



**DEPT. OF MECHANICAL ENGINEERING**

**TRIDENT ACADEMY OF TECHNOLOGY,  
BHUBANESWAR**

**LECTURE NOTES**

**ON**

**INTRODUCTION TO PHYSICAL METALLURGY  
AND ENGINEERING MATERIALS**

**B. Tech**

**3<sup>rd</sup> Semester**

**By**

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**Department of MECH**

## **MEPC2002 INTRODUCTION TO PHYSICAL METALLURGY AND ENGINEERING MATERIALS (3-0-0)**

**Course Objectives:**“This course aims to equip students with fundamental knowledge of physical metallurgy and engineering materials so that students will understand the structure, properties, processing, and performance of various engineering materials, enabling them to select and apply appropriate materials in mechanical design and manufacturing processes.”

### **MODULE-I(08hrs)**

Philosophy behind study of material science, Classification and properties of engineering materials. Crystal structures, Mechanism of crystallization, Defects in crystal structure, Plastic deformation by slip and twinning, Effects of cold working on properties, Review of strengthening methods, Hot working

### **MODULE-II(06hrs)**

Constitutions of Alloys: Pure metal, Intermediate alloy phase, solid solution: Substitutional and interstitial. Hume- Rothery Rules Phase Diagram: Binary phase diagram, phase diagram rules, iron-carbon equilibrium diagram, phase transformation in iron-carbon system, Lever rules

### **MODULE-III(05hrs)**

Heat Treatment of Steels: Structure and properties of common engineering materials, Annealing: different types of annealing, Normalizing, Hardening

### **MODULE-IV(06hrs)**

Time Temperature Transformation (TTT) diagram, different cooling curves and transformation on continuous cooling, Tempering, sub-zero treatment of steel, Defects due to heat treatment. Surface Hardening of Steels: Induction hardening, Flame hardening, Case hardening: Carburizing, Nitriding, Cyaniding, carbonitriding, Diffusion coating.

### **MODULE-V(05hrs)**

Introductory Ideas on Ferrous Alloys, Effect of alloying elements on the properties of steels, general classification of steels, Steel designation, Cast Iron. Nonferrous Alloys: Plastics, Ceramics, Composite materials, Common applications of various materials

### **Course Outcomes:**

**Upon completion of the course, students will be able to:**

<b>CO1</b>	Understand the crystal structure and classification of engineering materials.
<b>CO2</b>	Understand the classification of ferrous and nonferrous alloy and study their applications.

<b>CO3</b>	Interpret the phase diagrams of materials.
<b>CO4</b>	Understand heat treatment and surface hardening processes affecting mechanical properties of metals and alloys.
<b>CO5</b>	Understand the effect of alloying and composite materials.

**Books:**

- Introduction to Physical Metallurgy by Avner, Tata McGraw Hill
- Materials Science and Engineering by W.D. Callister, Wiley and Sons Inc.
- Physical Metallurgy: Principles and Practice by Ragahvan, PHI

## 1.1 Introduction to Material Science and Metallurgy

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Material is that from which anything can be made. It includes a wide range of metals and non-metals that are used to form the finished product.

Material science is the study of the structure-properties relationship of engineering materials such as ferrous; non-ferrous materials, polymers, ceramics, composites, and some advanced materials.

It is important to study material science because of the following reasons:

- ▶ For the selection of material for a particular application based on their performance and cost.
- ▶ To understand the limitations of a particular material for different applications.
- ▶ To be able to understand the change in the properties of a material with use.
- ▶ For creating new material which will have the desired properties.
- ▶ Metallurgy is the study of metals related to their extraction from ore, refining, production of alloys along with their properties.
- ▶ The scientific methods are used to evaluate, plan, produce a perfect metallurgical process.

A metallurgical field may be classified as follows:

1. Extractive Metallurgy
2. Mechanical Metallurgy
3. Physical Metallurgy

Extractive metallurgy is the branch that deals with the separation of metals by various Chemical processes from the ores.

- ▶ Mechanical metallurgy deals with the mechanical working as well as testing of mechanical properties of materials.
- ▶ Physical metallurgy deals with the structures of metals and alloys after deformation and treatment of metals.
- ▶ Hence, the study of material science and metallurgy links the science of metals to the industries.

Also, this helps in completing demands from new applications and severe-service requirements.

## 1.2 Classification of Materials

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Most engineering materials may be classified into the following types

- |                                     |                       |
|-------------------------------------|-----------------------|
| a) Metals (Ferrous and Non-ferrous) | b) Ceramics           |
| c) Composite                        | d) Semiconductors     |
| e) Organics                         | f) Advanced materials |

### a) Metals

- ▶ Metals are very important in the industrial application and play a major role in the day-to-day life of human beings.
- ▶ There are many metal parts and objects, which are used in engineering applications.
- ▶ The commonly used metal are Iron, Aluminium, Copper, Magnesium, etc

## **b) Ceramics**

- ▶ Ceramics generally consist of oxides, nitrides, carbides, silicates or borides of various metals.
- ▶ Ceramic materials contain compounds of metallic and non-metallic elements such as MgO, SiO<sub>2</sub>, SiC, glasses, etc.
- ▶ Ceramics are any inorganic, non-metallic solids, processed or used at high temperatures.
- ▶ The commonly used ceramic materials are Sand, Cement, Abrasive, Glass, Concrete, Plaster, etc

## **c) Organics**

- ▶ Organics are polymeric materials composed of carbon compounds. (Polymers are solids composed of long molecular chains).
- ▶ Organic materials may be natural, synthetic or manufactured and based chemically on carbon.  
The commonly used organics are Rubber, Plastics, Lubricants, Wood, Textiles, Fuels, etc.

## **d) Composites**

- ▶ Composite materials consist of more than one material type.
- ▶ For example, fiber-glass in which glass fibers are embedded within a polymeric material.

## **e) Semiconductors**

- ▶ Semiconductors have electrical properties that are intermediate between the electrical conductors and insulators.
- ▶ The electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of impurity atoms, of which concentrations may be controlled over very special regions.

## **f) Advanced Materials**

- ▶ Advanced materials are used in advanced or high technology applications.
- ▶ They consist of newly developed properties.
- ▶ These materials are used in the field of telecommunication, computers, aeronautics, electronics, etc.
- ▶ Advanced materials are Biomaterials, Nanomaterials, magnetic materials, High and low-temperature material, Dielectric materials, Cryogenics material, etc.

## **1.3 Selection of Materials**

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The selection of materials and the manufacturing processes are integral parts of the design of a machine element. In fact, the design of any machine element begins with the selection of material.

There are a large number of engineering materials available and many more are adding up day by day. The material selection is not an easy job and involves the trial and error method.

- ▶ The choice of the materials depends upon the following factors:

### **1. Availability of materials**

- ▶ The materials which are available readily and in abundance in the market should be selected.
- ▶ As far as possible, the materials which are not available easily should be avoided.

### **2. Cost of material**

- ▶ In today's world of competition, cost plays a significant role in the success of the product.
- ▶ The material should be selected such that the total cost should be minimum and within the specified limit.

- ▶ The total cost includes the cost of material and the cost of processing the material.

### **3. Manufacturing considerations**

- ▶ The manufacturing considerations play a vital role in material selection. The selected material should be suitable for the required manufacturing processes.
- ▶ For example, if the body of the machine is to be made by the casting process, the material suitable for the casting process must be selected.
- ▶ However, if the material is found suitable for all other considerations, sometimes the manufacturing process can be changed, if feasible.

### **4. Material properties**

- ▶ The material properties, in general, and mechanical properties, in particular, govern the selection of the materials.
- ▶ The different mechanical properties considered are static strength, fatigue strength, stiffness, elasticity, plasticity, ductility, brittleness, malleability, hardness, toughness, resilience, creep, etc.

## **1.4 Engineering Requirements of Materials**

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Nowadays there is a tremendous increase in the availability of materials along with demands from various applications and service conditions.

- ▶ Materials should fulfill the engineering requirements so that they can be successfully used for making various components.
- ▶ The properties of the selected material help the component to perform its operation successfully while in use.
- ▶ The following are the various engineering requirements which material should fulfill
  - a) Fabrication requirements
  - b) Service requirements
  - c) Economic requirements

### **1. Fabrication requirements**

- ▶ These requirements include the ability of the material to be able to get shaped or machined by various forming and manufacturing processes. For example, casting, forging, machining, sintering, etc.
- ▶ Also, the material should be able to join easily by welding, brazing, etc.
- ▶ The properties of materials such as machinability, ductility, castability, weldability, heat-treatability, etc. are related to fabrication requirements.

### **2. Service requirements**

- ▶ The material selected for the particular application should withstand all the service demands and severe service conditions.
- ▶ Selected material for a component should function properly during the service life of the component.
- ▶ Properties of materials such as strength, toughness, wear resistance, corrosion resistance, etc. are related to the service requirements.

### **3. Economic requirements**

- ▶ This demand implies that the component should be made from the material at the minimum possible cost.
- ▶ All the variables should be properly selected to achieve optimum cost and quality of a material.

- ▶ Both technical and marketing parameters should be selected properly for the minimum overall cost.

## 1.5 Properties of Materials

Property of a material is a factor that influences qualitatively or quantitatively the response of a given material under the action of forces, temperatures, pressures, etc.

- ▶ The property indicates that, whether a material is suitable or unsuitable for particular use in industry.
- ▶ The material property is independent of the dimension or shape of the material.
- ▶ The various material properties are divided into the following groups:
  1. Mechanical Properties
  2. Thermal Properties
  3. Electrical Properties

### Mechanical Properties

- ▶ Mechanical properties include those characteristics of a material that describe its behavior under the action of external forces.
- ▶ The knowledge of the mechanical properties of materials is very essential in order to construct a mechanically fool-proof structure.

Some of the important mechanical properties are as follows:

- |                 |                 |                    |                 |
|-----------------|-----------------|--------------------|-----------------|
| 1. Elasticity   | 2. Plasticity   | 3. Toughness       | 4. Resilience   |
| 5. Strength     | 6. Stiffness    | 7. Ductility       | 8. Malleability |
| 9. Brittleness  | 10. Brittleness | 11. Fatigue        | 12. Creep       |
| 13. Weldability | 14. Formability | 15. Machineability |                 |

### 1. Elasticity

- ▶ It is the property of a material to regain its original shape after deformation when the external forces are removed.
- ▶ This property is required for materials used in tools and machines.
- ▶ It is important to note that, steel is more elastic than rubber.

### 2. Plasticity

- ▶ The property of a material that retains the deformation produced under the load permanently is called plasticity.
- ▶ This property is essential in stamping, press work, forgings, ornamental work, etc.

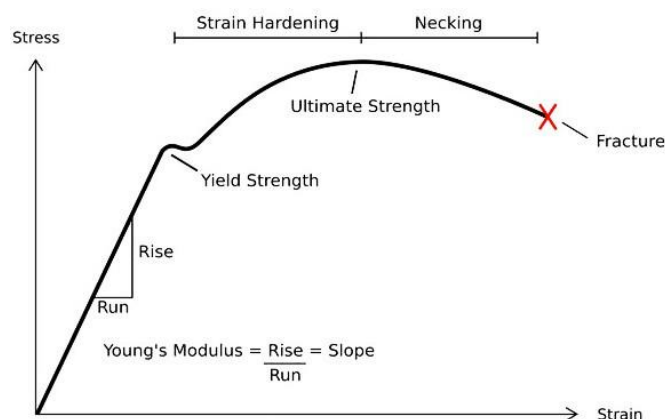


Fig.1.1 – Stress Strain Diagram For Material

### 3. Toughness

- ▶ Toughness is the total amount of energy absorbed by the material before its failure.
- ▶ It is the complete area under the stress-strain curve i.e. summation of the elastic and plastic region.
- ▶ This property is essential in parts subjected to shock and impact loads.

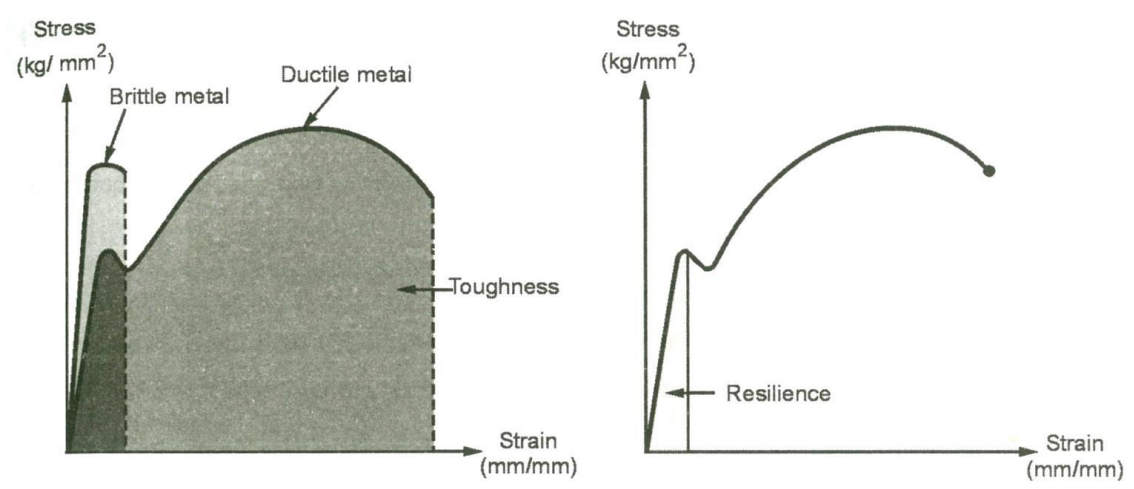


Fig.1.2 – Toughness and Resilience

### 4. Resilience

- ▶ The resilience of a material is defined as the total amount of energy absorbed by the material during its elastic deformation.
- ▶ This property is essential for springs, shock absorbers, etc.
- ▶ The area under the stress-strain curve in the elastic region indicates resilience.

### 5. Strength

- ▶ It is the ability of a material to resist the externally applied forces without failure.
- ▶ It is measured in kg/mm<sup>2</sup> or N/mm<sup>2</sup>.

### 6. Stiffness

- ▶ It is the ability of a material to resist deformation under stress.
- ▶ It is also defined as the force or load per unit deflection. It is measured in N/mm.

### 7. Ductility

- ▶ It is defined as the ability of a material to undergo plastic deformation under tensile loading, before its fracture.
- ▶ Also, ductility is the property of a material by which it can be drawn into fine wires. For example, a rubber.

### 8. Malleability

- ▶ It is defined as the ability of a material to be formed by hammering or rolling.
- ▶ It is the capacity of a material to withstand deformation under compression without failure.
- ▶ The main difference between ductility and malleability is that the ductility is considered as tensile property and malleability is considered as compressive property.

## 9. Brittleness

- ▶ It is the property of breaking of a material with little permanent distortion.
- ▶ Brittleness of material is opposite to ductility. For example glass, concrete block, etc.

## 10. Hardness

- ▶ It is an important property of metals.
- ▶ It is defined as the resistance of metal to plastic deformation usually by indentation.
- ▶ It is also defined as resistance to scratch, abrasion or cutting.

## 11. Fatigue

- ▶ When a material is subjected to repeated stresses or loading, it fails at stresses below the yield point stress. Such type of failure of material is called fatigue.
- ▶ Fatigue failure is caused by means of a progressive crack formation which is generally of microscopic size.
- ▶ It is considered while designing shafts, gears, springs, etc.

## 12. Creep

- ▶ When a material is subjected to constant stresses at high temperatures for a long period of time, it will undergo a slow and permanent deformation which is called creep.
- ▶ It is considered while designing boilers, I. C. engines, pumps, turbines, etc.

## 13. Weldability

- ▶ Weldability is defined as the capacity of a material to be welded under fabrication conditions imposed in a specific and suitably designed structure and to perform satisfactorily in the intended service.
- ▶ It indicates that metal with good weldability can be welded readily so as to perform satisfactorily in the fabricated structure.

Weldability includes,

- ▶ Metallurgical compatibility of a metal.
- ▶ The ability of the metal or alloy to be welded with mechanical soundness.
- ▶ Serviceability of the resulting welded joint.

## 14. Formability

- ▶ It is defined as the property of a material to be formed by compressive or tensile forces in tool and die arrangement.
- ▶ This term is generally used for sheet forming processes like bending, stamping, stretch forming, deep drawing, etc.

## 15. Machineability

- ▶ The machinability of a material indicates how machinable the material is.

When it is stated that material P is more machinable than material Q, it means that,

- ▶ Less power is required to machine material P.
- ▶ Lower tool wear is obtained with material P.
- ▶ Better surface finish can be achieved with material P.

- ▶ Machinability is also defined as the property of the material which governs the ease or difficulty with which it can be machined under a given set of conditions.

## 1.6 Structure - Properties - Performance Relationship

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The structure - properties - performance relationship forms the basis for optimum selection of material for a particular task.

- ▶ The optimum solution for material selection for product and system performance depends upon the properties of a material.
- ▶ These properties are related to the internal structure of a material. Hence the structure and properties of the material and performance are correlated.
- ▶ The structure must be controlled to ensure the desired properties of materials which in turn influence the performance of the system.
- ▶ This co-relationship is important and must be considered during both processing steps of production and in service.
- ▶ On the other hand, during processing and service, there IS a change in properties of materials due to altered internal structure.
- ▶ The performance of a material depends on the internal structure of the component.
- ▶ These internal arrangements involve electrons, atoms, crystals, and microstructures. The properties of material originating from the internal structures of that material.

## 1.7 Levels of Internal Structure

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The structure is the heart of the material science that connects processing methods of materials with its properties.

- ▶ Also, it is the spatial distribution of things seen and unseen in a material.

The following are the levels of internal structure required to study the various materials:

- a) Nuclear structure
- b) Atomic structure
- c) Molecular structure
- d) Microstructure
- e) Macrostructure

### a) Nuclear structure

- ▶ It determines the nuclear properties of a material.
- ▶ Nuclear structure studies the properties of nuclei in terms of nuclear mass and shapes, characteristic energy levels and radioactive decay.
- ▶ These structures can be studied by Nuclear Magnetic Resonance (NMR) spectroscopy, laser spectroscopy, Mossbauer studies, etc.
- ▶ These methods are used to identify nuclear ground-state properties like masses, charge radii, spins and moments, etc.

### b) Atomic structure

- ▶ The atomic structure of any material is an important factor in understanding the physical and chemical properties.

- ▶ Also, the properties of materials can be altered by manipulating the position of the atoms or substituting any other atom.
  - ▶ Atoms and atomic arrangements constitute the building blocks of advanced materials.
  - ▶ X-ray crystallography, spectroscopy techniques are used to determine atomic structures.
- c) Molecular structure**
- ▶ Molecules are made up of the number of atoms joined together by a covalent bond.
  - ▶ The geometrical structure of the molecule is one of the most important and fundamental parameters in distinguishing the materials.
  - ▶ Molecular spectroscopy, electron gas diffraction, etc. techniques are used to reveal molecular structure.
- d) Microstructure**
- ▶ Microstructure IS defined as the structure of material ranges between 0.1 to 100.
  - ▶ It is revealed by a microscope above 25X magnification and can strongly influence the physical properties such as strength, toughness, ductility, high/low-temperature behavior, etc.
  - ▶ The microstructure is usually related to the grain size. The grains and grain boundaries seen in the micrograph are part of the microstructure.
  - ▶ Microstructure examination involves higher power techniques such as optical microscopy, electron microscopy, X-ray diffraction, etc.
- e) Macrostructure**
- ▶ Macrostructure is defined as the structure that is revealed by visual examination with little or no magnification. It ranges from 100 and above.
  - ▶ It is revealed either by machining or by macro etch test.
  - ▶ The study of macrostructure gives an idea about discontinuities in metal such as cavities, porosity, gas bubbles, etc.
  - ▶ Also, it reveals the distribution of impurities and non-metallic inclusions, shape, and distribution of grains in various parts of the component.

## 1.8 References

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Sidney H Avner "Introduction to Physical metallurgy" 2<sup>nd</sup> Edition 2011 Tata Mc Graw- Hill Publication.

O. P. Khanna "Material Science and Metallurgy" Dhanpat Rai Publications.

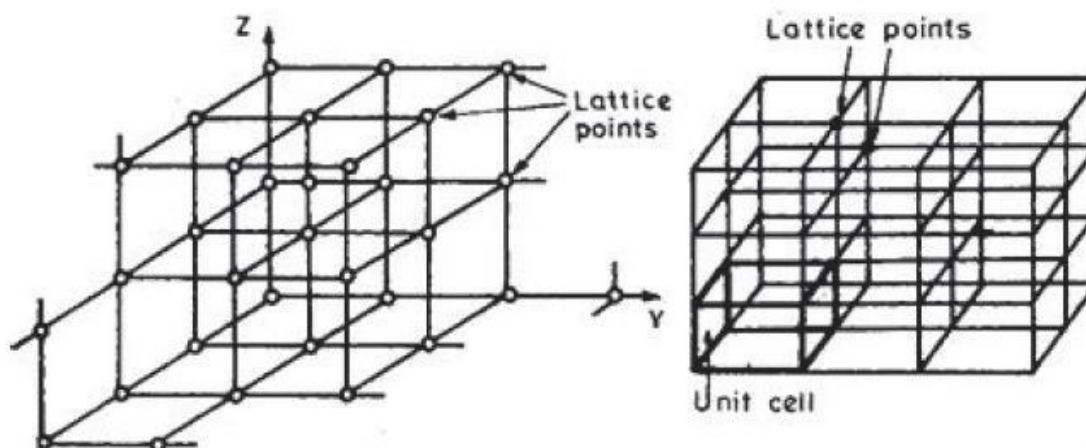
## 2.1 Introduction

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- ▶ Crystallography is the study of the crystal formation of solids, including:
    - X-ray determination of lattice structures, Crystal habit, (i.e. the form of a crystal), The shape and defects of crystals. When applied to metals, this science is called metallography.
  - ▶ Crystallography is that branch of science in which the internal structure of crystals, their properties, external or internal symmetries of crystals are studied.
  - ▶ Crystalline materials consist of atoms or molecules arranged in a regular and orderly manner in a three-dimensional pattern.
  - ▶ The various terms associated with crystallography are:
    1. Crystal
    2. Structure
    3. Space lattice
    4. Unit cell
    5. Crystallographic planes
    6. Lattice parameter
    7. Miller indices
    8. Atomic packing factor
    9. Coordinate number, etc.
1. A Crystal is a solid whose constituent atoms or molecules are arranged in a systematic geometric pattern.
  2. The structure implies the arrangement and disposition of the atoms within a crystal.
  3. The atoms arrange themselves in distinct pattern in space called a space lattice.
  4. The unit cell is the smallest group of atoms possessing the symmetry of the crystal.
  5. The layers of atoms or the planes along which atoms are arranged are known as atomic or crystallographic planes.
  6. Characteristic intercepts and interfacial angles of a crystal constitute the lattice parameters of a cell.
  7. Miller Indices is a system of notation for designating crystallographic planes and directions of crystals.
  8. Atomic packing factor is the ratio of the volume of the atoms per unit cell to the total volume occupied by the unit cell.
  9. Coordinate number is the number of nearest atoms directly surrounding a given atom in a crystal i.e., nearest neighbours to an atom in crystal.

## 2.2 Unit Cell and its Lattice Parameters

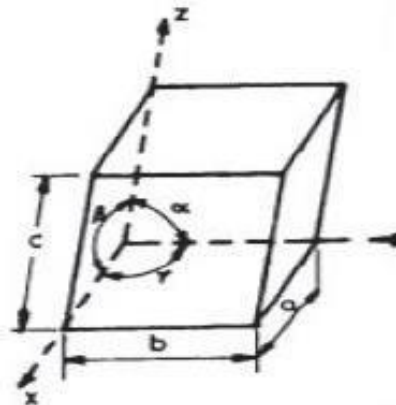
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*Fig.2.1 – Unit cell and lattice parameter*

- ▶ Lattice is the regular geometrical arrangement of points in crystalspace.
- ▶ The atoms arrange themselves in distinct pattern; in space, called a space lattice.
- ▶ Space lattice is the three dimensional network of imaginary lines connecting the atoms.

- ▶ A Space lattice can be considered as an infinite array of points in space, so arranged that it divides space into equal volumes with no space excluded.
- ▶ An important characteristic of a space lattice is that every point has identical surroundings.
- ▶ Space lattice or crystal lattice is the arrangement of atoms in a crystal.
- ▶ As already explained above, a space lattice can be considered as an infinite array of points in space, so arranged that it divides space into equal volumes with no space excluded. Every point, which is called a lattice point, has identical surroundings with every other point.
- ▶ The smallest volume that contains the full pattern of repetition is called a unit cell.
- ▶ Identical unit cells must completely fill the space when they are packed face to face, thus generating a space lattice. If a unit cell is so chosen that it contains lattice points only at its corners, it is called a primitive unit cell or simple unit cell.
- ▶ A primitive unit cell contains only one lattice point because each point at eight corners is shared equally with eight adjacent unit cells. The edge length of the unit cell, called a lattice constant or a lattice parameter, is a lattice translation in a given direction. Simple monoclinic, Triclinic, simple cubic are known as primitive cells. Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces.
- ▶ Fig. shows the unit cell geometry, which is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell.
- ▶ Within this framework, an x, y, z coordinate system is established with its origin at one of the unit cell corners; each of the x, y, and z axis coincide with one of the three parallelepiped edges that extend from this corner, as illustrated in Fig.



*Fig.2.2 – Description A unit cell with x, y and z coordinate axis, showing axial lengths (a, b, and c) and  $\alpha, \beta$  and  $\gamma$*

- ▶ The unit cell geometry is completely defined in terms of six parameters: the three edge length a,b, and c and three interaxial angles  $\alpha, \beta$  and  $\gamma$ . These are indicated in Fig. and are sometimes termed the Lattice Parameters of a crystal structure.
- ▶ On this basis, there are found crystals having seven different possible combinations of a,b, and  $\alpha, \beta$  and  $\gamma$ . Each of which represents a distinct function of crystal system.

## 2.3 Bravais Lattices

- ▶ Bravais lattices are the fourteen basic crystal lattices.
- ▶ Bravais showed that there are only fourteen possible different networks of lattice points

- ▶ Therefore, there are only 14 standard space lattices (Fig. 35.9) that are needed to describe all possible arrangements of points in space consistent with translational periodicity. Every crystal structure is based on one of the possible space lattices.
- ▶ There are only 14 independent ways of arranging points in three dimensions in a crystal.
- ▶ Bravais lattices named after their originator Mr. Bravais, are the 14 distinguishable three-dimensional space lattices that can be generated by repeated translation of three non-coplanar vectors  $a$ ,  $b$ , and  $c$  of a unit cell in three-dimensional space.
- ▶ Seven sets of the axis, are needed to construct the fourteen Bravais lattice. Accordingly, all crystalline solids can be classified into 7 crystal systems.
- ▶ The fourteen Bravais lattices continue in three dimensions. Each indicated point has identical surroundings.
- ▶ The fourteen Bravais lattices are explained below:

### 1. Simple Monoclinic Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a \neq b \neq c$  and interaxial angle  $\alpha = \gamma = 90 \neq \beta$

### 2. End Centered Monoclinic Lattice

- ▶ It has lattice points at the eight corners and at two face centers, opposite to each other. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = 90 \neq \gamma$ .

### 3. Triclinic Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha \neq \beta \neq 90 \neq \gamma$ .

### 4. Hexagonal Lattice

- ▶ It has pointed at the twelve corners of the hexagonal prism and at the centers of the two hexagonal faces of the unit cell. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = 90$  and  $\gamma = 120$ .

### 5. Rhombohedral Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a = b = c$  and an interaxial angle.  $\alpha = \beta = \gamma \neq 90$

### 6. Simple Orthorhombic Lattice

- ▶ It has lattice points at the eight corners of the unit. Cell. It has vectors  $a \neq b \neq c$  and interaxial angle  $\alpha = \beta = \gamma = 90$

### 7. Body-Centered Orthorhombic Lattice

- ▶ It has lattice points at the eight corners and at the body center. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90$ .

### 8. End-Centered Orthorhombic Lattice

- ▶ It has lattice points at the eight corners and at two face centers opposite to each other. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90$ .

