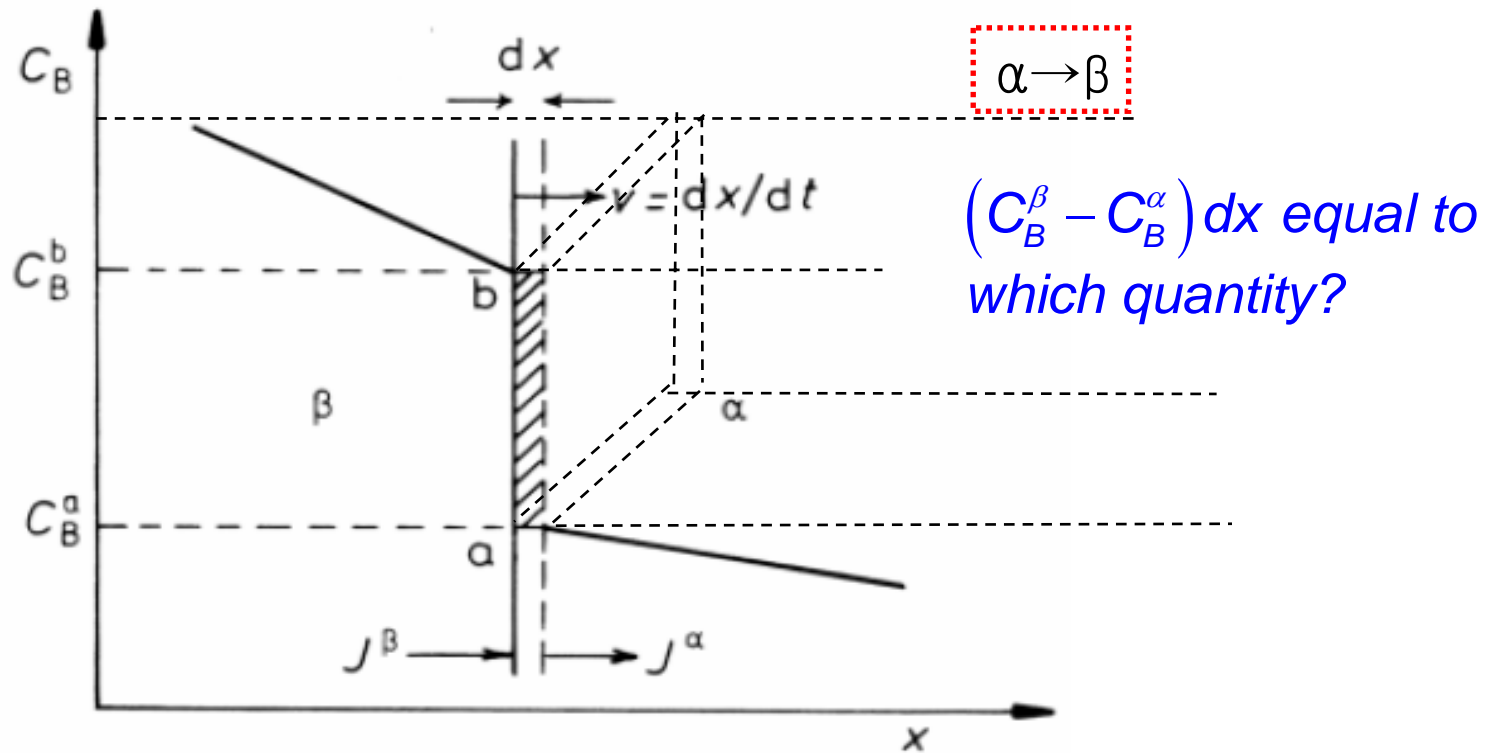which quantity?

Fig. 2.30. Concentration profile across the α/β interface and its associated movement assuming diffusion control.

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Local equilibrium is assumed.

A flux of B towards the interface from the β phase

$$J_B{}^\beta = -\tilde{D}(\beta)\frac{\partial C_B{}^b}{\partial x}$$

A flux of B away from the interface into the α phase

$$J_B{}^\alpha = -\tilde{D}(\alpha)\frac{\partial C_B{}^a}{\partial x}$$

In a time dt, there will be an accumulation of B atoms given by

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2} \implies \frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

- $[J_B\text{-}J_A]\, dt$

$dCdx$

$$\left\{-\left(\tilde{D}(\beta)\frac{\partial C_B^b}{\partial x}\right) - \left(-\tilde{D}(\alpha)\frac{\partial C_B^a}{\partial x}\right)\right\} dt = (C_B^b - C_B^a)dx$$

$$v = \frac{dx}{dt} = \frac{1}{(C_B{}^b - C_B{}^a)}\left\{\tilde{D}(\alpha)\frac{\partial C_B{}^a}{\partial x} - \tilde{D}(\beta)\frac{\partial C_B{}^b}{\partial x}\right\}$$

(velocity of the α/β interface)

Contents in Phase Transformation

상변태를
이해하는데
필요한 배경

(Ch1) 열역학과 상태도**: Thermodynamics**

(Ch2) 확 산 론**: Kinetics**

(Ch3) 결정계면과 미세조직
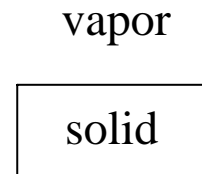
대표적인 상변태

(Ch4) 응 고**: Liquid $\rightarrow$ Solid**

(Ch5) 고체에서의 확산 변태**: Solid $\rightarrow$ Solid (Diffusional)**

(Ch6)고체에서의 무확산 변태**: Solid $\rightarrow$ Solid (Diffusionless)**

3. Crystal interfaces and microstructure

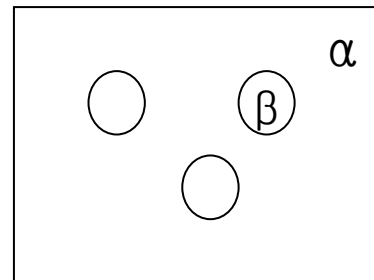• **Types of Interface**

1. Free surface (solid/vapor interface)

vapor

solid

2. Grain boundary (α/α interfaces)

> **same composition, same crystal structure**

> **different orientation**

3. inter-phase boundary (α/β interfaces)

> **different composition &**

   crystal structure

α

β

$\Rightarrow$ defect

$\Rightarrow$ energy $\uparrow$