CHAPTER 5: DIFFUSION IN SOLIDS

ISSUES TO ADDRESS...

• How does diffusion occur?

• Why is it an important part of processing?

• How can the rate of diffusion be predicted for some simple cases?

• How does diffusion depend on structure and temperature?
DIFFUSION DEMO

- Glass tube filled with water.
- At time $t = 0$, add some drops of ink to one end of the tube.
- Measure the diffusion distance, $x$, over some time.
- Compare the results with theory.
**DIFFUSION: THE PHENOMENA (1)**

- **Interdiffusion**: In an alloy, atoms tend to migrate from regions of large concentration.

Initially:

- **Cu** (100%) and **Ni** (0%) concentration profiles.

After some time:

- Concentration profiles have changed, indicating diffusion has occurred.

Adapted from Figs. 5.1 and 5.2, *Callister 6e*.
DIFFUSION: THE PHENOMENA (2)

• **Self-diffusion**: In an elemental solid, atoms also migrate.

Label some atoms

After some time
**DIFFUSION MECHANISMS**

**Substitutional Diffusion:**

- applies to substitutional impurities
- atoms exchange with vacancies
- rate depends on:
  - number of vacancies
  - activation energy to exchange.

![Diagram of diffusion processes](image)

increasing elapsed time
DIFFUSION SIMULATION

• Simulation of interdiffusion across an interface:

• Rate of substitutional diffusion depends on:
  --vacancy concentration
  --frequency of jumping.

(Courtesy P.M. Anderson)
INTERSTITIAL SIMULATION

• Applies to interstitial impurities.
• More rapid than vacancy diffusion.
• Simulation:
  --shows the jumping of a smaller atom (gray) from one interstitial site to another in a BCC structure. The interstitial sites considered here are at midpoints along the unit cell edges.

(Courtesy P.M. Anderson)
PROCESSING USING DIFFUSION (1)

• Case Hardening:
  --Diffuse carbon atoms into the host iron atoms at the surface.
  --Example of interstitial diffusion is a case hardened gear.

• Result: The "Case" is
  --hard to deform: C atoms "lock" planes from shearing.
  --hard to crack: C atoms put the surface in compression.

Fig. 5.0, Callister 6e. (Fig. 5.0 is courtesy of Surface Division, Midland-Ross.)
PROCESSING USING DIFFUSION (2)

• **Doping** Silicon with P for n-type semiconductors:

• **Process:**

  1. Deposit P rich layers on surface.
  2. Heat it.
  3. Result: Doped semiconductor regions.

![Magnified image of a computer chip](image)

Fig. 18.0, Callister 6e.
• Flux:

\[ J = \frac{1}{A} \frac{dM}{dt} \Rightarrow \left[ \frac{\text{kg}}{\text{m}^2 \text{s}} \right] \text{ or } \left[ \frac{\text{atoms}}{\text{m}^2 \text{s}} \right] \]

• Directional Quantity

• Flux can be measured for:
  -- vacancies
  -- host (A) atoms
  -- impurity (B) atoms
CONCENTRATION PROFILES & FLUX

• Concentration Profile, \( C(x) : [\text{kg/m}^3] \)

\[ \text{Cu flux} \quad \text{Ni flux} \]

Concentration of Cu [\text{kg/m}^3]

Concentration of Ni [\text{kg/m}^3]

Position, \( x \)

• Fick's First Law:

\[ J_x = -D \frac{dC}{dx} \]

flux in \( x \)-dir. [\text{kg/m}^2 \cdot \text{s}]

Diffusion coefficient [\text{m}^2/\text{s}]

concentration gradient [\text{kg/m}^4]

• The steeper the concentration profile, the greater the flux!

Adapted from Fig. 5.2(c), Callister 6e.
**STABLE STATE DIFFUSION**

- **Steady State**: the concentration profile doesn't change with time.

