Phase Transformation of Materials

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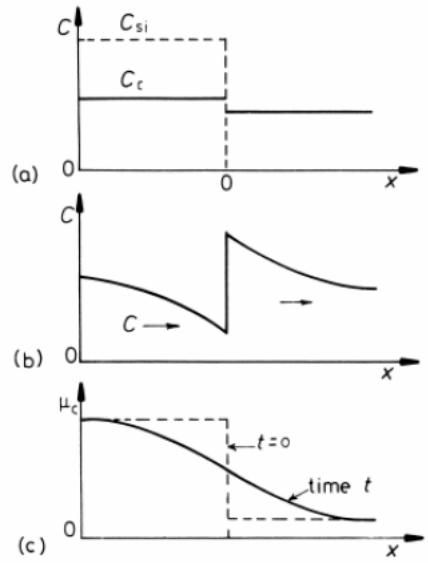
Diffusion in ternary alloys



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 (chemical potential of carbon) in solution.

② M_{Si} (sub.) ≪ M_C (int.), M : mobility

Fig. 2.23. (a) Carbon and silicon distribution in iron at t = 0. (b) Carbon distribution after high-temperature anneal. (c) Chemical potential of carbon v. distance.

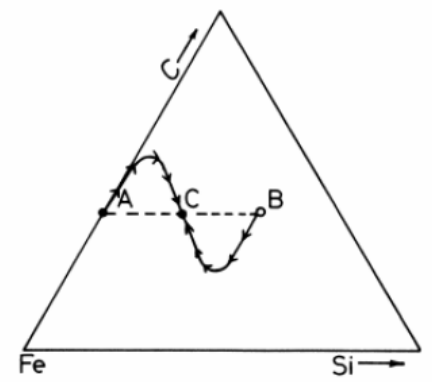


Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B) on opposite sides of the diffusion couple in Fig. 2.23. C is the final equilibrium composition of the whole bar. (After L.S. Darken, *Trans. AIME*, 180 (1949) 430, © American Society for Metals and the Metallurgical Society of AIME, 1949.)

High-diffusivity paths

Defect (grain boundary, dislocation, surface) :

more open structure

⇒ fast diffusion path

Diff. along lattice	$D_l = D_{lo} \exp(-\frac{Q_l}{RT})$
Diff. along grain boundary	$D_b = D_{bo} \exp(-\frac{Q_b}{RT})$
Diff. along free surface	$D_s = D_{so} \exp(-\frac{Q_s}{RT})$

$$D_s > D_b > D_l$$

But area fraction → lattice > g.b > surface

A atoms diffusing along the boundary will be able to penetrate much deeper than atoms which only diffuse through the lattice. (Fig 2.25) In addition, as the concentration of solute builds up in the boundaries atoms will also diffuse from the boundary into the lattice.

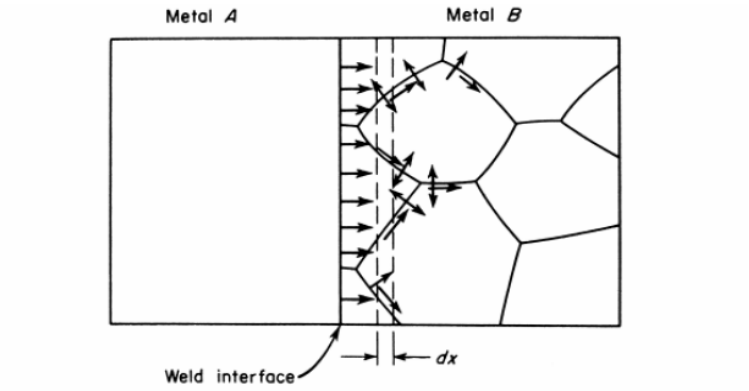


Fig. 2.25. The effect of grain boundary diffusion combined with volume diffusion. (After R.E. Reed-Hill, *Physical Metallurgy Principles, 2nd edn.*, Van Nostrand, New York, 1973.)

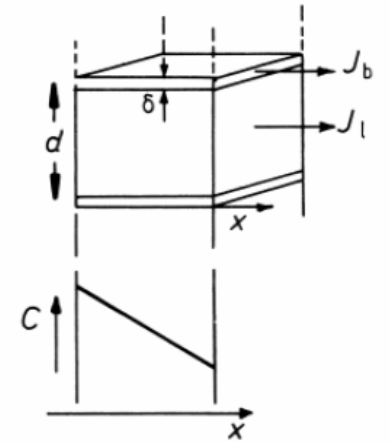


Fig. 2.26 Combined lattice and boundary fluxes during steady-state diffusion through a thin slab of material.

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

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

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

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 $D_b\delta > D_l d$. Due to the low activation energy for diffusion along grain boundaries, 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.

