

CHAPTER - III

PHYSICAL METALLURGY

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3.1 INTRODUCTION

Physical Metallurgy deals with the relationship between structure and properties of metals and alloy. The process adopted for metal extraction from the ores and subsequent fabrication influences the structure. The properties of interest are mainly those demanded by engineers such as strength, ductility toughness and corrosion resistance. Thus physical metallurgy provides a vital link in making, shaping, treating and using of metals and alloys. Physical metallurgy deals with the nature, structure and physical properties of metals and alloys, together with the mechanism of varying such properties.

Crystal Structure

All materials are composed of a very large number of atoms that are bonded together in some manner. The cohesion between the atoms is dependent upon the character of the individual elements. The bond formed between atoms can be classified as ionic bond and covalent bond. Another type of bond, similar to that of covalent type, is metallic bond in which there is complete freedom of the electrons when a group of atoms becomes associated. The relative free movement of electrons in metals accounts for electrical and thermal conductivity. The bonds formed by the free electrons are nondirectional and that leads to considerable flexibility in the directions along which the metal atoms can be displaced during plastic deformation.

Since there is no linkage between atoms in the metallic bond, metal atoms try to surround themselves by as many similar atoms as possible. The atoms arrange themselves in a distinct pattern in space, called a space lattice. When atoms approach each other, two opposing forces influence the internal energy, an attractive force between the electrons and both positive nuclei; and a repulsive force between the positive nuclei and also between the electrons. The first force tends to decrease the internal energy and the second force tends to increase it. At some distance, these two forces will just balance each other and the total internal energy will be a minimum, corresponding to an equilibrium distance no is different for each elements and is determined by measuring the distance of closest approach of atoms in the solid state. To specify a given point in a lattice in a structure, its coordinates are preferred to the crystal axes. Each space lattice has seven different systems of axes, each with specified equality or inequality of lengths and angles. These are the basis of the seven crystal systems. The smallest unit having the full symmetry of a crystal is known as unit cell (Fig.1). The specific unit cell of each metal is defined by its parameters which are the edges of the unit cell a , b , c and the angles α (between b and c), β (between c and a) and γ (between a and b) and are listed in Table I.

There are two ways in which atom may be packed so as to have the closest possible packing. One method of packing is to start with a layer of spheres, with each sphere in contact with adjacent spheres in the same plane. Another plane of spheres above the first is placed in such a manner that each sphere in the second layer rests in a pocket between the spheres of the first layer and touches three spheres in the layer below it. A third layer of spheres is placed so that each of the atoms is above the pockets of the first layer that were not filled by the second layer. Then there is a fourth layer of spheres, which will be exactly above the spheres of first layer. This continues on in the sequence "abc, abc", where 'a' is the first layer, 'b' is the second layer, 'c' is the third layer and 'a' repeats as fourth layer. This type of packing leads to FCC structure. In HCP structure, the third layer of spheres is placed in such a way that the spheres will be directly over the spheres of the first layer.

Alloying

Metals in their pure form are seldom used in engineering applications. Most of the metallic materials used in engineering are combinations of metals known as alloys. When two metals are melted together and crystallized, a single crystal structure may form. In the unit cell of this crystal, both the metal atoms are present in proportion to their concentration. This structure is known as a solid solution.

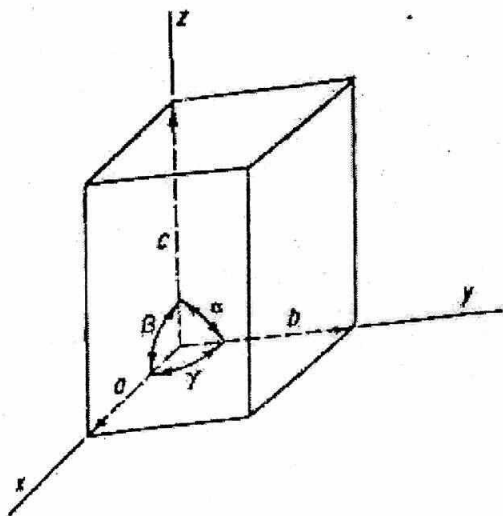


Fig.1 : Unit cell illustrating lattice parameters

Table 1 : Various crystal systems

1	Cubic	Three equal axes, mutually perpendicular $a = b = c$; $\alpha = \beta = \gamma = 90^\circ$
2	Hexagonal	Three equal coplanar axes at 120° and a fourth unequal axis perpendicular to their plane $a = b \neq c$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
3	Tetragonal	Three perpendicular axes, only two equal $a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$.
4	Rhombohedral (trigonal)	Three equal axes, not at right angles $a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$
5	Orthorhombic	Three unequal axes, all perpendicular $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
6	Monoclinic	Three unequal axes, one of which is perpendicular to the other two $a \neq b \neq c$; $\alpha = \gamma = 90^\circ \neq \beta$
7	Triclinic	Three unequal axes, no two of which are perpendicular $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$

3.2 SOLID SOLUTION

Metals may combine to form alloys by completely dissolving in each other. If the solute atoms occupy position between the present atoms, it is called substitutional solid solution. When the solute and solvent atoms are arranged in a regular fashion on the atomic sites, it is called ordered solid solution (superlattice). Perfect order is possible only when the two metals are mixed in some fixed proportion i.e. 1:1, 3:1, etc. If the solute atoms occupy position between the lattice sites of the parent atoms, it is called an interstitial solid solution.

Hume Rothery studied a number of alloy systems and formulated the conditions that former extensive substitutional solubility. These are as follows:

- i) The size difference between the parent atom and the solute atom must be less than 15%
- ii) The electronegativity difference between the metals must be small
- iii) The valency of the atoms must be same. A metal of lower valence tends to dissolve more of a metal of higher valence tends to dissolve more of a metal of a higher valence and vice-versa.
- iv) It is important to note that solubility tends to be favoured when the crystal structure of the two metals is of the same type.

Intermetallic Alloy phase or Compounds:

When a compound is formed, the elements lose their individual identity and characteristic properties to a large extent. The compound is having its own characteristic physical, mechanical and chemical properties. Most compounds, like pure metals, also exhibit a definite melting point within narrow limits of temperature. It is then referred to as a congruent melting phase.

Electron compounds are found to exist at or near compositions in each system that has a definite ratio of valence electrons to atoms. These phases are having similar lattice structures of the systems.

Thermodynamics and Kinetics:

The commercial importance of metals lie principally in their ability to combine with one another to produce substances having a wide range of properties that may not be achieved with pure metals alone. In considering the relation of the constituents that make up alloys at different temperatures, pressures and combinations, one specifies the two or more metallic elements that are being considered and the variables to which these elements will be subjected. An alloy system is a combination of two or more elements forming alloys, which are considered within a specified range of temperature, pressure and concentration

Systems are classified according to the number of components that constitute the system. In a particular alloy system, the components may combine within a certain temperature range to form two homogeneous coexisting portions. Each of these portions will be of different composition and will have different properties. Each portion is homogeneous throughout and regardless of sampling in that portion; the compositions will be the same. These homogenous physically distinct portions of the system are called phases. The system at equilibrium may contain fixed volume fractions of a number of phases.

Williard Gibbs developed a relationship between the number of coexisting phases, the number of components making up the system and the number of variables. The relation is a statement of the phase rule, which in general is expressed as,

$$p - c = V - F$$

where, p is the number of phases in equilibrium, c is the number of components in the system, V is the variables: temperature and pressure and F is the number of degrees of freedom. If the pressure is constant as it is generally in most metallurgical considerations, then the phase rule can be written as,

$$p - c = I - F$$

The equilibrium state of a system can be specified in terms of its thermodynamic properties. A closed system at constant temperature and pressure has minimum Gibbs free energy in its equilibrium state. Iron exhibits FCC, BCC and HCP crystal structures, but at the temperature and pressure of interest, the stable structure is the one for which the Gibbs's free energy is the lowest. When the pressure and temperature are not constant, the equilibrium state is identified with the help of other thermodynamic properties.

Most of the transformations of interest occur at constant temperature and pressure. Therefore, Gibbs free energy is often used to investigate equilibrium.

If a closed system at constant pressure is capable of existing ones suitable temperature ranges either as phase α or as a different phase β , the variations of the free energies of these phases can be as shown in Fig.2. ΔG is the free energy change associated with the transformation of one phase to the other.

The equilibrium transition temperatures, T_e , is defined such that $T = T_e$ when $\Delta G_T = 0$. At $T < T_e$, $\Delta G(\alpha \rightarrow \beta) > 0$, α is the stable phase and β transforms to α . When $T > T_e$, $\Delta G(\alpha \rightarrow \beta) < 0$, β becomes the stable phase and α transforms to β . At $T = T_e$, $\Delta G(\alpha \rightarrow \beta) = 0$ and $\Delta H_{T_e} = T_e \Delta S_{T_e}$. Since the slopes of the two free energy curves at T_e in Fig.4 are different, the entropy of transformation, ΔS_{T_e} and the enthalpy of transformation, ΔH_{T_e} are not equal to zero.

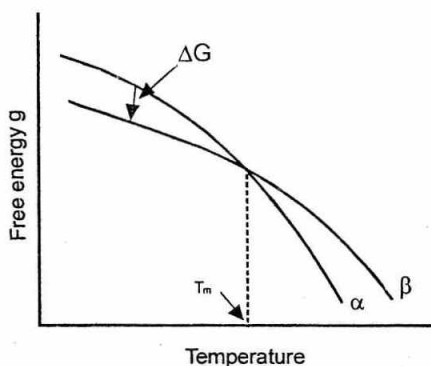


Fig.2 : Variation on free-energy of two phase with temperature

$$\begin{aligned} \Delta G(\alpha \rightarrow \beta) &= G(\beta) - G(\alpha) \\ &= \Delta H(\alpha \rightarrow \beta) - T \Delta S(\alpha \rightarrow \beta) \end{aligned}$$

3.3 DIFFUSION

Diffusion plays a key role in phase transformations of solids. To establish a logical co-relationship between structure and properties of materials, structural control is essential to obtain optimum properties, which in turn depends on diffusion. The process of diffusion can be defined as the mass flow process by which atoms or molecules change their relative positions with respect to their neighbors within a phase under the influence of thermal energy and a gradient. The gradient may be chemical potential owing to difference in concentration difference or due to temperature or stress or electric field or gravitational field. In the foregoing discussion we will highlight the gradient caused by concentration variation.

