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Imperfections in solids

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Nature is not perfect and so are the crystals, they may contain various types of imperfections and defects that influence many of their physical and mechanical properties. This influence could be beneficial as different types of defects can be intentionally introduced to produce specific characteristics within the material. (1)

Defects in Metals

Since crystallization does not occur in a regular perfect fashion, metals can have various types of defects which can be classified into 4 main categories: point, linear, interfacial and volume defects. (2)

1. Point defects (0-dimensional)

Point defects are zero-dimensional defects which occur when there is a missing, displaced, or extra atom. (2)

i. Vacancy defect

Vacancy is the simplest point defect where an atom is missing from one of the lattice sites (Figure 1). It may result from imperfect packing during crystallization, or due to increased thermal vibrations of the atoms at elevated temperature. Vacancies are important in determining the rate at which atoms or ions can move around (atomic diffusion). All crystalline solids have vacancies as it is impossible to create a material that is free of vacancies. The equilibrium number of vacancies $N\upsilon$ can be calculated through this equation: (1,2)

$$N\upsilon = N \exp(-\frac{Q\,\upsilon}{kT})$$

Where N is the total number of atomic sites, Q_υ is the energy required to form a vacancy, K is the Boltzmann's constant which is equal to 1.38 × 10−23 J/atom·K and T is the temperature in kelvins, therefore when temperature increase, the number of vacancies increase exponentially with temperature. (1,2)

ii. Self-interstitial defect

It is a type of point defects where the atom leaves it normal lattice site and occupies an interstitial site (Figure 1). In metal, self-interstitial defects produce large distortion in the surrounding lattice as the atom is much larger than the interstitial site it occupies, as a result, the probability of formation of this defect is low and much lower than vacancies. (2)

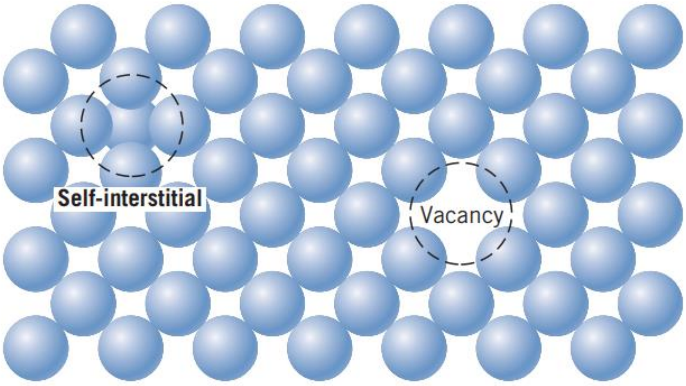


Figure 1: Two-dimensional representations of a vacancy and a self-interstitial.

iii. Impurities

Pure metals containing one type of atom does not exist, impurities will always be present. Impurities can be added intentionally to give specific properties to the material. (2)

The addition of impurity atoms to a metal could result in the formation of a **solid solution**. Solid solutions are made up of two components: a **solvent** which is the compound found in largest amount and a **solute** which presents in minor concentration. (2)

There are two types of solid solutions: *substitutional* and *interstitial*. (2)

In substitutional solid solution, the impurity atom replaces the original host atom (Figure 2), there are four rules that determine the degree of solubility of the solute in solvent, known as the ***Hume–Rothery rules***. According to these rules, substitutional solid solutions may form if the solute and solvent have: (2)

1. *Atomic radii difference less than 15%.* If more, the solute atoms will create substantial lattice distortions and a new phase will form.
2. *Same crystal structure.*
3. *Similar electronegativities,* if there is a large difference in electronegativity, the metals tend to form intermetallic compounds instead of solid solutions.
4. *Similar valency,* if all other factors are equal, A metal will have greater tendency to dissolve a metal with higher valency than one with lower valency. (2)

Figure 3: *Substitutional solid solution of copper in nickel.*

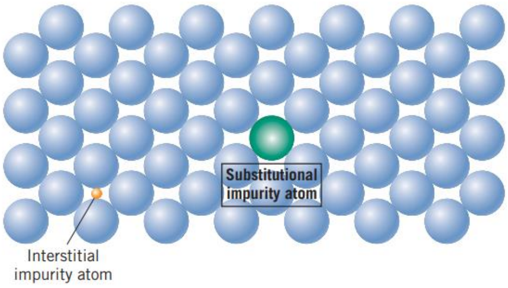
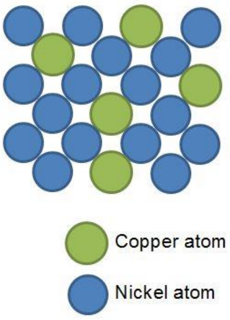


Figure 3: Substitutional solid solution of copper in nickel.



In interstitial solid solution, the impurity atoms fill the interstitial spaces between the host atoms (Figure 2). Metals have relatively high atomic packing factor, so their interstitial spaces are relatively small. Even if the impurity atom is very small, it would still be larger than the interstitial site causing lattice distortion (Figure 4). **Steel** is an example of interstitial solid solution where carbon atoms, *in maximum concentration of 2%,* occupy interstitial sites in the iron crystal structure since they are small enough to occupy these spaces with some strain (Figure 5). (2,3)

Figure 4: Lattice distortion by interstitial impurity atom.

