Chapter 4. Imperfection in solids

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It is very important to have a knowledge about imperfections and the roles they play in affecting the behaviour of materials. The properties of some materials are influenced by the presence of imperfections. Example: sterling silver (92.5% silver – 7.5% copper) is much harder and stronger than pure silver.

Ideal solids do not exist; all materials contain a large number of various defects or imperfections. **Crystalline defect** is a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Based on their geometry or dimensionality, crystalline defects are classified as:
- Point defects,
- Linear defects [1],
- Interfacial / boundary defects [2],
- Impurities.
4.1. Point defects

4.1.1. Point defects in metals

A vacancy is the simples point defects. It is normally occupied from which an atom is missing. It is not possible to produce a material without any of these defects. A self-interstitial is an atom from the crystal that is crowded into an interstitial site.
\[ N_v = N \exp \left( - \frac{Q_v}{kT} \right) \]

Where:
- \( N_v \) = the equilibrium number of vacancies,
- \( N \) = the total number of atomic sites,
- \( Q_v \) = the energy required for the formation of a vacancy,
- \( T \) = absolute temperature (K)
- \( K \) = Boltzmann’s constant
  \[ = 1.38 \times 10^{-23} \text{ J/atom K} = 8.62 \times 10^{-5} \text{ eV/atom K} \]

For most metals, \( N_v/N \approx 10^{-4} \) (below melting temperature). It indicates that one lattice site out of 10,000 will be empty.
4.1. Point defects
4.1.2. Point defects in ceramics

Ceramics materials consists of cations and anions, there are 3 types of point defects:
- Anion vacancies
- Cation vacancies
- Cation interstitial
Defect structure is important to determine the types and the concentrations of atomic defects in ceramics. Electroneutrality is the state that exists when there are equal numbers of positive and negative charges from the ions. As a result there are 2 types of defects in ceramics: Frenkel defect and Schottky defect.
The presence of an Fe$^{3+}$ ion disturbs the electroneutrality of the crystal (charge excess by +1).

The formation of 2 ions of Fe$^{3+}$

The formation of 1 ion of Fe$^{2+}$ vacancy
4.1. Point defects
4.1.3. Impurities in solids

4.1.3.1. Impurities in metals

It is impossible to obtain a pure metal (consist only one type of atoms). With sophisticated techniques, it is difficult to refine metals up to 99.9999%. At this level, $10^{22}$ to $10^{23}$ impurity atoms are present in 1 m$^3$ of material.

Alloys are metal in which impurity atoms are added intentionally to obtain specific properties.

Solid solution is method of the addition of impurity atoms to a metal. The metal’s properties depend on the kinds and concentrations of impurity, and the treatment of formation of the alloy. Solvent or host atom is the element in the greatest amount; solute is the element in a minor concentration.

Process: the solute atoms are added to host material without new structures are formed. The impurity atoms are randomly and uniformly dispersed within the host material.
The degree of the solute dissolves in the host material depend on several factors:

1. **Atomic size factor**
   If the difference of atomic radii between the 2 atoms is less than about 15%, appreciable quantities of solute may be accommodated by the host material. Otherwise, the solute atoms will create substantial lattice distortions and a new phase will form.

2. **Crystal structure**
   The crystal structures of both metals must be the same.

3. **Electronegativity**
   The more electropositive one element and the more electronegative the other, the greater to form intermetallic compound.

4. **Valences**
   The equal valence is good. A metal has a tendency to dissolve another metal of higher valency

   **Good example:**
   Copper and nickel alloy
   \[ r_{\text{Cu}} : 0.128 \text{ nm}; \ r_{\text{Ni}} : 0.125 \text{ nm} \]
   \[ \text{EN}_{\text{Cu}} : 1.9; \ \text{EN}_{\text{Ni}} : 1.8 \]
   \[ \text{Val Cu} : +1; \ \text{val Ni}: +2 \]
   both FCC
There are 2 types of impurity point defects: Substitutional and interstitial.

**Substitutional point defect:** the solute atom replace the host atom.

**Interstitial point defect:** the impurity atoms fill the voids among the host atoms. The atomic diameter of an interstitial impurity must be smaller than that of the host atoms.