Imperfections:

Imperfection in crystals can be classified according to their geometry: point defect, line defect and surface defect.

Point defects are of various kinds e.g., vacancy, interstitialcy, interstitial impurity and substitutional impurity. If an atom is missing from its site in the lattice leads to formation of vacancy (Fig.) When an atom is getting displaced from its regular position into an interstitial position is known as interstitialcy defect (Fig.3). Generally, a crystal contains a certain amount of defects at a given temperature. The fraction of vacancies n/N in a crystal at temperature T can be given by

$$n/N = \exp (-\Delta H_f/kT)$$

Where, n : number of defects N : total number of atomic sites, and ΔH_f : enthalpy for the formation of a vacancy.

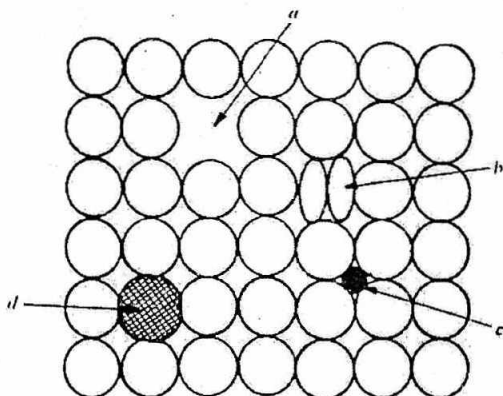


Fig. 3 : Point defects in Crystals: (a) Vacancy, (b) Interstitialcy, (c) Interstitial impurity and (d) Substitutional impurity

Line defects are known as dislocations. Dislocations are categorized as the edge dislocation and the screw dislocation (Fig.4). A dislocation is characterized by a vector known as Burgers Vector, b . For an edge dislocation the Burgers vector is perpendicular to the edge dislocation line. The Burgers vector for a screw dislocation is parallel to the dislocation line. However, the dislocations in real crystals are some combination of the edge and the screw types. These are known as mixed dislocations. The Burgers vector of a mixed dislocation remains invariant along the length of the dislocation line. It has two components: one parallel to the dislocation line (screw component) and the other parallel to the dislocation (edge component).

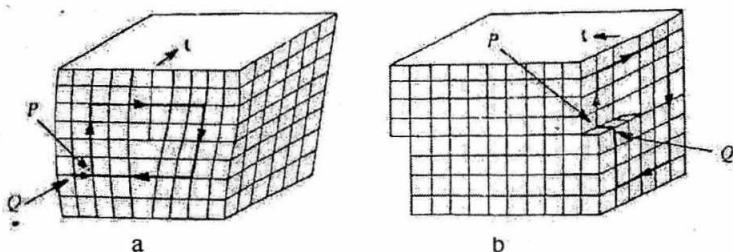


Fig. 4 : (a) Edge and (b) screw dislocations

Dislocation plays an important role in the plastic deformation of metals and alloys. Perfect crystals that are free of dislocation known as whisker possess very high strength. Presence of a few dislocations is sufficient to make the crystal weak.

Stacking faults are known as surface defects. Within the stacking sequence of FCC crystal i.e., ABC ABC, locally an improper stacking of CA CA (i.e. HCP stacking) may be created and this thin region is known as stacking fault. Stacking fault has surface energy. Another type of surface defect is grain boundary. They are categorized as tilt boundaries, twist boundaries and twin boundaries.

Laws of Diffusion:

The gradient due to concentration and diffusional phenomenon was initially illustrated by A. Fick in 1855. Considering unidirectional diffusion, mathematically it is given by

$$\frac{dn}{dt} = -D.A. \frac{dc}{dx}$$

where dn/dt : Number of moles of diffusion species passing through a cross sectional area A , perpendicular to the diffusion direction x per unit time; c : concentration of the species in mol. m^{-3} ; D : proportionality factor known as diffusivity or diffusion co-efficient and material's property depending upon medium in which diffusion occurs and the temperature (m^2s^{-1}).

In terms of flux J , the expression can be simplified to

$$J = -1/A. \frac{dn}{dt} = -D. \frac{dc}{dx}$$

Under steady state, flux transfer across any plane remains same along the diffusion distance i.e. concentration-distance profile does not vary with time. It refers, for independent D , the gradient is constant and the profile is straight line. If D is a function of concentration, the profile is not straight line. Non-steady state flow of mass is described by Fick's second law. For a given instant, flux at different cross sectional plane varies along diffusion direction. Moreover flux at a assigned cross section is a function of time. So, concentration-distance profile changes with time.

Mechanism of diffusion

Depending on the position of the atoms within the crystal structure for any solid solution, diffusion may take place by four mechanisms and they are given below in a nutshell (Fig.5):

- i) Interstitial mechanism – When the atoms are small enough to occupy interstitial sites of any system, can diffuse by jumping from one interstitial site to another (Fig.5a).
- ii) Vacancy mechanism – Substitutional atoms can diffuse by interchanging positions with a neighboring vacant sites giving rise to the vacancy mechanism (Fig.5b).
- iii) Interstitialcy mechanism – An atom from a regular site moves into an interstitial site and displaces another atom from regular site to an interstitial site. It means two atoms share a common lattice site and are displaced from it (Fig.5c).
- iv) Ring mechanism – Three or four atoms in the form of a ring rotate, thereby exchange their position. This process when repeated again and again with a different set of atoms in the ring each time can move an atom far away from its initial position (Fig.5d).

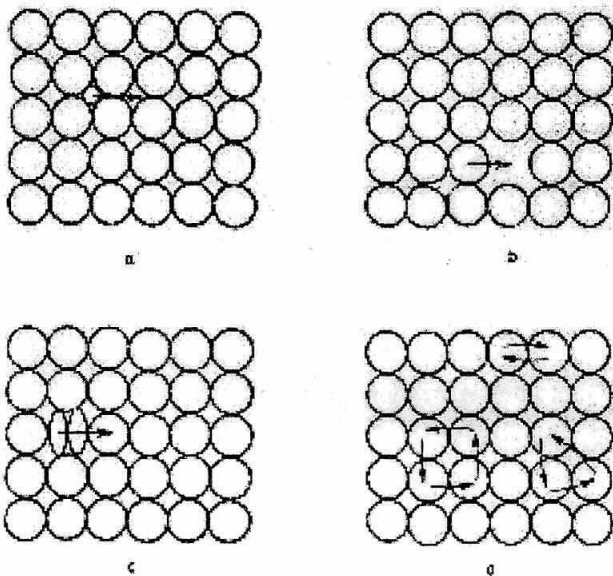


Fig.5 : (a) Interstitial, (b) vacancy, (c) interstitialcy, (d) direct exchange and ring mechanisms of diffusion

3.4 PHASE TRANSFORMATION

Equilibrium Diagrams:

The study of the interrelation of phases in an alloy system at different temperature and for different alloy compositions is of importance in understanding the characteristics of alloys. Generally, there are equilibrium relationships in that they correspond to the state of the minimum free energy of the system. The best method of representing these data is in the form of phase diagram, also known as equilibrium diagram.

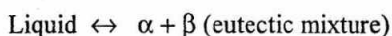
An equilibrium diagram may be defined as a plot of the composition of phases as a function of temperature in any alloy system under equilibrium conditions. Equilibrium diagrams may be classified according to the relation of the components in the liquid and solid states as follows:

1. Components completely soluble in the liquid state
 - a) Completely soluble in the liquid state (Type-I)
 - b) Partly soluble in the solid state, the eutectic reaction (Type-II)
 - c) Insoluble in the solid state, the eutectic reaction (Type-III)
 - d) Formation of a congruent - melting intermediate phase (Type-IV)
 - e) The peritectic reaction (Type-V)
2. Components partly soluble in the liquid state and completely soluble in the solid state, the monotectic reaction (Type-VI)
3. Components insoluble in the liquid state and insoluble in the solid state (Type-VII)
4. Transformation in the solid state
 - a) Allotropic change
 - b) Order-disorder
 - c) The eutectoid reaction
 - d) The peritectoid reaction

The equilibrium diagram makes it possible to determine the proportion of existing phases at any given temperature. Consider an alloy containing 80% A and 20% B at temperature T in Fig.6. At this temperature, the alloy is composed of the solid solution and the liquid, the solid and the alloy as a whole indicated by n, m and o, respectively. It can be shown that the amount of solid solution and liquid will be inversely proportional to the distances from the point representing the composition of the alloy to the points representing the composition of the phase in question.

Type I: Since the metals are completely soluble in the solid state, the only type of solid phase formed will be a constitutional solid solution. (Fig.7). The area below the solid line is a single-phase region and any alloy in this region will consist of a homogeneous solid solution. Between the liquidus and the solidus lines, there exist a two-phase region consisting of a mixture of a liquid solution and a solid solution.

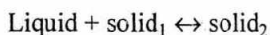
Type II: The most common and therefore, the most important type of system in which there is partial solubility in the solid state (Fig.7). Alloy in this system in which there is partial solubility crystals of pure A or pure B but always a solid solution or mixture of solid solutions. i.e., α , β and $(\alpha + \beta)$. a and b are also known as terminal solid solution or they are next to the axes. Point E, where the liquidus lines meet at a minimum is known as the eutectic point. The two solids that make up the eutectic mixture are given by the examination of the eutectic-temperature line, α of composition F and β of composition G. The eutectic reaction may be written as



Type III: A system in which the components are completely soluble in the liquid state and insoluble in the solid state. Since the two metals are assumed to be completely insoluble in the solid state, it should be apparent that when freezing starts the only solid that can form is a pure metal (Fig.8).