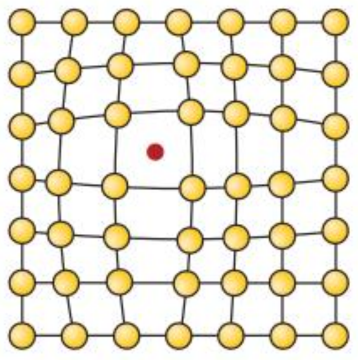
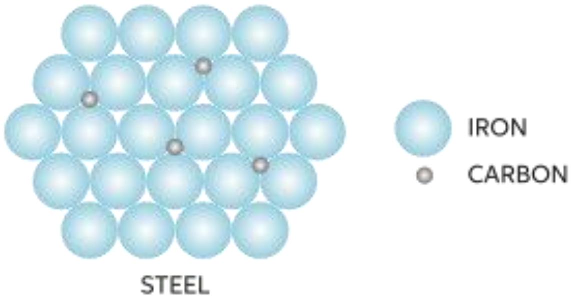


Figure 5: Interstitial solid solution of carbon in iron.



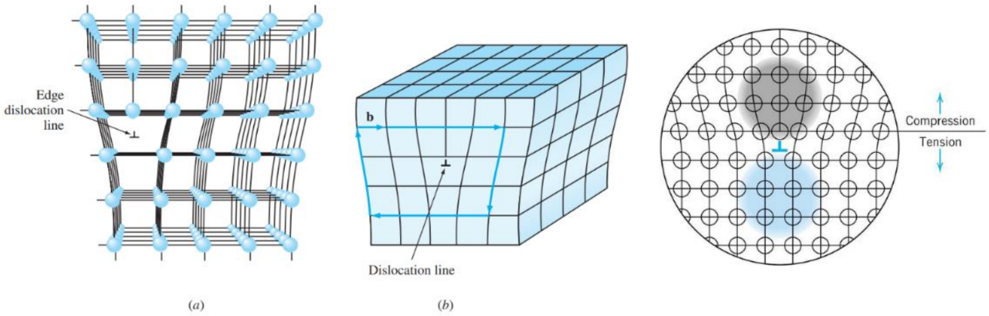
2. Linear defects (1-dimensional)

Linear defects, *also known as* ***dislocations***, are one-dimensional defect around which some of the atoms are misaligned. They are introduced into the material during solidification or when the material is permanently deformed. These defects cause distortion centered around a line. There are three types of dislocations: edge, screw and mixed dislocation. (2,5)

i. Edge dislocation

Edge dislocation is created when an extra half plane of atoms is inserted in the middle of the crystal, The bottom edge of this inserted half plane represents the edge dislocation. The dislocation line is indicated by the symbol ⊥. The atoms above the dislocation line are squeezed together (region of compressive strain), and those below are pulled apart (region of tensile strain). The lattice distortion around the dislocation is expressed in terms of the **Burgers vector b** which is **perpendicular** to the edge-dislocation line. (Figure 6) (3,5)

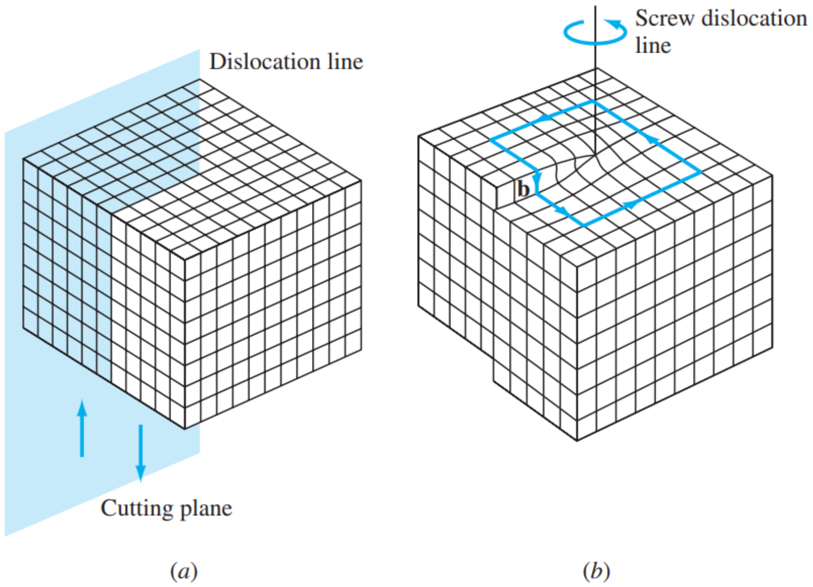
Figure 6: (a) Edge dislocation in a crystalline lattice. (b) Edge dislocation that indicates the orientation of its Burgers vector b. (c) Strain fields surrounding an edge dislocation.



