

# **Material Science**

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Module-1

## **Introduction**

## Contents

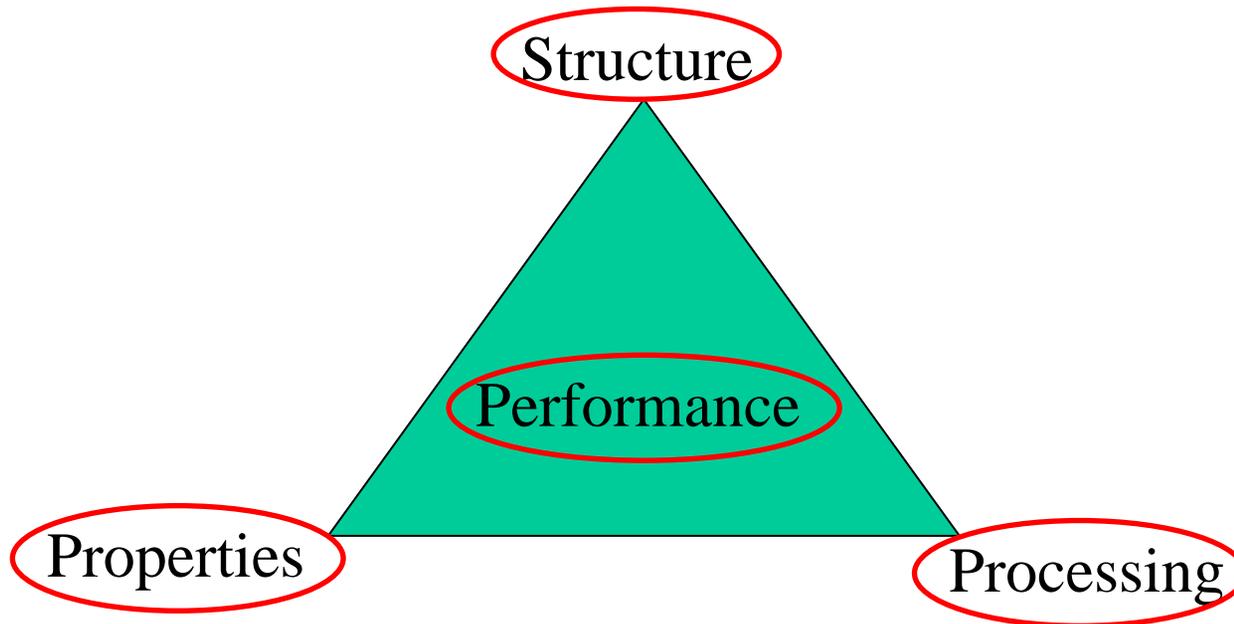
- 1) Historic perspective and Materials Science
- 2) Why study properties of materials,  
Classification of materials
- 3) Advanced materials, Future materials and  
Modern materials' needs

# Historic perspective

- Materials are very important in development of human civilization. In respect, their names are associated in history, e.g. stone age, Bronze age, Iron age, etc.
- With time humans discovered new materials and also techniques to produce known materials. This is an ongoing process for coming centuries, i.e. no end in sight!

# Materials Science

- It can be defined as science dealing the relationships that exist between the structures and properties of materials, which are useful in practice of engineer's profession.
- Basic components and their interrelationship:



# Properties of Materials

- All solid engineering materials are characterized for their properties.
- Engineering use of a material is reflection of its properties under conditions of use.
- All important properties can be grouped into six categories: Mechanical, Electrical, Thermal, Magnetic, Optical, and Deteriorative.
- Each material possess a structure, relevant properties, which dependent on processing and determines the performance.

# Why Study Properties of Materials?

- Since there are thousands of materials available it is almost impossible to select a material for a specific task unless otherwise its properties are known.
- There are several criteria on which the final decision is based on.
- There are less chances of material possessing optimal or ideal combination of properties.
- A need to trade off between number of factors!

- The classic **example** involves strength and ductility:
  - Normally material possessing strength have limited ductility. In such cases a reasonable compromise between two or more properties are important.
  - A second selection consideration is any deterioration of material properties during service operations.
  - Finally the overriding consideration is economics.

# Classification of Materials

- Three basic groups of solid engineering materials based on atomic bonds and structures:

Metals

Ceramics

Polymers

- Classification can also be done based on either properties (*mechanical, electrical, optical*), areas of applications (*structures, machines, devices*). Further we can subdivide these groups.
- According to the present engineering needs:  
Composites, Semiconductors, Biomaterials

# Metals

- Characteristics are owed to non-localized electrons (metallic bond between atoms) i.e. electrons are not bound to a particular atom.
- They are characterized by their high thermal and electrical conductivities.
- They are opaque, can be polished to high lustre. The opacity and reflectivity of a metal arise from the response of the unbound electrons to electromagnetic vibrations at light frequencies.
- Relatively heavier, strong, yet deformable.

**E.g.:** Steel, Aluminium, Brass, Bronze, Lead, Titanium, etc.

# Ceramics

- They contain both metallic and nonmetallic elements.
- Characterized by their higher resistance to high temperatures and harsh environments than metals and polymers.
- Typically good insulators to passage of both heat and electricity.
- Less dense than most metals and alloys.
- They are harder and stiffer, but brittle in nature.
- They are mostly oxides, nitrides, and carbides of metals.
- Wide range: traditional (*clay, silicate glass, cement*) to advanced (*carbides, pure oxides, non-silicate glasses*).

**E.g.:** Glass, Porcelain, Minerals, etc.

# Polymers

- Commercially called *plastics*; noted for their low density, flexibility and use as insulators.
- Mostly are of organic compounds i.e. based on carbon, oxygen and other nonmetallic elements.
- Consists large molecular structures bonded by covalent and van der Waals forces.
- They decompose at relatively moderate temperatures (100-400 C).
- Application: packaging, textiles, biomedical devices, optical devices, household items, toys, etc.

**E.g.:** Nylon, Teflon, Rubber, Polyester, etc.

# Composites

- Consist more than one kind of material; tailor made to benefit from combination of best characteristics of each constituent.
- Available over a very wide range: natural (*wood*) to synthetic (*fiberglass*).
- Many are composed of two phases; one is matrix – which is continuous and surrounds the other, dispersed phase.
- Classified into many groups: (1) depending on orientation of phases; such as particle reinforced, fiber reinforced, etc. (2) depending on matrix; metal matrix, polymer matrix, ceramic matrix.

**E.g.:** Cement concrete, Fiberglass, special purpose refractory bricks, plywood, etc.

# Semiconductors

- Their electrical properties are intermediate when compared with electrical conductors and electrical insulators.
- These electrical characteristics are extremely sensitive to the presence of minute amounts of foreign atoms.
- Found very many applications in electronic devices over decades through integrated circuits. It can be said that semiconductors revolutionized the electronic industry for last few decades.

# Biomaterials

- Those used for replacement of damaged or diseased body parts.
- Primary requirements: must be biocompatible with body tissues, must not produce toxic substances.
- Important materials factors: ability to support the forces, low friction and wear, density, reproducibility and cost.
- All the above materials can be used depending on the application.
- A classic **example**: hip joint.

**E.g.:** Stainless steel, Co-28Cr-6Mo, Ti-6Al-4V, ultra high molecular weight polyethelene, high purity dense Al-oxide, etc.

# Advanced materials

- Can be defined as materials used in high-tech devices i.e. which operates based on relatively intricate and sophisticated principles (e.g. computers, air/space-crafts, electronic gadgets, etc.).
  - These are either traditional materials with enhanced properties or newly developed materials with high-performance capabilities. Thus, these are relatively expensive.
  - Typical applications: integrated circuits, lasers, LCDs, fiber optics, thermal protection for space shuttle, etc.
- E.g.:** Metallic foams, inter-metallic compounds, multi-component alloys, magnetic alloys, special ceramics and high temperature materials, etc.

## Future materials

- Group of new and state-of-the-art materials now being developed, and expected to have significant influence on present-day technologies, especially in the fields of medicine, manufacturing and defense.
- Smart/Intelligent material system consists some type of sensor (*detects an input*) and an actuator (*performs responsive and adaptive function*).
- Actuators may be called upon to change shape, position, natural frequency, mechanical characteristics in response to changes in temperature, electric/magnetic fields, moisture, pH, etc.

## Future materials (contd...)

- Four types of materials used as actuators:
  - Shape memory alloys
  - Piezoelectric ceramics
  - Magnetostrictive materials
  - Electro-/Magneto-rheological fluids
  
- Materials / Devices used as sensors:
  - Optical fibers
  - Piezoelectric materials
  - Micro-electro-mechanical systems (MEMS)
  - etc.

## Future materials (contd...)

### ➤ Typical applications:

- By incorporating sensors, actuators and chip processors into system, researchers are able to stimulate biological human-like behavior.
- Fibers for bridges, buildings, and wood utility poles.
- They also help in fast moving and accurate robot parts, high speed helicopter rotor blades.
- Actuators that control chatter in precision machine tools.
- Small microelectronic circuits in machines ranging from computers to photolithography prints.
- Health monitoring detecting the success or failure of a product.

## Modern materials' needs

- Engine efficiency increases at high temperatures; requires high temperature structural materials.
- Use of nuclear energy requires solving problems with residue, *or* advance 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.

# Material Science

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Module-2

**Atomic Structures, Interatomic  
Bonding and Structure of  
Crystalline Solids**

## Contents

- 1) Atomic Structure and Atomic bonding in solids
- 2) Crystal structures, Crystalline and Non-crystalline materials
- 3) Miller indices, Anisotropic elasticity and Elastic behavior of Composites
- 4) Structure and properties of polymers
- 5) Structure and properties of ceramics

# Atomic structure

- Every atom consists of a small nucleus composed of protons and neutrons, which is encircled by moving electrons in their *orbitals*, specific energy levels.
- In an atom, there will be always equal number of protons and electrons
- The top most orbital electrons, valence electrons, affect most material properties that are of interest to engineer. **E.g.:** chemical properties, nature of bonding, size of atom, optical/magnetic/electrical properties.
- Electrons and protons are negative and positive charges of the same magnitude being  $1.60 \times 10^{-19}$  coulombs.
- Neutrons are electrically neutral.
- Protons and neutrons have approximately the mass,  $1.67 \times 10^{-27}$  kg, which is larger than that of an electron,  $9.11 \times 10^{-31}$  kg.

## Atomic structure (contd...)

- Atomic number ( $Z$ ) - is the number of protons per atoms.
- Atomic mass ( $A$ ) - is the sum of the masses of protons and neutrons within the nucleus.
- Atomic mass is measured in atomic mass unit ( $amu$ ) where  $1\text{amu} = \frac{1}{12}$  the mass of most common isotope of carbon atom, measured in grams.
- $A \cong Z + N$ , where  $N$  is number of neutrons.
- **Isotopes** - atoms with same atomic number but different atomic masses.
- A mole is the amount of matter that has a mass in grams equal to the atomic mass in  $amu$  of the atoms. Thus a mole of carbon has a mass of 12 grams.

## Atomic structure (contd...)

- The number of atoms or molecules in a mole of substance is called the Avogadro's number,  $N_{ay}$ .  $N_{ay} = 1 \text{ gram} / 1 \text{ amu} = 6.023 \times 10^{23}$ .

**E.g.:** Calculating the number of atoms per  $\text{cm}^3$ ,  $n$ , in a piece of material of density  $\delta$  ( $\text{g}/\text{cm}^3$ )

$$n = N_{av} \times \delta / M, \quad \text{where } M \text{ is the atomic mass in } amu.$$

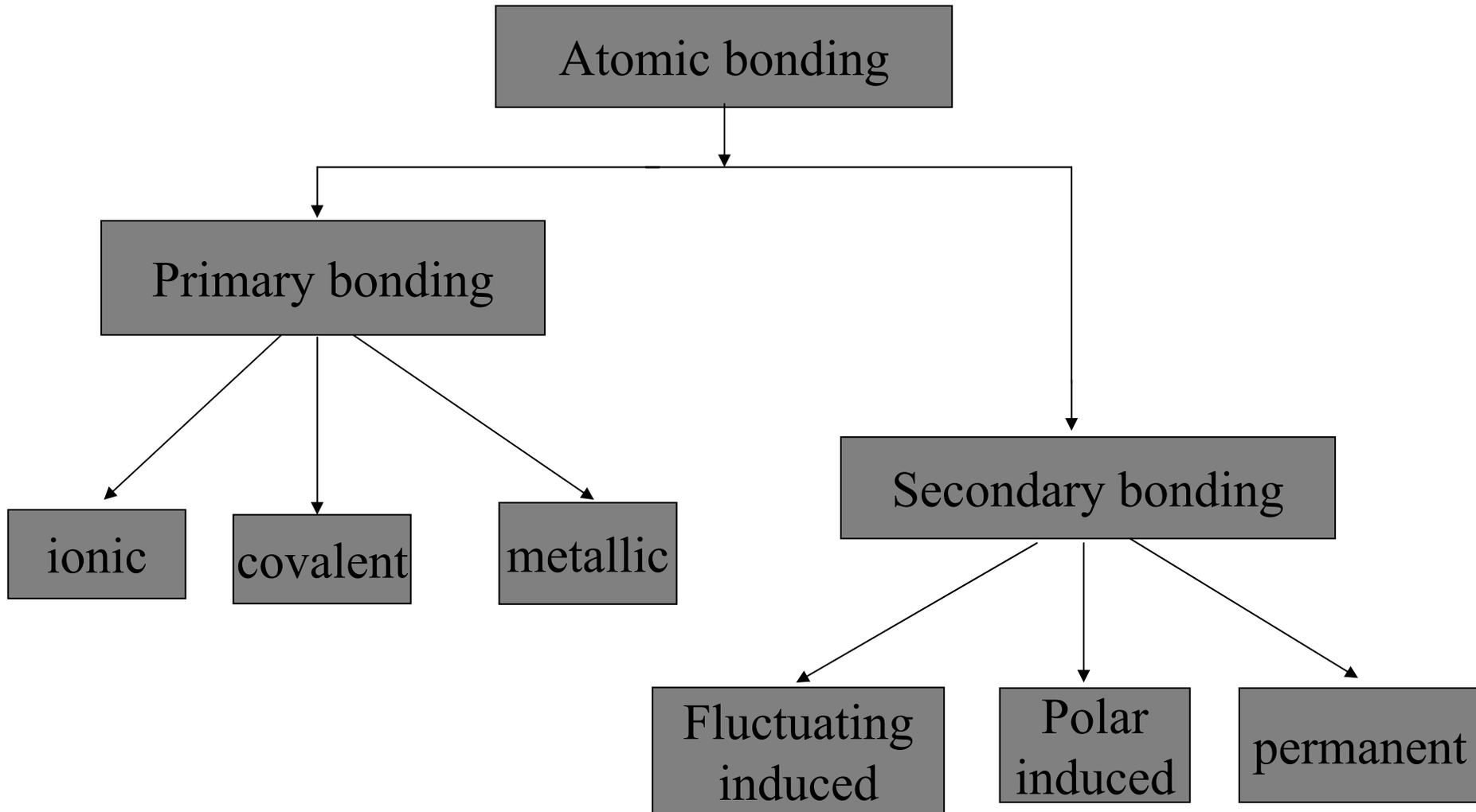
Thus, for graphite (carbon) with a density  $\delta = 1.8 \text{ g}/\text{cm}^3$  and  $M = 12$ ,  $n = 6.023 \times 10^{23} \text{ atoms/mol} \times 1.8 \text{ g}/\text{cm}^3 / 12 \text{ g/mol} = 9 \times 10^{22} \text{ atoms}/\text{cm}^3$ .

- Most solid materials will have atomic density in the order of  $6 \times 10^{22}$ , that's about 39 million atoms per centimeter.
- Mean distance between atoms is in the range of 0.25 nm. It gives an idea about scale of atomic structures in solids.

# Atomic Bonding in Solids

- Two questions need to be answered: why the atoms are clustered together?, and how they are arranged?
- Bonds are two kinds – Primary, and Secondary
- Primary bonds – relatively stronger. Exists in almost all solid materials.  
**E.g.:** Ionic, Covalent, and Metallic bonds.
- Secondary bonds – relatively weaker bonds. Exists in many substances like water along with primary bonds.  
**E.g.:** Hydrogen, and van der Waals forces.

# Atomic Bond in Solids



# Primary inter-atomic bonds

- These bonds invariably involves valence electrons.
- Nature of bond depends on electron arrangement in respective atoms.
- Atoms tend to acquire stable electron arrangement in their valence orbitals by transferring (ionic), sharing (covalent, and metallic) valence electrons. This leads to formation of bonds.
- Bond energies are in order of 1000 kJ/mol.

# Ionic bond

- This primary bond exists between two atoms when transfer of electron(s) results in one of the atoms to become negative (has an extra electron) and another positive (has lost an electron).
- This bond is a direct consequence of strong Coulomb attraction between charged atoms.
- Basically ionic bonds are non-directional in nature.
- In real solids, ionic bonding is usually exists along with covalent bonding.

**E.g.:** NaCl. In the molecule, there are more electrons around Cl, forming  $\text{Cl}^-$  and fewer electrons around Na, forming  $\text{Na}^+$ .

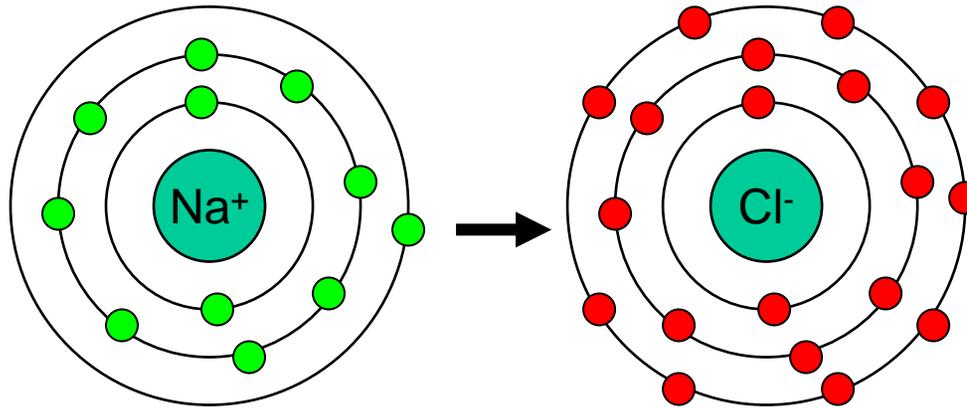


Fig.1 Schematic representation of ionic bonding.  
Here, Na is giving an electron to Cl to have stable structure

# Covalent bond

- This bond comes into existence if valence electrons are shared between a pair of atoms, thus acquire stability by saturating the valence configuration.
- Covalent bonds are stereospecific i.e. each bond is between a specific pair of atoms, which share a pair of electrons (of opposite magnetic spins).
- Typically, covalent bonds are very strong, and directional in nature.

**E.g.:** H<sub>2</sub> molecule, where an electron from each of the atom shared by the other atom, thus producing the covalent bond.

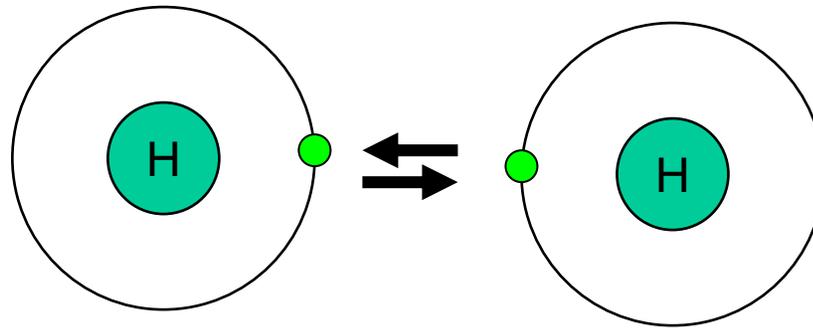


Figure 2. Schematic representation of covalent bond in Hydrogen molecule (sharing of electrons)

# Metallic bond

- This bond comes into existence if valence electrons are shared between number of atoms, i.e. arranged positive nucleuses are surrounded by electron pool.
- Shared electrons are not specific to a pair of atoms, in contrast to Covalent bond, i.e. electrons are delocalized.
- As shared electrons are delocalized, metallic bonds are non-directional.
- Very characteristic properties of metals like high thermal and electrical conductivities are result of presence of delocalized electron pool.

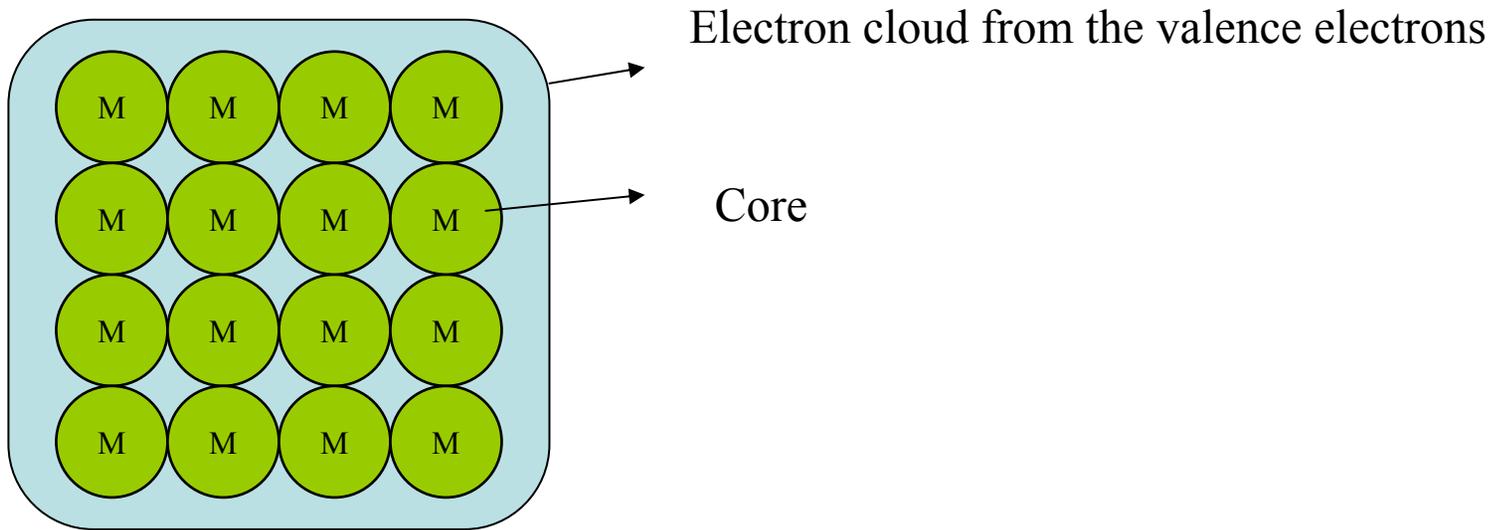


Figure 3. Metallic bonding

## Secondary inter-atomic bonds

- These bonds involves atomic *or* molecular dipoles.
- Bonds can exists between induced and permanent dipoles (polar molecules).
- Bond comes into existence because of Columbic attraction between positive end of one dipole and negative end of another dipole.
- Bond energies are in order of 10 kJ/mol

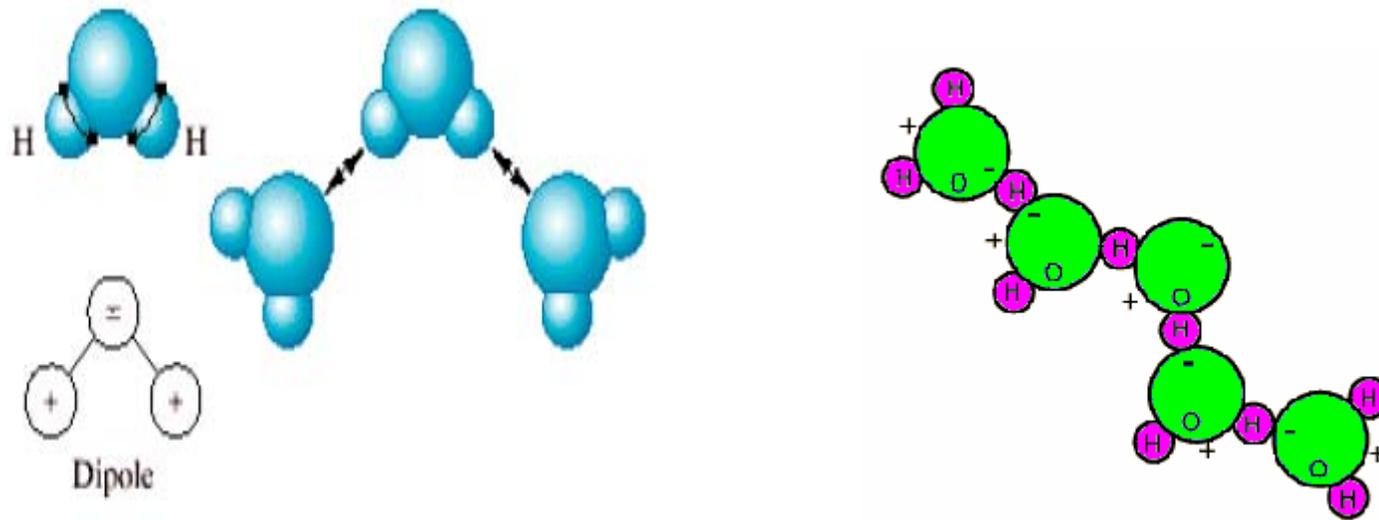


Figure 4. Dipole bonds in water

## Secondary inter-atomic bonds (contd...)

- Existence of these depends on three kinds of dipoles – fluctuating dipoles, Polar-molecule dipoles and Permanent dipoles.
- Permanent dipole bonds are also called Hydrogen bonds as covalently bonded hydrogen atoms – for example C-H, O-H, F-H – share single electron becomes positively charged proton that is capable of strong attractive force with the negative end of an adjacent molecule.
- Hydrogen bonds is responsible for water to exist in liquid state at room temperature.

# Crystal Structures

- All solid materials are made of atoms/molecules, which are arranged in specific order in some materials, called *crystalline solids*. Otherwise *non-crystalline* or *amorphous solids*.
- Groups of atoms/molecules specifically arranged – crystal.
- *Lattice* is used to represent a three-dimensional periodic array of points coinciding with atom positions.
- *Unit cell* is smallest repeatable entity that can be used to completely represent a crystal structure. It is the building block of crystal structure.

# Unit cell

It is characterized by:

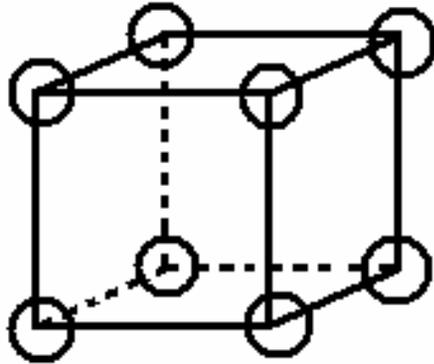
- Type of atom and their radii,  $R$
- Cell dimensions (Lattice spacing  $a$ ,  $b$  and  $c$ ) in terms of  $R$  and
- Angle between the axis  $\alpha$ ,  $\beta$ ,  $\gamma$
- $a^*$ ,  $b^*$ ,  $c^*$  - lattice distances in reciprocal lattice ,  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$  - angles in reciprocal lattice
- Number of atoms per unit cell,  $n$
- Coordination number ( $CN$ )– closest neighbors to an atom
- Atomic packing factor,  $APF$

Most common unit cells – Face-centered cubic, Body-centered cubic and Hexagonal.

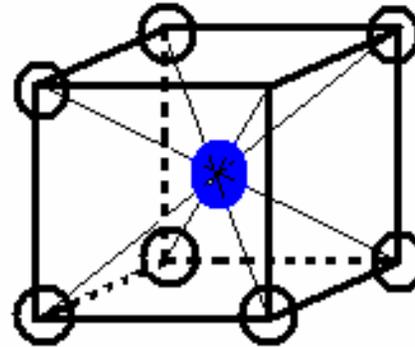
# Common Crystal Structures

| Unit Cell              | $n$ | $CN$ | $a/R$        | $APF$ |
|------------------------|-----|------|--------------|-------|
| Simple Cubic           | 1   | 6    | $4/\sqrt{4}$ | 0.52  |
| Body-Centered Cubic    | 2   | 8    | $4/\sqrt{3}$ | 0.68  |
| Face-Centered Cubic    | 4   | 12   | $4/\sqrt{2}$ | 0.74  |
| Hexagonal Close Packed | 6   | 12   |              | 0.74  |

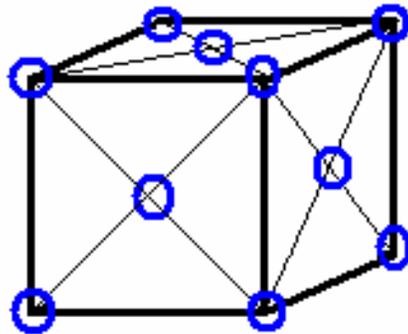
# Schematic Unit Cells



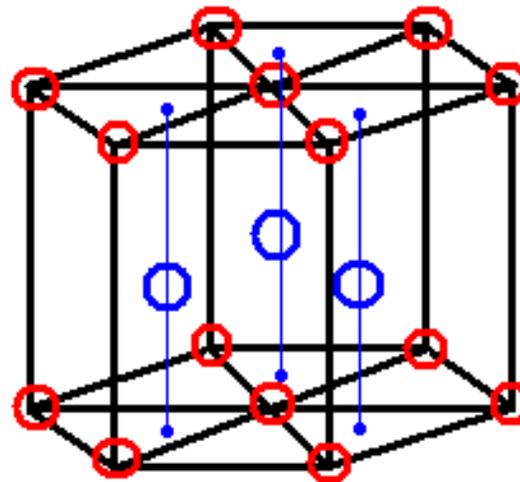
Simple Cubic



Body Centered Cubic



Face Centered Cubic



Hexagonal Close Packed

# Miller indices

- A system of notation is required to identify particular direction(s) or plane(s) to characterize the arrangement of atoms in a unit cell
- Formulas involving Miller indices are very similar to related formulas from analytical geometry – simple to use
- Use of reciprocals avoids the complication of infinite intercepts
- 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

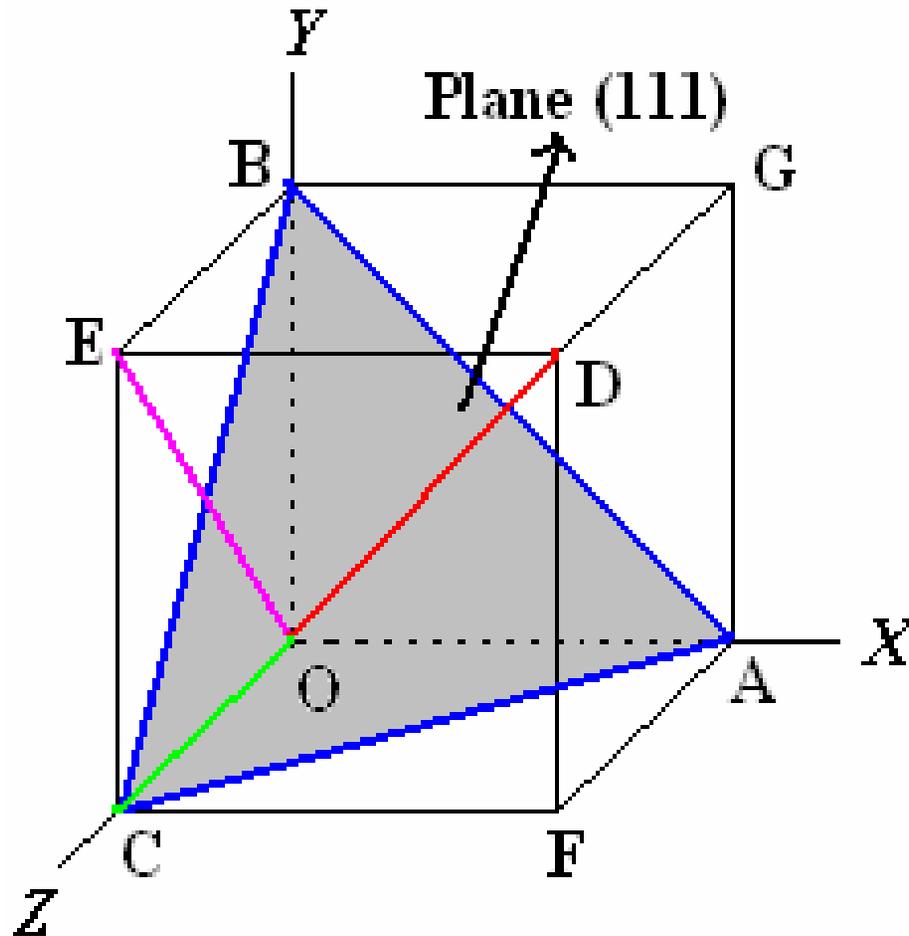
## Miller indices - Direction

- A vector of convenient length is placed parallel to the required direction
- The length of the vector projection on each of three axes are measured *in terms of 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  $\langle uvw \rangle$

## Miller indices - Plane

- 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}

# Miller indices - Examples



— Direction [001]

— Direction [011]

— Direction [111]

Plane ACEG (101)

Plane OAGB (001)

## Miller indices – Useful Conventions

- If a plane is parallel to an axis, its intercept is at infinity and its Miller index will be zero
- *Never alter negative numbers.* This implies symmetry that the crystal may not have! Use bar over the number to represent negative numbers.
- A plane or direction of family is not necessarily parallel to other planes or directions in the same family
- The smaller the Miller index, more nearly parallel the plane to that axis, and vice versa
- Multiplying or dividing a Miller index by constant has no effect on the orientation of the plane
- 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)

## Useful Conventions for cubic crystals

- $[uvw]$  is normal to  $(hkl)$  if  $u = h$ ,  $v = k$ , and  $w = l$ . **E.g.:**  $(111) \perp [111]$
- $[uvw]$  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  $u_1u_2 + v_1v_2 + w_1w_2 = 0$
- Inter-planar distance between family of planes  $\{hkl\}$  is given by:

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

- Angle between two planes is given by:

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

## Miller-Bravis indices

- Miller indices can describe all possible planes/directions in any crystal.
- However, Miller-Bravis indices are used in hexagonal systems as they can reveal hexagonal symmetry more clearly
- Indices are based on four axes – three are coplanar on basal plane at  $120^\circ$  apart, fourth axis is perpendicular to basal plane
- Both for planes/directions, extra index is given by

$$t = -(u+v), i = -(h+k)$$

where plane is represented as  $[uv tw]$ , and a direction is represented by  $(hkil)$

E.g.: Basal plane –  $(0001)$ , Prismatic plane –  $(10\bar{1}0)$

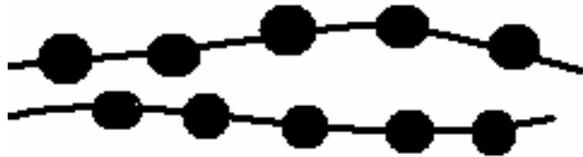
# Polymers - definition

- Polymers are made of basic units called *mers*
- These are usually Hydrocarbons – where major constituent atoms are Hydrogen and Carbon
- When structure consists of only one *mer*, it is monomer. If it contains more than one *mer*, it is called polymer
- *Isomers* are molecules those contain same number of similar *mers* but arrangement will be different  
E.g.: Butene and Isobutene
- When a polymer has ONE kind of *mers* in its structure, it is called *homopolymer*
- Polymer made with more than one kind of *mers* is called *copolymer*

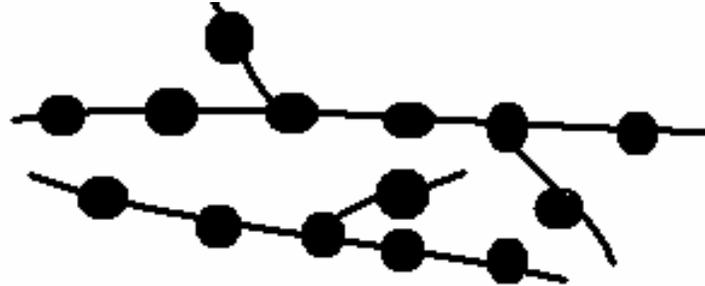
# Polymer structures

- Linear, where mer units are joined together end to end in single chains. E.g.: PVC, nylon.
- Branched, where side-branch chains are connected to main ones. Branching of polymers lowers polymer density because of lower packing efficiency E.g.: Bakelite
- Cross-linked, where chains are joined one to another at various positions by covalent bonds. This cross-linking is usually achieved at elevated temperatures by additive atoms. E.g.: vulcanization of rubber
- Network, trifunctional mer units with 3-D networks comes under this category. E.g.: epoxies, phenol-formaldehyde.

