Introduction to Engineering Materials
ENGR2000
Chapter 4: Imperfections in Solids
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Learning Objectives

1. Describe both vacancy and self interstitial defects
2. Calculate the equilibrium number of vacancies in a material at some specified temperature
3. Name the two types of solid solutions, provide a brief written definition and/or sketch
4. Given the mass and atomic weights of two or more elements in a metal alloy, calculate the weight percent or atom percent of each element
The **structure** of a material  
- arrangement of its internal components

- **Subatomic structure**  
  - Electrons & nuclei within the individual atoms

- **Atomic structure**  
  - Atoms & molecules within the material

- **Microscopic structure**  
  - Large groups of atoms aggregated together

- **Macroscopic structure**  
  - Elements that may be viewed with the naked eye
4.1 Introduction

- Imperfections or defects in crystal structures
  - ‘mistakes’ in atomic arrangement
  - single atoms (point defects)
  - rows of atoms (linear defects)
  - planes of atoms (planar defects)
  - 3D clusters of atoms (volume defects)
• **Vacancies:** Point Defects in Metals
  - vacant atomic sites in a structure.

• **Self-Interstitials:**
  - "extra" atoms positioned between atomic sites.
4.2 Vacancies and Self-Interstitials

- **Self-interstitials in metals**
  - Atom from the crystal is crowded into an interstitial site
    - Introduces relatively large distortions  Why?
    - How probable would you expect this to be?

Which is more likely a self interstitial site or a vacancy? Why?
Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

\[
\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)
\]

- No. of defects
- Activation energy
- Temperature

Boltzmann's constant
- (1.38 x 10^{-23} \text{ J/atom-K})
- (8.62 \times 10^{-5} \text{ eV/atom-K})

Each lattice site is a potential vacancy site

- No. of defects
- No. of potential defect sites
Measuring Activation Energy

- We can get $Q_v$ from an experiment.

- Measure this...

- Replot it...

\[
\frac{N_v}{N} = \exp \left( - \frac{Q_v}{kT} \right)
\]

- $\frac{N_v}{N}$: exponential dependence!
- $\ln \frac{N_v}{N}$: slope $\frac{Q_v}{k}$

defect concentration
Example 4.1

- Calculate the equilibrium number of vacancies per cubic meter for Cu at 1000 °C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density for Cu are 63.5 g/mol and 8.4 g/cm³, respectively.
Given:

\[ T = 1273 \, K, Q_v = 0.9 \, eV / \text{atom}, A_{Cu} = 63.5 \, g / \text{mol}, \rho = 8.4 \, g / cm^3 \]

# of atomic sites per m³ i.e. per unit volume:

\[ \frac{n}{V} = \frac{N_A \rho}{A_{Cu}} = 8.0 \times 10^{28} \, \text{atoms} / m^3 = N \]

# of vacancies per m³:

\[ N_v = N \exp \left( - \frac{Q_v}{kT} \right) \]

\[ = 8 \times 10^{28} \frac{\text{atoms}}{m^3} \exp \left( - \frac{0.9 \, eV}{8.62 \times 10^{-5} \frac{eV}{K} (1273K)} \right) \]

\[ = 2.2 \times 10^{25} \, \text{vacancies} / m^3 \]
4.3 Impurities in Solids

• Alloys
  – Impurity atoms added intentionally to impart specific characteristics to metals

• Solid solutions
  – Solute or impurities
  – Solvent or host material
Solid Solutions

- Solid solutions are formed when...
  - Solute atoms are added to the solvent
  - Crystal structure is maintained
  - No new structures are formed

They are compositionally homogenous? How so?

Impurity atoms are randomly and uniformly dispersed within solid
Substitutional solid solutions

- Solute or impurity atoms substitute for the solvent or host atoms.
Hume-Rothery Rules

• Factors that determine the degree to which the solute dissolves in the solvent
  1. Atomic size – difference in atomic radii must be less than ~15%.
  2. Crystal structure – same for metals of both atom types.
  3. Electro negativity->larger the difference -> more likelihood they will form an intermetallic compound instead of a substitutional solid solution.
  4. Valences – other factors being equal, a metal of lower valency has more of a tendency to dissolve another metal of higher valency than vice versa
Substitutional solid solutions

- **Cu & Ni solution**
  - Atomic radii for Cu & Ni are 0.128 nm & 0.125 nm.
  - Both have FCC crystal structure
  - EN values are 1.9 & 1.8
  - Valences are +1 & +2.
Interstitial solid solutions

- Solute or impurity atoms fill the interstices or voids among the solvent or host atoms.
Interstital solid solutions

How do you think the atomic radii of a solute compares to that of the solvent for interstitial solid solutions?