## 9. Face Centered Orthorhombic Lattice

- ▶ It has lattice points at the eight corners and at the six face centers of the unit cell. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 10. Simple Cubic Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a = b = c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 11. Body-Centered Cubic Lattice

- ▶ It has lattice points at the eight corners and at the body center. It has vectors  $a = b = c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 12. Face Centered Cubic Lattice

- ▶ It has lattice points at the eight corners and at the face centers of the unit cell. It has vectors  $a = b = c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 13. Simple Tetragonal Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a = b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 14. Body-Centered Tetragonal Lattice

- ▶ It has lattice points at the eight corners and at the body center. It has vectors  $a = b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

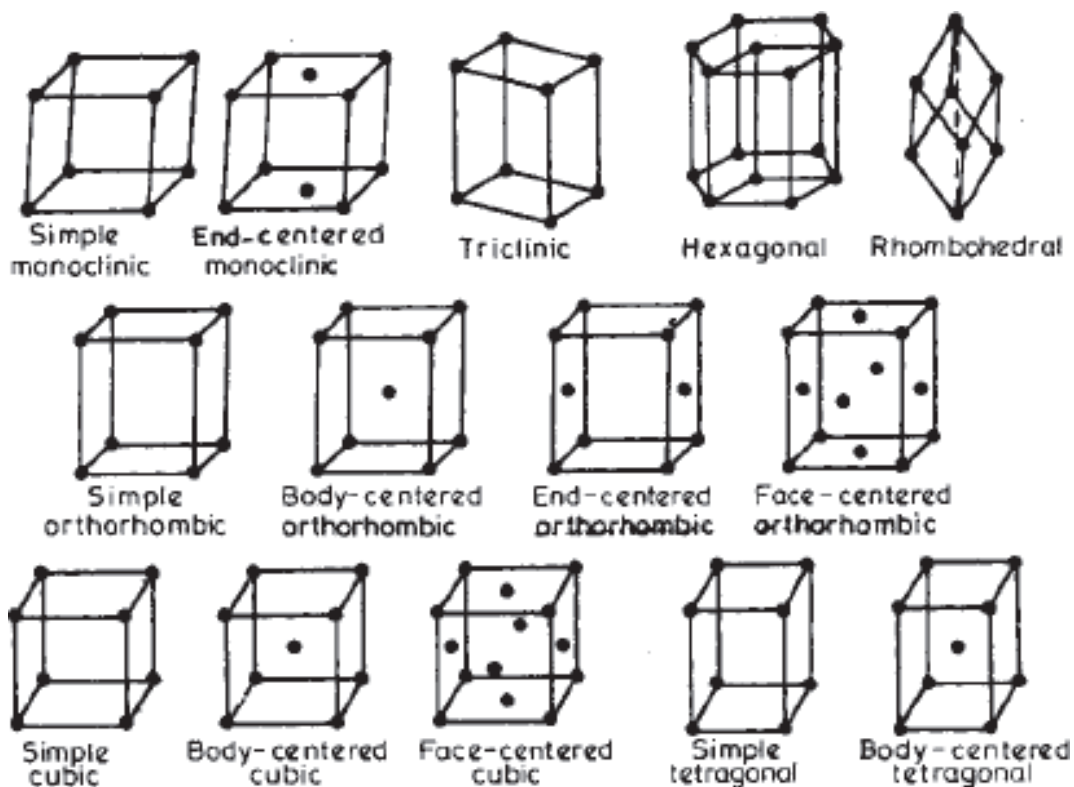


Fig.2.3 - Bravais Lattice

## 2.4 Coordination Number

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- ▶ Every atom in a crystal is surrounded by other atoms. By the term coordination number, we mean the number of nearest atoms that are directly surrounding a given atom.
- ▶ The coordination number may also be defined as the nearest neighbors to an atom in a crystal.
- ▶ Fig 2.3 shows that the coordination number of carbon atom is four because it has four hydrogen atoms around it.
- ▶ When the coordination number is larger, the structure is more closely packed.
- ▶ Coordination numbers for a simple cubic, BCC and FCC lattice have been discussed below:

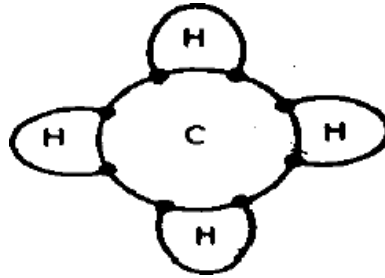


Fig.2.4 - Coordination number

### 1. Simple Cubic Structure

- ▶ There is one atom at each of the (eight) corners of the cube. Any corner atom has four nearest-neighbor atoms in the same plane and two nearest neighbors (one exactly above and other exactly below) in a vertical plane.
- ▶ Hence coordination number for simple cubic structure is  $4 + 2 = 6$ .

### 2. Body-Centered Cubic (B.C.C.) Structure

- ▶ In the B.C.C. structure, there is one atom at each corner of the cube and one atom at the center of the cube. For any corner atom of the unit cell, the nearest atoms are the atoms that are at the centers of unit cells.
- ▶ As such a corner atom is surrounded by eight unit cells having eight body-centered atoms, hence the coordination number is 8.
- ▶ Similarly, by considering the central atom of each unit cell, we can say that the coordination number is 8 because every centered atom is surrounded by eight equidistant neighbors.
- ▶ Hence, the coordination number for the B.C.C. structure is 8.

### 3. Face-centred Cubic (F.C.C.) Structure

- ▶ In the F.C.C. structure, there is one atom at each corner of the cube and one atom at the center of each face of the cube.
- ▶ For any corner atom of the unit cell, the nearest is the face-centered atoms.
- ▶ For any corner atom, there will be 4 face-centered atoms of the surrounding unit cells in its own plane, 4 face-centered atoms below this plane and 4 face-centered atoms above this plane.
- ▶ Hence the coordination number for this case is  $4 + 4 + 4 = 12$

## 2.5 Crystal Structure of Metals

### 1. Body-Centered Cubic (B.C.C.)

If the atoms are represented as spheres, the center atom touches each corner atom but they do not touch each other. Since each corner atom is shared by eight adjoining cubes and the atom in the center cannot be shared by any other cubes.

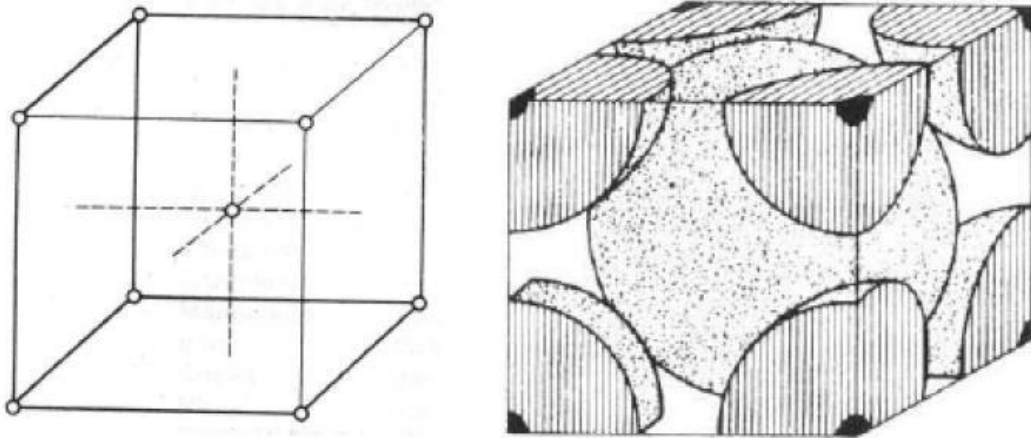


Fig.2.5 –Unit Cell Of B.C.C. Structure

The unit cell of the B.C.C. structure contains.

$$\begin{aligned} 8 \text{ atom at the corner} \times \frac{1}{8} &= 1 \text{ Atom} \\ 1 \text{ center atom} &= 1 \text{ Atom} \\ \text{Total} &= 2 \text{ Atom} \end{aligned}$$

### 2. Face Centered Cubic (F.C.C.)

In addition to an atom at each corner of the cube, there is one in the center of each face but none in the center of the cube. Each face atom touches its nearest corner atom. Since each corner atom is shared by eight adjoining cubes and each face is shared by only one adjacent cube.

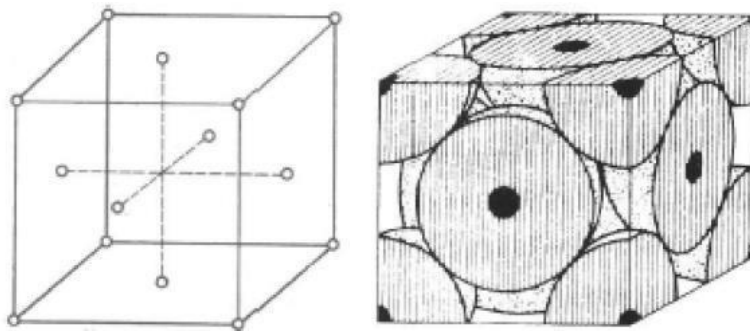


Fig.2.6 –Unit cell of F.C.C. structure

$$\begin{aligned} 8 \text{ atom at the corner} \times \frac{1}{8} &= 1 \text{ Atom} \\ 6 \text{ Face-centered Atom} \times \frac{1}{2} &= 3 \text{ Atom} \\ \text{Total} &= 4 \text{ Atom} \end{aligned}$$

This indicates that the F.C.C. structure is more densely packed than the B.C.C. structure.

Example: Aluminum, Nikle, Copper, Gold, Silver, Lead, Platinum, Gamma Iron

### 3. Close Packed Hexagonal (H.C.P.)

C.P.H. shows two based planes in the form of regular hexagons with atoms at each corner of the hexagon and one atom at the center. In addition, there are three atoms in the term of a triangle midway between the two based plane. If the based plane is divided into six equilateral triangles, the additional 3 atoms are nested in the center of an alternate equilateral triangle.

Unit cell of BCC & FCC can be specified by the lattice parameter „a“. The hexagonal unit cell required with hexagonal „a“ and distance between base plane „c“. this determines the axial ratio cross-section  $\left(\frac{c}{a}\right)$ . The axial

ratio varies from 1.58 for beryllium to 1.88 cadmium.

The atomic packing factor is 0.74.

Example: Zinc, Cadmium, Beryllium, magnesium.

No. of atoms in H.C.P.

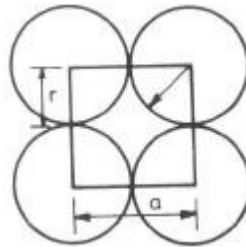
$$\begin{aligned} N &= \frac{N_c}{6} + \frac{N_F}{2} + \frac{N_i}{1} = \frac{12}{6} + \frac{2}{2} + \frac{3}{1} \\ &= 2 + 1 + 3 \\ &= 6 \end{aligned}$$

### Atomic Radius

Assume that atoms are spherical in space and are in contact in a crystal. Atomic radius can be designed as half the distance between the centers of two neighboring atoms.

The atomic radius of simple cubic structure „a“ is the lattice parameter

$$\text{Here, } a = 2r \quad r = \frac{a}{2}$$



### 1. Atomic Radius of F.C.C. Structure

Here a = Lattice parameter

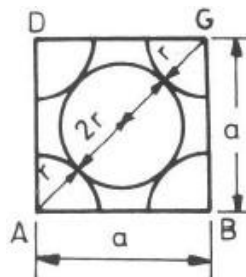
r = Atomic radius

$$AC^2 = AB^2 = BC^2$$

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

$$16r^2 = 2a^2$$

$$r = \frac{a\sqrt{2}}{4}$$



### 2. Atomic Radius of B.C.C. Structure

Let a = Lattice parameter

r = Atomic Radius

Let, Here

$$AG = r + 2r + r = 4r$$

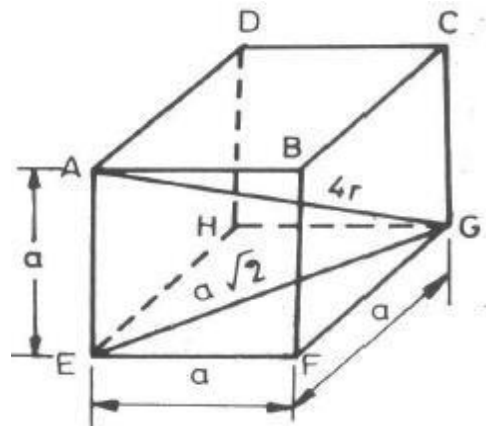
$$\text{Let } EG^2 = a^2 + a^2 = 2a^2$$

$$AG^2 = AE^2 + EG^2$$

$$(4r)^2 = a^2 + 2a^2 = 3a^2$$

$$16r^2 = 3a^2$$

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



## Atomic Packing Factor (APF)

### 1. APF For The Simple Cubic Structure

$$APF = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \text{or } a = 2r$$

$$APF = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{8a^3} \right) = 0.52$$

$$APF = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \text{or } a = 2r$$

$$APF = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{8a^3} \right) = 0.52$$

### 2. APF For F.C.C. Structure

$$APF = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 4 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \frac{a\sqrt{2}}{4}$$

$$APF = 4 \times \left( \frac{\frac{4}{3} \pi \left( \frac{a\sqrt{2}}{4} \right)^3}{a^3} \right)$$

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

$$= 0.74$$

### 3. APF For B.C.C. Structure

$$\text{APF} = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 2 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \frac{a\sqrt{3}}{4}$$

$$\text{APF} = 2 \times \left( \frac{\frac{4}{3} \pi \left( \frac{a\sqrt{3}}{4} \right)^3}{a^3} \right)$$

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

$$= 0.74$$

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$$\text{APF} = 2 \times \left( \frac{\frac{4}{3} \pi \left( \frac{a\sqrt{3}}{4} \right)^3}{a^3} \right)$$

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

$$= 0.74$$

## 2.6 Crystallography Planes and Directions (Miller Indices)

- ▶ The layers of atoms or the planes along which atoms are arranged are known as atomic or crystallographic planes.
- ▶ As one becomes more and more involved in the study of crystals, the need for symbols to describe the orientation in space, of important crystallographic planes and directions becomes evident.
- ▶ The Miller system of designating indices for crystallographic planes and directions is universally accepted for the purpose.
- ▶ Miller index is a system of notation that denotes the orientation of the faces of a crystal and the planes and directions of atoms within that crystal.

### Miller Indices for Planes

- ▶ One corner of the unit cell is assumed to be the origin (O) of the space coordinates, then find the intercepts on the three-axis in multiples or fractions of the unit distances on each axis (if a plane is parallel to, an axis it intersects it at infinity).
- ▶ For example, consider a plane ABC. It intersects X-axis at 1 unit, Y-axis at 3 units and Z-axis at 2 units from origin O.
- ▶ With this fill in the first (i) line of Table (ii) Take the reciprocal of these numbers; see (ii) line of Table

	X	Y	Z	
Intersection	1	3	2	...(i)
Reciprocal	$\frac{1}{1}$	$\frac{1}{3}$	$\frac{1}{2}$	...(ii)
		(3 × 2 = 6)		
	$\frac{1}{1} \times 6$	$\frac{1}{3} \times 6$	$\frac{1}{2} \times 6$	
	6	2	3	...(iii)
Miller indices	(623)			

Fig.2.7 – Miller indices of a plane

- ▶ (ii) Take the reciprocal of these numbers; see (ii) line of Table (iii) Change these reciprocals to the smallest integers having the same ratio, i.e., by multiplying each reciprocal (or fraction) by the same number such as the common denominator. Refer line (III) of Table (iv) Enclose the values in parenthesis Figs. (b), (c), (d) and (e) show a number of crystallographic planes and their miller indices in a cubic lattice.
- ▶ If a plane cuts any axis on the negative side of the origin, the index will be negative and is indicated by placing a minus sign above the index, as For example, the miller indices of plane ODEF which goes through the origin (O) cannot be determined without changing the location of the origin. Change the origin from point O to point P. The plane ODEF intersects X-axis and Z-axis at infinity but intersects Y-axis at -1. The plane has, therefore, miller indices at (010).

### Miller Indices for Directions

- ▶ The crystallographic direction can be defined as a line joining any two points of the lattice. For example, in Fig. 2.7 (a) OQ OD and OE are all crystallographic directions. Direction indices are simply the vector components of the directions resolved along each of the axes.
- ▶ Consider direction OE The point E lies in the plane OEFG. OE is 1 unit along X-axis, it neither intercepts Y-axis nor Z-axis. Thus the coordinates of point E and the miller indices of direction OE is [100] (x = 1, y = 0, z = 0).
- ▶ Similarly line OC, passes through the origin and the point C having .coordinates x = 0y = 0, z = 1; and thus the miller indices are [011]. Based on the same reasoning, the indices of OD is [111]. A general rule for finding the Miller indices of a crystallographic direction is:
- ▶ Draw a vector from origin parallel to the direction whose indices are desired. For example, if indices of AE are desired, draw a line OH parallel to AE through origin O. Draw CE in the downward direction (dotted), let it cut OH at I and then draw IJ parallel to X-axis to cut Z-axis.
- ▶ Now OI is the line that passes through the origin and is parallel to EA whose indices are to be determined. The point I have coordinates x =1, y =0,z = -1 and thus the indices of line EA is [101] (Parallel lines have the same indices)

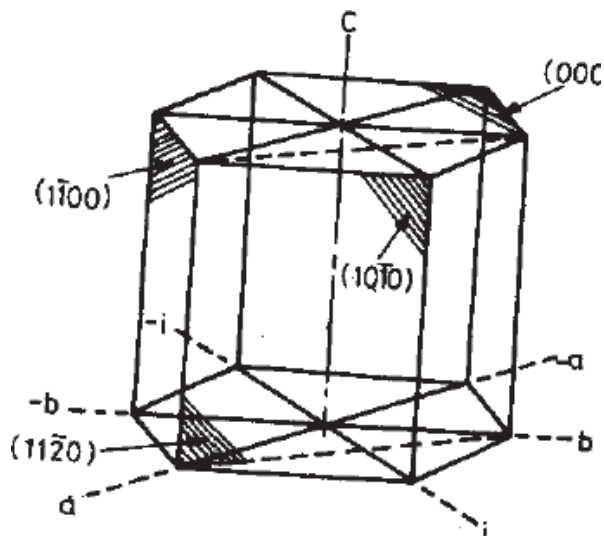
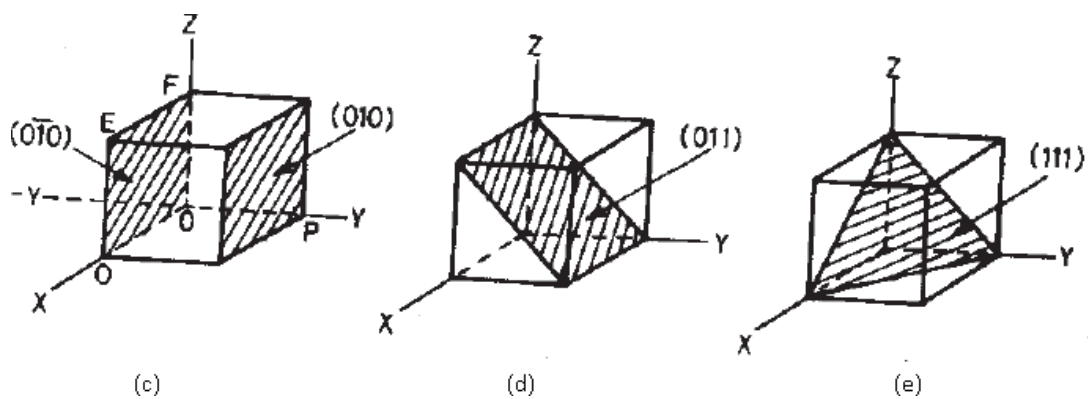
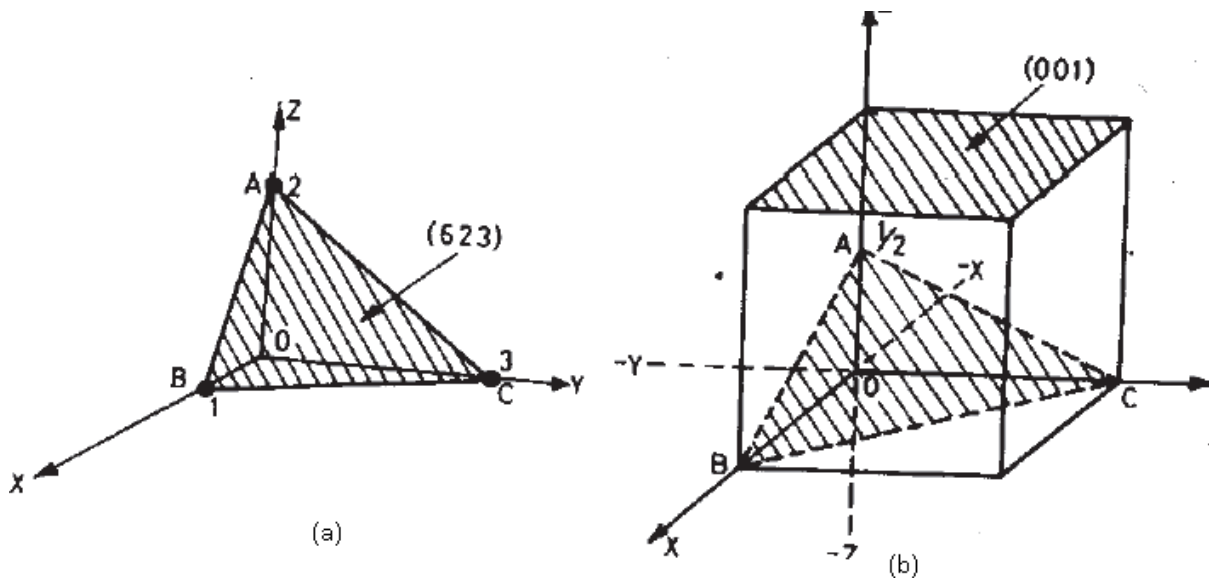


Fig.2.8 – (a) Miller Indices

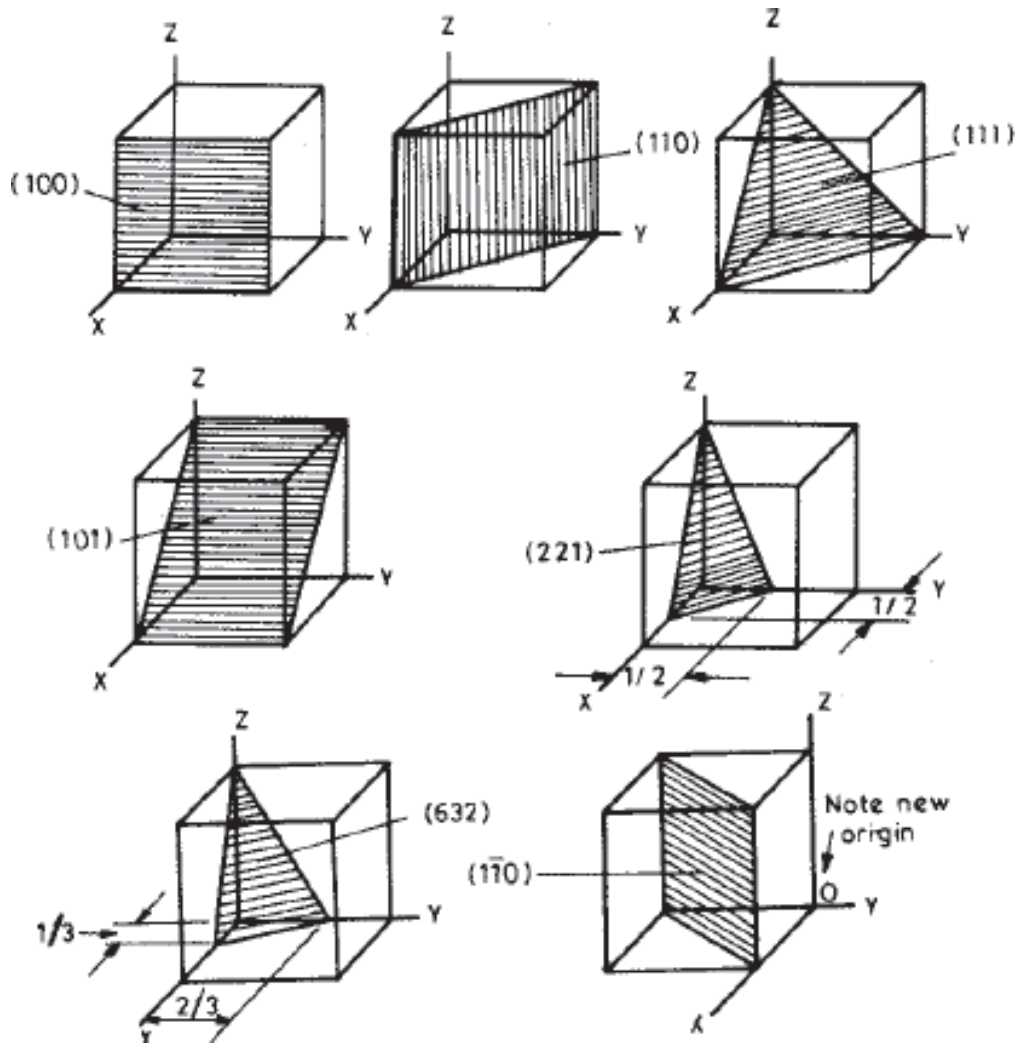


Fig.2.9 – (b) Miller Indices

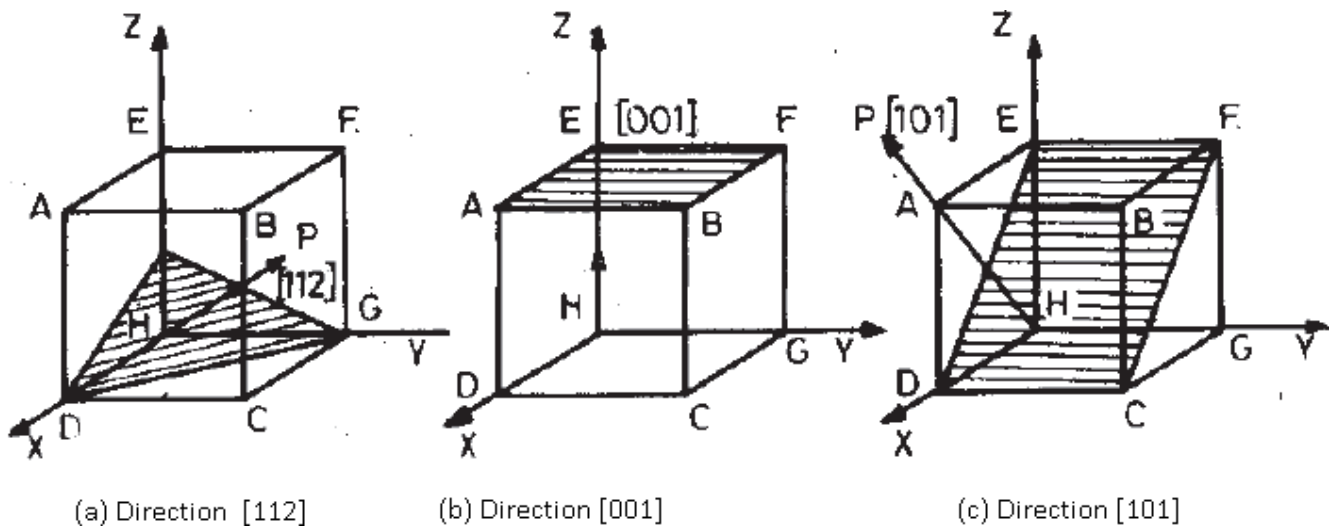


Fig.2.10 – (c) Miller Indices

## 2.7 Polymorphism and Allotropy

- The ability of the material to have more than one structure is called polymorphism.

- ▶ It is the behavior of material to show different crystal structures at a certain temperature or within a temperature range.
- ▶ The atomic arrangement may change according to change in temperature such a change in the crystal structure is called polymorphic change.
- ▶ If the change in the crystal structure is reversible then polymorphic change is known as allotropy.
- ▶ For example, iron ( $\alpha$ -Fe) is BCC at room temperature but it becomes FCC ( $\gamma$ -Fe) when heated to above 910°C.
- ▶ On further heating, to above 1400°C it revered to BCC ( $\delta$ -Fe)
- ▶ These changes are reversed on cooling hence iron changes its structure by allotropic change.

## 2.8 Diffusion in Solids

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- ▶ 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 processes play a crucial role in many solid-state phenomena and in the kinetics of microstructural changes during metallurgical processing and applications; typical examples include phase transformations, nucleation, recrystallization, oxidation, creep, sintering, ionic conductivity, and intermixing in thin-film devices.
- ▶ Direct technological uses of diffusion include solid electrolytes for advanced battery and fuel cell applications, the semiconductor chip and microcircuit fabrication and surface hardening of steels through carburization. The knowledge of the diffusion phenomenon is essential for the introduction of a very small concentration of an impurity in a solid-state device.

