2. Defects and Diffusion in Materials

2.0 Introduction:

We know that a perfect crystal is a periodic arrangement of atoms in the lattice arrays in all directions. Real crystals show deviation from perfect regular lattice structure, i.e., they have a large number of defects. Any deviation in the crystal from the perfect atomic periodicity is called lattice defect.

Thus, lattice defect is the state in which the lattice arrays of atoms are not continuous throughout the crystal.

2.1 Types of Defects:

The crystal defects arise due to the presence of imperfections. Crystal defects can be classified on the basis of their geometry as

l. Point defects
2. Line defects
3. Surface or plane defects
4. Volume defects

2.01 Point defects:

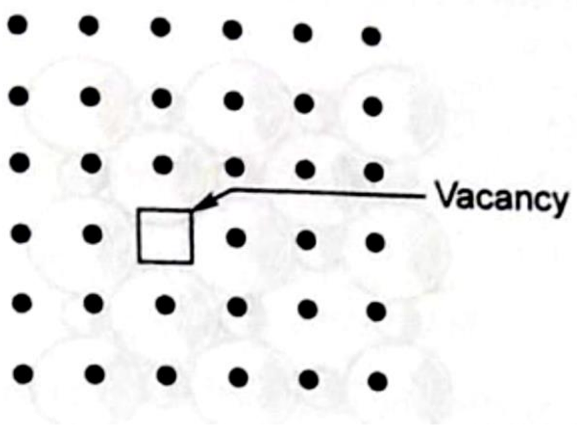
The simplest category of crystal defect is point defect. The point defects are imperfect point like region in the defects crystal. Their influence extends to only a few atoms diameters beyond their lattice positions.

The point defects are

(a) Vacancy defect
(b) Substitutional impurity defect
(c) Interstitial impurity defect

(a) Vacancy defect:

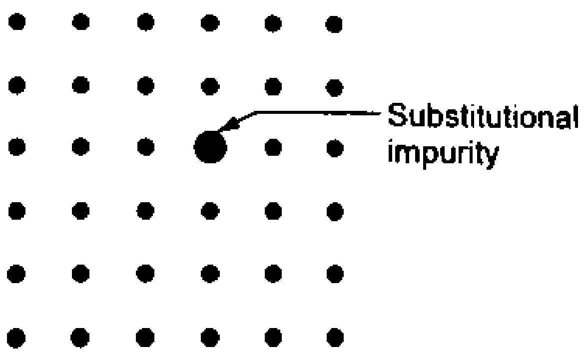
When an atom is missing from its normal position, then the defect is called as vacancy point defect. This is shown in fig.

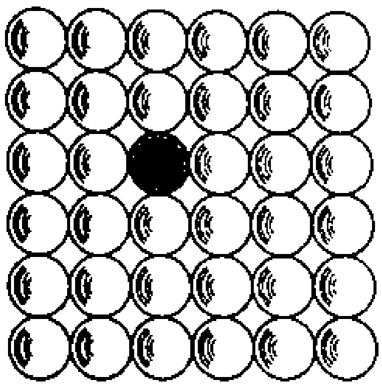


Vacancies may be single, two, or more. In metals, the vacancies are created by thermal excitation. At sufficiently high temperatures, the atoms of the solid vibrate vigorously about their regular positions. If an atom acquires enough energy, then it leaves its site completely. Now a vacancy is created. This vacancy is called a vacancy defect in a crystal.

(b) Substitutional impurity defect:

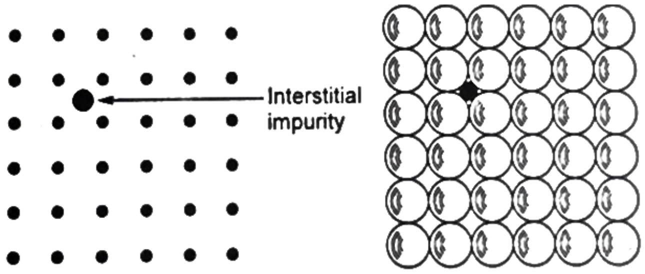
A foreign atom may replace a regular atom-giving rise to substitutional impurity. Pentavalent or trivalent impurity atoms doped in silicon or germanium are also substitutional impurities in the crystal. The substitutional impurity is shown in fig.





(c) Interstitial impurity defect:

When a foreign atom occupies the void space between the atoms of the crystal, then it is known as interstitial impurity. The interstitial impurity is shown in fig.

