NOTES ON MATERIALS ENGINEERING

UNIT-1 CRYSTALLOGRAPHY

UNIT-1

CRYSTALLOGRAPHY

Introduction

Materials Science – Investigating relationships that exist between the structure and properties of materials

Materials Engineering – on the basis of the structure-property correlations, designing or engineering the structure of a material to produce a pre-determined set of properties

Engineering materials is a branch of science which deals with the study of existing materials, their properties, functions, uses and effects over different compositions and mixtures. It provides the reader a broad knowledge of materials over a wide range.

We should proper knowledge of materials as the selection of a specific material for a particular use is a very complex process. However, one can simplify the choice if the details about (i) operating parameters, (ii) manufacturing processes, (iii) functional requirements and (iv) cost considerations are known.

Atomic Structure of metals

Atomic Structure

Atoms are composed of electrons, protons, and neutrons. Electrons and protons are negative and positive charged particles respectively. The magnitude of each charged particle in an atom is 1.6×10^{-19} Coulombs. The mass of the electron is negligible with respect to those of the proton and the neutron, which form the *nucleus* of the atom. The unit of mass is an atomic mass unit (*amu*) = 1.66 $\times 10^{-27}$ kg, and equals 1/12 the mass of a carbon atom. The Carbon nucleus has Z=6, and A=6, where Z is the number of protons, and A the number of neutrons. Neutrons and protons have very similar masses, roughly equal to 1 *amu* each. A neutral atom has the same number of electrons and protons, Z. A *mol* is the amount of matter that has a mass in grams equal to the atomic mass in *amu* of the atoms. Thus, a mole of carbon has a mass of 12 *grams*. The number of atoms in a mole is called the Avogadro number, $Nav = 6.023 \times 10^{23}$. Note that Nav = 1 *gram*/1 *amu*.

Atomic bonding in solids

The atoms are bound to each other by number of bonds. These inter-atomic bonds are primarily of two kinds: Primary bonds and Secondary bonds. Ionic, Covalent and Metallic bonds are relatively very strong, and grouped as primary bonds, whereas van der Waals and hydrogen bonds are relatively weak, and termed as secondary bonds

Ionic Bonding: This bond exists between two atoms when one of the atoms is negative (has an extra electron) and another is positive (has lost an electron). Then there is a strong, direct Coulomb attraction. Basically ionic bonds are non-directional in nature. An example is NaCl

Covalent Bonding: In covalent bonding, electrons are shared between the atoms, to saturate the valency. The simplest example is the H2 molecule, where the electrons spend more time in between the nuclei of two atoms than outside, thus producing bonding. Covalent bonds are stereo-specific i.e. each bond is between a specific pair of atoms, which share a pair of electrons (of opposite magnetic spins). Typically, covalent bonds are very strong, and directional in nature.

Metallic Metals characterized high thermal electrical **Bonding:** are by and conductivities. Thus, neither covalent nor ionic bonding are realized because both types of bonding valence electrons preclude conduction. However. localize the and strong bonding does occur in metals

Hydrogen bonding: It occurs between molecules as covalently bonded hydrogen atoms – for example C-H, O-H, F-H – share single electron with other atom essentially resulting in positively charged proton that is not shielded any electrons. This highly positively charged end of the molecule is capable of strong attractive force with the negative end of an adjacent molecule

Crystal structures

All metals, a major fraction of ceramics, and certain polymers acquire crystalline form when solidify, i.e. in solid state atoms self-organize to form *crystals*. Crystals possess a long-range order of atomic arrangement through repeated periodicity at regular intervals in three dimensions of space. When the solid is not crystalline, it is called amorphous. Examples of crystalline solids are metals, diamond and other precious stones,

Lattice is used to represent a three-dimensional periodic array of points coinciding with atom positions. *Unit cell* is smallest repeatable entity that can be used to completely represent a crystal structure. Thus it can be considered that a unit cell is the building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions

Crystal System

A regular and repetitious pattern in which atoms or groups of atoms (i.e. molecules) of a crystalline material arrange themselves is known as a crystal structure. All crystalline solids may be classified into seven crystal systems or structures, which are described below:

- (1) Cubic Structure:- In this crystal arrangement, three equal axes are at right angles.
- (2) **Tetragonal Structure:-** In this crystal arrangement, three axes are at right angles, two of these axes are equal while third one is different.
- (3) **Orthorhombic Structures:-** In this crystal arrangement, three unequal axes are at right angles.
- (4) **Rhombohedral Structures:-** In this crystal arrangement, three equal axes are equally included but at an angle other than a right angle.
- (5) **Hexagonal Structure:-** In this crystal arrangement, three equal axes are in one plane at 120° to each other, and a fourth axis normal to this plane. The interval along the fourth axis is unique.
- (6) **Monoclinic Structure:-** In this crystal arrangement, there are three unequal axes. One of the axes is at right angles to the other two axes, but the other two axes are not at right angles to each other.
- (7) **Triclinic Structure:-** In this crystal arrangement, three unequal axes a unequally inclined and none being at right angles

Crystal system	Lattice type	No. of lattices	Relation between primitives	Interface angles	Examples
Cubic	P, F, C	3	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	Au, NaCl, CaF ₂ , CrCl, CaO (I)}
Monoclinic	Р, В	2	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	2H ₂ O, NaSO ₄ , CaSO ₄ , FeSO ₄ }
Triclinic	Р	1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	K ₂ Cr ₂ O ₇ , CuSO ₄ , K ₂ S ₂ O ₈
Tetragonal	P, C	2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	NiSO ₄ , Sn, TiO ₃ , and SnO ₂
Orthogonal	P, B, F, C	4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	MgSO ₄ , KNO ₃ , and BaSO ₄
Rhombohedral (Trigonal) (orthorhombic)	P or R	1	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$	SiO ₂ , CaSO ₄ , and CaCO ₃
Hexagonal	Р	1	$a = b \neq c$	$\alpha = \beta = 90^{\circ} \gamma = 120^{\circ}$	AgCl, SiO2, Zn and Graphite

Crystal Structures for Metallic Elements:- Generally, the metallic elements crystallize in one of the following three structures.

- I. Body centered cubic structure (B.C.C):- In this type crystal structure, the unit cell has one atom at each corner of the cube and one at body centre of the cube. Examples- α iron(below 910° C), δ-iron(1400°C to 1539°C),W,V,Mo,Cr,Li,Na,K.
- II. II. Face centered cubic structure (F.C.C):- In this type of crystal structure, the unit cell has an atom at each corner of the cube and in addition has one atom at the centre of each face. Examples- γ -iron (910°C to 1400°C), Cu, Ag, Al, Ni, Pb, Pt.



Hexagonal Close Packed

III. Hexagonal close-packed structure (H.C.P) :- In this type of crystal structure, the unit cell has one atom at each of the twelve corners of the hexagonal prism, one atom at the centre of the two hexagonal faces and three atoms symmetrically arranged in the body of the cell. Examples- Mg, Zn, Ti, Zr, Cd.

Body-centered Cubic **Structure** (BCC): The cell of BCC system unit has at each which shared the adjoining eight cubes an atom corner. are by and one at the body centre (Fig. 3.16). Obviously, each unit cell share 8 atoms one on each of its corners in addition to one atom at the body centre. Hence

the share of each cube = $\frac{1}{8}$ th of each corner atom.

 \therefore Total no. of atoms = $\frac{1}{8} \times 8 = 1$ atom

BCC crystal has one atom at the centre = 1 atom

 \therefore Total atoms in BCC unit cell = 1 + 1 = 2 atoms

(Body diagonal)² = Sum of the squares of all the three sides $(4r)^2 = a^2 + a^2 + a^2$ $a = \sqrt{\frac{16r^2}{3}} = \frac{4r}{\sqrt{3}}$ Volume = $2 \times \frac{4}{3} \pi r^3$ $= 2 \times \frac{4}{3} \pi \left(\frac{a\sqrt{3}}{4}\right)^3$

$$r = \frac{a\sqrt{3}}{4}$$

Volume of unit cell = $a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$

 $APF = \frac{(Number of atoms) \times (Volume of one atom)}{Volume of unit cell}$

$$= \frac{2 \times \frac{4}{3} \pi r^3}{\left(4r/\sqrt{3}\right)^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

Face-centered Cubic Structure (FCC): In this type of lattice structure, also known as cubic packed structure, the atoms are located at the eight corners of the cube and at the centre of each face



Each face atom in FCC structure is shared by two unit cells, or we can say that one face of the FCC unit contains 1/2 atom.

No. of atoms in all six faces = $\frac{1}{2} \times 6 = 3$ No. of atoms in all corners = $\frac{1}{8} \times 8 = 1$

Total atoms in FCC unit cell = 1 + 3 = 4 atoms
 From the geometry of FCC structure

...

 $a = \sqrt{8} r = 2\sqrt{2} r$ Volume of 4 atoms = $4 \times \frac{4}{3} \pi r^3$

 $a^2 + a^2 = 4r^2$

$$= 4 \times \frac{4}{3} \frac{\left(a\sqrt{2}\right)^3 \pi}{(4)^3}$$
$$= \frac{16}{3} \pi a^3 \times \frac{2\sqrt{2}}{64} = \frac{\pi}{6}\sqrt{2} a^3$$
$$APF = \frac{4 \times \frac{4}{3} \pi r^3}{\left(2\sqrt{2} r\right)^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$



..

Hexagonal Closed Packed (HCP) Structures: In HCP structures, the unit cell contains one atom at each corner of the hexagonal prism, Face Centered Cubic one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell

Each corner atom is shared by six other unit lattices or each corner has 1/6 atom.

Number of atoms in upper hexagonal plane

$$=\frac{1}{6}\times 6=1$$

Number of atoms in lower hexagonal plane

$$=\frac{1}{6}\times 6=1$$

We note that each central atom is shared by two unit cells which means upper and lower planes contain atom each.

 $\frac{1}{2}$

Total number of central atoms in both, upper and lower planes = $\frac{1}{2} \times 2 = 1$...

and there are three intersititial atoms.