Type IV: When one phase changes into another phase isothermally and without any change in chemical composition, it is said to be a congruent phase transformation. The alloy X in Fig. 9 goes from a liquid phase to a single solid phase at constant temperature without a change in composition, and is therefore a congruent-melting alloy.

Type V: In the peritectic reaction, a liquid and a solid react isothermally to form a new solid on cooling. The reaction is expressed as



Type VI: Substances that are partly soluble in each other in the liquid state are said to have a miscibility gap.

Type VII: There are many combinations of metals, which are practically insoluble in each other. When cooled, the two metals appear to solidify at their individual freezing points into two distinct layers with a sharp line of contact and almost no diffusion. An alloy system, which comes very close to this type, is that between Al and Pb.

There are several equilibrium changes and reactions, which take place entirely in the solid state.

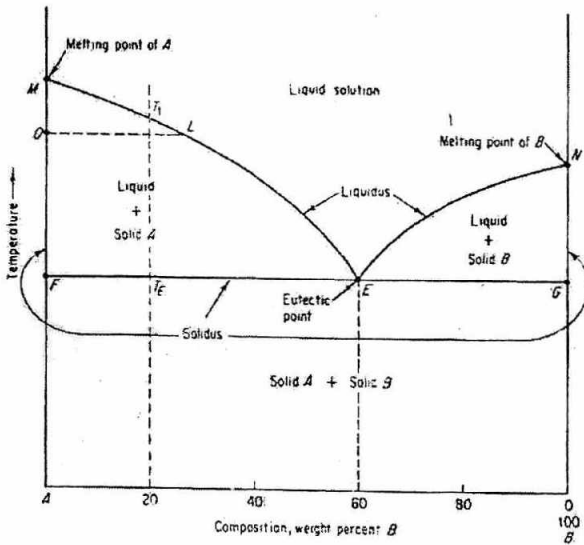


Fig. 7 : Type II Eutectic Phase Diagram showing Eutectic

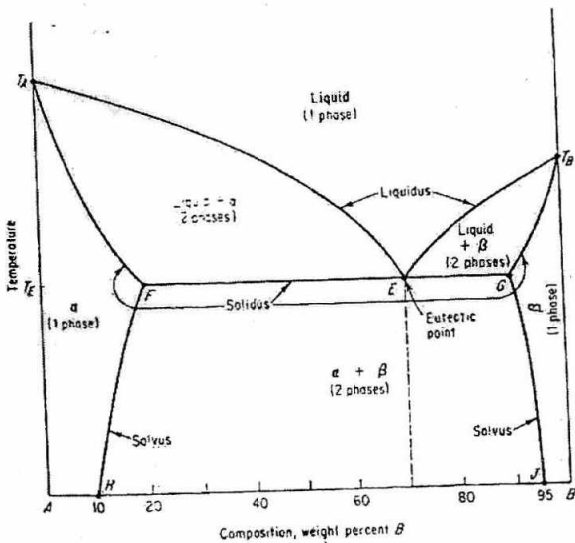


Fig. 8 : Type III Phase Diagram

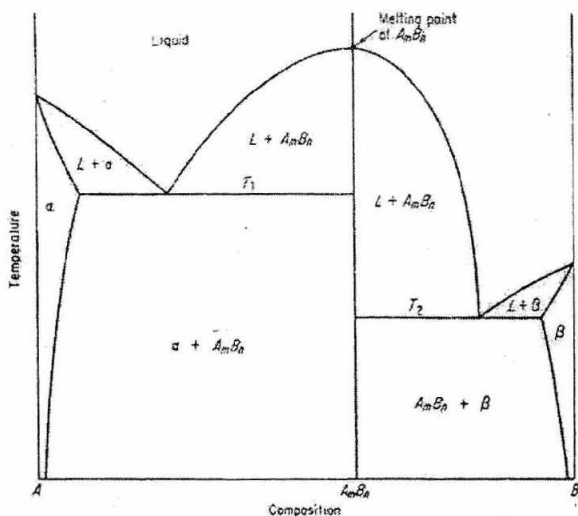


Fig.9 : Type IV Phase diagram

Allotropy: Several metals may exist in more than one type of crystal structure depending upon temperature. Iron, tin, manganese and cobalt are examples of metals, which exhibit this kind of transformation, i.e., allotropic transformation.

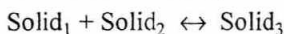
Order-disorder transformation: Generally, in the formation of a substitutional type of solid solution, the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. The alloy is said to be in a disordered condition. Some of this random solid solution, when cooled slowly, undergoes a rearrangement of the atoms where the solute atoms move into definite positions in the lattice. This structure is known as an ordered solid solution or superlattice. On the equilibrium diagram, the ordered solutions are frequently designated as α' , β' , etc. and the area in which they are found is usually bounded by a dot-dash line.

Eutectoid Reaction: This is a common reaction in the solid state. It is very similar to the eutectic reaction but does not involve the liquid, thus, a solid phase transforms on cooling into two new solid phases (Fig.10). The reaction may be written as



The resulting microstructure shows alternate layers of Solid_2 and Solid_3 in an extremely fine mixture.

Peritectoid Reaction: This reaction may be written in general as



The new solid phase is usually an intermediate alloy, but it may also be a solid solution. Fig. 11 shows that two solid phases α and β react to form an intermediate phase γ . The equation may be written as $\alpha + \beta \leftrightarrow \gamma$

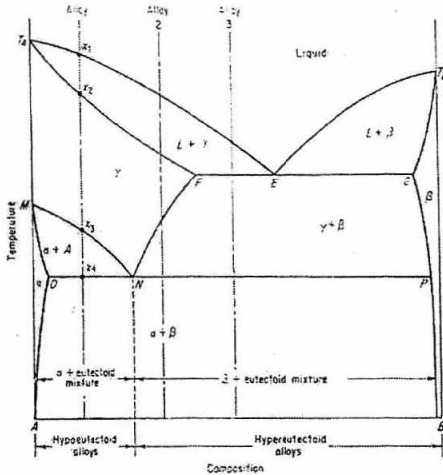


Fig. 10 : Eutectoid reaction

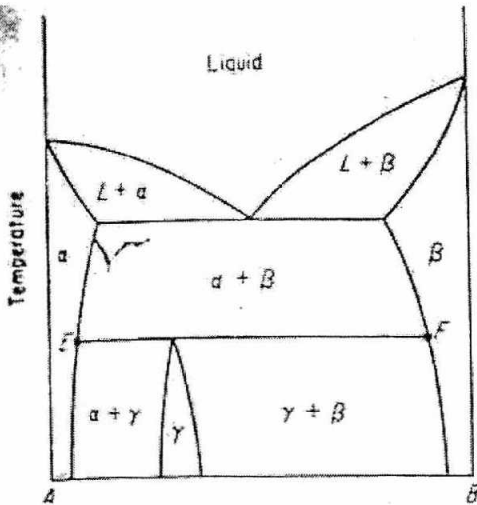


Fig. 11 : Peritectoid reaction

Microstructural changes during cooling:

Generally, the cooling rates are not slow enough to obtain equilibrium conditions. The continuous adjustments in compositions of the phases required for equilibrium do not take place. Consider an alloy of composition 70A-

30B that is getting cooled from above the liquidus (Fig.12). The first solid to crystallize has a composition C_{γ_1} . With the progress of solidification, the composition of the solid phase should shift along with solidus to C_{γ_2} , C_{γ_3} , etc. Diffusion of atoms inside the solid phase is required to have these compositional changes. However, diffusion in the solid phase is quite slower than in the liquid phase. So, the solid that solidifies at any instant in local equilibrium with the liquid in contact with that. The solid thus formed at a lower temperature does not have the composition according to that of the equilibrium diagram. Thus a gradient of composition develops from C_{γ_1} at the center, which solidifies first to C_{γ_5} at the periphery, which solidifies last. The average composition of the phase is shown by the dotted line in Fig.13. This is well deviated from the equilibrium composition. Solidification is complete at a lower temperature, T_5 , where the average composition of the solid becomes equal to the overall composition of the alloy. This phenomenon is called coring. The extent of coring increases, with increasing separation between the liquidus and the solidus, i.e., in alloy with a wide freezing range.

A homogenizing treatment is required to remove the compositional variations that accompany coring or surrounding. The alloy is heated to a high temperature and held there for a prolonged period yields a homogeneous solid solution.

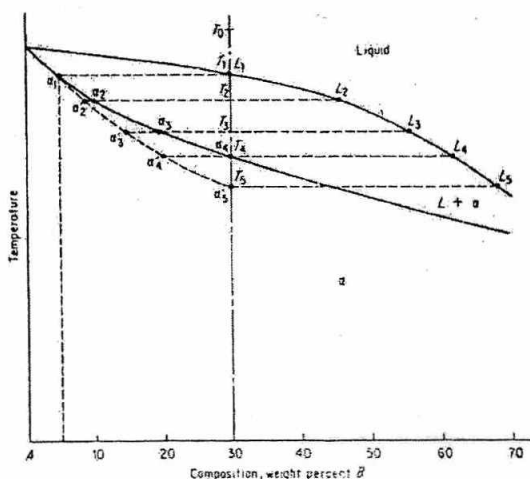


Fig.12 : Nonequilibrium cooling: the origin of coring

3.5 SOLIDIFICATION

Generally, commercial metals and alloys are frozen from a liquid phase into their final shape, called castings or into intermediate forms, i.e., ingot. Ingots later worked into the final product.

