

PHYSICAL METALLURGY

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Physical metallurgy is that branch of science which deals with the general relationship between the composition ,structure and properties of metals and alloys , as well as the changes brought about by thermal , chemical and mechanical treatment.

The aim of physical metallurgy as a science is to establish the physical laws governing the structure of an alloy and its properties and to find the best possible composition, manufacturing techniques and treatment of the alloy to obtain the required physical and mechanical properties.

The production of a summary description of nature in the form of scientific laws is a fundamental aim of science.

Crystal structure of metals:

All metals and their alloys are crystalline solids. They differ from amorphous solids, in which the atoms are arranged chaotically, in that crystalline solids have a definite and orderly internal structure repeated in 3-D.

Crystallography:

The scientific field concerned with the study of crystal structure is termed as crystallography

Crystal: A crystal is a periodic array of atoms in 3 dimensional spaces.

The crystal structure can be described with respect to a net of 3-D net of straight lines, called the lattice

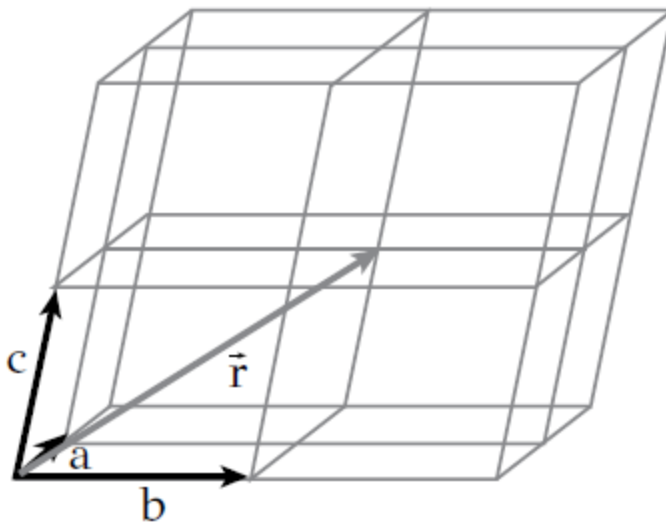


Figure:

The lattice divides space into cells defined by the unit vectors a , b , c . The cells are in contact on all faces and fill spaces entirely. The cell is then called the unit cell.

Atoms in crystalline material can be arranged in fourteen possible lattices, called Bravais lattices.

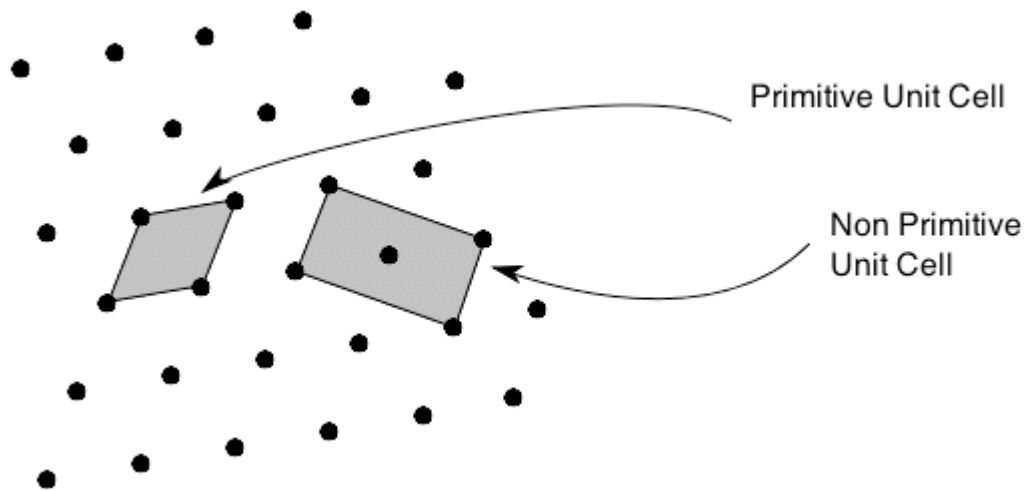
The space lattice of a crystal is described by means of a three dimensional co-ordinate system in which the co-ordinate axes coincide with any three edges of the crystal that intersect at one point and do not lie in a single plane

Seven different co ordinate systems of reference axes are employed to describe crystal structure

Crystal System	Axes and angles	Examples
Triclinic	$a \neq b \neq c$ $\hat{\alpha} \neq \hat{\beta} \neq \hat{\gamma} \neq 90^\circ$	K_2CrO_7
Monoclinic	$a \neq b \neq c$ $\hat{\alpha} = \hat{\gamma} = 90^\circ \neq \hat{\beta}$	$\beta - S$ $CaSO_4 \cdot 2H_2O$ (Plaster)
Orthorhombic	$a \neq b \neq c$ $\hat{\alpha} = \hat{\beta} = \hat{\gamma} = 90^\circ$	$\alpha - S$ Ga Fe_3C (Cementite)
Tetragonal	$a = b \neq c$ $\hat{\alpha} = \hat{\beta} = \hat{\gamma} = 90^\circ$	$\beta - Sn$ TiO_2
Cubic	$a = b = c$ $\hat{\alpha} = \hat{\beta} = \hat{\gamma} = 90^\circ$	Cu, Ag, Au Fe $NaCl$
Hexagonal	$a_1 = a_2 = a_3 \neq c$ $\hat{\alpha} = \hat{\beta} = 90^\circ, \gamma = 120^\circ$ Three equal coplanar axes at 120° angle. The fourth axis is perpendicular to them	Zn, Cd, Mg
Rhombohedral	$a_1 = a_2 = a_3 \neq c$ $\hat{\alpha} = \hat{\beta} = 90^\circ, \gamma = 120^\circ$ Three equal coplanar axes at 120° angle. The fourth axis is perpendicular to them	As, Sb, Bi

Primitive cell:

A primitive cell may be defined as a geometrical shape , which when repeated indefinitely in three dimension generates a space lattice and has lattice points only at its corners i.e. a primitive cell has only one effective lattice point per primitive cell.



The metal atoms act as electron donors, have one to three valence electrons. These electrons are donated to the whole crystal, since there are no other atoms, to act as electron acceptors and form other bonds, as ionic or covalent bonds. In this way the valence electrons are shared between the atoms of the crystal, forming a cloud of free electrons.

Metallic crystals consist of positive metal ions surrounded by the electron cloud.

In metallic bonding, the attraction between the array of positive metal ions and the free electron cloud balances the repulsion between the positive metal ions and is responsible for the structural stability of the crystal.

