LECTURE NOTE ON

INTRODUCTION TO PHYSICAL METALLURGY AND ENGINEERING MATERIALS

(MEPC2002)

B.TECH 3RD SEMESTER, MECHANICAL ENGINEERING

Prepared by:

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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:

CO1	Understand the crystal structure and classification of engineering materials.
CO2	Understand the classification of ferrous and nonferrous alloy and study their applications.
CO3	Interpret the phase diagrams of materials.
CO4	Understand heat treatment and surface hardening processes affecting mechanical properties of metals and alloys.
CO5	Understand the effect of alloying and composite materials.

INTRODUCTION

Metallurgy refers to the science and technology of metals. The subject area can be considered as a combination of chemistry, physics and mechanics with special reference to metals. In later years, metallurgy has expanded into materials science and engineering encompassing metallic, ceramic and polymeric materials. Metallurgy is an ancient subject linked to the history of mankind. The development of civilizations from Stone Age, Bronze Age and Iron Age can be thought of as the ages of naturally available ceramic materials, followed by the discovery of copper that can be produced relatively easily and iron that needs higher temperatures to produce. These follow the pattern of the Ellingham diagram known to all metallurgists. Faraday introduced the concept of electrolysis which revolutionized metal production. Today, we are able to produce highly reactive metals by electrolysis.

The prime objective to produce metals and alloys is to have materials with optimized properties. These properties are related to structure and thus, physical as well as mechanical properties form essential parts of metallurgy. Properties of metals and alloys enable the choice of materials in production engineering.

MATERIALS SCIENCE AND ENGINEERING

The discipline of materials science involves **investigating the relationships that exist between the structures and properties of materials**. In contrast, materials engineering is, on the basis of these structure–property correlations, designing or engineering the structure of a material to produce a predetermined set of properties.

OBJECTIVE OF MATERIAL SCEINCE

1. To understand the structure, properties, processing and performance of the principal classes of materials, and to understand and exploit the relationships between these four aspects of materials.
2. Concerns with the interdisciplinary study of materials for engineering and other practical purposes.
3. Deals with all materials, e.g. metals, ceramics, glasses, polymers woods and stones

PHYSICAL METALLURGY

Physical metallurgy is one of the two main branches of the scientific approach to metallurgy, which considers in a systematic way the physical properties of metals and alloys. It is basically the fundamentals and applications of the theory of phase transformations in metal and alloys, Also it deals with

- Evolution of structure in solid as it forms from liquid.
- Effect of alloy elements / impurities on the transformation process.
- Effect of processing technique on the evolution of structure.

- Structure property relation.

OBJECTIVE OF PHYSICAL METALLURGY

1. To provide a basic understanding of the underlying principles that determines the evolution of structure in metals and alloys during their processing and its relation with their properties and performance in service.
2. Understanding the behavior of materials particularly structure property correlation will help selecting suitable material for a particular application.
3. To know the effect of for instance the chemical composition, heat treatment and production process on the final component in order to achieve components with optimal properties.

Structure

‘‘Structure’’ is at this point a nebulous term that deserves some explanation. In brief,

i. The structure of a material usually relates to the arrangement of its internal components.
ii. Subatomic structure involves electrons within the individual atoms and interactions with their nuclei.
iii. On an atomic level, structure encompasses the organization of atoms or molecules relative to one another.
iv. The next larger structural realm, which contains large groups of atoms that are normally agglomerated together, is termed ‘‘microscopic,’’ meaning that which is subject to direct observation using some type of microscope.
v. Finally, structural elements that may be viewed with the naked eye are termed ‘‘macroscopic.’’

Property

Property is a material trait in terms of the kind and magnitude of response to a specific imposed stimulus. Generally, definitions of properties **are made independent of material shape and size.**

While in service use, all materials are exposed to external stimuli that evoke some type of response. For example, a specimen subjected to forces will experience deformation; or a polished metal surface will reflect light.

Virtually all important properties of solid materials may be grouped into six different categories: such as:

i. Mechanical
ii. Electrical
iii. Thermal
iv. Magnetic
v. Optical
vi. Deteriorative.

Mechanical properties relate deformation to an applied load or force; examples include elastic modulus and strength.

Electrical properties, such as electrical conductivity and dielectric constant, the stimulus is an electric field.

The thermal behaviour of solids can be represented in terms of heat capacity and thermal conductivity.

Magnetic properties demonstrate the response of a material to the application of a magnetic field.

Optical properties, the stimulus are electromagnetic or light radiation; index of refraction and reflectivity are representative optical properties.

Finally, **deteriorative characteristics** indicate the chemical reactivity of materials.

In addition to structure and properties, two other important components are involved in the science and engineering of materials, viz. ‘‘**processing**’’ and ‘‘**performance**.’’

Interrelationship between processing, structure, properties, and performance

With regard to the relationships of these four components, the structure of a material will depend on how it is processed. Furthermore, a material’s performance will be a function of its properties. **Thus, the interrelationship between processing, structure, properties, and performance is linear**, as depicted in the schematic illustration shown in Figure.

Processing ⇨ **Structure** ⇨ **Properties** ⇨ **Performance**

We now present an example of these processing-structure-properties-performance principles with Figure 1., a photograph showing three thin disk specimens placed over some printed matter. It is obvious that the optical properties (i.e., the light transmittance) of each of the three materials are different; the one on the left is transparent (i.e., virtually all of the reflected light passes through it), whereas the disks in the center and on the right are, respectively, translucent and opaque. All of these specimens are of the same material, aluminum oxide, but the leftmost one is what we call a single crystal—that is, has a high degree of perfection—which gives rise to its transparency. The center one is composed of numerous and very small single crystals that are all connected; the boundaries between these small crystals scatter a portion of the light reflected from the printed page, which makes this material optically translucent. Finally, the specimen on the right is composed not only of many small, interconnected crystals, but also of a large number of very small pores or void spaces. These pores also effectively scatter the reflected light and render this material **opaque**. Thus, the structures of these three specimens are different in terms of

crystal boundaries and pores, which affect the **optical transmittance properties**. Furthermore, each material was produced **using a different processing technique**. And, of course, if optical transmittance is an important parameter relative to the ultimate in-service application, **the performance of each material will be different**.

Figure 1. Three thin disk specimens of aluminum oxide that have been placed over a printed page in order to demonstrate their differences in light-transmittance characteristics. The disk on the left is transparent (i.e., virtually all light that is reflected from the page passes through it), whereas the one in the center is translucent (meaning that some of this reflected light is transmitted through the disk). The disk on the right is opaque—that is, none of the light passes through it. These differences in optical properties are a consequence of differences in structure of these materials, which have resulted from the way the materials were processed. (Specimen preparation, P. A. Lessing; photography by S. Tanner.)

WHY STUDY MATERIALS SCIENCE AND ENGINEERING?

The more familiar an engineer or scientist is with the various characteristics and structure property relationships, as well as processing techniques of materials, the more proficient and confident he or she will be to make judicious materials choices based on these criteria.

All engineers need to know about materials. Even the most "immaterial", like software or system engineering depend on the development of new materials, which in turn alter the economics, like software-hardware trade-offs. Increasing applications of system engineering are in materials manufacturing (industrial engineering) and complex environmental systems.

Innovation in engineering often means the clever use of a new material for a specific application. For example: plastic containers in place of age-old metallic containers. It is well learnt lesion that engineering disasters are frequently caused by the misuse of materials. So it is vital that the professional engineer should know how to select materials which best fit the demands of the design - economic and aesthetic demands, as well as demands of strength and durability. Beforehand the designer must understand the properties of materials, and their limitations. Thus it is very important that every engineer must study and understand the concepts of Materials Science and Engineering. This enables the engineer

- To select a material for a given use based on considerations of cost and performance.
- To understand the limits of materials and the change of their properties with use.
- To be able to create a new material that will have some desirable properties.
- To be able to use the material for different application.

CLASSIFICATION AND SELECTION OF MATERIALS

Material

A material is that out of which any product is to be made for fulfilling the requirement. Materials comprised a wide range of metals and non metals which must be operated upon to form the end product.

Engineering materials

Engineering always emphasises on usefulness of whether the basic law can be applied or not, sometimes some approximation or empirical rule may be taken from practical application part of view. A material is named as engineering material if it satisfies four basic requirements

1. Manufacturing requirement
2. Service requirement
3. Economic requirement
4. Availability requirement

1. Manufacturing/ Fabrication requirement

The fabrication requirements mean that the material should be able to get shaped.(cast, forged , formed , machined, sintered) and joined (welded, brazed) easily. Fabrication requirements relate themselves with materials.

a. Machinability
b. Ductility
c. Castability
d. Heat treatability
e. Weldability

2. Service requirement

This requirement indicates that the selected material should sustain the service demands.

For example the pipeline of water supply system should have a good corrosion resistance that is why the selected pipeline material should have good corrosion resistance properties in the presence of water as well as atmosphere.

3. Economic requirement

This requirement indicates about the minimum possible cost without compromising service requirement. Minimum overall cost can be achieved by optimum selection of both technical and marketing features.

For example: electrical distribution conductors are made by aluminium not in copper through copper is having good conductivity than aluminium same time cost of copper is much higher than aluminium.

4. Availability requirement

This requirement indicates that selected material should be available plentily in the peripheral market, but after globalisation this requirement are not much affecting the selection process. In the contrary availability also affects the cost of the material. Basically for high rate of mass production. This requirement plays an important role.

For an example coke producers are near the coal mines on petroleum refinery.

CLASSIFICATION OF ENGINEERING MATERIALS

The factors which form the basis of various systems of classifications of materials in material science and engineering are:

(i) The chemical composition of the material,
(ii) The mode of the occurrence of the material in the nature,
(iii) The refining and the manufacturing process to which the material is subjected prior it acquires the required properties,
(iv) The atomic and crystalline structure of material and
(v) The industrial and technical use of the material.

A. Based on state (phase) of a given material

i. Gas
ii. Liquid
iii. Solid

B. Based on atomic structure (arrangement of atoms, molecules , ions)

i. Crystalline

    ii. Qasi crystalline
    iii. Amorphous
    iv. Intermediate state(between crystalline and amorphous ie. Partly crystalline are also possible : polymers are partly crystalline

C. Based bond structure

    i. Metals
    ii. Semimetals
    iii. Semiconductors
    iv. Insulations

D. Based on size of entitiy

    i. Nano crystal
    ii. Nano quasicrystalline

E. Based on electrical conduction

    i. Conductors (Al, Cu,Ni)
    ii. SEMICONDUCTOR (Ge, Si)
    iii. Insulators (alumina, polythene)

F. Based on ductility

    i. Ductile – metals, alloy
    ii. Brittle- ceramics, inorganic glasses

Common engineering materials that fall within the scope of material science and engineering may be classified into one of the following six groups:

i. Metals (ferrous and non-ferrous) and alloys
ii. Ceramics
iii. Organic Polymers
iv. Composites
v. Semi-conductors
vi. Biomaterials
vii. Advanced Materials

METALS

Metals are element substances which readily give up electrons to form metallic bonds and conduct electricity. Atoms in metals and their alloys are arranged in orderly manner and relatively dense.

Reason of wide spread application in structural application

a. These materials are relatively stiff and strong
b. Yet are ductile also (capable of large amount of deformation without fracture)
c. Are resistance to fracture

The above reasons accounts for their wide spread use in structural application

Some of the important basic properties of metals are:

(a) Metals are usually good electrical and thermal conductors,
(b) At ordinary temperature metals are usually solid,
(c) To some extent metals are malleable and ductile,
(d) The freshly cut surfaces of metals are lustrous,
(e) When struck metal produce typical sound, and
(f) Most of the metals form alloys.

Metallic materials possess specific properties like plasticity and strength. Few favourable characteristics of metallic materials are high lustre, hardness, resistance to corrosion, good thermal and electrical conductivity, malleability, stiffness, the property of magnetism, etc. Metals may be magnetic, non-magnetic in nature.

These properties of metallic materials are due to:

- **(i) The atoms of which these metallic materials are composed and**
- **(ii) The way in which these atoms are arranged in the space lattice.**

Metallic materials are typically classified according to their use in engineering as under:

i. ***Pure Metals**:* Generally it is very difficult to obtain pure metal. Usually, they are obtained by refining the ore. Mostly, pure metals are not of any use to the engineers. However, by specialised and very expensive techniques, one can obtain pure metals (purity ~ 99.99%), e.g. aluminium, copper etc.

ii. ***Alloyed Metals:*** Alloys can be formed by blending two or more metals or atleast one being metal. The properties of an alloy can be totally different from its constituent substances, e.g. 18-8 stainless steel, which contains 18% chromium and 8% nickel, in low carbon steel, carbon is less than 0.15% and this is extremely tough, exceedingly ductile and highly resistant to corrosion. We must note that these properties are quite different from the behaviour of original carbon steel.

iii. ***Ferrous Metals:*** Iron is the principal constituent of these ferrous metals. Ferrous alloys contain significant amount of non-ferrous metals. Ferrous alloys are extremely important for engineering purposes. On the basis of the percentage of carbon and their alloying elements present, these can be classified into following groups:

   a. ***Mild Steels***: The percentage of carbon in these materials range from 0.15% to 0.25%. These are moderately strong and have good weldability. The production cost of these materials is also low.

   b. ***Medium Carbon Steels***: These contains carbon between 0.3% to 0.6%. The strength of these materials is high but their weldability is comparatively less.

   c. ***High Carbon Steels:*** These contains carbon varying from 0.65% to 1.5%. These materials get hardened tough by heat treatment and their weldability is poor. The steel formed in which carbon content is upto 1.5%, silica upto 0.5%, and manganese upto 1.5% along with traces of other elements is called plain carbon steel.

   d. ***Cast Irons:*** The carbon content in these substances varies between 2% to 4%. The cost of production of these substances is quite low and these are used as ferrous casting alloys.

iv. ***Non-Ferrous Metals:*** These substances are composed of metals other than iron. However, these may contain iron in small proportion. Out of several non-ferrous metals only six are available in sufficient quantity reasonably at low cost and used as common engineering metals. These are aluminium, tin, copper, nickel, zinc and magnesium. Some other non-ferrous metals, about fourteen in number, are produced in relatively small quantities but these are of vital importance in modern industry. These include chromium, mercury, cobalt, tungsten, vanadium, molybdenum, antimony, cadmium, zirconium, beryllium, niobium, titanium, tantalum and manganese.

v. ***Sintered Metals:*** These materials possess very different properties and structures as compared to the metals from which these substances have been cast. Powder metallurgy technique is used to produce sintered metals. The metals to be sintered are first obtained in powered form and then mixed in right calculated proportions. After mixing properly, they are put in the die of desired shape and then processed with certain pressure. Finally, one gets them sintered in the furnace. We must note that the mixture so produced is not the true alloy but it possesses some of the properties of typical alloys.

vi. ***Clad Metals:*** A ‘sandwich’ of two materials is prepared in order to avail the advantage of the properties of both the materials. This technique is termed as cladding. Using this technique stainless steel is mostly embedded with a thick layer of mild steel, by rolling the two metals together while they are red hot. This technique will not allow corrosion of one surface. Another example of the use of this technique is cladding of duralium with thin sheets of pure aluminium. The surface layers, i.e. outside layers of aluminium resist corrosion, whereas inner layer of duralumin imparts high strength. This technique is relatively cheap to manufacture.

CERAMICS

- Ceramics are compounds between metallic and non-metallic elements; they are most frequently oxides, nitrides, and carbides.
- The wide range of materials that falls within this classification includes ceramics that are composed of clay minerals, cement, and glass.
- These materials are typically insulative to the passage of electricity and heat, and are more resistant to high temperatures and harsh environments than metals and polymers.
- With regard to mechanical behaviour, ceramics are hard but very brittle.

IMPORTANT CHARACTERISTICS

- Relatively stiff and strong as compared to metals
- Typically very hard

- Extremely brittle (highly susceptible to fracture)
- Typically insulative to passage of heat and electricity
- Resistance to high temperature than metals and polymer
- Optical characteristics:- transparent, translucent and opaque

Examples:-

i. Traditional ceramics
  5. Clay minerals
    1) Cement
    2) Glass
    3) Feldspar

ii. Morden or advanced ceramics
    1) Al_2O_3
    2) SiC
    3) MgO
    4) BeO
    5) Si_3N_4

POLYMER

- Polymers include the familiar plastic and rubber materials.
- Many of them are organic compounds that are chemically based on carbon, hydrogen, and other non-metallic elements.
- Furthermore, they have very large molecular structures.
- These materials typically have low densities and may be extremely flexible.

IMPORTANT CHARACTERISTICS

- Low density
- Not as stiff nor as strong
- Extremely ductile and pliable (plastic) which means easily formed into complex shapes
- Relatively inert
- Tendency to soften, decompose at modest temperature
- Low electrical conductivities and non magnetic

EXAMPLES

1) Polyethylene
2) Nylon
3) Poly vinyl chloride (PVC)
4) Polycarbonate
5) Polystyrene
6) Silicon rubber

COMPOSITES

- A number of composite materials have been engineered that consist of more than one material type. Fiber glass is a familiar example, in which glass fibers are embedded within a polymeric material.
- A composite is designed to display a combination of the best characteristics of each of the component materials. Fiber glass acquires strength from the glass and flexibility from the polymer.
- Many of the recent material developments have involved composite materials.

IMPORTANT CHARACTERISTICS

- They are better than any of the individual components as regards to their properties like strength, stiffness, heat resistance, etc.

EXAMPLES

1) Steel-reinforced concrete,
2) Dispersion hardened alloys.
3) Vinyl coated steel,
4) Whisker-reinforced plastics.
5) Fibre-reinforced plastics,
6) Carbon-reinforced rubber.

SEMICONDUCTORS

- Semiconductors have electrical properties that are intermediate between the electrical conductors and insulators.
- Furthermore, the electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of impurity atoms, which concentrations may be controlled over very small spatial regions.
- The semiconductors have made possible the advent of integrated circuitry that has totally revolutionized the electronics and computer industries (not to mention our lives) over the past two decades.
- Semiconductors form the backbone of electronic industry. The semiconductors have made possible the advent of integrated circuitary that has totally revolutionized the electronics and computer industries. They affect all walks of life whether it is communications, computers, biomedical, power, aviation, defence, entertainment, etc.
- The field of semiconductors is rapidly changing and expected to continue in the next decade.

- Organic semiconductors are expected to play prominent role during this decade. Diamond as semiconductor will also be important. Optoelectronic devices will provide three dimensional integration of circuits, and optical computing.

BIOMATERIALS

- Biomaterials are employed in components implanted into the human body for replacement of diseased or damaged body parts.
- These materials must not produce toxic substances and must be compatible with body tissues (i.e., must not cause adverse biological reactions).
- All of the above materials—metals, ceramics, polymers, composites, and semiconductors—may be used as biomaterials.

ADVANCED MATERIALS

- Materials that are utilized in high-technology (or high-tech) applications are sometimes termed ***advanced materials***.
- By high technology we mean a device or product that operates or functions using relatively intricate and sophisticated principles; examples include electronic equipment (VCRs, CD players, etc.), computers, fiberoptic systems, spacecraft, aircraft, and military rocketry. These advanced materials are typically either traditional material whose properties have been enhanced or newly developed, high-performance materials.
- Furthermore, they may be of all material types (e.g., metals, ceramics, polymers), and are normally relatively expensive.

EXAMPLE

Materials that are used for lasers, integrated circuits, magnetic information storage, liquid crystal displays (LCDs), fiber optics, and the thermal protection system for the Space Shuttle Orbiter.

MODERN MATERIALS' NEEDS

In spite of the tremendous progress that has been made in the discipline of materials science and engineering within the past few years, there still remain technological challenges, including the development of even more sophisticated and specialized materials, as well as consideration of the environmental impact of materials production.

Some comment is appropriate relative to these issues so as to round out this perspective.

1) **ISSUE:** Reducing the weight of transportation vehicles (automobiles, aircraft, trains, etc.), as well as increasing engine operating temperatures, will enhance fuel efficiency

NEED: New high strength, low-density structural materials remain to be developed, as well as materials that have higher-temperature capabilities, for use in engine components.

2) **ISSUE:** The direct conversion of solar into electrical energy has been demonstrated. Solar cells employ some rather complex and expensive materials.
NEED: To ensure a viable technology, materials that are highly efficient in this conversion process yet less costly must be developed.

3) **ISSUE:** Many materials that we use are derived from resources that are non-renewable,that is, not capable of being regenerated. These include polymers, for which theprime raw material is oil, and some metals.
NEED: These non-renewable resources are gradually becoming depleted, which necessitates: 1) the discovery of additional reserves, 2) the development of new materials having comparable properties with less adverse environmental impact, and/or 3) increased recycling efforts and the development of new recycling technologies.

Some typical needs, thus, of modern materials needs are listed in the following:

- Engine efficiency increases at high temperatures: requires high temperature structural materials
- Use of nuclear energy requires solving problem with residues, or advances in nuclear waste processing.
- Hypersonic flight requires materials that are light, strong and resist high temperatures.
- Optical communications require optical fibers that absorb light negligibly.
- Civil construction – materials for unbreakable windows.
- Structures: materials that are strong like metals and resist corrosion like plastics.

IMPORTANT GROUPING OF MATERIALS

Material group	***Important characteristics***	***Examples***
1. Metals and Alloys	Lusture, hardness, thermal and electricalconductivity, resistance to corrosion, malleability,stiffness and the property ofmagnetism	Iron and steels, aluminium, copper, silver,gold, zinc, magnesium, brasses, bronzes,manganin, invar, super alloy, boron, rareearthalloys, conductors, etc.
2. Ceramics and Glasses	Thermal resistance, hardness, brittleness, opaqueness to light, electrical insulation abrasiveness, high temperature strength and resistance to	Silica, soda-lime-glass, concrete, cement, refractories, Ferrites and garnets, ceramic superconductors, MgO, CdS, Al_2O_3, SiC, $BaTiO_3$, etc.

	corrosion	
3. Organic Polymers	Soft, light in weight, poor conductors of electricity and heat, dimensionally unstable, ductile, combustible, low thermal resistance	*Plastics:* PVC, PTFE, polyethylene, polycarbonate *Fibres:* terylene, nylon, cotton, natural and synthetic rubbers, leather *Other uses:* refrigerants, explosives, insulators, lubricants, detergents, fuels, vitamins, medicines for surface treatment, adhesives, fibre-reinforced plastics, etc.
4. Composites (i) Metals and alloys and ceramics (ii) Metals and alloys and organic polymers (iii) Ceramics and organic polymers	They are better than any of the individual components as regards to their properties like strength, stiffness, heat resistance, etc.	Steel-reinforced concrete, dispersion hardened alloys. Vinyl coated steel, whisker-reinforced plastics. Fibre-reinforced plastics, carbon-reinforced rubber.

PROPERTIES OF ENGINEERING MATERIALS

- The term property in a broader sense may be defined as the quality which defines the specific characteristics of a material.
- Property of a material (material property) is a factor that influences qualitatively or quantitatively, the response of a given material to impose stimuli and constraints.

❖ **The following factors put together, determines the properties of material**

1) Composition
2) Phase present and their distribution
3) Defect structure (in phases and between the phases)
4) Residual stress (can have origins and one may have to travel across length scale)

❖ **The material property is independent of the dimensions or shape of the material.**

❖ **Properties of a material are determined by two important characteristics.**

- Atomic structure (the way atoms, ions, molecules arranged in the material)
- Electromagnetic structure (bonding character). The way the electrons / charges are distributed and spin associated with electron.

The properties materials comes under different kinds of classifications such as

a. Chemical properties

b. Physical properties
c. Mechanical properties
d. Dimensional properties
e. Processing properties

CHEMICAL PROPERTIES

Chemical properties are related to the structure of materials and their arrangements.
The following are the important chemical properties considered for materials in engineering industries.

a. Composition
b. Crystal structure
c. Microstructure
d. Stereo specificity
e. Corrosion resistance
f. Chemical reactivity

PHYSICAL PROPERTIES

Physical properties are the properties based on the physical nature such as colour, dimension etc. The physical properties can be classified are as follows

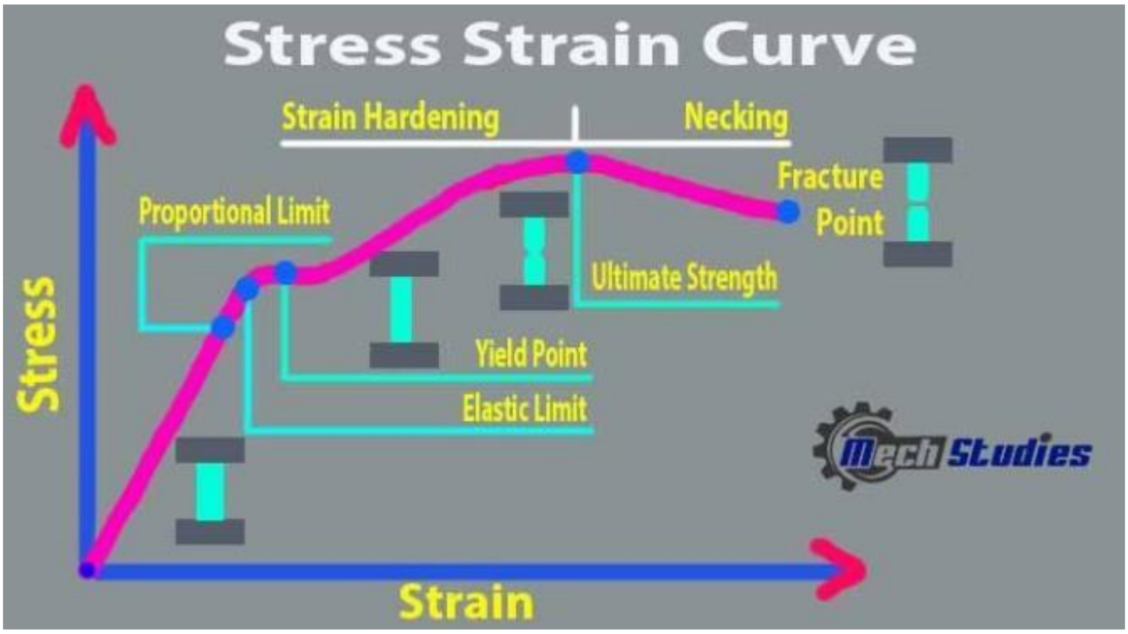
- General physical properties
  a. Dimension
  b. Colour
  c. Appearance
  d. Density
  e. Porosity
- Thermal properties
  a. Melting point
  b. Specific heat
  c. Heat capacity
  d. Thermal expansion
  e. Thermal conductivity
  f. Thermal stability
  g. Thermal shock resistance
  h. Thermal spalling
  i. Heat resistance
- Electrical properties
  a. Resistivity and conductivity

    b. Dielectric constant
    c. Dielectric strength
- Magnetic properties
    a. Permieability
    b. Magnetic field intensity
    c. Magnetic induction
    d. Magnetic flux
    e. Hysteresis
    f. Superconductivity
- Optical properties
    a. Reflection and refraction
    b. Dispersion
    c. Refractive index
    d. Interference
    e. Diffraction
    f. Polarisation

MECHANICAL PROPERTIES

Mechanical properties are the characteristics of the materials that describe the behaviour under the **action of external forces**. Most of the mechanical properties can be experimentally determined. The selection of materials mainly depends on the mechanical properties since it determines the behaviour of engineering materials under applied forces. There are various mechanical properties that influences its effect on the engineering material which are given below

1. Elasticity
2. Plasticity
3. Toughness
4. Resilience
5. Tensile strength
6. Yield strength
7. Impact strength
8. Ductility
9. Malleability
10. Brittleness
11. Hardness
12. Fatigue
13. Creep
14. Wear resistance



Elasticity

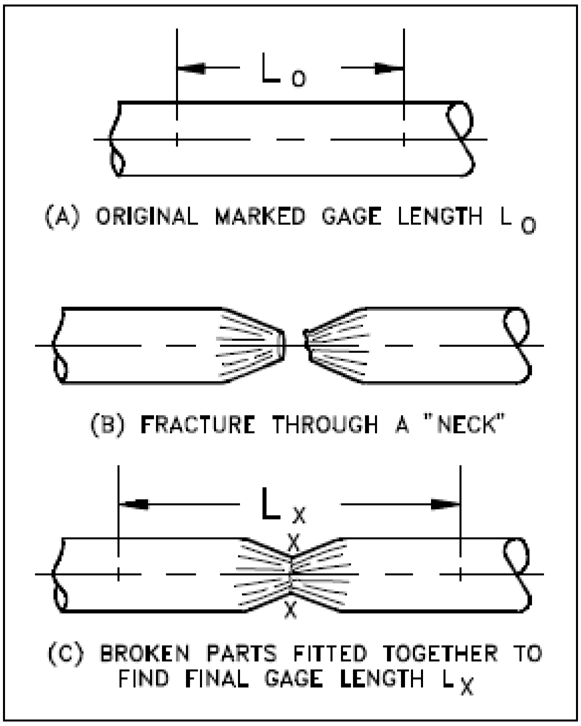
- It is a property of a material which enables it to regain its original shape and size after deformation within elastic imit.
- It is defined as the property of a material to regain its original shape and size after deformation when the external forces are removed.
- It is also called as the tensile property of material
- Example: steel, rubber

Plasticity

- Ability to deform non-elastically without rupture. It is the ability of a material to be permanently deformed (without fracture) even after the load is removed.
- Metals posses more plasticity at high temperature.
- Plasticity increases with increase of temperature.
- Plastic deformation takes place only after the elastic range has been exceeded.
- Example: clay, lead etc are the materials which are plastic at room temperature.
- This property finds its use in forming, shaping and extruding operation of metals.

Ductility

- It is defined as the property of a metal by virtue of which it can be drawn into wires or elongated before rupture takes place.
- It is measured by the percentage of elongation and percentage of reduction in area before rupture of test piece
- Its value is expressed as elongation.



Measuring elongation after fracture

$$\textit{percent elongation} = \frac{\textit{final gage length} - \textit{initial gage length}}{\textit{initial gage length}}$$

$$= \frac{l_f - l_o}{l_o} = \textit{inches per length } \times 100$$

Reduction of area is the proportional reduction of the cross-sectional area of a tensile test piece at the plane of fracture measured after fracture.

$$\textit{percent reduction of area}(RA) = \frac{\textit{area of original crossection} - \textit{minimum final area}}{\textit{area of original crossection}}$$

$$= \frac{A_O - A_{min}}{A_O} = \frac{\textit{decrease in area}}{\textit{original area}} = \frac{\textit{squre inches}}{\textit{squre inches}} \times 100$$

The reduction of area is reported as additional information (to the percent elongation) on the deformational characteristics of the material. The two are used as indicators of ductility, the ability of a material to be elongated in tension. Because the elongation is not uniform over the entire gage length and is greatest at the center of the neck, the percent elongation is not an absolute measure of ductility. (Because of this, the gage length must always be stated when the percent elongation is reported.) The reduction of area, being measured at the minimum diameter of the neck, is a better indicator of ductility.

- Metals with more than 15% elongation are considered as ductile. Metals with 5 to 15 % elongations are considered intermediate ductility.
- Metals 5 % elongations are considered as brittle.

- Example: Gold, Platinum, Silver, Iron, Copper, Al, Ni, Zn, Tin and Lead

- The ductility of many metals can change if conditions are altered. An increase in temperature will increase ductility. A decrease in temperature will cause a decrease in ductility and a change from ductile to brittle behaviour.
- So if a material is tested at high temperature, displacement of atomic plane is fast implies sample produces more plastic strain implies elongation at breaking point will be produced. Ductility will be high.

$$(\%\Delta lmax)_{low\ temp} < (\%\Delta lmax)_{room\ temp} < (\%\Delta lmax)_{high\ temp}$$

$$ductility_{low\ temp} < ductility_{room\ temp} < ductility_{high\ temp}$$

$$\boldsymbol{ductility \propto \frac{1}{strentgh} \propto temperature}$$

Brittlness

- The term brittleness may be defined as the property of a metal by virtue of which it will fracture without any **appreciable deformation**.
- Material failure with little deformation, low % elongation and % area reduction.
- Metals with less than 5% elongation are known to be brittle ones
- Example: cast iron, concrete, brass, ceramics

$$\boldsymbol{brittleness \propto strength \propto \frac{1}{ductility} \propto \frac{1}{tempearture}}$$

Hardness

- The term hardness may be defined as the property of a metal by virtue of which it is able to resist abrasion, indentation and scratching by harder bodies.
- Resistance to scratching and denting.
- Hardness of a material is determined by comparing its hardness with ten standard minerals.

Several methods for hardness testing

Those most often used are

1. Brinell
2. Rockwell
3. Vickers
4. Tukon
5. Slerscope

6. files test.

The first four are based on indentation tests and **the fifth on the rebound height of a diamond-tipped metallic hammer.** The file test establishes the characteristics of how well a file takes a bite on the material.

With increasing order of their hardness

$$talc < gypsum < calcite < fluorite < apatite < orthoclase < quartz < topaz < corundum < diamond$$

- $\boldsymbol{hardness \propto strength}$

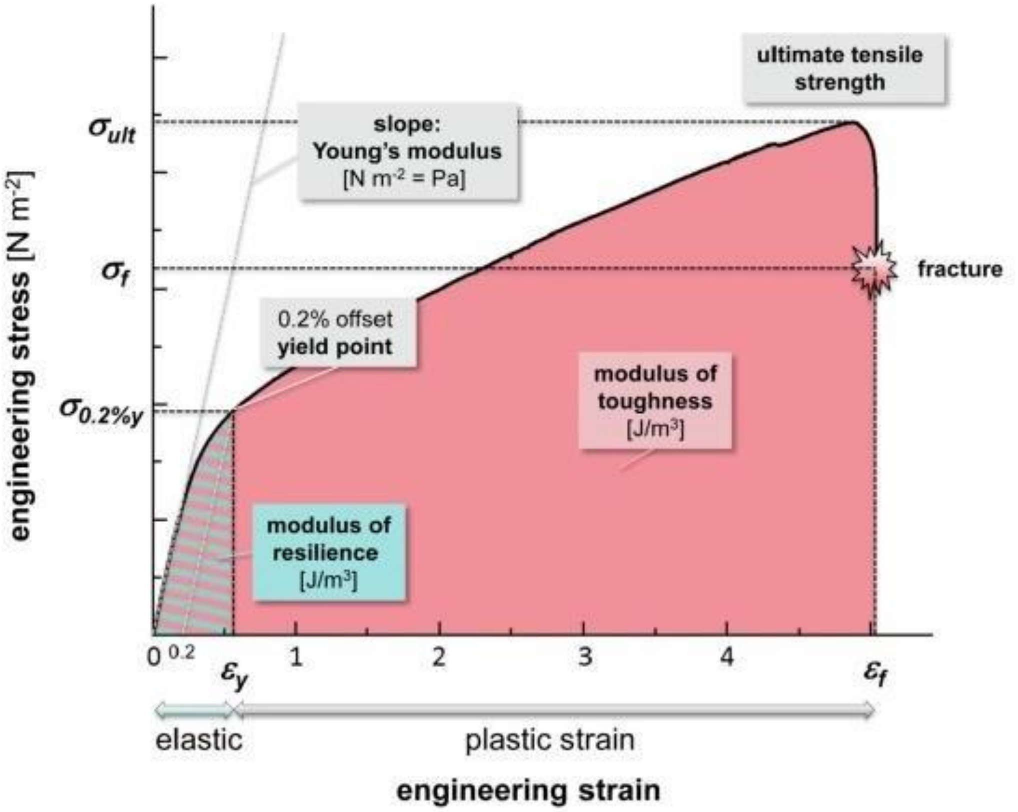
Toughness

- The term toughness may be defined as the property of a metal by virtue of which it can absorb maximum energy before fracture takes place.
- Other definition is amount of energy per unit volume that a material can absorb before rupture.
- It can also define materials resistance to fracture when stressed.
- Toughness can be determined by integrating the stress strain curve

$$\frac{energy}{volume} = \int_0^{\epsilon_f} \sigma \, d\epsilon \; where \; \epsilon = strain$$

$$\epsilon_f = strain\ upto\ failure$$

$$\sigma = stress$$



Toughness of a ductile material:

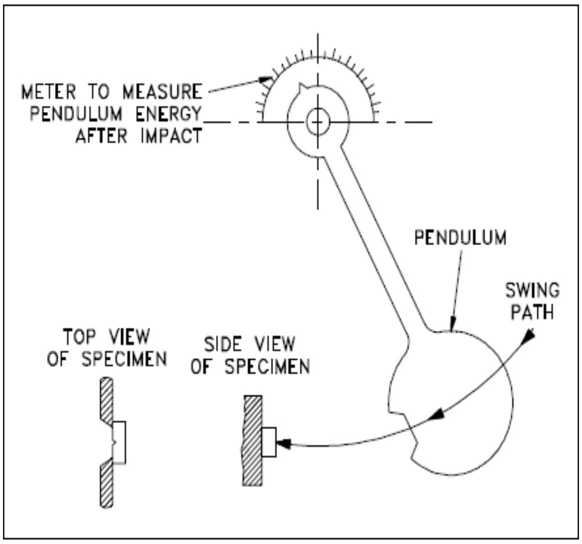
- By calculating the area under the stress versus strain curve upto failure point, the toughness of the material can be determined.

$$area = stress(\sigma) \times strain(\epsilon) = energy = toghness_{\ ductile}$$

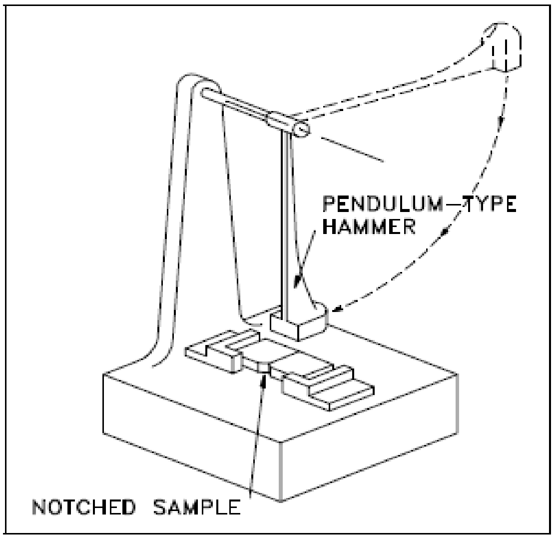
- A ductile material contains high toughness than a brittle material because the $area_{ductile} > area_{brittle}$ which implies $toughness_{ductile} > toughness_{brittle}$

Toughness of a brittle material:

Area under stress- strain curve upto failure point in case of brittle material is very low implies difficult to measure accurately without error implies measured fracture toughness is a error value. Therefore to measure the toughness of a brittle material ***IZOD or CHARPY*** **test** is used



Material toughness test



charpy test equipment

A v notch made sample is fixed as a cantilever beam and it is subjected to failure by hitting with a hammer of weight W_0. The entire load will act at the notch point and it will fail but during failure time, the sample will absorb highest energy from the hammer known as toughness of the material.

By applying toughness equation, toughness can be determined

Case 1

In IZOD test method one end of the sample is fixed and the other end is in free condition implies non uniform stress will be produced implies it will fail earlier than the actual value implies measured toughness is slightly error value.

Case 2

To overcome this drawback, in CHARPY test the sample will be kept on two point supported beam under stress free condition and subjected to failure as shown in figure implies measured toughness is highly accurate.

This method cannot be used in **case of a ductile material** because during hitting of the hammer it will undergo bending instead of failure. A v notch is created in the sample to initiate the failure in the sample with less weight of the hammer.

NOTE

The fracture toughness of a ductile material can be measured by tensile test but in case of brittle material either IZOD or CHARPY test will be used.

Resilience

- Resilience is closely related to toughness.

- Resilience is the capacity of a material to absorb energy when it is elastically deformed and up to elastic limit without shape change in elastic zone.
- The associate property is the modulus of resilience which is strain energy per unit volume required to stress a material from an unloaded state up to the point of yielding.
- A material contains good strength and good ductility means it will posses high resilience.
- A material contains high resilience means it will absorb energy effectively against failure without undergoing maintaining dimensional accuracy of the component.

Strength

- Strength is **the ability of a material to resist deformation**.
- The strength of a component is usually considered based on the maximum load that can be borne before failure is apparent.
- If **under simple tension** the permanent deformation (plastic strain) that takes place in a component before failure, the load-carrying capacity, at the instant of final rupture, will probably be less than the maximum load supported at a lower strain because the load is being applied over a significantly smaller cross-sectional area.
- **Under simple compression**, the load at fracture will be the maximum applicable over a significantly enlarged area compared with the cross-sectional area under no load.
- This obscurity can be overcome by utilizing a nominal stress figure for tension and shear. This is found by dividing the relevant maximum load by the original area of cross section of the component.
- Thus, **the strength of a material is the maximum nominal stress it can sustain**. The nominal stress is referred to in quoting the "strength" of a material and is always qualified by the type of stress, such as tensile strength, compressive strength, or shear strength.

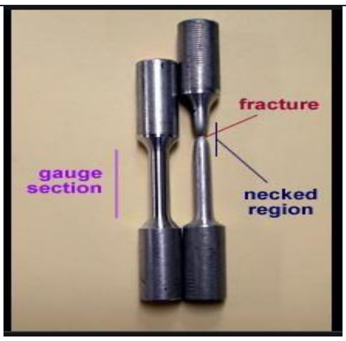
When a force is applied to a metal, layers of atoms within the crystal structure move in relation to adjacent layers of atoms. This process is referred to as *slip*. Grain boundaries tend to prevent slip. The smaller the grain size, the larger the grain boundary area**. Decreasing the grain size through cold or hot working of the metal tends to retard slip and thus increases the strength of the metal.**

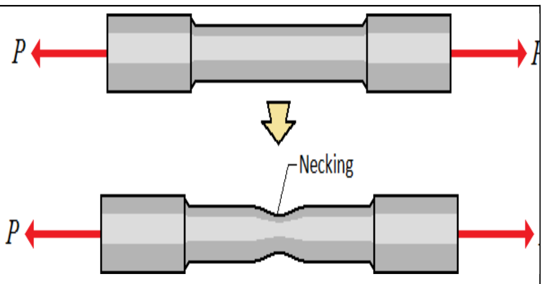
Tensile strength:

- Tensile strength is a measure of strength and ductility of the material.
- Ultimate tensile strength is the force required to fracture a material.
- Tensile strength can be experimentally determined by the given formula.

$$tensile\ strength\ = \frac{maximum\ tensile\ load\ applied}{original\ crosssectional\ area} = \frac{p_{max}}{A}$$

- The ultimate tensile strength P_{max}can be determined by the stress strain graph. The unit used for tensile strength is N/m^2.





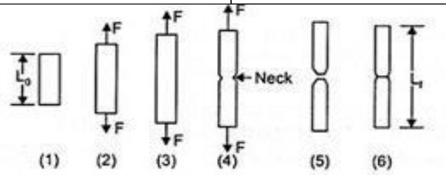


FIGURE : Typical progress of a tensile test : (1) beginning of test, no load; (2) uniform elongation and reduction of cross-sectional area; (3) continued elongation, maximum load reached; (4) necking begins, load begins to decrease; and (5) fracture. If pieces are put back together as in (6), final length can be measured.

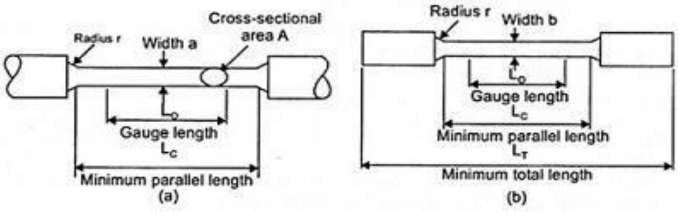


FIGURE : Properties of tensile test specimens : (a) cylindrical (b) flat.

Yield strength

- Higher yield strength shows greater resistance for the plastic deformation.
- Yield strength of a material is that value of stress at which the plastic deformation of the material starts.
- In other words it is the ability of the material to resist plastic deformation.
- The point at which stress due to strain suddenly increases is the yield point or yield strength.
- Yield strength is given by the formula

$$yeild\ strength = \frac{load\ at\ yeild\ point}{area\ of\ crossection} = \frac{p_{yeild}}{A_o}$$

- The unit use for yield strength is also N/m^2

Impact strength

- Impact strength is a combination of **toughness** and **strength of the material** and it is the capacity of the material to resist or absorb shock energy.
- Impact strength is directly related to the structure, rate of loading, temperature, notches etc.
- The impact strength can be directly determined by the Izod and Charpy test.
- Impact strength is measured in N/m^2
- Impact strength depends on grain size.
- Usually coarse grain structure reduces impact strength.

Shear strength

- Shear strength determines the materials tendering to withstand forces acting tangential causing crystal dislocation due to the relative movement of the layers.
- Shear strength of a material is the maximum value of tangential stress applied to shear it off across the resisting section.
- The shear strength can be given by the formula.

$$shear\ strength = \frac{maximum\ tangential\ load}{original\ crossection\ area} = \frac{p_{tangential}}{A_0}$$

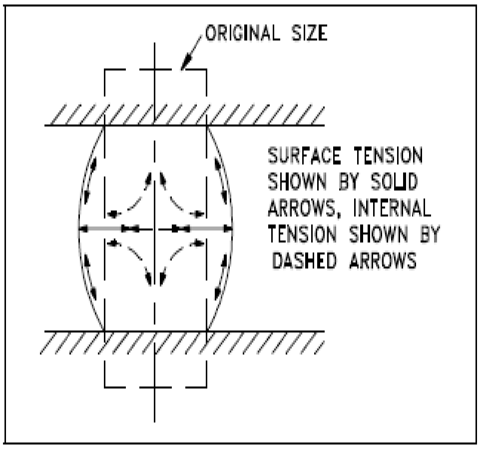
Compression strength

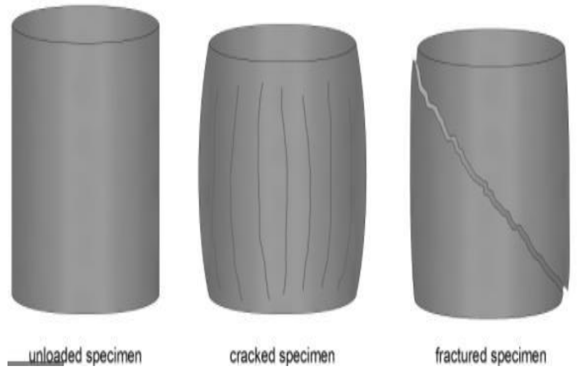
- The compression strength is mainly useful for materials like **ceramics and polymers**
- It gives the detail regarding breaking power.
- The compressive strength of a material is the maximum value of compressive stress applied to break it off by crushing.
- It is given by the formula

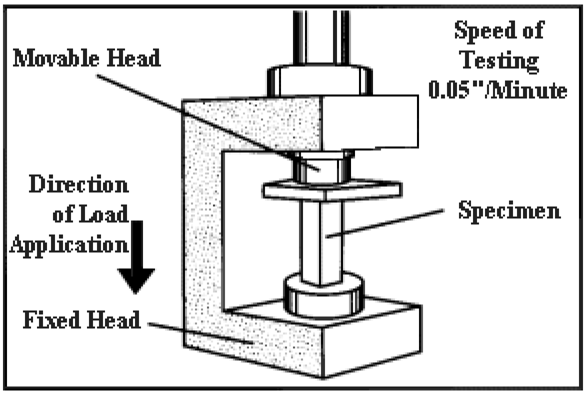
$$compressive\ strength = \frac{maximum\ compressive\ load}{original\ crossectional\ area} = \frac{p_{compressive}}{A_0}$$

Malleability

- Malleability and ductility has similar characteristics but with the little difference.
- Where ductility is the ability of a material to deform easily upon the application of a tensile force, malleability is the ability of a metal to exhibit large deformation or plastic response when being subjected to **compressive force**.
- Generally hammering and rolling operations are performed only on materials having good malleability.
- Malleability is the ability of a metal to be made as *thin sheets* by hammering where as the ductility is the ability of the metal to be drawn *as wire* with minimum radius or diameter.







Malleable Deformation of Cylinder under Uniform Axial Compression

Have you ever experienced the aggravation of having to expend considerable effort to tear open a small plastic package that contains nuts, candy, or some other confection? You probably have also noticed when a small incision (or cut) has been made into an edge, as appears in photograph (a), that a minimal force is required to tear the package open. This phenomenon is related to one of the basic tenets of fracture mechanics: an applied tensile stress is amplified at the tip of a small incision or notch.

The (b) photograph is of an oil tanker that fractured in a brittle manner as a result of the propagation of a crack completely around its girth. This crack started as some type of small notch or sharp flaw. As the tanker was buffeted about while at sea, resulting stresses became amplified at the tip of this notch or flaw to the degree that a crack formed and rapidly elongated, which ultimately led to complete fracture of the tanker.

The (c) photograph is of a Boeing 737-200 commercial aircraft (Aloha Airlines flight 243) that experienced an explosive decompression and structural failure on April 28, 1988. An investigation of the accident concluded the cause was metal fatigue that was aggravated by crevice corrosion in as much as the plane operated in a coastal (humid and salty) environment. Stress cycling of the fuselage resulted from compression and decompression of the cabin chamber during short hop flights. A properly executed maintenance program by the airline would have detected the fatigue damage and prevented this accident. (Photograph of the oil tanker by Neal Boenzi. Reprinted with permission from The New York Times. Photograph of the Boeing 737-200 courtesy of Star Bulletin/Dennis Oda/© AP/Wide World Photos.

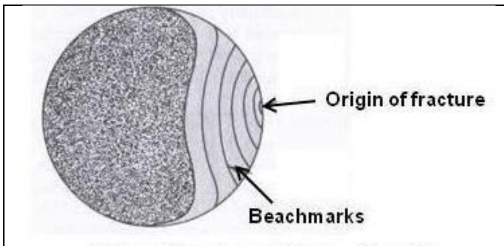
(a)

(b)

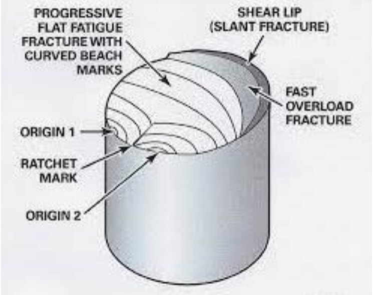
(c)

Fatigue

- Fatigue strength shows the endurance of the material to repeated load.
- Fatigue is a kind of failure in metals or alloys which is caused by *repeated fluctuating loads.*
- This is an important property to be noted for the proper maintenance of *machine parts, bridges, aircrafts etc.*
- Fatigue is a phenomenon that leads to fracture or failure that takes place under repeated fluctuating stress.
- Fatigue ends up with the propagation of cracks fracture etc.
- The fatigue test is a dynamic type of test when a material is subjected to repeating or fluctuating loads.
- By the help of fatigue testing machines S-N curve (S-stress, N-no of cycles of load applied) can be plotted that predicts endurance limit or fatigue limit.



Fatigue Fracture with Beachmarks



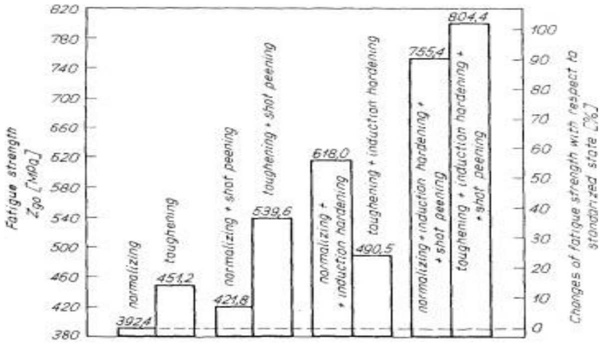
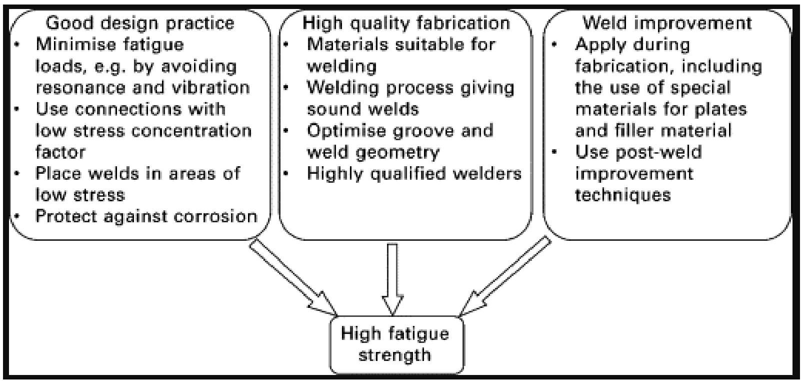


Fig. 2. Fatigue strength increase of steel 30HGSA after various surface treatments.



Good design practice
- Minimise fatigue loads, e.g. by avoiding resonance and vibration
- Use connections with low stress concentration factor
- Place welds in areas of low stress
- Protect against corrosion

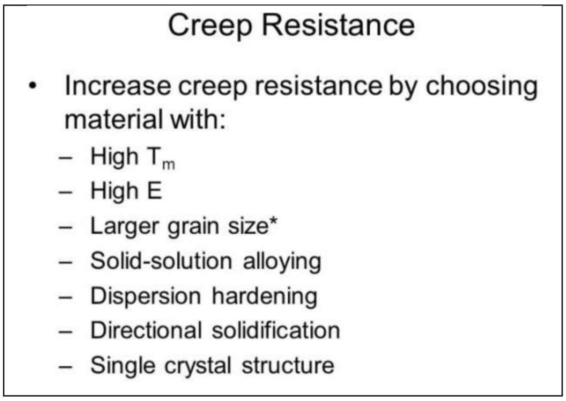
High quality fabrication
- Materials suitable for welding
- Welding process giving sound welds
- Optimise groove and weld geometry
- Highly qualified welders

Weld improvement
- Apply during fabrication, including the use of special materials for plates and filler material
- Use post-weld improvement techniques

High fatigue strength

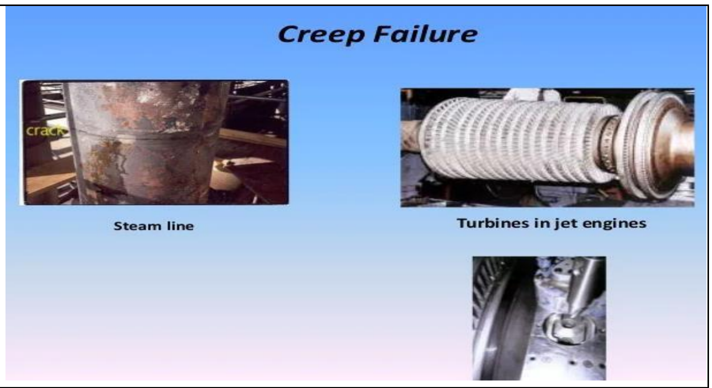
Creep

- Over a long period of time materials subjected to time- dependent strain may undergo deformation. This effect is known as a creep.
- Creep can be defined as the time- dependent and permanent deformation of materials when subjected to a constant load or stress.
- For metals creep tendency is notable at temperature greater than 0.5Tm, Tm is absolute melting temperature. Machine such as turbine rotors in jet engine, steam generators etc. Under go time- dependent strain at elevated temperature and pressure that can cause deformation, which is known as creep.
- The creep tendency is predominanent in polymers even at slightly higher temperature or normal temperature.



Creep Resistance

- Increase creep resistance by choosing material with:
  - High T_m
  - High E
  - Larger grain size*
  - Solid-solution alloying
  - Dispersion hardening
  - Directional solidification
  - Single crystal structure



Wear resistance

Wear is the unintentional removal of solid material from rubbing surface. Wear resistance is defined as the ability to resist **wear and abrasion.**

Adhesive wear

- Referred to galling, scuffing or scoring
- Characterized by an intensive interaction between two bearing surface resulting from mutual adhesion of the metal at the junction.

Cause

- Heavy tearing of rubbing surface

Abrasive wear

- It is the removal by ploughing or gouging out from the surface of material by another body much harder than the abraded surface

Cause

- Due to presence of hard particle introduced as dust or other incidental impurities between two sliding surface or to the rubbing of a hard surface against a soft one.

Extent of wear depends on size, shape, hardness of the particle

FACTORS AFFECTING MECHANICAL PROPERTIES

Mechanical properties are those which define the behaviour of a material under applied loads

Mechanical properties of materials are affected due to

1. **Alloy content:** such as addition of W, Cr etc. Improves hardness and strength of materials.
2. **Fine grain size:** fine grain size materials exhibit higher strength of materials.
3. **Crystal imperfection:** such as dislocation reduce the strength of materials.

4. **Excessive cold working**: produce strain hardening and the material may crack.
5. **Manufacturing defect:** such as cracks, blow holes tc reduces the strength of the materials.

PROCESSING PROPERTIES

1. Weldability
2. Solderability
3. Workability or formability
4. Castability
5. Machinability

BONDING IN SOLIDS

All solids of universe are composed of a large no atoms. Atoms can be defined as the smallest unit which take part in chemical combination. Atoms are arranged in a solid in some regular manner.

WHY STUDY Atomic Structure and Interatomic Bonding?

An important reason to have an understanding of interatomic bonding in solids is that in some instances, the type of bond allows us to explain a material's properties.

- For example, consider carbon, which may exist as both graphite and diamond. Whereas graphite is relatively soft and has a "greasy" feel to it, diamond is the hardest known material. In addition, the electrical properties of diamond and graphite are dissimilar: diamond is a poor conductor of electricity, but graphite is a reasonably good conductor. These disparities in properties are directly attributable to a type of interatomic bonding found in graphite that does not exist in diamond.

In the processing/structure/properties/performance scheme, reasons for studying atomic structure and interatomic bonding are as follows:

- For silicon, its electron configuration determines the type of primary bonding , which in turn affects its electron band structure.
- For polymer fibers, electron configurations of the constituent elements (i.e., C, H) affect the type of primary bonding , bonding type has an influence on the structures of polymer molecules.

Bond energy

The bong energy can also be expressed as the energy of formation of one mole of a substance its atoms or ions when brought together from an infinite distance to the equilibrium position.

Bond can be classified into two groups.

1. **Primary bond**

2. Secondary bond

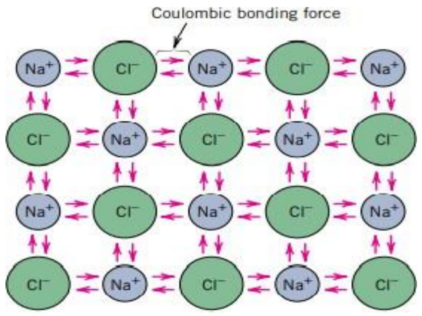
Primary bonds are those bonds where the bond energy is very high. **Ionic bond, covalent bond and metallic bond are the examples of primary bond**.
Secondary bonds are those bonds where the bond energy is very low. **Vander walls bond is the example of secondary bond.**

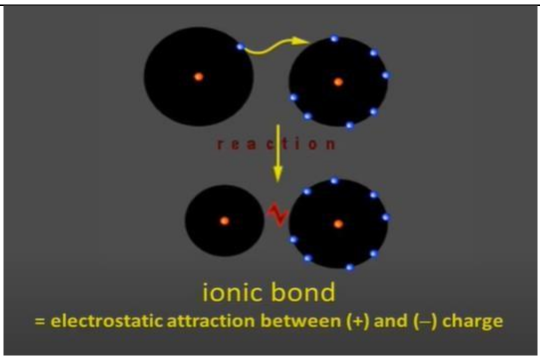
Ionic Bond

1. This type of bonding exists due to *electrostatic force of attraction* between *positive and negative ions of different elements*.
2. This type of bonding is formed between *two different elements* one of the atom loses its valence electron and other accepts it. The ions so formed attract each other and an ionic bond is formed.
3. Due to their crystalline structure, ionic solids *have high hardness*.
4. The ionic solids have very *low thermal and electrical conductivities*.
5. The ionic solids have *high melting and boiling temperatures*.
6. The ionic solids are *not malleable and ductile*.
7. The ionic solids *are soluble in water*.
8. The ionic compounds exist in the *solid form* only.

Ionic bonding

Ionic bonding is perhaps the easiest to describe and visualize. It is always found in compounds that are composed of both metallic and nonmetallic elements, elements that are situated at the horizontal extremities of the periodic table. Atoms of a metallic element easily give up their valence electrons to the nonmetallic atoms. In the process all the atoms acquire *stable or inert gas configurations* and, in addition, an electrical charge; that is, they become ions. Sodium chloride (NaCl) is the classic ionic material. A sodium atom can assume the electron structure of neon (and a net single positive charge) by a transfer of its one valence *3s* electron to a chlorine atom. After such a transfer, the *chlorine ion has a net negative charge* and an electron configuration identical to that of *argon*. In sodium chloride, all the sodium and chlorine exist as ions. This type of bonding is illustrated schematically in Figure.





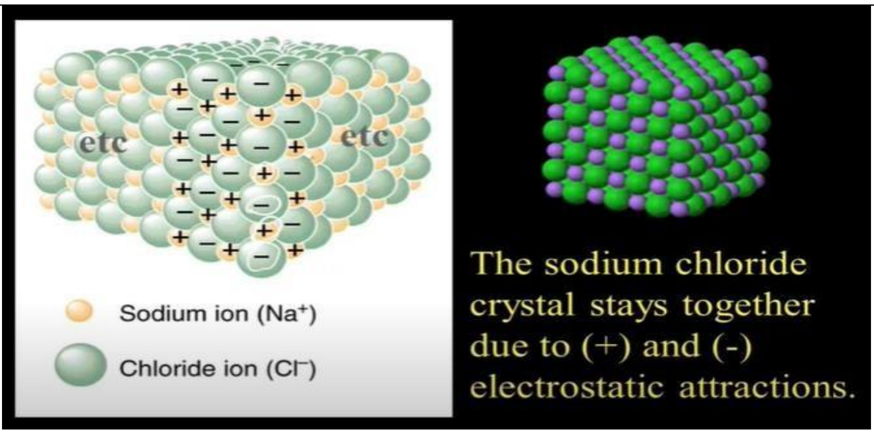


Figure: Schematic representation of ionic bonding in sodium chloride (NaCl) and NaCl structure.

Coulombic force

The attractive bonding forces are coulombic; that is, positive and negative ions, by virtue of their net electrical charge, attract one another.

- Ionic bonding is termed nondirectional; that is, the magnitude of the bond is equal in all directions around an ion.
- It follows that for ionic materials to be stable, all positive ions must have as nearest neighbors negatively charged ions in a three dimensional scheme, and vice versa. The predominant bonding in ceramic materials is ionic.

Covalent Bond

1. This type of bonding exists due to the electrostatic force of attraction between atoms which share the electron pairs to form a covalent bond.
2. This type of bonding is formed due to sharing of electron pairs between the atoms of same or different elements.
3. Except diamond, silicon and carbide, etc., the covalent solids have low hardness.
4. The covalent *solids have low thermal and electrical conductivities*.
5. The covalent solids have lower the covalent solids have lower in comparison to ionic solids.
6. The covalent solids are *not malleable and ductile*.
7. The covalent solids are *soluble in toluene and benzene* etc.
8. The covalent compounds exist in *solid, liquid and gaseous form*.

- In covalent bonding, stable electron configurations are assumed by the sharing of electrons between adjacent atoms. Two atoms that are covalently bonded will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms.
- Covalent bonding is schematically illustrated in Figure, for a molecule of methane (CH_4).

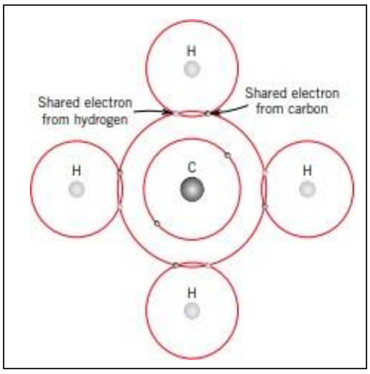


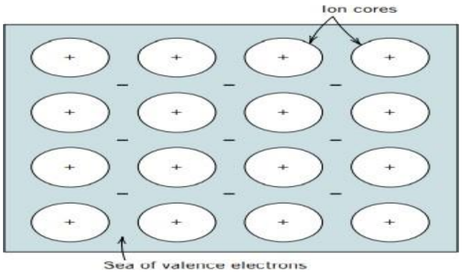
Figure: Schematic representation of covalent bonding in a molecule of methane (CH_4).

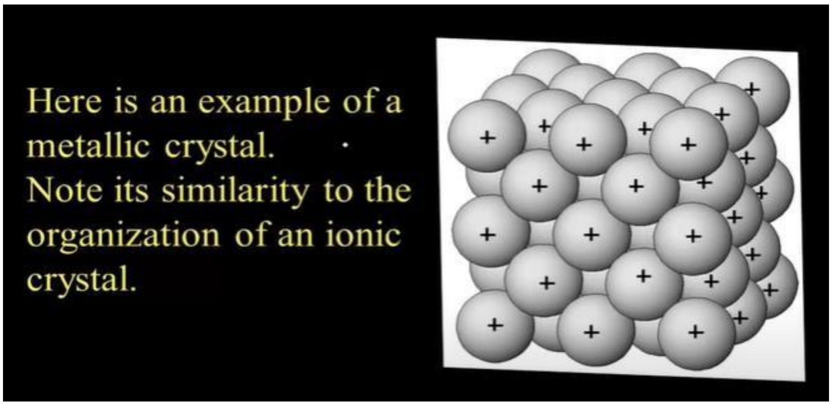
- The carbon atom has four valence electrons, whereas each of the four hydrogen atoms has a single valence electron. Each hydrogen atom can acquire a helium electron configuration (two 1*s* valence electrons) when the carbon atom shares with it one electron. The carbon now has four additional shared electrons, one from each hydrogen, for a total of eight valence electrons, and the electron structure of neon.
- The covalent bond is directional; that is, it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.
- Many nonmetallic elemental molecules (H_2, Cl_2, F_2, etc.) as well as molecules containing dissimilar atoms, such as CH_4, H_2O, HNO_3, and HF, are covalently bonded.
- Furthermore, this type of bonding is found in elemental solids such as diamond (carbon), silicon, and germanium and other solid compounds composed of elements that are located on the right-hand side of the periodic table, such as gallium arsenide (GaAs), indium antimonide (InSb), and silicon carbide (SiC).

Metallic Bond

1. This type of bonding exists due to electrostatic force of attraction between *electron clouds* and *positive ions* of same or different metals.

- Metallic bonding, the final primary bonding type, is found in metals and their alloys. A relatively simple model has been proposed that very nearly approximates the bonding scheme.
- Metallic materials have one, two, or at most, three valence electrons. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal. They may be thought of as belonging to the metal as a whole, or forming a "sea of electrons" or an "electron cloud." The remaining no nvalence electrons and atomic nuclei form what are called ion cores, which possess a net positive charge equal in magnitude to the total valence electron charge per atom.
- Figure is a schematic illustration of metallic bonding. The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another.
- Consequently the metallic bond is nondirectional in character. In addition, these free electrons act as a "glue" to hold the ion cores together.
- Metallic bonding is found in the periodic table for Group IA and IIA elements and, in fact, for all elemental metals.

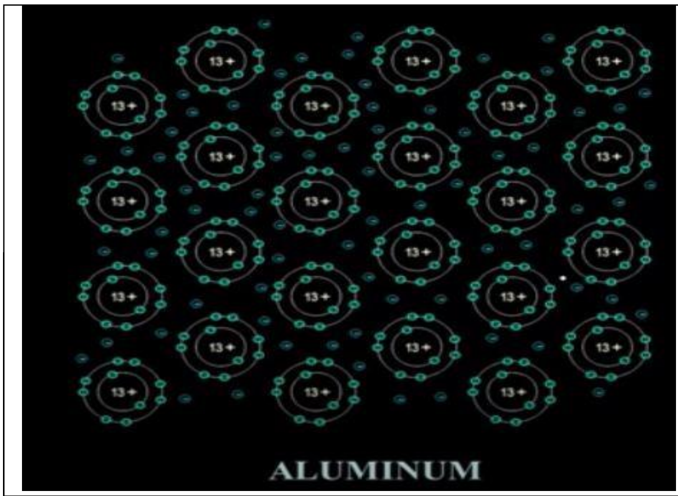


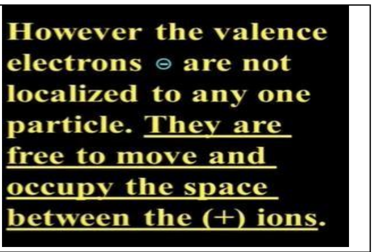


Here is an example of a metallic crystal.
Note its similarity to the organization of an ionic crystal.

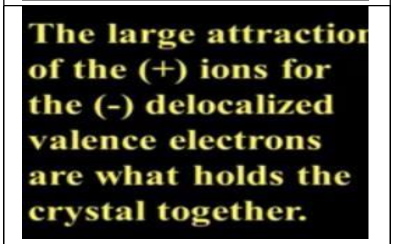
Figure: Schematic illustration of metallic bonding.

- Some general behaviors of the various material types (i.e., metals, ceramics, polymers) may be explained by bonding type.
- For example, metals are good conductors of both electricity and heat, as a consequence of their free electrons.
- By way of contrast, ionically and covalently bonded materials are typically electrical and thermal insulators because of the absence of large numbers of free electrons.
- At room temperature, most metals and their alloys fail in a ductile manner; that is, fracture occurs after the materials have experienced significant degrees of permanent deformation. This behavior is explained in terms of deformation mechanism, which is implicitly related to the characteristics of the metallic bond. Conversely, at room temperature ionically bonded materials are intrinsically brittle as a consequence of the electrically charged nature of their component ions.



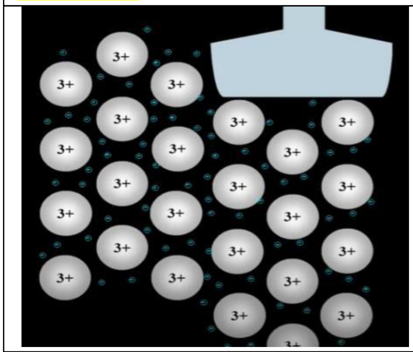


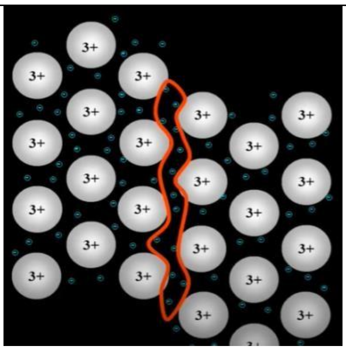
However the valence electrons ⊖ are not localized to any one particle. They are free to move and occupy the space between the (+) ions.

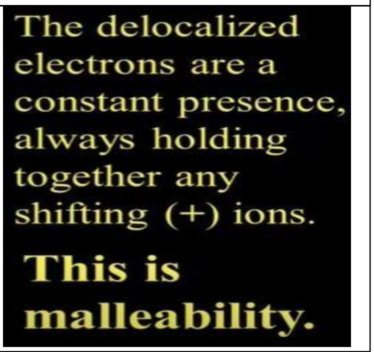


The large attraction of the (+) ions for the (-) delocalized valence electrons are what holds the crystal together.

Why the metallic crystals are malleable in nature & Why metallic crystal does not break with the application of hammering?

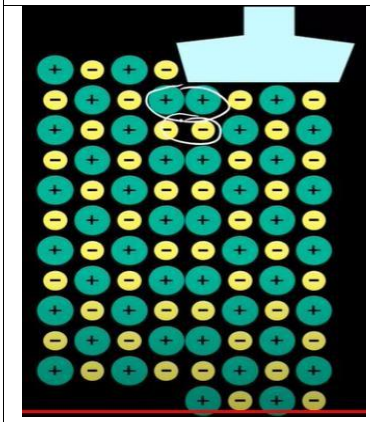


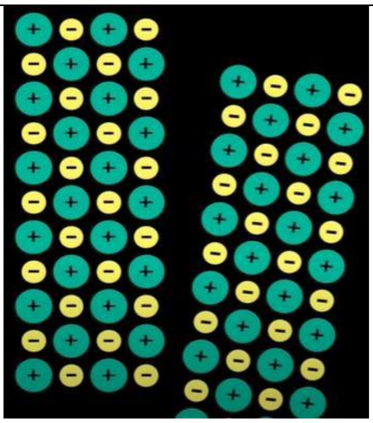


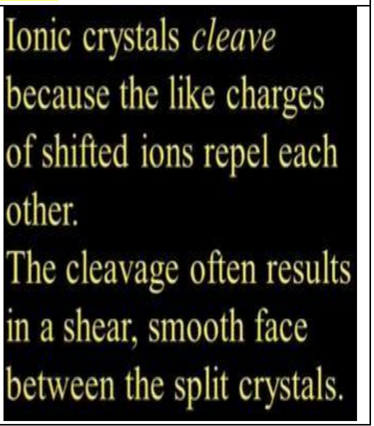

The delocalized electrons are a constant presence, always holding together any shifting (+) ions.

This is malleability.

Why the ionic crystals are not malleable in nature?






Ionic crystals *cleave* because the like charges of shifted ions repel each other.

The cleavage often results in a shear, smooth face between the split crystals.

Why do metals have large number of free electrons?

1. The atoms of **metals have** larger size due to which the holding capacity of the nucleus decreases at the outermost orbital. And therefore the **electrons** in the outermost shell **are free electrons** as they **can** be removed easily.

2. In metals, the electrons in the outer most shells are loosely bound to the nucleus. Even at room temperature, there are a large number of free electrons which are moving inside the metal in a random manner.

Source-Read more on Sarthaks.com - https://www.sarthaks.com/889235/why-do-metals-have-a-large-number-of-free-electrons

Effect of metallic bond on properties

1. The strong attraction between the (+) ions in the crystal for the delocalized electrons *results not only in malleability*
2. This structure makes metals *hard and strong, with a high melting point.*
3. In general, the more delocalized electrons, the *tougher the metal*. Transition metals have the most delocalized electrons and are the strongest.
4. Delocalized electrons also *carry electric current and heat* due to their ability to move through the crystal.
5. Delocalized electrons readily absorb and re-emit visible frequency photons, giving metals their *characteristic lustrure.*

SECONDARY BONDING OR VAN DER WAALS BONDING

- Secondary, van der Waals, or physical bonds are weak in comparison to the primary or chemical ones. Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present.
- Secondary bonding is evidenced for the inert gases, which have stable electron structures, and, in addition, between molecules in molecular structures that are covalently bonded.
- Secondary bonding forces arise from atomic or molecular **dipoles**. In essence, an electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule.
- The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one, as indicated in Figure.
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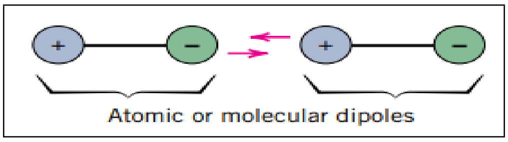


Figure: Schematic illustration of van der Waals bonding between two dipoles.

- Dipole interactions occur between *induced dipoles*, *between induced dipoles and polar molecules (which have permanent dipoles),* and *between polar molecules*.
- Hydrogen bonding, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents.

General characteristics of bond types

Property	**Metallic bond**	**Covalent bond**	**Ionic bond**	**Secondary bond**
Example	Cu, Ni, Fe	Diamond, silicon carbide	NaCl, $CaCl_2$	Wax, Ar
Mechanical	Weaker than ionic or covalent bond Tough and ductile Nondirectional	Very hard and brittle Fails by cleavage Strongly directional	Hardness increases with ionic charge Fails by cleavage Nondirectional	Weak and soft Can be plastically deformed
Thermal	Moderately high melting points Good conductors of heat	Very high melting points Thermal insulators	Fairly high melting points Thermal insulators	Low melting points
Electrical	Conductors	Insulators	Insulators	Insulators
Optical	Opaque and reflecting	Transparent or opaque High refractive index	Transparent Colored by ions	Transparent

CRYSTALLOGAPHY

INTRODUCTION

Crystallography is the study of crystal formation of solids including

- X-ray determination of lattice structure

- Crystal habit (the form of a crystal)
- The shape and defects of crystal

When crystallography is applied to metals, this science is called as metallography

Definition: crystallography is that branch of science in which the internal structures of crystal, their properties, external or internal symmetries of crystals are studied.