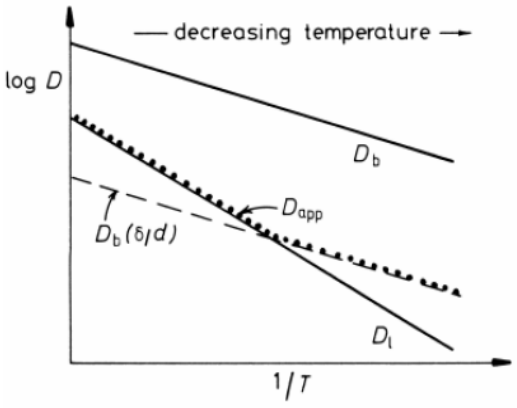


Fig. 2.27 Diffusion in a polycrystalline metal.

Diffusion along dislocations

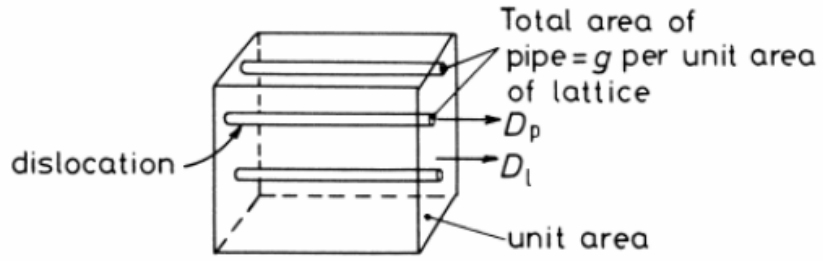


Fig. 2.28. Dislocations act as a high conductivity path through the lattice.

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

ex) annealed metal ~ 10^5disl/mm^2 $\perp$ accommodates 10 atoms in the cross-section, matrix contains 10^{13} atoms mm^{-2}

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

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

Diffusion in multiple binary system

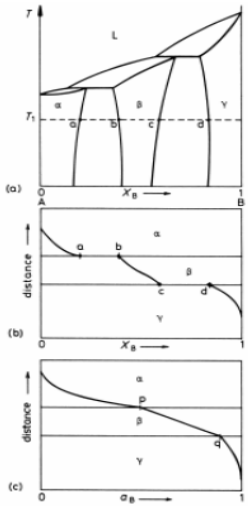


Fig. 2. 29 (a) A hypothetical phase diagram. (b) A possible diffusion layer structure for pure A and B welded together and annealed at T_1. (c) A possible variation of the activity of B (a_B) across the diffusion couple.

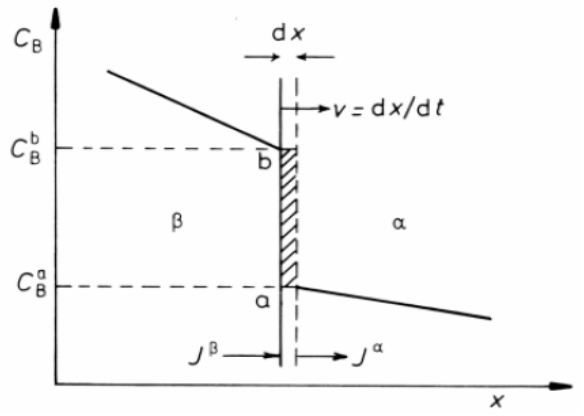


Fig. 2.30. Concentration profile across the α/β interface and its associated movement assuming diffusion control.

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

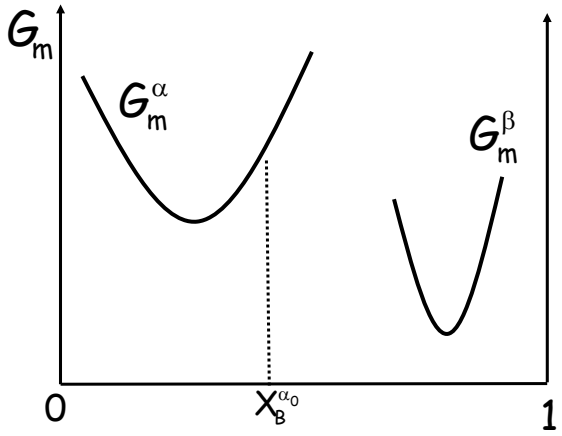
In a time dt, there will be an accumulation of B atoms given by