Goldschmidt and Laves described the basic principles of space filling of metals:

- (1) Atoms in a crystal structure are stacked in closed packed arrangements in order to efficiently fill space.
- (2) Atoms occupy positions in a closed packed arrangement resulting in the highest symmetry
- (3) Atoms are stacked as to have the largest number of nearest neighbors.

Atomic packing factor:

The efficiency for filling space can be described by the atomic packing factor, APF, which is the ratio of volume of the atoms belonging to the unit cell by the unit cell volume

$$APF = \frac{Z \cdot \frac{4}{3} \pi R^3}{V_c}$$

Where Z is the number of atoms per unit cell

R is the atomic radius

Atomic radii:

In metals, it is convenient to consider atom as being spherical (HARD BALL MODEL) with a radius, r equals to one half the inter-atomic distance, or the distance of closest approach between atoms:

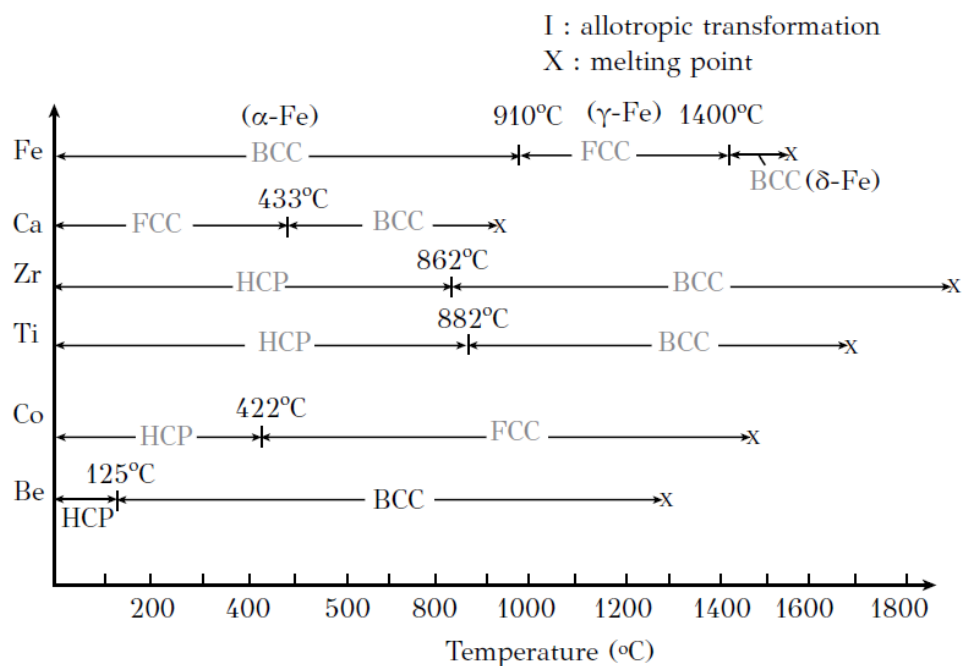
Co- ordination number Z :

It is defined as the number of nearest neighbors to a given atom in a crystal structure.

Allotropy:

Several metal change crystal structure with a change in temperature or pressure or even when subjected to a thermal or mechanical treatment.

The different crystal structures of a metal are called allotropic forms and the phenomenon is called allotropy.



The major effect of crystal structure refers to the following issues:

- (i) Alloying
- (ii) plastic deformation
- (iii) Diffusion

The most common crystal structures in common metals are

- (i) Body Centered Cubic(BCC) crystal structure
- (ii) Face centered cubic (FCC) Crystal structure
- (iii) Hexagonal close packed (HCP) crystal structure

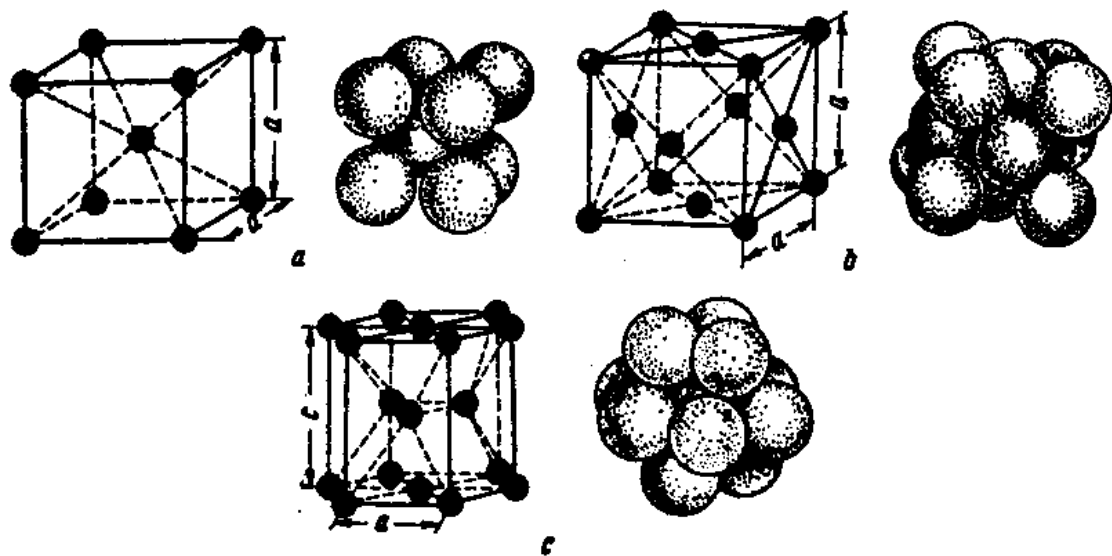


Fig. 2. Types of crystal lattices of metals and packing of atoms:
a—body-centred cubic, b—face-centred cubic, c—hexagonal

Atomic packing factor of BCC 0.68

Atomic packing factor of FCC 0.74

Atomic packing factor of HCP 0.74

Miller indices for planes:

These indices describe the orientation of crystal planes with respect to the reference axes, using the following procedure

- (a) Find the intersection of the plane with the axes
- (b) Take the inverse of these numbers
- (c) Find the smallest integers with the same ratio h,k,l
- (d) Enclose these integers in parentheses

In the hexagonal system, four indices ($hkil$) are used.

These indices correspond to the intersection of a plane with axes a_1 , a_2 , a_3 and c .

The first 3 indices are related by the expression $i=-(h+k)$

Miller indices of a direction:

The miller indices are simply the vector components of the direction resolved along each of the co-ordinate axes and reduced to smallest integers i.e. the components of the vector along the three axes are determined as multiples of the unit vector corresponding to each direction.

Imperfections in metallic materials:

The main characteristics of a crystal structure is the periodic arrangement of atoms .However in real metals , the crystal structure is not perfect and contain several types of imperfections , which disrupts the periodicity of the crystal.

