Surface, volume defect and effectof imperfections on properties of crystalline solids.

Surface defects

These are two dimensional imperfections that lies in the metal with polycrystalline structures or they are also called as interfacial defects can be defined as boundaries that have two dimensional imperfections in crystalline solids, and have different crystal structures and/or crystallographic orientations on either side of them. They refer to the regions of distortions that lie about a surface having thickness of a few atomic diameters. For example: external surfaces, grain boundaries, twin boundaries, stacking faults, and phase boundaries. These imperfections are not thermodynamically stable, rather they are meta-stable imperfections. They arise from the clustering of line defects into a plane.

External surface: The environment of an atom at a surface differs from that of an atom in the bulk; especially the number of neighbors (coordination) at surface is less. Thus the unsaturated bonds of surface atoms give rise to a surface energy. This result in *relaxation* (the lattice spacing is decreased) or *reconstruction* (the crystal structure changes). To reduce the energy, materials tend to minimize, if possible, the total surface area.

Grain boundaries: Crystalline solids are, usually, made of number of grains separated by grain boundaries. Grain boundaries are several atoms distances wide, and there is mismatch of orientation of grains on either side of the boundary as shown in *figure-3.6*. When this misalignment is slight, on the order of few degrees (< 10°), it is called *low angle grain*

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boundary. These boundaries can be described in terms of aligned dislocation arrays. If the low grain boundary is formed by edge dislocations, it is called *tilt boundary*, and *twist boundary* if formed of screw dislocations. Both tilt and twist boundaries are planar surface imperfections in contrast to high angle grain boundaries. For *high angle grain boundaries,* degree of disorientation is of large range (> 15°). Grain boundaries are chemically more reactive because of grain boundary energy. In spite of disordered orientation of atoms at grain boundaries, polycrystalline solids are still very strong as cohesive forces present within and across the boundary.
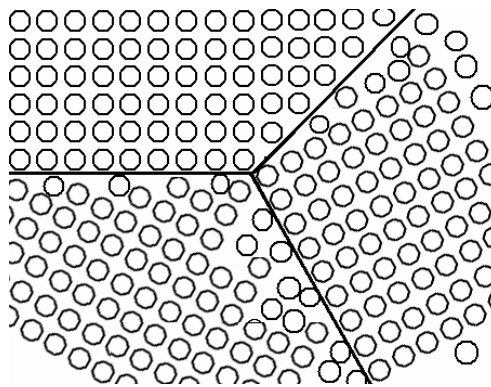

Fig 10: *Schematic presentation of grain boundaries*.

Tilt boundaries: *If the low grain boundary is formed by edge dislocations, it is called **tilt boundary**. A tilt boundary, between two slightly misaligned grains as an array of edge dislocations. Rotation axis is parallel to the boundary plane.*
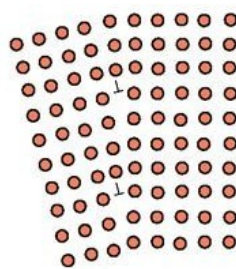

Fig 11: Tilt boundaries

Twist boundaries: *If the low grain boundary is formed by screw dislocations, it is called **twist boundary**. Rotation axis is perpendicular to the boundary plane*

Twin boundaries: It is a special type of grain boundary across which there is specific mirror lattice symmetry. Twin boundaries occur in pairs such that the orientation change introduced by one boundary is restored by the other (*figure-*). The region between the pair of boundaries is called the twinned region. Twins which forms during the process of recrystallization are called *annealing twins*, whereas *deformation twins* form during plastic deformation. Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure. Annealing twins are typically found in metals that have FCC crystal structure (and low stacking fault energy), while mechanical/deformation twins are observed in BCC and HCP metals. Annealing twins are usually broader and with straighter sides than mechanical twins. Twins do not extend beyond a grain boundary.
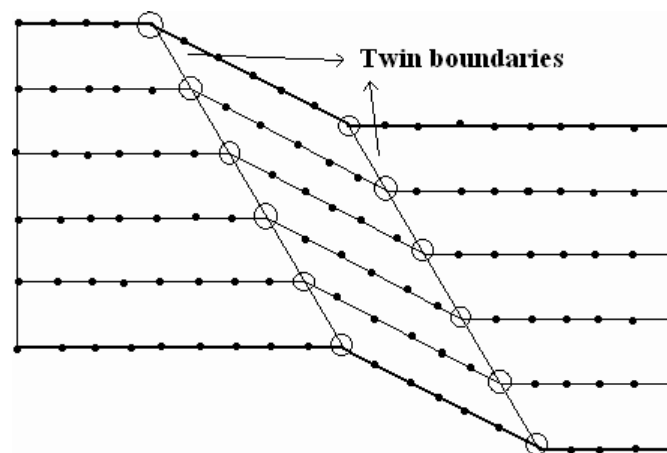