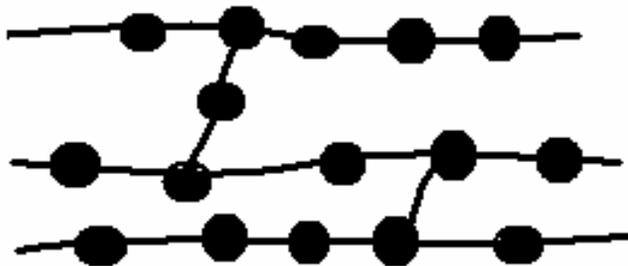
# Polymer structures



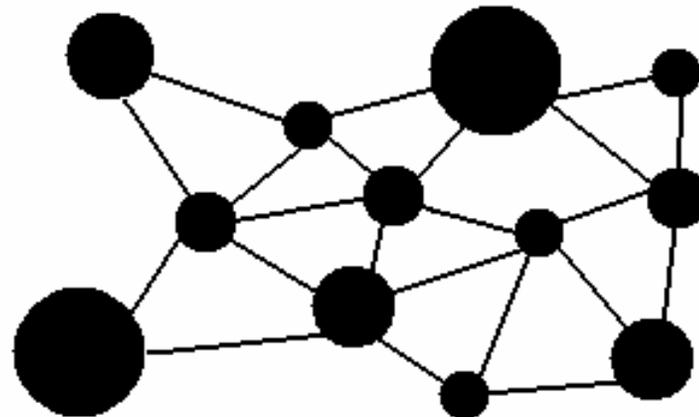
Linear



Branched



Cross-linked



Network

**Schematic presentation of polymer structures.**

Individual *mers* are represented by solid circles.

## Thermo-sets – Thermo-plasts

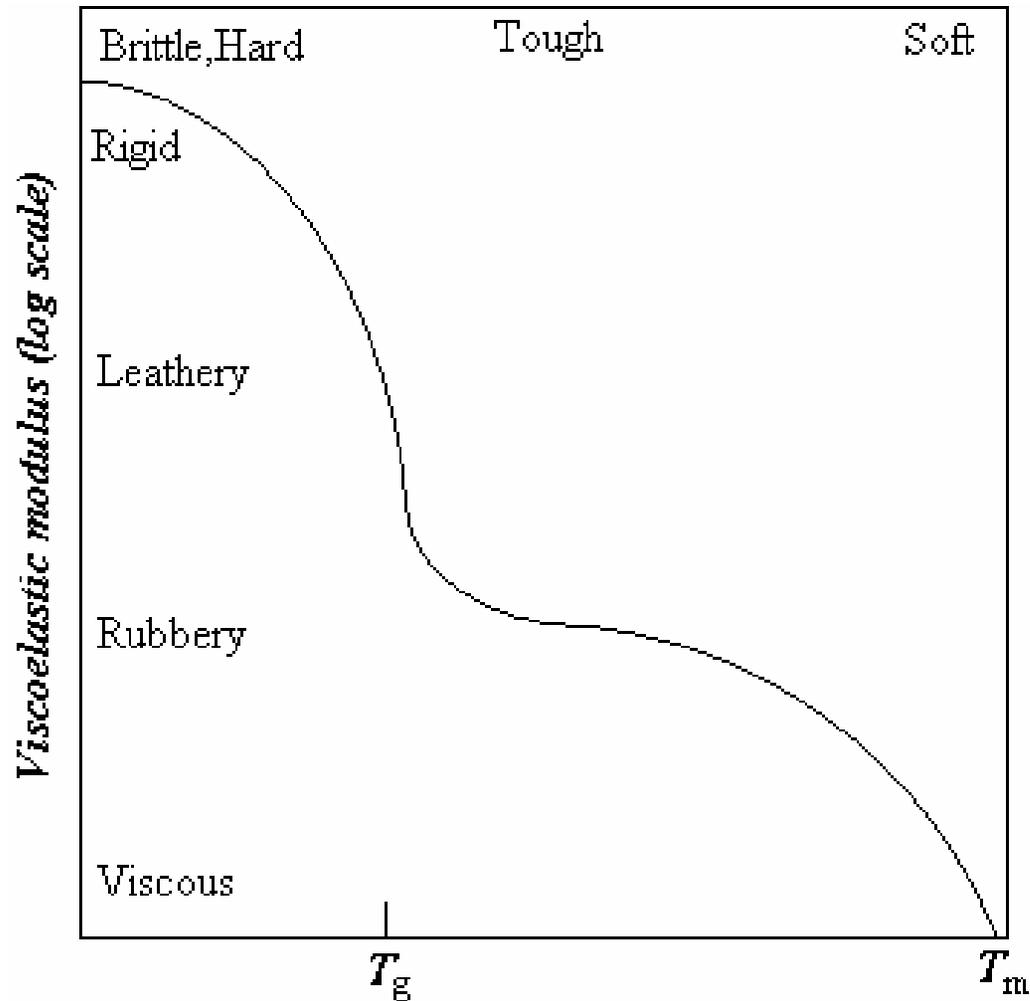
- Polymers mechanical response at elevated temperatures strongly depends on their chain configuration
- Based on this response polymers are grouped in to two - thermo-sets and thermo-plasts
- Thermo-sets: become permanently hard when heated, and do not soften during next heat cycle. During first heating covalent bonds forms thus extensive cross-linking takes place. Stronger and harder than thermo-plasts.  
*E.g.:* Vulcanized rubber, epoxies, some polyester resins
- Thermo-plasts: softens at high temperatures, and becomes hard at ambient temperatures. The process is reversible. Usually made of linear and branched structures.  
*E.g.:* Polystyrene, Acrylics, Cellulosics, Vinyls

# Polymer crystallinity

- Crystallinity in polymers is more complex than in metals
- Polymer crystallinity range from almost crystalline to amorphous in nature
- It depends on cooling path and on chain configuration
- Crystalline polymers are more denser than amorphous polymers
- Many semicrystalline polymers form *spherulites*. Each spherulite consists of collection of ribbon like chain folded lamellar crystallites.

E.g.: PVC (Poly Vinyl Chloride)

# Polymer properties



*Low ← Temperature → High*

*Impact ← Loading rate → Sustained*

# Ceramics

- Ceramics are inorganic and non-metallic materials
- Atomic bonds in ceramics are mixed – covalent + ionic
- Proportion of bonds is specific for a ceramic
- Ionic bonds exist between alkalis/alkaline-earth metals and oxygen/halogens.
- Mostly oxides, carbides, nitrides of metals are ceramics

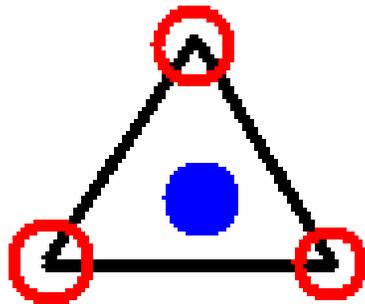
E.g.: Sand, Glass, Bricks, Marbles

# Ceramic structures

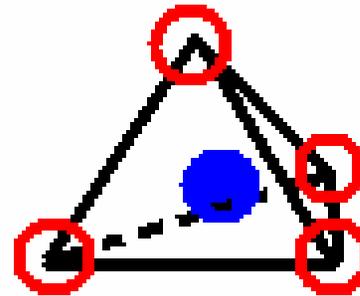
- Building criteria for ceramic structures:
  - maintain neutrality
  - closest packing
- Packing efficiency can be characterized by coordination number which depends on cation-anion radius ratio ( $r_c/r_a$ )

|  |            |                  |                  |                  |                  |            |
|--|------------|------------------|------------------|------------------|------------------|------------|
| <b><i>Cation-anion<br/>radius ratio<br/>(<math>r_c/r_a</math>)</i></b> | <<br>0.155 | 0.155 –<br>0.225 | 0.225 –<br>0.414 | 0.414 –<br>0.732 | 0.732 –<br>1.000 | ><br>1.000 |
| <b><i>Coordination<br/>number</i></b>                                  | 2          | 3                | 4                | 6                | 8                | 12         |

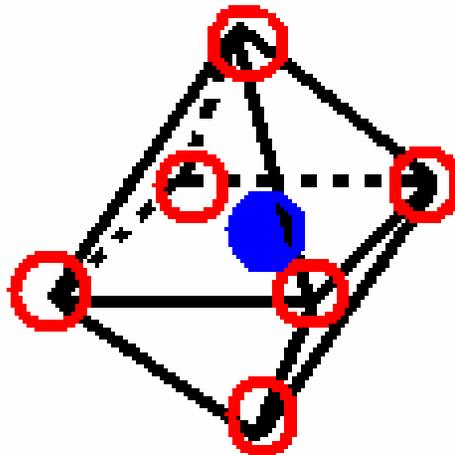
# Ion arrangement – Coordination numbers



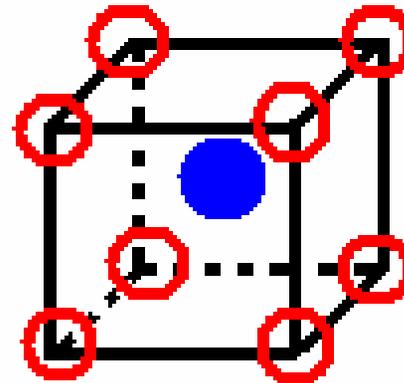
CN = 3



CN = 4



CN = 6



CN = 8

# Ceramic crystal structures

- AX-type: most common in ceramics. They assume different structures of varying coordination number (CN).

Rock salt structure – CN=6.

E.g.: NaCl, FeO

Cesium Chloride structure – CN=8

E.g.: CsCl

Zinc Blende structure – CN=4

E.g.: ZnS, SiC

- A<sub>m</sub>X<sub>p</sub>-type: number of anions and cations are different (m≠p). One unit cell is made of eight cubes.

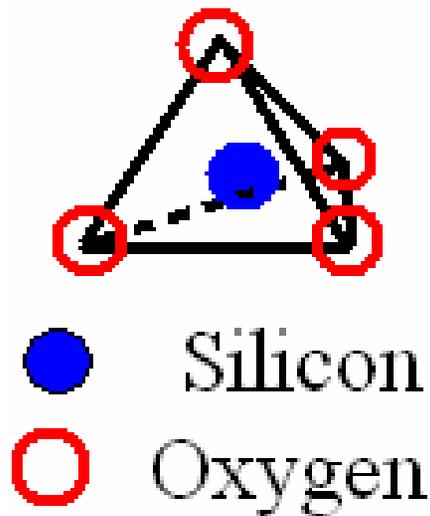
E.g.: CaF<sub>2</sub>, ThO<sub>2</sub>

- A<sub>m</sub>B<sub>n</sub>X<sub>p</sub>-type: when ceramic contains more than one kind of cations. Also called *perovskite crystal structure*.

E.g.: BaTiO<sub>3</sub>

# Silicates

- Most common ceramic in nature – Silicates, as constituent elements – silicon and oxygen – are most abundant in earth's crust.
- Bond between  $\text{Si}^{4+}$  and  $\text{O}^{2-}$  is weak ionic and very strong covalent in nature. Thus, basic unit of silicates is  $\text{SiO}_4^{4-}$  tetrahedron.



## Silicates (contd...)

- In Silica ( $\text{SiO}_2$ ), every oxygen atom the corner of the tetrahedron is shared by the adjacent tetrahedron.
- Silica can be both crystalline (quartz) and amorphous (glass)
- Crystalline forms of silica are complicated, and comparatively open...thus low in density compared with amorphous glasses
- Addition of network modifiers ( $\text{Na}_2\text{O}$ ) and intermediates ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ) lowers the melting point...thus it is easy to form. E.g.: Bottles.
- In complicated silicates, corner oxygen is shared by other tetrahedra....thus consists  $\text{SiO}_4^{4-}$ ,  $\text{Si}_2\text{O}_7^{6-}$ ,  $\text{Si}_3\text{O}_9^{6-}$  groups
- Clays comprises 2-D sheet layered structures made of  $\text{Si}_2\text{O}_5^{2-}$

# Carbon

- Carbon is not a ceramic, but its allotropic form - Diamond - is
- Diamond:
  - C-C covalent bonds, highest known hardness,
  - Semiconductor, high thermal conductivity, meta-stable
- Graphite - another allotropic form of carbon
  - layered structure - hexagonal bonding within planar layers, good electrical conductor, solid lubricant
- Another allotropic form -  $C_{60}$  - also called Fullerene / Bucky ball. Structure resembles hallow ball made of 20 hexagons and 12 pentagons where no two pentagons share a common edge.
- Fullerenes and related nanotubes are very strong, ductile - could be one of the important future engineering materials

# Imperfections in ceramics

- Imperfections in ceramics – point defects, and impurities. Their formation is strongly affected by charge neutrality
- *Frenkel-defect* is a vacancy-interstitial pair of cations
- *Schottky-defect* is a pair of nearby cation and anion vacancies
- Impurities:
  - Introduction of impurity atoms in the lattice is likely in conditions where the charge is maintained.
  - E.g.: electronegative impurities that substitute lattice anions or electropositive substitutional impurities

# Mechanical response of ceramics

- Engineering applications of ceramics are limited because of presence of microscopic flaws – generated during cooling stage of processing.
- However, as ceramics are high with hardness, ceramics are good structural materials under compressive loads.
- Plastic deformation of crystalline ceramics is limited by strong inter-atomic forces. Little plastic strain is accomplished by process of slip.
- Non-crystalline ceramics deform by viscous flow.
- Characteristic parameter of viscous flow – viscosity. Viscosity decreases with increasing temperature. However, at room temperature, viscosity of non-crystalline ceramics is very high.

## Mechanical response of ceramics (contd...)

- Hardness – one best mechanical property of ceramics which is utilized in many application such as abrasives, grinding media
- Hardest materials known are ceramics
- Ceramics having Knoop hardness about 1000 or greater are used for their abrasive characteristics
- Creep – Ceramics experience creep deformation as a result of exposure to stresses at elevated temperatures.
- Modulus of elasticity,  $E$ , as a function of volume fraction of porosity,  $P$ :  $E = E_0 (1 - 1.9 P + 0.9 P^2)$
- Porosity is deleterious to the flexural strength for two reasons:
  - reduces the cross-sectional area across where load is applied
  - act as stress concentrations

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Module-3

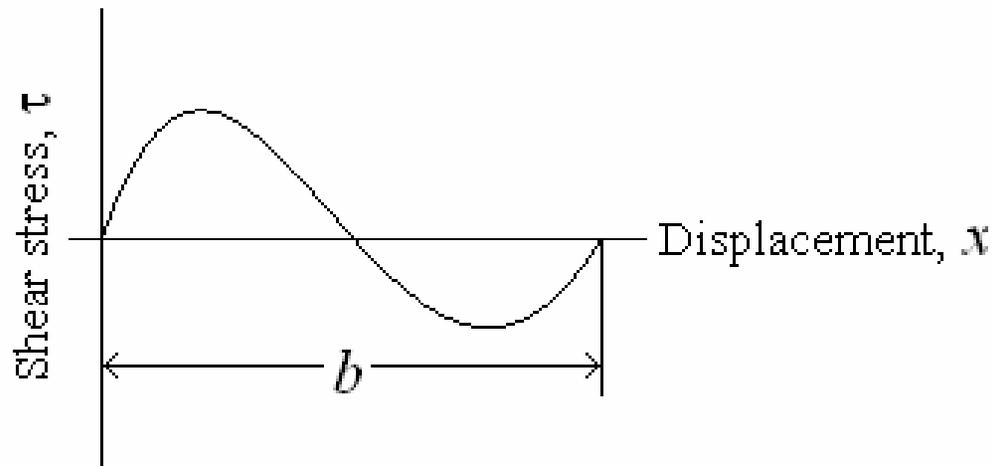
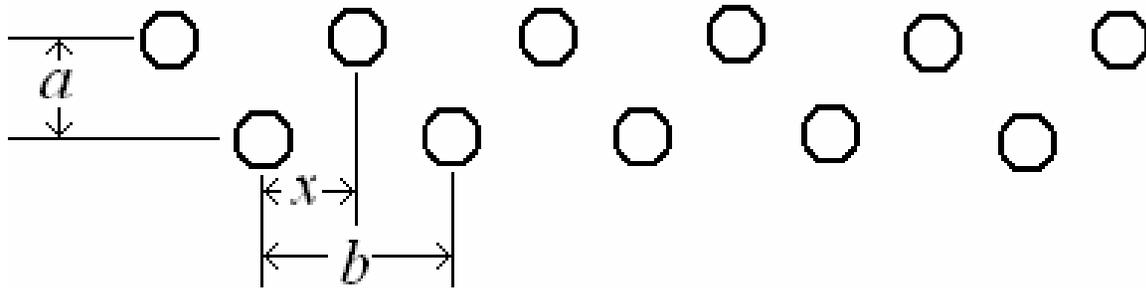
# **Imperfections in Solids**

## Contents

- 1) Theoretical yield strength, Point defects and Line defects or Dislocations
- 2) Interfacial defects, Bulk or Volume defects and Atomic vibrations

# Theoretical yield strength

- Ideal solids are made of atoms arranged in orderly way.



## Theoretical yield strength (contd...)

- Using a *sin* function to represent the variation in shear stress

$$\tau = \tau_m \sin \frac{2\Pi x}{b} \quad \tau \approx \tau_m \frac{2\Pi x}{b}$$



$$\tau = G\gamma = \frac{Gx}{a}$$

(Hooke's law)



$$\tau_m = \frac{G}{2\Pi} \frac{b}{a}$$

If  $b \approx a$

$$\tau_m = \frac{G}{2\Pi}$$

$G \approx 20-150 \text{ GPa}$

➔ Shear strength  $\approx 3-30 \text{ GPa}$

(ideal)

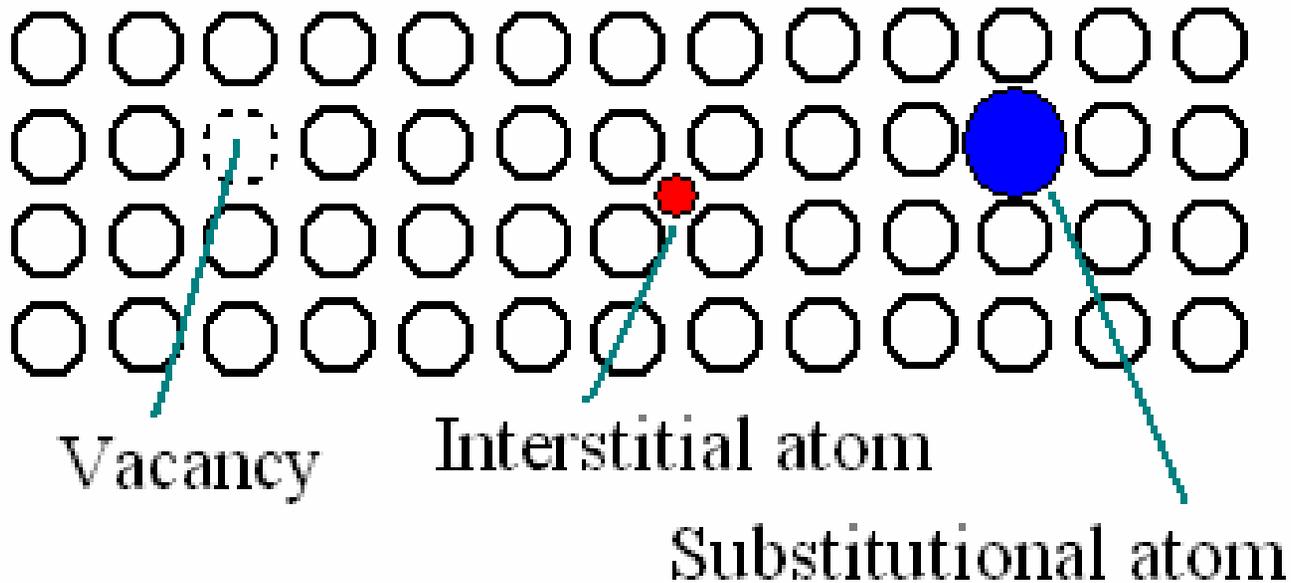
Real strength values  $\approx 0.5-10 \text{ MPa}$

## Theoretical yield strength (contd...)

- Theoretical strength of solids shall possess an ideal value in the range of 3-30 GPa.
- Real values observed in practice are 0.5-10 MPa.
- The assumption of perfectly arranged atoms in a solid may not valid.....i.e. atomic order must have been disturbed.
- Disordered atomic region is called *defect* or *imperfection*.
- Based on geometry, defects are: Point defects (zero-D), Line defects (1-D) *or* Dislocations, Interfacial defects (2-D) and Bulk *or* Volume defects (3-D).

## Point defects

- Point defects are of zero-dimensional i.e. atomic disorder is restricted to point-like regions.
- Thermodynamically stable compared with other kind of defects.

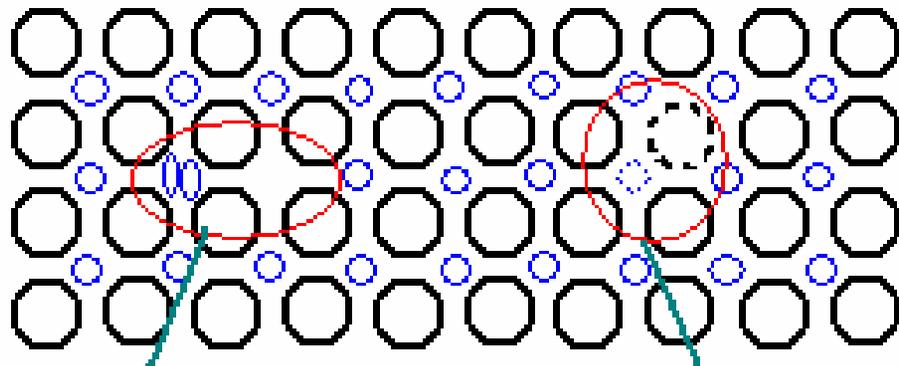


## Point defects (contd...)

- Fraction of vacancy sites can be given as follows:

$$\frac{n}{N} = e^{-Q/kT}$$

- In ionic crystals, defects can form on the condition of charge neutrality. Two possibilities are:



Frenkel defect

Schottky defect

## Line defects

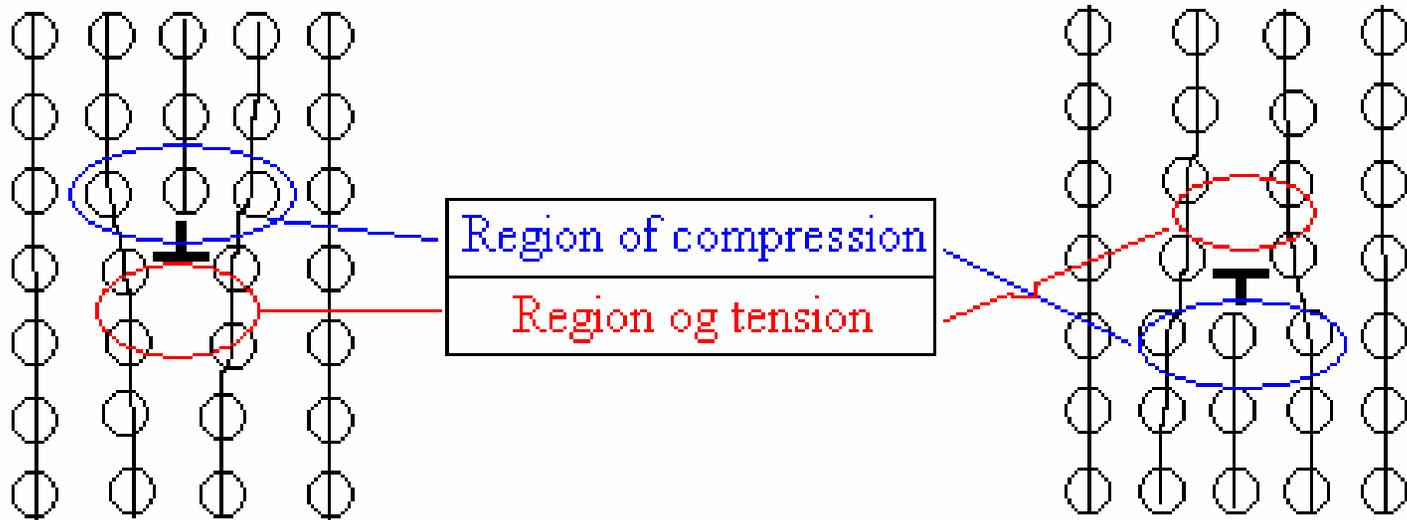
- *Line defects* or *Dislocations* are abrupt change in atomic order along a line.
- They occur if an incomplete plane inserted between perfect planes of atoms *or* when vacancies are aligned in a line.
- *A dislocation is the defect responsible for the phenomenon of slip, by which most metals deform plastically.*
- Dislocations occur in high densities ( $10^8$ - $10^{10}$  m<sup>-2</sup> ), and are intimately connected to almost all mechanical properties which are in fact structure-sensitive.
- Dislocation form during plastic deformation, solidification or due to thermal stresses arising from rapid cooling.

## Line defects – Burger's vector

- A dislocation is characterized by Burger's vector,  $\mathbf{b}$ .
- It is unique to a dislocation, and usually has the direction of close packed lattice direction. It is also the slip direction of a dislocation.
- *It represents the magnitude and direction of distortion associated with that particular dislocation.*
- Two limiting cases of dislocations, edge and screw, are characterized by Burger's vector perpendicular to the dislocation line ( $\mathbf{t}$ ) and Burger's vector parallel to the dislocation line respectively. Ordinary dislocation is of mixed character of edge and screw type.

# Line defects – Edge dislocation

- It is also called as *Taylor-Orowan dislocation*.
- It will have regions of compressive and tensile stresses on either side of the plane containing dislocation.

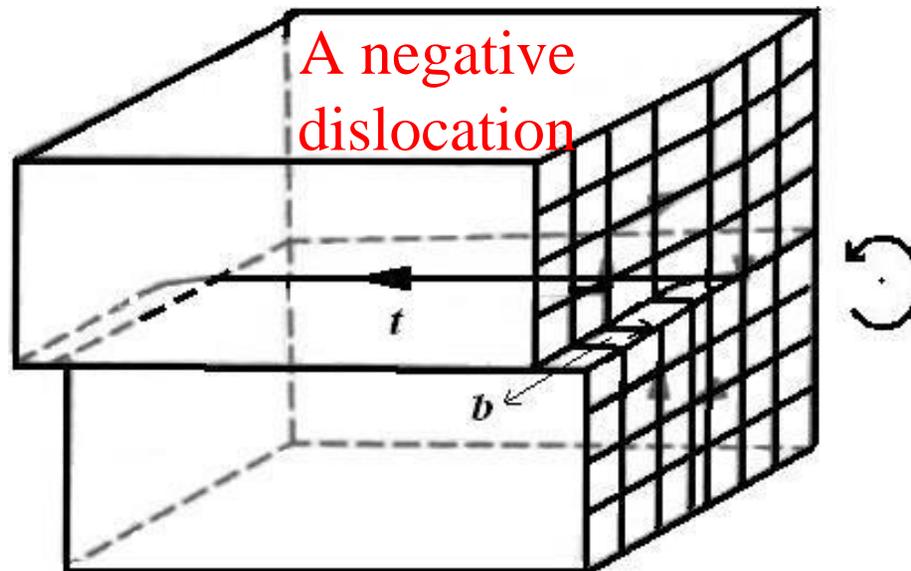


Positive Edge dislocation

Negative Edge dislocation

# Line defects – Screw dislocation

- It is also called as *Burger's dislocation*.
- It will have regions of shear stress around the dislocation line
- For positive screw dislocation, dislocation line direction is parallel to Burger's vector, and vice versa.



## Line defects – Dislocation motion

- Dislocations move under applied stresses, and thus causes plastic deformation in solids.
- Dislocations can move in three ways – glide/slip, cross-slip and climb – depending on their character. Slip is conservative in nature, while the climb is non-conservative, and is diffusion-controlled.
- *Any dislocation can slip, but in the direction of its burger's vector.*
- *Edge dislocation moves by slip and climb.*
- *Screw dislocation moves by slip / cross-slip.* Possibility for cross-slip arises as screw dislocation does not have a preferred slip plane as edge dislocation have.

## Line defects – Dislocation characteristics

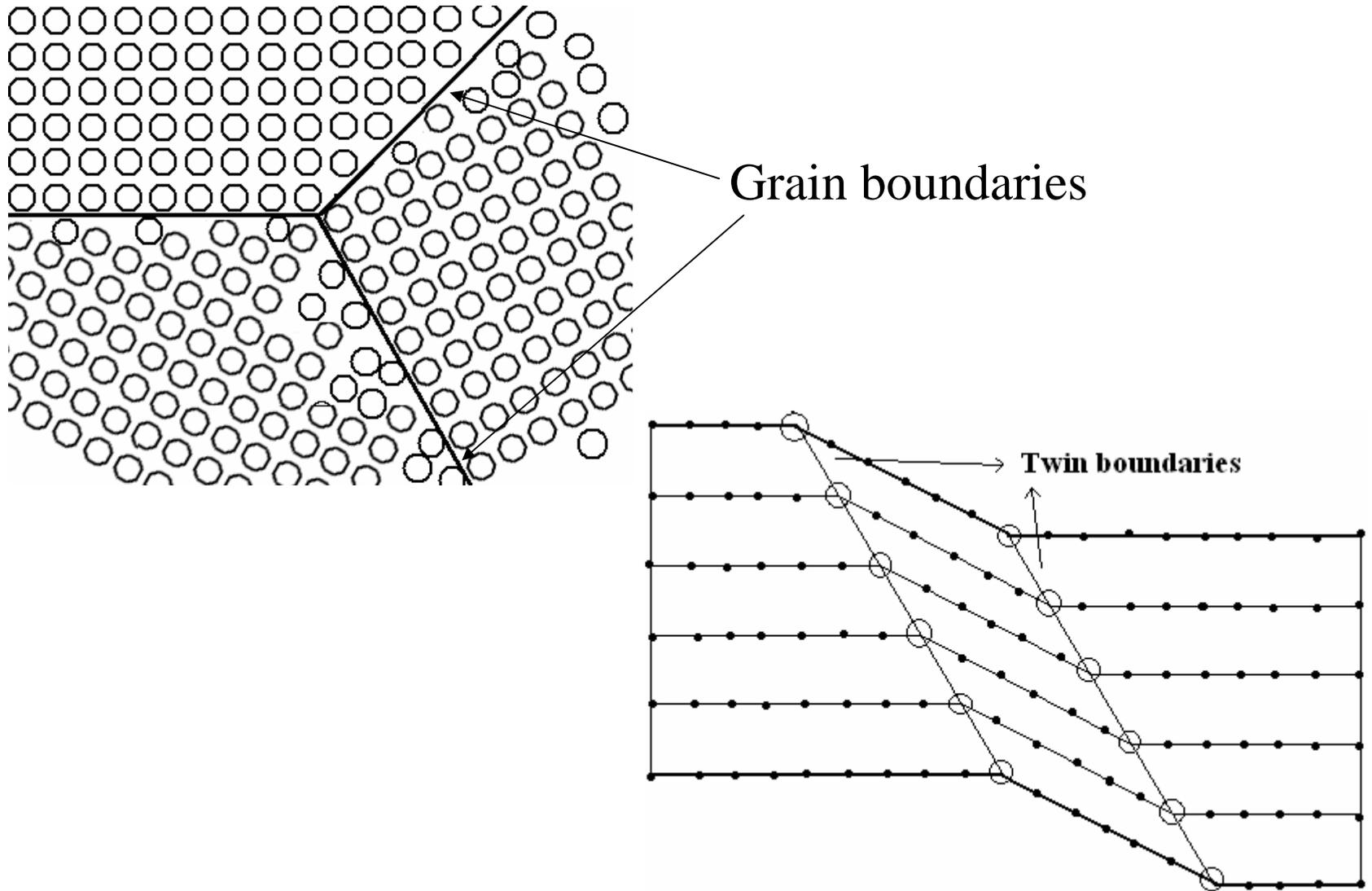
- A dislocation line cannot end abruptly inside a crystal. It can close-on itself as a loop, either end at a node or surface.
- Burger's vector for a dislocation line is invariant i.e. it will have same magnitude and direction all along the dislocation line.
- Energy associated with a dislocation because of presence of stresses is proportional to square of Burger's vector length. Thus dislocations, at least of same nature, tend to stay away from each other.
- Dislocations are, thus, two types – full and partial dislocations. For *full dislocation*, Burger's vector is integral multiple of inter-atomic distance while for *partial dislocation*, it is fraction of lattice translation.

## Interfacial defects

- An interfacial defect is a 2-D imperfection in crystalline solids, and have different crystallographic orientations on either side of it.
- Region of distortion is about few atomic distances.
- They usually arise from clustering of line defects into a plane.
- These imperfections are not thermodynamically stable, but meta-stable in nature.

**E.g.:** External surface, Grain boundaries, Stacking faults, Twin boundaries, Dislocations and Phase boundaries.

## Interfacial defects (contd...)



## Bulk or Volume defects

- Volume defects are three-dimensional in nature.
- These defects are introduced, usually, during processing and fabrication operations like casting, forming etc.

E.g.: Pores, Cracks, Foreign particles

- These defects act like stress raisers, thus deleterious to mechanical properties of parent solids.
- In some instances, foreign particles are added to strengthen the solid – dispersion hardening. Particles added are hindrances to movement of dislocations which have to cut through or bypass the particles thus increasing the strength.

## Atomic vibrations

- Atoms are orderly arranged, but they are expected to vibrate about their positions where the amplitude of vibration increases with the temperature.
- After reaching certain temperature, vibrations are vigorous enough to rupture the inter-atomic forces causing melting of solids.
- Average amplitude of vibration at room temperature is about  $10^{-12}$ m i.e. thousandth of a nanometer.
- Frequency of vibrations is the range of  $10^{13}$  Hz.
- Temperature of a solid body is actually a measure of vibrational activity of atoms and/or molecules.

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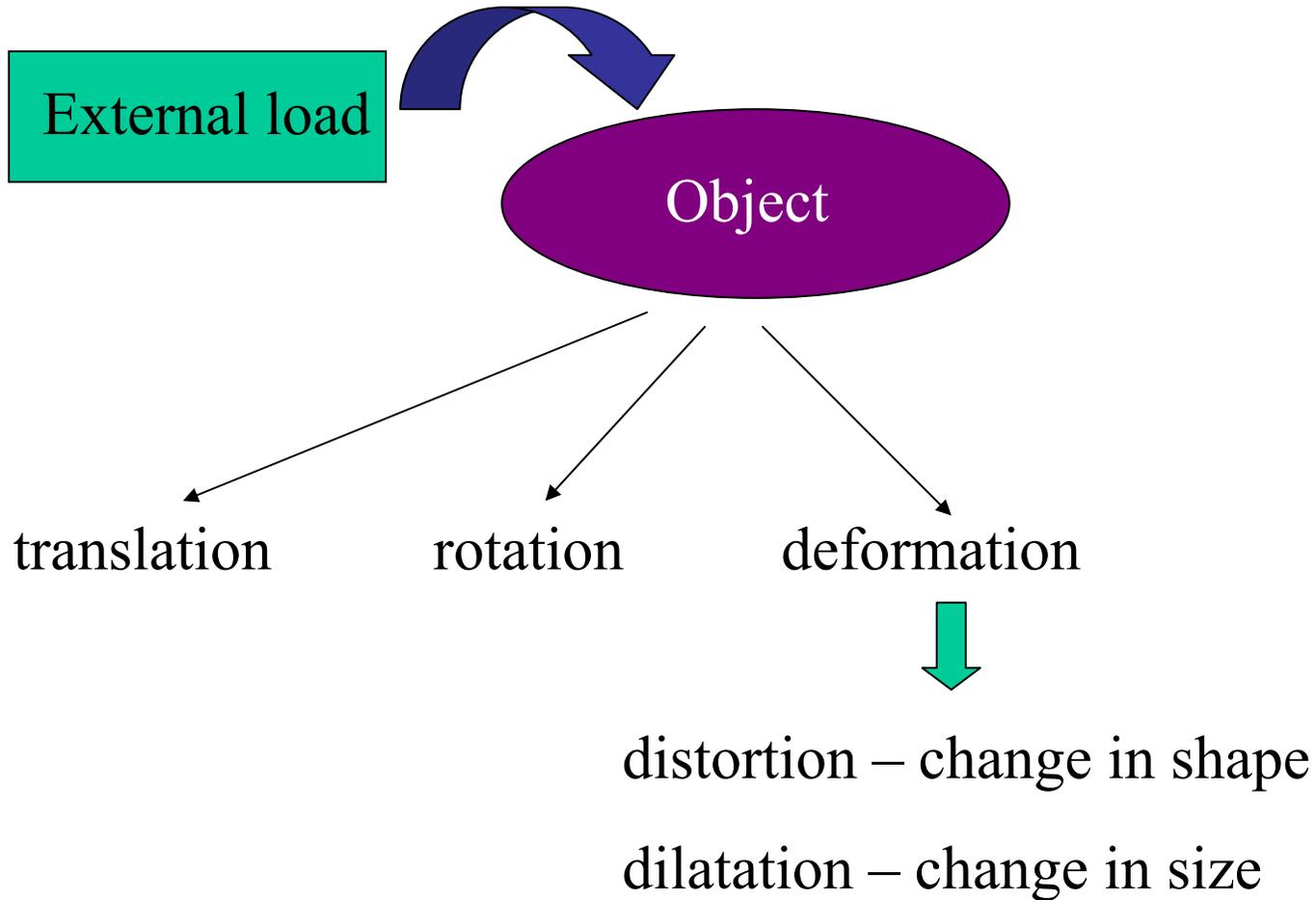
Module-4

## **Mechanical Properties of Metals**

## Contents

- 1) Elastic deformation and Plastic deformation
- 2) Interpretation of tensile stress-strain curves
- 3) Yielding under multi-axial stress, Yield criteria, Macroscopic aspects of plastic deformation and Property variability & Design considerations

# Mechanical loads - Deformation



# Deformation – function of time?

**Temporary / recoverable**

**Permanent**

time independent –

**elastic**

time independent –

**plastic**

time dependent –

**anelastic** (under load),

**elastic aftereffect** (after removal of load)

time dependent –

**creep** (under load),

combination of recoverable and permanent, but time dependent – **visco-elastic**

# Engineering Stress – Engineering Strain

- Load applied acts over an area.
- Parameter that characterizes the load effect is given as load divided by original area over which the load acts. It is called *conventional stress* or *engineering stress* or simply *stress*. It is denoted by  $s$ .
- Corresponding change in length of the object is characterized using parameter – given as per cent change in the length – known as *strain*. It is denoted by  $e$ .

$$s = \frac{P}{A_0}, e = \frac{L - L_0}{L_0}$$

- As object changes its dimensions under applied load, engineering stress and strain are not be the true representatives.