- **Apply Fick's First Law**:  
  \[ J_x = -D \frac{dC}{dx} \]

- **If** \( J_x(\text{left}) = J_x(\text{right}) \), then  
  \[ \frac{dC}{dx}_{\text{left}} = \frac{dC}{dx}_{\text{right}} \]

- **Result**: the slope, \( dC/dx \), must be constant (i.e., slope doesn't vary with position)!
EX: STEADY STATE DIFFUSION

- Steel plate at 700C with geometry shown:

- Q: How much carbon transfers from the rich to the deficient side?

\[
J = -D \frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9} \text{ kg/m}^2\text{s}
\]

Adapted from Fig. 5.4, Callister 6e.
NON STEADY STATE DIFFUSION

• Concentration profile, \( C(x) \), changes with time.

• To conserve matter:

\[
\frac{J(\text{right}) - J(\text{left})}{dx} = -\frac{dC}{dt}
\]

\[
\frac{dJ}{dx} = -\frac{dC}{dt}
\]

• Fick's First Law:

\[
J = -D \frac{dC}{dx}
\]

or

\[
\frac{dJ}{dx} = -D \frac{d^2C}{dx^2}
\]

(if \( D \) does not vary with \( x \))

• Governing Eqn.:

\[
\frac{dC}{dt} = D \frac{d^2C}{dx^2}
\]
EX: NON STEADY STATE DIFFUSION

• Copper diffuses into a bar of aluminum.

• General solution:

\[
\frac{C(x, t) - C_0}{C_S - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]

"error function"

Values calibrated in Table 5.1, *Callister 6e.*

Adapted from Fig. 5.5, *Callister 6e.*
PROCESSING QUESTION

• Copper diffuses into a bar of aluminum.
• 10 hours at 600°C gives desired C(x).
• How many hours would it take to get the same C(x) if we processed at 500°C?

Key point 1: $C(x,t_{500°C}) = C(x,t_{600°C})$.
Key point 2: Both cases have the same $C_o$ and $C_s$.

• Result: $Dt$ should be held constant.

\[
\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf} \left( \frac{x}{\sqrt{2Dt}} \right) \rightarrow (Dt)_{500°C} = (Dt)_{600°C}
\]

\[
5.3 \times 10^{-13} \text{m}^2/\text{s} \quad 10 \text{hrs}
\]

• Answer:

\[
t_{500°C} = \frac{(Dt)_{600°C}}{D_{500°C}} = 110 \text{hr}
\]

Note: values of D are provided here.
• The experiment: we recorded combinations of $t$ and $x$ that kept $C$ constant.

\[
\frac{C(x_i, t_i)}{C_s} = \frac{C_o}{C} \approx 1 - \text{erf} \left( \frac{x_i}{2 \sqrt{D t_i}} \right) = \text{(constant here)}
\]

• Diffusion depth given by:

\[
x_i \propto \sqrt{D t_i}
\]
• Experimental result: $x \sim t^{0.58}$
• Theory predicts $x \sim t^{0.50}$
• Reasonable agreement!
DIFFUSION AND TEMPERATURE

- Diffusivity increases with T.

\[ D = D_0 \exp \left( \frac{Q_d}{RT} \right) \]

- Experimental Data:

  \[ D \text{ has exp. dependence on } T \]
  
  Recall: Vacancy does also!

  \[ D_{\text{interstitial}} >> D_{\text{substitutional}} \]

  - C in \( \alpha \)-Fe
  - C in \( \gamma \)-Fe
  - Zn in Cu
  - Fe in \( \alpha \)-Fe
  - Fe in \( \gamma \)-Fe
  - Al in Al
  - Cu in Cu

  Adapted from Fig. 5.7, Callister 6e. (Date for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)
SUMMARY: STRUCTURE & DIFFUSION

Diffusion FASTER for...

• open crystal structures
• lower melting T materials
• materials w/secondary bonding
• smaller diffusing atoms
• cations
• lower density materials

Diffusion SLOWER for...

• close-packed structures
• higher melting T materials
• materials w/covalent bonding
• larger diffusing atoms
• anions
• higher density materials
ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: