

Materials Science (PHY 3204/MEC 2206)
Additional Lecture Note and Course Work

Instruction

1. Carefully read up the lecture notes given to you earlier.
2. Read the lecture note on Defects in Materials given below and additional file attached in the email on defects in materials.
3. In addition to 1 and 2 above, read about electro-positivity and electro-negativity and how they affect the properties and structure of materials. You will need to search for further information through online sources for this
4. The course work is given on the last page of this document. Submit on or before Friday 4th November 2022.

Defects in Materials

Materials are often stronger when they have defects. Bonding of materials plus crystal structure and defects gives materials their unique properties. The study of defects is divided according to their dimension:

1. Point defects: vacancies and interstitials. Impurities.
2. Linear defects: dislocations (edge, screw, mixed)
3. Planar defects: Grain boundaries, surfaces.
4. Volume defects: pores, cracks.

A vacancy is a lattice position that is vacant because the atom is missing. It is created when the solid is formed. There are other ways of making a vacancy, but they also occur naturally as a result of thermal vibrations. Vacancies are always present in crystals and they are particularly numerous at high temperatures, when atoms are frequently and randomly change their positions leaving behind empty lattice sites.

An interstitial is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self-interstitial) or an impurity atom.

In the case of vacancies and interstitials, there is a change in the coordination of atoms around the defect. This means that the forces are not balanced in the same way as for other atoms in the solid, which results in lattice distortion around the defect.

All real solids are impure. A very high purity material, say 99.9999% pure (called 6N – six nines) contains $\sim 6 \times 10^{16}$ impurities per cm^3

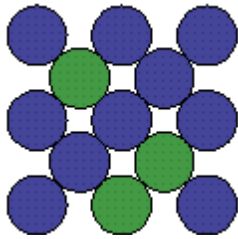
Impurities are often added to materials to improve the properties. For instance, carbon added in small amounts to iron makes steel, which is stronger than iron. Boron impurities added to silicon drastically change its electrical properties.

Solid Solution

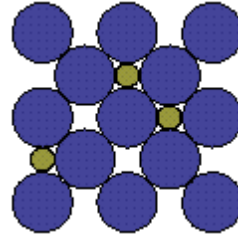
Solid solutions are made of a host (solvent or matrix) which dissolves the solute (minor component). The ability to dissolve is called solubility. Solid solutions are:

- homogeneous
- maintain crystal structure
- contain randomly dispersed impurities (substitutional or interstitial)

Whether the addition of impurities results in formation of solid solution or second phase depends the nature of the impurities, their concentration and temperature, pressure



Substitutional Impurity



Interstitial impurities

Factors for high solubility

1. Similar atomic size (to within 15%) Atomic size factor - atoms need to “fit” \Rightarrow solute and solvent atomic radii should be within $\sim 15\%$
2. Similar crystal structure Crystal structures of solute and solvent should be the same
3. Similar electronegativity Electro-negativities of solute and solvent should be comparable (otherwise new inter-metallic phases are encouraged, a compound is formed)
4. Similar valence
5. Atomic radius-For fcc, bcc, hcp structures the voids (or interstices) between the host atoms are relatively small \Rightarrow atomic radius of solute should be significantly less than solvent

Composition can be expressed in weight percent, useful when making the solution, and in atomic percent, useful when trying to understand the material at the atomic level

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Atom percent, useful when trying to understand the material at the atomic level

Weight percent (wt %): weight of a particular element relative to the total alloy weight. For two-component system, concentration of element 1 in wt. % is

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

m_1 and m_2 are masses of the two components

Atom percent (at %): number of moles (atoms) of a particular element relative to the total number of moles (atoms) in alloy. For two-component system, concentration of component 1 in at. % is

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

where $n_{m1} = m_1/A_1$, m_1 is mass in grams of component 1 and A_1 is atomic mass of component 1

Composition Conversion

Weight % to Atomic %

$$C_1^{at} = \frac{C_1^{wt} A_2}{C_1^{wt} A_2 + C_2^{wt} A_1} \times 100$$

$$C_2^{at} = \frac{C_2^{wt} A_1}{C_1^{wt} A_2 + C_2^{wt} A_1} \times 100$$

Atomic % to Weight %

$$C_1^{wt} = \frac{C_1^{at} A_1}{C_1^{at} A_1 + C_2^{at} A_1} \times 100$$

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From Weight % to mass per unit volume (g/cm³)

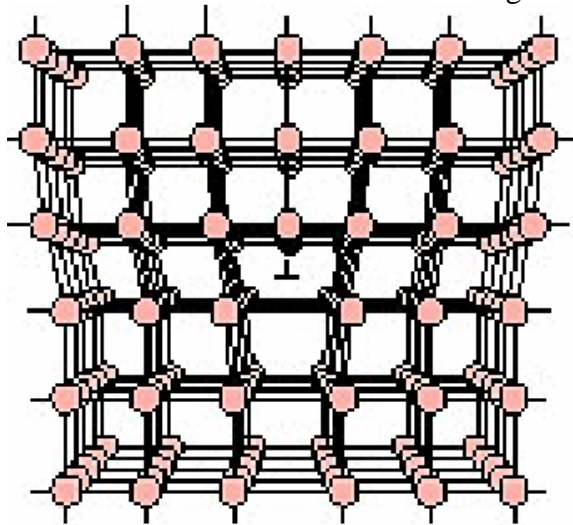
$$C_1 = \frac{C_1^{wt}}{\frac{C_1^{wt}}{\rho_1} + \frac{C_2^{wt}}{\rho_2}}$$

$$C_2 = \frac{C_2^{wt}}{\frac{C_1^{wt}}{\rho_1} + \frac{C_2^{wt}}{\rho_2}}$$

Where C_1 and C_2 are concentrations of the first and second components in g/cm³

Linear Defects or Dislocation

Dislocations are abrupt changes in the regular ordering of atoms, along a line (dislocation line) in the solid. The interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the dislocation core. Dislocations also create small elastic deformations of the lattice at large distances.

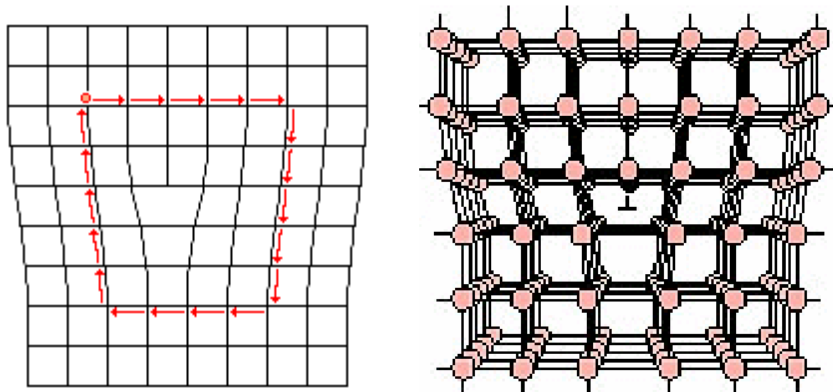


They occur in high density and are very important in mechanical properties of material. They are characterized by the Burgers vector, found by doing a loop around the dislocation line and noticing the extra interatomic spacing needed to close the loop. The Burgers vector in metals points in a close packed direction.

Description of Dislocations—Burgers Vector

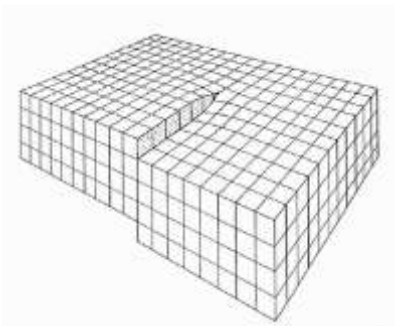
To describe the size and the direction of the lattice distortion caused by a dislocation we should introduce so called **Burgers vector \mathbf{b}** . To find the Burgers vector, we should make a circuit from atom to atom counting the same number of atomic distances in all directions. If the

circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector.



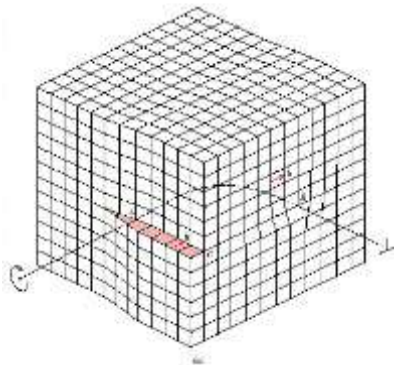
Dislocations shown above have Burgers vector directed perpendicular to the dislocation line. These dislocations are called **edge dislocations**. Edge dislocations occur when an extra plane is inserted. The dislocation line is at the end of the plane. In an edge dislocation, the Burgers vector is perpendicular to the dislocation line.

Screw dislocations result when displacing planes relative to each other through shear. In this case, the Burgers vector is parallel to the dislocation line. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).



Mixed/partial dislocations

The exact structure of dislocations in real crystals is usually more complicated than the ones shown in this pages. Edge and screw dislocations are just extreme forms of the possible dislocation structures. Most dislocations have mixed edge/screw character.



Planar or Interfacial Defect

Another type of defect is interfacial defect, the environment of an atom at a surface differs from that of an atom in the bulk, in that the number of neighbours (coordination) decreases. This

introduces unbalanced forces which result in relaxation (the lattice spacing is decreased) or reconstruction (the crystal structure changes). The density of atoms in the region including the grain boundary is smaller than the bulk value, since void space occurs in the interface. Surfaces and interfaces are very reactive and it is usual that impurities segregate there. Since energy is required to form a surface, grains tend to grow in size at the expense of smaller grains to minimize energy. This occurs by diffusion, which is accelerated at high temperatures.