The solidification of metals occurs by nucleation and growth. For nucleation, liquid metals may be cooled to temperature far below their equilibrium freezing points before solidification begins. This is known as super cooling. The rate at which the interface between the liquid and the solid moves during solidification is a function of degree of solidification. The interface motion is also affected by the sign of the temperature gradient in front of the interface.

If the temperature increases from the interface into the liquid and the temperature gradient is linear and perpendicular to the interface, the interface maintains a stable shape and moves forward on a unit.

Dendritic freezing is a common phenomenon in many alloy systems. The driving force for dendritic growth is thermal supercooling. There is another factor which can lead to this is known as constitutional supercooling. This results when a solid freezes with a composition different from that of the liquid from which it forms. It can be well represented by Fig. 13a where at temperature T , liquid of composition, C_1 is in equilibrium with solid of composition, C_s . The liquid composition C_1 is greater than the average composition C_0 of the melt. The liquid composition decreases with increasing distance from the interface (Fig. 13b). As a function of distance, it shows that the actual temperature gradient in the liquid ahead of the interface is such that the liquid at every point is at a temperature above the liquidus temperature (Fig. 13c). Therefore there is no supercooling ahead of the interface, which is stable and flat. The actual temperature profile in the liquid is such that the temperature at every point between x and y is lower than the equilibrium liquidus temperature (Fig. 13d). Any protrusions formed in this region feel supercooled and does not melt back (Fig. 13f). As the supercooling is due to compositional effect, this phenomenon is known as constitutional supercooling.

Nucleation and Growth:

According to thermodynamics, a driving force for phase transformation arises when the free energy of the present phase becomes higher than that of the product phase with a change in temperature or pressure. At that time, thermal fluctuations result in the formation of very tiny particles of the product phase within the parent phase. These tiny particles can grow by transfer of atoms across this interface. The transformation can be divided into two steps that occur sequentially:

1. The formations of tiny particles that are stable to further thermal fluctuations and will not dissolve. These tiny particles are known as nucleus. The process is known as nucleation.
2. The increase in size of the particles. The process is known as growth.

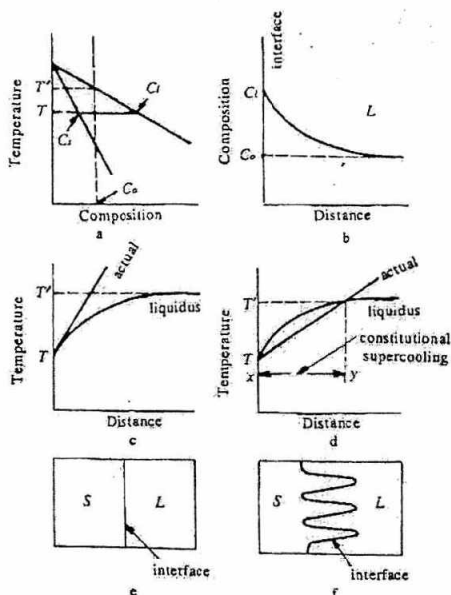


Fig.13 : Constitutional supercooling

A high nucleation rate means a large number of grains. When this is combined with a low growth rate, which will lead to a fine grain structure. On the other hand, a low nucleation rate combined with a high growth rate yields a coarse grain structure. An increase in cooling rate lowers the effective transformation temperature and results in the combination of a high nucleation rate and a relatively slow growth rate. Thus, it results in a fine grain size. This is also known as under cooling effect.

3.6 STRENGTHENING MECHANISM

Strength is inversely proportional to dislocation mobility and there are a number of possible factors, which affect the strength. Crystal structure determines the number and type of slip systems, fixes the Burgers vector and determines the stress required for the motion of dislocations. The fine grain size is often desired for high strength; large solute additions help in increase in strength and phase transformation may be utilized to increase strength.

It was empirically established by Hall and Petch that the tensile yield stress was related to grain size by $\sigma_0 = \sigma_i + K'd^{-1/2}$ where σ_0 : yield stress, σ_i : friction stress opposing the movement of dislocations, K' unpinning constant and d = grain diameter.

The introduction of soluble atoms into solid solution in the solvent lattice lead to an alloy stronger than the pure metal. If the solute and solvent atoms are mostly similar in size, the alloy will be called substitutional solid solution. If the solute atoms are much smaller than the solvent atoms, they form interstitial solid solutions.

Many commercial alloys contain a heterogeneous microstructure consisting of two or more metallurgical phases. The strengthening produced by second phase particles is usually additive to the solid solution strengthening produced in the matrix. The presence of second phase particles in the continuous matrix phase results in localized internal stresses, which modify the plastic properties of the continuous phase.

The strengthening produced by a finely dispersed insoluble second phase in a metallic matrix is known as dispersion hardening. This is similar to precipitation hardening or age hardening. For precipitation hardening, the second phase must be soluble at an elevated temperature, but must exhibit decreasing solubility with decreasing temperature. The second phase in dispersion-hardening systems have very little solubility in the matrix, even at elevated temperatures. There is atomic matching on coherency between the second phase particles and the matrix in dispersion-hardened system. The degree of strengthening depends on the volume fraction, average particle diameter and mean interparticle spacing.

Strain hardening or cold working is an important industrial process that is used to harden metals or alloys that do not respond to heat treatment. The cold worked state is having higher internal energy compared to that of the undeformed material. With increasing temperature, the cold worked state becomes more and more unstable. Eventually the metal solutions and reverts to a strain-free condition. The overall process by which this occurs is known as annealing. The annealing process can be divided into three distinct processes: recovery, recrystallization and grain growth. Recovery is defined as the restoration of the physical properties of the cold worked metal without observable change in microstructure. Recrystallization is the replacement of the cold worked structure by a new set of strain-free grains. Recrystallization is dependent on the amount of prior deformation, temperature, time, initial grain size, composition and amount of polygonization on recovery prior to recrystallization.

3.7 HEAT TREATMENT OF STEEL

Fe-Fe₃C Phase diagram:

The basis for the understanding of the heat treatment of steels is the Fe-Fe₃C phase diagram. The Iron-Iron carbide phase diagram is also known as Iron-Carbon equilibrium diagram. But the term iron-carbon is incorrect

in strict sense because the phase, which constitutes the binary phase diagram, is cementite, and not carbon and graphite. The term Iron- cementite is also not strictly correct because the cementite phase is metastable. In the metallurgical practice both the terms namely, iron-carbon and iron-cementite phase diagrams are used (Fig. 14).

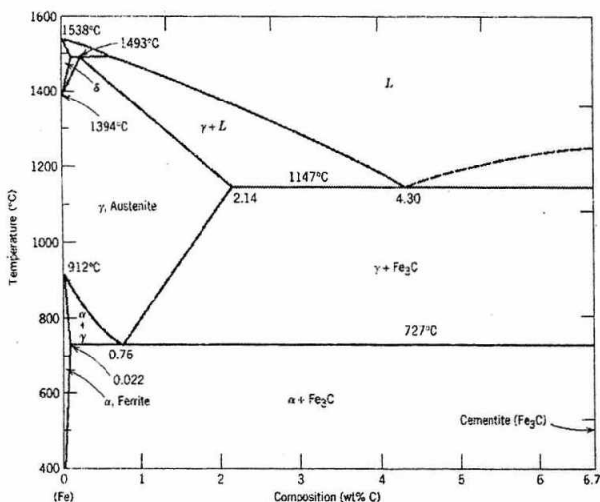
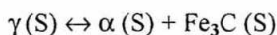


Fig. 14 : Iron-Iron Carbide diagram

The solubility of carbon varies in different forms of iron. In delta iron, maximum solid solubility of carbon is 0.1 percent. In gamma iron, the maximum solid solubility of carbon is 2.03 percent. Austenite is a solid solution of carbon in FCC iron and solute atoms occupy interstitial positions in this lattice. In α -iron, carbon has limited solid solubility of about 0.008 percent at room temperature. The maximum solubility of carbon in ferrite is 0.025 percent. The solid solution of carbon in α -iron is known as ferrite. The word “ferrite” is derived from the Latin word “ferrum” which stands for iron.

There are three reactions which occur in iron-cementite phase diagram (i) peritectic reaction, (ii) eutectic reaction, and (iii) eutectoid reaction. Out of these only eutectoid reaction is important as far as heat treatment of steels are concerned. A detailed analysis of the phase transformations at the peritectic and eutectic points of the iron-carbon system are not essential in a study of steels. In iron – carbon alloy with 0.8 percent carbon, the austenite is transformed into ferrite and cementite by eutectoid reaction on cooling at 723°C. Thus,



In heat treatment of steels, the liquid phase is always avoided. Some important boundaries at single-phase fields have been given special names:

- A_1 , the so-called eutectoid temperature, which is the minimum temperature for austenite
- A_3 , the lower-temperature boundary of the austenite region at low carbon contents, that is, the $\tilde{a}/(\tilde{a} + \tilde{\alpha})$ boundary
- A_{cm} , the counterpart boundary for high carbon contents, that is, the $\gamma/(\gamma + Fe_3C)$

If alloying elements are added to the iron-carbon alloy (steel), the position of the A_1 , A_3 , and A_{cm} boundaries and the eutectoid composition are changed. It suffices here to mention that

- All important alloying elements decrease the eutectoid carbon content
- The austenite-stabilizing elements manganese and nickel decrease A_1
- The ferrite-stabilizing elements chromium, silicon, molybdenum, and tungsten increase A_1

The Fe-Fe₃C phase diagram represents *metastable* equilibrium (as opposed to *stable* equilibrium); but because Fe₃C decomposition (a + graphite) is so slow, the Fe-Fe₃C phase diagram will prove more useful in most practical heat-treating conditions.