Total number of atoms in HCP crystal = 1 + 1 + 1 + 3 = 6*.*..

$$APF = \frac{2(4/3)\pi r^3}{a(a\sin 60^\circ)c}$$

where r is the atomic radius. Using c = 1.633a and a = 2r, one obtains,

$$APF = \frac{\pi\sqrt{2}}{6} = 0.74$$

Crystalline and Non-crystalline materials

Single Crystals: Crystals can be single crystals where the whole solid is one crystal. Then it has a regular geometric structure with flat faces.

Polycrystalline Materials: A solid can be composed of many crystalline grains, not aligned with each other. It is called *polycrystalline*. The grains can be more or less aligned with respect to each other. Where they meet is called a grain boundary.

Non-Crystalline Solids: In amorphous solids, there is no long-range order. But amorphous does not mean random, since the distance between atoms cannot be smaller than the size of the hard spheres. Also, in many cases there is some form of short-range order. For instance, the tetragonal order of crystalline SiO₂ (quartz) is still apparent in amorphous SiO₂ (silica glass)

Crystallographic notation of atomic planes

Crystal Directions: To specify the direction of a straight line joining lattice points in a crystal lattice, we choose any lattice point on the line as the origin and express the vector joining this to any other lattice point on the line as follows:

$$\vec{r} = n_1'\vec{a} + n_2'\vec{b} + n_3'\vec{c}$$

The direction of the line is represented by the set of integers n_1, n_2 , and n_3 . If these integer numbers have common factors, they are removed and the direction is denoted by $[n_1, n_2, n_3]$.



The

The direction [111] is the line passing through the origin O and point P. It may be noted that the point P is at a unit cell distance from each axis. The direction [100] is the line passing through origin O and point Q. obviously, the point Q is at a distance 1, 0, 0 from x, y and z axes respectively. The direction [101] is the line passing through the origin O and the point R. Again, the

point R is at a unit cell distance of 1, 0, 1 from x, y and z axes respectively.

equivalent directions are grouped together in the symbol <100>, where the bracket <> represents the whole family.



Crystallographic Planes: The crystal lattice may be regarded as made-up of an aggregate of a set of parallel equidistant planes, passing through the lattice points, which are known as lattice planes, or atomic planes. For a given lattice, one can choose the lattice planes in different ways

Miller evolved a method to designate a set of parallel planes in a crystal by three numbers h, k and l, usually written within brackets thus (h, k, l) known as *Miller indices* of the plane. *Determination of Miller Indices:* (a) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes, i.e. x, y, z axes now, express the above intercepts as multiples of the unit cell dimensions, or lattice parameters along the axes, i.e. axes (c) Take the reciprocal of intercepts (d) Now, reduce these reciprocals to the smallest set of integral numbers

$$\frac{1}{p}:\frac{1}{q}:\frac{1}{r}=h:k:l$$

and enclose within a bracket These integers within the bracket are Miller indices. In general it is denoted by (h, k, l)



Fig. Lattice planes in a cubic system. Negative intercepts are indicated on negative coordinates

Miller indices of a direction are simply the vector components of the direction resolved along each of the co-ordinate axis, expressed as multiples of the unit cell parameters and reduced to their simplest form. They are denoted by [hkl] (to distinguish it from the (hkl) plane).

Polymorphism

Polymorphism is the ability of a solid material to exist in more than one form or crystal structure. We can find this characteristic in any <u>crystalline</u> material such as <u>polymers</u>, mineral, metal, etc. There are several forms of polymorphism as follows:

- Packing polymorphism depending on the differences in the crystal packing
- Conformational polymorphism the presence of different conformers of the same molecule

The variation of the conditions during the crystallization process is the main reason that is responsible for the occurrence of the polymorphism in crystalline materials. These variable conditions are as follows:

- Polarity of solvent
- Presence of impurities
- The level of supersaturation at which the material starts to crystalize
- Temperature
- Changes in stirring conditions

	Polymorphism	Allotropy
DEFINITION	Polymorphism is the ability of a solid material to exist in more than one form or crystal structure.	Allotropy is the existence of two or more different physical forms of a chemical element.
OCCURRENCE	Polymorphism occurs in chemical compounds.	Allotropy occurs in chemical elements.
DESCRIPTION OF STRUCTURE	Describes the differences in crystal structures of compounds.	Describes the differences in atomic arrangement of compounds having the atoms of the same chemical element.

Allotropy

Allotropy is the existence of two or more different physical forms of a chemical element. These forms exist in the same physical state, mostly in the solid state. Therefore, these are different structural modifications of the same chemical element. Allotropes contain atoms of the same chemical element that binds with each other in different ways.

Moreover, these different forms may have different physical properties because they have different structures and chemical behavior may vary as well. One allotrope may convert into another when we change some factors such as pressure, light, temperature, etc. Therefore these physical factors affect the stability of these compounds. Some common examples for allotropes are as follows:

- Carbon diamond, graphite, graphene, fullerenes, etc.
- Phosphorous white phosphorous, red phosphorous, diphosphorous, etc.
- Oxygen dioxygen, ozone, tetraoxygen, etc.
- Boron amorphous boron, alpha rhombohedral boron, etc.
- Arsenic yellow arsenic, grey arsenic, etc.

Imperfection in solids

Any irregularity in the pattern of crystal arrangement in a solid lattice is called imperfection in solids. The occurrence of defects takes place when crystallization (the process of formation of crystals) occurs at a very fast or at an intermediate rate. This is because particles don't get enough time to arrange themselves in a regular pattern.

Defects exists any all solid materials. For ease of their characterization, defects are classified on the basis of their geometry, which is realistic as defects are disrupted region in a volume of a solid. Defects are:

- a. Point defects (zero-dimensional)
- b. Line defects (single dimensional)
- c. Surface defects (two dimensional)
- d. Volume defects (three dimensional)

Point defects, as the name implies, are imperfect point-like regions in the crystal. Typical size of a point defect is about 1-2 atomic diameters. Different point defects are explained in the following paragraphs.

A *vacancy* is a vacant lattice position from where the atom is missing. It is usually created when the solid is formed by cooling the liquid. There are other ways of making a vacancy, but they also occur naturally as a result of thermal excitation, and these are thermodynamically stable at temperatures greater than zero



An *interstitial atom* or *interstitialcy* is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the rest surrounding it (self interstitial) *or* a foreign impurity atom. Interstitialcy is most probable if the atomic packing factor is low.

Another way an impurity atom can be fitted into a crystal lattice is by substitution. A *substitutional atom* is a foreign atom occupying original lattice position by displacing the parent atom.

In ionic crystals, existence of point defects is subjected to the condition of charge neutrality. There are two possibilities for point defects in ionic solids.

When an ion displaced from a regular position to an interstitial position creating a vacancy, the pair of vacancy-interstitial is called *Frenkel defect*. Cations are usually smaller and thus displaced easily than anions. Closed packed structures have fewer interstitials and displaced ions than vacancies because additional energy is required to force the atoms into the interstitial positions. A pair of one cation and one anion can be missing from an ionic crystal, without violating the condition of charge neutrality when the valency of ions is equal. The pair of vacant sites, thus formed, is called *Schottky defect*. This type of point defect is dominant in alkali halides. These *ion-pair vacancies*, like single vacancies, facilitate atomic diffusion

Line defects Dislocations:

Line imperfections (one-dimensional defects) are also called Dislocations. They are abrupt changes in the regular ordering of atoms along a line (dislocation line) in the solid. They occur in high densities and strongly influence the mechanical properties of material. They are characterized by

the Burgers vector (\mathbf{D}), whose direction and magnitude can be determined by constructing a

loop around the disrupted region and noticing the extra inter-atomic spacing needed to close the loop. The Burgers vector in metals points in a close packed lattice direction. It is unique to a dislocation. Dislocations occur when an extra incomplete plane is inserted. The dislocation line is at the end of the plane. Dislocations can be best understood by referring to two limiting cases - Edge dislocation *and* Screw dislocation.



Positive Edge dislocation

Negative Edge dislocation

)r

Edge dislocation or *Taylor-Orowan dislocation* is characterized by a Burger's vector that is perpendicular to the dislocation line. It may be described as an edge of an extra plane of atoms within a crystal structure. Thus regions of compression and tension are associated with an edge dislocation. Because of extra incomplete plane of atoms, the atoms above the dislocation line are squeezed together and are in state of compression whereas atoms below are pulled apart and experience tensile stresses. Edge dislocation is considered *positive* when compressive stresses

present above the dislocation line, and is represented by \perp . If the stress state is opposite i.e. compressive stresses exist below the dislocation line, it is considered as negative edge dislocation, and represented by \top . A schematic view of edge dislocations

Screw dislocation or Burgers dislocation has its dislocation line parallel to the Burger's vector. A screw dislocation is like a spiral ramp with an imperfection line down its axis. Screw dislocations result when displacing planes relative to each other through shear. Shear stresses are associated with the atoms adjacent to the screw dislocation; therefore extra energy is involved as it is in the case of edge dislocations. Screw dislocation is considered positive if Burger's vector and *t*-vector or parallel, and vice versa. (*t*-vector – an unit vector representing the direction of the dislocation line). A positive screw



dislocation is represented by "C' a dot surrounded by circular direction in clock-wise direction", whereas the negative screw dislocation is represented by "O', a dot surrounded by a circular direction in anti-clock-wise direction". A schematic view of a negative screw dislocation

Surface defects

Interfacial defects can be defined as boundaries that have two dimensional imperfections in crystalline solids, and have different crystal structures and/or crystallographic orientations on either side of them. For example: external surfaces, grain boundaries, twin boundaries, stacking faults, and phase boundaries. These imperfections are not thermodynamically stable, rather they are meta-stable imperfections.

Grain boundaries: Crystalline solids are, usually, made of number of grains separated by grain boundaries. Grain boundaries are several atoms distances wide, and there is mismatch of orientation of grains on either side of the boundary as shown in *figure* When this misalignment is slight, on the order of few degrees ($< 10^{\circ}$), it is called *low angle grain boundary*. These boundaries can be described in terms of aligned dislocation arrays. If the low grain boundary is formed by edge dislocations, it is called *tilt boundary*, and *twist boundary* if formed of screw dislocations. Both tilt and twist boundaries are planar surface imperfections in contrast to high angle grain boundaries. For *high angle*

grain boundaries, degree of disorientation is of large range (> 15°). Grain boundaries are chemically more reactive because of grain boundary energy. In spite of disordered orientation of atoms at grain boundaries, polycrystalline solids are still very strong as cohesive forces present within and across the boundary.



