Lecture 1
"Defects in the Crystalline Structure"

Imperfections:

Perfect model of crystal

- Real crystals are never perfect, there are always defects! Actually, all crystals are imperfect.

- Controlling defects is one of the main goals of materials science and engineering.

- Crystal defects are imperfections in crystals caused by deviations from the individual lattice structure.

- "Crystals are like people, it's their defects that make them more interesting."

- Imperfections give properties of crystalline solids, i.e., they dominate the material properties.

- They always contain a considerable density of defects and imperfections that affect their physical, chemical, and mechanical properties.

- The existence of defects also plays an important role in various technological processes and phenomena such as annealing, precipitation, diffusion, sintering, oxidation, and others.

- It should be noted that defects do not necessarily have adverse effects on the properties of materials.
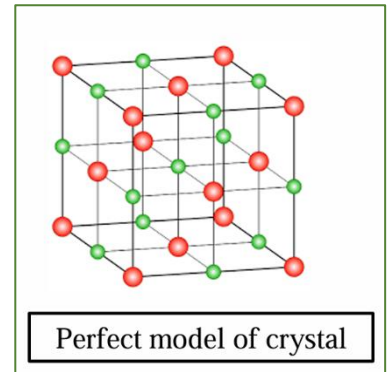
A crystalline defect refers to a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to the geometry or dimensionality of the defect.
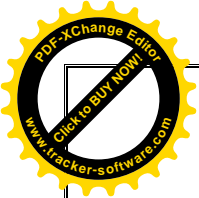
We can classify defects by dimensions to:

1. **Point defects.**
2. **Line defects.**
3. **Planar or surface defects.**
4. **Volume or bulk defects.**

Point Defects:

Types of Point Defects

- Vacancy

- Interstitial

- Substitutional (Larger - Smaller)

- Frenkel

- Schottky

A/ Vacancies

The simplest of the point defects is a vacancy or vacant lattice site, one normally occupied but from which an atom is missing (Figure 4.1). All crystalline solids contain vacancies, and, in fact, it is not possible to create such a material that is free of these defects. The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal. The equilibrium number of vacancies N_v for a given quantity of material (usually per meter cubed) depends on and increases with temperature according to

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

In this expression, N is the total number of atomic sites (most commonly per cubic meter), Q_v is the energy required for the formation of a vacancy (J/mol or
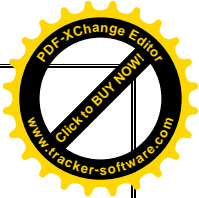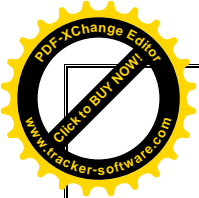
eV/atom), T is the absolute temperature in kelvins, and k is the gas or Boltzmann's constant. The value of k is 1.38×10^{-23} J/atom.K, or 8.62×10^{-5} eV/atom.K, depending on the units of Q_v. Thus, the number of vacancies increases exponentially with temperature.

Number-of-Vacancies Computation at a Specified Temperature

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

Solution

This problem may be solved by using Equation 4.1; it is first necessary, however, to determine the value of N—the number of atomic sites per cubic meter for copper, from its atomic weight A_{Cu}, its density ρ, and Avogadro's number N_A, according to

$$N = \frac{N_A \rho}{A_{Cu}} \tag{4.2}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}}$$

$$= 8.0 \times 10^{28} \text{ atoms/m}^3$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

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

$$= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right]$$

$$= 2.2 \times 10^{25} \text{ vacancies/m}^3$$

A self-interstitial is an atom from the crystal that is crowded into an interstitial site—a small void space that under ordinary circumstances is not occupied. This kind of defect is also represented in Figure 4.1. In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated. Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations that are significantly lower than for vacancies.
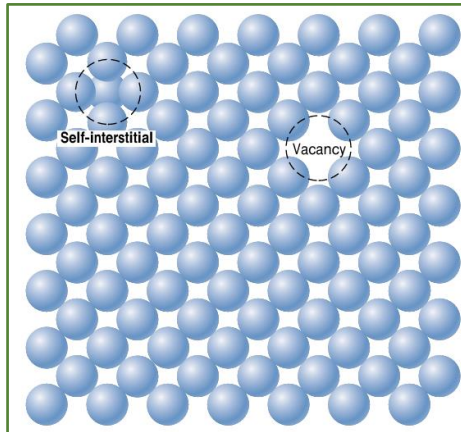
Figure (2): Two-dimensional representations of a vacancy and a self-interstitial.

