CHAPTER 4:
IMPERFECTIONS IN SOLIDS (Defects)

ISSUES TO ADDRESS...

• What types of defects arise in solids?

• Can the number and type of defects be varied and controlled?

• How do defects affect material properties?

• Are defects desirable or undesirable?
TYPES OF IMPERFECTIONS

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms
- Dislocations
- Grain Boundaries

Point defects

Line defects

Area defects
POINT DEFECTS

- **Vacancies**: vacant atomic sites in a structure.
- **Self-Interstitials**: "extra" atoms positioned between atomic sites.
Point Defects: Vacancies and Interstitials

- Vacancy: Missing Atom
- Interstitial: Extra atom inside lattice
Point Defect: Foreign atom, (impurity, dopant, solute)

Can be

• Substitutional (occupying lattice site)
• Interstitial

Often depends upon relative sizes
Quantitative Calculation of Point Defects

- Point Defects increase randomness in crystals, and therefore, “Entropy”.

- To maximize entropy, all crystals will have an equilibrium concentration of point defects for thermodynamic reasons

- This concentration can be deduced from thermodynamic principles
EQUILIBRIUM CONCENTRATION OF POINT DEFECTS

Boltzmann's constant

\( \frac{N_D}{N} = \exp \left( \frac{-Q_D}{kT} \right) \)

- No. of defects
- Activation energy
- Temperature

No. of potential defect sites.

Each lattice site is a potential vacancy site.

Boltzmann's constant

- \( 1.38 \times 10^{-23} \text{ J/atom K} \)
- \( 8.62 \times 10^{-5} \text{ eV/atom K} \)
MEASURING ACTIVATION ENERGY

• We can get $Q$ from an experiment.

• Measure this...

\[
\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)
\]

• Replot it...

\[
\ln\frac{N_D}{N}
\]

defect concentration
ESTIMATE VACANCY CONC.

- Find the equil. # of vacancies in 1m$^3$ of Cu at 1000C.
- Given:
  \[ \rho = 8.4 \text{ g/cm}^3 \quad A_{\text{Cu}} = 63.5\text{g/mol} \]
  \[ Q_V = 0.9\text{eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mole} \]
ESTIMATING VACANCY CONC.

- Find the equil. # of vacancies in 1m³ of Cu at 1000°C.

- Given:
  \( \rho = 8.4 \text{ g/cm}^3 \quad \text{ACu} = 63.5 \text{g/mol} \)
  \( Q_V = 0.9 \text{eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mole} \)

\[
\frac{N_D}{N} = \exp\left(-\frac{Q_D}{kT}\right) = 2.7 \cdot 10^{-4}
\]

For 1m³, \( N = \rho \times \frac{N_A}{\text{ACu}} \times 1\text{m}³ = 8.0 \times 10^{28} \text{ sites} \)

- Answer:
  \( N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28} \text{ sites} = 2.2 \times 10^{25} \text{ vacancies} \)
Two outcomes if impurity (B) added to host (A):

- **Solid solution** of B in A (i.e., random dist. of point defects)

- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)

**Substitutional solid soln.** (e.g., Cu in Ni)

**Interstitial solid soln.** (e.g., C in Fe)

Second phase particle -- different **composition**

-- often different structure.
Conditions for substitutional solid solution (S.S.)

- **W. Hume – Rothery rule**
  - 1. $\Delta r$ (atomic radius) < 15%
  - 2. Proximity in periodic table
    - i.e., similar electronegativities
  - 3. Same crystal structure for pure metals
  - 4. Valency
    - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency
Imperfections in Metals (iii)

Application of Hume-Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Radius (nm)</th>
<th>Crystal Structure</th>
<th>Electronegativity</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.1278</td>
<td>FCC</td>
<td>1.9</td>
<td>+2</td>
</tr>
<tr>
<td>C</td>
<td>0.071</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.046</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.1445</td>
<td>FCC</td>
<td>1.9</td>
<td>+1</td>
</tr>
<tr>
<td>Al</td>
<td>0.1431</td>
<td>FCC</td>
<td>1.5</td>
<td>+3</td>
</tr>
<tr>
<td>Co</td>
<td>0.1253</td>
<td>HCP</td>
<td>1.8</td>
<td>+2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1249</td>
<td>BCC</td>
<td>1.6</td>
<td>+3</td>
</tr>
<tr>
<td>Fe</td>
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<td>+2</td>
</tr>
<tr>
<td>Ni</td>
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<td>FCC</td>
<td>1.8</td>
<td>+2</td>
</tr>
<tr>
<td>Pd</td>
<td>0.1376</td>
<td>FCC</td>
<td>2.2</td>
<td>+2</td>
</tr>
<tr>
<td>Zn</td>
<td>0.1332</td>
<td>HCP</td>
<td>1.6</td>
<td>+2</td>
</tr>
</tbody>
</table>

Table on p. 118, *Callister & Rethwisch 8e.*
Impurities in Solids

Specification of composition

- **weight percent**
  \[ C_1 = \frac{m_1}{m_1 + m_2} \times 100 \]
  
  \( m_1 = \text{mass of component 1} \)

- **atom percent**
  \[ C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \]
  