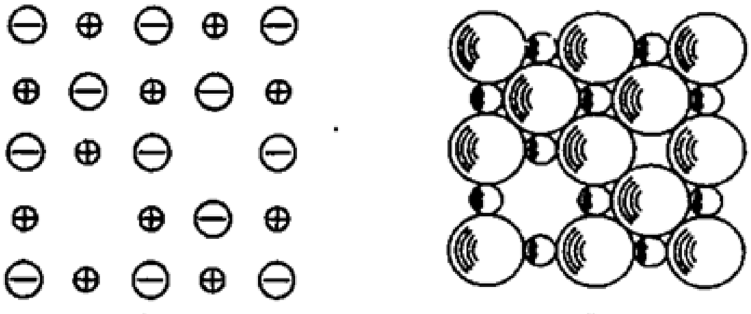


In crystals, there is some empty or space which is not occupied by the atoms of the crystal. If a small sized atom occupies the void space in the parent crystal without disturbing the parent atoms from their regular sites, then it is called as interstitial impurity.

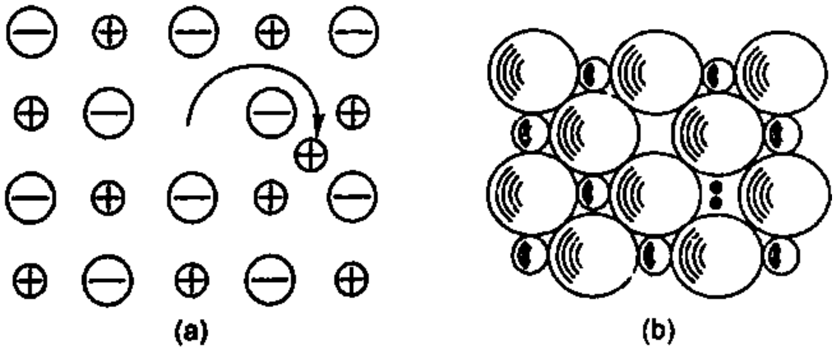
Schottky and Frenkel defects:

A pair of one cation and one anion can be missing from an ionic crystal. Such a pair of vacant ion sites is called Schottky defect.

In alkali halides or non-metallic crystals, a vacancy at a positive ion-site requires a local readjustment of charge in the surrounding crystal, so that a charge neutrality is maintained in the crystal as a whole. Thus, if there is a vacancy in a positive ion-site, the charge neutrality may be achieved by creating vacancy in neighbouring negative-ion site. Such a pair of vacant sites is called Schottky defect. This is shown in fig.


(a) (b)

When an atom is transferred from its regular lattice site to an interstitial position (void space between atoms, i.e., the position not normally occupied by an atom) is called as Frenkel defect. This defect is shown in fig.



This defect is produced when the crystal is exposed to a high energy radiation. The radiation may knock out atom or atoms to force it or them into interstitial spaces.

Frenkel Vs Schottky Defects

- Both the defects occur in non-metallic crystals like ionic crystals.
- Schottky defect is related to vacancies while Frenkel defects are interstitial in nature.
- Schottky defects are dominant in closed packed structures such as NaCI while Frenkel defects are prevalent in open structures such as those of silver halides.
- Both the defects are temperature dependent.
- In general, both the defects are caused by thermal fluctuations.
- The number of Schottky defects are proportional to number of atoms in the crystal (N) while the number of Frenkel defects is proportional to $\sqrt{(NN_i)}$ where N is number of atoms in the crystal and N_i is number of interstitial atoms.

2.02 Line defects:

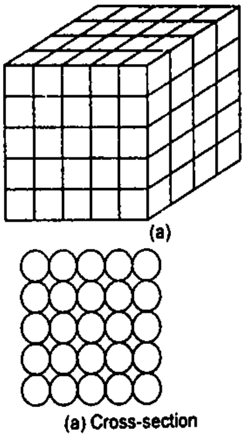
The line defects are known as dislocations. In geometrical sense, the line defect is a one dimensional defect. These defects take place due to dislocation or distortion of atoms along a line in some direction. A dislocation is defined as a disturbed region between two substantially perfect parts of a crystal.

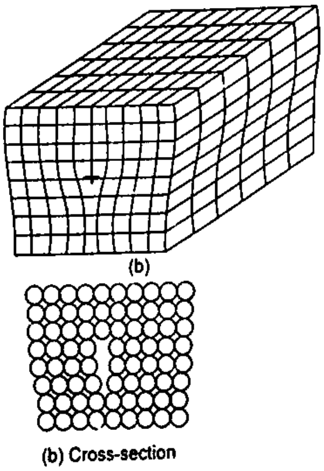
The two types of dislocations are :

(1) Edge dislocation, and (2) Screw dislocation.