Twin boundaries: It is a special type of grain boundary across which there is specific mirror lattice symmetry. Twin boundaries occur in pairs such that the orientation change introduced by one boundary is restored by the other (*figure-3.7*). The region between the pair of boundaries is called the twinned region. Twins which forms during the process of recrystallization are called *annealing twins*, whereas *deformation twins* form during plastic deformation.



Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure. Annealing twins are typically found in metals that have FCC crystal structure (and low stacking fault energy), while mechanical/deformation twins are observed in BCC and HCP metals. Annealing twins are usually broader and with straighter sides than mechanical twins. Twins do not extend beyond a grain boundary.

Stacking faults: They are faults in stacking sequence of atom planes. Stacking sequence in an FCC crystal is ABC ABC ABC ..., and the sequence for HCP crystals is AB AB AB.... When there is disturbance in the stacking sequence, formation of stacking faults takes place. Two kinds of stacking faults in FCC crystals are: (a) ABC AC ABC...where CA CA represent thin HCP region which is nothing but stacking fault in FCC, (b) ABC ACB CABC is called *extrinsic* or *twin*

stacking fault. Three layers ACB constitute the twin. Thus stacking faults in FCC crystal can also be considered as submicroscopic twins. This is why no microscopic twins appear in FCC crystals as formation of stacking faults is energetically favorable

Volume defects

Volume defects as name suggests are defects in 3-dimensions. These include pores, cracks, foreign inclusions and other phases. These defects are normally introduced during processing and fabrication steps. All these defects are capable of acting as stress raisers, and thus deleterious to parent metal's mechanical behavior

Diffusion

Diffusion refers to the transport of atoms through a crystalline or glassy solid. Many processes occurring in metals and alloys, especially at elevated temperatures, are associated with self-diffusion or diffusion.

Diffusion can be *defined* as the mass flow process in which atoms change their positions relative to neighbors in a given phase under the influence of thermal and a gradient.

Diffusion mechanisms

In pure metals self-diffusion occurs where there is no net mass transport, but atoms migrate in a random manner throughout the crystal. In alloys inter-diffusion takes place where the mass transport almost always occurs so as to minimize compositional differences. Various atomic mechanisms for self-diffusion and inter-diffusion have been proposed. *Figure below* presents schematic view of different atomic diffusion mechanisms. The most energetically favorable process involves an interchange of places by an atom and a neighboring vacancy – *vacancy diffusion*. This process demands not only the motion of vacancies, but also the presence of vacancies. The unit step in vacancy diffusion is an atom breaks its bonds and jumps into neighboring vacant site.



Diffusion mechanisms.

In *interstitial diffusion*, solute atoms which are small enough to occupy interstitial sites diffuse by jumping from one interstitial site to another. The unit step here involves jump of the diffusing atom from one interstitial site to a neighboring site. Hydrogen, Carbon, Nitrogen and Oxygen diffuse interstitially in most metals, and the activation energy for diffusion is only that associated with motion since the number of occupied, adjacent interstitial sites usually is large.

Substitutional diffusion generally proceeds by the vacancy mechanism. Thus interstitial diffusion is faster than substitutional diffusion by the vacancy mechanism. During *self-diffusion* or *ring mechanism* or *direct-exchange mechanism*, three or four atoms in the form of a ring move simultaneously round the ring, thereby interchanging their positions. This mechanism is untenable because exceptionally high activation energy would be required.

A *self-interstitial* is more mobile than a vacancy as only small activation energy is required for self-interstitial atom to move to an equilibrium atomic position and simultaneously displace the neighboring atom into an interstitial site. However, the equilibrium number of self-interstitial atoms present at any temperature is negligible in comparison to the number of vacancies. This is because the energy to form a self-interstitial is extremely large.

Steady-state diffusion

Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux. It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time. A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown in *figure*



Steady-state diffusion

Non-steady-state diffusion

Steady-state diffusion is described by Fick's first law which states that flux, J, is proportional to the concentration gradient. The constant of proportionality is called diffusion coefficient (diffusivity), D (cm²/sec). diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs. Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. for the one-dimensional case, *Fick's first law* is given by

$$J_x = -D\frac{dc}{dx} = \frac{1}{A}\frac{dn}{dt}$$

where D is the diffusion constant, dc/dx is the gradient of the concentration c, dn/dt is the number atoms crossing per unit time a cross-sectional plane of area A. The minus sign in the equation means that diffusion occurs down the concentration gradient.

Non-steady-state diffusion

Most interesting cases of diffusion are non-steady-state processes since the concentration at a given position changes with time, and thus the flux changes with time. This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or depleted from a region (which may cause them to accumulate in another region). *Fick's second law* characterizes these processes, which is expressed as:

$$\frac{dc}{dt} = -\frac{dJ}{dx} = \frac{d}{dx} \left(D \frac{dc}{dx} \right)$$

where dc/dt is the time rate of change of concentration at a particular position, x. If D is assumed to be a constant, then

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

Factors that influence diffusion

Ease of a diffusion process is characterized by the parameter D, diffusivity. The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

- Diffusing species: If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand if the size of substitution species is almost equal to that of parent atomic size, substitution diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.
- Temperature: Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion. Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

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

where D_0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature. From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between *(lnD)* and *(l/T)*. Thus by plotting and considering the intercepts, values of Q and D_0 can be found experimentally.

- Lattice structure: Diffusion is faster in open lattices or in open directions than in closed directions.
- Presence of defects: As mentioned in earlier section, defects like dislocations, grain boundaries act as short-circuit paths for diffusing species, where the activation energy is diffusion is less. Thus the presence of defects enhances the diffusivity of diffusing species.

Theories of plastic deformation

Deformation often referred to strain, is the change in the size and shape of an object due to the change in temperature or an applied force. Depending on the size, material and the force applied, various forms of deformation may occur. Based on these factors, deformation is classified into the following:

- Elastic Deformation The deformation caused is reversible and the deformation disappears after the removal of applied forces. A classic example of elastic deformation is the stretching of a rubber band.
- **Plastic Deformation** The deformation is irreversible and it stays even after the removal of the applied forces. Example, bending of steel rods.

Plastic deformation is studied in experiments with spring where <u>Hooke's law</u> is explained to differentiate between the plastic materials and elastic materials.

Plastic deformation is defined as a process in which the object due to applied force changes its size or shape in a way that is not reversible. Plastic deformation is seen in many objects including:Plastics, Metals, Soils, Rocks & Concrete

The mechanisms that cause plastic deformation differ widely. Plasticity in metals is a consequence of dislocations while in brittle materials such as concrete, rock and bone, plasticity occurs due to the slippage of microcracks. There are two prominent mechanisms of plastic deformation in metals and they are

- Slip
- Twinning

Slip is the prominent mechanism of deformation in metals. A slip involves the sliding of blocks of crystal over one another along different crystallographic planes known as slip planes. In twinning, the portion of crystals takes up an orientation related to the orientation of the rest of the untwined lattice in a symmetrical and definite way.

Given below in a table are the various differences between slip and twinning

Slip	Twinning
Occurs in discrete multiples of atomic spacing	The movement of atoms is lesser in atomic spacing
The orientation of the crystal above and below the slip plane is the same after deformation as before.	Orientation difference takes places across the twin plane
Occurs over a wide plane	Every atomic plane is involved
Slip occurs when shearing stress on the slip plane in the slip direction strikes a threshold value known as the critical resolved shear stress.	No critical resolved shear stress for twinning.
Takes places in several milliseconds	Takes place in few microseconds
Slip lines are present in even or odd numbers	Twin lines occur in pair

Recovery

Recovery is a process that kicks in at low temperatures; in this stage, the excess defects are annealed out, dislocations of opposite signs annihilate each other, and dislocations align to form low energy configurations, namely tilt and twist boundaries. Recovery is a process by which deformed grains can reduce their stored energy by the removal or rearrangement of defects in their crystal structure. These defects, primarily dislocations, are introduced by plastic deformation of theintroduced by plastic deformation of the material and act to increase the yield strength of a material. Recovery is a process that kicks in at low temperatures; in this stage, the excess defects are annealed out, dislocations of opposite signs annihilate each other, and dislocations align to form low energy configurations, namely tiltform low energy configurations, namely tilt and twist boundaries

Recrystallisation

Recrystallisation is defined as the process in which grains of a crystal structure come in a new structure or new crystal shape. \neg A precise definition of recrystallisation is \neg A precise definition of recrystallisation is difficult to state as the process is strongly related to several other processes, most notably recovery and grain growth. In some cases it is difficult to precisely define the point at which one process begins and another ends The recrystallization behavior of a particular metal alloy is sometimes specified in terms of a **recrystallization temperature**, the temperature at which recrystallization just reaches completion in 1 h.Recrystallisation is the process in which deformed grains are replaced by strain-free grains. It is generally observed that higher cold work ϖ It is generally observed that higher cold work and smaller initial grain size lead to finer recrystallised grains. The driving force for recrystallisation is the stored strain energy in the material The temperature at which a given material completely recrystallises in an hour is defined as the recrystallisation temperature. The recrystallisation temperature is low if the degree of deformation is high and/or if the temperature of deformation is low and/or if the initial grain size is small.initial

grain size is small. The recrystallisation temperature is also very sensitive to the purity of the material

Grain Growth

After recrystallization is complete, the strain-free grains will continue to grow if the metal specimen is left at the elevated temperature (Figures 7.21d to 7.21f); this phenomenon is called grain growth. Grain growth does not need to be preceded by recovery and recrystallization; it may occur in all polycrystalline materials, metals and ceramics alike. Energy is associated with grain boundaries, as explained in Section 4.6. As grains increase in size, the total boundary area decreases, yielding an attendant reduction in energy: the driving force the total this is for grain growth. Grain growth occurs by the migration of grain boundaries. Obviously, not all grains can enlarge, but large ones grow at the expense of small ones that shrink. Thus, the average grain size increases with time, and at any particular instant there exists a range of grain sizes. Boundary motion is just the short-range diffusion of atoms from one side of the boundary to the other. The directions of boundary movement and atomic motion are opposite to each other

UNIT-2 PHASE TRANSFORMATION

Phase Transformation

The understanding of phase diagrams for alloy systems is extremely important because there is a strong correlation between microstructure and mechanical properties, and the development of microstructure of an alloy is related to the characteristics of its phase diagram. In addition, phase diagrams provide valuable information about melting, casting, crystallization, and other phenomena.

