

# Diff. In Dilute Substitutional Alloys

$$X_B \sim 0, X_A \sim 1$$

$$\tilde{D} = D_B$$

- Normally  $D_B > D_A$  in dilute sol.
- (solute atom > solvent atom in size )
- Solute – Vacancy pair

## Atomic Mobility

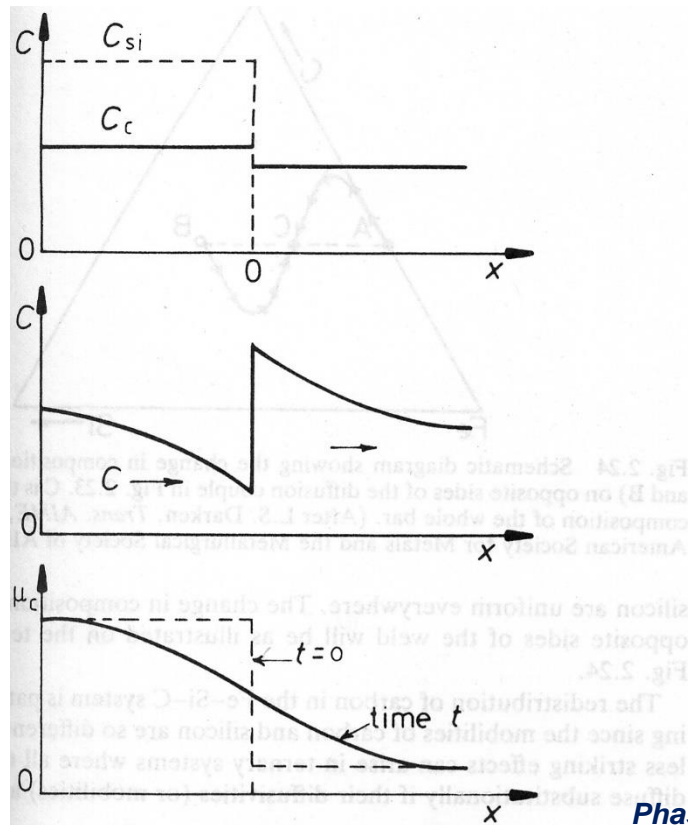
- $D_B = M_B RT$  ( for ideal dilute solution )
- Prove that  $D_B = M_B RT \left[ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right]$

# Diffusion In Ternary Alloy

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

① Si raises the  $\mu_C$  (chemical potential of carbon) in solution.