(1) Edge Dislocation:

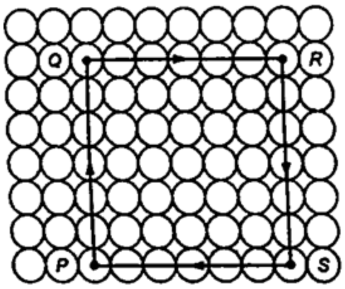
In a perfect crystal, the atoms are arranged in both vertical and horizontal plane parallel to the side faces as shown in fig. (a). If one of these vertical planes does not extend to full length but ends in between within the crystal as shown in fig. (b), then it is called edge dislocation. Therefore, in this defect, a line of atoms is not in proper position or, part of vertical layer of atoms is removed.



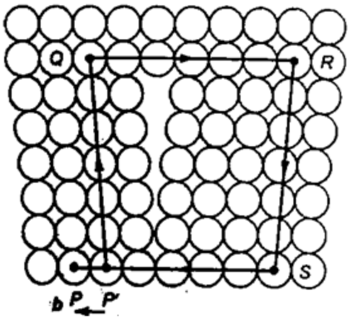


Burgers Vector

To understand the concept of Burgers vector, let us consider two crystals one perfect and the other with edge dislocation as shown in figures (a) and (b) respectively.



(a) Perfect crystal



(b) Edge dislocation

Burgers vector of a dislocation is determined by tracing a Burgers circuit. The procedure for drawing the Burgers circuit is as follows:

Let us consider the Burgers circuit in case of perfect crystal [Fig. (a)]. The Burgers circuit is realized by drawing a rectangular from point P (centre of an atom). Starting from point P, we go up by 6 steps (say) to a point Q, then move towards right by 6 steps (say) to a point R, further move down by 6 steps to a point S and finally move towards left by 6 steps to reach the starting point P. This gives a closed circuit PQRS known as Burgers circuit. In this particular case, the Burgers circuit is square.

Let us consider that the above procedure is repeated in case of imperfect crystal [Fig. (b)]. In this case, we end at a point P' instead of starting point P. Therefore, to come back to the starting point P, we have to advance an extra step backward, i.e., a distance P' P.

Now, we define Burgers vector.

The magnitude and the direction of the backward step P'P is defined by a vector called Burgers vector.

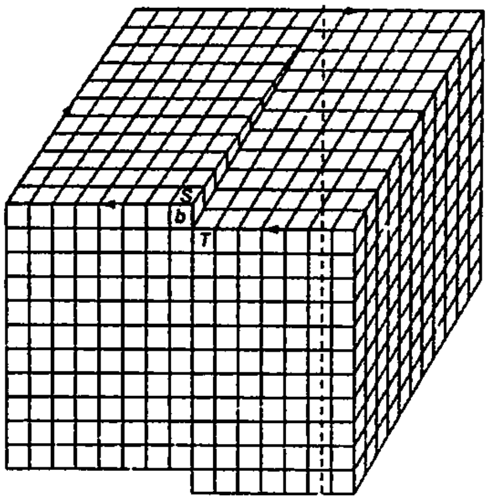
Burgers vector = P' P = b

The Burgers vector is perpendicular to the edge of dislocation. The Burgers vector's direction depends on the direction of circuit considered.

(2) Screw Dislocation:

Screw dislocation is defined as a displacement of the atoms in one part of a crystal relative to the rest of the crystal. The screw dislocation forms a ramp around the dislocation line.

Fig. shows when a part of a crystal is displaced relative to the rest of the crystal. It important to mention here that the displacement terminates with in the crystal.

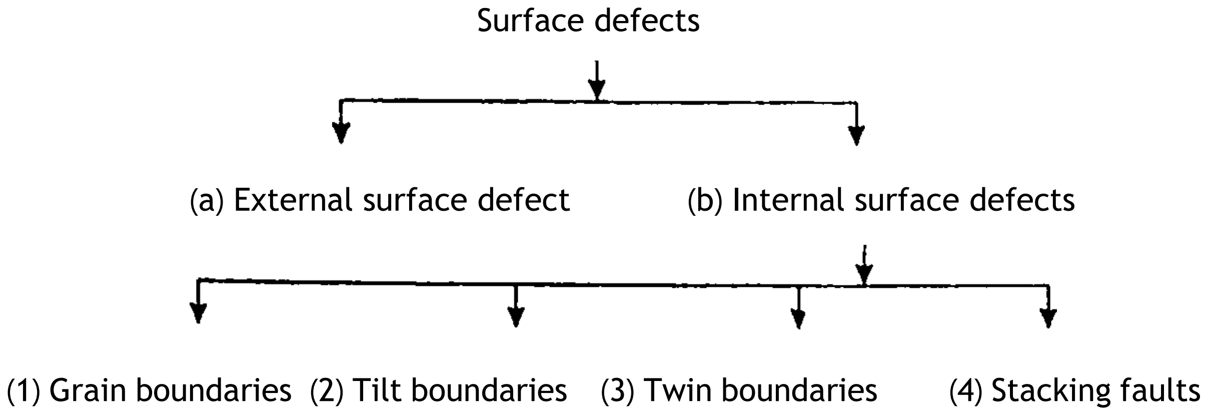


Distinction between Edge and Screw Dislocation:

