2023 Fall

"Phase Transformation in Materials"

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Contents in Phase Transformation

Background to understand phase transformation

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(Ch1) Thermodynamics and Phase Diagrams
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(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative Phase transformation

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(Ch4) Solidification: Liquid \rightarrow Solid
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(Ch5) Diffusional Transformations in Solid: Solid → Solid

(Ch6) Diffusionless Transformations: Solid → Solid

Contents for previous class

Interstitial Diffusion / Substitutional Diffusion

- Steady-state diffusion— Fick's First Law
- **→** Concentration varies with position.
- Non-steady-state diffusion: Fick's Second Law
- **→** Concentration varies with time and position.
- 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

Contents for previous class

• Diffusion : Movement of atoms to reduce its chemical potential μ.

driving force: Reduction of G

Down-hill diffusion movement of atoms from a high C_B region to low C_B region. **Up-hill diffusion** movement of atoms from a low C_B region to high C_B region.

- Interstitial Diffusion / Substitution Diffusion
 - Steady-state diffusion Fick's First Law_____

$$J_{B} = \frac{1}{6} \Gamma_{B} (n_{1} - n_{2}) = -\left(\frac{1}{6} \Gamma_{B} \alpha^{2}\right) \frac{\partial C_{B}}{\partial x} = -D_{B} \frac{\partial C_{B}}{\partial x}$$

→ Concentration varies with position. (atoms m⁻² s⁻¹)

- Nonsteady-state diffusion - Fick's Second Law

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$
 Concentration varies with time and position.

- For random walk in 3 dimensions, after n steps of length α
- Effect of Temperature on Diffusivity

$$r = \alpha \sqrt{(\Gamma t)} = f(D) = 2.4 \sqrt{Dt}$$

$$\log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T}\right)$$
4

The section is completed with 4 example solutions to Fick's 2nd law: carburisation, decarburisation, diffusion across a couple and homogenisation.

The solutions given are as follows:

Process	Solution			
Homogenization	$C = C_{\text{mean}} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \exp\left(-\frac{t}{\tau}\right)$			
	C_{mean} = Mean concentration b_0 = Initial concentration amplitude l = half-wavelength of cells t = relaxation time			
Carburization	$C = C_{\rm S} - (C_{\rm S} - C_0) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$			
	$C_S = Surface concentration$ $C_0 = Initial bulk concentration$			
Decarburization	$C = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ $C_0 = \text{Initial bulk concentration}$			
Diffusion Couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$			
	C_1 = Concentration of steel 1 C_2 = Concentration of steel 2			

Contents for today's class

Q. Interstitial diffusion vs Substitutional diffusion

- 1. Self diffusion in pure material
- 2. Vacancy diffusion
- 3. Diffusion in substitutional alloys

Interstitial Diffusion / Substitutional Diffusion

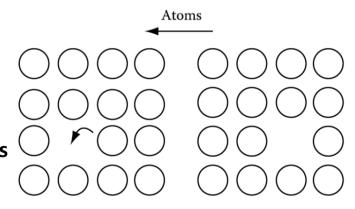
- Diffusion in dilute interstitial alloys ~ relatively simple because the diffusing atoms are <u>always surrounded by vacant sites</u> to which they can jump whenever they have enough to overcome the energy barrier for migration.
- In substitutional diffusion,

An atom can only jump if there happens to be vacant site at one of the adjacent lattice positions

Probability of vacancy x probability of jump

- → amenable to a simple atomic model: self-diffusion (순금속의 자기확산)
- 1. Self diffusion in pure material

The rate of self-diffusion can be measured experimentally by introducing a few radioactive A atoms (A*) into pure A and measuring the rate at which penetration occurs at various temperatures. Since A* and A atoms are chemically identical their jump frequencies are almost identical.



Diffusion coefficient
$$D_{A}^{*} = D_{A} = \frac{1}{6} \Gamma_{A} \alpha^{2}$$

most likely to occur back into the same vacancy

$$D_{\mathsf{A}}^* = f D_{\mathsf{A}}$$

 $D_{\Delta}^* = f D_{\Delta}$ (f: correlation factor) close to unity

Assumption

: unrelated to the previous jump

The next jump is not equally probable in all directions.

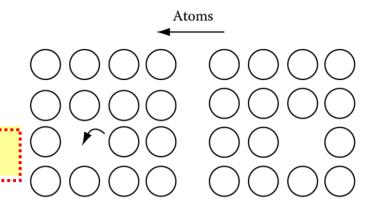
Q. Interstitial diffusion vs Substitutional diffusion

- 1. Self diffusion in pure material
- 2. Vacancy diffusion
- 3. Diffusion in substitutional alloys

2.3 Substitutional diffusion

2.3.1. Self diffusion in pure material

Probability of vacancy x probability of jump



What would be the jump frequency in substitutional diffusion?

An atom next to a vacancy can make a jump provided

it has enough thermal energy to overcome ΔG_m . $\rightarrow \exp(-\Delta G_m/kT)$

Jump frequency

$$\rightarrow$$
 exp(- Δ G_m/kT)

The probability that an adjacent site is vacant

$$\rightarrow zX_v$$

cf)
$$\Gamma = vz \exp \frac{-\Delta G_m}{RT}$$

for interstitials

Z= # of nearest neighbours

$$X_{V} = X_{V}^{e} = \exp \frac{-\Delta G_{V}}{RT}$$

$$D_A = \frac{1}{6} \Gamma_A \alpha^2$$

$$D_{A} = \frac{1}{6}\Gamma_{A}\alpha^{2}$$

$$D_{A} = \frac{1}{6}\alpha^{2} zv exp \frac{-(\Delta G_{m} + \Delta G_{v})}{RT}$$

For most metals: $v \sim 10^{13}$, fcc metals: z = 12, $\alpha = a/\sqrt{2}$

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$$D_{A} = \frac{1}{6}\alpha^{2} zv \exp \frac{-(\Delta G_{m} + \Delta G_{V})}{RT}$$

$$\Delta G = \Delta H - T\Delta S$$

$$D_{A} = \frac{1}{6}\alpha^{2} zv \exp \frac{\Delta S_{m} + \Delta S_{V}}{R} \exp(-\frac{\Delta H_{m} + \Delta H_{V}}{RT})$$

Z=number of nearest neighbors/ v= temperature independent frequency

For most metals: $v \sim 10^{13}$, fcc metals: z = 12, $\alpha = a/\sqrt{2}$

$$D_{A} = D_{0} \exp(-\frac{Q_{SD}}{RT})$$

$$D_{0} = \frac{1}{6}\alpha^{2}zv \exp\frac{\Delta S_{m} + \Delta S_{V}}{R}$$

$$Q_{SD} = \Delta H_{m} + \Delta H_{V}$$

$$\therefore \text{ self-diffusion requires the presence of vacancies}$$

~Same with interstitial diffusion except that the activation energy for self-diffusion has an extra term

* interstitial diffusion

Thermally activated process jump frequency

$$\Gamma_B = Z \nu \exp(-\Delta G_m / RT)$$
 Z: nearest neighbor sites

v: vibration frequency

 ΔG_m : activation energy for moving

$$\left\{ \Delta G_m = \Delta H_m - T \Delta S_m, D_B = \frac{1}{6} \Gamma_B \alpha^2 \right\}$$

$$D_B = \left[\frac{1}{6}\alpha^2 Z \nu \exp(\Delta S_m / R)\right] \exp(-\Delta H_m / RT)$$

$$\Delta H_m \equiv Q_{ID}$$

$$D_{B} = D_{B0} \exp \frac{-Q_{ID}}{RT_{\kappa}}$$
 (Arrhenius-type equation)

Temperature Dependence of Diffusion

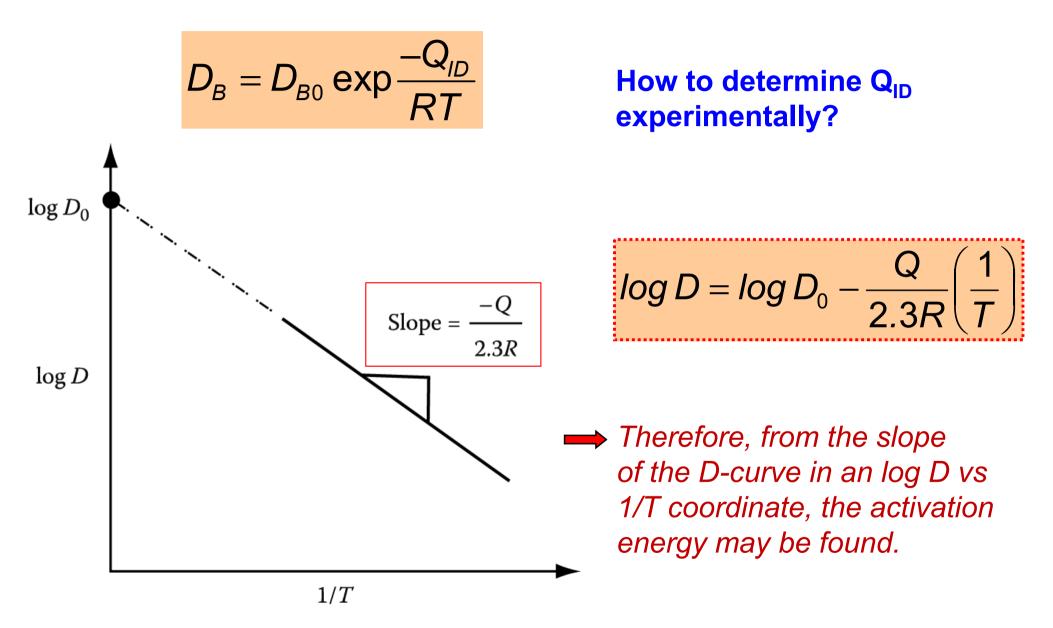


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

Experimental Determination of D

 Deposit a known quantity (M) of a radioactive isotope A*

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$
 (2.18)

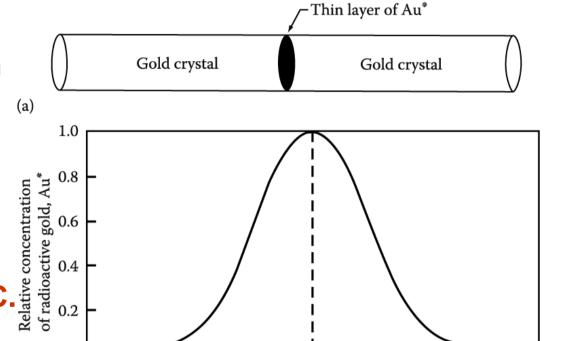
1) Solution for the infinite boundary condition

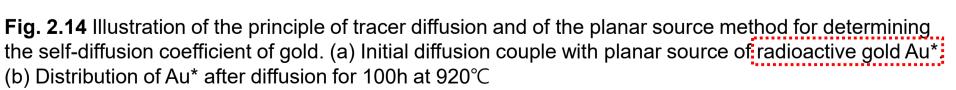
$$C = \frac{M}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt})$$

M: quantity·m⁻²/ C: quantity·m⁻³

2) Solution for the semi-infinite B.C.

$$C = \frac{M}{\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt})$$





(b)

-1.2

-0.9

-0.6

-0.3

0

Distance, x, mm

0.3

0.6

0.9

1.5

Table 2.2 Experimental Data for Substitutional Self-Diffusion in Pure Metals at Atmospheric Pressure

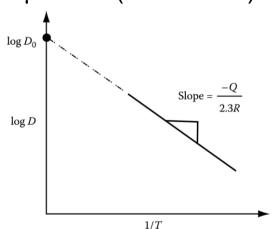
Class	Metal	T _m (K)	$D_0 \ ({ m mm}^2\ { m s}^{-1})$	Q (kJ mol^{-1})	$\frac{Q}{RT_{m}}$	$Q(T_{ m m}) \ (\mu m m^2 \ s^{-1})$
bcc (rare earths)	ε-Pu	914	0.3	65.7	8.7	53
	δ-Ce	1071	1.2	90.0	10.1	49
	γ-La	1193	1.3	102.6	10.4	42
	γ-Yb	1796	1.2	121.0	8.1	3600
bcc (alkali metals)	Rb	312	23	39.4	15.2	5.8
	K	337	31	40.8	14.6	15
	Na	371	24.2	43.8	14.2	16
4	Li	454	23	55.3	14.7	9.9
bcc (transition metals)	β-Τ1	577	40	94.6	19.7	0.11
	Eu	1095	100	143.5	15.8	14
	Er	1795	451	302.4	20.3	0.71
	α-Fe ^a	1811	200	239.7	15.9	26
	δ-Feª	1811	190	238.5	15.8	26
	β -Ti	1933	109	251.2	15.6	18
	$\beta - Z\rho$	2125	134	273.5	15.5	25
	Cr	2130	20	308.6	17.4	0.54
	V	2163	28.8	309.2	17.2	0.97
	Nb	2741	1240	439.6	19.3	5.2
	Mo	2890	180	460.6	19.2	0.84
	Ta	3269	124	413.3	15.2	31
hcp ^a	W	3683	4280	641.0	20.9	3.4
	Cd	594	∥c5	76.2	15.4	0.99
			⊥c 10	79.9	16.2	0.94
	Zn	692	∥ c 13	91.6	15.9	1.6
			⊥c 18	96.2	16.7	0.98
	Mg	922	c 100	134.7	17.6	2.3
,			⊥c 150	136.0	17.8	2.9
fcc	Pb	601	137	109.1	21.8	0.045
	Al	933	170	142.0	18.3	1.9
	Ag	1234	40	184.6	18.0	0.61
	Au	1336	10.7	176.9	15.9	1.3
	Cu	1356	31	200.3	17.8	0.59
	Ni	1726	190	279.7	19.5	0.65

For a given structure and bond type, Q/R T_m is roughly constant;

 \implies Q is roughly proportional to $T_{\rm m}$.