Fig 12. *A pair of twin boundaries*

Stacking faults: They are faults in stacking sequence of atom planes. Stacking sequence in an FCC crystal is ABC ABC ABC …, and the sequence for HCP crystals is AB AB AB…. When there is disturbance in the stacking sequence, formation of stacking faults takes place. Two kinds of stacking faults in FCC crystals are: (a) ABC AC ABC…where CA CA represent thin HCP region which is nothing but stacking fault in FCC, (b) ABC ACB CABC is called *extrinsic* or *twin stacking fault*. Three layers ACB constitute the twin. Thus stacking faults in FCC crystal can also be considered as submicroscopic twins. This is why no microscopic twins appear in FCC crystals as formation of stacking faults is energetically favorable. Stacking fault energy varies in range 0.01-0.1 J/m^2. Lower the stacking fault energy, wider the stacking fault, metal strain hardens rapidly and twin easily. Otherwise, metals of high stacking fault energy i.e. narrower stacking faults show a deformation structure of banded, linear arrays of dislocations.

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Phase boundaries exist in multiphase materials across which there is sudden change in physical/chemical characteristics.

The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this mid-plane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 mid-plane interior atoms. If a and c represent, respectively, the short(basal) and long 9 height) parameters of unit cell dimensions of Fig a, the c/a ratio should be 1.633 . The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively
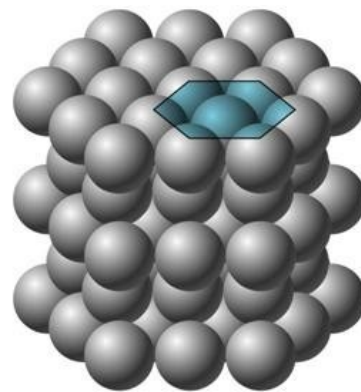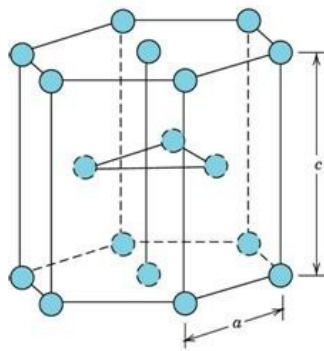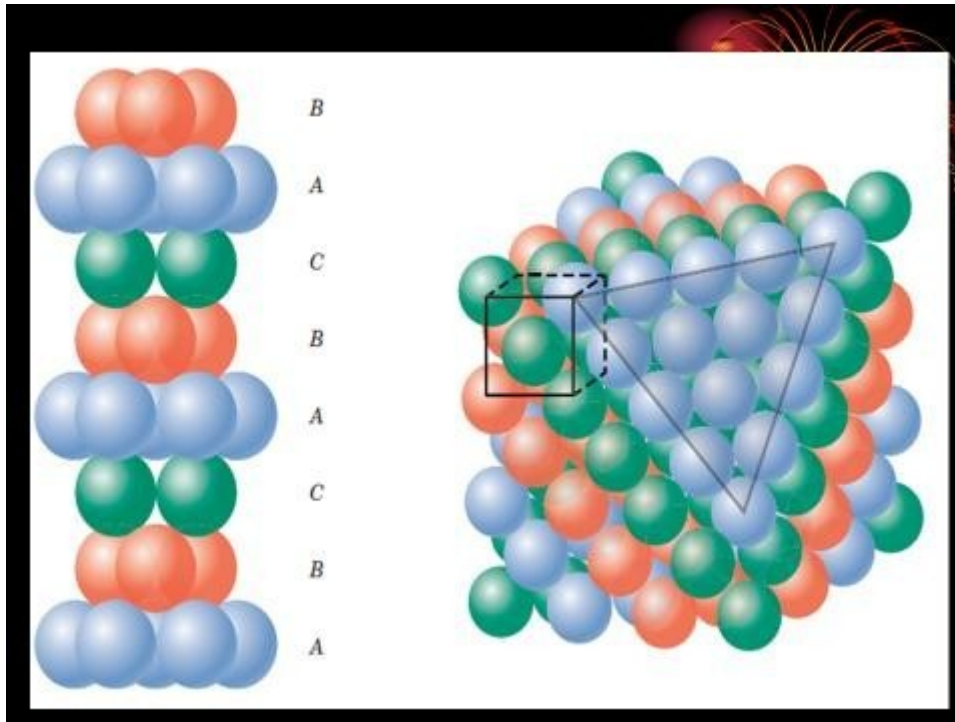