ii. Screw dislocation

Screw dislocation is formed by a shear stress that is applied to produce the distortion. It is called a screw dislocation because the planes of atoms in the crystal lattice trace a helical path around the dislocation line. The vector required to complete the loop, ***Burgers vector b***, is parallel to the screw dislocation. (5) (Figure 7)

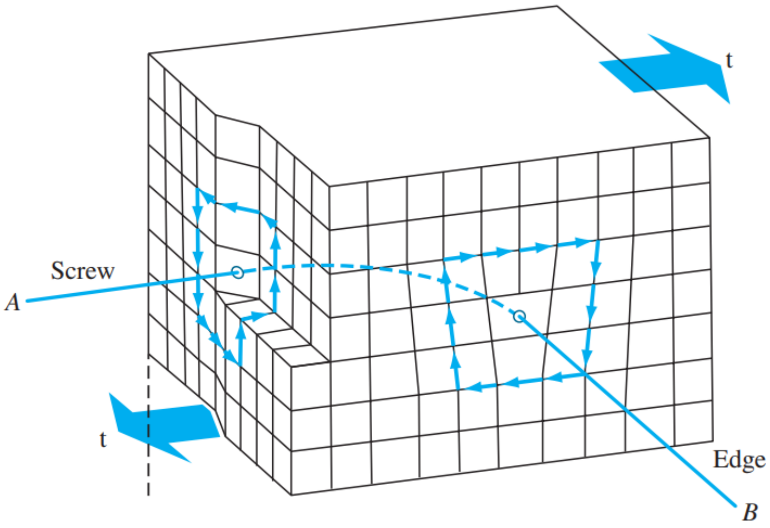
Figure 7: Formation of a screw dislocation. (a) A perfect crystal is sliced by a cutting plane, and up and down shear stresses are applied parallel to the cutting plane to form the screw dislocation in (b). (b) A screw dislocation is shown with its slip or Burgers vector b parallel to the dislocation line.



iii. Mixed dislocation

Most metals have large number of mixed dislocations, which have both **edge** and **screw** components with a transition region between them. Burgers vector is neither perpendicular nor parallel to the dislocation line. The Burgers vector remains the same for all portions of the mixed dislocation even though there is a change in the direction and nature of the dislocation within the crystal (e.g., from edge to mixed to screw). (Figure 8) (2)

Figure 8: Mixed dislocation in a crystal. Dislocation line AB is pure screw type where it enters the crystal on the left and pure edge type where it leaves the crystal on the right, For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw.



C. Interfacial defects (2-dimensional)

Those are surface defects that separate regions of material with different crystalline structure or orientation. Interfacial imperfections include external surfaces, grain boundaries, phase boundaries, twin boundaries, and stacking faults.(2)

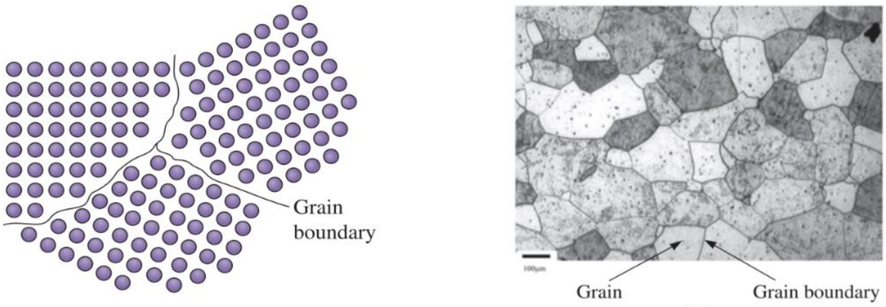
i. External Surface

It is the surface along which the crystal structure terminates. It is considered a defect because the atoms at the surface are not equally bonded from all sides, they have higher surface energy when compared to the atoms at the bulk of the crystal. The higher energy makes the atoms at the surface of the material susceptible to erosion and reaction with elements in the environment. (5)

ii. Grain boundaries

Most metals are polycrystalline, consisting of many grains with different orientation. The grains are separated from each other by **grain boundaries** (Figure 9). They are created during solidification when crystals formed from different nuclei grow simultaneously and meet each other. The grain boundary is a very narrow zone probably just several atom distances wide. Within this region, there is an atomic mismatch due to the transition from the crystalline orientation of one grain to that of an adjacent one. (2)

Figure 9: (a) Diagram showing the grains orientation and grain boundaries. (b) Grains and grain boundaries in a stainless-steel sample.



(a) **(b)**

Atoms at the grain boundaries have irregular arrangement, as a result, they have higher energy. This higher energy state makes the grain boundaries more chemically reactive than the grains themselves. Since grain boundaries are regions of atomic mismatch and less dense atomic packing, Impurities tend to segregate at these regions. (3,6)

Depending on the degree of crystallographic misalignment between adjacent grains, grain boundaries are classified into *low-angle grain boundaries* and *high-angle boundaries* (Figure 10). Low-angle grain boundaries can be viewed as an array of dislocations, giving two types of grain boundaries: tilt and twist boundaries. *Tilt boundary* can be viewed as a series of parallel edge dislocations. It occurs when the axis of rotation is parallel to the plane of the grain boundary (Figure 11). *Twist boundary* can be viewed as an array of screw dislocations, it occurs when the axis of rotation is perpendicular to the plane of the grain boundary. (2)

Figure 10: Schematic diagram showing low and high-angle grain boundaries.

