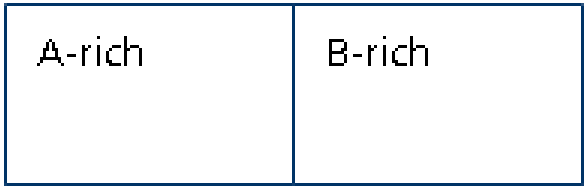
Diffusion in Substitutional Alloys

❖ **Binary substitutional diffusion**



D_A, D_B (intrinsic diffusion coefficient): diffusion relative to the lattice

J_A, J_B : across a given lattice plane (moving)

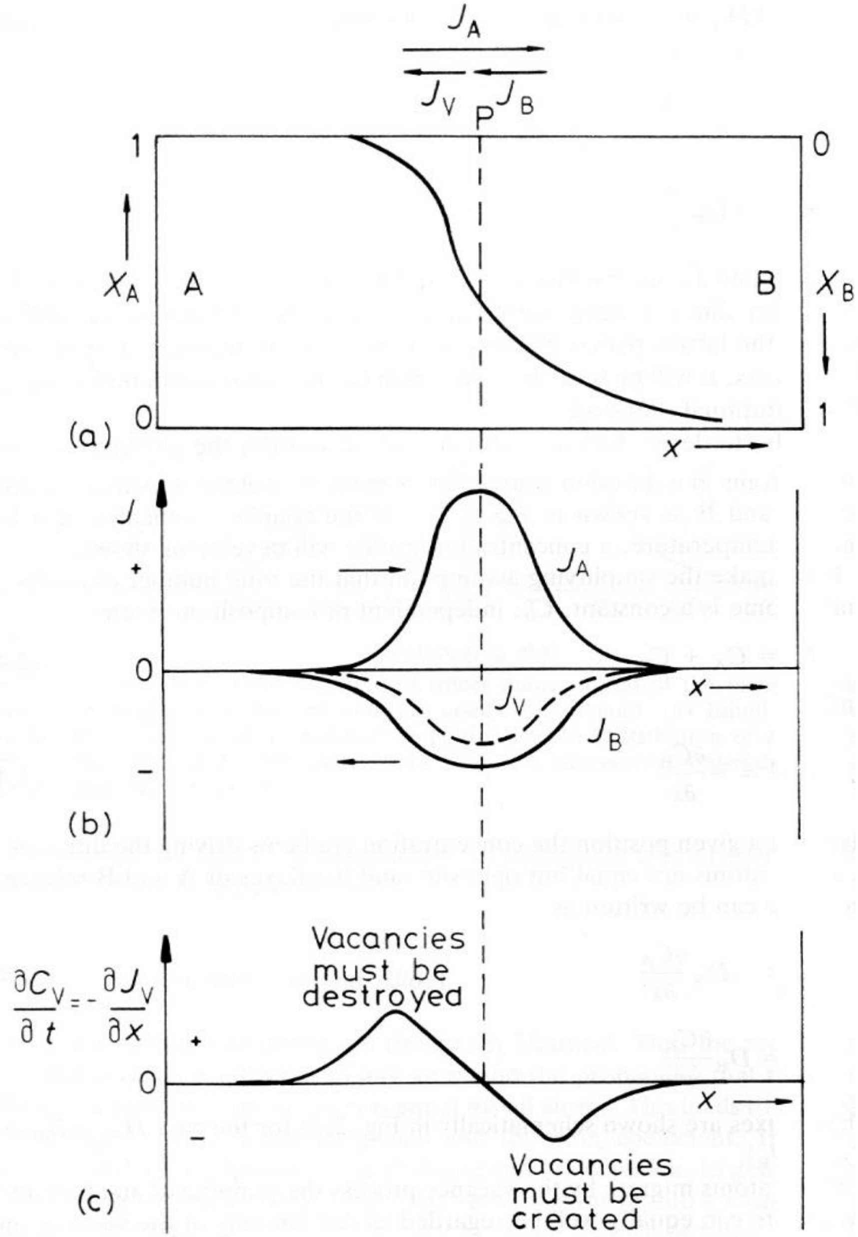
$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad , \quad J_B = -D_B \frac{\partial C_B}{\partial x}$$