B/ Interstitially (Self-Interstitial):

An atom occupies an interstitial site (which is not its normal site), Normally, it requires large energy to create an interstitial. The size of an interstitial site is very small, particularly in close-packed crystal structures that are much more elastically strained (displaced) than around a vacancy.
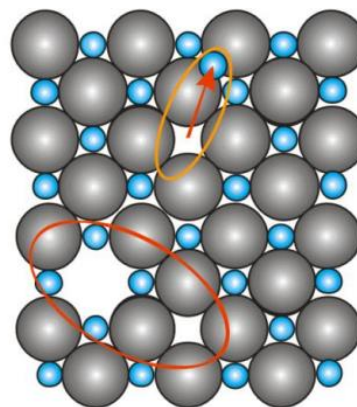
C/ Frenkel Defect:

When an atom is shifted from a normal lattice site (thus creating vacancy) and is forced into an interstitial position, the resulting pair of point defects (a vacancy as well as the interstitial) together is called a Frenkel defect.

D/ Schottky Defects:

A missing positive ion and negative ion from the crystal.

Impurity Atoms (Substitutional or Interstitial Type): an impurity (foreign) atom if present on the lattice by substituting the lattice site atom. Substitutional atoms may either be larger than the normal atom in the lattice (in which case, the surrounding atoms are compressed, or smaller (causing the surrounding atoms to be in tension). The number of defects is relatively independent of temperature.

An interstitial defect: the small-sized atoms present in the interstitial site. Therefore, the surrounding lattice is compressed and distorted. The number of interstitial atoms in the structure remains constant, even when the temperature is changed. Normally, the concentration of these atoms in very pure materials is lower than the concentration of vacancies. Foreign atoms also play a role in changing the electrical conductivity of the semiconductors.