Structural imperfections have a strong influence on physical and mechanical properties of metals as well as on the evolution of phase transformation in metallic materials

Imperfections can be classified into dimensions

Point defect such as vacancies and interstitials

Linear imperfections such as edge and screw

Surface imperfections, such as grain boundaries and interfaces

Three dimension defects, such as voids and inclusions

Importance of imperfections in the behavior and properties of metals and alloys:

All the above defects play a key role in mechanical behavior of metals and the development of microstructure through phase transformations.

For example, several phase transformations take place by atomic diffusion, where point defects, such as vacancies are essential. In addition; diffusion can be accelerated by the presence of dislocations or grain boundaries, which act as high diffusivity paths.

The plastic deformation of metals takes place by dislocation glide, while strengthening is accomplished by impeding dislocation motion.

The most common obstacles to dislocation glide are other dislocations, second phase particles or precipitates and grain boundaries

The 3-D imperfections, such as voids inclusions, play a key role in the ductile fracture of the metals

UNIT-2:

Alloy:

An alloy is a metallic solid or liquid formed from an intimate combination of two or more elements.

Any chemical element may be used for alloying.

But the only ones used in high concentration are metals

The intimate combination is usually brought about by dissolving the alloy elements in one another in the liquid states.

The parent metal or solvent, in the largest concentration, is melted first in a crucible and solid pieces of the alloy addition in weighed amounts are then dropped in, dissolved and stirred.

We now consider solid alloys. Suppose that, by freezing a liquid alloy or by some other means, we introduce into a pure solid metal some atoms of another element. The atoms are then in some way allowed to move about, rearrange themselves and change the crystal structure until they come to thermodynamic equilibrium among themselves. What is the structure of this alloy?

To study this question, it is convenient to think of the two atoms as

- (1) Indifferent to each other
- (2) Attracting one another
- (3) Repelling one another

In other words internal energy

- (a) Stays unchanged
- (b) Decreases
- (c) Increases

Case-1

Indifferent to each other

If the atoms are indifferent to each other they behave as if belonging to same species and they become mixed together so thoroughly that the alloy is homogeneous right down to the atomic scale.

Case-2

If unlike atoms are attracted together the nature of the resulting alloy varies widely according to the factors determining the attraction. When the structure formed from true metals is often an ordered solid solution or superlattice in which two species are arranged in some regular alternating pattern.

If the components differ electronically, the bond between them becomes partly ionic and the structure is usually termed as intermetallic compound.

Case-3 If unlike atoms are attracted less than like the two types tend to separate into distinct and different crystals joined at mutual grain boundaries. Some grains are rich in atoms of one type; others are rich in those of the other. The microscopically heterogeneous mixtures are termed as phase mixtures.

-A phase mixture however, not always an indication that unlike atoms are attracted less than like.

Solid solution:

When the liquid solution of the two metals crystallizes and if a solid of only single crystal structure forms, then a solid solution has formed.

A solid solution can exist over a range of composition

Anywhere within this range the material is fully homogeneous and its structure and properties differ only infinitesimally from those of neighboring compositions.

Solid solution can either be

-Substitutional

-Interstitial

-In substitutional solid solution the atoms share a single common array of atomic sites

-in interstitial solutions the atoms of one component are small enough to fit into the interstitial spaces between those of the other which are themselves arranged in crystalline order.

-The equilibrium distribution of atoms in substitutional solution generally depends on temperature

Various distributions are possible

-clustered (like neighbors preferred)

Ordered (unlike neighbors preferred)

The next question is what determines the solid solubility of one metal in another?

The pioneering work of Hume-Rothery and his research school has led to the following general answers

(1)Atomic size factor

(2)The electrochemical factor

(3)Relative valency factor

Solidification:

The process of solidification is the mechanism of transformation of liquid material to solid material

A liquid metal normally solidifies by crystallization

Metals can be produced in the glassy or amorphous solid state –hard but non crystalline but only with utmost difficulty.

Crystallization:

Crystallization ideally is a sharp change of state from the disordered atomic arrangement of the crystal, at a single temperature (ideal freezing point =ideal melting point)

At any temperature, the thermodynamically stable state is the one which has the lowest free energy and consequently, any other state tends to change to the other stable form.

The equilibrium temperature for transition between two states is the temperature at which they have the same free energy

The free energy of the liquid is higher than that of the crystal at low temperature, where the internal energy largely determines the free energy but it falls more steeply than that of the crystal as the temperature is increased, due to the extra entropy of the liquid and crosses that of the crystal at the melting point, the solidification can occur spontaneously.

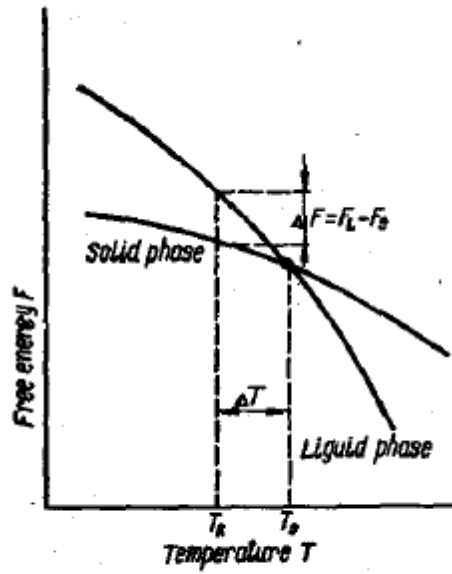


Fig. 13. Free energy vs temperature for the liquid and solid states

Variation of ΔG with T

$$\Delta G = G_{\text{solid}} - G_{\text{liquid}}$$

$$= (H_{\text{solid}} - H_{\text{liquid}}) - T(S_{\text{solid}} - S_{\text{liquid}})$$

At

$$T = T_m \text{ (melting point)}$$

$$\Delta G = 0$$

$$\Delta H = T_m (S_{\text{solid}} - S_{\text{liquid}})$$

$$\Rightarrow S_{\text{solid}} - S_{\text{liquid}} = \frac{\Delta H}{T_m}$$

$$\text{So } \Delta G = \frac{\Delta H \Delta T}{T_m}$$

Where ΔT is the amount of supercooling

Degree of supercooling:

The difference between the equilibrium temperature (T_m) of solidification and the temperature T at which solidification process proceeds under given conditions is called the degree of supercooling

$$\Delta T = T_m - T$$

At very low rate of cooling the degree of supercooling is small and the solidification process proceeds at a temperature near to the

The degree of supercooling increases with an increase in the rate of cooling and the solidification process proceeds at temperature of freezing

Mechanism of solidification:

Phenomena associated with the process of solidification are complex and varied .It is especially difficult to conceive the initial stages of the process when the first crystal or crystallization appears.