Almost all materials have more than one phase in them. Thus engineering materials attain their special properties. Macroscopic basic unit of a material is called component. It refers to a independent chemical species. The components of a system may be elements, ions or compounds.

A *phase* can be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics i.e. it is a physically distinct from other phases, chemically homogeneous and mechanically separable portion of a system. A component can exist in many phases.

E.g.: Water exists as ice, liquid water, and water vapor. Carbon exists as graphite and diamond.

When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a disparity in one or the other set of properties is sufficient. The following terms are frequently used in the study of solid phases and phase diagrams: *(i) System:* A system may be composed of solids, liquids, gases or their combinations and may have metals and non-metals separately or in any combination. It is explained as the whole complex of phases of one or several components at different pressures and compositions. A system is so isolated from its surroundings that it is unaffected by solids, liquids, gases or their combinations and may have only to the extent permitted by the investigator.

(*ii*) Components: These are the substances, either chemical elements or chemical compounds, whose presence is essential and sufficient to make a system. A pure metal is called a one-component system, an alloy of two metals is called a binary or two component system, etc. (*iii*) Phase: It is a homogeneous portion of a system that has uniform physical and chemical

characteristics. The number of phases in a system is the number of different substances that exist in it in a homogeneous system.

(iv) Phase diagram: A graphical representation of the relationships between environmental constraints (e.g. temperature and sometimes pressure), composition, and regions of phase stability, ordinarily under conditions of equilibrium.

Most phase diagrams are prepared by using slow cooling conditions whereby phases are in equilibrium. One can get following important informations from the phase diagrams

(a) Phases at different composition and temperature(b) Equilibrium solubility of one element or compound in another element.

(c) Melting points of different phases in an alloy.

(d) Temperature of solidification or range of solidification of an alloy.

(v) *Phase Equilibrium:* The state of a system where the phase characteristics remain constant over indefinite time periods. At equilibrium the free energy is a minimum. In an equilibrium diagram, liquid is one phase and solid solution is another phase.

(vi) Phase Transformation: A change in the number and/or character of the phases that constitute the microstructure of an alloy

Gibbs phase rule

The construction of phase diagrams—as well as some of the principles governing the conditions for phase equilibria—are dictated by laws of thermodynamics. One of these is the **Gibbs phase rule**, proposed by the nineteenth-century physicist J. Willard Gibbs

In a system under a set of conditions, number of phases (P) exist can be related to the number of components (C) and degrees of freedom (F) by Gibbs phase rule. Degrees of freedom refers to the number of independent variables (e.g.: pressure, temperature) that can be varied individually to effect changes in a system.

Thermodynamically derived Gibbs phase rule: P+F=C+2

In practical conditions for metallurgical and materials systems, pressure can be treated as a constant (1 atm.).

Thus Condensed Gibbs phase rule is written as: P+F=C+1

Equilibrium phase diagram

A diagram that depicts existence of different phases of a system under equilibrium is termed as *phase diagram*. It is actually a collection of solubility limit curves. It is also known as *equilibrium* or *constitutional diagram*.

Equilibrium phase diagrams represent the relationships between temperature, compositions and the quantities of phases at equilibrium. These diagrams *do not* indicate the dynamics when one phase transforms into another.

Useful terminology related to phase diagrams: liquidus, solidus, solvus, terminal solid solution, invariant reaction, intermediate solid solution, inter-metallic compound, etc.

Phase diagrams are *classified* according to the number of component present in a particular system.

Phase diagram Useful information

Important information, useful in materials development and selection, obtainable from a phase diagram:

- It shows phases present at different compositions and temperatures under slow cooling (equilibrium) conditions.

- It indicates equilibrium solid solubility of one element/compound in another

- It suggests temperature at which an alloy starts to solidify and the range of solidification.

- It signals the temperature at which different phases start to melt.

- Amount of each phase in a two-phase mixture can be obtained.

Unary phase diagram

If a system consists of just one component (e.g.: water), equilibrium of phases exist is depicted by *unary phase diagram*. The component may exist in different forms, thus variables here are temperature and pressure.



Binary phase diagram

If a system consists of two components, equilibrium of phases exist is depicted by *binary phase diagram*. For most systems, pressure is constant, thus independently variable parameters are temperature and composition.

An explanation of the principles governing, and the interpretation of phase diagrams can be demonstrated using binary alloys even though most alloys contain more than two components.

Binary phase diagrams are maps that represent the relationships between temperature and the quantities of equilibrium, compositions and phases which influence the at microstructure of an alloy. Many microstructures develop from phase transformations, the changes that occur when the temperature is altered (typically upon cooling). This may involve the transition from one phase to another or the appearance or disappearance of a phase. Binary phase diagrams are helpful in predicting phase transformations and the resulting microstructures, which may have equilibrium or nonequilibrium character

Two components can be either two metals (Cu and Ni), or a metal and a compound (Fe and Fe3C), or two compounds (Al2O3 and Si2O3), etc.

Two component systems are classified based on extent of mutual solid solubility (a) completely soluble in both liquid and solid phases (isomorphous system) and (b) completely soluble in liquid phase whereas solubility is limited in solid state.For isomorphous system - E.g.: Cu-Ni, Ag-Au, Ge-Si, Al ₂O₃-Cr₂O₃.

BINARY EUTECTIC SYSTEMS

Another type of common and relatively simple phase diagram found for binary alloys is shown in Figure for the copper-silver system; this is known as a binary eutectic phase diagram. A number of features of this phase diagram are important and worth noting. First, three single-phase regions are found on the diagram: a, b, and liquid. The a phase is a solid solution rich in copper; it has silver as the solute component and an FCC crystal structure. The b-phase solid solution also has an FCC structure, but copper is the solute. Pure copper and pure silver are also considered to be a and b phases, respectively.



The solubility limit for the a phase corresponds to the boundary line, labeled *CBA*, between the a/(a + b) and a/(a + L) phase regions; it increases with temperature to a maximum [8.0 wt% Ag at 779C (1434F)] at point *B*, and decreases back to zero at the melting temperature of pure copper, point *A* [1085C (1985F)]. At temperatures below 779C (1434F), the solid solubility limit line separating the a and a b phase regions is termed a **solvus line**; the boundary *AB* between the a and a *L* fields is the **solidus line**, as indicated in Figure 9.7. For the b phase, both solvus and solidus lines also exist, *HG* and *GF*, respectively, as shown. The maximum solubility of copper in the b phase, point *G* (8.8 wt% Cu), also occurs at 779C (1434F). This horizontal line *BEG*, which is parallel to the composition axis and extends between these maximum solubility positions, may also

be considered a solidus line; it represents the lowest temperature at which a liquid phase may exist for any copper–silver alloy that is at equilibrium. There are also three two-phase regions found for the copper–silver system An important reaction occurs for an alloy of composition *CE* as it changes temperature in passing through *TE*; this reaction may be written as follows:

$$L(C_E) \xrightarrow{\text{cooling}}_{\text{heating}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

$$L(71.9 \text{ wt\% Ag}) \xrightarrow[\text{beating}]{\text{country}} \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag})$$

a liquid phase is transformed into the two solid a and phases at the temperature T_E ; the opposite reaction occurs upon heating. This is called a **eutectic reaction**

Hume-Ruthery conditions

Extent of solid solubility in a two element system can be predicted based on Hume-Ruthery conditions. If the system obeys these conditions, then complete solid solubility can be expected. Hume-Ruthery conditions:

- > Crystal structure of each element of solid solution must be the same.
- > Size of atoms of each two elements must not differ by more than 15%.
- Elements should not form compounds with each other i.e. there should be no appreciable difference in the electro negativities of the two elements.
- Elements should have the same valence.

Solid Solution

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained, and no new structures are formed. In other words, when elements completely dissolve in each other in liquid and or solid state the resulting phase is called *solid solution*



(a) Solid solutions (b) substitutional solid solutions and (c) interstitial solid solution

Substitutional Solid Solution When the two metals in solid solution form a single face centred cubic lattice, i.e., in general solute or impurity atoms replace or substitute for the host atoms, is called as substitutional solid solution

Interstitial Solid Solutions These can form, for instance, on melting together transition metals and non-metals with a small atomic radius (H, N, C or B). The possibility of obtaining an interstitial solution is mainly determined by the size factor; i.e., the size of a solute atom must be equal to or slightly smaller than the size of an interstitial void.

IRON CARBON EQULIBRIUM DIAGRAM

Figure below shows the iron-carbon equilibrium diagram representing the entire range of ironcarbon alloys. Diagram indicates transformations that take place in an alloy of iron-carbon from pure iron to cementite carbon content 6.67%). The carbon percentages is represented on the horizontal axis and the temperature on the vertical axis. We have also shown the names of the phases existing at temperatures and concentrations determined by the lines (boundaries) of these areas on the equilibrium diagram. The curve ABCD is called the liquidus. All alloys represented by compositions and temperatures in the region above ABCD are completely liquids. Point A in the diagram represent the melting point of pure iron (1539°C). Point D represent the melting point (1539°C) of iron carbide or cementite. With the fall in the temperature of the liquid along the line ABC, crystals of austenite separate from the liquid. Similarly, in the same way, crystals of iron carbide (Fe3C) separate from the liquid along the line CD. High temperature transformation (- Fe - Fe or Fe Fe) take place at upper left hand portion of phase diagram (Fig. 9.21). The peritectic reaction HJB represents the formation of austenite. i.e. solid solution of carbon in gamma iron (-Fe or Fe). crystals of -iron (Fe) begin to separate from the liquid along the line AB. We know that a solid solution of carbon in -iron (Fe) at high temperatures is known as -iron (Fe). The complete solidification of iron-carbon alloys proceeds along the line HJECF called the solidus. The alloys containing 0.18 to 1.7% carbon represent the solidus HJE and those with carbon contents ranging from 1.7 to 6.67% become solid along the line ECF at temperature 1130°C.