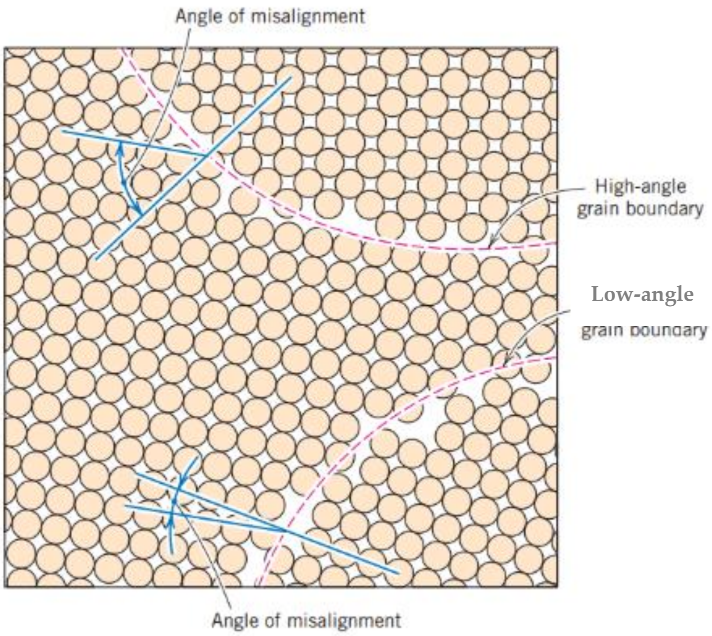
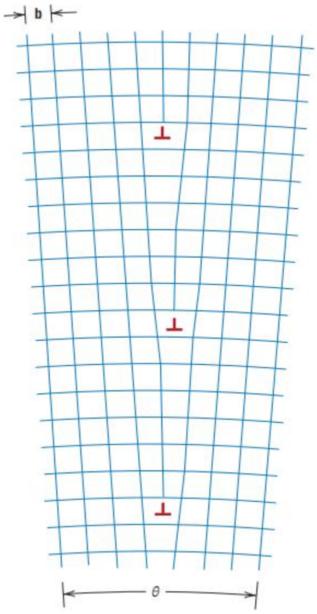


Figure 11: Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.



iii. Phase boundaries

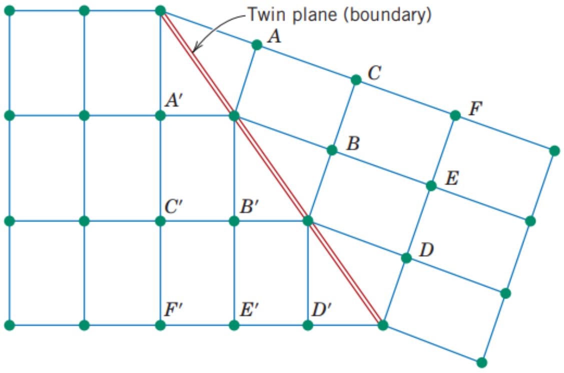
They are the boundaries that exist in multi-phase materials, in which there is a different phase on each side of this boundary and each phase has its own physical and chemical properties. (2)

iv. Twin boundaries

They are a special type of grain boundaries at which the atomic arrangement on one side of the boundary is a mirror image of the arrangement of atoms of the other side (Figure 12). The region of material between these boundaries called a twin. They are produced either by applied mechanical shear forces (mechanical twins) or by annealing heat treatments (annealing twins). (2,3)

Other possible interfacial defects include stacking faults and domain walls. Stacking faults occur when there is an interruption in the stacking sequence of the atomic layers in a crystal. Domain wall is a boundary that separates regions having different directions of magnetization in magnetic materials. (2)

Figure 12: Diagram showing a twin plane or boundary.



4. Volume defects (3-dimensional)

Volume defects or bulk defects are clusters of point defects. They include discontinuities such as pores, microcracks, inclusions, and other phases. These defects can be introduced during processing and fabrication steps. (2,5)

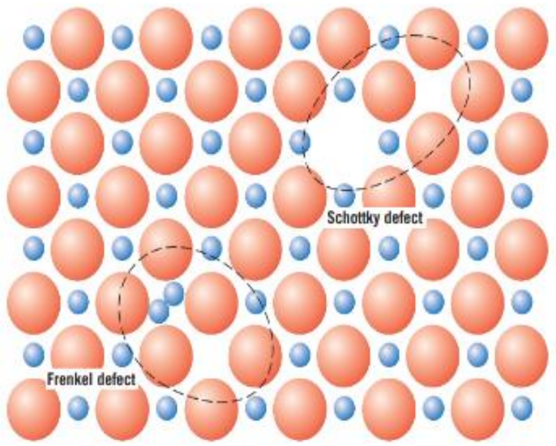
III. Defects in Ceramics

Ceramic materials are inorganic and nonmetallic materials, they are composed of metallic and non-metallic elements. So, their crystal structure is more complex than metals. Their atomic bonding ranges from purely ionic to totally covalent. Regarding ceramic materials with predominantly ionic atomic bonding, the crystal structure is composed of electrically charged ions; positively charged cations and negatively charged anion. The cations are normally smaller than anions as they lost their valence electrons when ionized. The crystal must be electrically neutral; the cation positive charges must be equal to the anion negative charges. When atomic defects occur, the electroneutrality state must be maintained, because of that, defects in ceramic do not occur alone, they usually come in pairs. Frenkel and Schottky defects are two of the most common defects that occurs in ceramic materials. (7)