It has been established at the present time that in liquid metal as distinct from the vaporous state where atoms are chaotically arranged, a certain “order” may be observed in atomic arrangement ,notwithstanding the high mobility of the atoms ,due to the forces of interaction between them.

X-ray research has shown that at temperatures near to solidification, groups of atoms may come together in small volumes of the liquid metal; they have an atomic arrangement near to that in the solid metal. These groups of clusters may appear, exist for certain time and then fall apart to appear again at some other place .Under definite conditions, however , such.....and become centers of crystallization or nuclei.

The formation of nuclei is facilitated by unequal distribution of energy between the atoms of a substance; however there are always a certain number of atoms possessing energy of a quantity either smaller or larger than the average value.

The random and tentative deviations in the energy separate atoms or regions of atom from the average value for the given temperature are called fluctuation of energy.

Numerous investigations have proved that nuclei of a great variety of size may appear in freezing. Not all nuclei however are capable of further growth. The formation of nuclei changes the free energy of the system. The appearance of a nucleus and its growth a crystal will reduce the amount of free energy per unit volume due to the lesser free energy of a unit volume of a solid in comparison to the liquid state.

At the same time, the appearance of an interface between the nucleus and the liquid medium causes an increase in the free energy of the system. Since atoms on the interface possess higher potential energy. Therefore a certain amount of energy is expended to form this interface between the phases. This additional energy is equal to the product of the nucleus surface area and the surface tension.

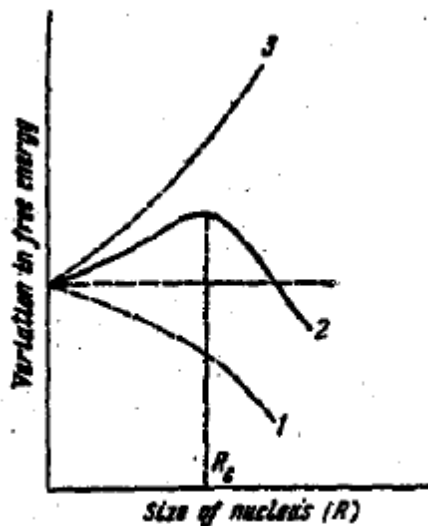


Fig. 17. Variation of the free energy of a metal upon the formation of a nucleus

It is evident from the curve 2 of the above figure that the growth of nucleus having a ratio less than R_c is impossible since this is accompanied by an increase in free energy.

In nuclei with radii less than R_c , the ratio of the surface area to the volume is large. The increase in free energy associated with the formation of the interface is greater than the reduction in free energy due to the formation of a nucleus. This increases the free energy of the system.

If a nucleus appears with a radius exceeding R_c , it will be stable and capable of further growth since an increase in its size will reduce the free energy of the system.

The minimum size of the nucleus (R_c) capable of growth at a given temperature, is called the critical size of the nucleus.

Thermodynamic calculations shows that the size of the critical nucleus depends on the degree of supercooling .

The higher the degree of supercooling i.e. the lower the temperature at which the freezing proceeds ,the smaller the size of the critical nucleus will be.

The formation of nuclei in the liquid metal or nucleation, in accordance with the above described mechanism is called the spontaneous nucleation.

Work required to form a nucleus on an existing surface is substantially less than that required for spontaneous nucleation in the liquid metal.

It must be noted; however **that** foreign inclusion will facilitate nucleation only if the surface tension between the nuclei and the inclusion is less than that at the interface between the liquid phase and solid crystals.

It has been established that the nearer the crystallographic structure of the nuclei being formed is to that of the solid particles in the liquid metal, the less the surface tension at the interfaces.

The growth of a formed nucleus ,usually called $3-D$ nucleus ,proceeds by building up new single-atom layers on its surface .These are called $2-D$ nucleus .

The rate of solidification depends on:

(1)The rate of nucleation

(2) The linear rate of crystal growth

Rate of nucleation (R_N)

No of $3-D$ nuclei appearing per unit time in a unit volume ($1/\text{mm}^2\text{sec}$)

Linear rate of crystal growth:

The rate of increase in the linear dimensions of crystal per unit time (mm per sec)

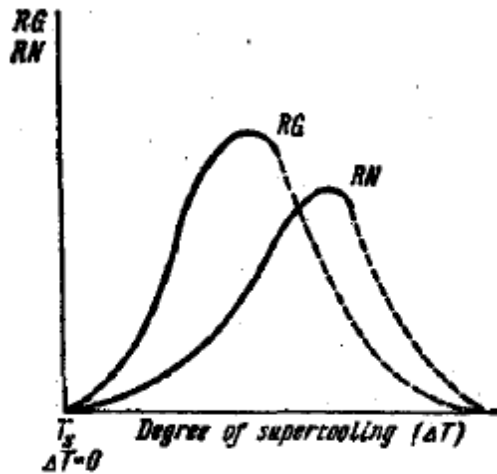


Fig. 19. Effect of the degree of supercooling on the rates of nucleation (R_N) and crystal growth (R_G)

It is evident from the above figure that at the equilibrium temperature T_m both R_G and R_N increase and reach a maximum at a definite rate of supercooling and drop again.

The maximum of R_G is always reached at less supercooling than that of R_N .

Increased rate of solidification, due to an increased degree of supercooling, may be explained by the reduction in the critical size of the nucleus and consequently, by less work required for its formation

At high degrees of supercooling, however, the mobility of the atoms are reduced by the increase in viscosity of the liquid phase. This impedes nucleation and reduces R_G and R_N curves.

The larger the number of nuclei and slower their growth, the smaller the crystals will be that grow out of each nucleus (the smaller the metal grains)

Formula

Since R_N increases faster than R_G for higher degrees of supercooling, the higher the degree of supercooling the smaller the grain will be

As a very high degree of supercooling cannot be achieved in liquid metal, smaller grain size is obtained in actual practice, at the present time, not by increasing the rate of cooling, but by introducing dispersion particles into the metal. These particles either facilitate nucleation or create conditions for slow crystal growth. This principle is the basis for the widely used industrial method of reducing grain size, known as modification.

The crystals which form in the process of solidification of metal may have many different structures depending on the rate of cooling, the type and amount of admixtures or impurities in the melt

Dendritic

Lamellar

Needle-type

Acicular

.

Perfect crystals of proper external shape can be obtained only if crystallization develops under conditions when the degree of supercooling is slight and the metal has a very high purity.

In great majority of cases, branched or tree-like crystals are obtained, which are called dendrites.

The nucleus develops to form a dendritic crystal chiefly along the direction of maximum linear rate of growth. As a result, the long branches are formed first. They are so-called axes of the first order (primary axes of the dendrite) and they branch out in various directions from the initial nucleus.