At point C in Fig. 9.21 (4.3% carbon), austenite and cementite are simultaneously precipitated from

the alloy to form the eutectic, also called as Lede-burite. The iron-carbon phase diagram (Fig. 9.21) indicates a peritectic point J, a eutectic point C, and a eutectoid point S. The following reactions take place at these points:

(i) During the *peritectic reaction* (horizontal line *HJB* at 1401°C)

Cooling

Heating

$$\delta$$
-Iron (Fe $_{\delta}$) + liquid $\overleftarrow{\text{Cooling}}_{\text{Heating}}$ Austenite
 $F_H + L_B \rightarrow A_J$

(ii) At point C the eutectic reaction takes place (4.3%, 1130°C). This can be represented as

or

or

or

→ Austenite + Cementite (Lede-burite eutectic mixture)

$$L_C \to [A_E + C_{em}]$$

Liquid -

(c) At point S (723°C), the eutectoid transformation can be expressed as

Solid
$$\xrightarrow{\text{Cooling}}_{\text{Heating}}$$
 Ferrite + Cementite or Pearlite (eutectoid mixture)
 $A_S \rightarrow [F_P + C_{em}]$



Iron-carbon equilibrium diagram representing the entire range of iron-carbon alloys

Important phases found on the iron-iron carbide phase diagram are

I. α-ferrite (BCC),

- II. γ -austenite (FCC),
- III. δ -ferrite and

IV. iron carbide [or cementite (Fe₃C)].

The following phases are involved in the transformation, occurring with iron-carbon alloys:

- I. L Liquid solution of carbon in iron;
- II. δ-ferrite Solid solution of carbon in iron. Maximum concentration of carbon in δ-ferrite is
 0.09% at 2719 °F (1493°C) temperature of the peritectic transformation. The crystal structure of δ-ferrite is BCC (cubic body centered).
- III. Austenite interstitial solid solution of carbon in γ-iron. Austenite has FCC (cubic face centered) crystal structure, permitting high solubility of carbon up to 2.06% at 2097 °F (1147 °C). Austenite does not exist below 1333 °F (723°C) and maximum carbon concentration at this temperature is 0.83%.
- IV. α -ferrite solid solution of carbon in α -iron. α -ferrite has BCC crystal structure and low solubility of carbon up to 0.025% at 1333 °F (723°C). α -ferrite exists at room temperature.
- V. Cementite iron carbide, intermetallic compound, having fixed composition Fe₃C.
 Cementite is a hard and brittle substance, influencing on the properties of steels and cast irons.
- VI. Alloys, containing up to 0.51% of carbon, start solidification with formation of crystals of δferrite. Carbon content in δ-ferrite increases up to 0.09% in course solidification, and at 2719 °F (1493°C) remaining liquid phase and δ-ferrite perform peritectic transformation, resulting in formation of austenite.

Alloys, containing carbon more than 0.51%, but less than 2.06%, from primary austenite crystals in the beginning of solidification and when the temperature reaches the curve ACM primary cementite stars to form. Iron-carbon alloys, containing up to 2.06% of carbon, are called *steels*. Alloys, containing from 2.06 to 6.67% of carbon, experience eutectic transformation at 2097 °F (1147 °C). The eutectic concentration of carbon is 4.3%.

In practice only hypoeutectic alloys are used. These alloys (carbon content from 2.06% to 4.3%) are called *cast irons* When temperature of an alloy from this range reaches 2097 °F (1147 °C), it contains primary austenite crystals and some amount of the liquid phase. The latter decomposes by eutectic mechanism to a fine mixture of austenite and cementite, called **ledeburite**.

All iron-carbon alloys (steels and cast irons) experience eutectoid transformation at 1333 °F (723°C). The eutectoid concentration of carbon is 0.83%.

When the temperature of an alloy reaches 1333 °F (733°C), austenite transforms to pearlite (fine ferrite-cementite structure, forming as a result of decomposition of austenite at slow cooling conditions)

Hypoeutectoid steels (carbon content from 0 to 0.83%) consist of primary (proeutectoid) ferrite (according to the curve A3) and pearlite.

Eutectoid steel (carbon content 0.83%) entirely consists of pearlite.

Hypereutectoid steels (carbon content from 0.83 to 2.06%) consist of primary (proeutectoid)cementite (according to the curve A_{CM}) and pearlite.

Cast irons (carbon content from 2.06% to 4.3%) consist of proeutectoid cementite C_2 ejected from austenite according to the curve A_{CM} , pearlite and transformed ledeburite (ledeburite in which austenite transformed to pearlite).

Time-Temperature-Transformation (TTT) diagram

Time-Temperature-Transformation (TTT) diagram or S-curve refers to only one steel of a particular composition at a time, which is applicable to all carbon steels. This diagram is also called as Ccurve isothermal (decomposition of austenite) diagram and Bain's curve. The effect of timetemperature on the microstructure changes of a steel can be shown by TTT diagram. These diagrams are extensively used in the assessment of the decomposition of austenite in heat-treatable steels. We have seen that the iron-carbon phase diagram does not show time as a variable and hence the effects of different cooling rates on the structures of steels are not revealed. Moreover, equilibrium conditions are not maintained in heat treatment. Although, the iron-carbon equilibrium diagram reveals on the phases and corresponding microstructures under equilibrium conditions but several useful properties of the steels can be obtained under non equilibrium conditions, e.g. variable rates of cooling as produced during quenching and better transformation of austenite into pearlite and martensite. The steels with different percentage of carbon, give different TTT diagrams. The diagram shows the rate at which austenite is transformed, at a given temperature, from all austenite to coarse pearlite; to fine pearlite, to upper bainite to lower bainite, martensite plus residual austenite, depending upon the carbon content. The transformation of the austenite takes the liquid place at а constant temperature, i.e., bath temperature in which the component is cooled for the required time. Since the changes takes place at a constant temperature, it is known as Isothermal Transformation. One can determine the amount of microstructural changes by the microscopic examination of the sample.

In order to construct a TTT diagram, a number of small specimens of steel are heated to a temperature at which austenite are stable and then rapidly cooled to temperatures, e.g. 650° C, 600° C, 250° C, etc. The specimens are held isothermally at these temperatures for different periods of time until the austenite is completely decomposed. Experimentally, it is observed that at the start of the cooling shown by the points *B*1, *B*2, *B*3 and *B*4, there is no decomposition of austenite. This time period is referred as *incubation period*. After this, austenite starts to decompose into the ferrite-cementite mixtures. After the lapse of a certain period of time, the process of decomposition of austenite is stopped

The isothermal transformation of the austenite in steel containing 0.8% carbon is shown in Figure For the sake of convenience, the time scale in such diagrams is logarithmic, since the decomposition of austenite takes from a fraction of a second to hours. One obtains two different curves by plotting the starting and end points of the decomposition of austenite.



. The transformation of austenite takes place in the area between these two curves. We can see from Figure above, the important products of austenite decomposition. Above 723° C, for the steel represented, austenite is the only stable phase. Below this temperature, the stability first rapidly decreases with temperature in cooling rate. Experimentally it is found to be least stable at about 500-550°C and below this temperature range starts to increase. A diffusionless transformation of austenite into a hardened steel structure called martensite is observed at temperatures between 250 and 50°C. The temperatures, at which the martensite starts and finishes are marked by *Ms* and *Mf*

. *Ms* stands for the temperature at which the formation of martensite begins and *Mf* stands for the temperature at which the formation of martensite ends. We may note that this is a super-saturated solid solution of carbon in -iron.

A ferrite-cementite mixture with coarse pearlite is obtained at temperatures near *Ar*1 (700°C). The product of austenite decomposition (a mixture of ferrite-cementite), lamellar in structure, and finer pearlite is obtained between 700°C and 550°C, which is known as *sorbite*. An evenly dispersed mixture of ferritecementite (troostite) is obtained, when the temperature is lowered too between 550°C to 500°C. A needlelike structure known as accicular troostite (or bainite) is obtained when the temperature is lowered from 500°C to 300°C. We may note that Bainite is harder, stronger and tougher than pearlite. Bainite steel is more ductile than pearlitic steel for same level of hardness. We note that with fall in temperature, the ferritecementite mixture will be harder due to the increased rate of dispersion. The TTT diagram is changed by alloying other elements added to carbon-steel. The effect of Cr, Ni, molybdenum is to shift the TTT diagram to the right, i.e. more time is required, at any particular temperature, for transformation from pearlite to bainite. Normally, the TTT diagrams are derived from data obtained for transformation at constant temperature.



If the continuous cooling is considered (as stated above); the TTT diagram is shifted to the right and downward. Such a diagram is referred to as a *continuous cooling transformation curve*.

Let the specimen of steel is cooled continuously below the lower critical point, i.e., $723^{\circ}C$ at various cooling rates. Let the inclined curves V1, V2, V3, . . . on temperature-time graph represent these cooling processes. The slowest cooling rate is represented by the curve V1. Slightly higher cooling rate is represented by the curve V 2. Still more rapid cooling rates are represented by the V3, V4 and V5. We may note that these curves are straight lines.

 V_2 and V_3 and others between them have more slope also intersect the line *Ms*. Obviously, the martensite is formed at the end of transformation. However, it has reported that martensite is never formed at such cooling rates. Perhaps, this may be due to the fact that the curves V_2 and V_3 and others intersect both the transformation curves. Thus the complete transformation of the austenite takes place at points b_2 and b_3 respectively. No austenite is left in the steel beyond these points. This means that nothing is to be transformed into martensite

Applications of TTT diagrams

- \checkmark It provides information for microstructures formed during cooling of austenite
- \checkmark It is used in heat treatment of steel
- \checkmark It shows what structures can be expected after various rates of cooling
- ✓ It shows how time of cooling effects microstructure & properties of steel.

UNIT-3 HEAT TREATMENT

Heat treatment

Heat treatment refers to the heating and cooling operations required to alter the properties of metals, alloys plastic and ceramic materials. Changes in material's properties result from changes made in microstructure of the material. Heat treatment can be applied to ingots, castings, semi-finished products, welded joints and various elements of machines and instruments. During heat-treatment of a metal piece, when it is heated to a definite temperature followed by cooling at a suitable rate, there occur changes in the micro-constituents of the metal. These changes in the microconstituents of the metal may be in their nature, form, size and distribution in the metal piece.