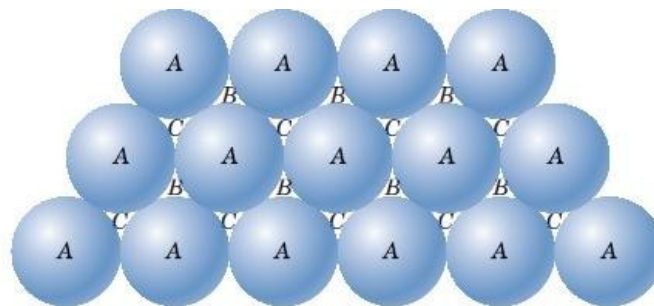Figure 13. HCP structure.

Figure 14: Staking Sequence.

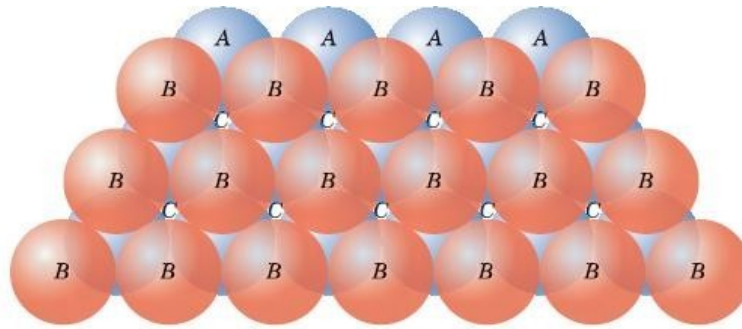Figure 15: Representation of atomic planes.

Figure 16: Atomic planes

Volume defects

As name suggests are defects in 3-dimensions. These include pores, cracks, foreign inclusions and other phases. These defects are normally introduced during processing and fabrication steps. All these defects are capable of acting as stress raisers, and thus deleterious to parent metal's mechanical behavior. However, in some cases foreign particles are added purposefully to strengthen the parent material. The procedure is called dispersion hardening where foreign particles act as obstacles to movement of dislocations, which facilitates plastic deformation. The second-phase particles act in two distinct ways – particles are either may be cut by the dislocations or the particles resist cutting and dislocations are forced to bypass them. Strengthening due to ordered particles is responsible for the good high-temperature strength on many super-alloys. However, pores are detrimental because they reduce effective load bearing area and act as stress concentration sites.

Effects of imperfections on crystal properties

The crystal imperfections can lead to variation of mechanical, electrical, magnetic and optical properties in a material. The different types of imperfections have their significant impact on the base property of the material. This variation of the properties is utilized to the suitable application in the industry.

A perfect crystal, with every atom of the same type in the correct position, does not exist. All crystals have some defects. Defects contribute to the mechanical properties of metals. In fact, using the term "defect" is sort of a misnomer since these features are commonly intentionally used to manipulate the mechanical properties of a material. Adding alloying elements to a metal is one way of introducing a crystal defect. Nevertheless, the term "defect" will be used, just keep in mind that crystalline defects are not always bad.