While the primary dendrites grow in length, branches of the second order (m) evolve from the edges and grow in a perpendicular direction. Axes of the 3rd order (n) evolve and grow on second order axes and so forth.

A stage is eventually reached at which the spaces between the branches are filled with solidifying metal. Upon further freezing of the metal and development of the dendritic crystal, all of the liquid metal in the spaces solidifies.

From the structure of an ingot three structural zones may be distinguished. Solidification of the liquid metal begins at the surface of the mould and proceeds at first, chiefly in the thin layer of highly supercooled liquid adjacent to this surface. This leads to the formation of a zone of fine crystallites.

A second zone of elongated columnar crystallites (zone of transcrystallisation) follows immediately the first zone. The crystallites grow in the direction of heat removal i.e. normal to the mould walls.

The subsequent growth of columnar crystallites from the mould walls proceeds by advancement of first-order branches into the molten metal and the evolution of higher order branches.

Slow cooling of metal which is not overheated (as in castings of heavy cross section) will create conditions favorable for crystal nucleation in the central part of the ingot. This will form a 3rd structural zone in the central part of the ingot consisting of equiaxed randomly oriented crystallites.

Unit 3

Free energy diagrams as shown below given the composition at which various phases or phase mixtures are stable at a given temperature. From several such diagrams at different temperatures we can construct the phase diagram (equilibrium diagram /constitutional diagram)

F

Which marks out the composition limits of the phases in a given alloy system as a function of temperature

The phase diagram is of utmost importance in metallurgy. It gives a blueprint of alloy system from which we can anticipate at what composition alloys are likely to have useful properties, what treatments we must give to alloys to develop their properties to best effect, and what treatments are likely to be harmful and must be avoided.

Importance of phase diagram/equilibrium diagram:

- (1) To predict the temperature at which freezing or melting begins ,or ends for any specific alloy composition in an alloy system
- (2) To predict the safe temperature of working ,or heat treatment
- (3) To determine the number of phases ,composition of phases present in any given alloy at a specific temperature
- (4) To calculate the relative amounts of the phases present in a two phase alloy
- (5) To describe the freezing or melting of an alloy
- (6) To predict the microstructure of an alloy at any given temperature
- (7) To predict the possible heat treatment which can be given
- (8) To choose the composition to develop best properties
- (9)

Most combinations of metals have the property of unlimited mutual solubility in the liquid state.

Certain metals for example, Lead and Iron, are the almost completely insoluble in each other and separate according to their specific gravity in the liquid state.

Complete insolubility is rarely encountered; Limited solubility in the liquid state is more frequent

In such a case, a homogeneous liquid solution will be obtained if the amount of metal B is added to metal A does not exceeds its maximum temperature .If on the other hand the amount of added metal B exceeds its maximum solubility in A ,the liquid will separate into two layers.

- (1) Equilibrium diagram of a binary system in which components form a mechanical mixture of crystals in the solid state and completely mutually soluble in the liquid state
- (2) Equilibrium diagram of a system whose components are mutually soluble in both the liquid and solid state
 - (a) Components have unlimited solubility in both the liquid and solid states
 - (b) Complete mutual solubility in the liquid state and limited solubility in the solid state and in which the solid state solubility decreases with temperature
 - (c) Components have complete mutual solubility in the liquid state and limited solubility in the solid state (alloys with peritectic transformation)
- (3) Equilibrium diagram of a system in which the components have unlimited solubility in the liquid state and form chemical compounds on solidification
 - (a) Components have complete mutual solubility in the liquid state and form stable chemical compounds after solidification
 - (b) Equilibrium diagram of a system of components that form an unstable chemical compound upon solidification and which decomposes upon reheating before melting, by a peritectic reaction, forming a solid solution and a liquid phase
- (4) Equilibrium diagram of a system whose components are subject to allotropic transformations

ISOMORPHOUS SYSTEMS/ISOMORPHOUS EQUILIBRIUM DIAGRAM:

2(a) mentioned above are called isomorphous system

Two components are completely soluble in the liquid state and are completely soluble in the solid state

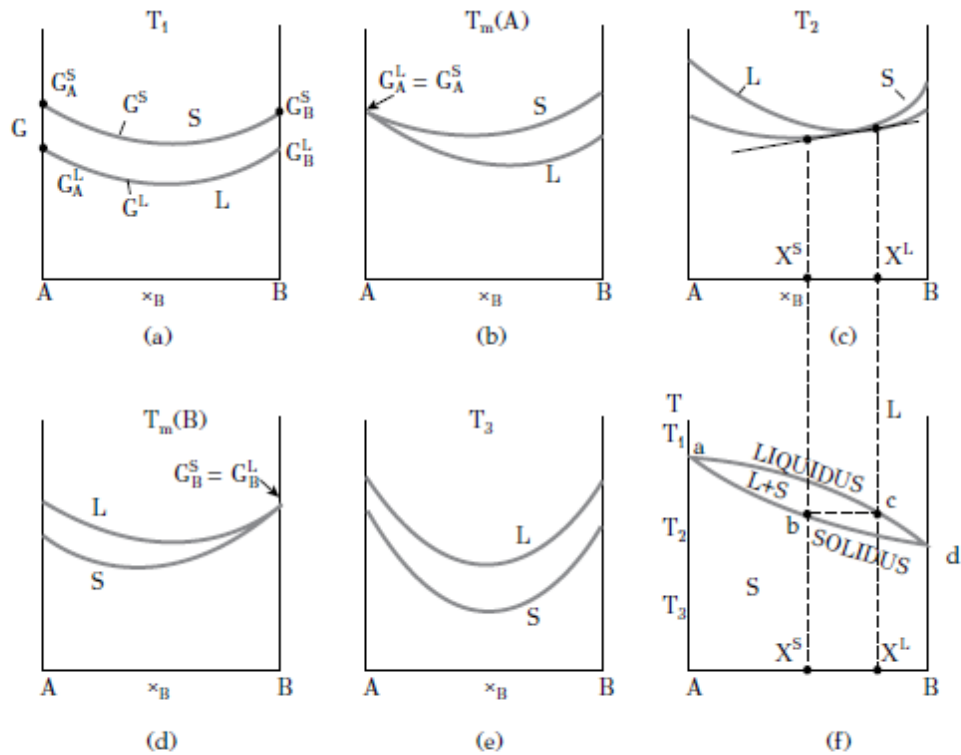


Figure 4.10: Construction of a phase diagram in a binary system exhibiting complete solid solubility, from the respective free energy curves of the solid and liquid phases.