The application or purpose of heat treatment is to achieve any one or more objectives cited as follows:

- > To remove strain hardening of a cold worked metal and to improve its ductility.
- To relieve internal stresses set up during cold-working, casting, welding and hot-working treatments
- > To remove gases from castings, to soften a metal to improve its machinability, and to increase the resistance to wear, heat and corrosion.
- To improve the cutting ability, i.e., hardness of a steel tool, to improve grain structure after hot working a metal and to remove effects of previously performed heat-treatment operations.
- > To improve magnetization property, especially of steels, for producing permanent magnets
- > To refine grain structure after hot working a metal.
- > To soften and toughen a high carbon steel piece.
- To produce a single phase alloy in stainless steel, and to produce a hard, wear resistant case on a tough core of a steel part.
- > To harden non-ferrous metals and alloys, especially aluminum alloys and to produce a single phase alloy in stainless steel.
- To produce a hard, wear resistant case on a tough core of a steel part and to toughen a hardened steel piece at the cost of its hardness

The principle of the theory of heat treatment is that when an alloy has been heated above a certain temperature, it undergoes a structural adjustment or stabilization when cooled to room temperature. The cooling rate plays an important role in this operation.

The structural modification is mainly based on the cooling rate. The heat treatments are normally applied to hypo-eutectoid carbon steels. For steel the eutectoid reaction in the iron-carbon diagram involves the transformation and decomposition of austenite into pearlite, cementite or martensite.

Processes of Heat treatment

The principal kinds of heat treatment are:

(i) Annealing (ii) Normalising (iii) Hardening (iv) Tempering (v) Case hardening (vi) Surface hardening .Each of them has a number of varieties.

This is a kind of heat treatment after which a metal or alloy acquires a structure close to the equilibrium one. A material is exposed to an elevated temperature for an extended time period and then slowly cooled. Normally, annealing is carried out to (i) relative stresses (ii) increase softness, ductility and toughness; and/or (iii) produce a specific microstructure. The temperature of heating in annealing depends on the composition of an alloy and the particular kind of the process; the rate of cooling from the annealing temperature is usually not high (within 30-200°C/h). There are variety of annealing heat treatments possible. These are characterized by the changes that are induced, which many times are microstructural and are responsible for the alteration of the mechanical properties.

An annealing process consists of three stages: (i) heating to the desired temperature, (ii) holding or 'soaking' at that temperature, and (iii) cooling, usually to room temperature. In these annealing procedures, time is an important parameter. There exist temperature gradients between the outside and interior portions of the piece during heating and cooling. The magnitudes of temperature gradients depend on the size and geometry of the piece. If the rate of temperature, change is too great, temperature gradients and internal stresses may be induced that may lead to wraping or even cracking. Moreover, the actual annealing time must be long enough to allow for any necessary transformation reactions. An annealing temperature is also an important consideration. Since diffusional processes are normally involved and therefore annealing may be accelerated by increasing the temperature. The various types of annealing operations are: (i) Full annealing, (ii) Process annealing, (iii) Spheroidise annealing and (iv) Diffusion annealing

Full-annealing

This operation removes all structural imperfections by complete recrystallization. This operation is often utilized in low and medium carbon steels that will be machined or will experience extensive plastic deformation during a forming operation. This operation consists of:

(i) Heating the hypoeutectoid steel to about 50-70°C above the upper critical temperature (for hypoeutectoid steels) and by the same temperature above the lower critical temperature for hypereutectoid steels until equilibrium is achieved. This ensures that the metal is heated thoroughly and phase transformation has taken place throughout the whole volume.

(ii) The alloy is then furnace cooled; i.e., the heat-treating furnace is turned off and both furnace and steel cool to room temperature at the same rate, which takes several hours. The micro-structural product of full anneal is coarse pearlite (in addition to any proeutectoid phase) that is relatively soft and ductile. The full-annealing cooling procedure is time consuming; however, a microstructure having small grains and a uniform grain structure results

Process annealing

This is a heat treatment that is used to negotiate the effects of cold work, i.e. to soften and increase the ductility of a previously strain hardened metal. Process annealing is commonly utilized during fabrication procedures that require extensive plastic deformation, to allow a continuation of deformation without fracture or excessive energy consumption. It is the recrystallization of cold work, i.e., recovery and recrystallization processes are allowed to occur. Ordinarily a fine grained microstructure is desired, and therefore, the heat treatment is terminated before appreciable grain growth has occurred. In other words, the exact temperature depends upon the extent of cold working, grain size, composition and time held at heat. Surface oxidation or scaling may be prevented or



minimized by annealing at relatively low temperature (but above the recrystallization temperature) or in a non oxidizing atmosphere. Process annealing is very useful in mild steels and low carbon steels

Spheroidise annealing

In this the work pieces are first heated to about their re-crystallization temperature and then these

are cooled slowly. Like process annealing this stress-relief may also be performed on any metal.

the piece is heated to the recommended temperature, held there long enough to attain a uniform temperature, and finally cooled to room temperature in air

Diffusion annealing

In this the ferrite iron is heated and produces homogeneity by rapid diffusion the steel is heated to a temperature considerably over the A_3 point, i.e. above the critical range for a time period. Then rapid cooling is performed to a temperature below the lower critical temperature. Now, immediately reheating is done to a point just over the upper critical temperature for a time period. Finally, slow cooling allowed to room temperature.

Normalizing

This is used as a finishing treatment for carbon steels giving higher strength than annealing. There is no serious loss of ductility too. Heating and soaking in this process is same as in the full annealing but part is allowed to cool in air so that cooling rate is much faster. An annealing heat treatment called normalizing is used to refine the grains (i.e., to decrease the average grain size) and produce a more uniform and desirable size distribution. Fine grained pearlite steels are tougher than coarse-grained ones. The fine grain structure increases the yield and ultimate strengths, hardness and impact strength. Normalizing is accomplished by heating at approximately 55 to 85°C above the upper critical temperature, which is, of course, dependent on composition.

Normalizing often applied to castings and forgings is stress relieving process. To some extent, it increases strength of medium carbon steel. It improves machinability, when applied to low carbon steel. Alloy steels in which the austenite a procedure termed austenizing is very stable can be normalized to produce hard

martensitic structure. Cooling in air produces high rate of cooling which can decompose the austenitic

structures in such steels and martensite is produced. This increases the hardness to great extent •

Hardening

It is a kind of heat treatment which forms a non-equilibrium structure in an alloy. Non-equilibrium structures can be produced by heat treatment only in cases when the alloy being treated undergoes certain transformations in solid solutions, decomposition of a high-temperature solid solution by eutectoid reaction, etc. To form a non-equilibrium structure in an alloy, it is heated above the temperature of the phase transformation in the solid state and then cooled (chilled) quickly; fast cooling is essential for preventing the equilibrium transformation during cooling. Structural and tool-making alloys are hardened in order to increase their strength. Alloys undergoing a eutectoid transformation under the equilibrium conditions can be strengthened by hardening quite substantially. Their strength increases either due to the martensitic phase change or due to a reduction of the temperature of eutectoid reaction; in both cases there forms a fine grained eutectoid mixture. If the hardening procedure has resulted in that the metal at room temperature (20-25°C) has the fixed state of high temperature solid solution, the strengthening effect immediately after hardening is insignificant; it will be pronounced mainly on a repeated low-temperature heating or after holding at 20-25°C.

In alloys possessing special properties, hardening makes it possible to change the structuresensitive physical and chemical properties, for instance increases the electric resistance, coercive force or corrosion resistance.

Hardening capacity and hardenability are important characteristics of steels. Hardening capacity is defined as the surface hardness of a hardened article and depends mainly on the carbon content of the steel. We may note that the influence of alloy composition on the ability of a steel alloy to transform to martensite for a particular quenching treatment is related to parameter hardenability Tempering

Tempering and ageing are the kinds of heat treatment which are applied to hardened alloys; they involve certain phase transformations which make the metal structure approach the equilibrium.

The term 'tempering' is usually applied to steels and other alloys undergoing a polymorphic transformation in hardening (two-phase aluminium, bronzes, some titanium alloys) and the term 'ageing' to alloys which undergo no polymorphic transformations in hardening (aluminium alloys, austenitic steels, nickel alloys, etc.). Tempering releases the stresses and reduces the brittleness.

Tempering causes the transformation of the martensite into less brittle structure, i.e., a fine pearlistic structure termed as troostite. Troostitie is much tougher, although somewhat softer than martensite. Most c.s. cutting tools have this type of structure. Once the tempering temperature has been reached, it is normal to quench the steel. All structures resulting from tempering are termed tempered martensite.

Surface hardening in steels

Surface hardening of articles, like most methods of surface strengthening (chemical heat treatment, strain hardening, knurling, etc.) offers an additional advantage that large compressive stresses appear in the surface layers of hardened articles.

A number of components require only a hard surface to resist wear and tear and a tough core to resist shock loads instead of complete component being made hard. These two properties do not exist in one steel. For toughness, one finds that the core should not exceed 0.3% carbon content, also sometimes it is not desirable to harden complete component. For example, it is undesirable to have case harden screw threads. The threads would be brittle and distortion during hardening would need expensive thread grinding operations to correct the distortions. Surface hardening is classified into two types:

Selective heating of the surface layers: In this case, the time available to change the microstructure of steel is short. Obviously, hardened and tempered steels respond well but annealed steels do not. Moreover, composition of the steel must be such that the quenching will produce martensite and so harden the steel. Clearly, carbon content to be 0.4% or more.

Flame hardening can be one of the method of selective heating. The surface of a component is heated to 850°C with an oxyacetylene flame and quenched with cold water immediately. Flame heating transforms the structure of the surface layers to austenite and quenching changes the austenite surface layers to martensite resulting into a hard surface. Depth of hardening depends on the heat supplied per unit time. Flame hardening is mostly used in case of carbon and alloy steels having carbon content 0.4% to 0.6, e.g. shafts, gears, cylinder linears, crank shafts bearing journals, etc.



Depth of harden zone is controlled by adjusting the flame intensity, heating time and speed of travel.Overheating may results in cracks after quenching Used for shaft, teeth of gears, mill rolls, spindles etc. making

Advantages

Economic

- Thinner cases can be obtained by increasing speed of heating
- Large machine parts can be harden easily
- Portable equipments
- Precise control on case properties
- Can be done even after finishing

Another method of selective heating is induction hardening. Steel components are placed within a coil through which a high frequency is allowed to pass. Surface layers of the component are heated between 850-1000°C. Subsequently cooling transforms the austenite to martensite. High frequency current are generated using:

- Motor generators with frequency of 1000 to 10000 cycles/second and a capacity of 1kW.
- Motor generators with frequency of 10000 to 100000 cycles/second and a capacity of 1kw.