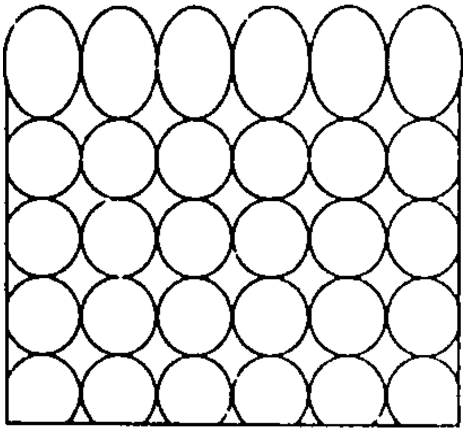
S.No.	Edge Dislocation	Screw Dislocation
1.	It involves an extra row of atoms above or below the slip plane.	In this dislocation, the distortion follows a helical path either right handed or left handed.
2.	The edge of the atomic plane is formed internal to the crystal.	Distortion of the lattice near the screw dislocation takes place.
3.	It is perpendicular to Burger's vector.	Screw dislocation lies parallel to Burger's vector.
4.	Edge dislocation moves in the direction of Burger's vector.	It moves perpendicular to Burger's vector.
5.	Force required to form and move an edge dislocation is small.	Larger forces are required to form and move screw dislocations.

2.03 Surface defects:

Surface defects arise from a change in the stacking of atomic planes on or a boundary. The classification is as follows.



(a) External Surface Imperfections

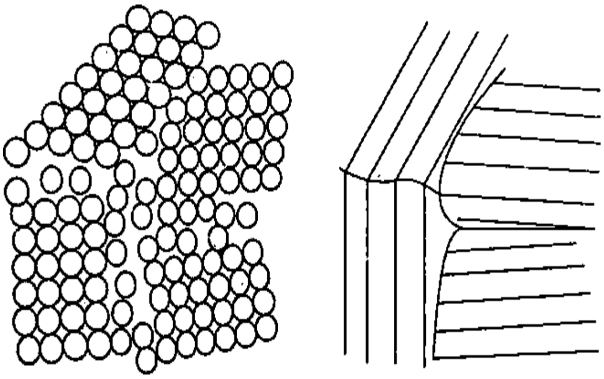


Finite dimension of the crystal itself is a defect because the atomic bonds do not extend beyond the surface. At the boundary, the atomic bonds are terminated. As a result, the atoms on the surface cannot be compared with the atoms within the crystal. The atoms on the surface have neighbours on one side whereas the atoms inside the crystal have neighbours on either side as shown in fig. This is known as external surface imperfection.

(b) Internal Surface Imperfections:

The internal surface defects are defects which occur inside the crystal. They are caused by grain boundaries, tilt boundaries, twin boundaries and stacking faults. We shall discuss these one by one.

(1) Grain Boundaries:



This is a two dimensional imperfection. When a piece of iron or copper solidifies or recrystallizes, new crystals form in different part. They grow and impinges on each other. The atoms held in between are attracted by crystals on either side and depending on the forces, the atoms occupy equilibrium positions. These positions at the boundary region between two crystals are distorted. The boundary region is called a crystal boundary or a grain boundary. The grain boundary is shown in fig. The crystal orientation changes sharply.

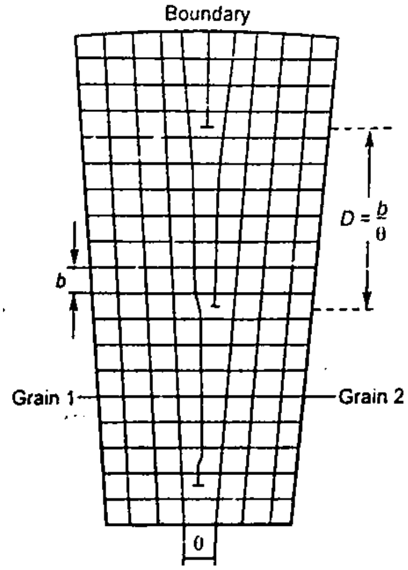
(2) Tilt Boundaries:

When the orientation difference between two neighbouring crystals is less than 10^0, then it is called as low-angle boundary. In general, low angle boundaries can be described by suitable array of dislocation.

Fig. shows a low angle tilt boundary. In tilt boundary, the neighbouring crystals are tilted with respect to each other by only a small angle.