Point defects of crystals

Vacancy   Interstitial impurity   Self-interstitial

Substitution impurity   Frenkel defect

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Figure 4-1 Point defects: (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom, (e) Frenkel defect, and (f) Schottky defect. All of these defects disrupt the perfect arrangement of the surrounding atoms.
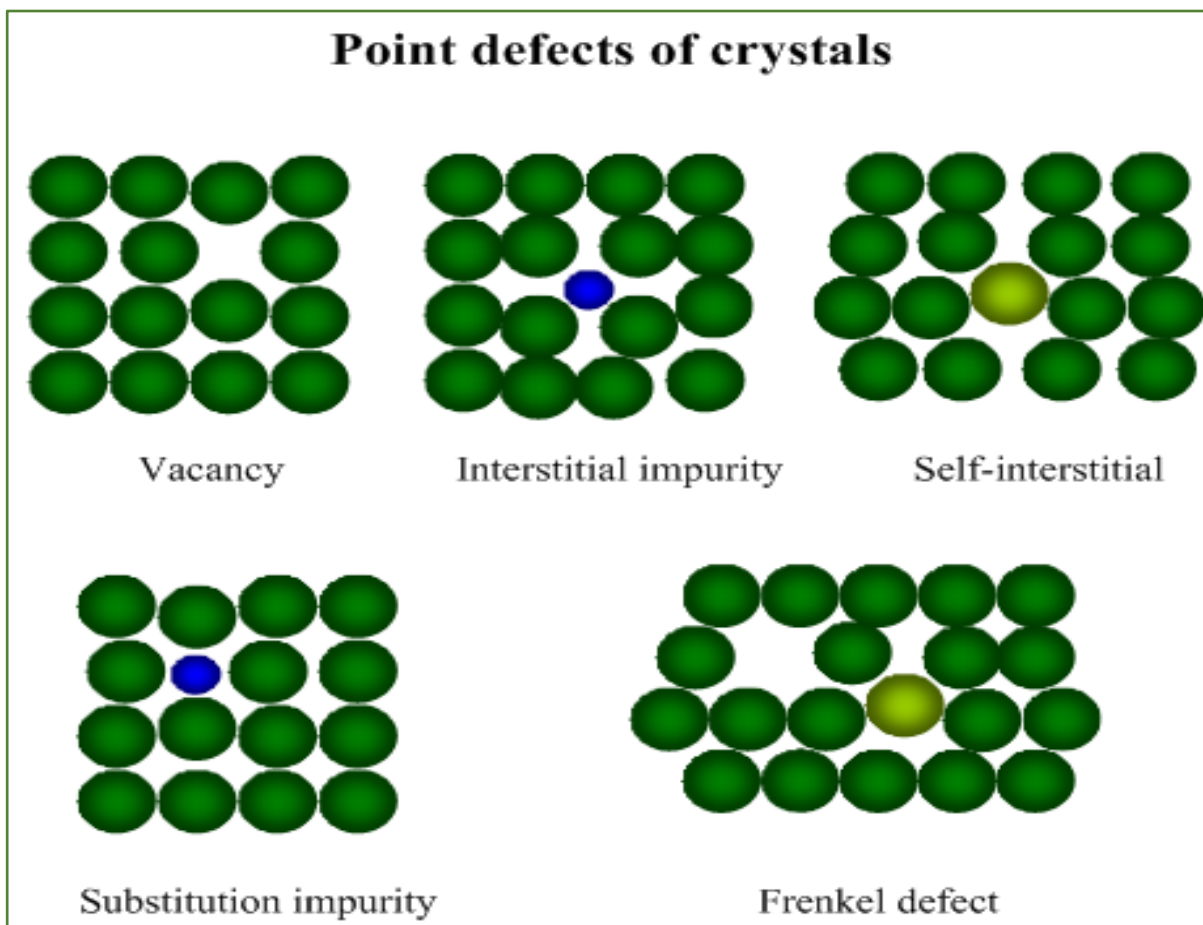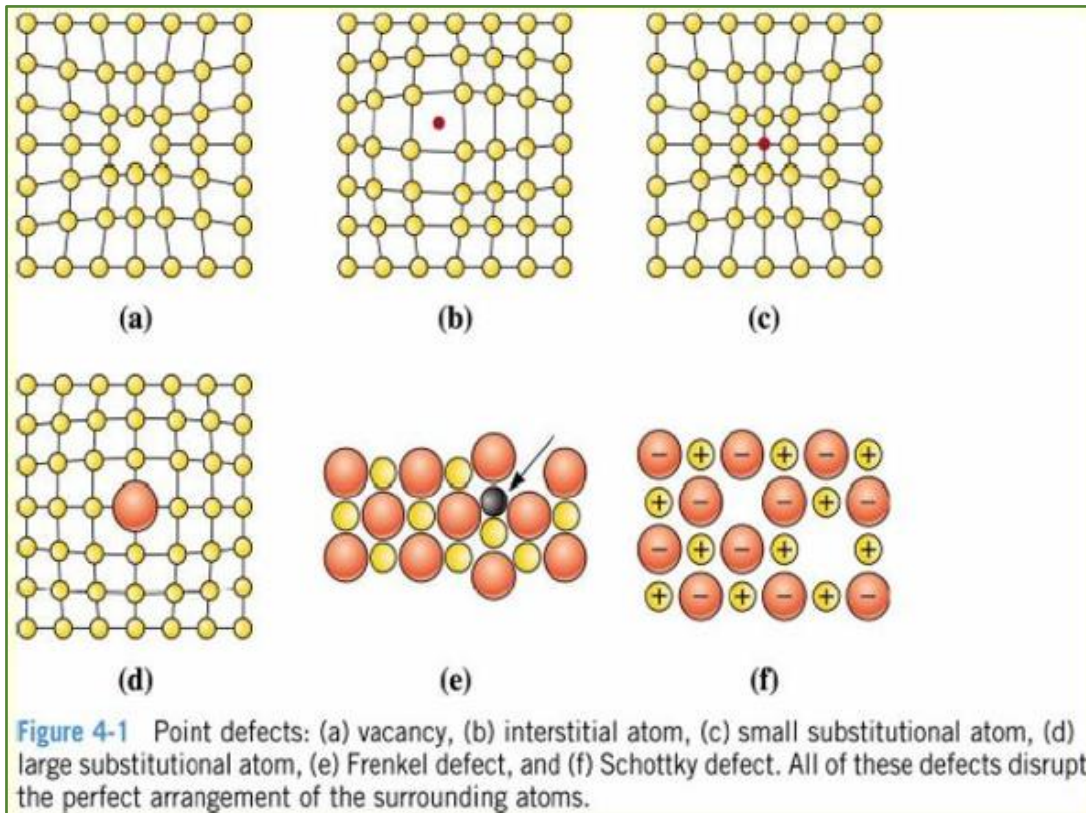
It is often necessary to express the **composition (or concentration)** of an alloy in terms of its constituent elements. **The two most common ways to specify composition are weight (or mass) percent and atom percent.**