Various terms associated with crystallography are as follows

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

CRYSTAL STRUCTURES

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another.

A **crystalline material** is one in which

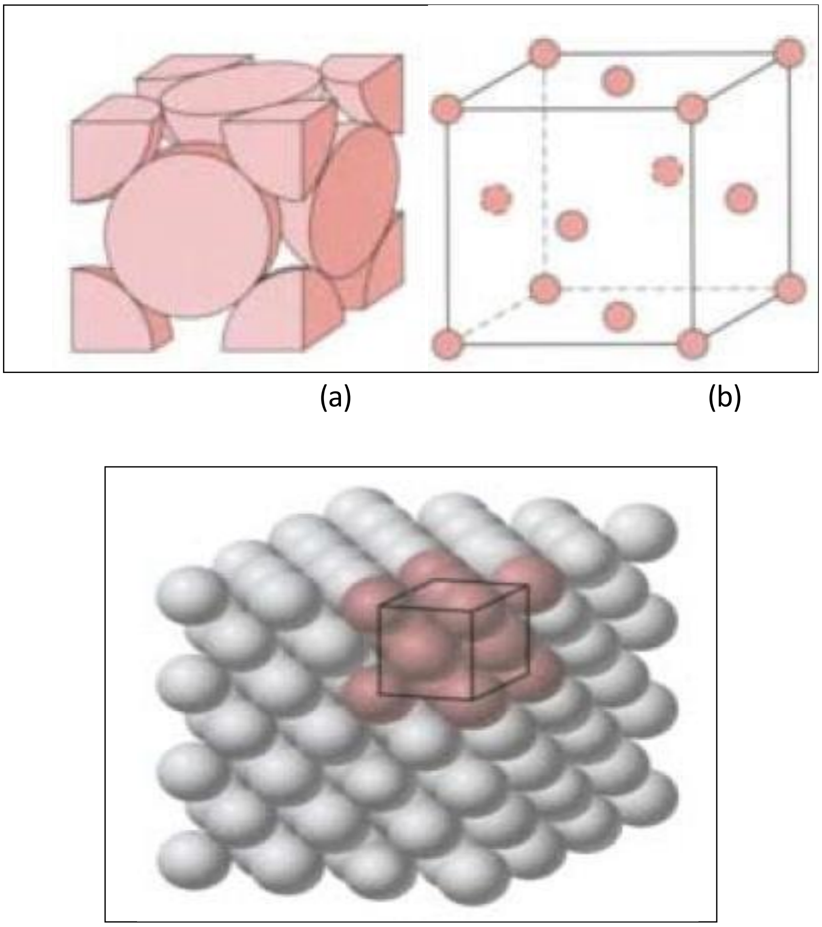
- The atoms are situated in a repeating or periodic array over large atomic distances; that is, long-range order exists,
- Upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbour atoms.
- All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions.

Atomic hard sphere model

When describing crystalline structures, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the atomic hard sphere model in which spheres representing nearest-neighbour atoms touch one another.

An example of the hard sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure.

In this particular case all the atoms are identical. Sometimes the term lattice is used in the context of crystal structures; in this sense *''lattice'' means a three-dimensional array of points coinciding with atom positions (or sphere centers).*



(a) (b)

(c)

(a) A hard sphere unit cell representation, (b) a reduced-sphere unit cell, c) an aggregate of many atoms

- The structure implies the arrangement and disposition of the atoms within a crystal.
- A *crystal structure* consists of atoms arranged in a pattern that repeats periodically in three-dimensional geometric lattice.
- The forces of chemical bonding cause this repetition.
- It is this repeated pattern which control properties like strength, ductility, conductivity (property of conducting or transmitting heat, electricity, etc.), and shape
- All metals, a major fraction of ceramics, and certain polymers acquire crystalline form when solidify, i.e. in solid state atoms self-organize to form crystals.
- *Crystals possess a long-range order of atomic arrangement through repeated periodicity at regular intervals in three dimensions of space*.
- When the solid is not crystalline, it is called amorphous.
- Examples of crystalline solids are metals, diamond and other precious stones, ice, graphite. Examples of amorphous solids are glass, amorphous carbon (a-C), amorphous Si, most plastics.

- There is very large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex structures for ceramics and some polymers.

Some very common crystal structures and relevant properties are listed in table

Unit Cell	***n***	***CN***	***a/R***	***APF***
Simple Cubic	1	6	4/√4	0.52
Body-Centered Cubic	2	8	4/√3	0.68
Face-Centered Cubic	4	12	4/√2	0.74
Hexagonal Close Packed	6	12		0.74

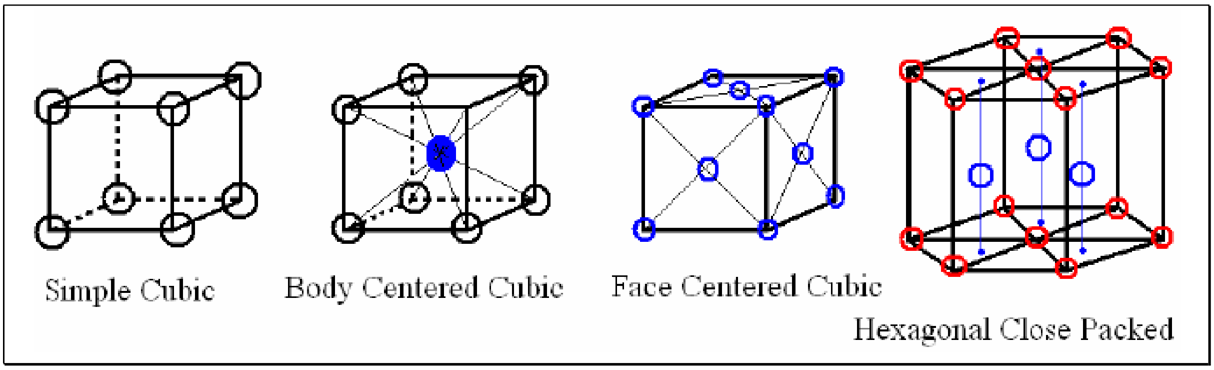


Fig.: Common metallic crystal structures.

Lattice points and space lattice

- *The atomic arrangement in crystal is called the crystal structure*. In perfect crystal, there is a regular arrangement of atoms.
- In a model of a crystal, ions, atoms or molecules that constitute its structure can be imagined to be spheres which touch one another and are arranged regularly in different directions.
- In a simple model of crystal structure, spheres are replaced by points representing the centres of ions, atoms or molecules. The periodicity in the arrangement of ions, atoms or molecules generally varies in different directions.
- It is very convenient to imagine points in space about which these atoms, ions or molecules are located. Such points in space are called lattice points. The totality of lattice points forms a *crystal lattice or space lattice*. If all the atoms, molecules or ions at the lattice points are identical, the lattice is called a Bravias lattice.
- The space lattice of a crystal is described *by means of a three-dimensional co-ordinate system in which the coordinate axis coincide with any three edges of the crystal* that intersect at one point and do not lie in a single plane.

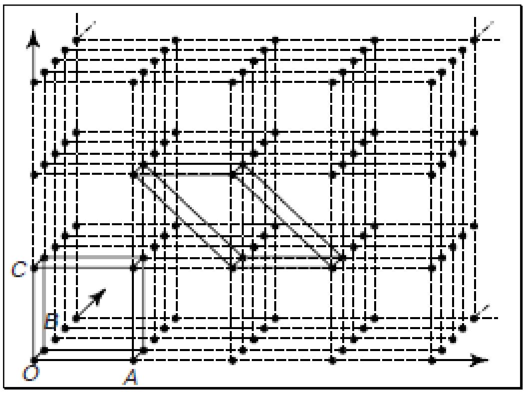


Fig: A space lattice, two possible unit cells and an environment of a point

BASIS

The space lattice has been defined as an array of imaginary points which are so arranged in space that each point has identical surroundings.

We must note that the crystal structure is always described in terms of atoms rather than points.

Thus in order to obtain a *crystal structure*, an atom or a group of atoms must be placed on each lattice point in a regular fashion.

Such an atom or a group of atoms is called the basis and these acts as a *building unit or a structural unit* for the complete crystal structure. Obviously, a lattice combined with a basis generates the crystal structure.

Mathematically one can express it as

$$\mathit{space\ lattice}\ + \mathit{basis}\ \rightarrow \mathit{crystal\ structure}$$

The generation of a crystal structure from a two-dimensional lattice is illustrated in Fig . The basis consists of two atoms, represented by ○ and •, having orientation as shown in Fig.. The crystal structure is obtained by placing the basis on each lattice point such that the centre of the basis coincides with the lattice point.

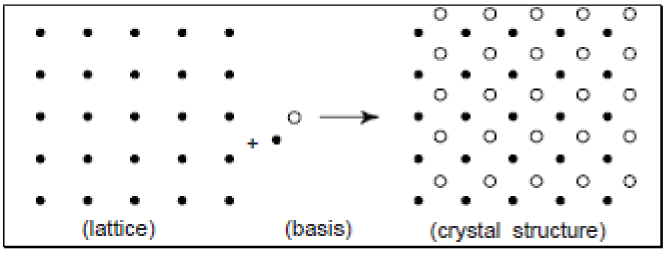


Figure. Generation of crystal structure

CRYSTALLINE AND NON-CRYSTALLINE MATERIALS

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

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

Non-Crystalline Solids: In amorphous solids, there is no long-range order. *But amorphous does not mean random, since the distance between atoms cannot be smaller than the size of the hard spheres.* Also, in many cases there is some form of short-range order. For instance, the tetragonal order of crystalline SiO_2 (quartz) is still apparent in amorphous SiO_2 (silica glass).

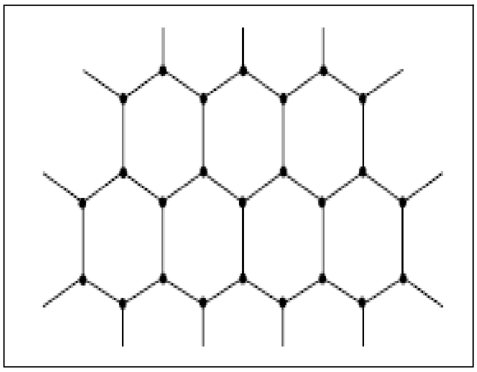


Fig. Crystalline (highly order structure)

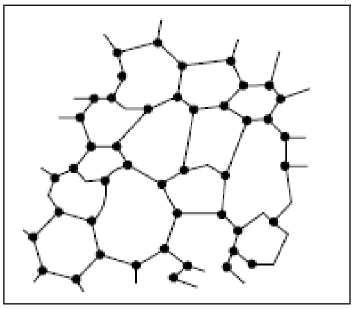


Fig. amorphous solids or Non-Crystalline Solids

CRYSTAL

- **Definition:**
  1. A crystal is a solid whose constituent atoms or molecules are arranged in a systematic geometric pattern under the action of its molecular forces.
  2. A 3 D translationally periodic arrangement of atoms in space is called as crystal
- Crystal is a physical object.
- It has physical properties (density, weight, electrical conductivity)
- Crystal are also known as *grains*
- The boundary separating the two adjacent is called as *grain boundary*
- $CRYSTAL = LATTICE\ + MOTIF\ OR\ BASIS$

LATTICE

- **Definition:**
  1. A 3D periodic arrangement of point in space
- It is a geometrical concept
- No physical properties. Only geometrical properties.

MOTIF

- **Definition:**

  An atom or group of atoms associated with each lattice point is called as motif or basis of a crystal.

- It also called as *linking bridge*.

NOTE

Lattice gives you underlying periodicity of crystal. Motif gives you atom or group of atom which is periodically repeated.

Lattice tells you how to repeat. Motif tells you what to repeat.

UNIT CELL

- The unit cell is the smallest group of atoms possessing the symmetry of the crystal.
- Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn within the aggregate of spheres which in this case happens to be a cube.

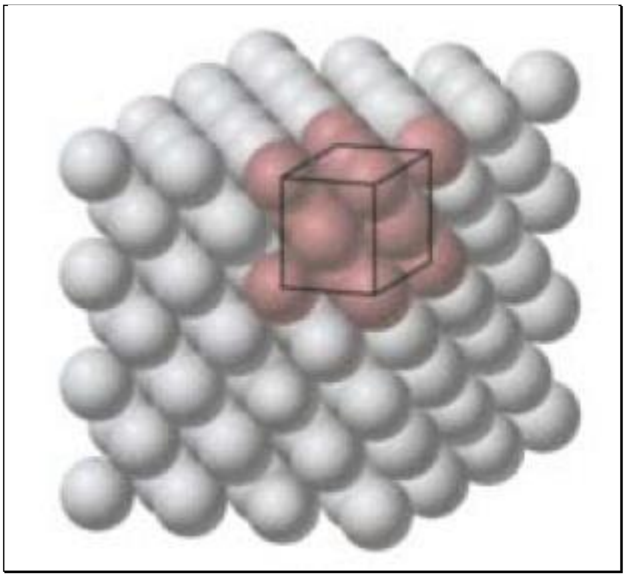


Figure: Unit cells is drawn within the aggregate of spheres

Why it is called as basic structural unit or building block of the crystal structure?

A unit cell is chosen to represent the *symmetry* of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure

Definition

1. A region of space which can generate the entire lattice (or crystal) by repetition through lattice translation.
2. Commonly unit cell is a parallelogram (in 2D) or a parallelepiped (3D) with corners at lattice points.

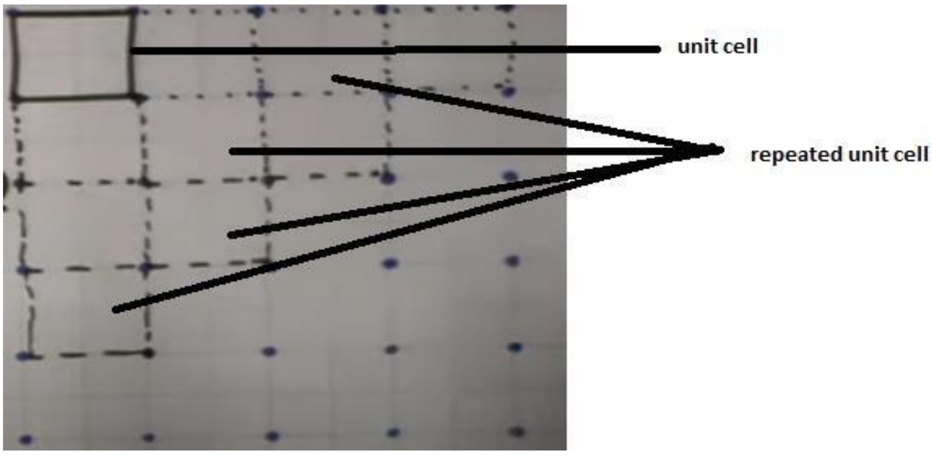
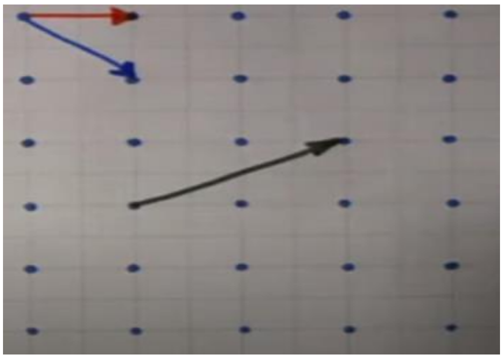


Fig: Example of 2D unit cell

Lattice translation:- Any vector from one lattice point to another lattice point.

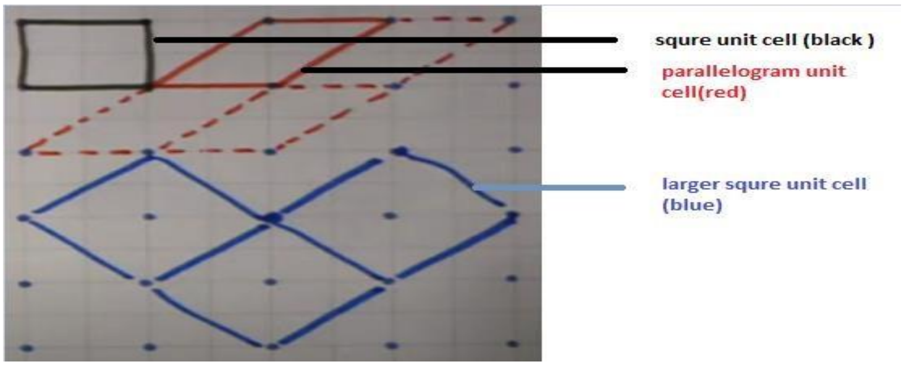


- It defines the crystal structure **by virtue of its geometry and the atom positions within**. Convenience usually dictates that parallelepiped corners coincide with centers of the hard sphere atoms.

Furthermore, more than one a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the *highest level of geometrical symmetry*.

Non –uniqueness of unit cell

A given lattice can have many (infinitely many) unit cells.



Important properties of the unit cells are

- The type of atoms and their radii R.
- Cell dimensions (Lattice spacing a, b and c) in terms of R and
- Angle between the axis α, β, γ
- a*, b*, c* - lattice distances in reciprocal lattice, α*, β*, γ* - angle in reciprocal lattice
- n, number of atoms per unit cell. For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, 1/m.
- CN, the coordination number, which is the number of closest neighbors to which an atom is bonded.
- APF, the atomic packing factor, which is the fraction of the volume of the cell actually occupied by the hard spheres. APF = Sum of atomic volumes/Volume of cell.

ATOMIC OR CRYSTALLOGRAPHIC PLANES

The layers of atoms or the planes along which atoms are arranged are known as atomic or crystallographic planes

LATTICE PARAMETER OF A CELL

- The length of three edges of the unit cell (or of three basis vectors) and the three interaxial angles between them are called the lattice parameters.
- According to unit cell configurations and/or atomic arrangements 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 axes coincides with one of the three parallelepiped edges that extend from the corner.

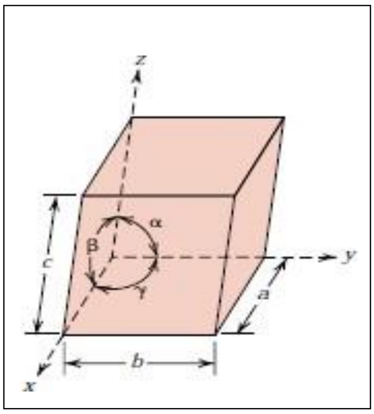


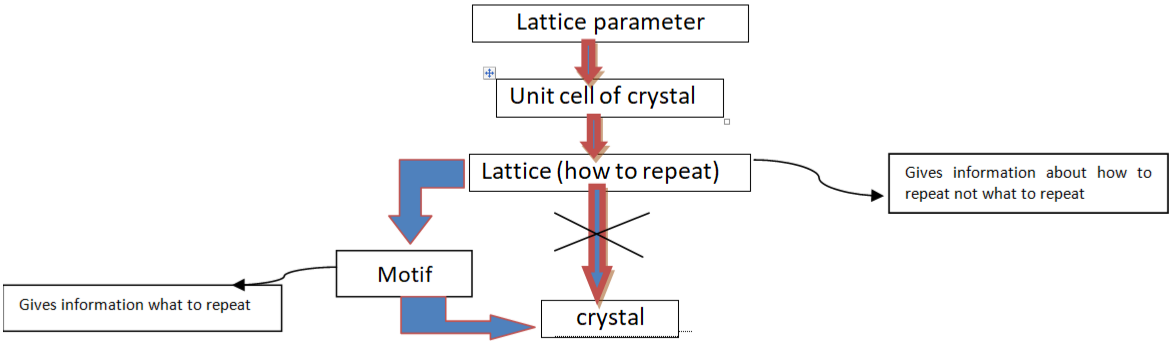
Figure: A unit cell with x, y, and z coordinate axes, showing axial lengths (a, b, and c) and inter axial angles α, β, γ

The unit cell geometry is completely defined in terms of six parameters:

a) the three edge lengths a, b, and c
b) the three inter axial angles α, β, γ

Edge length a, b, c and inter axial angles α, β, γ are termed as lattice parameter

- ❖ In a unit cell by varying lattice parameter the volume of the box can be changed implies shape of the box can be changed called as structural change.
- ❖ After fixing volume of the unit cell *by varying the atomic arrangement inside the unit cell,* strength of the material can be changed called as substructure change.



There are four sub structure that are existing as shown in figure.

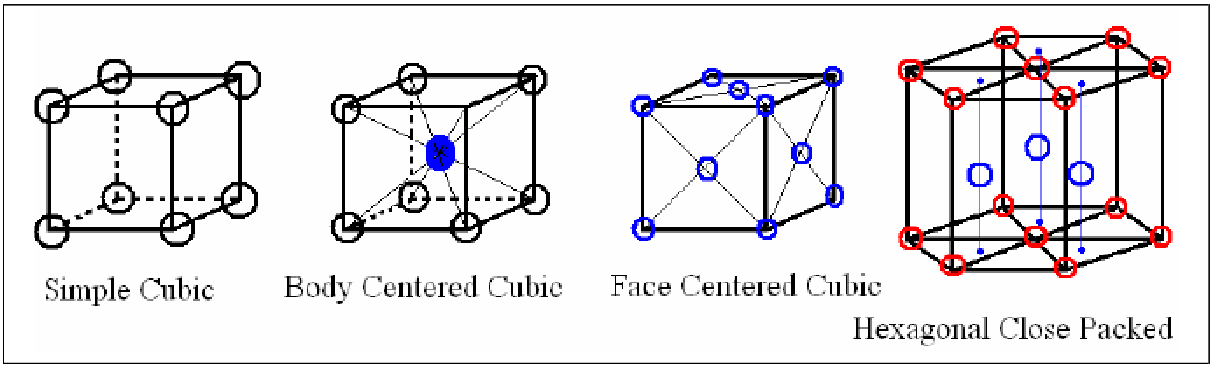


Figure. Types of Substructure of unit cell

MILLER INDICES

- Miller indices are a system of notation for designing crystal planes and direction of crystal.
- It is necessary to characterize the crystal to identify specific directions and planes. Specific methods are employed to define crystal directions and crystal planes.

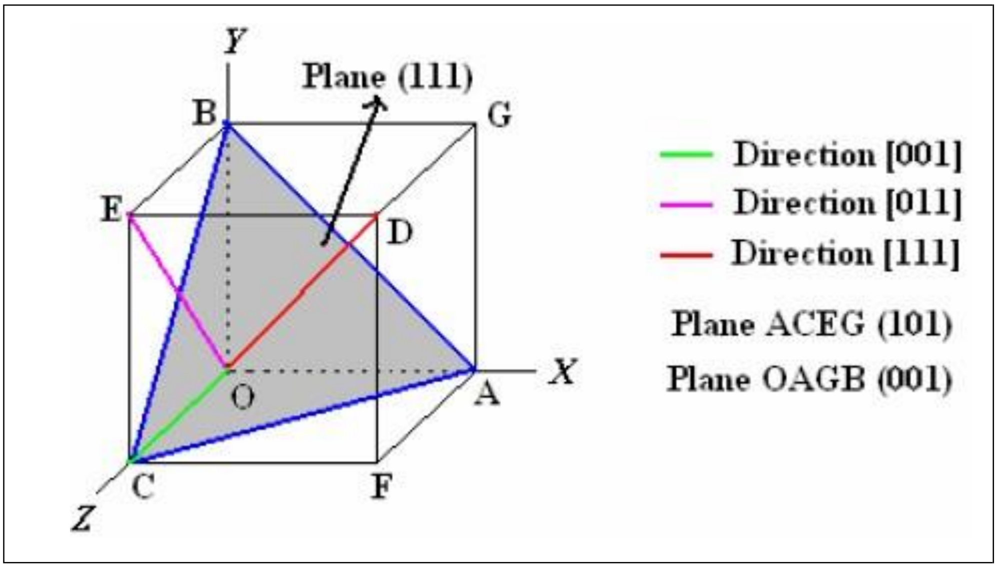


Fig.: Miller indices in a cubic crystal.

ATOMIC PACKING FACTOR (APF)

Atomic packing factor is the Ratio of the volume of the atoms per unit cell to the total volume occupied by the unit cell.

$$APF = \frac{volume\ of\ the\ atoms\ per\ unit\ cell}{total\ volume\ occupied\ by\ the\ unit\ cell}$$

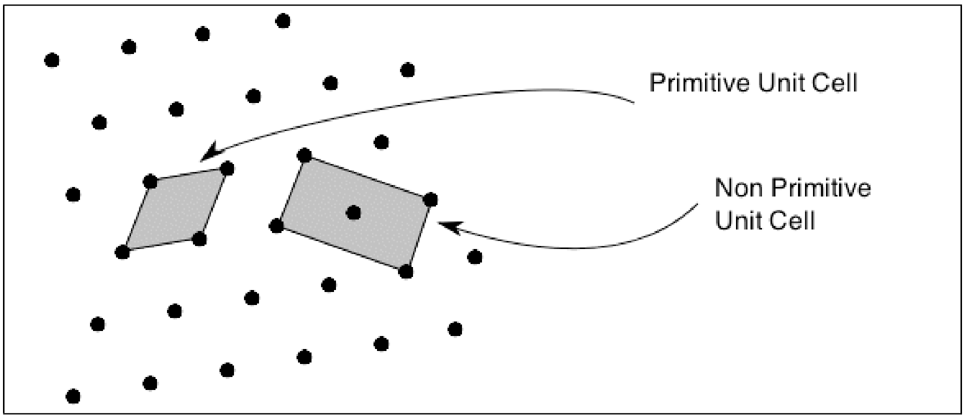
COORDINATION NO

Coordination no is the number of nearest atoms directly surrounding the given atom in a crystal.

PRIMITIVE CELLS & NON-PRIMITIVE UNIT CELL

Primitive unit cell: *Lattice point only at the corners of the cell*

Non-primitive unit cell: *Lattice points at its corner as well as at some other points.*



*There are two distinct types of unit cell: **primitive** and **non-primitive**.*

- *Primitive unit cells contain only one lattice point, which is made up from the lattice points at each of the corners.*
- *Non-primitive unit cells contain additional lattice points, either on a face of the unit cell or within the unit cell, and so have more than one lattice point per unit cell.*

This may be defined as a geometrical shape which, when repeated indefinitely in 3-dimensions, will fill all space and is equivalent of one lattice point, i.e. **the unit cell that contains one lattice point only at the corners**. We must note that in some cases the unit cell may coincide with the primitive cell, but in general the former differs from the latter in that it is not restricted to being the equivalent of one lattice point. **The unit cells, which contain more than one lattice point, are called non-primitive cells.** The unit cells may be primitive cells, but all the primitive cells need not to be unit cells.

CRYSTAL CLASSES

The atoms or molecules or ions in crystalline state are arranged in a *regular, repetitive* and *symmetrical pattern*, but the crystal will have the external symmetrical shape only, if no restraint is imposed during crystal growth. Crystals possess symmetry in that any given direction in the crystal corresponds to one or more directions which are exactly the same with respect to properties being considered. The symmetry of crystals is investigated by means of symmetry operations, as a result of which the crystal coincides with itself in various positions. The simplest of such operations (*rotation, reflection and translation*- *parallel displacement*) are associated with the elements of symmetry. The simplest elements of symmetry are *the axis and planes of symmetry*. The shape of the crystal is said to be symmetrical if it possesses one or more elements of symmetry. A group of symmetry operations, consisting commonly of a combination of rotations, reflections and rotations with reflection, is called a symmetry class.

The elements of symmetry are:

(i) The Symmetry Plane: The shape of the crystal is said to be symmetrical about a plane if it divides the shape into two identical halves or into two halves which are mirror images of one another. We must note that only in an ideal crystal the faces are of exactly same size.

(ii) The Symmetry Axis: If we can rotate the shape about an axis so that the shape occupies the same relative position in space more than once in a complete revolution, such an axis is called to be axis of symmetry. Such axes may be *either 2, 3, 4 or 6 fold*. The axis of symmetry causes the crystal to occupy more than one congruent position during rotation about that axis during rotation by 360°.

(iii) **The Centre of Symmetry:** Within a crystal, there is some point about which crystallographically similar faces are arranged in parallel and corresponding positions, e.g., the centre of the cube is a centre of symmetry. *We must note that a tetrahedron has no such centre*. A cube has highly symmetrical shape and contains many planes and axis of symmetry (Fig.).

- The axis of the symmetry is the imaginary line, passing through the center of the crystal, about which the crystal may be rotated so that it presents an identical environment, i.e. appearance more than once in the course of its rotation. When rotation around its axis presents the same appearance once, we call it as one-fold symmetry. One can determine the folds of symmetry by rotating the crystal through 360°, 180°,90°, 60°, and so on to obtain 1, 2, 3, 4 fold symmetry. We must note that the limit for crystalline solids six-fold symmetry.

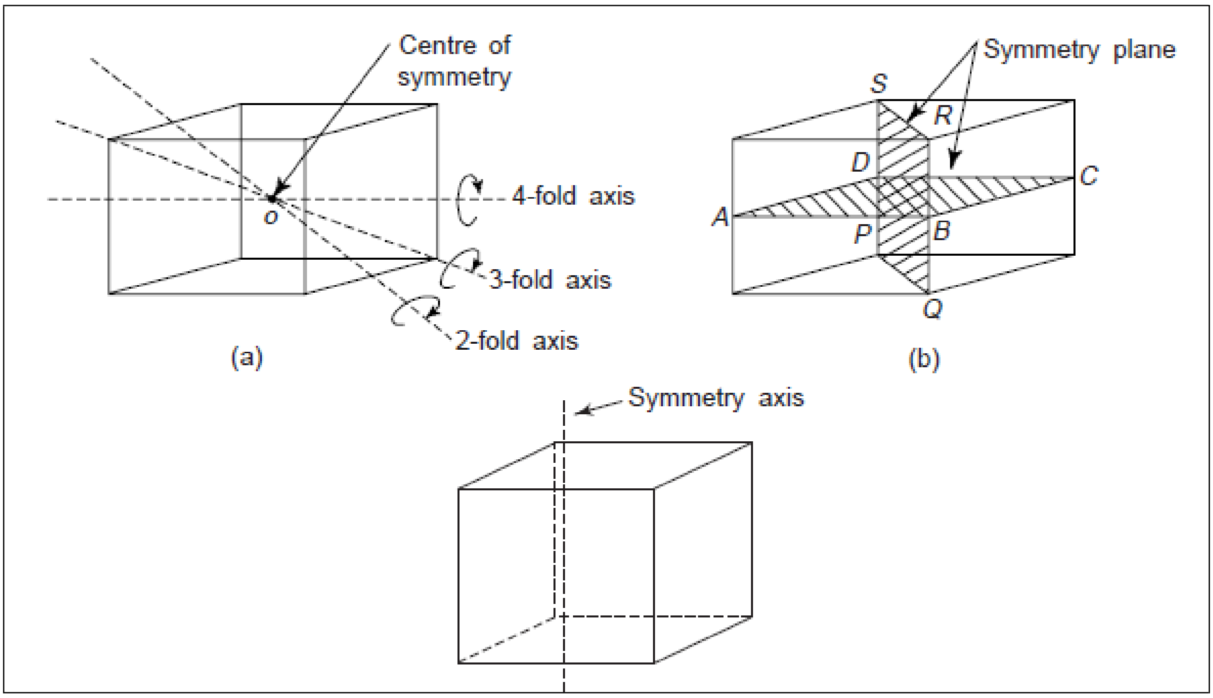


Fig: The elements of symmetry (a) axis and (b) planes

The principal axes of a cube are four-fold, i.e. during each complete rotation about the axis; the crystal passes four through identical positions. The body diagonal axes are three-fold and there are six two-fold axes. The vertical axis of hexagonal prism is a six-fold axes. A symmetry operation is one that leaves the crystal and its environment invariant. Symmetry operations performed about a point or a line are called *point group symmetry operations* and symmetry operation performed by translations as well is called *space group symmetry operations*. We must note that crystals exhibit both types of symmetries independently and in compatible combinations. The following are the different point group symmetry elements that are exhibited by crystals: (i) centre of symmetry or inversion centre, (ii) reflection symmetry and (iii) rotation symmetry.

CRYSTAL SYSTEM

If all the atoms at the lattice points are identical, the lattice is said to be *Bravais lattice.*

Bravais lattice for two dimension

- There are four systems and five possible Bravais lattices in two dimensions (Fig.)

- The four crystal systems of two dimensional spaces are *oblique, rectangular, square and hexagonal.*
- The rectangular crystal system has two Bravais lattices, namely, rectangular primitive and rectangular centered. In all, there are **five Bravais lattices** which are listed in Table 3.1 along with the corresponding point groups.

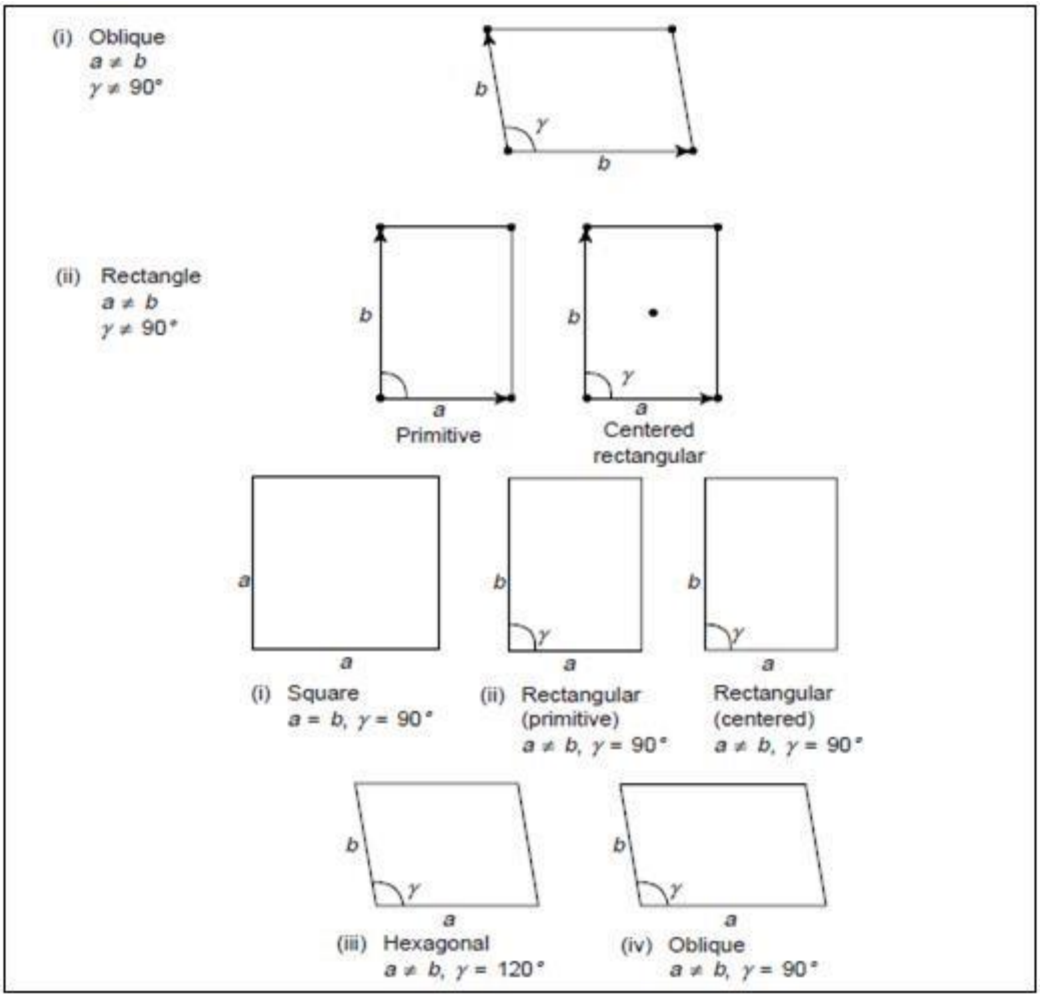
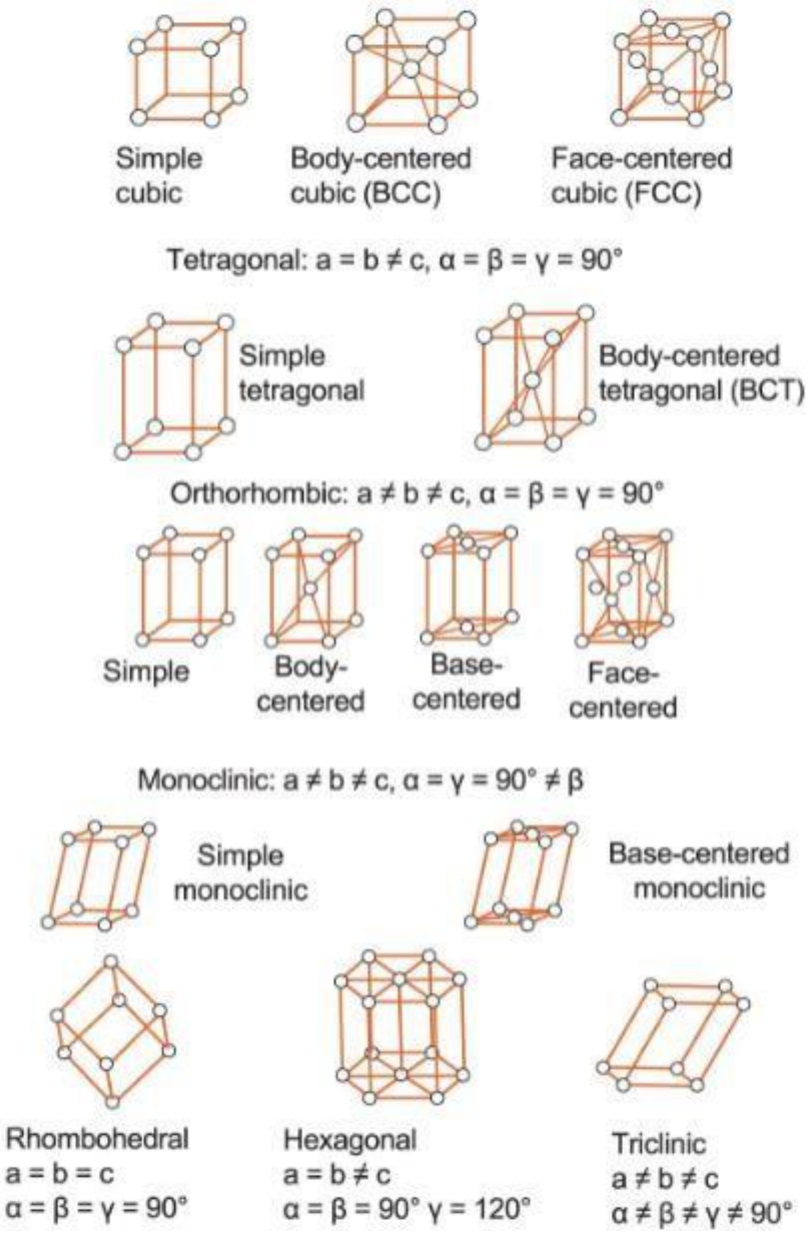
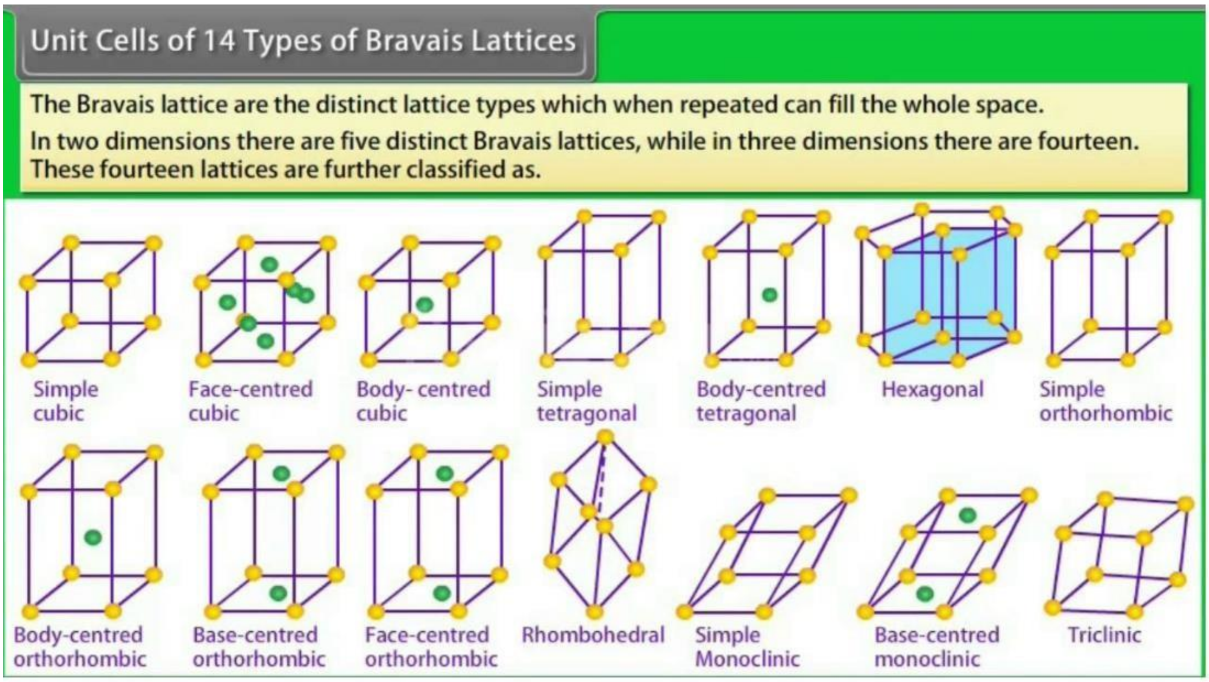


Fig: Bravais lattice for two dimension

BRAVAIS LATTICE FOR THREE DIMENSIONS

Based on pure symmetry considerations, there are only fourteen independent ways of arranging points in three-dimensional space, such that each arrangement is in accordance or in confirmation with the definition of a space lattice. These *14 space lattices* with *32 point groups* and *230 space groups* are called Bravais lattices


Simple cubic
Body-centered cubic (BCC)
Face-centered cubic (FCC)
Tetragonal: a = b ≠ c, α = β = γ = 90°
Simple tetragonal
Body-centered tetragonal (BCT)
Orthorhombic: a ≠ b ≠ c, α = β = γ = 90°
Simple
Body-centered
Base-centered
Face-centered
Monoclinic: a ≠ b ≠ c, α = γ = 90° ≠ β
Simple monoclinic
Base-centered monoclinic
Rhombohedral
a = b = c
α = β = γ = 90°
Hexagonal
a = b ≠ c
α = β = 90° γ = 120°
Triclinic
a ≠ b ≠ c
α ≠ β ≠ γ ≠ 90°



Unit Cells of 14 Types of Bravais Lattices

The Bravais lattice are the distinct lattice types which when repeated can fill the whole space.

In two dimensions there are five distinct Bravais lattices, while in three dimensions there are fourteen. These fourteen lattices are further classified as.

Figure. The 14- Bravais space lattices

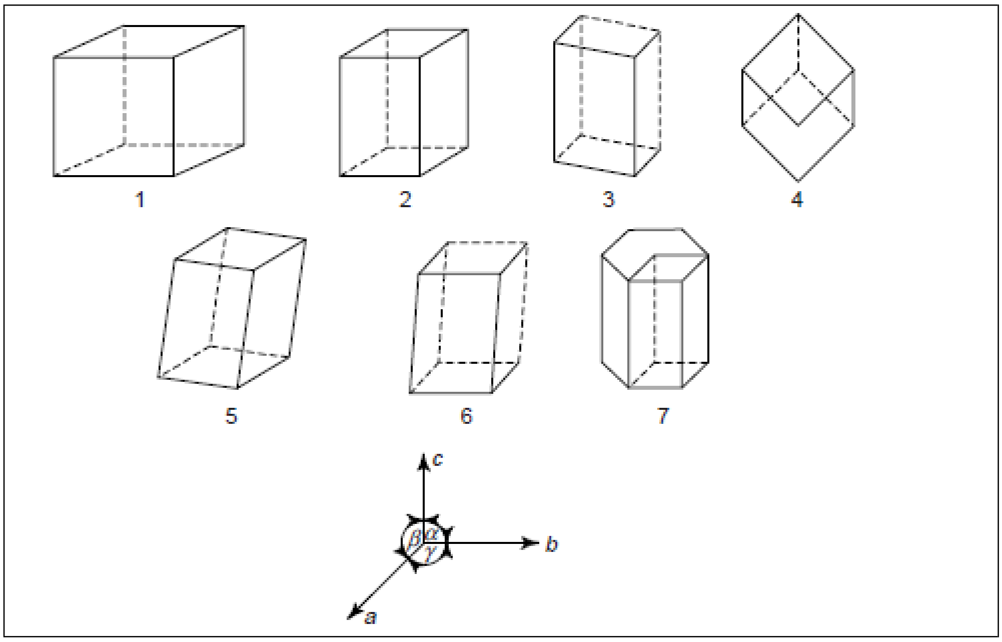
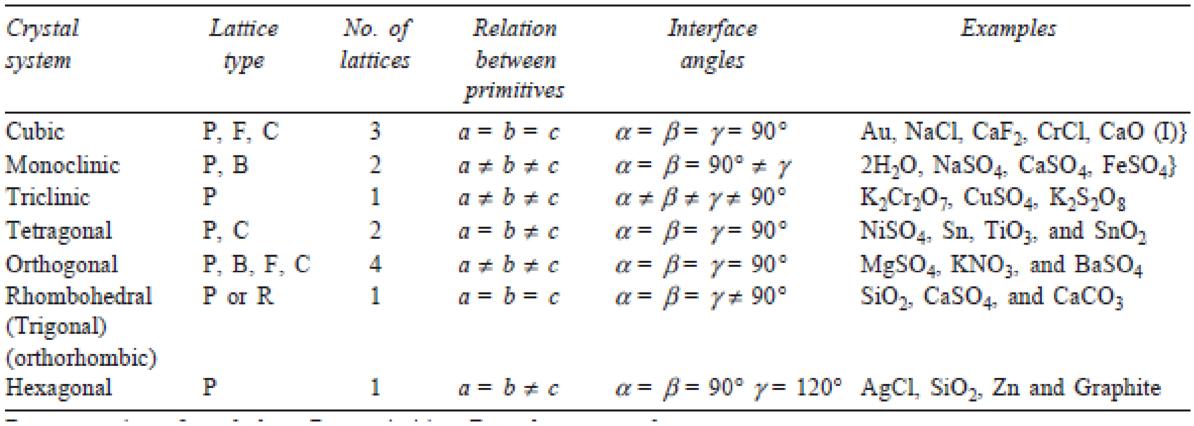


Figure. Seven basic crystal systems with reference axis.

Table. Seven crystal system with examples



Crystal system	*Lattice type*	*No. of lattices*	*Relation between primitives*	*Interface angles*	*Examples*
Cubic	P, F, C	3	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Au, NaCl, CaF_2, CrCl, CaO (I)}
Monoclinic	P, B	2	$a \neq b \neq c$	$\alpha = \beta = 90° \neq \gamma$	$2H_2O$, $NaSO_4$, $CaSO_4$, $FeSO_4$}
Triclinic	P	1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4$, $K_2S_2O_8$
Tetragonal	P, C	2	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	$NiSO_4$, Sn, TiO_3, and SnO_2
Orthogonal	P, B, F, C	4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$MgSO_4$, KNO_3, and $BaSO_4$
Rhombohedral (Trigonal) (orthorhombic)	P or R	1	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	SiO_2, $CaSO_4$, and $CaCO_3$
Hexagonal	P	1	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	AgCl, SiO_2, Zn and Graphite

Representation of symbols: $P \rightarrow Primitive, B \rightarrow base\ centered,\ C \rightarrow body\ centred\ and\ F \rightarrow face\ centred$

CRYSTAL STRUCTURE FOR METALLIC ELEMENTS

The most common types of space lattice or unit cells with which most common metals crystallise, are

(i) Body-centered cubic structures (BCC)

(ii) Face-centered cubic structures (FCC)

(iii) Hexagonal closed-packed structures (HCP)

BODY-CENTERED CUBIC STRUCTURES (BCC)

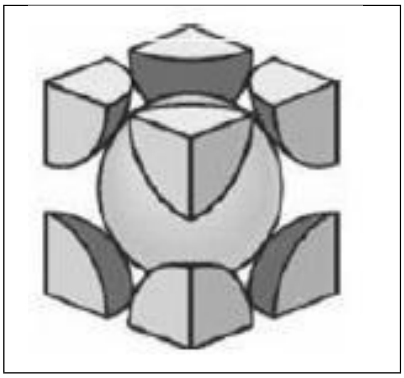


Figure. Arrangement of atoms in BCC structure

- **Because of presence of extra body centred atom all the 1/8th portion will not touch each other.**
- **But the body centred atom will have contact with all the 1/8th part.**

1) No of atoms per unit cell

$$N = \frac{N_C}{8} + \frac{N_F}{2} + \frac{N_B}{1} + \frac{N_{ba}}{2}$$

$where\ N_C - no\ of\ corner\ atoms,\quad N_F = no\ of\ face\ centre\ atoms,\quad N_B = no\ of\ body\ centre\ atom,\quad N_{ba} = no\ of\ base\ centre\ atoms$

$$N = \frac{8}{8} + 0 + \frac{1}{1} + 0 = 2$$

So no of atoms per unit cell in bcc structure is 2

2) Atomic packing factor

$$\text{Atomic packing factor} = \frac{\text{Average no of atoms per unit cell} \times \text{volume of an atom}}{\text{total volume of the unit cell}}$$

From the figure $b^2=a^2+a^2=2a^2$

$C^2=b^2+a^2 \longrightarrow c^2=2a^2+a^2$

$C^2=3a^2 \longrightarrow (4r)^2=3a^2 \longrightarrow r^2=\frac{3a^2}{16}$

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

r= atomic radius

a=lattice parameter

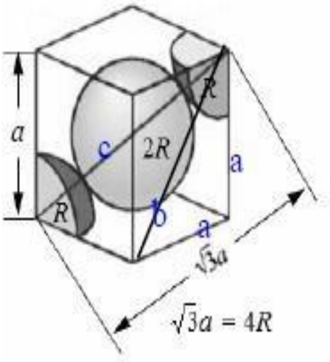


Figure. Calculation of atomic radius

$$\text{Atomic packing factor} = \frac{\text{Average no of atoms per unit cell} \times \text{volume of an atom}}{\text{total volume of the unit cell}}$$

$$= \frac{2 \times \frac{4}{3}\pi r^3}{a^3} = \frac{2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3} = \frac{8 \times 3\sqrt{3} \times \pi \times a^3}{3 \times 64a^3} = 0.68$$

$so\ atomic\ packing\ factor(APF)_{BCC} = 0.68 \text{ or } 68\%$

3) Coordination no

Body centre atom is in contact with all the corner atoms with a distance of R(same distance). So coordination no (Z) =8

4) Atomic radii

The atoms touch each other along the diagonal of the cube as shown in Fig. Obviously , the diagonal in this case is 4r, Also,

$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$

$AD^2 = AC^2 + CD^2 = 2a^2 + a^2 = 3a^2$

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

or $a = \frac{4r}{\sqrt{3}}$ and $2r = \frac{\sqrt{3}a}{2}$

$r = \frac{\sqrt{3}a}{4}$, area $a^2 = \frac{16r^2}{3}$

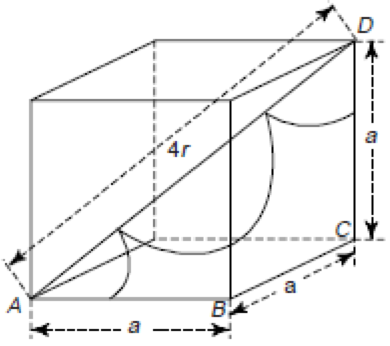


Figure. Calculation of atomic radius

FACE-CENTERED CUBIC STRUCTURES (FCC)

- A face centred cubic (FCC) unit cell consists of
    a. Eight corner atoms
    b. Six face centred atoms
- In this type of lattice structure, also known as cubic packed structure, the atoms are located at the eight corners of the cube and at the centre of each face. This type of structure is more common among metals than the BCC structure. It is also formed in ceramic crystals. Cu, Al, Ag, Au, Ca, $\propto -Fe, \beta - Co, \gamma - iron$(910°C to 1400°C) are common examples of metals possessing this type of structure.
- A metal with FCC structure has four times as many atoms as it has unit cells. This means the FCC structure is more densely packed than BCC structure.

1. No of atoms per unit cell

$$N = \frac{N_C}{8} + \frac{N_F}{2} + \frac{N_B}{1} + \frac{N_{ba}}{2}$$

$where\ N_C -\ no\ of\ corner\ atoms,\quad N_F = no\ of\ face\ centre\ atoms,\quad N_B = no\ of\ body\ centre\ atom,\quad N_{ba} = no\ of\ base\ centre\ atoms$

$$N = \frac{8}{8} + \frac{6}{2} + 0 + 0 = 4$$

So no of atoms per unit cell in bcc structure is 4.

2. Atomic packing factor

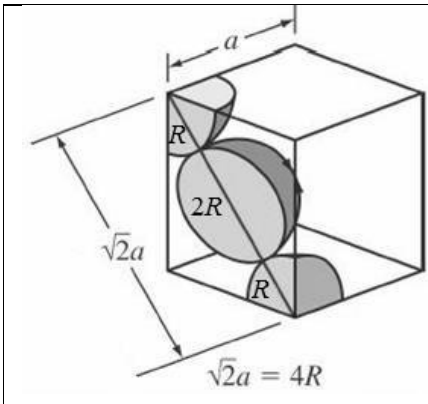


Figure. Calculation of atomic radius

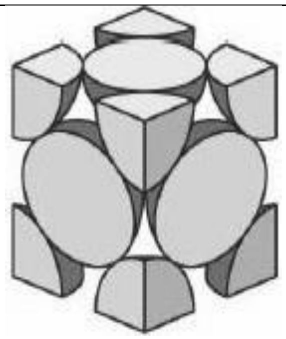


Figure. Arrangement of atoms in FCC

From this figure; first we can calculate atomic radius:

$(4r)^2=a^2+a^2 \rightarrow 16r^2=2a^2 \rightarrow r^2=\frac{2a^2}{16}$

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

$$\text{Atomic packing factor}=\frac{\text{Average no of atoms per unit cell}\times\text{volume of an atom}}{\text{total volume of the unit cell}}$$

$$=\frac{4\times\frac{4}{3}\pi r^3}{a^3}=\frac{4\times\frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}=\frac{16\times2\sqrt{2}\pi a^3}{3\times64a^3}=0.74$$

So atomic packing factor (APF) of FCC structure= 0.74 or 74%

That is 74 percent volume of an fcc unit cell is occupied by atoms and remaining 26 percent volume of unit cell is vacant.

3. Coordination no

Case-1

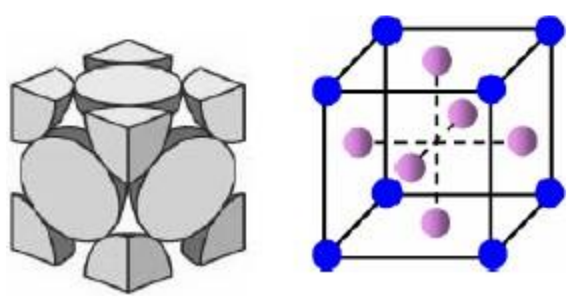


Figure. Arrangement of atoms in FCC

In the FCC lattice each atom is in contact with 12 neighbour atoms. FCC coordination number Z = 12. For example, the face centered atom in the front face is in contact with four corner atoms and four other face centered atoms behind it (two sides, top and bottom) and is also touching four face centered atoms of the centered unit cell in front of it.

Case-2

Let us consider a corner atom

1. **In its own plane:** corner atom has four face centered atoms. These face centered atoms are its nearest neighbours
2. **In a plane just above the corner atom**: it has four more face centered atoms as nearest neighbours
3. **In a plane which lies just below this corner atom**: it has yet four more face centred atoms as its nearest neighbours.

So for an atom in a face centred cubic unit cell no of nearest neaghbour atom is **12**

4. Atomic radii

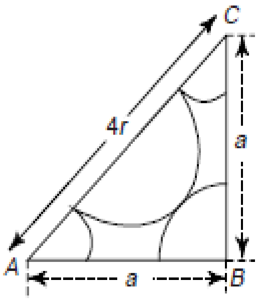


Figure. Triangle showing the relationship between radius r and side of edge a

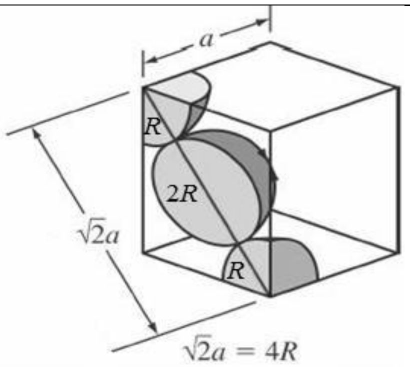


Figure. Calculation of atomic radius

Atoms within this structure touch along the diagonal of any face of the cube.

The diagonal has a length of 4r.

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

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

$$r^2 = \frac{2a^2}{16}$$

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

and area $=a^2=8r^2$

NOTE

Intrestingly the interatomic distances, 2r re 2% or 3% smaller than when the coordination no is eight(in (BCC), than when it is equal to twelve(in FCC &HCP). For example, inter atomic distances of BCC iron is $2.4824a^0$ but $2.50\ a^0$ in FCC iron.

Hence less the coordination no imples less the no of nearest neighbouring atoms implies possible of closer approach of atoms as there are less electronic repulsion due to less no of nearest ions

HEXAGONAL CLOSE PACKED (HCP)

In HCP structures, the unit cell contains one atom at each corner of the hexagonal prism, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. The HCP structure does not constitute a space lattice because the surroundings of the interior atoms and the corner atoms are different. This type of structure is denser than the simple hexagonal structure. The total number of atoms inside the NCP structure is 6.

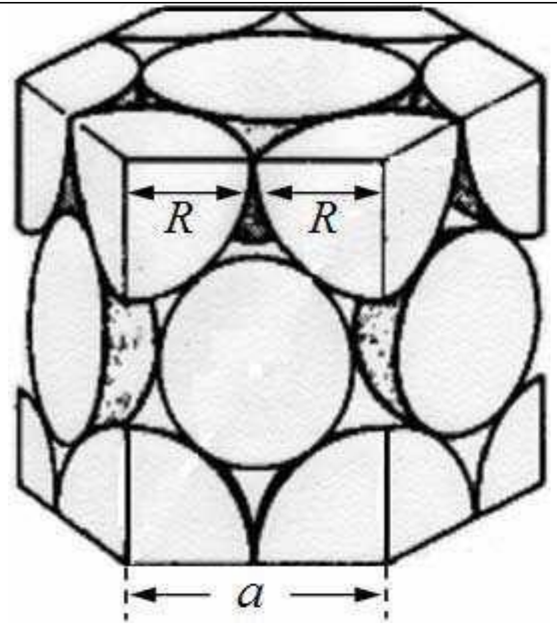


Figure. Arrangement of atoms

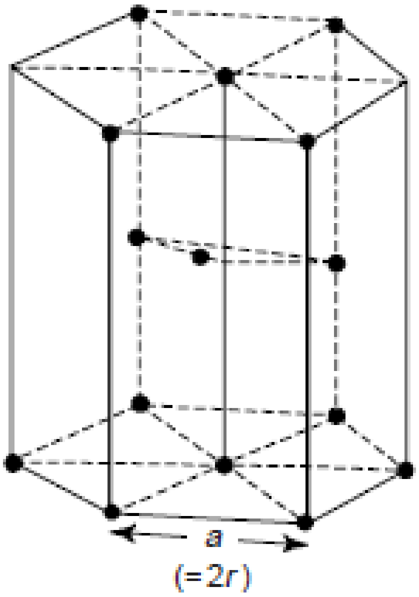


Figure. HCP unit cell

1. No of atoms per unit cell

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

Number of atoms in upper hexagonal plane

Number of atoms in lower hexagonal plane

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

Total number of central atoms in both, upper and lower planes =

and there are three intersititial atoms.

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

2. Atomic packing factor

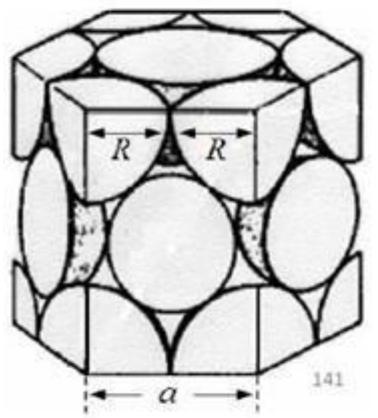
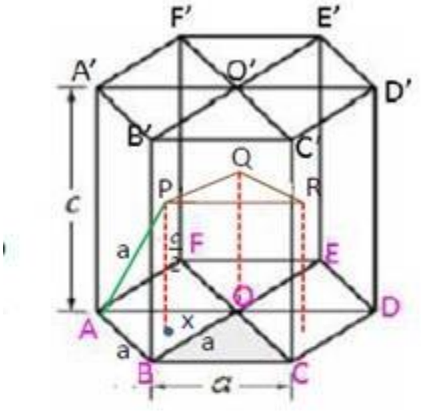
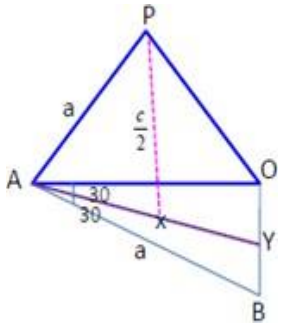
		

Figure. Arrangment of atoms	*Figure. Calculation of atomic radius*	*Figure. Relation between c and a*

Consider any one triangle, let us consider Δ AOB. ‘P’ is the centre of triangle

APOB –tetrahedron

In the triangle ΔAYB

$$\cos 30^0 = \frac{AY}{AB}$$

The diameter between any neighboring atoms is ‘a’ from the figure ‘AB’= a

$$AY = AB \cos 30^0 = \frac{a\sqrt{3}}{2}$$

From the figure ‘AX’ is orthocenter so,

$$AX = \frac{2}{3}AY = \frac{2}{3} \times \frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$

$$\text{Atomic packing factor(APF)} = \frac{\text{Average no of atoms per unit cell} \times \text{volume of an atom}}{\text{total volume of the unit cell}}$$

$$\text{Atomic packing factor} = \frac{6 \times \frac{4}{3}\pi r^3}{\text{total volume of the unit cell}}$$

In cubic a=b=c so volume=a3 but in the case of HCP a = b ≠ c

Volume of unit cell = Area of base of hexagonal X Height

Volume of unit cell = 6 x area of ΔAOB X C

$$\text{Volume of unit cell} = 6 \times \frac{1}{2} \times \text{OB} \times \text{AY} \times \text{C}$$

$$= 6 \times \frac{1}{2} \times \text{a} \times \frac{a\sqrt{3}}{2} \times c = ca^2\,\frac{3\sqrt{3}}{2}$$

$$\text{APF} = \frac{6 \times \frac{4}{3}\pi r^3}{ca^2\,\frac{3\sqrt{3}}{2}} = \frac{6 \times \frac{4}{3}\pi\,\frac{a^3}{8}}{ca^2\,\frac{3\sqrt{3}}{2}} = \frac{2\pi a}{c \times 3\sqrt{3}} = 0.74$$

$$\boldsymbol{APF_{HCP} = 0.74 \text{ or } 74\%}$$

Obviously, in an ideal HCP structure, 74% of the total volume is occupied by atoms

We further note that the APF value for HCP structure is identical to the APF of an FCC metal because each has a co-ordinate number of 12. The common examples of HCP structure are Be, Mg, Zn, Cd, Ti, Co, Hf, Se, Te, etc.

3. Coordination no

The coordination number of an HCP structure can be calculated as follws. Let us consider a face centred atom in the bottom layer. This face centred atom is surrounded by six corner atoms. These corner atoms are the nearest neighbours. The middle layer has three atoms which are nearest neighbours to the face centred atom. A unit cell, which lies below our reference unit cell also has three middle layer atoms. These three atoms are also the nearest neighbours for the face centred atom. Therefore the total number of nearest neighbours is 6+3+3=12

4. Atomic radius

THE ATOMICRADIUS OF AN HCP CRYSTAL STRUCTURE CAN BE CALCULATED AS FOLLOWS.

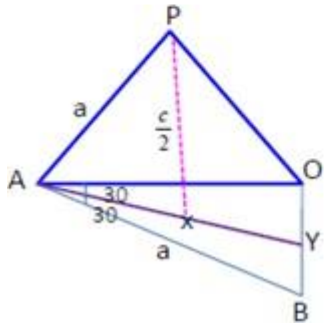
Let us consider any two corner atoms. Each and every corner atom touches each other. Therefore

a=2r

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

The atomic radius, r = a/2

5. C/A RATIO

Consider Δ APX $(AP)^2 = (AX)^2 + (XP)^2$ $\boldsymbol{a^2 = \frac{a^2}{3} + \frac{c^2}{4} \to a^2 - \frac{a^2}{3} = \frac{c^2}{4} \to \frac{c^2}{4} = \frac{2a^2}{3}}$ $\frac{c^2}{a^2} = \frac{8}{3} \to \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$	

DIAMOND STRUCTURE

A face centerd with 4 body atoms at a distance of $\frac{a}{4}$ from the opposite corners of the two opposite body diagonal is known as diamond structure.

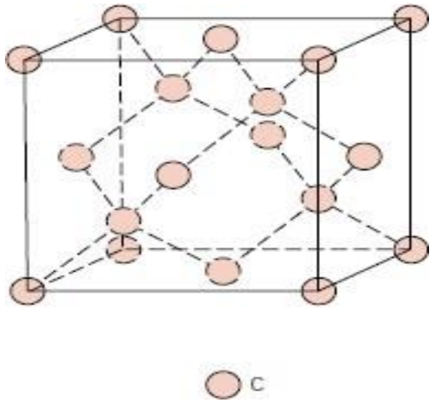


Figure: A unit cell for diamond cubic crystal structure.

1. **No of atoms per unit cell**

$$\boldsymbol{N = \frac{N_C}{8} + \frac{N_F}{2} + \frac{N_B}{1} + \frac{N_{ba}}{2}}$$

$$\boldsymbol{N = \frac{8}{8} + \frac{6}{2} + \frac{4}{1} + 0 = 8}$$

2. **Atomic packing factor**

Nearest neighbor distance=$\frac{a\sqrt{3}}{4}$

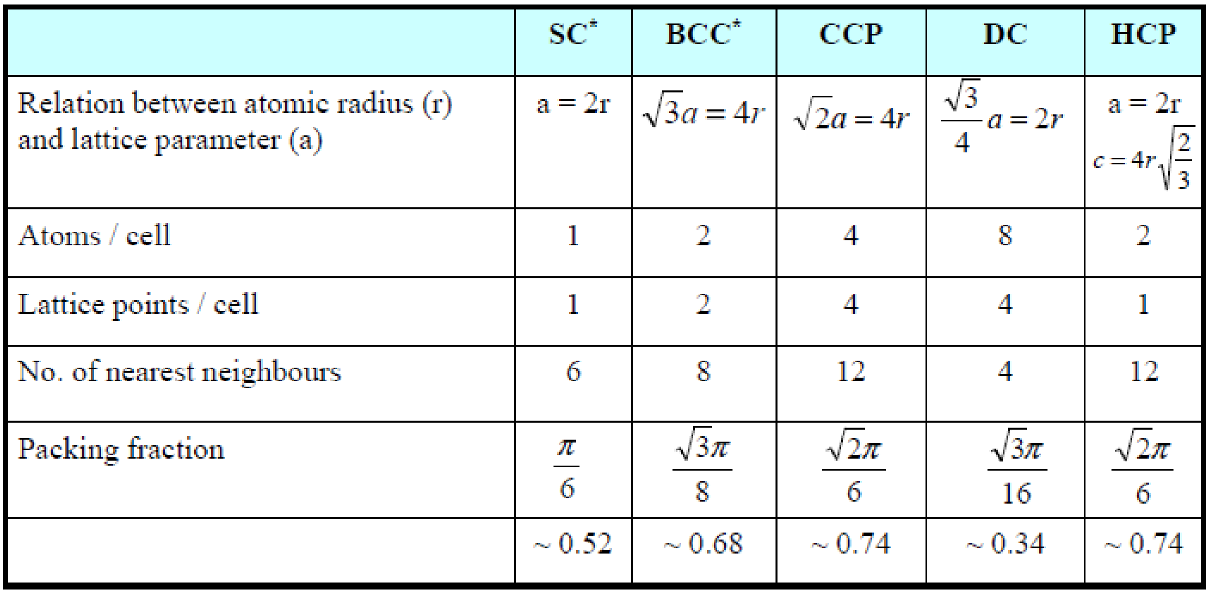
Radius of each sphere=$\frac{a\sqrt{3}}{8}$

Volume of unit cell=a^3

$$APF = \frac{no\ of\ atoms\ per\ unit\ cell \times volume\ of\ each\ sphere}{total\ volume\ of\ unit\ cell}$$

$$APF = \frac{N \times \frac{4}{3} \times \pi R^3}{a^3} = \frac{8 \times \frac{4}{3} \times \pi (\frac{a\sqrt{3}}{8})^3}{a^3} = \frac{\pi\sqrt{3}}{16} = .34$$

Table. Common cubic crystal structures with relationship of atomic radius with lattice parameter, atoms/cell, lattice points/cell, coordination no and APF



	SC*	BCC*	CCP	DC	HCP
Relation between atomic radius (r) and lattice parameter (a)	a = 2r	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	$\frac{\sqrt{3}}{4}a = 2r$	a = 2r $c = 4r\sqrt{\frac{2}{3}}$
Atoms / cell	1	2	4	8	2
Lattice points / cell	1	2	4	4	1
No. of nearest neighbours	6	8	12	4	12
Packing fraction	$\frac{\pi}{6}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$	$\frac{\sqrt{3}\pi}{16}$	$\frac{\sqrt{2}\pi}{6}$
	~ 0.52	~ 0.68	~ 0.74	~ 0.34	~ 0.74

CASE 1

If a material forms with simple cubic and BCC structure then $strength_{BCC} > strength_{sc}$ because BCC contains more no of atoms in the unit cell implies no of bonding will be more implies strength will be high. Also BCC contains high packing factor than simple cubic(SC) implies atoms are closely spaced implies binding energy among the atoms will be more implies strength will be more.

Also $density(\rho)_{BCC} > density(\rho)_{SC}$

NOTE: IN GENERAL A MATERIAL WITH HIGH DENSITY OR WEIGHT WILL BE TRY TO EXHIBIT HIGH STRENTH

CASE2

If a material forms with simple cubic , BCC AND FCC structure then

$$strength_{FCC} > strength_{BCC} > strength_{sc}$$
$$density(\rho)_{FCC} > density(\rho)_{BCC} > density(\rho)_{SC}$$

CASE 3

If a material forms with HCP and FCC structure then

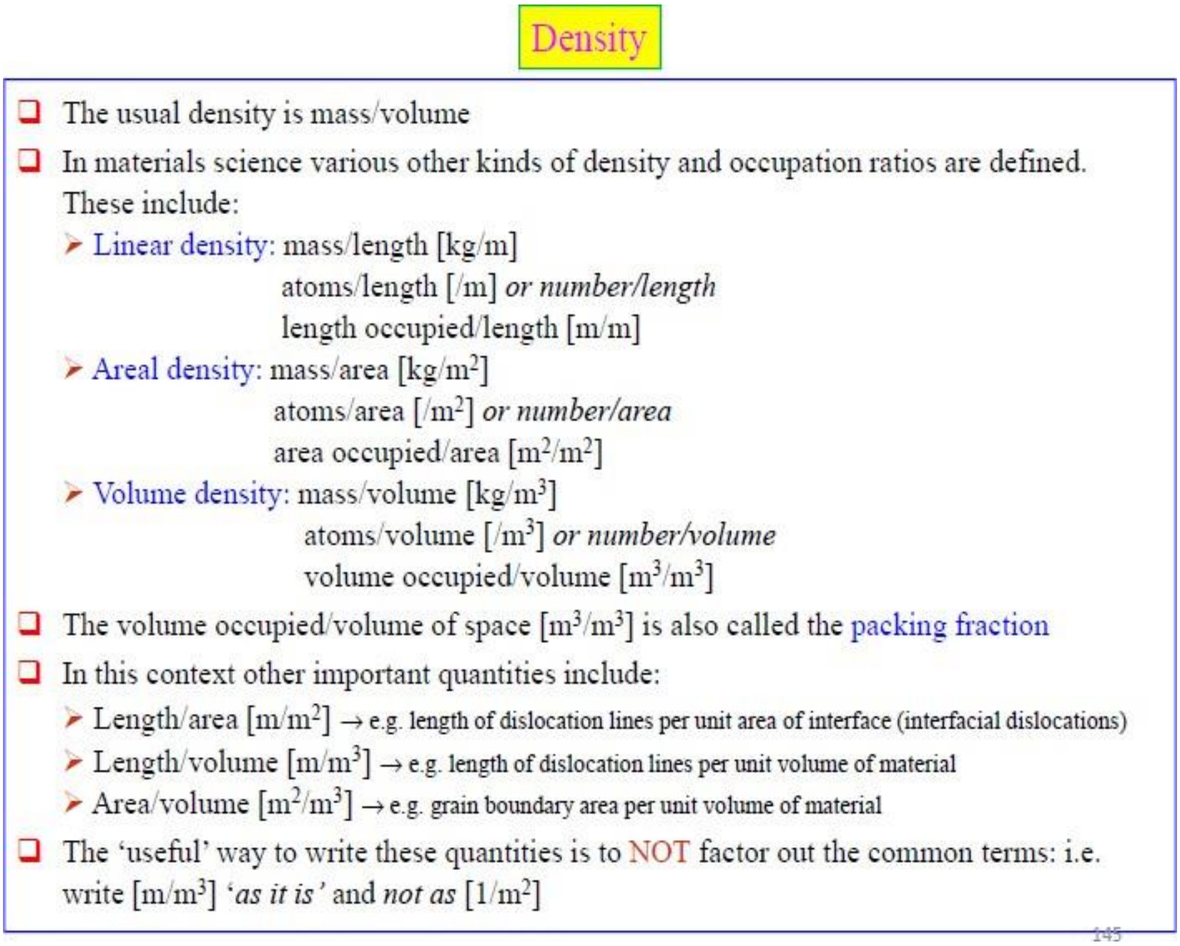
$$strength_{FCC} > strength_{HCP}$$

Because during formation of FCC lattice no gaps will formed among the lattice atom implies binding energy will be high. During formation of HCP structure gaps will form among the lattice atoms implies binding energy will be less implies strength is less

CASE 4

Diamond structure exhibits more hardness and strength eventhough it has low packing factor because carbon atoms will form bonding with carbon atoms itself with sp^3 bonding, which contains highest binding energy among the atoms implies hardness and strength is extremely high

NOTE: PRODUCTION METHOD DECIDES GRAIN SIZE IMPLIES GRAIN SIZE DECIDES ATOMIC ARRANGEMENT IMPLIES ATOMIC ARRANGEMENT DECIDES A STRUCTURE IMPLIES STRUCTURE DECIDES THE STRENGTH OF THE MATERIAL.