### Types of Diffusion

- i. Self Diffusion: It is the transition of a thermally excited atom from a site of the crystal lattice to an adjacent site or interstice.
- ii. Inter Diffusion: This is observed in binary metal alloys such as the Cu-Ni system.
- iii. Volume Diffusion: This type of diffusion is caused due to atomic movement in bulk in materials.
- iv. Grain Boundary Diffusion: This type of diffusion is caused due to atomic movement along the grain boundaries alone.
- v. Surface Diffusion: This type of diffusion is caused due to atomic movement along the surface of a phase.

### Diffusion Mechanism

- ▶ Diffusion is the transfer of unlike atoms which is accompanied by a change of concentration of the components in certain zones of an alloy. Various mechanisms have been proposed to explain the processes of diffusion. Almost all of these mechanisms are based on the vibrational energy of atoms in a solid.
- ▶ Direct interchange, cyclic, interstitial, vacancy, etc. are the common diffusion mechanisms. Actually, however, the most probable mechanism of diffusion is that in which the magnitude of energy barrier (activation energy) to be overcome by moving atoms is the lowest.
- ▶ Activation energy depends on the forces of interatomic bonds and crystal lattice defects which facilitate diffusion transfer (the activation energy at grain boundaries is only one half of that in the bulk of a grain). For metal atoms, the vacancy mechanism of diffusion is the most probable and for elements with a small atomic radius (H, N, and C), the interstitial mechanism. Now, we will study these mechanisms.
- ▶ Vacancy Mechanism: This mechanism is a very dominant process for diffusion in FCC, BCC and HCP metals and solid solution alloy. The activation energy for this process comprises the energy required to create a vacancy and that required to move it. In a pure solid, the diffusion by this mechanism is shown.
- ▶ Diffusion by the vacancy mechanism can occur by atoms moving into adjacent sites that are vacant. In a pure solid, during diffusion by this mechanism, the atoms surrounding the vacant site shift their

equilibrium positions to adjust for the change in a binding that accompanies the removal of a metal ion and its valency electron.

- ▶ We can assume that the vacancies move through the lattice and produce random shifts of atoms from one lattice position to another as a result of atom jumping. Concentration changes take place due to diffusion over a period of time. We must note that vacancies are continually being created and destroyed at the surface, grain boundaries and suitable interior positions, e.g. dislocations. Obviously, the rate of diffusion increases rapidly with increasing temperature.
- ▶ If a solid is composed of a single element, i.e. pure metal, the movement of a thermally excited atom from a site of the crystal lattice to an adjacent site or interstice is called self-diffusion because the moving atom and the solid are the same chemical-element.
- ▶ The self-diffusion in metals in which atoms of the metal itself migrate in a random fashion throughout the lattice occurs mainly through this mechanism. We know that copper and nickel are mutually soluble in all proportions in solid-state and form substitutional solid solutions, e.g., plating of nickel on copper excited atom from a site of the crystal lattice to an adjacent site or interstice is called self-diffusion because the moving atom and the solid are the same chemical-element. The self-diffusion in metals in which atoms of the metal itself migrate in a random fashion throughout the lattice occurs mainly through this mechanism.

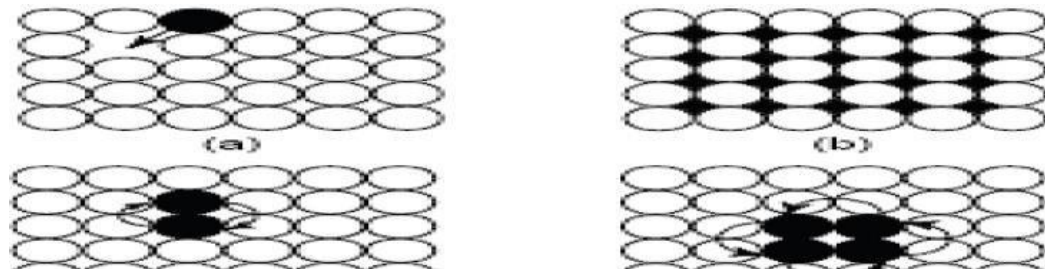


Fig.2.11 – Diffusion

## 2.9 Crystallization

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- ▶ Crystallization is the (natural or artificial) process of formation of which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. In chemical engineering, crystallization occurs in a crystallizer. Crystallization is, therefore, an aspect of precipitation, obtained through a variation of the solubility conditions of the solute in the solvent, as compared to precipitation due to chemical reaction.

## 2.10 Mechanism of Crystallization

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- ▶ The crystallization process consists of two major events, nucleation and crystal growth. Nucleation is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region), that become stable under the current operating conditions.
- ▶ These stable clusters constitute the nuclei. However, when the clusters are not stable, they dissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such critical size is dictated by the operating conditions (temperature, supersaturation, etc.). It is at the stage of nucleation that the atoms arranged in a defined and periodic manner that defines the crystal structure □ note that "crystal structure" is a special term that refers to the relative arrangement of the atoms, not the macroscopic properties of the crystal (size and shape), although those are a result of the internal crystal structure.
- ▶ The crystal growth is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation exists.

- ▶ Supersaturation is the driving force of the crystallization, hence the rate of nucleation and growth is driven by the existing supersaturation in the solution. Depending upon the conditions, either nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained (control of crystal size and shape constitutes one of the main challenges in industrial manufacturing, such as for pharmaceuticals).
- ▶ Once the supersaturation is exhausted, the solid-liquid system reaches equilibrium and the crystallization is complete unless the operating conditions are modified from equilibrium so as to supersaturate the solution again.
- ▶ Many compounds have the ability to crystallize with different crystal structures, a phenomenon called polymorphism. Each polymorph is, in fact, a different thermodynamic solid state and crystal polymorphs of the same compound exhibit different physical properties, such as dissolution rate, shape (angles between facets and facet growth rates), melting point, etc. For this reason, polymorphism is of major importance in the industrial manufacture of crystalline products.

## 2.11 Nucleation

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- ▶ It is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organization. Nucleation is typically defined to be the process that determines how long we have to wait before the new phase or self-organized structure, appears.
- ▶ Nucleation is often found to be very sensitive to impurities in the system. Because of this, it is often important to distinguish between heterogeneous nucleation and homogeneous nucleation. Heterogeneous nucleation occurs at nucleation sites on surfaces in the system. Homogeneous nucleation occurs away from a surface.
- ▶ Nucleation the initial process that occurs in the formation of a crystal from a solution, a liquid, or a vapor, in which a small number of ions, atoms, or molecules become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grows.
- ▶ Nucleation processes are classed as heterogeneous or homogeneous. In the former, the surface of some different substance, such as a dust particle or the wall of the container, acts as the center upon which the first atoms, ions, or molecules of the crystal become properly oriented; in the latter, a few particles come into correct position in the course of their random movement through the bulk of the medium.
- ▶ Heterogeneous nucleation is more common, but the homogeneous mechanism becomes more likely as the degree of supersaturation or supercooling increases. Substances differ widely in the likelihood that they will crystallize under conditions in which the crystalline state is the inherently stable one; glycerol is a well-known example of a compound prone to supercooling.

## 2.12 Crystal Growth

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- ▶ Once the first small crystal, the nucleus, forms acts as a convergence point (if unstable due to supersaturation) for molecules of solute touching or adjacent to the crystal so that it increases its own dimension in successive layers.
- ▶ The pattern of growth resembles the rings of an onion, as shown in the picture, where each color indicates the same mass of solute; this mass creates increasingly thin layers due to the increased surface area of the growing crystal.
- ▶ The supersaturated solute mass the original nucleus may capture in a time unit is called the growth rate and is a constant specific to the process. The growth rate is influenced by several physical factors, such as surface tension of the solution, pressure, temperature, relative crystal velocity in the solution, Reynolds number, and so forth.

### **The main values to control are, therefore**

- ▶ Supersaturation value, as an index of the quantity of solute available for the growth of the crystal.
- ▶ Total crystal surface in-unit fluid mass, as an index of the capability of the solute to fix onto the crystal.
- ▶ Retention time, as an index of the probability of a molecule of solute to come into contact with an existing crystal.
- ▶ Flow pattern, again as an index of the probability of a molecule of solute to come into contact with an existing crystal (higher in laminar flow, lower in turbulent flow, but the reverse applies to the probability of contact).
- ▶ The first value is a consequence of the physical characteristics of the solution, while the other define a difference between a well and poorly designed crystallizer.

## **2.13 Imperfection in Crystals**

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- ▶ For a crystalline solid we have tacitly assumed that perfect order exists throughout the material on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or imperfections.
- ▶ As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of meant a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to geometry or dimensionality of the defect.

### **Point Defects In Metals**

- ▶ The simplest of the point defects is a vacancy, or vacant lattice site, one normally occupied from which an atom is missing All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects.
- ▶ The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal.

## **2.14 References**

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Sidney H Avner ” Introduction to Physical metallurgy 2<sup>nd</sup> Edition 2011 Tata Mc Graw- Hill Publication.

O. P. Khanna “Material Science and Metallurgy” Dhanpat Rai Publications.

# CRYSTAL IMPERFECTIONS

## 3.1.a) CRYSTAL IMPERFECTIONS

In ideal crystal (perfect crystal) the atomic arrangement is perfectly regular and continuous thought.

But in real crystal due to some reasons the regular orientation of atoms may be disturbed at a point, along a line or in a region.

### Definition

*The disturbance occurred in the regular orientation of atoms is called crystal defect of imperfections.*

Some properties of crystal defects are structure sensitive i.e., properties such as mechanical strength, ductility, crystal growth, magnetic hysteresis, dielectric strength are greatly affected by relatively minor changes in crystal structure caused by imperfections.

Some other properties of crystals are structure-insensitive i.e. properties such as stiffness and density are not affected by the presence of imperfections.

### Classification of crystal imperfections (or) Defects

Crystalline imperfections are classified on the basis of their geometry as follows.

#### 1. Point Defects

- (a) Vacancies
- (b) Interstitials
- (c) Impurities

#### 2. Line Defects

- (a) Edge dislocations
- (b) Screw dislocations

#### 3. Surface Defects

- (a) Grain boundaries

- (b) Tilt boundaries
- (c) Twin boundaries
- (d) Stacking faults

#### **4. Volume Defects**

- (a) Cracks

### **1. Point Defects**

**Point defects are crystalline irregularities of atomic dimensions. They are imperfect points like regions in crystal. One or two atomic diameter is the typical size of point imperfection.**

Point defect takes place due to imperfect packing of atoms during crystallisation. They produced distortion in side the crystal structure.

#### **Types of Point Defects**

- (a) Vacancies
- (b) Interstitials
- (c) Impurities

#### **(a) Vacancy**

In crystallography, a vacancy is simplest a type of point defect in a crystal. A defect in which an atom is missing from one of the lattice sites is known as a "vacancy" defect.

Whenever one or more atoms are missing from a normally occupied position as shown in figure, the defect caused is known as vacancy.

The atoms surrounding the vacancies are displaced inward thereby distorting the regularity of arrangement. There are different kinds of vacancies like Frenkel defect, Schottky defect, Colour centre, etc.

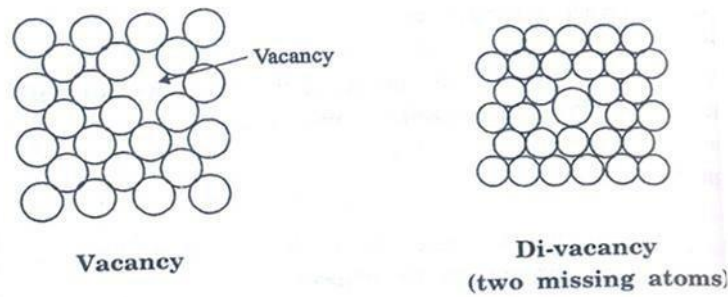


Fig:3.1.1 Vacancy

(i) **Schottky Defect**

It refers to the missing of pair of positive and negative ions in an ionic crystal.

A neutral defect that involves paired vacancies on the cation and anion sub lattices is called a **Schottky defect**.

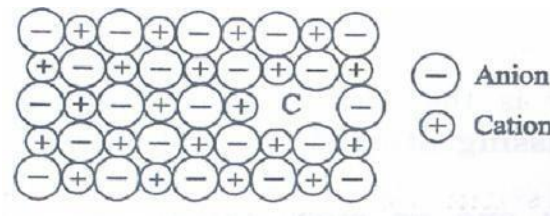


Fig 3.1.2 Schottky Defect

(ii) **Frankel Defects**

A vacancy associated with interstitial impurity is called Frenkel defect.

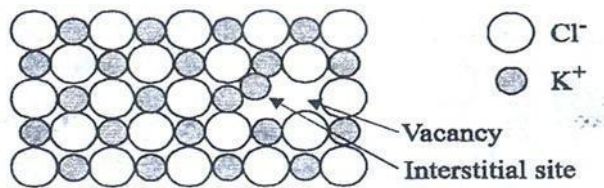


Fig 3.1.3 Frankel Defects

Here a missing atoms occupies interstitial position .This defect always occurs in ionic crystal, If a positive ion moves into an interstitial site in an ionic crystal, a cation vacancy is created in normal site, this *vacancy- interstitial* pair is known as **Frenkel defect**.

## (b) Interstitial Defect

When an extra atom occupies interstitial space within the crystal structure without removing the parent atom, the defect is called interstitial defect.

### Types of interstitial defect

#### (i) Self-interstitial

#### (ii) Foreign interstitial

#### (i) Self-interstitial

If an atom from the same crystal occupies an interstitial site, then it is called self-interstitial.

#### (ii) Foreign interstitial

If an impurity atom (foreign atom) occupies the interstitial position without replacing the parent atom, it is called foreign interstitial.

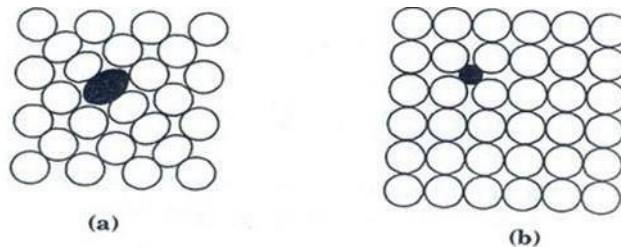


Fig 3.1.4 Foreign interstitial

- These can exist only in ionic and covalent crystals.
- Here the impurity atom has a very small size as that of the host atoms.

## (c) Impurities

When foreign atoms (impurities) are added to crystal lattices, they are known as impurities. The defect is called an impurity defect.

The impurity atoms may fit in the structure in two ways giving rise to two kinds of impurities defects. They are

- (i) Substitutional impurity defect
- (ii) Interstitial impurity defect

(i) **Substitutional Impurities**

A substitutional impurity refers to a foreign atom that replaces a parent atom in the Lattice.

Substitutional impurities changes the electrical properties enormously.

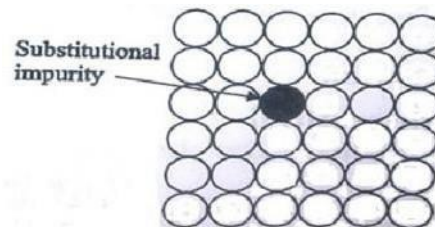


Fig 3.1.5- Substitutional impurities

**Example**

1. n-type and p-type semiconductor have substitutional impurities from V<sup>th</sup> group and III<sup>rd</sup> group elements. This is used to producing many electronic devices like diode and transistors.
2. During the production of brass alloy, zinc atoms are doped in copper lattice. Here zinc atoms are called as substitutional impurities.

## ii) Interstitial impurity defect



Fig 3.1.6- Interstitial impurity defect

An interstitial impurity is a small size atom occupying the empty space(interstitial) in the parent crystal, without dislodging any of the parent atoms from their sites.

An atom can enter into interstitial or empty space only when it is substantially smaller than parent atom.

### **Example**

In FCC iron, the atomic radius of iron atom is 0.225nm. The carbon atoms with atomic radius 0.078nm can occupy empty space in FCC lattice as interstitial impurities.

### **3.1.1 Line defect or dislocation: (one dimensional Effect)**

This defect due to dislocation or distortion of atoms along a line are known as

line defects.

In line defect, a portion of line of atoms is missing or displaced from its regular site.

### **Types of line defects**

There are two types of line defects

(a) Edge dislocation and

(b) Screw dislocations

#### **(a) Edge Dislocation**

An edge dislocation arises when one of the atomic planes forms only partially and does not extend through the entire crystal.

The atomic plane AB abruptly terminates at B. It is viewed as an extra plane inserted in between a set of parallel planes.

The edge of such a plane forms a line defect and it is called an edge dislocation.

The atomic row 1 passing through point B has one atom more than row 2 adjacent to it.

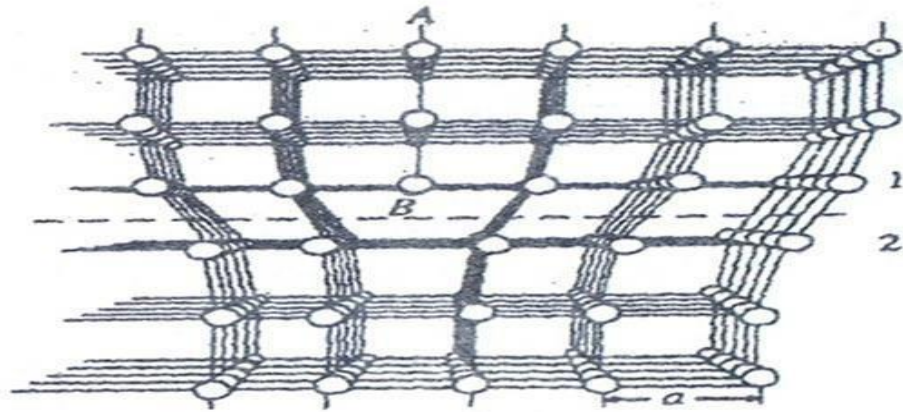


Fig 3.1.7- Edge Dislocation

### Classification of edge dislocation

Edge dislocations are symbolically represented by or depending on whether the incomplete plane starts from top or bottom of the crystal.

There are two configurations are referred as

- (i) Positive edge dislocation
- (ii) Negative edge dislocations

#### (i) Positive edge dislocation

If the extra plane of atoms is above the slip plane of the crystal than the edge dislocation is called positive as shown in figure. It is denoted by the symbol  $\perp$ .

#### (ii) Negative edge dislocations

If the extra plane of atoms is below the slip plane than the edge dislocation is called negative. It is denoted by the symbol  $\top$ .

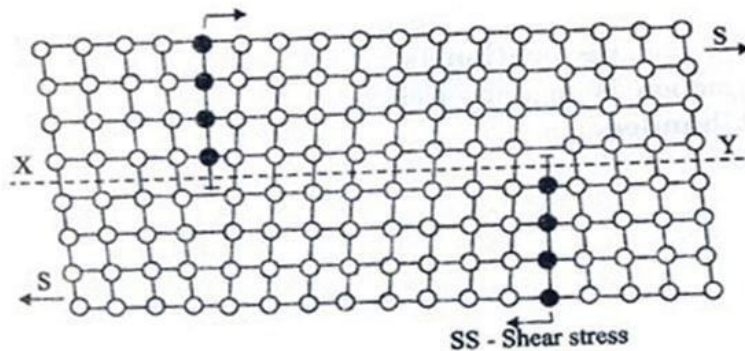


Fig 3.1.8- Negative edge dislocations

### (iii) Screw dislocations

**Screw dislocation is due to a displacement of atoms in one part of a crystal relative to rest of the crystal.**

The displacement terminates within crystal. This dislocation forms a spiral ramp around dislocation line.

In screw dislocation, the realignment of atoms about which crystal planes are warped to give an effect similar to threads of screw.

**The row of atoms marking the termination of the displacement is the screw dislocation. EF indicates the dislocation line**

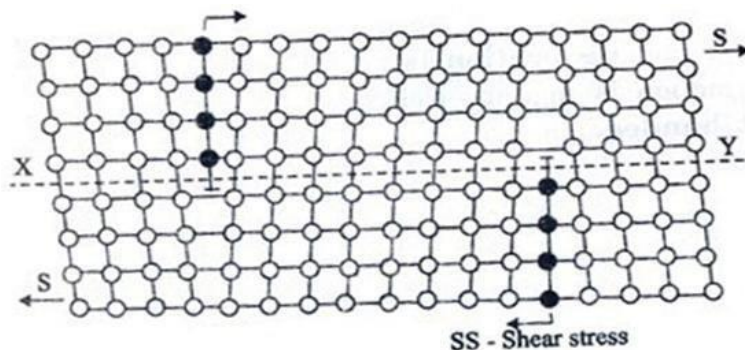


Fig 3.1.9- Screw dislocations

The term screw represents that one part of the crystal is moving in spiral

manner about dislocation line.

## BURGER'S VECTORS

The dislocation lines are expressed by a burger vector. It indicates the amount and direction of shift in lattice on slip plane. The figure shows a perfect crystal and crystal with a positive edge dislocation.

Consider a point starting from p in figure (b) which moves in particular direction as shown and it completes atomic distance in the form of a circuit called Burger circuit or burger loop.

If the same circuit is drawn starting from pin figure. Then the circuit would not complete, this is because of the presence of a dislocation.

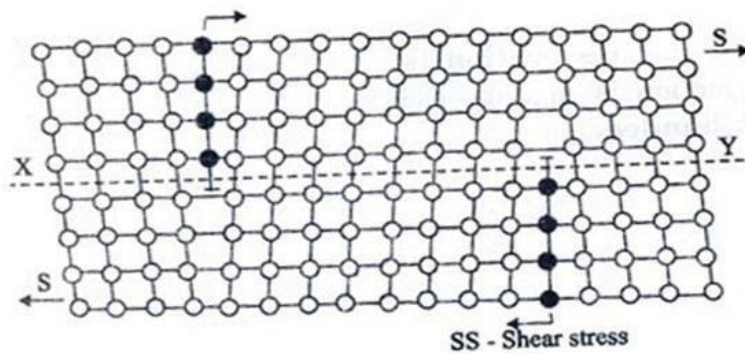


Fig 3.1.9- Burger's vectors

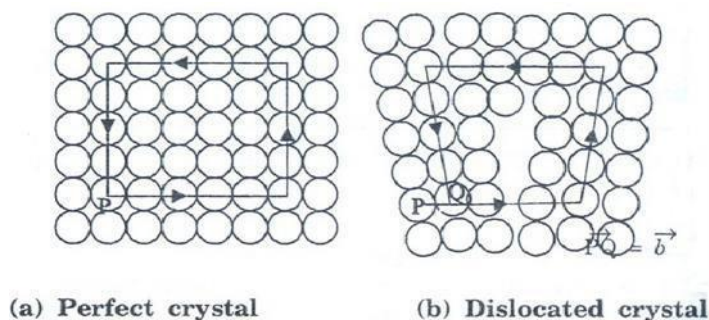


Fig 3.1.10 -a) Perfect Crystal and b) Dislocated Crystal

If we wish to arrive at starting point p from Q, then we must move an extra distance as shown in figure. The vector  $b+PQ$  connects end point with starting point. This is Burger's vector of the dislocation.

## **SURFACE DEFECTS(PLANE DEFECTS)**

**The defects on the surface of material are called as surface defect or plane defects.**

They are also known as two dimensional imperfections.

Surface defects are due to a change in the stacking of atomic planes on or across a boundary. Some important internal surface defects.

- (i) Grain boundaries
- (ii) Tilt and twist boundaries
- (iii) Twin boundaries
- (iv) Stacking fault
- (v) Grain boundaries

### **(i) Grain boundaries**

*Whenever the grains of different orientations separate the general pattern of atoms and exhibits a boundary the defect caused is called grain boundary.*

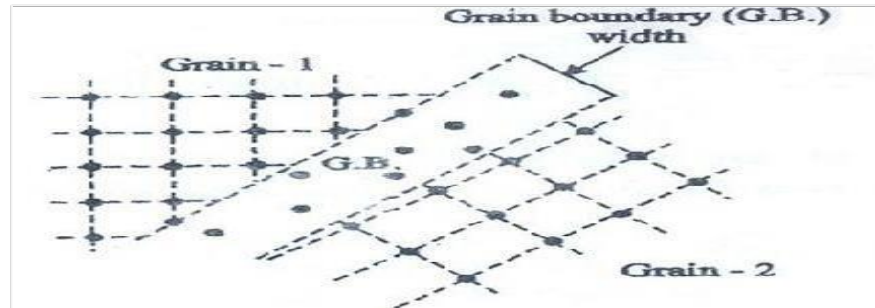


Fig 3.1.11- Grain boundaries

A grain boundary is formed when two growing grain surface meet. The shape of the grains is usually influenced by the presence of surrounding grains.

**(i) Tilt and twist boundaries**

Tilt boundary is another surface imperfection. It is an array of parallel edge dislocations of same sign (i.e. either) arranged one above other in an array or series.

Tilt boundary is a type of low angle boundary (less than 10°)

By rotation of an axis in the boundary, it is possible to bring the axis of two bordering grains into coincidence, then

Angle of tilt,  $\tan \theta = \frac{b}{D}$

D-dislocation spacing

b-length of Burger's vector

When angle very small, then  $\tan \theta = \theta$ ,

$$\theta = \frac{b}{D}$$

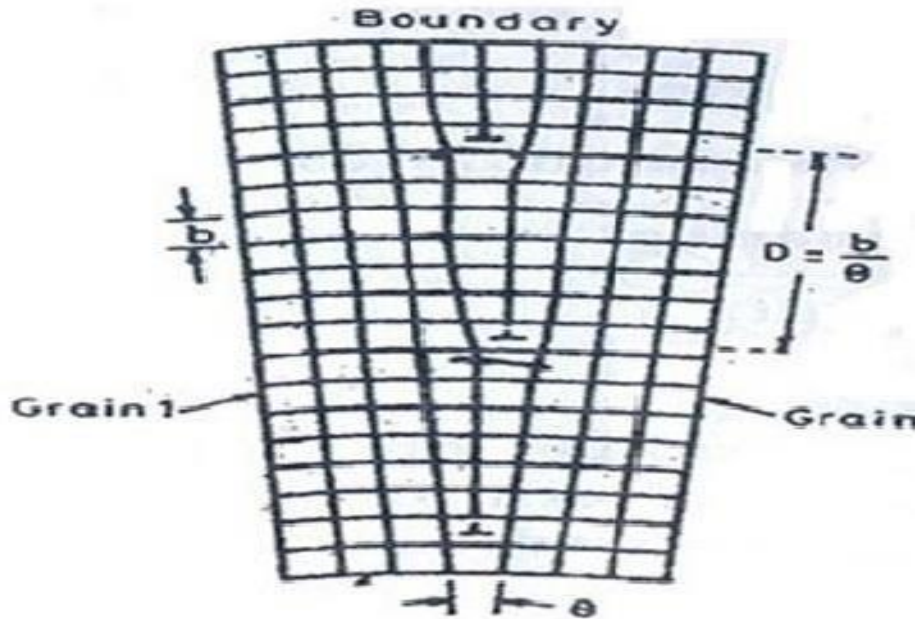


Fig 3.1.12- Tilt and twist boundaries

### **Twist boundaries**

**Twist boundaries are another type of low angle boundaries.** It consists of at least two sets of parallel screw dislocations lying in the boundary. In two boundaries, the rotation is about an axis normal to the boundary.

### **(ii) Twin boundaries**

#### **Twin boundaries are another surface imperfections**

If the boundary in which the atomic arrangement on one side of the boundary is somewhat a mirror image of the arrangement of atoms of the other side. This defect caused is called twin boundary.

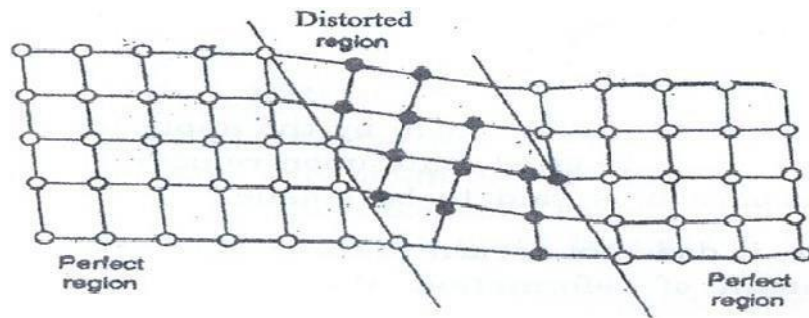


Fig 1.1.13- Twin boundaries

## STACKING FAULTS

It is the kind of surface imperfection. Whenever the stacking of atoms is not in proper sequence though the crystal, defect caused is called stacking effect.

### Explanation

Figure shows that the proper sequences of atomic plans if we read from bottom to top A-B-C-A-B-C-A-B-C.

