Phase Transformation of Materials

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

Data selected mainly from A.M. Brown and M.F. Ashby, 'Correlations for Diffusion Constants', *Acta Metallurgica*, **28**: 1085 (1980).

Class	Metal	T_m / K	D_0 / mm^2 s^{-1}	Q / kJ mol^{-1}	Q/RT_m	$D(T_m)$ / μm^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
	Li	454	23	55.3	14.7	9.9
bcc (transition metals)	β-Tl	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*	1811	200	239.7	15.9	26
	δ-Fe*	1811	190	238.5	15.8	26
	β-Ti	1933	109	251.2	15.6	18
	β-Zr	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
	W	3683	4280	641.0	20.9	3.4
hcp*	Cd	594	∥c 5	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	∥c100	134.7	17.6	2.3
			⊥c150	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

2.3.1 Self Diffusion

For a given structure and bond type,
Q/RT_m is roughly constant; Q is roughly proportional to T_m.

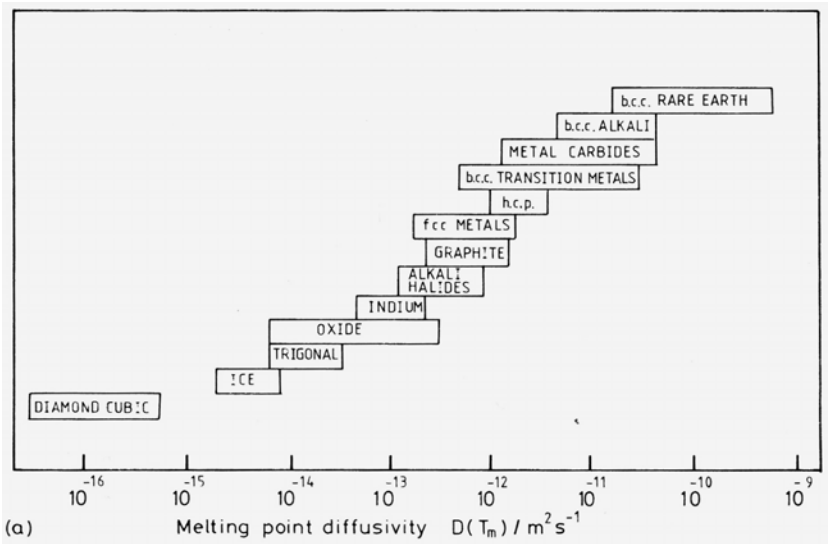
ex) for fcc and hcp, $Q/RT_m \sim 18$ and
$D(T_m) \sim 1\ \mu m^{-2}s^{-1}$ $(10^{-12}\ m^2s^{-1})$

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

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

T/T_m : homologous temperature

2.3.1 Self Diffusion



2.3.1 Self Diffusion

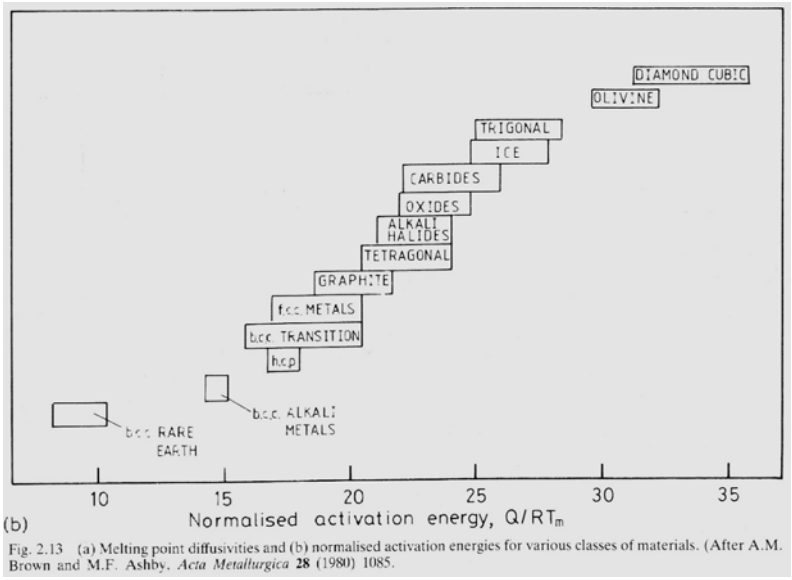


Fig. 2.13 (a) Melting point diffusivities and (b) normalised activation energies for various classes of materials. (After A.M. Brown and M.F. Ashby, *Acta Metallurgica* **28** (1980) 1085.