Density

- ❑ The usual density is mass/volume
- ❑ In materials science various other kinds of density and occupation ratios are defined. These include:
  - ➢ Linear density: mass/length [kg/m]
    atoms/length [/m] *or number/length*
    length occupied/length [m/m]
  - ➢ Areal density: mass/area [kg/m^2]
    atoms/area [/m^2] *or number/area*
    area occupied/area [m^2/m^2]
  - ➢ Volume density: mass/volume [kg/m^3]
    atoms/volume [/m^3] *or number/volume*
    volume occupied/volume [m^3/m^3]
- ❑ The volume occupied/volume of space [m^3/m^3] is also called the packing fraction
- ❑ In this context other important quantities include:
  - ➢ Length/area [m/m^2] → e.g. length of dislocation lines per unit area of interface (interfacial dislocations)
  - ➢ Length/volume [m/m^3] → e.g. length of dislocation lines per unit volume of material
  - ➢ Area/volume [m^2/m^3] → e.g. grain boundary area per unit volume of material
- ❑ The 'useful' way to write these quantities is to NOT factor out the common terms: i.e. write [m/m^3] '*as it is*' and *not as* [1/m^2]

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PLANAR DENSITY

Planar density (PD) refers to density of atomic packing on a particular plane.

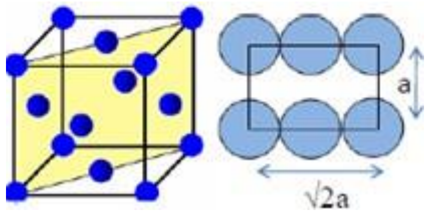
$$Planar\ Density = \frac{number\ of\ atoms\ on\ a\ plane}{area\ of\ plane}$$

Example-1

There are 2 atoms(1/4 x 4 corner atoms +1/2 x 2 side atoms) in the {110} plane in the FCC lattice.

Planar density of {110} planes in the FCC crystal

$$PD_{(110)} = \frac{2}{a\sqrt{2}a} = \frac{\sqrt{2}}{a^2}$$

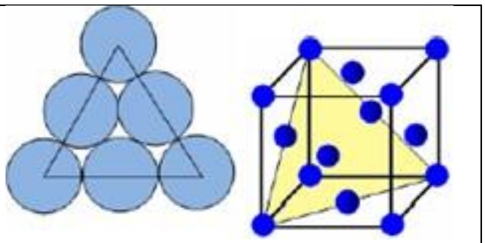


Example-1

In the {111} planes of the FCC lattice there are 2 atoms (1/6 x 3 corner atoms + ½ x 3 side atoms).

Planar density of {111} planes in the FCC crystal

$$PD_{(111)} = \frac{2}{\frac{1}{2}\sqrt{2}a \times \sqrt{2}a\frac{\sqrt{3}}{2}} = \frac{4}{\sqrt{3}a^2}$$



This is higher than{110} and any other plane. Therefore, {111} planes are most densly packed planes in the FCC crystal

LINEAR DENSITY

Linear density (LD) is the no of atoms per unit length along a particular direction.

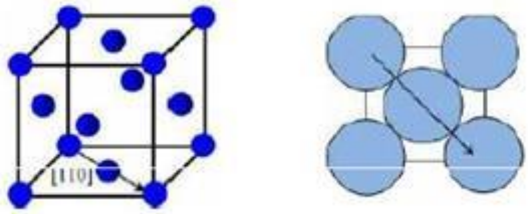
$$linear\ density = \frac{number\ \ of\ atoms\ on\ the\ direction\ vector}{length\ of\ the\ direction\ vector}$$

Example

<110> direction in the FCC lattice have 2 atoms (1/2 x 2 corner atoms + 1 centre atom) the length is $\sqrt{2}a$

Linear density of <110> direction in FCC crystal

$$LD_{[110]} = \frac{2}{\sqrt{2}a} = \frac{\sqrt{2}}{a}$$



This is the most densely packed direction in the fcc lattice

THEORETICAL DENSITY

Theoretical density calculation from crystal structure

Theoretical density =$\rho = \frac{nA}{V_C N_A}$

$\text{n} = \text{number of atoms in the unit cell}, \ \text{A} = \text{atomic weight}, \text{V}_\text{C} = \text{volume of unit cell}, \text{N}_\text{A} = \text{Avogadros's Number} \ (6.023 \text{ x } 10^{23}$

Example

Calculate the theoretical density of Aluminium (Al)

Given: Al is FCC structure; lattice parameter is 4.05 A$^{0;}$ n=4, atomic weight of Al is 26.98 g/mol

$$\rho = \frac{\text{nA}}{\text{V}_\text{C}\text{N}_\text{A}} = \frac{4 \times 26.98}{(4.05 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 2.697\text{g/cc}$$

MILLER INDICES

It is understood that properties of materials depend on their crystal structure, and many of these properties are directional in nature. For example: elastic modulus of BCC iron is greater parallel to the body diagonal than it is to the cube edge. Thus it is necessary to characterize the crystal to identify specific directions and planes. Specific methods are employed to define crystal directions and crystal planes.

Methodology to define crystallographic directions in cubic crystal:

- A vector of convenient length is placed parallel to the required direction.
- The lengths of the vector projection on each of three axes are measured in unit cell dimensions.
- These three numbers are made to smallest integer values, known as indices, by multiplying or dividing by a common factor.
- The three indices are enclosed in square brackets, [uvw]. A family of directions is represented by <uvw>.

For each of the three axes, there will exist both positive and negative coordinates. Thus negative indices are also possible, which are represented by a bar over the appropriate index. For example, the $[1\bar{1}1]$ direction would have a component in the _y direction. Also, changing the signs of all indices produces an antiparallel direction; that is, $[\bar{1}1\bar{1}]$ is directly opposite to $[1\bar{1}1]$. If more than one direction or plane is to be specified for a particular crystal structure, it is imperative for the maintaining of consistency that a positive–negative convention, once established, not be changed.

The [100], [110], and [111] directions are common ones; they are drawn in the unit cell shown in Figure

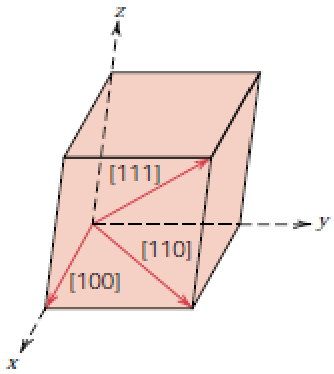
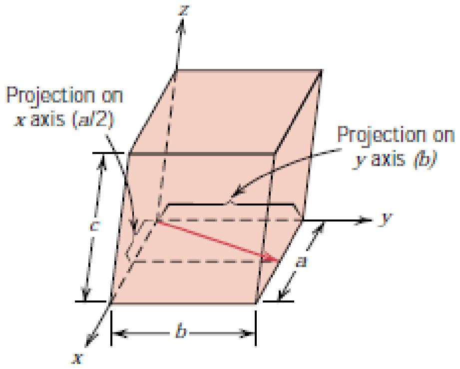


Figure: The [100], [110], and [111] directions

EXAMPLE

Determine the indices for the direction shown in the accompanying figure.



SOLUTION

The vector, as drawn, passes through the origin of the coordinate system, and therefore no translation is necessary. Projections of this vector onto the x, y, and z axes are, respectively, a/2, b, and 0c, which become $\frac{1}{2}$, 1, and 0 in terms of the unit cell parameters (i.e., when the a, b, and c are dropped). Reduction of these numbers to the lowest set of integers is accompanied by multiplication of each by the factor 2. This yields the integers 1, 2, and 0, which are then enclosed in brackets as [120].

This procedure may be summarized as follows:

	x	y	z
Projections	a/2	b	0c
Projections (in terms of a, b, and c)	$\frac{1}{2}$	1	0
Reduction	1	2	0
Enclosure		[120]	

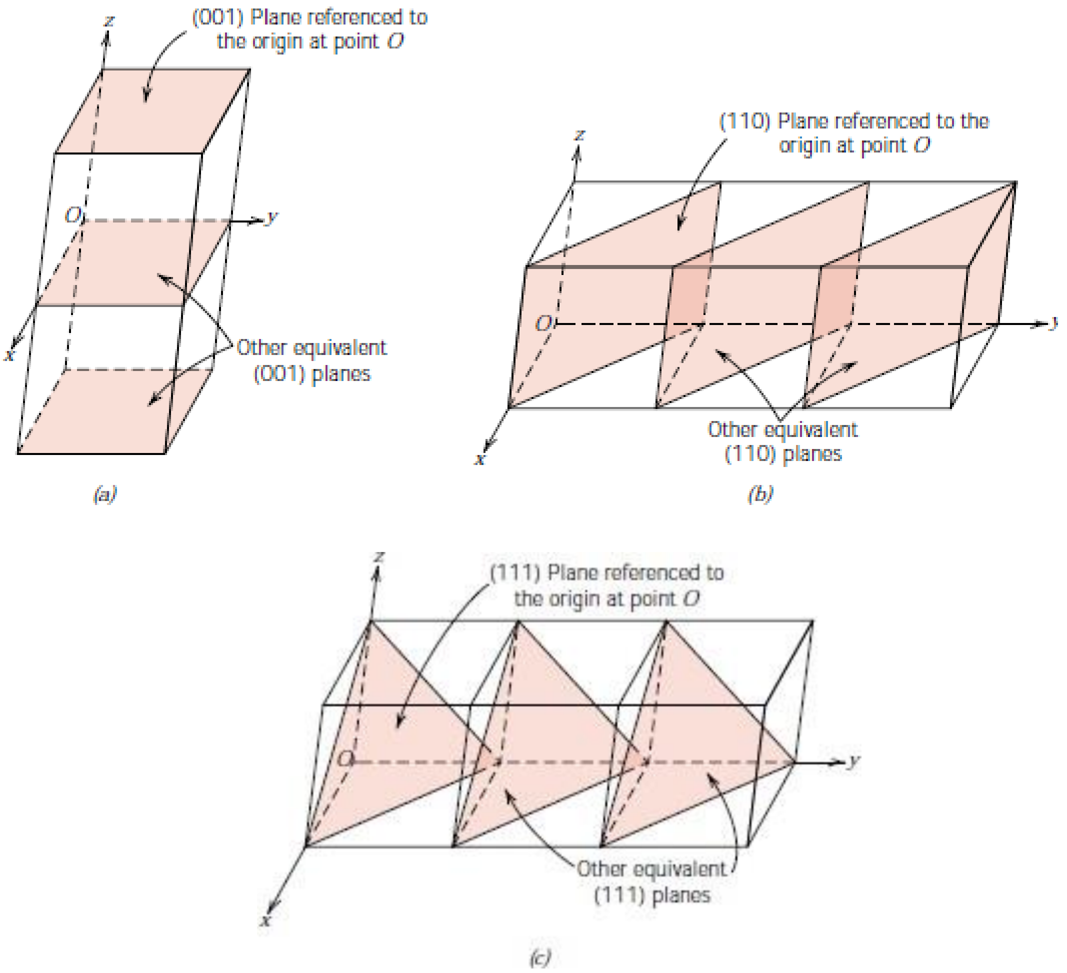
Methodology to define crystallographic planes in cubic crystal:

- Determine the intercepts of the plane along the crystallographic axes, in terms of unit cell dimensions. If plane is passing through origin, there is a need to construct a plane parallel to original plane.
- Take the reciprocals of these intercept numbers.
- Clear fractions.
- Reduce to set of smallest integers.
- The three indices are enclosed in parenthesis, (hkl). A family of planes is represented by {hkl}.

For example, if the x-, y-, and z- intercepts of a plane are 2, 1, and 3. The Miller indices are calculated as:

- Take reciprocals: 1/2, 1/1, 1/3.
- Clear fractions (multiply by 6): 3, 6, 2.
- Reduce to lowest terms (already there). => Miller indices of the plane are (362).

EXAMPLE

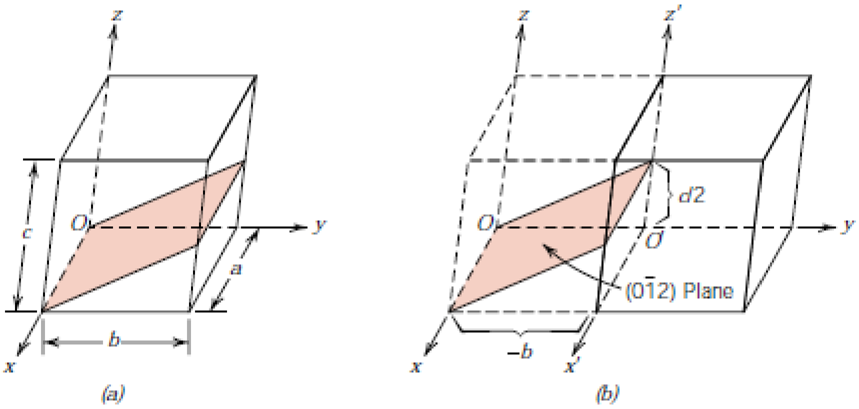


(a) (b) (c)

FIGURE : Representations of a series each of (a) (001), (b) (110), and (c) (111) crystallographic planes.

EXAMPLE

Determine the Miller indices for the plane shown in the accompanying sketch (a).



(a)

(b)

SOLUTION

Since the plane passes through the selected origin O, a new origin must be chosen at the corner of an adjacent unit cell, taken as O′ and shown in sketch (b). This plane is parallel to the x axis, and the intercept may be taken as ∞a. The y and z axes intersections, referenced to the new origin O′, are $-$b and c/2, respectively. Thus, in terms of the lattice parameters a, b, and c, these intersections are ∞, -1, and $\frac{1}{2}$. The reciprocals of these numbers are 0, -1, and 2; and since all are integers, no further reduction is necessary. Finally, enclosure in parentheses yields (0$\bar{1}$2).

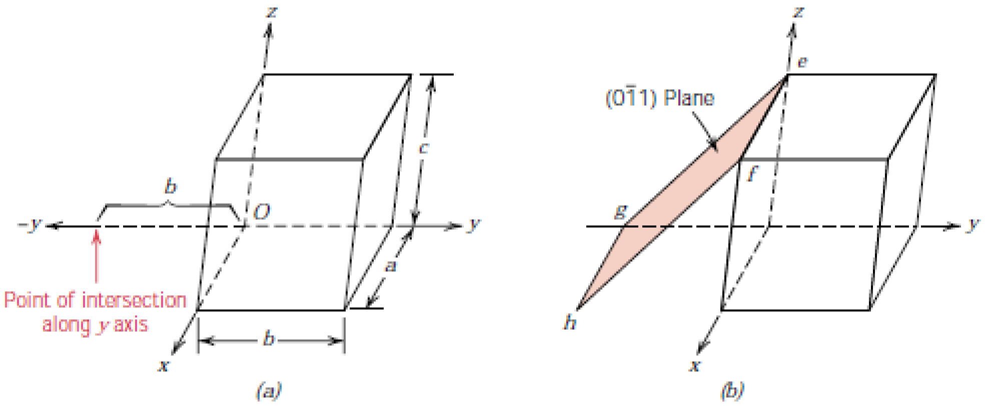
These steps are briefly summarized below:

	x	y	z
Intercepts	∞ a	$-$b	c/2
Intercepts (in terms of lattice parameters)	∞	-1	$\frac{1}{2}$
Reciprocals	0	-1	2
Reductions (unnecessary)			
Enclosure		(0$\bar{1}$2)	

Construct a (0$\bar{1}$1) plane within a cubic unit cell.

SOLUTION

To solve this problem, carry out the procedure used in the preceding example in reverse order. To begin, the indices are removed from the parentheses, and reciprocals are taken, which yields ∞, -1, and 1. This means that the particular plane parallels the x axis while intersecting the y and z axes at $-$b and c, respectively, as indicated in the accompanying sketch (a). This plane has been drawn in sketch (b). A plane is indicated by lines representing its intersections with the planes that constitute the faces of the unit cell or their extensions. For example, in this figure, line ef is the intersection between the (0$\bar{1}$1) plane and



the top face of the unit cell; also, line gh represents the intersection between this same (0$\bar{1}$1) plane and the plane of the bottom unit cell face extended. Similarly, lines eg and fh are the intersections between (0$\bar{1}$1) and back and front cell faces, respectively.

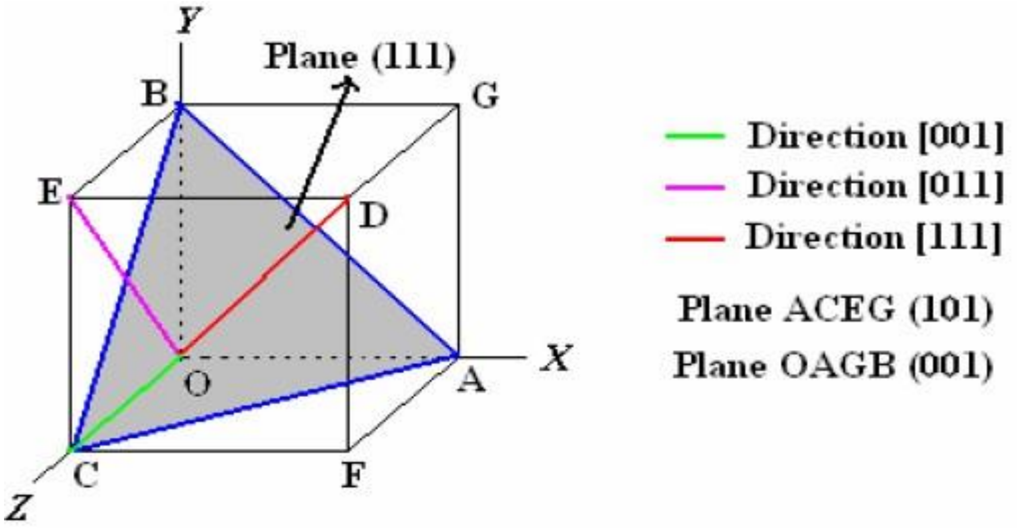


Figure: depicts Miller indices for number of directions and planes in a cubic crystal.

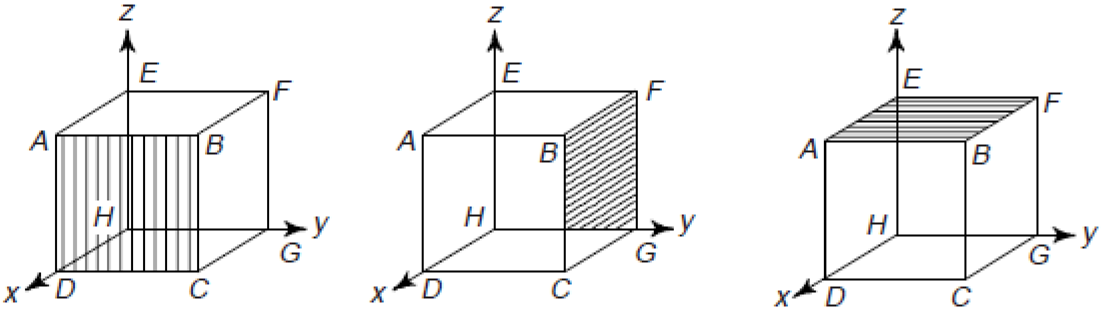
Some useful conventions of Miller notation:

- If a plane is parallel to an axis, its intercept is at infinity and its Miller index will be zero.
- If a plane has negative intercept, the negative number is denoted by a bar above the number. Never alter negative numbers. For example, do not divide -1, -1, -1 by -1 to get 1,1,1. This implies symmetry that the crystal may not have!
- The crystal directions of a family are not necessarily parallel to each other. Similarly, not all planes of a family are parallel to each other.
- By changing signs of all indices of a direction, we obtain opposite direction. Similarly, by changing all signs of a plane, a plane at same distance in other side of the origin can be obtained.

- Multiplying or dividing a Miller index by constant has no effect on the orientation of the plane.
- The smaller the Miller index, more nearly parallel the plane to that axis, and vice versa.
- When the integers used in the Miller indices contain more than one digit, the indices must be separated by commas. E.g.: (3,10,13)
- By changing the signs of all the indices of (a) a direction, we obtain opposite direction, and (b) a plane, we obtain a plane located at the same distance on the other side of the origin.

REPRESENTATION OF CRYSTAL PLANES IN CUBIC UNIT CELL

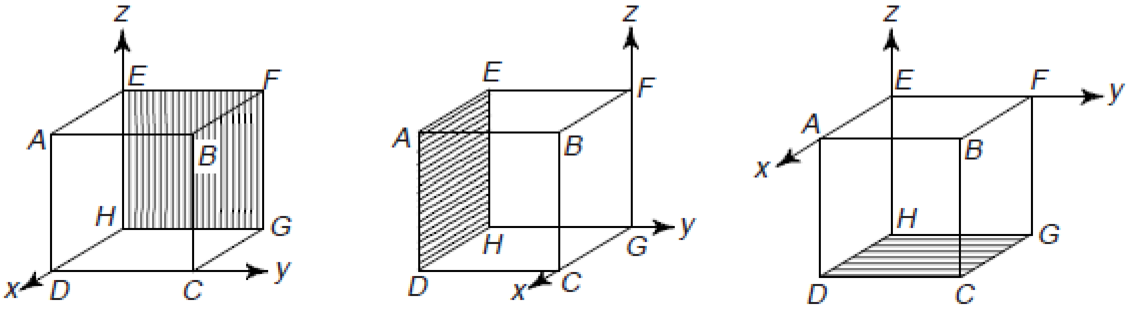
(100), (010) and (001) represent the Miller indices of the cubic planes *ABCD*, *BFGC* and *AEFB* respectively.



(a) Plane (100) (b) Pane (010) (c) Plane (001)

Crystal panes obtained by shifting the origin

Obviously, the above mentioned three planes represent the three faces of the cubic unit cell. We can represent the other three faces of the cube by shifting the origin of the coordinate system to another corner of the unit cell, e.g. the plane *EFGH* may be represented by shifting the origin from point *H* to point *D*

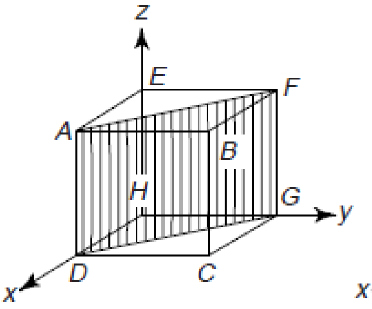


(a) Plane $(\bar{1}00)$ (b) Plane $(0\bar{1}0)$ (c) Plane $(00\bar{1})$

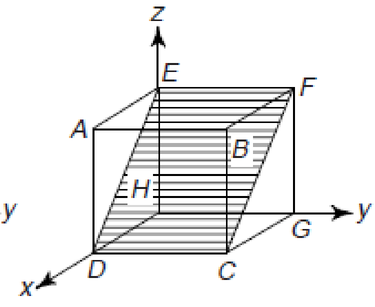
In figure (a) We note that now the values of the intercepts are—1 along x-x axes, ∞ along y-y and z-z axes. Thus the Miller indices are $(\bar{1}0\ 0)$. Similarly, we obtain Miller indices for the planes *AEHD* and *DHGC* as $(\bar{1}00)$ and $(00\bar{1})$ respectively by shifting the origin to the points *G* and *E.*

All the six faces of the cubic unit cell have same geometry, i.e. they are of the same form. Thus Miller indices of all the six planes are represented by {100}. This represents a set of six planes (100), (010), (001), ($\bar{1}$ 0 0), (0$\bar{1}$ 0) and (0 0 $\bar{1}$)

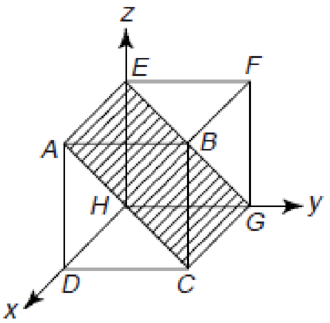
Similarly {110} represents a set of six planes (110), (101), (011), ($\bar{1}$ 1 0), ($\bar{1}$01), and (0 $\bar{1}$ 1)



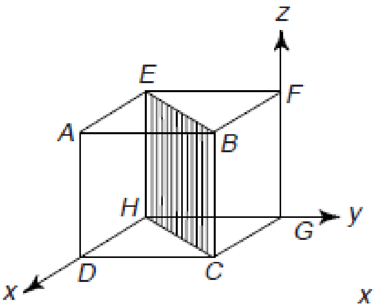
(a) Plane (110)



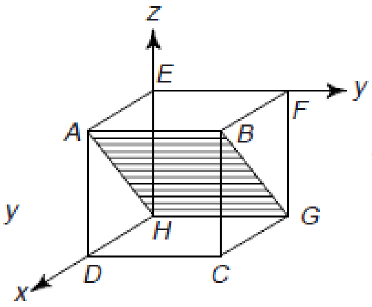
(b) Plane (101)



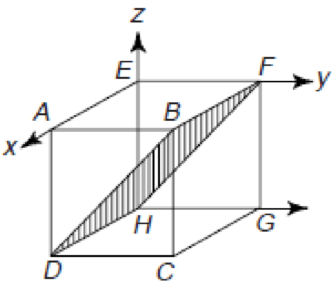
(c) Plane (011)



(d) Plane ($\bar{1}$ 10)



(e) Plane (10 $\bar{1}$)



(f) Plane (01 $\bar{1}$)

SKETCHING THE PLANE FROM A GIVEN MILLER INDICES

From a given Miller indices, one can sketch the planes. The procedure is as follows:

(i) First, take the reciprocal of the given Miller indices. These reciprocals represent the intercepts in terms of the axial units along x-x, y-y and z-z axes respectively. For example, if the given Miller indices are

(211), then its reciprocals or intercepts will be 1/2, 1/1 and 1/1 or 0.5, 1, 1 respectively.

(ii) Now, we should sketch the plane with intercepts. Here with 0.5, 1, 1 along x-x, y-y and z-z axes respectively

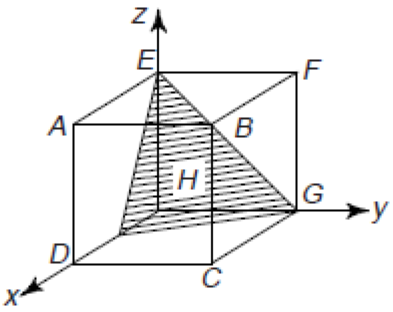


Figure: Plane (211)

More conventions applicable to cubic crystals only:

- $[uvw]$ is normal to (hkl) if $u = h, v = k, and\ w = l$. E.g.: $(111) \perp [111]$
- Inter-planar distance between family of planes $\{hkl\}$ is given by

$$d_{\{hkl\}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- $[uvw]$ is parallel to (hkl) if $hu + kv + lw = 0$
- Two planes $h_1k_1l_1$ and $h_2k_2l_2$ are normal if $h_1h_2 + k_1k_2 + l_1l_2 = 0$.
- Two directions $[u_1v_1w_1]$ and $[u_2v_2w_2]$ are normal if $u_1u_2 + v_1v_2 + w_1w_2 = 0$
- Angle between two planes is given by :

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}$$

The same equation applies for two directions

Why Miller indices are calculated in that way?

- Using reciprocals spares us the complication of infinite intercepts.
- Formulas involving Miller indices are very similar to related formulas from analytical geometry.
- Specifying dimensions in unit cell terms means that the same label can be applied to any plane with a similar stacking pattern, regardless of the crystal class of the crystal. Plane (111) always steps the same way regardless of crystal system.

CRYSTAL IMPERFECTION

Why Study *Imperfections in Solids?*

The properties of some materials are profoundly influenced by the presence of imperfections. Consequently, it is important to have knowledge about the types of imperfections that exist, and the roles they play in affecting the behavior of materials. For example, the mechanical properties of pure metals experience significant alterations when alloyed (i.e., when impurity atoms are added)—e.g., sterling silver (92.5% silver-7.5% copper) is much harder and stronger than pure silver. Also, integrated circuit microelectronic devices found in our computers, calculators, and home appliances function because of highly controlled concentrations of specific impurities that are incorporated into small, localized regions of semiconducting materials.

INTRODUCTION

By ‘‘crystalline defect’’ is 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. Several different imperfections are discussed in this chapter, including point defects (those associated with one or two atomic positions), linear (or one-dimensional) defects, as well as interfacial defects, or boundaries, which are two-dimensional. Impurities in solids are also discussed, since impurity atoms may exist as point defects.

Crystal:

A crystal is a solid composed of toms and, ions or molecules arranged in a pattern which is repetitive in three dimensions.

Ideal crystal:

The atomic arrangement is purely regular and continuous throughout. An ideal crystal is perfect.

Real crystal:

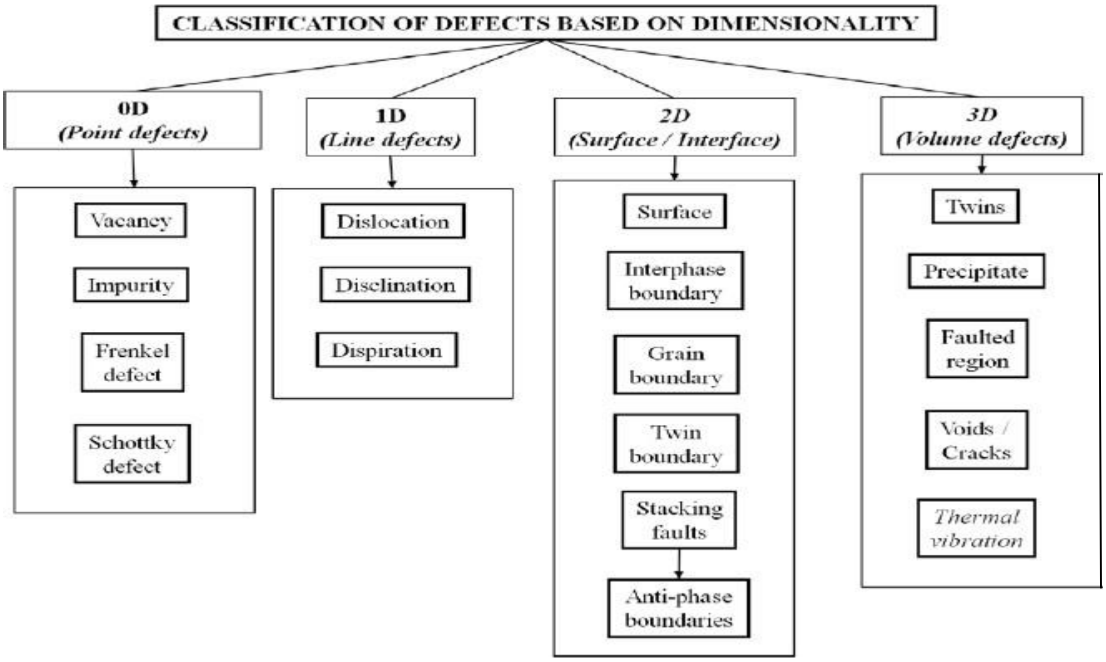
Real crystals are never perfect as in castor welded objects; lattice distortion and various imperfection, irregularities or defects are generally present in them. Therefore yield stress, physical and mechanical properties of metals and alloys are affected by imperfection.

Defects

$$strength\ of\ the\ material \propto \frac{1}{defect\ intensity}$$

- In any material if the defect size is more, strength of the material will be les therefore $strength \propto \frac{1}{defect}$
- Production of defects in a material depends on the method of production.
- Physical discontinuity in the lattice is called defects.

CLASSIFICATION OF CRYSTAL IMPERFECTION



All the defects and imperfection in crystal classified into four main divisions

1. **Point defects (zero dimensional)**
    a. Vacancies
    b. Interstitials
    c. Impurities
    d. Electronic defects
    e. Frenkel defect
    f. Schottky defect

2. **Line defects(one dimensional)**
    a. Edge dislocation
    b. Screw dislocation

3. **Planar, surface, interfacial or grain boundaries defects(two dimensional)**
    a. Grain boundaries
    b. Tilt boundaries
    c. Twin boundaries

4. **Volume defects**
    a. Crack or stacking faults

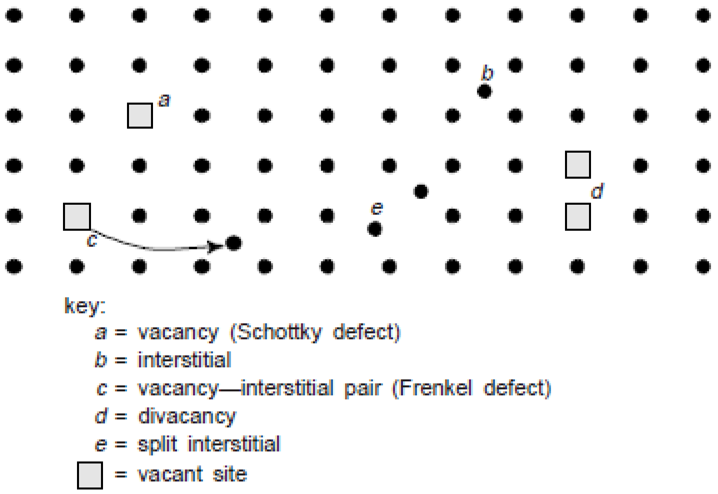


Fig: Some simple defects in a lattice

POINT DEFECTS (ZERO DIMENSIONAL) (MISSING ATOMS)

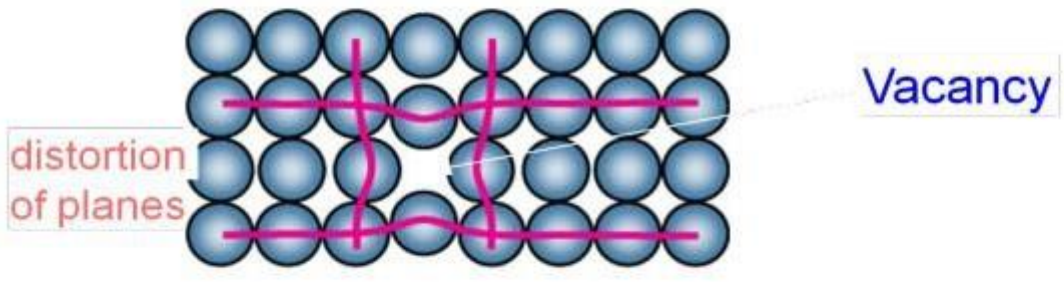
If the defect is confined to a single atom is known as point defects.

a. VACANCIES

- Missing of atoms from regular lattice de is known as vacancy.
- Vacancies are present invariably in all materials.
- Atoms around the vacancy displaced.
- Tensile stress field produced in the vicinity.
- The vacancy type of defect can result from imperfect packing during the crystallization process, or it may be due to increased thermal vibrations of the atoms brought about by elevated temperature.
- Vacancy creates deficiency of bondings with surrounding atoms in the lattice implies strength decreases

Example

- Porosity



DISPLACEMENT OF ATOMS

- Movement of atom from one lattice to another lattice side.
- Displacement of atom does not change the no of bonding with surrounding atoms implies strength remain same but it may change other properties. Of the material.

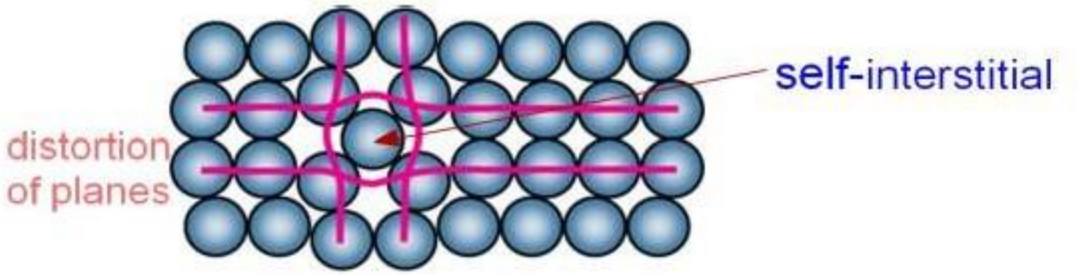
Example:

- In the pure form of silicon, it is electrically bad conductor but by adding Al or P , free electrons will travel through the vacancies in the lattice implies electron will move implies become as electrically good conductor.

b. SELF-INTERSTITIALS

- In a closed packed structure of atoms in a crystal if the atomic packing factor is low, an extra atom may be lodged within the crystal structure. This is known as interstitial position, i.e. voids.
- An extra atom can enter the interstitial space or void between the regularly positioned atoms only when it is substantially smaller than

the parent atoms otherwise it will produce atomic distortion. The defect caused is known as interstitial defect.



- In close packed structures, e.g. FCC and HCP, the largest size of an atom that can fit in the interstitial void or space have a radius about 22.5% of the radii of parent atoms.
- Interstitialcies may also be single interstitial, di-interstitials, and tri-interstitials

NOTE:

VACANCY AND INTERSTITIALCY ARE INVERSE PHENOMENA.

c. FRENKEL DEFECT

- When an ion displaced from a regular position to an interstitial position creating a vacancy, the pair of vacancy-interstitial is called *Frenkel defect*
- Frenkel defect is a combination of vacancy and interstitial defects
- These defects are less in number because energy is required to force an ion into new position.
- This type of imperfection is more common in ionic crystals, because the positive ions, being smaller in size, get lodged easily in the interstitial positions.

d. SCHOTTKY DEFECT:

- These imperfections are similar to vacancies.
- A pair of one cation and one anion can be missing from an ionic crystal, without violating the condition of charge neutrality when the valency of ions is equal. The pair of vacant sites, thus formed, is called *Schottky defect*.

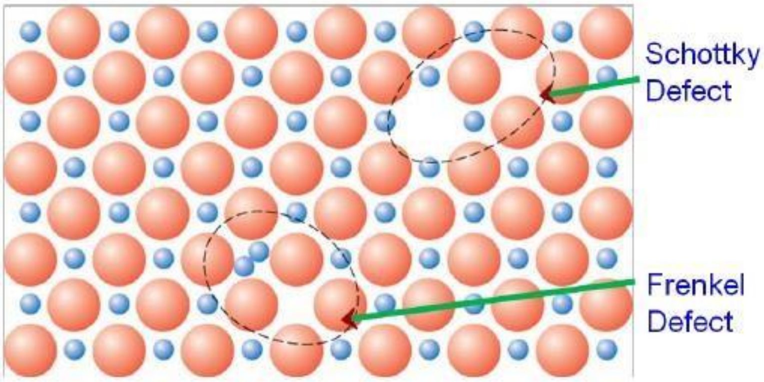
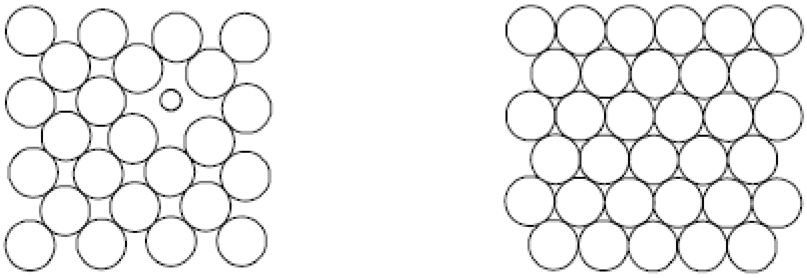
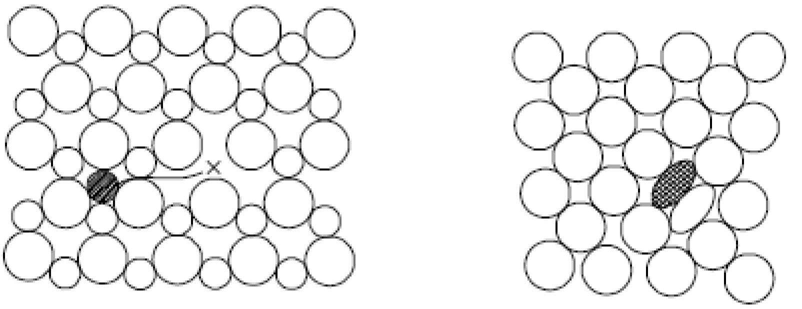


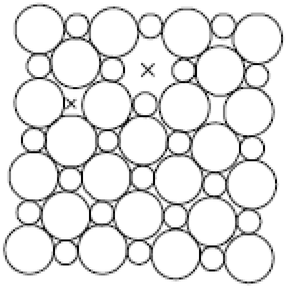
Figure: showing Frenkel defect and Schttky defect



(a) Vacancy defect (b) Interstitial defect



(c) Frenkel defect (d) Substitutional defect



(e) Schottky defect

Fig: point defects in a crystal lattice

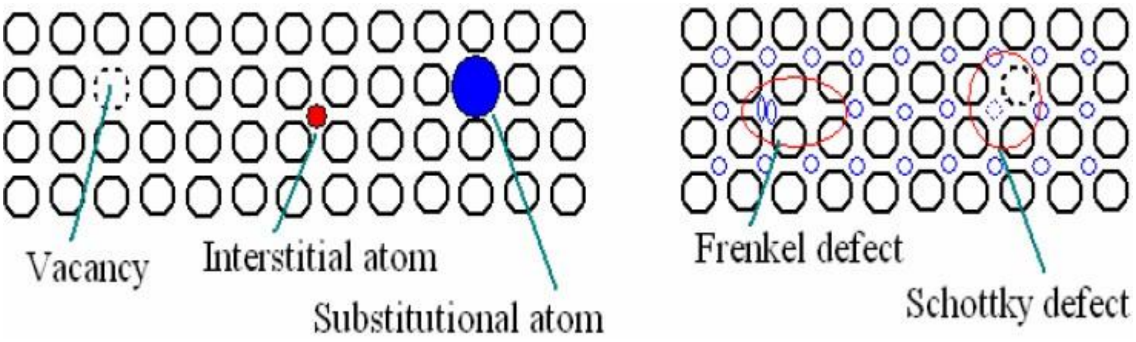


Fig: schematic depiction of point defects

e. **IMPURITIES**

- Impurities give rise to compositional defects.

- Impurities may be small particle(slag inclusion in metal) or a foreign atom (metal) in lattice
- The atomic radii and electronic structure of foreign atom is different from host atom. So it acts as a centre of distortion.
- Impurity (foreign atom) is introduced into crystal structure as
  1. Substitutional impurity atom/ substitutional inclusions
  2. Interstitial impurity/ interstitial inclusion

1. Substitutional impurity atom/ substitutional inclusions

- The foreign atom occupy the lattice atom position by removing the lattice atom
- A substituional impurity atom is an atom of a different type than the bulk atom which replaces one of the bulk atoms in lattice.
- Substituinal impurity atoms are usually close in size to bulk atom.
- Substitutional atom does not change the no of bonding implies strength remain same but other properties like thermal, electrical, optical and chemical properties can change.

Condition for substitutional inclusions

$$diameter\ of\ foreign\ atom\ (d_x) = diameter\ of\ lattice\ atom (d_l)$$

$$valency\ of\ X = valency\ of\ L$$

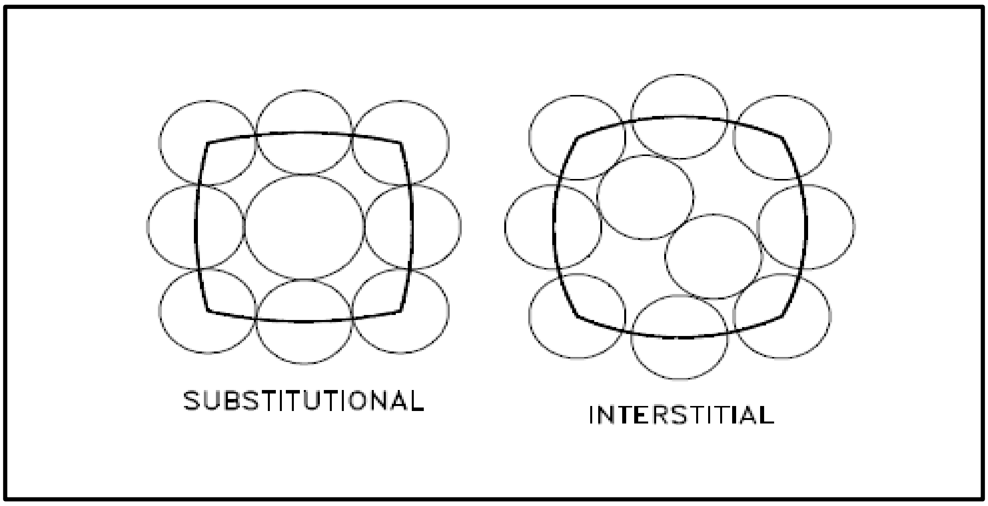
Example

- Addition of chromium(Cr) atom to steel improve corrosion resistance but strength remain same.
- Zinc atoms in bras. Zinc(Zn) atoms with a radius of 0.133nm have replaced some of the copper which have a radius of 0.128nm.

2. Interstitial impurity / interstitial inclusion

- The foreign atom is occupying the empty space available in the lattice without disturbing the lattice atom.
- Interstitial impurity atoms are much smaller than the atom in the bulk matrix.
- Interstitial inclusions increases the no of bonding implies strength increases.

Fig:



substitutional and interstitial inclusions

Condition for interstitial inclusions

$$diameter\ of\ foreign\ atom\ (d_x)\ \gg diameter\ of\ lattice\ atom(d_l)$$
$$valency\ of\ X > valency\ of\ L$$

Example

1. Addition of carbon tom(with a radius of 0.071nm) to iron to make steel and improve strength of steel
2. Carbon atom (with a radius of 0.071nm) fit nicely in the open spaces between the large (0.12nm) iron atoms.

EFFECT OF POINT DEFECT

1) The presence of a point imperfection introduces distortions in the crystal.
2) In the case of impurity atom, because of its difference in size, elastic strains are created in the regions surrounding the impurity atom.
3) All these factors tend to increase the potential energy of the crystal called ***'enthalpy'***. The work done for the creation of such a point defect is called the '***enthalpy of formation***' of the point imperfection

LINE DEFECTS

- Line imperfections (one-dimensional defects) are also called Dislocations.
- The defects which take place due to dislocation or distortion of atoms along a line some direction are called as line defects.
- The line defects also takes place when a central portion of a crystal lattice slips without disturbing the outer portion.

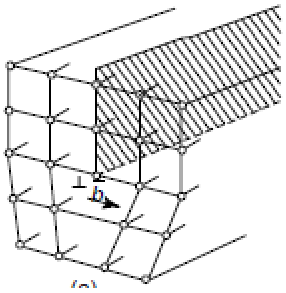
- They are abrupt changes in the regular ordering of atoms along a line (dislocation line) in the solid.
- They occur in high densities and strongly influence the mechanical properties of material.
- They are characterized by the Burgers vector (***b***), whose direction and magnitude can be determined by constructing a loop around the disrupted region and noticing the extra inter-atomic spacing needed to close the loop.

Types of line defects

1. Edge dislocation.
2. Screw dislocation

❖ EDGE DISLOCATION

- An edge dislocation in its cross-section is essentially the edge of an 'extra' half-plane
- In the crystal lattice. The lattice around dislocation is elastically distorted. This type of dislocation is formed by adding an extra partial plane of atoms to the crystal



- Figure shows a cross-section of a crystal where atoms (shown by dots) arranged in a perfect orderly manner. When an extra half plane is inserted from the top, the displacement of atoms is shown in Fig. We note that top and bottom of the crystal above and below the line *XY* appears perfect. When the extra half plane is inserted from the top, the defects so produced is represented by ⊥ (inverted tee) and if the extra half plane is inserted from the bottom, the defects so produced is represented by *T* (Tee).

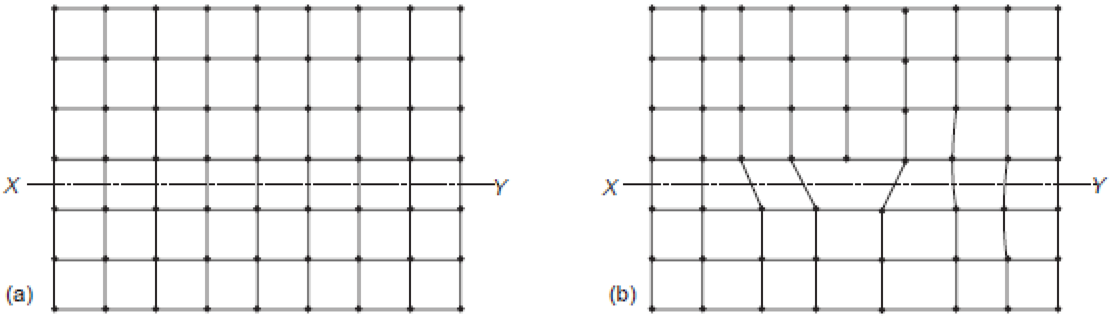


Fig: edge dislocation caused by an extra partial plane of atoms in the crystal

- Edge dislocation or Taylor-Orowan dislocation is characterized by a Burger's vector that is perpendicular to the dislocation line.
- It may be described as an edge of an extra plane of atoms within a crystal structure. Thus regions of compression and tension are associated with an edge dislocation.
- Because of extra incomplete plane of atoms, the atoms above the dislocation line are squeezed together and are in state of compression whereas atoms below are pulled apart and experience tensile stresses.
- Edge dislocation is considered positive when compressive stresses present above the dislocation line, and is represented by ⊥. If the stress state is opposite i.e. compressive stresses exist below the dislocation line, it is considered as negative edge dislocation, and represented by ⊤. A schematic view of edge dislocations are shown in figure.

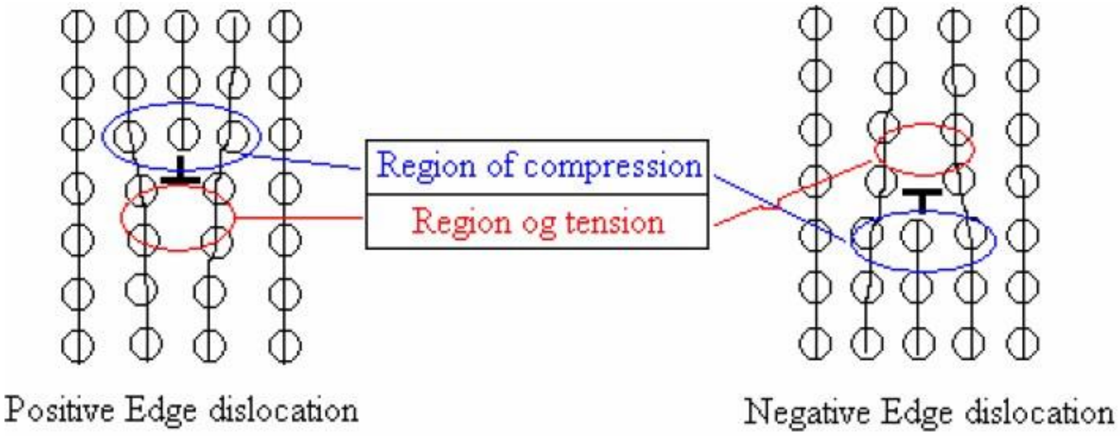


Figure: Edge dislocation

THE BURGERS VECTOR

The criterion of distortion is what is called the Burgers vector. It can be determined if a closed contour is drawn around a zone in an ideal crystal by passing from one site to another as shown in Fig. (a) and then the procedure is repeated a zone in a real crystal containing a dislocation. As may be seen from Fig. (b), the contour described in real crystal turns out to be unclosed. The vector required for the closing the contour is the Burgers vector. The Burgers vector of an edge dislocation is equal to the interatomic space and perpendicular to the dislocation line.

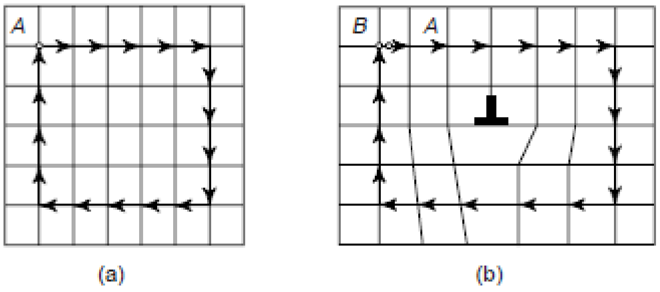


Fig: determination burger vector (BA)

The Burgers vector of a dislocation is an important property of a dislocation because, if the Burgers vector and the orientation of the dislocation line are known, the dislocation is completely described. Figure shows a method of determining the Burgers vector applied to a positive edge dislocation.

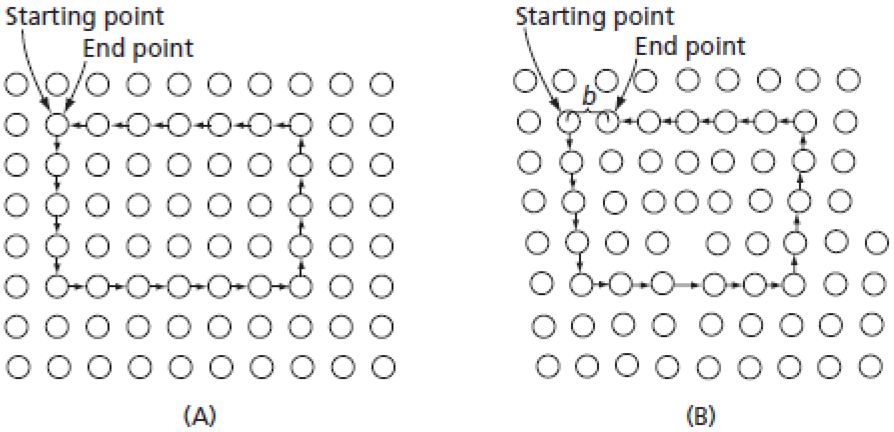


Fig: The Burgers circuit for an edge dislocation: (A) Perfect crystal and (B) crystal with dislocation

It is first necessary to choose arbitrarily a positive direction for the dislocation. In the present case, let us assume it to be the direction out of the paper. In Fig. A a counter clockwise circuit of atom-to-atom steps in a perfect crystal closes, but when the same step- by-step circuit is made around a dislocation in an imperfect crystal (Fig. B), the end point of the circuit fails to coincide with the starting point. The vector *b* connecting the end point with the starting point is the Burgers vector of the dislocation.

This procedure can be used to find the Burgers vectors of any dislocation if the following rules are observed:

1. The circuit is traversed in the same manner as a rotating right-hand screw advancing in the positive direction of the dislocation.
2. The circuit must close in a perfect crystal and must go completely around the dislocation in the real crystal.
3. The vector that closes the circuit in the imperfect crystal (by connecting the end point to the starting point) is the Burgers vector.

❖ SCREW DISLOCATION

- *Screw dislocation* or *Burgers dislocation* has its dislocation line parallel to the Burger’s vector.
- A screw dislocation is like a spiral ramp with an imperfection line down its axis.

- Screw dislocations result when displacing planes relative to each other through shear. Shear stresses are associated with the atoms adjacent to the screw dislocation; therefore extra energy is involved as it is in the case of edge dislocations.
- Screw dislocation is considered positive if Burger’s vector and *t*-vector or parallel, and vice versa. (***t***-vector – an unit vector representing the direction of the dislocation line).
- A positive screw dislocation is represented by ““⟳” a dot surrounded by circular direction in clock-wise direction”, whereas the negative screw dislocation is represented by ““⟲” a dot surrounded by a circular direction in anti-clock-wise direction”. A schematic view of a negative screw dislocation is shown in *figure.*

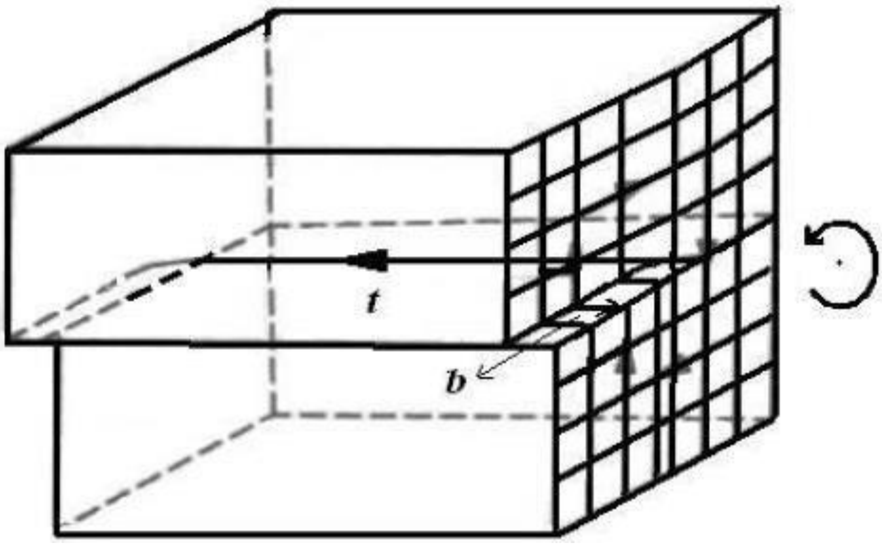


Figure: Negative screw dislocation.

The following effects of screw dislocation are of great importance.

a. Probably, the force required to form and move a screw dislocation is somewhat greater than that required to initiate an edge dislocation.

b. Without breaking the continuity of the lattice, the plastic deformation is possible under low stress.

c. Screw dislocation causes distortion of the crystal lattice for a considerable distance from the centre of the line and takes the form of spiral distortion of the planes. We must remember that the dislocations of both types, i.e., combinations of edge and screw, are closely associated with the crystallization as well as deformation.

It is now possible to summarize certain characteristics of both edge and screw dislocations.

1. Edge dislocations:
    a. An edge dislocation lies perpendicular to its Burgers vector.
    b. An edge dislocation moves (in its slip plane) in the direction of the Burgers vector (slip direction). Under a shear-stress sense⇆ N a positive dislocation ⊥moves to the right, a negative one T to the left.
2. Screw dislocations:
    a. A screw dislocation lies parallel to its Burgers vector.
    b. A screw dislocation moves (in the slip plane) in a direction perpendicular to the Burgers vector (slip direction).

SURFACE AND GRAIN BOUNDARY DEFECTS

The defects which take place on the surface of a material are known as surface defects or Plane defects.

Cause of surface defects:

Surface defects may takes place due to

- Impreferred packing of the atoms during crystallisation
- Defective orientation of the surface.
- change in the stacking of atomic planes on or across a boundary

Types of surface defects

Basically surface imperfections are of two types:

a) External
b) Internal.

External surface imperfections

- The external surface of a material is an imperfection itself because the atomic bonds do not extend beyond it.
- The surface atoms have neighbours on one side only while atoms inside the crystal have neighbours on either side of them (Fig.).
- Since surface atoms are not entirely surrounded by others, they possess higher energy than that of internal atoms. For most metals, the energy of surface atom is of the order 1 J/m2.

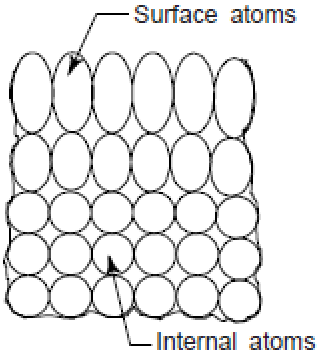


Figure: External surface defects

INTERNAL SURFACE IMPERFECTIONS

The internal surface imperfections are manifested by such defects as

- Grain boundaries
- Tilt boundaries
- Twin boundaries
- Stacking faults

GRAIN BOUNDARIES

- Grain boundary imperfections are those surface imperfections which separate crystals or grains of different orientation in a polycrystalline aggregation during nucleation or crystallization. The shape of a grain is usually influenced by the presence of surrounding grains.
- The lattices of adjacent grains are oriented at random and differently and a boundary between any two grains is essentially a transition layer of thickness of 1–5 nm. This layer may have a disordered arrangement of atoms, dislocation of clusters, and an elevated concentration of impurities.
- In grain boundaries the atomic packing is imperfect and between two adjacent grains, there is a transition zone that is not aligned with either grain as shown in figure.

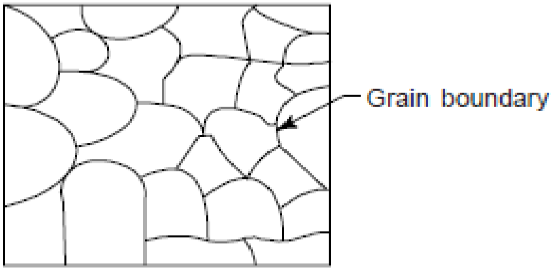


Figure: areas of disorder at grain boundary

- As a result, we note that boundary atoms in such cases cannot have a perfect complement of surrounding atoms. The mismatch with orientation of the adjacent grain produces a less efficient packing of atoms along the boundary. Thus, the atoms along the boundary have a higher energy than those within the grains.

- The higher energy of the boundary atoms is also important for the nucleation of polymorphic phase changes. The boundary between two crystals which have different crystalline arrangements or different compositions is called an interphase boundary or commonly called an interface.

Characteristics of grain boundaries

a. Region of orientation mismatch
b. High energy regions
c. Regions of heavy impurity concentration
d. Low melting point regions

HIGH ANGLE GRAIN BOUNDARIES

- The lower atomic packing along the boundary favours atomic diffusion. When the orientation difference between neighbouring grains is more than 10°–15°, boundaries are called high angle grain boundaries shown in fig.(a)

LOW ANGLE GRAIN BOUNDARIES

- Each grain in turn consists of *subgrains or blocks*. A subgrain is a portion of a crystal of a relatively regular structure.
- Subgrain boundaries are formed by walls of dislocations which divide a grain into a number of subgrains or blocks [Fig. (b)].
- Angle of misorientation between adjacent subgrains are not large (not more than 5°), so that their boundaries are termed 'low angle'.
- Low angle boundaries can also serve as places of accumulation of impurities

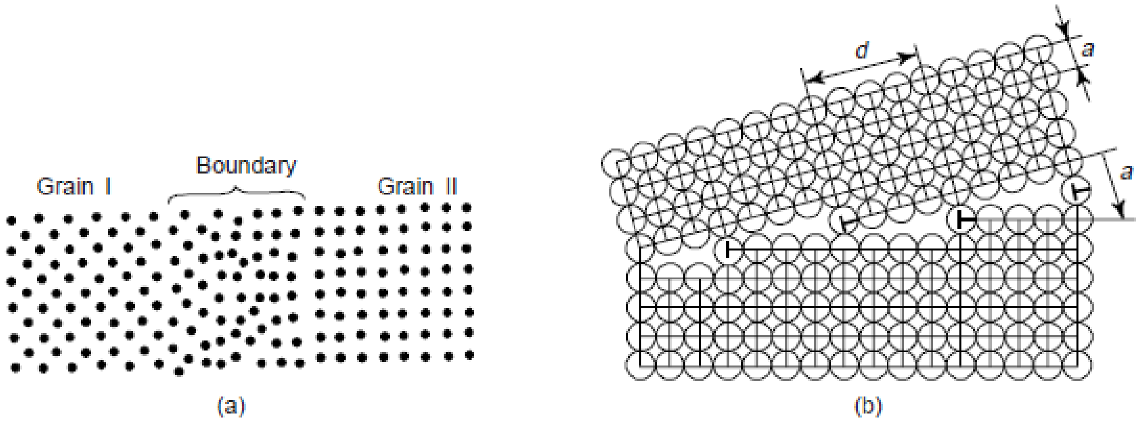


Figure: schemes of (a) High angle grain boundaries and (b) Low angle grain boundaries

TILT BOUNDARIES

- This is another type of surface defect called low-angle boundary as the orientation difference between two neighbouring crystals is less than 10°.
- This is why the disruption in the boundary is not so drastic as in the high angle boundary. This type of boundary is associated with relatively little energy and is composed of edge dislocations lying one above the other.
- In general, one can describe low-angle boundaries by suitable arrays of dislocation. The angle or tilt, $\theta = \frac{b}{D}$[Fig.], where b is the magnitude of Burgers vector and B is the average vertical distance between dislocations.

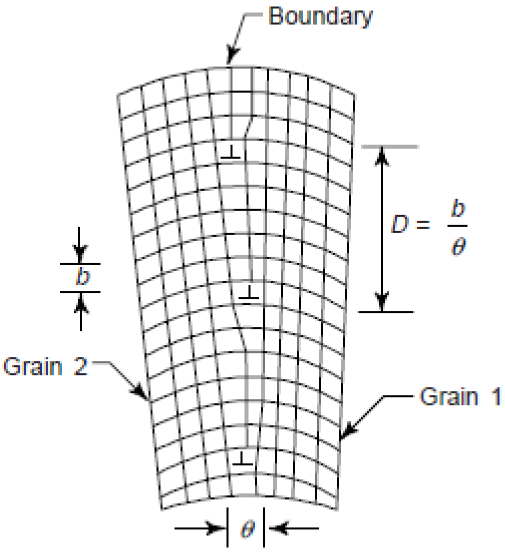


Fig: tilt boundaries

TWIN BOUNDARIES

- This is another planar surface imperfection. The atomic arrangement on one side of a twin boundary is a mirror reflection of the arrangement on the other side.
- Twinning may result during crystal growth or deformation of materials.
- Twin boundaries occur in pairs, such that the orientation change introduced by one boundary is restored by the other.
- The region between the pair of boundaries is termed as the *twinned region*.
- One can easily identify twin boundaries under an optical microscope.

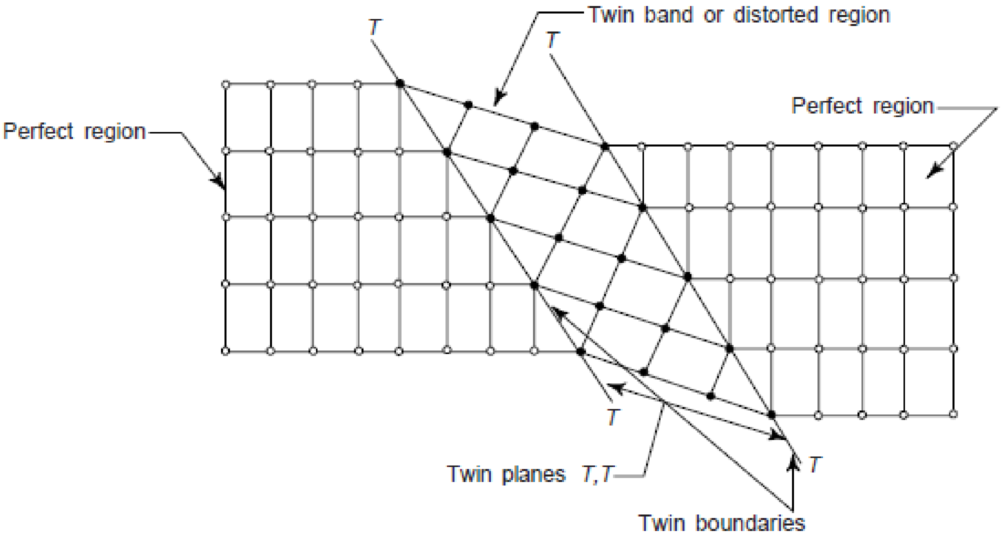


Figure: twin boundaries

- **Twin boundaries can be formed by two reasons**
  a) Permanent deformation (Twins which form during the process of recrystallization, i.e., in the process of mechanical working are known as mechanical twins)
  b) Whereas twins formed as a result of annealing after plastic deformation are known as annealing twins.

STACKING FAULT

This is a part of an atomic plane confined between dislocations and in which the regular order of alternation of atomic layers is disturbed.

This type of fault arises from the stacking of one atomic plane out of sequence on another while the lattice on either side of the fault is perfect.

For instance, in FCC lattice alloys, close packed atomic layers are normally in an alternation *ABC ABC AB* …. On passing through a stacking fault, their alternation may change, for instance, to *ABC BCA BC*….

The BCBC alternation is typical of an HCP lattice, and therefore the stacking fault in the case considered represents, as it were, a thin plate of an HCP lattice in the structure of an FCC lattice.

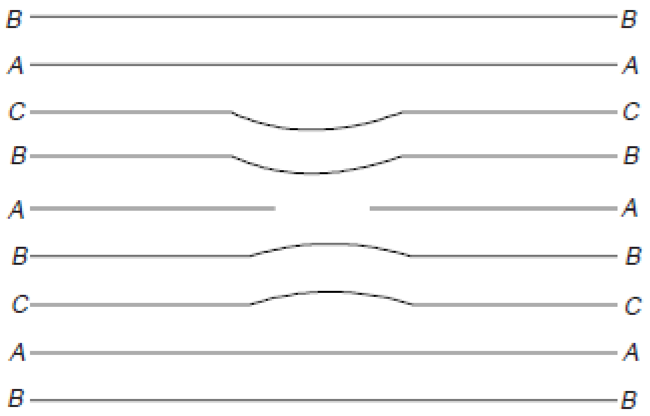


Figure: fault in stacking sequence in a FCC crystal

Figure shows the faults in the structure of an FCC crystal. Here the stacking sequence of an ideal FCC crystal is described as *ABC ABC* . . . and the stacking fault may change the sequence *ABC ACAB*.

Influence of Surface defects on mechanical and physical properties of materials

a) Grain boundaries influence mechanical properties and physical properties. The yield strength _y is associated with the grain size d by the relation.

$$\sigma_y = \sigma_0 + kd^{-\frac{1}{2}}$$

$$whre\ \sigma_0\ and\ k\ are\ constants\ for\ a\ given\ material.$$

b) With finer grain, a material has higher yield strength and toughness and is less susceptible to brittle failure.

c) The size of subgrains has a similar, though less strong, effect on mechanical properties.

d) Diffusion along boundaries of grains and subgrains occur many times quicker than in other directions in a crystal, especially on heating.

e) Interactions of defects, their displacements in crystals, and variations of their concentrations all these factors can change the properties of metals and are of high practical significance.

VOLUME DEFECTS

- Volume defects as name suggests are defects in 3-dimensions. These include pores, cracks, foreign inclusions and other phases.
- Volume imperfections, e.g. cracks may arise when there is only small electrostatic dissimilarity between the stacking sequences of close packed planes in metals.
- Moreover, when clusters of atoms are missing, a large vacancy or void is got which is also a volume imperfection.
- Foreign particle inclusions, large voids or noncrystalline regions which have the dimensions of the order of 0.20 nm are also termed volume imperfections.

- These defects are normally introduced during processing and fabrication steps.
- All these defects are capable of acting as stress raisers, and thus deleterious to parent metal’s mechanical behaviour.
- However, in some cases foreign particles are added purposefully to strengthen the parent material. The procedure is called dispersion hardening where foreign particles act as obstacles to movement of dislocations, which facilitates plastic deformation. The second-phase particles act in two distinct ways – particles are either may be cut by the dislocations or the particles resist cutting and dislocations are forced to bypass them. Strengthening due to ordered particles is responsible for the good high-temperature strength on many super-alloys.
- However, pores are detrimental because they reduce effective load bearing area and act as stress concentration sites.

EFFECT ON PROPERTY

- There are some properties of materials such as stiffness, density and electrical conductivity which are termed structure-insensitive, are not affected by the presence of defects in crystals while there are many properties of greatest technical importance such as mechanical strength, ductility, crystal growth, magnetic.

- Hysteresis, dielectric strength, condition in semiconductors, which are termed structure sensitive are greatly affected by the-relatively minor changes in crystal structure caused by defects or imperfections.

MODULE II

CONCEPT OF PLASTIC DEFORMATION OF METALS

For most metallic materials, elastic deformation persists only to strains of about 0.005. As the material is deformed beyond this point, Hooke's law ceases to be valid, i.e. stress is no longer proportional to strain, and permanent, nonrecoverable, or plastic deformation occurs.

Plastic deformation can occur under tensile, compressive and torsional stresses. The rate of plastic deformation is controlled by applied stress, strain rate and temperature control. The ability of metals to undergo plastic deformation is called ductility. In a plastic deformation of a metal, a change in shape occurs concurrently with changes in a number of metal properties; in particular, cold deforming increases the strength of a metal. The ductility of a metal ensures the structural strength of elements under a load and neutralizes the effect of stress concentrations. To perform processes such as rolling, forging, extrusion, spining, pressing, drawing, stamping, etc., plastic deformation is intensionally carried out.

From an atomic perspective / on a microscopic scale, plastic deformations are based on irreversible displacement of atoms through substantial distances from their equilibrium. Obviously, plastic deformation corresponds to the breaking of bonds with original atom neighbours and then reforming bonds with new neighbours a large number of atoms or molecules move relative to one another, upon removal of the stress they do not return to their original positions. Figure shows plastic deformation of a long range material.

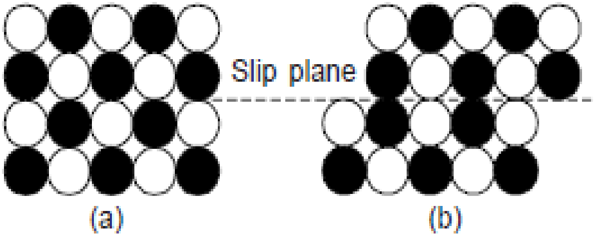


Fig.: plastic deformation, (a) prior to deformation, (b) after the passage of one unit of dislocation

The mechanism of this deformaton is different for crystalline and amorphous materials. For crystalline solids, deformation is accomplished by means of a process called slip, which involves the motion of dislocations. Plastic deformation in non-crystalline solids (as well as liquids) occurs by a viscous flow mechanism.

Mechanisms of plastic deformation in metals

- Plastic deformation, as explained in earlier section, involves motion of dislocations. There are two prominent mechanisms of plastic deformation, namely ***slip*** and ***twinning***.

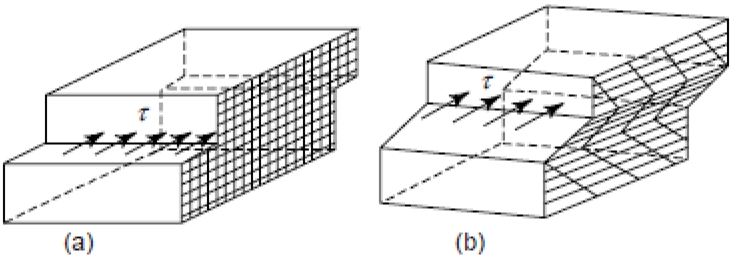


Figure: shemes of plastic deformation (a) by slip, (b) by twinning

- The process by which plastic deformation is produced by dislocation motion is termed slip.
- **On the microscopic level**, plastic deformation corresponds to the motion of dislocations in response to an externally applied shear stress.
- **Macroscopic plastic** deformation simply corresponds to permanent deformation that results from the movements of dislocations, or slip, in response to an applied shear stress.
- It involves sliding of blocks of crystal over one other along definite crystallographic planes, called ***slip planes***. In physical words it is analogous to a deck of cards when it is pushed from one end.
- Slip occurs when shear stress applied exceeds a critical value. During slip each atom usually moves same integral number of atomic distances along the slip plane producing a step, but the orientation of the crystal remains the same.
- Steps observable under microscope as straight lines are called ***slip lines***.
- The close packed directions have the smallest translation distance. Feasible combination of a slip plane together with a slip direction is considered as a slip system. The common slip systems are given in table-1.

Table 1: ***Slip systems for different crystal structures.***

Crystal	Occurrence	Slip planes	Slip directions
FCC		{111}	<110>
BCC	More common Less common	{110} {112}, {321}	<111>
HCP	More common Less common	Basal plane Prismatic & Pyramidal planes	Close packed directions
NaCl		{110}	<110>

Critical Resolved Shear Stress for Slip

The stress at which slip starts in a crystal depends on the relative orientation of the stress axis with respect to the slip plane and the slip direction. When a tensile stress σ is applied to a crystal (Figure), the shear stress τ_R resolved on a slip plane whose normal makes an angle $\boldsymbol{\phi}_1$ with the stress axis, along a slip direction inclined at an angle $\boldsymbol{\phi}_2$ to this axis, is given by

$$\tau_R = \sigma \cos\theta \cos\varphi$$

This is termed resolved shear stress (τ_R). The equation is known as Schmid's law and the term $\cos\theta \cos\varphi$ is called Schmid's sector. In general, $\theta + \varphi \neq 90^0$, since it need not be the case that the tensile axis, the slip plane normal, and the slip direction all lie in the same plane. The resolved shear stress τ_R should reach a critical value called the critical resolved shear stress τ_{cr} (CRSS) for plastic deformation to start. If the slip plane and slip direction are inclined at an angle 45° to the tensile axis, critical shear stress will be given by

$$\tau_{cr} = \sigma \cos 45^0 \cos 45^0 = \frac{\sigma}{2}$$

$$Stress = \left(\frac{force}{area}\right)_{1D}$$

$$\tau = \left(\frac{F\cos\alpha}{A / \cos\theta}\right).$$

$$\tau_{RSS} = \sigma \cos\theta \cos\varphi.$$

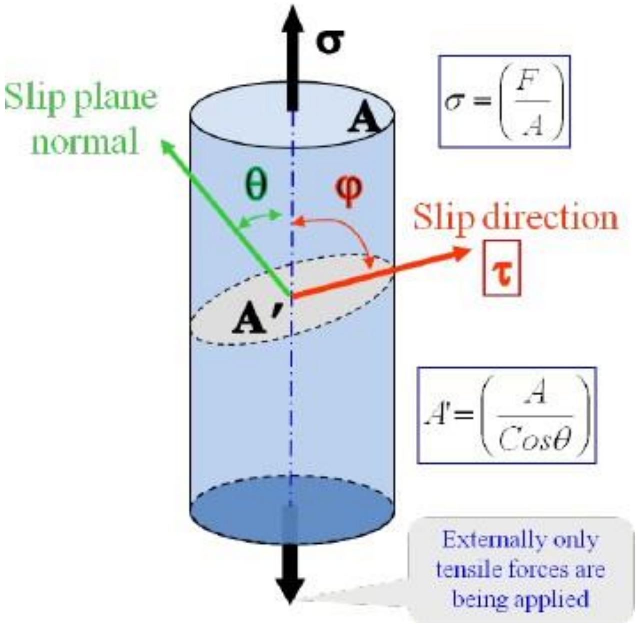


Fig: The resolved shear stress(τ) on a slip plane along a slip direction

Obviously, the critical resolved shear stress will always be less than half the tensile stress. The component of shear stress in the direction of slip is called "*critical shear stress*" and is a constant for each material, and depends upon the type of material. It is affected by the rate of deformation purity of the material, temperature etc. With the rise in temperature, the critical shear stress value decreases, and the thermal mobility of material increases.