But figure(b) shows the sequence of atomic planes as A-B-C-A-B-A-B-A-B-C

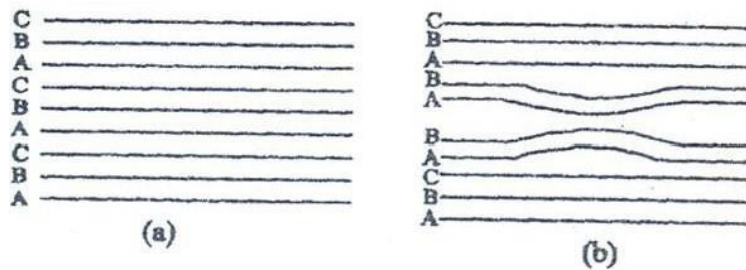


Fig:3.1.14 - stacking faults

The region in which the stacking fault occurs (A-B-A-B) forms a thin region of hexagonal close packing in FCC crystal.

### 3.1-b)ROLE OF IMPERFECTION IN PLASTIC DEFORMATION

#### Dislocation sand plastic deformation

Suppose a crystal is deformed by the application of stresses. Now it returns to its original state upon removal of the stresses, then the deformation is said to be elastic.

However, it does not return to its original state, i.e., retains a certain amount of deformation is said to be elastic.

It is generally believed that in most of the crystals the plastic deformation results from the slip of one part of the crystal relative to another.

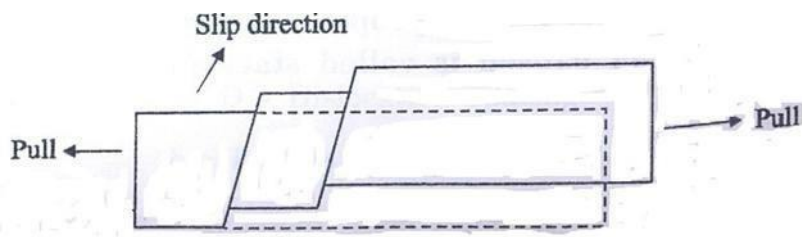


Fig:3.1.14 - Dislocation

If we confine ourselves with the plastic deformation which is composed of an increase in length only, then the figure is used to explain how such a process may lead to an increase in length of a crystal under the influence of tension.

Since slip is caused by the presence of dislocation, connections between plastic deformation and dislocations must obviously exist.

## 4.1 Introduction

---

- ▶ Phase diagrams, also known as Equilibrium Diagrams are a very important tool in the study of alloys.
- ▶ A phase diagram has temperature as its ordinate (Y-axis) & alloy composition as abscissa (X-axis).
- ▶ Ideally, the phase diagram will show the phase relationship under equilibrium conditions, in which there is no change with the time.
- ▶ Equilibrium conditions may be approached by extremely slow heating and cooling so that if a phase change is to occur, sufficient time is allowed.

## 4.2 Useful Terminology

---

- ▶ **System:** A system is a substance (or group of substances) so isolated from its surroundings that it is unaffected by these and is subjected to changes in the overall composition, temperature, pressure or total volume only to the extent allowed by the investigator.
- ▶ **Alloy System:** It is defined as a combination of two or more elements, forming alloys that are considered within a specified range of temperature, pressure, and concentration.
- ▶ **Component:** It is a unit of the composition variable of the system. A system having one component is called a Unary system and the system having two, three and four components are known as Binary, Ternary, and Quaternary systems, respectively.
- ▶ **Phase:** A phase can be defined as any part or portion of a chemical system that possesses distinctive physical characteristics, is limited by definite bonding surfaces, and may conceivably be mechanically separated from its surroundings.
- ▶ **Structural constituent:** The association of phases in a recognizably distinct fashion may be referred to as a structural constituent of the alloy.
- ▶ **Solid solution:** It consists of atoms of at least two different types where solute atoms occupy either substitutional or interstitial positions in the solvent lattice and the crystal structure of the solvent is maintained.
- ▶ **Solubility limit:** For almost alloy systems, at a specific temperature, a maximum of solute atoms can dissolve in the solvent phase to form a solid solution. The limit is known as the solubility limit. In general, solubility limit changes with temperature. If solute available is more than the solubility limit that may lead to the formation of different phases, either a solid solution or compound.
- ▶ **Phase equilibrium:** It refers to the set of conditions where more than one phase may exist. It can be reflected by the constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However, the state of equilibrium is never completely achieved because of the very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of the solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts, and their spatial arrangement or distribution.

## 4.3 Cooling Curves

---

- ▶ A method to determine the temperature at which phase changes (liquid $\rightleftharpoons$ solid) occur in an alloy system, consists of following the temperature as a function of time as different alloys in the system are very slowly cooled.

- ▶ The data obtained in this manner forms a cooling curve for each of the alloys. (Fig4.1)
- ▶ This method is useful in,
  - Studying the changes that occur during the solidification of alloys and also in determining transformations subsequent to solidification.

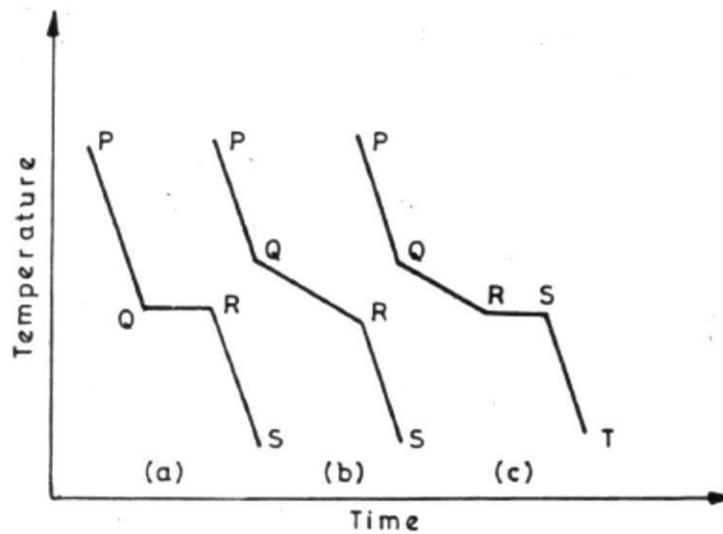


Fig.4.1 - Cooling curves for (a) Pure Metal or compound  
 (b) Binary solid solution  
 (c) Binary eutectic system

There are mainly three types of cooling curves.

**a. Cooling curve of pure metal or compound**

- ▶ The liquid metal cools from P to Q. First crystals begin to form at point Q.
- ▶ From Q to R, the melt liberates the latent heat of fusion in such amounts that the temperature from Q to R remains constant until the whole mass has entirely solidified (at point R). Between Q and R the mass is partly liquid and partly solid.
- ▶ On further cooling from R to S, the solid metal cools and tends to reach room temperature.
- ▶ The slopes of PQ and RS lines depend on the specific heats of liquid and solid metals respectively.

**b. Cooling curve of a binary solid solution**

- ▶ Curve portion PQ is similar no matter it is for a pure metal or for a binary system consisting of two metals forming a solid solution.
- ▶ However, in a binary system, during freezing (i.e.QR) period, the temperature does not remain constant, but it drops along line QR till the whole mass is solid at point R.
- ▶ The dropping trend of QR indicates that the alloy does not solidify at a constant temperature, but it possesses a freezing range which is due to the changes in the composition of the solid and liquid phases which naturally result in variable freezing (or melting) points.
- The solid cool along RS to attain the room temperature.

**c. Cooling curve of a binary eutectic system**

- ▶ In this system, the two components are completely soluble in the liquid state but entirely insoluble in solid-state.
- ▶ The liquid cools along PQ until the temperature Q is reached.
- ▶ At Q, one component that is in excess will crystalize and the temperature will drop along QR.

- ▶ At point R the liquid composition has been reached at which the two components crystallize simultaneously from the solution.
- ▶ The temperature remains constant until the whole mass is solid.
- ▶ Cooling from S to T is as usual.
- ▶ Fig 4.2 shows a series of cooling curves for different alloys in a completely soluble system (such as Cu-Ni system).
- ▶ The figure shows how a phase equilibrium diagram (shown dotted) can be constructed from the cooling curves of different alloys in the system.

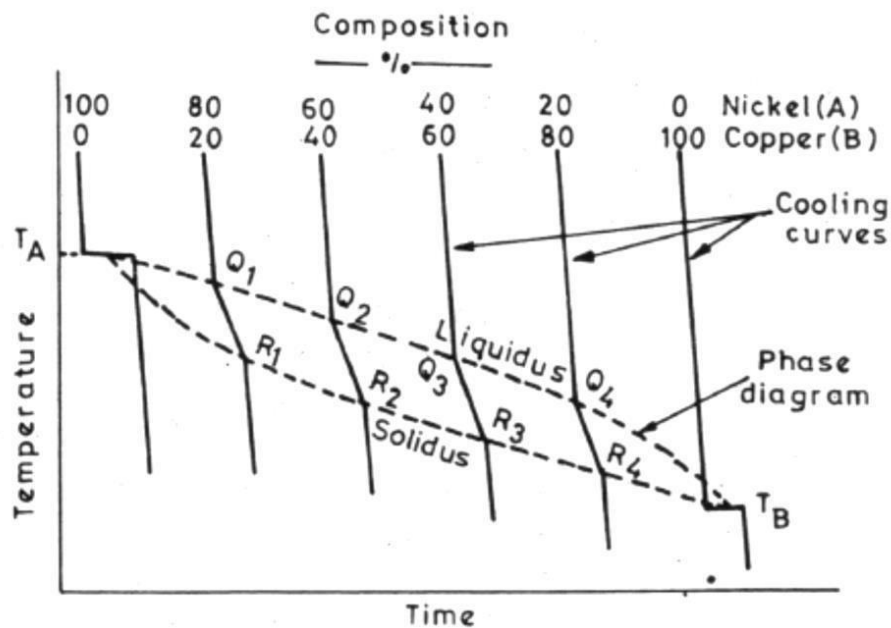


Fig.4.2 - Series of cooling curves giving rise to a phase diagram

## 4.4 Phase Diagram

- ▶ A huge amount of information concerning the phase changes in many alloys systems has been accumulated and the best way to record this data is in the form of the Phase diagram, which is also termed as Equilibrium diagram or Constitutional diagram.
- ▶ An equilibrium diagram shows the limits of composition and temperature within which the various constituents or phases of an alloy are stable.
- ▶ Changes of structure and the composition of the constituents in equilibrium at a fixed temperature can be determined from a phase diagram.
- ▶ If two metals of a binary solid solution (such as Cu-Ni) system are mixed in various proportions, melted and then cooled, and a cooling curve is constructed for each composition Fig .4.2 the resulting diagram obtain joining Q<sub>1</sub>, Q<sub>2</sub>, Q<sub>3</sub>...and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>...will be the phase diagram.
- ▶ Q<sub>1</sub>, Q<sub>2</sub>, Q<sub>3</sub>... is the temperature at which solidification completed.
- ▶ This phase diagram shows two different and distinct phases; one is a liquid metal solution and the other is a solid solution.
- ▶ Within these two phases or within liquidus and solidus, the two phases i.e., liquid and solid exist together, which can be mechanically separated by decantation of the liquid phase.

- ▶ Liquidus is the line above which the alloy is in a liquid state and from where the solidification starts.
- ▶ Solidus is that line below which the alloy is in solid-state and where solidification completes.
- ▶ If in a phase diagram adequate time is provided to attain equilibrium conditions, if equilibrium conditions are not achieved then the non –equilibrium solidification results in porous, dendritic material.

## 4.5 Interpretation of Phase Diagram

### Rule-1: Prediction of Phases

- ▶ From a phase diagram, specific information can be obtained only if temperature and composition are specified.
- ▶ For example, the state of the alloy of composition 30% Bismuth can be determined only with reference to a certain temperature. Thus when this alloy is at 1200 °F, point
- ▶ It is located (Fig 5.3) and when it is at 900°F and 600°F, points 2 and 3 are located respectively.
- ▶ The next step is to determine the phase or phases present at points numbers 1, 2, and 3.
- ▶ Point-1: With 30% Bi 70% Sb alloy at 1200°F, the only liquid phase is present.
- ▶ Point-2: With the same alloy but at 900°F, two phases are present, i.e. Liquid solution and Solid solution.
- ▶ Point-3: With the same alloy, but at 600°F, only one phase, i.e. the solid solution is present.
- ▶ A similar analysis can be made for any other alloy composition and temperature in the phase diagram.

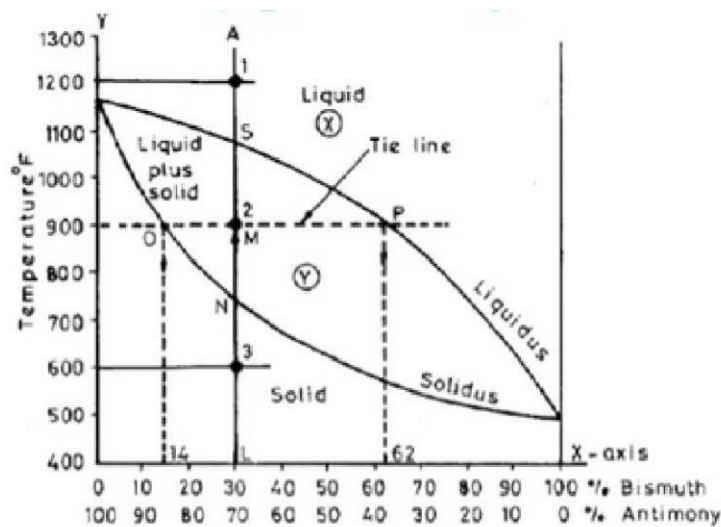


Fig.4.3 - Interpretation of phase diagram (Sb – Bi)

### Rule 2: Phase Composition

- ▶ To find out the composition of phases which are stable at a given temperature (say 900°F, Fig 4.4), draw a horizontal (isothermal) line, OP at the given temperature.
- ▶ The projections upon the X-axis of the intersections (i.e. O & P) of the isothermally with the solidus and liquidus respectively, give the compositions of the solid and liquid, which co-exist in equilibrium at that temperature.

For Example,

- ▶ The liquid phase (point P) has a composition of roughly 62% Bismuth.
- ▶ Solid-phase (point O) has the composition roughly 14% Bismuth.

### Rule 3: Lever Arm Principle

- ▶ Besides indicating the number of phases and phase composition, the phase diagram also tells the proportion of co-existing phases at any given temperature.
- ▶ To determine the relative amount of two phases, erect an ordinate at a point (say 30% Bi) on the composition scale which gives the total or overall composition of the alloy.
- ▶ The intersection of this composition vertical (AL) and a given isothermal line OP (i.e. point M) is the fulcrum of a simple lever system and OM and MP are lever arms,(fig 4.4).
- ▶ This is called as the lever rule because the amount of a given phase multiplied by its lever arm is equal to the amount of the other phase multiplied by its (i.e. other) lever arm.
- ▶ The lever rule or principle may be expressed mathematically as:

- ▶ The amount of solid phase,

$$\frac{MP}{OP} \times 100 = \frac{(62-30)}{(62-14)} \times 100 = 62.67\%$$

- ▶ The amount of liquid phase,

$$\frac{OM}{OP} \times 100 = \frac{(30-14)}{(62-14)} \times 100 = 33.33\%$$

## 4.6 Gibbs Phase Rule

---

- ▶ Phase rule, known as Gibbs Phase Rule, establishes the relationship between the number of degrees of freedom (F), the number of components (C), and the number of phases (P).
- ▶ It is expressed mathematically as follows:

$$\mathbf{P + F = C + 2}$$

Where

P = Number of Phases (e.g. solid, liquid etc.)

F = Number of a degree of freedom or the number of physical variables (pressure, temperature, concentration) that can be independently changed without altering the equilibrium, i.e., without causing the disappearance of a phase or the formation of new phase in the system.

C = number of components in the system; for example, Pb and Sn are the components of the Pb and Sn equilibrium diagram (fig 5.7).

- ▶ In metallurgical systems where pressure is regarded as remaining fixed at one atmosphere, the pressure variable is often omitted and the equation is simplified in to,

$$\mathbf{P + F = C + 1}$$
$$\mathbf{F = C + 1 - P}$$

- ▶ Since the degree of freedom cannot be less than zero,
- ▶ So,  $C + 1 - P \geq 0$ , or  $P \leq C + 1$
- ▶ This means the number of Phases (P) in a system cannot exceed the number of components plus one.
- ▶ Therefore in a Binary system having value  $C=2$ , not more than  $2+1=3$  phases may be in equilibrium.

- ▶ Considering the figure 5.4, it is required to determine the number of degrees of freedom using the phase rule.
  1. Point X, in the region above the liquidus  
 Number of components  $C=2$ , since it is a binary system of Bi and Sb,  
 Number of phases  $P=1$ (liquid)  
 Applying the rule,  $F = C + 2 - P$   

$$= 2+2-1$$
  

$$= 3 \text{ degrees of freedom}$$
  2. Point Y, between the liquidus and solidus  
 Number of components  $C=2$   
 Number of phases  $P=2$ (liquid and solid)  
 Applying the rule,  $F = C + 2 - P$   

$$=2+2-1$$
  

$$=2 \text{ degrees of freedom}$$

## 4.7 Classification of Equilibrium Diagrams

---

- ▶ An equilibrium diagram has been defined as a plot of the composition of phases as a function of temperature in any alloy system under equilibrium conditions.
- ▶ Equilibrium diagram may be classified according to the relation of the components in the liquid and solid states as follows:
  1. Components completely soluble in the liquid state,
    - a. and also completely soluble in the solid state,
    - b. but partially soluble in the solid-state (eutectic reaction)
    - c. but insoluble in the solid-state(eutectic reaction)
    - d. The peritectic Reaction
  2. Components partially soluble in the liquid state,
    - a. but completely soluble in the solid-state,
    - b. And partly soluble in the solid-state.
  3. Components are completely insoluble in a liquid state and completely insoluble in the solid-state.

## 4.8 Two Metals Completely Soluble In the Liquid and Solid-State

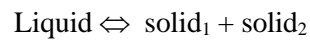
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### Solid States

- ▶ A system that illustrates an equilibrium diagram in which there is complete solubility in the liquid and solid states is that of Antimony – Bismuth system shown in figure 4.4.
- ▶ Since the two metals are completely soluble in the solid-state, the only type of solid solution formed will be a substitutional solid solution.
- ▶ Actually, the solidification of a liquid alloy of this type consists of two processes :
  - i. a. Formation of crystals in the melt (at say point S),  
 b. Growth of crystals (just as at point M).
  - ii. Homogenization of the composition in various parts of each crystal:
    - a. By diffusion between core and encasement.
    - b. By diffusion between core and melt.

## 4.9 Eutectic System

- ▶ In a eutectic reaction, when a liquid solution of fixed composition, solidifies at a constant temperature, forms a mixture of two or solid-phase without an intermediate pasty stage. This process reverses on heating.



- ▶ In the eutectic system, there is always a specific alloy, known as eutectic composition (fig 4.4), that freezes at a lower temperature than all other compositions.
- ▶ Under conditions approaching equilibrium (slow cooling), it (specific alloy) freezes at a single temperature like pure metal.
- ▶ In other respects, the solidification reaction of this composition is quite different from that of a pure metal since it freezes to form a mixture of two different solid phases.
- ▶ At the eutectic temperature, two solids form simultaneously from a single liquid phase.
- ▶ The eutectic temperature and composition determine a point on the phase diagram called a eutectic point.

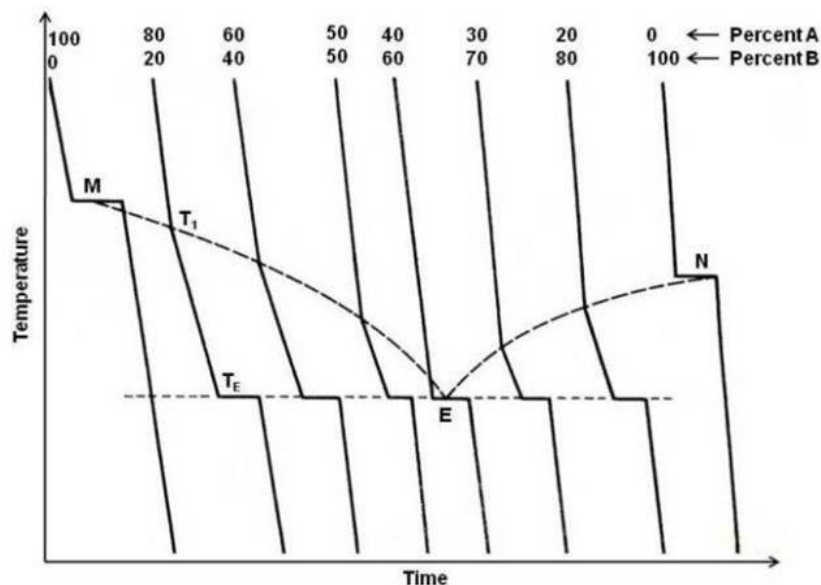


Fig.4.4 - Cooling curves for two metals insoluble in solid-state

- ▶ Binary alloy eutectic system can be classified as:
  - One in which, two metals are completely soluble in the liquid state but are insoluble in each other in solid-state.
  - The other in which, two metals are completely soluble in the liquid state but are partly soluble in each other in the solid-state.
- a. Two metals are completely soluble in the liquid state but completely insoluble in the solid-state.**
  - ▶ Technically, no two metals are completely insoluble in each other. However, in some cases the solubility is so restricted that for practical purposes they may be considered insoluble, e.g. Tin – Zinc or Bismuth – Cadmium.
  - ▶ Fig 5.5 shows cooling curves for a series of two metals that are insoluble in the solid-state such as Bismuth and Cadmium. The figure also shows, how by joining a1b1, a1b2... the point, the equilibrium diagram for such a system can be obtained.

- ▶ To explain this type of system it is necessary to consider the cooling and solidification of three compositions 1, 2 and 3.(fig 4.5)

**Alloy-1:** 20% Cd and 80% Bi

- ▶ Contrary to alloy 3, in this case, a crystal of pure Bi form first, enriching the melt with Cd.
- ▶ The composition of the melt (or liquid) moves to the right until ultimately the point E is reached and the remaining liquid solidifies as eutectic (40% Cd and 60% Bi).

**Alloy-2:** 40% Cd and 60% Bi (Eutectic alloy)

- ▶ No solidification occurs until the melt reaches the eutectic temperature (140°C)
- ▶ At the eutectic temperature, the two pure metals crystallize together to give a characteristically fine aggregate [Fig. 4.5 (C)] known as a eutectic.
- ▶ Eutectic consists of alternate layers of Cd and Bi which form at the eutectic temperature (140°C in this case).

**Alloy-3:** 80% Cd and 20% Bismuth.

- ▶ As the temperature falls to T1, crystal nuclei of pure Cd begin to form. Since pure Cd is deposited, it follows that the liquid becomes richer in Bi; the composition of liquid moves to left 3 and as indicated by the diagram, no further Cd deposits until the temperature falls to T2.
- ▶ At T2 more Cd is deposited and dendrites begin to develop from the already formed nuclei (Fig. 4.5 (D)).
- ▶ The growth of the Cd dendrites, on the one hand, and the consequent enrichment of the remaining liquid in Bi, on the other, continues until the temperature has fallen to 140°C, the eutectic temperature in this case.
- ▶ The remaining liquid then contains 40% Cd and 60% Bi, the eutectic composition.

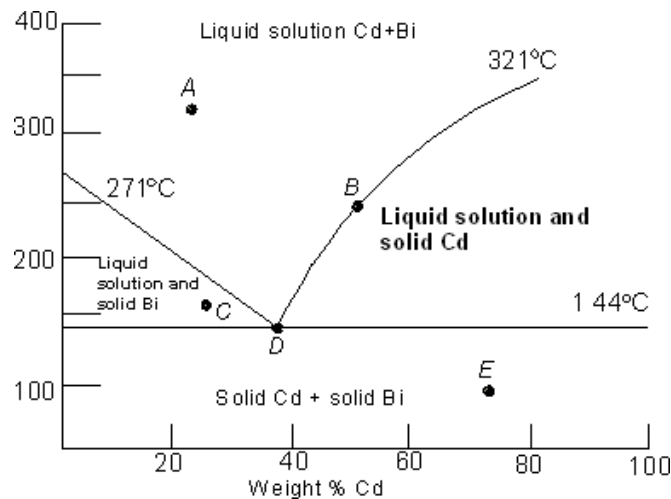


Fig.4.5 - The Bismuth – Cadmium Equilibrium Diagram

#### 4.10 Two Metals Completely Soluble In The Liquid State, But Only Partly Soluble In The Solid-State

- ▶ Since most metals show some solubility for each other in the solid-state, this type is the most common and, therefore, the most common alloy system.
- ▶ Metals such as Pb-Sn and Pb-Sb are partly soluble in each other in the solid-state.

- ▶ Fig. 4.6 shows the Tin-Lead equilibrium diagram with microstructure obtained under the non-equilibrium condition of solidification.
- ▶ The figure shows that:
  - ▶ (i) The tin will dissolve up to a maximum of 2.6% Pb at the eutectic temperature, forming the solid solution  $\alpha$ .
  - ▶ (ii) The lead will dissolve up to a maximum of 19.5% at the eutectic temperature, giving the solid solution  $\beta$ .
  - ▶ (iii) The slope of AB and CD indicates that the solubility of Pb into sn( $\alpha$ ) and that of sn into Pb( $\beta$ ) decrease as the temperature falls.
- ▶ Consider an alloy of composition Z (70%Pb – 30%Sn). As the melt temperature falls to T<sub>1</sub>, dendrites of composition Y will deposit.
- ▶ The alloy solidifies as a solid solution until at 183° C, the last layer of solid to form is of composition C (80.5% Pb – 19.5% Sn).

## 4.11 Peritectic Reaction

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- ▶ It is the reaction that occurs during the solidification of some alloys where the liquid phase reacts with a solid phase to give a solid phase of different structures.
- ▶ The reaction reverses on melting.
 
$$\text{Liquid } 1 + \text{Solid } 1 \xrightleftharpoons[\text{Temperature}]{\text{Constant}} \text{Solid } 2$$
- ▶ Like solid solution formation and eutectic reaction, the peritectic reaction is also a mechanism of solidification shown by various metal systems, but it is comparatively less common.
- ▶ A peritectic reaction is, actually, just the opposite of the eutectic reaction.
- ▶ Refer to Fig. 4.6 showing the peritectic reaction.
- ▶ Assuming very slow rates of cooling, the peritectic reaction will occur only in those Pt-Ag alloys that contain between 12 and 69% silver (Ag).
- ▶ Consider a liquid (melt) of composition Z, i.e., containing 25% Ag. Solidification
- ▶ commence at T<sub>1</sub> and dendrites of  $\alpha$ , initially of composition W, being forming
- ▶ Selective crystallization of  $\alpha$  continues down to T<sub>p</sub>, the peritectic temperature; when the alloys reach this temperature, it is composed of solid  $\alpha$ -dendrites of composition B and liquid of composition D in the proportion  $\alpha$ : liquid = RD: RB.

$$\frac{\text{Weight of } \alpha \text{ (composition B)}}{\text{Weight of } \delta \text{ (composition C)}} = \frac{RC}{BR}$$

- ▶ Consider another alloy Y.
- ▶ The first stage in the solidification of alloy Y is the same as in alloy Z: solidification begins at T<sub>2</sub> and when the peritectic is reached, the alloy consists, similarly, of dendrites of  $\alpha$ , of composition B and liquid of composition D, but in the proportions,  $\alpha$ : liquid = Y<sub>1</sub>D: Y<sub>1</sub>B

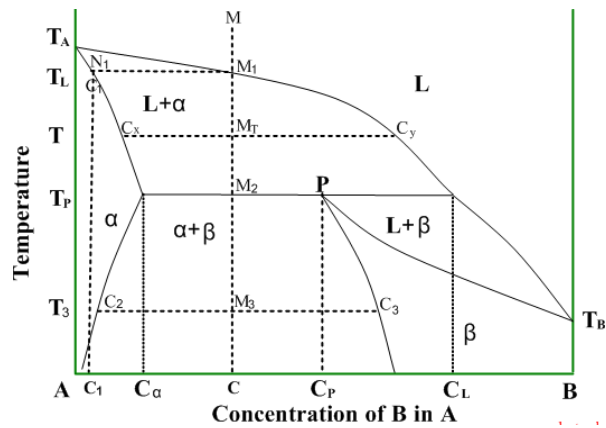
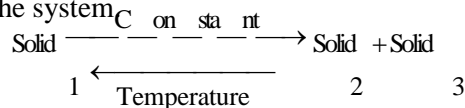


Fig.4.6 - Peritectic Reaction

- ▶ At peritectic temperature all the  $\alpha$  reacts with some of the liquid to form  $\delta$  of composition C, the proportion of  $\delta$  to remaining liquid is  $Y_1D: Y_1C$ .
- ▶ After the peritectic reaction has occurred, the temperature falls and the remaining liquid tends to solidify as  $\delta$  which changes in composition along  $CY_2$ . At  $Y_2$  solidification will be completed and the structure will consist of crystal of uniform  $\delta$  (of the same composition as that of the original liquid).
- ▶ In actual practice, fast cooling tends to produce heterogeneous grains and may cause some  $\alpha$  to be retained in the center of the ( $\delta$ ) grains.