Within each class, $D(T_m)$ and D_0 are approximately constants.

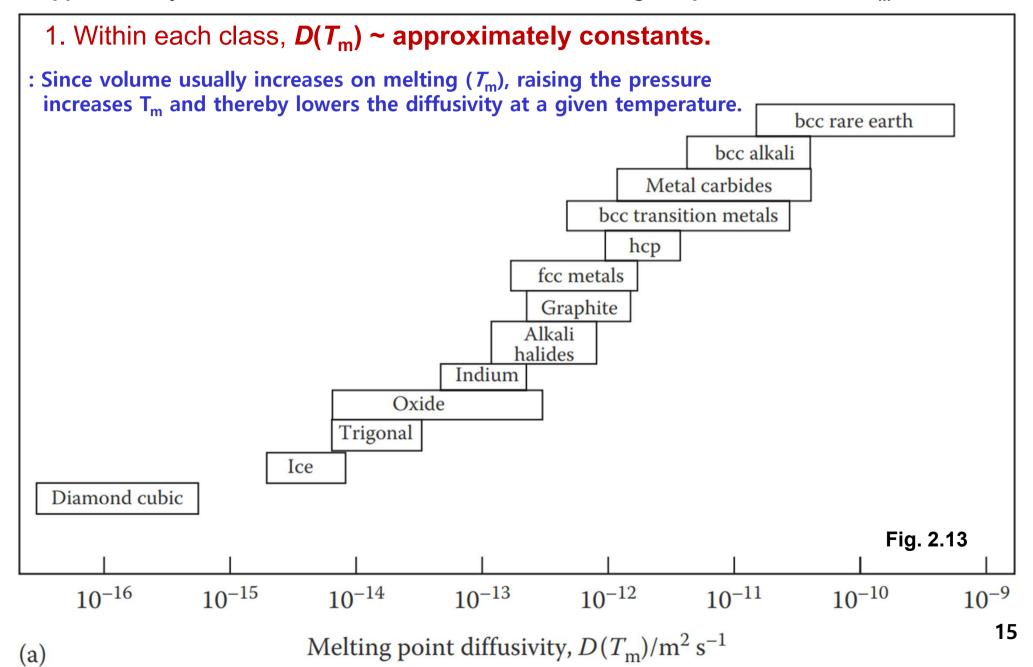
Most close-packed metals ex) for fcc and hcp, Q/RT_m ~ 18 and $D(T_m) \sim 1 \ \mu m^2 s^{-1} \ (10^{-12} \ m^2 s^{-1})$



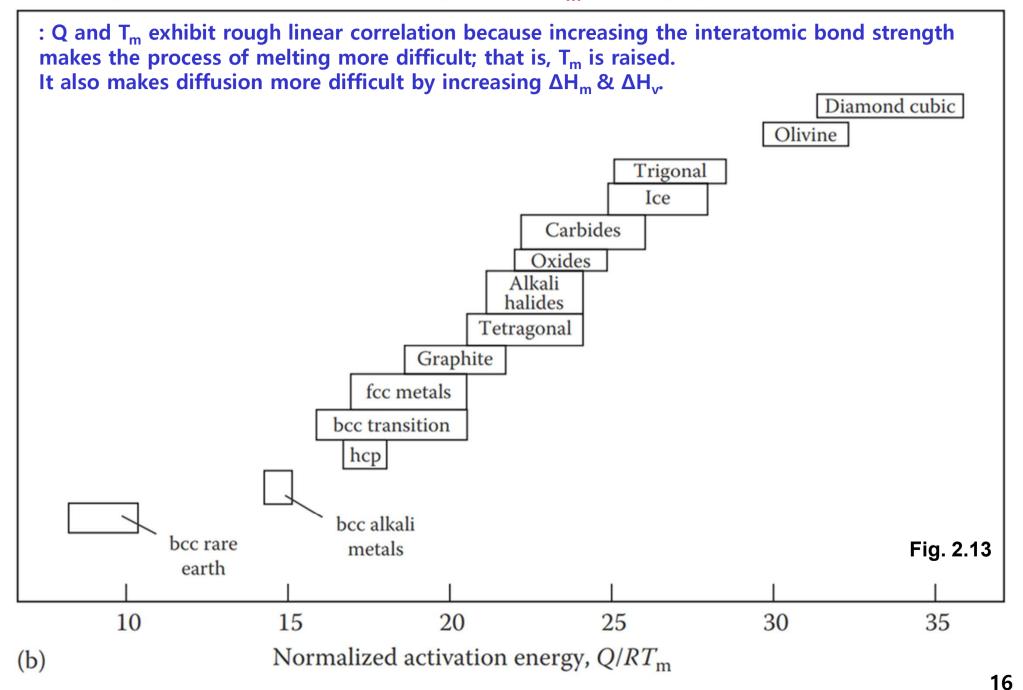
For a given structure and bond type, $D(T/T_m) \sim constant$

T/T_m: homologous temperature

- * Melting point diffusivities for various classes of materials:
- : The diffusion coefficients of all materials with a given crystal structure and bond type will be approximately the same at the same fraction of their melting temperature, i.e. $D(T/T_m) = const.$



For a given structure and bond type, Q/RT_m is roughly constant;



Consider the effect of temperature on self-diffusion in Cu:

ex) At 800°C,
$$D_{cu}$$
= 5 × 10⁻⁹ mm²s⁻¹, α = 0.25 nm Γ_{Cu} :?

$$D_B = \frac{1}{6} \Gamma_B \alpha^2$$

$$\Gamma_{Cu} = 5 \times 10^5 \, jumps \, s^{-1}$$

After an hour, diffusion distance (x)?

How do we determine D_{Cu} at low temperature such as 20°C?

Hint) From the data in Table 2.2, how do we estimate D_{Cu} at 20°C?

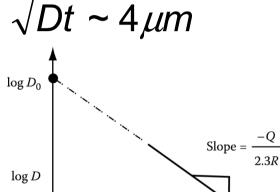


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

1/T

$$\Gamma_{Cu} \sim 10^{-20} jumps \ s^{-1}$$

→ Each atom would make one jump every 10¹² years!

Q. Interstitial diffusion vs Substitutional diffusion

- 1. Self diffusion in pure material
- 2. Vacancy diffusion
- 3. Diffusion in substitutional alloys

2.3.2. Vacancy diffusion

All the surrounding atoms are possible jump sites of a vacancy, which is analogous to interstitial diffusion.

$$D_{v} = \frac{1}{6}\alpha^{2}\Gamma_{v}$$

$$= \frac{1}{6}\alpha^{2}zv \exp(\Delta S_{m}/R) \exp(-\Delta H_{m}/RT)$$

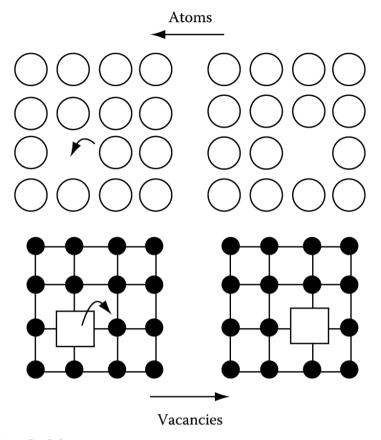


Fig. 2.16 The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.

Comparing D_v with the self-diffusion coefficient of A, D_A,

$$D_{v} = D_{A} / X_{v}^{e}$$

This shows in fact that the diffusivity of vacancy ($D_{\underline{v}}$) is many orders of magnitude greater than the diffusivity of substitutional atoms ($D_{\underline{A}}$).

Q: Diffusion in substitutional alloys?

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

$$J_{A}' = J_{A} + J_{A}^{v} = -\widetilde{D}\frac{\partial C_{A}}{\partial x} = \widetilde{D}\frac{\partial C_{B}}{\partial x}$$

$$J_{B}' = J_{B} + J_{B}^{v} = -\widetilde{D}\frac{\partial C_{B}}{\partial x} = \widetilde{D}\frac{\partial C_{A}}{\partial x}$$

$$\frac{\partial C_{A}}{\partial t} = \frac{\partial}{\partial x}\left(\widetilde{D}\frac{\partial C_{A}}{\partial x}\right)$$

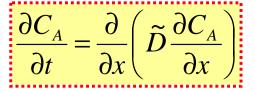
$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right)$$

Fick's 1st law for substitutional alloy Fick's 2nd law for substitutional alloy

침입형 확산에서 Fick의 법칙 고정된 격자면의 이동 고려

2.3.3. Diffusion in substitutional alloys

: A원자/B원자의 상호확산을 통한 격자면의 이동 고려



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

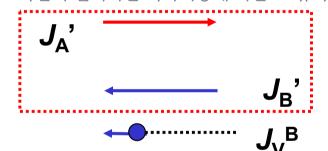
$$J_A' = J_A + J_v^A = J_A + vC_A = -\widetilde{D}\frac{\partial C_A}{\partial x}$$



고정된 격자 내에서 확산에 의한 유속



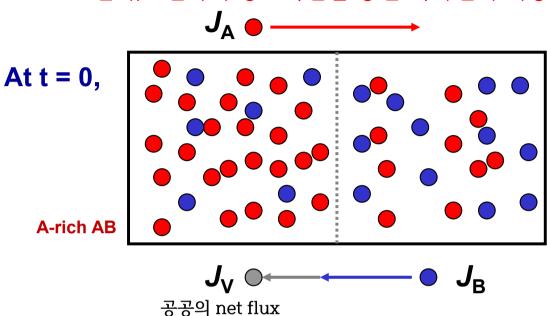
B-rich AB 확산이 일어나는 격자이동에 의한 A 유속

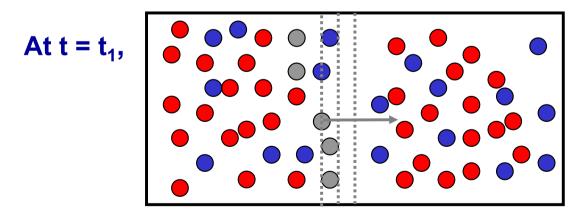


확산이 일어나는 격자이동에 의한 B 유속

고정된 격자 내에서 확산에 의한 유속

$$J'_{B} = J_{B} + J_{v}^{B} = J_{B} + vC_{B} = -\tilde{D}\frac{\partial C_{B}}{\partial x}$$
$$\therefore J'_{B} = -J'_{A}$$

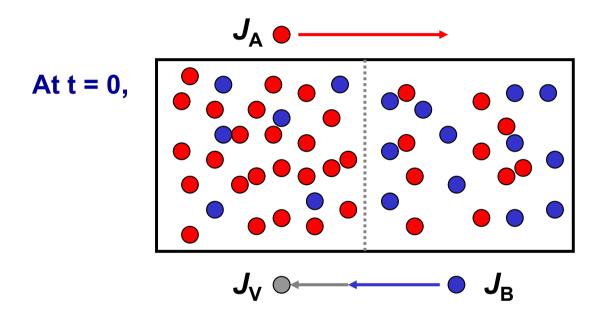


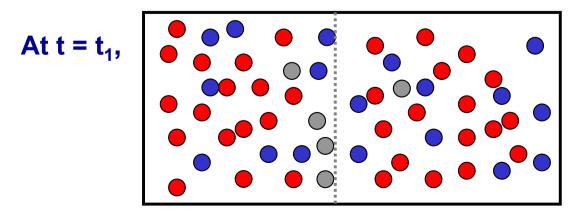


A원자와 B원자가 서로 다른 속도로 도약 → 농도 구배에 의한 속도 + 격자면 이동에 의한 속도

2.3.3. Diffusion in substitutional alloys

- * During self-diffusion, all atoms are chemically identical. : probability of finding a vacancy and jumping into the vacancy ~ equal
- * In binary substitutional alloys, each atomic species must be given its own intrinsic diffusion coefficient D_A or D_B .