i. Frenkel defect

It is a type of point defect where a positive cation leaves its normal position and move to an interstitial site. It is a combination of both cation vacancy and cation interstitial type of defects. It occurs when there is a large difference in the size between the anion and cation where the cation is much smaller and will fit better in the interstitial sites. The number of cations and anions remain equal, as a result, charge neutrality is maintained. Frenkel defect does not have any impact on the density of the crystal (Figure 13). (7,8)

Figure 13: Schematic diagram showing Frenkel and Schottky defects in ionic solids.



ii. Schottky defect

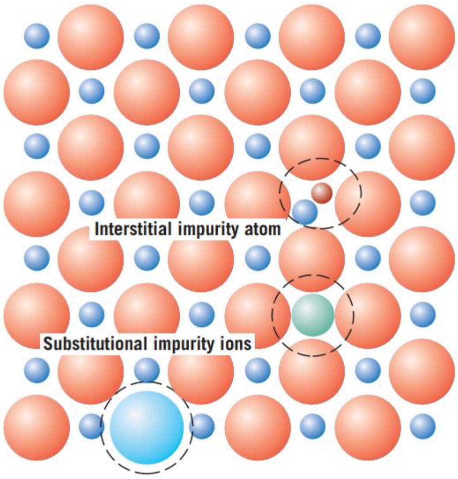
It is another type of point defect where an anion and a cation are removed from the interior of the crystal and placed at an external surface. It is a combination of both cation and anion vacancies, it occurs when the anion and cation have similar size. Since they carry opposite charges, charge neutrality is maintained. However, there is a decrease in the density of the crystal since a fraction of ions leave the crystal (Figure 14). (7,9)

In both, Frenkel and Schottky defects, the ratio of anions to cations is not changed by the defect, so the ceramic compound is said to be stoichiometric. However, if there is any deviation from the ratio of anions to cations as predicted by the chemical formula, the ceramic compound is said to be nonstoichiometric. (7)

iii. Impurities

Impurity atoms can form substitutional and interstitial solid solutions in ceramics as they do in metals. For an interstitial solid solution to occur, the radius of the impurity ion must be relatively small in comparison to the anion. However, for a substitutional solid solution to occur, the size and charge of the impurity ion must be nearly the same as one of the host ions whether a cation or an anion. If the impurity ion has a different charge than that of the host ion, crystal must compensate for this difference in charge by the formation of lattice defects so that the electroneutrality is maintained (Figure 14). (7)

Figure 14: Schematic representations of interstitial, anion-substitutional and cation-substitutional impurity atoms in an ionic compound.



Note: Common ceramic materials include Silica. Silica can be crystalline or amorphous. In amorphous silica, the atoms have a short-range order. It is made up of continuous network of connected structured tetrahedral units consisting of one silicon surrounded by four oxygen (Figure 15). Coordination defects are the main type of defects found in these amorphous solids. They are a kind of defect when the atom has different coordination compared to the atoms of similar type in the structure. A coordination defect can occur in silica due to oxygen vacancy; the neighboring silicon will have coordination number of three instead of the typical four (Figure 16). (10)

Figure 15: (a) Structural Unit of Silica, (b) Amorphous Silica.

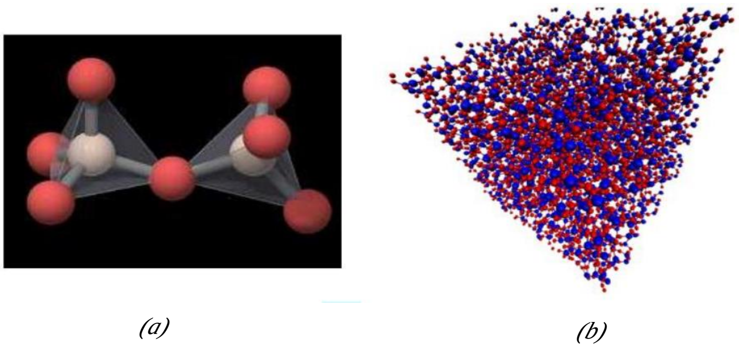
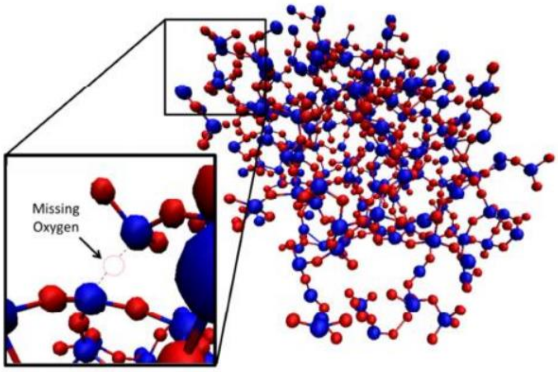

(a) *(b)*

Figure 16: Diagram showing coordination defect in an amorphous structure where silica is surrounded by three oxygen atoms instead of four.