②  $M_{Si}(\text{sub.}) \ll M_C(\text{int.})$ ,  $M$  : mobility



- Interface: local equilibrium
- System: partial equilibrium

# High Diffusion path

Defect (grain boundary, dislocation, surface) : more open structure

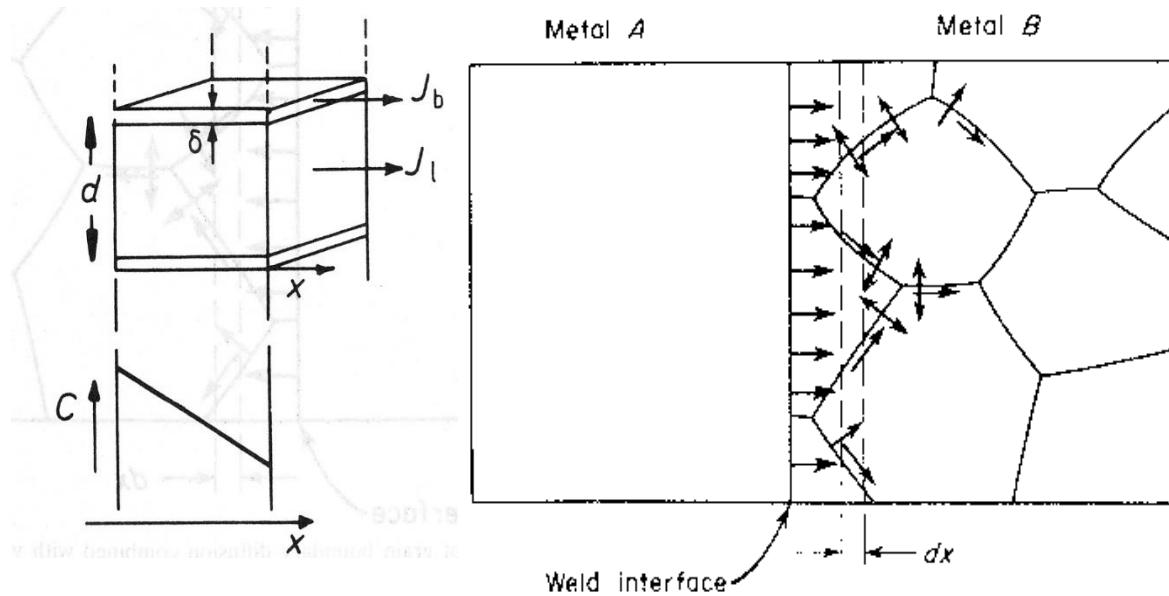
⇒ fast diffusion path

- ✓ Diff. along lattice  $D_l = D_{l_0} \exp\left(-\frac{Q_l}{RT}\right)$
- ✓ Diff. along grain boundary  $D_b = D_{b_0} \exp\left(-\frac{Q_b}{RT}\right)$
- ✓ Diff. along free surface  $D_s = D_{s_0} \exp\left(-\frac{Q_s}{RT}\right)$

❖  $D_s > D_b > D_l$

❖ But area fraction → lattice > g.b > surface

# Lattice vs. Grain Boundary Diffusion



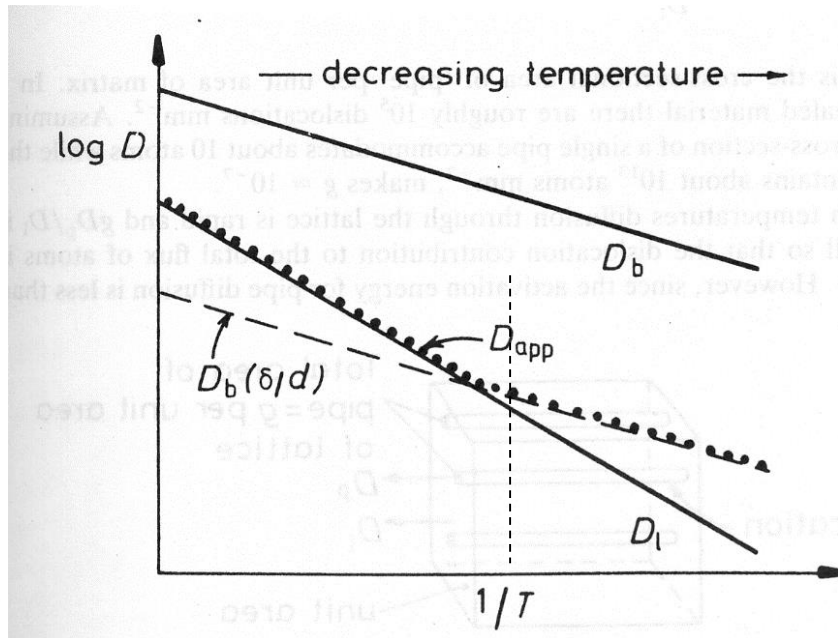
$$J_l = -D_l \frac{dC}{dx} \quad J_b = -D_b \frac{dC}{dx}$$

$$J = \frac{(J_b \cdot \delta + J_l \cdot d)}{d} = -\left(\frac{D_b \delta + D_l \delta}{d}\right) \frac{dC}{dx}$$

$$\therefore D_{\text{apparent}} = D_l + D_b \frac{\delta}{d} \quad \text{or} \quad \frac{D_{\text{app}}}{D_l} = 1 + \frac{D_b}{D_l} \frac{\delta}{d}$$