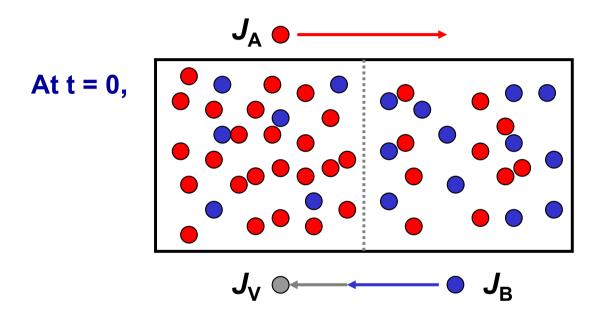


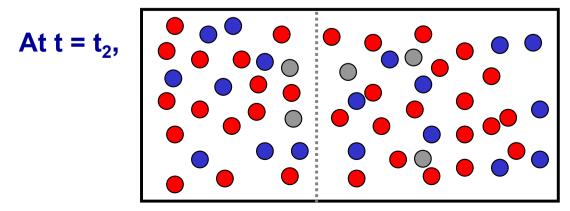
Kirkendall effect

Creation/destruction of vacancies is accomplished by *dislocation climb*.

2.3.3. Diffusion in substitutional alloys

- * During self-diffusion, all atoms are chemically identical. : probability of finding a vacancy and jumping into the vacancy ~ equal
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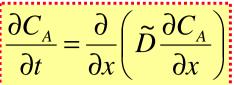


Kirkendall effect

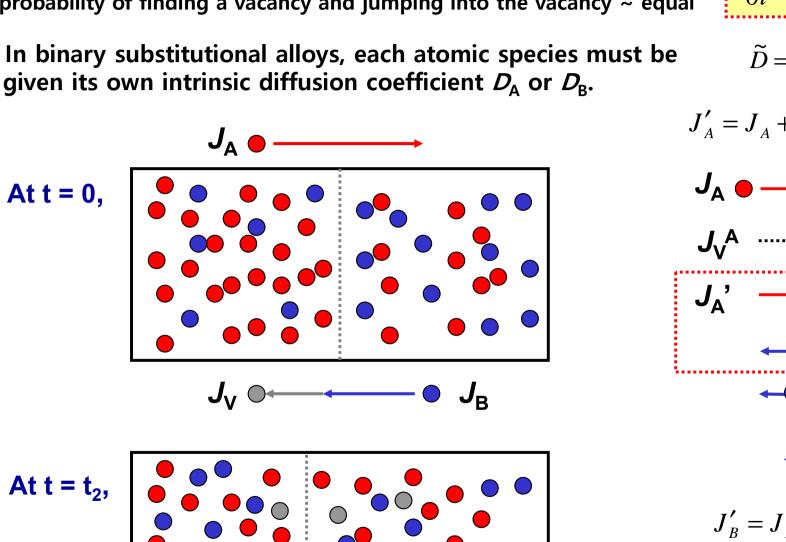
Creation/destruction of vacancies is accomplished by *dislocation climb*.

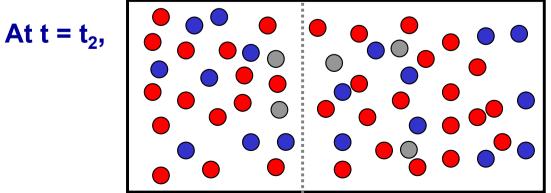
3. Diffusion in substitutional alloys

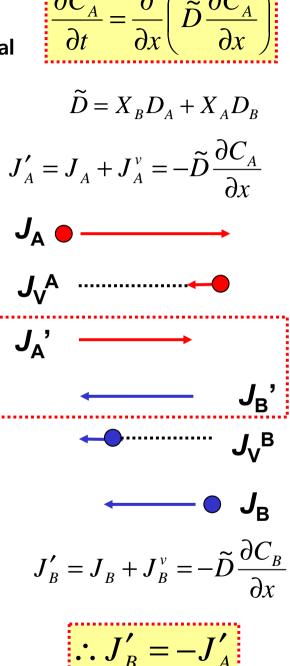
* During self-diffusion, all atoms are chemically identical. : probability of finding a vacancy and jumping into the vacancy ~ equal



* In binary substitutional alloys, each atomic species must be







1) INTERDIFFUSION

Assume that C_0 : total number of atoms (A, B) per unit volume = constant, independent of composition

$$\frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$$

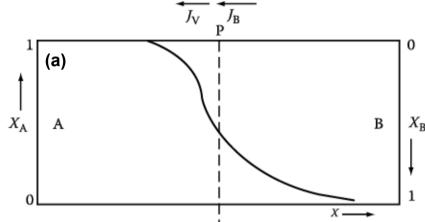


 $C_o = C_A + C_B$ and $\frac{\partial C_A}{\partial v} = -\frac{\partial C_B}{\partial v}$ * If the couple is annealed at a high enough temp., a concentration profile will develop as shown.

Fluxes of A and B atoms across a given lattice plane ~ equal

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$J_{A} = -D_{A} \frac{\partial C_{A}}{\partial x} \qquad J_{B} = -D_{B} \frac{\partial C_{B}}{\partial x} = D_{B} \frac{\partial C_{A}}{\partial x}$$



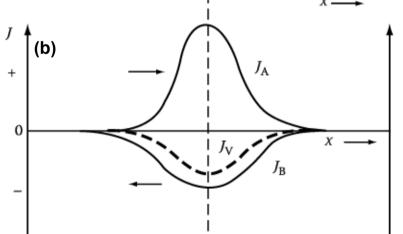
Due to the difference in diffusivities, a flux difference is created.

$$\left|J_{\scriptscriptstyle A}\right|\!>\!\left|J_{\scriptscriptstyle B}\right|$$

Flux of vacancies

$$J_A
ightarrow J_{v,A} = -J_A \qquad J_B
ightarrow J_{v,B} = -J_B$$

$$J_V + \quad J_B \quad = \quad -J_A$$



 $J_V = -J_A - J_B$ (a net flux of vacancies)

Fig. 2.15 Interdiffusion and vacancy flow.

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

$$\therefore J_{B} = -D_{B} \frac{\partial C_{B}}{\partial x} = D_{B} \frac{\partial C_{A}}{\partial x}$$
 25

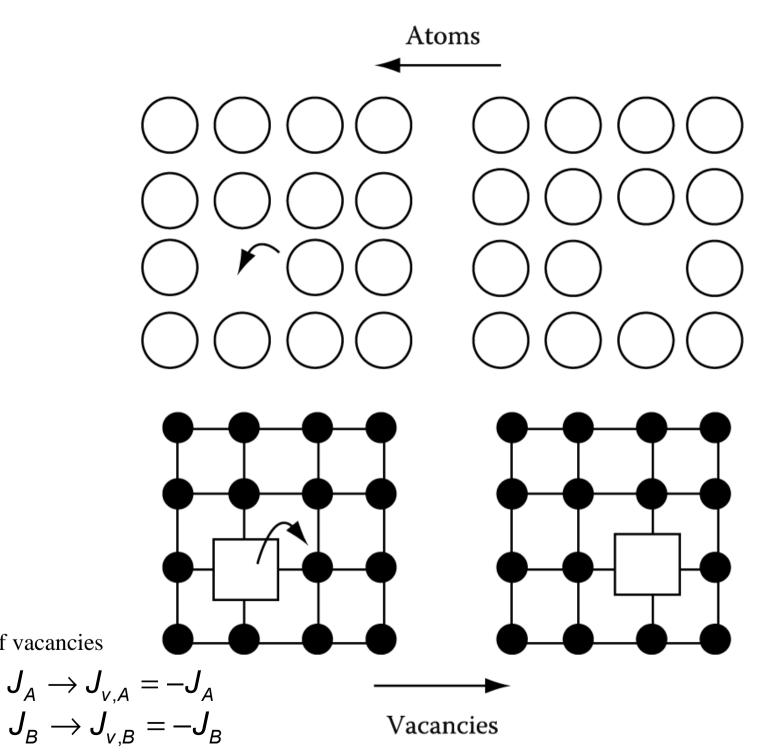


Fig. 2.16 The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.

Flux of vacancies

$$J_V = -J_A - J_B$$
 (a net flux of vacancies)
= $(D_A - D_B) \frac{\partial C_A}{\partial x}$

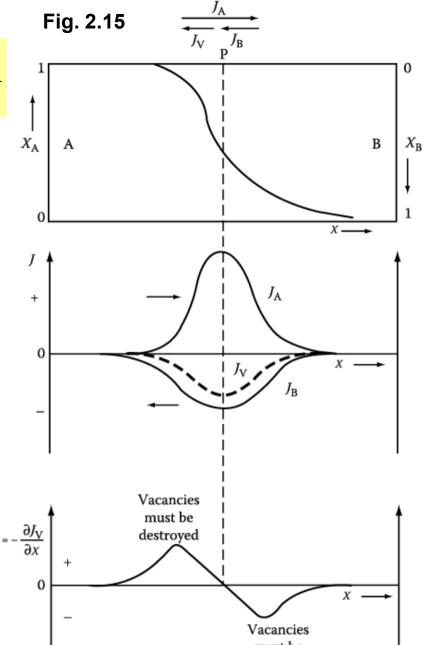
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

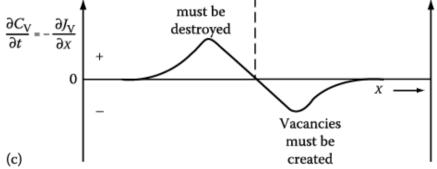
$$\frac{\partial C_{v}}{\partial t} = -\frac{\partial J_{v}}{\partial x} \text{ vs. } x?$$

What would become of excess vacancy?

$$\partial C_V / \partial t = -\partial J_V / \partial x$$
 (Fig. 2. 15c)

$$cf) \quad \frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}$$





In order to maintain the vacancy concentration everywhere near equilibrium, vacancies must be created on the B-rich side and destroyed on the A-rich side.

* Net flux of vacancies across the middle of the diffusion couple → "Movement of lattice"

(b)

Kirkendall effect

Creation/destruction of vacancies is accomplished by *dislocation climb*.

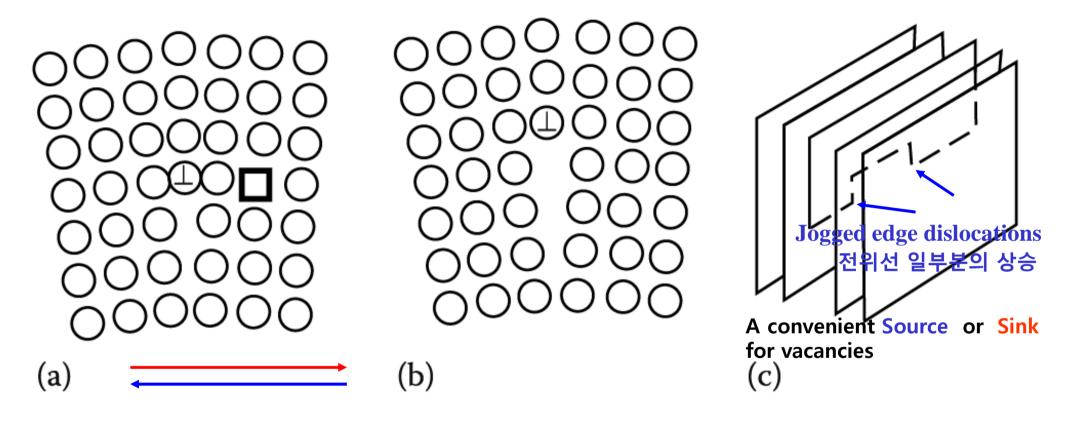


Fig. 2.17 (a) before, (b) after: <u>a vacancy is absorbed at a jog on an edge dislocation</u> (positive climb). (b) before, (a) after: <u>a vacancy is created by negative climb of an edge dislocation</u>.