- τ_{RSS} is maximum (P/2A) when $\Phi = \lambda = 45^0$

- If the tension axis is normal to slip plane i.e. λ=90^0 or if it is parallel to the slip plane i.e. Φ=90^0 then τ_{RSS}=0 and slip will not occur as per Schmid's law.

- Schmid's law : slip is initiated when $\tau_{RSS} \geq \tau_{CRSS}$

τ_{CRSS} is a material parameter, which is determined from experiments.

- Yield strength of a single crystal $\sigma_y = \dfrac{\tau_{CRSS}}{\cos\theta \cos\varphi}$

Factors affecting critical shear stress

(i) The critical stress value is less for pure metals, i.e. purity of metals reduces the critical stress.
(ii) Surface effects, e.g. surface films greatly enhance the critical shear stress.
(iii) The thermal mobility increases with rise in temperature but critical shear stress decreases.
(iv) Rate of deformation and the extent of initial deformation also help in raising the critical shear stress.
(v) Deformation and slip in *polycrystalline materials* is somewhat more complex. Because of the random crystallographic orientations of the numerous grains, the direction of the slip varies from one grain to another.

Problem

Consider a single crystal of BCC iron oriented such that a tensile stress is applied along a [010] direction.

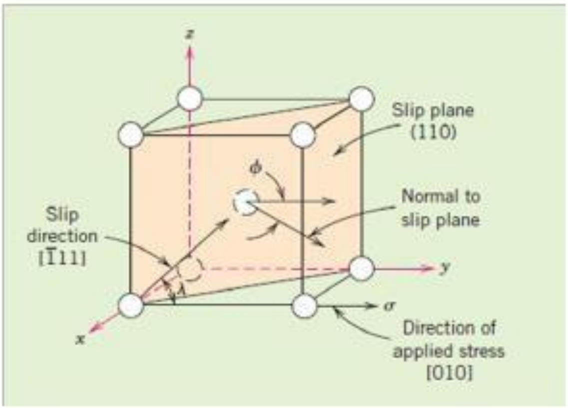
(a) Compute the resolved shear stress along a (110) plane and in a [111] direction when a tensile stress of 52 MPa (7500 psi) is applied

(b) If slip occurs on a (110) plane and in a $[\bar{1}\,1\,1]$ direction, and the critical resolved shear stress is 30 MPa (4350 psi), calculate the magnitude of the applied tensile stress necessary to initiate yielding.

Solution

Determine the value of the angle between the normal to the (110) slip plane (i.e., the [110] direction) and the [010] direction using [u1v1w1] = [110], [$u_2v_2w_2$] = [010] and the following equation

$$\theta = \cos^{-1}\left(\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}}\right)$$



$$\Phi = \cos^{-1}\left(\frac{(1)(0) + (1)(0) + (0)(0)}{\sqrt{[(1)^2 + (1)^2 + (0)^2][(0)^2 + (1)^2 + (0)^2]}}\right)$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45^0$$

Similarly determine the value of λ, the angle between [$\bar{1}$ 1 1] and [010] directions as follows:

$$\lambda = \cos^{-1}\left(\frac{(-1)(0) + (1)(1) + (1)(0)}{\sqrt{[(-1)^2 + (1)^2 + (1)^2][(0)^2 + (1)^2 + (0)^2]}}\right)$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7^0$$

Then calculate the value of τ RSS using the following expression

$$\tau_{RSS} = \sigma \cos\Phi \cos\lambda.$$

$$= (152MPa) \cos 45 \cos 54.7$$

$$= 21.3MPa$$

$$= 13060psi$$

Yield strength σ_y

$$\sigma_y = \frac{\tau_{CRSS}}{\cos\theta \cos\varphi}$$

$$\sigma_y = \frac{30MPa}{\cos 45 \cos 54.7}$$

$$= 73.4MPa$$

Dislocation theory

Edge and screw are the two fundamental dislocation types. In an edge dislocation, localized lattice distortion exists along the end of an extra half-plane of atoms, which also defines the dislocation line. A screw dislocation may be thought of as resulting from shear distortion; its dislocation line passes through the center of a spiral, atomic plane ramp. Many dislocations in crystalline materials have both edge and screw components; these are mixed dislocations Plastic deformation corresponds to the motion of large numbers of dislocations. An edge dislocation moves in response to a shear stress applied in a direction perpendicular to its line.

❖ Mechanics of dislocation motion(**On the microscopic level)**

The mechanics of dislocation motion are represented in Figure 1

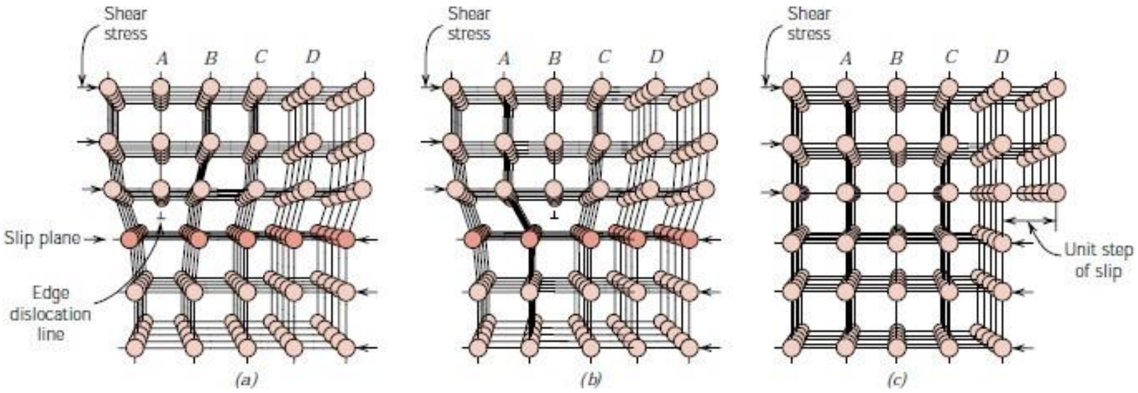


Figure 1: Atomic rearrangements that accompany the motion of an edge dislocation as it moves in response to an applied shear stress. (a) The extra halfplane of atoms is labeled A. (b) The dislocation moves one atomic distance to the right as A links up to the lower portion of plane B; in the process, the upper portion of B becomes the extra half-plane. (c) A step forms on the surface of the crystal as the extra half-plane exits.

- Let the initial extra half-plane of atoms be plane A. When the shear stress is applied as indicated **(Figure 1a),** plane A is forced to the right; this in turn pushes the top halves of planes B, C, D, and so on, in the same direction.
- If the applied shear stress is of sufficient magnitude, the interatomic bonds of plane B are severed along the shear plane, and the upper half of plane B becomes the extra half-plane as plane A links up with the bottom half of plane B **(Figure 1b).**
- This process is subsequently repeated for the other planes, such that the extra half-plane, by discrete steps, moves from left to right by successive and repeated breaking of bonds and shifting by interatomic distances of upper half-planes.
- Before and after the movement of a dislocation through some particular region of the crystal, the atomic arrangement is ordered and perfect; it is only during the passage of the extra half-plane that the lattice structure is disrupted.

- Ultimately this extra half-plane may emerge from the right surface of the crystal, forming an edge that is one atomic distance wide; this is **shown in Figure 1c**.
- The process by which plastic deformation is produced by dislocation motion is termed slip; the crystallographic plane along which the dislocation line traverses is the slip plane, as indicated in **Figure 1**.

❖ Macroscopic plastic deformation

- Macroscopic plastic deformation simply corresponds to permanent deformation that results from the movement of dislocations, or slip, in response to an applied shear stress, as represented in **Figure 2a**.
- The motion of a screw dislocation in response to the applied shear stress is shown in **Figure 2b**; the direction of movement is perpendicular to the stress direction. For an edge, motion is parallel to the shear stress.

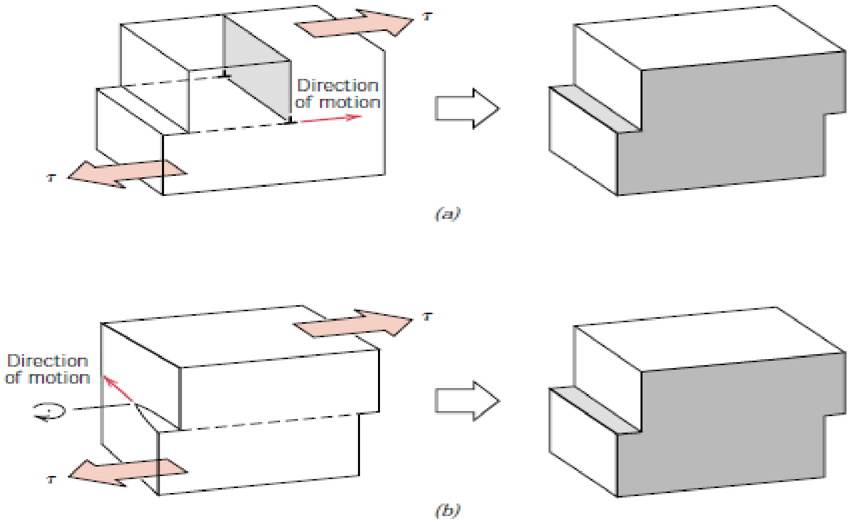


Figure 2: The formation of a step on the surface of a crystal by the motion of (a) an edge dislocation and (b) a screw dislocation. Note that for an edge, the dislocation line moves in the direction of the applied shear stress; for a screw, the dislocation line motion is perpendicular to the stress direction

- However, the net plastic deformation for the motion of both dislocation types is the same. (See Figure .2)
- The direction of motion of the mixed dislocation line is neither perpendicular nor parallel to the applied stress, but lies somewhere in between.

Representation of the analogy between caterpillar and dislocation motion.

- Dislocation motion is analogous to the mode of locomotion employed by a caterpillar **(Figure 3).** The caterpillar forms a hump near its posterior end by pulling in its last pair of legs a unit leg distance.

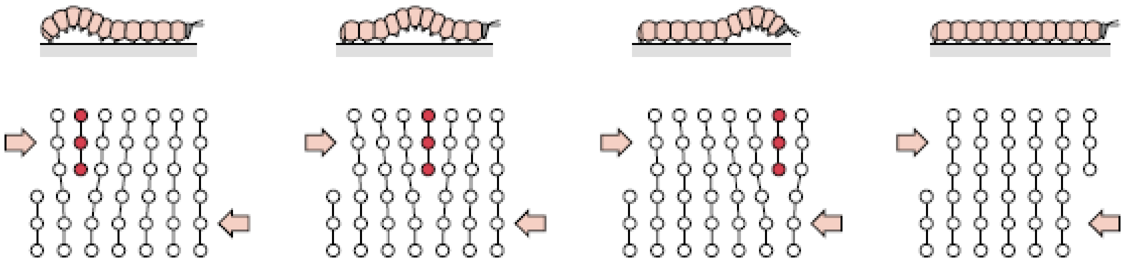


FIGURE 3: Representation of the analogy between caterpillar and dislocation motion.

- The hump is propelled forward by repeated lifting and shifting of leg pairs. When the hump reaches the anterior end, the entire caterpillar has moved forward by the leg separation distance. The caterpillar hump and its motion correspond to the extra half-plane of atoms in the dislocation model of plastic deformation.

CHARACTERISTICS OF DISLOCATIONS

1. All metals and alloys contain some dislocations that were introduced during solidification, during plastic deformation, and as a consequence of thermal stresses that result from rapid cooling.
2. The number of dislocations, or dislocation density in a material, is expressed as the total dislocation length per unit volume or, equivalently, the numbe of dislocations that intersect a unit area of a random section.
3. The units of dislocations are per square millimeter.
4. For heavily deformed metals the density may be as high as 10^9 to 10^{10}/mm^2.
5. Heat treating a deformed metal specimen can diminish the density to on the order of 10^5 to 10^6/ mm^2. A typical dislocation density for ceramic materials is between 10^2 and 10^4 /mm^2. When metals are plastically deformed, some fraction of the deformation energy (~5%) is retained internally and the remainder is dissipated as heat.
6. The major portion of this stored energy is as strained energy associated with dislocations. During plastic deformation, the number of dislocations increases dramatically.

DEFORMATION BY SLIP AND TWIN

- Plastic deformation, as explained in earlier section, involves motion of dislocations. There are two prominent mechanisms of plastic deformation, namely ***slip*** and ***twinning***.

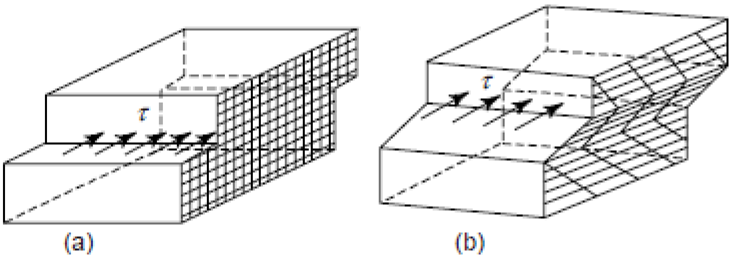


Figure: shemes of plastic deformation (a) by slip, (b) by twinning

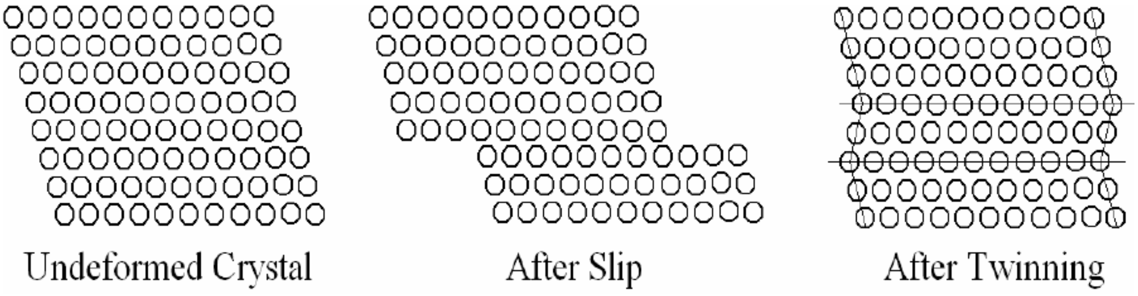


Figure-: ***Schematic presentation of different plastic deformation mechanism.***

DEFORMATION BY SLIP

- The process by which plastic deformation is produced by dislocation motion is termed slip.
- **On the microscopic level**, plastic deformation corresponds to the motion of dislocations in response to an externally applied shear stress.
- **Macroscopic plastic** deformation simply corresponds to permanent deformation that results from the movements of dislocations, or slip, in response to an applied shear stress.
- It involves sliding of blocks of crystal over one other along definite crystallographic planes, called ***slip planes***. In physical words it is analogous to a deck of cards when it is pushed from one end.
- Slip occurs when shear stress applied exceeds a critical value. During slip each atom usually moves same integral number of atomic distances along the slip plane producing a step, but the orientation of the crystal remains the same.
- Steps observable under microscope as straight lines are called ***slip lines***.
- The close packed directions have the smallest translation distance. Feasible combination of a slip plane together with a slip direction is considered as a slip system. The common slip systems are given in table-1.
-

Table 1: ***Slip systems for different crystal structures***

Crystal	Occurrence	Slip planes	Slip directions
FCC		{111}	<110>
BCC	More common Less common	{110} {112}, {321}	<111>

HCP	More common Less common	Basal plane Prismatic & Pyramidal planes	Close packed directions
NaCl		{110}	<110>

DEFORMATION BY TWIN

- The second important mechanism of plastic deformation is twinning.
- It results when a portion of crystal takes up an orientation that is related to the orientation of the rest of the untwined lattice in a definite, symmetrical way.
- The twinned portion of the crystal is a mirror image of the parent crystal.
- The plane of symmetry is called twinning plane.
- Each atom in the twinned region moves by a homogeneous shear a distance proportional to its distance from the twin plane.
- The lattice strains involved in twinning are small, usually in order of fraction of inter-atomic distance, thus resulting in very small gross plastic deformation.
- The important role of twinning in plastic deformation is that it causes changes in plane orientation so that further slip can occur.
- If the surface is polished, the twin would be still visible after etching because it possesses a different orientation from the untwined region.
- This is in contrast with slip, where slip lines can be removed by polishing the specimen.

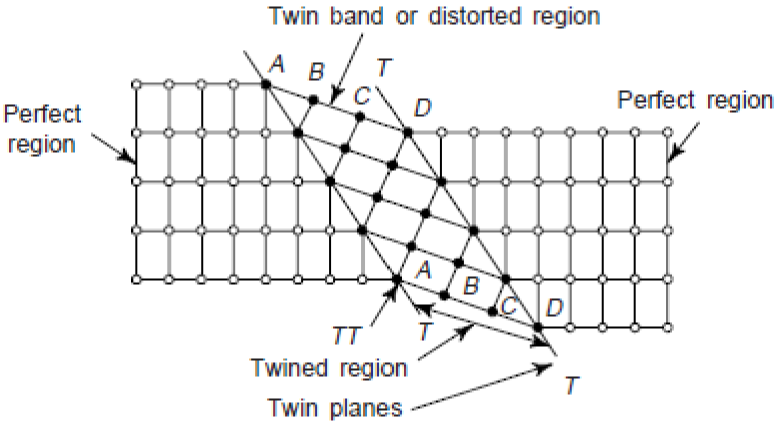


Fig.: deformation in a crystal by twinning.

- Twinning also occurs in a definite direction on a specific plane for each crystal structure. However, it is not known if there exists resolved shear stress for twinning.
- Twinning generally occurs when slip is restricted, because the stress necessary for twinning is usually higher than that for slip.
- Thus, some HCP metals with limited number of slip systems may preferably twin. Also, BCC metals twin at low temperatures because slip is difficult.

- Of course, twinning and slip may occur sequentially or even concurrently in some cases.

Twinning systems for some metals are given in table 2 ..

Table .2: twin planes and directions

Crystal	Example	Twin planes	Twin directions
FCC	Ag,Au,Cu	(111)	<110>
BCC	$\alpha - Fe$,Ta	(112)	<111>
HCP	Zn,Cd,Mg,Ti	1012	<1011>

COMPARISON BETWEEN SLIP AND TWINNING

A comparison between slip and twinning is presented in Table 3

	Slip	**Twinning**
(i) Orientation	The orientation of the crystal above and below the slip plane remains same after deformation.	. Twin causes orientation difference in the crystal across the twin plane
(ii) Movement during the process	Slip usually occurs in discrete multiples of atomic spacing.	. The movement of atoms are much smaller in comparison to atomic spacing.
(iii) Deformation planes and directions	Slip occurs on relatively wide planes. Usually, the slip plane is the plane of greatest atomic density, and the slip direction is the closest packed direction within the slip plane.	In twinning, every atomic plane is involved in the deformation in the twinned region of the crystal. For each crystal twin occurs in a definite direction on a specific crystallographic plane
(iv)Time	Slip takes several million seconds to occur, i.e. there is a delay time of several million seconds prior to forming of one slip band	Twins can form in a few microseconds only
(v) Stress	Slip takes place when the shearing stress on the slip plane in the slip direction reaches a threshold value called the *critical resolved shear stress.*	Resolved critical shear stress in twinning almost has no role

A comparison between slip and twinning is presented in Table 4

	during/in slip	**during/in twinning**
Crystal orientation	Same above and below the slip plane	Differ across the twin plane
Size (in terms of inter-atomic distance)	Multiples	Fractions
Occurs on	Widely spread planes	Every plane of region involved
Time required	Milli seconds	Micro seconds
Occurrence	On many slip systems simultaneously	On a particular plane for each crystal

DEFORMATION OF POLYCRYSTALLINE METALS

For polycrystalline metals, because of the random crystallographic orientations of the numerous grains, the direction of slip varies from one grain to another. For each, dislocation motion occurs along the slip system that has the most favourable orientation (i.e., the highest shear stress).

Why greater stresses are requires for deformation of polycrystalline metals?

In case of polycrystalline metals, greater stresses are required to initiate slip and the attendant yielding since they are stronger than their single-crystal equivalents. Even though a single grain may be favourably oriented with the applied stress for slip, it cannot deform untill the adjacent and less favourably oriented grains are capable of slip also, this requires a higher applied stress level

The characteristics of polycrystalline metals are as follows:

(i) (When polycrystalline metals are loaded, various grains have random orientation for slip.

(ii) Greater stress is required due to random orientations and therefore, the resolved shear stress is not constant but varies with grain orientation.

(iii) Under load condition, all crystals of a polycrystalline metal are perfectly elastic. There are a number of slip planes within a crystal. Considerable structural changes result in deformation.

(iv) Contrary to single crystals, polycrystalline metals show elastic after effects. Application of this effect is in work hardening.

(v) A significant amount of permanent deformation and an appreciable amount of yielding can be obtained in the polycrystalline crystals of metals after elastic deformation.

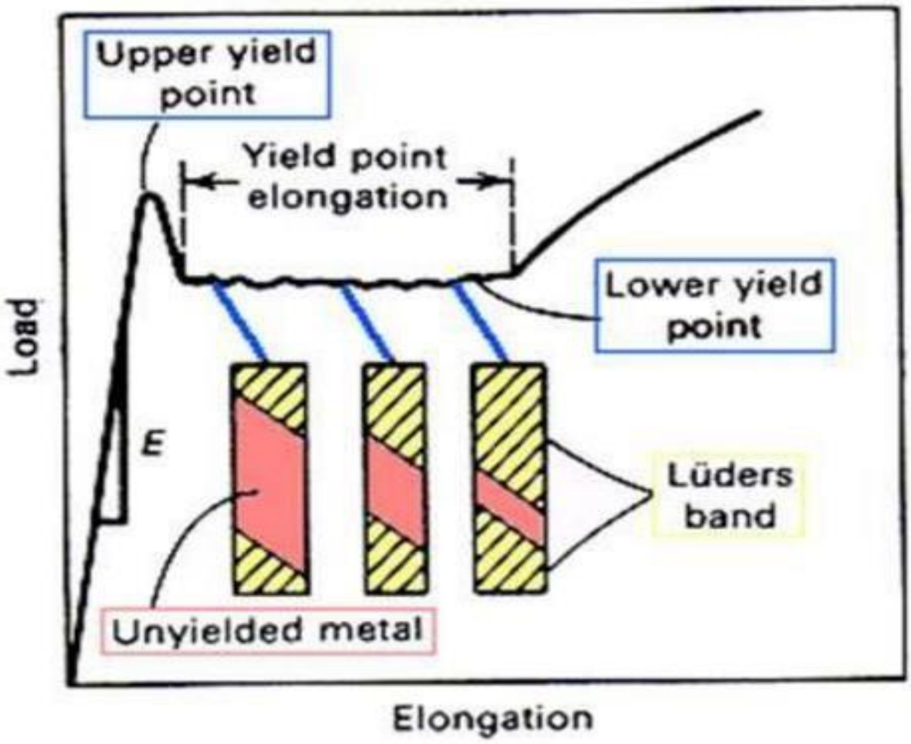
YIELD POINT PHENOMENON AND RELATED EFFECTS

A yield point phenomenon is not shown by every material. It occurs especially in mild steel or in low carbon steel. In a flow curve or stress-strain diagram the transition from elastic region to plastic region is witnessed by a sudden drop in stress (upper and lower yield point) followed by constant stress is known as stretched stress or popularly known as yield point phenomena.

Reason behind decrease in stress

Now to know the reason behind decrease in stress we need to go atomic level and consider the presence of edge dislocation the carbon atom's size is very large comparison with the interstices presence in the steel. It will always want to reduce the compression stress which is acting on it due to its presence inside the interstices. So it will move and will occupy the other half of the plane present in the edge dislocation as the space is more in this case. Now when stress is applied on the body some amount of extra stress (upper yield stress) is required in order to remove the carbon atoms present on the dislocation. Once they are removed, the material come backs to its original position and it required normal amount of stress to deform. For this reason we encounter a sudden decrease in stress.

- Metals particularly low carbon steel, show a localised heterogeneous transition from elastic to plastic deformation →yeild point elongation.



- The load after the upper yield point suddenly drop to approximately constant value (lower yield point) and then rises with further strain.
- The elongation which occurs at constant load is called as the yield point elongations which are heterogeneous deformation.
- L$\ddot{u}$der bands or stretcher strains are formed at approximately 450 to the tensile axis during yield point elongation and propagate over the specimen.

Note: the yield point phenomenon has also been observed in other metals such as Fe,Ti,Mo,Cd,Zn,Al alloys.

Cottrell atmosphere

In materials science, the concept of the **Cottrell atmosphere** was introduced by A. H. Cottrell and B. A. Bilby in 1949 to explain how dislocations are pinned in some metals by boron, carbon, or nitrogen interstitials.

Cottrell atmospheres occur in body-centered cubic (BCC) and face-centered cubic (FCC) materials, such as iron or nickel, with small impurity atoms, such as boron, carbon,or nitrogen.[As these interstitial atoms distort the lattice slightly, there will be an associated residual stress field surrounding the interstitial. This stress field can be relaxed by the interstitial atom diffusing towards a dislocation, which contains a small gap at its core (as it is a more open structure), see Figure 1. Once the atom has diffused into the dislocation core the atom will stay. Typically only one interstitial atom is required per lattice plane of the dislocation.

Once a dislocation has become pinned, a large force is required to unpin the dislocation prior the yielding, thus at room temperature, the dislocation will not get unpinned. This produces an observed upper yield point in a stress–strain graph. Beyond the upper yield point, the pinned dislocation will act as Frank–Read source to generate new dislocations that are not pinned. These dislocations are free to move in the crystal, which results in a subsequent lower yield point, and the material will deform in a more plastic manner.

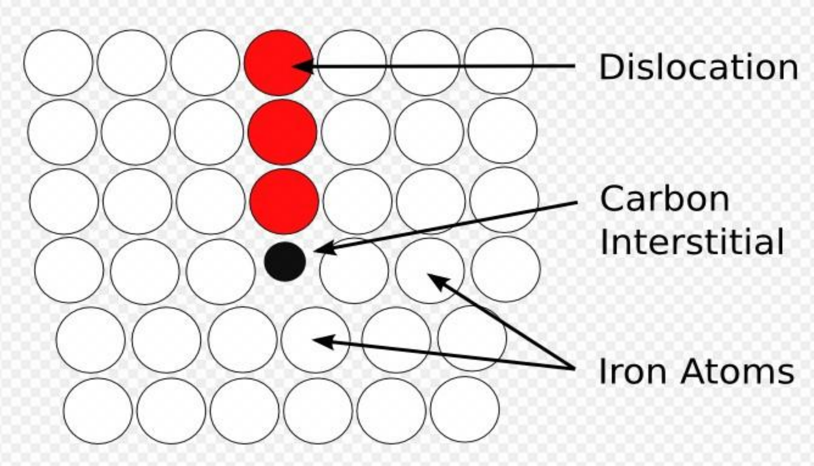


Figure: carbon interstitial diffused in dislocation

RELATED EFFECTS OF YIELD POINT PHENOMENON

1. Lüders bands and stretcher strains

- These represents the markings on the surface of a tensile test sample, formed at the points of stress concentration like fillets. These bands are usually at 45° to the tensile axis when several bands are formed, the stress-strain curve is irregular during yield point elongation. Lüders bands distinguish those portions of the sample that have yielded form those which have not. These bands are formed because of *jogs*.
- Arrival of the upper yield point is indicated by the formation of these. Lüder bands can be observed at a number of positions on the sample, e.g. at both the ends on the gauge length. When Lüder bands propagate and cover the whole length, the flow will increase with strain. The yield point elongation ends here.
- In drawing and stamping operations,L üders bands produce rough appearance on the surface of the metal sheet and have to be avoided on the finished products. In order to control this uneven yielding effect, one will have to overstrain the sheets prior to pressing operations, by means of temper roll pass. This helps to eliminate the yield point phenomenon.

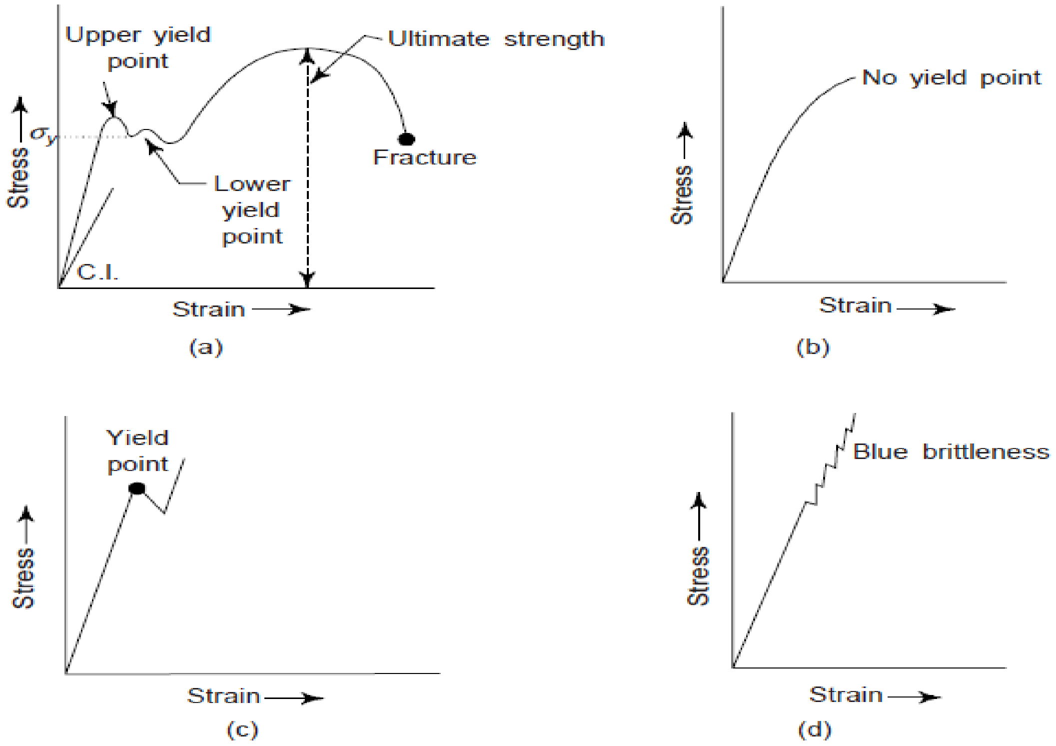


Figure: Stress-strain behaviour founds for some steels demonstrating the yield point phenomenon and related effects. (a) Anchored atmosphere (first test) (b) free atmosphere (unloaded) and (c) strain aging (anchored atmosphere)

2. Strain Ageing

- This is associated with yield point phenomenon and refers to changes in the properties of an over strained alloy with time.
- In order to remove the yield point, if the test sample which has been overstrained, is allowed to rest or age after plastic deformation, the yield point returns with higher stress during the retest (**Fig. c**).
- However, if the specimen is unloaded and rested without ageing then the yield point will occur (**Fig. b)** due to weak dislocation effects from the atmosphere of carbon and nitrogen atoms. Carbon and nitrogen atoms form new interstitials and anchor the dislocations.
    - In strain ageing of iron, nitrogen plays a more important role than carbon because nitrogen has higher solubility and diffuses easily.
    - Strain ageing or strain-age-hardening is accompanied by hardening due to increase in stress value.
    - When the sample, after test of **Fig. (a)** is unloaded and allowed to rest or age for some time and then retested, when the yield point as in **Fig. (c),** reappears with a higher stress value. The said phenomenon is observed. Commercial iron and steel show this behaviour.
    - This has an important effect on the study of fatigue and creep behaviour of some metals.

3. Blue Brittleness

- When the temperature range of the test is raised; the yield point becomes less pronounced and blue brittleness effect is produced.
- For plain carbon steel the temperature range is 200^0 to 370°C. However, this effect appears at about 160^0 to 300°C **(Fig.d).**
- We can see that the section of the stress vs. Strain diagram shows a steeper curve with rapid formation of successive yield points due to **quick diffusion and dislocation effects.**

4. Orange Peel Effects

- During stretching, these markings appear on metals. This is observed in coarse grained metals at low-temperature-forming operations and it is also a surface roughening phenomenon. This effect is eliminated by grain refinement.
- Interstitial atoms (C, O, H, and N) can contribute largely to the strengthening effect if they accumulate on dislocations and lock these, thus forming segregations or *cottrell atmospheres*.

  - Such atmospheres anchor the dislocations and higher stresses are required to free a dislocation. However, the value of this stress should be corresponding to upper yield points.
  - We may note that free dislocations lower the yield point. Cottrell atmospheres give yield point and blue brittleness as shown by stress-strain diagrams.

COLD WORKING

Cold working is deformation carried out under conditions where recovery processes are not effective.

Structural changes during cold working of polycrystalline metals and alloys

- **Changes in shape and size of grains**: The equiaxed grains on deformation are elongated in the direction of acting force i.e. stretched in the direction of main tensile deformation stress–say, in the direction of rolling or wire drawing.
- **Changes in orientation of grains**: Preferred orientation or texture of is the state of severely cold worked metal in which certain crystallographic planes of the grains orient themselves in a preferred manner with respect to the direction of the stress (or maximum strain).
- **Changes in internal structure of grains**: during cold working around 15% of the work of the deformation gets absorbed in the material (rest is lost as heat). This stored energy is the form of energy of crystal defects. Plastic deformation increases the concentration of point defects. With increase of cold working, the number of stacking-faults increases, thus density of extended dislocations increases. The number of kinks, jogs, dipoles, prismatic loops increase. The most important internal change of structure is increase in density of dislocation from $10^6 – 10^8$ cm^{-2} in annealed state to $10^{10} – 10^{12}$ by moderate cold working.

PREFERRED ORIENTAION

Isotropic.

- Usually, ordinary alloys show no effect of direction on their elastic properties.
- Amorphous solids, liquids and gases are isotropic, i.e., their properties are same in every plane and every direction.
- A poly-crystalline material is mostly isotropic because of random orientation character

Anisotropic

- Physical and mechanical properties of a material are determined by the arrangement of atoms, these crystals are anisotropic. Their properties change according to the plane or direction along which they are measured.

- The spacing of atoms in crystalline material, differ on different planes and different directions along these planes.

Preferred orientation.

- Alloys are made up of millions of very tiny crystals.
- If the crystals are randomly oriented, the elastic properties will be same in all directions.
- It is possible for crystals to assume identical orientation i.e., try to align themselves in a common axial direction by casting, rolling or heat treatment processes. Such a direction is known as preferred orientation.

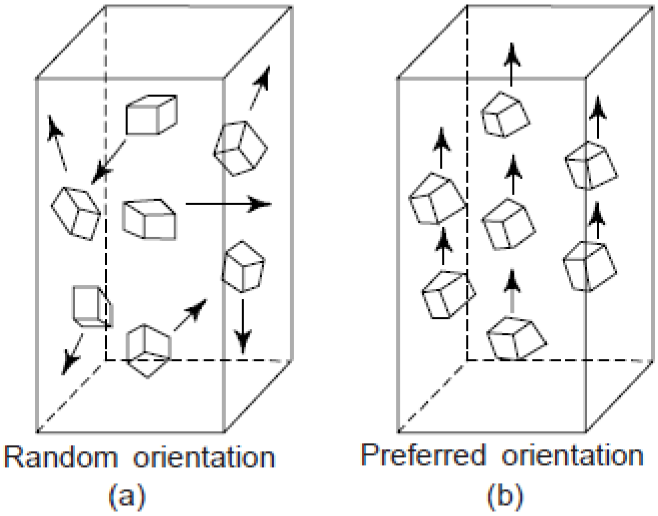


Figure: Preferred orientation. Grains are represented by cube (a) random orientation and (b) preferred orientation

Development of preferred orientation

- One can develop the preferred orientation by mechanical working.
- **During plastic deformation the slip planes of all crystals are caused to rotate into more favourable directions with respect to the direction of critical shear stress.**
- X-ray methods are used to determine or detect them.
- Heat treatment cannot eliminate preferred orientation, once it has been developed by mechanical working.

Preferred orientation finds following engineering applications:

1. Directional properties, e.g. strength and magnetic permeability are quite useful in crystals of some metals, e.g. silicon steels, and quite undesirable in many others.
2. The formation of a strong preferred orientation can cause anisotropy in mechanical properties. This means that during fabrication, different mechanical properties can be obtained in different directions.
3. The manufacture of transfer cores of iron sheets helps in orienting the core iron in the direction of the magnetic field. This helps in saving a large amount of electrical energy dissipated as heat in the iron core by eddy currents.

4. Preferred orientation causes the loss of ductility in semi finished products likes wires and sheets. In cold rolled sheets, the preferred orientation is developed which results in lower tensile strength, lower yield strength and lower ductility across the grain, i.e. transverse to the rolling direction, than parallel to it. If one wants to have more strength, ductility, etc., in transverse direction too, then he has to break up preferred orientation. One can achieve this by cross-rolling the sheets (for deep drawing purposes), i.e. rolling alternatively in two directions at right angles to each other.
5. Preferred orientation has been found useful in cast metals having columnar growth.

ANNEALING OF COLD WORKED MATERIALS

- Annealing is an important industrial process to relieve the stresses from cold working.
- During cold working grain shape changes, while material strain hardens because of increase in dislocation density. Between 1-10% of the energy of plastic deformation is stored in material in the form of strain energy associated with point defects and dislocations.
- On annealing i.e. on heating the deformed material to higher temperatures and holding, material tends to lose the extra strain energy and revert to the original condition (restore the optimum physical properties, i.e.: ductility or electrical conductivity with a simultaneous decrease in hardness and strength) before deformation by the processes of recovery and recrystallization which may be followed by grain growth.

RECOVERY

- This is the first stage of restoration after cold working where physical properties of the cold-worked material are restored without any observable change in microstructure.
- This term implies **all changes in the fine structure and properties of a metal** which involve **no changes in the microstructure** of the deformed metal
- During recovery, some of the stored internal strain energy is relieved by virtue of dislocation motion (in the absence of an externally applied stress).
- Also, physical properties such as electrical and thermal conductivities and the like are recovered to their precold-worked states

Recovery is further subdivided into two stages: ***strain-relief crystallization*** and ***polygonization*.**

Strain-relief crystallization involves

1. Diminishes the number of point-defects, mainly vacancies
2. Includes dislocation climb

3. Involves a release of residual stresses due to Redistribution of dislocations
4. Decreases the electric resistance and increases the density of a metal

Polygonization involves

1. The formation of new low angle boundaries within each grain.
2. Boundaries can form by slip and climb of dislocations; as a result, a grain is divided into **subgrains, or polygons which are free of dislocations**

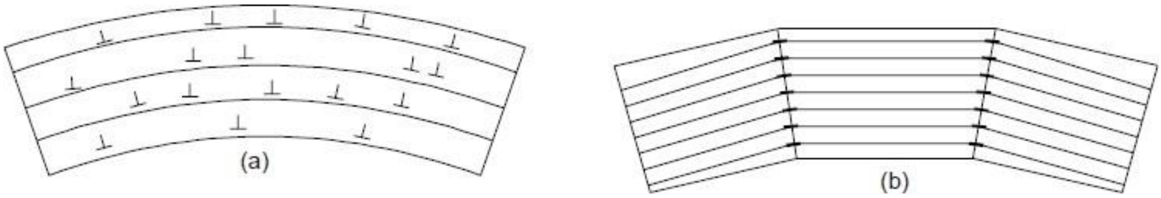


Figure: scheme of Polygonization (a) strain hardened metal prior to polygonization, (b) after polygonzation

RECRYSTALLIZATION

- Recrystallization is the formation of a new set of strain-free and equiaxed grains (i.e., having approximately equal dimensions in all directions) that have low dislocation densities and are characteristic of the precold-worked condition.
- It is nucleation and growth of new strain-free crystals from the cold worked metal. Kinetics of recrystallization resembles a phase transformation.
- **Two distinct nucleation mechanisms have been identified**.
    a. Strain-induced boundary migration, where a strain-free nucleus is formed when one of the existing grain boundaries into its neighbour, leaving a strain-free recrystallized region.
    b. New grains are formed in the regions of sharp lattice curvature through subgrain growth. This seems to predominate at high strains, with nuclei appearing at grain boundaries or at inclusions or second phase particles.

Recrystallization temperature

- It starts on heating to temperatures in the range of 0.3-0.5 Tm, which is above the recovery stage. There is no crystal structure change during recrystallization. This process is characterized by recrystallization temperature.
- Recrystallization temperature which is defined as the temperature at which 50% of material recrystallizes in one hour time.

- It can be defined as the temperature at which a given alloy in a highly cold-worked state completely recrystallizes in 1h.

- As recrystallization behaviour is influenced by temperature. Hence recrystallization temperature is not a fixed temperature in the sense of a melting temperature.

- Recrystallization temperature is strongly dependent on the purity of a material. Pure materials may recrystallizes around 0.3 T_m, while impure materials may recrystallizes around 0.5-0.7 T_m.

Factors influence recrystallization behaviour are

a. Amount of deformation
b. temperature
c. time
d. initial grain size
e. composition
f. amount of recovery or polygonisation
g. Method of deformation.

The laws of recrystallization are:

a. A minimum amount of deformation is needed to cause recrystallization.
b. Smaller the degree of deformation, higher the temperature required to cause recrystallization.
c. Recrystallization rate increases exponentially with temperature. Doubling the annealing time is approximately equivalent to increasing the annealing temperature 10°C.
d. Greater degree of deformation and lower annealing temperature, the smaller the recrystallized grains.
e. Larger the original grain size, the greater the amount of cold-work required to produce equivalent recrystallization temperature.
f. The recrystallization temperature decreases with increasing impurity of motel. Alloying always raise recrystallization temperature.
g. The amount of deformation required to produce equivalent recrystallization behaviour increases with increased temperature of working.

During this stage of annealing **impurity atoms tend to segregate at grain boundaries, and retard their motion and obstruct the processes of nucleation and growth. This *solute drag effect*** can be used to retain cold worked strength at higher service temperatures. Presence of second phase particles causes slowing down of recrystallization – ***pinning action of the particles.***

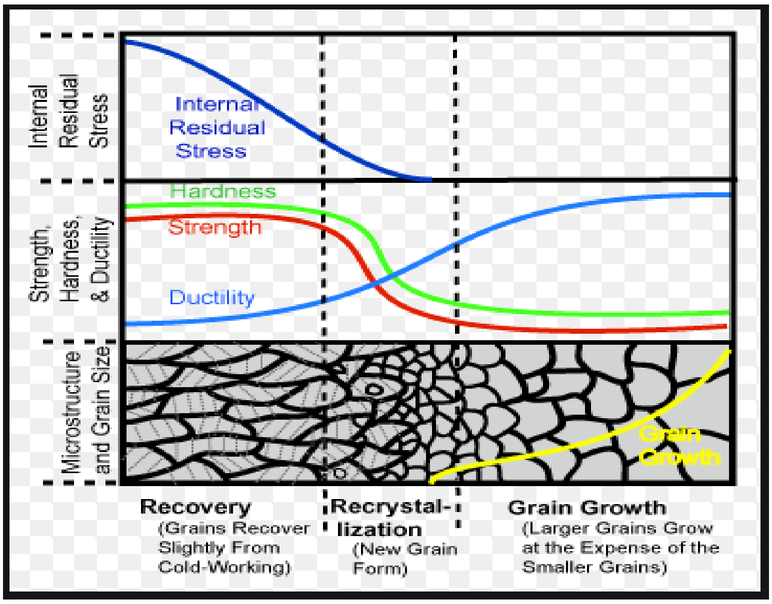


Figure: comparison of mechanical properties during Recovery, Recrystallization and Grain growth

GRAIN GROWTH

This stage follows complete crystallization if the material is left at elevated temperatures. However, grain growth does not need to be preceded by recovery and recrystallization; it may occur in all polycrystalline materials. During this stage newly formed strain-free grains tend to grow in size. This grain growth occurs by the migration of grain boundaries. Driving force for this process is reduction in grain boundary energy i.e. decreasing in free energy of the material. As the grains grow larger, the curvature of the boundaries becomes less. This results in a tendency for larger grains to grow at the expense of smaller grains. In practical applications, grain growth is not desirable. Incorporation of impurity atoms and insoluble second phase particles are effective in retarding grain growth.

Because the driving force for grain growth is lower than the driving force for recrystallization, grain growth occurs slowly at a temperature where recrystallization occurs at substantially high speeds. However, grain growth is strongly temperature dependent.

Grain growth occurs by the passage of atoms from one grain to a neighbouring grain through the boundary; in this process some grains diminish in size and even disappear, while others become large and devour adjacent grains. Grain growth is accelerated with an increase of temperature. The higher the temperature of heating, the larger the recrystallized grains.

For many polycrystalline materials, the grain diameter d varies with time t according to the relationship

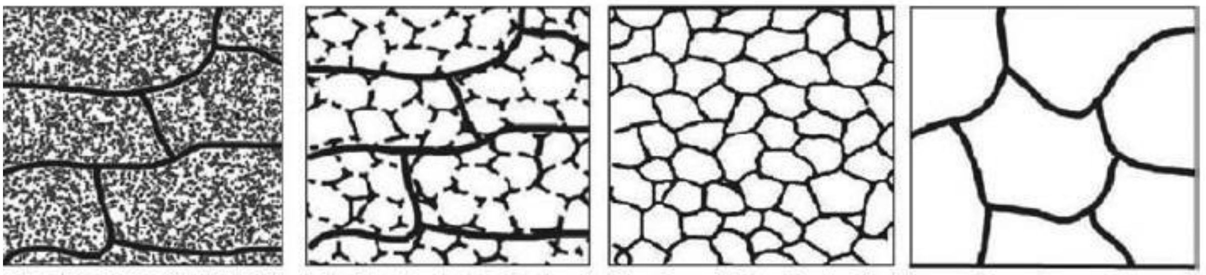
$$d^n - d_0^n = Kt$$

Where d_0 is the initial grain diameter at time t = 0, and K and n are time-independent constants; the value of n is generally equal to or greater than 2.

In a polycrystalline metal the yield stress (σ_y) increases with decrease in grain size; as per the following relation: $\sigma_y = \sigma_i + kd^{-\frac{1}{2}}$ where σ_i is yield stress for a crystal having no grain boundaries, *d* is grain diameter and *k* is Hall-Petch constant

Grain growth depends upon a number of factors, e.g.

(i) annealing temperature and time
(ii) degree of previous cold work
(iii) effect of insoluble mixtures to the metal
(iv) addition of some alloying elements
(v) rate of heating and cooling



(a) (b) (c) (d)

Fig. (a) Work hardening, (b) recovery, (c) recrystallization, and (d) grain growth during annealing.

HOT WORKING

- When metals are worked above recrystallization temperature (or 0.7 T_{mp} approximately), they recrystallize while being deformed and they remain soft. Metal billets are stressed and given massive deformation. This process is called *hot working*.
- During this process the metal is in a plastic state and it readily takes the desired shape.
- In hot working hardening due to deformation and softening due to annealing occur simultaneously.

Temperature

- Cold working process is carried out below the recrystallization temperature whereas hot working processes are carried out at temperatures above the recrystallization range.
- The upper limit of hot working is the temperature at which metal begins to melt and usually it is about 40°C below the melting point of the material
- The temperature in intermediate pass is kept well above the minimum hot working temperature so that energy in deforming metal may be saved.

- The working temperature in last pass is just above the minimum hot working temperature
- This *finishing temperature* is usually above the minimum recrystallization temperature.

Stress involved

- Usually, hot working processes are at a given compressive stress, e.g. as in rolling, forging extrusion, etc.

Speed

The speed of hot working operation at a given temperature can be calculated by considering the amount of time required for recrystallization. Operation has to be performed rapidly at higher temperature. In comparison to metals, alloys are more difficult to work.

Example

The common hot working processes are rolling, hot drawing, hot spinning, hot extruding, Forging welding, hot piercing, etc.

Note: Lead, however, is hot-worked at room temperature because of its low melting temperature. At the other extreme, molybdenum is cold-worked when deformed even at red heat because of its high recrystallization temperature

CONCEPT OF ALLOY FORMATION

A homogeneous mixture of two or more metals or a metal and a non-metal when fused together at a certain temperature forms a new metal after solidification, termed as an alloy.

The basic knowledge of structural properties of alloys is still in large part empirical, and indeed, it will probably never be possible to derive formulas which will predict which metals to mix in a certain proportion and with a certain heat treatment to yield a specified property or set of properties.

Concept

However, a set of rules exists which describes the qualitative behaviour of certain group of alloys. These rules are

1. Statements concerning the relative sizes of constituent atoms for alloy formation,
2. Concerning what kinds of phases to expect in terms of the valence of the constituent atoms.

The rules were discovered in a strictly empirical way

The present theoretical understanding of alloys

3. Consists of rudiomentary theories which describe how the rules arise from the basic principles of physics.
4. Understanding of the manufacturing process itself.
5. The behaviour of the material during both processing and in-service performance.

6. Process modelling developed which enable to take the microstructural specification for a given composition, which controls the properties of the material, and define an optimum manufacturing route to provide the desired material and performance.

Alloys may be prepared by different technological methods: melting, sintering of a powders mixture, high temperature diffusion of an alloying element into the base metal, plasma and vapour deposition of different elements, electroplating etc

The solid state an alloy may be present in one or more of the following forms:

1. As a solid solution
2. As an intermediate phase or intermediate chemical compound
3. As a finely divided mechanical mixture of solid solution
4. As a finely divided mechanical mixture of the metals
5. As a finely divided mechanical mixture of chemical compounds of metals, the individual metals and solid solutions.

CLASSIFICATION OF ALLOYS

Alloys are classified as

a) Binary alloys, composed of two components;
b) Ternary alloys, composed of three components;
c) Multicomponent alloys.

Metal alloys by virtue of composition, are often grouped into two classes:

a) Ferrous
b) Non-ferrous.

Ferrous alloys are those in which iron is the principal constituent, include steels and cast irons. The nonferrous alloys are all alloys that are not iron based.

The alloying elements are added to improve one or more of the following properties:

a) Tensile strength, hardness and toughness
b) Corrosive and oxidation resistance
c) Machinability
d) Elasticity
e) Hardenability
f) Creep strength
g) Fatigue resistance

SOLID SOLUTION

When we add a specific amount of sugar to water, the sugar dissolves in the water and the process eventually forms syrup. Here, the water is called solvent and sugar is called solute. The syrup contains both the solvent and solute, and it commonly referred as liquid solution. The composition is homogeneous throughout the solution. Of course, there is a limit on the concentration of sugar that can be added to water and is called solubility limit beyond which no more sugar can be added to the solvent

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

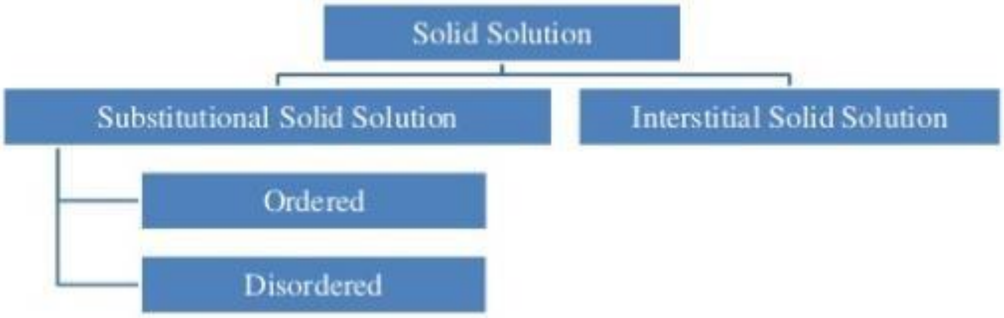
Solid solutions form readily when solvent and solute atoms have similar sizes and electron structures, so that it is compositionally or chemically homogeneous and the component atoms of the elements cannot be distinguished physically or separated mechanically. There is a homogeneous distribution of the constituents in the solid state so as to form a single phase or solid solution. The solute atoms are randomly and uniformly dispersed in the solvent matrix.

However, the **solubility of solute in the solvent** depends on various factors such as

1. **Atomic size factor:** Appreciable quantities of solute can dissolve in the solvent only when the difference in atomic radii between the two atoms is less than about ±15%±15%. Otherwise, the solute atoms will create substantial lattice distortions and a new phase can be formed.
2. ***Crystal structure:*** For appreciable solid solubility the crystal structures for both the solvent and solute must be same.
3. ***Electronegativity:*** The more electro-positive one element and the more electro-negative the other, such cases will form intermetallic compound instead of forming a substitutional solid solution. Thus, the electronegativities of the solute atom and solvent atom must be comparable.

Basically, solid solutions are of two types:

1. **Substitutional Solid Solution**
2. **Interstitial Solid Solutions**



HUME-ROTHERY'S RULE

While developing an alloy, it is frequently desirable to increase the strength of the alloy by adding a metal that will form a solid solution. Hume-Rothery has framed *empirical rules* that govern the choice of alloying elements in the formation of substitutional solutions. We may note that if an alloying element is chosen at random, it is likely to form an objectionable intermediate phase instead of a solid solution. Extensive solid solubility by substitution occurs, when

1. ***The solute and solvent atoms do not differ by more than 15% in size***, i.e. diameter. Within this limit of size factor, each of the metals will be able to dissolve appreciably (to the order of 10%) in the other metal. However, if the atomic size factor is greater than 15%, solid solution formation tends to be severely limited and is usually only a fraction of one percent.
2. ***The electronegativity difference between the elements is small***. If the chemical affinity of two metals is greater, then the solid solubility will be more restricted. When the chemical affinity of two metals is great, they tend to form an intermediate phase rather than a solid solution.
3. ***The valency and the crystal structures of the elements are the same.*** If the alloying element has a different valence from that of the base metal, the number of valence electrons per atom (called the electron ratio), will be changed by alloying. We may note that the crystal structures are more sensitive to a decrease in the electron ratio than to an increase. Obviously, a metal of high valence can dissolve only a small amount of lower valence metal; whereas the lower valence metal may have good solubility for a higher valence metal. Moreover, only metals that have the same type of lattice (for example FCC) can form a complete series of solid solutions. For complete solubility, it is found that the size factor must usually be less than 8%. Examples of binary and ternary systems exhibiting complete solid solubility are Cu- Ni and Ag-Au-Pt respectively.

Substitutional Solid Solution

When the two metals in solid solution form a single face centred cubic lattice, i.e., in general solute or impurity atoms replace or substitute for the host atoms, is called as substitutional solid solution. One may also define solid solutions as crystalline phases of a variable composition. Atoms of a solute B can be arranged in the crystal lattice of a solvent A either by substituting for some atoms of the latter in the crystal lattice or by occuping the interatomic spaces between atoms, or interstices.

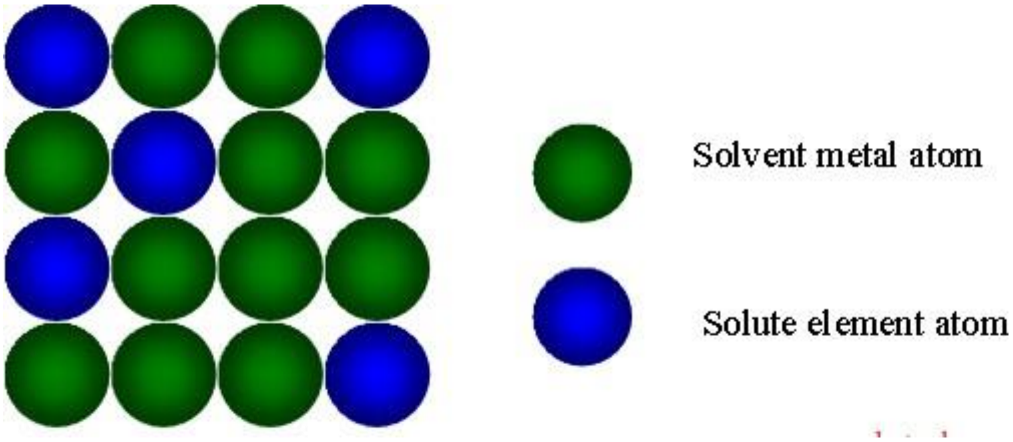


Fig.: **substitutional solid solution**

Condition for substitutional solid solution

1. The *atoms of the two metals be of almost same size*, i.e., the difference in atomic radii between the two atom types be less than about ±15%. Otherwise the solute atoms will create substantial lattice distortion and a new phase will form
2. *Solid solubility the crystal structures for metals of both atoms must be same*. If one element has more electropositivity and the other more electronegativity, then there is greater likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
3. *Other factors being equal, i.e. atomic size, crystal structure and electronegativity.*
4. *A metal will have more of a tendency to dissolve another metal of higher valency than one of a lower valency.*

Example

- Copper and nickel to form monel.
- Brass, an alloy of copper and zinc
- Copper (solute) can be added to Gold (solvent) to form Copper-Gold solid solution.
-

Substitutional solid solutions are of two types:

1. Random substitutional solid solutions
2. Ordered substitutional solid solutions.

Random substitutional solid solutions

When there is no order in the substitution of the two metal elements (**Fig. (a)),** the chance of one metal element occupying any particular atomic site in the crystal is equal to the atomic percent of the element in the alloy. Obviously, in such a situation the concentration of solute atoms can vary considerably throughout the lattice structure. Such type of the resulting solid solution is called a ***random* or *disordered* substitutional solid solution.**

In other words, This is formed when the alloying element(solute) atoms do not occupy any specific orderly position but replace the atoms in lattice structure of base metal (solvent) atoms at random then the phase is known as disordered or random sustitutional solid solution. It is normally observed at high temperature

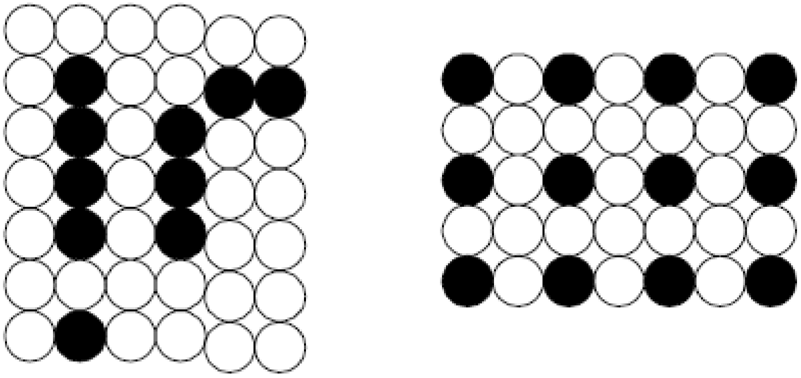
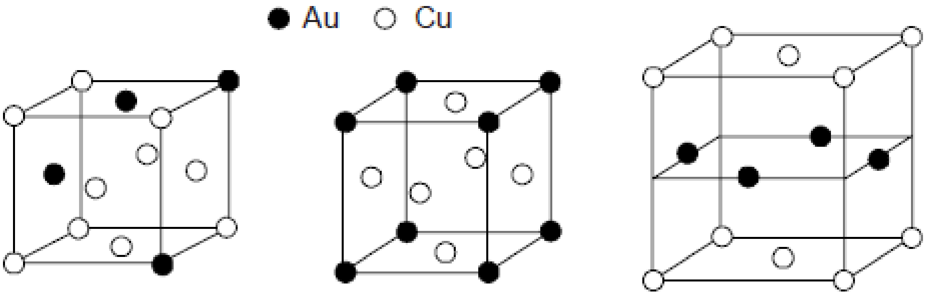

(a) (b)

Fig.: (a) Random substitutional solid solutions and (b) Ordered substitutional solid solutions.



(a) (b) (c)

Fig: crystal lattice of Cu-Au alloys (a) disordered solid solution (b) ordered solid solution of $AuCu_3$ alloys and (c) ordered solid solution of AuCu alloys

Ordered substitutional solid solutions.

Many substitutional solid solutions can be in an ordered state at relatively low temperatures, i.e. unlike atoms of two elements are distributed between the sites of the space lattice not statistically, but in a perfectly definite order. **Such solid solutions are called ordered; the term 'superstructure'** is also in use. Such ordering is common at low temperatures because greater thermal agitation tends to destroy the orderly arrangement. **[Fig. (b)].**

In other words, This is formed when the alloying element (solute) atoms occupy specific orderly positions in the lattice structure of base metal (solvent) atoms then the phase is known as ordered substitutional solid solution. It is normally observed at room temperature.

Ordered solid solutions can be found in systems with either substantial or unlimited solubility in the solid state; in that case complete ordering can occur with concentrations of the solid solution elements corresponding to simple atomic ratios of the components of the type, say ***AB* or *AB*$_3$.**

Partial ordering may be observed in systems with concentration ratios close to the indicated ones.

Can we have this disorders structure at room temperature?

Of course yeah, you can have a disordered structure room temperature. Any dilute solid solutions are disordered. This is at very high disorder concentration this is 50 50, but if you have let us say 1percent Zinc in Copper or for example, Copper-Nickel very good example, Copper-Nickel all the way it is FCC. So, you cannot distinguish which is Copper which is Nickel. So, Copper-Nickel for example, is like this. So, at any concentration, each atom is mixture of Copper and Nickel. The probability of each site being occupied by Copper and Nickel is determined by their fraction. So, if it is Copper-Nickel 50 by 50, each atom is copper 50 percent Copper 50 percent Nickel. It is not realistically it will be either Copper or Nickel, but probability wise it is 50 percent Copper, 50 percent Nickel. If it is 25 percent Copper, 75 percent Nickel, it will be 25 percent Copper, 75 percent (Refer Time: 24:38). So, there is a; so, this is the Disordered Solid Solution which remains FCC even at room temperature. No matter what the fraction of two elements is ok.

Interstitial Solid Solutions

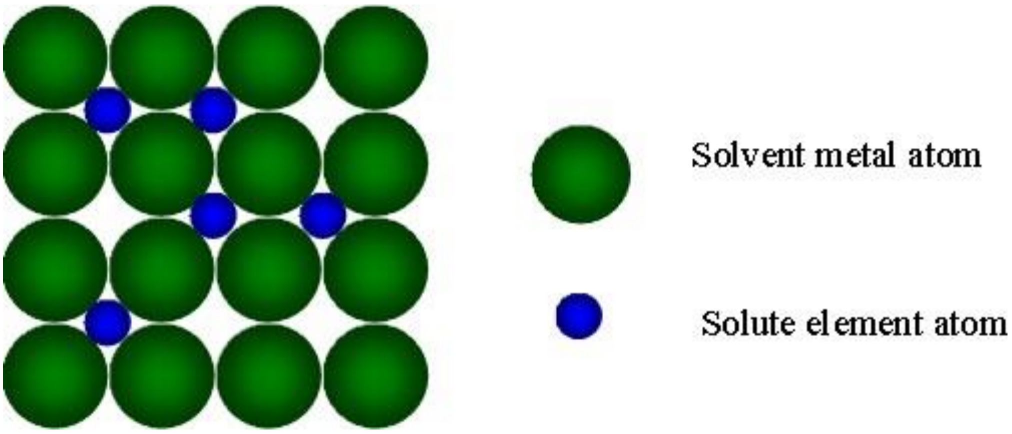


Fig.: Interstitial Solid Solutions

These can form, for instance, on melting together transition metals and non-metals with a small atomic radius (*H*, *N*, *C* or *B*).

Condition for Interstitial Solid Solutions

1. The size factor; i.e., the size of a solute atom must be equal to or slightly smaller than the size of an interstitial void.

2. Due to limited solubility form preferably in solvents having an HCP or FCC lattice with interstices of a radius of 0.41 *R*, where *R* is the radius of a solvent atom. In BCC lattices, the solubility is low, since the size of interstices does not exceed 0.29 *R*.

Example:

- solid solution of carbon in , which has an FCC lattice, can dissolve upto 2.14% (by mass) of carbon
- Nitrogen for maintaining stainless steel in austenitic condition for nitriding condition
- Hydrogen when introduced into steels during welding operations.

Effect of Interstitial solid solution on properties

1. Lattice distortions appearing on the formation of interstitial solid solutions are stronger than those in the substitutional solid solutions, because of which the properties of alloys can be changed more drastically.
2. As the concentration of a solute in a solid solution increases, this increases noticeably the electric resistance, coercive force, hardness and strength
3. But decreases the ductility and toughness.

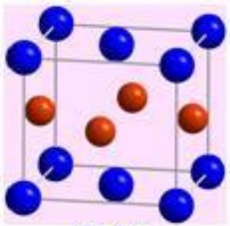
Order-disorder Transformations

- Ordinarily in the formation of substitutional type of solid solution the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. The alloy is said to be in a ‘disordered’ condition.

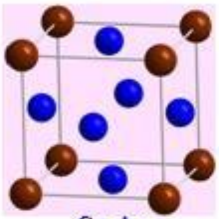
- Some of these random solid solutions, if cooled slowly, undergo a rearrangement of the atoms where the solute atoms move into definite positions in the lattice. This structure is known as an *ordered solid solution or superlattice.*

- Ordering is most common in metals that are completely soluble in the solid state, and usually the maximum amount of ordering occurs at a simple atomic ratio of the two elements.

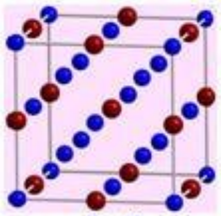
- For this reason, the ordered phase is sometimes given a chemical formula, such as AuCu and $AuCu_3$ in the gold-copper alloy system. On the equilibrium diagram, the ordered solutions are frequently designated as α’ , β’ , etc. or α’ , α’’ , etc., and the area in which they are found is usually bounded by a dot-dash line.



CuAu



Cu$_3$Au



Fe$_3$Al

- When the ordered phase has the same lattice structure as the disordered phase, the effect of ordering on mechanical properties is negligible. Hardening associated with the ordering process is most pronounced in those systems where the shape of the unitcell is changed by ordering.
- Regardless of the structure formed as a result of ordering, an important property change produced, even in the absence of hardening, is a significant reduction in electrical resistance. Notice the sharp decrease in electrical resistivity at the compositions which correspond to the ordered phases AuCu and AuCu$_3$.

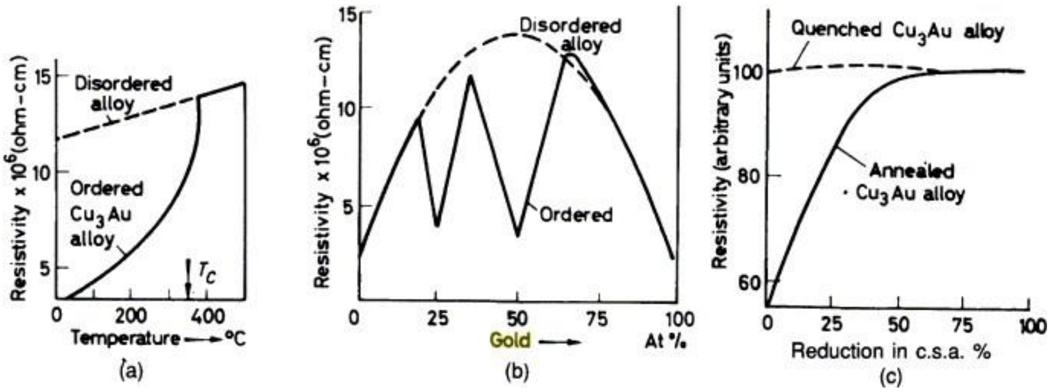


FIGURE: Effect of (a) temperature, (b) composition, (c) deformation on the resistivity of copper-gold alloys

Module III

PHASE DIAGRAM

Introduction

Phase diagram also known as equilibrium diagram or constitutional diagram is very important tool in the study of alloys. When the graphical representation deals with phases which are in equilibrium with the surrounding it is called as equilibrium diagram. Otherwise it is called as phase diagram. A phase diagram is plotted with temperature as ordinate (y axis) and alloy composition as abscissa (x axis).

Phase diagram enables

1. Phase content of an alloy to be determines at any particular temperature and composition.
2. Enable the phase transformation to be followed in heating and cooling the alloy under equilibrium condition.(in reversible case)

Why phase diagram is called as equilibrium diagram?

As phase diagram determines phase composition of an alloy for a particular temperature and composition under equilibrium condition (slow heating and cooling) which shows/exhibit/manifest the reversal of process hence it is called as equilibrium diagram.

Need of phase diagram:

a) Generally properties of material depend on (i) number, (ii) amount, (iii) type, (iv) the form (shape and size) of phase present. Properties can be changed by altering these quantities. So study of phase relationship plays an important role for understanding the properties of material.

b) Again state of material depends on variables/ conditions i.e. (i) composition, (ii) temperature, (ii) pressure. So best way to understand these effects, phase or equilibrium diagram needed.

So phase diagram is a function of temperature (T), pressure (P) and composition.

$$phase\ diagram = f(T, P\ \&\ composition)$$

It enables

a) Phase content of an alloy at particular temperature (T) and composition

b) Phase transformation under equilibrium condition(slow cooling and slow heating)

c) A blue print of the alloy system from which
    (i) Useful properties at what composition
    (ii) Improved properties with best effect with which treatment
    (iii) Which treatment will give harmful and which will be avoided can be anticipated.

Alloy: a substance which composed of two or more chemical elements such that metallic atoms predominate in composition and metallic bond predominates. The element which is larger proportion is called base metal and other elements present are called as alloying elements.

Classification of phase diagram

(i) Unary (or one component) phase diagram

a. Pressure on vertical axis (Y-axis)
b. Temperature on horizontal axis(X axis)

(ii) Binary (or two component) phase diagram

a. Temperature on vertical axis (Y-axis)
b. Alloy on horizontal axis(X axis)

(iii) Binary (or two component) phase diagram

a. Temperature on vertical axis (Y-axis)
b. Concentration on horizontal axis(X axis)

The following terms are used in study of solid phase and phase diagram.

1. System

- A system may be composed of solids, liquids and gases or their combination and may have metals and non metals separately or in any combination.
- A system is isolated from surrounding, unaffected by solids, liquids and gases (substances present in it are free to react only with each other)

Classification of systems

a) Unary system: having one component (pure metal)
b) Binary system: having two component(alloy of two metals)

Systems having three or four components are known as tertiary and quaternary system

2. Component

- A component is a unit of composition variable in the system.
- The components may be (i) elements (ii) ions (iii) compounds
- It refers to independent chemical species.

3. Solubility limit

- For an alloy system at some specific temperature there is maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution is called solubility limit.

Example: sugar-water ($C_{12}H_{22}O_{11}$-H_2O)

- Sugar will dissolve in water up to certain limit called solubility limit. Further addition of sugar will result in setting of sugar particles at bottom thus forming two separate systems.
   a) Sugar water syrup liquid solution
   b) Solid crystal of undissolved sugar.

Explanation with example

- To illustrate this concept, consider the sugar–water ($C_{12}H_{22}O_{11}$–H_2O) system. Initially, as sugar is added to water, a sugar–water solution or syrup forms. As more sugar is introduced, the solution becomes more concentrated, until the solubility limit is reached, or the solution becomes saturated with sugar. At this time the solution is not capable of dissolving any more sugar, and further additions simply settle to the bottom of the container. Thus, the system now consists of two separate substances: a sugar–water syrup liquid solution and solid crystals of undissolved sugar.
- This solubility limit of sugar in water depends on the temperature of the water and may be represented in graphical form on a plot of temperature along the ordinate and composition (in weight percent sugar) along the abscissa, as shown in **Figure**. Along the composition axis, increasing sugar concentration is from left to right, and percentage of water is read from right to left. Since only two components are involved (sugar and water), the sum of the concentrations at any composition will equal 100 wt%. The solubility limit is represented as the nearly vertical line in the figure. For compositions and temperatures to the left of the solubility line, only the syrup liquid solution exists; to the right of the line, syrup and solid sugar coexist. The solubility limit at some temperature is the composition that corresponds to the intersection of the given temperature coordinate and the solubility limit line. For example, at 20^{0}C the maximum solubility of sugar in water is 65 wt%. As **Figure** indicates, the solubility limit increases slightly with rising temperature.

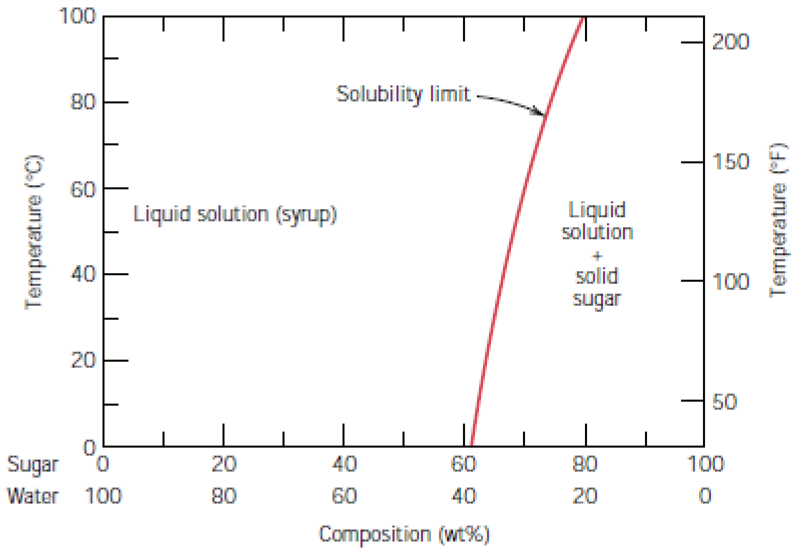


Figure: The solubility of sugar (C12H22O11) in sugar–water syrup.

4. Phase

- It is a homogeneous portion of a system that has uniform physical and chemical characteristics.
- Sometimes, a single-phase system is termed ‘‘homogeneous.’’ Systems composed of two or more phases are termed ‘‘mixtures’’ or ‘‘heterogeneous systems.’’ Most metallic alloys, and, for that matter, ceramic, polymeric, and composite systems are heterogeneous.
- Phase satisfy the following
  - (i) Physically distinguishable
  - (ii) Chemically homogeneous
  - (iii) Mechanically separable
- Example: water can exist in three form (i) solid (ii) liquid (iii) gas. These three forms are called as phase

Importants and objective of phase diagram

(1) Shows the phases which exist in equilibrium for any combination of temperature and alloy composition

(2) Shows relationship between composition, temperature and structure of an alloy in series.

(3) Provides knowledge of phase composition and phase stability as a function of temperature, pressure and composition

(4) Predict the phase transformations and the resulting microstructures which may have equilibrium or non-equilibrium character

(5) Find out what phases are present but also to assure that the alloy is in the stable equilibrium state.

Equilibrium is reached when the Gibbs free energy of the system has reached to its lowest possible value.

(6) Permits to study and control processes. Such as

  a. Phase separation
  b. Solidification of metals
  c. Purification of metals
  d. Structural changes produced by heat treatment

(7) It marks liquidus and solidus.