Where  $D_b \delta > D_l d$  grain boundary diffusion is important

- ❖ Width of grain boundary:  $\sim 0.5\text{nm}$ , grain size:  $1\sim 1000\ \mu\text{m}$
- ❖  $D_b > D_l$  ( always ), Also  $Q_b \sim 0.5Q_l$  in FCC materials  
→ Contribution depends on temperature



$D_{g.b}$  is important  
below  $0.75 \sim 0.8T_m$

High T – lattice diff. Low T – g.b diff.

# Diffusion along Pipe

$g$ : Cross-sectional area of pipe per unit area of matrix ( $\delta$ /dimension)

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

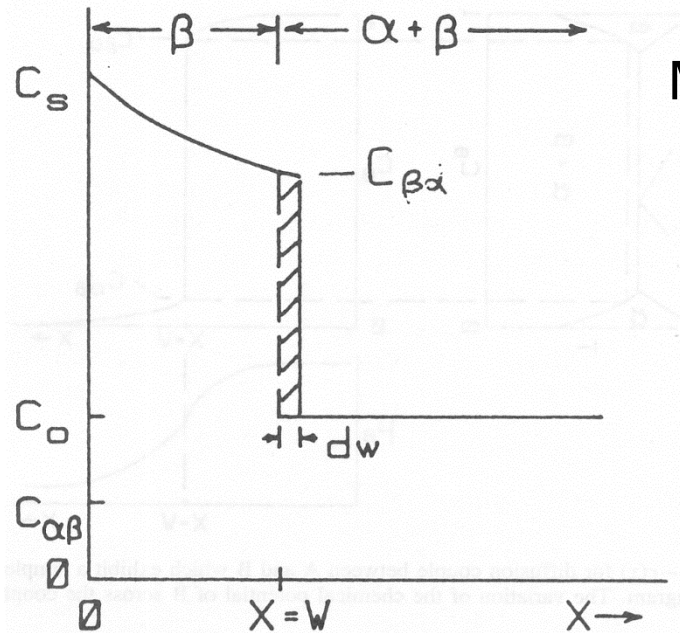
ex) annealed metal  $\sim 10^5$  disl/mm<sup>2</sup>

Pipe accommodates 10 atoms in the cross-section, matrix contains  $10^{13}$  atoms mm<sup>-2</sup>