(c) Perspective drawing of a jogged edge dislocation.

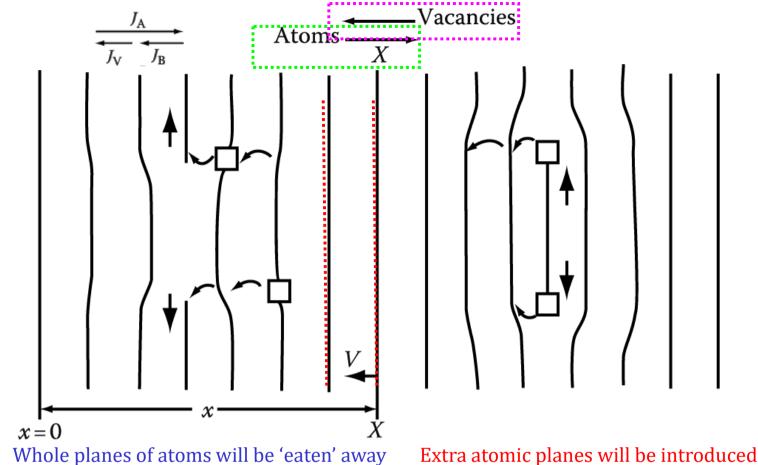


Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.

2) velocity of the movement of the lattice plane is related to the net flux of vacancies across the middle of the diffusion couple, such that

$$Av \cdot \delta t \cdot C_0 = J_v A \cdot \delta t \longrightarrow J_v = C_0 v$$
 # of removed atoms # of vacancies crossing the plane
$$v = \frac{1}{C_0} (D_A - D_B) \frac{\partial C_A}{\partial x} = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

 X_A : mole fraction of A atoms, v: marker velocity (velocity of the lattice plane)

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.

(균질화 시간 혹은 확산쌍의 위치에 따른 조성 변화)

Derivation of the Fick's 2nd law for substitutional alloys

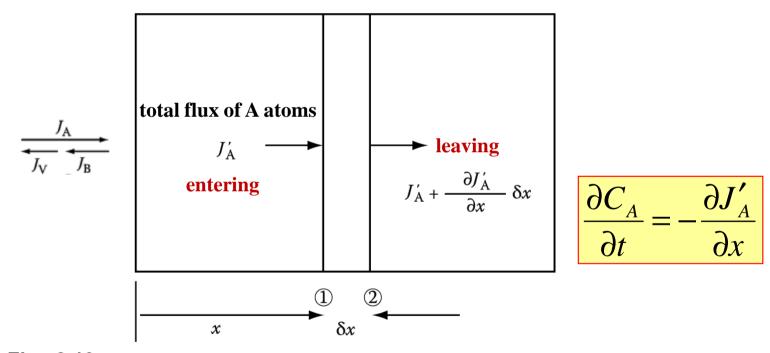


Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

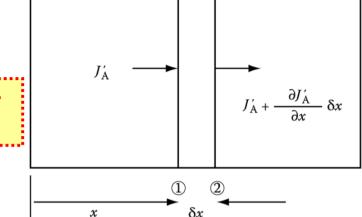
 $\mathbf{J'}_{\mathbf{A}}$: total flux of A atoms across a stationary plane with respect to the specimen

3) Derivation of the Fick's 2nd law for substitutional alloys

J'_A: total flux of A atoms across a stationary plane with respect to the specimen

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J_A'}{\partial x}$$

A Diffusive flux due to diffusion relative to the lattice + A flux due to the velocity of the lattice



$$J_A' = J_A + vC_A$$

$$= -D_A \frac{\partial C_A}{\partial x} + vC_A$$

$$v = \frac{1}{C_0} (D_A - D_B) \frac{\partial C_A}{\partial x} = (D_A - D_B) \frac{\partial X_A}{\partial x} \quad X_A = C_A / C_0$$

$$= -(X_B D_A + X_A D_B) \frac{\partial C_A}{\partial x}$$

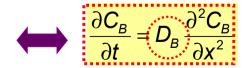
$$=-\widetilde{D}\frac{\partial C_A}{\partial x}$$

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

$$= -\tilde{D}\frac{\partial C_A}{\partial x} \qquad \qquad \tilde{D} = X_B D_A + X_A D_B \qquad \qquad J_B' = -\tilde{D}\frac{\partial C_B}{\partial x} = \tilde{D}\frac{\partial C_A}{\partial x}$$

(Darken's equation, interdiffusion coefficient)

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right)$$
 Fick's 2nd law for substitutional alloy $\longleftrightarrow \frac{\partial C_B}{\partial t} = \overline{D_B} \frac{\partial^2 C_B}{\partial x^2}$



$$\therefore J_B' = -J_A'$$

Only difference with ID : diffusion coefficient 31

Q: How can we determine D_A and D_B ? in substitutional alloys?

By measuring velocity of a lattice (v) and interdiffusion coefficient (\tilde{D})

$$v = (D_A - D_B) \frac{\partial X_A}{\partial X} = (D_B - D_A) \frac{\partial X_B}{\partial X} \qquad \Longrightarrow \quad \widetilde{D} = X_B D_A + X_A D_B$$

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 ?

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

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

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)?

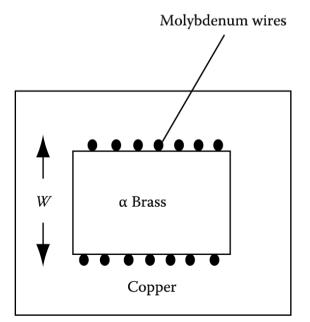


Fig. 2.20 An experimental arrangement to show the Kirkendall effect

The displacement of wires during diffusion was first observed by Smigelskas and Kirkendall in 1947 and is usually known as the Kirkendall effect.

Creation/destruction of vacancies is accomplished by dislocation climb.

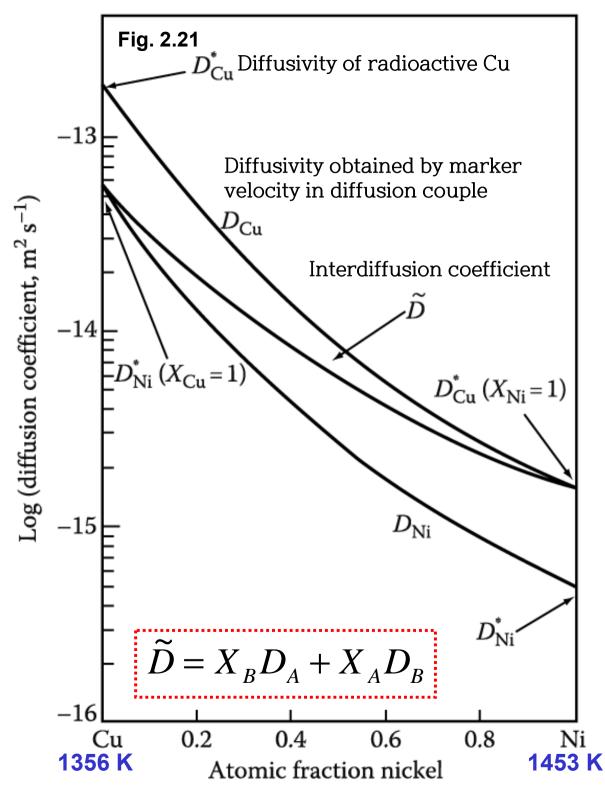
$$D_{Zn} > D_{Cu}$$

After annealing at a high temperature, it was found that the separation of the markers (w) had decreased. 33

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D.

 \mathbf{D}_{Cu} , \mathbf{D}_{Ni} , (\tilde{D}) are all composition dependent, increasing as \mathbf{X}_{Cu} increases.



• 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.

$$\widetilde{D} = \widetilde{D}_0 \exp(-Q/RT)$$

Variation of \tilde{D} with composition:

- For a given crystal structure, \underline{D} at T_m is roughly constant. Therefore if adding B to A decreases T_m , \tilde{D} will increase at a given temperature, and vice verse.
- For both interstitial and substitutional alloys, diffusion is more rapid in bcc (0.68) than in a close-packed lattice (FCC~0.74).
 α, Ferrite
 γ, Austenite

Ex) diffusion of carbon in Fe at 1183 K, $D_C^{\alpha}/D_C^{\gamma}$ ~100 Self-diffusion coefficients for Fe at 1133 K, $D_{Fe}^{\alpha}/D_{Fe}^{\gamma}$ ~100

BCC_more open and less lattice distortion

2.3.4 Diffusion in dilute substitutional alloys

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

(interdiffusion coefficient)

For Dilute Substitutional Alloys

if
$$X_A \approx 1$$
, $\tilde{D} = D_B$

The rate of homogenization in dilute alloys is controlled by how fast the solute (B) atoms can diffuse.

In this case, D_B is called <u>'impurity diffusion coefficient'.</u>
~ can be measured by using radioactive tracers like self-diffusion

- * D_B in a dilute solution of B in A is greater than D_A .
- The reason for this is that the <u>solute atoms can attract vacancies</u> so that there is more than a random probability of finding <u>a vacancy next</u> to a solute atom with the result that they can <u>diffuse faster than solvent</u>.
- 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. In this case the solute-vacancy pair can diffuse through the lattice together.

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D.

 D_{Cu} , D_{Ni} , (\tilde{D}) are all composition dependent, increasing as X_{Cu} increases.

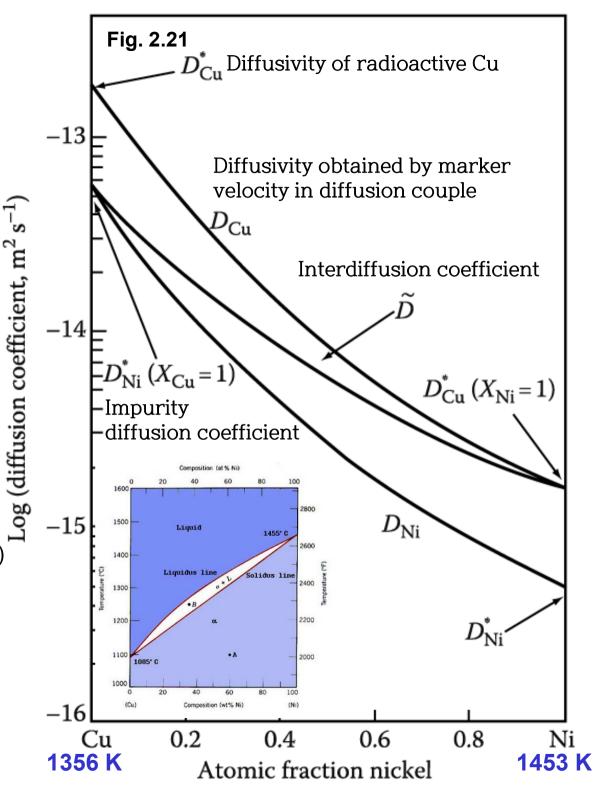
* Concentration of A & B at any x after t

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right) \quad \text{Eq. (2.53)}$$

- By solving (2.53) with appropriate BCs, \rightarrow Possible to obtain $C_A(x, t)$ and $C_B(x, t)$
- Characteristic relaxation time for an Homogenization anneal

$$\tau = \frac{l^2}{\pi^2 \tilde{D}} \quad \tau : \text{relaxation time}$$

(The range of composition is small enough that any effect of composition on \tilde{D} can be ignored)