The angle of tilt is given by $\theta = \frac{b}{D}$

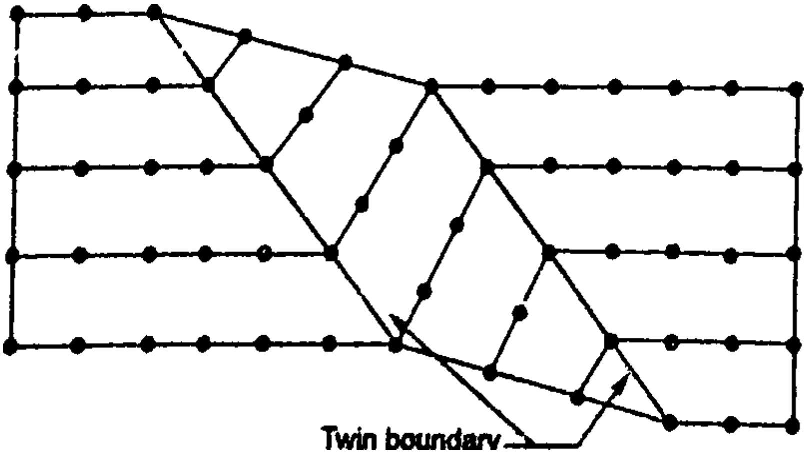
where b = Burgers vector, and D = average vertical distance between dislocations



(3) Twin Boundaries:

When the atomic arrangement on one side of a boundary is a mirror reflection of the arrangement on the other side, then it is called as twin boundary.

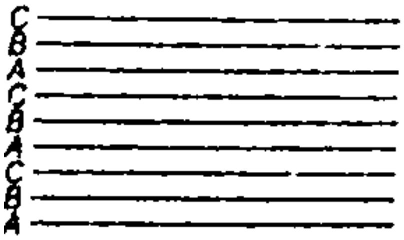
The twin boundary is shown in fig. As they occur in pair, they are called twin boundaries. At one boundary, orientation of atomic arrangement changes. At the other boundary, it is resorted back. The region between the pair boundaries is called the twinned region.

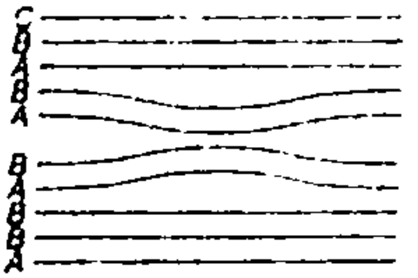


(4) Stacking Faults:

When the staking of atomic planes is not in a proper sequence throughout the crystal, the fault caused is known as stacking fault. Fig. shows a stacking fault.

For example. the stacking sequence in FCC crystal is described by A-B-C-A-B-C-A-B-C-. But the stacking fault may change the sequence as A-B-C-B-A-B-A-B-C. The region in which the stacking fault occurs (A-B-A-B) forms a thin region and it becomes HCP. This thin region is a surface imperfection and is called a stacking fault.





2.04 Volume defects:

The volume defects such as cracks may arise in crystals when they are grown or while they are used.

- In growing a crystal, it is possible a small electrostatic dissimilarity between the stacking layers may result in a crack.
- Presence of large vacancy or void space, when cluster of atoms are missed is also considered as volume imperfection.
- While growing a crystal, there is every possibility of inclusions foreign particles and non-crystalline regions which have the dimensions of the order of 0.2 nm. These are also called volume imperfections.
- The cracks may also generate when the crystal is used in some device application and is subjected to sudden thermal waves.
- Using optical microscope, presence of volume defects can be detected.

2.05 Production and removal of defects:

Production of defects:

Following are sources of production of defects:

I. Deformation
2. Irradiation
3. Quenching

(1) Deformation :

When crystals are subjected to various kinds of situations during manufacturing and fabrications, they are deformed. The deformations may be geometrically linear, angular or complex. As a result, the dislocations enter into the crystal.

(2) Irradiation:

When the crystals are irradiated with high energy particles excess points defects are produced in the crystal. The high energy particles collide with lattice atoms and displace them thereby forming point defects. The number of point defects produced in this manner is independent of temperature but depends only on the nature of the crystal and irradiating particles.

(3) Quenching:

The fraction of vacant lattice sites in a metal increases rapidly with temperature. One of the methods producing an excess number of point defects at given temperature is by quenching (quick cooling) from a higher temperature.

In this process, the heated metal is suddenly dipped into a cooling a medium. The cooling material may be cold water, oil, air and fused salts.

Removal of defects:

Following few methods of removing defects.

1. Annealing
2. Recovery

1. Annealing:

Annealing removes all structural imperfections by complete recrystallization.

Annealing involves the following three processes.

- ☞ Heating to a desired temperature.
- ☞ Holding at that temperature for specified time.
- ☞ Cooling, usually to room temperature.

In annealing processes, time is an import parameter.

Annealing of steel is done to impart softness to it. In this process, the steel is heated above its critical temperature (approximately 723^0C). After this, this is hold at this temperature for about one hour. Finally, it is cooled slowly in the furnace at a rate of about 30^0 to 15^0C/hour. After cooling, the steel is changed into different forms.