2.3.1 Self Diffusion

ex) At 800°C, $D_{Cu} = 5 \times 10^{-9}$ mm^{2}s^{-1}, α = 0.25 nm $\quad \Gamma_{Cu}$: ?

$$D_B = \frac{1}{6}\Gamma_B \alpha^2 \qquad \Gamma_{Cu} = 5 \times 10^5 \; jumps \; s^{-1}$$

After an hour, diffusion distance (x)? $\quad \sqrt{Dt} \sim 4\,\mu m$

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?

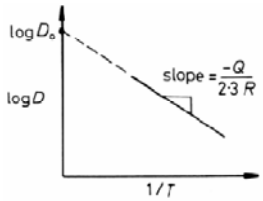


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

At 20°C, $D_{Cu} \sim 10^{-34}$ mm^{2}s^{-1} $\quad \Gamma_{Cu} \sim 10^{-20} \; jumps \; s^{-1}$

→ Each atom would make one jump every 10^{12} years!

2.3.1 Self Diffusion

Experimental Determination of D

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

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

Solution for the boundary condition

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

M : quantity m^{-2}
C : quantity m^{-3}

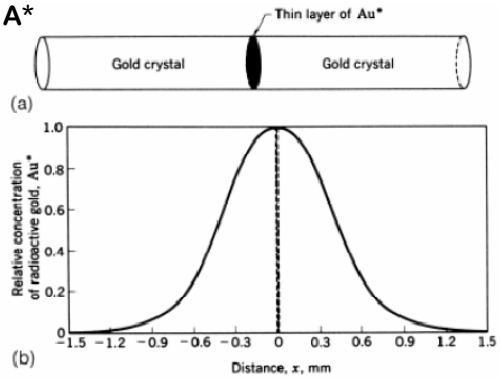


Fig. 2.14 Illustration of the principle of tracer diffusion and of the planar source method for determining the self-diffusion coefficient of gold. (a) Initial diffusion couple with planar source of radioactive gold Au*. (b) Distribution of Au* after diffusion for 100h at 920°C. (After A.G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1971.)

2.3.2 Vacancy diffusion

The jumping of atoms into vacant sites can equally well be considered as the jumping of vacancies onto atoms sites. A vacancy is always surrounded by sites to which it can jump like interstitials.

$$D_V = \frac{1}{6}\alpha^2 \Gamma_V = \frac{1}{6}\alpha^2 z\nu \exp\frac{\Delta S_m}{R} \exp\frac{-\Delta H_m}{RT}$$

Which is larger, D_V or D_A? **How much larger?**

$$D_V = D_A / X_V^e$$

This shows in fact that the diffusivity of vacancy (D_v) is many orders of magnitude greater than the diffusivity of substitutional atoms (D_A).

2.3.3 Diffusion in substitutional alloys

The rate at which solvent (A) and solute (B) atoms can move into a vacancy is not equal, and each atomic species must be given its own 'intrinsic' diffusion coefficient D_A and D_B.

Fick's *1st* law relative to the lattice:

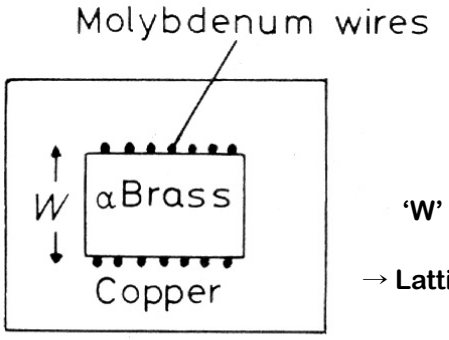
$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

J_A, J_B: Fluxes of atoms across a given lattice plane

2.3.3 Diffusion in substitutional alloys

INTERDIFFUSION



$D_{Zn} > D_{Cu}$

'W' decreases with time.

→ Lattice moves with diffusion.

Fluxes of A and B atoms across a given lattice plane

$$J_A = -D_A \frac{\partial C_A}{\partial x}, \quad J_B = -D_B \frac{\partial C_B}{\partial x} \qquad \frac{\partial C_A}{\partial x} \approx -\frac{\partial C_B}{\partial x} \qquad |J_A| > |J_B|$$