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

# Moving Boundary Problem

## ❖ Diffusion in Multiple Binary System



Mass balance

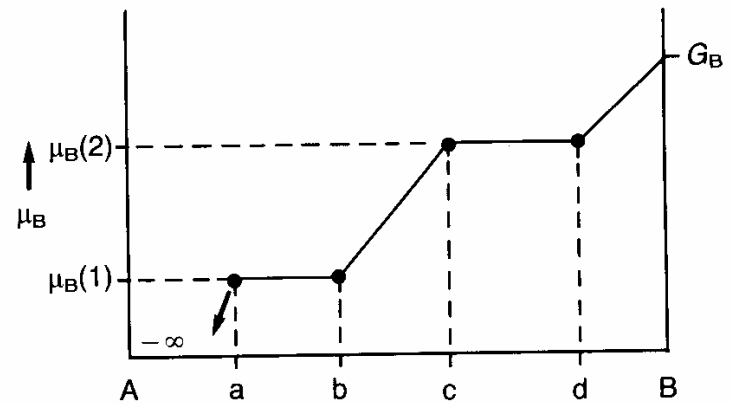
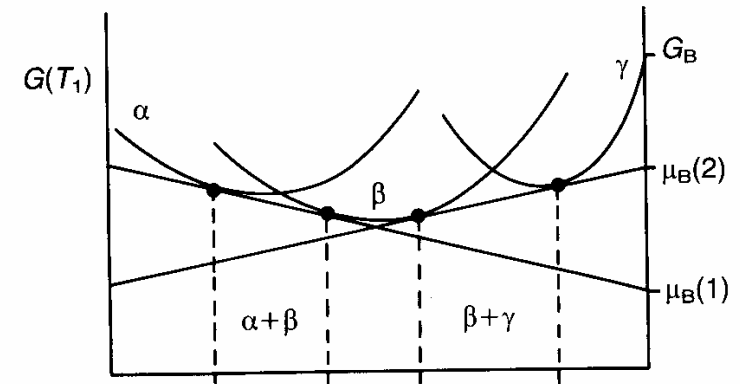
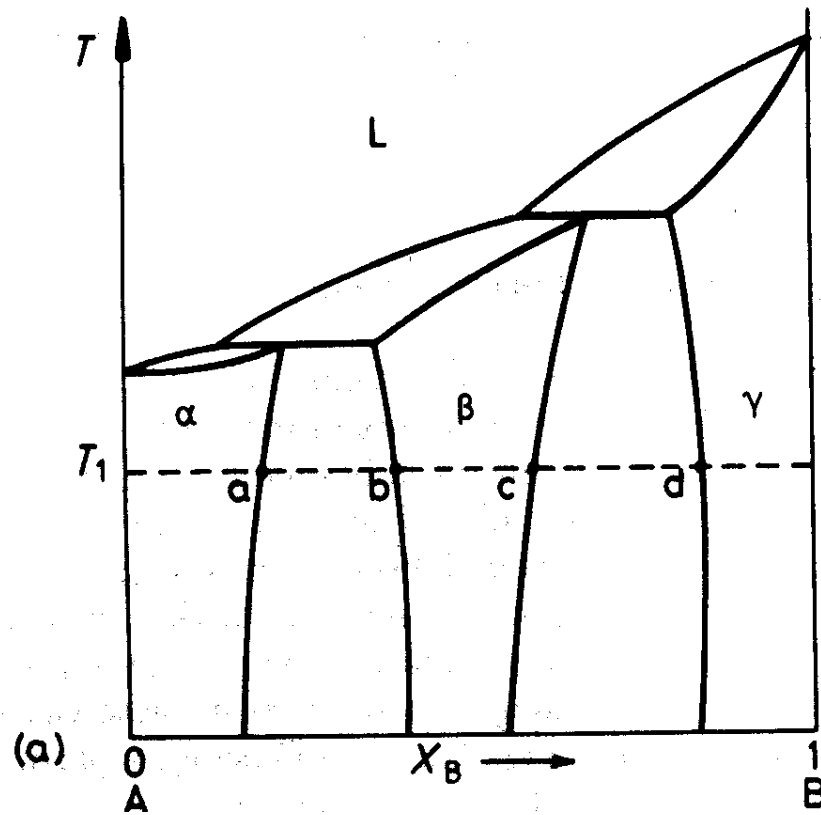
$$(J_B^\beta - J_B^\alpha) dt = (C_B^b - C_B^a)(dx \cdot 1)$$