Total # of atoms/unit volume = C_0 (constant, independent of composition)

Then, $C_o = C_A + C_B$

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

$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad , \quad J_B = +D_B \frac{\partial C_A}{\partial x}$$



$$J_A = -D_A \frac{\partial C_A}{\partial x} \ , \quad J_B = +D_B \frac{\partial C_A}{\partial x}$$

If $D_A > D_B$, then $J_A > J_B$

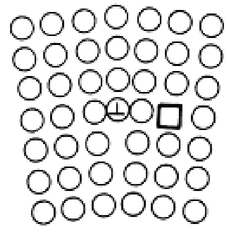
$$J_v = -J_A - J_B$$

$$= (D_A - D_B) \frac{\partial C_A}{\partial x} \qquad \ldots\ldots \ (1)$$

variation in J_v across the diff. couple

Supersaturated vacancies

$\rightarrow$ Equilibrium should be maintained by dislocation motion

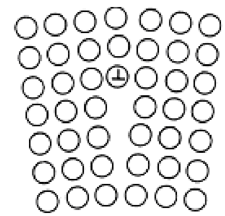


(a)

dislocation climb-up

$\downarrow$

lattice plane **destroyed**

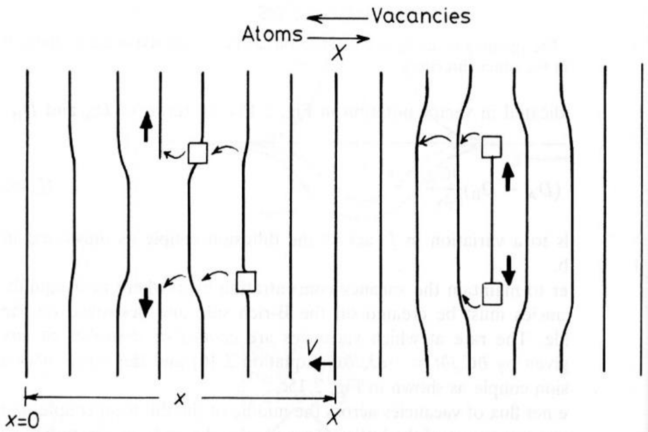


(b)

dislocation climb-down

$\downarrow$

lattice plane **created**



$\Rightarrow$ **Movement of lattice**

- Velocity of the lattice plane : v
- Volume swept out $(Av\delta t)$ contains $(Av\delta tC_0)$ atoms

  = total # of vacancy crossing the plane $(J_v A\delta t)$

$$\therefore J_v = C_0 v \qquad \ldots\ldots \text{(2)}$$

from (1) and (2)

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

$$X_A \left(= \frac{C_A}{C_0} = mole\ \ fraction\ of\ \ A\ \right)$$

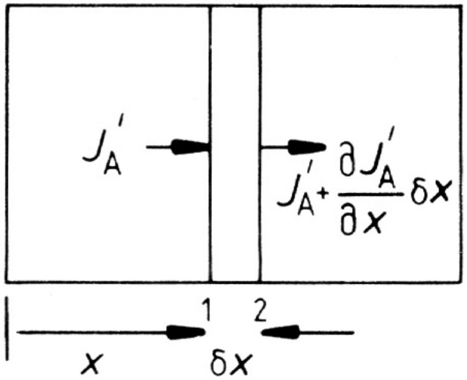
$$v = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

Practical question

⑴ Time for homogenization

⑵ Change in composition at a fixed position relative to the end of specimen

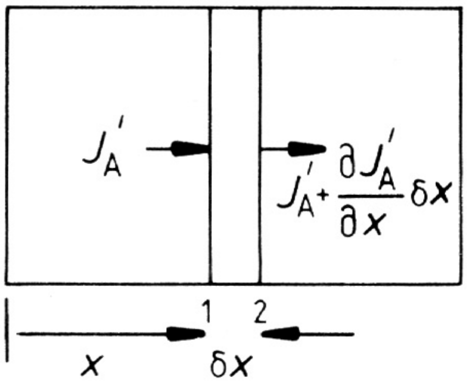
- **Variation in J_v across the diffusion couple.**