The basis for weight percent (wt%) is the weight of a particular element relative to the total alloy weight. For an alloy that contains two hypothetical atoms denoted by 1 and 2, the concentration of 1 in wt%, C_1, is defined as:

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

where m_1 and m_2 represent the weight (or mass) of elements 1 and 2, respectively. The concentration of 2 is computed in an analogous manner.

When an alloy contains more than two (n) elements, Equation (4.3a) takes the form:

$$C_1 = \frac{m_1}{m_1 + m_2 + m_3 + \cdots + m_n} \times 100$$

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The basis for atom percent (at%) calculations is the number of moles of an element in relation to the total moles of the elements in the alloy. The number of moles in some specified mass of a hypothetical element 1, n_{m1}, may be computed as follows:

$$n_{m1} = \frac{m_1'}{A_1}$$

Here, m_1 and A_1 denote the mass (in grams) and atomic weight, respectively, for element 1. Concentration in terms of atom percent of element 1 in an alloy containing element 1 and element 2 atoms, C1 is defined by:

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

In like manner, the atom percent of element 2 is determined. Atom percent computations also can be carried out on the basis of the number of atoms instead of moles, because one mole of all substances contains the same number of atoms.

Linear Defects – Dislocations:

Line defects, or dislocations, are lines along which whole rows of atoms in a solid are arranged anomalously. The resulting irregularity in spacing is most severe along a line called the line of dislocation. Line defects can weaken or strengthen solids. Dislocations are generated and move when stress is applied. The motion of dislocations allows slip–plastic deformation to occur.

- Dislocation is the region of localized lattice distortion that separates the slipped and unslipped portion of the crystal. The upper region of the crystal over the slip plane has slipped relative to the bottom portion.
- The line (AD) between the slipped and unslipped portions is the dislocation. The magnitude and direction of slip produced by dislocation (pink shaded) is the Burger vector of the dislocation.
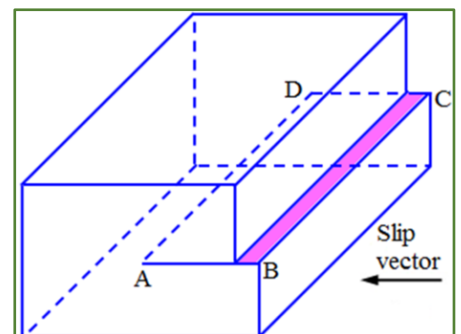
The Burgers vector is a quantitative characteristic describing the distortions of the crystal lattice around a dislocation.

There are two basic types of dislocations: Edge dislocation and the Screw dislocation.

A/ Edge Dislocations:

Edge dislocations occur when an **extra half-plane is inserted**. The slip plane is at the end of the plane. This line runs along the top of the extra half-plane. The inter-atomic bonds are significantly distorted only in the immediate around of the dislocation line.