# True Stress – True Strain

➤ *True* or *Natural* stress and strain are defined to give true picture of the instantaneous conditions.

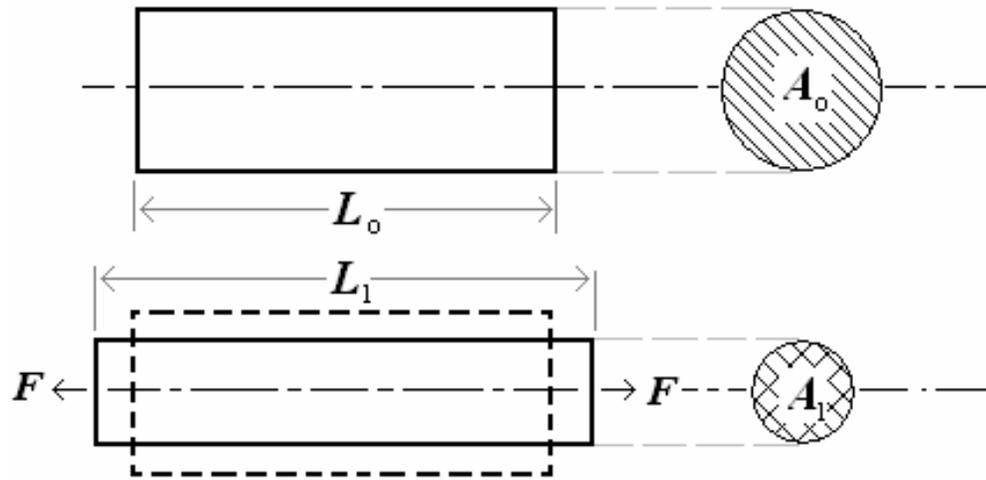
➤ True strain:

$$\varepsilon = \sum \frac{L_1 - L_0}{L_0} + \frac{L_2 - L_1}{L_1} + \frac{L_3 - L_2}{L_2} + \dots \quad \varepsilon = \int_{L_0}^L \frac{dL}{L} = \ln \frac{L}{L_0}$$

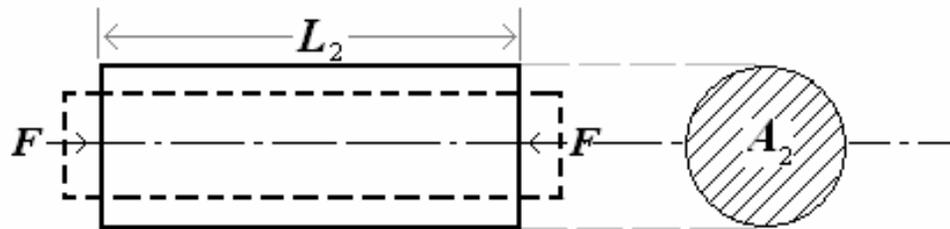
➤ True stress:

$$\sigma = \frac{P}{A} = \frac{P}{A_0} \frac{A_0}{A} = s(e + 1)$$

# Different loads – Strains

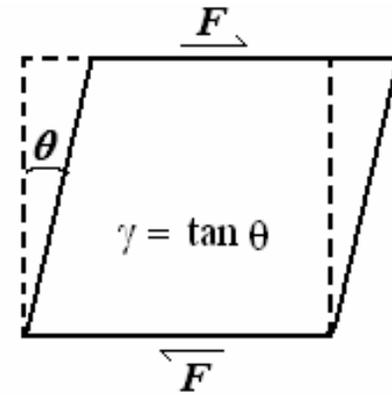


Tensile deformation

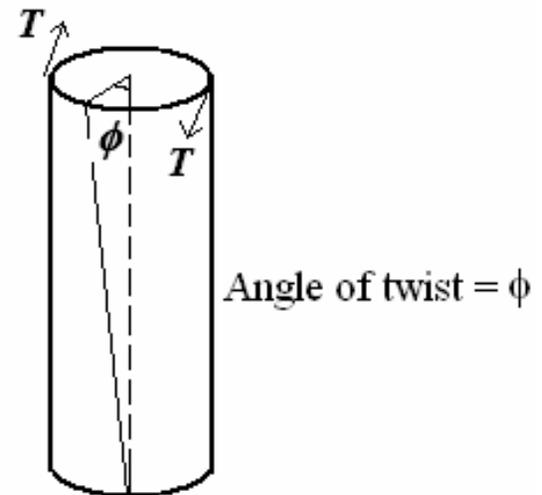


Compressive deformation

Linear strains



Shear strain



Torsional strain

## Elastic deformation

- A material under goes elastic deformation first followed by plastic deformation. The transition is not sharp in many instances.
- For most of the engineering materials, complete elastic deformation is characterized by strain proportional to stress. Proportionality constant is called *elastic modulus* or *Young's modulus*,  $E$ .

$$\sigma \propto \varepsilon \qquad \sigma = E\varepsilon$$

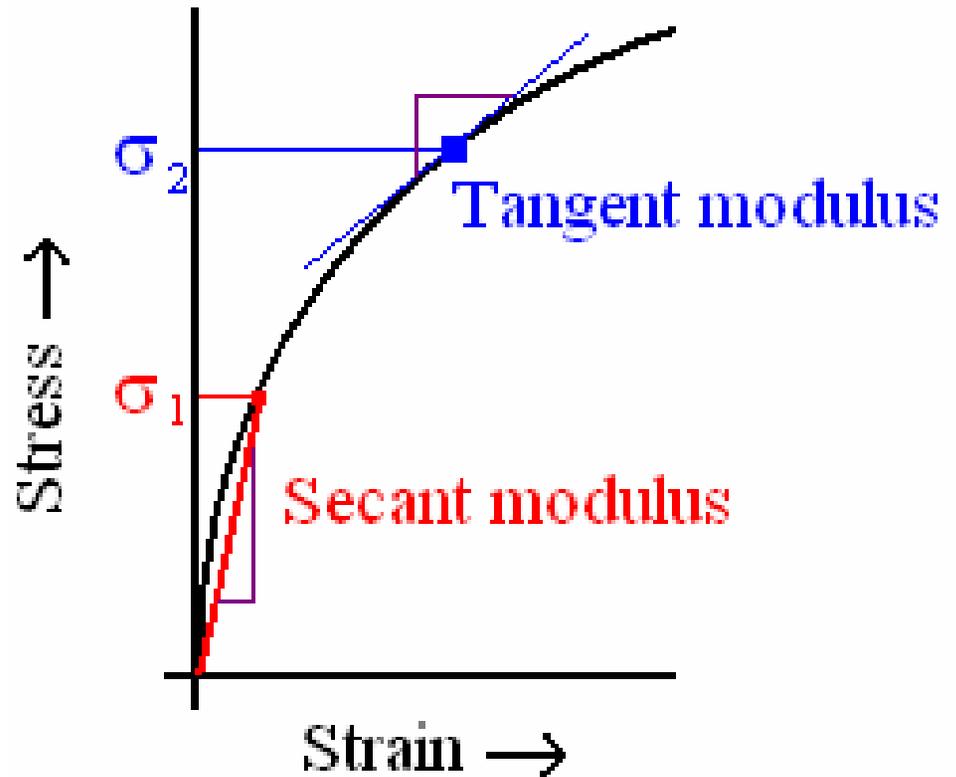
- Non-linear stress-strain relation is applicable for materials.  
E.g.: rubber.

## Elastic deformation (contd...)

- For materials without linear stress-strain portion, either tangent or secant modulus is used in design calculations.

The tangent modulus is taken as the slope of stress-strain curve at some specified level.

Secant module represents the slope of secant drawn from the origin to some given point of the  $\sigma$ - $\epsilon$  curve.



## Elastic deformation (contd...)

- Theoretical basis for elastic deformation – reversible displacements of atoms from their equilibrium positions – stretching of atomic bonds.
- Elastic modulus measures *stiffness* of material. It can also be a measure of resistance to separation of adjacent atoms.
- Elastic modulus =  $f/n$  (inter-atomic forces)  
=  $f/n$  (inter-atomic distance)  
=  $f/n$  (crystal structure, orientation)  
=> For single crystal elastic modulus are not isotropic.
- For a polycrystalline material, it is considered as isotropic.
- Elastic modulus slightly changes with temperature (decreases with increase in temperature).

## Elastic deformation (contd...)

- Linear strain is always accompanied by lateral strain, to maintain volume constant.
- The ratio of lateral to linear strain is called Poisson's ratio ( $\nu$ ).
- Shear stresses and strains are related as  $\tau = G\gamma$ , where  $G$  is shear modulus or elastic modulus in shear.
- Bulk modulus or volumetric modulus of elasticity is defined as ratio between mean stress to volumetric strain.  
$$K = \sigma_m / \Delta$$
- All moduli are related through Poisson's ratio.

$$G = \frac{E}{2(1 + \nu)}$$

$$K = \frac{\sigma_m}{\Delta} = \frac{E}{3(1 - 2\nu)}$$

## Plastic deformation

- Following the elastic deformation, material undergoes plastic deformation.
- Also characterized by relation between stress and strain at constant strain rate and temperature.
- Microscopically...it involves breaking atomic bonds, moving atoms, then restoration of bonds.
- Stress-Strain relation here is complex because of atomic plane movement, dislocation movement, and the obstacles they encounter.
- Crystalline solids deform by processes – slip and twinning in particular directions.
- Amorphous solids deform by viscous flow mechanism without any directionality.

## Plastic deformation (contd...)

- Because of the complexity involved, theory of plasticity neglects the following effects:
  - Anelastic strain, which is time dependent recoverable strain.
  - Hysteresis behavior resulting from loading and unloading of material.
  - Bauschinger effect – dependence of yield stress on loading path and direction.
- Equations relating stress and strain are called *constitutive equations*.
- A true stress-strain curve is called *flow curve* as it gives the stress required to cause the material to flow plastically to certain strain.

## Plastic deformation (contd...)

- Because of the complexity involved, there have been many stress-strain relations proposed.

$$\sigma = fn(\varepsilon, \dot{\varepsilon}, T, \text{microstructure})$$

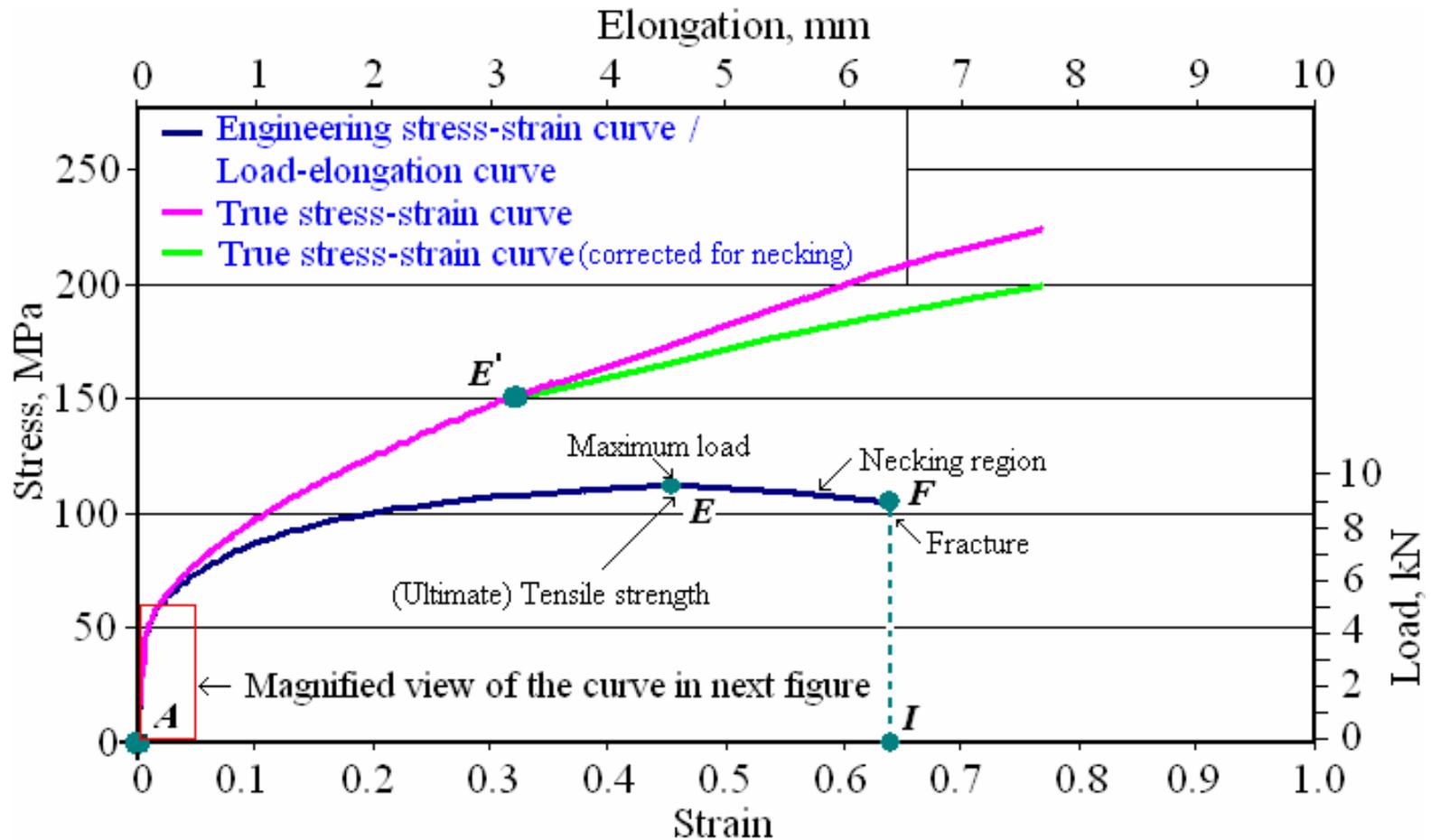
$$\sigma = K\varepsilon^n \quad \text{Strain hardening exponent, } n = 0.1-0.5$$

$$\sigma = K\dot{\varepsilon}^m \quad \text{Strain-rate sensitivity, } m = 0.4-0.9$$

$$\sigma = K(\varepsilon_0 + \varepsilon)^n \quad \text{Strain from previous work} - \varepsilon_0$$

$$\sigma = \sigma_0 + K\varepsilon^n \quad \text{Yield strength} - \sigma_0$$

# Tensile stress-strain curve



A – Starting point

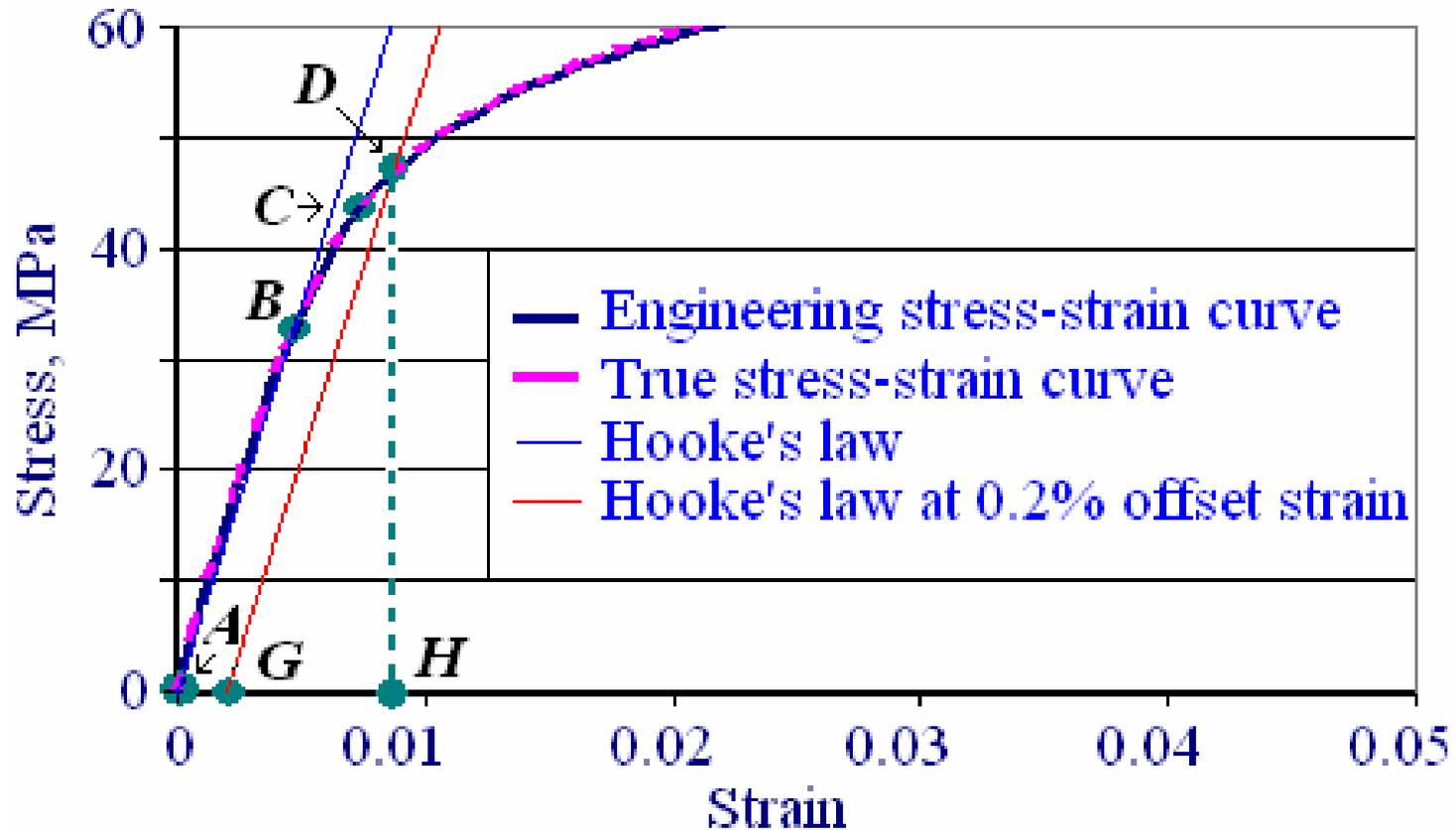
E – Tensile strength

E' – Corresponding to E on flow curve

F – Fracture point

I – Fracture strain

## Tensile stress-strain curve (contd...)



A – Starting point

C – Elastic limit

G – 0.2% offset strain

B – Proportional limit

D – Yield limit

H – Yield strain

## Tensile stress-strain curve (contd...)

- Apart from different strains and strength points, two other important parameters can be deduced from the curve are – resilience and toughness.
- Resilience ( $U_r$ ) – ability to absorb energy under elastic deformation
- Toughness ( $U_t$ ) – ability to absorb energy under loading involving plastic deformation. Represents combination of both strength and ductility.

$$U_r = \frac{1}{2} s_0 e_0 = \frac{1}{2} s_0 \frac{s_0}{E} = \frac{s_0^2}{2E} \quad \text{area ADH}$$

$$U_t \approx s_u e_f \approx \frac{s_0 + s_u}{2} e_f \quad \text{area AEFI} \quad U_t \approx \frac{2}{3} s_u e_f \quad (\text{for brittle materials})$$

# Yielding under multi-axial stress

- With on-set of necking, uni-axial stress condition turns into tri-axial stress as geometry changes takes place. Thus flow curve need to be corrected from a point corresponding to tensile strength. Correction has been proposed by Bridgman.

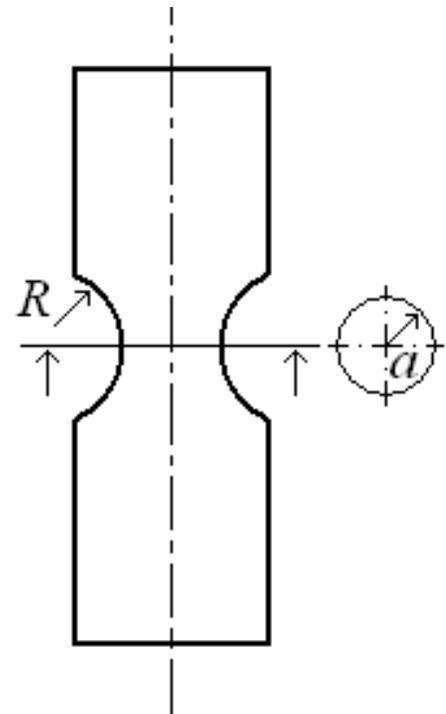
$$\sigma = \frac{(\sigma_x)_{avg}}{(1 + 2R/a) [\ln(1 + a/2R)]}$$

where

$(\sigma_x)_{avg}$  measured stress in the axial direction,

$a$  – smallest radius in the neck region,

$R$  – radius of the curvature of neck



## Yield criteria

- von Mises or Distortion energy criterion:  
yielding occurs once second invariant of stress deviator ( $J_2$ ) reaches a critical value. In other terms, yield starts once the distortion energy reaches a critical value.

$$J_2 = k^2 \quad J_2 = \frac{1}{6} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]$$

Under uni-axial tension,  $\sigma_1 = \sigma_0$ , and  $\sigma_2 = \sigma_3 = 0$

$$\frac{1}{6}(\sigma_0^2 + \sigma_0^2) = k^2 \Rightarrow \sigma_0 = \sqrt{3}k$$

$$\Rightarrow \sigma_0 = \frac{1}{\sqrt{2}} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]^{1/2}$$

$$k = \frac{1}{\sqrt{3}} \sigma_0 = 0.577 \sigma_0 \quad \text{where } k \text{ – yield stress under shear}$$

## Yield criteria (contd...)

- Tresca or Maximum shear stress criterion  
yielding occurs once the maximum shear stress of the stress system equals shear stress under uni-axial stress.

$$\tau_{\max} = \frac{\sigma_1 - \sigma_3}{2}$$

Under uni-axial tension,  $\sigma_1 = \sigma_0$ , and  $\sigma_2 = \sigma_3 = 0$

$$\tau_{\max} = \frac{\sigma_1 - \sigma_3}{2} = \tau_0 = \frac{\sigma_0}{2} \Rightarrow \sigma_1 - \sigma_3 = \sigma_0$$

Under pure shear stress conditions ( $\sigma_1 = -\sigma_3 = k$ ,  $\sigma_2 = 0$ )

$$k = \frac{\sigma_1 - \sigma_3}{2} = \frac{1}{2} \sigma_0$$

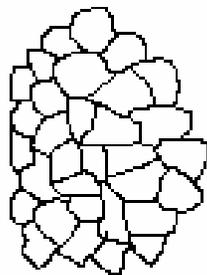
# Macroscopic aspects – Plastic deformation

- As a result of plastic deformation (Dislocation generation, movement and (re-)arrangement ), following observations can be made at macroscopic level:

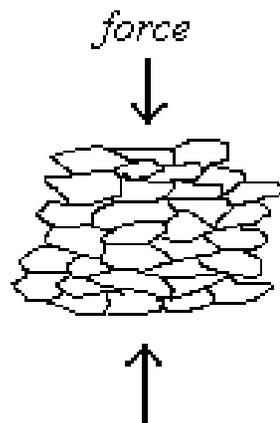
dimensional changes

change in grain shape

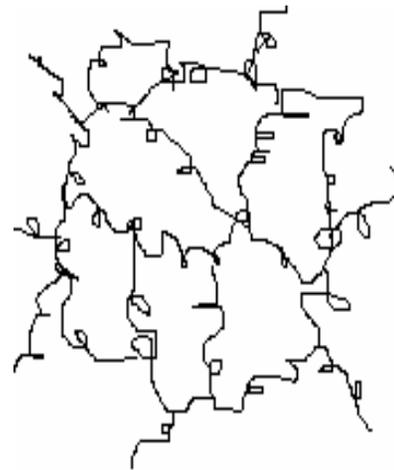
formation of cell structure in a grain



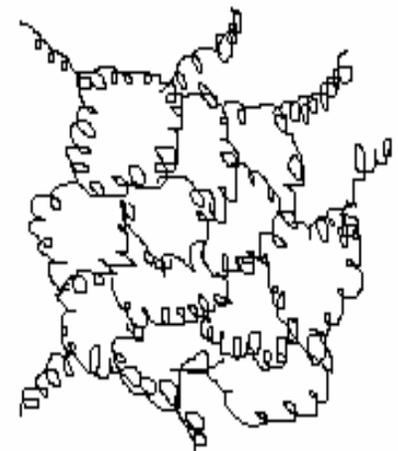
*equi-axed grains*



*deformed grains*

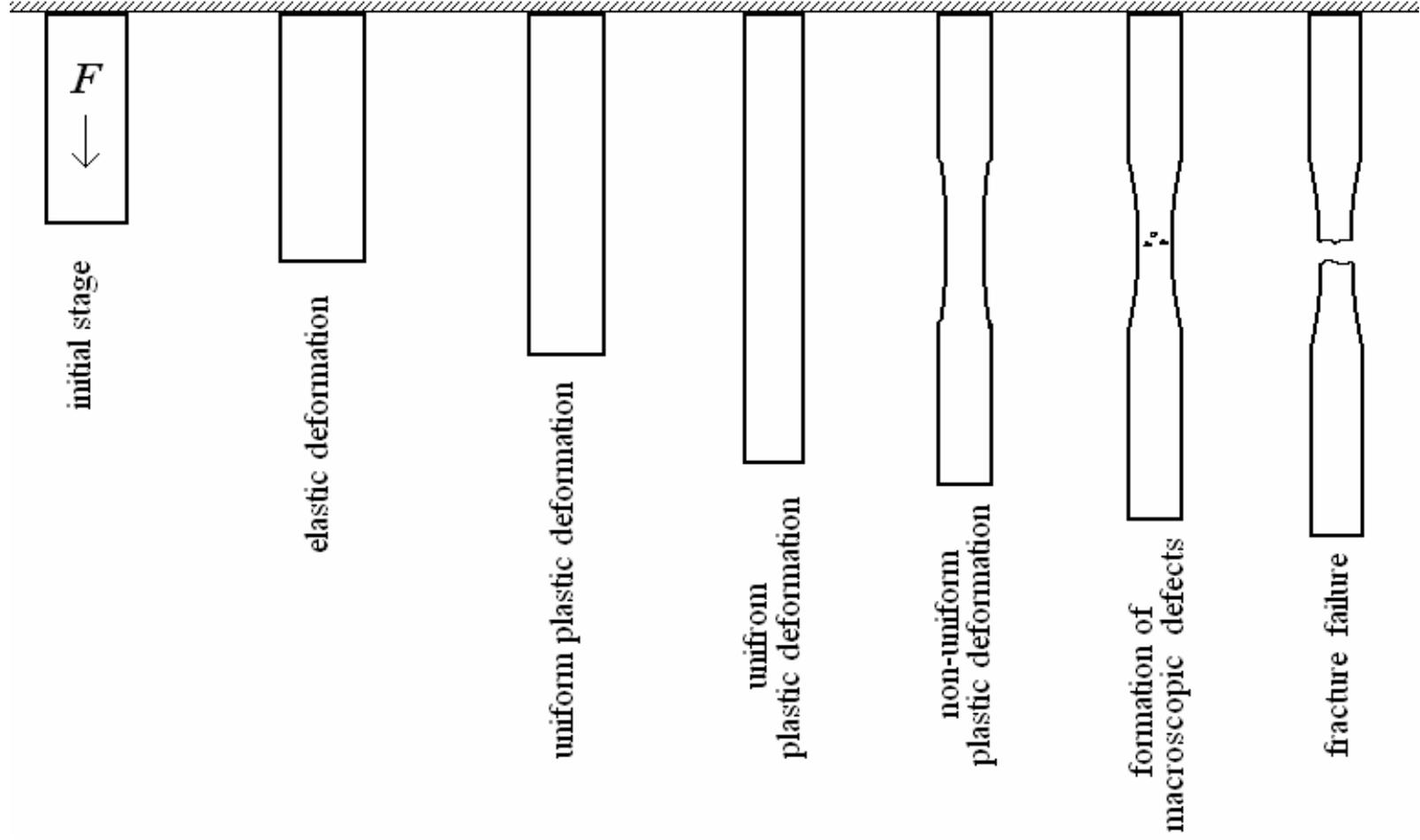


*initial cell structure*



*denser cell structure*

# Macroscopic aspects – Plastic deformation (contd...)



# Property variability

- Scatter in measured properties of engineering materials is inevitable because of number of factors such as:

test method

specimen fabrication procedure

operator bias

apparatus calibration, etc.

Average value of  $x$  over  $n$  samples.

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

Scatter limits:

$$\bar{x} - s, \quad \bar{x} + s$$

Property variability measure –  
Standard deviation

$$s = \left[ \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1} \right]^{1/2}$$

## Design consideration

- To account for property variability and unexpected failure, designers need to consider tailored property values. Parameters for tailoring: safety factor ( $N$ ) *and* design factor ( $N'$ ). Both parameters take values greater than unity only.

E.g.: Yield strength

$$\sigma_w = \sigma_y / N$$

$$\sigma_d = N' \sigma_c$$

where  $\sigma_w$  – working stress

$\sigma_y$  – yield strength

$\sigma_d$  – design stress

$\sigma_c$  – calculated stress

## Design consideration (contd...)

- Values for  $N$  ranges around: 1.2 to 4.0.
- Higher the value of  $N$ , lesser will the design efficiency i.e. either too much material *or* a material having a higher than necessary strength will be used.
- Selection of  $N$  will depend on a number of factors:
  - economics
  - previous experience
  - the accuracy with which mechanical forces
  - material properties
  - the consequences of failure in terms of loss of life or property damage.

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Module-5

**Diffusion**

## Contents

- 1) Diffusion mechanisms and steady-state & non-steady-state diffusion
- 2) Factors that influence diffusion and non-equilibrium transformation & microstructure

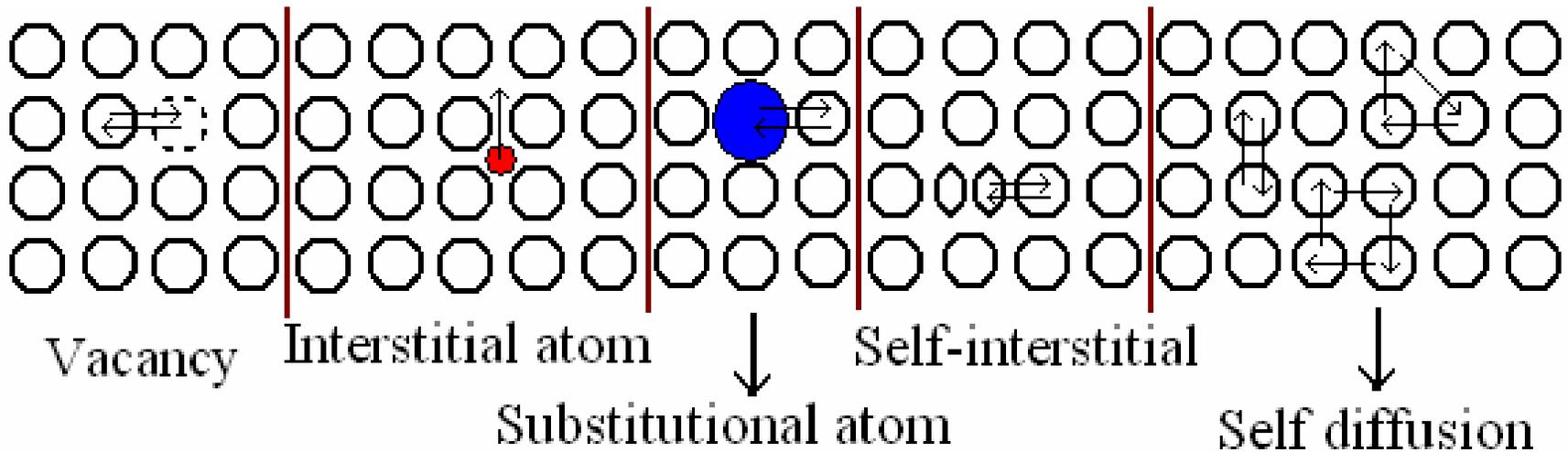
# Diffusion phenomenon

- *Definition* – Diffusion is the process of mass flow in which atoms change their positions relative to neighbors in a given phase under the influence of thermal and a gradient.
- The gradient can be a compositional gradient, an electric or magnetic gradient, or stress gradient.
- Many reactions in solids and liquids are diffusion dependent.
- Diffusion is very important in many industrial and domestic applications.

E.g.: Carburizing the steel, annealing homogenization after solidification, coffee mixing, etc.

# Diffusion mechanisms

- From an atomic perspective, diffusion is a step wise migration of atoms from one lattice position to another.
- Migration of atoms in metals/alloys can occur in many ways, and thus corresponding diffusion mechanism is defined.



## Diffusion mechanisms (contd...)

- Most energetically favorable diffusion mechanism is vacancy mechanism. Other important mechanism is interstitial mechanism by which hydrogen/nitrogen/oxygen diffuse into many metals.
- In ionic crystal, Schottky and Frankel defects assist the diffusion process.
- When Frenkel defects dominate in an ionic crystal, the cation interstitial of the Frenkel defect carries the diffusion flux. If Schottky defects dominate, the cation vacancy carries the diffusion flux.
- In thermal equilibrium, in addition to above defects, ionic crystal may have defects generated by impurities and by deviation from stoichiometry.

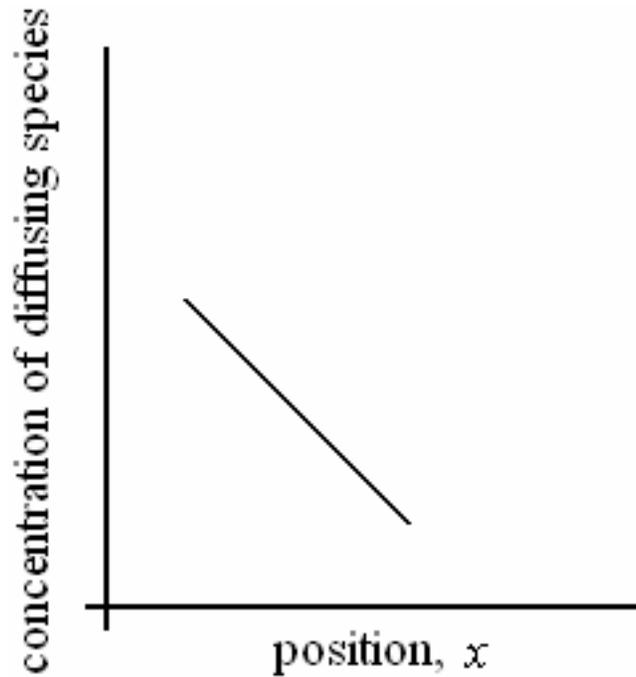
## Diffusion mechanisms (contd...)

- Diffusion that occurs over a region is volume diffusion.
- Diffusion can occur with aid of linear/surface defects, which are termed as short-circuit paths. These enhances the diffusivity.
- However, diffusion by short-circuit paths (e.g.:dislocaions, grain boundaries) is small because the effective cross-sectional area over which these are operative is small.
- Diffusion can occur even in pure metals that is not noticeable. Diffusion that occurs in alloys which is noticeable called *net diffusion* as there occurs a noticeable concentration gradient.

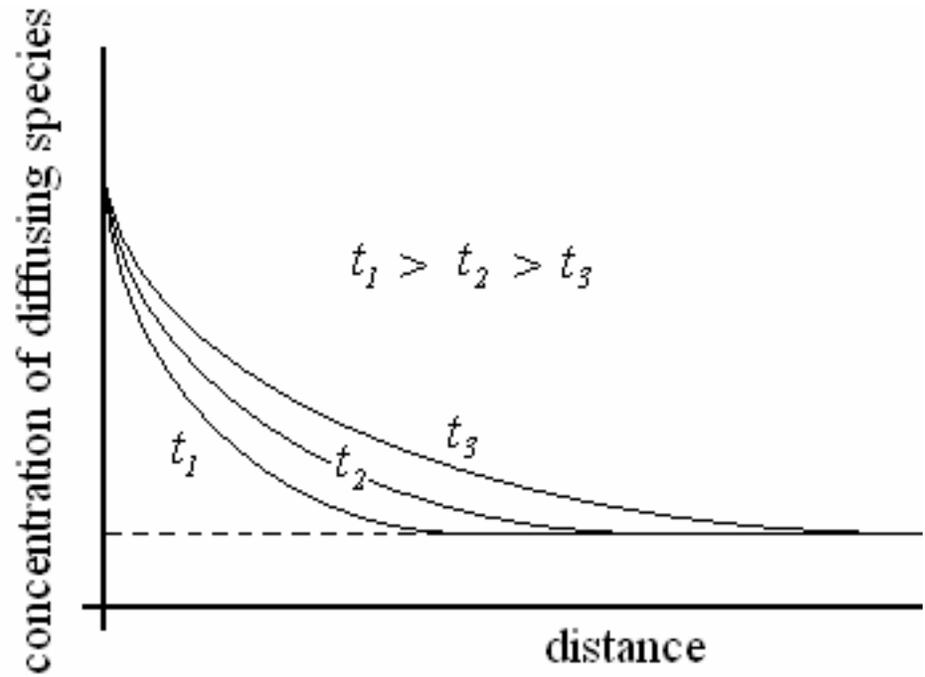
## Diffusion – time function?