Annealing serves the following objectives:

(i) Softens the steel

(ii) Refines the grain structure

(iii) Improves ductility of steel

(iv) Enhances the machinability.

Types of Annealing processes

The various types of annealing operations are :

(I) Full annealing

(2) Process annealing or partial annealing

(3) Spheroidise annealing

(4) Diffusion annealing

(1) Full Annealing:

This operation removes all structural imperfections by complete recrystallization. This operation is often utilized in low and medium carbon steels.

The process consists of heating steel to about 50-70^{0}C its critical temperature until equilibrium is achieved. This is hold at this temperature for a considerable time. Finally, this is furnace cooled, i.e., heat furnace is turned off and both furnace and steel are allowed to cool to room temperature slowly. The process takes several hours.

After this process, the steel structure becomes chemically homogeneous and gets soft.

(2) process Annealing or Partial Annealing:

In this process, the steel is heated to 550-650^{0}C which is a little below the critical temperature. It is held there for a prolonged duration. After this, it is slowly cooled. This results in formation of pearlite. New crystals of the same structure are formed after the heating-cooling operation.

(3) Spheroidise Annealing:

This process is normally applied to high carbon steel by heating below lower critical temperature approximately 680^{0}C. It is hold for a long time at this temperature. Finally, cooled slowly below 600^{0}C. Obviously this is a time consuming process.

Tool steels for cutting tools, measuring instrument and cold forming dies are produced by this process.

This type of heat treatment produces carbide in the form of round or globular (spheroids) instead of plates. Due to this fact, the process is known as spheroidise annealing.

(4) Diffusion Annealing:

For the jobs above critical temperature (about 820^{0}C), the diffusion annealing is employed. This is followed by full annealing to obtain fine grained structure.

This process is used in heavy castings to make austenitic (a metallic, non-magnetic solid solution of carbon and iron) grains homogeneous.

2. Recovery:

The term 'recovery' may be defined as the process of removing all the changes in fine structure and properties of a metal that take place during heat treatment. They are:

- ☞ Some of the internal strain energy is relieved by virtue of dislocation motion without any externally applied stress.
- ☞ Internal (residual) stresses are relieved.
- ☞ Some reduction in number of dislocations and dislocation configurations.
- ☞ Microstructure remains unaffected.
- ☞ Physical properties such as electrical and thermal conductivities are recovered to their precooled worked states.

Recovery is further subdivided into following two states :

(i) **Strain-relief crystallization:** This is a stage at which the number of point-defects, mainly vacancies diminishes in a number of metals such as aluminium and iron.

(ii)

(ii) **Polygonization:** This is a kind of recovery involving formation of new long angle boundaries within each grain. These boundaries can form by slip and climb of dislocations; as a result, a grain is divided into sub grains, or polygons which the free of dislocations.

2.06 Diffusion in solids:

Diffusion is a phenomenon by which atoms or molecules from higher concentration region will slowly migrate towards the lower concentration region. Even though it is taking place in a slow manner, the rate of diffusion can be increased by increasing the temperature of the material. For diffusion, there should be activation energy, which originates from the thermal vibration of atoms of molecules. Further, there should be vacant sites and interstitials in the atomic lattice.

Types of diffusion:

The process of diffusion is broadly classified as follows:

(1) Microscopic diffusion (2) Macroscopic diffusion

(1) **Microscopic Diffusion:**

This diffusion concerns with the movement of individual atoms and molecules. This is a random process, i.e., each atom or molecule follows a random path. Microscopic view considers the system on atomic or molecular level. Microscopic diffusion is further classified into following types:

(i) Self diffusion : In this case, thermally excited atom from a site of crystal lattice jumps to an adjacent site.

(ii) Inter-diffusion : This is observed in binary metal-alloys such as Cu-Ni system.

(iii) Volume diffusion: In this case, the atomic movement takes place throughout the volume of solid.

(iv) Surface diffusion: In this type of diffusion, the atomic movement takes place along the surface of the system.

(v) Grain boundary diffusion: In this type of diffusion, the atoms diffuse along the grain boundaries.

(vi) Pipe diffusion : This diffusion takes place along the dislocation edge.

(2) Macroscopic Diffusion:

This is a mass flow process, i.e., a large number of atoms and molecules take part in the diffusion process. It is important to mention that the process takes part in a pre-defined direction and not in a random direction.