In Edge dislocations the Burger vector is perpendicular to the dislocation line and the distortion produces an extra half-plane above the slip plane
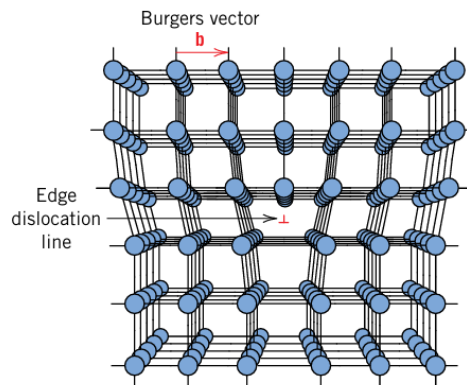

Figure (6): The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective.
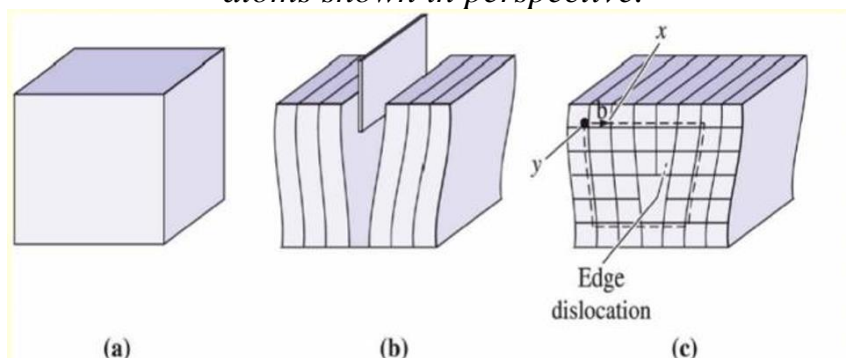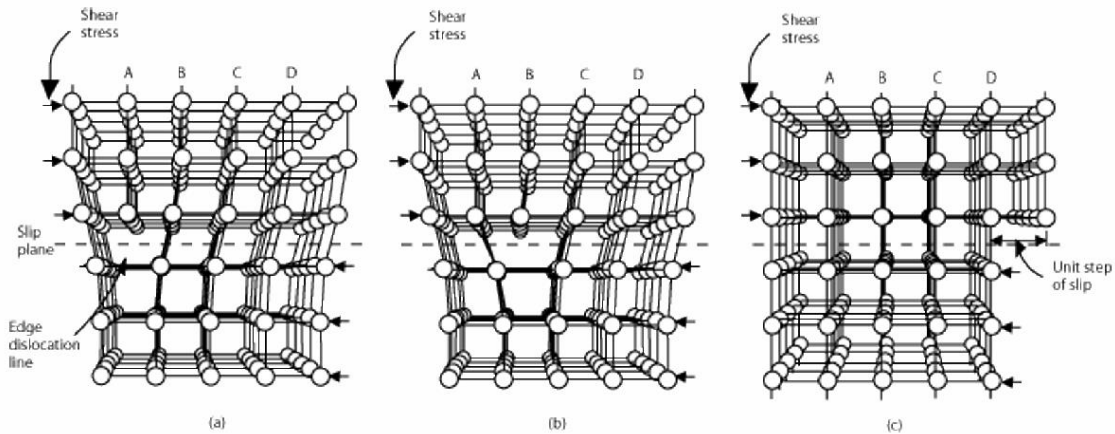

Figure 4-5 The perfect crystal in (a) is cut and an extra plane of atoms is inserted (b). The bottom edge of the extra plane is an edge dislocation (c). A Burgers vector **b** is required to close a loop of equal atom spacings around the edge dislocation. (Adapted from J.D. Verhoeven, Fundamentals of Physical Metallurgy, Wiley, 1975.)

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The dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in the image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half.

However, only a small fraction of the bonds is broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously. The edge dislocation moves parallel to the direction of stress.