Note: liquidus is a line in an equilibrium diagram which indicates the tempearature of beginning of solidification or complition of melting whareas solidus is the line in as equilibrium diagram which indicates completion of siolidification or beginning of melting.

THE PHASE RULE OR GIBB'S PHASE RULE OR CONDENSED PHASE RULE

This expresses mathematically the general relationships for the existence of stable phases corresponding to the equilibrium conditions.

It enables us

1. To predict and check the processes that occur in alloys during heating or cooling
2. To determine whether the solidification process takes place at a constant temperature or within a certain temperature interval
3. Indicate the number of phases that can exist simultaneously in a system.

The phase rule known as Gibb's phase rule establishes the relationship between the no of phase (P), the no of component (C) and the no of degrees of freedom (F). The relationship can be expressed mathematically as

$$P + F = C + n$$

Where $P = No\ of\ phases$ in eqilibrium

$F = No\ of\ degrees\ of\ freedom$ that is no. of independent variables

$C = No\ of\ component\ in\ the\ alloy\ system$

$n = no\ of\ physical\ varibles\ like\ pressure, temperature\ and\ concentarion, composition$, That can be independently changed without altering the equilibrium

Thermodynamic variables for Gibb's phase rule

- Pressure and temperature (if both are variables)
- If pressure is fixed, then only temperature is variable.

Composition variable

- Phase composition are considered as variables
- Overall alloy composition is not a variable expect when we have a single phase equilibrium when alloy composition is also the phase composition.

How many composition variables we have?

If there are C components then one need to specify the C-1 compositions for each phase therefore for P phases one needs P(C-1) composition variables.

Thus the total no of variables (V) = P(C-1) +2: if pressure and temperature are variables
V=P(C-1) +1 if pressure remain constant and temperature is variable.

Degree of freedom

F=No of thermodynamic variables which can be specified independently without changing the phases in equilibrium

Since there is thermodynamic equilibrium there are equilibrium relations between the thermodynamic variables. If we specify certain no of variables, others are automatically fixed by these equilibrium relations.

Case-1

Since the non composition variables includes the two external parameters namely temperature (T) and pressure (P) hence rule can be written as $P + F = C + 2$ WHERE n=2

Case-2

In metallurgical systems where pressure is regarded as fixed at one atmosphere, the pressure variable is omitted so rule can be written as $P + F = C + 1$ where n=1 (applicable for binary phase diagram)

So $F = C + 1 - P$, Since degree of freedom F can never be less than zero, therefore $C + 1 - P \geq 0$ or $P \leq C + 1$ which means that the no of phases in the system cannot exceed the no of component plus one.

COOLING CURVE (TIME- TEMPERATURE CURVE)

Figure shows a cooling curve which is distinctly divided into two portions

a) Exhibiting the fall of temperature of time
b) Exhibit that the temperature remains practically constant over a period of time.

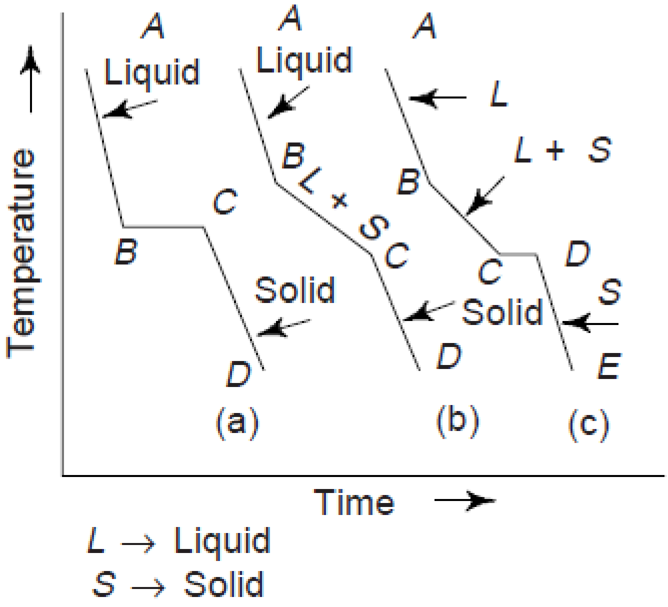


Figure: (a) cooling curve for pure metal or compound, (b) Cooling curve for binary solid solution,(c) Cooling curves of binary eutectic system

(a) cooling curve for pure metal or compound

From A to B

Pure metals cools from A to B and first crystal begins to form at B.

From B to C

Liquid metals liberate latent heat of fusion from B to C till the entire mass has solidified (at point C) without any change in temperature.

In between B and C mass is partly liquid and partly solid.

From C to D

The solid cools and tend to reach the room temperature. The slopes AB and CD depend upon specific heats of liquid and solid metals respectively.

(b) Cooling curve for binary solid solution

- **The curve AB and CD** of binary solid solution is same as that of pure metals but line BC, is not horizontal as in pure metals
- **The line BC** is inclined indicating that binary solid solutions do not freeze at constant temperature but they posses freezing range BC which varies with the composition of an alloy.
- The temperature drops along line BC during freezing till whole mass has been solidified at point C.

(c) Cooling curves of binary eutectic system

Eutectic system is one in which two components are completely soluble in liquid state but entirely insoluble in solid state

In AB

Liquid cools along AB until temperature B is reached

At B and in line BC

At B, one component that is excess will crystallize and temperature will drop along BC.

At point C and in line CD

At point C, the liquid composition has been reached at which two components crystallize simultaneously from the solution at constant temperature CD until the whole mass has been solidified at D. Cooling from D to E is as usual.

CONSTRUCTION OF A PHASE DIAGRAM OR CONSTITUTIONAL DIAGRAM

Depending upon the number of components and solubility characteristic, the phase diagrams are usually categorised as follows:

a. ***Solid Solution Type:***
   - Two metals are completely soluble in solid as well as in liquid state.
   - They have the same type of lattice and similar atomic size.
   - Copper and Nickel form an isomorphous system.

b. ***Eutectic Type:***
   - When two metals are completely soluble in the liquid state but partly or completely insoluble in the solid state, is termed as eutectic type
   - Fe-C, Al-Mn, Pb-Sn form an eutectic system.

c. ***Peritectic Type:***

- Liquid and solid combine to form a new solid. The melting points of two metals differ considerably.
- Ag and Pt form such a system.

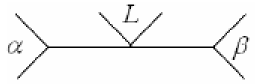
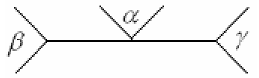
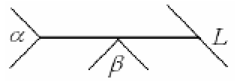
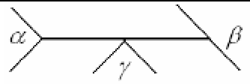
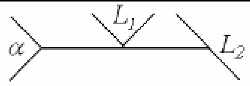
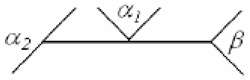
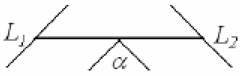
d. Monotectic Type:

- The two liquid solutions are not soluble in each other over a certain composition range,
- In this type one liquid decomposes into another liquid solid
- Cu and Pb form monotectic system.

e. Eutectoid Type:

- In this one solid decomposes into two different solids. Obviously, solid to solid transformation takes place
- Fe-C, Cu-Zn, Al-Cu, Cu-Sn, etc form eutectoid system.
- The crystal structure of new phase is known as the ***Widmanstatten structure***

Table-5: *Summary of invariant reactions in binary systems.*

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$		Fe-C, 4.27% C, 1147 °C
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$		Fe-C, 0.80% C, 723 °C
Peritectic	$L + \alpha \leftrightarrow \beta$		Fe-C, 0.16%C, 1495 °C
Peritectoid	$\alpha + \beta \leftrightarrow \gamma$		
Monotectic	$L_1 \leftrightarrow L_2 + \alpha$		Fe-C, 0.51%C, 1495 °C
Monotectoid	$\alpha_1 \leftrightarrow \alpha_2 + \beta$		
Syntectic	$L_1 + L_2 \leftrightarrow \alpha$		

Construction of a phase diagram for alloys of two metals *A* and *B* in their various compositions, using the data from the cooling curves is shown in Fig. In order to get the actual phase diagram, the arrestment points have been joined. There is complete intersolubility in the liquid and solid phases in the diagram.

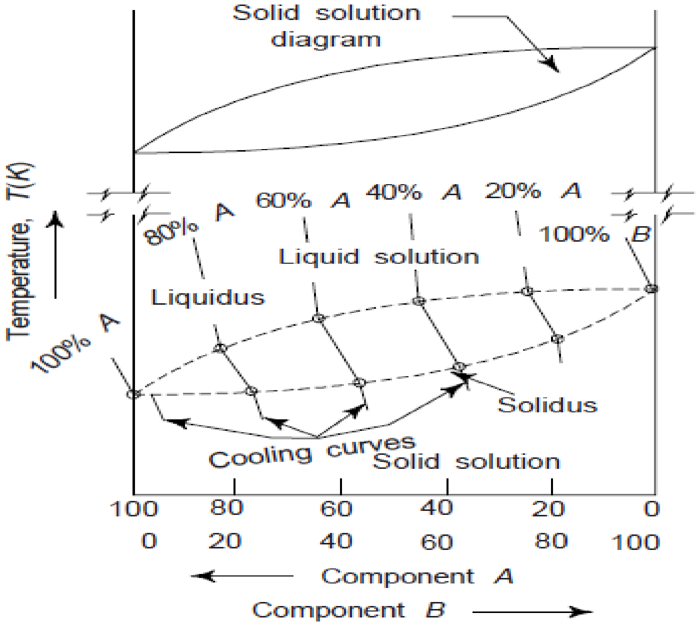


Figure: A phase diagram resulting from a series of cooling curve.

The upper line corresponds to the temperature at which the alloy starts to solidify the liquids. The lower line shows the complete solidification and is called the *solidus*. A mixture of solid and liquid exists between two lines. i.e. between *liquidus* and solidus and represents the alloys in a *semisolid* state. The figure is known as *equilibrium diagram*. To designate solid solutions in phase diagrams. Greek letters α, β, γ etc. are commonly used.

THE LEVER RULE

If an alloy consists of more than one phase, the amount of each phase present can be found by applying the lever rule to the phase diagram.

Importants of Lever Rule

a. Helps to calculate the relative proportions of solid and liquid material present in the mixture at any given temperature.
b. The number and composition of phases can be obtained from the phase diagram.
c. In a two phase region, one can determine the relative amount of each phase that is present from the phase diagram.

The lever rule can be explained by considering a simple balance. The composition of the alloy is represented by the fulcrum, and the compositions of the two phases by the ends of a bar. The proportions of the phases present are determined by the weights needed to balance the system.

So,
Fraction of phase 1 = (C2 - C) / (C2 - C1)
and,
Fraction of phase 2 = (C - C1) / (C2 - C1).

Using a relationship known as *lever rule* (or the inverse lever rule), which is applied as follows:

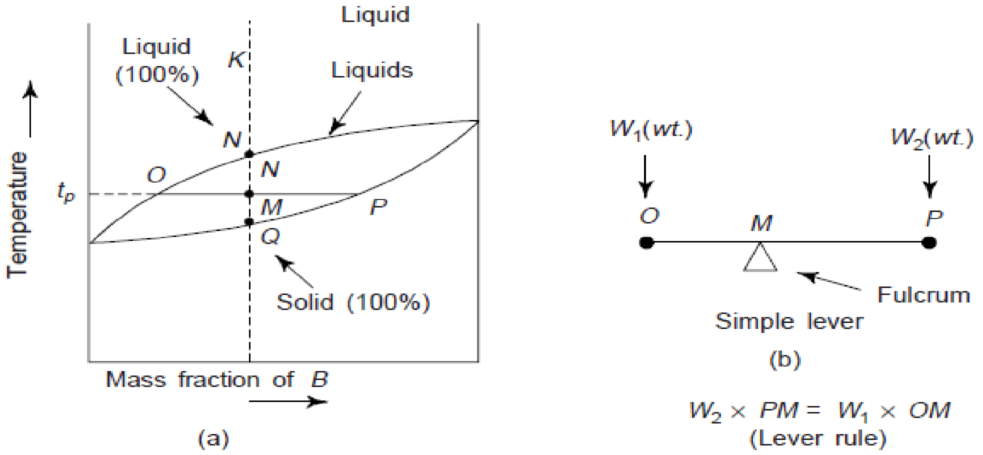
a. Construct the tie line across the two-phase region at the temperature of the alloy.
b. The overall alloy composition is located on the tie line.
c. The fraction of one phase is computed by taking the length of the line from the overall alloy composition to the phase boundary for the other phase, and dividing the total tie line-length.
d. One can determine the fraction of the other phase in the same manner.
e. In case if phase percentages are desired, each phase fraction is multiplied by 100. When the composition axis is scaled in weight percent; the phase fractions computed using the lever rule are mass fractions – the mass (or weight) of a specific phase divided by the total alloy mass (or weight). The mass of each phase is computed from the product of each phase fraction and the total alloy mass.

Explanation of Lever Rule Using One Example

- To determine the relative amounts of two phases, erect an ordinate or vertical line at a point on composition scale which gives the total composition of the alloy.
- The intersection of this ordinate with the given isothermal line denotes the fulcrum of a simple lever system.
- From **Fig. (a**) it is clear that the ordinate *KL* intersects the temperature line at a point *M*. However, the relative lengths of lever arm *OM* and *MP* (**Fig. (b))** multiplied by the amount of phases present must balance. From **Fig. (a)** it is clear that the length *MP* represents the amount of liquid and the length *OM* represents the amount of solid. Therefore

The percentage of solid present=$\frac{OM}{OP} \times 100 = \frac{OP-MP}{OP} \times 100$

The percentage of liquid present=$\frac{MP}{OP} \times 100 = \frac{OP-OM}{OP} \times 100$



(a)

(b)

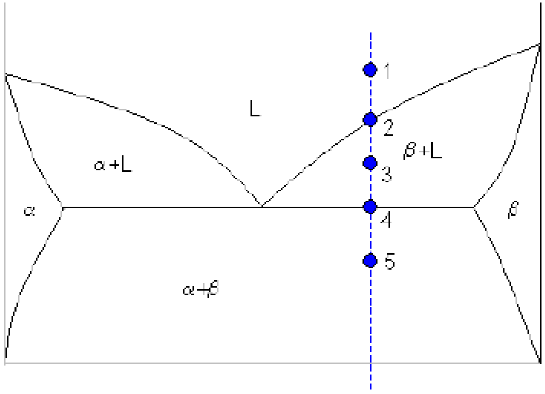
$W_2 \times PM = W_1 \times OM$
(Lever rule)

Figure: lever rule derivation using phase diagram

From **Fig**. *OM* + *MP* = *OP*, which represents the total composition of alloy between liquids and solidus, say at temperature *tp*.
The *OMP* (isothermal) can be considered a **tie line** since this line joins the composition of two phases in equilibrium at a specific temperature *tp*.

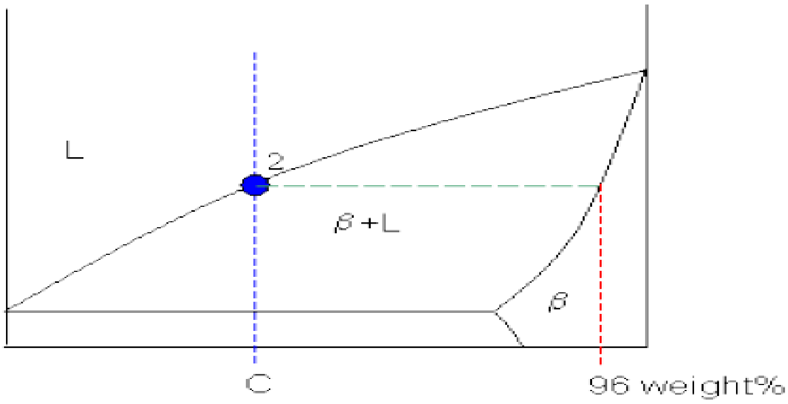
Application of Lever Rule

Lever rule applied to a binary system



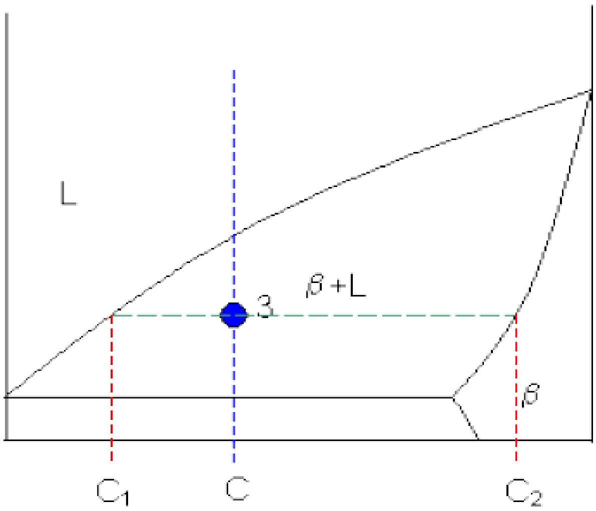
Point 1
At point 1 the alloy is completely liquid, with a composition C. Let
C = 65 weight% B.

Point 2
At point 2 the alloy has cooled as far as the liquidus, and solid phase starts to form. Phase first forms with a composition of 96 weight% B. The green dashed line below is an example of a *tie-line*. A tie-line is a horizontal (i.e., constant-temperature) line through the chosen point, which intersects the phase boundary lines on either side.



Point 3

A tie-line is drawn through the point, and the lever rule is applied to identify the proportions of phases present.



Intersection of the lines gives compositions C_1 and C_2 as shown.

Let

C1 = 58 weight% B

and

C2 = 92 weight% B

So,

Fraction of solid = (65 - 58) / (92 - 58) = 20 weight%

and

Fraction of liquid = (92 - 65) / (92 - 58) = 80 weight%

Point 4

Let

C3 = 48 weight% B

and

C4 = 87 weight% B

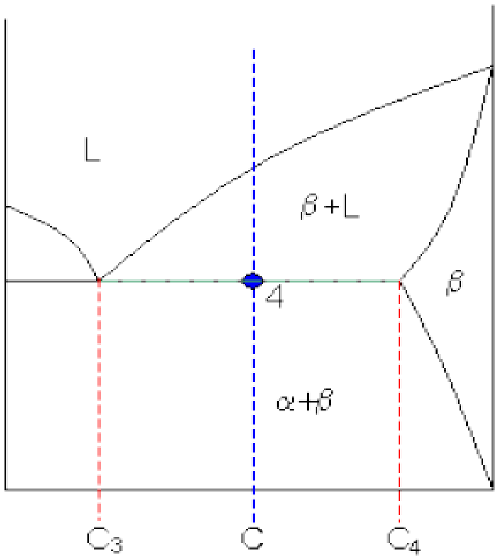
So

fraction of solid = (65 - 48) / (87 - 48) = 44 weight%.

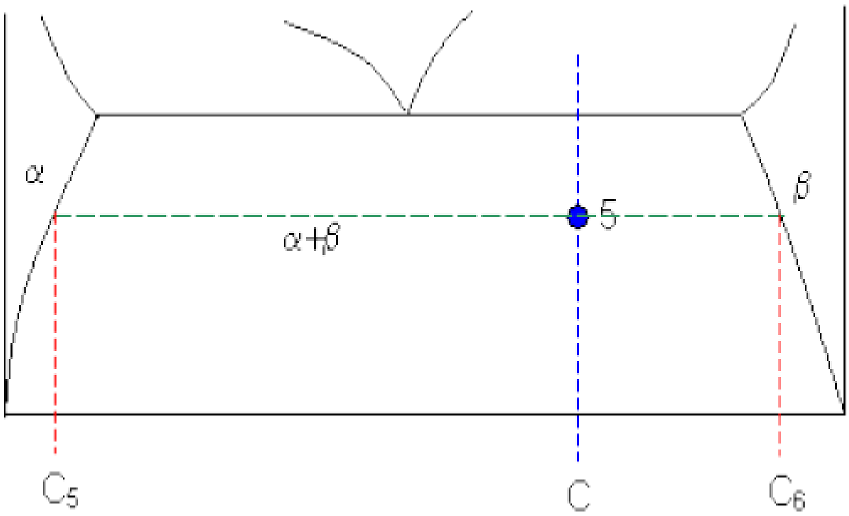
As the alloy is cooled, more solid phase forms.

At point 4, the remainder of the liquid becomes a eutectic phase of ⟨and

fraction of eutectic = 56 weight%



Point 5



Let
C5 = 9 weight% B
and
C6 = 91 weight% B
So
fraction of solid = (65 - 9) / (91 - 9) = 68 weight%
and
fraction of solid = (91 - 65) / (91 - 9) = 32 weight%.

ALLOTROPIC TRANSFORMATION

ALLOTROPY

Allotropy OR allotropism meaning "Allos" means other and "tropos" meaning manner. Allotropy is the property of same chemical elements exists in two or more different form, in the same physical state known as allotropes of these elements. Many metals can exist in more than one crystalline form; this phenomenon is called as allotropy.

Examples: allotropes of carbon (C)

a. Diamond (carbon atoms are bonded together in tetrahedral lattice arrangement.)
b. Graphite (carbon atoms are bonded together in sheets of a hexagonal lattice)
c. Grapheme (single sheet of graphite)
d. Fullerene (carbon atoms are bonded together in spherical, tabular or ellipsoidal formation.

All the above allotropes differ in crystalline structure.

ALLOTROPES OF IRON

Iron perhaps the best known example of allotropy in a metal.

At atmospheric pressure there are three allotropic forms of iron.

(1) Alpha iron (α) → ferrite(low temperature ferrite)
(2) Gamma iron (β) → austenite
(3) Delta iron (δ) → high temperature ferrite

At very high pressure

(4) Fourth form exists: called as epsilon iron (ε) hexaferrum

Phase Diagram of Pure Iron

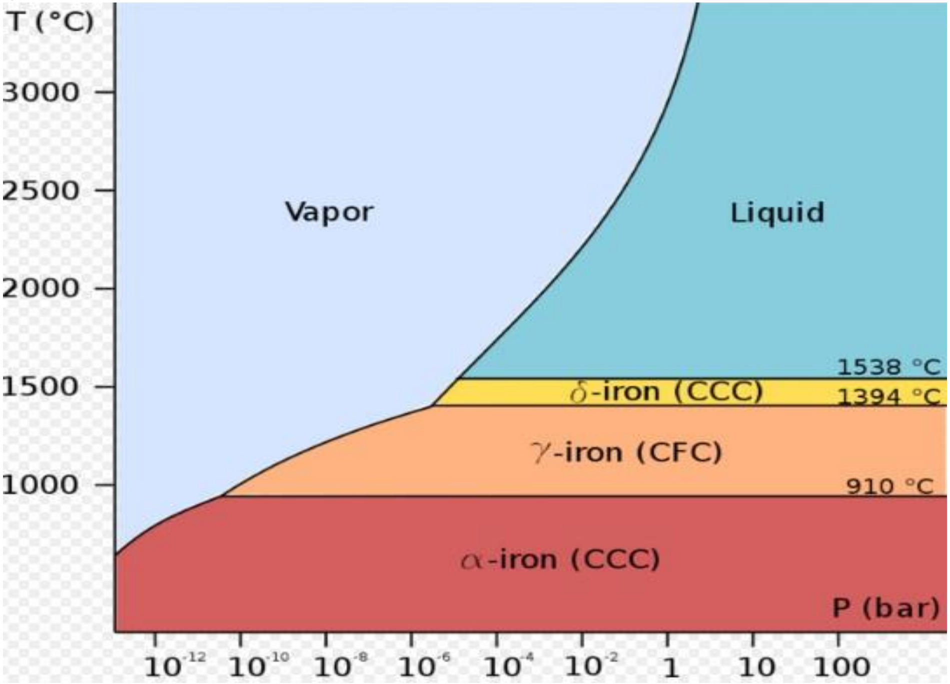


Figure: phase diagram of pure iron

COOLING CURVE OF PURE IRON

After the freezing of pure iron, there are three thermal arrest temperature in solid state (excluding freezing temperature) called as critical temperature.

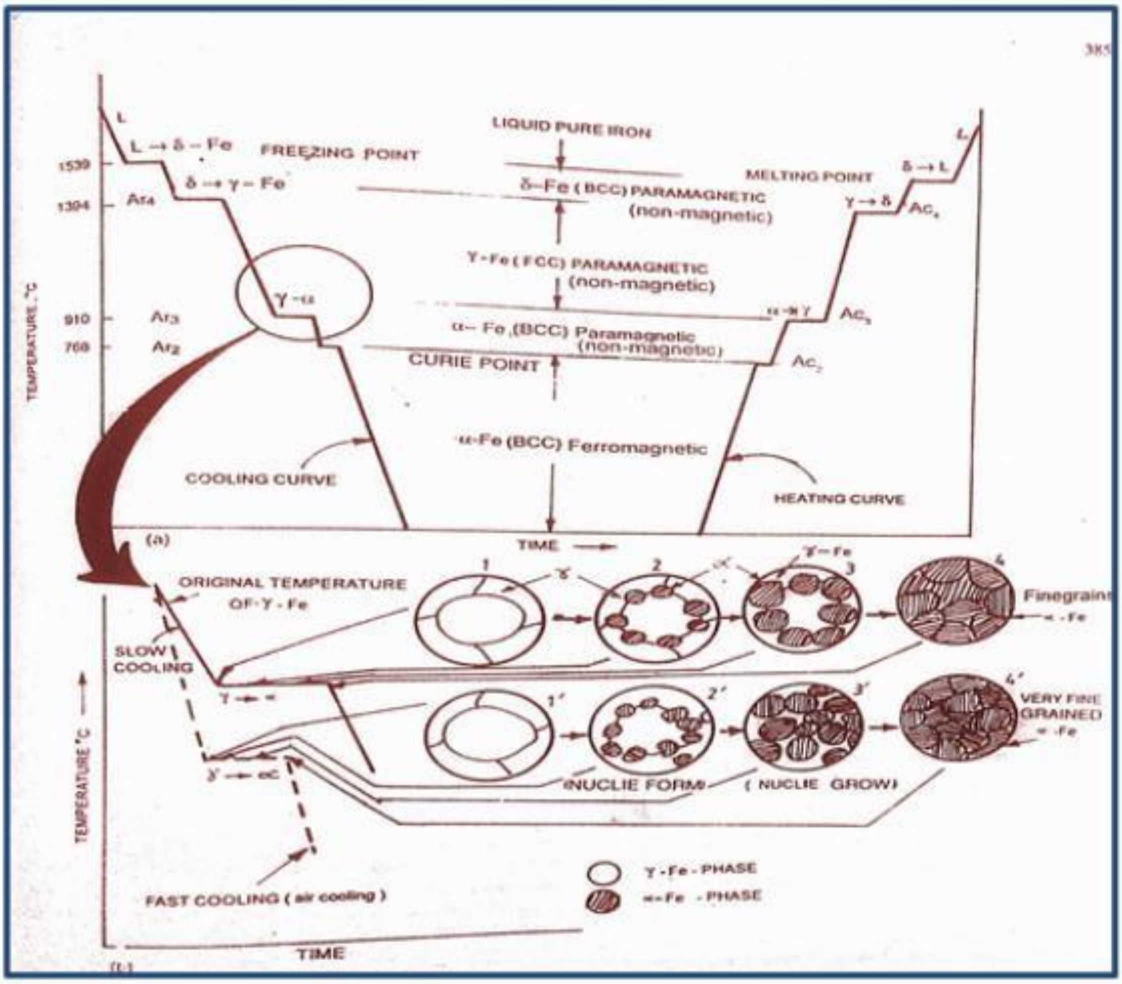
They are designated as

$$A_4 \rightarrow A\ means\ arrest\ , A_4\ temp@\ \delta \rightarrow \gamma\ transformation$$

$$A_3\ temp@\ \gamma\ \rightarrow \alpha\ transformation$$

$$A_2\ temp@\ \alpha_{paramagnetic}\ \rightarrow \alpha_{ferromagnetic}\ transformation$$

Temperature 768^0 is called as Curie temperature (named after Madam Curie). It is not a allotropic transformation temperature



During cooling

Temperature are named as

Ar_4, Ar_3, Ar_2 *where A means arrest and* **r** *means a french word refroidissement means cooling*

During heating

Temperature are named as

Ac_4, Ac_3, Ac_2 *where A means arrest and* **c** *means a french word chauffage means heating*

The values of these temperatures are

$$Ar_4\ , Ar_3\ , Ar_2\ = Ac_4\ , Ac_3\ , Ac_2\ = 1400^0, 910^0\ \&768^0\ respectively$$

I. At 768^0 temperature and above

It is evident from the cooling curve diagram that iron which exists below 768^0 is called $\boldsymbol{\alpha}$ iron.

- Average no of atom is 2.
- It is magnetic in nature.
- $\boldsymbol{\alpha}$ Iron is also called as low temperature ferrite.

The temperature 768^0 is called as Curie temperature.

At temperature 768^0, $\boldsymbol{\alpha}$ Iron changes magnetic properties from magnetic to non magnetic iron.

$$\boxed{magnetic\ \alpha\ iron\ (BCC) \overset{\Delta\ \&\nabla\ @768^0}{\Leftrightarrow=======\Rightarrow} non\ magnetic\ \alpha\ iron\ (BCC)}$$

This is a time dependent phenomenon. The iron above 768^0 is never magnetic again.

II. At 910^0 temperature and above

The iron exists below 910^0 and above 768^0 is non magnetic α iron (BCC)

- It is also called as $\boldsymbol{\alpha}$ Iron.
- Structure is BCC
- Average no is 2

$$\boxed{non\ magnetic\ \alpha\ iron\ (BCC) \overset{\Delta\ \&\nabla\ @910^0}{\Leftrightarrow=======\Rightarrow} non\ magnetic\ \alpha\ iron\ (FCC)}$$

At 910^0 temperature non magnetic $\boldsymbol{\alpha}$ Iron transform to nonmagnetic $\boldsymbol{\gamma}$ iron.

Above 910^0, crystal structure transformation takes place. $\boldsymbol{\alpha}$ Iron which is BCC transfer into $\boldsymbol{\gamma}$ iron which is FCC in nature with average no -4

III. At 1400^0 temperature and above

- At temperature 1400^0 temperature $\boldsymbol{\gamma}$ iron (austenite) transform to δ iron (BCC)
- δ iron is called as high temperature ferrite.
- When $\boldsymbol{\gamma}$ iron is heated at 1400^0, again phase transformation takes place that is BCC structure is formed δ iron.

$$\boxed{\gamma\ \text{iron(FCC)} \overset{\Delta\ \&\nabla\ @1400^0}{\Leftrightarrow========\Rightarrow} \delta\ \text{iron(BCC)}}$$

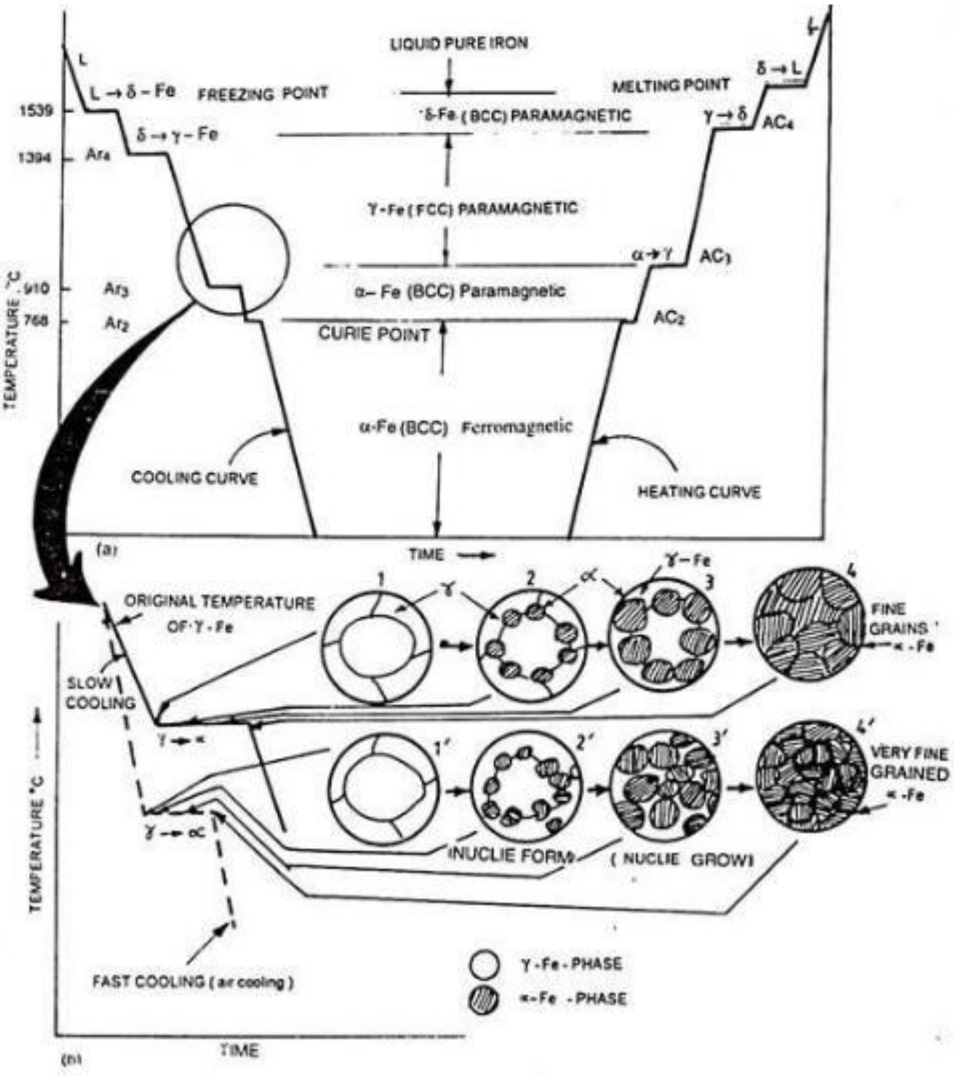
IV. At 1539^0 temperature and above

When δ iron (high temperature ferrite is heated at 1539^0 solid iron melts liquid state.

$$\boxed{\delta\ \text{iron(BCC)} \overset{\Delta\ \&\nabla\ @1539^0}{\Leftrightarrow========\Rightarrow} liquid}$$

Thermodynamically reversible allotropic transformations are called as polymorphic transformation.

The transformations in the cooling curve of pure iron takes place at constant temperature and all these are called time dependent transformation.



Effect of non equilibrium cooling

The equilibrium solidification of a solid solution alloy assumes that the rate of cooling is infinitely slow, so that **complete equilibrium** by means **of convection (in the liquid)** and **diffusion (in the solid**) could be achieved at each stage of the process**.**

Under actual conditions of industrial casting practice however the rate of solidification is much faster than the rate of diffusion, and thus the solid phase is unable to attain uniformity and equilibrium.

Due to this the core (centre) of each dendrite (or grain) contains higher amount of high melting metal than the surface of dendrite (or inter-dentritic region)

CORING

In the production of Cu-Ni alloy, there is insufficient time for complete diffusion to take place. This leads to lack of uniformity in the structure of the metal. This is termed a *cored* structure, which give rise to less than the optimal properties.

In copper nickel solid solution (for example 70Ni 30 Cu alloy), the core has more nickel content than the equilibrium amount, so that outer fringes (inter-dentritic spaces) contain correspondingly more copper than the equilibrium content. ***The variation of composition from the core of the dentrite to the interdentritic space (content of nickel decreases continuosly from the core to the centre of the interdentritic space) is called as dendritic-segregation. Dentritic- segregation on a microscopic scale is called coring***

The degree of coring in an alloy system depends on

a) the diffusivity of the two unlike atoms in the solid solution and
b) The time available for diffusion.

Time available for diffusion depends on the solidification rate,

a) short for chill-casting (more intense coring)
b) Relatively long for sand-castings because of lower heat transfer rates of sands.

EFFECT OF CORING ON MATERIAL PROPERTIES

a) results in weakness
b) brittleness of castings because of different composition near the grain boundaries
c) susceptibility to corrosion
d) cause intergranular corrosion
e) lack uniformity of mechanical and physical properties

CORING IN Cu-Ni

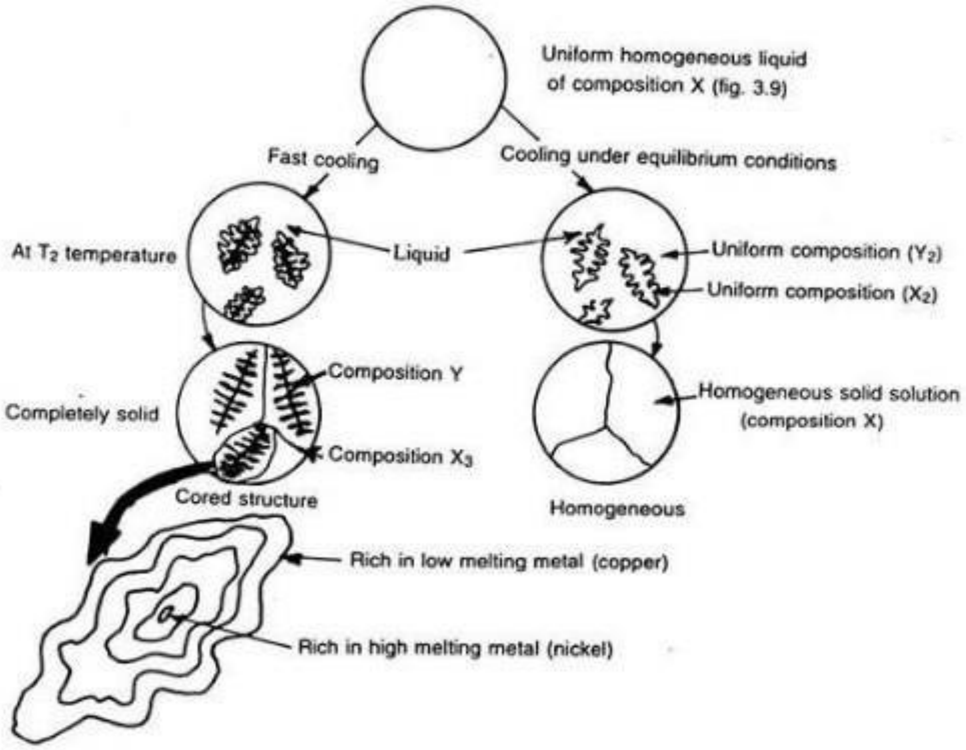


Fig. Effect of non-equilibrium cooling of solid solution alloy (70 Ni 30 Cu). The result is coring

Since the rate of chemical attack with an etchant varies with the composition, proper etching of polished surface usually reveals coring.

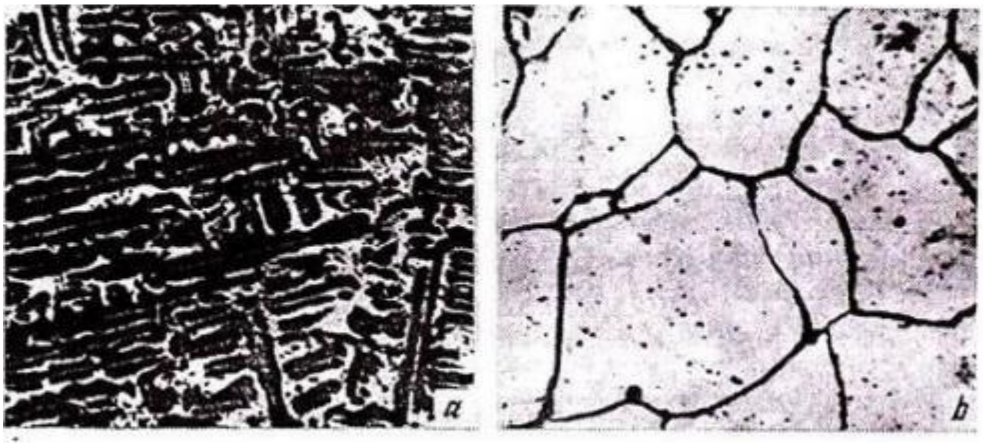


Fig. (a) Microstructure of cored structure cored CU-Ni alloy, (b) effect of homogenising on it

Let us examine the solidification of 70% Ni, 30% Cu alloy when cooled at a faster rate than equilibrium cooling. Under equilibrium conditions, the composition of the liquid phase varies continuously along the liquidus and that of solid along the solidus.
Even under non-equilibrium conditions, there is not often much undercooling of the liquid, and diffusion and convection currents within the liquid are usually rapid enough to maintain it at very nearly the composition indicated by liquidus curve XX_1X_3 **(Fig.).**

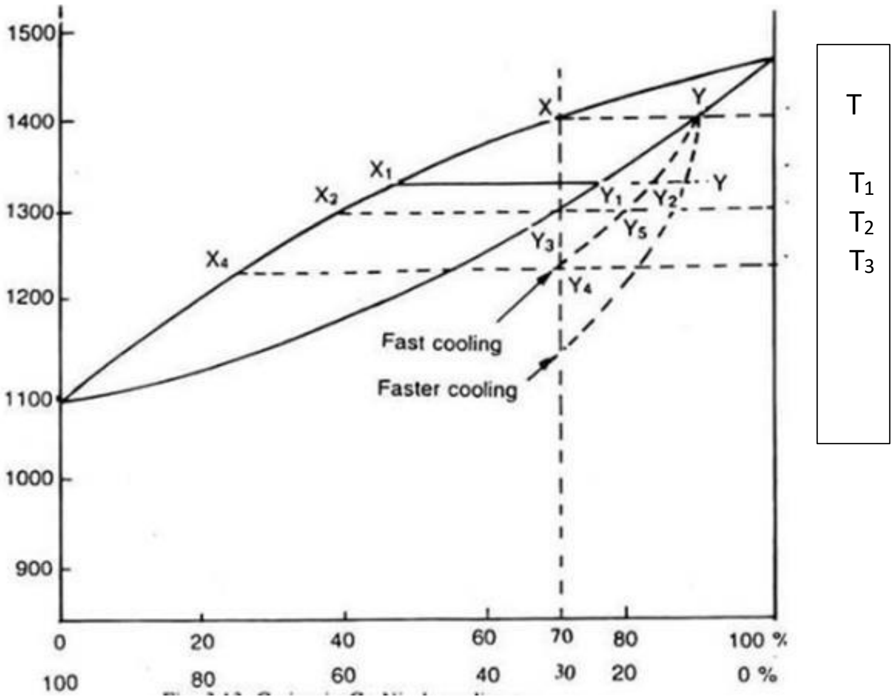


Fig. Coring in Cu-Ni phase-diagram

The solidification of this alloy begins at T, freezing a solid solution of composition Y. As the temperature drops, then at T_1 the liquid have composition of X_1 and the solid solution now freezing is of composition Y_1.

Since the diffusion is too slow (cooling rate is fast) to keep pace with the crystal growth, not enough time is being allowed to achieve uniformity in the solid, thus its average composition may be between Y and Y_1, say Y_1.

As the temperature decreases, the average composition of the solid solution departs still further from equilibrium conditions. It appears that the composition of the solid follows a 'non-equilibrium' solidus line $YY_2\ Y_5\ Y_4$ shown dotted in **Fig.** Under equilibrium cooling, the solidification should be complete at however, since the average composition of the solid solution at this temperature is and has not become equal to the average composition of the alloy, some liquid must be present in the alloy (which can be calculated by using lever rule with lever length of $X_3\ Y_5$ and fulcrum at Y_3).

The solidification is completed at T_3 as at this temperature the composition of the solid solution Y_4 coincides with the alloy composition (X). The last traces of liquid to solidify have the composition X_4, much richer in copper than obtained under equilibrium conditions. Faster the rate of cooling, the greater is the composition range in the solidified alloy, i.e., there is an increased temperature range over which liquid and solid are present, and last freezing occurs at a much lower temperature than predicted by phase diagram. This solidi- fying liquid is much richer in low melting metal (here copper). The real microstructure of the alloy may differ substantially from the equilibrium structure.

Coring takes place not only in an isomorphorous system like Cu-Ni having complete solid solubility, but almost in all equilibrium diagrams exhibiting certain ranges of solidification. Greater is the gap between liquidus and solidus, more pronounced is the coring, which becomes still intense if the temperatures of freezing of alloys are low.

Though diffusivity of both types of atoms at such temperatures is important, but normally it is very slow. The process of diffusion at low temperatures is very slow, more so because the number of vacancies, which aid diffusion, decrease exponentially with the drop of temperature. That is why, cast tin-bronzes are invariably found cored even the commercial castings of brasses and stainless steels are cored.

The problem of coring can be solved by one of the following methods

1. **Use of Slow Cooling Rates during Solidification of the Alloys:**

   Slow, or almost equilibrium cooling rates prevent the formation of coring because then, enough time is available for the diffusion to occur to homogenise the solid phase. But this method is normally not adopted commercially, because slow cooling rates produce coarse-grained castings, which develop inferior properties.

As more time is needed, the productivity decreases. Moreover slow cooling rates may not be practically feasible if a casting has been designed to be produced, say by chill-casting method. Even sand-casting method is fast enough to give coring.

2. Homogenisation of Cored Castings

Homogenisation is a prolonged annealing treatment at a temperature high enough so that diffusion within the alloy is relatively rapid, but still safely below the depressed solidus, so that burning of the alloy does not occur. Grain boundary regions will melt first in as much as they are richer in low-melting component. This produces a sudden loss in mechanical integrity due to the thin-liquid film that separates the grains. For example, a 70% Ni 30% Cu alloy casting must be heated below T_3 temperature **(Fig.),** below the depressed solidus.

If the temperature of homogenising is fixed (looking at solidus temperature in the equilibrium diagram), below T_2 and above T_3, the liquation of the grain boundaries occurs, called 'burning', impairing the shape and physical properties of the casting.

A burnt alloy is permanently damaged, because oxidation occurs at the grain boundaries. The alloy cannot be salvaged by any heat or and mechanical treatment. However, over-heated alloy, due to heating below but very close to depressed solidus, which shows decreased ductility and toughness, can be salvaged by proper heat, or and mechanical treatment.

The time required to homogenise a given cored alloy varies with grain size, extent of coring, temperature of diffusion, diffusion rate at this temperature in the alloy. The homogenising time can in some cases be reduced by first cold-working and then doing homogenising annealing.

As recrystallisation occurs during annealing and recrystallisation increases a diffusion rate. More important is that cold working reduces interdendritic distance, that is, the distance through which atoms have to diffuse. Thus, homogenisation is faster. Most hot-worked, or cold-worked and annealed products have homogeneity which approaches the equilibrium state. **Fig. (b)** Illustrates homogenised casting.

Uses of Phase Diagrams:

1. To Predict the Temperature at which Freezing, or Melting Begins, or Ends for any Specific Alloy Composition in an Alloy System:

Draw a vertical line representing the composition of the specific alloy, say X in Fig. 3.39. Its intersections with the solidus (T_2) and liquidus (T_1) indicate the temperature below which, at equilibrium, the alloy is completely solid, and above which, it is completely liquid respectively.

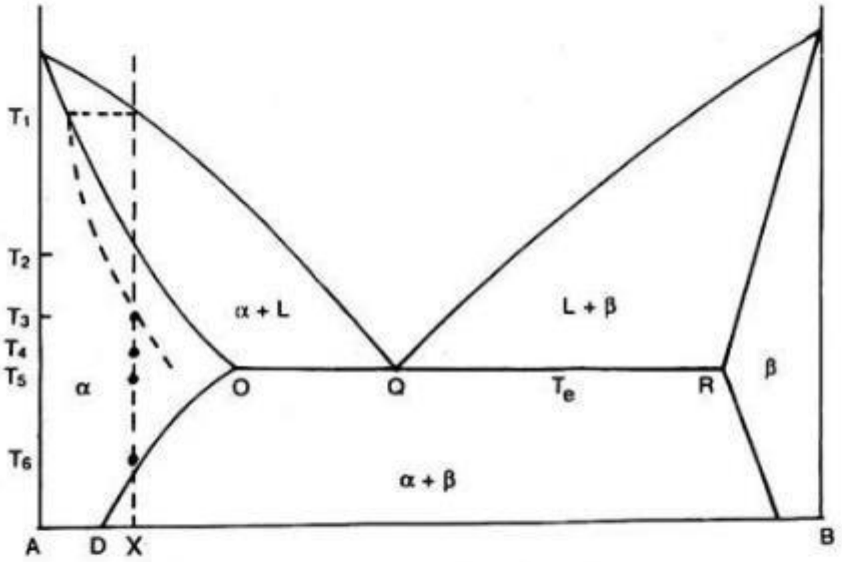


Fig. 3.39. Eutectic with partial solid solubility diagram.

On heating, melting begins at T_2 and is completely liquid above T_1 temperature. If an alloy is to be cast, then, the temperature of the molten alloy has to be higher than T_1. In order to fill the mould completely before freezing blocks of any thin section in it, the alloy should be at least 50°C higher than its liquidus temperature, T_1.

2. **To Predict the Safe Temperature of Working, or Heat Treatment:**

The temperature of hot working, or heat treatment should be less than (at least 30°C) its solidus temperature to give allowances for the impurities present in it and for the temperature fluctuations in the furnace. Heating the alloy above T_2 temperature, causes partial melting, called burning of the alloy.

The 'sweat out' molten metal leaves behind voids whose interior surface gets oxidised (which cannot be welded during hot working). A burnt alloy is good only for scrap. If the alloy is in cored state, then a homogenising temperature above T_3, shall again cause 'burning' of the alloy. A safer temperature is T_4.

If for age hardening, the solutionising temperature T6 is chosen instead of T_6, grain growth of α-phase occurs which cannot be refined later on.

3. **To Determine the Number of Phases, Types of Phases, Composition of Phases Present in any given Alloy at a Specific Temperature:**

The primary function of an equilibrium diagram is to graphically show the extent and boundaries of composition-temperature regions within which an alloy exists as a single phase, or as two-phases. Thus, the fields of the diagram are so labelled that the number and the general nature of the phases present, under equilibrium conditions, in a specific alloy at a particular temperature are indicated on the diagram.

If the point with coordinates of a specific composition and a particular temperature lies in single-phase field, then the alloy is either unsaturated homogeneous liquid, or solid solution with composition as of the alloy.

Such a point in a two-phase field indicates both the phases to be saturated solutions, which could be liquid solutions, solid solutions, or a liquid and a solid solution. If the composition of the alloy is changed at the same temperature but still being within the two-phase field, the number, type, or the composition of the phases do not change but their relative amounts get changed.

A horizontal line in a binary phase diagram indicates a particular temperature and a range of alloy compositions at which three-phases can coexist at equilibrium. Such a line separates either a two-phase field from some other two-phase field which has only one phase in common with it, or a two-phase field from a one-phase field that is different from either of these two phases.

4. To Calculate the -Relative Amounts of the Phases Present in a Two-Phase Alloy:

Lever rule has been used to calculate the amounts of the two phases present in a two-phase field.

5. To Describe the Freezing or Melting of an Alloy:

Cooling of a number of alloys from the molten state to room temperature is described with the help of the equilibrium diagram. During slow heating of the alloy, the changes would be exactly reversed.

6. To Predict the Microstructure of an Alloy at any given Temperature:

It is a major advantage of equilibrium diagrams to make usefully accurate predictions of the microstructure developed in an alloy at a specific temperature, or after an actual or proposed heat treatment. It is more important to a metallurgist as the microstructure controls the properties of an alloy.

For example, the shape of the pure element which is separating with the fall of temperature is quite important. Zinc has HCP crystal structure and strongly anisotropic. When zinc crystals are growing freely in liquid, growth tends to be more along one or another of its close packed directions.

Thus, there develops acicular (needle-shaped) crystals. Zinc in a eutectic mixture does not find the same opportunity for free growth. Thus, it is present as finely distributed phase with another phase in eutectic mixture.

7. To Predict the Possible Heat Treatment which can be given:

The presence of a solvus line in a phase diagram, which if shows decrease of solid solubility (‘OD’ in **Fig**.) with the decrease of temperature indicates the chance of giving precipitation-hardening heat treatment to the alloys in the system. The presence of eutectoid reaction in a phase diagram helps to predict possible heat treatments like annealing, normalising, or hardening.

It is possible to predict what heat treatments are likely to be harmful and must be avoided. For example, if the shape of an alloy is not to be changed by mechanical working, and if no phase transformation occurs during heating, or cooling, then heating such an alloy to high temperatures shall coarsen the grains with resulting inferior properties developed in it. The coarse grains cannot be refined again.

8. To Choose the Composition to Develop Best Properties:

The composition of the alloy can be chosen which gives the best properties. An alloy having maximum solute content indicated by the solubility limit by the solvus line can develop maximum hardness by precipitation hardening. If the solute content is more (or less), the maximum hardness attained is less.

The maximum tensile and yield strengths are developed if a slowly cooled alloy (if alloy is to be used in annealed state) has 100% eutectic structure, or 100% eutectoid structure, if one of the two reactions occurs in the phase diagram, but the ductility is low. Good ductility is present if the amount of these mixtures is minimum, or it should be a single phase alloy. The castability in an alloy system is best at the eutectic point of the system.

Limitations of Phases Diagrams:

Phase diagrams play an extremely useful role in the interpretation of the microstructures developed in alloys, but have several restrictions:

1. Phase diagrams show only equilibrium state of alloys (i.e., under very slow cooling rates), but alloys under normal industrial practice are rarely cooled under equilibrium conditions.
2. Phase diagrams do not indicate whether a high temperature phase can be retained at room temperature by say fast quenching.
3. Phase diagrams do not indicate whether a particular transformation (for example eutectoid transformation) can be suppressed, and what should be the rate of cooling of the alloy to-avoid the transformation.
4. These diagrams do not indicate the phases produced by fast rates of cooling such as martensite is not shown in $Fe-Fe_3C$ phase diagram. These, thus, do not indicate the temperature of start of such transformations (Ms, etc.) and their kinetics of formation.
5. Even under equilibrium conditions, the diagrams do not indicate the character of the transformations. These do not indicate the rate at which the equilibrium shall be attained.
6. The most important limitation is that the diagram gives information only on the constitution of alloys, like the number of phases present at a point, but does not give information about structural distribution of the phases, i.e., does not indicate the size, shape, distribution of the phases, which effect the mechanical properties of the alloys.

The structural distributions of phases are affected by the surface energy between phases and the strain energy produced by the transformation. For example, if the beta phase, in a mixture of alpha and beta, is in small amounts, and is entirely distributed with alpha grains, the mechanical properties shall be largely governed by the alpha phase, but if beta is present around the grain boundaries of alpha, then the strength and ductility of the alloy is largely dictated by properties of beta-phase.

LIMITATION OF Fe-Fe_3C PHASE DIAGRAM

1) Fe-Fe_3C diagram represents behavior of steels under equilibrium conditions, whereas the
2) actual heat treatments of steels are normally under non-equilibrium conditions.
3) The diagram does not indicate the character of transformation of austenite such as to bainite, or martensite.
4) The diagram does not indicate the presence of metastable phases like martensite, or bainite.
5) It does not indicate the temperature of start of martensite Ms or bainite Bs .
6) It does not indicate the kinetics of the transformation of austenite to martensite, bainite or even pearlite.
7) It does not indicate the possibilities of suppressing the pearlitic or bainitic transformations.

IRON – CEMENTITE PHASE DIAGRAM

INTRODUCTION

It is the most important binary system in engineering alloys.

- The Fe-C (or more precisely the Fe-Fe3C) diagram is an important one.
- Iron-cementite diagram is not a true equilibrium daiagram, since equilibrium means no change of phase with time however long it may be. Graphite is more stable form of carbon. Cementite is a metastable phase, which decomposes to graphite if allowed long periods of time. Graphitization, however, rarely occurs in steels and may take years to form. Also the decomposition rate of cementite is very slow. Thus cementite, though a metastable phase, can be taken to be practically stable.
- Fe-Fe_3C diagram even though represents metastable conditions, can be assumed to represent equilibrium state relevant to the behavior of most steels in practice. Fe- Fe_3C diagram is, thus, called as phase diagram.
- Cementite is not a equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.
- The alloys of iron caron system containing 0 to 2.1%C are called as steels. Those containing from 2.1% to 6.7%c are called as cast iron.
- It is interesting to know that iron- carbon alloys exist in different phases in steel and cast iron.

- In steel iron and carbon exists as two separate phase, ferrite and cementite.
  a) **Ferrite** is a solid solution of carbon of carbon in α-iron with negligible amount of carbon.
  b) **Cementite** is an intermettalic called iron-carbide (Fe_3C). Cementite is a stable phase in steels only. But not stable in cast iron under all condition. Hence cementite is called a metastable phase.

Phase diagram of iron carbon system

In this diagram, the carbon composition (weight percent) is plotted along the horizontal axis and temperature along the vertical axis. The diagram shows the phase present at varies temperature for slowly cooled iron-carbon alloys carbon with carbon content up to 6.7%C.

This diagram gives us information about the following points.

a) Solid phases in the phase diagram.
b) Invariant reaction in the phase diagram
c) Critical temperature
d) Eutectoid, hypereutectoid and hypereutectoid steels.

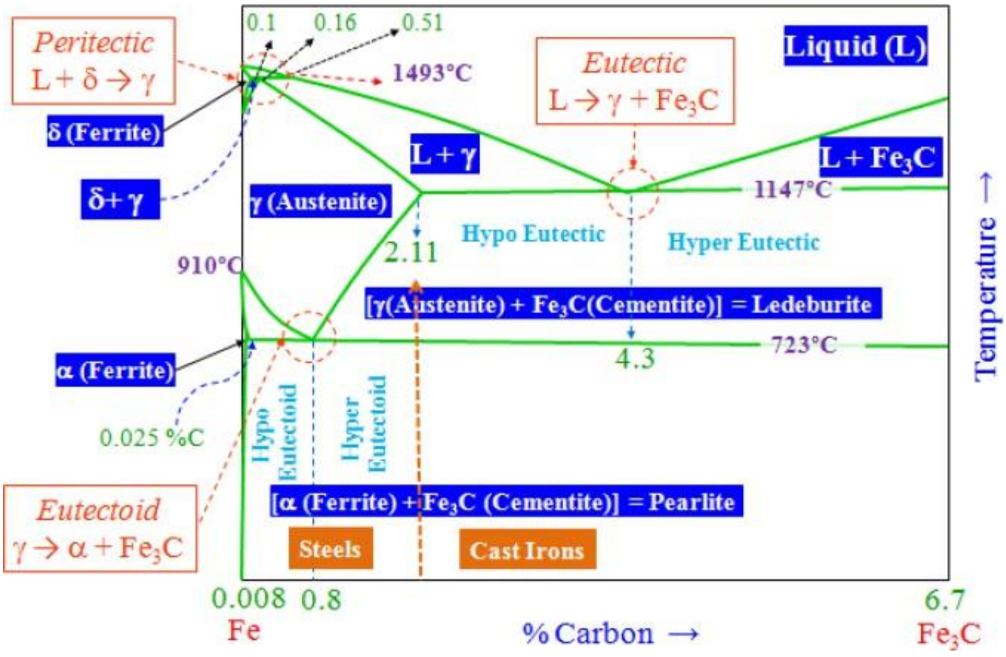


Fig. Iron-cementite diagram labelled in general terms

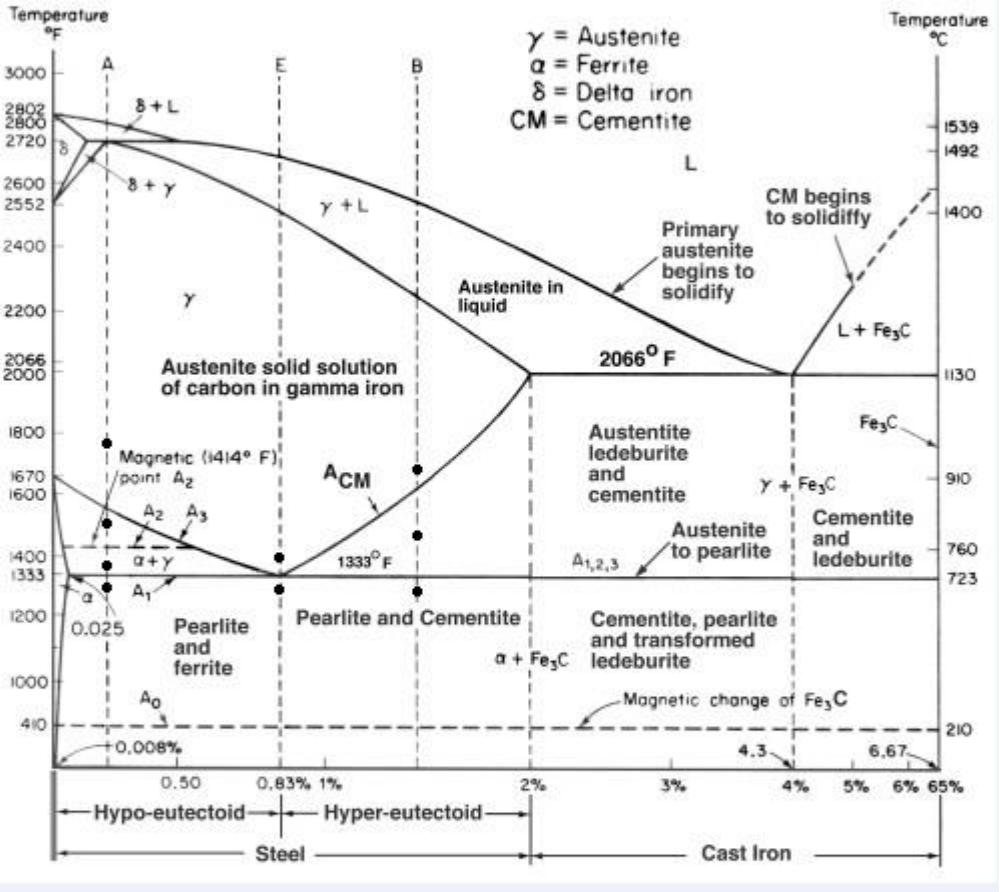
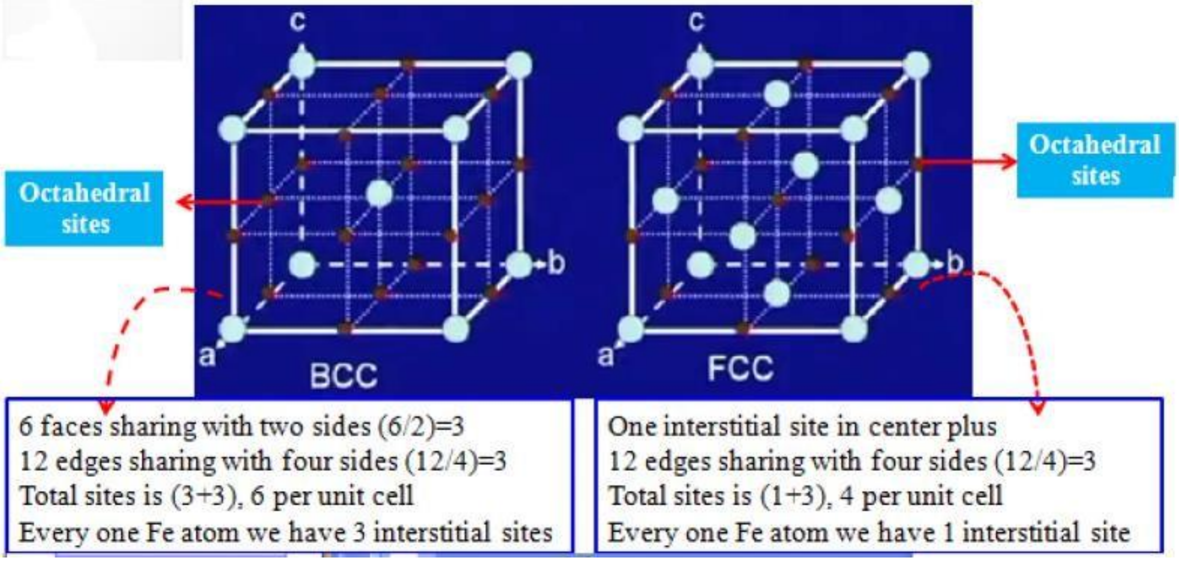


Fig. Iron-cementite diagram labelled in general terms

Carbon Solubility in Iron

Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice?

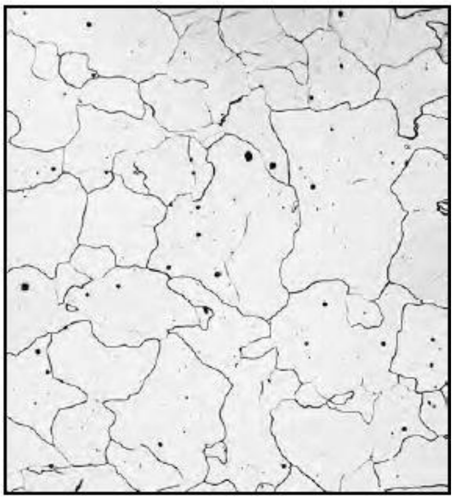


6 faces sharing with two sides (6/2)=3
12 edges sharing with four sides (12/4)=3
Total sites is (3+3), 6 per unit cell
Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
12 edges sharing with four sides (12/4)=3
Total sites is (1+3), 4 per unit cell
Every one Fe atom we have 1 interstitial site

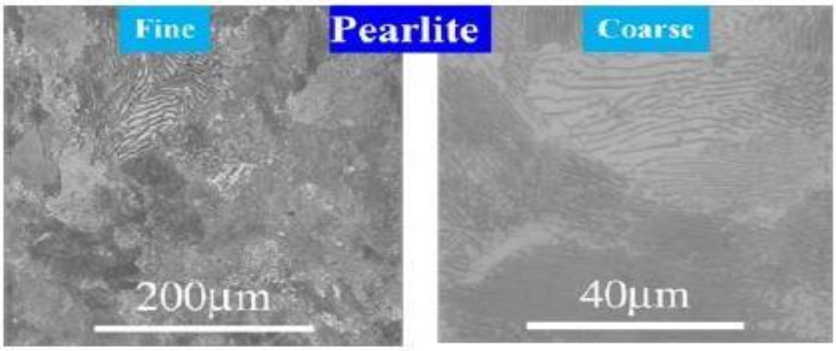
SOLID PHASES IN IRON-IRON CARBIDE PHASE DIAGRAM.

- **α ferrite**



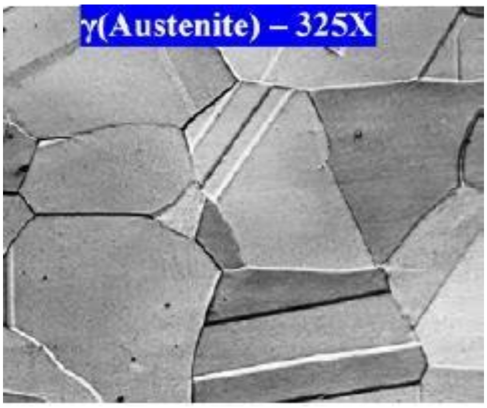
  a) It is defined as interstitial solid solution of carbon in α iron which is BCC structure.
  b) At 0.008%of carbon it corresponds to α iron.
  c) **Solubility of carbon**: maximum solubility of carbon in α ferrite is 0.02 % at 723^0 C
  d) The solubility of carbon in α ferrite decreases with decrease in temperature until it is about 0.008%C at 0^0c.
  e) The $\boldsymbol{\alpha}$ ferrite is soft ductile and highly magnetic
  f) Its density is 7.88gm/cm^3 and tensile strength is about 310MP.
  g) Softest phase in Fe-Fe3C phase diagram.. less strength and High ductility

- **Pearlite (α + Fe3C)**
  a) Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723ºC on very slow cooling.
  b) It is very fine platelike or lamellar mixture of ferrite and cementite. The fine fingerprint mixture called pearlite is shown in below figure.
  c) Tensile strength – 120,000 psi or 825 Mpa
  d) Elongation – 20 percent in 2 in.
  e) Hardness – HRC 20, HRB 95-100, or BHN 250-300
  f) Soft Phase than Austenite but posses better strength than Ferrite



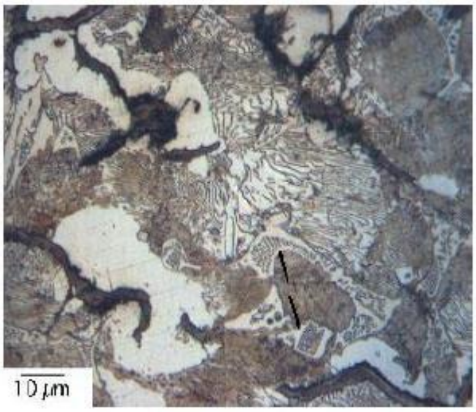
- **Austenite (γ)**
  a) It is defined as the interstitial solid solution of carbon in $\boldsymbol{\gamma}$ **iron** which is of FCC structure.
  b) Its average no of atoms equal to 4
  c) It is nonmagnetic in nature.
  d) **Solubility of carbon:** In austenite solid solubility of carbon is much greater than α ferrite. The solubility of carbon in austenite reaches a maximum of 2.11% at 1148^0 C and then decreases to 0.8% at 723^0c
  e) Tensile strength – 150,000 psi or 1035 Mpa

f) Toughest phase among all… Strength along with optimum Ductility
g) Elongation – 10% in 2 in.
h) Hardness - 40 HRC and Toughness is high.



Ledeburite (γ+ Fe_3C)

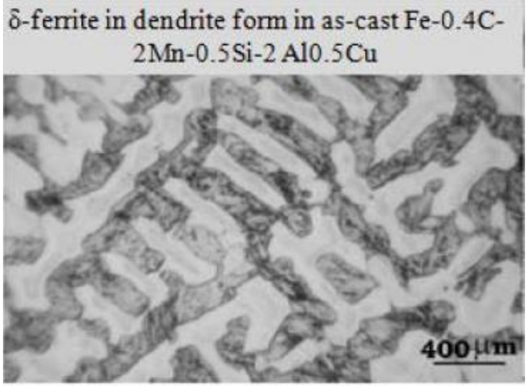
a) Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3%C and is formed at 1147ºC
b) Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
c) Not stable at room temperature.



Ferrite (δ)

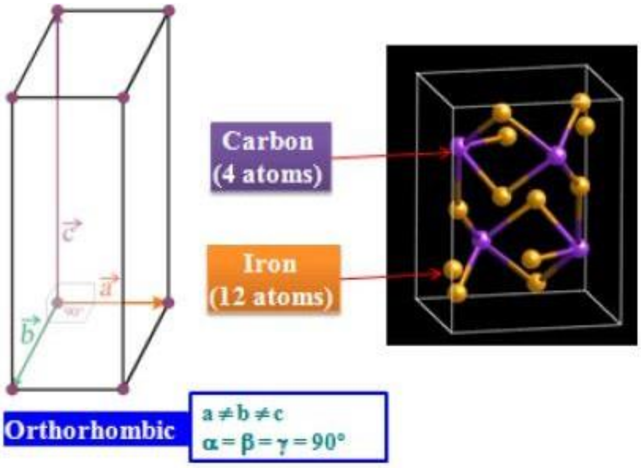
a) Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89Å) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between 1394- 1539°C.

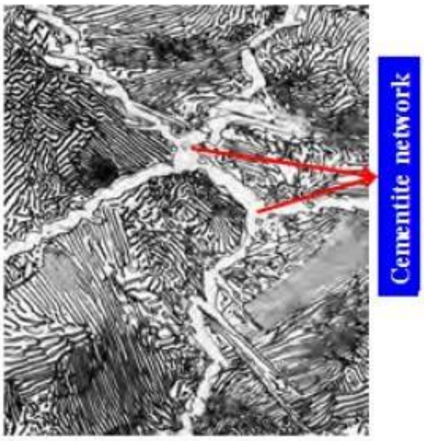
b) This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel especially duplex stainless steel.


δ-ferrite in dendrite form in as-cast Fe-0.4C-2Mn-0.5Si-2 Al0.5Cu

Cementite

a) It is an intermettalic compound of iron and carbon having a maximum carbon solubility of 7.67% in it
b) Its chemical formula is Fe_3C
c) Crystal structure is orthorhombic with 12 iron atoms and 4 carbon atoms per unit cell
d) Typically hard and brittle interstitial compound
e) The hardest structure that appears on the Fe-C diagram.
f) Density is 7.6gm/cm^3
g) It is magnetic below 210^{0}C





If C added to Fe it will produce Fe₃C (iron carbide) also known as cementite which exhibits more hardness and brittleness.

1. If the C content increase implies produces more iron carbide volume implies that plane exhibit more hardness. $\boxed{hardness_{Fe} < hardenss_{steel} < hardness_{cast\ iron}}$

$$\boxed{hardness_{Fe} < hardenss_{low\ C\ steel} < hardness_{midium\ C\ steel} < hardness_{high\ c\ steel} < hardness_{cast\ iron}}$$

2. If carbon content increases, hardness increases implies fracture decreases

$$\boxed{FT_{Fe} > FT_{LCS} > FT_{MCS} > FT_{HCS} > FI_{CI}}$$

3. If the carbon content increases hardness increases implies machinability will become difficult, therefore

$$\boxed{m/cbility_{Fe} > m/cbility_{LCS} > m/cbility_{MCS} > m/cbility_{HCS} > m/cbility_{CI}}$$

4. If carbon content increases then free iron decreases implies difficult to undergo corrosion implies corrosion resistance increases.

$$\boxed{CR_{Fe} < CR_{LCS} < CR_{MCS} < CR_{HCS} < CR_{CI}}$$

5. If the carbon content increases free iron decreases implies weldability is different

$$\boxed{weldability_{Fe} > weldability_{LCS} > weldability_{MCS} > weldability_{HCS} > weldability_{CI}}$$

These reactions which occur at some temperature during heating and cooling.

Peritectic reaction

- It occurs at 1492^{0}C at 0.18% carbon content where a mixture of liquid and solid converts into another solid phase upon cooling

$$\boxed{\delta + L \overset{\nabla\,\&\,\Delta}{\Leftrightarrow\!\!\Longrightarrow} \gamma}$$

- It is thermodynamics reversible reaction

$$\boxed{s_1 + L \to S_2}$$

S₁ and S₂ are solid solution

$$\boxed{\delta_{Fe} + L \xrightarrow{\nabla} \gamma_{Fe}}$$

Eutectic reaction

- It occurs at 1147^{0}C at 4.3% carbon content.

$$\boxed{L \overset{\nabla\,\&\,\Delta}{\Leftrightarrow\!\!\Longrightarrow} \gamma + Fe_3C}$$

$$\boxed{L \to S_2 + S_3}$$

- The mixture of $\gamma + Fe_3C$ formed in eutectic reaction is called ledeburite.
- This transformation is called as eutectic phase transformation.

Eutectoid reaction

- It occurs at 723^{0}C at 0.8% carbon content. It is also called as decomposition reaction because no liquid phase is involved. 723^{0}C and 0.8%C are called as eutectoid temperature and eutectoid composition.

$$\boxed{\gamma \overset{\nabla \,\&\Delta}{\Leftrightarrow\Longrightarrow} \alpha + Fe_3C}$$

- The mixture of $\alpha + Fe_3C$ formed is eutectoid reaction is called as Pearlite.
- At eutectoid point 3 phases will co-exist in equilibrium simultaneously.
- Carbon diffuses through the lattice structure and produces alternate plate α and Fe_3C. This structure is called pearlite and it is produced by diffusion.
- So pearlite is not having orthorhombic structure phase, it is a phase mixture of a α and Fe_3C . α is having BCC structure and Fe_3C is having orthorhomic structure.
- Pearlite is the eutectoid decomposition product of austenite.

CRITICAL TEMPERATURE LINE AND THEIR SIGNATURE.

- The horizontal line passing through 210^{0}C is A_0 line
- The horizontal line passing through 723^{0}C is A_1 line.
- The horizontal line passing through 768^{0}c is A_2 line.
- The line going on top of $(\alpha + \gamma)$ boundary is A_3 line.

A_1 line.

It occurs at 723^{0}C

It is called as lower critical temperature line. This line signifies Pearlite to austenite transformation on heating.

A_2 line

It occurs at 768^{0}c.

It is also called as Curie point temperature line.