IV. Defects in Polymers

Polymers are high molecular weight long-chain macromolecules. Generally, polymers are amorphous structure with randomly coiled and entangled chains. However, some chains align themselves to form crystalline regions within the remaining amorphous material (Figure 17). (11)

Defects in the polymer structure are due to the chain-like macromolecules and the nature of the crystalline state for polymers. The crystalline regions may have point defects like vacancies, interstitial atoms and impurity atoms similar to those found in metals. Chain ends are considered defects as they are chemically different from normal chains units. Vacancies are also associated with chain ends. Defects can also result from branches in the polymer chain, dangling chains, loose chains, and dislocations (Figure 18). (12)

Figure 17: Diagram of polymers a) Polymer containing only amorphous structure (b) Polymer containing amorphous and crystalline regions.

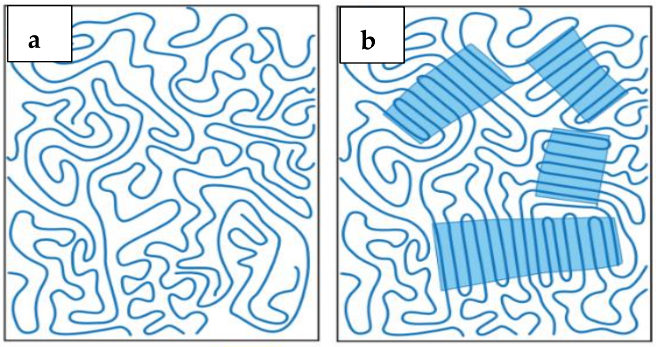
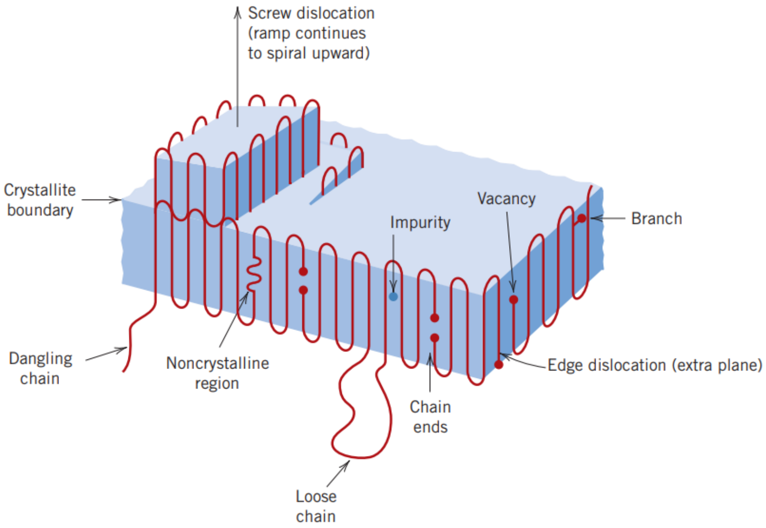


Figure 18: Schematic representation of defects in polymer crystallites.



V. Effect of defects on the properties of the material

Defects play an important role in influencing the properties of the materials, Dislocations are especially important in metals and alloys as they provide a mechanism for *plastic deformation*. When the applied stress is above the yield strength, it will cause bond breakage, dislocation movement and permanent deformation. This must be distinguished from *elastic deformation* where only stretching of the inter-atomic bonds occurs and no dislocation movement. The dislocation movement occurs through a process known as slip (Figure 19). (3)

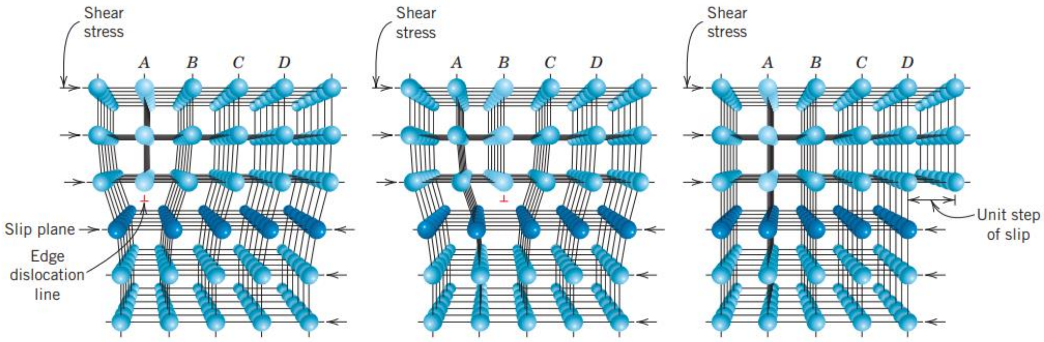
The slip process is important in understanding the mechanical behavior of metals:

1. It explains why the strength of metals is much lower than the value predicted from the metallic bond because only a tiny fraction of metallic bonds is being broken at any one time, rather than the whole row at once. So, the force required to deform a material is lower than expected.