• C in Fe
  – Atomic radii of C & Fe are 0.071 nm & 0.124 nm.
  – Max. concentration of C is ~2 %.
Cool video of the day

https://www.youtube.com/watch?v=urq8SuPMZ_w
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
    \[ C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \]
    \[ n_{m1} = \text{number of moles of component 1} \]

How is \( n_m \) related to mass, \( m_1 \) and atomic weight, \( A_1 \) of an element?

\[ n_{m1} = \frac{m_1}{A_1} \]
Composition Conversions

Density & atomic weights of alloys in terms of the concentrations:

\[ C'_1 = \frac{C_1A_2}{C_1A_2 + C_2A_1} \times 100 \quad 4.6a \]

\[ C'_2 = \frac{C_2A_1}{C_1A_2 + C_2A_1} \times 100 \quad 4.6b \]

\[ C_1 = \frac{C'_1A_1}{C'_2A_2 + C'_1A_1} \times 100 \quad 4.7a \]

\[ C_2 = \frac{C'_2A_2}{C'_2A_2 + C'_1A_1} \times 100 \quad 4.7b \]
Composition Conversions

Conversion of weight percent to mass per unit volume

\[
C_1'' = \frac{C_1}{C_1 + C_2} \times 10^3
\]

\[
C_2'' = \frac{C_2}{C_1 + C_2} \times 10^3
\]

Average composition density and atomic weight

\[
\rho_{ave} = \frac{100}{C_1 + C_2}
\]

\[
A_{ave} = \frac{100}{A_1 + A_2}
\]
Linear Defects
4.5 Dislocations

• **Dislocation**
  – A 1D defect around which some of the atoms are misaligned.
  – Edge dislocation
  – Screw dislocation
  – Mixed dislocation
Line Defects

Dislocations:
• are line defects,
• slip between crystal planes result when dislocations move,
• produce permanent (plastic) deformation.

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

slip steps
Edge Dislocation

- A linear defect that centers around the line (dislocation line) that is defined along the end of the extra half-plane of atoms.

Magnitude and direction of lattice distortion represented by **Burgers vector**

Extra half plane
Edge Dislocation

• Linear defect
• Centered on line that is defined along the end of the extra half plane of atoms (dislocation line)
• Atoms above dislocation line are squeezed together or pulled apart?
  Below dislocation line?
Screw Dislocation

• Formed by applied shear stress
• Upper front region of crystal shifted by one atomic distance to the right
• Burger’s vector is parallel to the unit tangent vector
  \( \vec{b} \parallel \vec{t} \)
• Linear and along a dislocation line
Screw Dislocation

Dislocation line
Burgers vector $\mathbf{b}$

C

A

D
Mixed Dislocation

- Neither pure edge or pure screw dislocation
TEM Image of Dislocations
Planar Defects
4.6 Interfacial Defects

• 2D boundaries that separate regions of materials with different crystal structures and/or crystallographic orientations
  – External surfaces
  – Grain boundaries
  – Twin boundaries
  – Stacking faults
  – Phase boundaries
External Surfaces

• Surface along which the crystal structure terminates.

• Surface atoms are not bonded to the maximum number of nearest neighbors, hence are in a higher energy state than interior atoms.
  – Surface energy or surface tension
Grain Boundaries

- Boundary separating crystals with different orientations.

**Figure 3.17** Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (a) Small crystallite nuclei. (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed. (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, An Introduction to the Study of Physical Metallurgy, 2nd edition, Constable & Company Ltd., London, 1915.)
Grain Boundaries

**Figure 4.7** Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.
Grain Boundaries

• Atoms bonded less regularly along grain boundary results in an interfacial or grain boundary energy!

• How might grain boundary energy
  – be related to the magnitude of angle between boundaries (proportional/inversely proportional)?
  – influence chemically reactivity
  – Be related to size of grains?
  – Impurity atomic presence?
  – Temperature?
Tilt Boundary

- Small angle grain boundary.
- An ordered arrangement of edge dislocations.

\[ \vec{b} \perp \vec{t} \]
Twist Boundary

- Angle of misorientation is parallel to the boundary
- An ordered arrangement of screw dislocations.

\[ \vec{b} \parallel \vec{t} \]
Phase Boundaries

• A phase is defined as a homogenous portion of a system that has uniform physical and chemical characteristics (Section 9.3)

• Exist in multiphase materials wherein a different phase exists on each side of the boundary

• Each of the constituent phases has its own distinctive physical or chemical characteristics
Twin Boundary

- A mirror image of the crystal structure across a boundary.
  - formed during plastic deformation from shear forces (mechanical twins)
  - formed during rapid cooling from high temperatures (annealing twins)

Occurs on a definite crystallographic plane and in a specific direction!
Miscellaneous Interfacial Defects

• Stacking faults
  – Interruption in stacking sequence of close packed planes ex. ABCABCABC for the FCC

• Ferromagnetic domain walls
  – boundaries have different directions of magnetization
Volume Defects
4.7 Bulk Defects

- Normally introduced during processing and fabrication
  - Pores
  - Cracks
  - Foreign inclusions
  - Other phases
Example

