§ 4 Imperfection in solids

Imperfection → point defects: vacancies & self-interstitials, impurity
Linear defects: dislocations
Plane defects: interfacial, external surface, grain boundaries, twin boundaries)
Bulk or volume defects: stalking faults
Pores, crack

Point defects (點缺陷)

§4.2 vacancies & self-interstitials

Vacancies: one normally occupied from which an atom is missing.

Principles of thermal dynamics: 必須要有 vacancies to increase entropy.
Equilibrium number of vacancies $N_v$.

$$N_v = N \exp \left(-\frac{Q_v}{kT} \right)$$ (function of material & temperature)

$N$: total # of atomic site
$Q_v$: energy required for the formation of vacancy
$K$: Boltzman’s constant = 1.38*10^{-23} J/atom-k

Ex. Equilibrium number of vacancies for Cu at 1000 °C

$Q_v = 0.9$ eV/atom, $w = 63.5$ g/mol

$$N = \frac{N_A \rho}{A_{Cu}} = \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)10^6 \text{ cm}^3/m^3}{63.5 \text{ g/mol}} = 8.0 \times 10^{28} \text{ atom/m}^3$$

$$N_v = N \exp \left(-\frac{Q_v}{kT} \right) = 8.0 \times 10^{28} \cdot \exp \left(\frac{0.9 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/k} \times 1273} \right) = 2.2 \times 10^{25} \text{ atom/m}^3$$

$N_v \approx 10^{-4}$ at its melting point.

☆ Types of point defects

(1) Vacancy
(2) Divacancy
(3) Missing ions
(4) Frenkel defect: A cation vacancy & a cation interstitial pair
(5) Self-interstitial: An atom from the crystal that is crowded into an interstitial
Shottky defect (ion pair vacancy) 为了维持电中性

Fig. 13.20

§ 4.3 Impurity in solids

Purity < 9.9999% \(10^{22} - 10^{23}\) impurity atom/m³

Alloys: material in which impurity atoms are added intentionally to tailor its properties.
Solder alloys: Pb₃₇Sn₆₃

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>207°C</td>
</tr>
<tr>
<td>Sn</td>
<td>232°C</td>
</tr>
<tr>
<td>Pb₃₇Sn₆₃</td>
<td>183°C</td>
</tr>
</tbody>
</table>

Solid solution (new second phase) Vs compound 化合物
Fe₃C (C, α phase, β phase)
Solute: minor component
Solvent

Impurity point defects
(a) Substitutional type(置换型): solute(impurity) atoms substitute for the host atoms
(b) Interstitial type(间隙型): solute atoms fill the voids or interstices among the host atoms

The requirements to form substitutional impurities:
(1) Atomic size difference \(<±15\%\)
(2) Same crystal structure
(3) Electro negativity (电负性)
(4) A metal with higher valences can be dissolved easier than the lower one

Ex. Ni/Cu \(r_{\text{Cu}} = 1.278\ Å, r_{\text{Ni}} = 1.246\ Å\), 可形成 100%互溶.
§ 4.4 Dislocation 差排

Dislocation: a linear or 1-D defect around which some of the atoms are mis-aligned.

Dislocation line:
(a) Edge dislocation
(b) Screw dislocation
Mixed dislocation (edge + screw)
Dislocation is defined by dislocation line & Burgers vector

(b) Screw dislocation
Fig. 4.4 center of the spiral
(c) Mixed dislocation

Figure 4.5

(a) Schematic representation of a dislocation that has edge, screw, and mixed character.
(b) Top view, where open circles denote atom positions above the slip plane. Solid circles, atom positions below.
At point A, the dislocation is pure screw, while at point B, it is pure edge.
For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw.
[Figure (b) from W. T. Read, Jr., Dislocations in Crystals, McGraw-Hill Book Company, New York, 1953.]
Burgers vector: describe the magnitude & direction of a dislocation.

Draw: Burgers circuit include dislocation line, $3 \rightarrow 3 \downarrow$ & 繞在 perfect lattice point 上
For perfect crystal, 會回到原點
For non-perfect crystal, 無法回到原點, (1) For edge dislocation: $b \perp$ dislocation line
$b // $ slip direction of dislocation line
(2) For screw dislocation: $b // $ dislocation line
$b \perp $ slip direction $\rightarrow$ explain
(3) Mixed: neither $\perp$ nor $//$

Theoretical value of fracture strength
But in real life $\sim$100000 times less than this value

§ 4.5 Interfacial defects
1. External surface: bonds of the surface atom are not satisfy
2. Grain boundary: low-angle G.B few degree
   High-angle G.B

![Interfacial defects diagram](image)

One simple low angle – tilt boundary

![Tilt boundary diagram](image)
3. Twin boundary specific mirror lattice symmetry
   FCC metals
   Annealing twin: fcc
   Deformation: bcc, hcp

   A B C A B C A B C
   A B C A B C B A C B A C

4. Stacking faults

   ABCABCABC
   ABCABC

§ 4.6 Bulk (volume) defect
Pores, cracks

§ 4.9 Microscopic Examination
Optical microscopic
Electronic microscopic

(1) Optical
   Fig. 4.11

   Grind
   Polishing
   Etching

(2) Electronic microscopy
   High energy electron: wavelength 0.03 Å
   (a) Scanning electron microscope (SEM)
       Magnifications: 10~5000X
   (b) Transmission electron microscopic (TEM)
       100000X
   (c) Scanning probe microscope
       10^6X
§ 4.10 Grain size determination
ASTM (American Society for Testing & Material)
Grain size number $n$
$N = 2^{n-1}$
# of grain in 1”x1” at 100x photo

☆ How to measure vacancy concentration?
\[ \frac{\Delta n_v}{n} = 3 \left( \frac{\Delta L}{L} - \frac{\Delta a}{a} \right) \]
\(\Delta L \cdot \Delta a\) are linear changes.

→ near the melting point
\[ \frac{\Delta n_v}{n} \approx 10^{-4} \]