Carbon is an impurity atoms for iron. The max conc of carbon is \( \approx 2\% \).

\[ r_C : 0.071 \text{ nm}; \]
\[ r_{Fe} : 0.124 \text{ nm}. \]
4.1. Point defects
4.1.3. Impurities in solids

4.1.3.2. Impurities in ceramics

Both cations and anions are present in ceramics, a substitutional impurity will substitute for the host ion to which it is most similar in an electrical sense.

For example:
In NaCl, impurity Ca$^{2+}$ and O$^{2-}$ ions would most likely substitute for Na$^+$ and Cl$^-$ ions, respectively.
A Frenkel or a Schottky defect does not alter the ratio of cations to anions. If no other defects are present, the material is said to be stoichiometric. **Stoichiometry** is defined as a state for ionic compounds wherein there is the exact ratio of cations and anions as predicted by the chemical formula. Example: NaCl

Stoichiometry  \[ \leftrightarrow \]  Nonstoichiometry

**Nonstoichiometry** may occur for some ceramic materials in which two valence (or ionic) states exist for one of the ion types. Example: in iron oxide / wüstite / FeO; the iron can be in Fe\(^{2+}\) and Fe\(^{3+}\), the number of each ion depends on temperature and the ambient oxygen pressure.
4.1. Point defects

4.1.4. Point defects in polymers

The defect concept in polymers is different with that in metals and ceramics. Chain ends in polymers are considered as defects; impurity atoms/ions or groups of atoms/ions that part of molecular structure may consider as interstitial defects.
4.1. Point defects

4.1.5. Specification of composition

In material with host and impurity atoms, it is important to express the composition or concentration of the impurity elements. The two most common ways to specify composition are weight (or mass) percent and atom percent.

The weight percent (wt%) or mass percent (mass%) is the weight or mass of a particular element relative to the total alloy weight or mass.

\[ C_1 = \frac{m_1}{m_1 + m_2} \times 100 \]

Where:
- \( C_1 \) = weight (or mass) percent (wt%),
- \( m_1 \) and \( m_2 \) = the weight (or mass) of elements 1 and 2, respectively.
The **atom percent** (at%) is the number of moles of an element relative to the total moles of the elements in the alloy.

\[
C_1' = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100 \quad \text{with} \quad n_{m_1} = \frac{m_1'}{A_{1_1}}
\]

Where:
- \( C_1' \) = the atom percent (at%)
- \( n_{m_1}, n_{m_2} \) = the number of moles in a mass of elements 1 and 2 respectively,
- \( m_1' \) = mass (g),
- \( A_{1_1} \) = atomic weight (g)
The composition relation between weight percent and atom percent

\[ C'_1 = \frac{C_1A_2}{C_1A_2 + C_2A_1} \times 100 \]
\[ C'_2 = \frac{C_2A_1}{C_1A_2 + C_2A_1} \times 100 \]
\[ C_1 = \frac{C'_1A_2}{C'_1A_2 + C'_2A_1} \times 100 \]
\[ C_2 = \frac{C'_2A_1}{C'_1A_2 + C'_2A_1} \times 100 \]
The concentration (kg/m\(^3\)) is the weight of one component per unit volume of material.

\[
C_1^* = \frac{C_1}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \times 10^3
\]

Where:
- \(C_1^*\) = concentration (kg/m3),
- \(C_1\) = weight percent (wt%),
- \(\rho_1, \rho_2\) = densities of elements 1 and 2 respectively (g/cm3)
4.2. Other imperfections

4.2.1. Dislocations – linear defects

A dislocation is a linear or [1] defect where some atoms are misaligned. Three types of dislocation:

a. **Edge dislocation / dislocation line**: a linear defect that centers around and perpendicular to the plane of the page.

b. **Screw dislocation**: a defect that may formed by a shear stress that is applied to produce distortion.

c. **Mixed dislocations**

**Burgers vector** (b) is a vector system to describe the magnitude and the direction of the lattice distortion associated with a dislocation.
Dislocations in crystalline materials can be observed using electron-microscope techniques.

The dark lines are the dislocations.
4.2. Other imperfections

4.2.2. Interfacial defects

Interfacial defects are boundaries that have [2] and normally separate regions of the materials that have different crystal structures and/or crystallographic orientation.