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

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

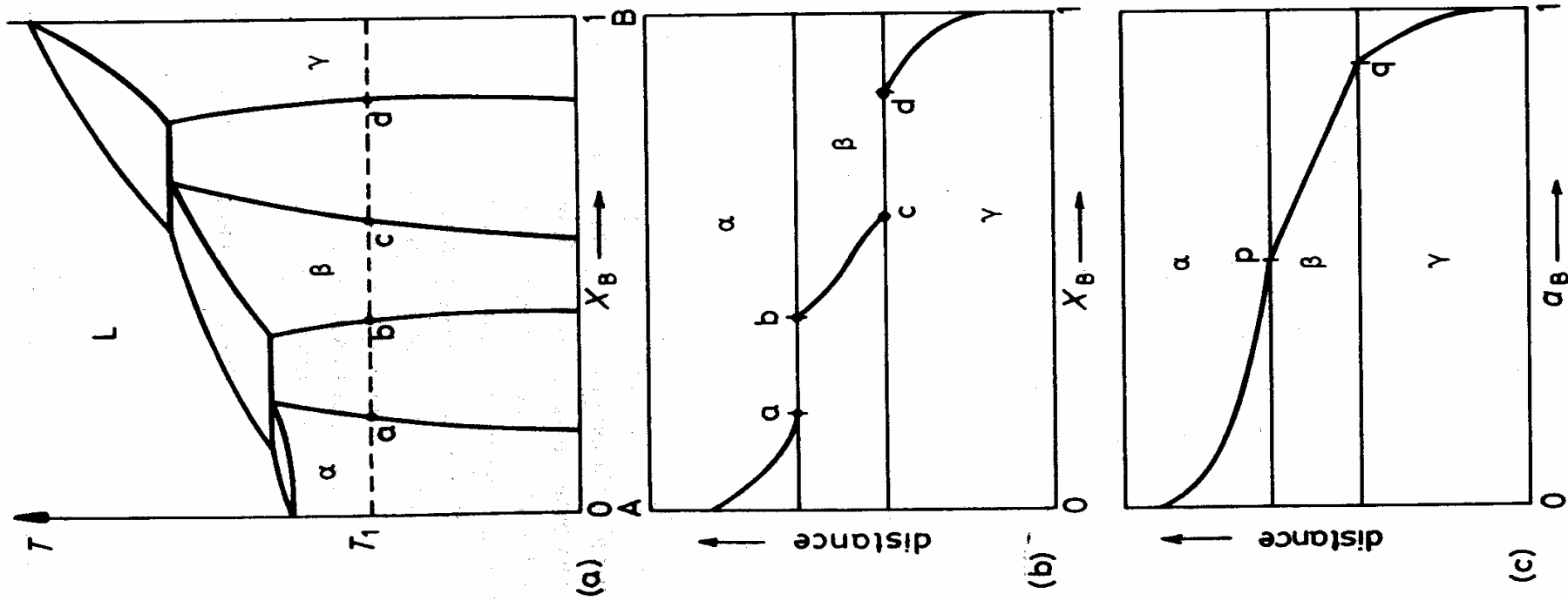
- ❖ Diffusion flux determines velocity (in local equilibrium)
- ❖ Reaction that passes Interface is important  
→ interface (reaction) controlled