Total flux of A across a stationary plane with respect to specimen

= a diffusing flux ($J_A = -D_A \frac{\partial C_A}{\partial x}$) w.r.t. lattice

+ flux due to lattice (vC_A)



Total flux of A across a stationary plane with respect to specimen

= a diffusing flux ($J_A = -D_A \frac{\partial C_A}{\partial x}$) w.r.t. lattice

+ flux due to lattice (vC_A)

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

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

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

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

$$J_A' = -\tilde{D}\frac{\partial C_A}{\partial x} \quad , \quad \tilde{D} = (X_B D_A + X_A D_B)$$

→ **Interdiffusion coefficient**

Likewise $$J_B' = -\tilde{D}\frac{\partial C_B}{\partial x} = \tilde{D}\frac{\partial C_A}{\partial x}$$ i.e. $$J_{B'} = J_{A'}$$

Using continuity equation,

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

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

Fick's 2nd law for substitutional alloy Darken's Eq

As long as the range of comp. is small

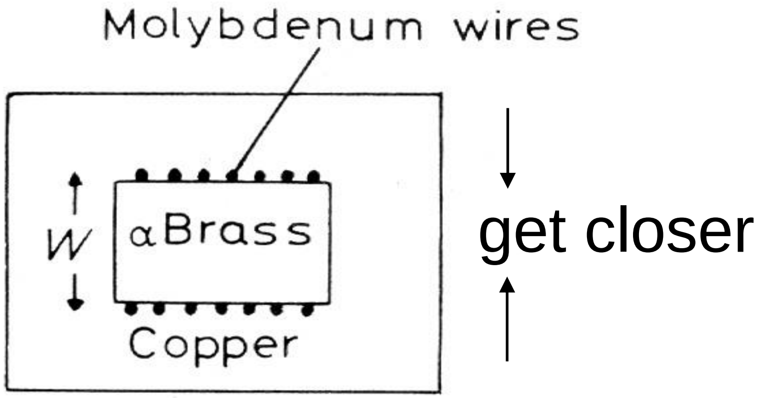
$$X_A D_B + X_B D_A \approx D_B \quad , \qquad \tilde{D} \neq f(comp.)$$

to know D_A, D_B , need to know v (by marker)

with known v & $\tilde{D}$ $\Rightarrow D_A, D_B$

$\tilde{D} = \tilde{D}_0 \exp(-\frac{Q}{RT})$ likewise, $D_A = D_{A0} \exp(-\frac{Q_A}{RT})$