  \( n_{m1} = \text{number of moles of component 1} \)
**COMPOSITION**

**Definition:** Amount of impurity (B) and host (A) in the system.

**Two descriptions:**

- **Weight %**
  
  \[ C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100 \]

- **Atom %**
  
  \[ C'_B = \frac{\# \text{ atoms of B}}{\text{total # atoms}} \times 100 \]

- **Conversion between wt % and at% in an A-B alloy:**
  
  \[ C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100 \]

- **Basis for conversion:**

  - mass of B = moles of B \times A_B
  - mass of A = moles of A \times A_A

  \[ C'_B = \frac{C_B/A_B}{C_A/A_A + C_B/A_B} \]

  atomic weight of B

  atomic weight of A

Mukhopadhyay...ME370
A certain mass of alloy contains 33g of Cu and 47g of Zn
Atomic Wt. of Cu is 63.55 and Zn is 65.39

Calculate atomic composition.
Likewise, for Zn

\[
n_{m_{\text{Zn}}} = \frac{47 \text{ g}}{65.39 \text{ g/mol}} = 0.719 \text{ mol}
\]

Now, use of Equation (4.5) yields

\[
C_{\text{Cu}}' = \frac{n_{m_{\text{Cu}}}}{n_{m_{\text{Cu}}} + n_{m_{\text{Zn}}}} \times 100
\]

\[
= \frac{0.519 \text{ mol}}{0.519 \text{ mol} + 0.719 \text{ mol}} \times 100 = 41.9 \text{ at%}
\]

Also,

\[
C_{\text{Zn}}' = \frac{0.719 \text{ mol}}{0.519 \text{ mol} + 0.719 \text{ mol}} \times 100 = 58.1 \text{ at%}
\]
Alloy has 5 at% Cu and 95 at% Pt
Atomic weights are: Cu – 63.55; Pt – 195.08

Calculate wt% of this alloy
\[
C_{Cu} = \frac{C'_{Cu} A_{Cu}}{C'_{Cu} A_{Cu} + C'_{Pt} A_{Pt}} \times 100
\]
\[
= \frac{(5)(63.55 \text{ g/mol})}{(5)(63.55 \text{ g/mol}) + (95)(195.08 \text{ g/mol})} \times 100
\]
\[
= 1.68 \text{ wt%}
\]

\[
C_{Pt} = \frac{C'_{Pt} A_{Pt}}{C'_{Cu} A_{Cu} + C'_{Pt} A_{Pt}} \times 100
\]
\[
= \frac{(95)(195.08 \text{ g/mol})}{(5)(63.55 \text{ g/mol}) + (95)(195.08 \text{ g/mol})} \times 100
\]
\[
= 98.32 \text{ wt%}
\]
LINE DEFECTS: DISLOCATIONS

- are line defects,
- cause slip between crystal plane when they move,
- produce permanent (plastic) deformation.

Schematic of a Zinc (HCP):
- before deformation
- after tensile elongation

slip steps
Line Defects-Dislocations
Edge Dislocation

**Figure 4.3** The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1976, p. 153.)
Line Defects-Dislocations
Screw Dislocation

Figure 4.4 (a) A screw dislocation within a crystal. (b) The screw dislocation in (a) as viewed from above. The dislocation line extends along line $AB$. Atom positions above the slip plane are designated by open circles, those below by solid circles.

(Figure b from W. T. Read, Jr., Dislocations in Crystals, McGraw-Hill Book Company, New York, 1953.)
INCREMENTAL SLIP

• Dislocations slip planes *incrementally*...
• The dislocation line (the moving red dot)...
  ...separates slipped material on the left from unslipped material on the right.

Simulation of dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)
BOND BREAKING AND REMAKING

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.

Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)
• Structure: close-packed planes & directions are preferred.

view onto two close-packed planes.

close-packed directions

close-packed plane (bottom) close-packed plane (top)
Dislocations and Crystal Structure

- Identify the closest packed Plane in FCC
- How many such planes are there in a given crystal?

- Identify the closest packed direction in FCC
- How many such directions are on each plane?
  [These together determine how many “slip systems” for dislocation to move]
Dislocations and Crystal Structure

- Identify the closest packed Plane in HCP
- How many such planes are there in a given crystal?

- Identify the closest packed direction in HCP
- How many such directions are on each plane?

[How many “slip systems” for dislocation to move? Compare to FCC]
Comparison among crystal structures:
FCC: many close-packed planes/directions;
HCP: only one plane, 3 directions;
BCC: none

Results of tensile testing.

Mg (HCP)

Al (FCC)
Grain boundaries:
- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- impede dislocation motion.

Schematic

Adapted from Fig. 4.7, Callister 6e.
Methods to Observe/Study Defects

- Point Defects are very subtle: Properties related to defects (such as electrical conductivity, density, optical properties etc.) need to be monitored.
- Line Defects related to ductility and plastic deformation in metals. Directly observable by Transmission Electron Microscopy.
- Grain Boundaries easier to observe by optical or scanning electron microscopy (discussed earlier).
Transmission Electron Microscope Image of Dislocations

**Figure 4.6** A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations. 51,450×. (Courtesy of M. R. Plichta, Michigan Technological University.)