Classify each of the following defects as point, linear, planar or volume defects:
(a) A screw dislocation  linear
(b) A low-angle twist boundary composed of screw dislocations  planar
(c) A vacancy  point
(d) A spherical cluster of 50 vacancies  volume
(e) A local region of atoms with a BCC structure within an FCC lattice  volume
(f) The boundary between the above BCC & FCC regions  planar
4.8 Atomic Vibrations
- as imperfections or defects

- Atoms in a solid material are vibrating about their lattice positions
- Not all atoms vibrate at the same frequency & amplitude or energy
- How does temperature relate to the vibrational activity of atoms and molecules?
4.8 Atomic Vibrations
- effect on properties of the material

• Temperature
  – Measure of the average vibrational activity of atoms and molecules

• Melting of a solid
  – Occurs when the vibrations are vigorous enough to rupture large numbers of atomic bonds
Optical Microscopy

• **Use of a light microscope (upper limit x2000)**
  – For opaque materials, only the surface is subjected to observation
  – Used in a reflecting mode, contrasts in image result from differences in reflectivity of the various regions
  – Investigations are often termed *metallographic*

• **Surface preparation**
  – grounded and polished (finer abrasive papers and powders)
  – Chemically treated (etching)
(a) Polished and etched grains as they might appear when viewed with an optical microscope. (b) Section taken through these grains showing how the etching characteristics and resulting surface texture vary from grain to grain because of differences in crystallographic orientation. (c) Photomicrograph of a polycrystalline brass specimen. 60×. (Photomicrograph courtesy of J. E. Burke, General Electric Co.)
Microscopic Examination

**Figure 4.12** (a) Section of a grain boundary and its surface groove produced by etching; the light reflection characteristics in the vicinity of the groove are also shown. (b) Photomicrograph of the surface of a polished and etched polycrystalline specimen of an iron-chromium alloy in which the grain boundaries appear dark. 100×. [Photomicrograph courtesy of L. C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD.)]
Optical Microscopy

- Small grooves form along grain boundaries as a result of etching.
- Luster of each grain depends on its reflective properties.
Electron Microscopy

- Image formed using beams of electrons
- Electrons accelerated across large voltages resulting in short wavelengths
- Electrons focused and image formed with magnetic lenses
Electron Microscopy

• Transmission Electron Microscopy (TEM)
  – Contrasts produced by beam scattering or diffraction
  – Thin foil form, why?
  – 1,000,000 x

• Scanning Electron Microscopy (SEM)
  – Reflected beams
  – Image displayed on a cathode ray tube (TV)
  – 50,000x

• Scanning Probe Microscopy (SPM)
  – Does not use light or electrons to generate image
  – Probe generates topographical map on an atomic scale
  – $10^9$x
4.11 Grain Size Determination

• Mean Intercept Length:  
  \[ \bar{\ell} = \frac{L_T}{PM} \]
  \( M \) – magnification,  
  \( L_T \) – total line length,  
  \( P \) – # of intersect sections

• Comparison method: American Society for Testing and Materials (ASTM) grain size number  
  \( G \) …

  \[ n = 2^{G-1}, n = \# \text{ of grains/in}^2 \text{ at a magnification of 100X} \]

  \( G \) = grain size number

• Does grain size # increase or decrease with decreasing grain size? Why?
Grain Size Determination

- Fine grained material
  - ASTM grain size 8 - 10
- Coarse grained material
  - ASTM grain size 2 - 3

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<th>Grain diameter (μm)</th>
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Example

• Assuming grains have a square shape, estimate the average grain size in microns of a material whose ASTM grain size numbers are 2 and 8 for two different conditions.
Edge length of square = $D$

$\Rightarrow 1$ grain occupies an area of $(D)^2 \text{in}^2$

Edge length at $100x = 100xD = D_{100}$

$\Rightarrow 1$ grain occupies an area of $(D_{100})^2 \text{in}^2$ at $100x$

$N = 2^{n-1} = \frac{1}{(D_{100})^2}$ # of grains / $\text{in}^2$

$\Rightarrow D_{100} = 2^{(1-n)/2} \text{in}$

$\Rightarrow D = \frac{2^{(1-n)/2}}{100} \text{in} = \frac{2^{(1-n)/2}}{100} \times (2.54 \text{cm/in}) \times (10^4 \mu \text{m/cm})$

For the two ASTM numbers:

$D_{ASTM \#2} = 180 \mu m$ and $D_{ASTM \#8} = 22.5 \mu m$

From Table:

$d_{ASTM \#2} = 180 \mu m$ and $d_{ASTM \#8} = 22.4 \mu m$
Design Problem 4.D1

- Al-Li alloys have been developed by the aircraft industry in order to reduce the weight and improve performance. A commercial aircraft skin material having a density of 2.55 g/cm$^3$ is desired. Compute the concentration of Li in wt.% that is required.
Design Problem 4.D2

- Copper (Cu) and platinum (Pt) both have the FCC crystal structure, and Cu forms a substitutional solid solution for concentrations up to approximately 6 wt% Cu at room temperature. Determine the concentration in weight percent of Cu that must be added to Pt to yield a unit cell edge length of 0.390 nm.