- Steady-state and Non-steady-state diffusion processes are distinguished by the parameter – diffusion flux,  $J$ .
- Flux is defined as number of atoms crossing a unit area perpendicular to a given direction per unit time.
- Thus flux has units of atoms/m<sup>2</sup>.sec *or* moles/m<sup>2</sup>.sec.
- If the flux is independent of time, then the diffusion process is called steady-state diffusion. On the other hand, for non-steady-state diffusion process, flux is dependent on time.

## Diffusion – time function? (contd...)



Steady-state diffusion



Non-steady-state diffusion

## Steady-state diffusion

- Steady-state diffusion processes is characterized by Fick's first law, which states that diffusion flux is proportional to concentration gradient.
- The proportionality constant,  $D$ , is called diffusion coefficient or diffusivity. It has units as  $\text{m}^2/\text{sec}$ .
- For one-dimensional case, it can be written as

$$J_x = -D \frac{dc}{dx} = \frac{1}{A} \frac{dn}{dt} \quad J_x \neq f(x, t)$$

where  $D$  is the diffusion constant,  $dc/dx$  is the gradient of the concentration  $c$ ,  $dn/dt$  is the number atoms crossing per unit time a cross-sectional plane of area  $A$ .

**E.g.:** Hydrogen gas purification using palladium metal sheet.

## Non-steady-state diffusion

- Most interesting industrial applications are non-steady-state diffusion in nature.
- Non-steady-state diffusion is characterized by Fick's second law, which can be expressed as

$$\frac{dc}{dt} = -\frac{dJ}{dx} = \frac{d}{dx} \left( D \frac{dc}{dx} \right) \qquad \frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

where  $dc/dt$  is the time rate of change of concentration at a particular position,  $x$ .

- A meaningful solution can be obtained for the above second-order partial equation if proper boundary conditions can be defined.

## Non-steady-state diffusion (contd...)

- One common set of boundary conditions and the solution is:

$$\text{For } t = 0, \quad C = C_0 \text{ at } 0 \leq x \leq \infty$$

$$\text{For } t > 0, \quad C = C_s \text{ at } x=0$$

$$C = C_0 \text{ at } x = \infty$$

- The solution is 
$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where  $C_x$  represents the concentration at depth  $x$  after time  $t$ .

- The term *erf* stands for Gaussian error function, whose values can be obtained from standard mathematical tables.

**E.g.:** Carburization and decarburization of steel, corrosion resistance of duralumin, doping of semi-conductors, etc.

## Influencing factors for diffusion

- Diffusing species: Interstitial atoms diffuse easily than substitutional atoms. Again substitutional atoms with small difference in atomic radius with parent atoms diffuse with ease than atoms with larger diameter.
- Temperature: It is the most influencing factor. Their relations can be given by the following Arrhenius equation

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

where  $D_0$  is a pre-exponential constant,  $Q$  is the activation energy for diffusion,  $R$  is gas constant (Boltzmann's constant) and  $T$  is absolute temperature.

## Influencing factors for diffusion (contd...)

- From the temperature dependence of diffusivity, it is experimentally possible to find the values of  $Q$  and  $D_0$ .
- Lattice structure: Diffusivity is high for open lattice structure and in open lattice directions.
- Presence of defects: The other important influencing factor of diffusivity is presence of defects. Many atomic/volume diffusion processes are influenced by point defects like vacancies, interstitials.
- Apart from these, dislocations and grain boundaries, i.e. short-circuit paths as they famously known, greatly enhances the diffusivity.

# Non-equilibrium transformation & microstructure

- Non-equilibrium transformation occurs, usually, during many of the cooling processes like casting process.
- Equilibrium transformation requires extremely large time which is in most of the cases impractical and not necessary.
- Alloy solidification process involves diffusion in liquid phase, solid phase, and also across the interface between liquid and solid.
- As diffusion is very sluggish in solid, and time available for it is less, compositional gradients develop in cast components.
- These are two kinds: coring and segregation.

# Non-equilibrium transformation & microstructure

(contd...)

- Coring: It is defined as gradual compositional changes across individual grains.
- Coring is predominantly observed in alloys having a marked difference between liquidus and solidus temperatures.
- It is often being removed by subsequent annealing and/or hot-working.
- It is exploited in zone-refining technique to produce high-purity metals.
- Segregation: It is defined as concentration of particular, usually impurity elements, along places like grain boundaries, and entrapments.
- Segregation is also useful in zone refining, and also in the production of rimming steel.

# Non-equilibrium transformation & microstructure

(contd...)

- *Micro-segregation* is used to describe the differences in composition across a crystal or between neighboring crystals.
- Micro-segregation can often be removed by prolonged annealing or by hot-working.
- *Macro-segregation* is used to describe more massive heterogeneities which may result from entrapment of liquid pockets between growing solidifying zones.
- Macro-segregation persists through normal heating and working operations.
- Two non equilibrium effects of practical importance:(1) the occurrence of phase changes *or* transformations at temperatures other than those predicted by phase boundary lines on the phase diagram, and (2) the existence of non-equilibrium phases at room temperature that do not appear on the phase diagram.

# **Material Science**

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Module-6

## **Dislocations and Strengthening Mechanisms**

## Contents

- 1) Dislocations & Plastic deformation and Mechanisms of plastic deformation in metals
- 2) Strengthening mechanisms in metals
- 3) Recovery, Recrystallization and Grain growth

# Plastic deformation – Dislocations

- Permanent plastic deformation is due to shear process – atoms change their neighbors.
- Inter-atomic forces and crystal structure plays an important role during plastic deformation.
- Cumulative movement of dislocations leads to gross plastic deformation.
- During their movement, dislocations tend to interact. The interaction is very complex because of number of dislocations moving over many slip systems in different directions.

## Plastic deformation – Dislocations (contd...)

- Dislocations moving on parallel planes may annihilate each other, resulting in either vacancies or interstitials.
- Dislocations moving on non-parallel planes hinder each other's movement by producing sharp breaks – jog (break out of slip plane), kink (break in slip plane)
- Other hindrances to dislocation motion – interstitial and substitutional atoms, foreign particles, grain boundaries, external grain surface, and change in structure due to phase change.
- Material strength can be increased by arresting dislocation motion.

# Plastic deformation mechanisms - Slip

- Mainly two kinds: slip and twinning.
- Slip is prominent among the two. It involves sliding of blocks of crystal over other along slip planes.
- Slip occurs when shear stress applied exceeds a critical value.
- Slip occurs most readily in specific directions (slip directions) on certain crystallographic planes.
- Feasible combination of a slip plane together with a slip direction is considered as a slip system.
- During slip each atom usually moves same integral number of atomic distances along the slip plane.

## Plastic deformation mechanisms – Slip (contd...)

- Extent of slip depends on many factors - external load and the corresponding value of shear stress produced by it, crystal structure, orientation of active slip planes with the direction of shearing stresses generated.
- Slip occurs when shear stress applied exceeds a critical value.
- In a polycrystalline aggregate, individual grains provide a mutual geometrical constraint on one other, and this precludes plastic deformation at low applied stresses.
- Slip in polycrystalline material involves generation, movement and (re-)arrangement of dislocations.
- During deformation, mechanical integrity and coherency are maintained along the grain boundaries.

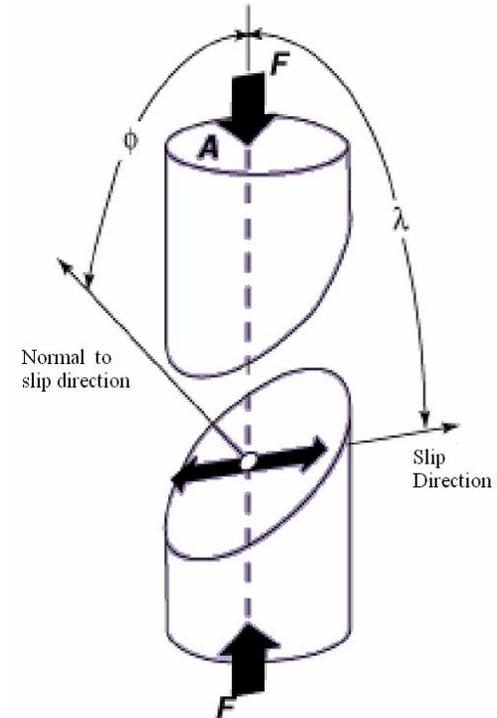
# Plastic deformation mechanisms – Slip (contd...)

➤ For single crystal, Schmid defined critical shear stress as

$$\tau_R = \frac{P \cos \lambda}{A / \cos \phi}$$

$$= \frac{P}{A} \cos \phi \cos \lambda = \sigma \cos \phi \cos \lambda$$

$$\Rightarrow m = \cos \phi \cos \lambda$$



Schematic model for calculating CRSS

- A minimum of five independent slip systems must be operative for a polycrystalline solid to exhibit ductility and maintain grain boundary integrity – von Mises.
- On the other hand, crystal deform by twinning.

## Slip systems

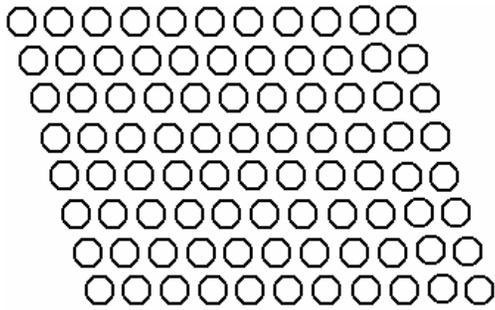
| <b>Crystal</b> | <b>Occurrence</b>          | <b>Slip planes</b>                             | <b>Slip directions</b>     |
|----------------|----------------------------|--|----------------------------|
| FCC            |                            | $\{111\}$                                      | $\langle 110 \rangle$      |
| BCC            | More common<br>Less common | $\{110\}$<br>$\{112\}, \{123\}$                | $\langle 111 \rangle$      |
| HCP            | More common<br>Less common | Basal plane<br>Prismatic & Pyramidal<br>planes | Close packed<br>directions |
| NaCl           |                            | $\{110\}$                                      | $\langle 110 \rangle$      |

# Plastic deformation mechanisms – Twinning

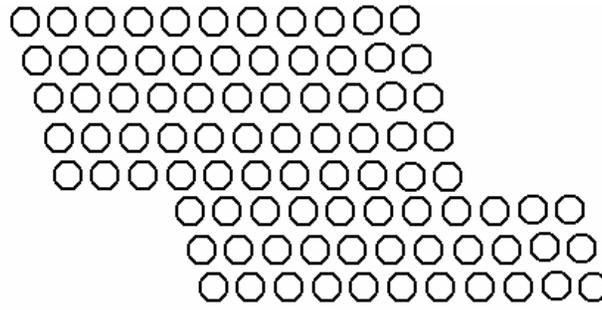
- It results when a portion of crystal takes up an orientation that is related to the orientation of the rest of the untwined lattice in a definite, symmetrical way.
- The important role of twinning in plastic deformation is that it causes changes in plane orientation so that further slip can occur.
- Twinning also occurs in a definite direction on a specific plane for each crystal structure.

| <b>Crystal</b> | <b>Example</b>   | <b>Twin plane</b> | <b>Twin direction</b> |
|----------------|------------------|-------------------|-----------------------|
| FCC            | Ag, Au, Cu       | (111)             | [112]                 |
| BCC            | $\alpha$ -Fe, Ta | (112)             | [111]                 |
| HCP            | Zn, Cd, Mg, Ti   | (10 $\bar{1}$ 2)  | [ $\bar{1}$ 011]      |

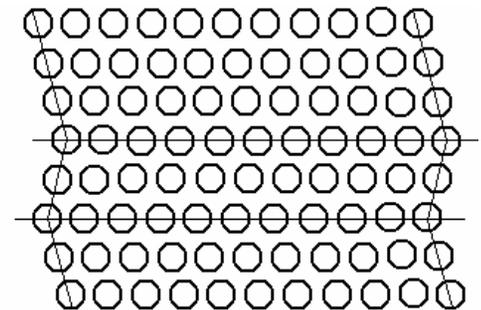
# Slip Vs. Twinning



Undeformed Crystal



After Slip



After Twinning

|  | <b>during/in slip</b>               | <b>during/in twinning</b>              |
|--|-------------------------------------|--|
| 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 |

# Strengthening mechanisms

- Material strength can be increased by hindering dislocation, which is responsible for plastic deformation.
- Different ways to hinder dislocation motion / Strengthening mechanisms:

*in single-phase materials*

- Grain size reduction
- Solid solution strengthening
- Strain hardening

*in multi-phase materials*

- Precipitation strengthening
- Dispersion strengthening
- Fiber strengthening
- Martensite strengthening

## Strengthening by Grain size reduction

- It is based on the fact that dislocations will experience hindrances while trying to move from a grain into the next because of abrupt change in orientation of planes.
- Hindrances can be two types: forcible change of slip direction, and discontinuous slip plane.
- Smaller the grain size, often a dislocation encounters a hindrance. Yield strength of material will be increased.
- Yield strength is related to grain size (diameter,  $d$ ) as Hall-Petch relation:

$$\sigma_y = \sigma_i + kd^{-1/2}$$

- Grain size can be tailored by controlled cooling or by plastic deformation followed by appropriate heat treatment.

## Strengthening by Grain size reduction (contd...)

- Grain size reduction improves not only strength, but also the toughness of many alloys.
- If  $d$  is average grain diameter,  $S_v$  is grain boundary area per unit volume,  $N_L$  is mean number of intercepts of grain boundaries per unit length of test line,  $N_A$  is number of grains per unit area on a polished surface:

$$S_v = 2N_L \quad d = \frac{3}{S_v} = \frac{3}{2N_L} \quad d = \sqrt{\frac{6}{\pi N_A}}$$

- Grain size can also be measured by comparing the grains at a fixed magnification with standard grain size charts.
- Other method: Use of ASTM grain size number (Z). It is related to grain diameter, D (in mm) as follows:

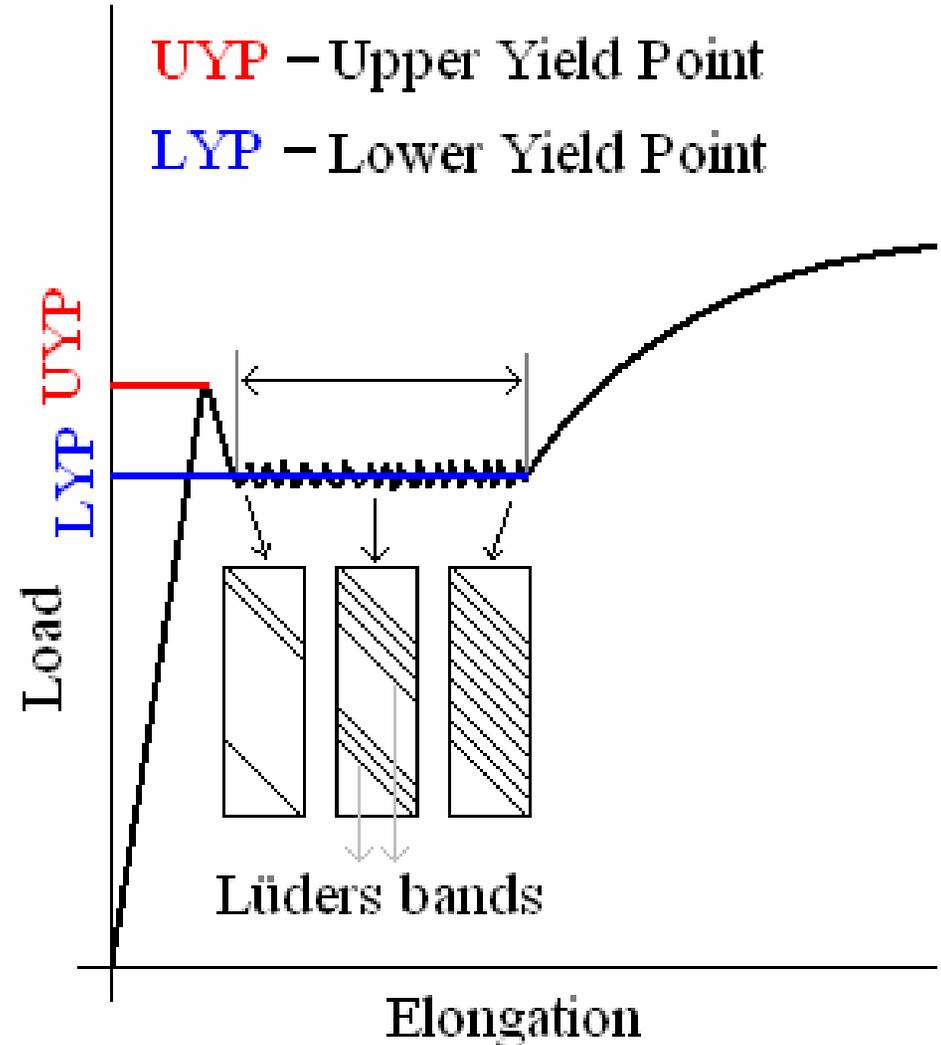
$$D = \frac{1}{100} \sqrt{\frac{645}{2^{G-1}}}$$

## Solid solution strengthening

- Impure foreign atoms in a single phase material produces lattice strains which can anchor the dislocations.
- Effectiveness of this strengthening depends on two factors – size difference and volume fraction of solute.
- Solute atoms interact with dislocations in many ways:
  - elastic interaction
  - modulus interaction
  - stacking-fault interaction
  - electrical interaction
  - short-range order interaction
  - long-range order interaction
- Elastic, modulus, and long-range order interactions are of long-range i.e. they are relatively insensitive to temperature and continue to act about  $0.6 T_m$ .

# Yield point phenomenon

- Localized, heterogeneous type of transition from elastic to plastic deformation marked by abrupt elastic-plastic transition – Yield point phenomenon.
- It characterizes that material needs higher stress to initiate plastic flow than to continue it.



## Yield point phenomenon (contd...)

- The bands are called Lüders bands / Hartmann lines / stretcher stains, and generally are approximately 45° to the tensile axis.
- Occurrence of yield point is associated with presence of small amounts of interstitial or substitutional impurities. It's been found that either unlocking of dislocations by a high stress for the case of strong pinning or generation of new dislocations are the reasons for yield-point phenomenon.
- Presence of Cottrell atmosphere is important for movement of interstitial atoms towards the dislocation.
- Magnitude of yield-point effect will depend on energy of interaction between solute atoms and dislocations and on the concentration of solute atoms at the dislocations.

## Strain hardening

- Phenomenon where ductile metals become stronger and harder when they are deformed plastically is called strain hardening *or* work hardening.
- Increasing temperature lowers the rate of strain hardening. Hence materials are strain hardened at low temperatures, thus also called cold working.
- During plastic deformation, dislocation density increases. And thus their interaction with each other resulting in increase in yield stress.
- Dislocation density ( $\rho$ ) and shear stress ( $\tau$ ) are related as follows:

$$\tau = \tau_0 + A\sqrt{\rho}$$

## Strain hardening (contd...)

- During strain hardening, in addition to mechanical properties physical properties also changes:
  - a small decrease in density
  - an appreciable decrease in electrical conductivity
  - small increase in thermal coefficient of expansion
  - increased chemical reactivity (decrease in corrosion resistance).
- Deleterious effects of cold work can be removed by heating the material to suitable temperatures – Annealing. It restores the original properties into material. It consists of three stages – recovery, recrystallization and grain growth.
- In industry, alternate cycles of strain hardening and annealing are used to deform most metals to a very great extent.

# Precipitation & Dispersion hardening

- Foreign particles can also obstructs movement of dislocations i.e. increases the strength of the material.
- Foreign particles can be introduced in two ways – precipitation and mixing-and-consolidation technique.
- Precipitation hardening is also called age hardening because strength increases with time.
- Requisite for precipitation hardening is that second phase must be soluble at an elevated temperature but precipitates upon quenching and aging at a lower temperature.

**E.g.:** Al-alloys, Cu-Be alloys, Mg-Al alloys, Cu-Sn alloys

- If aging occurs at room temperature – Natural aging
- If material need to be heated during aging – Artificial aging.

## Precipitation & Dispersion hardening (contd...)

- In dispersion hardening, fine second particles are mixed with matrix powder, consolidated, and pressed in powder metallurgy techniques.
- For dispersion hardening, second phase need to have very low solubility at all temperatures.

E.g.: oxides, carbides, nitrides, borides, etc.

- Dislocation moving through matrix embedded with foreign particles can either cut through the particles *or* bend around and bypass them.
- Cutting of particles is easier for small particles which can be considered as segregated solute atoms. Effective strengthening is achieved in the bending process, when the particles are submicroscopic in size.

## Precipitation & Dispersion hardening (contd...)

- Stress ( $\tau$ ) required to bend a dislocation is inversely proportional to the average interspacing ( $\lambda$ ) of particles:

$$\tau = Gb/\lambda$$

- Interspacing ( $\lambda$ ) of spherical particles:  $\lambda = \frac{4(1-f)r}{3f}$   
where  $r$  - particle radius,  $f$  - volume fraction

- Optimum strengthening occurs during aging once the right interspacing of particles is achieved.
  - Smaller the particles, dislocations can cut through them at lower stresses
  - larger the particles they will be distributed at wider distances.

# Fiber strengthening

- Second phase can be introduced into matrix in fiber form too.
- Requisite for fiber strengthening:
  - Fiber material – high strength and high modulus
  - Matrix material – ductile and non-reactive with fiber material
  - E.g.: fiber material –  $\text{Al}_2\text{O}_3$ , boron, graphite, metal, glass, etc.
  - matrix material – metals, polymers
- Mechanism of strengthening is different from other methods.
- Higher modulus fibers carry load, ductile matrix distributes load to fibers. Interface between matrix and fibers thus plays an important role.
- Strengthening analysis involves application of continuum, not dislocation concepts as in other methods of strengthening.

## Fiber strengthening (contd...)

- To achieve any benefit from presence of fibers, critical fiber volume which must be exceeded for fiber strengthening to occur:

$$f_{critical} = \frac{\sigma_{mu} - \sigma'_m}{\sigma_{fu} - \sigma'_m}$$

where  $\sigma_{mu}$  – strength of strain hardened matrix,  $\sigma'_m$  – flow stress of matrix at a strain equal to fiber breaking stress,  $\sigma_{fu}$  – ultimate tensile strength of the fiber.

- Minimum volume fraction of fiber which must be exceeded to have real reinforcement:

$$f_{min} = \frac{\sigma_{mu} - \sigma'_m}{\sigma_{fu} + \sigma_{mu} - \sigma'_m}$$

# Martensite strengthening

- This strengthening method is based on formation of martensitic phase from the retained high temperature phase at temperatures lower than the equilibrium invariant transformation temperature.
- Martensite forms as a result of shearing of lattices.
- Martensite platelets assumes characteristic lenticular shape that minimizes the elastic distortion in the matrix. These platelets divide and subdivide the grains of the parent phase. Always touching but never crossing one another.
- Martensite platelets grow at very high speeds (1/3rd of sound speed) i.e. activation energy for growth is less. Thus volume fraction of martensite exist is controlled by its nucleation rate.

## Martensite strengthening (contd...)

- Martensite platelets attain their shape by two successive shear displacements - *first* displacement is a homogeneous shear throughout the plate which occurs parallel to a specific plane in the parent phase known as the habit plane, *second* displacement, the lesser of the two, can take place by one of two mechanisms: slip as in Fe-C Martensite or twinning as in Fe-Ni Martensite.
- Martensite formation occurs in many systems.  
**E.g.:** Fe-C, Fe-Ni, Fe-Ni-C, Cu-Zn, Au-Cd, and even in pure metals like Li, Zr and Co. However, only the alloys based on Fe and C show a pronounced strengthening effect.
- High strength of Martensite is attributed to its characteristic twin structure and to high dislocation density. In Fe-C system, carbon atoms are also involved in strengthening.

# Recovery

- Annealing relieves the stresses from cold working – three stages: recovery, recrystallization and grain growth.
- Recovery involves annihilation of point defects.
- Driving force for recovery is decrease in stored energy from cold work.
- During recovery, physical properties of the cold-worked material are restored without any observable change in microstructure.
- Recovery is first stage of annealing which takes place at low temperatures of annealing.
- There is some reduction, though not substantial, in dislocation density as well apart from formation of dislocation configurations with low strain energies.

# Recrystallization

- This follows recovery during annealing of cold worked material. Driving force is stored energy during cold work.
- It involves replacement of cold-worked structure by a new set of strain-free, approximately equi-axed grains to replace all the deformed crystals.
- This process is characterized by recrystallization temperature which is defined as the temperature at which 50% of material recrystallizes in one hour time.
- The 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  $0.5-0.7 T_m$ , where  $T_m$  is absolute melting temperature of the material.

## Recrystallization laws

- A minimum amount of deformation is needed to cause recrystallization ( $R_x$ ).
- Smaller the degree of deformation, higher will be the  $R_x$  temperature.
- The finer is the initial grain size; lower will be the  $R_x$  temperature.
- The larger the initial grain size, the greater degree of deformation is required to produce an equivalent  $R_x$  temperature.
- Greater the degree of deformation and lower the annealing temperature, the smaller will be the recrystallized grain size.
- The higher is the temperature of cold working, the less is the strain energy stored and thus  $R_x$  temperature is correspondingly higher.
- The  $R_x$  rate increases exponentially with temperature.

# Grain growth

- Grain growth follows complete crystallization if the material is left at elevated temperatures.
- Grain growth does not need to be preceded by recovery and recrystallization; it may occur in all polycrystalline materials.
- In contrary to recovery and recrystallization, driving force for this process is reduction in grain boundary energy.
- Tendency for larger grains to grow at the expense of smaller grains is based on physics.
- In practical applications, grain growth is not desirable.
- Incorporation of impurity atoms and insoluble second phase particles are effective in retarding grain growth.
- Grain growth is very strongly dependent on temperature.

# **Material Science**

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Module-07

# **Phase Diagrams**

## Contents

- 1) Equilibrium phase diagrams, Particle strengthening by precipitation and precipitation reactions
- 2) Kinetics of nucleation and growth
- 3) The iron-carbon system, phase transformations
- 4) Transformation rate effects and TTT diagrams, Microstructure and property changes in iron-carbon system

# Mixtures – Solutions – Phases

- Almost all materials have more than one phase in them. Thus engineering materials attain their special properties.
- Macroscopic basic unit of a material is called component. It refers to a independent chemical species. The components of a system may be elements, ions or compounds.
- A phase can be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics i.e. it is a physically distinct from other phases, chemically homogeneous and mechanically separable portion of a system.
- A component can exist in many phases.  
**E.g.:** Water exists as ice, liquid water, and water vapor.  
Carbon exists as graphite and diamond.

## Mixtures – Solutions – Phases (contd...)

- When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a disparity in one or the other set of properties is sufficient.
- A solution (liquid or solid) is phase with more than one component; a mixture is a material with more than one phase.
- Solute (minor component of two in a solution) does not change the structural pattern of the solvent, and the composition of any solution can be varied.
- In mixtures, there are different phases, each with its own atomic arrangement. It is possible to have a mixture of two different solutions!

## Gibbs phase rule

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

$$P + F = C + 2$$

- In practical conditions for metallurgical and materials systems, pressure can be treated as a constant (1 atm.). Thus Condensed Gibbs phase rule is written as:

$$P + F = C + 1$$

## Equilibrium phase diagram

- A diagram that depicts existence of different phases of a system under equilibrium is termed as *phase diagram*.
- It is actually a collection of solubility limit curves. It is also known as *equilibrium* or *constitutional diagram*.
- Equilibrium phase diagrams represent the relationships between temperature, compositions and the quantities of phases at equilibrium.
- These diagrams *do not* indicate the dynamics when one phase transforms into another.
- Useful terminology related to phase diagrams: *liquidus*, *solidus*, *solvus*, *terminal solid solution*, *invariant reaction*, *intermediate solid solution*, *inter-metallic compound*, etc.
- Phase diagrams are classified according to the number of component present in a particular system.

## Phase diagram – Useful information

- Important information, useful in materials development and selection, obtainable from a phase diagram:
  - It shows phases present at different compositions and temperatures under slow cooling (equilibrium) conditions.
  - It indicates equilibrium solid solubility of one element/compound in another.
  - It suggests temperature at which an alloy starts to solidify and the range of solidification.
  - It signals the temperature at which different phases start to melt.
  - Amount of each phase in a two-phase mixture can be obtained.

# Unary phase diagram

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

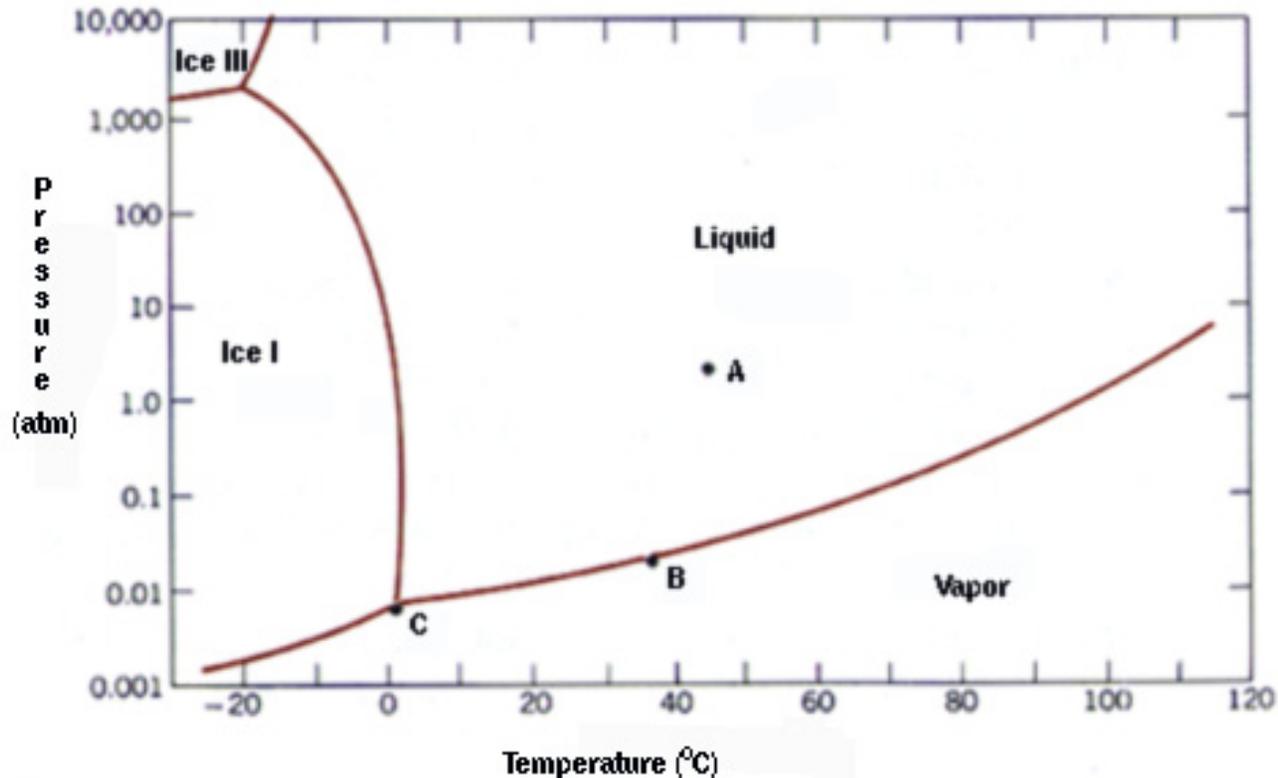


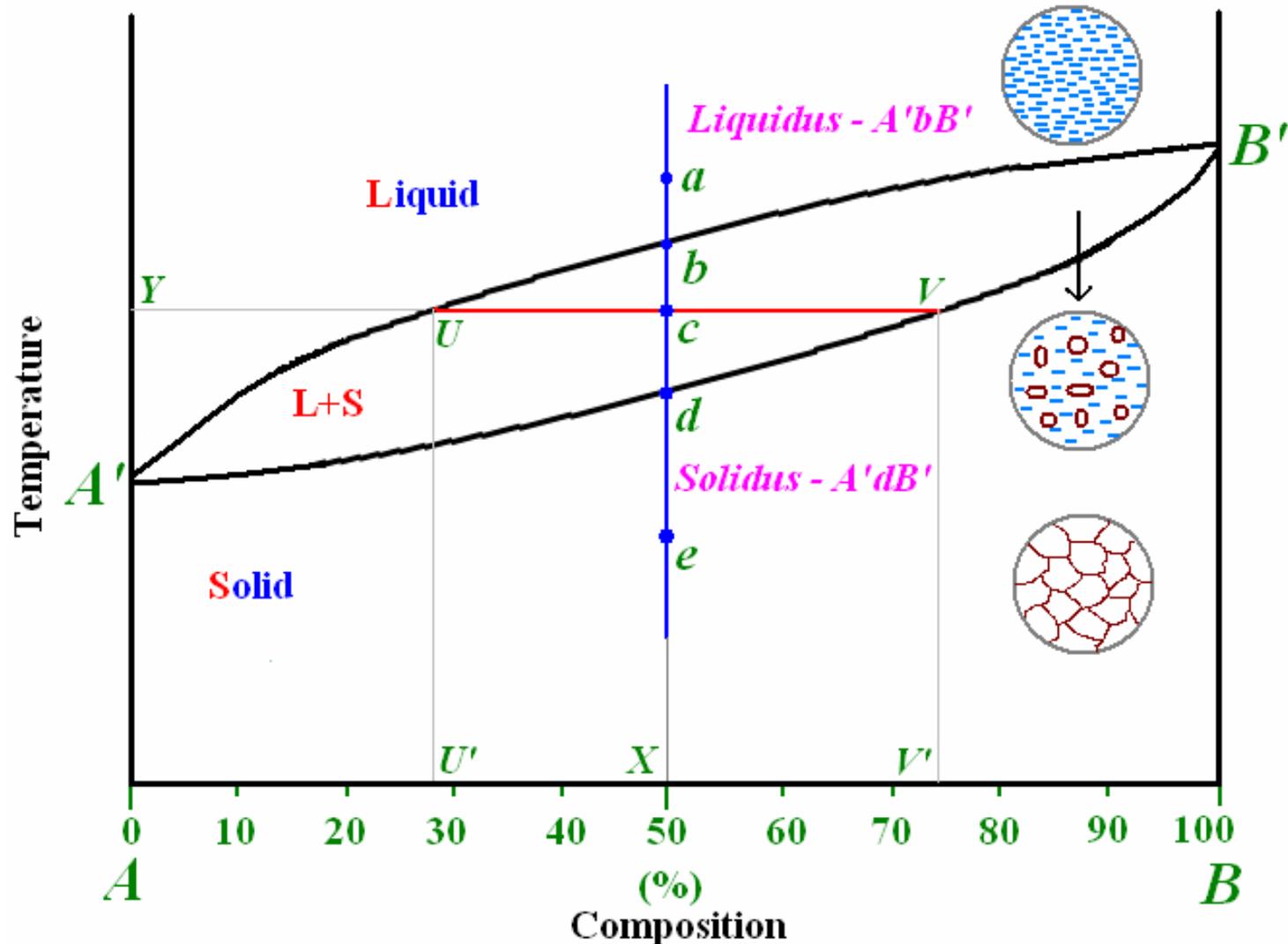
Figure-1: Unary phase diagram for water.

## Binary phase diagram

- If a system consists of two components, equilibrium of phases exist is depicted by *binary phase diagram*. For most systems, pressure is constant, thus independently variable parameters are – temperature and composition.
- Two components can be either two metals (Cu and Ni), or a metal and a compound (Fe and Fe<sub>3</sub>C), or two compounds (Al<sub>2</sub>O<sub>3</sub> and Si<sub>2</sub>O<sub>3</sub>), etc.
- Two component systems are classified based on extent of mutual solid solubility – (a) completely soluble in both liquid and solid phases (isomorphous system) and (b) completely soluble in liquid phase whereas solubility is limited in solid state.
- For isomorphous system - E.g.: Cu-Ni, Ag-Au, Ge-Si, Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>.

# Isomorphous binary system

- An isomorphous system – phase diagram and corresponding microstructural changes.



## Tie line – Lever rule

- At a point in a phase diagram, phases present and their composition (tie-line method) along with relative fraction of phases (lever rule) can be computed.
- Procedure to find equilibrium concentrations of phases (refer to the figure in previous slide):
  - A *tie-line* or *isotherm* ( $UV$ ) is drawn across two-phase region to intersect the boundaries of the region.
  - Perpendiculars are dropped from these intersections to the composition axis, represented by  $U'$  and  $V'$ , from which each of each phase is read.  $U'$  represents composition of liquid phase and  $V'$  represents composition of solid phase as intersection  $U$  meets liquidus line and  $V$  meets solidus line.