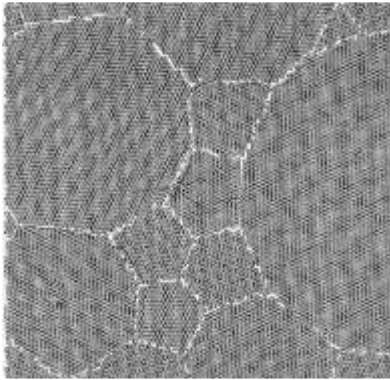
External Surfaces

Surface atoms have unsatisfied atomic bonds, and higher energies than the bulk atoms
 ⇒ Surface energy, γ (J/m²)

- Minimization of surface areas reduces the energy of the system (e.g. liquid drop)
- Solid surfaces can “reconstruct” to satisfy atomic bonds at surfaces.

Grain Boundaries

Polycrystalline material comprised of many small crystals or grains. The grains have different crystallographic orientation. There exists atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.



Surfaces and interfaces have structure that is different from the bulk and can be reactive → 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.

High and low angle grain boundaries

Depending on misalignments of atomic planes between adjacent grains we can distinguish between the low and high angle grain boundaries

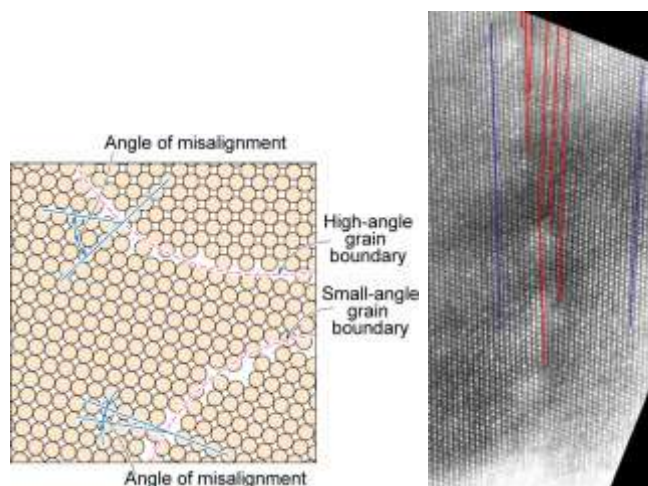


figure b

Small angle grain boundaries can be described as arrays of dislocations. This is a transmission electron microscope image of a small angle tilt boundary in Si. The red lines mark the edge dislocations, the angle between the blue lines corresponds to the tilt angle.

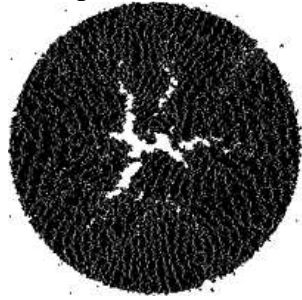
Small angle twist boundary can be represented by an array of screw dislocations (consider joint of two halves of a cube and twist an angle around the cross section normal) **Figure b**

Twin Boundaries

Low-energy **twin boundaries** with mirrored atomic positions across boundary may be produced by deformation of materials. This gives rise to **shape memory metals**, which can recover their original shape if heated to a high temperature. Shape-memory alloys are twinned and when deformed they untwin. At high temperature the alloy returns back to the original twin configuration and restore the original shape.

Volume Defect

A typical volume defect is porosity, often introduced in the solid during processing. A common example is snow, which is highly porous ice.



Atomic Vibrations

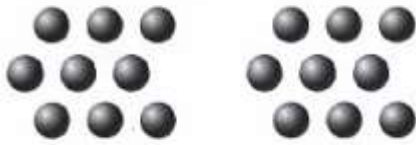
Atomic vibrations occur, even at zero temperature (a quantum mechanical effect) and increase in amplitude with temperature. Vibrations displace transiently atoms from their regular lattice site, which destroys the perfect periodicity.

Diffusion

Many important reactions and processes in materials occur by the motion of atoms in the solid (transport), which happens by diffusion. Inhomogeneous materials can become homogeneous by diffusion, if the temperature is high enough (temperature is needed to overcome energy barriers to atomic motion)

Diffusion Mechanism

Atom diffusion can occur by the motion of vacancies (vacancy diffusion) or impurities (impurity diffusion). The energy barrier is that due to nearby atoms which need to move to let the atoms go by. This is more easily achieved when the atoms vibrate strongly, that is, at high temperatures. There is a difference between diffusion and net diffusion. In a homogeneous material, atoms also diffuse but this motion is hard to detect. This is because atoms move randomly and there will be an equal number of atoms moving in one direction than in another. In inhomogeneous materials, the effect of diffusion is readily seen by a change in concentration with time. In this case there is a net diffusion. Net diffusion occurs because, although all atoms are moving randomly, there are more atoms moving in regions where their concentration is higher.