INTERDIFFUSION

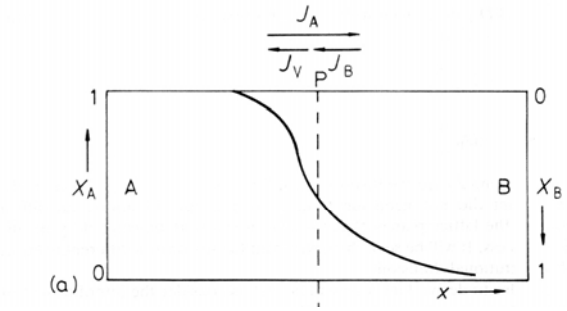
$$J_A \rightarrow J_{v,A} = -J_A$$

$$J_B \rightarrow J_{v,B} = -J_B$$

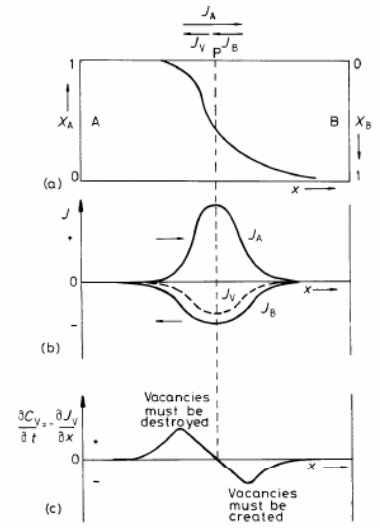
$$J_{v,(A,B)} = ?$$

$$J_{v,(A,B)} = -J_A - J_B$$

$$J_A = -J_{v,(A,B)} - J_B$$



J_A vs. x, J_B vs. x, and J_V vs. x?



$$\frac{\partial C_v}{\partial t} = -\frac{\partial J_v}{\partial x} \text{ vs. } x?$$

What would become of excess vacancy?

Fig. 2.15 Interdiffusion and vacancy flow. (a) Composition profile after interdiffusion of A and B. (b) The corresponding fluxes of atoms and vacancies as a function of position x. (c) The race at which the vacancy concentration would increase or decrease if vacancies were not created of destroyed by dislocation climb.

Interdiffusion of A and B in the sample made by welding two pieces together. (Fig. 2. 15)

Assume that the total number of atoms per unit volume is a constant (C_0), independent of composition.

$$C_o = C_A + C_B$$

C_o: Total number of atoms (A, B) per unit volume

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

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

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

Due to the difference in diffusivities, a flux difference is created. $|J_A| > |J_B|$

$$J_V + J_B = -J_A$$

$$J_V = -J_A - J_B \quad \text{(a net flux of vacancies)}$$

$$= (D_A - D_B)\frac{\partial C_A}{\partial x} \qquad \because J_B = -D_B \frac{\partial C_B}{\partial x} = D_B \frac{\partial C_A}{\partial x}$$

The rate at which the vacancy concentration would increase or decrease if vacancies were not created or destroyed by dislocation climb.

$\partial C_V / \partial t = -\partial J_V / \partial x$ (Fig. 2. 15c) $\quad cf)\ \frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}$

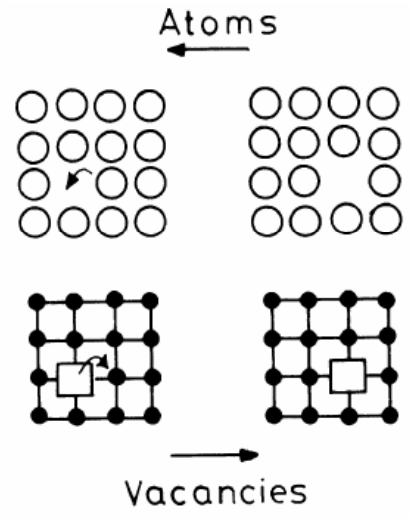


Fig. 2.16 The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.

Source or Sink for Vacancy

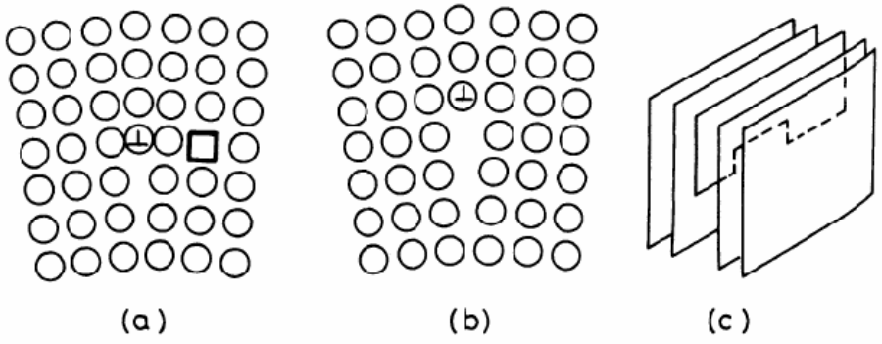


Fig. 2.17 (a) before, (b) after: a vacancy is absorbed at a jog on an edge dislocation (positive climb). (b) before, (a) after: a vacancy is created by negative limb of an edge dislocation. (c) Perspective drawing of a jogged edge dislocation.

If dislocation climbs continue to occur, what would happen?

Problems that will be asked in the next class

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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.

For this purpose, what would be the appropriate diffusivity for substitutional alloys?
Can you derive it?