## Tie line – Lever rule (contd....)

- Procedure to find equilibrium relative amounts of phases (*lever rule*):
  - A tie-line is constructed across the two phase region at the temperature of the alloy to intersect the region boundaries.
  - The relative amount of a phase is computed by taking the length of tie line from overall composition to the phase boundary for the other phase, and dividing by the total tie-line length. In previous figure, relative amount of liquid and solid phases is given respectively by:

$$C_L = \frac{cV}{UV}$$

$$C_S = \frac{Uc}{UV}$$

$$C_L + C_S = 1$$

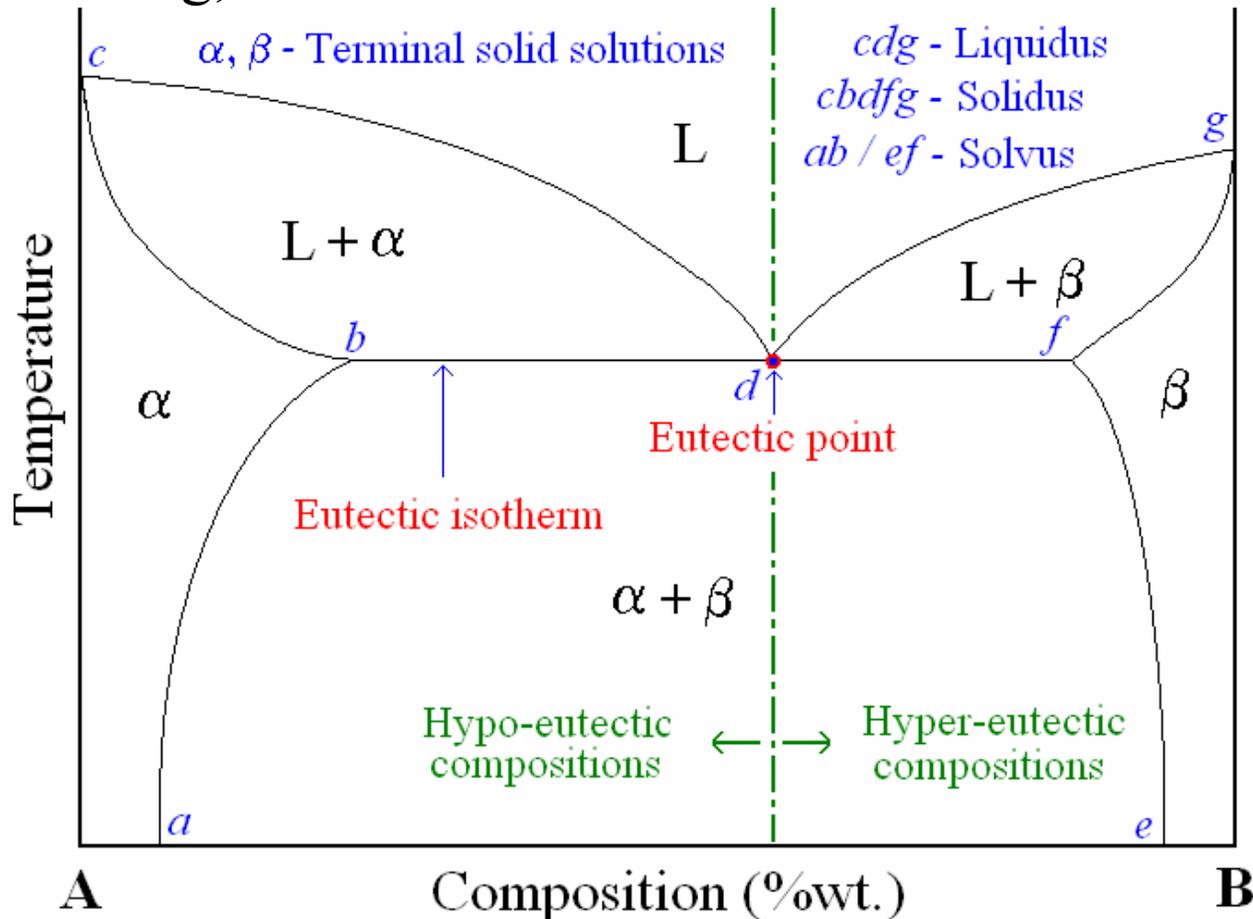
## Hume-Ruthery conditions

- Extent of solid solubility in a two element system can be predicted based on Hume-Ruthery conditions.
- If the system obeys these conditions, then complete solid solubility can be expected.
- Hume-Ruthery conditions:
  - Crystal structure of each element of solid solution must be the same.
  - Size of atoms of each two elements must not differ by more than 15%.
  - Elements should not form compounds with each other i.e. there should be no appreciable difference in the electronegativities of the two elements.
  - Elements should have the same valence.

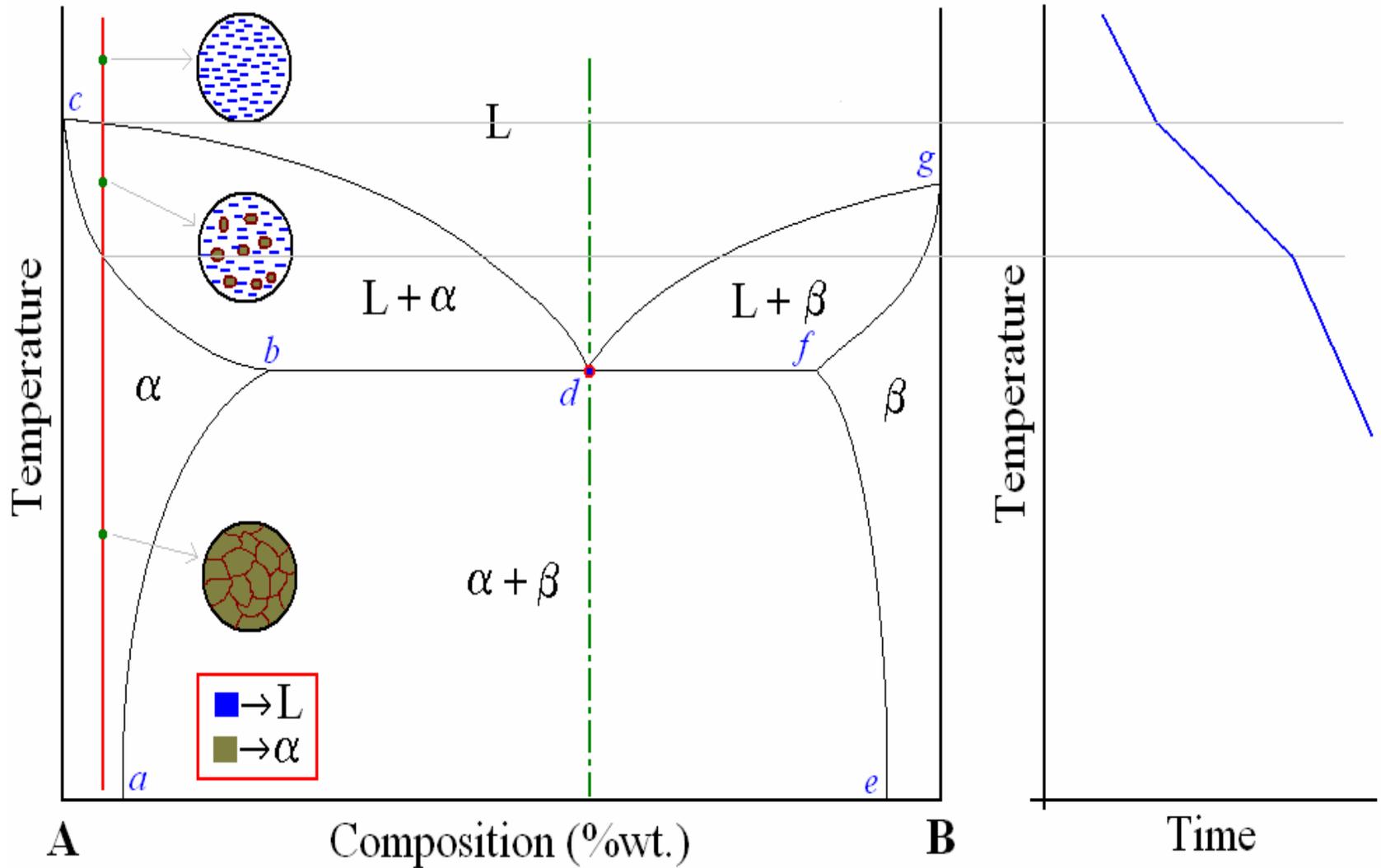
## Eutectic binary system

- Many of the binary systems with limited solubility are of eutectic type – eutectic alloy of eutectic composition solidifies at the end of solidification at eutectic temperature.

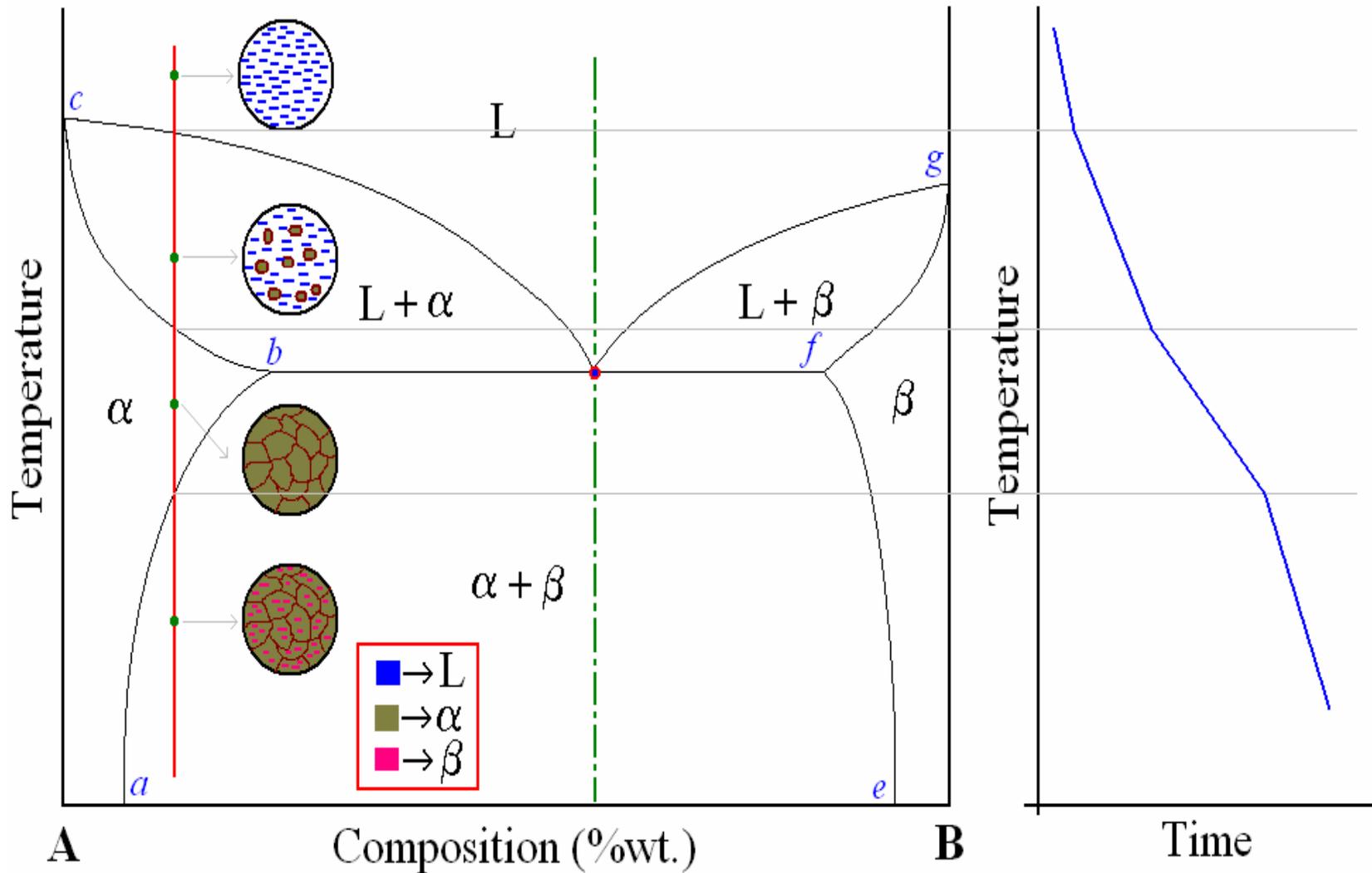
E.g.: Cu-Ag, Pb-Sn



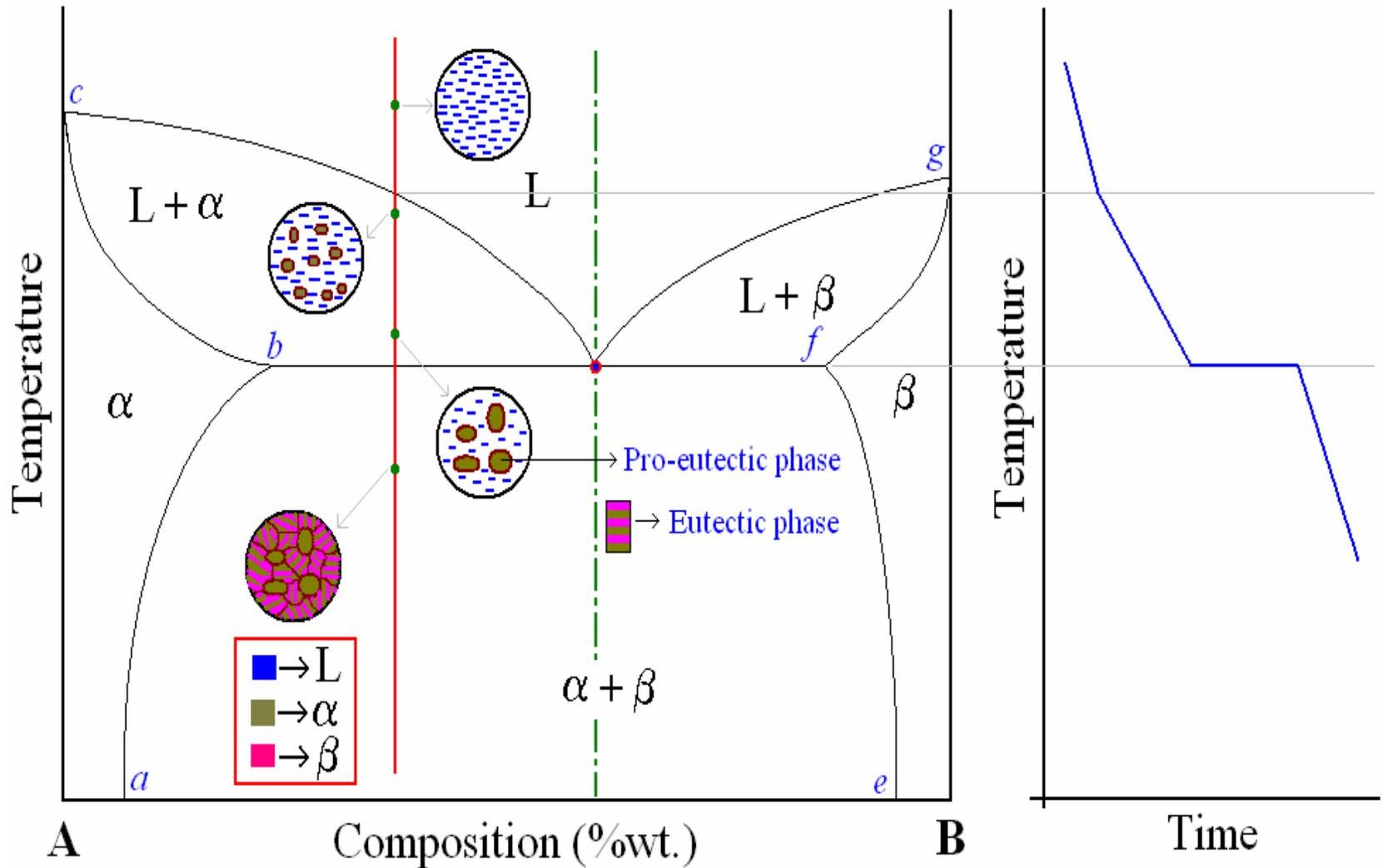
# Eutectic system – Cooling curve – Microstructure



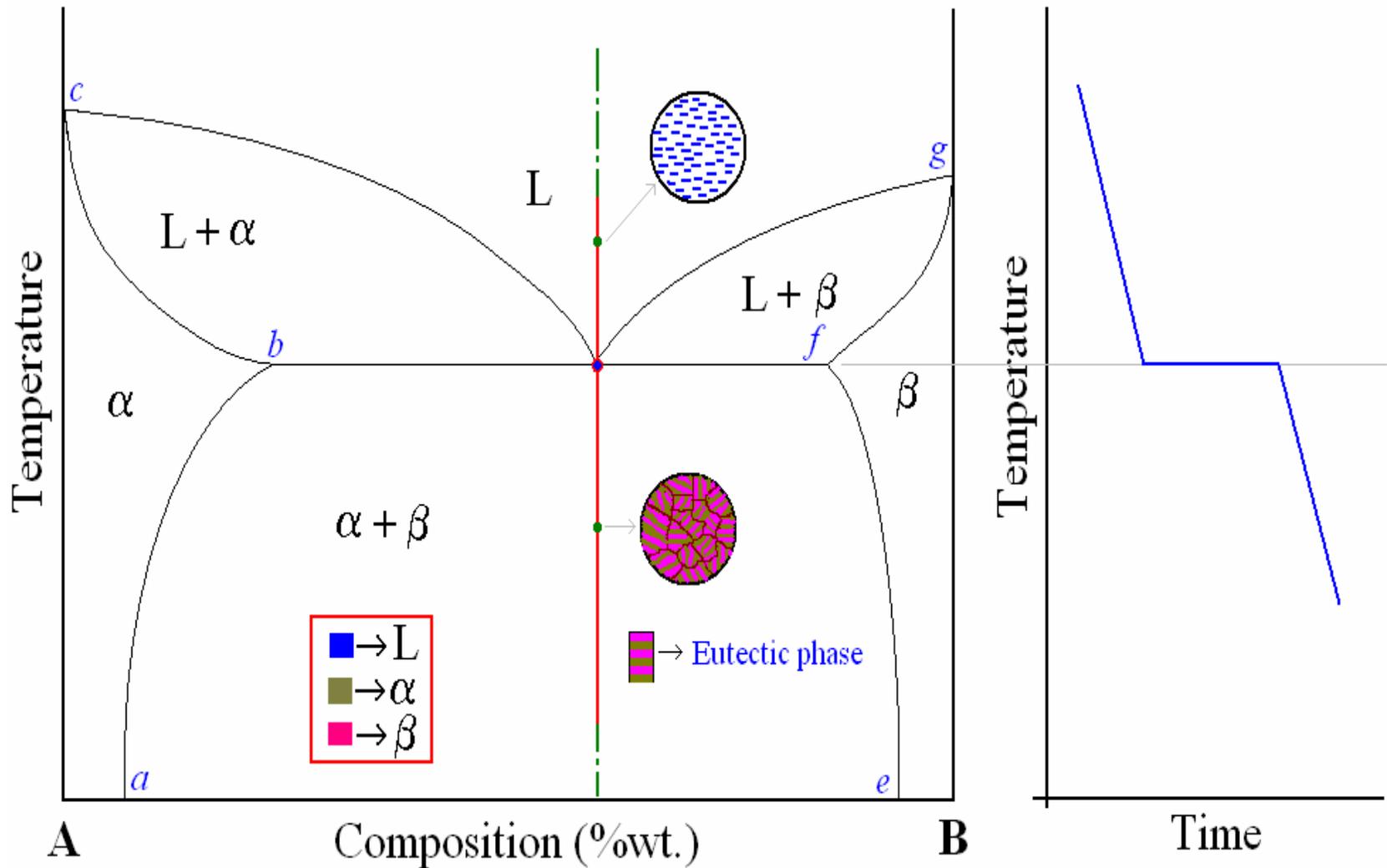
# Eutectic system – Cooling curve – Microstructure (contd....)



# Eutectic system – Cooling curve – Microstructure (contd....)



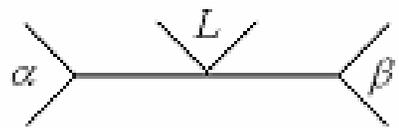
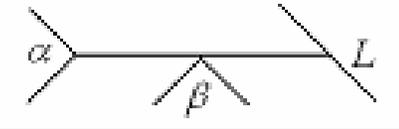
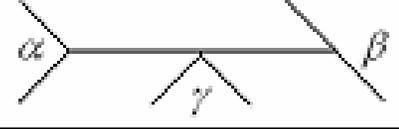
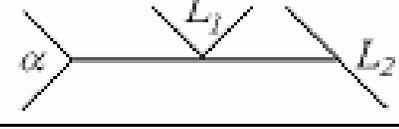
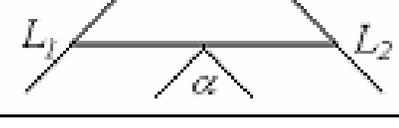
# Eutectic system – Cooling curve – Microstructure (contd....)



## Invariant reactions

- Observed triple point in unary phase diagram for water?
- How about eutectic point in binary phase diagram?
- These points are specific in the sense that they occur only at that particular conditions of concentration, temperature, pressure etc.
- Try changing any of the variable, it does not exist i.e. phases are not equilibrium any more!
- Hence they are known as invariant points, and represents *invariant reactions*.
- In binary systems, we will come across many number of invariant reactions!

## Invariant reactions (contd....)

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

## Intermediate phases

- Invariant reactions result in different product phases – terminal phases and intermediate phases.
- Intermediate phases are either of varying composition (intermediate solid solution) *or* fixed composition (inter-metallic compound).
- Occurrence of intermediate phases cannot be readily predicted from the nature of the pure components!
- *Inter-metallic compounds* differ from other chemical compounds in that the bonding is primarily metallic rather than ionic *or* covalent.  
*E.g.:* Fe<sub>3</sub>C is metallic, whereas MgO is covalent.
- When using the lever rules, inter-metallic compounds are treated like any other phase.

# Congruent, Incongruent transformations

- Phase transformations are two kinds – congruent and incongruent.
- Congruent transformation involves no compositional changes. It usually occurs at a temperature.  
E.g.: Allotropic transformations, melting of pure a substance.
- During incongruent transformations, at least one phase will undergo compositional change.  
E.g.: All invariant reactions, melting of isomorphous alloy.
- Intermediate phases are sometimes classified on the basis of whether they melt congruently or incongruently.  
E.g.:  $\text{MgNi}_2$ , for example, melts congruently whereas  $\text{Mg}_2\text{Ni}$  melts incongruently since it undergoes peritectic decomposition.

# Precipitation – Strengthening – Reactions

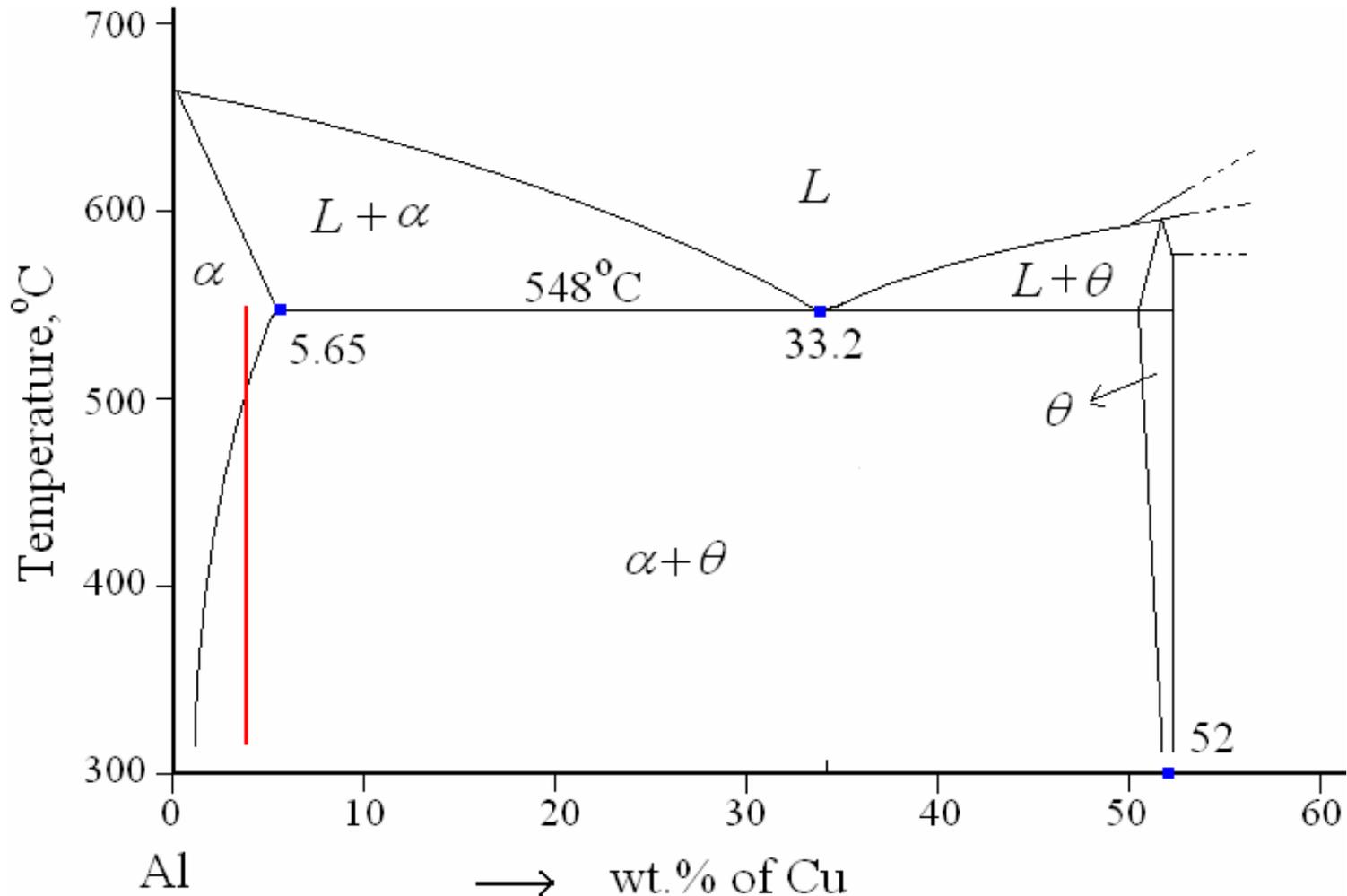
- A material can be strengthened by obstructing movement of dislocations. Second phase particles are effective.
- Second phase particles are introduced mainly by two means – direct mixing and consolidation, or by precipitation.
- Most important *pre-requisite* for precipitation strengthening: there must be a terminal solid solution which has a decreasing solid solubility as the temperature decreases.  
*E.g.:* Au-Cu in which maximum solid solubility of Cu in Al is 5.65% at 548° C that decreases with decreasing temperature.
- Three basic steps in precipitation strengthening: *solutionizing, quenching* and *aging*.

## Precipitation – Strengthening – Reactions (contd....)

- Solutionizing (solution heat treatment), where the alloy is heated to a temperature between solvus and solidus temperatures and kept there till a uniform solid-solution structure is produced.
- Quenching, where the sample is rapidly cooled to a lower temperature (room temperature). Resultant product – supersaturated solid solution.
- Aging is the last but critical step. During this heat treatment step finely dispersed precipitate particle will form. Aging the alloy at room temperature is called natural aging, whereas at elevated temperatures is called artificial aging. Most alloys require artificial aging, and aging temperature is usually between 15-25% of temperature difference between room temperature and solution heat treatment temperature.

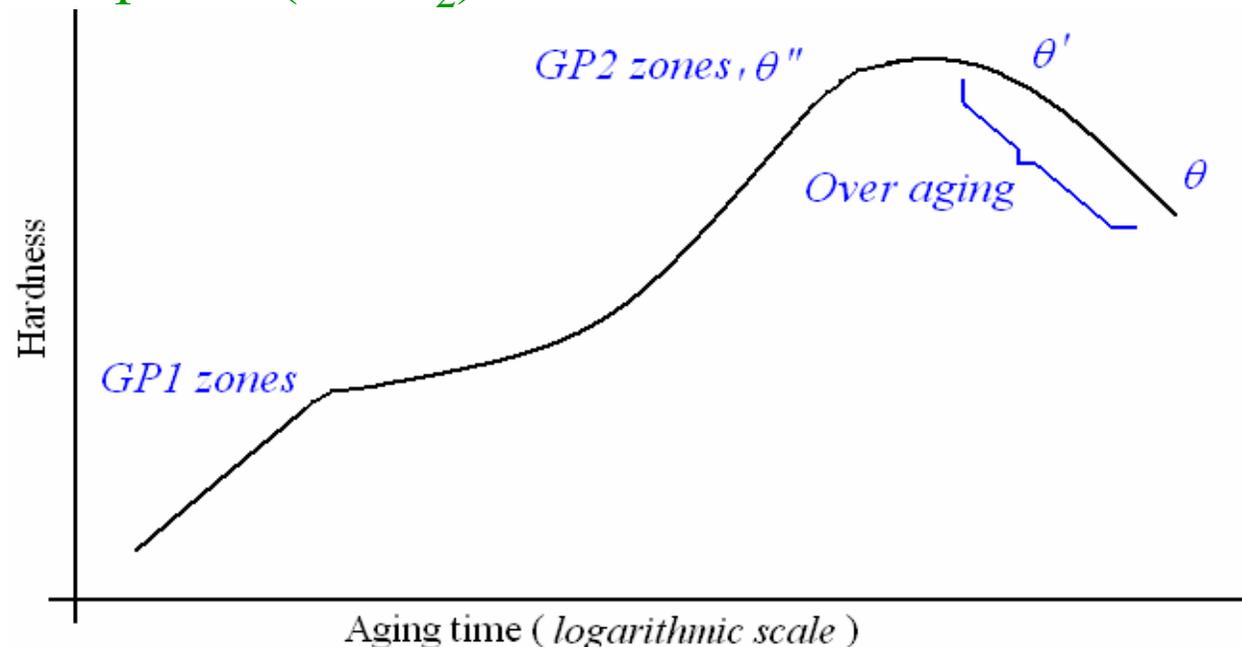
# Precipitation – Strengthening – Reactions (contd....)

- Al-4%Cu alloy is used to explain the mechanism of precipitation strengthening.



# Precipitation – Strengthening – Reactions (contd....)

- Al-4%Cu alloy when cooled slowly from solutionizing temperature, produces coarse grains – moderate strengthening.
- For precipitation strengthening, it is quenched, and aged!
- Following sequential reactions takes place during aging:  
Supersaturated  $\alpha$   $\rightarrow$  GP1 zones  $\rightarrow$  GP2 zones ( $\theta''$  phase)  $\rightarrow$   $\theta'$  phase  $\rightarrow$   $\theta$  phase ( $\text{CuAl}_2$ )



# Nucleation and Growth

- Structural changes / Phase transformations takes place by nucleation followed by growth.
- Temperature changes are important among variables (like pressure, composition) causing phase transformations as diffusion plays an important role.
- Two other factors that affect transformation rate along with temperature – (1) diffusion controlled rearrangement of atoms because of compositional and/or crystal structural differences; (2) difficulty encountered in nucleating small particles via change in surface energy associated with the interface.
- Just nucleated particle has to overcome the +ve energy associated with new interface formed to survive and grow further. It does by reaching a critical size.

## Homogeneous nucleation – Kinetics

- Homogeneous nucleation – nucleation occurs within parent phase. All sites are of equal probability for nucleation.
- It requires considerable under-cooling (cooling a material below the equilibrium temperature for a given transformation without the transformation occurring).
- Free energy change associated with formation of new particle

$$\Delta f = \frac{4}{3} \pi r^3 \Delta g + 4\pi r^2 \gamma$$

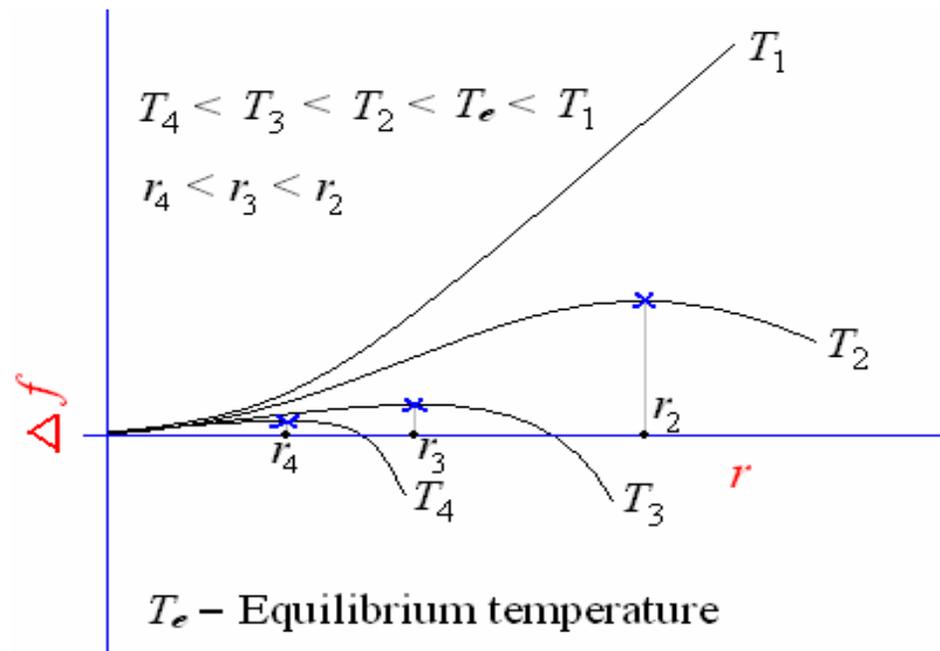
where  $r$  is the radius of the particle,  $\Delta g$  is the Gibbs free energy change per unit volume and  $\gamma$  is the surface energy of the interface.

## Homogeneous nucleation – Kinetics (contd...)

- Critical value of particle size (which reduces with under-cooling) is given by

$$r^* = -\frac{2\gamma}{\Delta g} \quad \text{or} \quad r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T}$$

where  $T_m$  – freezing temperature (in K),  $\Delta H_f$  – latent heat of fusion,  $\Delta T$  – amount of under-cooling at which nucleus is formed.



# Heterogeneous nucleation – Kinetics

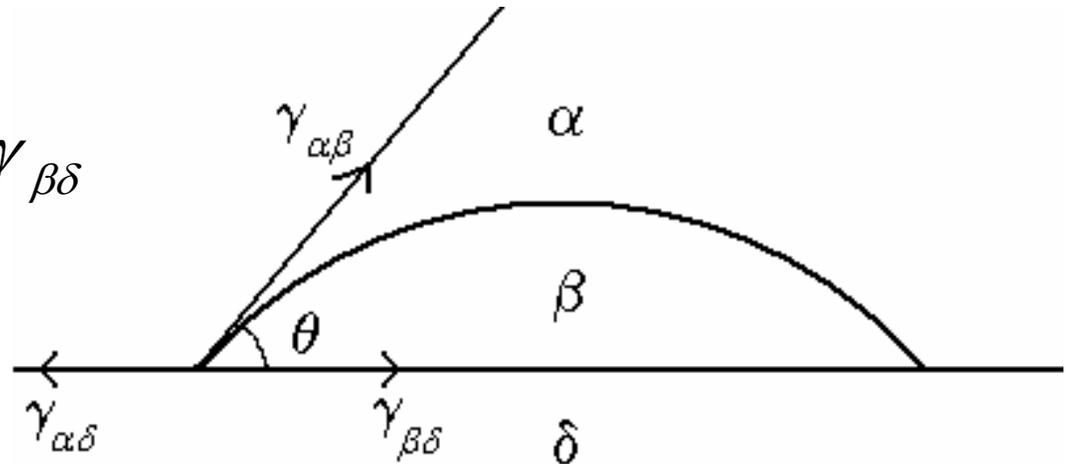
- In heterogeneous nucleation, the probability of nucleation occurring at certain preferred sites is much greater than that at other sites.

**E.g.:** During solidification - inclusions of foreign particles (*inoculants*), walls of container holding the liquid

In solid-solid transformation - foreign inclusions, grain boundaries, interfaces, stacking faults and dislocations.