## 4.12 Eutectoid Transformation (Reaction)

- ▶ Unlike Eutectic or Peritectic transformations which are liquid-solid transformations, Eutectoid involves a solid-solid transformation.
- ▶ Eutectoid reaction is an isothermal reversible reaction in which a solid phase (usually a solid solution) is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system



- ▶ Eutectoid point: The point in the equilibrium diagram indicating the composition of the eutectoid and its temperature of transformation.
- ▶ Eutectoid structure: The structure, frequently lamellar, produced by the simultaneous precipitation of the components of the eutectoid from the solid solution.
- ▶ Eutectoid reaction is found in many systems such as Cu-Al, Cu-Zn, Al-Mn, Cu-Be, etc.
- ▶ Fig. 4.7 shows an eutectoid-diagram.
- ▶ Consider the alloy-1 As it is slowly cooled by  $y$  solid solutions formed when the liquidus line cross at  $Y_1$ . More and more  $y$  is formed until the solidus line is cross at  $Y_2$ . it remains a uniform solid solution until the solvents line cross at  $Y_3$ . The pure metal A must now be started to undergo an allotropic change, forming the  $\alpha$  solid solution.
- ▶ The composition of  $y$  is gradually moving down and along the line ME;  $y$  solution becomes richer in metal B.
- ▶ When alloy reaches the eutectoid temperature  $T_e$ , the reaches eutectoid point E.

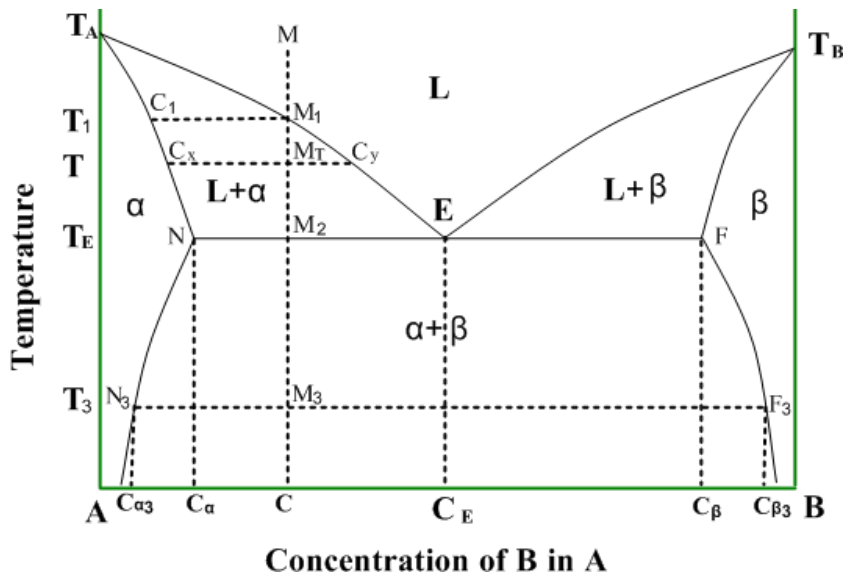
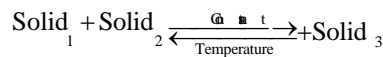


Fig.4.7 - Eutectoid diagram

- ▶ The microstructure at room temperature consists of primary  $\alpha$  of pro eutectoid  $\alpha$  which was formed between  $Y_3$  and  $Y_4$  surrounded by the eutectoid mixture of  $\alpha + \beta$ .

### 4.13 Peritectoid Transformation (Reaction)

- ▶ The peritectoid reaction is the transformation of two solids into a third solid.
- ▶ It is an isothermal reversible reaction in which a solid phase reacts with a second solid phase to produce yet a third solid phase on cooling.



- ▶ Fig. 4.8 shows a Peritectoid Diagram, which can be explained on lines similar to those for the eutectoid diagram (Refer section 4.12).
- ▶ L is the liquid phase.
- ▶  $\gamma$ ,  $\alpha$  and  $\beta$  are solid phases.
- ▶ A and B are two metals.
- ▶  $E_p$  is the peritectoid point.
- ▶  $T_p$  is the peritectoid temperature.

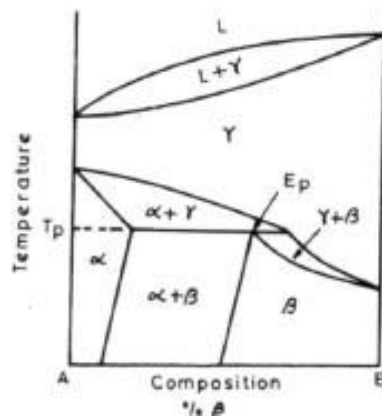


Fig.4.8 - Peritectoid diagram

## 4.14 Types of Solid Solutions

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Solid solutions occur in either of two distinct types, namely

Substitutional solid solution

1. Disordered
  2. Ordered
  3. Interstitial solid solution.
- ▶ **Substitutional Solid Solution:** In substitutional solid solution, there is a direct substitution of one type of atom for another so that solute atoms (Cu) enter the crystal to take positions normally occupied by solvent atoms (e.g., nickel atoms); In other words, in substitutional solid solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent. Substitutional solid solution forms when the solute and solvent atoms possess equal or approximately equal (within  $\pm 7.5\%$ ) diameters; for example, an atomic diameter of copper is  $2.551 \text{ \AA}$  and that of nickel is  $2.487 \text{ \AA}$ , and the two (i.e., Cu and Ni) form a substitutional solid solution. The great majority of the solid solutions are of a substitutional type.
  - ▶ **Disordered Substitutional Solid Solution:** In the formation of a substitutional solid solution the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. This alloy is said to be in a disordered condition. In the disordered condition, the concentration of solute atoms can vary considerably throughout the lattice structure.
  - ▶ When a disordered substitutional solid solution crystallizes from the melt, there is a natural tendency for the core of the dendrite to contain rather more atoms of the metal with a higher melting point, whilst the outer fringes of the crystal will contain correspondingly more atoms of the metal of the lower melting point.
  - ▶ Ordered substitutional solid solution: The alloy in the disordered condition, if it is cooled slowly, undergoes a rearrangement of the atoms because of the diffusion that takes place during cooling. Diffusion tends to produce a uniform distribution of solute and solvent atoms. The solute atoms move into definite orderly positions in the lattice.
  - ▶ This structure is now known as ordered substitutional solid solution or superlattice. Prolonged annealing tends to produce still more uniform and ordered solid solution. Cu- Zn, Au-Cu, Cu<sub>2</sub>MnAl are some examples of ordered structures.
  - ▶ **Interstitial Solid Solution:** Interstitial solid solution forms when solute atoms are very small as compared to the solvent atoms, they are unable to substitute solvent
  - ▶ atoms (because of the large difference in diameters of solvent and solute atoms) and can only fit into the interstices or spaces in the crystal lattice of solvent atoms
  - ▶ Those atoms which have atomic radii less than 1 angstrom ( $1 \text{ \AA}$ ) are likely to form interstitial, solid solutions. Such atoms are carbon ( $0.77 \text{ \AA}$ ), nitrogen ( $0.71 \text{ \AA}$ ), hydrogen ( $0.46 \text{ \AA}$ ), oxygen ( $0.6 \text{ \AA}$ ), etc. Actually, atomic size is not the only factor that determines whether or not an interstitial solid solution will form.
  - ▶ Small interstitial solute atoms dissolve much more readily in transition metals (such as Fe, Ni, Mn, Mo, Cr, W, etc.) than in other metals. Carbon forms an interstitial solid solution with F.C.C. iron during the solidification of steel but it can also be absorbed by solid iron provided the latter is heated to a temperature at which the structure is F.C.C. This is the basis of carburizing steels. Nitrogen also dissolves interstitially in solid steel, during the nitriding process.

## 4.15 Factors Governing Substitutional Solubility (Hume-Rothery Law)

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Several factors are now known, largely through the work of Hume-Rothery that controls the range of solubility in alloy systems. The different rules or factors are:

### 1. Crystal Structure Factor

- ▶ The crystal lattice structure of the two (metal) elements should be the same (i.e., both should be of b.c.c., f.c.c., or h.c.p. structure) for complete solubility, otherwise the two solutions would not merge into each other. Also, for complete solid solubility, the size factor must usually be less than 8%.

### 2. Relative Size Factor

- ▶ If two metals are to exhibit extensive solid solubility in each other it is essential that their atomic diameters shall be fairly similar, since it is essential that their atomic diameters shall be fairly similar, since atoms differing greatly in size cannot be accommodated readily in the same structure (as a substitutional solid solution) without producing excessive strain and corresponding instability. This is what is referred to when the term size-factor is employed and extensive solid solubility is encountered only when the two different atoms differ in size by less than 15%, called a favorable size factor (e.g., Cu-Ni). If the relative size factor is between 8% and 15%, the alloy system usually shows a minimum and if this factor is greater than 15%, substitutional solid solution formation is very limited.

### 3. Chemical-affinity Factor

- ▶ The greater the chemical affinity of two metals, the more restricted is their solid solubility. When their chemical affinity is great, two metals tend to form an intermediate phase rather than a solid solution. Generally, the farther apart the elements are in the periodic table, the greater is their chemical affinity.

### 4. Relative Valence (Valency) Factor

- ▶ Consider two atoms, one with large valence electrons and the other with a small number of valence electrons. It has been found that the metal of high valence can dissolve only a small amount of a lower valence metal, while the lower valence metal may have good solubility for the higher valence metal. For example, in the Al-Ni alloy system, both metals have f.c.c. structure. The relative size factor is approximately 14%. However; Ni is lower in valence than Al and thus solid nickel dissolves 5% aluminum, but the higher valence Al dissolves only 0.04% Ni.

## 4.16 References

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Sidney H Avner " Introduction to Physical metallurgy 2nd Edition 2011 Tata Mc Graw- Hill Publication.

O. P. Khanna "Material Science and Metallurgy" Dhanpat Rai Publications.

## 5.1 Allotropy of Iron

- ▶ The metal iron is a primary constituent of some of the most important engineering alloys.
- ▶ In an almost pure form, known as “ingot iron” it is used for drainage culverts, roofing, and ducts, and as a base for porcelain enamel in refrigerator cabinets, stoves, washing machines, etc

Carbon	: 0.012%	Tensile strength	: 40000 PSI
Manganese	: 0.017%	Elongation in 2 inch	: 40%
Phosphorous	: 0.005%	Hardness	: 30 HRB
Sulphur	: 0.025%		
Silicon	: Trace		

- ▶ Iron is an „allotropy metal“ which means that it can exist in more than one type of lattice structure depending upon temperature.

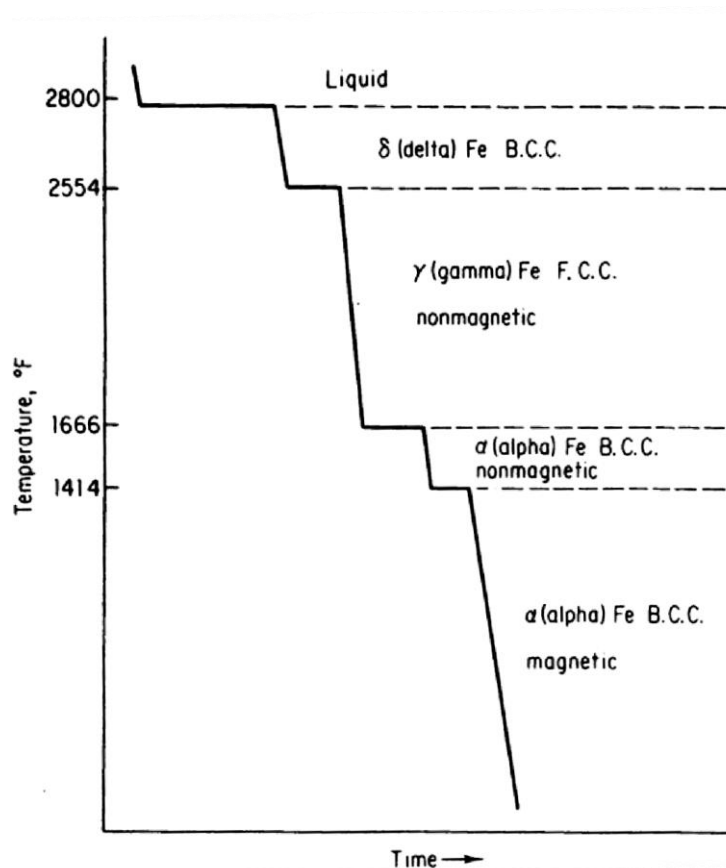


Fig.5.1 – Cooling curve for pure iron.

- ▶ When iron first solidifies at 2800°F, it is in the B.C.C.  $\delta$  (delta) form. Upon further cooling at 2554°F a phase change occurs and the atoms rearrange themselves into the  $\gamma$  (gamma) form, which is F.C.C. and non-magnetic. When the temperature reaches 1666°F, another phase change occurs from F.C.C. non-magnetic  $\gamma$  iron to B.C.C. non-magnetic  $\alpha$  (alpha) iron. Finally, at 1414°F,  $\alpha$  iron becomes magnetic without a change in the lattice structure.
- ▶ Originally, non-magnetic  $\alpha$  iron was called  $\beta$  iron until subsequent x-ray studies showed no change in lattice structure at 1414° F. Since this magnetic transformation does not affect the heat treatment of iron-carbon alloys.
- ▶ All the allotropic changes give off heat (exothermic) when the iron is cooled and absorb heat (endothermic) when the iron is heated (Refer Figure 5.1).

## 5.2 The Iron – Iron Carbide Diagram

- ▶ The temperature at which the allotropic changes take place in iron is influenced by alloying elements, the most important of which is carbon. The portion of the iron-carbon alloy system which is of interest is shown in Fig.5.2.
- ▶ This is the part between pure iron and interstitial compound, iron carbide,  $\text{Fe}_3\text{C}$ , containing 6.67% carbon by weight. Therefore, we will call this portion the iron- iron carbide equilibrium diagram.

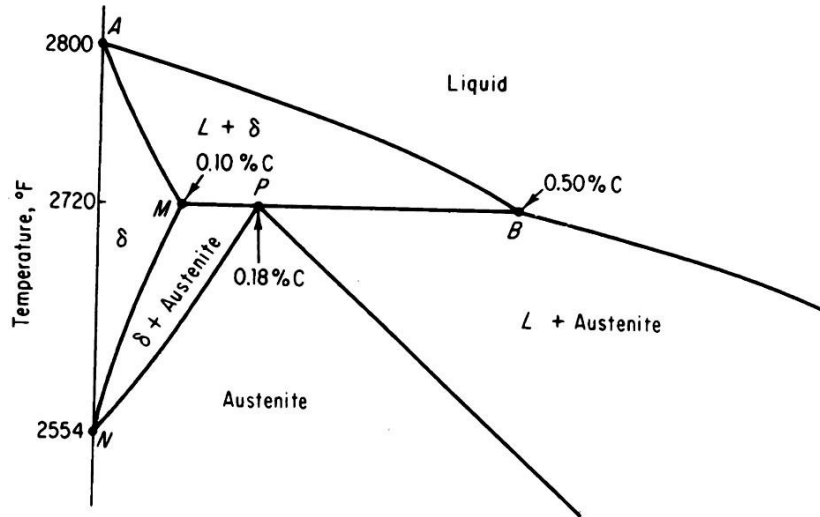
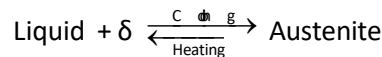


Fig.5.2 - The delta region for iron – iron carbon diagram

- ▶ The diagram shows three horizontal lines which indicate isothermal reactions. The  $\gamma$  solid solution is called austenite. The portion of the diagram in the upper left corner is expanded in Figure 5.2. This is known as the delta region, because of the  $\delta$  solid solution. The horizontal line at 2720°F is being a peritectic reaction. The equation of the peritectic reaction may be written as



- ▶ The maximum solubility of carbon in B.C.C.  $\delta$  iron is 0.10% (point M) while in F.C.C.  $\gamma$  iron the solubility is much greater. The presence of carbon influences the  $\delta$  iron to  $\gamma$  iron allotropic change.
- ▶ As carbon is added to iron, the temperature of the allotropic change increases from 2554°F to 2720°F at 0.10% carbon.
- ▶ Consider the significance of line NMPB. On cooling, the portion NM represents the beginning of the crystal structure changes from B.C.C.  $\delta$  iron to F.C.C.  $\gamma$  iron for alloys containing less than 0.10% carbon.
- ▶ The portion MP represents the beginning of this crystal structure change by means of a peritectic reaction for alloys between 0.10% and 0.18% carbon.
- ▶ For the alloys containing less than 0.18% carbon on cooling, the end of crystal structure change is given by line NP.
- ▶ On line PB, for alloy between 0.18 and 0.50% carbon, the allotropic change begins and ends at a constant temperature.
- ▶ Any alloy containing more than 0.50% carbon will cut the diagram to the right of point B and will solidify austenite only.
- ▶ No commercial heat treatment is done in the delta region.

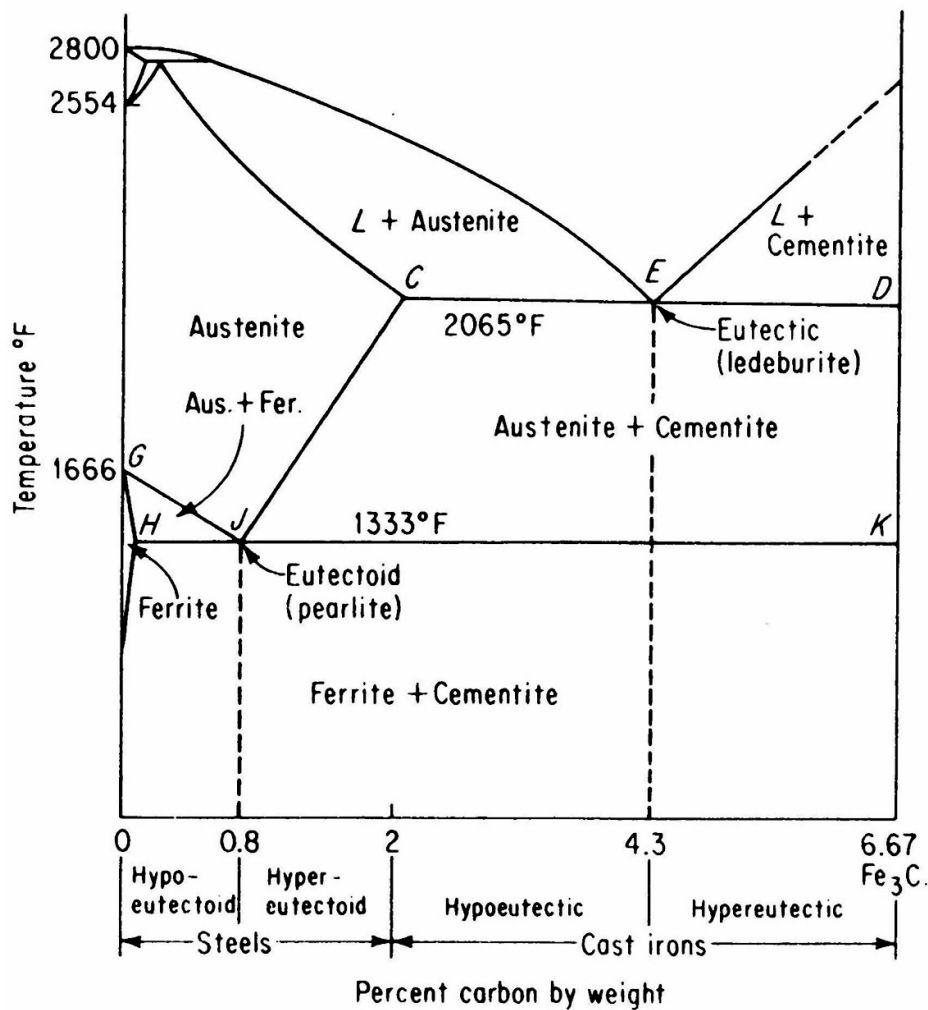


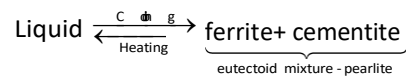
Fig.5.3 - The iron – iron carbide equilibrium diagram labeled with the common names for the structure.

- ▶ Figure 5.3 shows an eutectic reaction at 2065°F at horizontal line CED, at point E where 4.3% carbon. Since the horizontal line CED represents the eutectic reaction, whenever an alloy crosses this line the reaction must take place.
- ▶ Any liquid that is present when this line is reached must now solidify into the very fine intimate mixture of the two phases that are at either end of the horizontal line, namely austenite and iron carbide (called cementite). This eutectic mixture has given the name ledeburite and equation may be written as



- ▶ The eutectic mixture is not usually seen in the microstructure since austenite is not stable at room temperature and must undergo another reaction during cooling.
- ▶ There is a small solid solution area to the left of line GH. We know that 1666°F represents the changes in the crystal structure of pure iron from F.C.C.  $\gamma$  iron to B.C.C.  $\alpha$  iron. That area is a solid solution of a small amount of carbon dissolved in B.C.C.  $\alpha$  iron and is called „Ferrite“.
- ▶ The diagram shows a third horizontal line HJK, which represents a eutectoid reaction. The eutectoid point J is at 0.80% carbon and 1333°F. Any austenite present must now transform into the very fine eutectoid mixture of „Ferrite + Cementite“ called „Pearlite“.

- ▶ The equation may be written as



- ▶ On the basis of carbon content, the iron carbide diagram divides into two parts.

Alloys contain < 2% carbon → Steels.

Alloys contain > 2% carbon → Cast irons.

Steel < 0.8% carbon → Hypo eutectoid steels.

Steel in between 0.8% to 2% carbon → Hyper eutectoid steel.

Cast iron < 4.3% carbon → Hypo eutectoid Cast irons.

Cast iron > 4.3% carbon → hyper eutectoid Cast irons.

## 5.3 Definition of Structure

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### 1 Cementite: (Iron Carbide)

- ▶ Chemical formula Fe<sub>3</sub>C contains 6.67% carbon by weight.
- ▶ It is a typically hard and brittle interstitial compound of low tensile strength and high compressive strength.
- ▶ Its crystal structure is orthorhombic.

### 2 Austenite

- ▶ Austenite is the name given to  $\gamma$  solid solution.
- ▶ It is an interstitial solid solution of carbon dissolved in  $\gamma$  (F.C.C.) iron.
- ▶ Maximum solubility is 2% at 2065°F (point C).

### Properties

- ▶ Tensile strength 150000 PSI.
- ▶ Elongation 10% in 2 inches.
- ▶ Hardness Rockwell C40 approx.
- ▶ High toughness.
- ▶ It is normally not stable at room temperature

### 3 Leadeburite

- ▶ It is a eutectic mixture of austenite and cementite.
- ▶ It contains 4.3% carbon and is formed at 2065°F.

### 4 Ferrite

- ▶ It is the name given to  $\alpha$  solid solution.
- ▶ It is an interstitial solid solution of a small amount of carbon dissolved in  $\alpha$  (B.C.C.) iron.
- ▶ The maximum solubility is 0.025% carbon at 1333°F at point H and it dissolves only 0.008% carbon at room temperature.

- ▶ It is the soft structure that appears on the diagram.

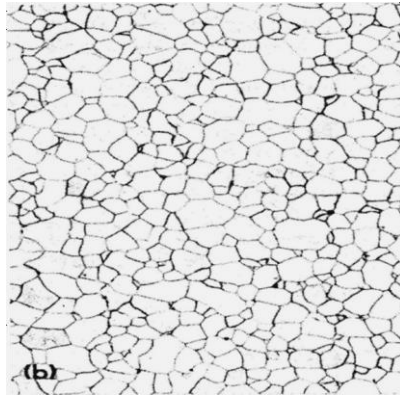


Fig.5.4 – Ferrite

### Properties:

- ▶ Tensile strength 40000 PSI.
- ▶ Elongation 40% in 2 inches.

### 5 Pearlite

- ▶ It is the eutectoid mixture containing 0.80 % carbon and is formed at 1333°F on very slow cooling.
- ▶ It is a very fine plate-like OR a lamellar mixture of ferrite and cementite. The fine fingerprint mixture called Pearlite shown in Figure 5.5(c). The white ferritic background or matrix which makes up most of the eutectoid mixture contains thin plates of cementite. The same structure magnified, 17000 times with an electron microscope shown in Figure 5.5(d).

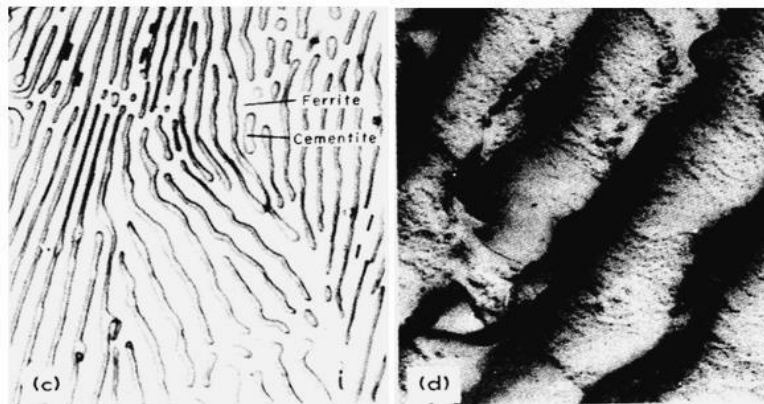


Fig.5.5 –( c) Pearlite with 2500X (d) Pearlite with 17000X

### Properties

- ▶ Tensile strength 120000 PSI
- ▶ Elongation 20% in 2 inch
- ▶ Hardness – Rockwell C20
- ▶ Rockwell B 95 -100
- ▶ BHN 250-300

## 5.4 Carbon Solubility in Iron

---

- ▶ Austenite, being F.C.C. with four atoms per unit cell, represents a much denser packing of atoms than ferrite, which is B.C.C. with two atoms per unit cell. This is shown by the expansion that takes place when austenite changes to ferrite on slow cooling. If the iron atoms are assumed to be spheres, it is possible, from the lattice dimensions and assuming the distance of the closest approach to be equal to the atom diameter, to calculate the amount of empty space in both crystal structures.
- ▶ The calculation shows that the percentage of unfilled space in the F.C.C. lattice is 25% and in the B.C.C. lattice 32%. In both austenite and ferrite, the carbon atoms are dissolved interstitially, that is, in the unfilled spaces of the lattice structure. In view of the above calculations, it may seem strange that the solubility of carbon in austenite is so much greater than it is in ferrite.

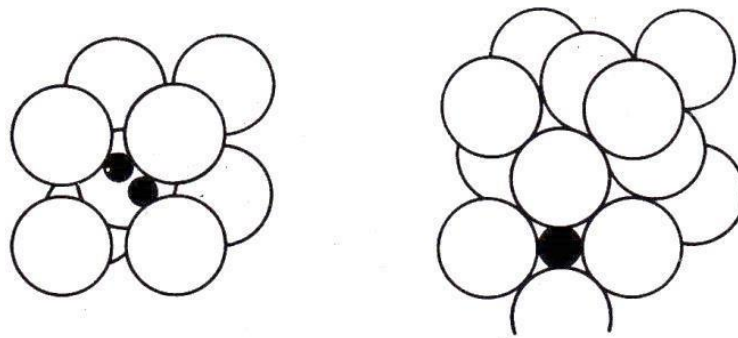


Fig.5.6 – Interstices of the B.C.C. (left) and F.C.C. (right).

- ▶ This seemingly unusual behavior may be explained by a study of Fig. 5.6. The largest hole in B.C.C. ferrite is halfway between the center of the face and space between the two corner atoms. Two of the four possible positions for a carbon atom on the front face of a body-centered cube are shown in Fig. 5.6.
- ▶ The largest interstitial sphere that would just fit has a radius of  $0.36 (10^{-8})$  cm. The largest hole in F.C.C. austenite is midway along the edge between two corner atoms. One possible position for a carbon atom on the front face of a face-centered cube is shown in Fig. 5.6.
- ▶ The largest interstitial sphere that would just fit has a radius of  $0.52 (10^{-8})$  cm. Therefore, austenite will have a greater solubility for carbon than ferrite. Since the carbon atom has a radius of about  $0.70 (10^{-8})$  cm, the iron atoms in austenite are spread apart by the solution of carbon so that, at the maximum solubility of 2%, only about 10% of the holes are filled. The distortion of the ferrite lattice by the carbon atom is much greater than in the case of austenite; therefore, the carbon solubility is much more restricted.