Steady State Diffusion

The flux of diffusing atoms, J , is expressed either in number of atoms per unit area and per unit time (e.g., atoms/m²-second) or in terms of mass flux (e.g., kg/m²-second). Steady state diffusion means that J does not depend on time. In this case, Fick's first law holds that the flux along direction x is

$$J = -D \frac{dC}{dx}$$

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$$J = -D \frac{dc}{dx}$$

Where dC/dx is the gradient of the concentration C , and D is the diffusion coefficient. The concentration gradient is often called the driving force in diffusion (but it is not a force in the mechanistic sense). The minus sign in the equation means that diffusion is down the concentration gradient.

Non-Steady State Diffusion

This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or that it is depleted from a region (which may cause them to accumulate in another region).

Factors influencing Diffusion

As stated above, there is a barrier to diffusion created by neighbouring atoms that need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion. Also, smaller atoms diffuse more readily than big ones, and diffusion is faster in open lattices or in open directions. Similar to the case of vacancy formation, the effect of temperature in diffusion is given by a Boltzmann factor:

$$D = D_0 \exp\left(\frac{-Q_d}{RT}\right)$$

Where D_0 – temperature-independent pre-exponential (m^2/s)

Q_d – the activation energy for diffusion (J/mol or eV/atom)

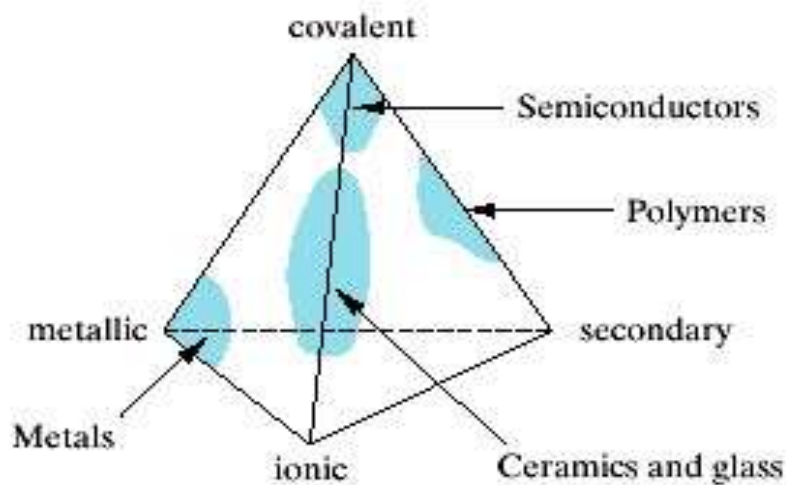
R – the gas constant ($8.31 \text{ J/mol}\cdot\text{K}$ or $8.62 \times 10^{-5} \text{ eV/atom}\cdot\text{K}$)

T – absolute temperature (K)

Diffusion occurs more easily along surfaces, and voids in the material (short circuits like dislocations and grain boundaries) because less atoms need to move to let the diffusing atom pass. Short circuits are often unimportant because they constitute a negligible part of the total area of the material normal to the diffusion flux

Relationship between structure and bonding in materials

The diagram presents the major relationship between structure of materials and the bonding that exists amongst them.



The diagram shows in a simple sense the relationship between bonding and structure of materials. In many materials more than one type of bonding is involved (ionic and covalent in ceramics, covalent and secondary in polymers, covalent and ionic in semiconductors. for example in the following materials, the nature of bonds that exist are shown

1. Metals: Metallic bond exists specifically in Metals
2. Ceramics: Ionic or Covalent bonds exist in Ceramics
3. Polymers: Covalent and Secondary
4. Semiconductors: Covalent or Covalent / Ionic

Coursework

1. What is diffusion coefficient and Diffusion flux?
2. Write the expression for Fick's First. Explain each parameter
3. Explain non steady state diffusion based on Fick's law.
4. Given that D = diffusion coefficient , D_0 = temperature-independent preexponential and Q_d = activation energy for diffusion and T = absolute temperature. From $D = D_0 \exp\left(-Q_d/RT\right)$ express Q_d in terms D , D_0 , R and T
5. At 300°C the diffusion coefficient and activation energy for Cu in Si are $D(300^\circ\text{C}) = 7.8 \times 10^{-11} \text{ m}^2/\text{s}$ $Q_d = 41.5\text{KJ/mol}$, what is the diffusion coefficient at 350°C ?
6. Explain the effect of electronegativity on bonding in materials.
7. What is Atomic Packing Factor (APF)?
8. Calculate APF for FCC and BCC