- Considering, force equilibrium during second phase formation:

$$\gamma_{\alpha\delta} = \gamma_{\alpha\beta} \cos \theta + \gamma_{\beta\delta}$$



## Heterogeneous nucleation – Kinetics (contd....)

$$\Delta f_{het}^* = \frac{4\pi\gamma_{\alpha\beta}^3}{3(\Delta g)^2} (2 - 3\cos\theta + \cos^3\theta) = \Delta f_{hom}^* \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

- When product particle makes only a point contact with the foreign surface, i.e.  $\theta = 180^\circ$ , the foreign particle does not play any role in the nucleation process  $\rightarrow$

$$\Delta f_{het}^* = \Delta f_{hom}^*$$

- If the product particle completely wets the foreign surface, i.e.  $\theta = 0^\circ$ , there is no barrier for heterogeneous nucleation  $\rightarrow$

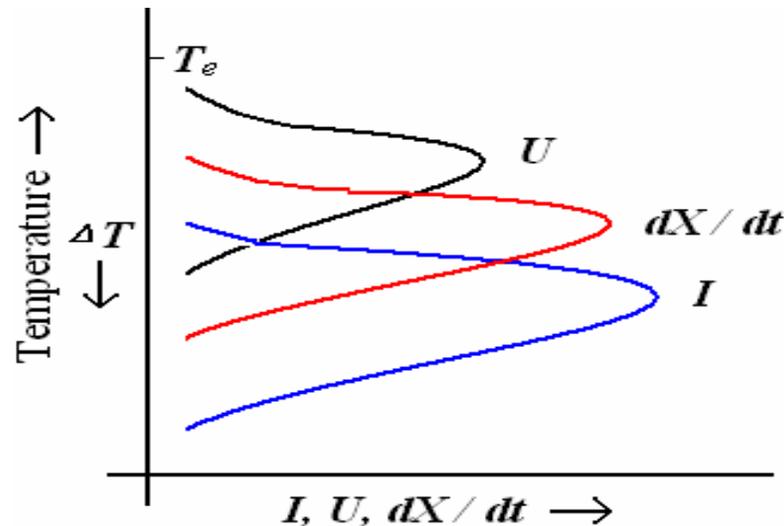
$$\Delta f_{het}^* = 0$$

- In intermediate conditions such as where the product particle attains hemispherical shape,  $\theta = 90^\circ \rightarrow$

$$\Delta f_{het}^* = \frac{1}{2} \Delta f_{hom}^*$$

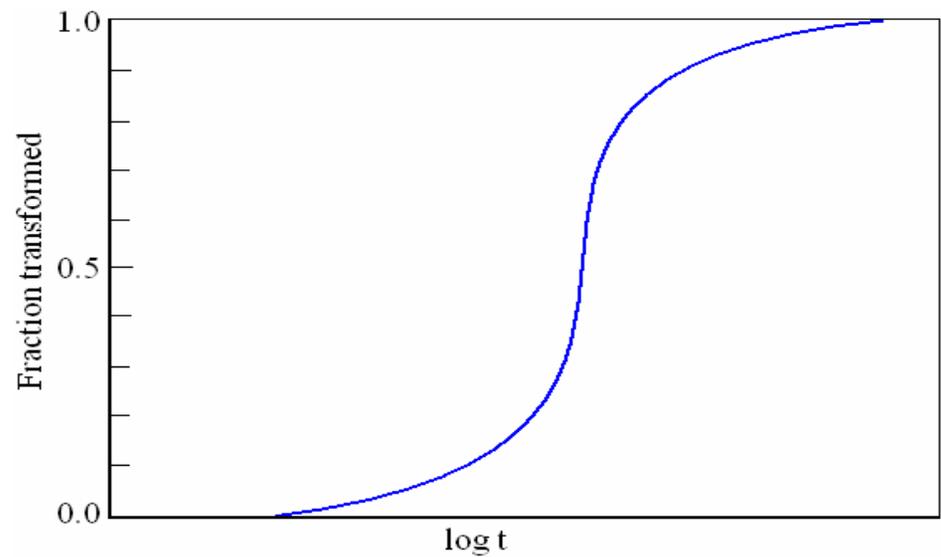
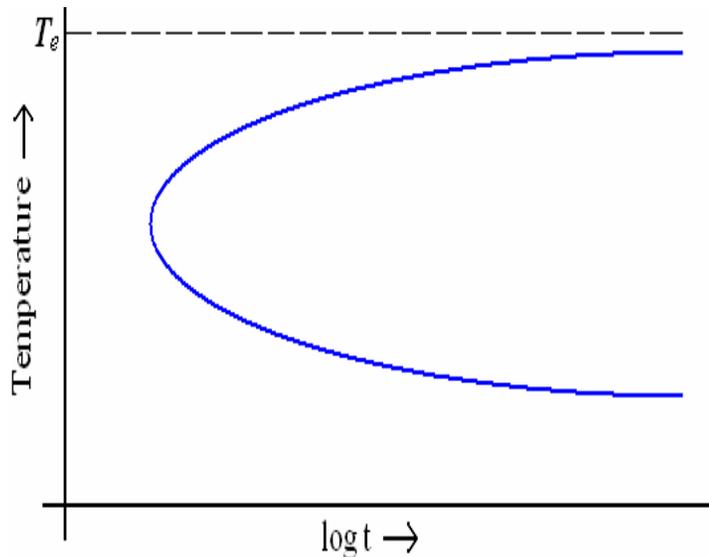
## Growth kinetics

- After formation of stable nuclei, growth of it occurs until equilibrium phase is being formed.
- Growth occurs in two methods – thermal activated diffusion controlled individual atom movement, or athermal collective movement of atoms. First one is more common than the other.
- Temperature dependence of nucleation rate ( $U$ ), growth rate ( $I$ ) and overall transformation rate ( $dX/dt$ ) that is a function of both nucleation rate and growth rate i.e.  $dX/dt = fn(U, I)$ :



## Growth kinetics (contd....)

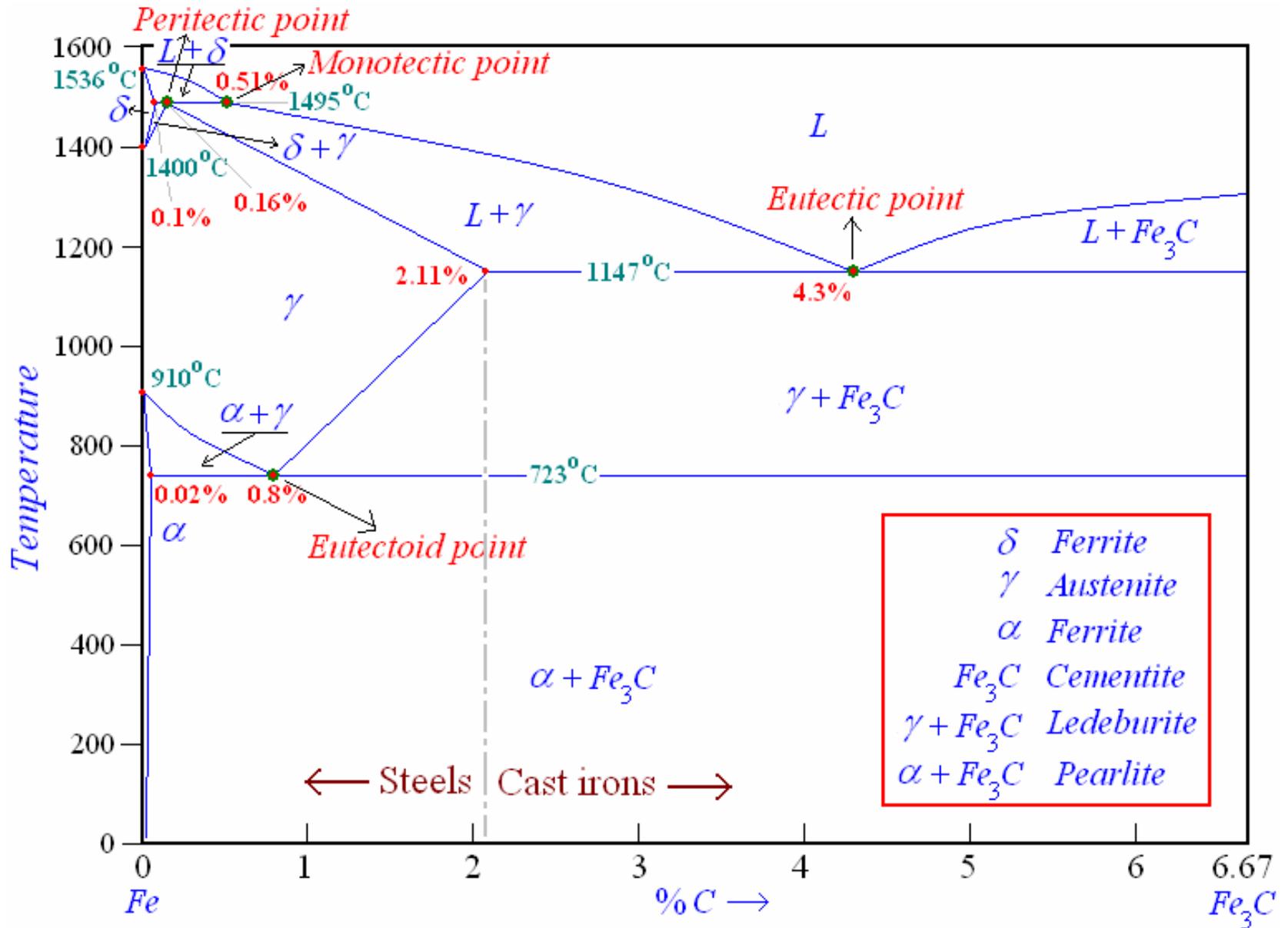
- Time required for a transformation to completion has a reciprocal relationship to the overall transformation rate, C-curve (time-temperature-transformation *or* TTT diagram).
- Transformation data are plotted as characteristic *S-curve*.
- At small degrees of supercooling, where slow nucleation and rapid growth prevail, relatively coarse particles appear; at larger degrees of supercooling, relatively fine particles result.



# Martensitic growth kinetics

- Diffusion-less, athermal collective movement of atoms can also result in growth – Martensitic transformation.
- Takes place at a rate approaching the speed of sound. It involves congruent transformation.  
*E.g.:* FCC structure of Co transforms into HCP-Co *or* FCC-austenite into BCT-Martensite.
- Because of its crystallographic nature, a martensitic transformation only occurs in the solid state.
- Consequently,  $M_s$  and  $M_f$  are presented as horizontal lines on a TTT diagram.  $M_s$  is temperature where transformation starts, and  $M_f$  is temperature where transformation completes.
- Martensitic transformations in Fe-C alloys and Ti are of great technological importance.

# Fe-C binary system – Phase transformations



# Fe-C binary system – Phase transformations (contd....)

- Fe-Fe<sub>3</sub>C phase diagram is characterized by *five individual phases*,:  $\alpha$ -ferrite (BCC) Fe-C solid solution,  $\gamma$ -austenite (FCC) Fe-C solid solution,  $\delta$ -ferrite (BCC) Fe-C solid solution, Fe<sub>3</sub>C (iron carbide) *or* cementite - an inter-metallic compound and liquid Fe-C solution **and** *four invariant reactions*:
- peritectic reaction at 1495 °C and 0.16%C,  $\delta$ -ferrite +  $L \leftrightarrow \gamma$ -iron (austenite)
  - monotectic reaction 1495 °C and 0.51%C,  $L \leftrightarrow L + \gamma$ -iron (austenite)
  - eutectic reaction at 1147 °C and 4.3 %C,  $L \leftrightarrow \gamma$ -iron + Fe<sub>3</sub>C (cementite) [ledeburite]
  - eutectoid reaction at 723 °C and 0.8%C,  $\gamma$ -iron  $\leftrightarrow \alpha$ -ferrite + Fe<sub>3</sub>C (cementite) [pearlite]

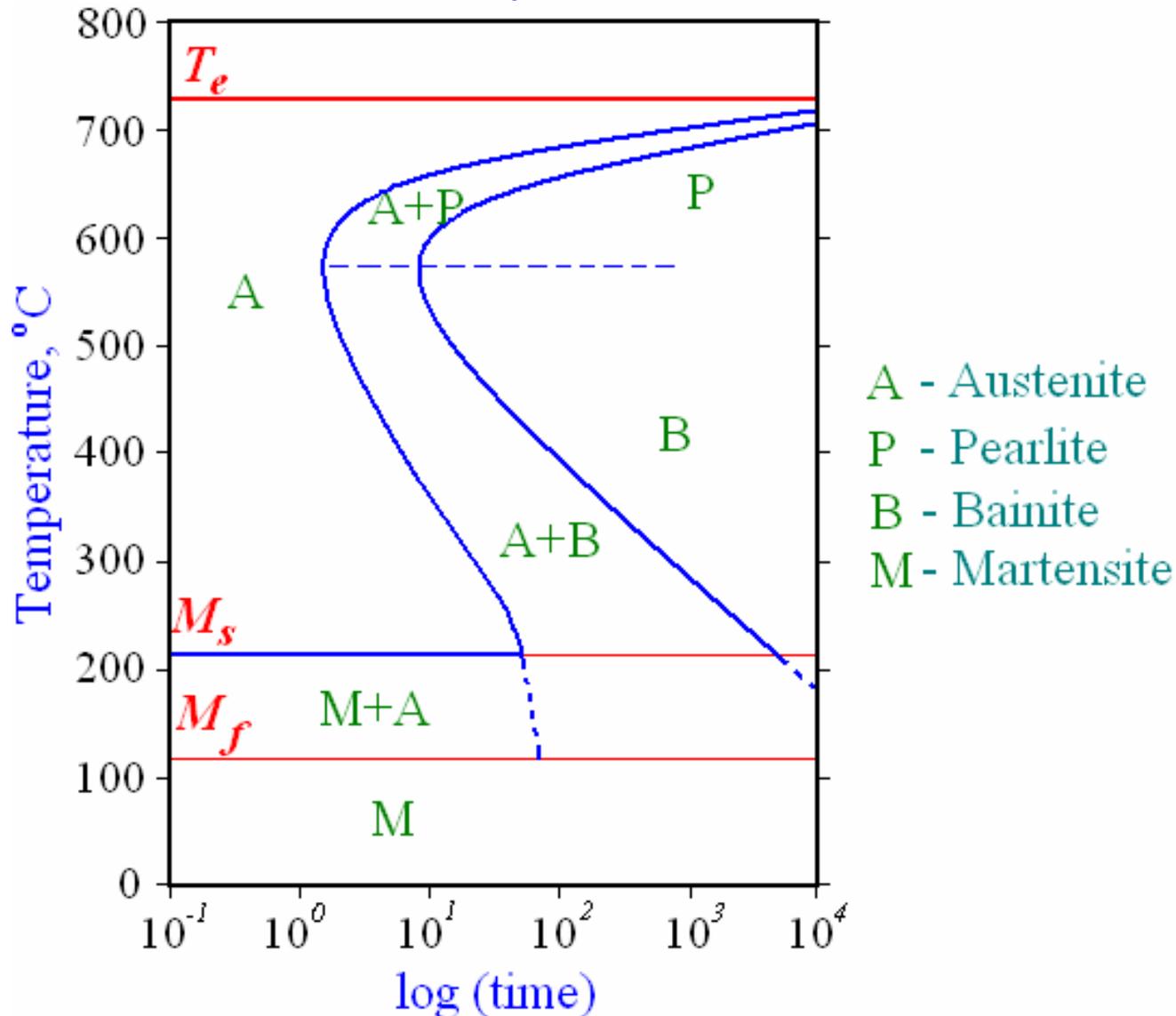
## Fe-C alloy classification

- Fe-C alloys are classified according to wt.% C present in the alloy for technological convenience as follows:

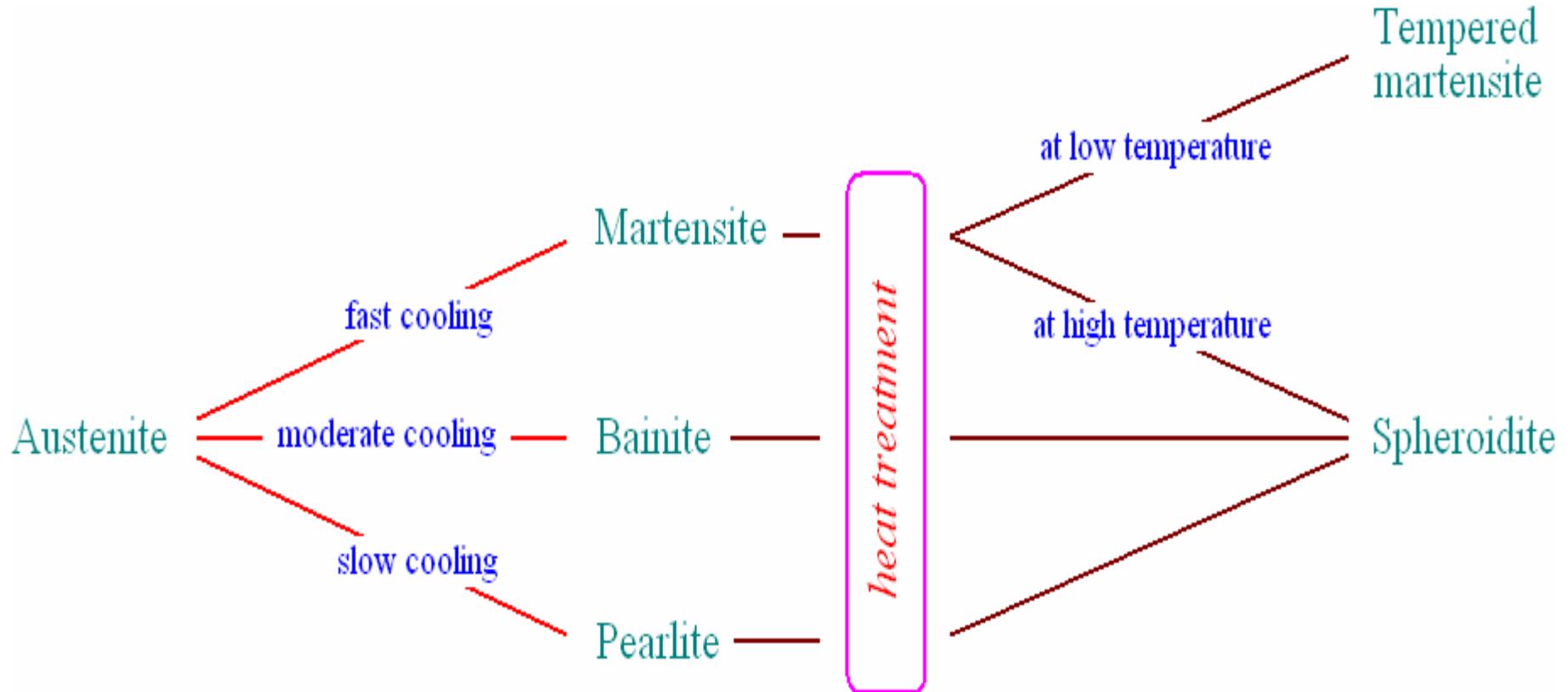
|                        |                  |
|------------------------|------------------|
| Commercial pure irons  | % C < 0.008      |
| Low-carbon/mild steels | 0.008 - %C - 0.3 |
| Medium carbon steels   | 0.3 - %C - 0.8   |
| High-carbon steels     | 0.8- %C - 2.11   |
| Cast irons             | 2.11 < %C        |

- Cast irons that were slowly cooled to room temperature consists of cementite, look whitish – *white cast iron*. If it contains graphite, look grayish – *gray cast iron*. It is heat treated to have graphite in form of nodules – *malleable cast iron*. If inoculants are used in liquid state to have graphite nodules – *spheroidal graphite (SG) cast iron*.

# TTT diagram for eutectoid transformation in Fe-C system



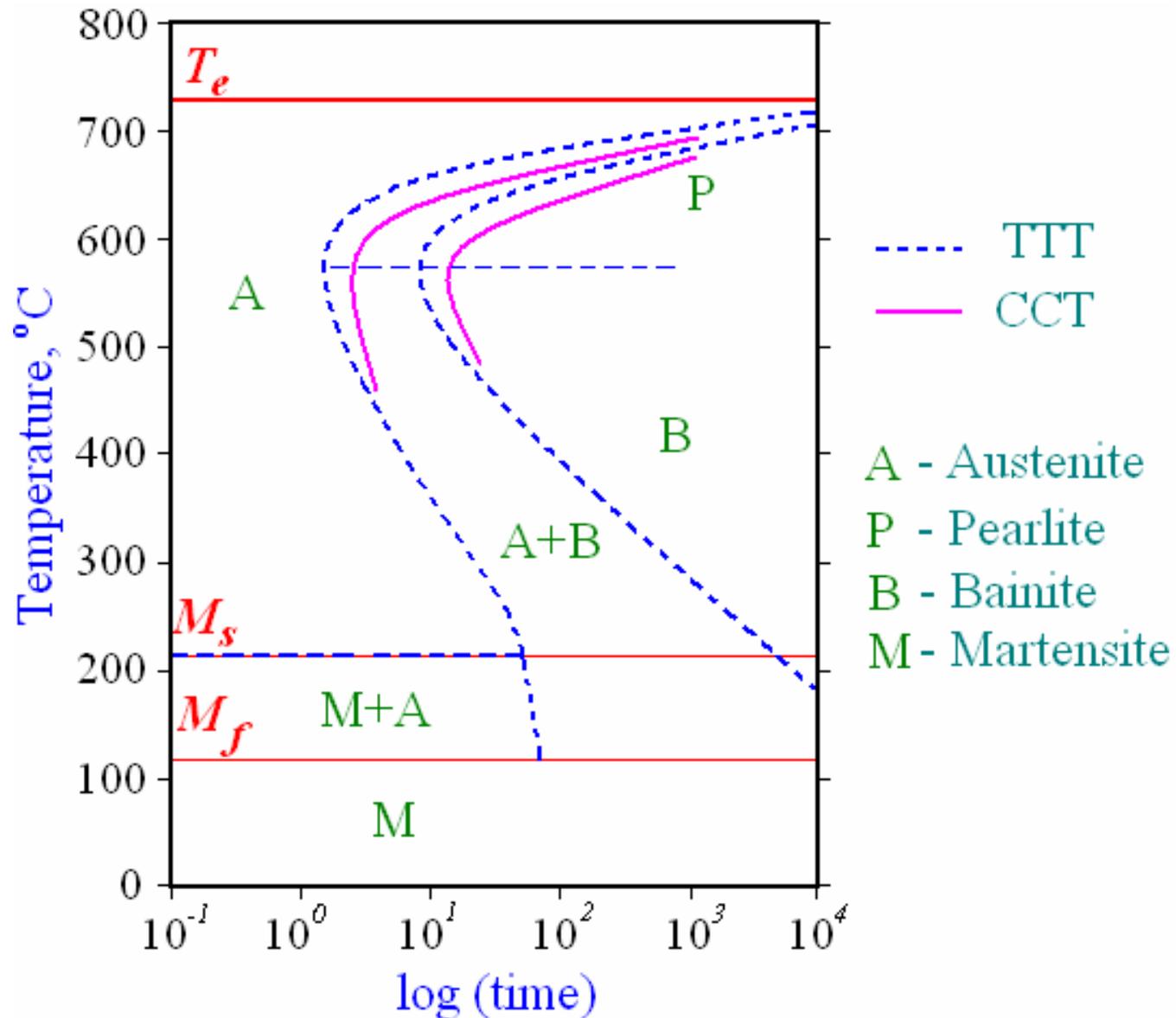
# Transformations involving austenite for Fe-C system



## CCT diagram for Fe-C system

- TTT diagram though gives very useful information, they are of less practical importance since an alloy has to be cooled rapidly and then kept at a temperature to allow for respective transformation to take place.
- Usually materials are cooled continuously, thus Continuous Cooling Transformation diagrams are appropriate.
- For continuous cooling, the time required for a reaction to begin and end is delayed, thus the isothermal curves are shifted to longer times and lower temperatures.
- Main difference between TTT and CCT diagrams: no space for bainite in CCT diagram as continuous cooling always results in formation of pearlite.

# CCT diagram for Fe-C system (contd....)





# Material Science

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**Failure**

## Contents

- 1) Fracture, ductile and brittle fracture
- 2) Fracture mechanics
- 3) Impact fracture, ductile-to-brittle transition
- 4) Fatigue, crack initiation and propagation, crack propagation rate
- 5) Creep, generalized creep behavior, stress and temperature effects

# Failure – Classification

- Failure of a material component is the loss of ability to function normally *or* to perform the intended job!
- Three general ways failure:
  - Excessive elastic deformation, E.g.: buckling. Controlled by design and elastic modulus of the material.
  - Excessive plastic deformation, Controlled by yield strength of the material. E.g.: loss of shape, creep and/ or stress-rupture at elevated temperatures.
  - Fracture, involves complete disruption of continuity of a component – under static load: brittle *or* ductile, under fluctuating/cyclic load: fatigue, mode in which most machine parts fail in service.

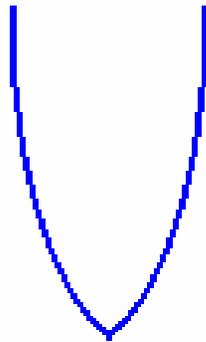
# Fracture

- Fracture *defined* as the separation or fragmentation of a solid body into two *or* more parts under the action of stress.
- Fracture is classified based on several characteristic features:

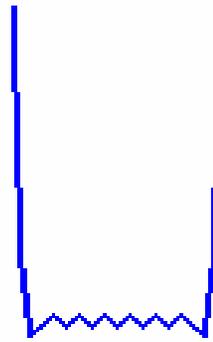
| <i>characteristic</i> | <i>terms used</i>      |                       |
|-----------------------|------------------------|-----------------------|
| Strain to fracture    | <b><i>Ductile</i></b>  | <b><i>Brittle</i></b> |
| Crystallographic mode | Shear                  | Cleavage              |
| Appearance            | Fibrous and gray       | Granular and bright   |
| Crack propagation     | Along grain boundaries | Through grains        |

# Fracture modes

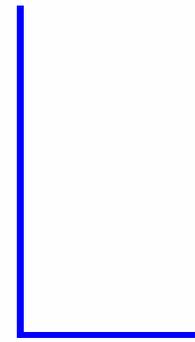
- Ductile and Brittle are relative terms.
- Most of the fractures belong to one of the following modes:  
(a) rupture, (b) cup-&-cone and (c) brittle.



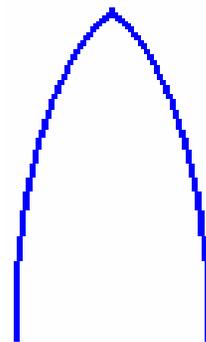
**Rupture**



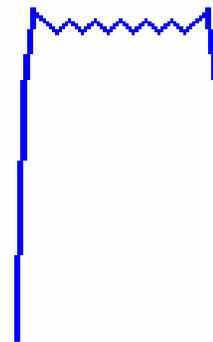
**Cup-&-Cone fracture**



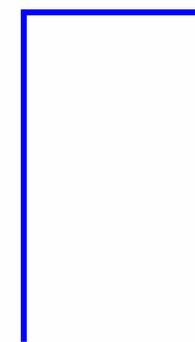
**Brittle fracture**



**(a)**



**(b)**



**(c)**

## Ductile fracture Vs Brittle fracture

| <i>Parameter</i>        | <i>Ductile fracture</i>    | <i>Brittle fracture</i> |
|-------------------------|----------------------------|-------------------------|
| Strain energy required  | Higher                     | Lower                   |
| Stress, during cracking | Increasing                 | Constant                |
| Crack propagation       | Slow                       | Fast                    |
| Warning sign            | Plastic deformation        | None                    |
| Deformation             | Extensive                  | Little                  |
| Necking                 | Yes                        | No                      |
| Fractured surface       | Rough and dull             | Smooth and bright       |
| Type of materials       | Most metals (not too cold) | Ceramics, Glasses, Ice  |

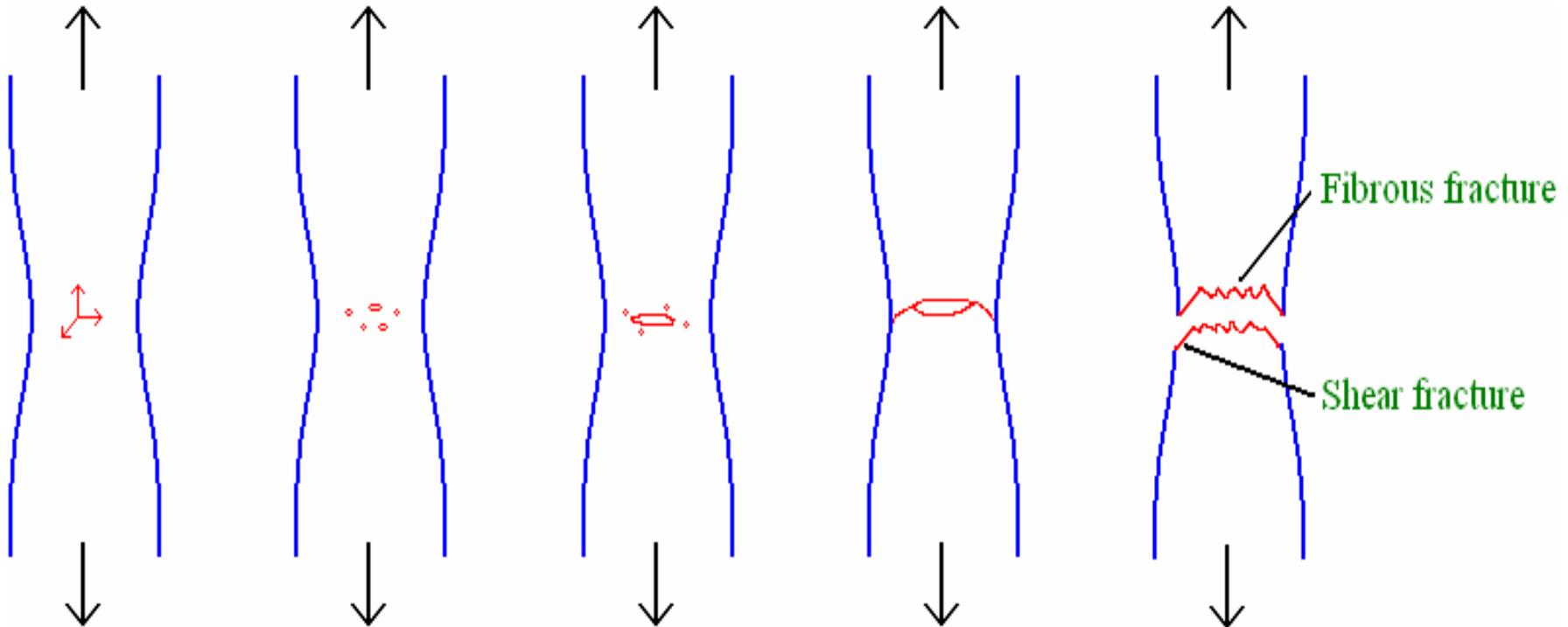
# Ductile fracture

- Ductile fracture in tension occurs after appreciable plastic deformation.
- It is usually preceded by necking.
- It exhibits three stages - (1) formation of cavities (2) growth of cavities (3) final failure involving rapid crack propagation at about 45° to the tensile axis.
- Fractography of ductile fracture reveals numerous spherical dimples separated by thin walls on the fractured surface.
- McClintock's strain to ductile fracture,  $\varepsilon_f$

$$\varepsilon_f = \frac{(1-n) \ln(l_0/2b_0)}{\sinh\left[(1-n)(\sigma_a + \sigma_b)/(2\bar{\sigma}/\sqrt{3})\right]}$$

## Ductile fracture (contd....)

- Stages of void nucleation, void growth, crack initiation and eventual fracture under ductile fracture mode:



# Brittle fracture

- Brittle fracture takes place with little *or* no preceding plastic deformation.
- It occurs, often at unpredictable levels of stress, by rapid crack propagation.
- Crack propagates nearly perpendicular to the direction of applied tensile stress, and hence called cleavage fracture.
- Most often brittle fracture occurs through grains i.e. transgranular.
- Three stages of brittle fracture - (1) plastic deformation that causes dislocation pile-ups at obstacles, (2) micro-crack nucleation as a result of build-up of shear stresses, (3) eventual crack propagation under applied stress aided by stored elastic energy.

## Brittle fracture – Griffith Theory

- Nominal fracture stress that causes brittle fracture in presence of cracks (length of interior crack= $2c$ ), the stress raisers,

$$\sigma_f \approx \left( \frac{E\gamma}{4c} \right)^{1/2}$$

- Griffith's criteria: a crack will propagate when the decrease in elastic energy is at least equal to the energy required to create the new crack surface. Thus for thin plates:  $\sigma = \left( \frac{2E\gamma}{c\pi} \right)^{1/2}$

- For thick plates:  $\sigma = \left( \frac{2E\gamma}{(1-\nu^2)c\pi} \right)^{1/2}$

- When plastic energy is also taken into account (Orowan's modification):

$$\sigma = \left( \frac{2E(\gamma + p)}{c\pi} \right)^{1/2} \approx \left( \frac{Ep}{c} \right)^{1/2}$$

# Fracture mechanics

➤ Relatively new field of mechanics, that deals with possibility whether a crack of given length in a material with known toughness is dangerous at a given stress level or not!

➤ Fracture resistance of a material in the presence of cracks, known as fracture toughness, is expressed in two forms.

(1) Strain-energy release rate,  $G$ : 
$$G = \frac{\pi\sigma^2 c}{E}$$

(2) Stress concentration factor,  $K$ : 
$$K = \alpha\sigma\sqrt{c\pi}$$

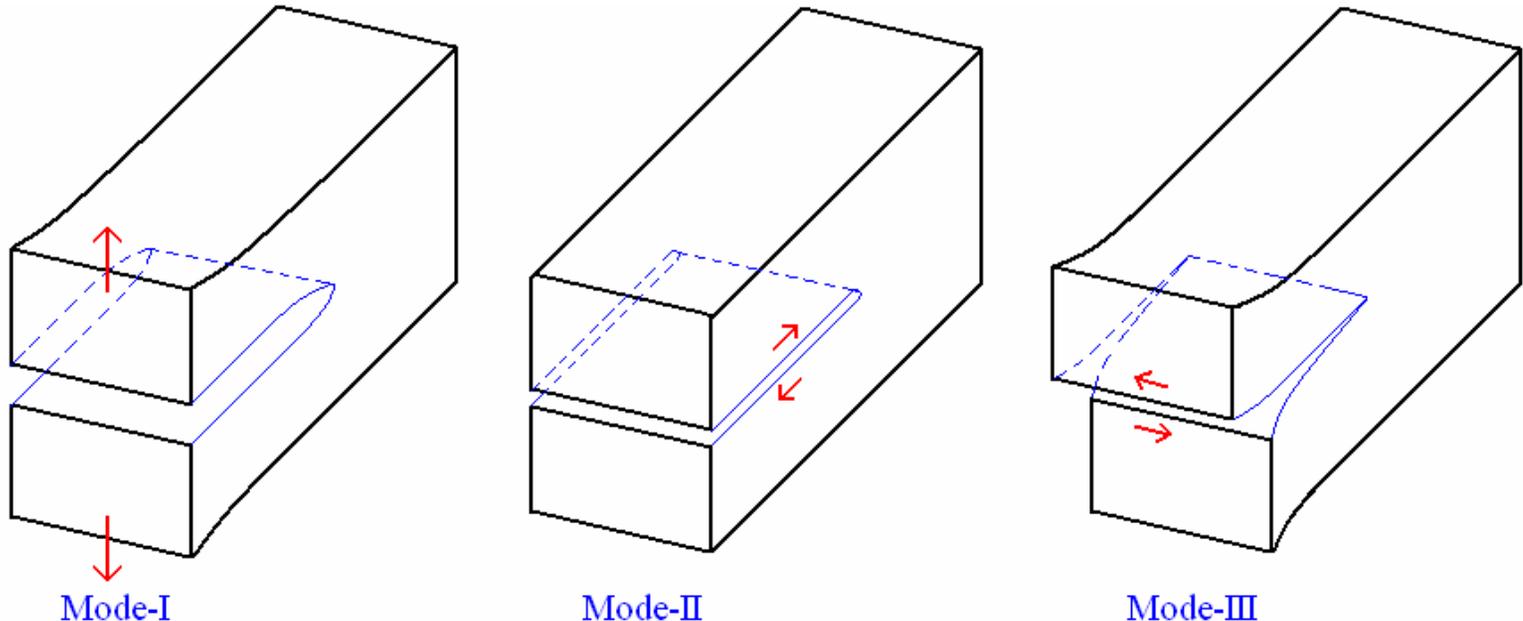
➤ Both parameters are related as:

For plane stress conditions i.e. thin plates:  $K^2 = GE$

For plane strain conditions i.e. thick plates:  $K^2 = GE/(1 - \nu^2)$

## Fracture mechanics (contd....)

- $K$  depends on many factors, the most influential of which are temperature, strain rate, microstructure and orientation of fracture. The value of  $K$  decreases with increasing strain rate, grain size and/or decreasing temperature.
- Depending on the orientation of fracture, three modes of fracture are identified as shown in the figure:



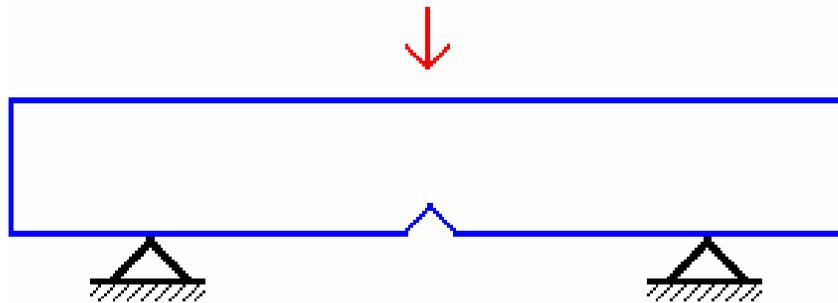
↑ Displacement of crack surfaces

## Notch-impact testing

- Ductile and Brittle are terms used to distinguish two extremes of fractures modes based on plastic deformation involved before fracture occurs.
- Three factors that aid transition from ductile to brittle-cleavage type of fracture are: (1) tri-axial state of stress (2) low temperature, and (3) rapid rate of loading.
- Since brittle fracture is most unpredictable, its been extend at a greater extent. Usually a notch will be introduced to simulate the conditions.
- A notch increases the tendency for brittle fracture by four means: (a) by producing high local stresses, (b) by introducing a tri-axial state of stress, (c) by producing high local strain hardening and cracking, and (d) by producing a local magnification to the strain rate.