2. It provides ductility in metals, if there are no dislocations, the metal would be brittle.

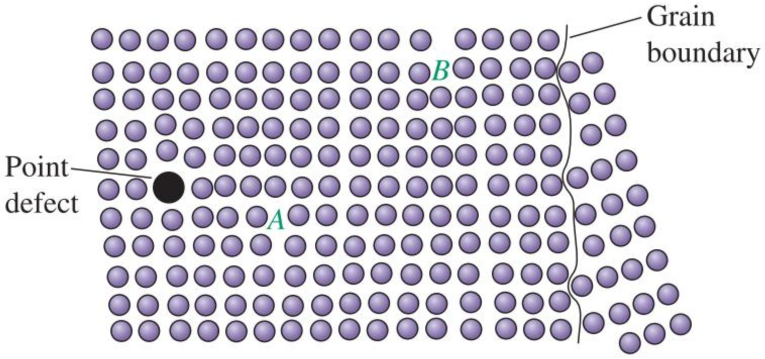
3. Controlling the mechanical properties of metals or alloys can be done by interfering with dislocation movement. Any obstacle that prevents dislocation movement will increase the strength since higher forces are needed to overcome this obstacle. (3)

Figure 19: Diagram showing motion of an edge dislocation as it moves in response to an applied shear stress.



Defects as point defects, dislocations, and grain boundaries act as "*stop signs*" for dislocations; they obstruct dislocation movement, As a result, higher stresses are needed to overcome these obstacles, therefore, the strength of the material is increased (Figure 20).⁽³⁾

Figure 20: *If the dislocation at point A moves to the left, its motion is hindered by the point defect. If the dislocation moves to the right, it interacts with the distorted lattice near the second dislocation at point B. If the dislocation moves farther to the right, its motion is obstructed by a grain boundary.*



Three common strengthening mechanisms are based on the three categories of defects in crystals: Strain Hardening, Solid-Solution Strengthening and Grain-Size Strengthening. These mechanisms work best for metallic materials because dislocation movement is easier in metals and alloys. (3)

Strain Hardening: By increasing the number of dislocations by cold working. since increasing the dislocation density causes more stop signs for dislocation motion. (3)

Solid-Solution Strengthening: By intentionally introducing substitutional or interstitial impurity atoms, solid-solution strengthening occurs. (3)

In both types of solid solutions, the impurity atoms will distort the lattice due to the difference in atomic size between solute and solvent. As a result, dislocation movement is inhibited which will lead to strengthening of the material, the degree of strengthening depends on: (4)

The difference in atomic size between solute and solvent, the larger the difference, the greater the strengthening.

The concentration of solute atoms, the higher the concentration, the greater the strengthening effect.

Grain-Size Strengthening: By reducing the grain size, the number of grains increase. Thus, the amount of grain boundary area increases, as a result, the strength of the material will increase. (3)

Other effects on the properties of materials:

Twin boundaries interfere with the slip process; thus, the strength of the material increases. (3)

Crystalline defects serve as scattering centers for electrons conduction in metals, increasing the number of defects, will decrease the electric conductivity. (3)

Cracks and pores have undesirable effects as they decrease the strength and fracture resistance of the materials. (3)

VI. Microscopic Examination

Structural elements and defects have a large influence on the properties of the materials. Some of these structural elements are of macroscopic dimensions which can be seen by naked eye. However, in most materials, they are in microscopic dimensions. As a result, they must be investigated using microscope. Microscopic examination is very useful in the study and characterization of materials. The common types of microscopes are optical, electron, and scanning probe microscopes. (2)

A. Optical Microscopy

Optical or light microscopy involves passage of visible light transmitted through or reflected from the sample through a single lens or multiple lenses to allow a magnified view of the sample. Surface preparation of the sample must be done first to reveal the microstructure details, this involves polishing and etching of the specimen surface in order to achieve a smooth and mirror-like finish. (2,5)

In polycrystalline materials, etching characteristics and resulting surface texture vary from grain to another due to different crystallographic orientation (Figure 21). Also, upon etching, atoms along grain boundaries are more chemically active and therefore dissolve faster than those within the grains, forming small grooves along the grain boundaries, these grooves are detectable under microscope as they reflect light at a different angle than the atoms within the grain, so they appear under microscope as dark lines (Figure 22). (2)

Figure 21: (a) How polished and etched grains might appear when viewed with an optical microscope. (b) Grains with different crystallographic orientation have different etching characteristics and resulting surface texture.