B/ Screw dislocations:

- The other type of dislocation is the screw dislocation where the Burger vector is parallel to the dislocation line (AD). The trace of the atomic planes around the screw dislocation makes a spiral or helical path (pink shade) like a screw and hence, the name.

- Screw dislocations result when displacing planes relative to each other through shear. the Burgers vector is parallel to the dislocation line.

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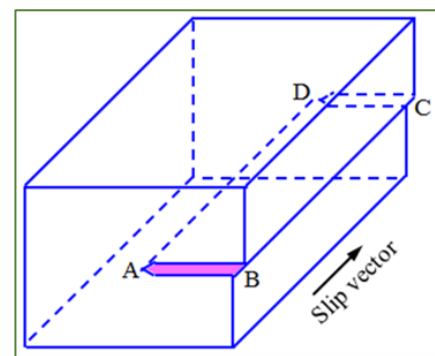
Interfacial Defects (Surface defects):

Come form: between different phases, or between different crystals. It may arise at the boundary between two grains, or small crystals, within a larger crystal. The rows of atoms in two different grains may run in slightly different directions, leading to a mismatch across the grain boundary. The actual external surface of a crystal is also a surface defect because the atoms on the surface adjust their positions to accommodate for the absence of neighboring atoms outside the surface

1) External Surfaces: The environment of an atom at a surface differs from that of an atom in the bulk, in that the number of neighbors (coordination) decreases. This introduces unbalanced forces which result in relaxation (the lattice spacing is decreased) or reconstruction (the crystal structure changes). Surface atoms have unsatisfied atomic bonds, and higher energies than the bulk atoms $\Rightarrow$ Surface energy, γ (J/m^2)
   • Surface areas tend to minimize (e.g. liquid drop)
   • Solid surfaces can "reconstruct" to satisfy atomic bonds at surfaces.

2) Grain Boundaries: Polycrystalline material comprised of many small crystals or grains. The grains have different crystallographic orientations. There exists atomic mismatch within the regions where grains meet. These regions are called grain boundaries.
   Surfaces and interfaces are reactive and impurities tend to segregate there. Since energy is associated with interfaces, grains tend to grow in size at the expense of smaller grains to minimize energy. This is accelerated at high temperatures. The density of atoms in the region including the grain boundary is smaller than the bulk value since void space occurs in the interface.
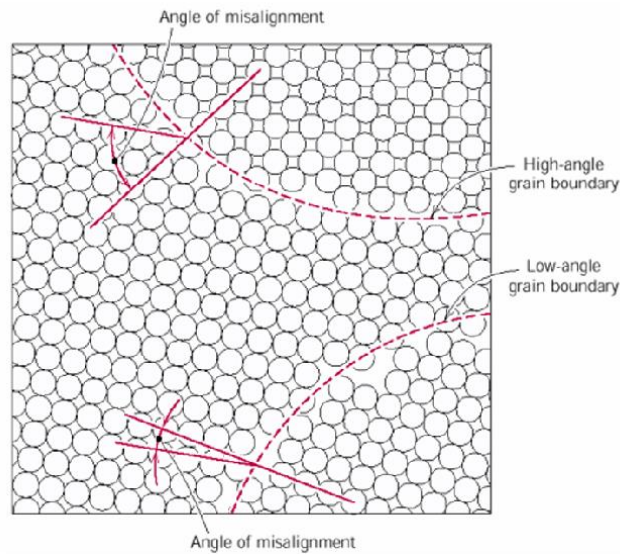
Interfaces between crystals are grain boundaries, as discussed earlier.

It is convenient to separate grain boundaries by the extent of the mis-orientation between the two grains.

• low angle grain boundaries: are those with a misorientation of less than about 11 degrees.

• high angle grain boundaries: whose misorientation is greater than about 11 degrees

Volume defects

    • Porosity

    • Cracks

    • Inclusions

- These defects form during manufacturing processes for various reasons and

are often harmful to the material.

- A lot of inclusions fall into the material during welding, thermal, mechanical,

or grinding. other processing. For example, during grinding.

- Example porosity reduces the thermal conductivity of material, but sometimes

porosity specifically increases for increase thermal isolate.