This line signifies magnetic to non magnetic transformation on heating.

Carbon content has no effect on Curie point temperature in iron carbon system of alloys

A_3 line (723^0-910^{0}C)

It is called as upper critical temperature line for hypoeutectoid steels.

A_3 line signifies the completion of ferrite to austenite transformation.

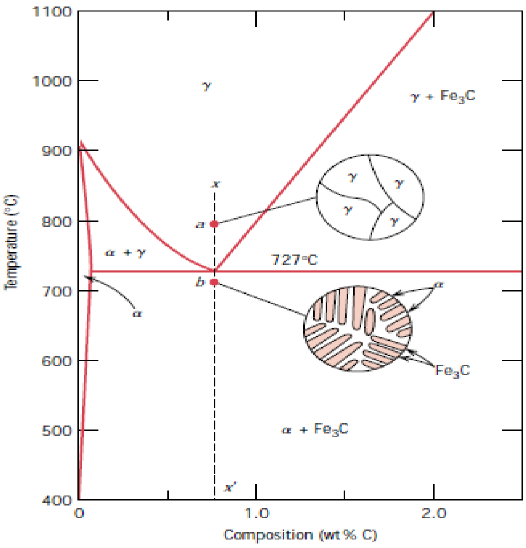
A_{cm} line (723^0-1147^{0}C)

It is called as upper critical temperature line for hypereutectoid steel.

A_{cm} line signifies the completion of cemntite transformation into austenite.

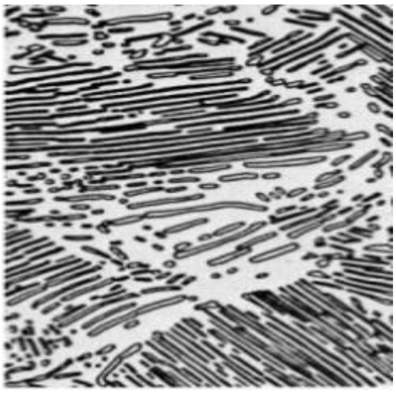
MICROSTRUCTURES INVOLVED IN EUTECTOID MIXTURE

Eutectoid reaction



- Phase changes that occur upon passing from the γ region into the α+ Fe_3C phase field.
- Consider, for example, an alloy of eutectoid composition (0.8%C) as it is cooled from a temperature within the γ phase region, say 800^0C – that is, **beginning at point 'a'** in figure and moving down vertical xx′. Initially the alloy is composed entirely of the austenite phase having composition 0.8 wt.% C and then transformed to α+ Fe_3C [pearlite]

MICROSTRUCTURE FOR EUTECTOID STEEL

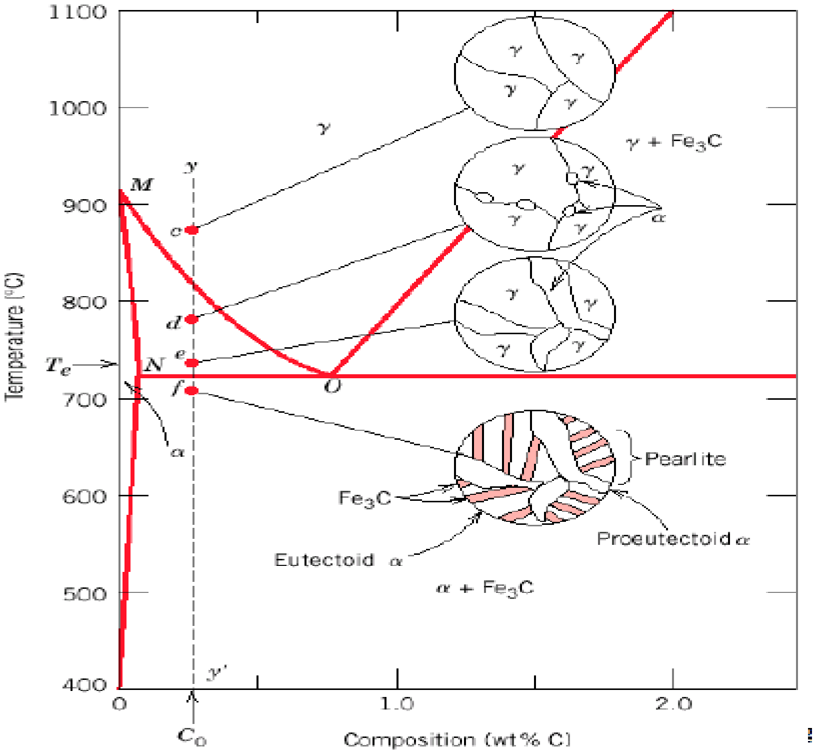


- The microstructure for this eutectoid steel that is slowly cooled through eutectoid temperature consists of alternating layers or lamellae of the two phases α and Fe_3C
- The pearlite exists as grains, often termed "colonies"; within each colony the layers are oriented in essentially the same direction, which varies from one colony to other.
- In the micrograph, The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark.

HYPOEUTECTOID REGION

- Hypo eutectoid region – 0.008 to 0.8 %C
- Consider vertical line yy′ in figure, at about 875^0C, point c, the microstructure will consist entirely of grains of the γ phase.
- In cooling to point d, about 775^0C, which is within the α+γ phase region, both these phases will coexist as in the schematic microstructure Most of the small α particles will form along the original γ grain boundaries.
- Cooling from point d to e, just above the eutectoid but still in the α+γ region, will produce an increased fraction of the phase and a microstructure similar to that also shown: the particles will have grown larger.
- Just below the eutectoid temperature, at point f, all the γ phase that was present at temperature e will transform pearlite. Virtually there is no change in α phase that

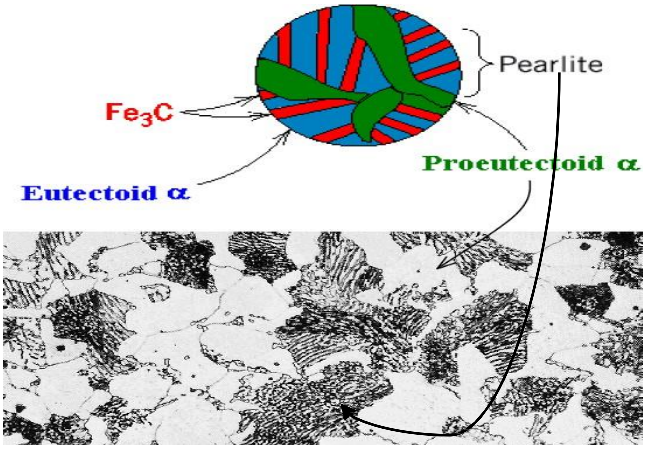
existed at point e in crossing the eutectoid temperature – it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies.



- Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the α+γ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, is termed proeutectoid (meaning pre- or before eutectoid) ferrite.

Microstructure of hypoeutectoid steel

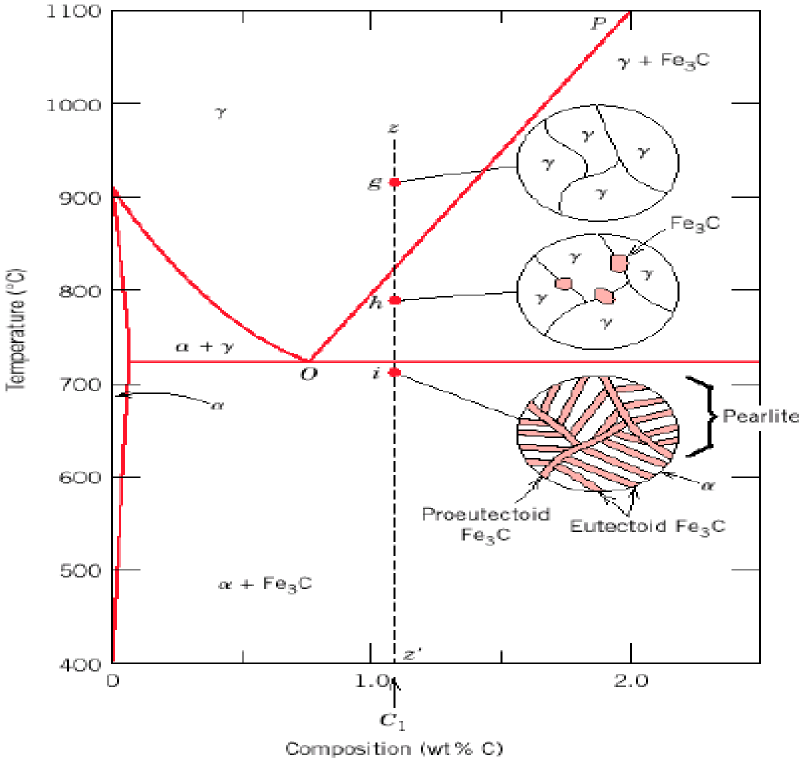
- Hypoeutectoid alloys contain proeutectoid ferrite (formed above the eutectoid temperature) plus the eutectoid perlite that contain eutectoid ferrite and cementite.



HYPER EUTECTOID REGION

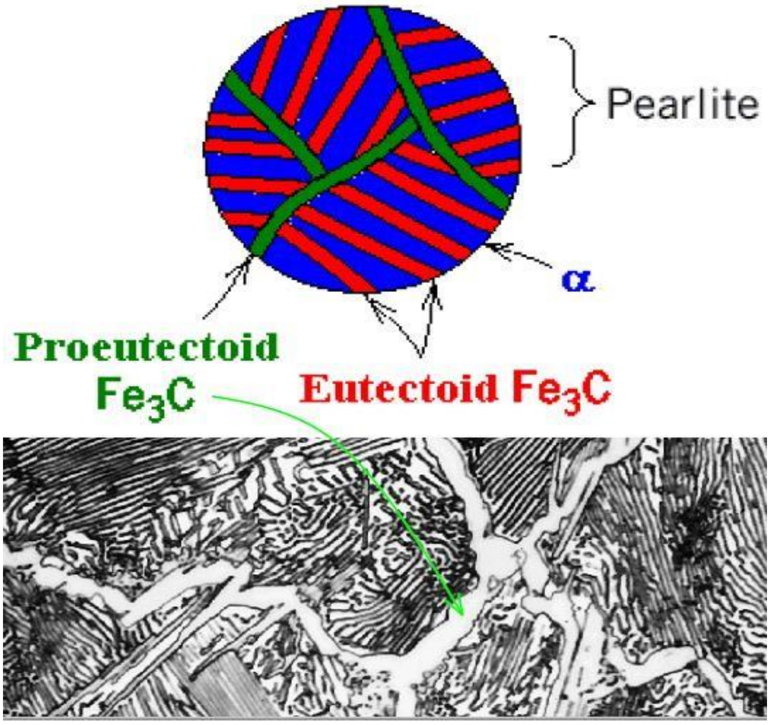
- Hyper eutectoid region – 0.8 to 2.1 %C
- Consider an alloy of composition C_1 in figure that, upon cooling, moves down the line zz′. At point g only the γ phase will be present and the microstructure having only gamma grains.

- Upon cooling into the γ+ Fe3C phase field – say to point h – the cementite phase will began to form along the initial γ grain boundaries, similar to the α phase in point d. this
- Cementite is called *proeutectoid cementite* that which forms before the eutectoid reaction.
- As the temperature is lowered through the eutectoid to point I, all remaining austenite of eutectoid composition is converted into pearlite; thus the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.

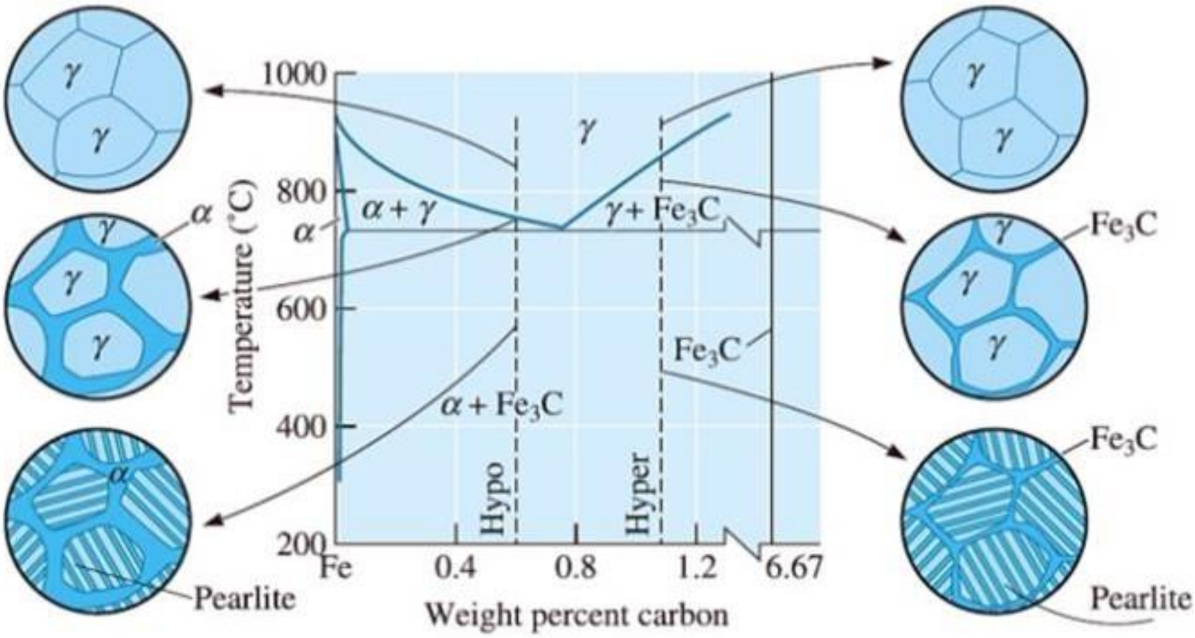


Microstructure of hypereutectoid steel

Hypereutectoid alloys contain proeutectoid cementite (formed above the eutectoid temperature) plus perlite that contain eutectoid ferrite and cementite.



The evolution of the microstructure of hypoeutectoid and hypereutectoid steels during cooling in relationship to the fe-fe_3C



Application of Lever rule in Fe-Fe3C phase diagram

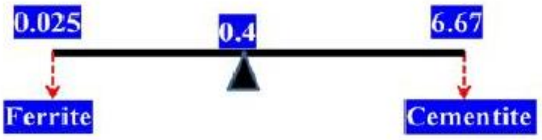
Solved Example

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following:

a) The amount of Fe_3C, ferrite (α) and pearlite

b) The amount of pearlite and proeutectoid ferrite (α)

a) The amount of Fe_3C and ferrite (α)



$$\text{Percentage of } Fe_3C = \frac{0.4-0.025}{6.67-0.025} * 100$$

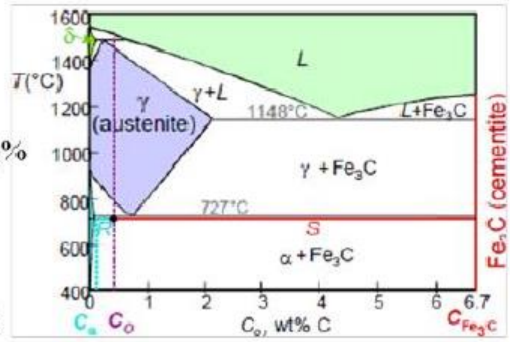
Percentage of Fe_3C in 0.4 %C steel is 5.64 %

Percentage of Ferrite (α) in 0.4 %C steel = (100- 5.64)%

Percentage of ferrite in 0.4 %C steel = 94.36%

or

$$\text{Percentage of ferrite} = \frac{6.67-0.4}{6.67-0.025} * 100 = 94.36\%$$



b) Phase fraction of pearlite and proeutectoid ferrite (α)

$$\textit{Percentage of pearlite} = \frac{0.4-0.025}{0.8-0.025} * 100$$

Percentage of pearlite = 48 %

Percentage of proeutectoid ferrite (α) in 0.4 %C steel = (100- 48)%

Percentage of proeutectoid ferrite (α) = 52 %

or

$$\textit{Percentage of proeutectoid ferrite} = \frac{0.8-0.4}{0.8-0.025} * 100 = 52\%$$

IRON GRAPHITE DIAGRAM

The stable diagram for Fe-C alloys is iron-graphite diagram is illustrated as shown in figure with dashed lines referring to precipitation of graphite and the solid lines to that of cementite. Graphite, being the stable phase may form as a result of direct precipitation from liquid or by the decomposition of previously formed cementite process called graphitisation. Primary graphite starts to solidify at temperatures represented by line CD’. The eutectic, now of austenite and graphite forms at 1153^{0}C. Secondary graphite separates out along the line Q'U' and eutectoid reaction occurs at 738^0C. The eutectoid mixture now consists of ferrite + graphite. Iron-graphite system is of importants far cast irons which are discussed separately. Silicon presence causes rapid graphitisation. If graphitisation is complete, the iron-graphite equilibrium diagram adequately represents the actual structures. When partial decomposition of iron carbide occurs, both Fe-Fe_3C diagram and iron-graphite diagram must be used.

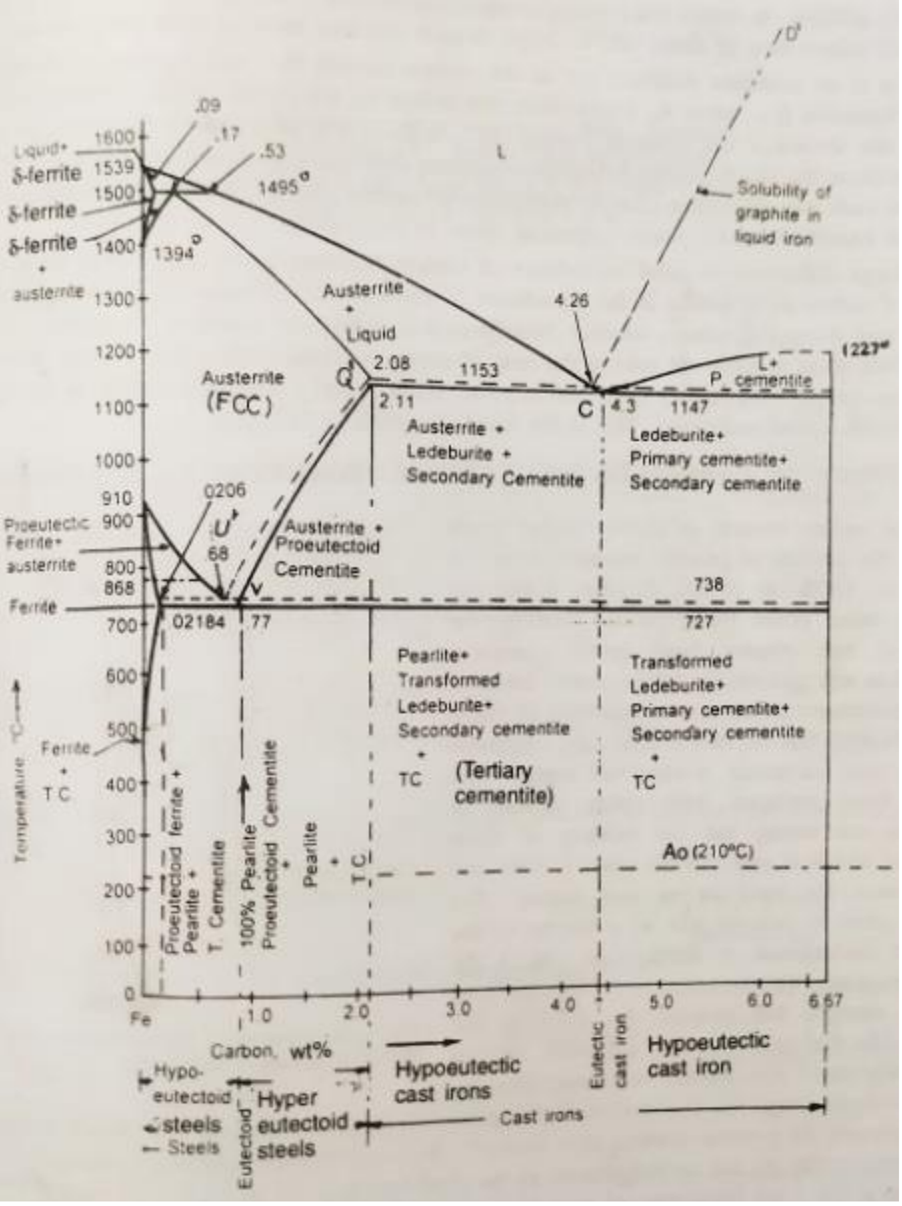
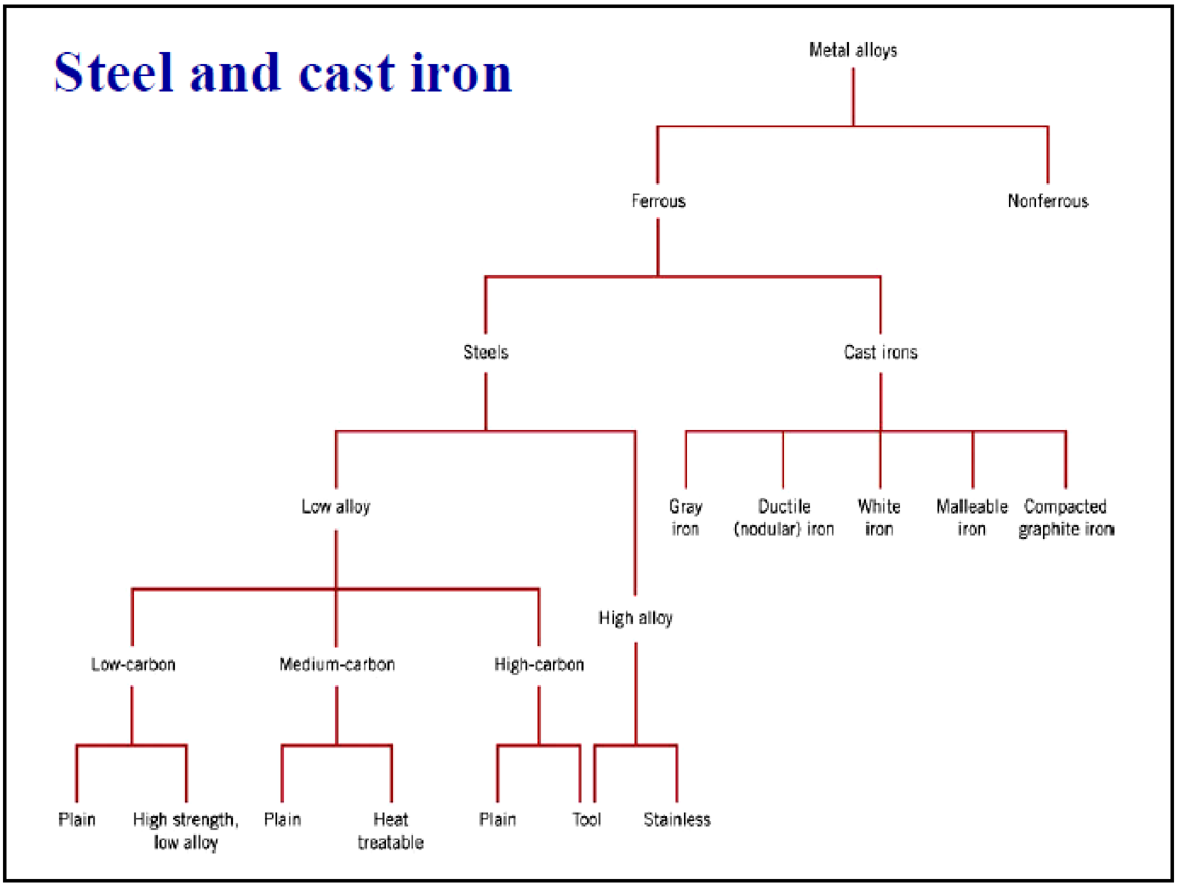


Fig. Iron-graphite equilibrium diagram

MICROSTRCURE AND PROPERTIES OF DIFFERENT ALLOYS



Stainless Steels

Stainless Steels are a large group of special alloys developed primarily to withstand corrosion. These steels contain chromium in excess of 12% by weight which imparts "stainless" characteristics to iron alloys.

AISI Grades of stainless steels:

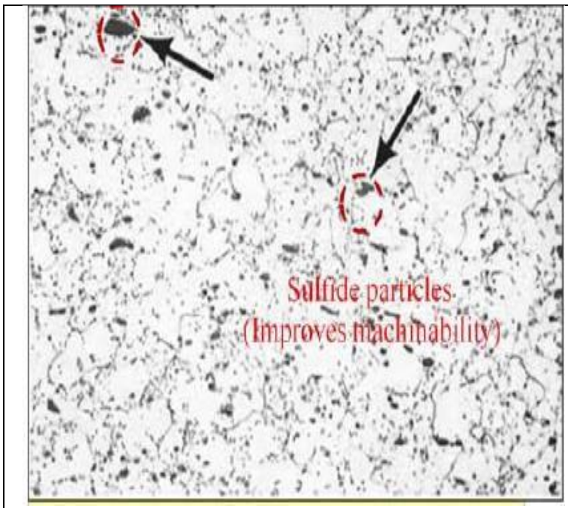
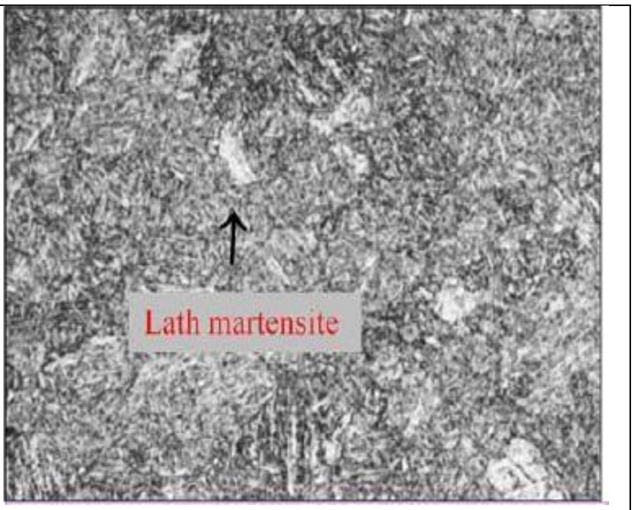
Series Designation	Groups
2xx	Chromium-Nickel-Manganese; Nonhardenable, Austenitic, Nonmagnetic
3xx	Chromium-Nickel; Nonhardenable, Austenitic, Nonmagnetic
4xx	Chromium; Hardenable, Martensitic, Magnetic
4xx	Chromium; Nonhardenable, Ferritic, Magnetic
5xx	Chromium; Low chromium; Heat-Resisting

Martensitic Stainless Steel

- These are primarily straight chromium steels with 11.5 to 18% Cr, 0.15% C, 1.25% Mn, and 1%Si.
- Common examples are 403, 410, 416, 420, 440A, 501 & 502 (AISI grades).
- Used for turbine blades and corrosion resistant applications.

Heat Treatment

- Process Annealing → 650 - 760 o C, increase ductility and machinability
- Austenitizing → 925 -1065 o C followed by oil quenching or air cooling, increase corrosion resistance and strength

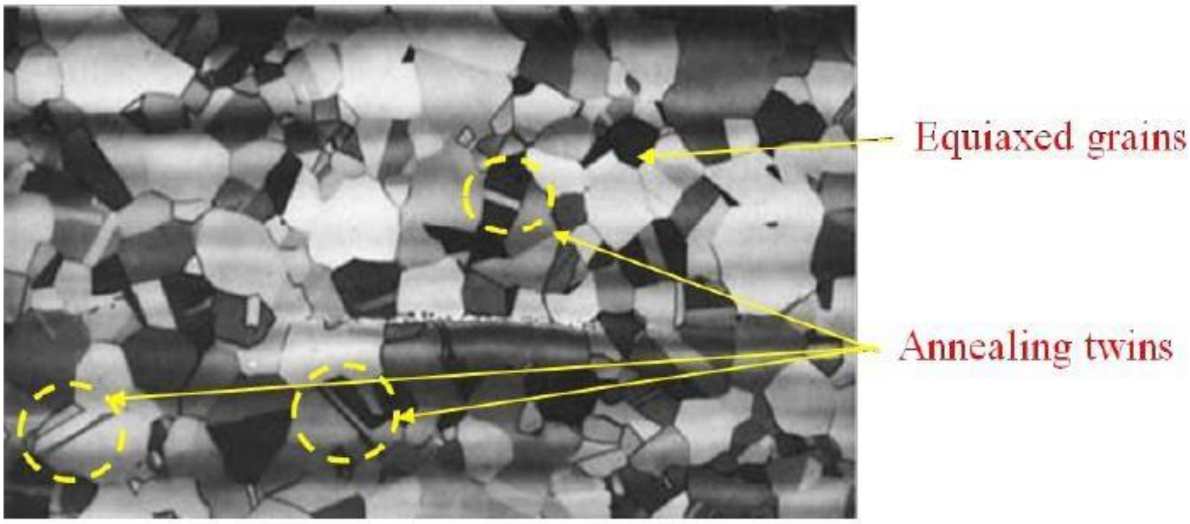
	
Microstructure of annealed 416stainless steel etched with Vilella's reagent	Microstructure of hardened type 403 stainless steel etched with 4% picral - HCL

Austenitic Stainless Steel

- These are chrome-nickel (3xx type) or chrome -nickel- manganese(2xx type) alloys.
- Total content of Ni and Cr is at least 23%.
- Difficult to machine but can be improved by addition of selenium of sulfur.
- Best high temperature strength and scaling resistance. Hence shows best corrosion resistance
- Used in chemical industry and for household and sanitary fittings.

Heat Treatment

- Cold working causes work hardening but hot working can easily be done.
- Annealing at high temperatures → Recrystallization and carbide solution
- Solution treatment → Dissolution of chromium carbides



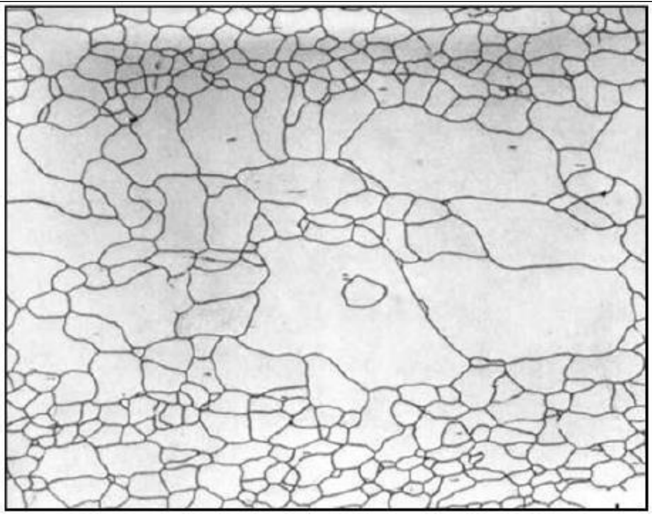
Microstructure of annealed type 316L austenitic stainless steel etched in 20% HCL, 2% NH4FHF, 0.8%PMP

Ferritic Stainless Steel

- These are primarily straight chromium steels with 14 to 27% Cr. Carbon is restricted both to maintain high toughness and ductility and to prevent austenite formation (As carbon expands the gamma loop)
- These steels can be cold formed easily and hence are used for deep drawn parts such as vessels for food and chemical industries and for architectural and automotive trim.

Heat Treatment

- Can be cold or hot worked.
- Annealing → 760 - 966oC, Recrystallization of cold-worked structures → achieves maximum softness, ductility and corrosion resistance.



Single-phase microstructure of an annealed ferritic stainless steel

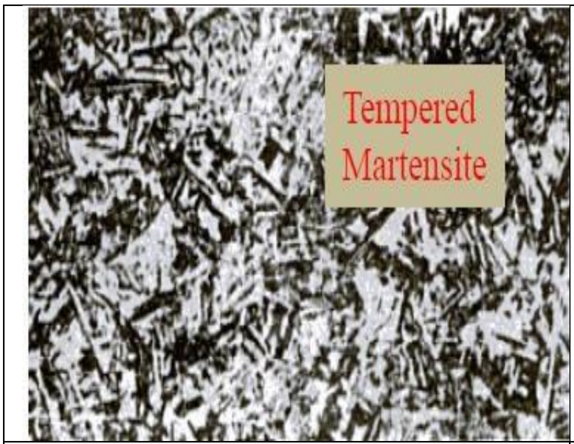
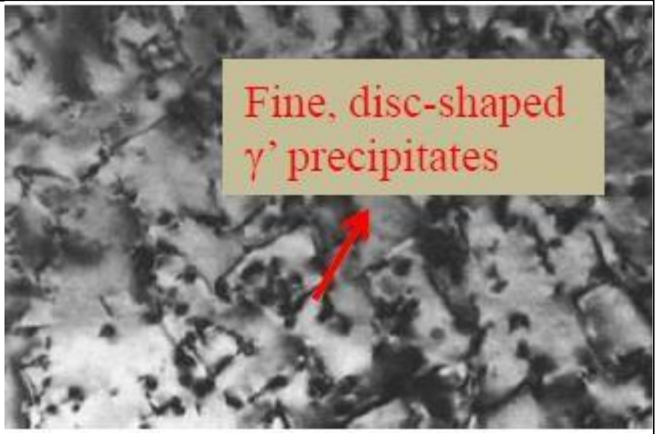
Fig. Microstructure of annealed ferritic stainless steel containing 26%Cr and 1%Mo etched electrolytically in 60% HNO_3-H_2O

PRECIPITATION HARDENED STAINLESS STEELS

- Contains Mo, Nb, Ti or Al in addition to basic composition. Ni content is generally less to reduce the stability of austenite.
- Common Grades are: 630/17-4 PH (17% Cr, 4%), 631/17-7 PH,15-5 PH etc.
- Provides high strength and toughness while maintaining the corrosion resistance of stainless steels. Also shows excellent elevated-temperature performance and are widely used in the aerospace industry.
- Strengthening is accomplished by the precipitation of intermetallic compounds such as Ni3Al in austenitic or ductile low-carbon martensitic matrices.

Heat Treatment

- These steels are usually solution – annealed followed by air cooling with the resultant transformation of austenite to martensite. After forming ageing (480-620 o C) is carried out to cause precipitation effect.
- More is the ageing temperature, better is the ductility, toughness and resistance to stress corrosion.

	
MICROSTRUCTURE OF 17-4PH ALLOY SOLUTION TREATED AT 10380C AGED AT 4950C	MICROSTRUCTURE OF AN AGED AUSTENITIC PRECIPITATION- HARDENING STAINLESS STEEL.

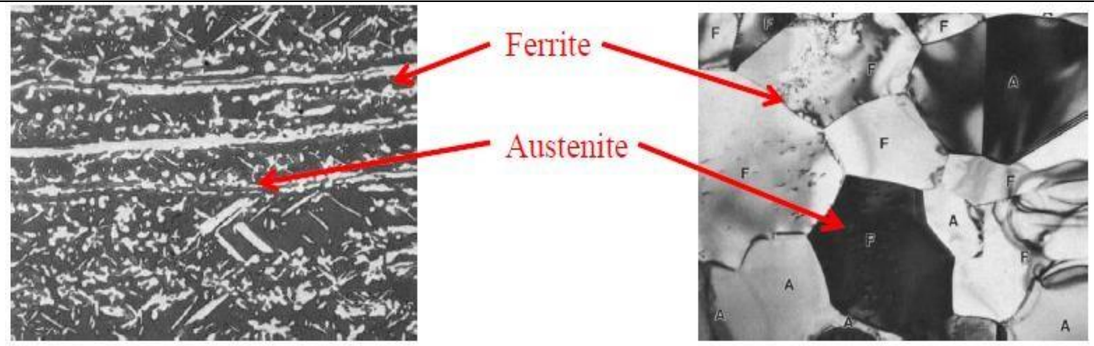
DUPLEX STAINLESS STEELS

- Duplex stainless steels by design have nearly balanced amounts of ferrite and austenite.
- Compositions of duplex stainless steels range from 17 to 30% Cr and 3 to 13% Ni.
- Molybdenum, a ferrite stabilizer, is also typically present.
- Shows higher strength and better resistance to stress corrosion. Decrease in ductility at low temperature is compensated by increased rates of strain hardening due to strain-induced transformation of austenite to martensite

- Used in petrochemical industry (for handling wet an dry CO_2, sour gas and oil products), heat exchanges (welded tubing), chemical, industries etc.

Heat Treatment

- Thermomechanical processing is accomplished in the two-phase ferrite austenite fields.
- Amounts of ferrite and austenite formed during hot working or annealing are a function of temperature. Higher temperatures produce larger amounts of ferrite. Hence, hot working temperatures must be kept between 1000 - 1200^{O}c

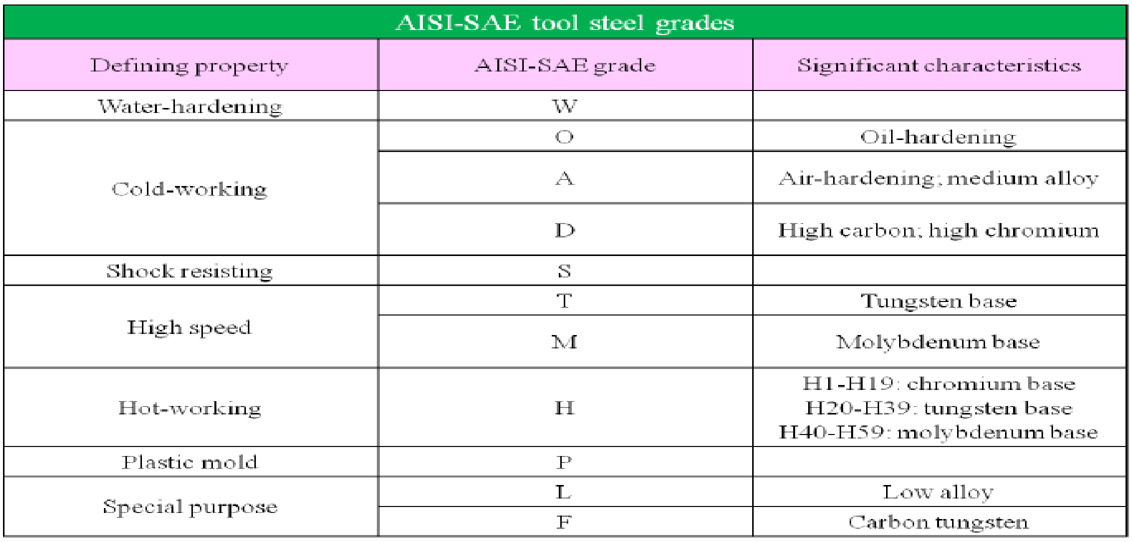


Microstructure of duplex stainless steel 7Mo-Plus	Microstructure of cold worked and annealed duplex stainless steel Al 2205

TOOL STEEL

- Tool steel refers to a variety of carbon and alloy steels that are particularly well- suited to be made into tools.
- Characteristics include high hardness, resistance to abrasion (excellent wear), an ability to hold a cutting edge, resistance to deformation at elevated temperatures (red-hardness).
- Tool steels are generally used in a heat-treated state.

Table -6. AISE-SAE tool steel grades



AISI-SAE tool steel grades		
Defining property	AISI-SAE grade	Significant characteristics
Water-hardening	W	
Cold-working	O	Oil-hardening
	A	Air-hardening; medium alloy
	D	High carbon; high chromium
Shock resisting	S	
High speed	T	Tungsten base
	M	Molybdenum base
Hot-working	H	H1-H19: chromium base H20-H39: tungsten base H40-H59: molybdenum base
Plastic mold	P	
Special purpose	L	Low alloy
	F	Carbon tungsten

- Shock resisting tool steels → Intended for applications requiring toughness and resistance to shock-loading such as hammers, chisels, punches, driver bits and others.
- Water hardening tool steels → Shallow hardened and relatively low resistance to softening. They are suitable for woodworking tools, hand-metal cutting tools such as taps and reamers and cutlery.
- Steels for Room Temperature Use (Classified according to their quenching media)
- Water hardened grades (W) → Plain carbon steels with 0.6-1.0 %C. These have a low hardenability, ie., martensite only to a depth of 0.5 in. V can be added (forms V_4C_3)to improve the hardness and wear resistance of these steels.
- Shock resistant grades (S) → Contain small amounts of Cr or Mo and are quenched in oil. They have lower C contents (0.5%) to improve impact strength.
- Oil hardened grades (O) → Small percentages of Cr and W with 0.9 %C. The have medium hardness and are used to short run cold forming dies.
- Air hardening grades (A) → Greater amounts of Cr and Mo and 1 %C. Used for complicated shapes and thread rolling. Mo and W are relatively expensive so they are only added in small amounts to give much improved hardenability.
- High carbon, high Cr grades (D grade) → 12 %Cr and 1.5-2.25 %C are extremely wear resistant and used for long run dies and for gauges. Chromium is a relatively low cost addition for increasing hardenability with the excess Cr, $Cr_{23}C_6$ is also formed, which improves wear resistance.

Steels for High Temperature Use

- **Chromium hot working steels (H grades)** → 5-7 % Cr, 0.4-1.0% V, 1.5-7.0% W, 1.5% Mo, 0.35% C. Medium hot working for Mg and Al extrusion die-casting dies.
- **Tungsten hot working steels (H)** → 9.5-12 % W, 3.5-12.0 % Cr, 0.35 % C. Hot working, extrusion and forging dies for brass, nickel and steel.
- **Tungsten high speed steel (T)** → 12-18 % W, 4.0 % Cr, 1-5 % V, 0.7-1.5 % C. Original high speed (HS) cutting steel with excellent HT wear resistance.
- **Molybdenum HS steel (M)** → 3.5-8.0 % Mo, 1.5-6.0 % W, 4.0 % Cr, 1-5 % V, 5 % Co, 0.8-1.5 % C. Used for 85% of US cutting steels before the advent of ceramic cutting tools.

HIGH STRENGTH LOW ALLOY (HSLA) STEELS

A general description of HSLA steel is as that containing:

1. Low carbon (0.03–0.25%) content to obtain good toughness, formability, and weldability,
2. One or more of the strong carbide-forming microalloying elements (MAEs) (e.g., V, Nb, or Ti),

3. A group of solid solution strengthening elements (e.g., Mn up to 2.0% and Si), and One or more of the additional MAEs (e.g., Ca, Zr) and the rare earth elements, particularly Ce and La, for sulfide inclusion shape control and increasing toughness.

- In many other HSLA steels, small amounts of Ni, Cr, Cu, and particularly Mo are also present, which increase atmospheric corrosion resistance and hardenability.
- A very fine ferrite grain structure in the final product produced by a combination of
- High Strength Low Alloy (HSLA) steels controlled rolling and controlled cooling with an optimum utilization of microalloying additions, in HSLA steels, is an important factor in simultaneously increasing strength and toughness and decreasing the ductile–brittle transition temperature (to as low as -70oC).
- Carbides (NbC, VC, TiC), nitrides (TiN, NbN, AlN), and carbo-nitrides (e.g., V(C,N), Nb(C,N), (Nb,V) CN, (Nb,Ti) CN) are the dispersed second-phase particles that act as grain size refiners or dispersive strengthening phases in HSLA steels.
- HSL A steels are successfully used as ship, plate, bar, structural sections, and forged bar products, and find applications in several diverse fields such as oil and gas pipelines; in the automotive, agricultural, and pressure vessel industries, in offshore structures and platforms and in the constructions of crane, bridges, buildings, ship buildings, railroad, tank cars, and power transmission an d TV towers.

Weathering steels

Steels containing ~0.1% C, 0.2–0.5%Cu, 0.5–1.0%Mn, 0.05–0.15%P, 0.15–0.90%Si, and sometimes containing Cr and Ni, exhibiting superior atmospheric corrosion resistance.
Typical applications include railroad cars, bridges, and unpainted buildings.

Control-rolled steels

Steels designated to develop a highly deformed austenite structure by hot rolling (according to a predetermined rolling schedule) that will transform to a very fine equiaxed ferrite structure on cooling

Pearlite-reduced steels

Steels strengthened by very fine-grained ferrite and precipitation hardening but with low carbon content, and therefore exhibiting little or no pearlite in the microstructure.

Dual-Phase steels

Steel comprising essentially fine dispersion of hard strong martensite but sometimes also retained austenite or even bainite in a soft and fine-grained ferrite matrix. The volume function of martensite is about 20–30%. Steels are characterized by continuous yielding (i.e., no yield point elongation), low yield stress (the YS/UTS ratio being around 0.50), high UTS, superior formability, and rapid initial work-hardening rate. Additionally, they possess greater resistance to onset of necking (i.e., plastic instability) in the uniaxial sheet material forming process to provide large uniform strain.

Micro alloyed steels

Conventional HSLA steels containing V, Ti, or Nb, as defined above. They exhibit discontinuous yielding behavior.

Acicular Ferrite steels

Very low -carbon (typically 0.03–0.06%) steels with enough hardenability (by Mn, Mo , Nb , and B additions) to transform on cooling to a very fine, high-strength acicular ferrite structure rather than the usual polygonal ferrite structure. In addition to high strength and good toughness , these steels have continuous yielding behavior.

Low carbon bainite steels

Steels are strengthened by bainite, with very fine grains and precipitations. They contain 0.02–0 .2% C, 0.6–1. 6% M n, 0.3–0. 6% Mo, and MAEs (such as V, Nb, Ti, and B), usually containing 0.4–0.7% Cr. The yield strength of these steels is higher than 490 M Pa, with good toughness.

Low carbon martensite steels

Steels are strengthened by martensite with high hardenability (by addition of Mo, Mn , Cr, Nb, and B) and fine grains (by Nb addition). These steels contain 0.05–0.25%C, 1.5–2.0% Mn , 0.20–0.50 Mo, and MAEs (such as Nb, Ti, V, and B). Some steels containing small amounts of Ni, Cr, and Cu, after rolling or forging, and directly quenching and tempering attain a low -carbon martensite structure with high yield strength (760–1100 MPa), high toughness (CVN 50–130J), and superior fatigue strength.

HIGH SPEED STEEL (HSS)

- HSS is a subset of tool steel, commonly used in tool bits and cutting tools. It is often used in power saw blades and drill bits.
- They are characterized by high carbon contents, sometimes up to 1.5%, and major additions of strong carbide forming elements such as chromium, molybdenum, tungsten and vanadium. Up to 12% Co is also included in some of the more complex grades.
- It can withstand higher temperatures without losing its temper (hardness) which allows it to cut faster than high carbon steel, hence the name.
- Other characteristics include high hardness, resistance to abrasion (excellent wear), an ability to hold a cutting edge, resistance to deformation at elevated temperatures (red-hardness).
- Modulus Of elasticity: 221GPa, Density : 8767 kg/m3 (↑ durability & hardness), Thermal Conductivity: 21W/m/K
- HSS are mainly of two types: Tungsten based ones (T grades), Molybdenum based ones (M grades)

Table. Three popular grades i high-speed steel

AISI-SAE grade	C%	W%	Mo%	Cr%	V%
T1	0.75	18		4	1
M1	0.8	2	8	4	1
M2	0.85	6	5	4	2

CAST IRON

The engineering and physical properties of cast iron vary with the type of iron; the designer must match the engineering requirements with all the properties of the specific type of cast iron being considered. Machinability, e.g., is significantly affected by the type of cast iron specified. Gray cast iron is the most machinable; the white cast irons are the least machinable.

White cast iron

- In which all the C is in the combined form as Fe3C (Cementite)
- The typical microstructure of white cast iron *(see next slide),* consisting of dendrites of transformed austenite (pearlite) in a white interdendritic network of cementite.
- Microstructure ® Pearlite + Ledeburite + Cementite
- White cast iron contains a relatively large amount of cementite as a continuous interdendritic network, it makes the cast iron hard and wear-resistant but extremely brittle and difficult to machine.
- ‘Completely white’ cast irons are limited in engineering applications because of this brittleness and lack of machinability. Mainly used in liners for cement mixers, ball mills and extrusion nozzles.
- A large tonnage of white cast iron is used as a starting material for the manufacturer of malleable cast iron.
- Hardness : 375 to 600 BHN, Tensile strength : 135-480 Mpa, Compressive strength: 1380 -
- 1725 Mpa
- White cast irons fall into three major groups: **Nickel Chromium White Irons**: containing 3-5%Ni, 1-4%Cr. Identified by the name Ni-Hard iron. The **chromium-molybdenum irons** (high chromium irons): 11-23%Cr, 3%Mo, and sometimes additionally alloyed with
- Ni or Cu. **25-28%Cr White Irons**: contain other alloying additions of Molybdenum and/or
- Nickel up to 1.5%

Typical white cast iron contains 2.5-3.5% C, 0.4-1.5% Si, 0.4-0.6% Mn, 0.1-0.4% P, 0.15% S, and balance Fe.

- During solidification, high internal stresses may be developed due to varying cooling rates across the cross section . These stresses can be relieved by heating white cast iron to about 500-550°C

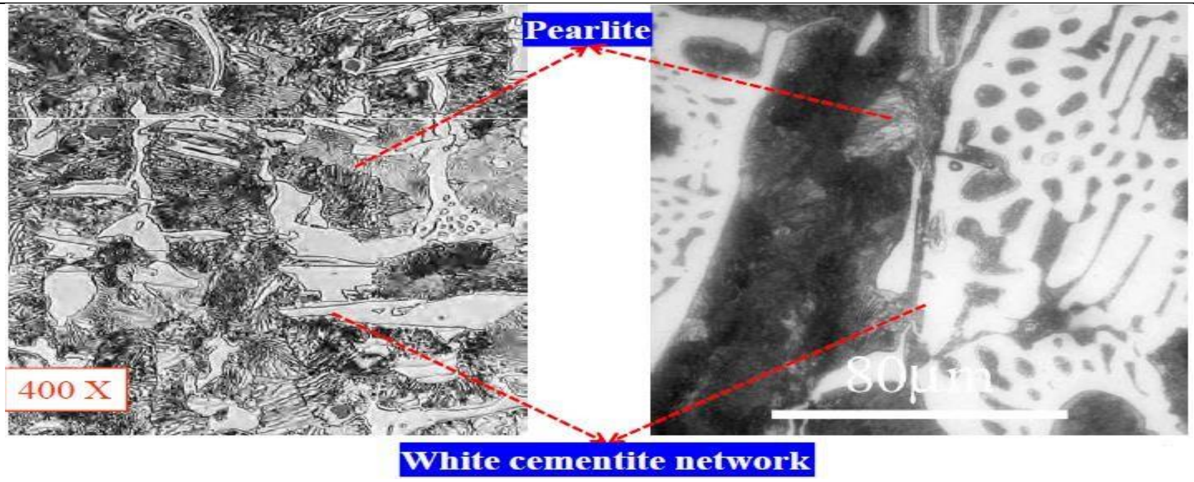


Figure: white cast iron

Gray cast iron

- Gray cast iron is obtained by cooling the molten metal slowly during solidification. A typical gray cast iron contains 2.5-3.5% C, 1.4-2.8% Si, 0.5-0.8% Mn, 0.1-0.9% P, and 0.06-0.12% S.
- Fractured surface of gray cast iron appears grey because of the presence of graphite. Hence the alloy is termed gray cast iron.
- In the manufacture of gray cast iron the tendency of cementite to separate into graphite and austenite or ferrite is favored by controlling alloy additions and cooling rates.
- These alloys solidify by first forming primary austenite. The initial appearance of combined carbon is in the cementite resulting from the eutectic reaction. With proper control of carbon content, temperature and the proper amount of graphitizing elements notably silicon, magnesium cerium and, alloy will follow the stable iron – graphite equilibrium diagram.
- For most of these cast irons, the graphite exists in the form of flakes (similar to corn flakes), which are normally surrounded by an α-ferrite or pearlite matrix.
- Mechanically, gray iron is comparatively weak and brittle in tension as a consequence of its microstructure; the tips of graphite flakes are sharp and pointed, and may serve as points of stress concentration when an external tensile stress is applied. Strength and ductility are much higher under compressive loads.
- Gray irons are very effective in damping vibrational energy. Base structures for machines and heavy equipment that are exposed to vibrations are frequently constructed of this material. In addition, gray irons exhibit a high resistance to wear.

- Furthermore, in the molten state they have a high fluidity at casting temperature, which permits casting pieces having intricate shapes; also, casting shrinkage is low.
- Finally, and perhaps most important, gray cast irons are among the least expensive of all metallic materials.
- Gray irons having different type of microstructures, it may be generated by adjustment of composition and/or by using an appropriate heat treatment.
- For example, lowering the silicon content or increasing the cooling rate may prevent the complete dissociation of cementite to form graphite. Under these circumstances the microstructure consists of graphite flakes embedded in a pearlite matrix.
- Tensile strength of gray cast iron varies from 100 Mpa to 340 Mpa

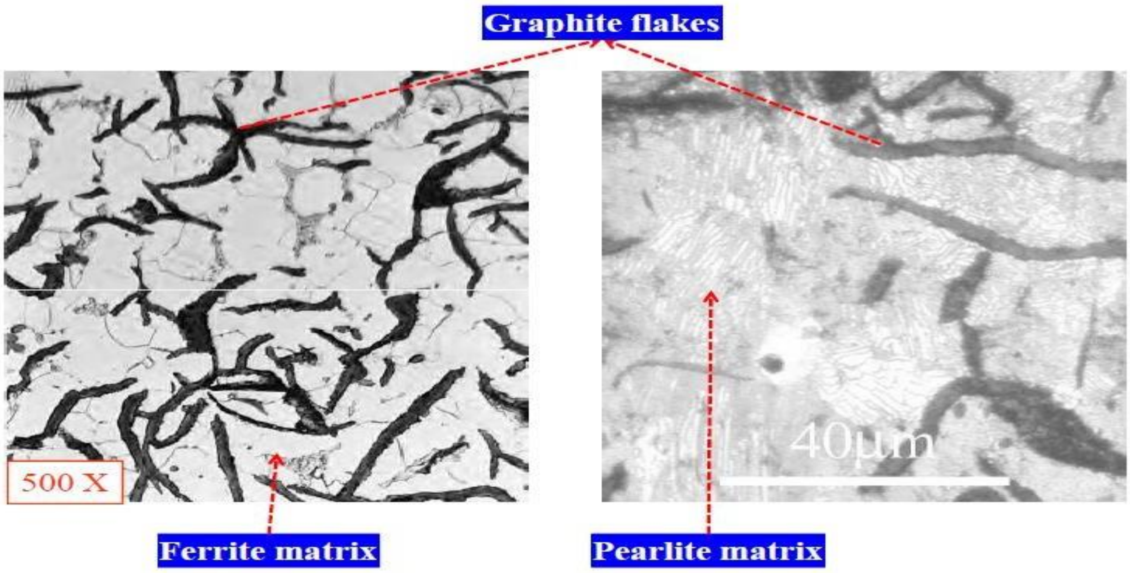


Figure: Microstructure of gray cast iron

Ductile cast iron: spheroidal graphite (SG) iron

- Ductile cast iron also called as Nodular cast iron, and Spherulitic cast iron.
- Graphite nodules instead of flakes *(in 2D section)*
- Mg (0.03-0.06)%, Ce, Ca (or other spheroidizing) elements are added
- The elements added to promote spheroidization react with the solute in the liquid to form heterogeneous nucleation sites
- The alloying elements are injected into mould before pouring
- It is thought that by the modification of the interfacial energy the ‘c’ and ‘a’ growth direction are made comparable leading to spheroidal graphite morphology.
- The graphite phase usually nucleates in the liquid pocket created by the pro-eutectic
- As compared to flaky graphite in grey cast iron, spheroidal graphite does not weaken the matrix considerably. For this reason the mechanical properties of SG iron are superior to gray iron.
- SG iron has tensile strength of 400-700 Mpa, Yield strength 270-390 Mpa, and percentage of elongation 10-20.

- Approx. chemical composition of SG iron is 3.0-3.6%C, 2.0-2.5%Si, 0.6%Mn, 0.04 max P, 0.04 max S, and balance Fe.

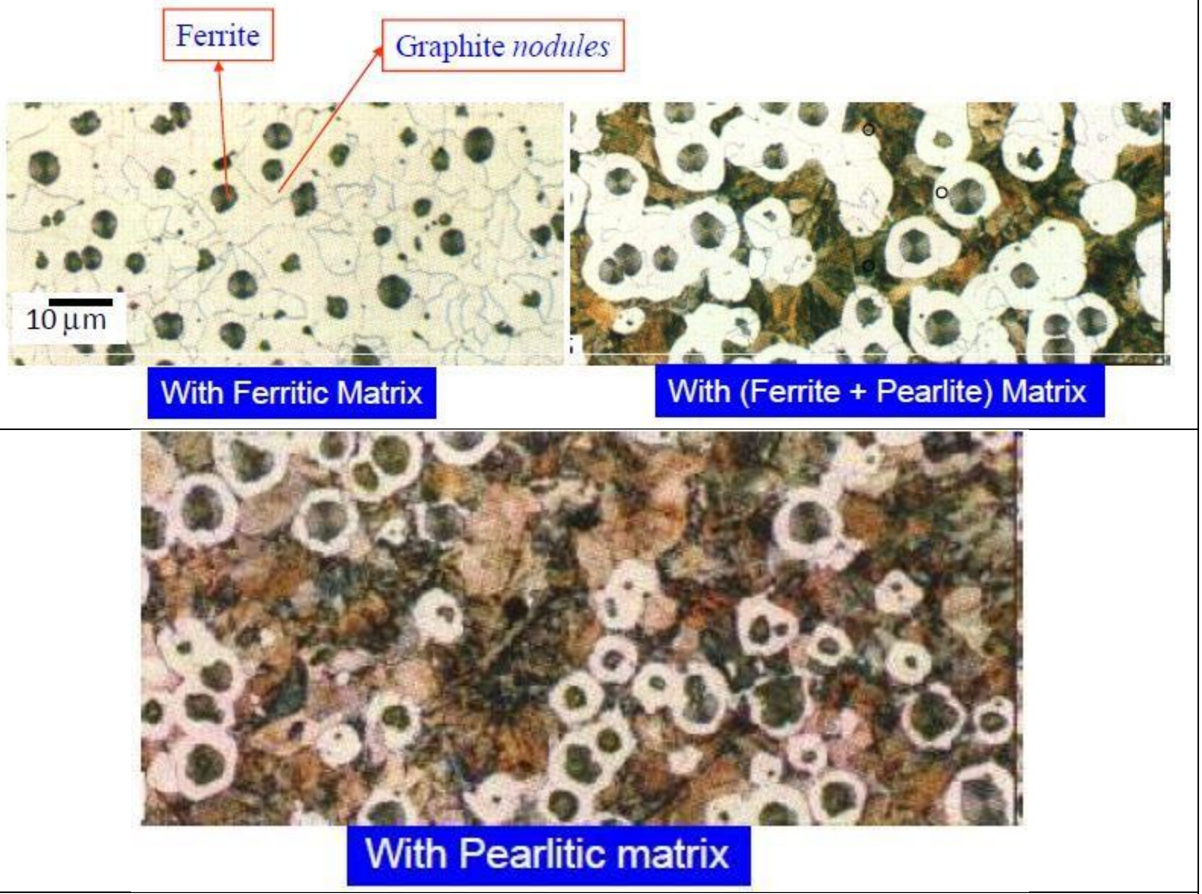


Figure: Microstructure of ductile iron with ferritic matrix, ferritic +pearlite matrix, pearlite marix

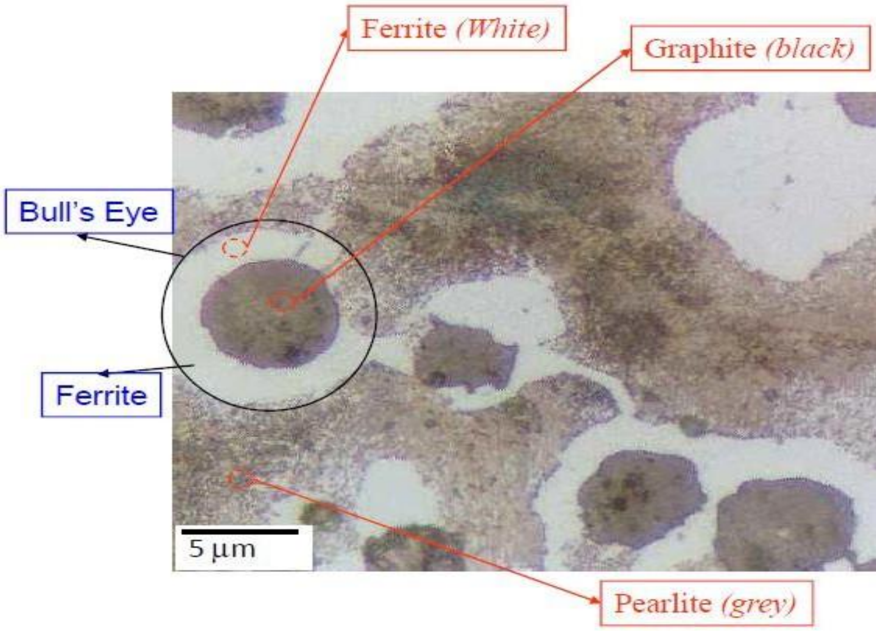
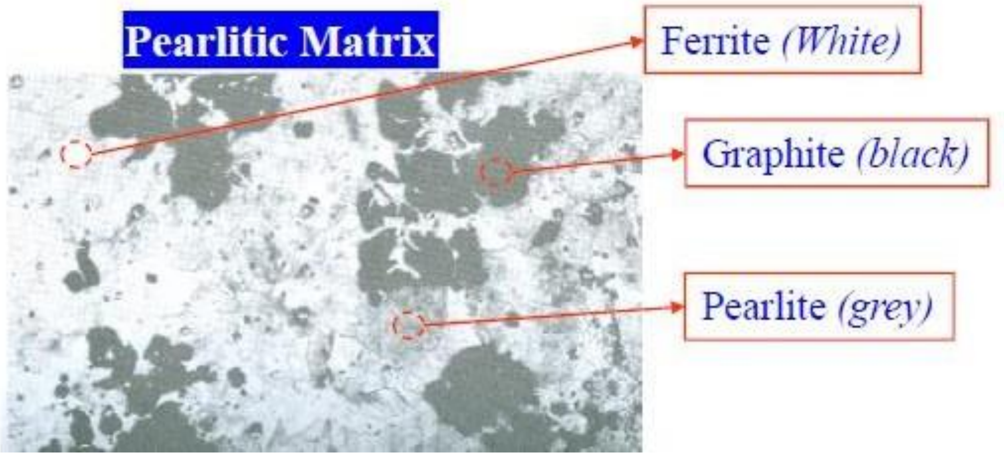


Figure: Microstructure of spheroidal graphite (SG) iron: nodular cast iron

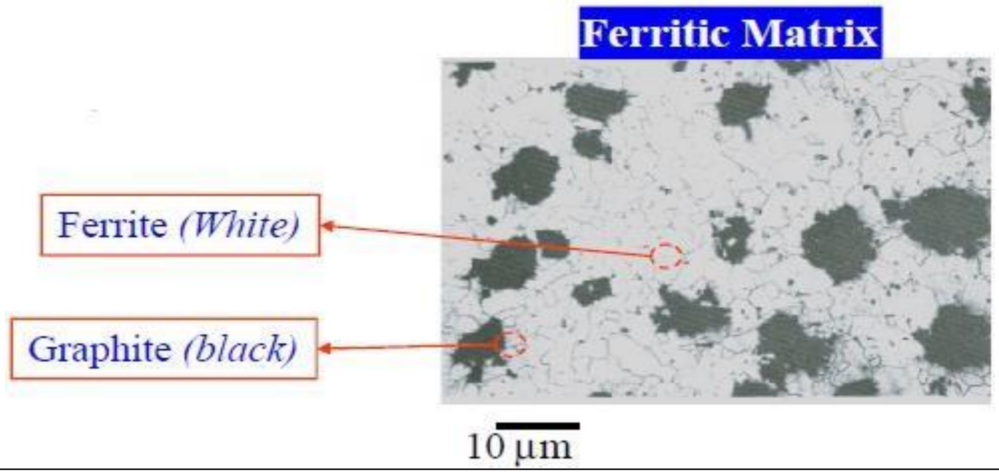
MALLEABLE CAST IRON

$$\text{white cast iron} \xrightarrow{\text{malleabilize(to increase ductile)}} \text{malleable cast iron}$$

- As we discussed earlier that cementite is actually a metastable phase. There is a tendency for cementite to decompose into iron and carbon. This tendency to form free carbon is the basis for the manufacture of malleable cast iron. The reaction of $Fe_3C \rightarrow 3Fe + C$ is favored by elevated temperatures, the existence of solid nonmetallic impurities, higher carbon contents, and the presence of elements that aid the decomposition of Fe_3C. Categorized into 3 categories: Ferritic, Pearlitic, and Martensitic Malleable Cast Iron. ferritic malleable Irons require a two stage annealing cycle. First: converts primary carbides to temper Carbon. Second: converts Carbon dissolved in Austenite at the first-stage annealing temperature to temper Carbon and Ferrite. Consists of temper Carbon in a matrix of Ferrite. Contain a slight amount of controlled Iron.
- Pearlitic: 1st stage identical to that of Ferrite. Casting is slowly cooled to approx 870°C.
- When the combined Carbon content of the Austenite is reduced to about .75% the castings are air cooled. Usually air blasted to avoid the formation of ferrite around the temper Carbon particles. Then, the castings are tempered to specified time.



Partially Malleabilized Iron →Incomplete Ferritizing Anneal



Fully Malleabilized Iron →Complete Ferritizing Anneal

Compacted graphite cast iron (CGI)

A relatively recent addition to the family of cast irons is *compacted graphite (CGI).*

- Micro structurally, the graphite in CGI alloys has a worm-like (or vermicular) shape; a typical CGI microstructure. In a sense, this microstructure is intermediate between that of gray iron and ductile iron and, in fact, some of the graphite (less than 20%) may be as nodules. The chemistries of CGIs are more complex than for the other cast iron types; compositions of Mg, Ce and other additives must be controlled so as to produce a microstructure **Vermicular shape** that consists of the worm-like graphite particles, while at the same time limiting the degree of graphite nodularity, and preventing the formation of graphite flakes. Furthermore, depending on heat treatment, the matrix phase will be pearlite and/or ferrite.
- CGI are now being used in a number of important applications – these include: diesel engine blocks, exhaust manifolds, gearbox housings, brake discs for high speed trains and flywheels.

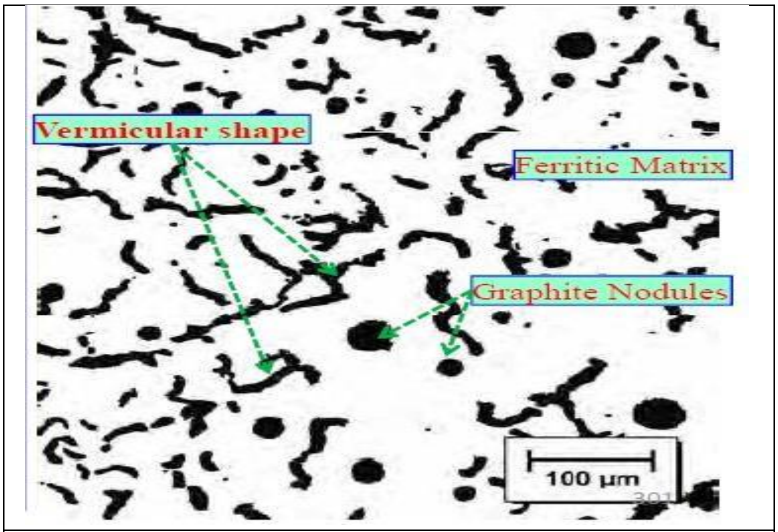


Figure.Mmicrostructure of *compacted graphite cast iron (CGI)*

MODULE IV

TIME-TEMPERATURE-TRANSFORMATION (TTT) DIAGRAMS

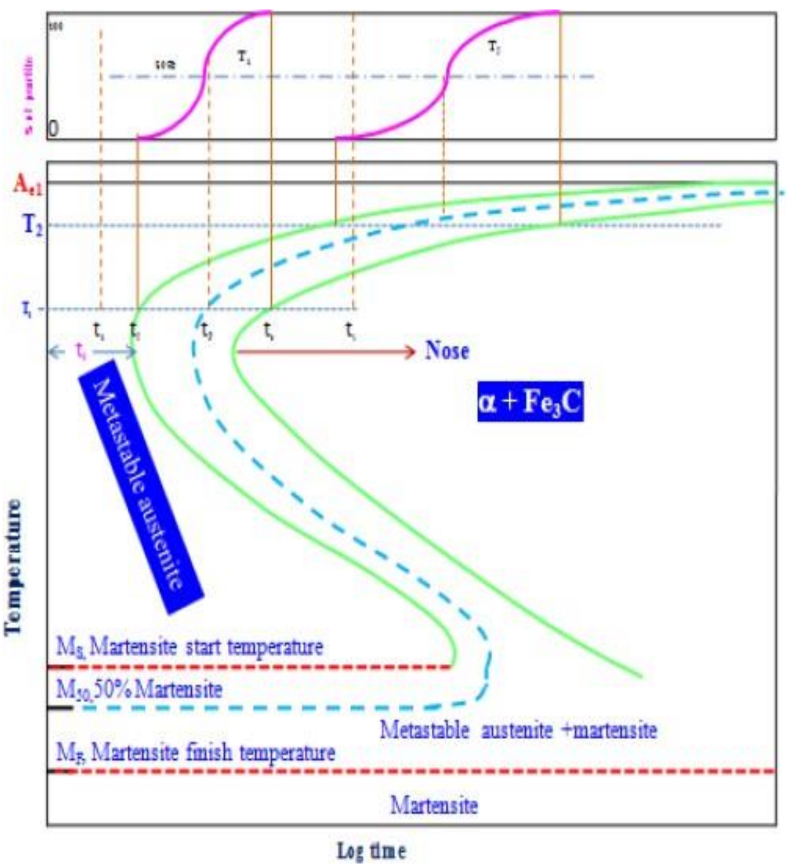
- Davenport and Bain were the first to develop the TTT diagram of eutectoid steel. They determined pearlite and bainite portions whereas Cohen later modified and included MS and MF temperatures for martensite.
- There are number of methods used to determine TTT diagrams. The most popular method is salt bath techniques combined with metallography and hardness measurement with addition of this we have other techniques like dilatometry, electrical resistivity method, magnetic permeability, i*n situ* diffraction techniques (X-ray, neutron), acoustic emission, thermal measurement techniques, density measurement techniques and thermodynamic predictions.
- TTT diagrams, also called as Isothermal (*temperature constant)* Transformation diagrams.
- TTT diagrams give the kinetics of isothermal transformations.

- For every composition of steel we should draw a different TTT diagram.
- For the determination of isothermal transformation (or) TTT diagrams, we consider *molten salt bath technique* combined with metallography and hardness measurements.
- In *molten salt bath technique* two salt baths and one water bath are used. Salt bath I is maintained at austenising temperature (780˚C for eutectoid steel). Salt bath II is maintained at specified temperature at which transformation is to be determined (below Ae_1), typically 700-250°C for eutectoid steel. Bath III which is a cold water bath is maintained at room temperature.
- In bath I numbers of samples are austenite at A_1+20-40°C for eutectoid, A_3+20-40°C for hypo-eutectoid steel and A_{Cm}+20-40°C for hyper-eutectoid steels for about an hour.
- Then samples are removed from bath I and put in bath II and each one is kept for different specified period of time say t_1, t_2, t_3, t_4,............,tn etc. After specified times, the samples are removed and quenched in cold water. The microstructure of each sample is studied using metallographic techniques. The type, as well as quantity of phases, is determined on each sample.

EQUIPMENTS FOR DETERMINATION OF TTT DIAGRAM

Description about curve

- The curve at extreme left represents the time required for transformation of austenite to pearlite at any given temperature.
- The extreme right curve of curve represents the time required for completing the transformation process.
- In between two curves, the points represent the partial transformation.



✓At T_1, incubation period for pearlite=t_2, Pearlite finish time =t_4

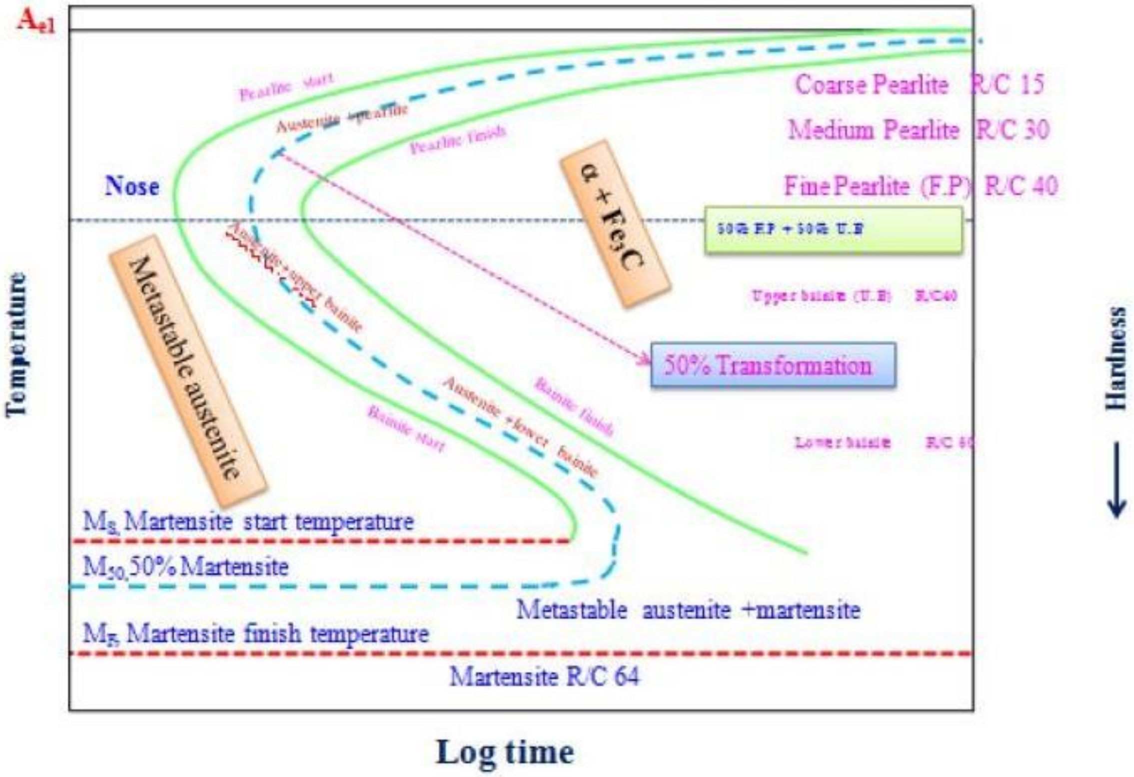
✓Minimum incubation period t_0 at the nose of the TTT diagram,

Important points to be noted:

✓ The x-axis is log scale. 'Nose' of the 'C' curve is in ~sec and just below T_E transformation times may be ~day.

✓ The starting phase (left of the C curve) has to γ.

✓ To the right of finish C curve is (γ+ Fe_3C) phase field. This phase field has more labels included.



Region of curves:

a. Pearlite (diffusion control)

- The eutectoid reaction is fundamental to the development of microstructure in steel alloys.
- $\gamma(0.76\%) wt\ C \leftrightharpoons \alpha\ (0.022\% wtC) + Fe_3C(6.07\ \%wt\ C)$
- Pearlite is the microstructural product of this transformation.
- Above eutectoid temperature:-only austenite (γ)exist.
- Below eutectoid temperature: nucleation and growth.
- The percentage of transformation product is related to the holding temperature and holding time.
- The thickness of the ferrite / cementite layer in pearlite depends on the temperature. With decreasing temperature the layer becomes progressively thinner.
- At temperature just below eutectoid, relatively thick layers (coarse pearlite) formed.
- At temperature of 540^{0}C, relatively thin layers (fine paerlite formed).

b. Bainite region

The time temperature transformation curves corresponds to the start and finish of transformation which extent into the range of temperature.