DIFFUSION MECHANISMS:

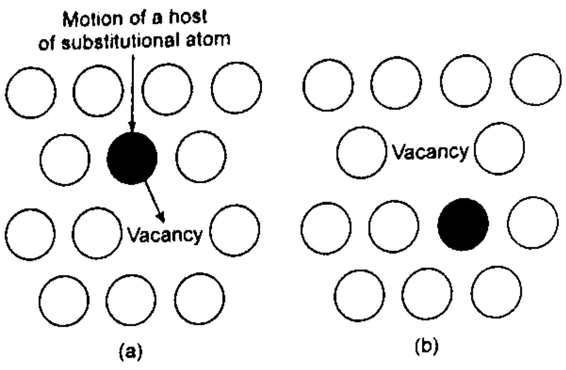
Almost all the mechanisms are based on vibrational energy of atoms in a solid. The important mechanisms are:

1. Vacancy mechanism
2. Interstitial mechanism
3. Direct interchange diffusion mechanism

1. Vacancy mechanism:

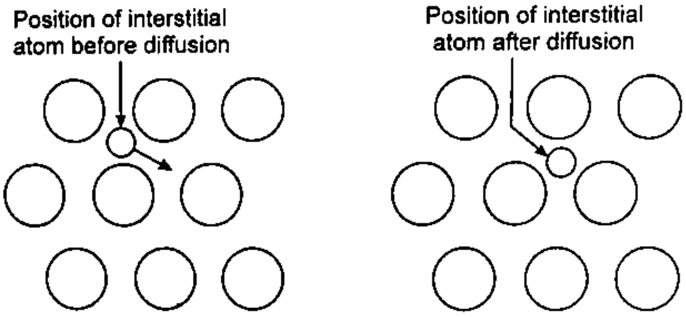
We know that vacancies are vacant atomic sites. The vacancy mechanism involves the shifting of atom from its normal lattice position to adjacent lattice site or vacancy. This is shown in fig. (a). This is known as vacancy diffusion. At the position of shifted atom a new vacancy is created as shown fig. (b).

For this diffusion process, vacancy/vacancies, is/are necessary. The vacancies are continually being created and destroyed, i.e., vacancies move through the lattice and produce random shift of atoms from one lattice position to another lattice position.



Vacancy diffusion is responsible for the phenomenon of creep in materials. It is bulk diffusion process. If a solid is composed of single element, i.e., pure metal, the movement of thermally excited atom from one site of crystal lattice to an adjacent site is called self-diffusion. The process of self-diffusion in gold and silver occurs by vacancy mechanism.

2. Interstitial Mechanism:

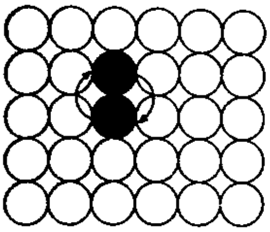


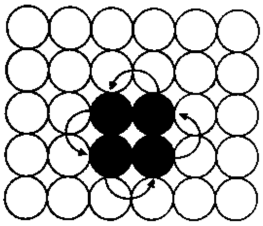
When a solid is composed of two or more elements whose atomic radii differ significantly, interstitial diffusion may take place. The large size atoms occupy lattice sites whereas smaller size atoms fit into the interstices created by the large atoms. In another words, we can say that this diffusion is similar to vacancy diffusion except that interstitial atoms stay on interstitial sites. Therefore, this diffusion mechanism involves atoms that migrate from an interstitial position to neighbouring one, which is empty as shown in fig. This diffusion mechanism is found for inter diffusion of impurities such as hydrogen, carbon, nitrogen, oxygen, etc. which have small atoms.

3. Direct Interchange Mechanism:

In this mechanism, the atoms exchange places through rotation about a mid-point. Two or more jump past each other and exchange positions but the number of sites remain constant as shown in (a and b).

Fig. (a) shows two atoms interchange mechanism while fig. (b) shows four atoms interchange mechanism.


(a)


(b)

Factors affecting diffusion:

l. Temperature : It increases the rate of diffusion.

2. Concentration : If the concentration in a single phase of the solid solution (alloy) varies, the value of diffusion coefficient also varies

3. Crystal structure : Diffusion rate increases with the crystals having low packing factor. Thus BCC has faster diffusion than FCC.

4. Grain boundaries : Diffusion along the grain boundaries decreases with the decreasing angle of tilt between the grains.

5. Grain size : The diffusion rate is more in a fine grained due to the presence of more grain boundaries than the coarse grained material.

2.07 Fick's laws of Diffusion:

Diffusion is a mass flow process, i.e., quantity of element that transported within another. This is a macroscopic view and a time dependent process. Diffusion can occur under the influence of concentration gradient, an electric or magnetic field gradient or a stress gradient. Here, we shall consider diffusion (mass flow) or rate of mass transfer under concentration gradient in one dimensional case.