G-X diagram for isomorphous equilibrium diagram

E.g Silver-Gold, Copper-Nickel

EUTECTIC EQUILIBRIUM DIAGRAM:

Typ1: Two components are completely soluble in liquid state and are completely insoluble in each other in solid state

Type 2: Two components are completely soluble in the liquid state and are partially soluble in the solid state

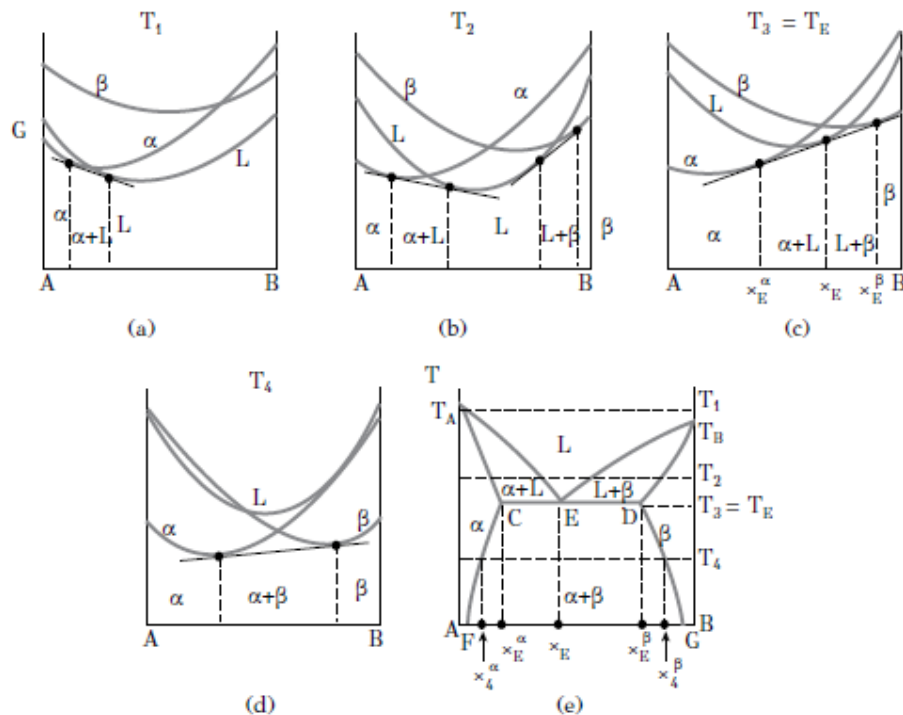


Figure 4.12: Construction of a eutectic phase diagram from the respective free energy curves.

G-X Diagram

E.g. Copper-Zinc

EUTECTOID EQUILIBRIUM DIAGRAM:

Eutectoid reaction is similar to eutectic reaction but involves only solids. Here, a solid solution upon cooling to some critical temperature, called eutectoid temperature is seen to transform completely through alternate precipitation of two solid phases both different from the parent solid solution occurring in solid state, and as the word ends in “-oid” indicates that the parent phase was a solid solution (and not a liquid solution)



PERITECTIC SYSTEM /EQUILIBRIUM DIAGRAM:

G-X Diagram for peritectic system

When two metals are completely soluble in the liquid state, show partial solubility in the solid state and if their melting point are vastly different from each other, then a peritectic phase diagram may result.

L (fixed composition) + S₁ (fixed composition) \longleftrightarrow S₂ (fixed composition)

Phase Rule:

The solidification of metal alloys is clearly demonstrated by means of equilibrium diagram which are convenient graphic representation of changes in states due to variations in temperature and concentration.

A system is here understood the whole complex of phases of one or several components at different pressures and compositions.

The components are the substances (Chemical elements or compounds) whose presence is necessary and sufficient to make up a system

For example, a pure metal comprises a one component system; an alloy of two metals is a two component system (binary) etc.

A phase is physically and chemically homogeneous portion of the system, separated from the other portion by a surface, the interface.

Phase Rule: It establishes the relationship [between the number of degrees of freedom, the number of components and the number of phases

Mathematically expressed as follows

$$F = C + n - P$$

In which

F is the number of degrees of freedom in the system (the number of variable factors)

C is the number of components of the system

P is the number of phases in equilibrium

n is the number of external factors (For example ,temperature and pressure)

Lever Rule:

Lever Rule states that the relative amount of a given phase is proportional to the length of the lever arm on the opposite side of the alloy point of the lever.

Lever rule is used to find the amount of phases present in only the two phase region of the binary equilibrium diagrams

Fe-C Phase diagram:

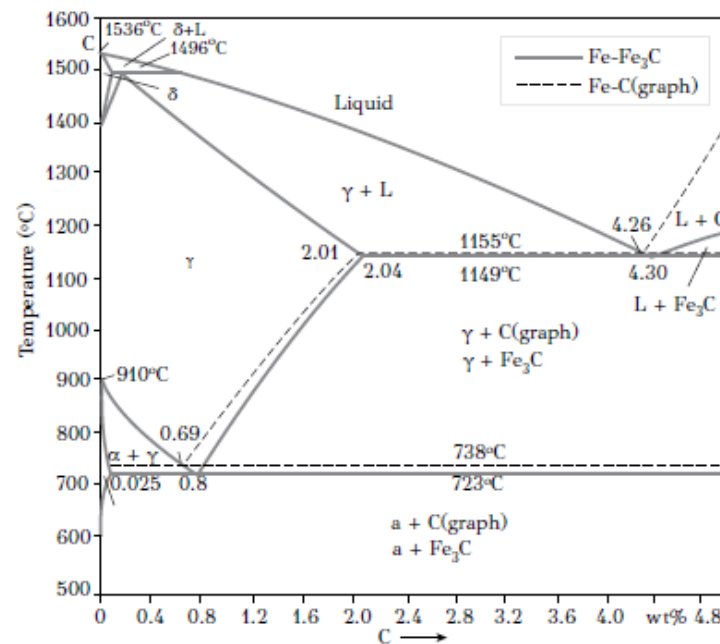


Figure 4.20: The binary Fe-C phase diagram. Full lines: equilibrium with cementite, dotted lines: equilibrium with graphite.

Dotted lines correspond to equilibrium of iron and graphite, which is the stable form of carbon, while the full lines correspond to the equilibrium of iron with (Fe₃C), which is a metastable form of carbon forming instead of graphite.

The difference between the two diagrams is small except in the region of the eutectic where the difference is appreciable.

Alpha, Ferrite (BCC)

Gamma, Austenite (FCC)

Delta, Ferrite (BCC)

Fe₃C, Cementite (Orthorhombic)

Below the Curie temperature (T_c) 768°C Alpha-Fe is Ferromagnetic while it is paramagnetic above T_c .