• Spark gap oscillator with frequency of 100000 to 400000 cycles/second and capacity of 25kW.

- Vacuum-tube oscillator at 500000 cycles/second and capacity of 20 to 50kW
- The part is places in induction coils made of copper tubes and is water cooled

When high frequency current is passed in induction coil it set up a magnetic field which results in heating of surface producing a SKIN EFFECT



The heating coil is often made of tube perforated with fine spray holes so that it can be used both for heating and quenching. We may note that the depth of heating produced by this method is related to the frequency of the alternating current. Higher the frequency of a.c. current less will be the hardened depth, but there will be more rapid rise in temperature.

Advantages

- Time is reduced
- Done foe external and internal surfaces
- No distortion
- High hardness can be obtained
- Shape can be controlled closely
- Depth of hardening can be controlled.

Used for Crankshaft, cams, piston rods, Spurgear etc. making

Case Hardening: In this method C and/or N2 are introduced in the surface layer. In *carburizing* the part is surrounded by material or atmosphere rich in carbon and on heating this carbon is first released and then absorbed in steel. More recently case carburizing is more effectively performed by heating steel part in the atmosphere of natural gas, coke even gas, butane or propane or the volatized form of liquid hydrocarbons like terpenes and benzene or the volatilized form of liquid hydrocarbons like terpenes. Volatilized form of alcohol and glycols or ketones have also been used. In these cases the thickness of hardened layer is proportional to root of the time of treatment in hour. The depth of hardness depends upon the number of times the process is repeated. The component is finally raised to a red heat and quenched in water. However, one will have to take the precaution that the part to be hardened should be covered with the compound.

Carburizing

This is another method of surface hardening. The composition of surface layers are changed. This process is usually carried out on a steel containing less than 0.2% carbon. Carburizing is usually employed for treating certain types of machine elements which have to have a wear-resistance working surface and tough core, gear wheels, shafts, pins, camshafts, cams, worms, etc. The initial medium for carburizing (carbon saturation) is usually called a *carburizer*. Two methods of

carburizing are in use: in a solid and in a gaseous carburizer. In both cases, however, the carburizing process passes through a gaseous phase.

Nitriding:

This is the process of diffusion saturation of steel surface with nitrogen. The component is heated in a mixture of ammonia and hydrogen so that nitrogen diffuses into the surface layers and hard nitride compounds are formed. The process is employed for increasing the wear resistance and endurance limit of machine elements (crankshafts, cylinder sleeves, worm gears, shafts, etc.). Prior to nitriding, steel articles are subjected to hardening and high temperature tempering (improving heat treatment) and finishing. After nitriding, they are ground and polished. In a nitriding process, the component is heated in a mixture of ammonia and hard nitride compounds are formed. Common nitriding is carried out at a temperature of 500-600°C in a muffle or container through which dissociating ammonia is being passed. This process is used with those alloys of steel which contain elements that form stable nitrides, e.g. chromium, molybdenum, tungsten, vanadium, aluminium, etc.

Cyaniding

Similar to carbonitriding, cyaniding also involves the diffusion of carbon and nitrogen into the surface of steel. It is also called liquid carbonitriding. The components are heated to the temperature of about $800 - 900^{\circ}$ C in a molten cyanide bath consisting of sodium cyanide, sodium carbonate and sodium chloride. After allowing the components in the bath for about 15 - 20 minutes, they are quenched in oil or water. Cyaniding is normally used for low-carbon steels, and case depths are usually less than 0.25 mm. It produces hard and wear resistance surface on the steels. Because of shorter time cycles, the process is widely used for the machine components subjected to moderate wear and service loads. The process is particularly suitable for screws, small gears, nuts and bolts.

Hardenability

Hardenability is one of the most important properties of a steel because it describes the ease with which a given steel can be quenched to form martensite or the depth to which martensite is formed on a given quench. The ability of steel to form martensite on quenching is referred to as the hardenability. Hardenability is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature. Steels with high hardenability form martensite even on slow cooling.

High hardenability in a steel means that the steel forms martensite not only at surface but to a large degree throughout the interior. To achieve this, the steel must be quenched at a rate sufficiently rapid to avoid the decomposition of austenite during cooling to such products as ferrite, pearlite and bainite. For the optimum development of strength, steel must be fully converted to martensite. Hardenability of a steel should not be confused with the hardness of a steel.

HARDNESS ≠*HARDENABILTY*

DETERMINATION OF HARDENABILITY

There are two methods to determine hardenability of steels

- Grossman's Method
- Jominy end quench method

In Grossman's method, we use round iron bars of different diameters. These bars are quenched in a suitable quenchant. Further, we determine the critical diameter (d_c) which is the maximum diameter of the rod which produced 50% martensite on quenching. The ideal diameter (D_I) is then determined from the curve. This type of experiment requires multiple austenitization and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.

JOMINY END QUENCH METHOD

Grossmans method requires multiple austenitization and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material. An alternative approach is to develop a more convenient standard test method that can be used for relative comparison of hardenability. The Jominy end-quench test is one such approach. The jominy end-quench test is specified in ASTM standard A255 and is a widely used method for quantifying hardenability. Its more reliable as more data are accumulated. Moreover, Jominy data have been collected on a large enough scale to offer a high degree of statistical certainty for many steels. These data have been correlated with measurements and/or calculations of dc. By using these correlations, a single Jominy test can be used to estimate dc and DI for a given steel (and austenite grain size)

The most commonly used method for determining hardenability is the end quench test developed by Jomini and Boegehold. The details of the test are covered in IS : 3848 – 1981 and ASTM A 255 The Jominy End Quench Test measures Hardenability of steels. Information gained from this test is necessary in selecting the proper combination of alloy steel and heat treatment to minimize thermal stresses and distortion when manufacturing components of various sizes



The hardenability of a steel is measured by a Jominy test: A round metal bar of standard size is transformed to 100% austenite through heat treatment, and is then quenched on one end with room-temperature water. The cooling rate will be highest at the end being quenched, and will decrease as distance from the end increases. The hardenability is then found by measuring the hardness along the bar: the farther away from the quenched end that the hardness extends, the higher the hardenability

Cooling rate and Jominy distance (distance from the quenched end) do not change with alloying elements as the rate of heat transfer is nearly independent of composition

STEPS IN JOMINY END QUENCH TEST

- First, a sample specimen rod either 100mm in length and 25mm in diameter, or alternatively, 102mm by 25.4mm is obtained.
- Second, the steel sample is normalized to eliminate differences in microstructure due to previous forging, and then it is austenitised. This is usually at a temperature of 800 to 900°C.
- Next, the specimen is rapidly transferred to the test machine, where it is held vertically and
- Sprayed with a controlled flow of water onto one end of the sample.
- This cools the specimen from one end, simulating the effect of quenching a larger steel component in water. Because the cooling rate decreases as one moves further from the quenched end, you can measure the effects of a wide range of cooling rates from vary rapid at the quenched end to air cooled at the far end
- After end quenching, longitudinal Flat Surfaces are ground on opposite sides of the test piece as per dimensions. The specimen is ground flat along its length to a depth of .38mm (15 thousandths of an inch) to remove decarburized material. This grinding is very important for correct positioning of the sample in the fixture and also for accurate repeatable and reliable test results.

Heat Treatment -Defects & Remedies

1) **Overheating-** Heating for long periods at temperatures considerably exceeding the normal values.

Remedies:-

- 1. For slight overheating-apply normal annealing and normalising.
- 2. For more apply double annealing and normalising.
- 2) **Burning-** Heating for a long period at a high temperature in an oxidation atmosphere or at temperatures near the melting point.

Remedies:-

- 1. 1st stage- use homogenising followed by double annealing.
- 2. 2nd stage- use forging followed by annealing.
- 3. 3rd stage- defect cannot remedied
- 3) **Oxidation-** Thick layer of scale on the surface of the steel article. Oxidation atmosphere in the heating furnace is the caused.

Remedies:-

- 1. Heat in furnaces with reducing , neutral or protective atmospheres.
- 2. Heat in boxes with used carburising agent or cast iron chips.
- 3. Heat in molten salt bathes

4) **Decarburisation-** loss of carbon in the suface layers of the articles. This is due to the oxidising atmosphere in the heating furnace.

Remedies:-

- 1. Heat in furnaces with reducing, neutral or protective atmosphere.
- 2. Machine off the decarburised layer if the machining allowances is sufficiently large.
- 3. Heat in molten salt bath.
- 4. Heat in boxes with used carburising agent.
- 5) **Quenching** cracks- this is due to the internal stresses due to volume changes at temperature, caused by martensitic transformation.

Remedies:-

1. Avoiding sharp projections, sharp corners, and sudden transitions from thick to thin sections

- 2. Apply austempering.
- 3. Temper immidiately after quenching.
- 4. Heat to the minimum suitable temperature for hardening.
- 6) **Warping-** asymmetrical deformation of the articles in quenching. This is due to volume changes in cooling or heating, non-uniform heating, internal stresses etc.

Remedies:-

- 1. Cool slowly in the martensitic range.
- 2. Apply surface hardening.
- 3. Heat uniformly for hardening.
- 4. Quench as uniformly as possible in hardening.
- 7) **Errosion** –reduction in size of the articles or loss of metals from its surface due to chemical reactios of chlorous salts and oxidation of metals.

Remedies-

- 1. Deoxidised salt bath with borax or ferrosilicon should be used.
- 2. Properly position the article in reference to the electrodes of electrical salt bath.
- 8) **Corrosion-** pitting or groove or non-uniform scale formation type destruction of the surface of an article due to heating in flame furnace , salt bath composition and oxidation.
- ➢ Remedies −
- 1. Carefully control salt composition.
- 2. Deoxidise the bath.
- 3. Eliminate the oxidising temperature atmosphere when heating in flame hardening.
- 9) Soft spots- zones on the surface of hardened articles with lower hardness due to decarburizations and inhomogeneity of structure.
- ➢ Remedies:-
- 1. Using more effective quenching medium.
- 2. Obtaining a homogenous structure , employing annealing or normalising before hardening.
- 3. Protecting against decarburisation in heating.