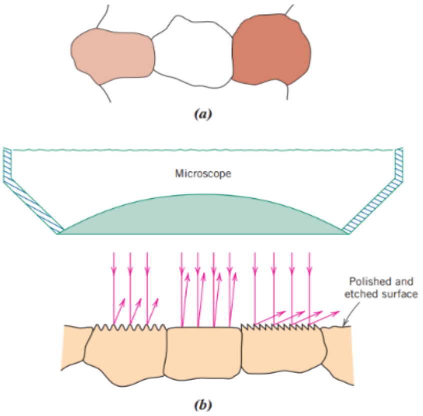
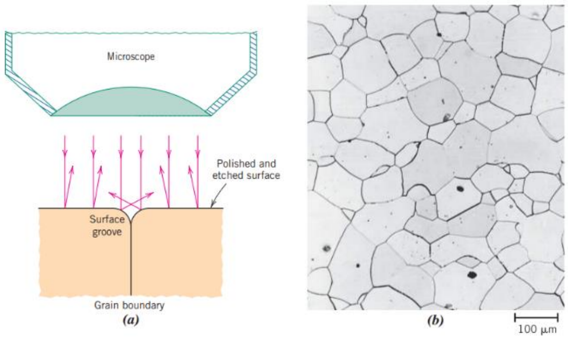


Figure 22: (a) Section of a grain boundary and its surface groove produced by etching, the light reflection characteristics are also shown. (b) Photomicrograph of the surface of a polished and etched polycrystalline specimen in which the grain boundaries appear dark.



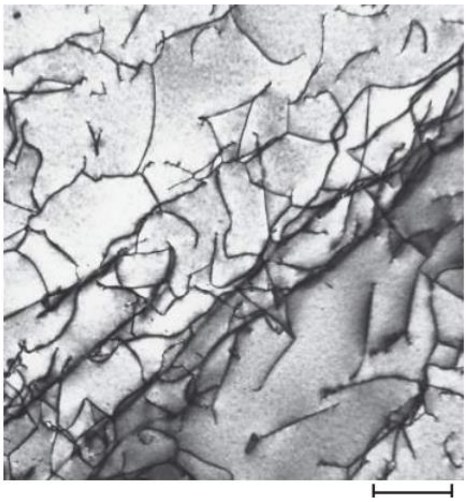
B. Electron Microscopy

The magnification of optical microscope is limited to 2000X which is insufficient for observation of very fine structural elements, in such cases, the electron microscope can be used. It uses a **beam of electrons** instead of light to form the image. It is characterized by **high magnification and resolving power** because of the short wavelengths of electron beams. The two types of electron microscopes are Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). (2)

Transmission Electron Microscopy (TEM)

TEM allows magnification up to 1,000,000× therefore it is commonly used to study dislocations (Figure 23). The image is formed by passing an electron beam through the specimen. The specimen preparation for TEM analysis is complex and requires highly specialized instruments. It should be very thin to allow transmission of electron through the specimen. The transmitted beam is then projected onto a fluorescent screen or photographic film. (2,5)

Figure 23: A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations.



Scanning Electron Microscopy (SEM)

SEM allows magnification from 10× to 50,000×. The surface of the specimen is scanned with ***electron beam***, the reflected beam is collected and then displayed on a screen. The surface of the specimen must be electrically conductive. If the material is nonconductive, it must be covered with a thin layer of conductive material, most commonly gold. This is done by using a device called a "sputter coater." (2,5)

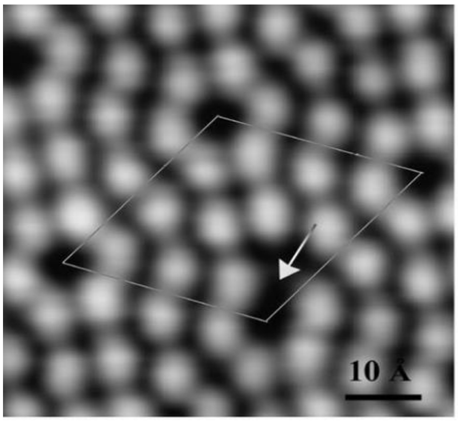
The main difference between SEM and TEM is that SEM creates an image by detecting reflected electrons, while TEM uses transmitted electrons (electrons that are passing through the sample) to create an image. As a result, TEM offers valuable information on the inner structure of the sample, while SEM provides information on the sample’s surface. (2)

C. Scanning Probe Microscopy

A scanning probe microscope (SPM) is used for studying surfaces at the *nanoscale* level. It allows magnification up to 10^9x which provides much better resolution than other microscopic techniques. SPMs use a tiny probe with a very sharp tip to scan the specimen’s surface, the probe does not touch the surface but traces the specimen nanometers above the surface. The movement of the probe allow generation of a 3D topographic image of the surface at the atomic scale (Figure 24).(2)

Scanning Tunneling Microscopes (STMs) and Atomic Force Microscopes (AFMs) are examples.

Figure 24: Scanning probe micrograph showing vacancy defect.



CONCLUSION

Materials are rarely perfect; they usually contain defects or imperfections that affect their properties either in a positive or a negative way. Several microscopes are used for examining such defects.

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