Fe-C diagram contains 3 invariant reactions:-

Peritectic 1496:

Eutectic 1149:

Eutectoid 723:

Gamma + Fe₃C is called ledeburite

Alpha + Fe₃C is called pearlite

In Fe – Graphite phase diagram:

- There is a minor change in the upper limit of the solubility of carbon in austenite and in liquid
- The eutectoid and eutectic temperature are little higher than Fe-Fe₃C diagram
- This diagram extends till 100% C

Iron forms a compound with carbon called cementite when the carbon content becomes more than the solubility limits of iron

Though carbon should be present as graphite as it has lower free energy than cementite yet cementite forms because the formation of cementite is more probable kinetically i.e. it is easier to form it, as only 6.67% C has to diffuse to segregate to form cementite whereas 100% C segregation is required to form graphite

Graphite being the stable phase may form as a result of direct precipitation from liquid or by the decomposition of previously formed cementite –process is called Graphitisation.

UNIT-4:

Solution:

A solution is a homogeneous mixture of two or more substances. The substances that are called solutes and the substance the solutes are dissolved in is called the solvent.

Alloying:

An alloy is a metallic solid or liquid formed from an intimate combination of two or more elements. Any chemical element may be used for alloying but the only ones used in high concentrations are metals. The process of combining two or more elements to form an alloy is called alloying.

Type of solid solution:

(1) Primary solid solution :

A solid solution can exist over a range of composition. Anywhere within this range the material is fully homogeneous and its structure and properties differ only infinitesimally from those of neighboring composition

-A few solid solutions extend continuously all the way from one pure metal to the other

-or, else the range of homogeneous composition is limited

When this limited range includes one of the pure components the solution is primary one

(2)Secondary Solid solution:

Solid solutions in alloys are also formed in intermediate ranges of composition which do not include pure component. These are called secondary solid solutions.

Also solid solutions can be

(1) **Substitutional** (Atoms share a single array of atomic sites)

(2) **Interstitial** (Atoms of one component are small enough to fit into interstitial spaces between those of the other)

A substitutional solid solution can be (i) fully random

(ii) Clustered (like neighbors favoured)

(iii) Ordered (unlike neighbors favoured)

Again ordered substitutional solid solution can have

- (i) A short range order
- (ii) A long range order

Superlattice : Regular alternation of unlike atoms throughout the entire crystal

Chemical compound Vs solid solutions:

- (i) The electro-chemical compounds satisfy.. the valency laws ,whereas solid solutions have a range of composition
- (ii) The compounds are formed between more electropositive and more electrotive elements such as Mg_2Si , Mg_3Sb_2 etc. The solid solutions normally have quite a large range of solubility
- (iii) The crystal structures of some compounds are simple of the type found in ionic crystals but different than the crystal lattice of the elements forming the compounds. But most compounds have complex crystalline structures. Primary solid solution has same crystal structure as the solvent element
- (iv) The properties of the compounds are much different than the properties of the elements forming them .These are essentially non-metallic brittle and bad conductor of electricity .The properties of solid solutions are metallic in nature and little different than the solvent metal.

Intermediate Phases:

Most alloy systems don't show complete solid solubility .When the amount of solute element (say solute B in solvent A) is more than the limit of solid solubility, a second phase also appears apart from the primary (terminal) solid solution of solute B in solvent A .This second phase in some cases may be the solid solution of element A in B (the second terminal solid solution)

Generally apart from these terminal solid solutions , the second phase which form is an intermediate phase .It is a phase formed at intermediate composition between the two primary (or terminal) solid solutions .The crystal structures of intermediate phase is different from both parent elements .Some of these intermediate phases have a fixed composition and are called intermetallic compounds.

Phase mixtures :

If unlike atoms are attracted less than like the two types tend to separate into distinct and different crystals joined at mutual grain boundaries .Some grains are rich in atoms of one type, others are rich in those of the other.

If the atoms are indifferent two one another they behave as if belonging to the same species and they become mixed together so thoroughly that the alloy is homogeneous right down to the atomic scale and form random solid solution.

If unlike atoms are attracted together, the nature of resulting alloy varies widely according to the factors determining the attraction when formed from true metals the structure is often an ordered solid solution or superlattice in which the two species are arranged in some regular alternating pattern.

Hume-Rothery Rule:

The pioneering work of Hume Rothery on a number of alloy systems led to the formation of conditions that favors extensive primary substitutional solid solubility. These empirical conditions are called Hume-Rothery's Rules:

- (1) Atomic size factor
- (2) Electro-Chemical Factor
- (3) Relative valency factor
- (4) Crystal structure factor

UNIT 5 :

Cast irons are basically iron-carbon alloys having carbon more than 2.11% i.e. more than the maximum solid solubility of carbon in Austenite

Very brittle, not amenable to deform

Easy to cast (due to lower melting point) into complicated shapes and cheap

-with alloying, good foundry practice and heat treatment, properties can be varied over wide range

Carbon can occur in cast iron as:

Combined carbon (Fe_3C) or free carbon (Graphite)

Shape and distribution of carbon is also important

Parameter that influence are

--Carbon content

--Alloy and impurity content

--Cooling rate during and after freezing

--Heat treatment after casting

Classification of Cast iron based on metallographic structure

--White cast iron

--Malleable cast iron (Free carbon as irregular particles)

--chilled cast iron (white cast iron at the surface and grey cast iron at the interior)

--Grey cast iron (flake graphite)

--Spheroidal graphite (SG) / ductile cast iron

Nodular cast iron (Free carbon as spheroids)

--alloy cast iron

Type of cast iron	Graphite	Ductility	
White	No	No	Fast cooling rate
Grey	Flakes	No	Slow cooling rates
Malleable	Anneal: Flake to nodule	Yes	White iron +Heat treatment
Nodular	Nodular	Yes	Additions made so that nodules of graphite form instead of flakes

Diagram

White cast iron:

--Fe₃C + Pearlite

--Hard and brittle

--Shows a white crystalline fractured surface

--excellent wear resistance

--High compressive stress

Malleable Cat Iron:

White cast iron+ Annealing treatment (900-950⁰ C for many days / cooling slowly)

-During annealing treatment graphite nucleates and grows from the Fe₃C to form nodules

Grey Cast Iron:

During Slow solidification carbon in Fe separates or graphitizes to form separate graphite flakes

Cast Iron: Factors affecting Graphitization

Cast Iron Carbon Equivalent

$$CE \text{ (wt\%)} = C + ((Si + P)/3)$$

A high cooling rate and low carbon equivalent favors the formation of white Cast Iron

A low cooling rate or a high carbon equivalent promotes grey Cast Iron.