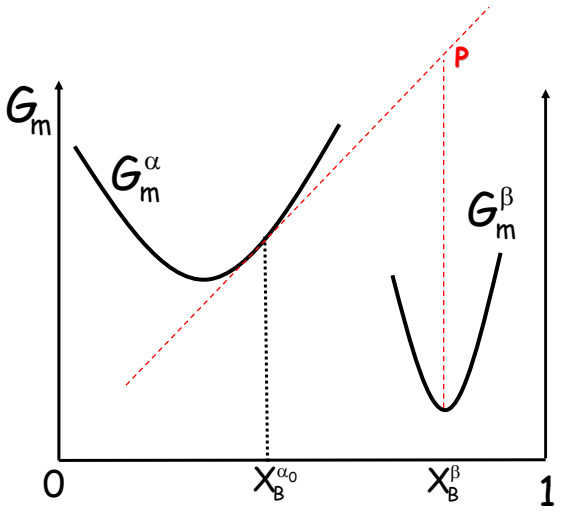
$$\left\{-\left(\tilde{D}(\beta)\frac{\partial C_B^b}{\partial x}\right)-\left(-\tilde{D}(\alpha)\frac{\partial C_B^a}{\partial x}\right)\right\}dt = (C_B^b - C_B^a)dx$$

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

(velocity of the α/β interface)

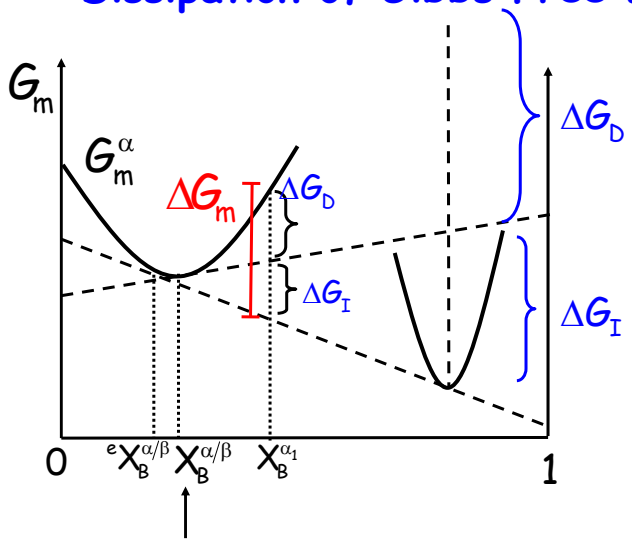
What is the driving force for precipitation of β from α?



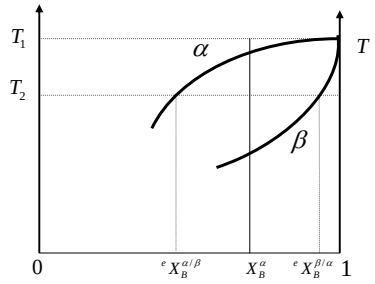


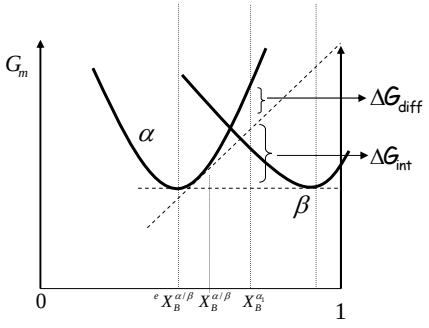
$$\Delta G = \bar{G}_A X_A^{\beta} + \bar{G}_B X_B^{\beta} - G_m^{\beta}(X_B^{\beta})$$

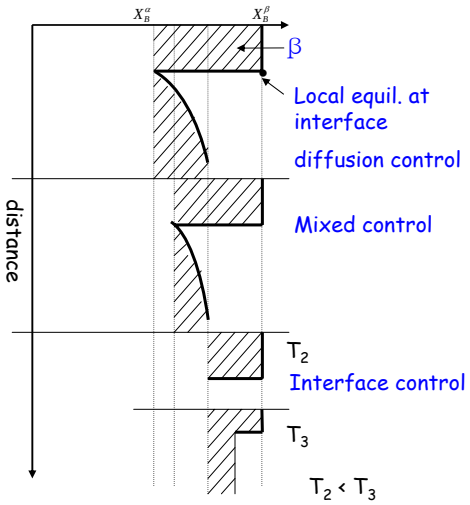
Dissipation of Gibbs Free Energy

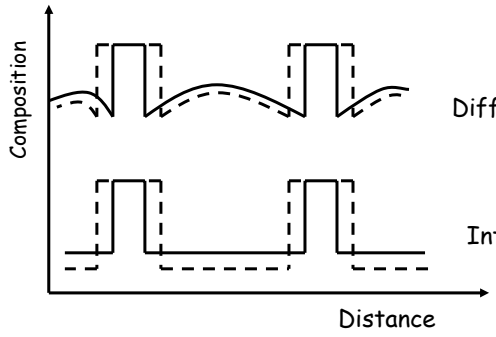


Composition of α at the β interface









$J_D = J_I$ → mass conservation in serial kinetic path

$J_D \approx M_D \cdot \Delta G_D$

$J_I \approx M_I \cdot \Delta G_I$

$\Delta G_{total} = \Delta G_D + \Delta G_I$

$M_I >> M_D \rightarrow \Delta G_D >> \Delta G_I$

$\rightarrow \Delta G_I \approx 0$ Local equilibrium