Contents for today's class

Substitution Diffusion

1. Self diffusion in pure material (by radioactive element)

Probability of vacancy x probability of jump

$$D_{A} = \frac{1}{6}\alpha^{2} \operatorname{zv} \exp \frac{-(\Delta G_{m} + \Delta G_{V})}{RT}$$

$$D_{A} = D_{0} \exp(-\frac{Q_{SD}}{RT})$$

$$D_A = D_0 \exp(-\frac{Q_{SD}}{RT})$$

$$Q_{SD} = \Delta H_m + \Delta H_V$$

2. Vacancy diffusion

$$D_{v} = \frac{1}{6}\alpha^{2}zv \exp(\Delta S_{m}/R) \exp(-\Delta H_{m}/RT)$$

Comparing D_{v} with the self-diffusion coefficient of A, D_{A} , $D_{v}=D_{A}/X_{v}^{e}$

$$D_{v} = D_{A} / X_{v}^{e}$$

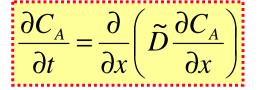
Diffusion in substitutional alloys

$$X_{V} = X_{V}^{e} = exp \frac{-\Delta G_{V}}{RT}$$

침입형 확산에서 Fick의 법칙 고정된 격자면을 통한 이동

3. Diffusion in substitutional alloys

: A원자/B원자의 상호확산을 통한 격자면의 이동 고려



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

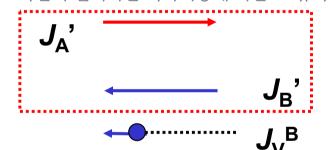
$$J_A' = J_A + J_v^A = J_A + vC_A = -\widetilde{D}\frac{\partial C_A}{\partial x}$$



고정된 격자 내에서 확산에 의한 유속



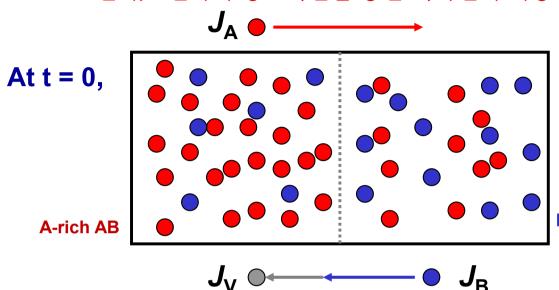
B-rich AB 확산이 일어나는 격자이동에 의한 A 유속

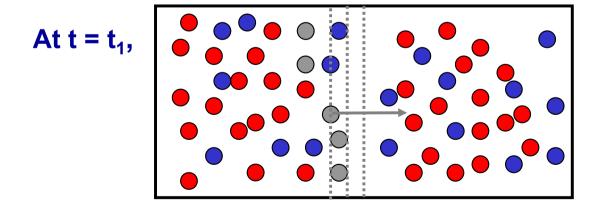


확산이 일어나는 격자이동에 의한 B 유속

고정된 격자 내에서 확산에 의한 유속

$$J'_{B} = J_{B} + J_{v}^{B} = J_{B} + vC_{B} = -\tilde{D}\frac{\partial C_{B}}{\partial x}$$
$$\therefore J'_{B} = -J'_{A}$$





공공의 net flux

A원자와 B원자가 서로 다른 속도로 도약 → 농도 구배에 의한 속도 + 격자면 이동에 의한 속도 The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D.

 D_{Cu} , D_{Ni} , (\tilde{D}) are all composition dependent, increasing as X_{Cu} increases.

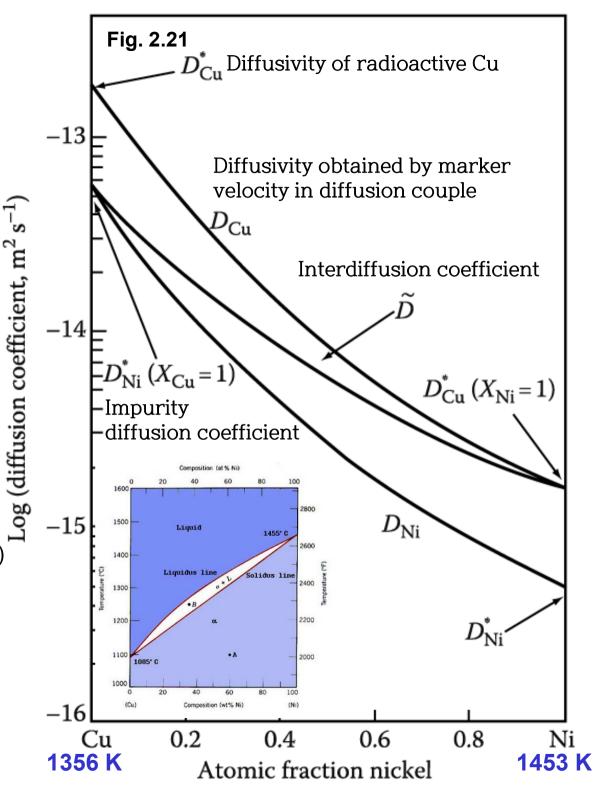
* Concentration of A & B at any x after t

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right) \quad \text{Eq. (2.53)}$$

- By solving (2.53) with appropriate BCs, \rightarrow Possible to obtain $C_A(x, t)$ and $C_B(x, t)$
- Characteristic relaxation time for an Homogenization anneal

$$\tau = \frac{l^2}{\pi^2 \tilde{D}} \quad \tau : \text{relaxation time}$$

(The range of composition is small enough that any effect of composition on \tilde{D} can be ignored)



2023 Fall

"Phase Transformation in Materials"