A study of the phase diagram shows that all the compositions containing less than 2.06 percent C pass through the austenite region on cooling from the liquid state to room temperature. Alloys in this interval are arbitrarily classed as steels. Steels with carbon content from 0.025 percent to 0.8 percent are called hypoeutectoid steels. Steels with carbon content of 0.8 percent are known as eutectoid steels. Steels with carbon content greater than 0.8 percent are called hypereutectoid steels.

Transformations in Eutectoid Steel

Let us consider a steel containing 0.8 percent carbon (x' in Fig. 15a). When the steel is in the austenite region at point 'a', the microstructure contains completely austenite grains. On cooling to temperature at 'b' in the figure (below the eutectoid point), all austenite will transform into 100 percent pearlite. Pearlite consists of alternate plate of Fe₃C and ferrite, with ferrite the continuous phase. An example of a pearlitic structure is shown in Fig. 16a where the dark areas are Fe₃C layers, the light phase is ferrite. Pearlite is not a phase, but a mixture of two phases—cementite and ferrite

The decomposition of austenite to form pearlite occurs by nucleation and growth. As in almost all the cases, nucleation occurs heterogeneously and not homogeneously. If the austenite is homogeneous (uniform

composition), nucleation occurs almost exclusively at grain boundaries. Let us assume that the active nucleus is a small lamella of cementite which forms at an austenite grain boundary and grows into one of the austenite grains. As this small plate grows in length and thickness (Fig. 15c). It removes carbon atoms from the austenite on either side of it. The carbon concentration of the austenite in contact with the cementite falls as a result, and eventually a carbon-concentration contour is achieved in the austenite. When the composition of the austenite next to the cementite reaches some more or less fixed value, ferrite nucleates and grows along the surface of the cementite plate (Fig. 15c). Since this ferrite lamella can contain almost no carbon, their continued growth is associated with a build-up of carbon at the ferrite-austenite interface. This build up continues until a new layer of cementite nucleates. Growth of this cementite layer will, in turn, induce formation of a new layer of ferrite, and as this process continues, the alternating lamellae of a pearlite colony are formed.

Classification of Steels

Name	Carbon content	Examples
Low carbon	0.05% - 0.32%	Sheet, structural
Medium carbon	0.35% - 0.55%	Machinery
High carbon	0.60% - 1.50%	Machine tools

Heat Treatment of Steels

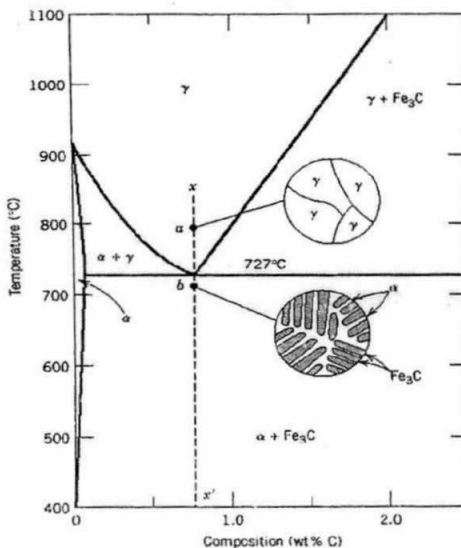


Fig. 15a : The Eutectoid Section of the Fe-Fe₃C diagram

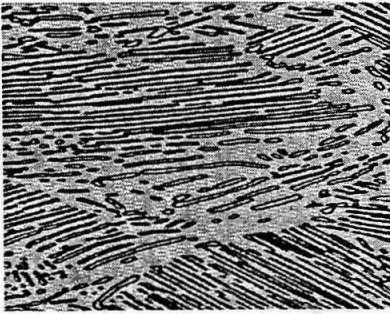


Fig 15b : *Microstructure of Pearlite*

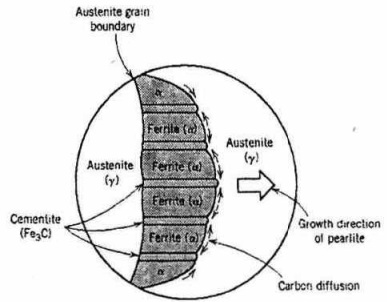


Fig.15c : *The Nucleation and Growth of Pearlite*

Heat treatment is defined as the heating and cooling operation(s) applied to metals and alloys in solid state so as to obtain the desired properties. The purpose of heat treatment is to improve in ductility, relieve internal stresses, refine grain size, and increase hardness or tensile strength and to achieve changes in chemical composition of metal surface as in the case of casehardening.

Time-Temperature Transformation (TTT) Curves:

The temperature of transformation controls the nature of decomposed product (of austenite), which in turn decides the resulting properties of steel. Therefore, the study of transformation temperature effect on the nature of decomposed product is of much importance. Both time and temperature of austenite transformation have significant impact on the nature and morphology of transformed product. Thus, a diagram which can include all the three parameters, i.e. time, temperature and transformation will be of great importance, specially to the heat treaters. Such a diagram is known as time temperature transformation (TTT) diagram. This diagram is also popularly known as isothermal transformation (IT) diagram or the C-curve.

The complete TTT diagram for an iron-carbon alloy of eutectoid composition is shown in Fig.16 where A stands for Austenite, B stands for Bainite, M stands for Martensite and P stands for Pearlite. Above approximately 550° C to 600° C, austenite transform completely to pearlite. Below this temperature to approximately 450° C, both pearlite and bainite formed. Finally, between 450° C and 210° C, the reaction product is bainite. The significance of the dotted line, which runs between the two curves, marking the beginning and end of isothermal transformations, should be mentioned.

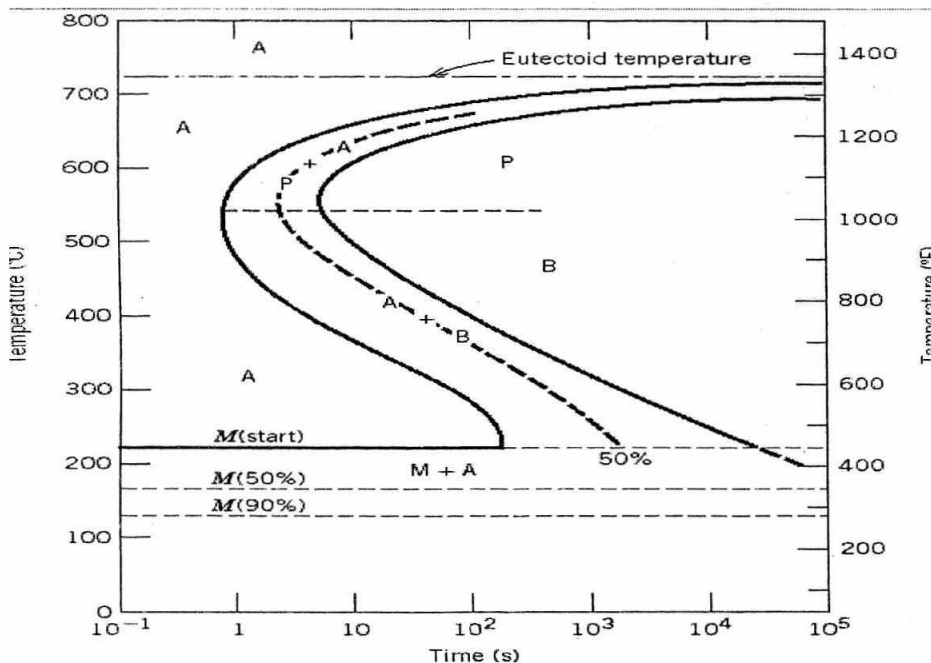


Fig.16 : TTT diagram for Eutectoid Steel

Continuous Cooling Transformation (CCT) Diagrams:

Continuous cooling transformation (CCT) diagrams can be obtained by techniques which is similar to that for TTT diagrams except that, in the case of CCT diagrams, points of start and end of austenitic transformation are recorded on continuous cooling. For the construction of CCT diagram for the eutectoid steel, a large number of small samples are heated above the lower critical temperature (A_1) to complete austenitic structure. From this temperature, specimens are cooled at a constant cooling rate, and points corresponding to start and finish of pearlite are determined. By repeating the same process at various cooling rates, different sets of start and end points for the pearlitic transformations are obtained. On joining start and end points, two curves, similar to those in TTT curves, corresponding to start and end of transformation, are obtained. Thus, a CCT diagram is obtained. The continuous-cooling-transformation diagram of an eutectoid steel is shown in Fig.17.

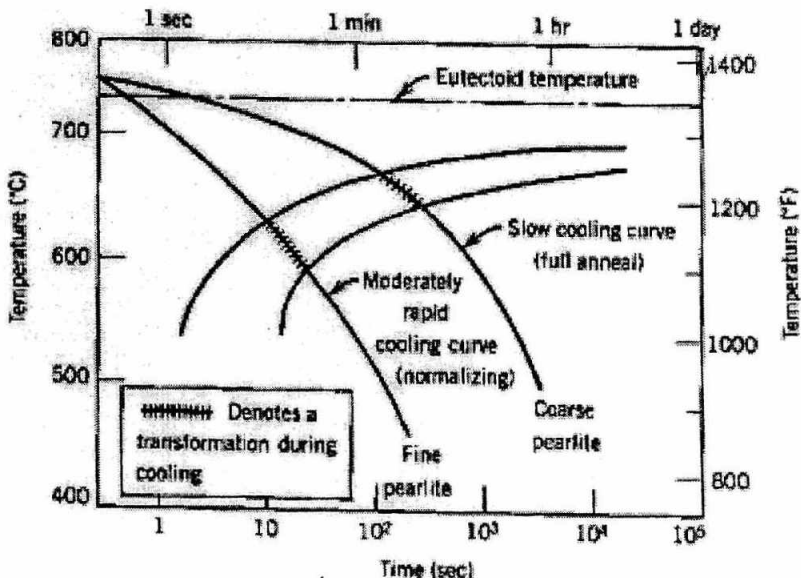


Fig. 17 : CCT Diagram for Eutectoid Steel

If the cooling curve is rapid enough to avoid transformation through the nose region, then the structure formed would be fully martensite. Therefore, in order to get a complete martensitic structure, the steel should be rapidly cooled in such a way that the transformation through the nose region of the C-curve is avoided. Thus cooling rate which is tangent to the nose of the C-curve would be the approximate **critical cooling rate (CCR)**. Any cooling rates slower than this produce some softer transformation product whereas the cooling rate faster than that will form only martensite.