General Characteristics /Advantages of Grey cast iron

- (I) Cheap
- (II) Low melting point
- (III) Fluid –Easy to cast , Especially advantageous into large complex shapes
- (IV) Excellent machinability
- (V) Excellent bearing properties
- (VI) Excellent damping properties
- (VII) Excellent damping properties
- (VIII) Excellent wear resistance
- (IX) Can be heat treated(Surface hardened)
- (X) Can be alloyed

Compressive strength >> tensile strength

Chilled Cast Iron:

--Obtained by casting against a chiller

--Surface is white Cast Iron (faster cooling rates)

--Harder / wear resistance surface

--Depth depends on composition

(C, Si decrease chill depth)

Carbide forming elements like Cr, Mo increase chill depth

Applications:

Railway Car wheels, Crushing Rolls, Heavy Machinery

Ductile/Nodular Cast Iron

--Grey Iron Composition

--Impurity level control important as it will affect nodule formation

--Have nodule instead of flakes if we add in 0.05 % Mg and/or Ce

--As cast structure: Graphite forms as nodules instead of flakes

Additions of Co/Mg poisons the easy growth direction and results change in Graphite morphology from flakes to spheres which occurs due to isotropic growth

Spheroidal Graphite cast iron usually has a pearlite matrix

Heat treated Spheroidal Graphite Cast Iron:

Annealing causes the carbon in the pearlite to precipitates on the existing graphite or to form further small graphite particles, leaving behind ferritic matrix

Austempered Ductile Cast Iron:

--The chemical composition of the Cast Iron is

Fe-3.52C-2.51Si -0.49Mn-0.15Mo-0.31Cu wt%

--austenised at 950⁰ C , austempered at 350⁰ C for 60 min

Graphitisation;

In iron-carbon alloys, graphite is more stable phase than cementite but kinetically, it is easier to form cementite than graphite

--6.67% carbon should segregate to nucleate cementite whereas 100% segregation of carbon is needed to nucleate graphite. Thus cementite forms more easily from austenite or from liquid as the energy for its nucleation, and the amount of diffusion required for its formation is much less than the graphite.

--When graphite forms directly from liquid, it is called primary graphitization but when graphite forms from the dissociation of cementite its called secondary Graphitisation.

--Slow cooling of liquid cast iron leads to the formation of grey cast iron , whereas fast cooling rate leads to white cast iron

--If the graphitization of secondary cementite is not complete, the microstructure at higher temperatures consists of austenite plus graphite plus cementite, which becomes at lower temperature (after the eutectoid reaction) as pearlite plus graphite cementite (mottled form)

--If all the secondary cementite (and not the cementite of pearlite) decomposes , the high temperature microstructure of austenite plus graphite would become at low temperature of pearlite plus graphite (complete pearlitic type)

--If the the decomposition of cementite of pearlite (Obtained due to eutectoid reaction) is completed, the microstructure consists of ferrite plus graphite and if its incomplete, the structure contains pearlite plus graphite plus ferrite

Unit-6:

Metallurgical microscopes:

--In comparison with a biological type , the metallurgical microscope differs in the manner by which the specimen is illuminated .Since a metallographic sample is opaque to light , the sample must be illuminated by reflected light.

--A horizontal beam of light from some light source is reflected by means of a plane glass reflector, downward through the microscope objective onto the surface of the specimen

--Some of this incident light reflected from the specimen surface will be magnified in passing through the plane glass reflector and be magnified again by the upper lens system.

--when a particular combination of objective and eyepiece is used at the proper tube length, the total magnification is equal to the product of the magnifications of the objective and eyepiece.

(1)Table type of metallurgical microscope

(2) Bench type metallurgical microscope

(Especially designed for both visual examination and permanent recording of metallographic structures by photographic method)

--The maximum magnification obtained with the optical microscope is about 2000X .The principal limitation is the wavelength of visible light which limits the resolution of fine detail in metallographic specimen.

Electron microscope:

--Under certain circumstances, high velocity electrons behave like light of very short wavelength. The electron beam associated with it a wavelength nearly 100000 times smaller than the wavelength of visible light thus increasing the resolving power tremendously

--Although in principle the electron microscope is similar to the electron microscope is similar to the light microscope its appearance is very much different .It is much larger because of the highly regulated power supplies that are needed to produce and control the electron beam. The entire

system must be kept pumped to a high vacuum since air would interfere with the motion of the electron.

--The lenses of the electron microscope are powerful magnetic fields of the coils and the image is brought into focus by changing the field strength of the coils while the coils remain in fixed position. In the optical microscope the image is brought into focus by changing the lens spacing.

--The electrons emitted by hot-tungsten filament cathode are accelerated, to form a high-velocity beam; by the anode. This beam is concentrated on the replica by the condensing lens. Depending on the density and thickness of the replica at each point, some of the electrons are absorbed or scattered while the remainder pass through the magnetic fields of the objective lens focuses and enlarges the electron beam that has passed through the replica.

Metallography or Microscopy:

It consists of the microscopic study of the structural characteristics of a metal or an alloy.

The aim of the metallographic study include the determination of the size and shape of the crystallites which constitute an alloy, revealment of structural characteristics of certain type of metal working operations, discovery of microdefects (non metallic inclusions, microcracks etc.) and in some cases, the determination of chemical content of alloys (for example, annealed carbon steels). Microstructures is an indication of the quality of mechanical properties etc.

--Metallographic investigations are conducted in specimens called microsections. These are prepared by cutting out small specimen, for example, a tin cube or a washer 10 to 15 mm high

--One face of the specimen is smoothed with a file or emery wheel and then ground with special emery paper arranged on thick plate glass or secured to a rapidly rotating wheel.

--The specimen is ground first by the coarsest available emery paper and successively by finer and finer grains until the finest available grade is reached. The direction of grinding is periodically changed through 90° .

--After grinding, the specimen is polished by rotating disc, covered with broadcloth, felt, or velvet, to which a very finely ground abrasive material (alumina, chromium oxide etc.) is continuously applied.

--Electropolishing or electrolyte polishing is often employed for preparing microsections. A DC with a density from 2A to 6A per square centimeter is passed through the electrolyte. Localised dissolving of the surface is obtained on the microsections. Aqueous solutions of acids, mixed with solvents that facilitate dissolution of the anode products, are usually employed as electrolytes.

--Electropolishing reduces the time required to prepare a microsection and completely eliminates deformation in the surface layers due to grinding. Such deformation may distort the actual character of the metal structure.

--Microstructure is revealed by etching the microsection with a special reagent called an etchant.

--Steel and cast iron are usually etched with 4 to 5% alcoholic solution of nitric or picric acid

A 0.5% aqueous solution of Hydrofluoric acid is extensively used for aluminum alloys and 8% ammonia solution of CuCl_2 is suitable for alloys

Sampling

Rough grinding

Mounting

Intermediate Polishing

Fine polishing

Etching