## 5.5 Slow Cooling of Steel

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- ▶ Alloy 1 (Figure 5.7) is a hypo eutectoid steel containing 0.20% carbon. In the austenite range, these alloys consist of uniform interstitial solid solution. Each grain contains 0.20% carbon dissolved in the space of the F.C.C. iron lattice structure (Figure 5.7(a)).
- ▶ Upon slow cooling, nothing happens until the line GJ is crossed at point  $X_1$ . This line is known as the upper critical temperature line on the hypo eutectoid side and is labeled  $A_3$ .
- ▶ The allotropic change from F.C.C. to B.C.C. iron takes place at  $1666^\circ\text{F}$  for pure and a decrease in temperature with increasing carbon content as shown by the  $A_3$  line. Therefore at  $X_1$ , ferrite must begin to form at the austenite grain boundaries (Figure 5.7(b)). As the cooling progress and the number of ferrite increases, the remaining austenite becomes richer in carbon.

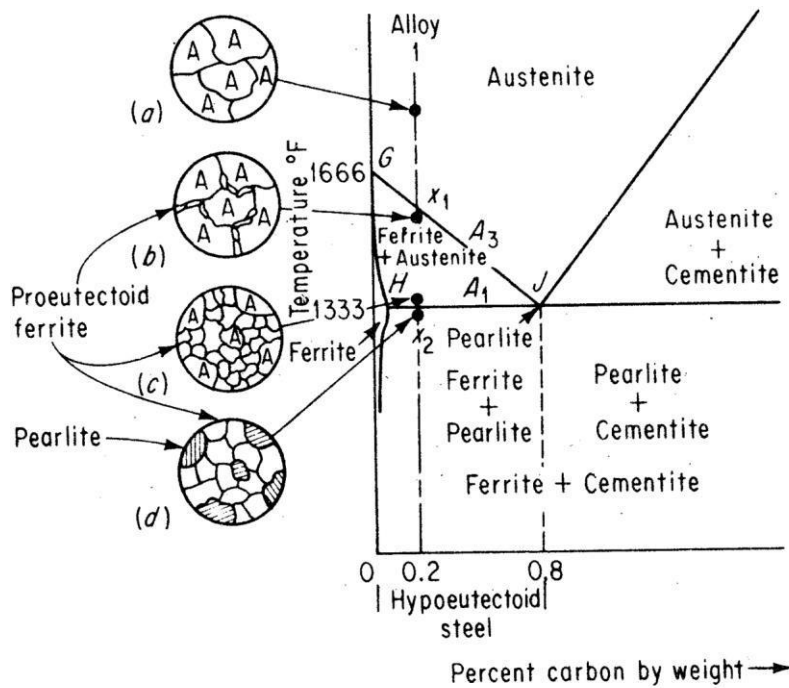
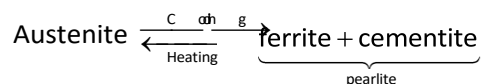


Fig.5.7 - Schematic representation of the changes in microstructure during the slow cooling of 0.2% carbon steel.

- a) Austenite
- b) Formation of ferrite grains at austenite grain boundaries.
- c) Growth of ferrite grains – composition of austenite is now 0.8% carbon
- d) Austenite transforms to pearlite at 1333°F

- ▶ Its carbon content is gradually moving down and to the right along the  $A_3$  line.
- ▶ Finally, the line HJ is reached at point  $X_2$ . This line is known as the lower critical temperature line on the hypo eutectoid side and is labeled  $A_1$ . The line  $A_1$  is the eutectoid temperature line and is the lowest temperature at which F.C.C. iron can exist under equilibrium condition
- ▶ Just above  $A_1$ , line the microstructure consists of 25% austenite and 75% ferrite (Figure 5.7(c)).



- ▶ Note that it is only austenite which is changing at the  $A_1$  line. Therefore when the reaction is complete the microstructure will show approximately 25% Pearlite and 75% ferrite (Figure 5.7(d)).
- ▶ Let us consider the eutectoid reaction in a little more detail. Austenite is to change to ferrite. Austenite is an interstitial solid solution with each remaining grain dissolving 0.8 % C in F.C.C. Fe. Ferrite, however, is B.C.C. Fe and dissolves very little carbon, so the change in the crystal structure cannot occur until the carbon atoms come out of solution.
- ▶ Therefore, the first step is the precipitation of the carbon atoms to form plates of cementite (iron carbide). In the area immediately adjacent to the cementite plate the iron is depleted of carbon, and the atoms may now rearrange themselves to form B.C.C. ferrite. Thin layers of ferrite are formed on each side of the cementite plate. The process continues by the formation of alternate layers of cementite and ferrite to give the fine fingerprint mixture known as pearlite. The reaction usually starts at the austenite grain boundary, with the pearlite growing along the boundary and into the grain, see Fig.5.8.

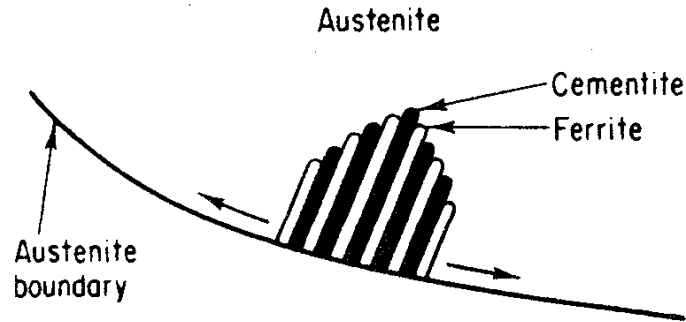


Fig.5.8 – Schematic picture of the formation and growth of pearlite

- ▶ Since ferrite and pearlite are stable structures, the microstructure remains substantially the same down to room temperature and consists of approximately 75 % pro eutectoid ferrite (formed between the  $A_3$  and  $A_1$  lines) and 25% pearlite (formed from austenite at the  $A_1$  line). Figure 5.9 (a) shows the microstructure of a 0.2 % C steel slow – cooled. As predicted, it consists of 75 % pro eutectoid ferrite (light areas) and 25% pearlite (dark areas). The dark areas in this micro certainly do not look like a mixture, which pearlite is supposed to be. Higher magnification (Fig.5.9 (b)), however, reveals the fine fingerprint mixture of pearlite.
- ▶ The changes just described would be the same for any hypo eutectoid steel. The only difference would be in the relative amount of ferrite and pearlite. The closer the carbon content to the eutectoid composition (0.8 % C), the more pearlite will be present in the microstructure. The microstructure of a 0.4 % C steel slow cooled (Fig.5.9(c)) shows approximately 50 % pearlite, while the eutectoid composition (0.8 % C) shows 100 % pearlite (Fig.5.9 (d)).
- ▶ Alloy 2 (Fig.5.10) is hypereutectoid steel containing 1% carbon. In the austenite range, this alloy consists of a uniform F.C.C. solid solution with each grain containing 1 % carbon dissolved interstitially (Fig.5.10(a)). Upon slow cooling, nothing happens until the line CJ is crossed at point  $x_3$ .
- ▶ This line is known as the upper- critical-temperature line on the hypereutectoid side and is labeled  $A_{cm}$ . The  $A_{cm}$  line shows the maximum amount of carbon that can be dissolved in austenite as a function of temperature. Above the  $A_{cm}$  line, austenite is an unsaturated solid solution. At the  $A_{cm}$  line, point  $x_3$ , the austenite is saturated in carbon.

As the temperature is decreased, the carbon content of austenite, that is, the maximum amount of carbon that can be dissolved in austenite moves down along the  $A_{cm}$  line toward point J. Therefore, as the temperature decreases from  $x_3$  to  $x_4$ , the excess carbon above the amount required to saturate austenite is precipitated as cementite primarily along the grain boundaries (Fig.5.10(b),(c)). Finally, the eutectoid – temperature line is reached at  $x_4$ . This line is called the lower – critical temperature line on the hypereutectoid side and is labeled  $A_{3,1}$ . Just above the  $A_{3,1}$  line, the microstructure consists largely of austenite, with the excess pro eutectoid cementite as a network surrounding the austenite grains. Applying Rule II with cementite on the right side of the line, the amount of cementite would be

$$\% \text{ cementite} = \frac{1.0 - 0.8}{6.67 - 0.8} \times 100 = 3.4 \%$$

- ▶ and the amount of austenite would be

$$\% \text{ austenite} = \frac{6.67 - 1.0}{6.67 - 0.8} \times 100 = 96.6 \%$$

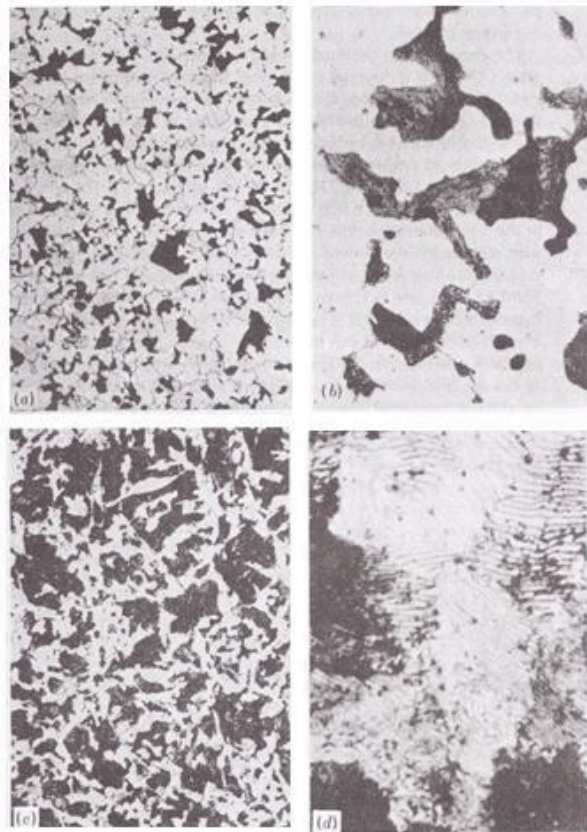


Fig.5.9 – of (a) 0.20 percent carbon steel, slow – cooled, 100X  
 (b) Same as (a), but at 500X;  
 (c) 0.40 percent carbon steel, slow – cooled, 100X;  
 (d) eutectoid (0.80 percent carbon)

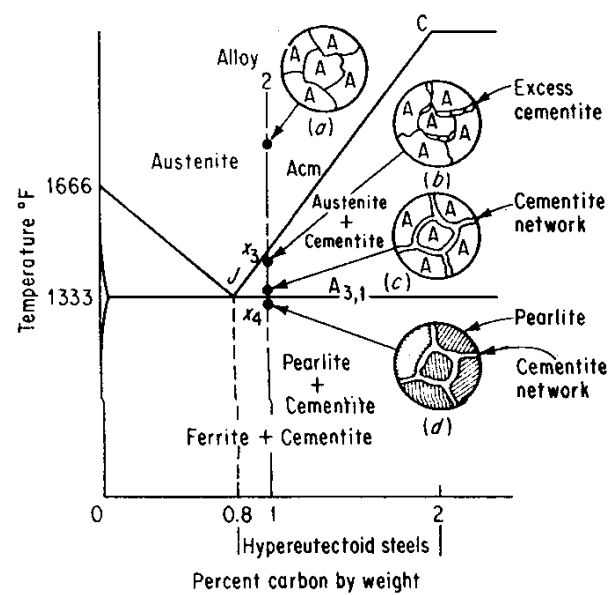


Fig.5.10 - Schematic representation of the changes in microstructure during the slow cooling of a 1.0 percent carbon steel. (a) Austenite; (b) formation of excess cementite at austenite grain boundaries;

(c) growth of excess cementite to form a network – austenite composition is now 0.8 percent carbon; (d) Austenite transforms to pearlite at 1333° F.

- ▶ The  $A_{3,1}$  line for hypereutectoid steels represent the beginning and the end of the allotropic change from F.C.C. austenite to B.C.C. ferrite. By the same process described earlier, the remaining austenite (containing 0.8 % carbon) transforms to the eutectoid mixture, pearlite (Fig.5.10 (d)). At room temperature, the microstructure consists of 96.6 % pearlite (formed from austenite at the  $A_{3,1}$  line) and a network of 3.4 % pro eutectoid cementite (formed between the  $A_{cm}$  and  $A_{3,1}$  lines). Look closely at Fig. 5.10(a), particularly where the pearlite areas meet, to see the thin, white pro eutectoid cementite network. The story just described would be the same for any hypereutectoid steel, slow – cooled. As the carbon content of the alloy increases, the thickness of the pro eutectoid cementite network generally increases. Figure 5.10 (b) shows the microstructure of a 1.2 % carbon steel. Both photomicrographs show very clearly the lamellar (platelike) structure of pearlite.
- ▶ The  $A_{3,1}$  line for hypereutectoid steels represent the beginning and the end of the allotropic change from F.C.C. austenite to B.C.C. ferrite. By the same process described earlier, the remaining austenite (containing 0.8 % carbon) transforms to the eutectoid mixture, pearlite (Fig.5.8 (d)).
- ▶ At room temperature, the microstructure consists of 96.6 % pearlite (formed from austenite at the  $A_{3,1}$  line) and a network of 3.4 % pro eutectoid cementite (formed between the  $A_{cm}$  and  $A_{3,1}$  lines). Look closely at Fig. 5.11(a), particularly where the pearlite areas meet, to see the thin, white pro eutectoid cementite network.



*Fig.5.11 - Photomicrographs of (a) 1 percent carbon steel, slow – cooled, 500X;  
(b) 1.2 percent carbon steel, slow – cooled, 300X.*

- ▶ The story just described would be the same for any hypereutectoid steel, slow – cooled. As the carbon content of the alloy increases, the thickness of the pro eutectoid cementite network generally increases. Figure 5.11(b) shows the microstructure of a 1.2 % carbon steel. Both photomicrographs show very clearly the lamellar (platelike) structure of pearlite.

- ▶ Note the difference in significance of the upper – critical – temperature lines, the  $A_3$  and  $A_{cm}$ . The former line involves an allotropic change, whereas the latter involves only a change in carbon solubility.
- ▶ The mechanical properties of an alloy depend upon the properties of the phases and the way in which these phases are arranged to make up the structure.
- ▶ Ferrite is relatively soft with low tensile strength, while cementite is hard with very low tensile strength. The combination of these two phases in the form of the eutectoid (pearlite) produces an alloy of much greater tensile strength than that of either phase. Since the amount of pearlite increases with an increase in carbon content for hypo eutectoid steels, the strength and Brinell hardness will also increase up to the eutectoid composition of 0.80 % carbon.
- ▶ The ductility, as expressed by percent elongation and reduction in area, and impact strength decrease with increasing carbon content. Beyond the eutectoid composition, the strength levels off and may even show a decrease due to the brittle cementite network. The Brinell hardness, however, continues to increase due to the greater proportion of hard cementite.

## 5.6 B.I.S System of Designation of Steel

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Steels are designated by a group of letters or numbers indicating any one of the following three properties:

- (i) Tensile strength;
- (ii) Carbon content; and
- (iii) Composition of alloying elements.

For example, Fe 360

- ▶ Indicates steel with a minimum tensile strength of 360 N/mm<sup>2</sup>.

Similarly, Fe E 250

- ▶ Indicates steel with a minimum yield strength of 250 N/mm<sup>2</sup>.

The designation of plain carbon steel consists of the following three quantities:

- (i) A figure indicating 100 times the average percentage of carbon;
- (ii) A letter C; and
- (iii) A figure indicating 10 times the average percentage of manganese.

For Example, 55C4

- ▶ Indicates plain carbon steel with 0.55% carbon and 0.4% manganese steel with 0.35

Similarly 40C8

- ▶ 0.45% carbon and 0.7–0.9% manganese

The designation of unalloyed free-cutting steels consists of the following quantities:

- (i) A figure indicating 100 times the average percentage of carbon;
- (ii) A letter C;
- (iii) A figure indicating 10 times the average percentage of manganese;
- (iv) A symbol „S“, „Se“, „Te“ or „Pb“ depending upon the element that is present and which makes the steel free cutting; and
- (v) A figure indicating 100 times the average percentage of the above elements that makes the steel free cutting.

For Example, 25C12S14

- ▶ indicates free cutting steel with 0.25% carbon, 1.2% manganese and 0.14% sulphur.

Similarly, 20C12Pb15.

- ▶ indicate free cutting steel with an average of 0.20% carbon, 1.2% manganese and 0.15% lead.

The term „alloy“ steel is used for low and medium alloy steels containing total alloying elements not exceeding 10%. The designation of alloy steels consists of the following quantities:

- A figure indicating 100 times the average percentage of carbon; and
- Chemical symbols for alloying elements each followed by the figure for its average percentage content multiplied by a factor. The multiplying factor depends upon the alloying element. The values of this factor are as follows:

Elements	Multiplying Factor
Cr, Co, Ni, Mn, 4 Si and W	4
Al, Be, V, Pb, Cu, Nb, Ti, Ta, Zr, and Mo	10
P, S, N	100

For example, 25Cr4Mo2

- ▶ alloy steel having an average 0.25% of carbon, 1% chromium and 0.2% molybdenum.

Similarly, 40Ni8Cr8V2

- ▶ an alloy steel containing average 0.4% of carbon, 2% nickel, 2% chromium and 0.2% vanadium.

Consider an alloy steel with the following composition:

Carbon = 0.12–0.18%      Silicon = 0.15–0.35%      Manganese = 0.40–0.60%      Chromium = 0.50–0.80%

- ▶ The average percentage of carbon is 0.16% and multiplying this value by 100, the first figure in the designation of steel is 16.
- ▶ The average percentage of silicon and manganese is very small and, as such, the symbols Si and Mn are deleted.
- ▶ The average percentages of nickel and chromium are 0.8 and 0.6, respectively, and the multiplying factor for both elements is 4. Therefore,
- ▶ Nickel:  $0.8 \times 4 = 3.2$  rounded to 3 or Ni3
- ▶ Chromium:  $0.6 \times 4 = 2.4$  rounded to 2 or Cr2.
- ▶ The complete designation of steel is 16Ni3Cr2.

The term „high alloy steels“ is used for alloy steels containing more than 10% of alloying elements. The designation of high alloy steels consists of the following quantities:

- a letter X
- a figure indicating 100 times the average percentage of carbon;
- chemical symbol for alloying elements each followed by the figure for its average percentage content rounded off to the nearest integer; and
- chemical symbol to indicate a specially added element to attain desired properties, if any. As an example, X15Cr25Ni12 is high alloy steel with 0.15% carbon, 25% chromium and 12% nickel. As a second example, consider steel with the following chemical composition:

carbon = 0.15–0.25%

silicon = 0.10–0.50%

manganese = 0.30–0.50%

nickel = 1.5–2.5%

chromium = 16–20%

The average content of carbon is 0.20%, which is denoted by a number (0.20 x 100) or 20. The

major alloying elements are chromium (average 8%) and nickel (average 2%). Hence, the designation of steel is X20Cr18Ni2.

Cast iron is an alloy of iron and carbon, containing more than 2% of carbon. In addition to carbon, cast iron contains other elements like silicon, manganese, sulphur, and phosphorus. There is a basic difference between steels and cast iron. Steels usually contain less than 1% carbon while cast iron normally contains 2 to 4% carbon.

Typical composition of ordinary cast iron is as follows:

Carbon = 3.0 – 4.0%

Silicon = 1.0 – 3.0%

Manganese = 0.5 – 1.0%

Sulphur = up to 0.1%

Phosphorus = up to 0.1%

Iron = remainder

For example, FG 200,(Grey Cast Iron)

- ▶ In general, means a grey cast iron with an ultimate tensile strength of 200 N/mm<sup>2</sup>.

BM 350 (Malleable Cast Iron)

- ▶ Blackheart malleable cast iron with a minimum tensile strength of 350 N/ mm<sup>2</sup>.

PM 600

- ▶ Pearlitic malleable cast iron with a minimum tensile strength of 600 N/mm<sup>2</sup>

WM 400

- ▶ White heart malleable cast iron with a minimum tensile strength of 400 N/mm<sup>2</sup>.

SG 800/2 (Ductile Cast Iron/ Nodular Cast Iron)

- ▶ Spheroidal graphite cast iron with a minimum tensile strength of 800 N/mm<sup>2</sup> and a minimum elongation of 2%.

## 5.7 References

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Sidney H Avner ” Introduction to Physical metallurgy 2<sup>nd</sup> Edition 2011 Tata Mc Graw- Hill Publication.

O. P. Khanna “Material Science and Metallurgy” Dhanpat Rai Publications.

V.B.Bhandari “Design of Machine Elements” 3<sup>rd</sup> Edition Tata Mc Graw- Hill Publication

## 6.1 Heat Treatment

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Heat treatment is defined as the combination of operations involving heating of metals or alloys in solid-state and cooling it at a suitable rate to obtain the desired properties

### Purpose of heat treatment

1. Relieving the internal stresses.
2. Refinement of grain size.
3. Improvement of ductility.
4. Increasing hardness or tensile strength.
5. Achieving changes in the chemical composition of the metal.
6. Improvement in machinability.

The parameter affects the heat treatment process

1. Temperature
2. Holding time
3. Rate of heating and cooling

## 6.2 Full Annealing

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### Method

This process consists of heating the steel to the proper temperature and then cooling slowly through the transformation range. Preferably in the furnace or in any good heat-insulating materials.

### Purpose

1. To refine the grain size
2. Induce softness
3. Improve electrical and magnetic properties
4. Improve machinability

### Structure Changes

Aim: We have 0.20% carbon steel (Hypoeutectoid steel) and desired to refine the grain size by annealing.

#### Process

- ▶ When this steel is heated, no change will occur until A<sub>1</sub>(lower critical temperature line) is crossed, when A<sub>1</sub> is crossed at that temperature pearlite area will transform to small grains of austenite by means of eutectoid reactions, but the original large ferrite grains will remain unchanged (Figure 6.1b). Cooling from this temperature will not refine the grain.
- ▶ Continued heating between A<sub>1</sub> and A<sub>3</sub> lines will allow the large ferrite grains to transform into small grains of austenite so that above A<sub>3</sub> (upper critical temperature line) line the entire microstructure will show only small grains of austenite. (Figure 6.1c)
  - a) Original structure. Coarse-grained ferrite and pearlite
  - b) Just above the A<sub>1</sub> line; pearlite has transformed into small grains of austenite, ferrite unchanged.
  - c) Above the A<sub>3</sub> line; only fine-grained austenite
  - d) After cooling at room temperature; fine-grained ferrite and small pearlite areas.
- ▶ Subsequent furnace cooling will result in small grains of pro eutectoid ferrite and a small area of coarse lamellar pearlite. (Figure 6.1d) So, proper annealing temperature for hypo eutectoid steel is approximately 50°F above the A<sub>3</sub> line.

- Refinement of the grain size of hypereutectoid steel will occur about 50°F above the lower critical temperature line ( $A_{3, 1}$ ). Heating above this temperature will coarsen the austenite grains which, on cooling will transform into large pearlite areas.

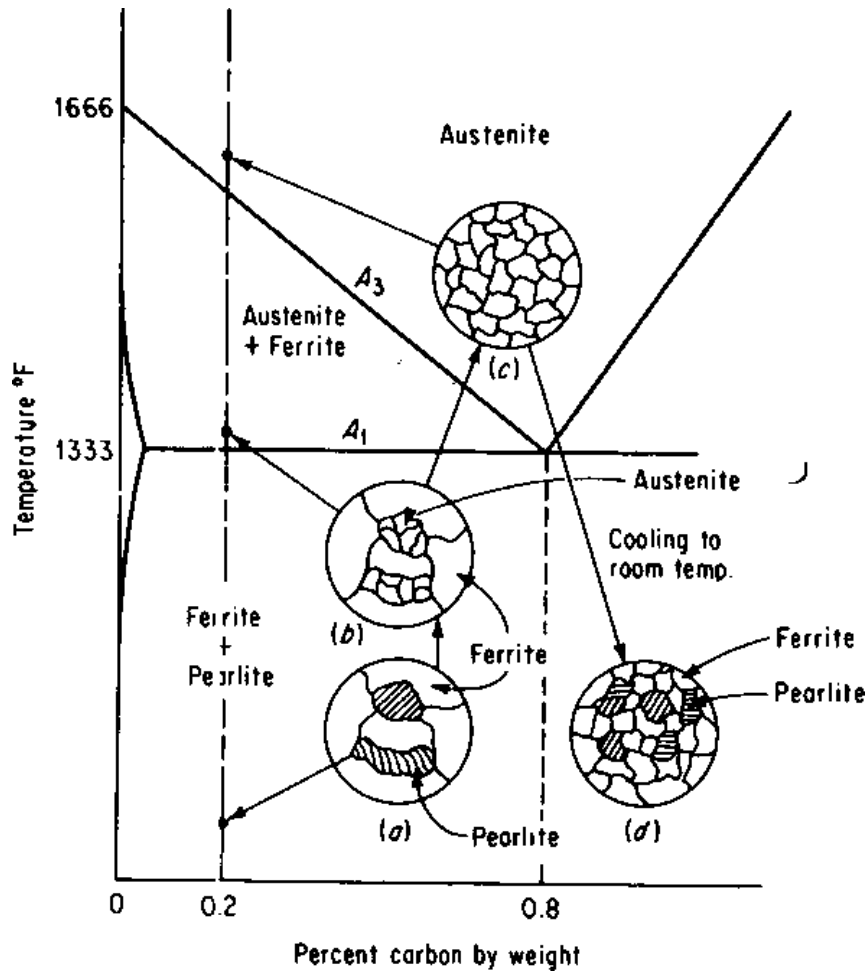


Fig.6.1 - schematic representation of the changes in microstructure during annealing of 0.20% carbon steel

- The microstructure of annealed hypereutectoid steel will consist of coarse lamellar pearlite areas surrounded by a network of pro eutectoid cementite (Fig.6.1). Because this excess cementite network is brittle and tends to be a plane of weakness, annealing should never be final heat treatment for hypereutectoid steels. The presence of a thick, hard grain boundary will also result in poor machinability.
- Approximate tensile strength of annealed hypo eutectoid steel may be determined by the proportion of ferrite and pearlite present.

$$\text{Approximate Tensile Strength} = \frac{40000 (\text{percent ferrite}) + 120000(\text{percent pearlite})}{100}$$

Example: Annealed 0.2% carbon steel

Approx 25% pearlite, 75% ferrite

$$\begin{aligned} \text{Approximate Tensile Strength} &= \frac{40000 (0.75) + 120000(0.25)}{100} \\ &= 60000 \text{ PSI} \end{aligned}$$

- This same idea cannot be applied to hypereutectoid steel since their strength is determined by the cementite network which forms the continuous phase. The presence of the brittle network results in a drop in tensile strength above 0.8% carbon.

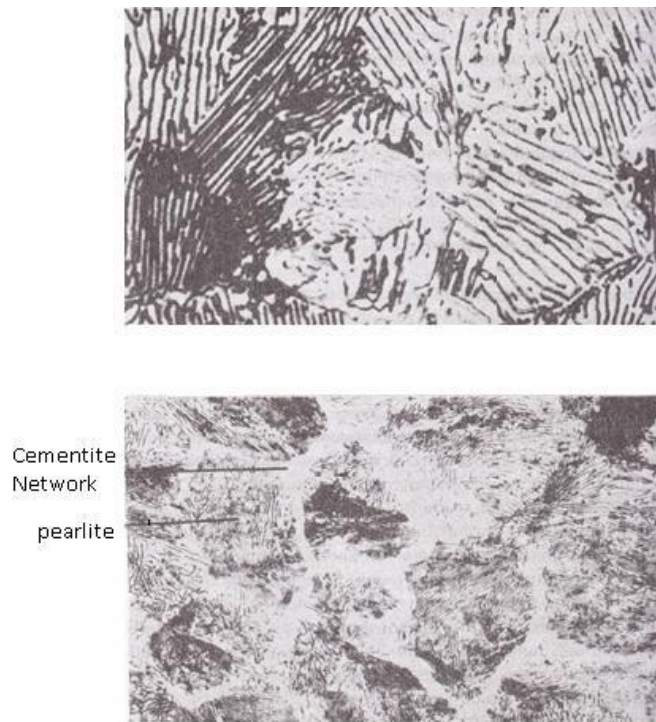


Fig.6.2 Photomicrographs of (a) 1 percent carbon steel, slow-cooled, 500X;  
 (b) 1.2 percent carbon steel, slow-cooled, 300X. Pearlite areas surrounded by a white pro-eutectoid cementite network. Note the increase in the thickness of the cementite network with the increase in carbon content.