Hardening

High hardness values can be obtained by a process known as **Hardening**. Hardening treatment consists of heating to hardening temperature, holding at a temperature, followed by rapid cooling such as quenching in water, oil or salt baths. Rapid cooling results in the transformation of austenite at considerably low temperatures into non-equilibrium products. The hardening temperature depends on chemical composition. For plain carbon steels, it depends on carbon content alone. Hypoeutectoid steels are heated to about 30-50°C above the upper critical temperature, whereas eutectoid and hypereutectoid steels are heated to about 30-50°C above the lower critical temperature.

The properties of steel developed by hardening depend on various factors. Important among these factors are (i) chemical composition of steel, (ii) size and shape of the steel part, (iii) hardening cycle, i.e heating rate, hardening temperature, holding time cooling rate, (iv) homogeneity and grain size of austenite, (v) quenching media, and (vi) surface condition of the steel part. All these factors are interrelated. In fact, these factors affect almost all heat treatment processes and are of great importance for hardening treatment, due to rapid cooling, which results in transformation of austenite to non-equilibrium product.

Hardenability

In a steel specimen of any appreciable size, the cooling rates at the surface and at the center are not the same. The difference in these rates naturally increases with the severity of the quench, or the speed of the cooling process. Thus, there will be little difference, at any instant, between the temperature at the surface and the center of a bar of the some size when it is furnace cooled (fully annealed). On the other hand, the same bar, if quenched in a rapid coolant such as iced brine, has markedly different cooling rates at the surface and at the center, which are capable of producing entirely different microstructures at the surface and center of the bar. If drastic cooling is carried out, martensite can also form at the center of the cross-section of steel because the cooling rate at the center may be exceed the critical cooling rate, and the steel may harden throughout the cross-section. However the drastic quenching may give rise to other undesirable effects such as warping and cracking of the steel. Therefore, hardenability of the steel is reflected by its ability to harden (by forming martensite) through out its cross-section while avoiding drastic quenching.

Factors influencing hardenability

A steel said to have high hardenability if austenite of the steel is transformed into martensite, even at the relatively slow cooling rates. Any factor, which shifts the nose of the C- curve of the CCT diagram to right, makes it easier to form a martensitic structure at a slower cooling rate. All common alloying (except cobalt) move the nose of the C-curve to the right. Therefore, they are said to increase the hardenability of steel. Thus, the shifting of the nose of the C-curve is associated with an increase in hardenability of steel. This statement can also be understood from another angle, i.e any variable, which checks the formation of pearlite, increases the hardenability of steel. Basically, the hardenability of steel depends on the effect of austenitic grain size, carbon content and alloying elements.

The relation between critical diameter (D_c), ideal critical diameter (D_I), and severity of quench (H) can be determined from the thermodynamic considerations. These relations are shown in Grossman master graph. In this

figure, ideal critical diameter D_I plotted as the abscissa, and the critical diameter D_c is plotted as the ordinate. A number of curves are plotted in this graph and each belongs to different rates of cooling. In every case, the rate of cooling is measured by the H-value or the severity of quench.

From this master graph, by knowing the value of D_c , the corresponding value for D_I can be found out. For example, assuming $D_c=1$ inch and $H=5$ (for agitated brine quench), the ideal critical diameter or hardenability works out to 1.2 inches with the help of Fig.18.

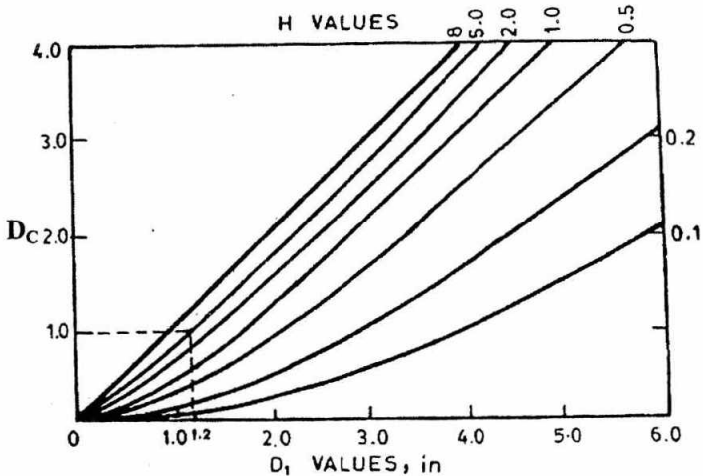


Fig.18 : Relation between ideal critical diameter (D_I) and critical diameter (D_c) using a quenching medium with a given cooling power H .

Problems Associated with Quenching

The differential cooling rates encountered by the heat treatment parts produces stresses that may lead to distortion and even cracking. During cooling two processes take place: (a) volume expansion due to martensite formation and (b) thermal contraction during cooling. Residual stresses and distortion arise because cooling rate is a function of section size or position in the part and therefore, the volume change occurs at different times in different locations during the cooling process. The stresses produced by different rates of cooling throughout the part produce distortion if the stresses generated are high enough to produce nonuniform yielding or plastic deformation on cooling.

Tempering

All steels that are hardened are subjected to subcritical heat treatment known as tempering. Any temperature up to the lower critical may be used

for tempering, thus an extremely wide variation in properties and microstructures ranging from those of as quenched martensite to spheroidised carbides in ferrites can be produced by tempering. It is balance of hardness and toughness required in service that determined the conditions of tempering for a given application.

Tempering in the range of 150°C to 200° C produces modest increase in toughness that is required for high strength and fatigue resistance as well as good wear resistance. Tempering above 425°C is used where high toughness is major requirement and strength is of secondary concern.

3.8 EFFECT OF ALLOYING ELEMENTS IN STEEL

The industries in last seventy years demanded steels with higher and higher tensile strength together with adequate ductility i.e. high strength to weight ratio. An increment in carbon content meets this demand in a limited fashion as in the heat treated condition the maximum strength is 700N/mm² at which, ductility and impact toughness fall rapidly. Plain carbon steel frequently necessitates water quenching accompanied by danger of distortion and cracking and even so only thin section can be hardened through out. So, heat treatable alloy steels have come into lime light to provide not only high strength with adequate ductility but also other attractive properties like corrosion resistance, high temperature oxidation resistance, improved creep properties depending on the arena of application.

Depending upon the effects of alloying elements, the alloying elements can be classified as follows,

- Elements, which tend to form carbides – Cr, W, Ti, Nb, V, Mo and Mn belong to this category.
- Elements which graphitise the carbide – Si, Co, Al and Ni are in this group.
- Elements which tend to stabilize austenite – Mn, Ni, Co and Cu influence this effect.
- Elements, which tend to stabilize ferrite – Cr, W, Mo, V and Si are the main elements in this group.

3.9 SURFACE MODIFICATIONS

Case hardening

Chemical heat treatment or case hardening consists of adding some element to the surface of the steel by diffusion of this element from surroundings at high temperature. The process takes place in three steps:

- Dissociation of external medium to liberate diffusing species.
- Contact of diffusing element with the surface of the steel.
- Penetration of the atom to the matrix of the metal.

The concentration of the element at the surface layer depends on activity of the surrounding medium and the rate of diffusion. The depth of penetration depends on temperature, time and concentration of diffusing element in the environment. There are different chemical treatments, which are in practice; they are illustrated below.

A. Carburizing – It is the process of adding carbon to the surface layer of steel containing 0.1-0.18% carbon. The main purpose of this process is to enhance the carbon content of surface layer (~0.8-1.0%) to obtain high wear resistance and endurance limit. Carbon can diffuse in steel in the atomic state, i.e. elemental carbon obtained by the dissociation of gases containing carbon (CO, CH₄ etc) at a temperature above Ac₃. Carbon diffuses in the lattice of gamma, makes it saturated and then a continuous layer of cementite may be formed. The carbon concentration varies along the cross section of the job. Upon slow cooling, the layers consist of hypereutectoid zone of pearlite and proeutectoid cementite, eutectoid zone of pearlite and hypoeutectoid zone of pearlite and ferrite from surface to core.

B. Nitriding – It is the process of adding nitrogen to the surface of steel by heating it in ammonia at 480-700°C. The process increases the hardness of surface layer, wear resistance, endurance limit and resistance to corrosion. A nitride layer can retain its hardness up to 600-650°C in comparison to carburized layer (~200-225°C). The process is extensively used for gears, cylinders of engines etc.

After nitriding, starting from surface the sequence of formation of different phases are as follows. When processing temperature is below 591°C, the α -phase is formed, which is the solid solution of nitrogen in bcc iron, after the saturation of α -phase, γ' (Fe₄N) begins to form having nitrogen content of 5.6-5.95%, further addition of nitrogen causes ϵ phase formation (Fe₂N) containing 8-11.2% nitrogen. As a result of diffusion naturally the surface layer consists of ϵ phase at the surface, succeeded by γ' and finally by α -phase. When the temperature is lowered, ϵ and α -phases decompose to liberate γ'' precipitate. Therefore at 20°C, from surface to core the phases are $\epsilon + \gamma'' - \gamma' - \alpha + \gamma''$.