- Above 550^{0}c- austenite transforms completely to pearlite.
- Below 550^{0}c- both pearlite and bainite are formed.
- Below 450^{0}c- only bianite is formed.

c. Martensite region

Martensite is formed when austenitized Fe-C alloys re readily cooled (or quenched) to a relatively low temperature that is

- Non equilibrium single phase
- Transformation of FCC to BCT (body centred tetragonal)
- The martensite grains nucleate and grow at a very rapid rate.

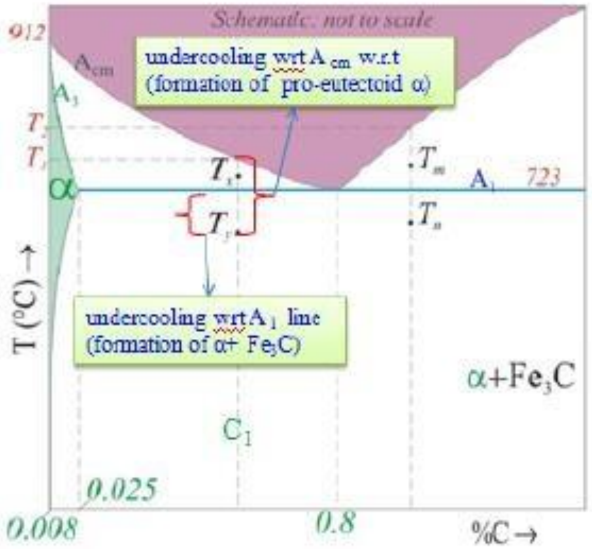
The fraction of Martensite formed is not a function of the time of hold, but the temperature to which we quench (between M_s and M_f).

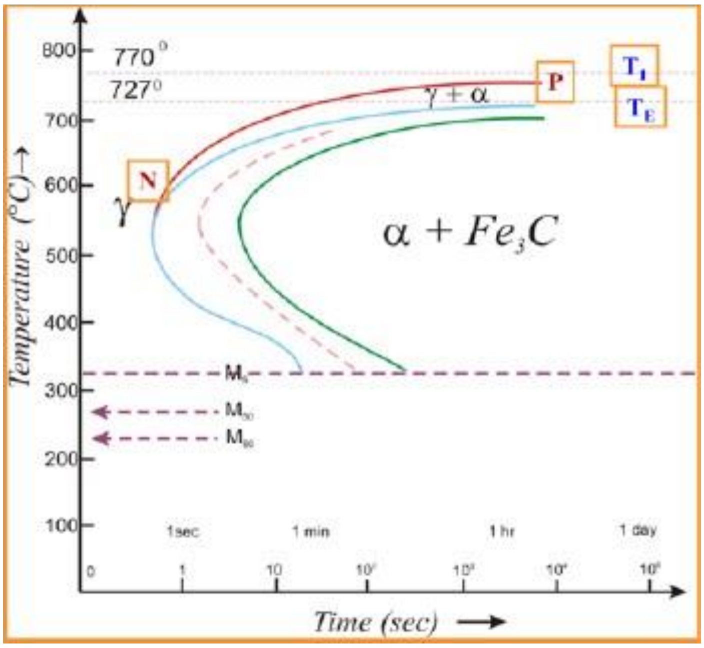
- The reason we see the formation of pro-eutectoid α first is that the undercooling w.r.t to A_{cm} is more than the undercooling w.r.t to A_1. Hence, there is a higher propensity for the formation of pro-eutectoid α.

TTT diagram for Hypo eutectoid steel

- In hypo- (and hyper-) eutectoid steels (say composition C_1) there is one more branch to the ‘C’ curve-NP *(marked in red).*

- The part of the curve lying between T_1 and T_E (marked in fig: n*ext slide*) is clear, because in this range of temperatures we expect only pro-eutectoid α to form and the final microstructure will consist of α and γ. *(E.g. if we cool to T_x and hold).*
- The part of the curve below T_E is a bit of a 'mystery' *(since we are instantaneously cooling to below T_E, we should get a mix of $\alpha + Fe_3C$ what is the meaning of a 'pro'-eutectoid phase in a TTT diagram? (remember 'pro-' implies 'pre-')*
- Suppose we quench instantaneously an hypo-eutectoid composition C_1 to T_x we should expect the formation of $\alpha+Fe_3C$ (and not pro-eutectoid α first).



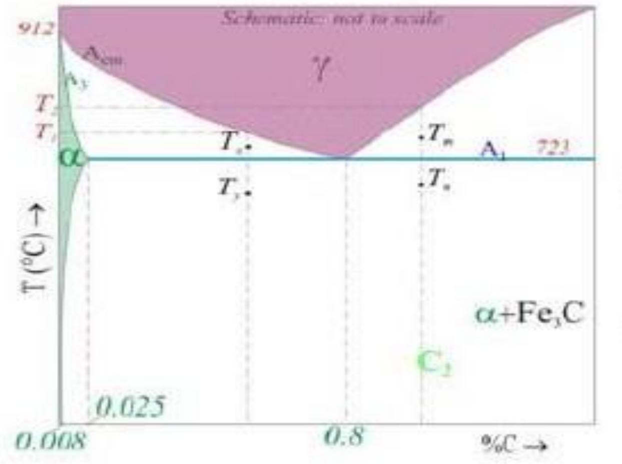


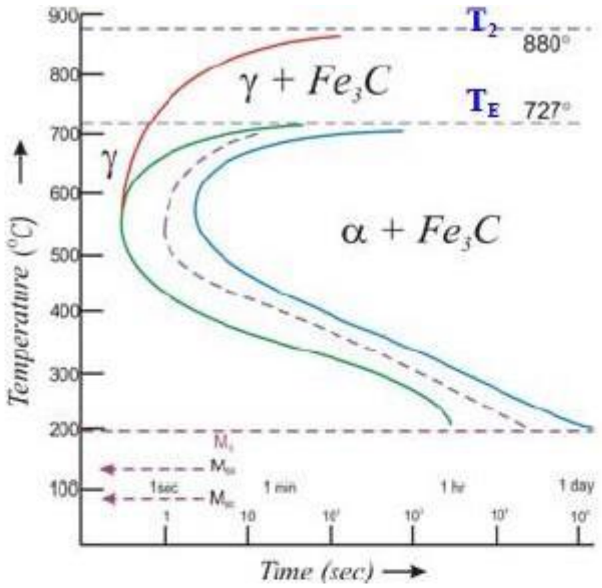
TTT diagram for Hyper eutectoid steel

Similar to the hypo-eutectoid case, hyper-eutectoid compositions C_2 have a $\gamma+Fe_3C$ branch.

For a temperature between T_2 and T_E (say Tm (not melting point- just a label)) we land up with γ+Fe_3C.

For a temperature below T_E (but above the nose of the 'C' curve) (say Tn), first we have the formation of pro-eutectoid Fe_3C followed by the formation of eutectoid γ+Fe_3C.





Factors affecting TTT diagram

1- Composition of steel-

- (a) Carbon wt%,
- (b) Alloying element wt%

2- Grain size of austenite

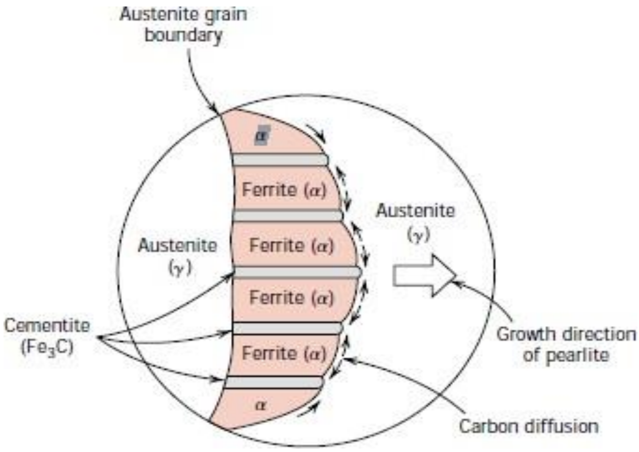
3- Heterogeneity of austenite

TTT diagram gives

a. Nature and type of transformation.
b. Rate of transformation.
c. Stability of phases under isothermal transformation conditions.
d. Temperature or time required to start or finish transformation.
e. Qualitative information about size scale of product.
f. Hardness of transformed products.

FORMATION OF PEARLITE FROM AUSTENITE AND DIRECTION OF CARBON DIFFUSION

Figure illustrates schematically microstructural changes that accompany this eutectoid reaction; here the directions of carbon diffusion are indicated by arrows. Carbon atoms diffuse away from the 0.022 wt% ferrite regions and to the 6.7 wt% cementite layers, as the pearlite extends from the grain boundary into the unreacted austenite grain. The layered pearlite forms because carbon atoms need diffuse only minimal distances with the formation of this



TRANSFORMATION OF AUSTENITE TO PEARLITE

Transformation of austenite to pearlite starts by formation of cementite nuclei at austenite grain boundaries (see **Fig**.). Carbon diffuses from the surrounding austenite to the cementite, and the growth of carbide begins. As carbon diffuses, the adjacent austenite is depleted in carbon and transforms to ferrite. With formation of ferrite, there is rejection of carbon from the ferrite region, i.e., effective enrichment of the adjacent austenite. This results in the formation of additional nuclei of cementite. Because of the alternate formation of cementite and ferrite, cementite can only grow away from the boundary of the original austenite grain as a platelet.

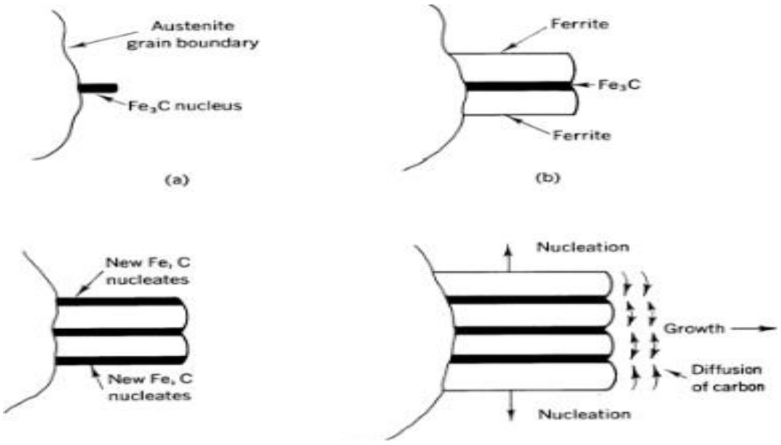


Fig. : Schematic representation of pearlite formation by nucleation and growth; (a) through (d) indicate successive steps in time sequence

Nucleation and growth of alternate plates of cementite and ferrite occur at several points along the austenite grain boundaries. This forms pearlite colonies, which are approximately hemispherical regions of alternate parallel plates of cementite and ferrite. These pearlite colonies grow until the entire austenite grain has been consumed and has become a pearlite structure. The process of pearlite formation is sometimes referred to as sidewise nucleation and edgewise growth.

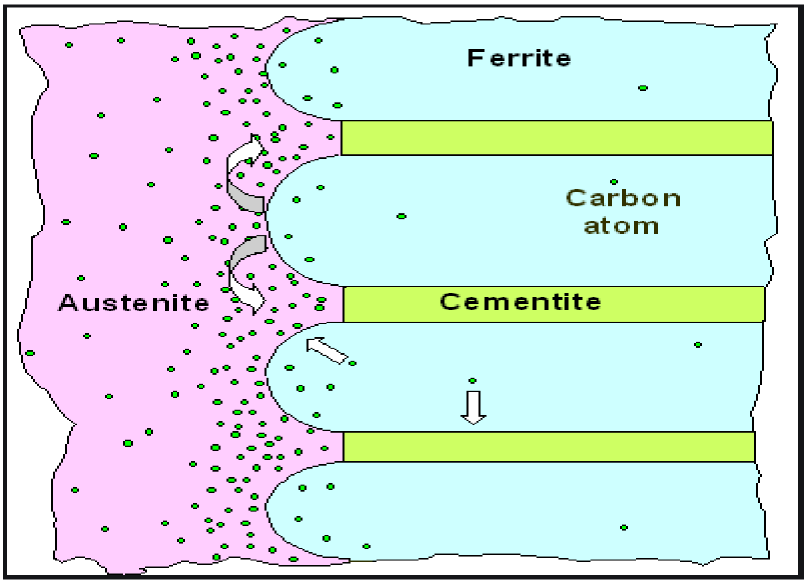
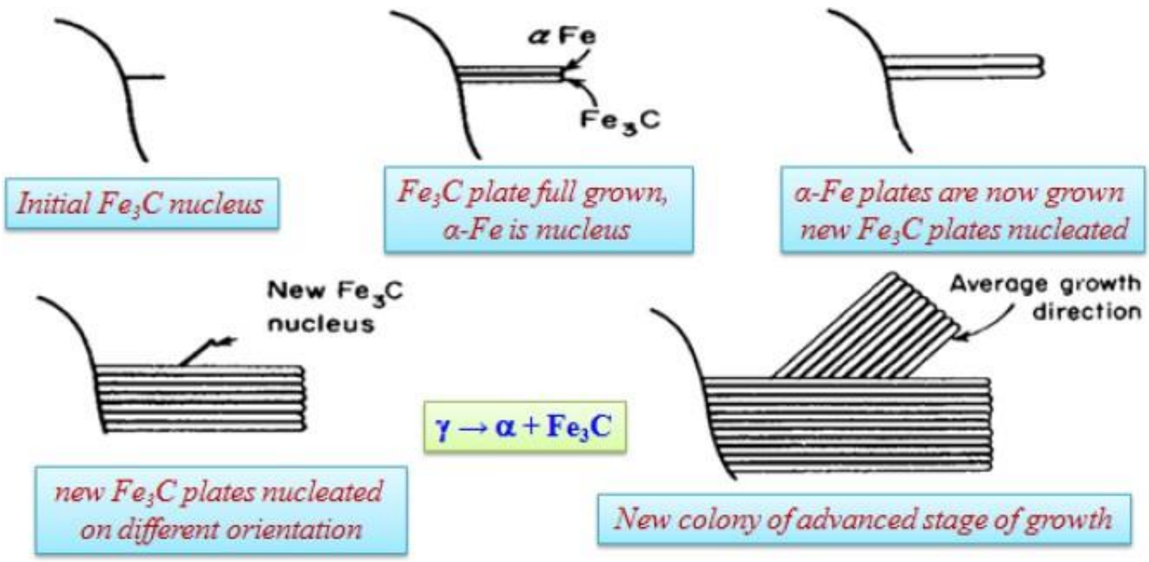


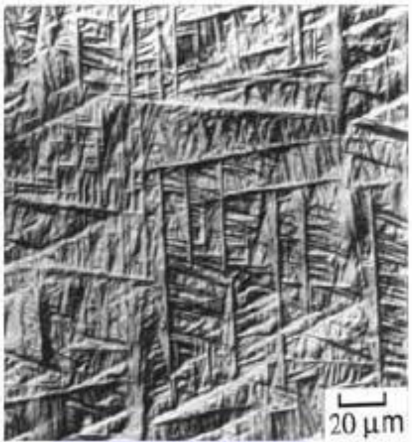
Fig.: Formation of the eutectic / eutectoid "zebra pattern" by minimizing carbon diffusion



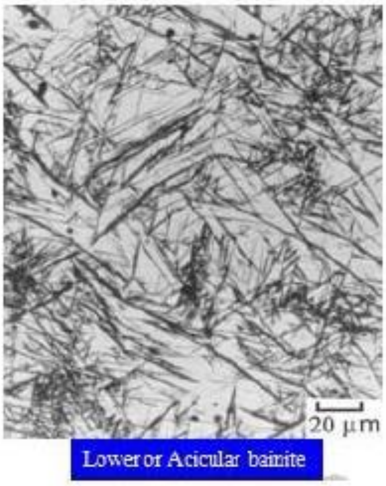
- Nucleation and growth
- Heterogeneous nucleation at grain boundaries
- Interlamellar spacing is a function of the temperature of transformation
- Lower temperature → finer spacing → higher hardness

Transformation to Bainite

- In between the nose region of approximately 510˚C and the Ms temperature, a new, dark-etching aggregate of ferrite and cementite appears. This structure, named after E.C.Bain, is called bainite.
- At upper temperatures of the transformation range, it resembles pearlite and is known as upper or feathery bainite. At low temperatures it appears as a black needlelike structure resembling martensite and is known as lower or acicular banite.

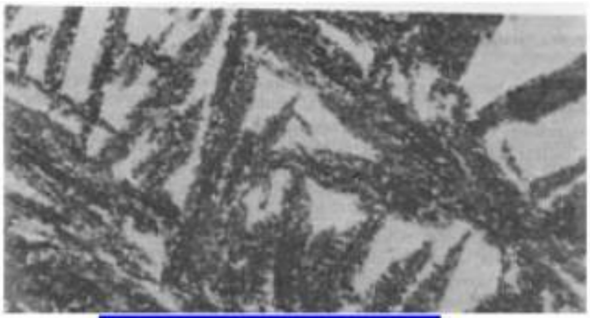


Upper or Feathery bainite

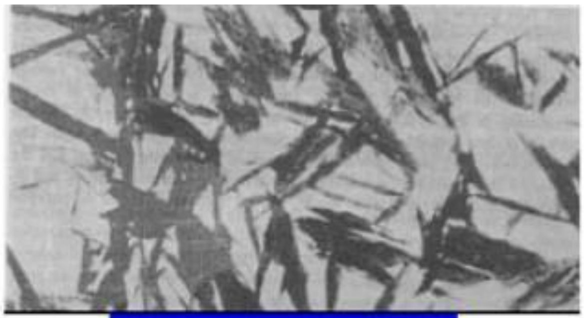


Lower or Acicular bainite

- Pearlite is nucleated by a carbide crystal, bainite is nucleated by a ferrite crystal, and this results in a different growth pattern.
- Acicular, accompanied by surface distortions
- ** Lower temperature → carbide could be ε carbide (hexagonal structure, 8.4% C)
- Bainite plates have irrational habit planes
- Ferrite in Bainite plates possess different orientation relationship relative to the parent Austenite than does the Ferrite in Pearlite



Bainite formed at 348°C



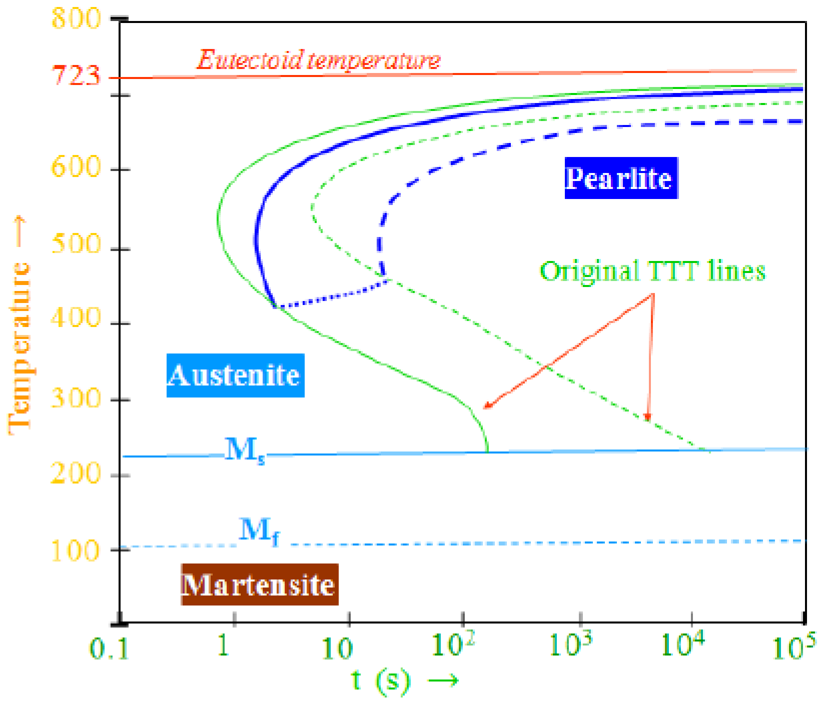
Bainite formed at 278°C

$$\gamma \rightarrow \alpha + Fe_3C^{**}$$

CONTINUOUS COOLING TRANSFORMATION DIAGRAMS (CCT DIAGRAM)

- The TTT diagrams are also called Isothermal Transformation Diagrams, because the transformation times are representative of isothermal hold treatment (following a instantaneous quench).

- In practical situations we follow heat treatments (T-t procedures/cycles) in which (typically) there are steps involving cooling of the sample. The cooling rate may or may not be constant. The rate of cooling may be slow (as in a furnace which has been switch off) or rapid (like quenching in water).
- Hence, in terms of practical utility TTT curves have a limitation and we need to draw separate diagrams called Continuous Cooling Transformation diagrams (CCT), wherein transformation times (also: products & microstructure) are noted using constant rate cooling treatments. A diagram drawn for a given cooling rate (dT/dt) is typically used for a range of cooling rates (thus avoiding the need for a separate diagram for every cooling rate).



- However, often TTT diagrams are also used for constant cooling rate experiments- keeping in view the assumptions & approximations involved.
- The CCT diagram for eutectoid steel is considered next.
- *Important difference between the CCT & TTT transformations is that in the* CCT case *Bainite cannot form.*

CONCEPT OF HEAT TREATMENT

Heat treatment of steels is the heating and cooling of metals to change their physical and mechanical properties, without letting it change its shape. Heat treatment could be said to be a method for strengthening materials but could also be used to alter some mechanical properties such as improving formability, machining, etc.

Heat treatment process consists of a metal or alloy to a specific predetermined temperature, holding at this temperature for required time and finally cooling from this temperature.

Definition

Heat treatment may be defined as an operation or combination of operations involving the heating and cooling of metal or alloy in its solid state with the objective of changing the characteristics of the material.

Normally properties of material can be varied within limits by several methods.

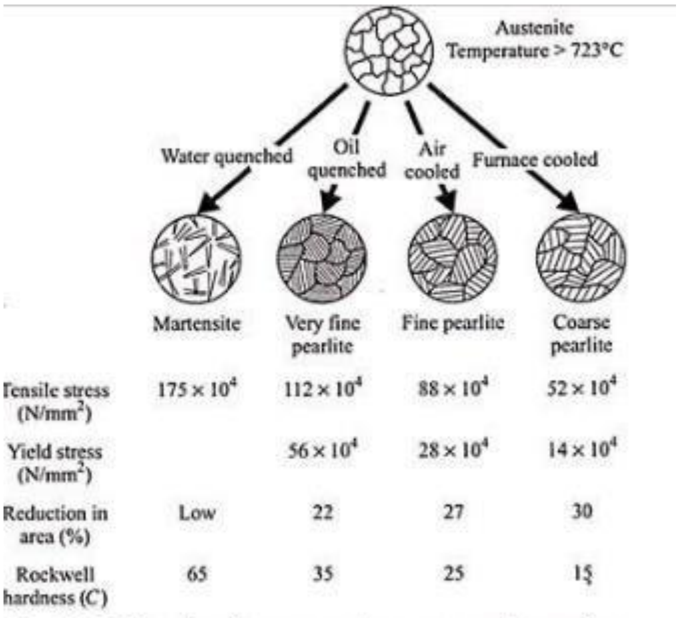
a. Heat treatment
b. Mechanical working
c. Alloying
d. Grain size control.

Objective

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

Principle heat treatment

- The principle of the theory of heat treatment is that when an alloy has been heated above a certain temperature, it undergoes a structural adjustment or stabilization when cooled to room temperature. The cooling rate plays an important role in this operation.
- Let us take a simple example where austenite steel (above 723°C) is cooled at different rates. Figure shows the various resulting structures along with a few mechanical properties.

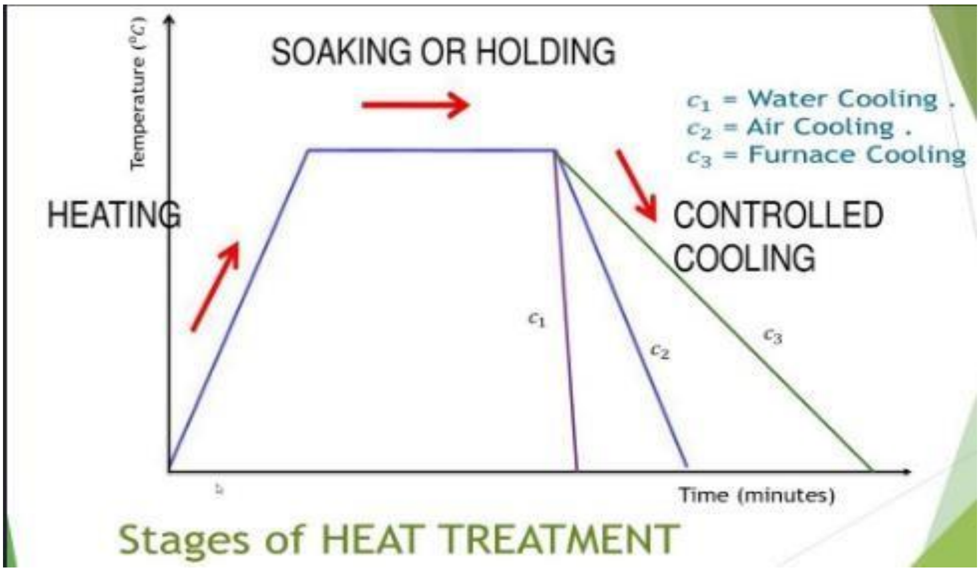


	Martensite	Very fine pearlite	Fine pearlite	Coarse pearlite
Tensile stress (N/mm^2)	175×10^4	112×10^4	88×10^4	52×10^4
Yield stress (N/mm^2)		56×10^4	28×10^4	14×10^4
Reduction in area (%)	Low	22	27	30
Rockwell hardness (C)	65	35	25	15

Fig. 1.29 Effect of cooling rate on microstructure and properties.

It is thus obvious that by changing only the rate of cooling, different phases can be achieved

Stages of heat treatment



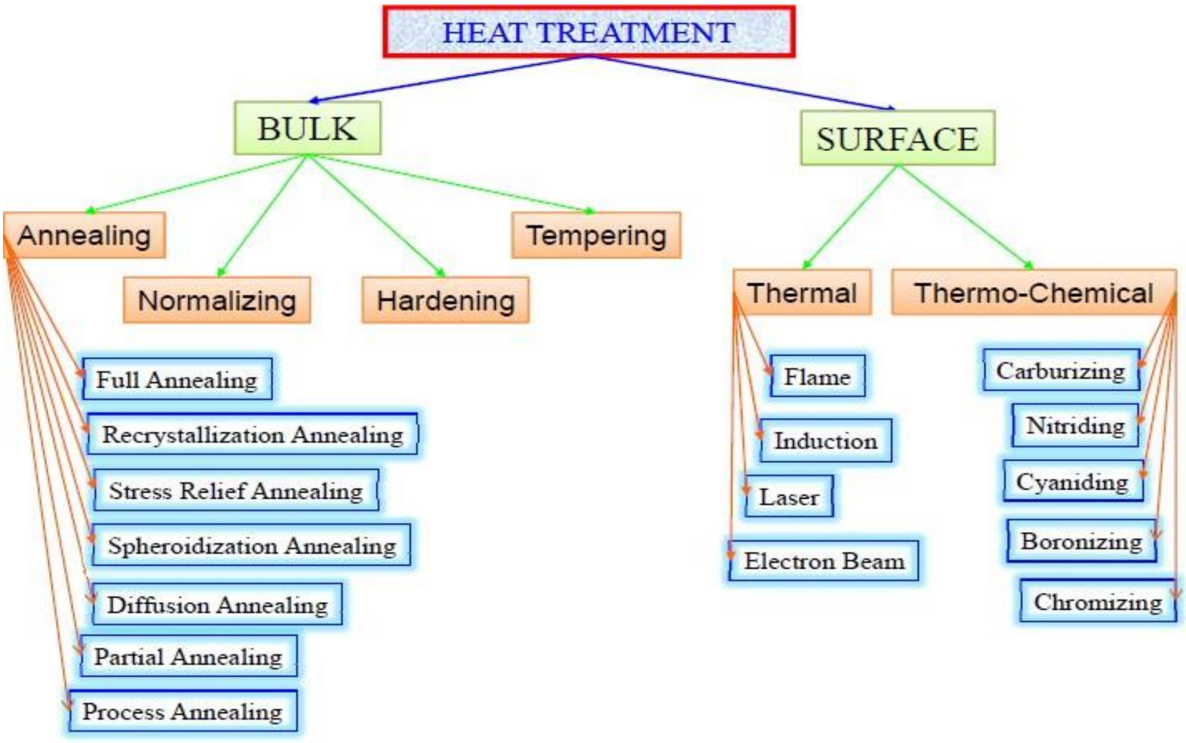
Every heat treatment process contains 3 steps

1. Heating: small grains will combine and form larger grains
2. Holding: all grains will turn into uniform shape and size.
3. Cooling: based on rate of cooling the final grain size will be decided.

Note-1: If a steel component is heated to high temperature followed by rapid cooling process implies larger grains will break into small grains implies hardness increases.

Note-2: if a steel component is heated to high temperature followed by slow cooling process then small grain will combine and form larger grains implies ductility increases.

GENERAL HEAT TREATMENT PROCESSES



ANNEALING

Annealing refers to heating the material to a predetermined temperature, soaking at this temperature then cooling it slowly normally in a furnace.

Annealing is the process involving heating above re-crystallization temperature, holding this temperature for some time and then slow cooling.

Note: One biggest disadvantages of annealing process is that material loses its strength and hardness after this process.

The various purposes of annealing heat treatment are

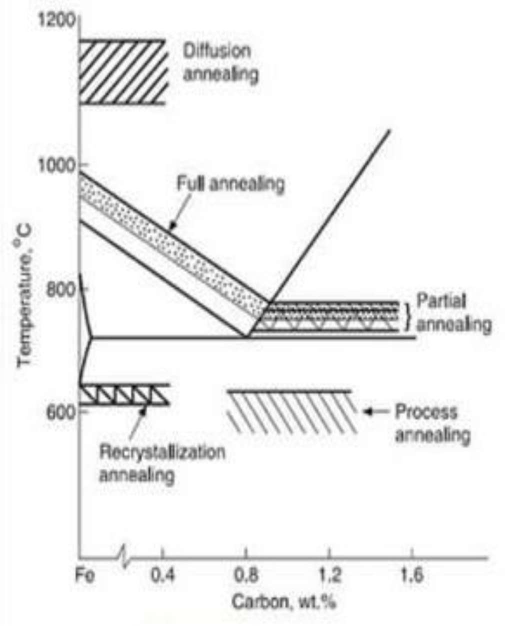
1. Internal stress relieving
2. Restore ductility and toughness
3. Refine grain size
4. Eliminate chemical non-uniformity and gaseous contents in steel

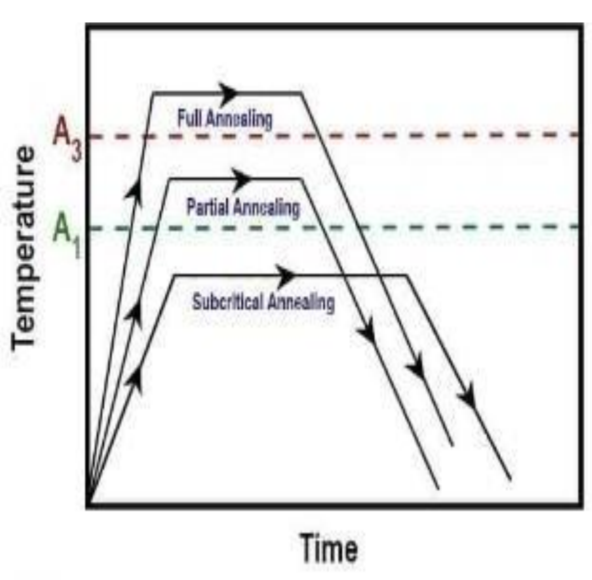
Stages of annealing process

1. **Recovery**- softening through removal of dislocation and internal stress
2. **Re-crystallization**- nucleation of new strain-free grains
3. **Grain growth**- coarsening of grains

Types of Annealing

1. Improvement in mechanical properties of cast or hot worked steel by referring the grains : Full annealing
2. Homogenisation of segregated casting and ingots of steels and alloy steels: Homogenising annealing (diffusion annealing)
3. Restore ductility of cold worked steels: Re-crystallisation annealing
4. Improve the machinability and cold formability particularly of high carbon steels and alloy steels.: Spherodisation annealing
5. Relieve the internal stress of cast, hot worked or welded structure: Stress relieving annealing.





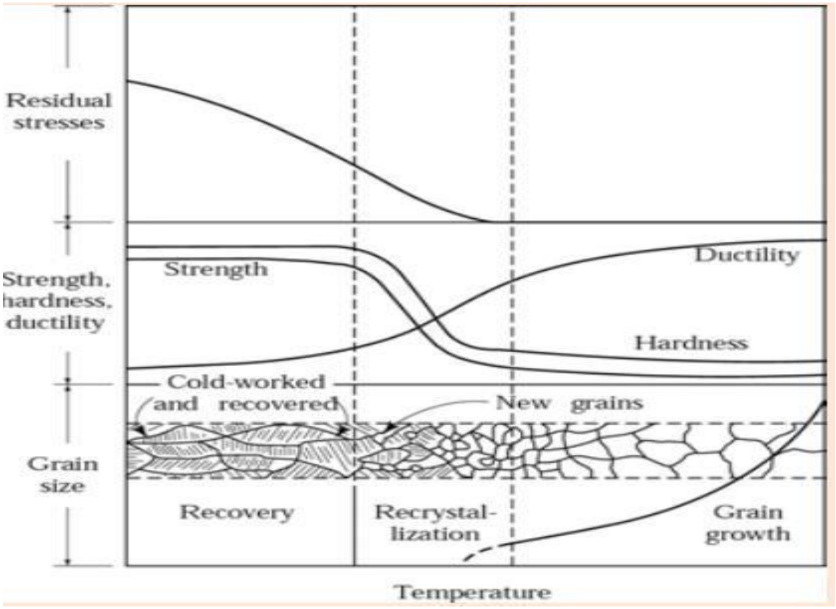


Fig. Schematic illustration of the effects of recovery, recrystallization and grain growth on mechanical properties and on the shape and size of grains

FULL ANNEALING

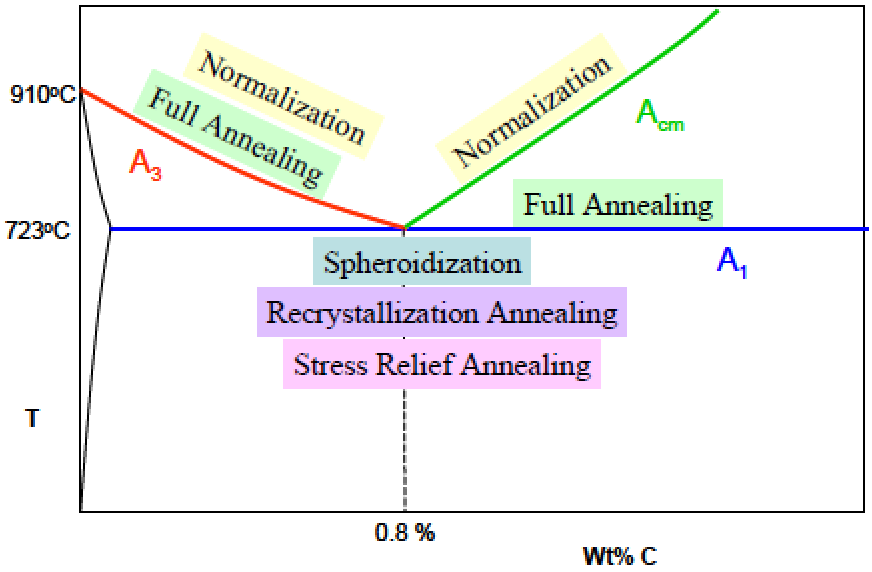
- Applicable to steels with %of carbon from 0-2.11%C (Low carbon steels, medium carbon steels, High carbon steels)

Process

- Full annealing consists of heating the steels to a temperature above its upper critical temperature, soaking there for sufficient time to obtain homogeneous austenite and then left to cool in the furnace (normally at rate of 50 to 30^{0}C/hour or in a container made of a heating insulating material(like as, lime)
- The steel is heated above A_3 (for hypo-eutectoid steels) and A_1 (for hyper-eutectoid steels) →(hold)→then the steel is furnace cooled to obtain Coarse Pearlite.
- Coarse Pearlite has ↓ Hardness, ↑ Ductility
- Not above Acm →to avoid a continuous network of proeutectoid cementite along grain boundaries (→path for crack propagation)

Heating rate , heating range and temperature range

- For **hypoeutectoid steels and eutectoid steels** temperature taken is AC_3 + (20-40^{0}C) to obtain single phase austenite.
- For **hypereutectoid steels temperature** taken is AC_1 + (20-40^{0}C) to obtain austenite + cementite.
- Normally the rate of cooling varies from 30^{0}C-200^{0}C and the holding time is 3-4 min/mm.



This process in general not employed for hypereutectoid steels.

Reason: Heating above upper critical temperature followed by slow cooling will result in considerable coarsening of austenite grains, formation of lamellar pearlite and network of cementite network at grain boundary. Neither coarse pearlite nor cementite network at grain boundary is desirable (inherent and poor mechanical properties).

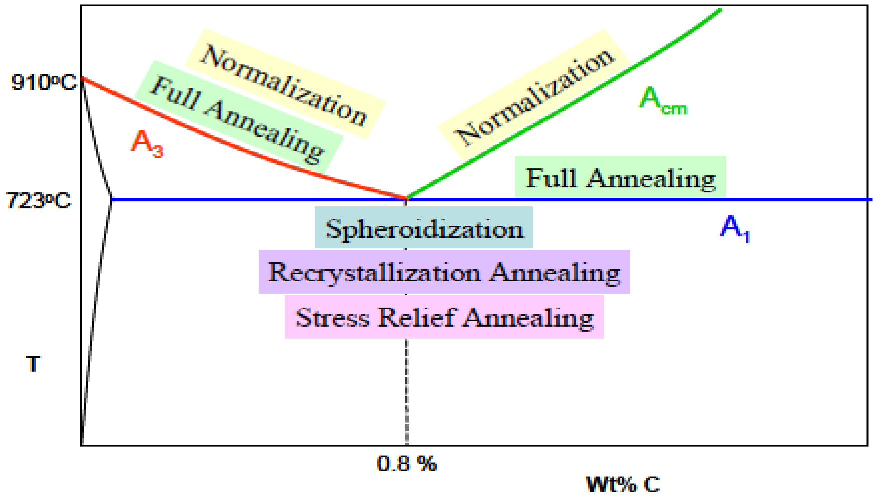
Objective of full annealing

- Improve ductility,
- Remove internal stress,
- Enhanced magnetic
- Electrical properties
- Refine the grain structure.

Re-crystallization Annealing

- The Heat below A_1→Sufficient time→ Recrystallization

Cold worked grains→ new stress free grains



PROCESS

- When cold worked metals are heated to a sufficiently high temperature, the badly deformed cold worked grains are replaced by new strain-free grains.

- This process is referred to as re-crystallization, which is distinct from the recovery process during stress relief. At a constant temperature, recovery starts rapidly and then decreases with time. On the other hand, re-crystallization, which is a nucleation and growth process, starts slowly and then builds up to a maximum rate before rapidly levelling off. Re-crystallization annealing of steel is done at **subcritical temperatures.**

- The *re-crystallization temperature* is often defined as the temperature required for the microstructure to undergo 50% re-crystallization in 30 min, and for complete re-crystallization in approximately one hour.

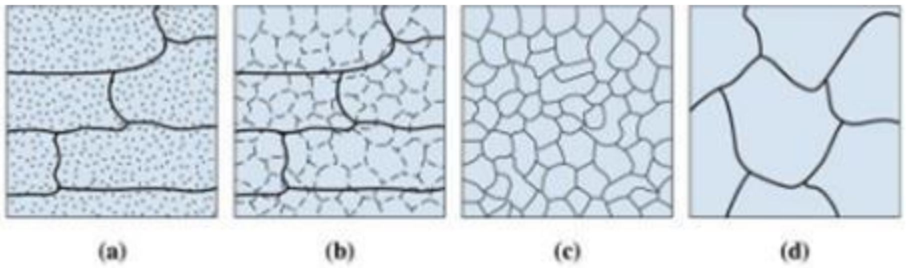


Figure. The effect of annealing temperature on the microstructure of cold-worked metals. (a) cold-worked, (b) after recovery, (c) after recrystallization and (d) after grain growth

OBJECTIVE OF RECRYSTALLIZATION ANNEALING

1. Re-crystallization annealing of can produce a new grain structure without inducing a phase change in cold worked metal.
2. Results in the nucleation and growth of new strain-free, equiaxed grains
3. Contain low dislocation density equivalent to the precold worked condition → annealed state
4. Restoration of mechanical properties → softening

The re-crystallized grain size is dependent

- On both the re-crystallization time and temperature, particularly the temperature. Higher temperatures tend to promote larger grain sizes

The temperature required for re-crystallization depends

- On the composition of the alloy
- In particular on the amount of cold work performed.
- Used in between processing steps (e.g. Sheet Rolling)

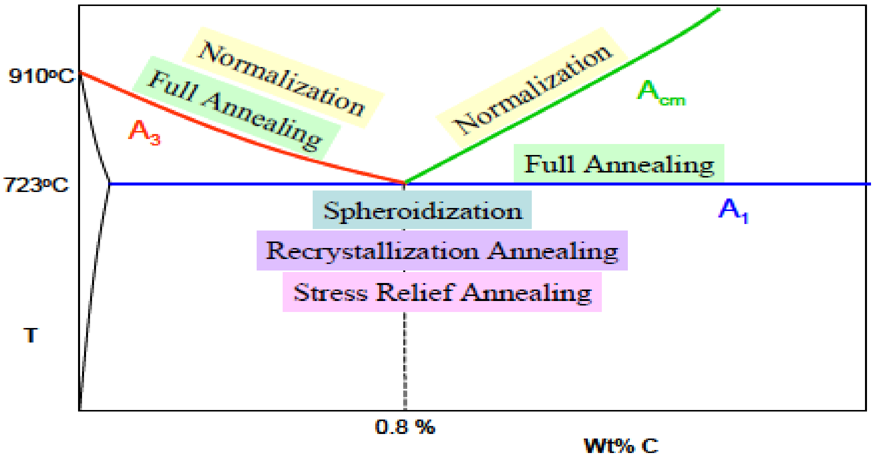
Application

- Used in between processing steps (e.g. Sheet Rolling)

Stress Relief Annealing

PROCESS

• Annealing involves uniform heating of a structure, or portion thereof, and holding at this temperature for a predetermined period of time, followed by uniform cooling. Stress relief temperatures are sufficiently high to help activate the microstructural process of *recovery,* such that stored internal strain energy is relieved by rearrangement of dislocations into lower-energy configurations without any change in the shape and orientation of grains.



CARE TAKEN DURING THE PROCESS

•. Care must be taken to ensure uniform cooling, particularly when a component is composed of variable section sizes. If the rate of cooling is not constant and uniform, new residual stresses can result that are equal to or greater than those that the heat-treating process was intended to relieve.

TEMPERATURE RANGE

Annealing at subcritical temperatures (below Ac1) includes three different temperature regions). The first is the temperature range for stress-relief annealing.

OBJECTIVE

1. can reduce distortion and high stresses from welding that can affect service performance. The presence of residual stresses can lead to stress-corrosion cracking (SCC) near welds and in regions of a component that has been cold strained during processing.
2. Stress-relief heat treating is used to relieve stresses from cold working

Spheroidization Annealing

- Heat below A_1, lower critical temperature. (Prolonged holding)
- Applicable to steel with carbon % 0.6 to 1.2(high carbon steel) which are difficult to machine.
- It causes the formation of all carbides in the steel in the form of very small globlules or spheroids like sphere.

PROCESS

The process consist of hating the steel near the lower critical temperature (730-770^{0}C), holding at this temperature and then cooling slowly to 600^{0}C . The rate of cooling in the furnace is 25-30^{0}C/hr.

PROCESS IN HYPOEUTECTOID STEELS

- In hypoeutectoid steels, prolonged holding at a temperature just below Ae1 accelerates the process of spheroidization. The process may take several hours. To improve on kinetics for full spheroidization, some treatments involve heating and cooling alternately between temperatures that are just above Ac1 and just below Ar1.

PROCESS IN HYPEREUTECTOID STEELS

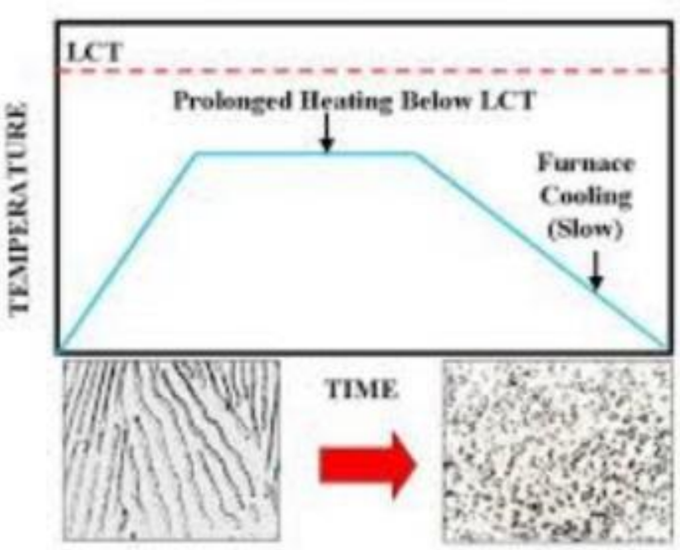
- spheroidization is done Heating of hypereutectoid steels above Ac1 is done to create dispersed cementite particulates. Heating to dissolve the carbide prevents reformation of a carbide network. If a temperature slightly above Ac1 is to be used, good loading characteristics and accurate temperature controls are required for proper results; otherwise, it is conceivable that Ac1 may not be reached and that austenitization may not occur.

OBJECTIVE

1. The shape and distribution of the carbides can be modified.
2. Spheroidization treatments are used to produce carbides with a more spherical morphology.
3. Cementite plates → Cementite spheroids →↑ Ductility
4. To improve machinability and improve toughness in hypereutectoid steels (C > 0.77%) and tool steels

DIFFERENT MORPHOLOGIES OF CEMENTITE CARBIDES IN A STEEL

1. The lamellar cementite of pearlite
2. A network of cementite along prior austenite grain boundaries in hypereutectoid steel.



QUESTIONS

How spheroidization helps to improve machinability, toughness, and formability?

- Because spherical shapes have lower surface energy than angular shapes, the lamellar shape of cementite in pearlite changes morphology to form spheroids. Portions of the lamellae “pinch off” (dissolve) to form a spheroid from the remaining portions of lamellae. This process can occur over a long period of time, or it can be accelerated by heat treatment. Depending on the steel, spheroidized carbides can lead to improved machinability, toughness, and formability.
- **Spherical grains offer uniform resistive force against the movement of tool bit with roll friction which implies machinability is easy.**

Why low carbon steels are not preferable for spherodizing for machining?

- In low-carbon steels, the typical purpose of spheroidizing is to improve the cold formability of steels. The formability of steel is altered significantly depending on whether carbides are spheroids or present as lamellae in pearlite. Low-carbon steels are seldom spheroidized for machining, because in the spheroidized condition they are excessively soft and “gummy,” cutting with long, tough chips.

What will happen if steel is kept too long at spheroidized-annealing temperature ?

- If the steel is kept too long at the spheroidized-annealing temperature, the cementite particles will coalesce and become elongated thus reducing machinability

Diffusion Annealing

- This process also known as homogenizing annealing, is employed to remove any structural non-uniformity.
- Dendrites, columnar grains and chemical inhomogeneities are generally observed in the case of ingots, heavy plain carbon steel casting, and high alloy steel castings. These defects promote brittleness and reduce ductility and toughness of steel.

PROCESS

- In diffusion annealing treatment, steel is heated sufficiently above the upper critical temperature (say, 1000-1200°C).the optimum temperature being 1150^{0}C at which diffusion proceeds quite easily. The steel is heated to 1150^{0}C as the highest rate available for the furnace. Holding time is kept at minimum, followed by cooling with the furnace for 6-8 hours to 800-850^{0}C and then further cooling in air. After cooling homogenizing castings undergo full annealing to refine their structures. Higher temperatures are selected to enable diffusion more and more.

OBJECTIVE

1. Employed to remove any structural non-uniformity.

Post processing heat treatment followed by diffusion annealing

- Segregated zones are eliminated and chemically homogeneous coarse grain steel is obtained by this treatment as a result of diffusion.
- The coarse grained structure can be refined either by plastic working for ingots or by employing a second heat treatment for castings.

Diffusion annealing on Hypoeutectoid, eutectoid and hypereutectoid steel

- Hypoeutectoid and eutectoid steel castings are given full annealing treatment, whereas hypereutectoid steel castings are either normalized or partially annealed for this purpose.

Process annealing

Process

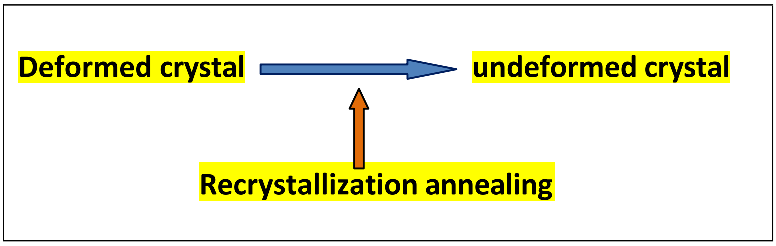
- It is the re-crystallization of cold-worked steel by heating below the lower critical temperature, and is held at this temperature for sufficient time and then cooled. Since it is a subcritical annealing, cooling rate is of little importance.
- The exact temperature depends upon the extent of cold working, grain size, composition and holding time.
- During re-crystallization the deformed grains are reoriented hence they increases plasticity and remove internal stresses.

It produces no change in microstructure and the process is primarily used for low carbon steels.

The purpose of this treatment

1. To reduce hardness
2. To increase ductility of cold-worked steel so that further working may be carried out easily.
3. To restore ductility of the cold worked metal.

It is an Intermediate operation and is sometimes referred to as in process annealing. The process is less expensive than Re-crystallization annealing.



During process annealing, recovery and crystallization takes place. During process annealing, new equiaxed, strain- free grains nucleate at high stress regions in the cold worked microstructure and hence hardness and strength decreases whereas ductility increases.

Annealed crystal (grain) $\xrightarrow[\text{Cold work}]{}$ **Deformed or strained Crystal**
(high energy state)

When a metal is cold worked, most of the energy goes into plastic deformation to change the shape and heat generation. However, a small portion of the energy, up to -5%, remains stored in the material. The stored energy is mainly in the form of elastic energy in the strain fields surrounding dislocation and point defects generated during the cold work.

By Process annealing cold worked are quite unstable due to the strain energy, by heating the cold worked material to high temperature where sufficient atomic mobility is available, the material can be process annealing where recovery and re-crystallization take place.

NORMALIZING

Purpose

1. To refine grain size,
2. To make its structure more uniform,
3. To make it more responsive to hardening, and
4. To improve machinability.

Applicable to steels with %C 0-2.11 % (low carbon steels, medium carbon steels and high carbon steels)

Process

- When steel is heated to a high temperature, the carbon can readily diffuse, resulting in a reasonably uniform composition from one area to the next. The steel is then more homogeneous and will respond to the heat treatment more uniformly.

- Normalizing is an austenitizing heating cycle followed by cooling in still or slightly agitated air. Typically, the temperatures for normalizing are approximately 55^0C (100^0F) above the upper critical line (that is, above Ac_3 for hypoeutectoid steels and above Acm for hypereutectoid steels).

- Heat above A_3 | Acm→ Austenization → Air cooling → Fine Pearlite (Higher hardness)

- In hypo-eutectoid steels normalizing is done 50^0C above the annealing temperature 50^0C
- In hyper-eutectoid steels normalizing done above Acm → due to faster cooling cementite does not form a continuous film along GB.
-

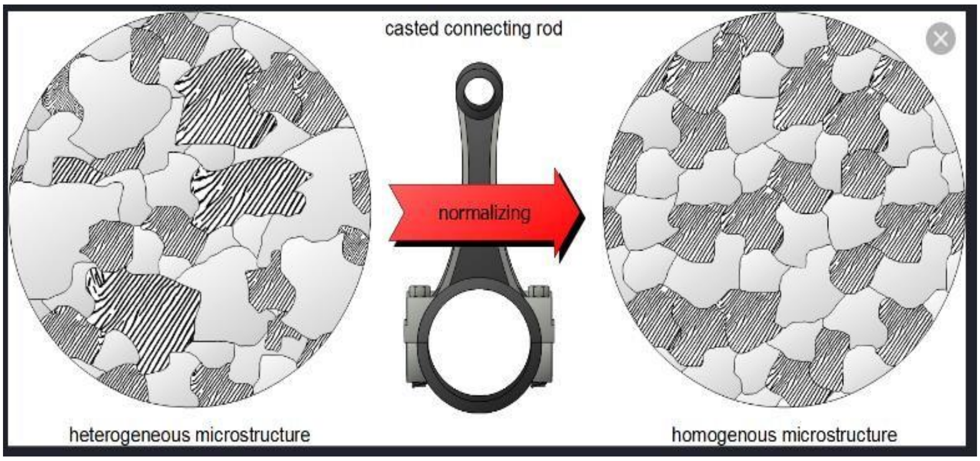


Fig. Normalizing of a casted connecting rod (transformation from heterogeneous microstructure to homogeneous microstructure

Difference between annealed product and normalized product

Annealed vs Normalized	
Annealed	Normalized
Less hardness, tensile strength and toughness	Slightly more hardness, tensile and toughness
Pearlite is coarse and usually gets resolved by the optical microscope.	Pearlite is fine and usually appears unresolved with optical microscope
Grain size distribution is more uniform	Grain size distribution is lightly less uniform
Internal stress are least	Internal stresses are slightly more.

Note: During normalising process due to atmospheric cooling the component will be partially oxidised and hence it posses high corrosion resistance.

HARDENING

Definition

- Certain applications demand high tensile strength and hardness values so that the components may be successfully used for heavy duty purposes. High tensile strength and hardness values can be obtained by a process known as Hardening.

- The maximum hardness of any steel is associated with a fully martensitic structure. This microstructure can be produced only if the cooling rate applied is higher than the critical cooling rate for the corresponding steel.

Process of hardening

Hardening process consists of four steps.

1. The first step involves heating the steel to above A_3 (higher critical temperature) temperature for hypoeutectoid steels and above A_1 (lower critical temperature) temperature for hypereutectoid steels by 50^0C.

2. The second step involves holding the steel components for sufficient socking time for homogeneous austenization.

3. The third step involves cooling of hot steel components at a rate just exceeding the critical cooling rate of the steel to room temperature or below room temperature. Due to rapid cooling carbon carbon freezes at its location and the microstructural appears like colloidal solution of cementite is ferrite. This microstructure is called as martensite which is very hard and brittle.

4. The final step involves the tempering of the martensite to achieve the desired hardness along with relieving of internal stresses and to achive the desires mechanical properties.

The hardening process is based on the metallurgical reaction of eutectoid. This reaction is dependent upon

a) Adequate C-content to produce hardening
b) Austenite decomposition
c) Heating rate and time
d) Quenching medium
e) Quenching rate
f) Size of the part
g) Surface condition

HARDENING METHOD

Conventional or direct quenching
Quenching in stages in sequence in different media
Spray Quenching
Quenching with self tempering
Austempering or Isothermal Quenching
Martempering

DEFECTS IN HARDENING

1. Mechanical properties are not up to specification

   Reason

   a) Insufficient fast cooling
   b) Presence of scale or oil
   c) Inadequate circulation of coolant
   d) Lower austenitising temperature

2. Soft spots soft areas on the hardened surface

   Reason

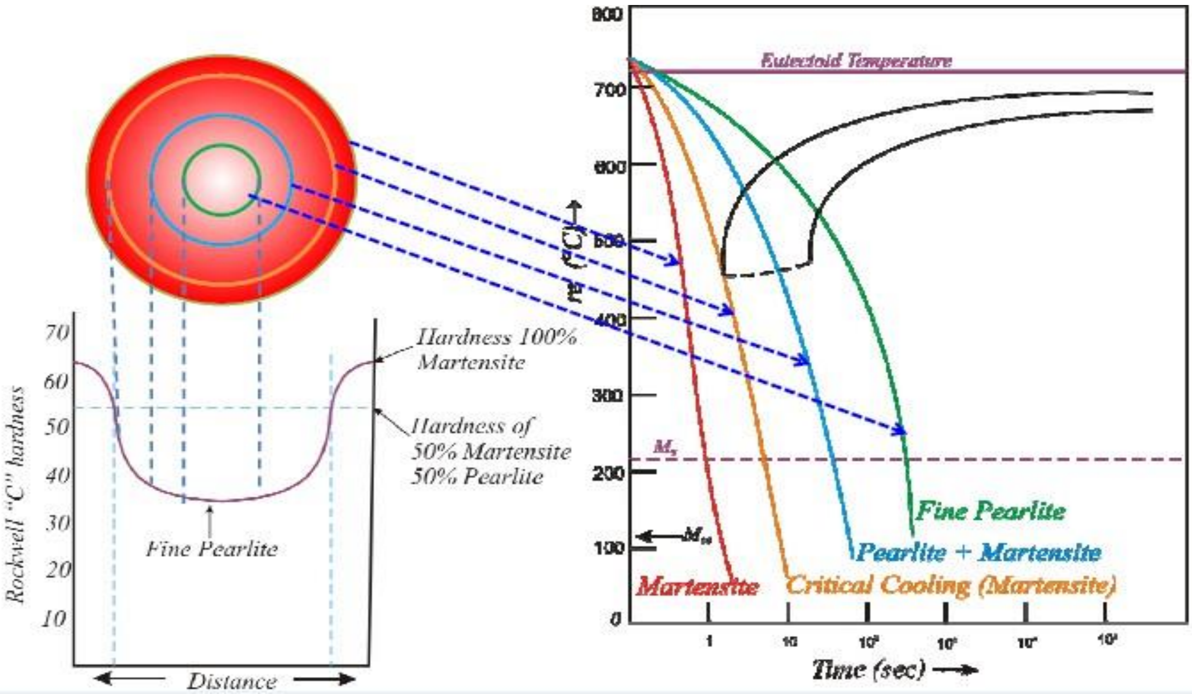
   a) Insufficient circulation of coolant
   b) Rough surface

3. Quench cracks due to residual stress produced.

HARDENABILITY

Hardenability is defined as the "susceptibility to hardening by rapid cooling", or as "the property, in ferrous alloys, that determines the depth and distribution of hardness produced by quenching". Both of these definitions emphasize hardness. As discussed previously, the source of hardening is the formation and presence of martensite, and therefore a third definition of hardenability, "the capacity of a steel to transform partially or completely from austenite to some percentage of martensite at a given depth when cooled under some given conditions," more accurately describes the physical process underlying hardening.

HARDNESS PROFILE IN A CYLINDER FROM CASE TO CORE



Typical hardness test survey made along A diameter of a quenched cylinder	**Schematic showing variation in cooling rate from surface to interior leading to different microstructures**

- **It is a qualitative measure of the rate at which hardness drops off with distance into the interior of a specimen as a result of diminished martensite content.**
- Hardenability is more related to depth of hardening of steel upon heat treat.
- The depth of hardening in plain carbon steel may be 2-3 mm Vs 50 mm in an alloy steel.
- A large diameter rod quenched in a particular medium will obviously cool more slowly than a small diameter rod given a similar treatment. Therefore, the small rod is more likely to become fully martensitic.

Determination of hardenability

Hardenability of steel is determined by the following methods

- Grossman's critical diameter method
- Jominy end quench test
- Estimation of hardenability from chemical composition
- Fracture test

Severity of Quench

The effectiveness of a given quenching medium is ranked by a parameter referred to as its "severity of quench." This measure of cooling or quenching power is identified by the letter "H" and is determined experimentally by quenching a series of round bars of given steel.

Note that apart from the nature of the quenching medium, the vigorousness of the shake determines the severity of the quench. When a hot solid is put into a liquid medium, gas bubbles form on the surface of the solid (interface with medium). As gas has a poor conductivity the quenching rate is reduced. Providing agitation (shaking the solid in the liquid) helps in bringing the liquid medium in direct contact with the solid; thus improving the heat transfer (and the cooling rate). The H value/index compares the relative ability of various media (gases and liquids) to cool a hot solid. Ideal quench is a conceptual idea with a heat transfer factor of ∞ ($\Rightarrow H = \infty$)

Table. The H value of various media (gases and liquids)

Process	Variable	H Value
Air	No agitation	0.02
Oil quench	No agitation	0.2
"	Slight agitation	0.35
"	Good agitation	0.5
"	Vigorous agitation	0.7
Water quench	No agitation	1.0
"	Vigorous agitation	1.5
Brine quench (saturated Salt water)	No agitation	2.0
"	Vigorous agitation	5.0
Ideal quench		∞

Severity of Quench as indicated by the heat transfer equivalent **H**

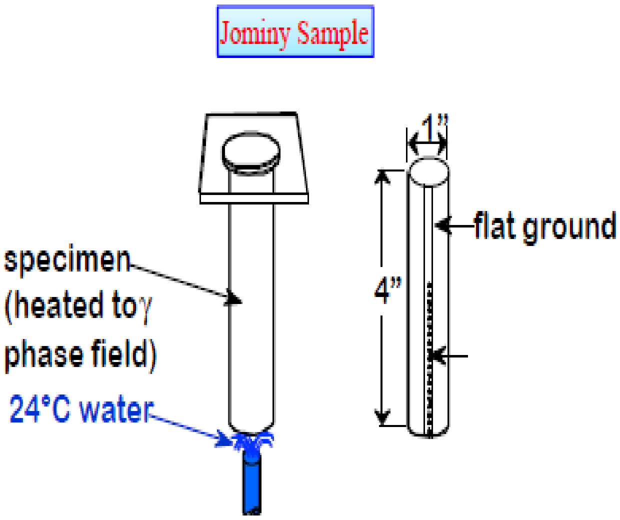
$$H = \frac{f}{K} \quad [m^{-1}]$$

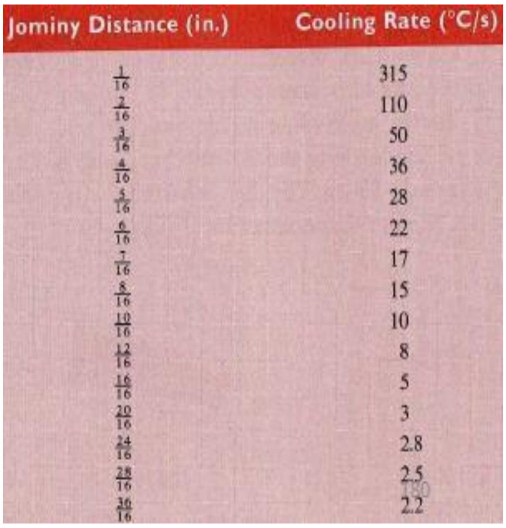
Jominy end quench test for Hardenability

- The most commonly used method for determining hardenability is the end quench test developed by Jominy and Boegehold
- Grossmans method requires multiple Austenitisation and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.
- An alternative approach is to develop a more convenient standard test method that can be used for relative comparison of hardenability. The Jominy end-quench test is one such approach.
- The Jominy end-quench test is specified in ASTM standard A255 and is a widely used method for quantifying hardenability. Its wide use adds to its value, since the utility of empirical relations and data comparison becomes more reliable as more data are accumulated.
- Moreover, Jominy data have been collected on a large enough scale to offer a high degree of statistical certainty for many steels.
- These data have been correlated with measurements and/or calculations of DC.
- By using these correlations, a single Jominy test can be used to estimate DC and DI for given steel (and austenite grain size).
- Information gained from this test is necessary in selecting the proper combination of alloy steel and heat treatment to minimize thermal stresses and distortion when manufacturing components of various sizes.

Jominy End Quench Method- Principle

- The hardenability of steel is measured by a Jominy test with following procedure.
- In conducting this test, a 1 inch round specimen 4 inch long is heated uniformly to the proper austenising temperature. It is then removed from the furnace and placed on a fixture where a jet of water impinges on the bottom face of the sample.
- After 10 min. on the fixture, the specimen is removed, and to cut along the longitudinal direction.
- And then Rockwell C scale hardness readings are taken at 1/16 inch, intervals from the quenched end. The results are expressed as a curve of hardness values vs. distance from the quenched end. A typical hardenability curve shown below for eutectoid steel.
- A number of Jominy end quench samples are first end- quenched for a series of different times and then each of them (whole sample) is quenched by complete immersion in water to freeze the already transformed structures.
- Cooling curves are generated putting thermocouple at different locations and recording temperature against cooling time during end quenching.
- Microstructures at the point where cooling curves are known are subsequently examined and measured by quantitative metallography. Hardness measurement is done at each investigated point.
- Based on metallographic information on investigated point the transformation start and finish temperature and time are determined. The transformation temperature and time also determined for specific amount of transformation.

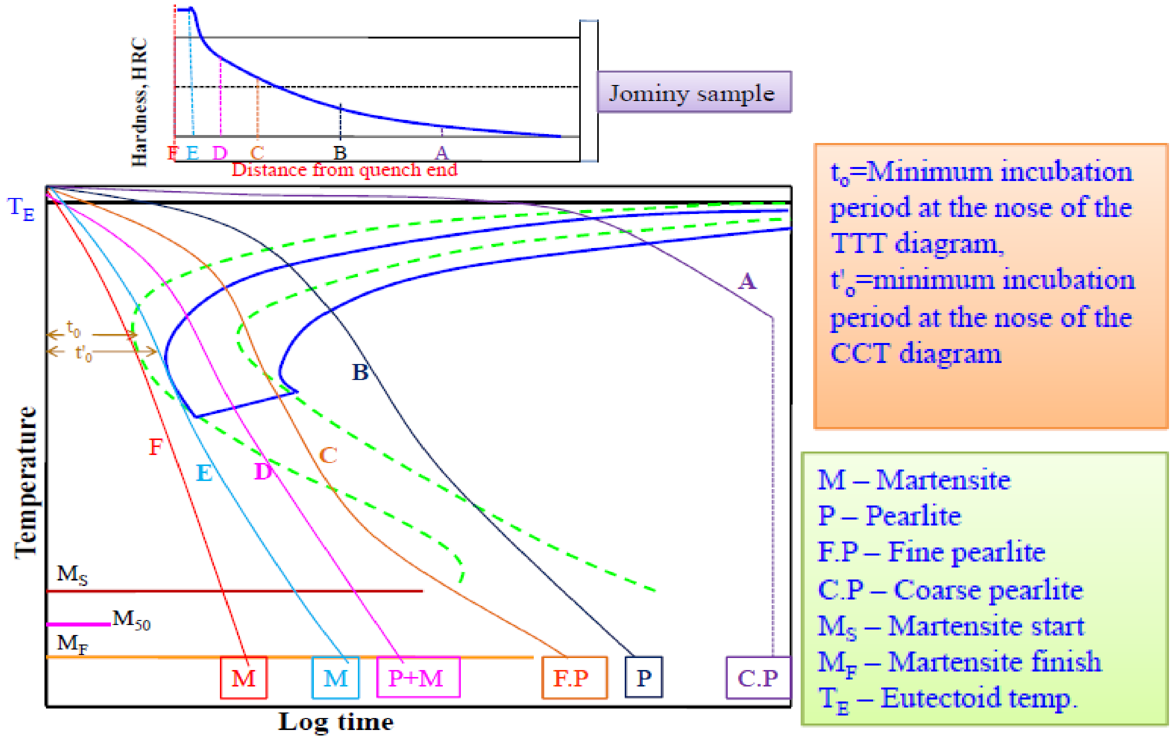




Jominy Distance (in.)	Cooling Rate (°C/s)
$\frac{1}{16}$	315
$\frac{2}{16}$	110
$\frac{3}{16}$	50
$\frac{4}{16}$	36
$\frac{5}{16}$	28
$\frac{6}{16}$	22
$\frac{7}{16}$	17
$\frac{8}{16}$	15
$\frac{10}{16}$	10
$\frac{12}{16}$	8
$\frac{16}{16}$	5
$\frac{20}{16}$	3
$\frac{24}{16}$	2.8
$\frac{28}{16}$	2.5
$\frac{36}{16}$	2.2

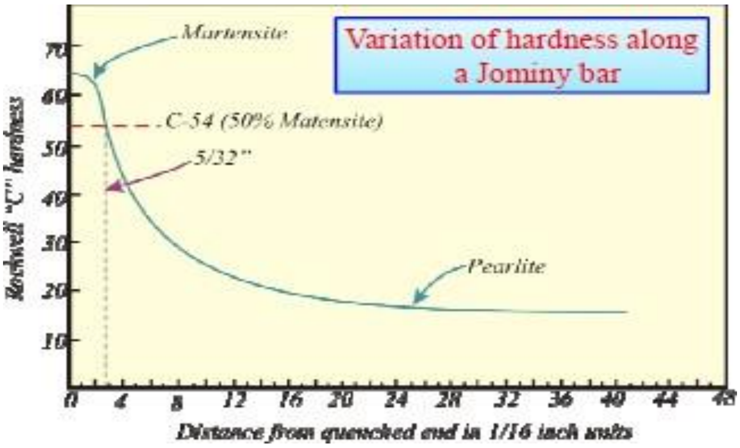
- These are located on cooling curves plotted in a temperature versus time diagram. The locus of transformation start, finish or specific percentage of transformation generate CCT diagram.

- A, B, C, D, E, F are six different locations on the Jominy sample shown in *Figure.* that gives six different cooling rates. The cooling rates A, B, C, D, E, F are in increasing order.
- The corresponding cooling curves are shown on the temperature log time plot. At the end of the cooling curve phases are shown at room temperature. Variation in hardness with distance from Jominy end is also shown in the diagram.

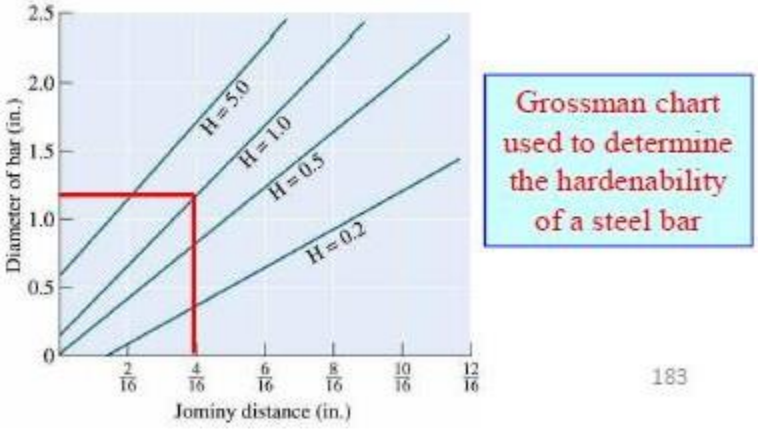


Determination of hardenability from Jominy curve

- After plotting the Jominy distance Vs Hardness curve, the Jominy distance having hardness equal to 50 % martensite is determined.
- Then the diameter of a rod having cooling rate similar to the cooling rate at the Jominy distance having 50 % martensite is determined from the graph correlating the Jominy distance with the diameter of the rod having similar cooling rate for water quenching.
- This diameter gives the hardenability of the steel in water quenching (having H value equal to 1).
- Hardenability in any other quenchants can be determined from the same graph.
- DI (hardenability in ideal quenching medium) can also be determined in a similar manner.
- We can determine hardenability for any other amount of martensite in the core in any quenchants in a similar way.



Variation of hardness along a Jominy bar



Grossman chart used to determine the hardenability of a steel bar

FACTOR AFFECTING THE HARDENABILITY

Slowing the phase transformation of austenite to ferrite and pearlite increases the hardenability of steels.

a) The most important variables which influence hardenability are
b) Quenching conditions
c) Austenitic grain size
d) Carbon content
Alloying elements

QUENCHING CONDITIONS

The fluid used for quenching the heated alloy effects the hardenability.

- Each fluid has its own thermal properties like…
  a) Thermal conductivity
  b) Specific heat
  c) Heat of vaporization
- These cause rate of cooling differences
- Ideal quenchant: It is one which brings down the surface temperature to room temperature instantaneously and keeps it at that temperature thereafter.

RETAINED AUSTENITE

- Austenite that is present in in the ferrous alloys even after the completion of the heat treatment process is referred to as retained austenite. In simple words, retained austenite is the untransformed austenite.
- Austenite transforms to martensite between Ms and Mf temperatures as it is essentially an athermal transformation. However, this transformation never goes to completion, i.e., 100% martensite (Mf temperature line is illustrated as dotted line in TTT diagrams).
- This is because at Mf , a small amount of (~1%) of austenite is present in highly stressed state along with ~99% martensite, and cannot transform to martensite because unfavourable stress conditions.
- Both Ms and Mf temperatures decrease with increase in carbon content. Therefore amount of retained austenite in hardened steels increase with increase in carbon content.
- All alloying elements, except Al and Co, lower the Ms temperature and hence enhance the amount of retained austenite. Therefore, both high carbon steels and high alloy steels are more prone to the presence of retained austenite.
- The substructure of retained austenite differs from that of the original austenite as it has as a higher density of imperfections like dislocations, stacking faults, etc. which are created by local plastic deformation of the austenite by martensite crystals.
- Tool steels may have retained- austenite in the range of 5-35%. At the surface of quenched steel, that restrains are minimum. R.A is less at surface than center of the part.

ADVANTAGES

- Ductility of austenite can help to relieve some internal stresses developed due to hardening, to reduce danger of distortion and cracks. 10% retained austenite along with martensite is desirable.
- The presence of 30-40% retained austenite makes straightening operation of the components possible after hardening. Straightening increases the hardness slightly.
- Non-distorting steels owe their existence to retained austenite. Here enough austenite is retained to balance the transformational contracting during heating, on the formation of austenite from ferrite carbide aggregate on the one hand, and the expansion corresponding

DISADVANTAGES

- The soft austenite if present, in large amounts, decreases the hardness of hardened steels.

- As retained austenite may transform to lower bainite, or to martensite, there takes place increase in dimensions of the part. Not only it creates problems in precision gauges, or dies, the neighboring parts may be put under stress by it. In the component itself, stresses may be created to cause distortion or cracking.
- Retained austenite decreases the magnetic properties of the steel.

TEMPERING

Objective:

1. Relieve internal stresses developed during hardening
2. Restore ductility and toughness with decrease in hardness and strength
3. To improve dimensional stability b decomposing retained austenite
4. To improve magnetic properties by by transforming non-magnetic retained austenite

Process

The martensite which is formed during quenching is too brittle and hence cannot b used in many cases. The residual stresses are also developed during martensite formation hence hardening should be followed by tempering. Tempering consists in heating the hardened steel to a temperature below the lower critical temperature holding it for some time and then cooling slowly. It is the final operation in heat treatment.

Some advantages of tempering are:

1. Residual stresses are relieved.
2. Ductility is improved
3. Toughness is increased

The higher the tempering temperature more will be the recrystallization phenomenon this will reduce hardness and increase toughness. The work is cooled slowly after tempering. The cooling rate considerably affects the residual stresses. The slower the cooling the lesser wiil be the stresses. Rapid cooling in water develops new thermal stresses.