CARBON, %	YIELD POINT, 1,000 PSI	TENSILE STRENGTH, 1,000 PSI	ELONGATION, % IN 2 IN.	REDUCTION IN AREA, %	BHN
<b>Normalized (hot-rolled steel):</b>					
0.01	25	45	45	71	90
0.20	45	64	35	60	120
0.40	51	85	27	43	165
0.60	60	109	19	28	220
0.80	70	134	13	18	260
1.00	100	152	7	11	295
1.20	100	153	3	6	315
1.40	96	148	1	3	300
<b>Annealed:</b>					
0.01	18	41	47	71	90
0.20	36	59	37	64	115
0.40	44	75	30	48	145
0.60	49	96	23	33	190
0.80	52	115	15	22	220
1.00	52	108	22	26	195
1.20	51	102	24	39	200
1.40	50	99	19	25	215

Fig.6.3 - Mechanical properties of normalized and annealed steels

# 1. Spheroidising Annealing

## Purpose

To improve the machinability and ductility of high carbon steel and air hardening alloy steel. This process will produce a spheroidal or globular form of carbide in a ferrite matrix

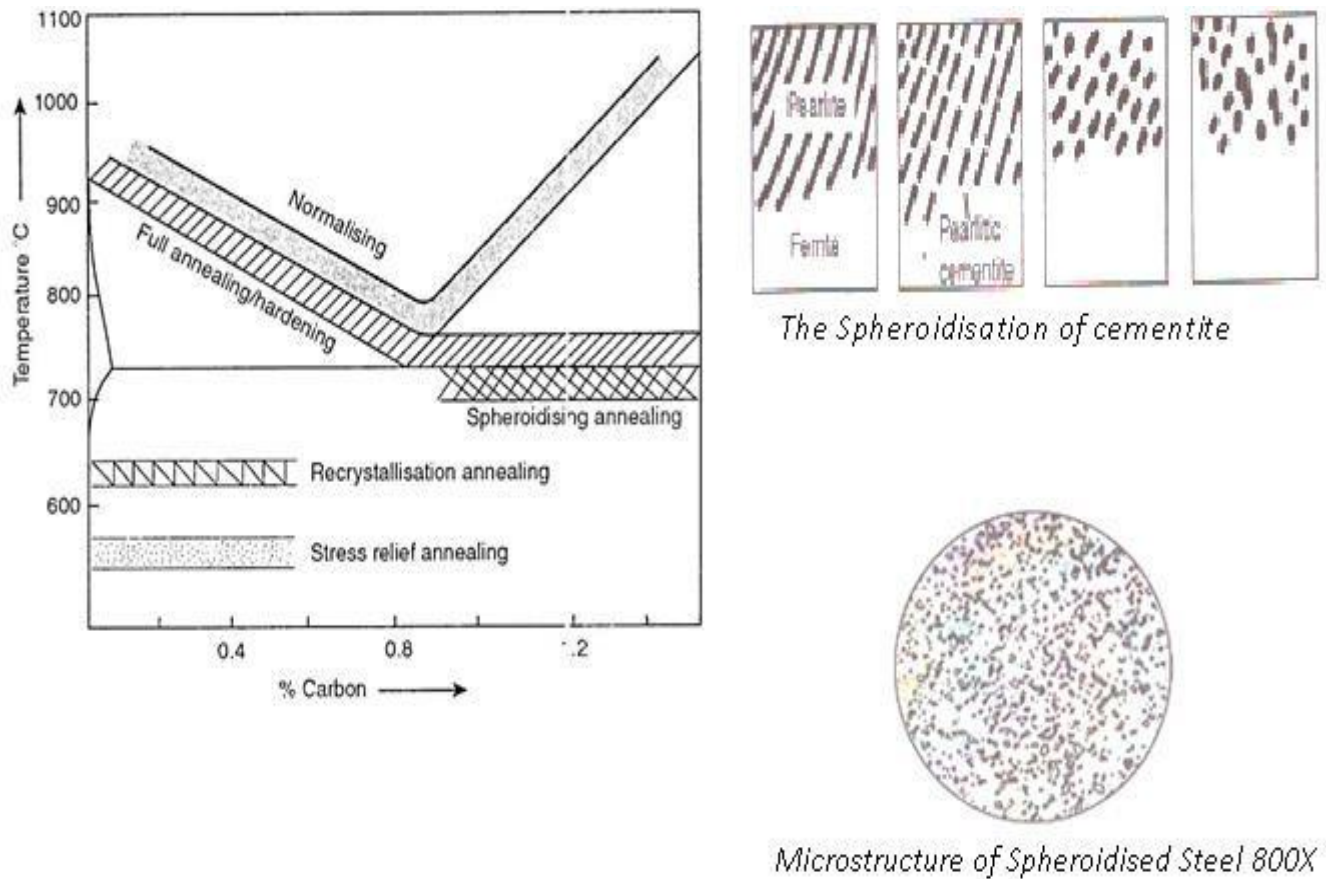


Fig.6.4 - Spheroidising Annealing

## Method to produce spheroids structure

1. The first method consists of heating steel to a temperature just below the lower critical temperature at that temperature for a prolonged period and followed by slow cooling.
2. The second method involves heating and cooling the steel alternately just above and below the lower critical temperature.
3. The third method consists of heating the steel to a temperature above the lower critical temperature followed by slow cooling to a temperature below the lower critical temperature and holding that temperature for a long period.

## Structure Change

In this process, no phase change takes place. The lamellar and free cementite into tiny spheroids due to surface tension effect. The final structure consists of spheroids of carbide in a matrix of ferrite.

The degree of spheroidisation depends on the heat treatment temperature and holding time. More ever fine pearlite coalesces more easily than the coarse pearlite.

## Applications

1. The microstructure of high carbon steel contains a network of cementite since the cementite plates are hard and brittle, the cutting tool cannot cut through this plate and it is subjected to a continuous shock load. Hence, this type of steel shows poor machinability. By the Spheroidising process, cementite plates are broken into tiny spheroids. This improves the machinability of high carbon steel.
2. During cold forming, lamellar shapes of cementite act as stress raisers and initiate crack formation. But spheroidal is less conductive stress concentration because of their rounded shape and prevents the initiation of cracks.

## 2. Stress Relief Annealing

### Purpose

- ▶ Residual stresses are induced during different operations like a solidification of casting, forming, machining, welding, grinding and phase transformation. Steels with residual stresses fail by stress corrosion cracking under a corrosive environment.
- ▶ These stresses also enhance the warpage and dimensional instability in steels.
- ▶ To eliminate or reduce residual stresses, steel is subjected to stress relief annealing.

### Method

- ▶ Steel is heated uniformly below the lower critical temperature line (1000°F to 1250°F) and held at this temperature for a sufficient period of time, followed by uniform cooling.
- ▶ The magnitude of stress relieved depends on the temperature and holding time.

### Structural change

- ▶ Since this process is carried out below the lower critical temperature to relieve only residual stress, no further microstructural changes occur during this process.

## 3. Process Annealing/ Recrystallisation Annealing

### Purpose

- ▶ This heat treatment is used in sheet and wire industry. Cold working of steels increase the hardness and strength but decrease the ductility. Moreover, the grains are deformed and residual stresses are deformed. So it is necessary to soften the metal to increase the ductility at the expense of hardness, for further cold working (example wire drawing). The annealing process employed for this is referred to as „Recrystallisation annealing“.

### Method

- ▶ The process consists of heating the steel above „Recrystallisation temperature“ or „below lower critical temperature“ (1000°F to 1250°F), holding at this temperature for a particular period of time then followed by cooling.

It depends on the following parameters.

1. Chemical composition
2. Amount of deformation
3. Holding time and initial grain size

### Structural changes

- ▶ The final structure after this treatment consists of strain-free equipped grains at the expense of deformation grains. Properly changes produced by cold working are removed and steel returns very nearly to its original properties.

- ▶ Therefore, hardness and strength decrease whereas the ductility increases.

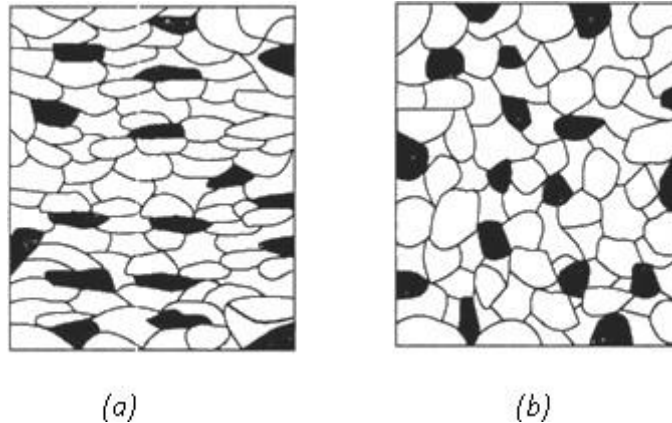


Fig.6.5 - Microstructure of (a) Cold worked steel  
(b) Recrystallized steel

### Application

- ▶ Manufacturing in steel wires, sheets or strips.

## 4. Normalizing

### Purpose

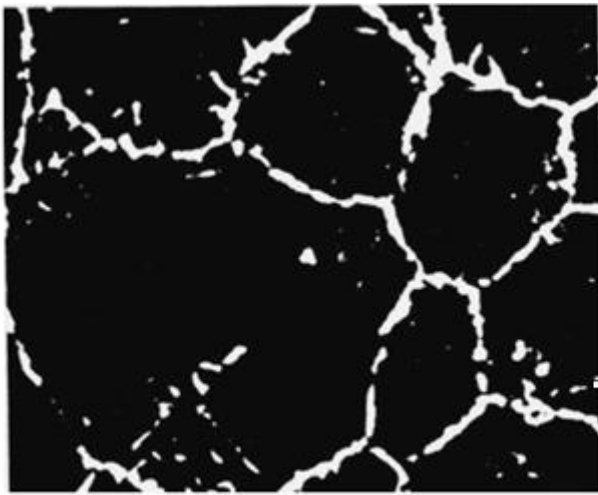
- ▶ The purpose of Normalizing is to perform harder and stronger steel than full annealing. So that for some applications normalizing may be final heat treatment.
- ▶ Normalizing may also be used to improve machinability modified and refine cast dendritic structure, refine the grain and homogenize the microstructure in order to improve the response in hardening operations.

### Method

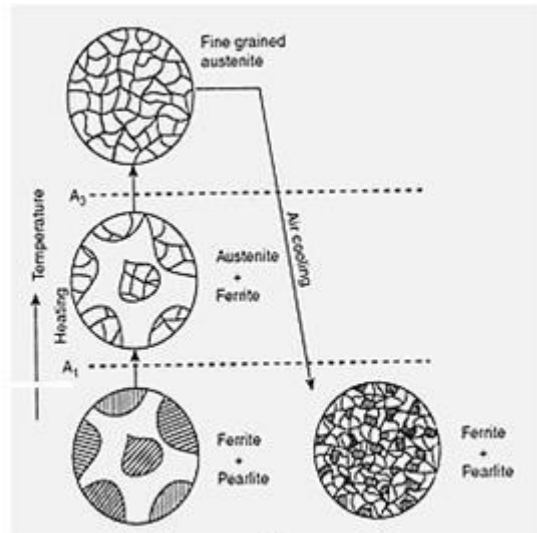
- ▶ Steel is heated to about approximately 100°F above the upper critical temperature ( $A_3$  or  $A_{cm}$ ), hold at that temperature for a sufficient period of time and then cooled in still air.
- ▶ The increase in cooling rate due to air cooling as compared with furnace cooling affects the transformation of austenite and resultant microstructure in several ways.

### Structural change

- ▶ In this process, the homogeneity of austenite increases since the temperature involved is more than that for annealing. It results in better dispersion of ferrite and cementite in the final structure. The grain size is finer in the normalized structure than in annealed one. This results in slightly higher strength and hardness but lower ductility than full annealing.
- ▶ Figure 6.6(b) shows the microstructure of normalized 0.5% carbon steel.
- ▶ In annealed condition 62% pearlite + 38% pro eutectoid ferrite. Due to air cooling, this sample has 10% pro eutectoid ferrite which is the white network surrounding the dark pearlite areas.
- ▶ For hypereutectoid steel, normalizing will reduce the continuity of pro eutectoid cementite network, and in some cases, it may be suppressed entirely.
- ▶ Since it was the presence of cementite network which reduces the strength of annealed hypereutectoid steels, normalized steel should show an increase in strength. (Table 6.1) particularly for steels containing more than 0.8% carbon.



(a)



(b)

Fig.6.6 – (a) Structural changes during normalizing.

(b) Normalized 0.50% carbon steel, heated to 1800°F and air-cooled

### Application

- ▶ Rolled and forged steels possessing coarse grains are subjected to normalizing for grain refinement.

Table 6.1 - Annealing and Normalizing

Normalizing	Annealing
1. Air cooling	1. Furnace cooling
2. Due to normalizing there are different cooling at different locations, hence different thickness regions will have different properties.	2. The furnace imposes identical cooling at all the locations so identical properties.
3. Microstructure contains less ferrite than annealing. ▶ Example: 0.5% carbon steel 10% ferrite and 90% pearlite	3. Microstructure contains less ferrite. ▶ Example: 0.5% carbon steel 38% ferrite and 62% pearlite
4. Ferrite cementite lamella in pearlite is fine.	4. Ferrite cementite lamellae in pearlite is coarse.
5. Comparatively higher strength and hardness.	5. Comparatively lower strength and hardness.
6. Less expensive	6. Here energy is needed and it is time-consuming so treatment is expensive.
7. It improves the machinability of low carbon steel.	7. It improves the machinability of medium carbon steel.

## 5. Hardening

### Purpose

The main purpose of hardening is to develop a high hardness level in components extended for heavy-duty service.

### Process

Hardening treatment consists of heating the steel to hardening temperature, holding at that temperature for a particular time followed by rapid cooling such as quenching in water, oil, salt bath.

- Hypo eutectoid steel is heated about 30-50°C above the upper critical temperature line (A3).

- b) Hyper eutectoid steel is heated about 30-50°C above the lower critical temperature line (A<sub>1</sub>).
- c) Rapid cooling means the cooling rate is just in excess of the critical cooling rate.

### Structure change

- ▶ In hypo eutectoid steel, ferrite and pearlite transform to austenite at hardening temperature. This austenite transforms to martensite on rapid cooling.
- ▶ In hypereutectoid steel, the foundation structure blends of cementite and martensite. Since cementite is harder than the martensite, the wear resistance is better than that achieved by martensite alone.

### Applications

- ▶ Tensile strength and yield strength are improved by hardening structural steel components like gears, shafts, bearings.
- ▶ The wear resistance and cutting ability of steel are increased.

## 6. Tempering

- ▶ Hardening treatment develops maximum hardness, excellent wear resistance and high strength in the steel.
- ▶ At the same time, it affects the property such as ductility and toughness. Hence in hardened condition steels are generally brittle.
- ▶ The degree of brittleness increased with increasing carbon content and severity in the cooling rate.
- ▶ More over, high residual stresses are developed due to the formation of martensite. Therefore hardening is always followed by another treatment known as tempering.

### Purpose

- ▶ The purpose of tempering is to relieve the residual stresses and improve the ductility and toughness of the steel. The gain in ductility and toughness is usually attained at the loss of hardness and wear resistance.

### Process

- ▶ The process consists of heating the steel below the lower critical temperature (typically 150 – 630 °C) followed by cooling in air or at any other desired cooling rate.

### Structural Changes

- ▶ As martensite is a supersaturated solid solution, if energy is supplied by tempering, it decomposes to a two-phase microstructure consisting of B.C.C.  $\alpha$  ferrite and small particles of carbide.

### Classification

1. Low-temperature tempering	about 200°C	high carbon and low alloy steel
2. Medium temperature tempering	about 200 - 400°C	coil and laminated spring
3. High-temperature tempering	about 400 - 650°C	medium carbon steel, shafts, gears

## 6.3 Factors Affecting the Hardening Process

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### 1. Hardening temperature

- ▶ Hypoeutectoid steel 30-50°C above the upper critical temperature line (A<sub>3</sub>).
- ▶ Hyper eutectoid steel 30-50°C above the lower critical temperature line (A<sub>1</sub>).

### 2. Holding time

- ▶ The recommended holding time is 1 hour for each 25mm thickness or diameter.

### 3. Quenching medium

- ▶ Different industrial quenching media available are water, brine, air, oil, molten salt bath, and synthetic quenchants.

- ▶ Quenching medium characteristics such as temperature, specific heat, and thermal conductivity, latent heat of vaporization, viscosity and agitation affect the cooling+

#### 4. Cooling rate

- ▶ The critical cooling rate (CCR) largely depends upon the alloying element. Alloy steel has less CCR and hence some of the alloy steels are hardened by air cooling.
- ▶ High carbon steels have slightly more CCR and have to be hardened by oil cooling.
- ▶ Medium carbon steels have still higher CCR hence water or brine quenching is required.

#### 5. Shape and size of steel parts

- ▶ Larger parts or parts with variable thickness are heated at a very slow rate because at a faster cooling rate, the thermal gradient is set up between the inner and outer surface or between the thick and thin surface.
- ▶ These parts are held at the hardening temperature for a sufficient period of time to attain a uniform temperature.
- ▶ The quenching medium contacts the surface of the parts only. So that the ratio of surface to mass is an important factor in determining the actual cooling rate.

#### 6. Surface condition

- ▶ The surface condition of the steel components also affects the hardening characteristics.
- ▶ The presence of scale, oil, grease, and other foreign particles are not desirable. Oil and grease burn during the heating and leave behind a residue which is bad conduction of heat. These residues, scale or foreign particles result in variable cooling rates at different points on the surface.

### 6.4 Surface Heat Treatment or Case Hardening

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- ▶ Numerous industrial applications require a hard wear resistance surface called the case and relatively soft, tough inside called core.
- ▶ Case hardening methods
  1. Carburizing
  2. Nitriding
  3. Cyaniding or carbonitriding
  4. Flame hardening
  5. Induction hardening
- ▶ The first three methods change the chemical composition
  - Carburizing – the addition of carbon
  - Nitriding – the addition of nitrogen
  - Cyaniding – the addition of both
- ▶ The last two methods do not change the chemical composition of the steel. In flame and induction hardening the steel must be capable of being hardened, therefore the carbon content must be about 0.3% or higher.

#### 1. Carburizing

- ▶ Carburizing is a process by which the carbon content of steel is increased.
- ▶ Low carbon steel, usually about 0.2% carbon or lower is placed in an atmosphere that contains a substantial amount of carbon monoxide.
- ▶ This process is used for machine parts including cams, pistons, gears, pump shafts, etc.
- ▶ The process consists of heating the steel to a temperature 1700°F (900-930°C) in contact with a carburizing medium, holding at that temperature for a sufficient period of time and cooling it to room temperature.

- ▶ As the steel is now in the austenite region and the solubility of carbon is more in this region, the carbon from the medium is diffused into austenite (1.2% of carbon at the surface).
- ▶ In this method, steel components to be carburizing are packed with carburizing medium in heat resistance boxes.
- ▶ The carburizing medium consists of an 80% mixture of charcoal coke and 20% barium carbonate (energizer). The boxes are placed in the furnace and heated to 230°C. The parts are maintained at this temperature until the desired degree of penetration is obtained.

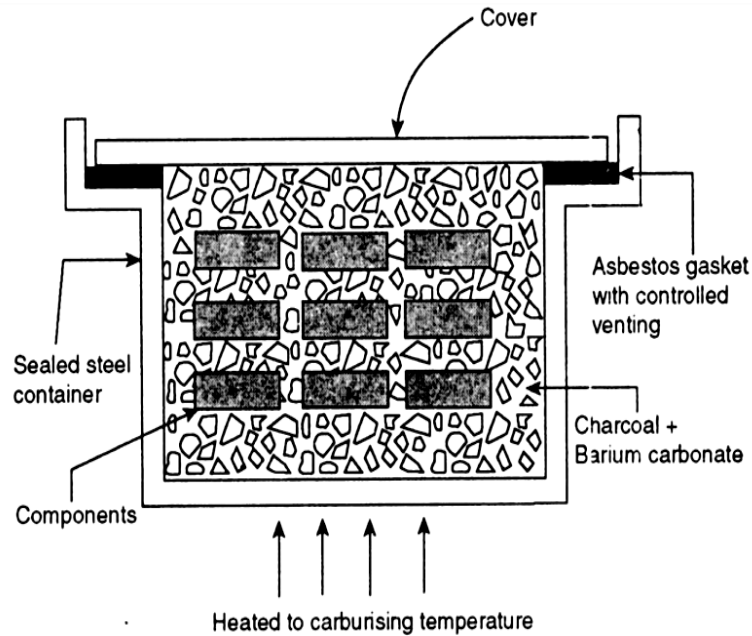
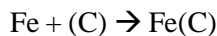


Fig.6.7 – Pack carburizing

1. Barium carbonate decomposes on heating  

$$\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2$$
2. In the presence of carburizing material,  $\text{CO}_2$  gives CO  

$$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$$
3. The main carburizing reaction takes place at the surface of the steel. The carbon produced is in nascent form and it diffuses into the steel



4. The  $\text{CO}_2$  produced reacts with the carburizing components to form more CO.  

$$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$$

- ▶ The depth obtained varies from 1 to 2 mm and carburizing time varied from 6 to 8 hrs.

#### Advantages

- ▶ It does not require the use of a prepared atmosphere.
- ▶ It is efficient and economical for industrial processing of parts in small lots or for large massive parts.

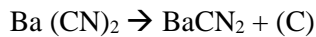
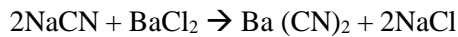
#### Disadvantages

- ▶ Not suitable for the production of thin carburized cases.
- ▶ Close control of surface carbon cannot be achieved.

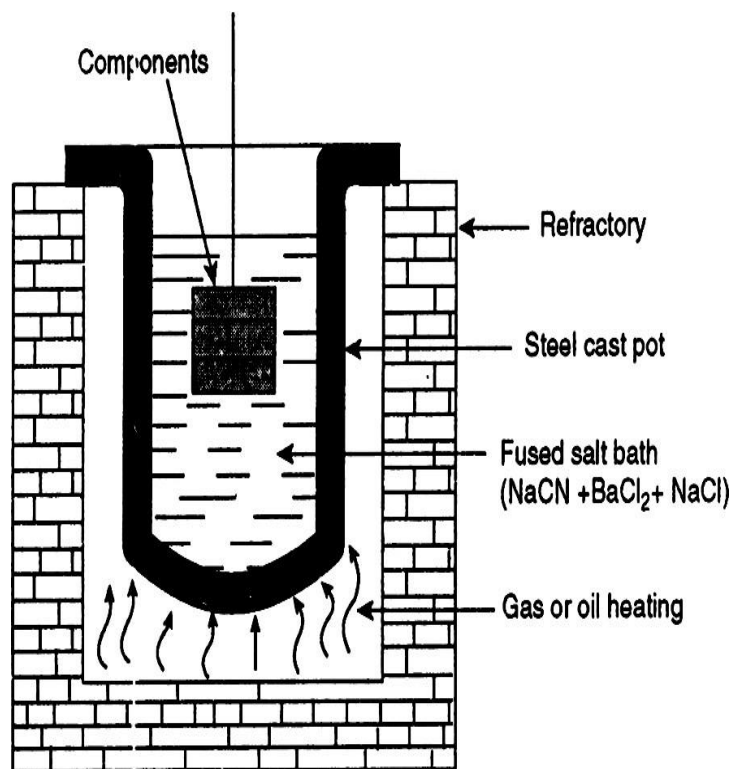
## 1. Liquid Carburizing

- ▶ Liquid carburizing is also known as salt bath carburizing. The carburizing medium is a fused salt bath composed of sodium cyanide (NaCN), sodium chloride (NaCl) and barium chloride (BaCl<sub>2</sub>). Both are melted in a steel cast pot type furnace heated by oil or gas.
- ▶ The process is carried out by immersing the steel components in both maintained at a temperature of 815 - 900°C for a period varying from 5 min to 1 hrs. Depending upon the case depth require. The components are then quenched.

- ▶ The reactions in the salt bath are as follows:



- ▶ The carbon atoms dissolve interstitially in the steel. A small amount of liberated nitrogen is also absorbed.
- ▶ This process gives a thin and clear hardened layer up to a case depth of 0.08 mm. A high-temperature salt bath is used for producing a deep case.



*Fig.6.8 - Liquid carburizing*

### Advantages

- ▶ Rapid and uniform heat transfer, low distortion, negligible surface oxidation and rapid absorption of carbon.
- ▶ Highly uniform case depths are obtained with uniform carbon content.
- ▶ The cycle time for liquid carburizing is shorter than gas or pack carburizing.

### Disadvantages

- ▶ Cyanide salts are extremely poisonous so the case is required during its storage and disposal.
- ▶ The salt sticks to the components and must be thoroughly washed after treatment.
- ▶ Regular checking and adjustment of both compositions are necessary to obtain uniform case depth.

## 2. Gas Carburizing

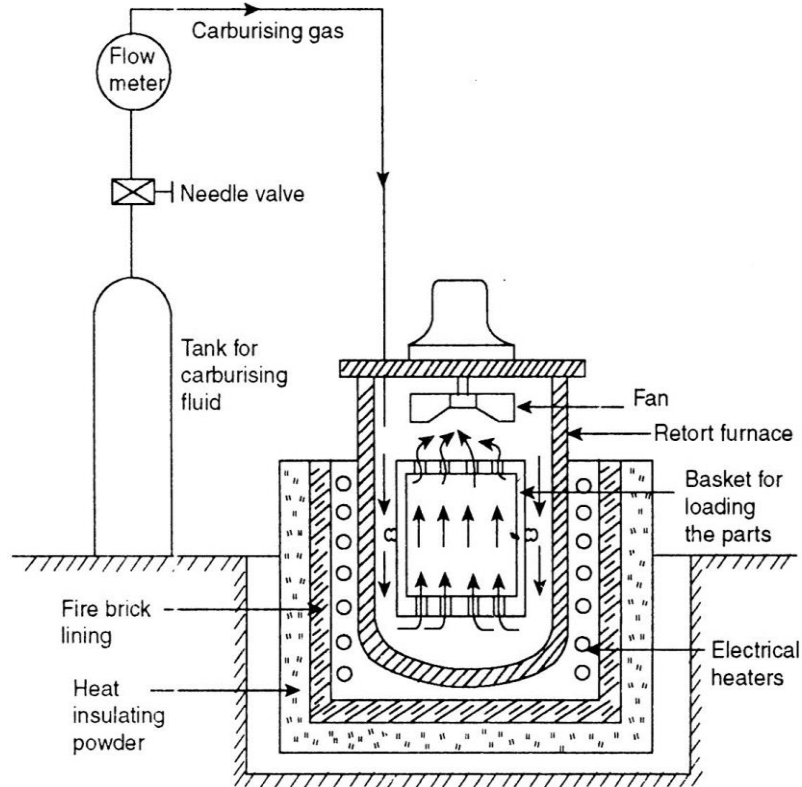


Fig.6.9 – Gas carburizing

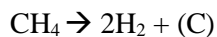
- ▶ This is the most widely used carburizing method for mass production.
- ▶ The steel is heated in contact with carbon monoxide or hydrocarbon which is readily decomposed at carburizing temperature. The hydrocarbon may be methane, propane, natural gas or vaporized fluid hydrocarbon.
- ▶ Gas carburizing is carried out in an airtight retort furnace capable of maintaining positive pressure.
- ▶ The furnace is initially purged (washout) with a carrier gas consisting of a mixture of CO, N<sub>2</sub>, and H<sub>2</sub>. The furnace operates at the carburizing temperature of 930°C.
- ▶ The components are loaded in the basket and lowered into the furnace so that a free flow of gas could pass around them. A fan is suited at the top of the furnace which circulates and mixes the gas.
- ▶ When the material reaches the carburizing temperature, methane or propane is added to maintain specific carbon potential.
- ▶ During gas carburizing the following reaction takes place:

1. The carbon monoxide in the carrier gas is the active carburizing agent.

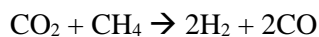


The carbon thus releases dissolved interstitially into the surface of the steel.

2. Methane also release carbon



3. Carbon dioxide formed in -1 reacts with methane



The concentration of carbon monoxide is thus maintained so that carburizing continuous.