C. Cyaniding – In this process both carbon and nitrogen is introduced to the surface layer of work by heating it in liquid medium. The work is heated and held at 820-960°C in a molten salt bath containing NaCN. The cyanided case contains 0.6-0.7% carbon and 0.8-1.2% nitrogen. In low temperature cyaniding, the job is quenched directly from cyaniding bath and subsequently tempered at 180-200°C. The hardness becomes 58-62 Rc.

At high processing temperature, carbon concentration becomes higher (~0.8-1.2%) than the nitrogen (~0.2-0.3%) at the surface layer of the job. After cyaniding the surface layer consists of carbonitrided e-phase and after hardening the cyanided and carburized cases have similar structure. After cyaniding, the work is cooled in air, then hardened by heating in salt bath/furnace and subsequently quenched. The final operation is low temperature tempering.

C. Carbonitriding – In this process the job is heated at 850-870°C in an endothermic controlled atmosphere having the gas mixture of carburizing gas, 5-15% un-processed natural gas and 3-10% ammonia for 2-10hrs to obtain a case hardened layer of 0.25-1.0mm thick. Carbonitriding is followed by quenching directly from furnace or after reheating. Martempering is frequently employed. Usual hardness becomes 60-62Rc after the complete processing.

Surface Hardening by Ion Implantation

Tool and die makers have always looked for the perfect solution, a hard, tough surface produced from easily workable but wear-resistant material. Perfection is not here yet, but the technique of ion implantation does offer major advantages, using a moderate temperature process to give significant increases in tool life of tools made from low carbon steels.

Laser transformation hardening

Transformation hardening is a well-established technique for the thermal hardening of steel. Like all thermal-hardening processes, the principle is to attempt to trap a structure as it exists at an elevated temperature and so preserve this structure at room temperature. Surface transformation hardening involves hardening only a thin layer on the surface of the component, leaving the desirable bulk properties of the material such as toughness and ductility unchanged. Laser transformation hardening involves the use of high intensity laser radiation to rapidly heat the surface of a steel into the austenitic region. Due to high rates of heat transfer, steep temperature gradients are set up which result in rapid cooling by conduction. This causes the transformation from austenite to martensite without the need for external quenching. This self-quenching occurs as the cold interior of the workpiece constitutes a sufficiently large heat sink to quench the hot surface by heat conduction to the interior at a rate high enough to prevent pearlite or bainite formation at the surface, resulting in martensite formation instead.

Electron Beam Hardening

Electron beam surface hardening is a process that uses the heat generated by the impingement of an electron beam on the surface of the material to

austenitize it, and then the austenitized layers are transformed to martensite because of very rapid conduction of heat into the cold interior of the workpiece. This effect is known as self-quenching and the cooling rates obtained are usually high enough to allow martensite formation, even in steels, which have very low hardening ability.

Plasma Hardening

The surface hardening of ferrous components such as grey cast iron and steel is traditionally done either by oxy-fuel flame or induction hardening. It is also possible to harden them with a laser. However, the surface hardening of ferrous specimens by a micro-plasma arc which makes use of a small controlled stream of ionised gas to heat the material to its austenitising temperature to effect hardening. As the stream of hot ionised gas comes into contact with a specimen, it rapidly heats up the surface. The heat is conducted into the bulk of the specimen causing self-quenching to occur and the formation of martensite since the quenching rate is high. This process has the ability to harden a selected area of a machine element that is subjected to wear.

3.10 LIGHT METALS AND ALLOYS

Light metals and their alloys have become of great importance for the construction of transportation equipment. These lightweight alloys have sufficiently high strength required for structural applications. The greatest application of light alloys is in the construction of aircraft. The extensive use of light alloys began with the discovery of precipitation hardening in these alloys.

Aluminium: Commercially pure aluminium with a specific gravity of 2.71 is 99% pure, the remainder consisting principally of iron and silicon. In the pure form, aluminum is used principally for cooking utensils and chemical equipment. On a weight basis, the electrical conductivity of aluminium is about 200% that of Cu. The Al alloys are used most extensively for structural purposes.

Alloying elements are added to aluminium castings to improve casting qualities as well as mechanical properties. The alloying elements commonly used for this purpose include Cu, Si, Mg and Mn, The improvement in mechanical properties due to alloying is due to

- (i) Solid solution strengthening
- (ii) Precipitation hardening
- (iii) Strain hardening by cold work.

Magnesium: Commercially pure Mg has a specific gravity of 1.74 and 99.8% pure. The pure metal is used largely in Mg base alloys, as a

deoxidizer and alloying agent in non-ferrous metals. Alloys of Mg are employed for structural purposes. The low specific gravity of Mg is offset by two disadvantages i.e., lack of stiffness and ease of oxidation. The alloying elements commonly added to Mg are Al, Zn, Mn and for special purposes Sn, Zr, Ce, Th and Be. Magnesium alloys may be classified as (i) casting or (ii) wrought alloys. The designations of the Mg base alloys follow the recommendation of ASTM. These consist of not more than two letters representing the alloying elements. These letters are followed by the respective percentages rounded off to whole numbers.

Selected Mg alloys may be rolled as sheet and plate, extruded on bars, shapes or tubing and forged by press or hammer forging depending on the specific alloy. These alloys are readily hot worked and formed at temperatures of 250°C – 400°C.

Titanium: Ti has a relatively high melting point of 1727°C, a low specific gravity of 4.5 and excellent resistance to corrosion at temperatures below 500°C. The strength of Ti alloys is 2-3 times that of the Al alloy and equal to some of the alloy steels. The modulus of elasticity of Ti is 16×10^6 lb/in², which means that it has greater stiffness than the Al alloys.

Ti exists in two allotropic forms, α at temperature upto 885°C and above this temperature. α -Ti is of the hexagonal structure while β is body centered cubic. Most of alloy elements decrease the α to β transformation temperature. Aluminium stabilizes the α phase at higher temperatures, which makes Al an important alloying element. Fe, Mn, Cr, Mo, V, Nb and Ta stabilize the β phase, thus decreasing the α - β transformation temperature. Additions of Nb and Ta lead to improved strength and help in preventing embrittlement caused by the presence of compounds of Ti and Al.

There are three general types of Ti alloy depending upon their structure: all α , α + β and all β . The α -alloys are not responsive to heat-treatment and hence do not develop the strength comparable to other alloys. α - β alloys are heat treatable and possess good ductility. These alloys are age hardenable. The β alloys have relatively low ductility for strengths comparable to other alloys.

3.11 CHARACTERIZATION TECHNIQUES

Metallography and Microscopy

Microstructure deals the size and shape of grains (crystals), the presence of crystal of different nature, their distribution and relative volume quantities, the shape of foreign inclusions and micro-voids, orientations of crystals and special crystallographic characteristics (twins, slip lines etc.). This branch

of science dealing with the microstructure of metals and alloys is termed as metallography.

Macro-structural examination is also a valuable method for studying crystalline materials. It can be studied by naked eyes or with a magnifying glass. Macro-structure can reveal the pattern of fracture, shrinkage cavities & voids and shape & size of large crystal. It can also detect cracks, chemical in-homogeneities, fibrous textures etc.

Irrespective of the microscope used, the success of any metallographic study is not only dependent on the microscope used but also it is very much dependent on the quality of the samples prepared. There are various sample preparation techniques for different microscope. Again, it also varies depending on the type of materials used.

OPTICAL MICROSCOPY

The optical microscopy remains the most important tool for micro structural studies in spite of the development of other sophisticated microscope (electron microscopy). The basic features of the microscope, till the century ago introduction by H.S.Scorby, remains same in spite of its latest development. It can be used to examine as polished as well as etched specimens.

The basic components are:

- Illumination system Condenser Light filters
- The objective lens The eyepiece Stage Stand

A variety of light sources are available for illuminating the objects. They are low voltage tungsten filament lamp, carbon arc illumination system, tungsten halogen filament lamp, sodium arc etc. Condenser is used to focus the light at the desired point. It is a adjustable lens free of aberration and coma. It is placed in front of the light source. Also a second adjustable-iris diaphragm is placed in the light path before the vertical illuminator.

To improve photo-microscopy or to alter contrast, filters are used. Various neutral density filters are used to reduce the intensity of the light. The objective lens is the most important component of the light microscope. Numerical aperture (NA) is the ability of a objective lens for the collecting of the reflective lights from the object. The NA is defined as:

$$NA = n \sin a$$

Where, 'n' is the minimum refractive index of the various materials between the specimen and the objective lens and 'a' is the half angle of the most oblique rays entering the front lens of the objective. As 'n' increases

the larger will be the NA or the greater is the light collecting ability of the objective lens. Also, it increases with 'a'.

The two most important limitation of an optical microscope are resolving power and depth of field. Factors that affect resolving power influence depth of field as well but in opposite direction. Thus one has to make compromise for getting optimum output. Both are dependent on wavelength (λ) of the illuminating light and NA. Resolution increases with decrease in λ and increase in NA respectively. The resolving power of an objective can be expressed as the inverse of the limit of resolution.

Resolving power = $1 / \text{limit of resolution}$

Limit of resolution = $0.5 \lambda / \text{NA}$ (for coherent illumination) and
= $0.61 \lambda / \text{NA}$ (for incoherent illumination e.g. in fluorescence)

An optical micrograph is presented in Fig.20.

HARDNESS TESTING

Classically hardness is defined as resistance to deformation of materials surface. Based on the concept of the resistance of a surface to abrasion Turner Sclerometer was developed where a diamond point was drawn across the surface until a visible scratch is generated. A list of hardness table is made where diamond (with a hardness index of 10) heads the list and talc (with a hardness index of 1) is at the foot of the list.

Since then a series of hardness measurement technique were developed. They were categorized in three groups on the basis of techniques used. They are (a) scratch hardness (b) indentation hardness and (c) rebound or dynamic hardness.