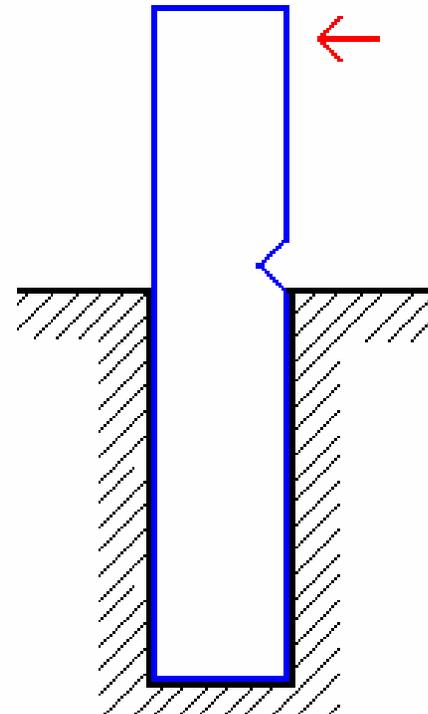
## Notch-impact testing (contd....)

- A material's susceptibility to different kinds of fracture is measured using notched specimen subjected to impact load. Further study involves examining the fracture surfaces, and calculation of ductility.
- Two kind of specimen configurations & loading directions:



Charpy specimen

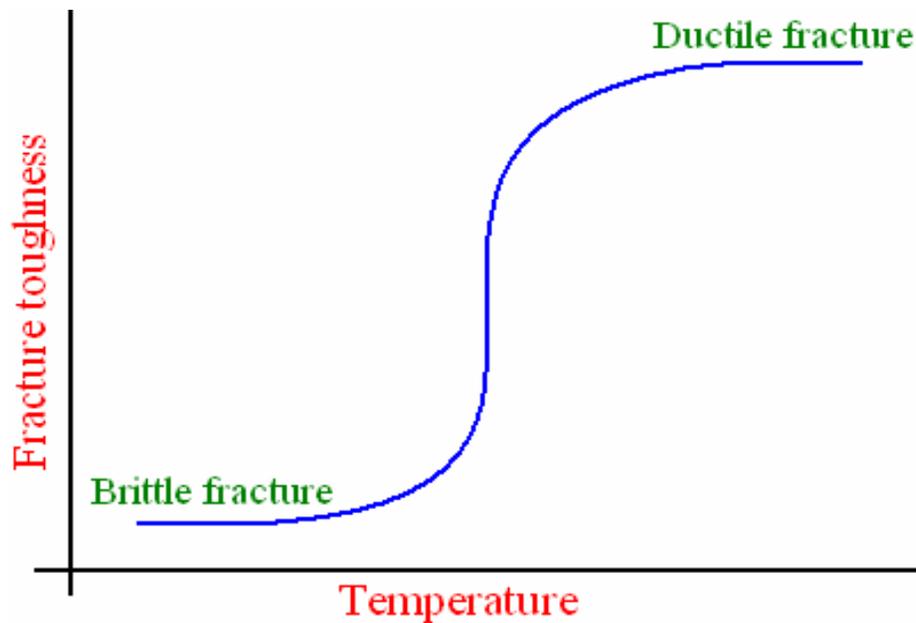
↑ Impact load direction



Izod specimen

# Ductile-to-Brittle transition

- Energy absorbed during the notch-impact is plotted as a function of temperature to know at what temperature range (DBTT) material fracture in a particular mode.



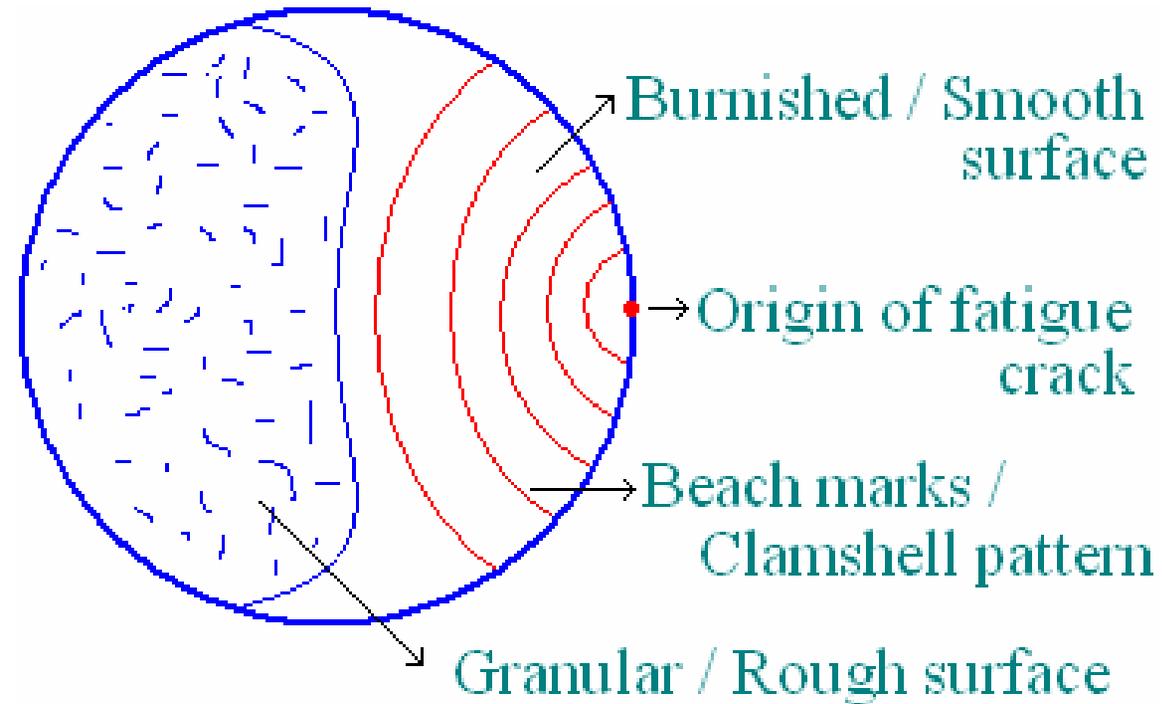
- In metals DBTT is around  $0.1-0.2 T_m$  while in ceramics it is about  $0.5-0.7 T_m$ , where  $T_m$  represents absolute melting temperature.

# Fatigue failure

- Failure that occurs under fluctuating/cyclic loads – Fatigue.
- Fatigue occurs at stresses that considerable smaller than yield/tensile stress of the material.
- These failures are dangerous because they occur without any warning. Typical machine components subjected to fatigue are automobile crank-shaft, bridges, aircraft landing gear, etc.
- Fatigue failures occur in both metallic and non-metallic materials, and are responsible for a large number fraction of identifiable service failures of metals.
- Fatigue fracture surface is perpendicular to the direction of an applied stress.

## Fatigue failure (contd....)

- Fatigue failure can be recognized from the appearance of the fracture surface:



- Any point with stress concentration such as sharp corner *or* notch *or* metallurgical inclusion can act as point of initiation of fatigue crack.

## Fatigue failure (contd....)

- Three basic requisites for occurrence of fatigue fracture are:  
(a) a maximum tensile stress of sufficiently high value (b) a large enough variation or fluctuation in the applied stress and (c) a sufficiently large number of cycles of applied stress.
- Stress cycles that can cause fatigue failure are characterized using the following parameters:

Range of stress,

$$\sigma_r = \sigma_{max} - \sigma_{min}$$

Alternating stress,

$$\sigma_a = \sigma_r / 2 = (\sigma_{max} - \sigma_{min}) / 2$$

Mean stress,

$$\sigma_m = (\sigma_{max} + \sigma_{min}) / 2$$

Stress ratio,

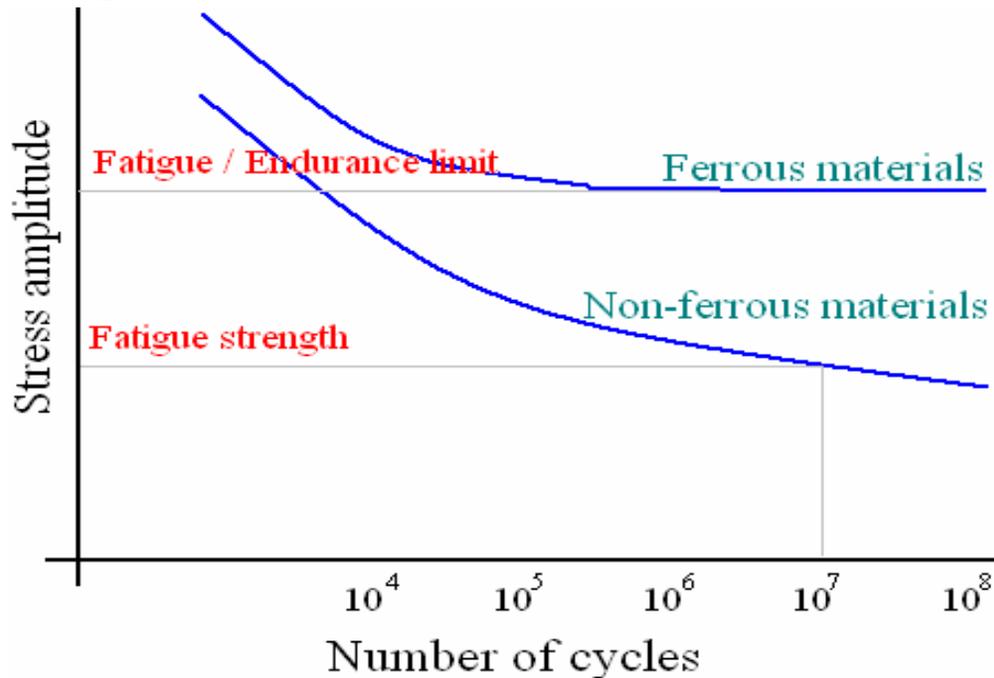
$$R = \sigma_{min} / \sigma_{max}$$

Amplitude ratio,

$$A = \sigma_a / \sigma_m = (1 - R) / (1 + R)$$

## Fatigue testing – Data presentation

- Fatigue test, usually, involves applying fluctuating load cyclically.
- A specimen of rotating beam type is often used because of its simplicity.
- Fatigue data is usually presented by plotting maximum stress ( $S$ ) against number of cycles to fracture ( $N$ ), using a logarithmic scale for the latter variable.



S-N curve can be represented by the Basquin equation:

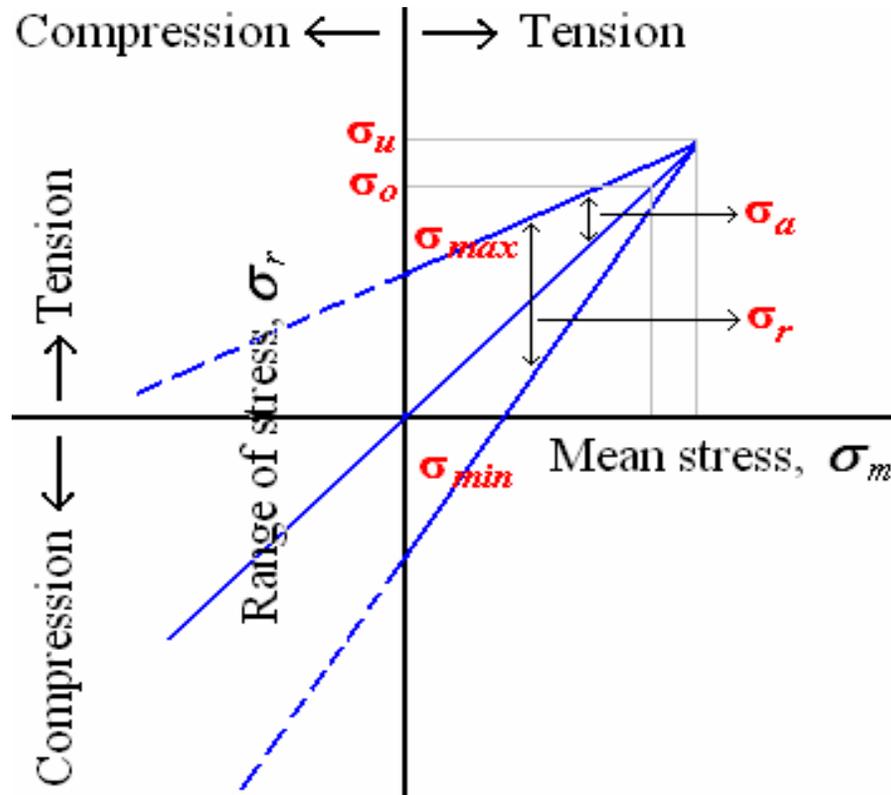
$$N\sigma_a^p = C$$

## Fatigue parameters

- Material fails under fatigue mode at higher number of stress cycles if stress applied is lower.
- After a limiting stress, ferrous materials won't fail for any number of stress cycles. This limiting stress is called – *fatigue limit / endurance limit*.
- For non-ferrous materials, there is no particular limiting stress i.e. as stress reduces, number of cycles to failure keep increasing. Hence stress corresponding to  $10^7$  cycles is considered as characteristic of material, and known as *fatigue strength*. Number of cycles is called *fatigue life*.
- *Endurance ratio* – ratio of fatigue stress to tensile stress of a material. For most materials it is in the range of 0.4-0.5.

# Fatigue data presentation – Goodman diagram

- The Goodman diagram presents the dependence of allowable stress ranges on mean stress for a material. Allowable stress range increases with increasing compressive mean stress i.e. compressive stress increases the fatigue limit.

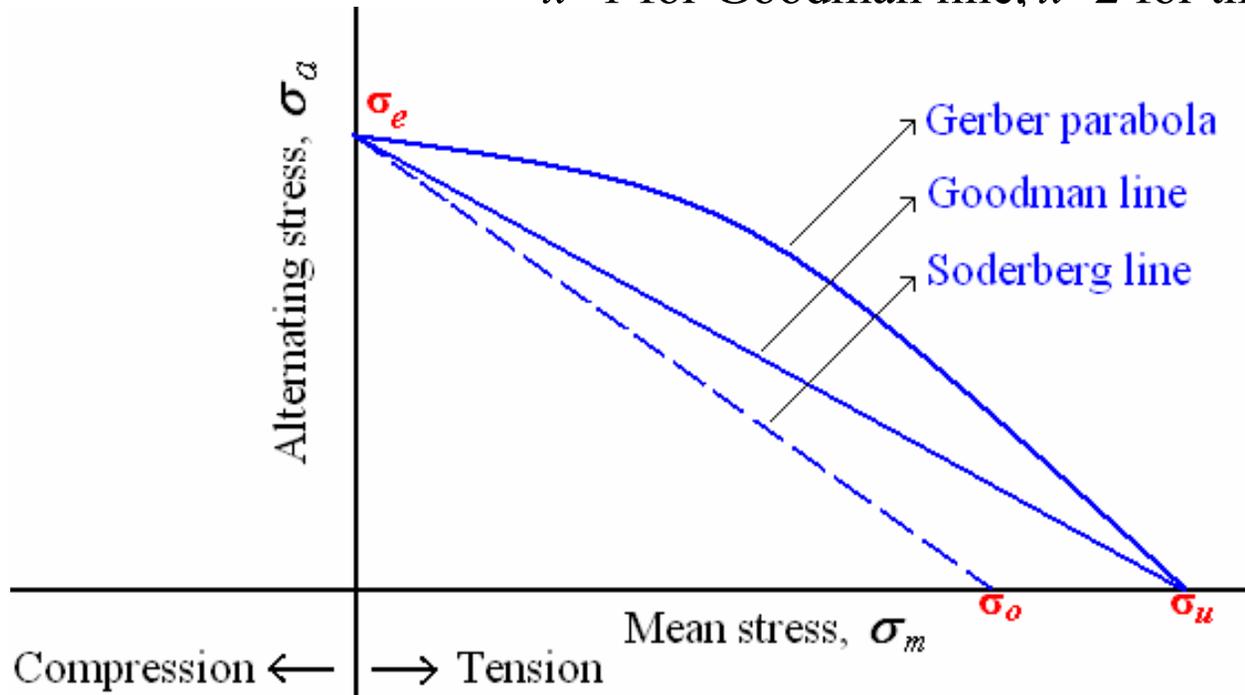


## Fatigue data presentation (contd....)

- An alternative method of presenting mean stress data is by using Heig-Soderberg diagram. The following equation summarizes the diagram:

$$\sigma_a = \sigma_e \left[ 1 - \left( \frac{\sigma_m}{\sigma_u} \right)^x \right]$$

$x=1$  for Goodman line,  $x=2$  for the Gerber parabola.



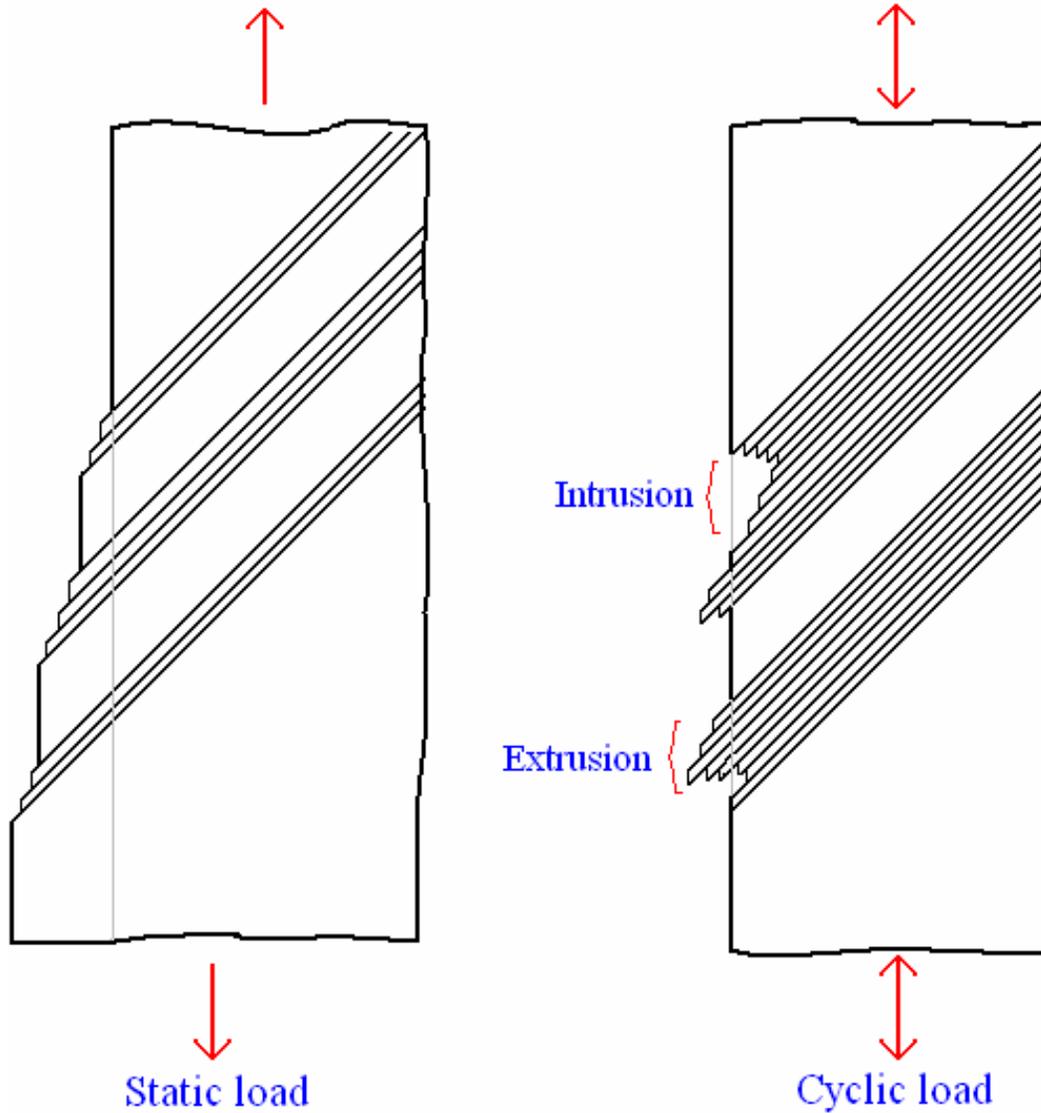
# Fatigue – Crack initiation & propagation

- Fatigue failure consists of four stages: (a) crack initiation – includes the early development of fatigue damage that can be removed by suitable thermal anneal (b) slip-band crack growth – involves the deepening of initial crack on planes of high shear stress (stage-I crack growth) (c) crack growth on planes of high tensile stress – involves growth of crack in direction normal to maximum tensile stress (stage-II crack growth) (d) final ductile failure – occurs when the crack reaches a size so that the remaining cross-section cannot support the applied load.
- Stage-I is secondary to stage-II crack growth in importance because very low crack propagation rates involved during the stage.

## Static load Vs Cyclic load

| <i>Feature</i>         | <i>Static load</i> | <i>Cyclic load</i>      |
|------------------------|--------------------|-------------------------|
| Slip ( <i>nm</i> )     | 1000               | 1-10                    |
| Deformation feature    | Contour            | Extrusions & Intrusions |
| Grains involved        | All grains         | Some grains             |
| Vacancy concentration  | Less               | Very high               |
| Necessity of diffusion | Required           | Not necessary           |

# Static load Vs Cyclic load (contd....)



## Fatigue crack growth: Stage-I Vs Stage-II

| <i>Parameter</i>             | <i>Stage-I</i>    | <i>Stage-II</i>                     |
|------------------------------|-------------------|-------------------------------------|
| Stresses involved            | Shear             | Tensile                             |
| Crystallographic orientation | Yes               | No                                  |
| Crack propagation rate       | Low (nm/cycle)    | High ( $\mu\text{m}/\text{cycle}$ ) |
| Slip on                      | Single slip plane | Multiple slip planes                |
| Feature                      | Feature less      | Striations                          |

# Fatigue crack propagation rate

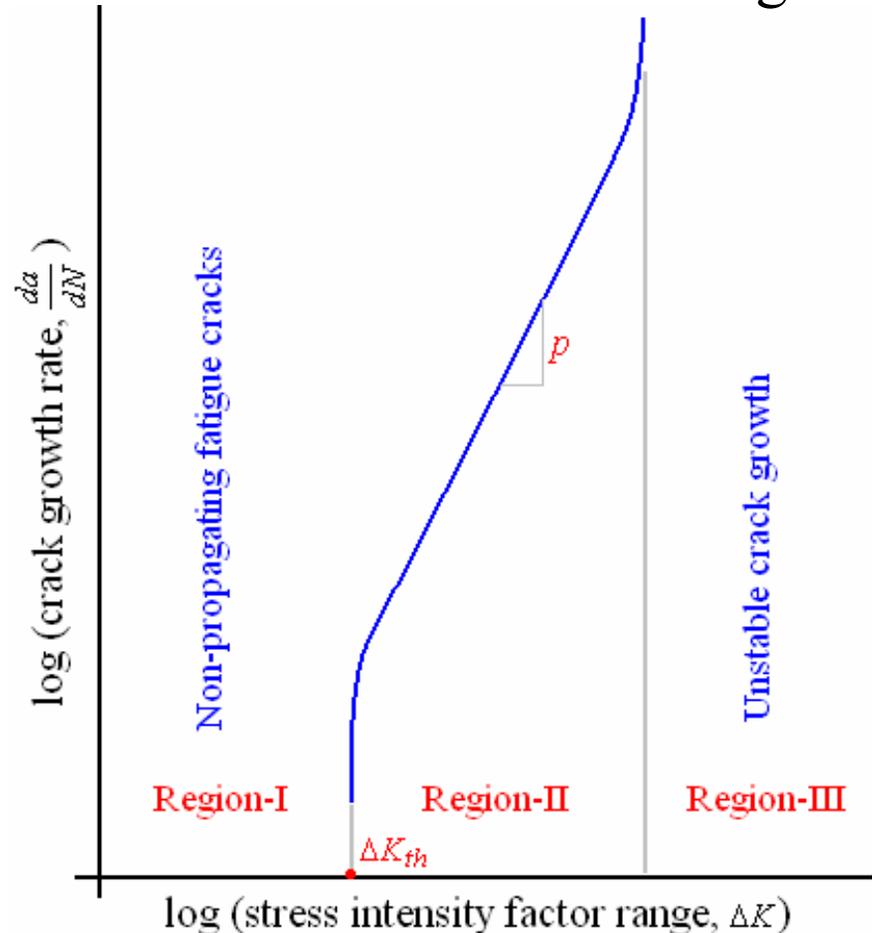
- Studies of fatigue crack propagation rate attained much importance because it can be used as fail-safe design consideration.

$$\frac{da}{dN} = fn(\sigma, a) = C\sigma_a^m a^n$$

- Paris law:

$$\frac{da}{dN} = A(\Delta K)^p$$

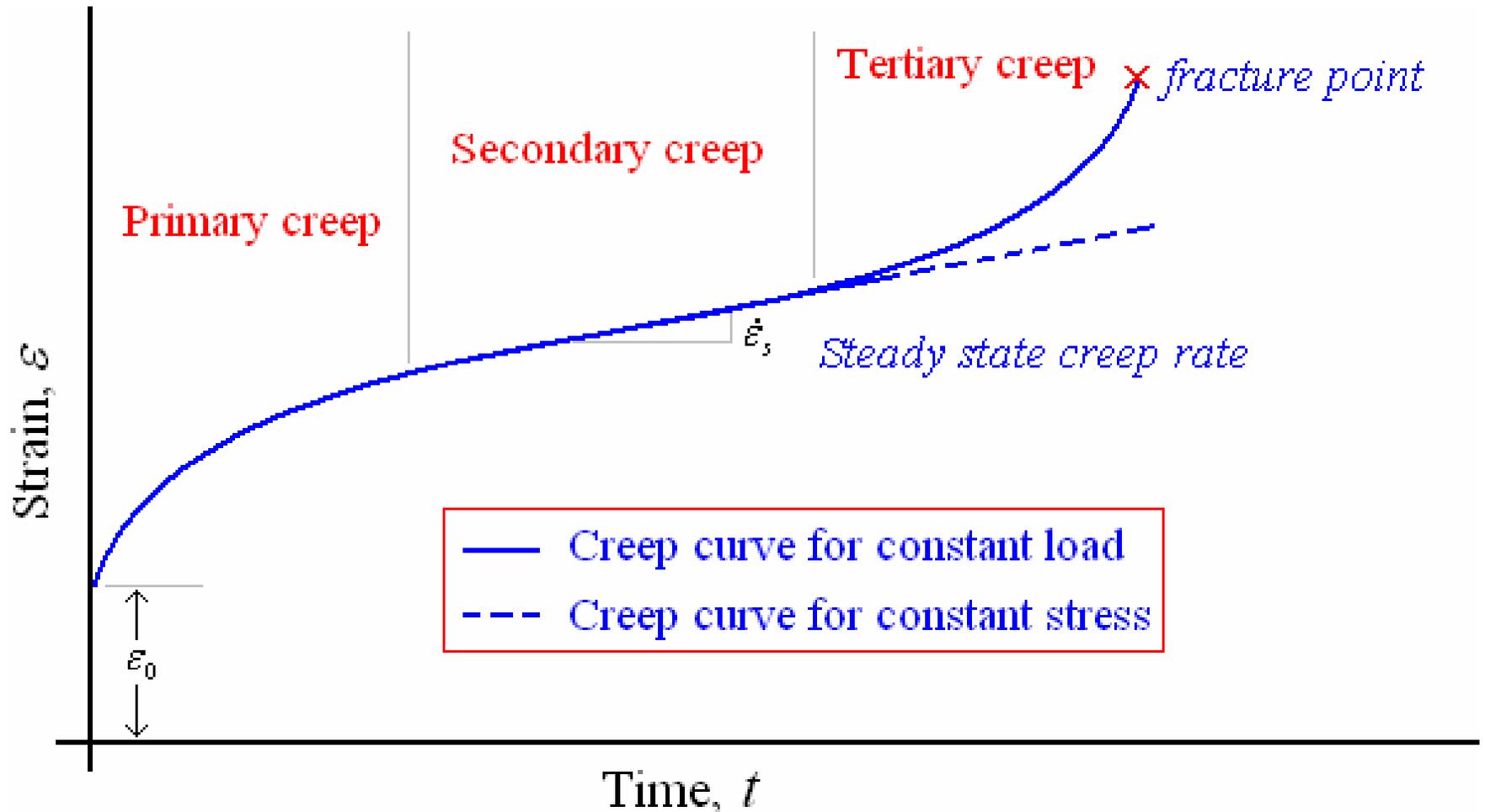
p= 3 for steels, 3-4 for Al alloys



# Creep failure

- Deformation that occurs under constant load/stress and elevated temperatures which is time-dependent is known as *creep*.
- Creep deformation (constant stress) is possible at all temperatures above absolute zero. However, it is extremely sensitive to temperature.
- Hence, creep is usually considered important at elevated temperatures (temperatures greater than  $0.4 T_m$ ,  $T_m$  is absolute melting temperature).
- Creep test data is presented as a plot between time and strain known as creep curve.
- The slope of the creep curve is designated as creep rate.

# Creep curve



## Creep curve (contd....)

- Creep curve is considered to be consists of three portions.
- After initial rapid elongation,  $\varepsilon_0$ , the creep rate decreases continuously with time, and is known as *primary* or *transient creep*.
- Primary creep is followed by *secondary* or *steady-state* or *viscous creep*, which is characterized by constant creep rate. This stage of creep is often the longest duration of the three modes.
- Finally, a third stage of creep known as, *tertiary creep* occurs that is characterized by increase in creep rate.
- Andrade creep equation:
$$\varepsilon = \varepsilon_0 (1 + \beta t^{1/3}) e^{kt}$$
- Garofalo creep equation:
$$\varepsilon = \varepsilon_0 + \varepsilon_t (1 - e^{-rt}) + \dot{\varepsilon}_s t$$

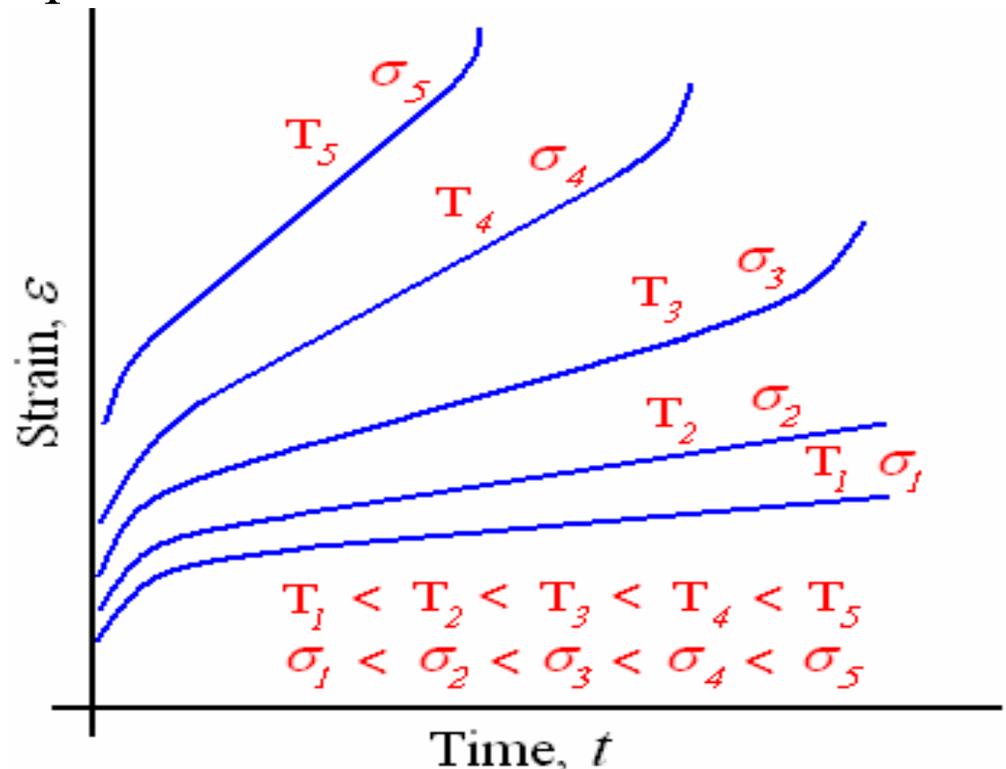
## Creep in different stages

- First stage creep is associated with strain hardening of the sample.
- Constant creep rate during secondary creep is believed to be due to balance between the competing processes of strain hardening and recovery. Creep rate during the secondary creep is called the minimum creep rate.
- Third stage creep occurs in constant load tests at high stresses at high temperatures. This stage is greatly delayed in constant stress tests. Tertiary creep is believed to occur because of either reduction in cross-sectional area due to necking or internal void formation. Third stage is often associated with metallurgical changes such as coarsening of precipitate particles, recrystallization, or diffusional changes in the phases that are present.

# Creep rate – Stress & Temperature effects

- Two most important parameter that influence creep rate are: stress and temperature.
- With increase in either stress or temperature (a) instantaneous elastic strain increases (b) steady state creep rate increases and (c) rupture lifetime decreases.

$$\dot{\varepsilon}_s = K_2 \sigma^n e^{-\frac{Q_c}{RT}}$$





# **Material Science**

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Module-09

## **Applications and Processing of Metals and Alloys**

## Contents

- 1) Types of metals and alloys
- 2) Fabrication of metals
- 3) Thermal processing of metals

# Materials – Classification

- Materials are classified into three basic groups based on their mechanical and physical nature as – metals, ceramics and polymers.
- For an engineer, especially, metals are more important owing to ability to carry loads and ease of manufacturing.
- Metallic materials are again classified for ease of selection and/or based on their tonnage of usage broadly into two classes – ferrous and non-ferrous.
- Ferrous materials – chief constituent is iron (*Fe*). **E.g.:** steel, cast iron.
- Metallic materials those are not ferrous are termed as non-ferrous materials. **E.g.:** Brass, Silver, Aluminium, Titanium.

# Ferrous materials - Introduction

- In engineering applications, lion share is served by ferrous materials.
  
- Factors account for it are:
  - availability of abundant raw materials combined with economical extraction
  - ease of forming
  - their versatile mechanical and physical properties.
  
- There are some drawbacks about ferrous materials:
  - poor corrosion resistance
  - high density i.e. low specific strength
  - low thermal and electrical conductivities

# Ferrous materials - Classification

- There are two classes – *steels* and *cast irons* – categorized based on carbon content.
- Steels: %C is up to 2.14%  
Cast irons: %C is above 2.14%
- Cast irons are called so because they are usually manufactured through casting technique owing to their brittle nature due to presence of iron carbide.
- Steels are serving major part of present engineering applications.
- However, cast irons mostly serve as structural components. E.g.: automobile motor casings, lathe bed, sliding guides in machinery.

# Steels

- In steels, C atoms occupies interstitial sites of Fe.
- Steels are classified based on their C content/alloying additions which in turn dictates their applications: plain carbon steels and alloying steels.
- **Plain carbon steels**
  - *Low-carbon steels*: % wt of C < 0.3
  - *Medium carbon steels*:  $0.3 < \% \text{ wt of C} < 0.6$
  - *High-carbon steels*: % wt of C > 0.6
- **Alloy Steel:**
  - High Strength Structural Steel
  - Tool Steels
  - Stainless steel

## Low carbon steels:

- Carbon present is not enough to strengthen them by heat treatment, hence are strengthened by cold work.
- They are easily weldable and machinable.
- Typical applications: tin cans, automotive body components, structural shapes, etc.

## Steels (contd....)

### ➤ Medium carbon steels:

- They are less ductile and stronger than low carbon steels.
- Heat treatable (austenitizing, quenching and tempering).
- Hardenability is increased by adding Ni, Cr, Mo.
- Used in various tempered conditions.
- Typical applications: gears, railway tracks, machine parts.

### ➤ High carbon steels:

- They are strongest and hardest of carbon steels.
- Heat treatable. Used in tempered or hardened conditions.
- Alloying additions – Cr, V, W, Mo
- Typical applications: Knives, razors, hacksaw blades, etc where high wear resistance is the prime requirement.

# HSLA and Stainless Steels

## ➤ High Strength Structural Steel

E.g.. HSLA (high strength low alloy) steels:

- They can be strengthened by heat treatment.
- Ductile and formable.
- Alloying addition – Cu, V, W, Ni, Cr, Mo, etc.
- Typical applications: support columns, pressure vessels, bridge beams.

## ➤ Tool Steels

General properties are : Wear and abrasion resistance, toughness, red hardness, non-deforming property and minimum cost.

## ➤ Stainless steels:

- They typical consists min.12% Cr along with other alloying elements, thus highly corrosion resistant owing to presence of chromium oxide.
- Three kinds - ferritic & hardenable Cr steels, austenitic and precipitation hardenable (martensitic, semi-austenitic) – based on presence of prominent microstructural constituent.

## Stainless Steels (contd....)

### ➤ Stainless steels:

- Typical applications – cutlery, surgical knives, storage tanks, domestic items
- *Ferritic steels* are principally Fe-Cr-C alloys with 12-14% Cr. And small additions of Mo, V, Nb, Ni.
- *Austenitic steels* contain 18% Cr and 8% Ni plus minor alloying elements. Ni stabilizes the austenitic phase assisted by C and N.
- For, *martensitic steels*  $M_s$  is made to be above the room temperature. These alloys are heat treatable. Major alloying elements are: Cr, Mn and Mo.
- Ferritic and austenitic steels are hardened and strengthened by cold work because they are not heat treatable.
- Austenitic steels are non-magnetic as against ferritic and martensitic steels, which are magnetic.