Kirkendall Effect

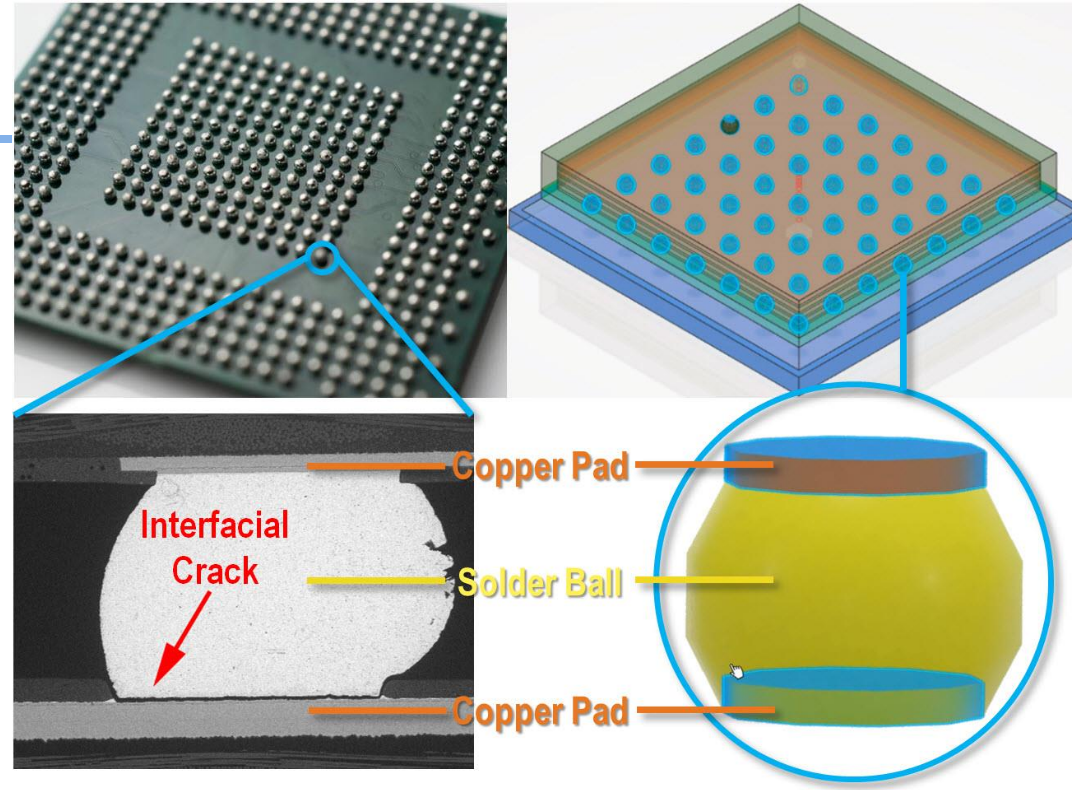


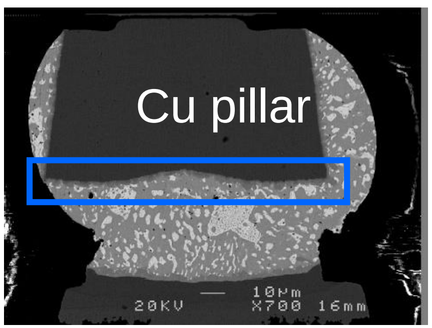
- $D_{Zn} > D_{cu}$
- Lower melting point materils (low atomic size) has higher D.

1. For a given crystal structure, $\tilde{D}(T_m)$=const. in if B was added to A, results in lower T_{m2} than $\tilde{D}(T_{m2})$ (after B added) will be higher than before.

2. Open structure →higher diff.
   Interstitial C in Fe $D_c^{\alpha} / D_c^{\gamma} \sim 100$
   Sub. Self diff $D_{Fe}^{\alpha} / D_{Fe}^{\gamma} \sim 100$

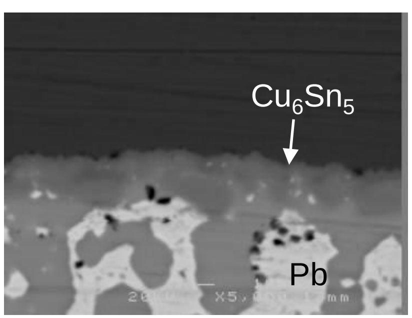
Kirkendall void





120℃

As reflowed



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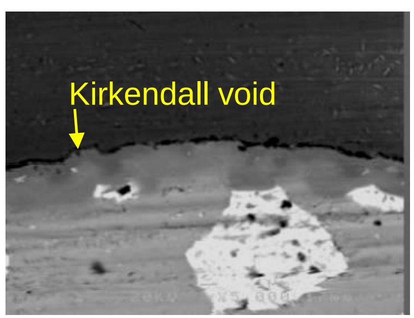

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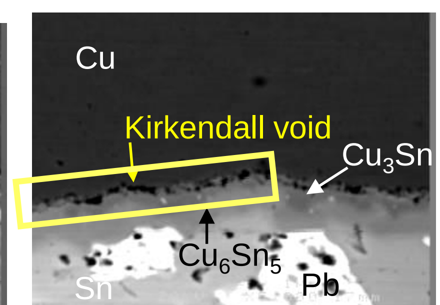

- Kirkendall voids formed at the interface between Cu and solder.