While indentation hardness is mainly used for metals and it has importance for engineering applications. In this case an indenter is used to make an impression on the metal surface. Then the hardness is measured through applied load and the area of impression. Various types of indenter are used to make the impression. Among them, the well known hardness measurement techniques (macro) are The Brinell test, the Meyer hardness, The Vickers hardness test or diamond pyramid hardness test, The Knoop hardness test, Rockwell hardness test etc.

In case of Brinell Hardness (BHN) steel balls of various diameters are used as indenters according to the materials to be tested. The load is also varied as per the diameters of the ball. It is one of the widely accepted hardness tests.

In addition of macro hardness measurement the micro hardness measurement is also widely used. Here the load is varied from 1 gm. to 2000

gms. It is used mainly to measure the hardness of individual phases or where it is necessary to measure the surface hardening. For thin film also it has application.

Scanning Electron Microscope

Scanning Electron Microscope (SEM) is an important instrument for materials characterization. It has unique capabilities for analyzing surfaces. SEM is an essential tool for microstructural studies and failure analysis.

It is analogous to the reflected optical/light microscope. But different sources are used to produce required illumination and get an image. The Optical Microscope (OM) form an image from light reflected from a specimen surfaces, where as SEM uses electron for image formation. The wavelength of these different sources result in different resolution levels. Electrons have much shorter wavelength (less than 0.5 \AA) than the light rays (photons). Therefore, it provides a better resolution. The enhanced resolution in turn permits higher magnification without the loss of detail. The max magnification of electron microscope is beyond 800000x theoretically. Due to the limitation of instrumental parameters, practical magnification and resolution are 300000x and 30 \AA in a conventional SEM. A SEM micrograph is presented in presented in Fig.22.

The other important capability of SEM is a high depth of field, which is the ability of, maintains focus across a field of view regardless of surface roughness. The combination of high resolution, extensive magnification range and high depth of field makes the SEM uniquely suited for the study of surfaces.

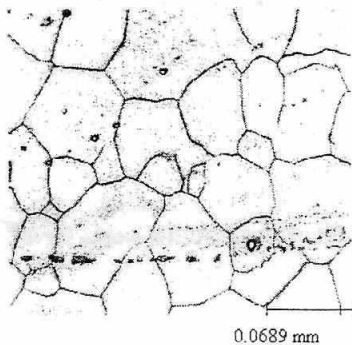


Fig. 19 : A typical Optical Micrograph

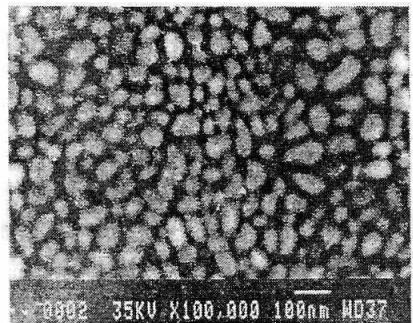


Fig. 20 : A typical SEM micrograph

Identification of the element is possible by measuring either the energy or wavelength of the X-rays respective by energy or wavelength dispersive

spectrometers (EDS/WDS). The X-rays are detected by spectrometers, which discriminate among either the energies or the wavelengths of the rays. EDS are most commonly associated with SEMs, whereas WDS are coupled to microprobes.

X-RAY DIFFRACTION

X-ray powder diffraction, interaction of X-rays with the specimen creates secondary “diffracted” beams of X-rays related to interplanar spacings in the crystalline powder according to a mathematical relation called “Bragg’s law” : $2d \sin\theta = n\lambda$

where, n is the order of diffraction, λ is the wavelength used, d is the interplanar spacing and 2θ is the diffraction angle (Fig.23).

The “angle” of the diffraction (denoted as θ by convention) is related to the interplanar spacing, d , by the Bragg law, and the intensity of the diffraction maximum is related to the strength of those diffractions in the specimen. The angles and intensities of diffractions are recorded electronically using a detector, electronics and specialized software resulting in a plot of θ vs intensity for the specimen (Fig.23b).

An observed powder diffraction pattern is the net effect of a convolution of: the diffraction ability of the sample (i.e. structure factor, F_{hkl}) and a complex system function. The observed intensity (y_{oi}) at the data point i is the result of: y_{oi} = sum of intensity of all Bragg peaks + the background. A diffraction pattern contains a host of information and it is the users’ interest to extract them. The said information on the offering may be: *i*) peak position → dimension of the unit cell *ii*) peak intensity @ content of the unit cell *iii*) peak broadening → crystallite size/micro strain *iv*) scaling factor → quantitative phase abundances etc.

Once the presence of crystalline phases in a polycrystalline aggregate is identified, the next task is to identify the various crystalline planes of each phases giving out their representative Bragg reflections. For first order reflections, we can rewrite the Bragg’s law as $\lambda=2d \sin\theta$, using this equation, for a known wavelength λ , we can easily estimate the crystallographic interplanar spacings (d) along various $[hkl]$ directions. Furthermore, for a cubic crystal, d and hkl are related by: $\lambda/d^2 = (h^2+k^2+l^2)/a^2$. Subsequently, by applying the structure factor restrictions, we can obtain a set of hkl planes corresponding to each d values (see the adjacent figure), which are represented on a particular diffraction pattern.

For some advanced users, a sophisticated application of the diffraction utility is in the ‘quantitative analysis’ using Rietveld method. In quantitative analysis, an attempt is made to determine structural characteristics and phase

proportions from the experimental data itself. In this analysis, standard patterns and structural data are used as a starting point; and the success involves in modeling the diffraction pattern such that the calculated pattern duplicates the experimental one.

Diffraction remains the premier tool for sampling the RS in materials. It is a non-destructive technique and the only one capable of providing absolute values for the entire stress tensor and with few assumptions. It does not require the stress free sample. The technique has kept pace with requirements of the researchers in the area of multiphase materials. The crystallographic interplanar atomic spacing acts as an internal microscopic strain gage and the reversible change in the distance between atoms is proportional to the stress acting on the planes. The stress can now be separated in to macro (peak shift) and micro (peak broadening) components, without the knowledge of the unstressed lattice parameter. XRD measures stress values as weighted averages of RS in the depth region, which depends upon materials absorption of X-rays $\approx 20 \mu\text{m}$ in steel.

The accuracy of the stress value depends upon the accuracy with which the shift in the diffraction peak position can be determined. The peak shift is determined by orienting the sample at different angles ($\pm \Psi$) to the incident X-ray beam, Fig.21. This way, a series of peak shift measurements can be made with planes of atoms oriented at different θ angles with respect to the sample surface and hence the surface stress. A straight line relationship is generally obtained in the plot between peak shift and $\text{Sin}^2\Psi$.

The slope of the plot along with Young's modulus (E) and Poisson's ratio (ν) for the diffracting plane gives the value of surface stress in terms of peak shift ' θ ' as follows:

$$\sigma_{\phi} = (2\theta_0 - 2\theta_{\Psi}) \cdot \left\{ \text{Cot}\left(\frac{\theta}{2}\right) \right\} \cdot \left\{ \frac{E}{(1+\nu)} \right\} \cdot \left(\frac{1}{\text{Sin}^2\Psi} \right) \left(\frac{\pi}{180} \right)$$

Where σ_{ϕ} is the stress along the azimuthal angle ϕ on the surface of the specimen, θ_0 and θ_{Ψ} correspond to the peak position at $\Psi=0$ and $\Psi \neq 0$ respectively as shown in the figure 1. The slope m of the plot in $(\theta_0, \theta_{\Psi})$ vs. $\text{Sin}^2\Psi$ is given by $\mu = [(1+\nu)/E] \cdot \sigma_{\phi}$, Fig. 22.

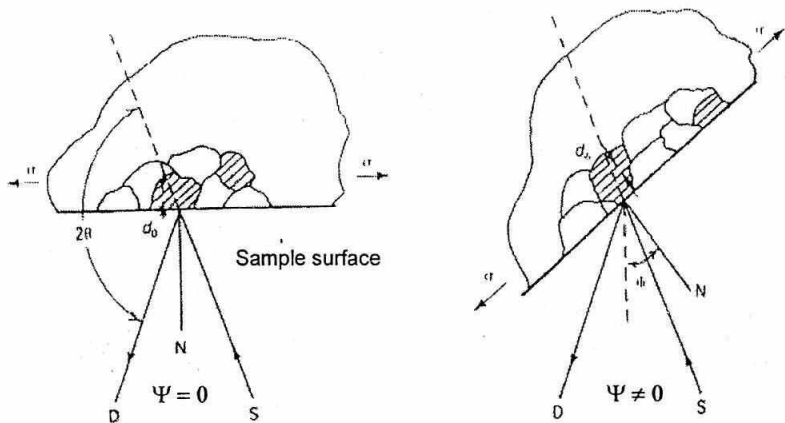


Fig. 21 : Figure shows the sample orientation with respect to beam orientation at $\psi = 0$ and $\psi \neq 0$ positions. S: Incident beam direction, D: Diffracted beam direction and N: Direction of the normal to specimen surface.

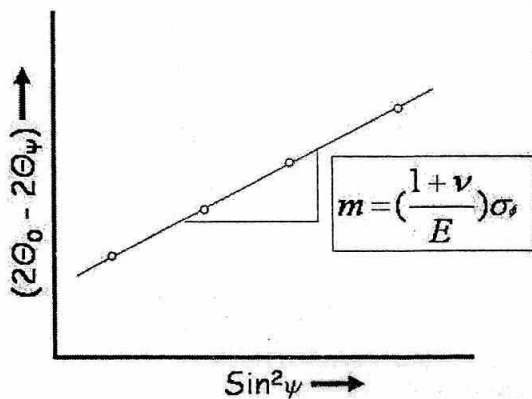


Fig. 22 : Relation between $\text{Sin}^2\psi$ and peaks shift is shown in the plot