2023.10.04

Eun Soo Park

Office: 33-313

Telephone: 880-7221

Email: espark@snu.ac.kr

Office hours: by an appointment

Contents in Phase Transformation

Background to understand phase transformation

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(Ch1) Thermodynamics and Phase Diagrams
```

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative Phase transformation

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(Ch4) Solidification: Liquid \rightarrow Solid
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(Ch5) Diffusional Transformations in Solid: Solid → Solid

(Ch6) Diffusionless Transformations: Solid → Solid

Contents for previous class

Interstitial Diffusion

- Steady-state diffusion— Fick's First Law
- **→** Concentration varies with position.
- Non-steady-state diffusion: Fick's Second Law
- **→** Concentration varies with time and position.

/ Substitutional 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

Contents for previous class (8_PTM 092723)

• Diffusion : Movement of atoms to reduce its chemical potential μ.

driving force: Reduction of G

Down-hill diffusion movement of atoms from a high C_B region to low C_B region. **Up-hill diffusion** movement of atoms from a low C_B region to high C_B region.

- Interstitial Diffusion / Substitution Diffusion
 - Steady-state diffusion Fick's First Law_____

$$J_{B} = \frac{1}{6} \Gamma_{B} (n_{1} - n_{2}) = -\left(\frac{1}{6} \Gamma_{B} \alpha^{2}\right) \frac{\partial C_{B}}{\partial x} = -D_{B} \frac{\partial C_{B}}{\partial x}$$

→ Concentration varies with position. (atoms m⁻² s⁻¹)

- Nonsteady-state diffusion - Fick's Second Law

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$
 Concentration varies with time and position.

- For random walk in 3 dimensions, after n steps of length α
- Effect of Temperature on Diffusivity

$$r = \alpha \sqrt{(\Gamma t)} = f(D) = 2.4 \sqrt{Dt}$$

$$\log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T}\right)$$

The section is completed with 4 example solutions to Fick's 2nd law: carburisation, decarburisation, diffusion across a couple and homogenisation.

The solutions given are as follows:

Process	Solution
Homogenization	$C = C_{\text{mean}} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \exp\left(-\frac{t}{\tau}\right)$
	C_{mean} = Mean concentration b_0 = Initial concentration amplitude l = half-wavelength of cells t = relaxation time
Carburization	$C = C_{\rm S} - (C_{\rm S} - C_0) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$
	$C_S = Surface concentration$ $C_0 = Initial bulk concentration$
Decarburization	$C = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ $C_0 = \text{Initial bulk concentration}$
Diffusion Couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$
	C_1 = Concentration of steel 1 C_2 = Concentration of steel 2

Contents for previous class (9_PTM 100223)

Substitution Diffusion

1. Self diffusion in pure material (by radioactive element)

Probability of vacancy x probability of jump

$$D_{A} = \frac{1}{6}\alpha^{2} \operatorname{zv} \exp \frac{-(\Delta G_{m} + \Delta G_{V})}{RT}$$

$$D_{A} = D_{0} \exp(-\frac{Q_{SD}}{RT})$$

$$D_A = D_0 \exp(-\frac{Q_{SD}}{RT})$$

 $Q_{SD} = \Delta H_m + \Delta H_V$

2. Vacancy diffusion

$$D_{v} = \frac{1}{6}\alpha^{2}zv \exp(\Delta S_{m}/R) \exp(-\Delta H_{m}/RT)$$

Comparing D_v with the self-diffusion coefficient of A, D_A , $D_v = D_A / X_v^e$

$$D_{v} = D_{A} / X_{v}^{e}$$

3. Diffusion in substitutional alloys

$$X_{V} = X_{V}^{e} = exp \frac{-\Delta G_{V}}{RT}$$

Q: Diffusion in substitutional alloys?

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

$$J_{A}' = J_{A} + J_{A}^{v} = -\widetilde{D}\frac{\partial C_{A}}{\partial x} = \widetilde{D}\frac{\partial C_{B}}{\partial x}$$

$$J_{B}' = J_{B} + J_{B}^{v} = -\widetilde{D}\frac{\partial C_{B}}{\partial x} = \widetilde{D}\frac{\partial C_{A}}{\partial x}$$

$$\frac{\partial C_{A}}{\partial t} = \frac{\partial}{\partial x}\left(\widetilde{D}\frac{\partial C_{A}}{\partial x}\right)$$

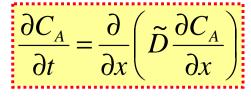
$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right)$$

Fick's 2nd law for substitutional alloy Fick's 1st law for substitutional alloy

2원계 치환형 확산에서 Fick의 법칙 적용 격자면의 이동 고려

2.3.3. Diffusion in substitutional alloys

: A원자/B원자의 상호확산을 통한 격자면의 이동 고려



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

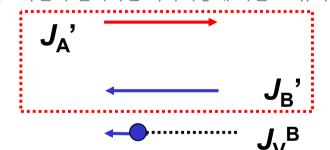
$$J_A' = J_A + J_v^A = J_A + vC_A = -\widetilde{D}\frac{\partial C_A}{\partial x}$$



고정된 격자 내에서 확산에 의한 유속



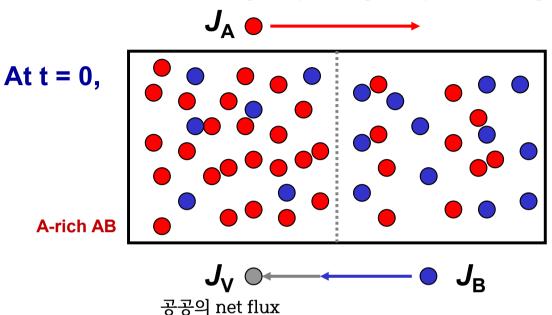
B-rich AB 확산이 일어나는 격자이동에 의한 A 유속

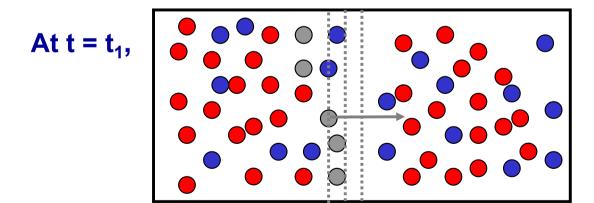


확산이 일어나는 격자이동에 의한 B 유속

고정된 격자 내에서 확산에 의한 유속

$$J'_{B} = J_{B} + J_{v}^{B} = J_{B} + vC_{B} = -\widetilde{D} \frac{\partial C_{B}}{\partial x}$$
$$\therefore J'_{B} = -J'_{A}$$





A원자와 B원자가 서로 다른 속도로 도약 → 농도 구배에 의한 속도 + 격자면 이동에 의한 속도

1) INTERDIFFUSION

Assume that C_0 : total number of atoms (A, B) per unit volume = constant, independent of composition

$$C_o = C_A + C_B$$
 and

$$\frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$$

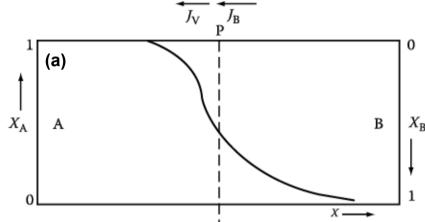


 $C_o = C_A + C_B$ and $\frac{\partial C_A}{\partial v} = -\frac{\partial C_B}{\partial v}$ * If the couple is annealed at a high enough temp., a concentration profile will develop as shown.

Fluxes of A and B atoms across a given lattice plane ~ equal

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$J_{A} = -D_{A} \frac{\partial C_{A}}{\partial x} \qquad J_{B} = -D_{B} \frac{\partial C_{B}}{\partial x} = D_{B} \frac{\partial C_{A}}{\partial x}$$



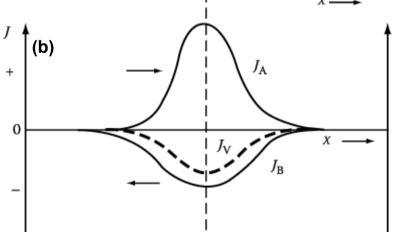
Due to the difference in diffusivities, a flux difference is created.

$$\left|\boldsymbol{J}_{\boldsymbol{A}}\right|\!>\!\left|\boldsymbol{J}_{\boldsymbol{B}}\right|$$

Flux of vacancies

$$J_A
ightarrow J_{v,A} = -J_A \qquad J_B
ightarrow J_{v,B} = -J_B$$

$$J_V + \quad J_B \quad = \quad -J_A$$



 $J_V = -J_A - J_B$ (a net flux of vacancies)

Fig. 2.15 Interdiffusion and vacancy flow.

9

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

$$\therefore J_{B} = -D_{B} \frac{\partial C_{B}}{\partial x} = D_{B} \frac{\partial C_{A}}{\partial x}$$

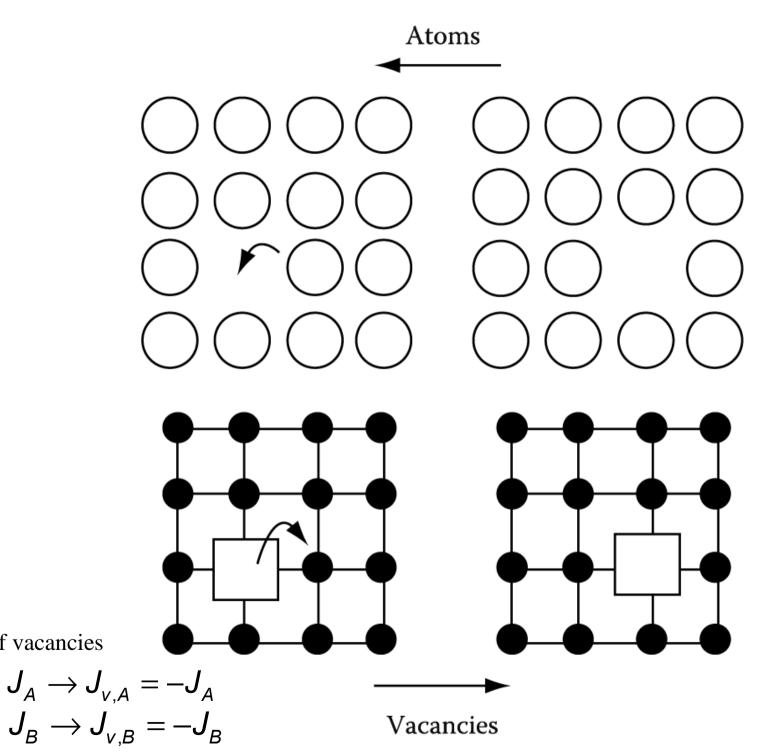


Fig. 2.16 The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.

Flux of vacancies

$$J_V = -J_A - J_B$$
 (a net flux of vacancies)
= $(D_A - D_B) \frac{\partial C_A}{\partial x}$

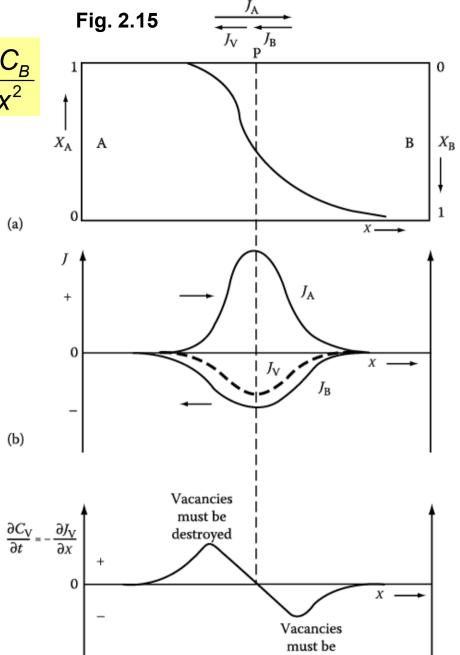
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

$$\frac{\partial C_{v}}{\partial t} = -\frac{\partial J_{v}}{\partial x} \text{ vs. } x?$$

What would become of excess vacancy?

$$\partial C_V / \partial t = -\partial J_V / \partial x$$
 (Fig. 2. 15c)

$$cf) \quad \frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}$$



created

In order to maintain the vacancy concentration everywhere near equilibrium, vacancies must be created on the B-rich side and destroyed on the A-rich side.

* Net flux of vacancies across the middle of the diffusion couple ightharpoonup "Movement of lattice"

(b)

(c)

Kirkendall effect

Creation/destruction of vacancies is accomplished by *dislocation climb*.

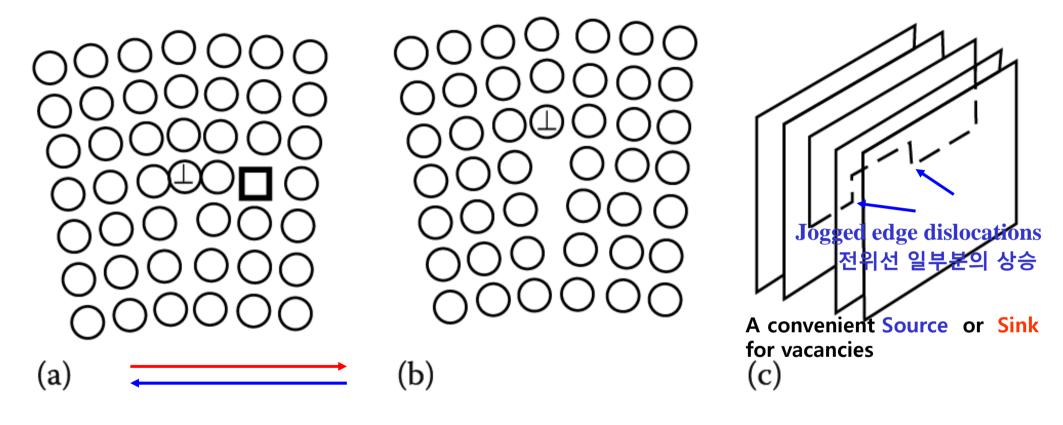


Fig. 2.17 (a) before, (b) after: <u>a vacancy is absorbed at a jog on an edge dislocation</u> (positive climb). (b) before, (a) after: <u>a vacancy is created by negative climb of an edge dislocation</u>.

(c) Perspective drawing of a jogged edge dislocation.

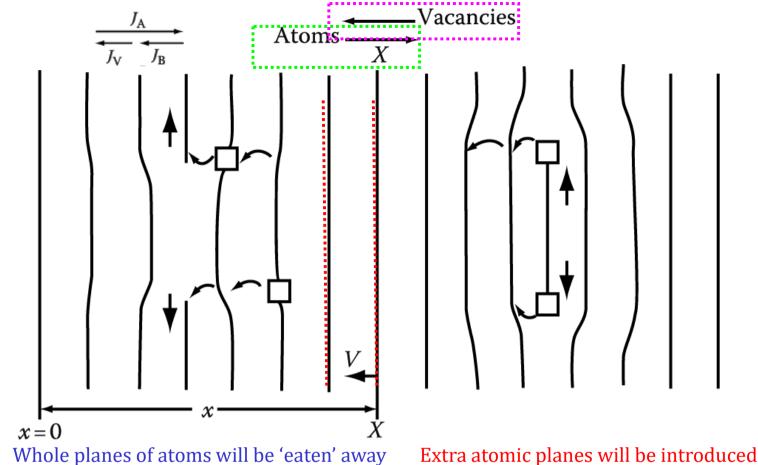


Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.