- ▶ Gas carburizing is commonly used to obtain thin carbon between 0.2 – 0.5 mm.

## Advantages

- ▶ This method is used for large volume production.
- ▶ Process provides accurate control of case depth and surface carbon content.
- ▶ It is a cleaner process.
- ▶ It allows quicker handling by direct quenching.
- ▶ Less labor cost but highly skilled personnel are required to maintain the necessary control.

## Heat treatment after carburizing

- ▶ After carburizing excess cementite ( $\text{Fe}_3\text{C}$ ) occurs as a network in the case and induces brittleness. However, a case containing 1% or more carbon may be soft at the surface after quenching due to the retention of austenite. Prolonged heating in the austenite range during carburizing introduces a coarse grain to the whole structure.
- ▶ The objective of heat treatment after carburizing are:
  1. To break the cementite network
  2. To achieve higher hardness at the surface
  3. To refine the coarse grains of the core and case.

## 3. Direct Quench

- ▶ In this method, the components are quenched in a quenching both directly, from the carburizing temperature and then tempered to reduce the brittleness of the case.
- ▶ Due to faster cooling from the austenite region, martensite is produced in the surface and reasonably fine ferrite is produced in the center. This process is good for only fine-grained steels.

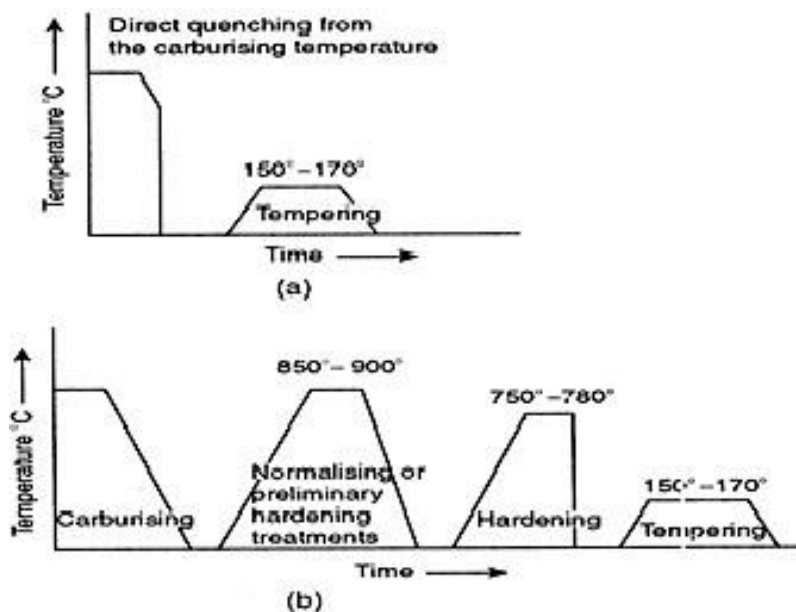


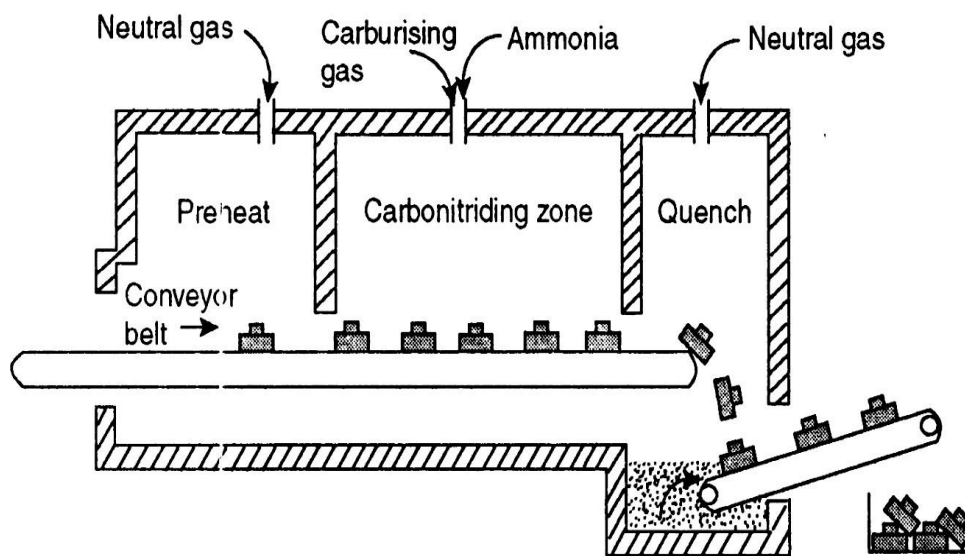
Fig.6.10 – Heat treatment for carburized steel (a) Direct quench  
(b) Double heat treatment

## 4. Double Heat Treatment

- ▶ If the steel is coarse-grained through the cross-section then double heat treatment required.
- ▶ Steps involved in the process are:

1. Slow cooling from the carburizing temperature to room temperature. This reduces the residual stresses which in turn reduce the tendency of distortion and cracking.
2. Reheating the steel above the upper critical temperature (850 - 900°C) and quenching. Austenite is finer at this temperature and these results in finer ferrite grains at the core. The additional advantage is that the carbide network also dissolves on heating and does not appear after quenching.
3. Reheating to a temperature just above the lower critical temperature (750 – 780°C) and quenching. By this treatment refining and hardening of the case are achieved. On quenching, austenite transforms to martensite at the surface of the steel. The core does not get hardened.
4. Tempering the steel to relieve internal stresses and brittleness of the case.
  - ▶ The carbonitriding process involves the diffusion of both carbon and nitrogen into the steel surface.
  - ▶ This process is specifically used for plain carbon steel (0.3 – 0.4% C) to improve the wear resistance.
  - ▶ This process is carried out in a gas atmosphere furnace. The gas mixture consists of carburizing gas which is a mixture of methane (5%), ammonia (15%) and remaining natural gas.
  - ▶ The process is performed at a lower temperature in the range of (800 - 870°C). The phase present in steel at this temperature is ferrite and austenite.
  - ▶ Carburizing gas is the source of carbon. Ammonia dissolves to provide nitrogen. Carbon and nitrogen diffuse simultaneously into the surface of the steel in the austenitic-ferritic condition.

## 5. Carbo Nitriding



*Fig.6.11 – Carbo nitriding*

- ▶ Nitrogen is more effective in increasing the Hardenability of the case when compared to carbon.
- ▶ After carbonitriding, quenching is done in oil followed by tempering at 150 - 180°C.
- ▶ The core depth is in the order of 0.05 – 0.75mm and having hardness approximately 60 – 65 HRC. The method is applied for bolts, nuts, and gears.

### Advantages

- ▶ It has advantages over carburizing as the lower heat-treating temperature is required and less drastic quench is needed. The less drastic quench significantly reduces the distortion.
- ▶ The wear resistance and surface Hardenability are better than the carburizing process.

## 6. Cyaniding

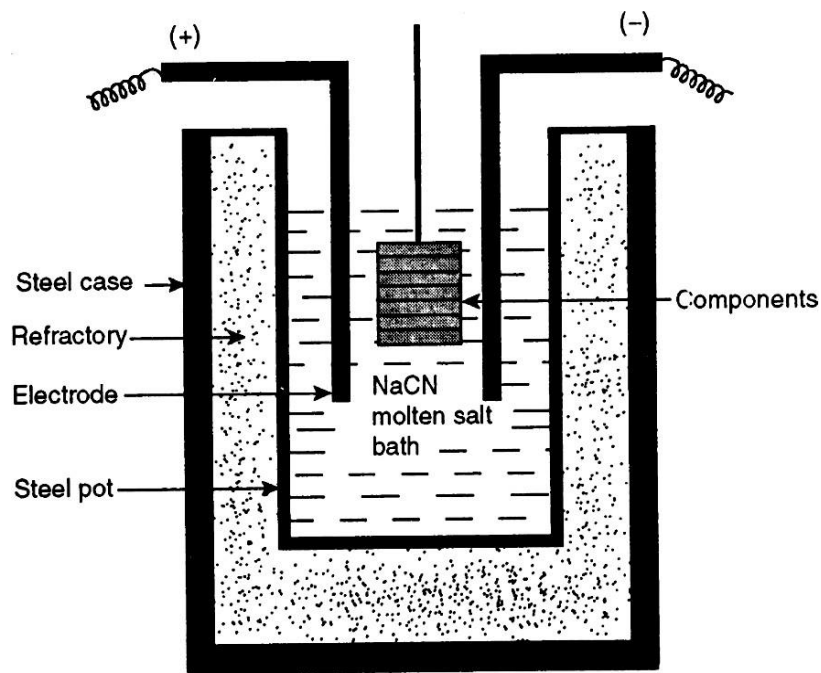


Fig.6.12 – Cyaniding

- ▶ The cyaniding process involves the diffusion of both carbon and nitrogen into the surface of the steel.
- ▶ This process is used for low carbon steel (0.2%C) and is similar to liquid carburizing because of the use of a cyanide salt bath.
- ▶ The steel is immersed in a molten salt bath of sodium cyanide heated by immersed electrodes. The concentration of sodium cyanide varies between 25% and 90%. The most commonly used concentration is 30%.
- ▶ The bath is heated at a temperature between 800 – 870 °C.
- ▶ The basic reaction in the bath are:
  1. Molten cyanide decomposes in the presence of air at the surface of the bath to produce sodium cyanate.
$$2\text{NaCN} + \text{O}_2 \rightarrow 2\text{NaCNO}$$
  2. Sodium cyanate further dissociates to liberate carbon and nitrogen.
$$4\text{NaCNO} \rightarrow \text{Na}_2\text{CO}_3 + 2\text{NaCN} + \text{CO} + 2(\text{N})$$
$$2\text{CO} \rightarrow \text{CO}_2 + (\text{C})$$
- ▶ Carbon and nitrogen are so formed are absorbed in the surface of the steel. After cyaniding, the process is quenched directly into oil or water.
- ▶ The case depth obtained is in the range of 0.025 – 0.25 mm and surface hardness is up to 65 HRC. It is used for small parts like nuts, bolts, and gears.

### Advantages

- ▶ Process is less time consuming.

### Disadvantages

- ▶ Sodium salts are very poisonous, care is required.
- ▶ This process is not suitable for parts which are subjected to shock, fatigue, and impact because nitrogen addition has an adverse effect on such properties.

## 7. Nitriding

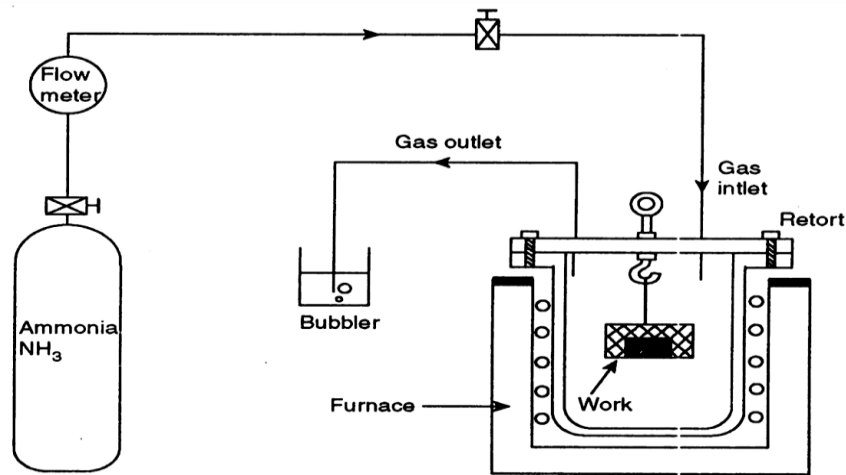
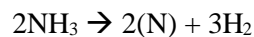


Fig.6.13 – Nitriding

- ▶ In the nitriding process, atomic nitrogen is diffused into the surface of the steel being treated.
- ▶ This process is more effective for special alloy steel containing aluminum, chromium, vanadium, and molybdenum. These elements form hard and stable nitrides as soon as they come into contact with nitrogen at the surface of the workpiece.
- ▶ Before being a nitride, the steel parts are heated to produce the required core property. The heat treatment is done by heating the steel to 930°C, quenching in oil followed by tempering. All rough and finish machining is carried out before nitriding.
- ▶ The steel parts are placed in a retort and heated to a temperature of about 550°C. At this temperature ammonia (NH<sub>3</sub>) gas is allowed to circulate. The ammonia gas dissociates as follows the equation.



- ▶ The atomic nitrogen is absorbed by the surface of steel forming nitrides both with iron and other elements. The parts are maintained at this temperature for about 40 – 100 hours according to the core required.
- ▶ Nitriding does not involve a quench and the parts are slowly cooled in the retort itself.
- ▶ Core depth in the range of 0.1 – 0.5 mm is obtained and hardness up to 1100 VHN.

### Application

- ▶ Nitriding is used for aircraft engine parts such as cams, cylinders, liners, valve stems, shaft, and piston rings. Nitride steels are more corrosion resistant and have higher endurance limit than most of the plain carbon carburized steels.
- ▶ Parts such as gauges, forming dies, bearing parts are surface hardened by nitriding.
- ▶ During nitriding „white layer“ of Fe<sub>4</sub>N and Fe<sub>2</sub>N formed at the outer layer of the surface. The white layer is brittle and hence has a determinate effect on the fatigue life of nitrided parts and this is normally removal.

### Advantages

- ▶ No quenching is required after nitriding, cracking or distortion is unlikely.
- ▶ Very high surface hardness is obtained. (1100 VHN)
- ▶ Resistance to corrosion is good.
- ▶ Fatigue resistance is important advantages.

- ▶ Hardness is retained up to 500°C whereas in carburized component hardness begins to fall at low temperature. (200°C)
- ▶ It is a very clean process compared with the cyanide bath.

### Disadvantages

- ▶ This process is economical only when a large number of components are to be treated.
- ▶ To obtain maximum hardness, special alloy steel has to be used.
- ▶ The cycle times are long requiring 50 – 90 hours to produce a maximum case depth of 0.5 – 0.8 mm.

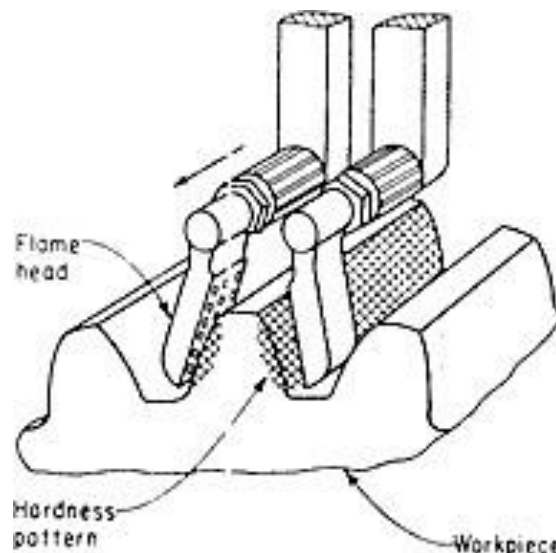
## 8. Flame Hardening

- ▶ Flame hardening and induction hardening do not change the chemical composition of the steel.
- ▶ In this process, the surface of the steel is heated by oxy-acetylene gas flame to austenitizing temperature followed by a quenching spray. The austenite is transformed into martensite.

The steel for flame hardening must have sufficient carbon content (0.3 – 0.6 %C).

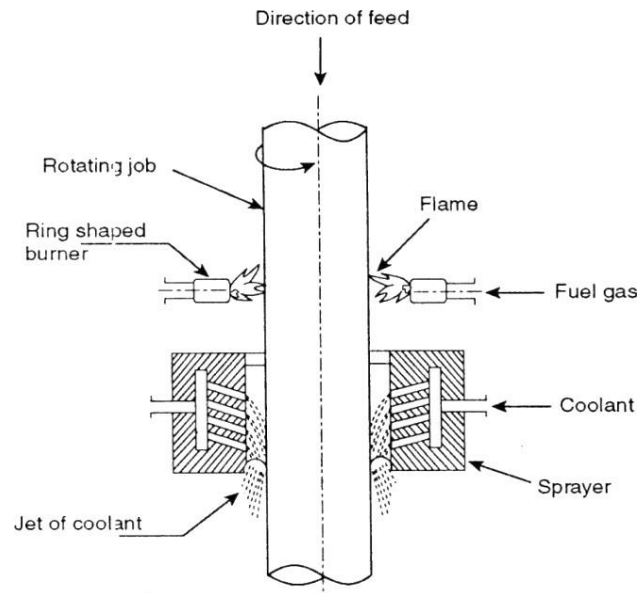
Methods of flame hardening:

1. Stationary (Torch and workpiece stationary)
  2. Progressive (Torch moving, workpiece stationary)
  3. Spinning (Torch stationary, workpiece moving)
  4. Progressive spinning (Torch and workpiece moving)
- ▶ In a stationary method, both torch and work are stationary. This method is used for spot hardening of small parts such as valve stems, open and wrenches, the tip of the screw, etc.
  - ▶ In the progressive method, the torch moves over a stationary workpiece. This is used for the hardening of large parts such as a way of lathe bed, teeth of large gears.



*Fig.6.14 – Progressive method of flame hardening, showing the hardness pattern developed*

- ▶ In the spinning method, the torch is stationary while the workpiece rotates such as precision gears, pulleys, and drums.
- ▶ In the progressive spinning method, in which the torch moved over a rotating workpiece. It is used for surface hardening of long circular parts such as shaft and rolls.



*Fig.6.15 - Flame hardening (progressive)*

- ▶ In all the procedures, provision must be made for rapid quenching after the surface has been heated to the required temperature.
- ▶ This may be accomplished by the use of water spray, by quenching the entire piece in water or oil or even air cooling in some steels.
- ▶ After quenching the parts should be stress relieved by heating in the range of (350 – 400 °F) and air-cooled. Such treatment does not appreciably reduce surface hardness.
- ▶ Hardness zone is much deeper than obtained by carburizing range from (1/8” – 1/4”) inch in depth. Thinner cases of an order of 1/16” can be obtained by increasing the speed of heating and quenching.

#### **Advantages**

- ▶ The required area can be hardened.
- ▶ Large machine surface can be hardened economically.
- ▶ Ability to treat component offer surface finishing, since there is a little scaling, decarburization or distortion.

#### **Disadvantages**

- ▶ The possibility of overheating and thus damaging the parts.
- ▶ The difficulty is producing a hardened zone less than 1/16” in depth.
- ▶ To obtain optimum results, a technique has to be developed for each design.

## 9. Induction Hardening

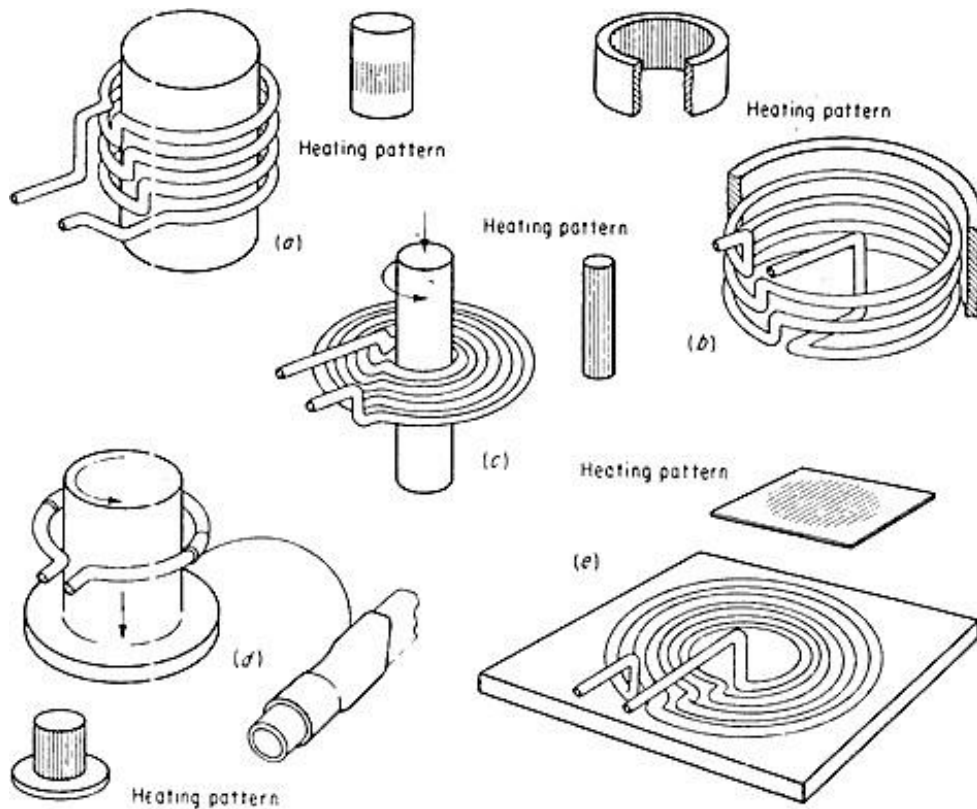


Fig.6.16 – Typical works coils for high – frequency units and the heat patterns developed by each.

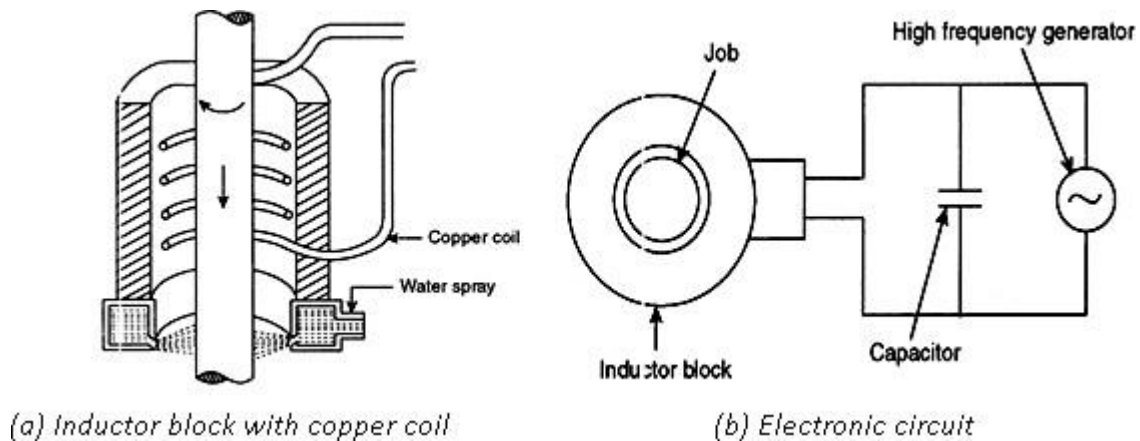


Fig.6.17 - Induction hardening

- ▶ Due to very fast heating and no holding time, the austenite formed fine and this result in fine-grained martensite.
- ▶ Induction hardening is normally followed by a low-temperature tempering at (160 – 200 °C).
- ▶ The depth of hardening is controlled by the frequency of alternating currents where
 
$$d \propto \frac{1}{f}$$
- ▶ The steels with carbon content 0.4 – 0.5% are more suitable for this process.

Table 6.2 - Homogeneous & Heterogeneous System

Frequency, Hz	Theoretical Depth on the Penetration of Electrical Energy, Inch	Practical Depth of Case Hardness, Inch
1000	0.059	0.180 to 0.350
3000	0.035	0.150 to 0.200
10000	0.020	0.100 to 0.150
120000	0.006	0.060 to 0.100
500000	0.003	0.040 to 0.080
1000000	0.002	0.010 to 0.030

### Applications

- ▶ Crankshaft, camshaft, axles, gears, rolls, bearing bars, brakes drums, overhead traveling crane wheels, etc.

### Advantages

- ▶ Fast heating and the absence of holding time leads to an increase in production rate.
- ▶ No decarburization occurs.
- ▶ Less distortion because the heating is only at the surface.
- ▶ Easy control over the depth of hardening by control of the frequency of supply voltage and time of holding.

### Disadvantages

- ▶ Because of the cost of the equipment, the process is not suitable for small scale production.
- ▶ Irregular shaped parts cannot be handled economically.
- ▶ High maintenance cost.

## 6.5 Austempering or Isothermal Quenching

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### Purpose

- ▶ Austempering is a hardening process. The purpose of Austempering is either to reduce the tendency towards distortion and cracking during conventional quenching or to improve the ductility and toughness while maintaining the hardness.

### Process

- ▶ Steel is heated above austenitizing temperature and then quenched in a bath maintained at a temperature just above Ms temperature within the bainitic region (between 400 – 800°F) 200 – 400 °C in general. It is held at that temperature in the salt bath for a sufficient period of time until all the austenite is transformed into bainite.
- ▶ Since the transformation occurs at a constant temperature, this process is known as „isothermal hardening“.
- ▶ After complete transformation, the steel is taken out of the bath and cooled to room temperature by any desired rate.

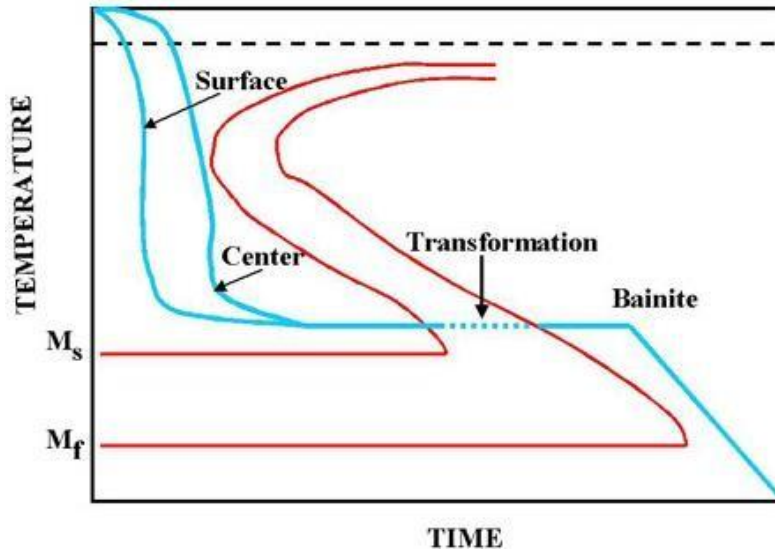


Fig.6.18 - Austempering

### Structural changes

- ▶ Depending on the transformation temperature the structure could be upper bainite or lower bainite. But the lower bainite is preferable as it has better mechanical properties than tempered martensite.

### Applications

- ▶ Austempering is applied for heat-treating components of intricate sections. Such components might distort or crack when they are treated by the conventional quench hardening. This is avoided in Austempering.

## 6.6 Martempering or Marquenching

### Purpose

- ▶ It is also a hardening process. The purpose of martempering is similar to Austempering.
- ▶ Martempering steels have fewer tendencies to crack, distort and develop residual stresses during heat treatment

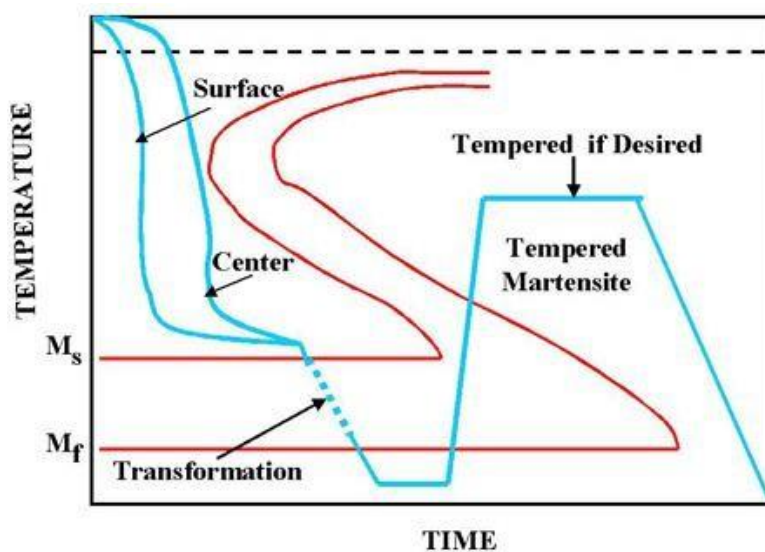


Fig.6.19 – Martempering

### **Process**

- ▶ In this process, the steel is heated to austenitizing temperature. It is then quenched in a constant temperature bath (180 – 250 °C) maintained above Ms temperature. It is held in this bath until the temperature is uniform through the part. Then it is removed the bath and cooled in air.
- ▶ This process removes most of the quenching stress.

### **Structure Changes**

- ▶ During cooling in air, the structure obtained is martensite. The steel is generally tempered in order to improve the property.

### **Application**

- ▶ This process is more suitable for high carbon steel and alloy steel.

## **6.7 References**

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