UNIT-4 FERROUS METALS AND THEIR ALLOYS

FERROUS METALS & ITS ALLOYS

Engineering Materials

A materials is that out of which something may be made, Engineering materials are those materials which can be used in engineering purposes. The knowledge of materials and their properties is of great significance for a engineer so that we can easily use them in different areas as required. The engineering materials are mainly classified as :

1. Metals and their alloys, such as iron, steel, copper, aluminium, etc.

2. Non-metals, such as glass, rubber, plastic, etc

The metals may be further classified as :(a) Ferrous metals, and (b) Non-ferrous metals.

Ferrous metals are those which have the iron as their main constituent, such as cast iron, wrought iron and steel.

Non-ferrous metals are those which have a metal other than iron as their main constituent, such as copper, aluminium, brass, tin, zinc, etc

Ferrous metals are those which have iron as their main constituent. The ferrous metals commonly used in engineering practice are cast iron, wrought iron, steels and alloy steels.

The principal raw material for all ferrous metals is pig iron which is obtained by smelting iron ore with coke and limestone, in the blast furnace



CAST IRON:

The cast iron is obtained by re-melting pig iron with coke and limestone in a furnace known as cupola. It is primarily an alloy of iron and carbon. The carbon contents in varies from 1.7 per cent to 4.5 per cent. It also contains small amounts of silicon, manganese, phosphorous and sulphur. Cast iron is a brittle material, therefore, it cannot be used in those parts of machines which are subjected to shocks. Cast iron has low cost, good casting characteristics, high compressive strength, wear

resistance and excellent machinability. The carbon in a cast iron is present in following two forms: 1. Free carbon or graphite, and 2. Combined carbon or cementite

TYPES OF CAST IRON

GREY CAST IRON.

It is an ordinary commercial iron having the compositions: Carbon = 3 to 3.5%; Silicon = 1 to 2.75\%; Manganese = 0.40 to 1.0\%; Phosphorous = 0.15 to 1%; Sulphur = 0.02 to 0.15\%; and the remaining is iron.

The grey colour is due to carbon is present in the form of free graphite. It has a low tensile strength, high compressive strength, no ductility & easily machined. A very good property of grey cast iron is that it acts as a lubricant. Due to this reason, it is used where sliding action is desired. It is used for machine tool bodies, automotive cylinder blocks, heads, housings, fly-wheels, pipes and pipe fittings.

WHITE CAST IRON.

The white cast iron has approximate compositions :Carbon = 1.75 to 2.3%;Silicon = 0.85 to 1.2%; Manganese = less than 0.4%; Phosphorus = less than 0.2% Sulphur = less than 0.12%, and remaining is iron.The white colour is due to no graphite and whole of the carbon is in the form of carbide (known as cementite) which is the hardest constituent of iron.

The white cast iron has a high tensile strength and a low compressive strength. Since it is hard, therefore, it cannot be machined with ordinary cutting tools but requires grinding as shaping process. The white cast iron may be produced by casting This used where a hard, wear resisting surface is desired for such products as for car wheels, rolls for crushing grains and jaw crusher plates

CHILLED CAST IRON

It is a white cast iron produced by quick cooling of molten iron. The quick cooling is generally called chilling and the cast iron so produced is called chilled cast iron.

Chills are used on any faces of a casting which are required to be hard to withstand wear and friction.

MOTTLED CAST IRON

It is a product in between grey and white cast iron in composition, colour and general properties. It is obtained in castings where certain wearing surfaces have been chilled.

MALLEABLE CAST IRON

The malleable iron is a cast iron-carbon alloy which solidifies in the cast condition in a graphite free structure, *i.e.* total carbon content is present in its combined form as cementite (Fe3C).

It is ductile and may be bent without breaking or fracturing the section. The tensile strength of the malleable cast iron is usually higher than that of grey cast iron

Used in brake supports, parts of agricultural machinery, pipe fittings, door hinges

ALLOY CAST IRON

It contain small percentages of other constituents likesilicon, manganese, sulphur and phosphorus. The alloy cast iron is produced by adding alloying elements like nickel, chromium, molybdenum, copper and manganese in sufficient quantities. It result in improvement of properties like increased strength, high wear resistance, corrosion resistance or heat resistance. The alloy cast irons are extensively used for automobile parts like cylinders, pistons, piston rings, crankshafts, camshafts, sprockets, wheels, pulleys, brake drums and shoes, parts of crushing and grinding machinery etc

STEEL

It is an alloy of iron and carbon, with carbon content up to a maximum of 1.5%.

- The carbon occurs in the form of iron carbide, because of its ability to increase the hardness and strength of the steel.
- Other elements *e.g.* silicon, sulphur, phosphorus and manganese are also present to greater or lesser amount to impart certain desired properties to it.
- A carbon steel is defined as a steel which has its properties mainly due to its carbon content and does not contain more than 0.5% of silicon and 1.5% of manganese

Types of Steel

- 1. Dead mild steel up to 0.15% carbon.
- 2. Low carbon or mild steel -0.15% to 0.45% carbon
- 3. Medium carbon steel 0.45% to 0.8% carbon
- 4. High carbon steel -0.8% to 1.5% carbon

ALLOY STEEL

A steel to which elements other than carbon are added in sufficient amount to produce an improvement in properties. It is done to increase wearing resistance, corrosion resistance and to improve electrical and magnetic properties, which cannot be obtained in plain carbon steels

The chief alloying elements used in steel are nickel, chromium, molybdenum, cobalt, vanadium, manganese, silicon and tungsten

EFFECT OF IMPURITIES ON CAST IRON

The effect of impurities on the cast iron is as follows:

SILICON. It may be present in cast iron upto 4%. It provides the formation of free graphite which makes the iron soft and easily machinable. It also produces sound castings free from blow-holes, because of its high affinity for oxygen.

SULPHUR. It makes the cast iron hard and brittle. Since too much sulphur gives unsound casting, therefore, it should be kept well below 0.1% for most foundry purposes.

MANGANESE. It makes the cast iron white and hard. It is often kept below 0.75%. It helps to exert a controlling influence over the harmful effect of sulphur.

PHOSPHORUS. It aids fusibility and fluidity in cast iron, but induces brittleness. It is rarely allowed to exceed 1%. Phosphoric irons are useful for casting of intricate design and for many light engineering castings when cheapness is essential

EFFECT OF IMPURITIES ON STEEL

1. *Silicon*. The amount of silicon usually ranges from 0.05 to 0.30%. Silicon is added in low carbon steels to prevent them from becoming porous. It removes the gases and oxides, prevent blow holes and thereby makes the steel tougher and harder.

2. *Sulphur.* It occurs in steel either as iron sulphide or manganese sulphide. Iron sulphide because of its low melting point produces red shortness, whereas manganese sulphide does not affect so much. Therefore, manganese sulphide is less objectionable in steel than iron sulphide.

3. *Manganese*. It serves as a valuable deoxidising and purifying agent in steel. Manganese also combines with sulphur and thereby decreases the harmful effect of this element remaining in the steel. When used in ordinary low carbon steels, manganese makes the metal ductile and of good bending qualities. In high speed steels, it is used to toughen the metal and to increase its critical temperature.

4. *Phosphorus.* It makes the steel brittle. It also produces cold shortness in steel. In low carbon steels, it raises the yield point and improves the resistance to atmospheric corrosion. The sum of carbon and phosphorus usually does not exceed 0.25%.

EFFECT OF ALLOYING ELEMENTS ON ALLOY STEEL NICKEL

It increases the strength and toughness of the steel. These steels contain 2 to 5% nickel and from 0.1 to 0.5% carbon An alloy containing 25% nickel possesses maximum toughness and offers the greatest resistance to rusting, corrosion and burning at high temperature.

A nickel steel alloy containing 36% of nickel is known as *invar*. It has nearly zero coefficient of expansion. So it is in great demand for measuring instruments and standards of lengths for everyday use

CHROMIUM

It is used in steels as an alloying element to combine hardness with high strength and high elastic limit. It also imparts corrosion-resisting properties to steel. The most common chrome steels

contains from 0.5 to 2% chromium and 0.1 to 1.5% carbon. The chrome steel is used for balls, rollers and races for bearings.

A *nickel chrome steel* containing 3.25% nickel, 1.5% chromium and 0.25% carbon is much used for armour plates. Chrome nickel steel is extensively used for motor car crankshafts, axles and gears requiring great strength and hardness.

TUNGSTEN

It prohibits grain growth, increases the depth of hardening of quenched steel and confers the property of remaining hard even when heated to red colour.

Steel containing 3 to 18% tungsten and 0.2 to 1.5% carbon is used for cutting tools. The principal uses of tungsten steels are for cutting tools, dies, valves, taps and permanent magnets. **VANADIUM**

It aids in obtaining a fine grain structure in tool steel. It increase tensile strength and elastic limit in low and medium carbon steels without a loss of ductility.

The *chrome-vanadium steel* containing about 0.5 to 1.5% chromium, 0.15 to 0.3% vanadium and 0.13 to 1.1% carbon have extremely good tensile strength, elastic limit, endurance limit and ductility. These steels are frequently used for parts such as springs, shafts, gears, pins and many drop forged parts

MANGANESE

It improves the strength of the steel in both the hot rolled and heat treated condition. The manganese alloy steels containing over 1.5% manganese with a carbon range of 0.40 to 0.55% are used extensively in gears, axles, shafts and other parts The principal uses of manganese steel is in machinery parts subjected to severe wear. These steels are all cast and ground to finish

SILICON

The silicon steels behave like nickel steels. These steels have a high elastic limit as compared to ordinary carbon steel. Silicon steels containing from 1 to 2% silicon and 0.1 to 0.4% carbon and other alloying elements are used for electrical machinery, valves in I.C. engines, springs and corrosion resisting materials.

MOLYBDENUM

A very small quantity (0.15 to 0.30%) of molybdenum is generally used with chromium and manganese (0.5 to 0.8%) to make molybdenum steel. These steels possess extra tensile strength and are used for air-plane fuselage and automobile parts. It can replace tungsten in high speed steel.