2) velocity of the movement of the lattice plane is related to the net flux of vacancies across the middle of the diffusion couple, such that

$$Av \cdot \delta t \cdot C_0 = J_v A \cdot \delta t \longrightarrow J_v = C_0 v$$
 # of removed atoms # of vacancies crossing the plane
$$v = \frac{1}{C_0} (D_A - D_B) \frac{\partial C_A}{\partial x} = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

 X_A : mole fraction of A atoms, v: marker velocity (velocity of the lattice plane)

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.

(균질화 시간 혹은 확산쌍의 위치에 따른 조성 변화)

Derivation of the Fick's 2nd law for substitutional alloys

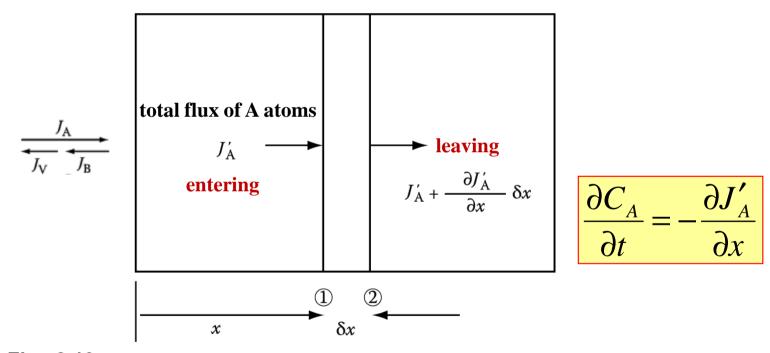


Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

 $\mathbf{J'}_{\mathbf{A}}$: total flux of A atoms across a stationary plane with respect to the specimen

3) Derivation of the Fick's 2nd law for substitutional alloys

J'_A: total flux of A atoms across a stationary plane with respect to the specimen

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J_A'}{\partial x}$$

A Diffusive flux due to diffusion relative to the lattice +

A flux due to the velocity of the lattice
$$J'_{A} = J_{A} + vC_{A}$$

$$= -D_{A} \frac{\partial C_{A}}{\partial x} + vC_{A}$$

$$v = \frac{1}{C_{0}} (D_{A} - D_{B}) \frac{\partial C_{A}}{\partial x} = (D_{A} - D_{B}) \frac{\partial X_{A}}{\partial x}$$

$$X_{A} = C_{A} / C_{0}$$

$$= -(X_B D_A + X_A D_B) \frac{\partial C_A}{\partial x}$$

$$= -\tilde{D} \frac{\partial C_A}{\partial C_A}$$

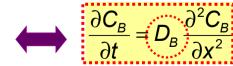
$$\widetilde{D} = X_B D_A + X_A D_B$$

$$= -\tilde{D}\frac{\partial C_A}{\partial x} \qquad \qquad \tilde{D} = X_B D_A + X_A D_B \qquad \qquad J_B' = -\tilde{D}\frac{\partial C_B}{\partial x} = \tilde{D}\frac{\partial C_A}{\partial x}$$

Fick's 1st law for substitutional alloy

(Darken's equation, interdiffusion coefficient)

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right)$$
 Fick's 2nd law for substitutional alloy
$$\longleftrightarrow \frac{\partial C_B}{\partial t} = \overline{D_B} \frac{\partial^2 C_B}{\partial x^2}$$



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

Only difference with ID : diffusion coefficient

Q: How can we determine D_A and D_B ? in substitutional alloys?

By measuring velocity of a lattice (v) and interdiffusion coefficient (\tilde{D})

$$v = (D_A - D_B) \frac{\partial X_A}{\partial x} = (D_B - D_A) \frac{\partial X_B}{\partial x} \qquad \Longrightarrow \quad \widetilde{D} = X_B D_A + X_A D_B$$

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 ?

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

$$\Longrightarrow \widetilde{D} = X_B D_A + X_A D_B$$

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)?

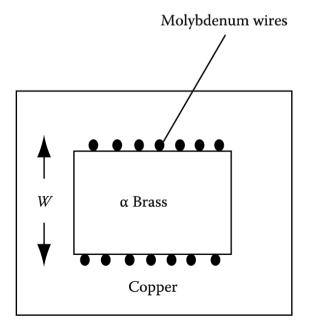


Fig. 2.20 An experimental arrangement to show the Kirkendall effect

The displacement of wires during diffusion was first observed by Smigelskas and Kirkendall in 1947 and is usually known as the Kirkendall effect.

Creation/destruction of vacancies is accomplished by dislocation climb.

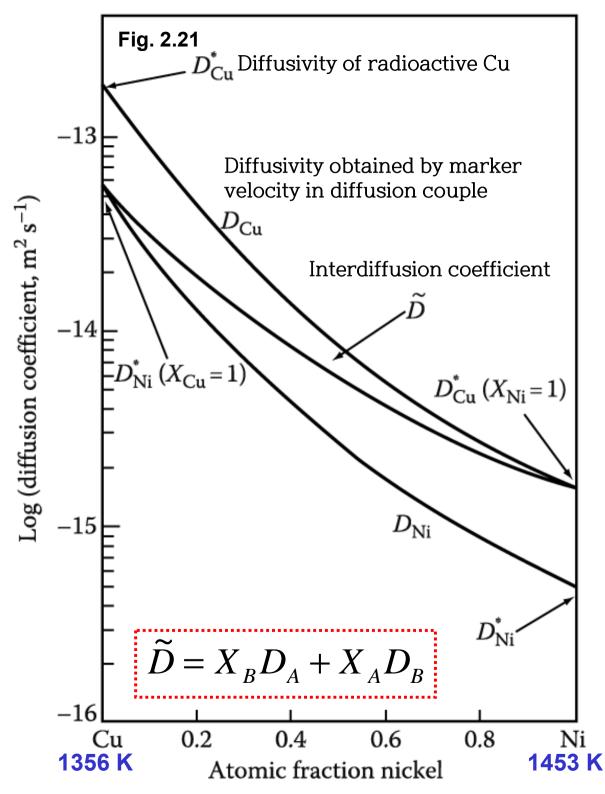
$$D_{Zn} > D_{Cu}$$

After annealing at a high temperature, it was found that the separation of the markers (w) had decreased. 17

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D.

 \mathbf{D}_{Cu} , \mathbf{D}_{Ni} , (\tilde{D}) are all composition dependent, increasing as \mathbf{X}_{Cu} increases.



• 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.

$$\widetilde{D} = \widetilde{D}_0 \exp(-Q/RT)$$

Variation of \tilde{D} with composition:

- For a given crystal structure, \underline{D} at T_m is roughly constant. Therefore if adding B to A decreases T_m , \tilde{D} will increase at a given temperature, and vice verse.
- For both interstitial and substitutional alloys, diffusion is more rapid in bcc (0.68) than in a close-packed lattice (FCC~0.74).
 α, Ferrite
 γ, Austenite

Ex) diffusion of carbon in Fe at 1183 K, $D_C^{\alpha}/D_C^{\gamma}$ ~100 Self-diffusion coefficients for Fe at 1133 K, $D_{Fe}^{\alpha}/D_{Fe}^{\gamma}$ ~100

BCC_more open and less lattice distortion

2.3.4 Diffusion in dilute substitutional alloys

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

(interdiffusion coefficient)

For Dilute Substitutional Alloys

if
$$X_A \approx 1$$
, $\tilde{D} = D_B$

The rate of homogenization in dilute alloys is controlled by how fast the solute (B) atoms can diffuse.

In this case, D_B is called <u>'impurity diffusion coefficient'.</u>
~ can be measured by using radioactive tracers like self-diffusion

- * D_B in a dilute solution of B in A is greater than D_A .
- The reason for this is that the <u>solute atoms can attract vacancies</u> so that there is more than a random probability of finding <u>a vacancy next</u> to a solute atom with the result that they can <u>diffuse faster than solvent</u>.
- 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. In this case the solute-vacancy pair can diffuse through the lattice together.

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D.

 \mathbf{D}_{Cu} , \mathbf{D}_{Ni} , (\tilde{D}) are all composition dependent, increasing as \mathbf{X}_{Cu} increases.

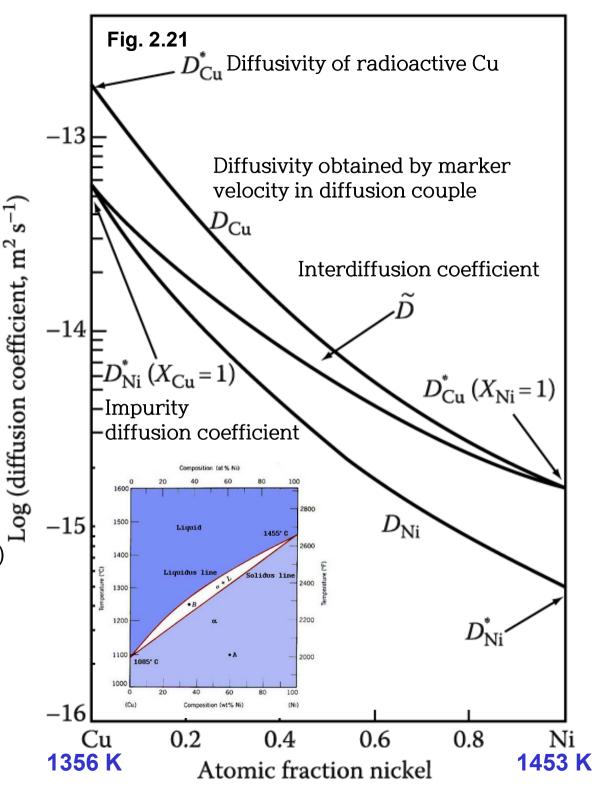
* Concentration of A & B at any x after t

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\widetilde{D} \frac{\partial C_A}{\partial x} \right) \quad \text{Eq. (2.53)}$$

- By solving (2.53) with appropriate BCs, \rightarrow Possible to obtain C_A (x, t) and C_B (x,t)
- Characteristic relaxation time for an Homogenization anneal

$$\tau = \frac{l^2}{\pi^2 \tilde{D}} \quad \tau : \text{relaxation time}$$

(The range of composition is small enough that any effect of composition on \tilde{D} can be ignored)



Contents for today's class (10_PTM 100423)

- 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

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

$$D_B = M_B RTF$$

Thermodynamic factor

$$D_{B} = M_{B}RTF$$

$$F = (1 + \frac{d \ln \gamma_{B}}{d \ln X_{B}})$$

2.4 Atomic mobility

- <u>Fick's first law</u>: assume that diffusion eventually stops when the concentration is the same everywhere → never true in practice due to lattice defect (농도구배만 고려)
- Higher concentrations in the vicinity of the "defect"
 - → Diffusion in the vicinity of these defects is affected by both the concentration gradient and the gradient of the interaction energy.(결함과의 상호작용에너지의 구배)
- Fick's law alone ~ insufficient
 to describe how to concentration will vary with distance and time.

e.g. Too big or too small solute atom

- → relatively high potential energy due to the "strain" in the surrounding matrix
- → However, this strain energy can be reduced if the atom is located in a position where it <u>better matches the space available</u>, i.e., near dislocations and in boundaries, where the matrix is already distorted.

2.4 Atomic mobility

- "Segregation" of atoms occur at crystal defects where the strain energy can be reduced. Segregation causes problems like temper embrittlement and dynamic strain aging. Fundamental kinetics of phase transformation are also affected by segregation.
- 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 1) 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. Fick's first law is merely a special case $J_B = -D_B \frac{\partial C_B}{\partial x}$ of this more general approach. ("previous approach")



$$J_{B} = v_{B}C_{B}$$

무질서한 도약에 의한 순 표류속도

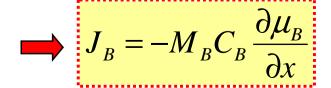
 $J_B = v_B C_B$ 2) A diffusion flux ~ a net drift velocity superimposed on the random jumping motion of each diffusing atom,

: remove differences in chemical potential ∞ chemical potential gradient

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