Note that in full annealing process the component will be heated to above 723^{0}C always but in tempering it is always heated to below 550^{0}C. Therefore $(grain\ size)_{annealed\ product} > (grain\ size)_{tempered\ component}$, $hardeness_{annealed\ product} < hardness_{tempered\ product}$, $ductility_{annealed\ product} > ductility_{tempered\ component}$

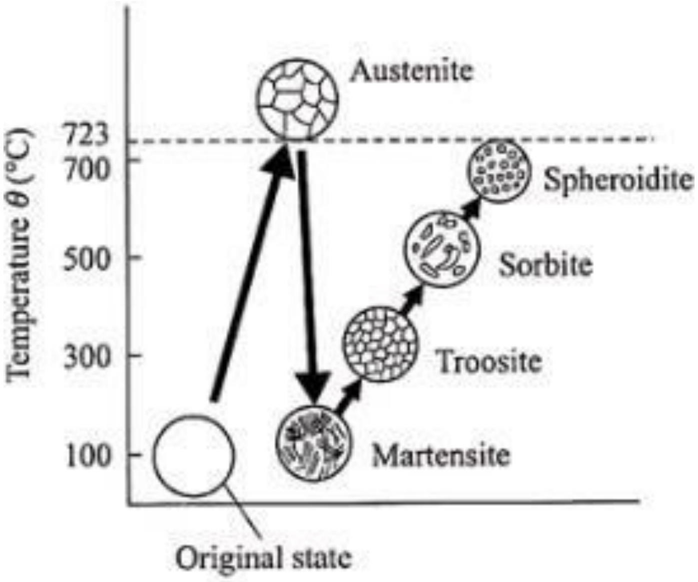


Fig.Tempering of martensite

Tempering is classified according to the tempering temperature, because it has much effect on properties of steel.

1. **High temperature Tempeing**(500-650^{0}C)

   It is employed at 500-650^{0}C. The resulting structure consists of **sorobite** which gives good strength and toughness. Residual stresses are completely relieved if holding temperature is 100-120^{0}C the holding time for 1-2hr to give desired properties to steel. High temperature tempering produces **spheriodite structure (sorbitic structure)** in plain carbon and low alloy steels.

   Application: This results in best combination of strength and toughness for machine components.

2. **Medium temperature tempering(350^0-500^{0}C)**

   This type of tempering is employed at 350-500^{0}C resulting steel structure consists of **troosite**. This process increases the endurance limit and elastic limit in range of hardness HRC. If water quenched after tempering, the piece developed compressive stresses in the surface to increase the endurance limit. After tempering the work is cooled in water then by increasing the endurance limit in case of springs. **Application**: This process is used for spring steels and die steels, springs of both types, coils and laminated.

3. **Low temperature tempering (1-2 hours in the range up to 250^{0}C)**

   The temperature employs at 250^{0}C and the holding time is 1-2 hours. This process reduces internal stresses, increases strength and toughness and provides high wear resistance.

Application: This method is employed in manufacturing of (plain carbon and low alloy steels) measuring tools and cutting tools. This is also employed to components which are surface hardened by carburizing nitriding or carbo-nitriding.

OPTICAL PROPERTIES

Engineering materials are important in everyday life because of their versatile structural properties. Other than these properties, they do play an important role because of their physical properties. Prime physical properties of materials include: electrical properties; thermal properties; magnetic properties; and optical properties. Optical properties play an important role in daily life. They have had a significant impact on the development of the communications infrastructure and the information technology. They are also useful in fields like medicine, manufacturing, astronomy, etc.

Basic concepts

Optical property of a material is related to the interaction of it with electromagnetic radiation. This radiation may have characteristics that fall in the visible light spectrum, or may be even out of it. Electromagnetic spectrum of radiation spans the wide range from γ-rays with wavelength as 10^{-12} m, through x-rays, ultraviolet, visible, infrared, and finally radio waves with wavelengths as along as 10^{5} m. visible light is one form of electromagnetic radiation with wavelengths ranging from 0.39 to 0.77 µm. It contains color bands from violet through red, as shown in the ***figure.*** White light is simply a mixture of all colors. The ultraviolet region covers the range from about 0.01 to about 0.40 µm, and the infrared region extends from about 0.75 to 1000 µm.

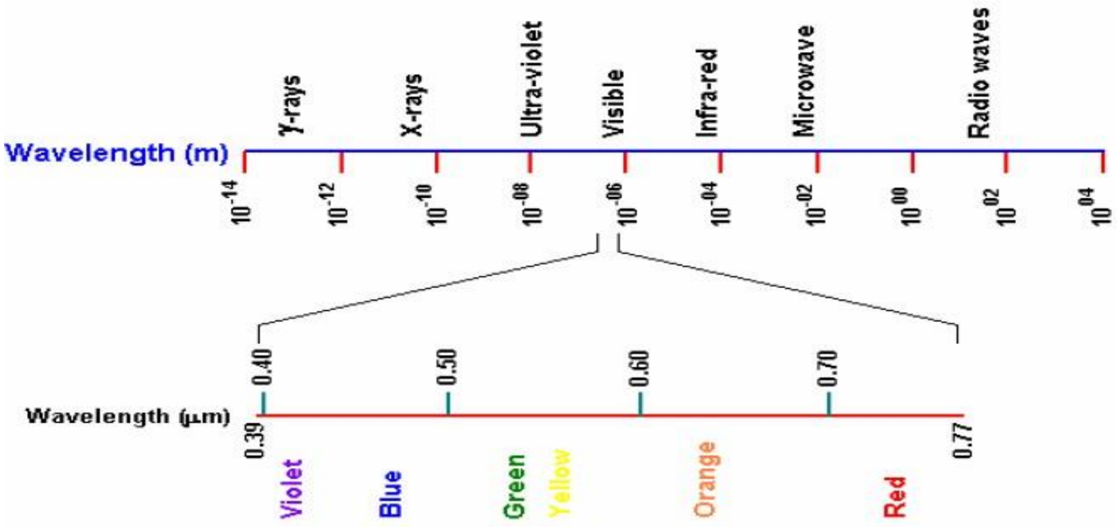


Figure: *Wave length spectrum of electro-magnetic waves.*

The true nature of the light will probably never be known. However, light can be considered as having waves and consisting of particles called photons. The important characteristics of the photons are related by the following equation. This equation allows us to consider the photon as a particle of energy, or as a wave with a characteristic wavelength and frequency.

$$E = h\nu = \frac{hC_0}{\lambda}$$

Where E-energy, h-Plank's constant (6.62 X10^{-34} J.sec), ν-frequency, $C_0 -$ speed of light in vacuum (3x108m/sec) and λ-wavelength

All materials interact in some way with light. Interaction of photons with the electronic or crystal structure of a material leads to a number of phenomena. The photons may give their energy to the material (absorption); photons give their energy, but photons of identical energy are immediately emitted by the material (reflection); photons may not interact with the material structure (transmission); *or* during transmission photons are changes in velocity (refraction).

At any instance of light interaction with a material, the total intensity of the incident light striking a surface is equal to sum of the absorbed, reflected, and transmitted intensities i.e

$$I_O = I_A + I_R + I_T$$

The intensity is defined as the number of photons impinging on a surface per unit area per unit time. Materials that are capable of transmitting light with relatively little absorption and reflection are called *transparent materials* i.e. we can see through them. *Translucent materials* are those through which light is transmitted diffusely i.e. objects are not clearly distinguishable when viewed through. Those materials that are impervious to the transmission of visible light are termed as *opaque materials*.

OPTICAL PROPERTIES OF METALS AND ALLOYS

Typical characteristic of metals with respect to crystal structure is that they possess a high-energy band that is only partially filled with electrons. When visible light in directed on a metal surface, the energy is used to excite electrons into unoccupied energy states above the Fermi level, thus making metals behave as opaque materials i.e. light is absorbed. Except of thin sections, metals strongly reflect and/or absorb incident radiation for long wavelengths to the middle of the ultraviolet range i.e. metals are opaque to all electromagnetic radiation on the low end of the frequency spectrum, from radio waves, through infrared, visible, into middle of the ultraviolet radiation. However, metals are transparent to high end frequencies, ex. x-ray and γ–ray radiation. Total absorption by metals is within a very thin outer layer, usually less than 0.1 µm; thus only metallic films thinner than 0.1 µm are capable of transmitting visible light.

Most of the absorbed radiation is emitted from the metallic surface in the form of visible light of the same wavelength as reflected light. The reflectivity of metals is about 0.95, while the rest of impinged energy is dissipated as heat. The amount of energy absorbed by metals depends on the electronic structure of each particular metal. For example: with copper and gold there is greater absorption of the short wavelength colors such as green and blue and a greater reflection of yellow, orange and red wavelengths. Other metals such as silver and aluminium strongly reflect all parts of the visible spectrum and show a white silvery color.

OPTICAL PROPERTIES OF NON-METALLIC MATERIALS

By virtue of their electron structure with characteristic energy band structures, non-metallic materials may be transparent to visible lights. Thus, all four optical phenomena such as absorption, reflection, transmission and refraction are important for these materials.

Refraction: When light photons are transmitted through a material, they causes polarization of the electrons in the material and by interacting with the polarized materials, photons lose some of their energy. As a result of this, the speed of light is reduced and the beam of light changes direction.

The relative velocity of light passing through a medium is expressed by the optical property called the index of refraction (n), and is defined as:

$$\boldsymbol{n = \frac{c_o}{c}}$$

Where c_0 – speed of light in vacuum, c – speed of light in the concerned material. If the angle of incidence from a normal to the surface is θ_i and the angle of refraction is θ_r, the refractive index of the medium, n, is given by

$$\boldsymbol{n = \frac{\sin\theta_i}{\sin\theta_r}}$$

Provided that the incident light is coming from a phase of low refractive index such as vacuum or air. Reflection and refraction of light is shown in *figure*

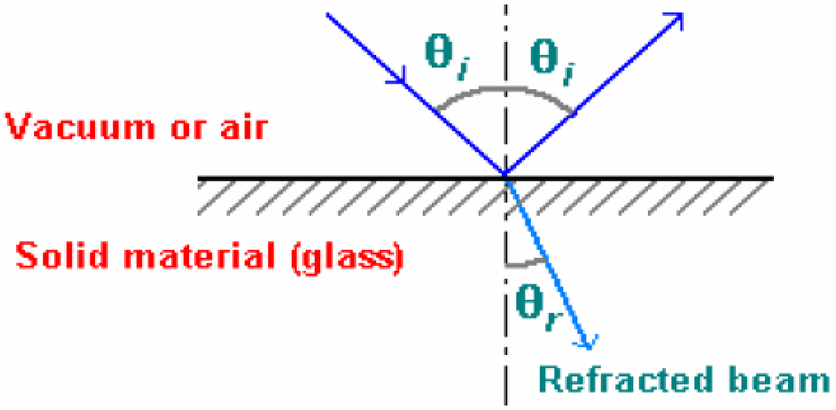


Figure-: *Reflection and refraction of light*.

The speed of light in a material can be related to its electrical and magnetic properties as:

$$c = \frac{1}{\sqrt{\mu.\varepsilon}}$$

Where ε – electrical permittivity, and μ – magnetic permeability. Thus,

$$c = \frac{c_0}{c} = \frac{\sqrt{\mu.\varepsilon}}{\sqrt{\mu_0.\varepsilon_0}} = \sqrt{\mu_r\varepsilon_r}$$

Since most substances are only slightly magnetic i.e. $\mu_r \approx 1$, then

$$n \cong \sqrt{\varepsilon_r}$$

Thus, for transparent materials, index of refraction and dielectric constant are related. Refractive indices of some materials are listed in the *table*.

Table. Refractive indices of some materials

Material	*Refractive index*	*Material*	*Refractive index*
Air	1.00	Epoxy	1.58
Ice	1.309	Polystyrene	1.60
Water	1.33	Spinel, $MgAl_2O_3$	1.72
Teflon	1.35	Sapphire, Al_2O_3	1.76
Silica glass	1.458	Rutile, TiO_2	2.68
Polymethyl methacrylate	1.49	Diamond	2.417
Silicate glass	1.50	Silicon	3.29
Polyethylene	1.52	Gallium arsenide	3.35
NaCl	1.54	Germanium	4.00

Snell's law of light refraction – refractive indices for light passing through from one medium with refractive index *n* through another of refractive index *n'* is related to the incident angle, *ϑ*, and refractive angle, *θ'*, by the following relation.

$$\frac{n}{n'} \quad \frac{\sin\theta'}{\sin\theta}$$

If light passes from a medium with a high refractive index to one with a low refractive index, there is a critical angle of incidence, θ_c which if increased will result in total internal reflection of the light. This angle is defined as θ' (refraction) = 90°.

Reflection: When a beam of photons strikes a material, some of the light is scattered at the interface between the two media even if both are transparent. Reflectivity, *R*, is a measure of fraction of incident light which is reflected at the interface, and is given by

$$R = \frac{I_R}{I_O}$$

Where I_0 and I_R are the incident and reflected bean intensities respectively. If the material is in a vacuum or in air:

$$R = \left(\frac{n-1}{n+1}\right)^2$$

If the material is in some other medium with an index of refraction of n_i, then:

$$R = \left(\frac{n-n_i}{n+n_i}\right)^2$$

The above equations apply to the reflection from a single surface and assume normal incidence. The value of *R* depends upon the angle of incidence. Materials with a high

index of refraction have a higher reflectivity than materials with a low index. Because the index of refraction varies with the wavelength of the photons, so does the reflectivity. In metals, the reflectivity is typically on the order of 0.90-0.95, whereas for glasses it is close to

0.05. The high reflectivity of metals is one reason that they are opaque. High reflectivity is desired in many applications including mirrors, coatings on glasses, etc.

Absorption: When a light beam in impinged on a material surface, portion of the incident beam that is not reflected by the material is either absorbed or transmitted through the material. The fraction of beam that is absorbed is related to the thickness of the materials and the manner in which the photons interact with the material's structure. Thus, according to *Bouguer's law*:

$$I = I_0 \exp(-\alpha . x)$$

where *I*- intensity of the beam coming out of the material, I_O - intensity of the incident beam, x-path through which the photons move, and α – linear absorption coefficient, which is characteristic of a particular material.

Absorption in materials occurs mainly by two mechanisms (1) Rayleigh scattering – where photon interacts with the electrons orbiting an atom and is deflected without any change in photon energy. This is significant for high atomic number atoms and low photon energies. Ex.: Blue color in the sunlight gets scattered more than other colors in the visible spectrum and thus making sky look blue. *Tyndall effect* is where scattering occurs from particles much larger than the wavelength of light. Ex.: Clouds look white. (2) Compton scattering – here incident photon knocks out an electron from the atom loosing some of its energy during the process. This is also significant for high atomic number atoms and low photon energies. *Photoelectric effect* occurs when photon energy is consumed to release an electron from atom nucleus. This effect arises from the fact that the potential energy barrier for electrons is finite at the surface of the metal. Absorption occurs at particular levels of photon energies, which are equal to that of binding energies. The energy at which this occurs is called the absorption edge.

Transmission: the fraction of beam that is not reflected or absorbed is transmitted through the material. Thus the fraction of light that is transmitted through a transparent material depends on the losses incurred by absorption and reflection. Thus,

R+A+T=1

Where *R* – reflectivity, *A* – aborptivity, and *T* – transmitivity. Each of these parameters are characteristic of material, and they also depend on light wavelength.

If the incident light is of intensity I_0, then the loss due to reflection at the front end of the material is RI_0. Thus the fraction of beam intensity entering the material is

$$I_{after\ reflection} = (1 - R)I_0$$

Once the beam enters the material, a portion of it is absorbed. Thus

$$I_{after\ absorption} = (1 - R)I_0 \exp(-\alpha . x)$$

Before the beam exits at the back surface, a portion of it will be reflected again. Thus

$$I_{after\ reflection\ at\ back\ surface} = R(1 - R)I_0 \exp(-\alpha . x)$$

Thus, the fraction of beam that is actually transmitted through the material is given by

$$I_{transmitted} = I_{after\ absorption} - I_{after\ reflection\ at\ back\ surfac}$$
$$= (1-R)I_0 \exp(-\alpha.x) - R(1-R)I_0 \exp(-\alpha.x)$$

Thus,

$$I_t = I_0(1-R)^2 \exp(-\alpha.x)$$

The process of light transmission is shown schematically in the *figure*

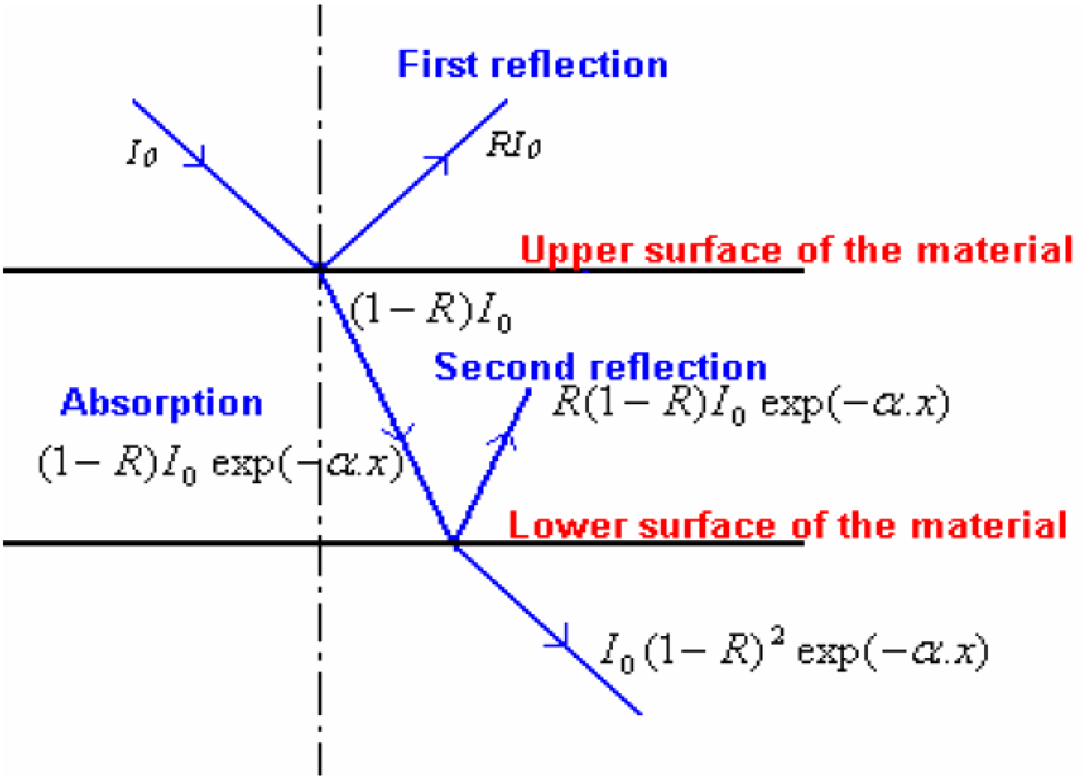


Figure-: *Light transmission*.

ATOMIC AND ELECTRONIC INTERACTIONS

The optical phenomena that occur in solid materials involve interactions between the electromagnetic radiation and atoms, ions, and/or electrons. Two of the most important of these interactions are: *(i) electronic polarization* and *(ii) electron energy transitions.*

ELECTRONIC POLARIZATION

One component of an electromagnetic wave is simply a rapidly fluctuating electric field $\vec{E}$. For the visible range of frequencies, this electric field interacts with the electron cloud surrounding each atom within its path in such a way as to induce electronic polarization, or to shift the electron cloud relative to the nucleus of the atom with each change in direction of electric field component. Two major consequences of this *electronic polarization* are: *(i)* some of the radiation energy may be absorbed, and *(ii)* light waves are retarded in velocity as they pass through the medium. The second consequence is manifested as *refraction*.

ELECTRON TRANSITIONS

The absorption and emission of electromagnetic radiation may involve electron transitions from one energy state to another. Let us consider an isolated atom the electron energy diagram for which is represented in **Fig**. . An electron may be excited from an occupied state $E1$ to a vacant and higher lying one, denoted by E_2, by the absorption of a photon of energy. The change in energy experienced by the electron, , depends on the frequency of radiation as follows:

$$E_2 - E_1 = \Delta E = hv$$

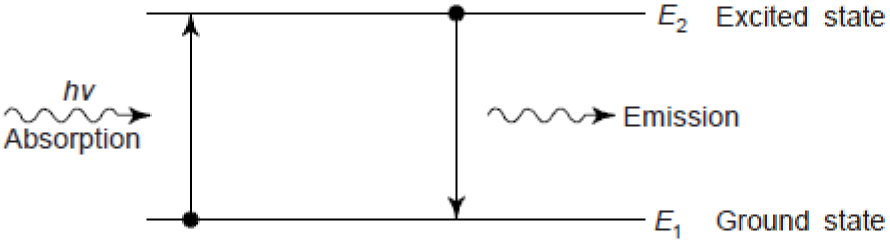


Figure: Atomic transition

We may note that the energy states for the atom are discrete and therefore, only specific ΔE_S exist between the energy levels; thus, only photons of frequencies corresponding to the possible $\Delta E'_S$ for the atom can be absorbed by electron transitions. Moreover, all of a photon's energy is absorbed in each excitation event.

The stimulated electron cannot remain in an *excited state* indefinitely; after a short time, electron falls or decays back into its *ground* or *lower energy state* or *unexcited level*, with a reemission of electromagnetic radiation. Several decay paths are possible. However, there must be a conservation of energy for absorption and emission electron transitions. Obviously, the optical characteristics of solid materials that relate to absorption and emission of electromagnetic radiation are explained in terms of *electron band structure* and the principles relating to electron transitions.

APPLICATION OF OPTICAL PHENOMENA

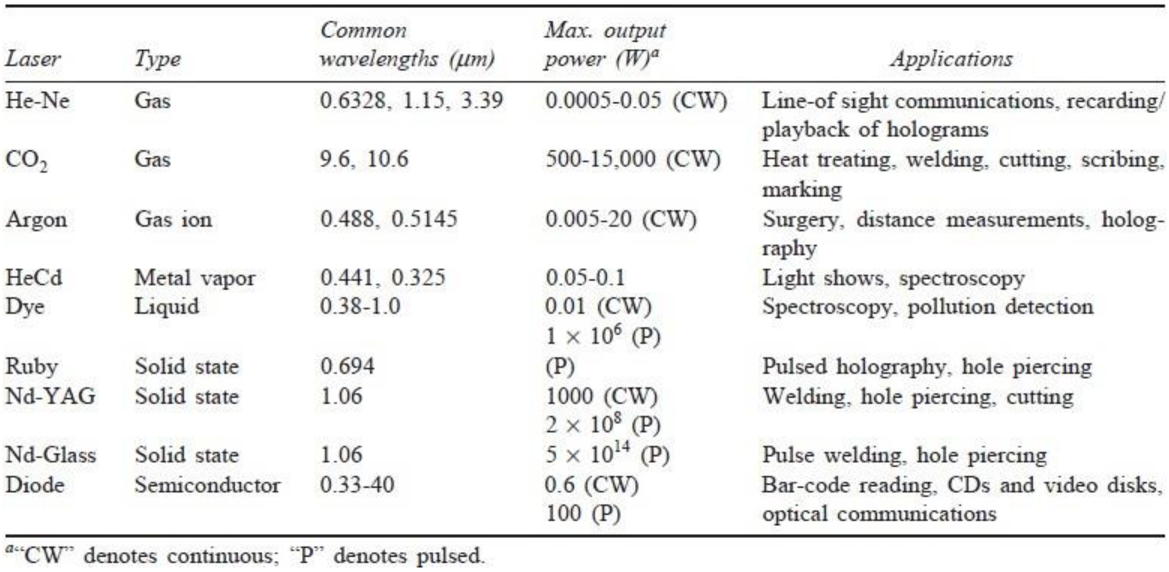
Light interacts with a material in many ways. Depending on the material, its crystal-/micro-structure, and also on the characteristics of incident light, there are many peculiar phenomena occurs, which are known as optical phenomena. These include: luminescence, lasers, thermal emission, photo-conductivity, and optical fibers.

LASER

The word 'laser' is an acronym for light amplification by stimulated emission of radiation. It is a source of highly pure intense beam of light. Laser action can occur in atoms, molecules in gases, liquids, solids, and flames, and ions. The emitted wavelength by laser source covers the ultraviolet to the radio frequency regions, the output power varying form a few MW to MW. Some lasers emit *continuous* waves while others, in pulses.

Table lists several common lasers and their characteristics.

Characteristics and application of few different types of lasers



Laser	*Type*	*Common wavelengths (μm)*	*Max. output power (W)^a*	*Applications*
He-Ne	Gas	0.6328, 1.15, 3.39	0.0005-0.05 (CW)	Line-of sight communications, recarding/ playback of holograms
CO_2	Gas	9.6, 10.6	500-15,000 (CW)	Heat treating, welding, cutting, scribing, marking
Argon	Gas ion	0.488, 0.5145	0.005-20 (CW)	Surgery, distance measurements, holography
HeCd	Metal vapor	0.441, 0.325	0.05-0.1	Light shows, spectroscopy
Dye	Liquid	0.38-1.0	0.01 (CW) 1×10^6 (P)	Spectroscopy, pollution detection
Ruby	Solid state	0.694	(P)	Pulsed holography, hole piercing
Nd-YAG	Solid state	1.06	1000 (CW) 2×10^8 (P)	Welding, hole piercing, cutting
Nd-Glass	Solid state	1.06	5×10^{14} (P)	Pulse welding, hole piercing
Diode	Semiconductor	0.33-40	0.6 (CW) 100 (P)	Bar-code reading, CDs and video disks, optical communications

^{a}"CW" denotes continuous; "P" denotes pulsed.

The phenomena involved in the laser action encompass interactions between atoms and molecules and electromagnetic fields. The salient features of laser radiation are: *(i)* directionality, *(ii)* high intensity, *(iii)* monochromaticity and *(iv)* coherence.

Laser applications are diverse. Since lasers beams may be focused to produce localized heating, they are used in some surgical procedures and for cutting, welding, and machining metals. Complex operations in surgery are performed with laser beams; such operations are less painful, bloodless, and quick. Lasers are also used in communication, computer circuitary, biology, meterology, military warfare, holography, etc.

Laser beams being highly directional, large distances can be measured accurately with their help, e.g. the distance of the moon from the earth has been measured with an error of only 15 cm in 384000 km. Lasers have opened up new researches on the interaction of matter with light and in *non-linear optics.*

OPTICAL FIBRES IN COMMUNICATION

An optical-fibre is a very thin and flexible medium of cylindrical shape. The three principal sections of a fibre are: *(i)* the *core*, *(ii)* the *cladding,* and *(iii)* the *jacket*. The innermost section, made of glass or plastic, is referred to as *core.* A glass or plastic coating surrounding the core is known as the *cladding.* The optical properties of the cladding are different from those of the *jacket*. It is made of plastic or polymer and other materials, and protects the structure from moisture, abrasion, mechanical shocks, and other environmental hazards. The actual working structure of the optical fibre is the core. The light entering the core at a suitable angle propagates through it, suffering a number of total internal reflections at the core-cladding interface. Optical fibres serve as cables for communications to carry optical signals from one end to the other over a wide band. A schematic diagram showing the components of an optical fibre communication system is shown in **Fig.** With the development of optical fibre technology, the field of communications has recently experienced a great revolution. Now, all telecommunications are transmitted via optical fibre rather than through conventional copper wires. Signal transmission through a metallic wire conductor is electronic, whereas using otpically transparent fibres, signal transmission is *photonic,* i.e. it uses photons of electromagnetic or light radiation. Use of optical fibres in communications has improved speed of transmission, information density, and transmission density, with a reduction in error rate; moreover, there is no electromagnetic interference with fibre optics.

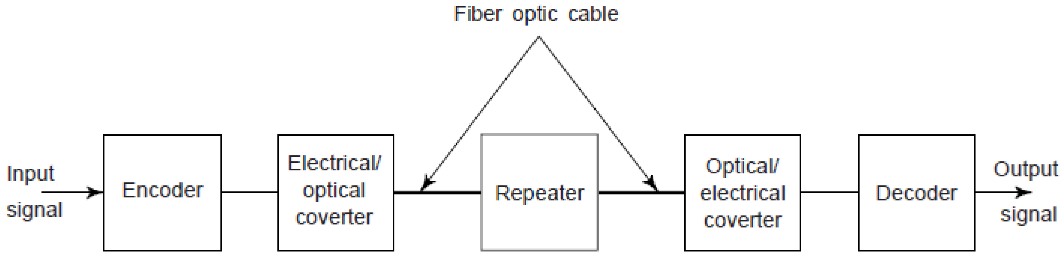


Fig: The components of an optical fibre communication system

High purity silica glass is used as the fibre material. Fibre diameters normally range between about 5 and 100 μm. The optical fibres are relatively flaw free and, thus, remarkably strong; during production the continuous fibres are tested to ensure that they meet minimum strength standards. Exceptionally pure and high-quality optical fibres are fabricated using advanced and sophisticated processing techniques. Impurities and other defects that absorb, scatter and thus attenuate the light beam must be eliminated.

MODULE V

THERMOSETTING AND THERMOPLASTIC

Though thermoset plastics and thermoplastics sound similar, they have very different properties and applications. The primary physical difference is that thermoplastics can be remelted back into a liquid, whereas thermoset plastics always remain in a permanent solid state. Think of thermoplastics as butter – butter can be melted and cooled multiple times to form various shapes. Thermoset is similar to bread in that once the final state is achieved, any additional heat would lead to charring.

A ***thermoplastic*** is a polymeric material or plastic that becomes soft and formable when heated and rigid when cooled. This process may be repeated a number of times without chemically altering the material.

A ***thermoset*** is a polymeric material that undergoes irreversible chemical changes when it is cured through heat, catalysts, or ultraviolet light: cross-linking prevents movement of molecular chains after curing. Once cured, the structure cannot be altered.

What is Thermoplastic?

We call thermoplastics '**Thermo-softening Plastics**' because we can melt down this material at high temperatures and can cool to gain back solid form. Thermoplastics are generally of high molecular weight. The polymer chains are linked together via intermolecular forces. We can easily break down these intermolecular forces if we supply sufficient energy. This explains why this polymer is moldable and will melt upon heating. When we provide enough energy to get rid of the intermolecular forces that hold the polymer as a solid, we can see the solid melting. When we cool it back, it gives off heat and re-forms the intermolecular forces, making it a solid. Therefore, the process is reversible.

Once the polymer is melted, we can mould it into different shapes; upon re-cooling, we can obtain different products as well. Thermoplastics also show different physical properties between the melting point and the temperature at which solid crystals are formed. Moreover, we can observe that they possess a rubbery nature between those temperatures. Some common thermoplastics include Nylon, Teflon, Polyethylene and Polystyrene

What is Thermoset?

We call thermosets 'Thermosetting Plastics'. They are able to withstand high temperatures without melting. We can obtain this property by toughening or hardening the soft and viscous pre-polymer through the introduction of cross-links between polymer chains. These links are introduced at chemically active sites (unsaturation etc.) with the aid of a chemical reaction. In common, we know this process as 'curing' and we can initiate it by heating the material above 200˚C, UV radiation, high energy electron beams and using additives. The cross links are stable chemical bonds. Once the polymer is cross-liked, it gets a very rigid and strong 3D structure, which refuses to melt upon heating. Therefore, this process is irreversible converting the soft starting material into a thermally stable polymer network.

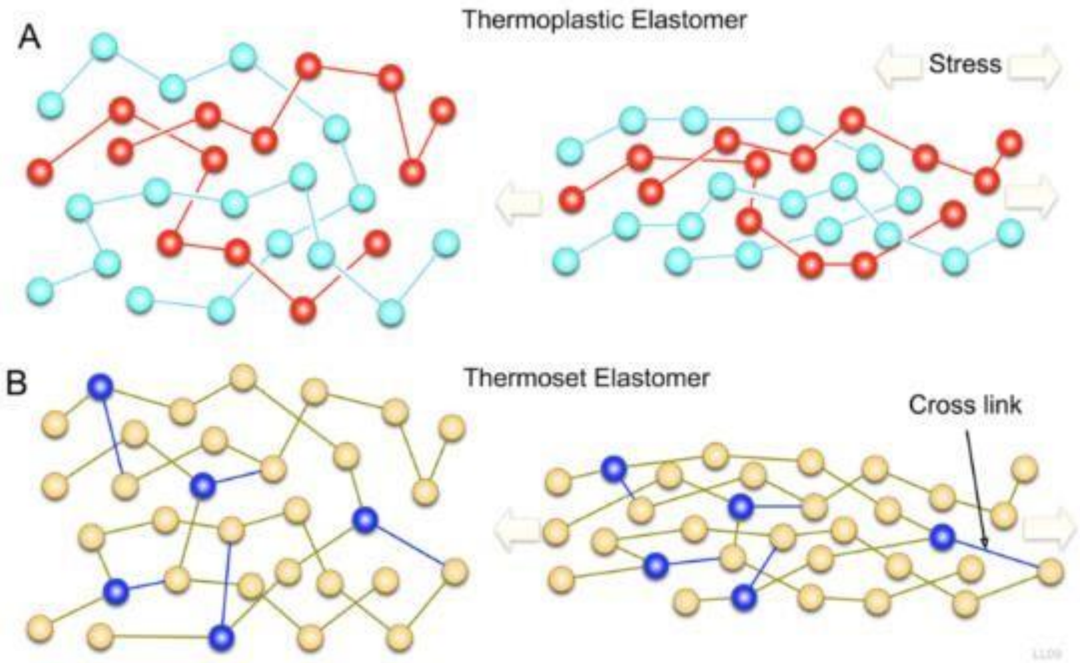


Figure 02: Comparison of Thermoplastic and Thermoset Elastomers

During the process of cross-linking, the molecular weight of the polymer increases; hence the melting point increases. Once the melting point goes above the ambient temperature, the material remains solid. When we heat up thermosets to uncontrollably high temperatures, they decompose instead of melting due to reaching the decomposition point before the melting point. Some common examples of thermosets include Polyester Fibreglass, Polyurethanes, Vulcanized Rubber, Bakelite, and Melamine.

THERMOSETTING	**THERMOPLASTIC**
Definition Thermoplastic is a substance that become plastic on heating and harden on cooling and is able to repaeat these process	**Definition** Thermoset is a polymer that is irreversibly hardened by curing from a soft solid or viscous liquid pre-polymer or resin
Thermoset Curing Process Thermoset plastics contain polymers that cross-link together during the curing process to form an irreversible chemical bond. The cross-linking process eliminates the risk of the product remelting when heat is applied, making thermosets ideal for high-heat	**Thermoplastics Curing Process** Thermoplastics pellets soften when heated and become more fluid as additional heat is applied. The curing process is completely reversible as no chemical bonding takes place. This characteristic allows thermoplastics to be remolded and recycled

applications such as electronics and appliances.	without negatively affecting the material's physical properties
Thermosetting plastics are often formed by the condensation polymerization.	Thermoplastics are usually formed by the addition of polymerization
it contains a 3D network structure constructed with strong covalent bonds.	It contains long-chain linear polymers and held together by weak Van der Waal forces
Features & Benefits Thermoset plastics significantly improve the material's mechanical properties, providing enhances chemical resistance, heat resistance and structural integrity. Thermoset plastics are often used for sealed products due to their resistance to deformation.	***Features & Benefits*** There are multiple thermoplastic resins that offer various performance benefits, but most materials commonly offer high strength, shrink-resistance and easy bendability. Depending on the resin, thermoplastics can serve low-stress applications such as plastic bags or high-stress mechanical parts.
Nature mouldable	**Nature** brittle
Strength Less strong compared to thermoset	**Strength** Comparatively stronger
Shape Can melt and obtain desired shapes	**Shape** Have a permanent shape
Recyclability Recycle	**Recyclability** Non-recyclable
Advantages ▪ High impact resistance ▪ More resistant to high temperatures than thermoplastics ▪ Highly flexible design ▪ Thick to thin wall capabilities ▪ Excellent aesthetic appearance ▪ High levels of dimensional stability ▪ Cost-effective	**Advantages** ▪ Excellent resistance to solvents, ▪ Fatigue strength, ▪ High resistance towards heat and high temperature ▪ Highly recyclable ▪ Aesthetically-superior finishes ▪ High-impact resistance ▪ Remolding/reshaping capabilities ▪ Chemical resistant ▪ Hard crystalline or rubbery surface options ▪ Eco-friendly manufacturing
Disadvantages ▪ Cannot be recycled ▪ More difficult to surface finish ▪ Cannot be remolded or reshaped	**Disadvantages** ▪ Generally more expensive than thermoset ▪ Can melt if heated

Thermoset as a Metal Alternative

Thermoset plastics have been successful in replacing traditional metal materials where they can provide value through improved performance at a lower cost.

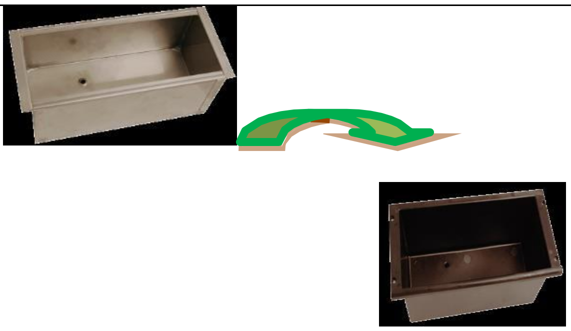
Thermoset Performance Benefits:

- Less Weight
- Design flexibility
- Dent resistance
- Corrosion resistance
- Heat resistance

WATER TANK CONVERSION

Significant cost savings were achieved by converting this stainless steel part to plastic.

The part is used inside the steamer boxes of fast food steamers for food preparation.



- Thermoset plastics are well suited to demanding requirements because they have the capability to withstand heat and pressure for long periods of time without failure, they are impact resistant, and they have exceptional electrical insulating properties. Their dimensional stability, creep resistance, chemical resistance, stiffness, and high temperature capabilities make them the preferred material where reliable performance in adverse conditions is imperative and can be used as a cost- savings alternative for metals.
- Phenolic and Polyesters are the two most commonly used materials for metal replacement. The ability to mold these materials into complex shapes makes them cost effective and also eliminates the need to machine features of a design which allows for closer tolerances. Dimensional stability of these materials guarantees that close tolerances can be controlled and repeated continually within ten-thousandths of an inch.

CERAMIC

- Ceramic are burnt in earth and its definition can be given in a negative way i.e. whatever is not a metal, non-metal and organic polymer is called a ceramic.
- The word "ceramic" is derived from the Greek word keramikos meaning pottery. It is related to the older Indo-European language meaning "to burn". Thus it was used, to refer to a product obtained through the action of fire upon earthen materials.

Properties of ceramic are:

1. They are extremely brittle
2. High thermal stability
3. High chemical stability (corrosion resistance)
4. High hardness
5. Low density compared to metals
6. High melting point or decomposition temperature
7. High hardness and very brittle
8. High elastic modulus and moderate strength
9. Low toughness
10. High electrical resistivity
11. Low thermal conductivity
12. High temperature wear resistance
13. Thermal Shock resistance
14. High corrosion resistance
15. In crystalline ceramics the crack propagation is usually through the grains (transgranular) and along specific crystallographic (or cleavage) planes, which are planes of high atomic density

Crystal Structure of ceramics

- Because ceramics are composed of at least two elements, and often more, their crystal structures are generally more complex than those for metals. The atomic bonding in these materials ranges from purely ionic to totally covalent; many ceramics exhibit a combination of these two bonding types, the degree of ionic character being dependent on the electronegativities of the atoms.
- For those ceramic materials for which the atomic bonding is predominantly ionic, the crystal structures may be thought of as being composed of electrically charged ions instead of atoms. The metallic ions, or **cations,** are positively charged, because they have given up their valence electrons to the nonmetallic ions, or **anions,** which are negatively charged.
- Two characteristics of the component ions in crystalline ceramic materials influence the crystal structure:
    1. The magnitude of the electrical charge on each of the component ions
    2. The relative sizes of the cations and anions.

- **The magnitude of the electrical charge on each of the component ions**

    - The crystal must be electrically neutral; that is, all the cation positive charges must be balanced by an equal number of anion negative charges. The chemical formula of a compound indicates the ratio of cations to anions, or the composition that achieves this charge balance. For example, in calcium fluoride, each calcium ion has a +2 charge (Ca^{2+}), and associated with each fluorine ion is a single negative charge (F^{-}). Thus, there must be twice as many F^{-} as Ca^{2+} ions, which is reflected in the chemical formula CaF_2 .

- **The relative sizes of the cations and anions.**
  - The second criterion involves the sizes or ionic radii of the cations and anions, r_C and r_A , respectively. Because the metallic elements give up electrons when ionized, cations are ordinarily smaller than anions, and, consequently, the ratio $\frac{r_C}{r_A}$ is less than unity. Each cation prefers to have as

    many nearest-neighbor anions as possible. The anions also desire a maximum number of cation nearest neighbors.

AX-TYPE CRYSTAL STRUCTURES

Some of the common ceramic materials are those in which there are equal numbers of cations and anions. These are often referred to as AX compounds, where A denotes the cation and X the anion. There are several different crystal structures for AX compounds; each is normally named after a common material that assumes the particular structure.

1. Rock Salt Structure

Perhaps the most common AX crystal structure is the *sodium chloride* (NaCl), or *rock salt,* type. The coordination number for both cations and anions is 6, and therefore the cation–anion radius ratio is between approximately 0.414 and 0.732. A unit cell for this crystal structure (**Figure**) is generated from an FCC arrangement of anions with one cation situated at the cube center and one at the center of each of the 12 cube edges. An equivalent crystal structure results from a facecentered arrangement of cations. Thus, the rock salt crystal structure may be thought of as two interpenetrating FCC lattices, one composed of the cations, the other of anions. Some of the common ceramic materials that form with this crystal structure are NaCl, MgO, MnS, LiF, and FeO.

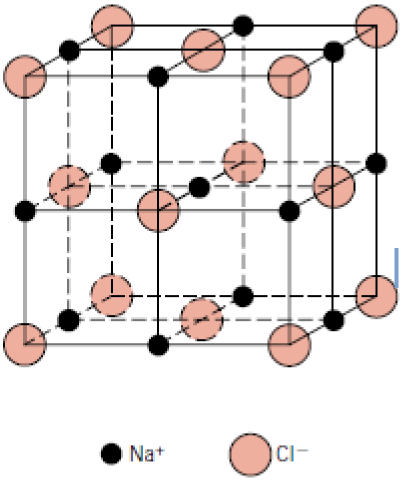


Figure: A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

2. Cesium Chloride Structure

Figure shows a unit cell for the *cesium chloride* (CsCl) crystal structure; the coordination number is 8 for both ion types. The anions are located at each of the corners of a cube, whereas the cube center is a single cation. Interchange of anions with cations, and vice versa, produces the same crystal structure. This is *not* a BCC crystal structure because ions of two different kinds are involved.

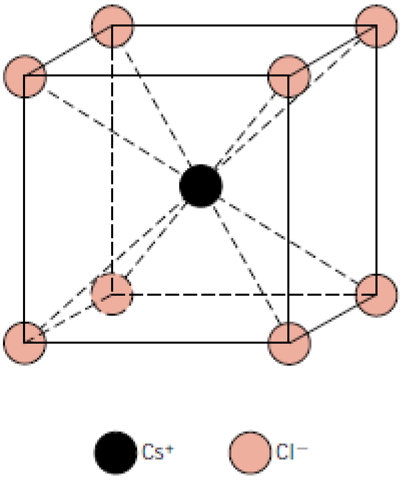


FIGURE. A unit cell for the cesium chloride (CsCl) crystal structure.

3. Zinc Blende Structure

A third AX structure is one in which the coordination number is 4; that is, all ions are tetrahedrally coordinated. This is called the *zinc blende,* or *sphalerite,* structure, after the mineralogical term for zinc sulfide (ZnS). A unit cell is presented in **Figure**; all corner and face positions of the cubic cell are occupied by S atoms, while the Zn atoms fill interior tetrahedral positions. An equivalent structure results if Zn and S atom positions are reversed. Thus, each Zn atom is bonded to four S atoms, and vice versa. Most often the atomic bonding is highly covalent in compounds exhibiting this crystal structure (Table), which include ZnS, ZnTe, and SiC.

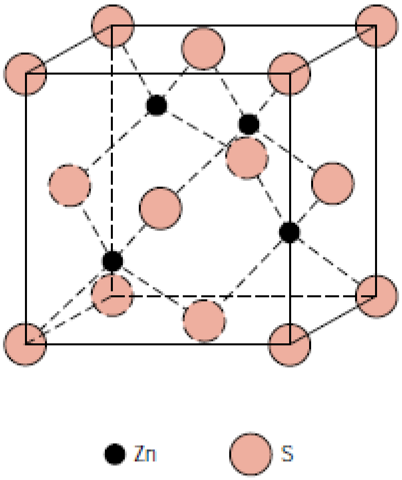


FIGURE. A unit cell for the zinc blende (ZnS) crystal structure.

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A*m*X*p*-TYPE CRYSTAL STRUCTURES

If the charges on the cations and anions are not the same, a compound can exist with the chemical formula A*m*X*p,* where *m* and/or $p \neq 1$. An example would be AX_2, for which a common crystal structure is found in *fluorite* (CaF_2). The ionic radii ratio r_C/r_A for CaF_2 is about 0.8 which gives a coordination number of 8. Calcium ions are positioned at the centers of cubes, with fluorine ions at the corners. The chemical formula shows that there are only half as many Ca^{2+} ions as F^{-} ions, and therefore the crystal structure would be similar to CsCl (**Figure**), except that only half the center cube positions are occupied by Ca^{2+} ions. One unit cell consists of eight cubes, as indicated in **Figure.** Other compounds that have this crystal structure include UO_2, PuO_2, and ThO_2.

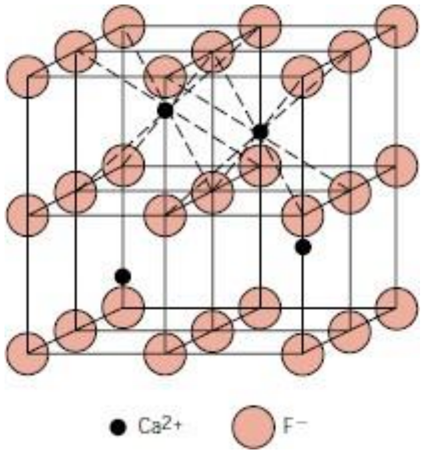


FIGURE. A unit cell for the fluorite (CaF_2) crystal structure.

A*m*B*n*X*p*-TYPE CRYSTAL STRUCTURES

It is also possible for ceramic compounds to have more than one type of cation; for two types of cations (represented by A and B), their chemical formula may be designated as AmBnXp. Barium titanate ($BaTiO_3$), having both Ba^{2+} and Ti^{4+} cations, falls into this classification. This material has a perovskite crystal structure. At temperatures above 120^0C

(248^0F), the crystal structure is cubic. A unit cell of this structure is shown in **Figure**; Ba^{2+} ions are situated at all eight corners of the cube and a single Ti^{4+} is at the cube center, with O^{2-} ions located at the center of each of the six faces.

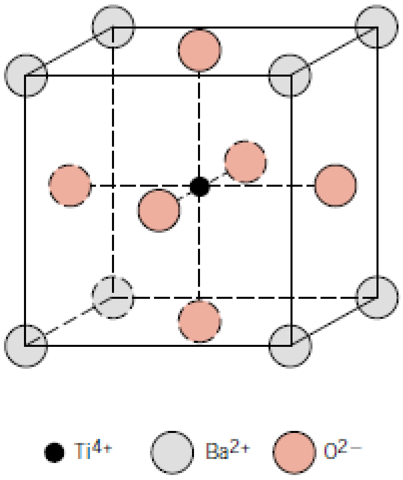
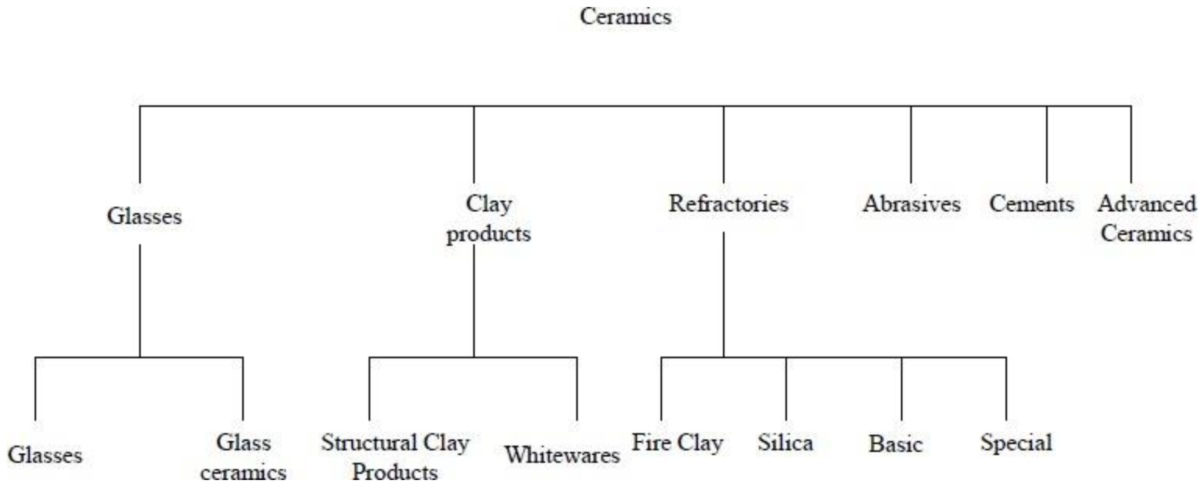


FIGURE: A unit cell for the perovskite crystal structure.

Classification of Ceramics Based on their Applications



APPLICATIONS

THERMAL	
Inslulation	High temperature furnace linings for insulation (oxide fibres such as alumina, silica and zirconia)
Refractroriness	High temperature furnace linings for insulation and containment of molten metal and slags
Thermal coductivity	Heat sinks for electronic packages
MAGNETIC AND SUPERCONDUCTIVITY	

Hard Magnets	Ferrite magnets [$(Ba, Sr)O.6Fe_2O_3$]
Soft magnets	Transformer cores [(Zn,M)Fe2O3 with M=Mn,Co, Mg]
superconductivity	Wires and SQUID magnetometers($YBa_2Cu_3O_7$)
OPTICAL	
Transparency	Windows (soda lime glasses), cables for optical communication (ultra-pure silica)
Translucency and chemical inertness	Heat and corrosion-resistant materials, usually for Na lamps(Al_2O_3)
Nonlinearity	Switching devices for optical computing ($LiNbO_3$)
IR transparency	Infrared laser windows (CaF_2,SrF_2,NaCl)
NUCLEAR APPLICATIONS	
Fission	Nuclear fuel (UO3,UC),fuel cladding (SiC), Neutron moderators (C, BeO)
Fusion	Tritium breeder materials (zirconates and silicates of Li,Li_2O_3), fusion reactor lining (C,SiC,SiC,Si_3N_4,B_4C)
CHEMICAL	
Catalyst	Filters (zerolites), purification of exhaust gases
Anticorrosion properties	Heat exchangers (SiC), Chemical equipment in corrosive environments
Biocompatibility	Artificial joint prostheses(Al_2O_3)
MECHANICAL	
Hardness	Cutting tools (SiC whisker reinforced Al_2O_3, Si_3N_4)
High temperature strength	Stators and turbine blades, ceramic engines (Si_3N_4)
Wear resistance	Bearings (Si_3N_4)
ELECTRIC AND DIELECTRIC	
Conductivity	Heat elements for furnaces (SiC, Zro_2, $MoSi_2$)
ferroelectricity	Capacitors (Ba-titanate-based materials)
Low-voltage insulators	Ceramic insulation (porcelain, steatite, forsterite)
Insulators in electronic applications	Substrates for electronic packaging and electrical insulators in general (Al_2O_3,AlN)
Insulators in hostile environments	SPARK PLUGS (Al_2O_3)
SEMICONDUCTING	Thermistors and heating elements (oxides of Fe, Co,Mn)

COMPOSITES

Many of our modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics, and polymeric materials. This is especially true for materials that are needed for aerospace, underwater, and transportation applications. For example, aircraft engineers are increasingly searching for structural materials that have low densities, are strong, stiff, and abrasion and impact resistant, and are not easily corroded. This is a rather formidable combination of characteristics. Frequently, strong materials are relatively dense; also, increasing the strength or stiffness generally results in a decrease in impact strength.

Generally speaking, a composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is realized. According to this **principle of combined action,** better property combinations are fashioned by the judicious combination of two or more distinct materials. Property trade-offs are also made for many composites.

Composites include multiphase metal alloys, ceramics, and polymers.
For example:

a. Pearlitic steels have a microstructure consisting of alternating layers of ferrite and cementite. The ferrite phase is soft and ductile, whereas cementite is hard and very brittle. The combined mechanical characteristics of the pearlite (reasonably high ductility and strength) are superior to those of either of the constituent phases.

There are also a number of composites that occur in nature.
For example:

b. Wood consists of strong and flexible cellulose fibers surrounded and held together by a stiffer material called lignin. Also, bone is a composite of the strong yet soft protein collagen and the hard, brittle mineral apatite.

Definition:

- A material which is composed of two or more materials at a microscopic scale and have chemically distinct phases.
- Heterogeneous at a microscopic scale but statically homogeneous at macroscopic scale.
- Constituent materials have significantly different properties.

Composite: Necessicity

Why do you need composite materials?

- Enhanced desired properties!

What are these desired properties?

- Strength
- Stiffness

- Toughness
- Corrosion resistance
- Wear resistance
- Reduced weight
- Fatigue life
- Thermal/Electrical insulation and conductivity
- Acoustic insulation
- Energy dissipation
- Attractiveness, cost
- Tailorable properties

Composite: Constituents

What are the constituents in a composite material?

1. **Reinforcement (dispersed phase)**
   a. discontinuous
   b. stronger
   c. harder
2. **Matrix:**
   a. Continuous

What are the functions of reinforcement?

1. Contribute desired properties
2. Load carrying
3. Transfer the strength to matrix

What are the functions of a matrix?

1. Holds the fibres together
2. Protects the fibres from environment
3. Protects the fibres from abrasion (with each other)
4. Helps to maintain the distribution of fibres
5. Distributes the loads evenly between fibres
6. Enhances some of the properties of the resulting material and structural component (that fibre alone is not able to impart). These properties are such as:
   a. transverse strength of a lamina
   b. Impact resistance
7. Provides better finish to final product

The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase. ''Dispersed phase geometry'' in this context means the shape of the particles and the particle size, distribution, and orientation; these characteristics are represented in Figure

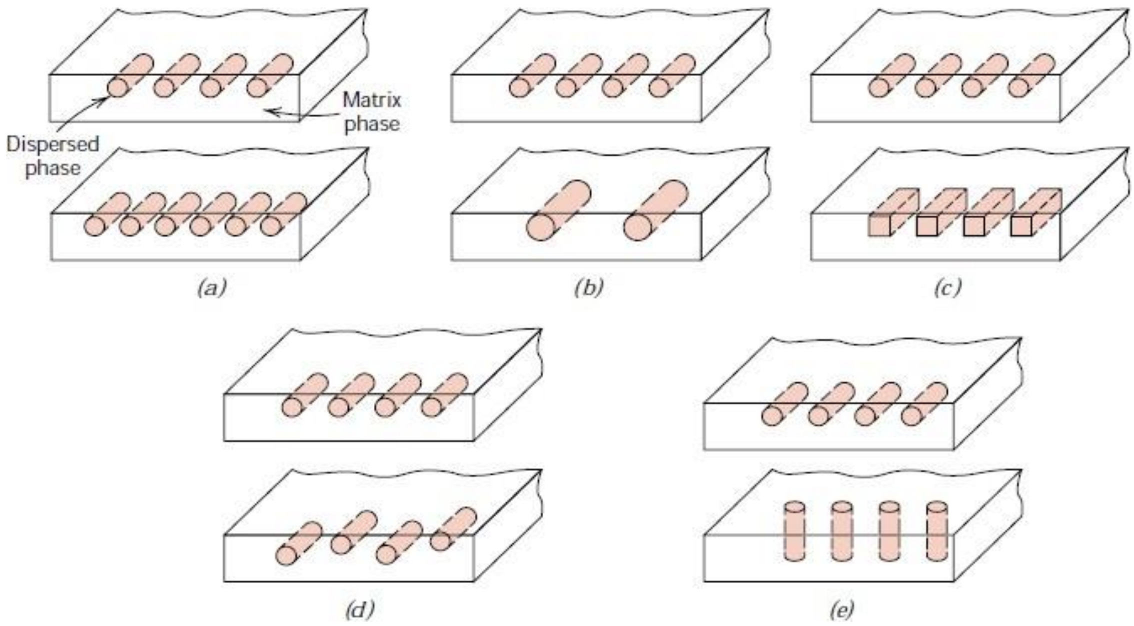


Figure Schematic representations of the various geometrical and spatial characteristics of particles of the dispersed phase that may influence the properties of composites: (*a*) concentration, (*b*) size, (*c*) shape, (*d*) distribution, and (*e*) orientation.

$\boldsymbol{Properties\ of\ composites} = f\ (properties\ of\ the\ constituent\ phases,$ their relative amounts, the geometry of the dispersed phase)

Geometry of the dispersed phase means

1. shape of the particles
2. the particle size
3. distribution
4. orientation

Classification of composites

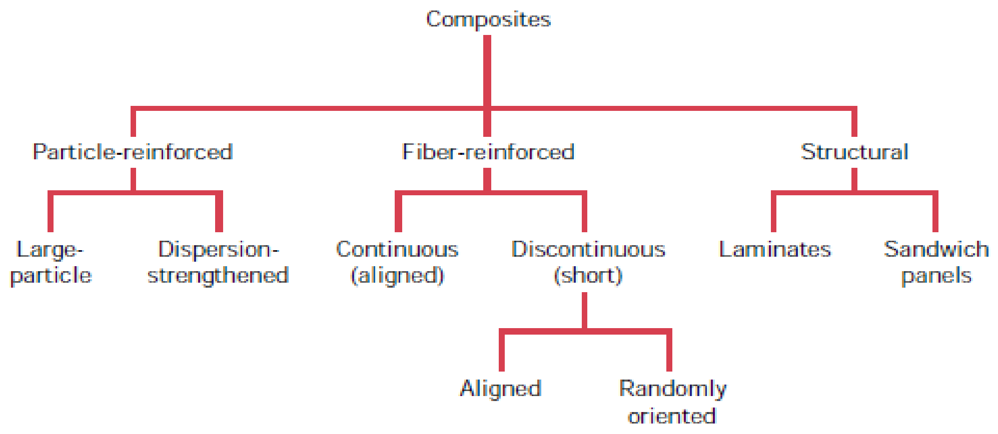


Figure A classification scheme for the various composite types

Classification of composite materials is shown in Figure, which consists of three main divisions—particle-reinforced, fiber-reinforced, and structural composites.

- The dispersed phase for particle-reinforced composites is equiaxed (i.e., particle dimensions are approximately the same in all directions);
- For fiber-reinforced composites, the dispersed phase has the geometry of a fiber (i.e., a large length-to diameter ratio of the order 1000).
- Structural composites are combinations of composites and homogenous materials.

AGGLOMERATED MATERIALS

Agglomerated materials are also called as composite materials. To agglomerate means to bind macroscopic particles together to form an integrated mass to serve a useful purpose. A number of engineering materials are formed by agglomeration of small particles into a useful product. For example:

a. Concrete is an agglomerated material. Its constituents are gravel, sand Portland cement and water.
b. Shell moulds are agglomerated materials. They have thin sand moulds bonded together with resin and polymerised hot by either a thermoplast ao a thermoset.
c. In the asphalt paving of high way agglomeration of asphalt and stone from an uniform bed and
d. The abrasive grains of grinding wheel are bonded together by either glass or a resin. however agglomerated materials differ from the composite materials by the fact that in the latter there are two distinct phases, a matrix and a dispersed phase where the matrix reinforces the dispersed phase but in the former the two phase evenly distributed in one another.

REINFORCED MATERIALS

a) Reinforced concrete

- Reinforced and prestressed concrete can be considered as the prototypes of morden composite materials.
- Cement concrete is a matrix of cement, water, sand, crushed stones/ gravel etc. Cement acts as binder for sand and stone chips. When the above substances are mixed, the mass sets and hardness.

  The hardness mass (i.e., plain cement concrete) is very strong in compression but is extremely weak in tension and thus it is used when the structure to be built will be in pure compression, e.g., a small (ground) platform for an electric furnace.
- Concrete is a heterogeneous material characterized by a high compressive strength (average quality concrete 28MPa or 4000psi, but a low tensile strength that is 10 or 15 times smaller than the compressive strength. When a concrete member is bent, failure occurs on the tension side of the member, resulting in cracks in the concrete mass. To

overcome this weakness, reinforced concrete has been designed in which steel in the form of rods, wires, bars or fibric is embedded in the fresh concrete. This minimises the development of tensile stress in concrete and produces material of much greater strength in compression, shear and tension. In reinforced concrete , steel bars carry the loads / stresses.

- If the tensile stress in the reinforcement (steel rods) exeeds the value of the copmpressive strength of concrete, the concrete surrounding , the reinforcement will develop tensile cracks. This cracking may not prove detrimental, since the bond between steel and concrete is sufficiently high to prevent the width of the cracks from becoming significant. However, if the width of the crcks is excessive, then concrete may become too permeable to moisture and corrosion of the steel reinforcement may ocur.
- The coefficient of thermal expansion of steel is so close to that of concrete, that, the adhesive bond between the interface steel- cement pastes is very strong and the steel is protected from corrosion by the highly alkaline environment (PH bout 12) of the cement paste.

  The adhesion of steel to the cement paste can be improved still further by imparting to steel rods special surface patterns that provide for better interlocking between the cement paste and the surface of steel rods.

Advantages of Reinforced cement concrete (RCC)

1. It is economical.
2. It is very durable and fire resisting.
3. Maintenance of RCC structure is negligible.
4. For practical purposes, it is impermeable to moisture penetration.
5. Different shapes can be obtained easily with RCC
6. RCC structures are not affected by vermins, fungus or other such insects.
7. Materials employed for RCC construction are easily available and in abundance.

b) Fibre reinforced Plastic (FRP)

- Such composites are composed of three components: (i) fibre or filaments (the dispersed phase) the cental pivotal part on which the whole composite stands (ii) polymeric materials (the matrix phase) which supports the central filament and (iii) the bonding agent which binds both the phases.

Characteristics

The composites should have the following characteristics to be an effective material for the requirement.

a. Mechanical properties like high strength and stiffness on weight basis, i.e. specifies strength = tensile strength/specific gravilty (s/ρ) and specific modulus = modulus of elasticity / specific gravity (E/ ρ) but lower density the composites.

Specific strength (s/ρ) and specific modulus (E/ρ) are the controlling factors for engineering uses. A high value is desirable for good mechanical necessity. Polymeric composites have low ultimate strength and glass. A 50-50 (glass and plastic) composite has (E/ρ)= 20000N.m/g, which is equivalent to most artificial composites. Glass a reinforced composite has E/ρ equivalent to metals. Higher values are also obtained with fused silica fibres but too expensive to use.

b. Nature and properties of both fibre and matrix phases as well as their volume fraction should be conducive for use.
c. Orientation and distribution of fibres in the matrix.
d. Aspect ratio (=length/dia of the fibre)
e. Strength of the interfacial bond, between the fibre phase and the matrix phase.

Requirement

Superior properties of the fibre reinforced composites, like high strength-yield, fatigue, creep and fracture, can be achieved with proper slection of the components.

The requirements are:

a. The fibres should have high mechanical properties preventing slip and crack formation as well as their propagation.
b. High load and shock bearing capacity- a load applied on the matrix transfer the stress to the fibre embedded through a plastic flow. A hard matrix and soft phase has good shock bearing capacity. On the reverse the strength and modulus increases at the cost of shock resistance.
c. For maximum strength and modulus maximum number of fibres per unit volume must be present for better load distribution.
d. The fibres must have anisotropic behaviour, i.e. must be continuous and aligned with a specific orientation which has a much higher strength than a random orientation and discontinuous alignment.
e. The coefficient of expansion must match for both the matrix and the fibre.
f. Both the phases must be chemically compatible and form a bond with each other.
g. The fibre must be stable at room as well as at elevated temperature.

(The fibre length (l) must be much above the critical length (lc), $l \gg lc$ where $lc=st.d/Ec$ (st= tensile strength, d = diameter of the fibre and Ec= fibre-matrix bond strength or shear yield strength).

For carbon and glass fibre-matrix combination the $lc \approx 1$mm (20-150times of the fibre diameter). If $l/lc \approx 15$ then the fibre is called continuous and $l<lc$ it is discontinuous.

c) METAL MATRIX COMPOSITE

The matrix in these composites is a ductile metal. These composites can be used at high service temperatures than their base metal counterparts. The reinforcement in these materials may improve specific stiffness, specific strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability.

In comparison to polymer-matrix composites, these materials have higher operating temperatures, non flammability and greater resistance to degradation by organic fluids. In comparison to PMCs, MMCs are much more expensive and therefore, their use is somewhat restricted. Alloys of aluminium, magnesium, titanium, and copper, and superalloys are used as matrix materials. The reinforcement may be in the form of particulates, both continuous and discontinuous fibres, and whiskers (concentrations range 10 to 60 Vol%) carbon, silicon carbide, boron, alumina, and refractory metals are continuous fibre materials, whereas silicon carbide whiskers, chopped fibres of alumina and carbon, and particulates of silicon carbide and alumina are discontinuous reinforcements sense, cermets fall within MMCs.

At elevated temperatures, some matrix-reinforcement combinations are highly reactive. This problem can be resolved either by using a protective surface coating to the reinforcement or by modifying the matrix alloy composition.

Application

Recently, automobile industries have begun to use MMCs in their products, e.g. some engine components have been introduced consisting of an aluminium-alloy matrix that is reinforced with alumina and carbon fibres. These MMCs is light in weight and can resist wear and thermal distortion. MMCs are also used in driveshafts (that have higher rotational speeds and reduced vibrational noise levels), forged suspension and transmission components, and extruded stabilizer. MMCs are used by aerospace industry. Aluminium alloy metal-matrix composites, boron fibres are used as the reinforcement for the Space Shuttle Orbiter, and continuous graphite fibres for Hubble Telescope.

Using refractory metals such as tungsten, the high temperature creep and rupture properties of some of the superalloys (Ni-and Co based alloys) may be enhanced by fibre reinforcement.

PROCESSING OF FIBER-REINFORCED COMPOSITES

To fabricate continuous fiber-reinforced plastics that meet design specifications, the fibers should be uniformly distributed within the plastic matrix and, in most instances, all oriented in virtually the same direction. Newly developed techniques (pultrusion, filament winding, and prepreg production processes) by which useful products of these materials are manufactured.

PULTRUSION

Pultrusion is used for the manufacture of components having continuous lengths and a constant cross-sectional shape (i.e., rods, tubes, beams, etc.). With this technique, illustrated schematically in **Figure**, continuous fiber *rovings,* or *tows,* are first impregnated with a thermosetting resin; these are then pulled through a steel die that preforms to the desired shape and also establishes the resin/fiber ratio. The stock then passes through a curing die that is precision machined so as to impart the final shape; this die is also heated in order to initiate curing of the resin matrix. Apulling device draws the stock through the dies and also determines the production speed. Tubes and hollow sections are made possible by using center mandrels or inserted hollow cores.

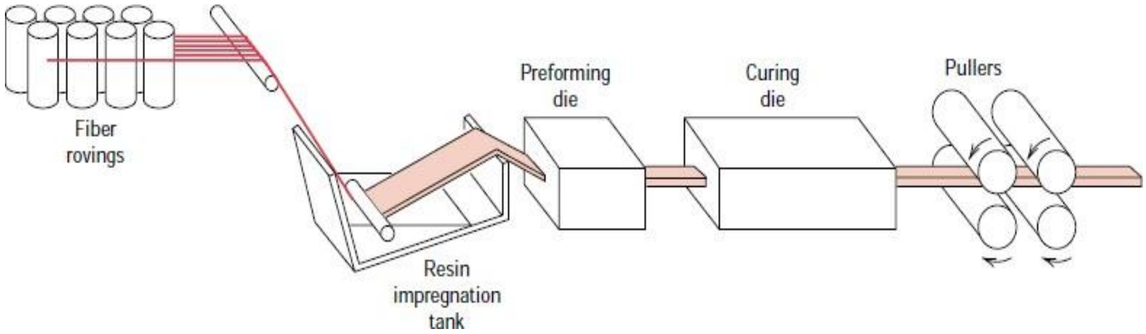


FIGURE schematic diagrams showing the pultrusion process.

Principal reinforcements are glass, carbon, and aramid fibers, normally added in concentrations between 40 and 70 vol%. Commonly used matrix materials include polyesters, vinyl esters, and epoxy resins. Pultrusion is a continuous process that is easily automated; production rates are relatively high, making it very cost effective. Furthermore, a wide variety of shapes are possible, and there is really no practical limit to the length of stock that may be manufactured.

A roving, or tow, is a loose and untwisted bundle of continuous fibers that are drawn together as parallel strands.

PREPREG PRODUCTION PROCESSES

Prepreg is the composite industry’s term for continuous fiber reinforcement preimpregnated with a polymer resin that is only partially cured. This material is delivered in tape form to the manufacturer, who then directly molds and fully cures the product without having to add any resin. It is probably the composite material form most widely used for structural applications. The prepregging process, represented schematically for thermoset polymers in **Figure**, begins by collimating a series of spool-wound continuous fiber tows.

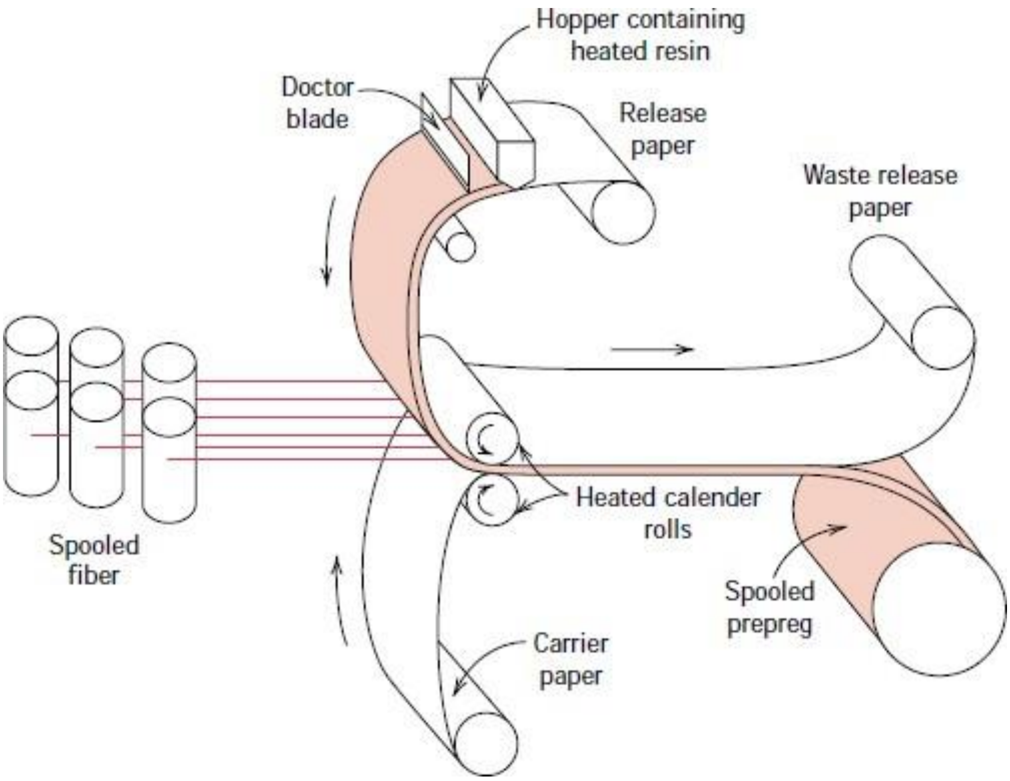


Figure Schematic diagram illustrating the production of prepreg tape using thermoset polymers.

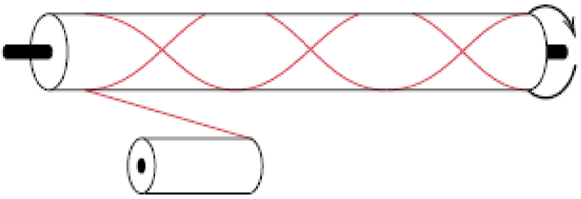
These tows are then sandwiched and pressed between sheets of release and carrier paper using heated rollers, a process termed ‘‘calendering.’’ The release paper sheet has been coated with a thin film of heated resin solution of relatively low viscosity so as to provide for its thorough impregnation of the fibers. A ‘‘doctor blade’’ spreads the resin into a film of uniform thickness and width. The final prepreg product—the thin tape consisting of continuous and aligned fibers embedded in a partially cured resin—is prepared for packaging by winding onto a cardboard core. As shown in **Figure**, the release paper sheet is removed as the impregnated tape is spooled. Typical tape thicknesses range between 0.08 and 0.25 mm (3 _ 103 and 102 in.), tape widths range between 25 and 1525 mm (1 and 60 in.), whereas resin content usually lies between about 35 and 45 vol%. At room temperature the thermoset matrix undergoes curing reactions; therefore, the prepreg is stored at 0^0C (32^0F) or lower. Also, the time in use at room temperature (or ‘‘out-time’’) must be minimized. If properly handled, thermoset prepregs have a lifetime of at least six months and usually longer. Both thermoplastic and thermosetting resins are utilized; carbon, glass, and aramid fibers are the common reinforcements. Actual fabrication begins with the ‘‘lay- up’’—laying of the prepreg tape onto a tooled surface. Normally a number of plies are laid up (after removal from the carrier backing paper) to provide the desired thickness. The lay- up arrangement may be unidirectional, but more often the fiber orientation is alternated to produce a cross-ply or angle-ply laminate. Final curing is accomplished by the simultaneous application of heat and pressure. The lay-up procedure may be carried out entirely by hand (hand lay-up), wherein the operator both cuts the lengths of tape and then positions them in the desired orientation on the tooled surface. Alternately, tape patterns may be machine cut, then hand laid. Fabrication costs can be further reduced by automation of prepreg lay- up and other manufacturing procedures (e.g., filament winding, as discussed below), which virtually eliminates the need for hand labor. These automated methods are essential for many applications of composite materials to be cost effective.

FILAMENT WINDING

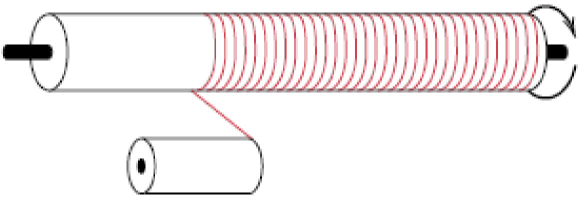
Filament winding is a process by which continuous reinforcing fibers are accurately positioned in a predetermined pattern to form a hollow (usually cylindrical) shape. The fibers, either as individual strands or as tows, are first fed through a resin bath and then continuously wound onto a mandrel, usually using automated winding equipment (**Figure**) After the appropriate number of layers have been applied, curing is carried out either in an oven or at room temperature, after which the mandrel is removed. As an alternative, narrow and thin prepregs (i.e., tow pregs) 10 mm or less in width may be filament wound. Various winding patterns are possible (i.e., circumferential, helical, and polar) to give the desired mechanical characteristics. Filament-wound parts have very high strength-to-weight ratios. Also, a high degree of control over winding uniformity and orientation is afforded with this technique. Furthermore, when automated, the process is most economically attractive.

Application

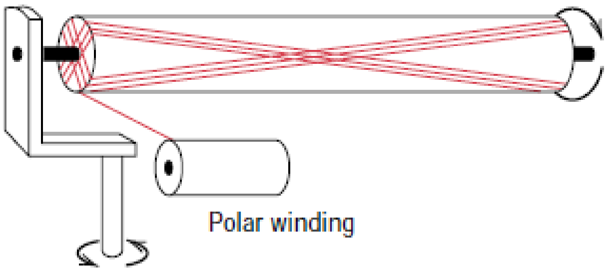
Common filament-wound structures include rocket motor casings, storage tanks and pipes, and pressure vessels. Manufacturing techniques are now being used to produce a wide variety of structural shapes that are not necessarily limited to surfaces of revolution (e.g., Ibeams). This technology is advancing very rapidly because it is very cost effective.



Helical winding



Circumferential winding



Polar winding

FIGURE . Schematic representations of helical, circumferential, and polar filament winding techniques.

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