Regarding the rate of mass transfer, Fick gave two laws known as Fick's laws. They are:

1. Fick's first law
2. Fick's second law

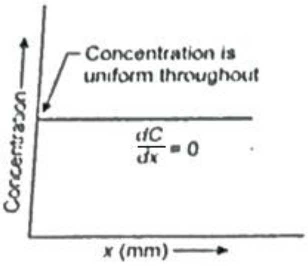
1. Fick’s first law:

This law describes the rate at which diffusion occurs. This law states that the quantity (dn) of a substance diffusing per unit time (dt) through surface area (A) is proportional to (i) concentration gradient (dC/dx) and (ii) the coefficient of diffusion (D). The law can be expressed as

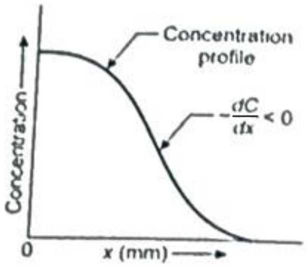
$$J = \frac{1}{A}\left(\frac{dn}{dt}\right) = -D\left(\frac{dC}{dx}\right)$$

The negative sign indicates that diffusion takes place down the concentration gradient.

This law can be used to describe the flow under steady state conditions. The steady state condition is shown in fig (a). Under the steady state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction.



(a)



(b)

The profile will be non-linear when D is a function of C as shown in fig (b). This law does not provide about the time dependence of the concentration.

2. Fick’s second law:

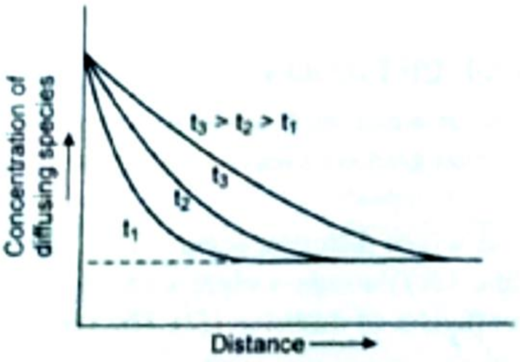
This law is an extension of Fick's first law to non-steady flow. If the concentration gradient varies in time and the diffusion coefficient is taken to be independent of concentration, the diffusion process is described by Fick's second law.

This law states that the rate of variation of concentration with time is proportional to the rate of variation of concentration gradient with distance.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Fig. shows the concentration profiles at three different diffusion times.



IMPORTANT UNIVERSITY QUESTIONS

LONG ANSWER QUESTIONS

1. What are different types of defects? Explain point defects, line defects and volume defects.
2. Explain vacancy defect, substitutional defect and interstitial defect in detail.
3. What are Schottky and Frenkel defects? Explain these defects in detail.
4. What is diffusion? Explain mechanism of diffusion.
5. State and explain Fick's laws of diffusion.

SHORT ANSWER QUESTIONS

1. What are crystal defects? Mention different types of defects.
2. Discuss point defects in crystals.
3. Explain the following defects :
   (i) Line defects, (ii) Surface defects
4. Compare and contrast Frenkel and Schottky defects.
5. Explain the production of dislocations.
6. Explain the following .
   (i) quenching, (ii) annealing, (iii) recovery

PROBLEMS

1. A plate of iron is exposed to a carbon-rich atmosphere on one side and carbon deficient atmosphere on the other side at 700 ^{0}C. If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm (5×10^{-3} and 10^{-2} m) beneath the carburizing surface are 1.2 and 0.8 kg/m^3 respectively. Assume a diffusion coefficient of 3 x 10^{11} m^2/s at this temperature.

   Sol.:

   According to Fick's first law, we have

$$J = -D\left(\frac{C_A - C_B}{x_A - x_B}\right)$$

$$= -(3\times10^{-11}\ \mathrm{m^2/s})\left[\frac{(1.2-0.8)\ \mathrm{kg/m^3}}{(5\times10^{-3}-10^{-2})\ \mathrm{m}}\right]$$

$$= 2.4\times10^{-9}\ \mathrm{kg/m^2 - s}$$

2. During a corrosion resistance process, the outward flux of copper atoms aluminium is 10^{21} m^2/s. The concentration of copper at room temperature is 2×10^{13} /m^3 on one side of aluminium which is 3 mm thick Calculate the diffusivity if concentration of copper on the other side of aluminium is limited to 4×10^6/m^3. Determine the concentration gradient also.

Sol.: The concentration gradient is,

$$\frac{dC}{dx} = \frac{(2\times10^{13})-(4\times10^{6})}{3\times10^{-3}}$$

$$= \mathbf{21.66\times10^{15}/m^4}$$

According to Fick's first Jaw of diffusion,

$$J = -D\left(\frac{dC}{dx}\right)$$

$$10^{21} = -D\times(21.66\times10^{15})$$

$$D = -\frac{10^{21}}{21.66\times10^{15}}$$

$$= \mathbf{-0.15\times10^{6}\ m^2/s}$$