Extrinsic point defects affect almost all engineering properties, but they are particularly important in semiconducting crystals, where extrinsic defects are used to control electrical properties, and in structural metals and alloys, where extrinsic defects are added to increase mechanical strength.

Donors and acceptors in semiconductors: Point defects are intentionally added to semiconductors to control the type and concentration of charge carriers. Consider, for example, boron (valence 3) as a substitutional solute in elemental silicon. The saturated covalent bonds in silicon are shown schematically in Fig 17a, and depend on the availability of four valence electrons per silicon atom. Since the bonds are saturated, silicon has very low conductivity in its pure state; pure silicon can only conduct electricity when electrons are excited into high energy electron states. If boron is added, as in Fig 17b, a valence electron is missing from the immediate environment of the boron atom, causing a hole in the bonding pattern. Electrons can then move from bond to bond by exchanging with the hole. The exchange requires some energy to separate the hole from the boron ion core, but this energy is small compared to that required to excite an electron from a Si-Si bond into a high-energy state. The room-temperature conductivity of Si increases significantly when a small amount of B is added. Electron-deficient solutes like boron that cause holes in the configuration of bonding electrons are called acceptors.
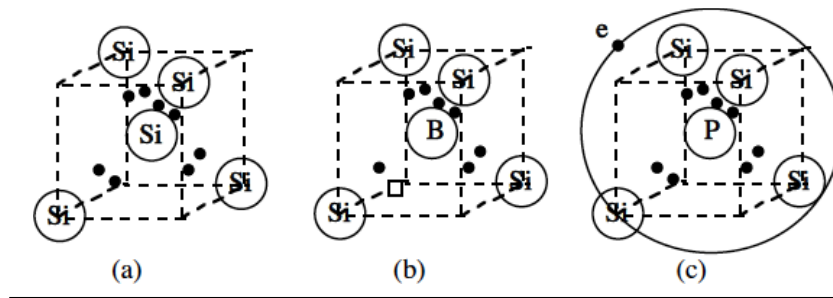
Fig 17: (a) Tetrahedral bonding configuration in Si. (b) Bonding around a B solute, showing a hole. (c) Bonding around a P solute, showing an electron (e) in a loose excited orbital.

The conductivity also rises when a solute with an excess of electrons is added to a semiconductor with saturated bonds. For example, let phosphorous (valence 5) be added to Si, as in Fig 17c. The 5 valence electrons of P are sufficient to fill the local covalent bonds with one electron left over. This electron can only go into an excited state, and orbits about the P ion core somewhat as shown in the figure. It requires a relatively small energy increment to free this electron from the P core, in which case it can transport current by moving through the lattice. The conductivity of Si rises dramatically if a small amount of P is added. Electron-excess solutes such as P in Si are called donors. Semiconductors whose electrical properties are controlled by electrically active solutes are called extrinsic semiconductors. Almost all of the semiconductors that are used in engineering devices are extrinsic.

Solution hardening in structural materials: The addition of solute atoms almost always increases the mechanical strength of a solid. The phenomenon is called solution hardening. It is due to the fact that the solute atom is always a bit too large or a bit too small to fit perfectly into the crystal lattice site it is supposed to occupy, and distorts the crystal lattice in its attempt to fit as well as possible. This distortion impedes the motion of the linear defects (dislocations) that are responsible for plastic deformation and, consequently, hardens the crystal. The distortion due to a substitutional solute is relatively small, though the associated hardening may be large enough to be useful in the engineering sense. The distortions due to interstitial atoms such as carbon and nitrogen are normally much greater because of the small size of the interstitial void in which they must fit. The hardening effect of interstitial solutes is large and technologically important; for example, high strength structural steels are alloys of

Fe and C.

Plastic deformation: It is important to note at this point that plastic deformation in a material occurs due to the movement of dislocations (linear defects). Millions of dislocations result for plastic forming operations such as rolling and extruding. It is also important to note that any defect in the regular lattice structure disrupts the motion of dislocation, which makes slip or plastic deformation more difficult. These defects not only include the point and planer defects. Dislocation movement produces additional dislocations, and when dislocations run into each other it often impedes movement of the dislocations. This drives up the force needed to move the dislocation or, in other words, strengthens the material.