# Multiphase Binary System (Phase Diagram and Chemical Potential)

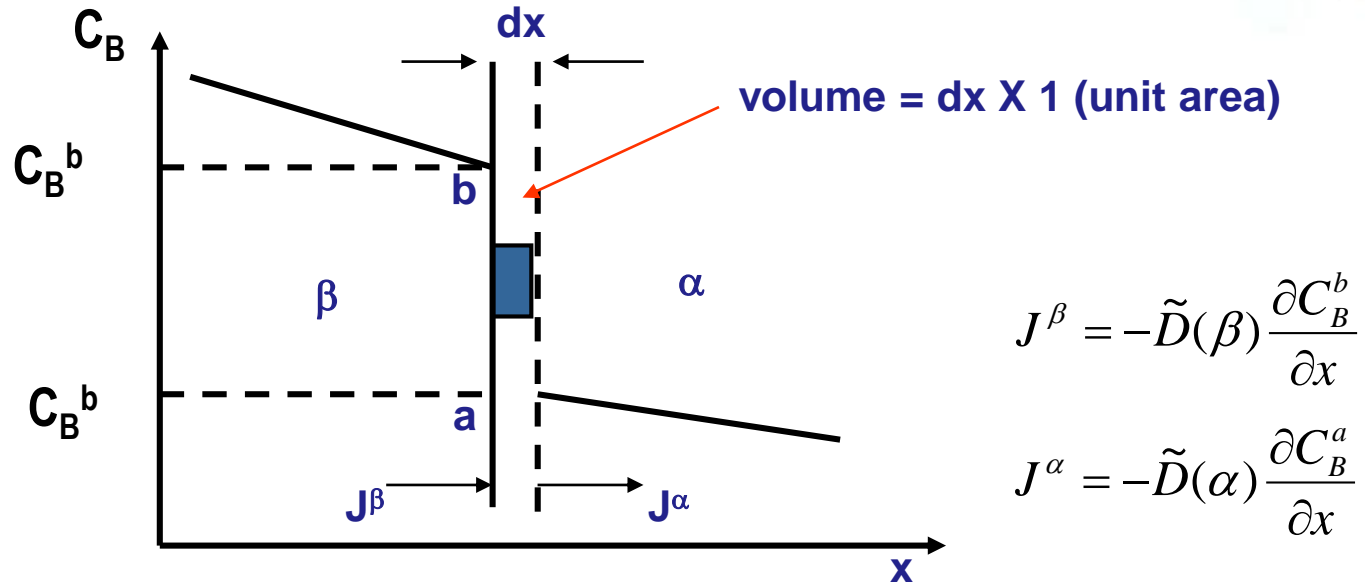




# Diffusion in Multiphase System



# Moving boundary problem



Amount of accumulated B atoms

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

Velocity of  $\alpha$ - $\beta$  interface

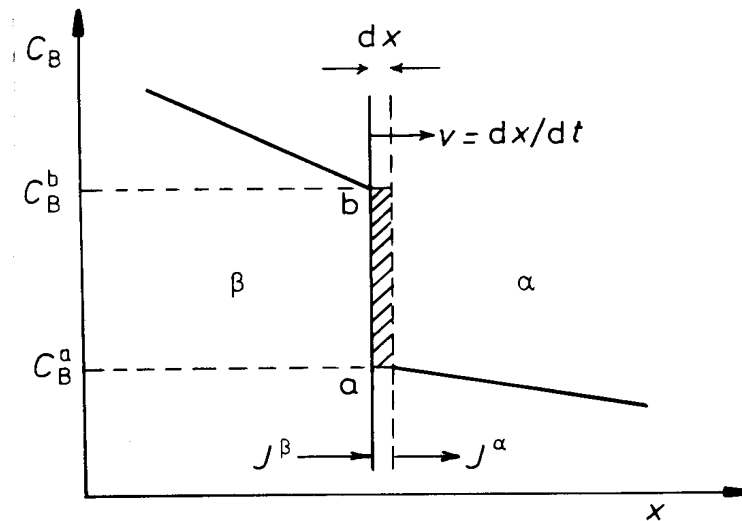
$$v = \frac{dx}{dt} = \frac{1}{(C_B^b - C_B^a)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^a}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^b}{\partial x} \right\}$$

## ❖ Diffusion Controlled :

Diffusion flux 가 velocity를 결정. (local equilibrium에 있을 경우)

## ❖ Interface (reaction) Controlled:

Interface를 뛰어넘는 계면 반응이 중요한 경우



▲ Concentration profile across the  $\alpha/\beta$  interface and its associated mo

# Kinetic parameters and measurements

- ❖ Thermodynamic variables : p, V, T, S, and m
- ❖ Kinetic parameters : atomic diffusivities, surface and interface energies, interfacial reaction constants, and enthalpy (heat) of formation
- ❖ When the dependence of the layer thickness (x) on time (t) measured, we can plot x versus t and x versus  $t^{1/2}$

$$x = Kt \qquad x^2 = 4\tilde{D}t$$
$$K = K_0 \exp\left(\frac{-E_a}{kT}\right) \qquad \tilde{D} = \tilde{D}_0 \exp\left(\frac{-E_a}{kT}\right)$$

We can get reaction constant (K), atomic diffusivity (D), activation energy