Several types of interfacial defects:
- External surfaces,
- Grain boundaries,
- Twin boundaries,
- Stacking faults,
- Phase boundaries.
4.2. Other imperfections

4.2.2. Interfacial defects

4.2.2.1. External surfaces

External surface is one of the most obvious boundaries, which the crystal structure terminates. On the surface, the atoms are not bonded to the maximum number of nearest neighbours and it results in a higher energy state than the atoms at interior positions (J/m$^2$).

To reduce this energy, materials tend to minimize the total surface area. *Example: liquid droplets have spherical shape.*

It is impossible for solid materials.
4.2. Other imperfections
4.2.2. Interfacial defects

4.2.2.2. Grain boundaries

Grain boundary is a boundary separating two small grains or crystal having different crystallographic orientation in polycrystalline materials.

Several types of grain boundaries:
- Small-angle grain boundary / dislocation arrays
  - Tilt boundary (angle of misorientation \perp boundary)
  - Twist boundary (angle of misorientation \parallel boundary)
- High-angle grain boundary

Impurity atoms often segregate along boundaries
4.2. Other imperfections

4.2.2. Interfacial defects

4.2.2.3. Twin boundaries

Twin boundary is a grain boundary in which there is a specific mirror lattice symmetry; atoms on one side of the boundary are located in mirror image positions of the atoms on the other side.

This defect is a result of the application of mechanical shear forces and during annealing following deformation. The mechanical twins occur in BCC and HCP metals, whereas the annealing twins occur in FCC metals.

4.2.2.4. Other defects

Stacking faults are found in FCC metals. Phase boundaries exist in multiphase materials after sudden change physical and/or chemical characteristics.
4.2. Other imperfections

4.2.3. Bulk or volume defects

Defects [3] are much larger than previous defects. There are several types of these defects: pores, cracks, foreign inclusions, and other phases.

These occur during processing and fabrication stages.

4.2.4. Atomic vibration

Every atom in a solid materials naturally vibrates very rapidly about its lattice position within the crystal. At any time, not all atoms vibrate at the same frequency, amplitude, and energy. A distribution of energy exists in the materials.

Example: a typical vibration at RT: $f \approx 10^{13}$ vibrations/sec,

\[ A \approx 1,00 \text{ nm} \]
4.3. Microscopic examination

In most materials the grains are in microscopic dimensions, with diameters in the order of microns. Microstructure relates to grain size and shape.

Microscopic observations are used optical, electron and scanning probe microscopes. Photomicrographs are photographs recorded by microscopes.

Microscopic examination is an extremely useful tool in the study and characterization of materials. The applications are:

- To understand the relation between the properties and structure (and defects),
- To predict the properties of materials,
- To design alloys with new elements combination,
- To determine whether or not a material has been correctly heat treated,
- To determine the mode of mechanical fracture.
4.3. Microscopic examination

4.3.1. Optical microscopy

Optical microscopy systems:
Using optical and illumination systems. The upper limit of magnification $\approx 2000 \times$

Metallographic technique
Specimen surface must be ground and polished to a smooth and mirrorlike finish. Etching procedure, especially for metal specimens.
4.3. Microscopic examination

4.3.2. Electron microscopy

Electron microscopy system:
Using accelerated electrons with $\lambda \approx 0.003$ nm. The electron beam is focused and the image is formed with a magnetic lenses.

**SEM**
The specimen surface is scanned with the electron beam and the reflected beam is collected then displayed on a CRT.

**TEM**
The electron beam passes through the specimen and the contrast of the internal microstructures are produced by differences in beam scattering produced between various elements of the microstructures.
4.3. Microscopic examination

**SPM**
A tiny probe with a very sharp tip is brought into very close proximity (in the order of nm) to the specimen surface to generate a topographical map on atomic scale.

Some advantages of SPM:
Nanometer scale examination with a magnification as high as 109.
Operated in a variety environments (vacuum, air, liquid).

**AFM**
A technique that is able to observe atomic structure of a specimen.
4.3. Microscopic examination

4.3.3. Grain size determination

Grain size often determines the properties of a polycrystalline material. The grain size is specified in terms of grain volume, diameter or area.

*Intercept Method:*  
Straight lines all the same length are drawn through several photomicrographs that show the grain structure. The grains intersected by each line segment are counted; the line length is then divided by an average number of grains intersected, taken over all the line segments. The average grain diameter is found by dividing this result by the linear magnification of the photomicrographs.

*Standard Comparison Charts Method:*  