: remove differences in chemical potential
$$\infty$$
 chemical potential $v_B = -M_B \frac{\partial \mu_B}{\partial x}$: ① chemical force causing atom to migrate "M_B": mobility of B atoms, a constant of proportion

"M_B": mobility of B atoms, a constant of proportionality



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

Relationship between M_B and D_B

$$J_{B} = -M_{B}C_{B}\frac{\partial \mu_{B}}{\partial x}$$

$$\therefore J_{B} = -M_{B} \frac{X_{B}}{V_{m}} \frac{RT}{X_{B}} (1 + \frac{\partial \ln \gamma_{B}}{\partial \ln X_{B}}) \frac{\partial X_{B}}{\partial x} = RT (1 + \frac{\partial \ln \gamma_{B}}{\partial \ln X_{B}}) \frac{\partial \ln X_{B}}{\partial x}$$

$$= -M_{B}RTF \frac{\partial C_{B}}{\partial x} = -D_{B} \frac{\partial C_{B}}{\partial x}$$

$$C_{B} = \frac{n_{B}}{V} = \frac{n_{B}}{(n_{A} + n_{B})V_{m}} = \frac{X_{B}}{V_{m}}$$

$$D_B = M_B RTF$$

For ideal or dilute solutions,

near $X_B \approx 0$, $\gamma_B = const.$ with respect to X_B

$$\therefore F = 1$$

$$D_{R} = M_{R}RT$$

$$\mu_{B} = G_{B} + RT \ln a_{B} = G_{B} + RT \ln \gamma_{B} X_{B}$$

$$\frac{\partial \mu_{B}}{\partial x} = \frac{\partial}{\partial x} (G_{B}^{0} + RT \ln \gamma_{B} X_{B})$$

$$= RT (\frac{\partial \ln \gamma_{B}}{\partial x} + \frac{\partial \ln X_{B}}{\partial x})$$

$$= RT (1 + \frac{\partial \ln \gamma_{B}}{\partial \ln X_{B}}) \frac{\partial \ln X_{B}}{\partial x}$$

$$C = \frac{n_{B}}{n_{B}} = \frac{n_{B}}{n_{B}} = \frac{X_{B}}{n_{B}}$$

$$V = (n_A + n_B)V_m - V_m$$

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

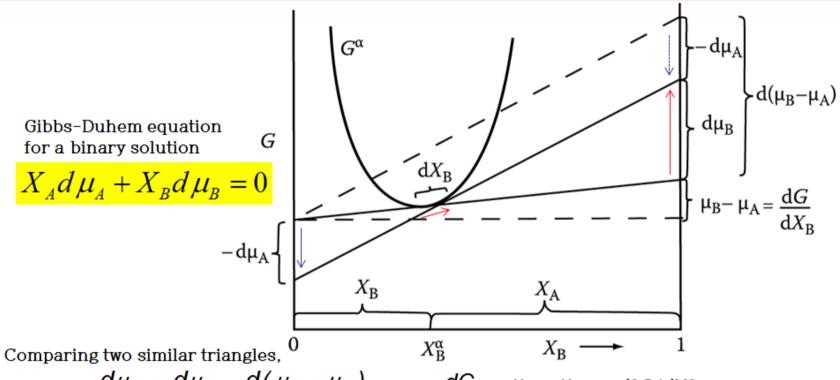
For non-ideal concentrated solutions, thermodynamic factor (F) must be included.

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

Additional Thermodynamic Relationships for Binary Solutions

The Gibbs-Duhem Equation क्षेत्र क्षेत्र गर्म गर्म श्री प्राप्त श्री स्वर्ग स्वरंग स्वर्ग स्वरंग स्व

be able to calculate the change in chemical potential (dµ) that result from a change in alloy composition (dX).



$$-\frac{d\mu_{A}}{X_{B}} = \frac{d\mu_{B}}{X_{A}} = \frac{d(\mu_{B} - \mu_{A})}{1} \iff \frac{dG}{dX_{B}} = \frac{\mu_{B} - \mu_{A}}{1} , \frac{d^{2}G/dX^{2}}{d^{2}G/dX_{B}^{2}} = d^{2}G/dX_{A}^{2}$$

Substituting right side Eq. & Multiply X_AX_R

" Gibbs-Duhem Equation $\textbf{X}_{\text{A}},\,\textbf{X}_{\text{B}}\,\textbf{vs.}\,\,\textbf{d}\mu_{\text{A}},\,\textbf{d}\mu_{\text{B}}$ γ_A, γ_B

 a_A , a_B

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2 G}{dX^2} dX_B$$

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

Eq. 1.65

- ② The diffusive flux is also affected by the gradient of strain energy, ∂E/∂x. 변형 € 구배도 확산에 영향
 - Ex) The expression for the chemical potential can be modified to include the effect of an "elastic strain energy term", E depends on the position (x) relative to a dislocation.

$$\mu_{B} = G_{B} + RT \ln \gamma_{B} X_{B} + E \qquad \Longrightarrow \qquad J_{B} = -D_{B} \cdot \frac{\partial C_{B}}{\partial x} - \frac{D_{B} C_{B}}{RT} \cdot \frac{\partial E}{\partial x}$$
Concentration gradient & strain E gradient

- 3 Atoms diffusing towards regions of high concentration can be found
 - a. when diffusion occurs in the presence of an electric field or a temperature gradient.
 - b. when the free energy curve has a <u>negative curvature</u>, which is known as spinodal decomposition.

Q: How does D^*_{AII} differ from D_{AII} ?

Tracer diffusion coefficient

Intrinsic diffusion coefficients

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

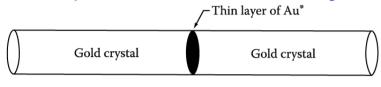
Thermodynamic factor

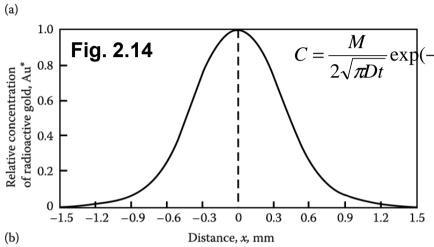
$$\tilde{D} = X_B D_A + X_A D_B = F\left(X_B D_A^* + X_A D_B^*\right) \qquad F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$$

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

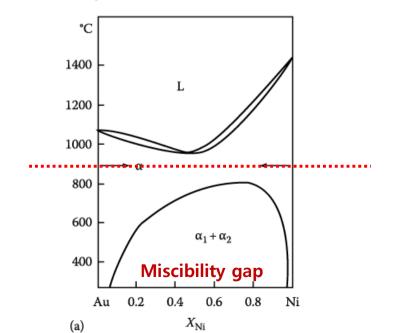
2.5 Tracer diffusion in binary alloys

1) Au* in Au or Au/X alloy





2) Au* in Au-Ni



Tracer diffusion coefficient (D^*_{Au}) in pure metal & Intrinsic diffusion coefficients (D_{Au}) in an alloy : possible to determine by radioactive tracers

$$\frac{x^2}{4Dt}$$
) \rightarrow $D = D^*_{Au}$ (tracer diffusion coefficient)

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

추적자 확산계수: 원자의 도약확률이 모든방향에서 일정

 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.

고유 확산계수: 원자의 도약확률 농도구배의 영향

If concentration gradient exhibit,

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

Au-Ni: 'dislike' each other

the rate of homogenization will therefore be slower.

Ex) Probability for the jumps made by Au atoms

in Ni-rich regions \downarrow \rightarrow "slower diffusivity"

 D^* versus D: On the other hand,

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. (M*=M)

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

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

$$D_{B}^{*} = M_{B}^{*}RT = M_{B}RT \qquad \longleftarrow \qquad D_{B} = M_{B}RT \left\{ 1 + \frac{d \ln \gamma_{B}}{d \ln X_{B}} \right\} = FM_{B}RT$$

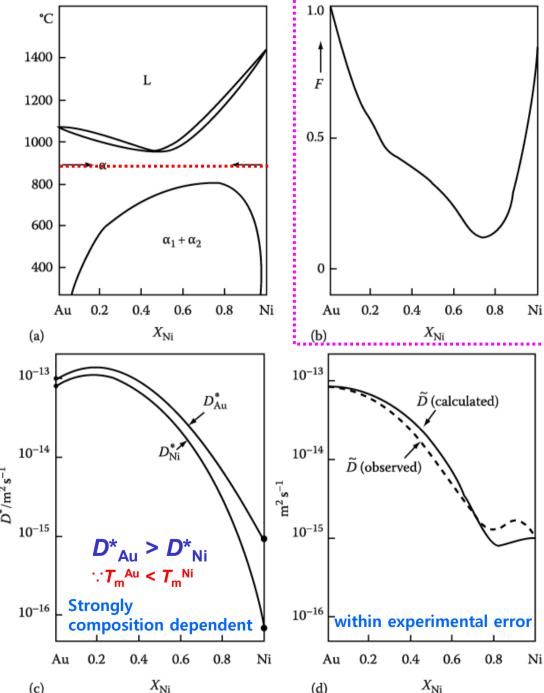
$$D_{A} = FD_{A}^{*}$$

$$D_{B} = FD_{B}^{*} \qquad \longrightarrow \qquad \tilde{D} = X_{B}D_{A} + X_{A}D_{B} = F\left(X_{B}D_{A}^{*} + X_{A}D_{B}^{*}\right)$$

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

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

2.5 Tracer diffusion in binary alloys



(d)

(c)

Fig. 2.22 Inter-diffusion 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).

1) Measured by diffusion couple experiment in Au-Ni: D

$$\overset{\mathbf{N}_{\mathbf{i}}}{\mathbf{v}} = (D_A - D_B) \frac{\partial X_A}{\partial X} = (D_B - D_A) \frac{\partial X_B}{\partial X} \implies \widetilde{D} = X_B D_A + X_A D_B$$

2) Calculated by tracer diffusion coefficient $D_{Au} \& D_{Ni}$:

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

- → The agreement is within the experimental error.
- Strong composition dependent, $Ni \uparrow \rightarrow \widetilde{D} \downarrow$

$$T_{\rm m}^{\rm Au} < T_{\rm m}^{\rm Ni}$$

Q: How do the compositions of ternary A and B alloys of diffusion couple change with time?

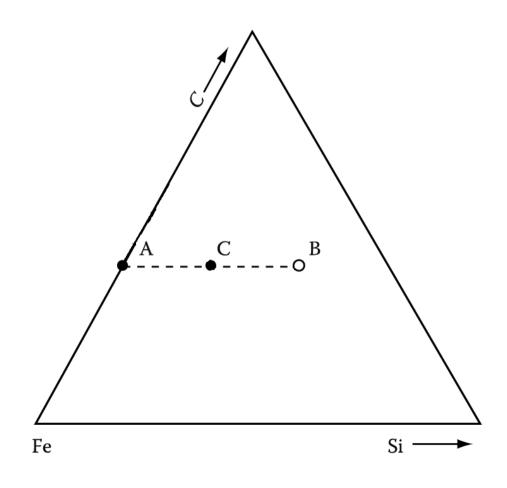
2.6 Diffusion in ternary alloys: Additional Effects

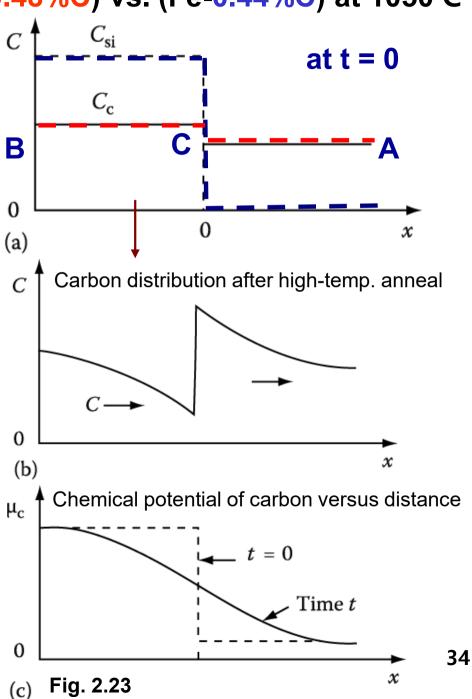
Example) Fe-Si-C system (Fe-3.8%Si-0.48%C) vs. (Fe-0.44%C) at 1050°C

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

C 이동: 고동도→ 저농도 영역 & Si-rich→Si 적은 영역

② M_{Si} (sub.) \ll M_{C} (interstitial solute), (M: mobility)





austenitized

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

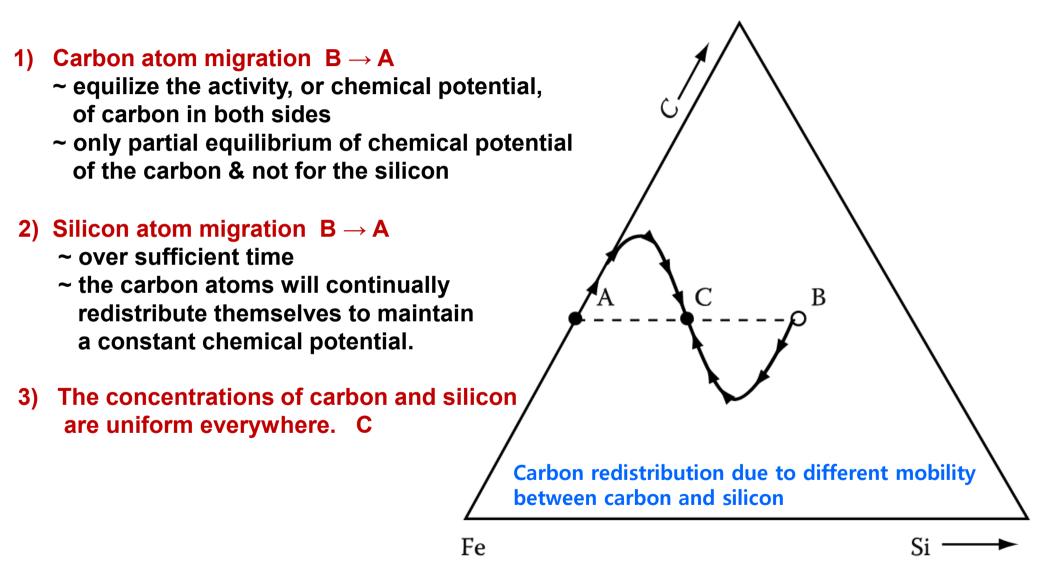


Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B) on opposite sides of the diffusion couple

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1.7.1 Full and Partial Equilibrium : Fe-M-C system

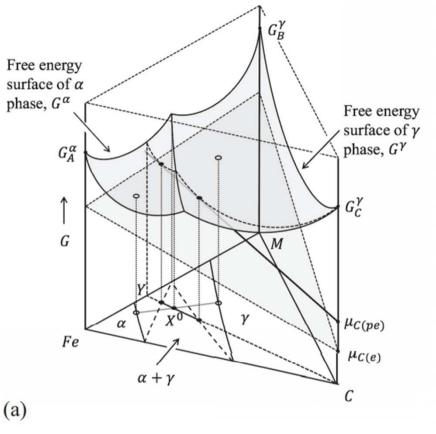
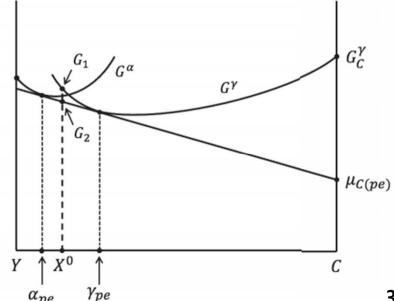


Fig. 1.49 (a) Schematic free energy diagram for the system Fe-M-C at a temperature (T2) where both the bcc α-Fe and fcc γ-Fe are stable. Fe and M are substitutional and C interstitial elements. Full equilibrium obtained by the common tangent plane to the free surfaces and para-equilibrium by the common tangent line alone compositions pointing toward C. The chemical potential of C for para-equilibrium, $\mu_{C(pe)}$ is greater than that for full equilibrium $\mu_{C(e)}$. Plan view of the corresponding Gibbs triangle. Note how tie-lines for paraequilibrium point towards the C corner of the triangle. (c) Section through the free energy surfaces for compositions with XM/Xfe constant, i.e., along the line YC.



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