# Cast irons

## ➤ Grey cast iron

- Cementite decomposes during solidification to form carbon flakes. Thus they are brittle.
- Fractured surface looks grey because of presence of graphite, hence the name.
- Possess good damping properties.
- Typical applications – base structures, machine beds

## ➤ White cast iron

- Cooled fast so that cementite does not decompose.
- Fractures surface looks whitish because of cementite, hence the name.
- They are brittle and extremely difficult to machine.
- Used as source materials for producing malleable iron.

## Cast irons (contd....)

### ➤ Nodular cast iron

- Alloying addition of Mg/Ce to grey cast iron melt results in graphite to form as nodules.
- They are stronger and ductile than grey cast iron.
- Typical applications – pump bodies, crank shafts, automotive components, etc.

### ➤ Malleable cast iron

- Formed by heat treating white cast iron. Heat treatment involves heating to 800-900C, keep it there for long hours, then cooling to room temperature.
- Cementite decomposes to form graphite and ferrite.
- Typical applications – railroad, connecting rods, marine and other heavy-duty services.

# Non-Ferrous materials

- Typical advantages of non-ferrous materials over ferrous materials:
  - high specific strength.
  - low density.
  - high electrical and thermal conductivities.
  - distinct properties thus used for specific purposes.
  - can be formed with ease.

E.g.: Al-alloys

Cu-alloys (brass, bronze)

Mg-alloys

Ti-alloys

Noble metals (E.g.: Ag, Au, Pt, Pa)

Refractory metals (E.g.: Nb, Mo, W and Ta)

# Fabrication of metals and alloys

- Four basic manufacturing processes:
- Casting – to give a shape by pouring in liquid metal into a mold that holds the required shape, and letting harden the metal without external pressure.
- Forming – to give shape in solid state by applying pressure.
- Machining – in which material is removed in order to give it the required shape.
- Joining – where different parts are joined by various means.
- Other important technique is powder metallurgy.

# Metal Casting – Metal Forming

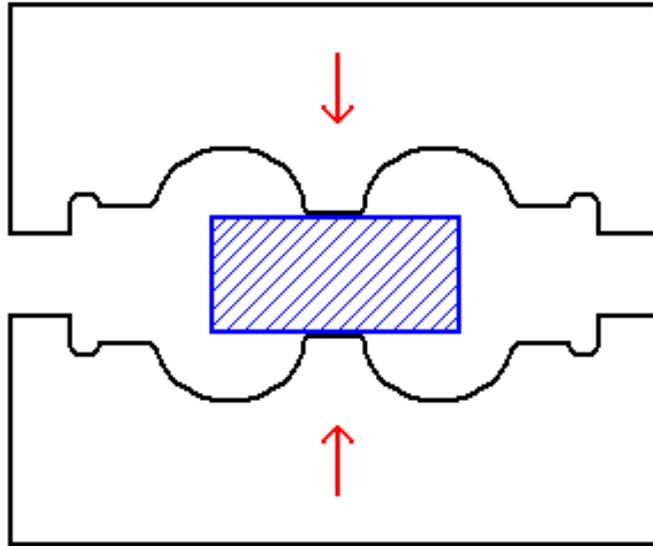
➤ Four important casting techniques are:

- Sand casting
- Die casting
- Investment casting
- Continuous casting

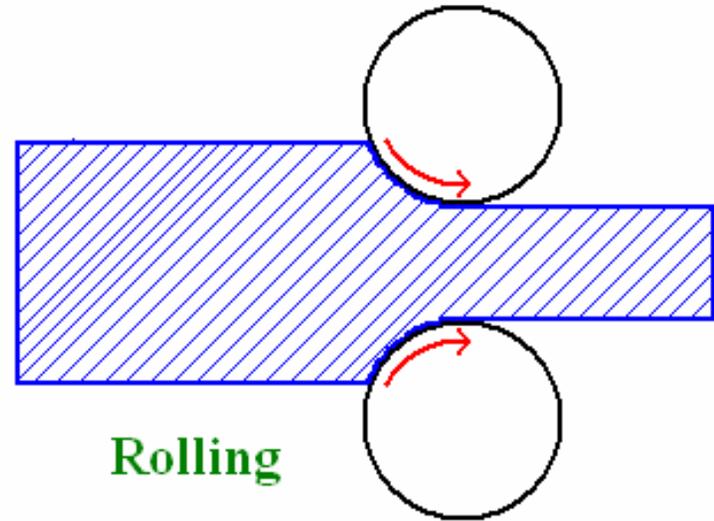
➤ Four important forming techniques are:

- Forging
- Rolling
- Extrusion
- Drawing

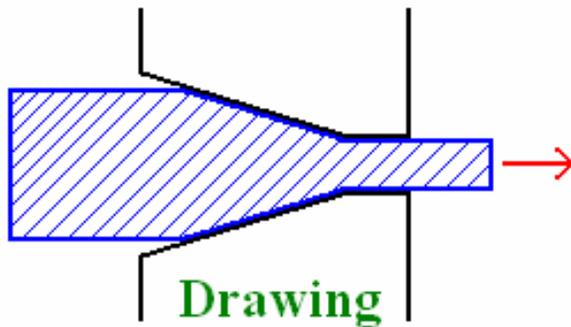
# Metal Forming techniques



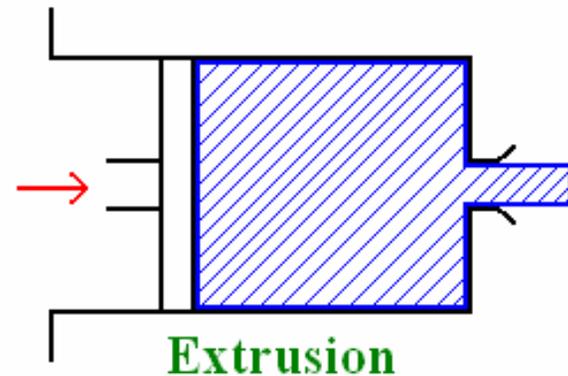
**Forging**



**Rolling**



**Drawing**



**Extrusion**

# Thermal processing

- Two main kinds of metal processing methods – mechanical and thermal.
- Thermal processing is also known as heat treatment.
- Purpose of heat treatment:
  - improvement in ductility
  - relieving internal stresses
  - grain size refinement
  - increase of strength
  - improvement in machinability and toughness
- Thermal processing factors – temperature up to which material is heated, length of time that the material is held at the elevated temperature, rate of cooling, and the surrounding atmosphere under the thermal treatment.

# Thermal processing methods

- Two kinds heat treating methods are – annealing and quenching & tempering.
- These differ in the way material is cooled from an elevated temperature.
- Annealing involves cooling the material slowly, allowing phase changes.
- Quenching (also known as *hardening*) means cooling the material at a rapid rate to arrest the equilibrium phase transformations.
- During annealing, material is cooled in air and/or heating furnace itself.
- For quenching, material is immersed in water / oil quench bath.

## Annealing techniques

- Process annealing – applied to cold worked materials to negate effects of cold work. Commonly sandwiched between two cold work operations. Improves ductility.
- Stress relief – purpose of it is to remove stresses. Temperatures are low such that cold work effects are not affected.
- Full annealing – used for products that are to be machined later-on. Cooling is done in furnace itself. Hardness and strength are restored by additional heat treatments after machining.
- Normalizing – used to refine the grains and produce a more uniform and desirable size distribution. It involves heating the component to attain single phase (e.g.: austenite in steels), then cooling in open air atmosphere.

# Quenching & Tempering

- Quenching operation is usually followed by tempering.
- Tempering involves heating martensitic steel at a temperature below the eutectoid transformation temperature to make it softer and more ductile. Here Martensite transforms to ferrite embedded with carbide particles.
- *Martempering* is used to minimize distortion and cracking. It involves cooling the austenitized steel to temperature just above  $M_s$  temperature, holding it there until temperature is uniform, followed by cooling at a moderate rate to room temperature before austenite-to-bainite transformation begins. The final structure of martempered steel is tempered Martensite.
- *Austempering* involves austenite-to-bainite transformation. Thus, the final structure of austempered steel is bainite.

# Case Hardening

- In case hardening, the surface of the steel is made hard and wear resistant, but the core remains soft and tough.

## ***Induction hardening***

- Here, an alternating current of high frequency passes through an induction coil enclosing the steel part to be heat treated.
- The induced *emf* heats the steel.
- Immediately after heating, water jets are activated to quench the surface.
- Martensite is produced at the surface, making it hard and wear resistant.
- The microstructure of the core remains unaltered.

## ***Flame hardening***

- Flame hardening is done by means of an oxyacetylene torch.
- Heating should be done rapidly by the torch and the surface quenched, before appreciable heat transfer to the core occurs

# Case Hardening

## *Laser hardening*

- A laser beam can be used for surface hardening.
- As laser beams are of high intensity, a lens is used to reduce the intensity by producing a defocused spot of size ranging from 0.5 to 25 mm.
- Proper control of energy input is necessary to avoid melting.
- Laser hardening has the advantage of precise control over the area to be hardened, an ability to harden reentrant surfaces, very high speed of hardening and no separate quenching step.

## *Carburizing*

- The surface layers of low carbon steel are enriched with carbon up to 0.8-1.0%.
- The source of carbon may be a solid medium, a liquid or a gas.
- In all cases, the carbon enters the steel at the surface and diffuses into the steel as a function of time at an elevated temperature.
- Carburizing is done at 920-950° C. This fully austenitic state is essential.
- If carburizing is done in the ferritic region, the carbon, with very limited solubility in ferrite, tends to form massive cementite particles near the surface, making the subsequent heat treatment difficult.

# Case Hardening

## Cyaniding

- Cyaniding is done in a liquid bath of NaCN, with the concentration varying between 30 and 97%.
- The temperature used for cyaniding is lower than that for carburizing and is in the range of 800-870° C.
- The time of cyaniding is 1-3 hr to produce a case depth of 0.25 mm or less

## Nitriding

- Nitriding is carried out in the ferritic region.
- No phase change occurs after nitriding.
- During nitriding, pure ammonia decomposes to yield nitrogen which enters the steel.
- The solubility of nitrogen in ferrite is small. Most of the nitrogen, that enters the steel, forms hard nitrides (e.g., Fe<sub>3</sub>N).
- The temperature of nitriding is 500-590° C.
- The time for a case depth of 0.02 mm is about 2 hr.
- In addition to providing outstanding wear resistance, the nitride layer increases the resistance of carbon steel to corrosion in moist atmospheres.



# Material Science

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Module-10

## Applications and Processing of Ceramics

## Contents

- 1) Types and applications of ceramics
- 2) Fabrication and processing of ceramics

## Introduction – Ceramics

- The word ‘ceramic’ is originated from greek word keromikos, which means ‘burnt stuff’.
- Ceramics are compounds of metallic and non-metallic elements.
- Characteristics of ceramics are:
  - high temperature stability
  - high hardness
  - brittleness
  - high mechanical strength
  - low elongation under application of stress
  - low thermal and electrical conductivities

## Classification – Ceramics

- Ceramics are classified in many ways. It is due to divergence in composition, properties and applications.
  
- Based on their composition, ceramics are:
  - Oxides
  - Carbides
  - Nitrides
  - Sulfides
  - Fluorides
  - etc.

# Classification – Ceramics

- Based on their specific applications, ceramics are classified as:
  - Glasses
  - Clay products
  - Refractories
  - Abrasives
  - Cements
  - Advanced ceramics for special applications

## Classification – Ceramics

- Based on their engineering applications, ceramics are classified into two groups as: traditional and engineering ceramics.
- Traditional ceramics – most made-up of clay, silica and feldspar
- Engineering ceramics – these consist of highly purified aluminium oxide ( $\text{Al}_2\text{O}_3$ ), silicon carbide ( $\text{SiC}$ ) and silicon nitride ( $\text{Si}_3\text{N}_4$ )

## Introduction – Processing ceramics

- The very specific character of ceramics – high temperature stability – makes conventional fabrication routes unsuitable for ceramic processing.
- Inorganic glasses, though, make use of lower melting temperatures. Most other ceramic products are manufactured through powder processing.
- Typical ceramic processing route: powder synthesis – green component (casting, extrusion, compaction) – sintering / firing.

## Processing ceramics – Glasses

- Most of them are silica-soda-lime variety.
- Raw materials are heated to an elevated temperature where melting occurs.
- Glass melt is processed by different route to form different products:

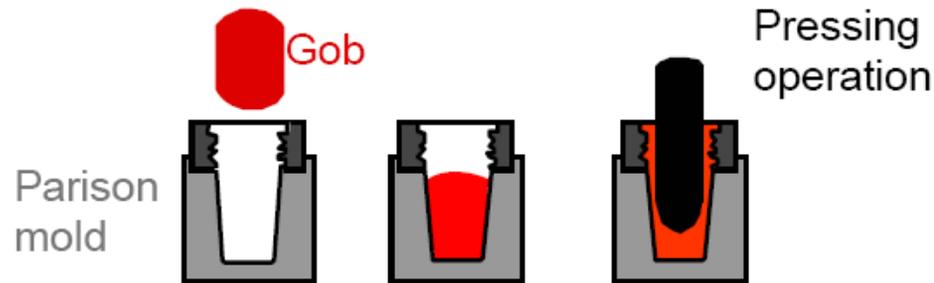
Pressing – to form shapes like plates and dishes

Blowing – used to produce objects like jars, bottles, light bulbs.

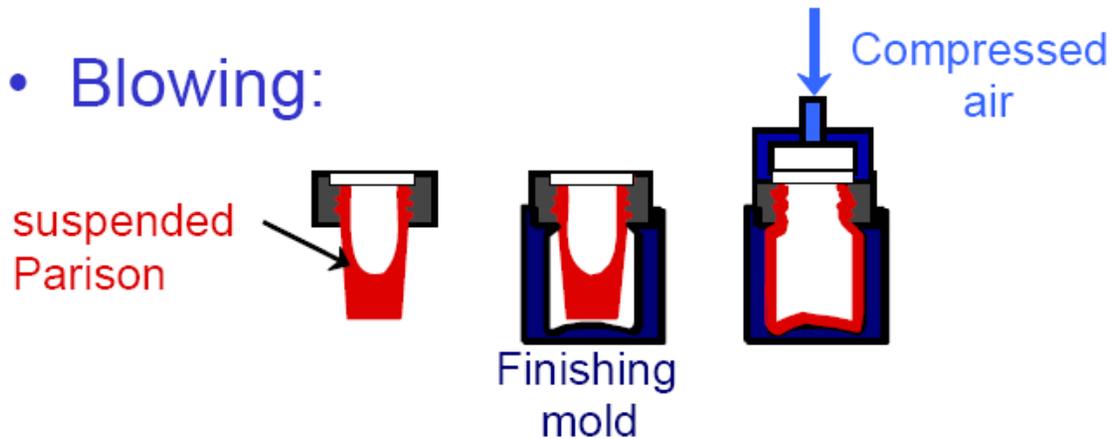
Drawing – to form lengthier objects like tubes, rods, whiskers, etc.

# Processing ceramics – Glasses

- **Pressing:** mold is steel with graphite lining; plates, dishes, cheap glasses



- **Blowing:**

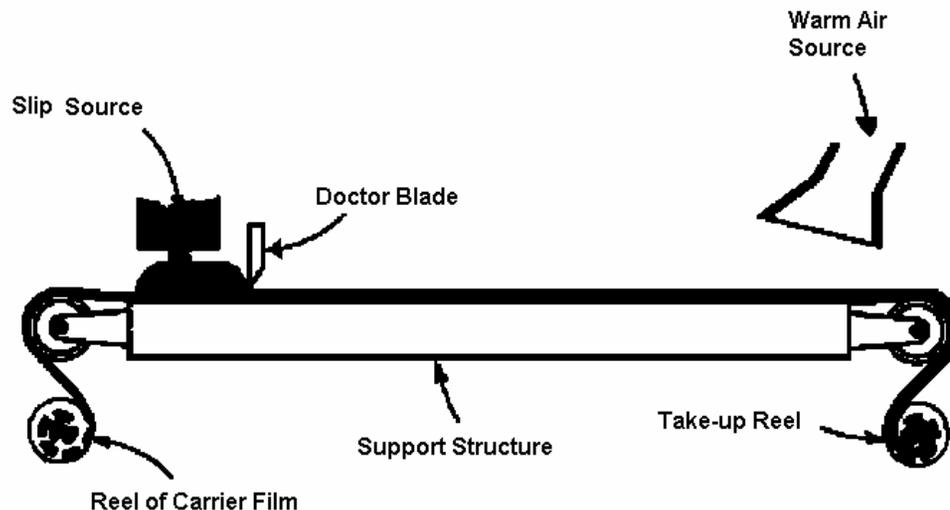


## Ceramic powder processing

- Ceramic powder processing route: synthesis of powder, followed by fabrication of green product which is then consolidated to obtain the final product.
- Synthesis of powder involves crushing, grinding, separating impurities, blending different powders.
- Green component can be manufactured in different ways: tape casting, slip casting, extrusion, injection molding and cold-/hot- compaction.
- Green component is then fired/sintered to get final product.

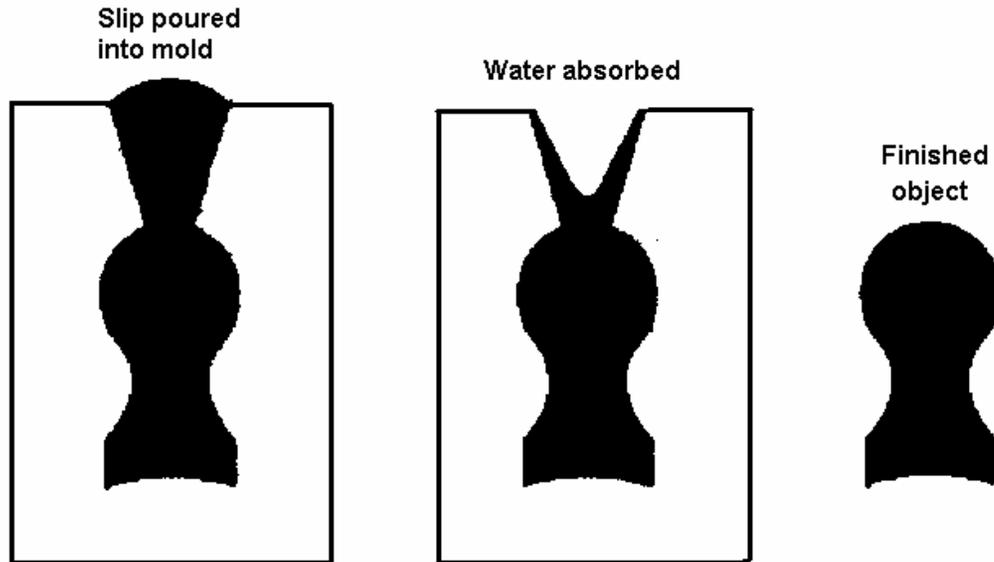
# Ceramic powder processing - Casting

- Slurry of ceramic powder is processed via casting routes – tape casting, and slip casting.
- Tape casting – also known as doctor blade process – used for making thin ceramic tapes. In this slurry of ceramic powder + binders + plasticizers is spread over plastic substrate. Tape is then dried using hot air. Later tape is subjected to binder burnout and sintering.



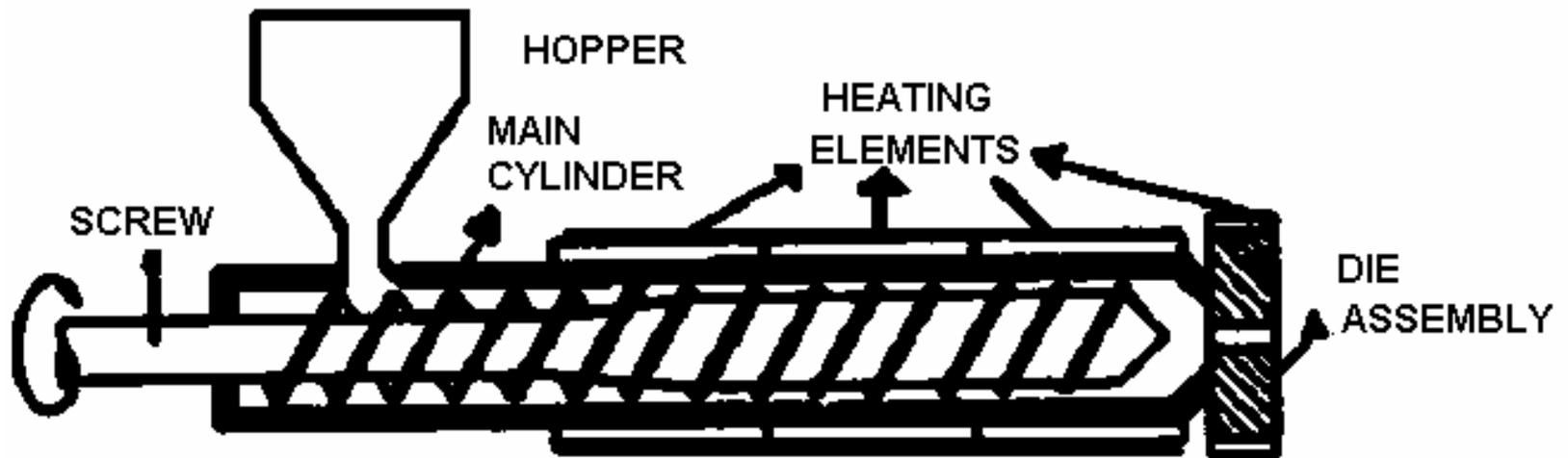
# Ceramic powder processing - Casting

- Slip casting – here aqueous slurry of ceramic powder is poured into plaster of Paris mold. As water begins to move out due to capillary action, thick mass builds along mold wall. It is possible to form solid piece by pouring more slurry.



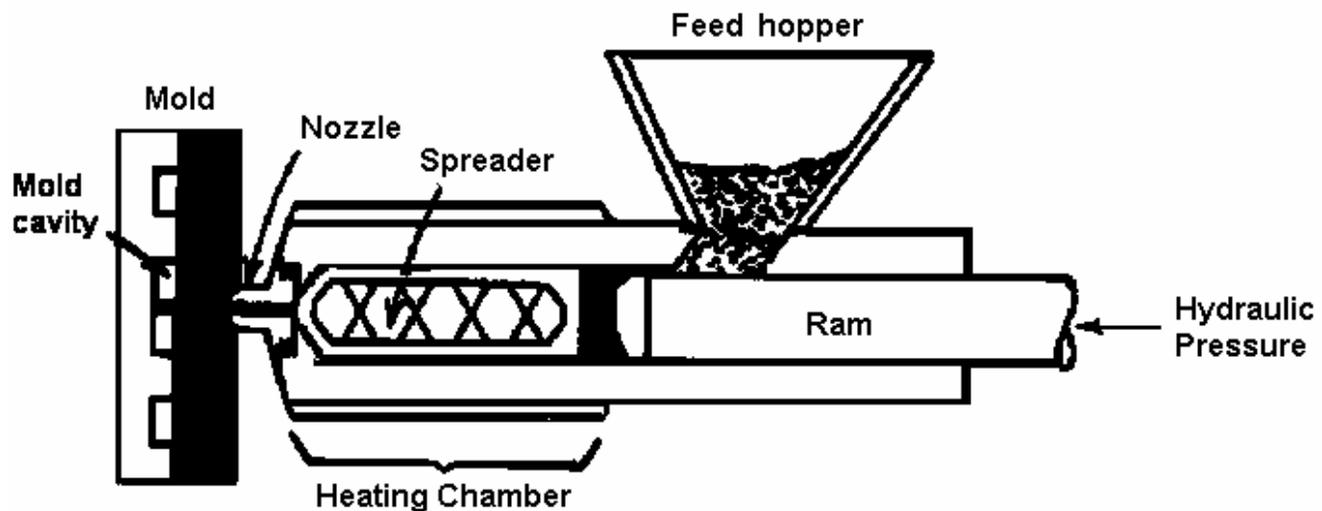
# Ceramic powder processing – Extrusion

- Extrusion – viscous mixture of ceramic particles, binder and other additives is fed through an extruder where continuous shape of green ceramic is produced. Then the product is dried and sintered.



# Ceramic powder processing –Injection molding

- Injection molding – it is similar to the process used for polymer processing. Mixture of ceramic powder, plasticizer, thermoplastic polymer, and additives is injected into die with use of a extruder. Then polymer is burnt off, before sintering rest of the ceramic shape. It is suitable for producing complex shapes.
- Extrusion and Injection molding are used to make ceramic tubes, bricks, and tiles.



## Ceramic powder processing – Compaction

- Ceramic powder is compacted to form green shapes of sufficient strength to handle and to machine.
- Basis for compaction – application of external pressure from all directions.
- In cold iso-static pressing (CIP), pressure is applied using oil/fluid, then green product is subjected to sintering.
- In hot iso-static pressing (HIP), pressure is applied at high temperatures thus compaction and sintering occurs simultaneously. It is expensive, but has certain advantages.

# Ceramic powder processing – Compaction, HIP

- HIP is used
  - when during CIP not enough strength is gained
  - almost nil porosity is the requirement
  - for Refractories and covalently bonded ceramics.
- Sintering – process of subjecting the green ceramic to elevated temperatures with the purpose of gaining mechanical integrity.
- Driving force for sintering – reduction in total surface area and thus energy.
- Diffusion (atomic- and bulk-) is responsible for growth of bonds at contact points of particles (necks). This lead to coalescence of particles, and eventual mechanical integrity.

# **Material Science**

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Module-11

## **Applications and Processing of Polymers**

## Contents

- 1) Polymer types and polymer synthesis and processing
- 2) Crystallization, melting and glass transition
- 3) Mechanical behavior of polymers
- 4) Mechanisms of deformation and strengthening of polymers

## Introduction – Polymers

- The word ‘polymer’ is originated from Greek word *meros*, which means ‘a part’.
- Polymers are primarily organic compounds, however few polymers are made of inorganic compounds.
- Characteristics of ceramics are:
  - low temperature stability
  - low hardness
  - low mechanical strength
  - high elongation under application of stress
  - low thermal and electrical conductivities
  - high sensitivity of properties to their morphology

## Classification – Polymers

- Polymers are classified in many ways. The prime classification based on their industrial usage is: plastics and elastomers.
- Plastic polymers are again classified based on their temperature dependence of their structure as follows:
  - thermoplasts and
  - thermosets

# Thermoplasts

- Plastics which softens up on heating and hardens up on cooling where the softening and hardening are totally reversible processes. Hence thermoplasts can be recycled.
- They consist of linear molecular chains bonded together by weak secondary bonds or by inter-winding.
- Cross-linking between molecular chains is absent in thermoplasts.

**E.g.:** Acrylics, PVC, Nylons, Perspex glass, etc.

# Thermosets

- Plastics which are ‘set’ under the application of heat and/or pressure. This process is not reversible, hence thermosets can not be recycled.
- They consist of 3-D network structures based on strong covalent bonds to form rigid solids. linear molecular chains bonded together by weak secondary bonds or by interwinding.
- Characterized by high modulus / rigidity / dimensional stability when compared with thermoplasts.

E.g.: Epoxies, Amino resins, some polyester resins, etc.

# Elastomers

- These polymers are known for their high elongations, which are reversible upon release of applied loads.
- They consist of coil-like molecular chains, which straightens up on application of load.
- Characterized by low modulus / rigidity / strength, but high toughness.

E.g.: natural and synthetic rubber.

# Polymer synthesis

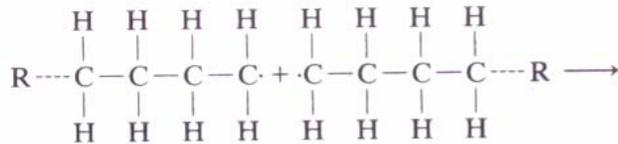
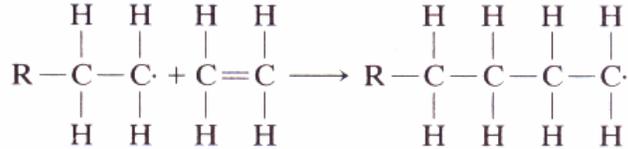
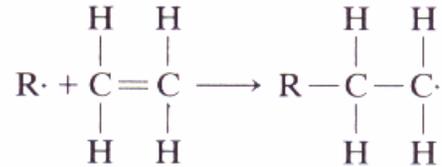
- Processing of polymers primarily limits to synthesis followed by forming.
- Polymers are synthesized by process known as polymerization.
- Polymerization is process in which multi-functional monomers are attached to form linear/3-D macro molecular chains.
- When polymerization process involves single kind of monomers i.e. in Additional polymerization, resultant macro-molecule's composition is an exact multiplication of composition of individual monomer.

# Polymer synthesis

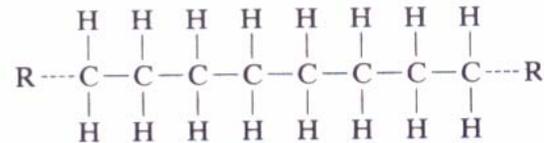
- Additional polymerization process involves three stages namely initiation, propagation and termination.
- Initiation process will be started by an initiator (e.g. benzoyl peroxide) which forms a reactive site where carbon atom of another monomer is attracted, upon which reaction site transfers to different place leading to molecular chain growth.
- As molecular chain grows longer, reaction rate decreases. However the growth process is terminated either by the combination *or* disproportionation process.

# Polymer synthesis

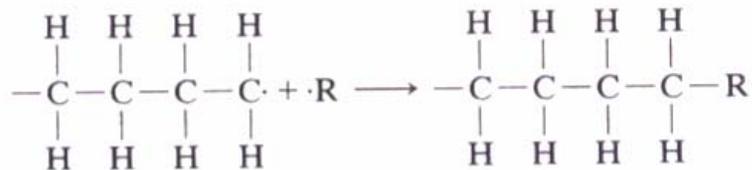
➤ E.g., polyethylene



Combination:



Disproportionation:



## Polymer synthesis

- Condensation polymerization process involves more than one monomer species. This process is also known as step growth polymerization.
- In condensation polymerization, smaller macro-molecule by-product such as water is eliminated.
- No resultant product has the chemical formula of mere one monomer.
- Repeat unit in condensation process itself is product of polymerization involving basic constituents.
- Reaction times for condensation polymerization is usually longer than those for additional polymerization.



## Degree of polymerization

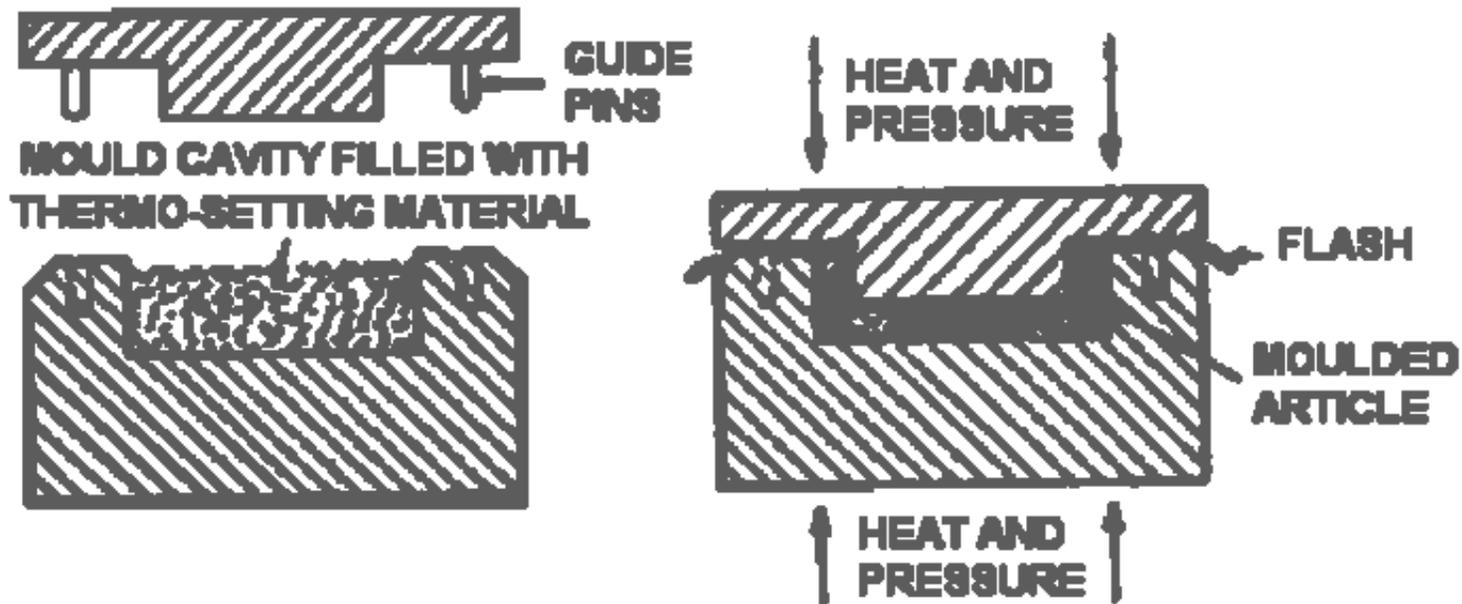
- Extant of polymerization is characterized in terms of 'degree of polymerization'.
- It is defined as number of mer units in molecular chain or ratio of average molecular weight of polymer to molecular weight of repeat unit.
- Average molecular weight is defined in two ways: *Weight average molecular weight* (based on weight fraction) and *Number average molecular weight* (based on the number fraction).
- Number average molecular weight is always smaller than the weight average molecular weight.

# Polymer forming

- Thermoplasts usually formed above their glass transition temperatures under application of pressure which ensures detailed product shape.
- Thermosets are formed in two stages – making liquid polymer and then molding it.
- Different molding techniques are employed to mold polymers –
  - compression molding
  - transfer molding
  - injection molding
  - blow molding
  - extrusion

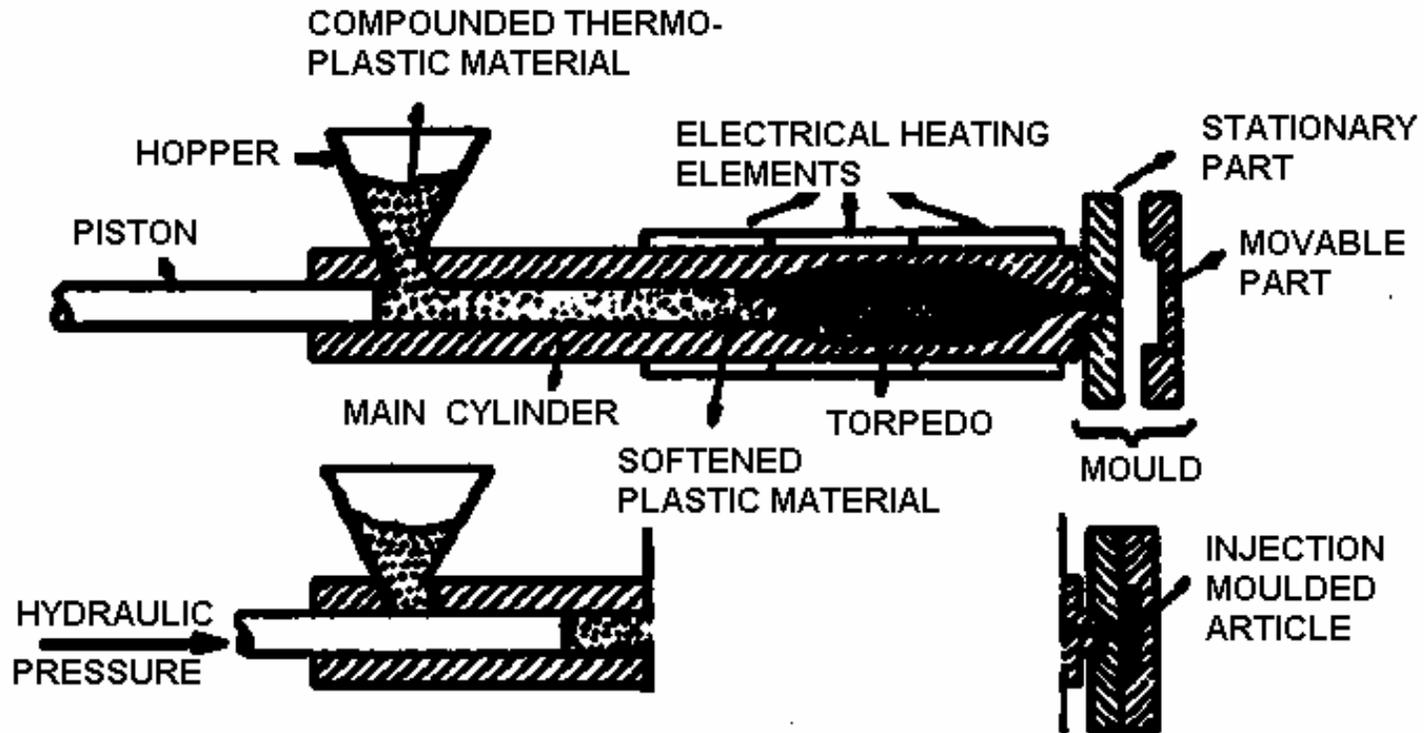
# Compression molding

- Involves placing appropriate amount of polymer with additives between heated male and female mold parts.
- After pouring polymer, mold is closed, and heat and pressure are applied, causing viscous plastic to attain the mold shape.



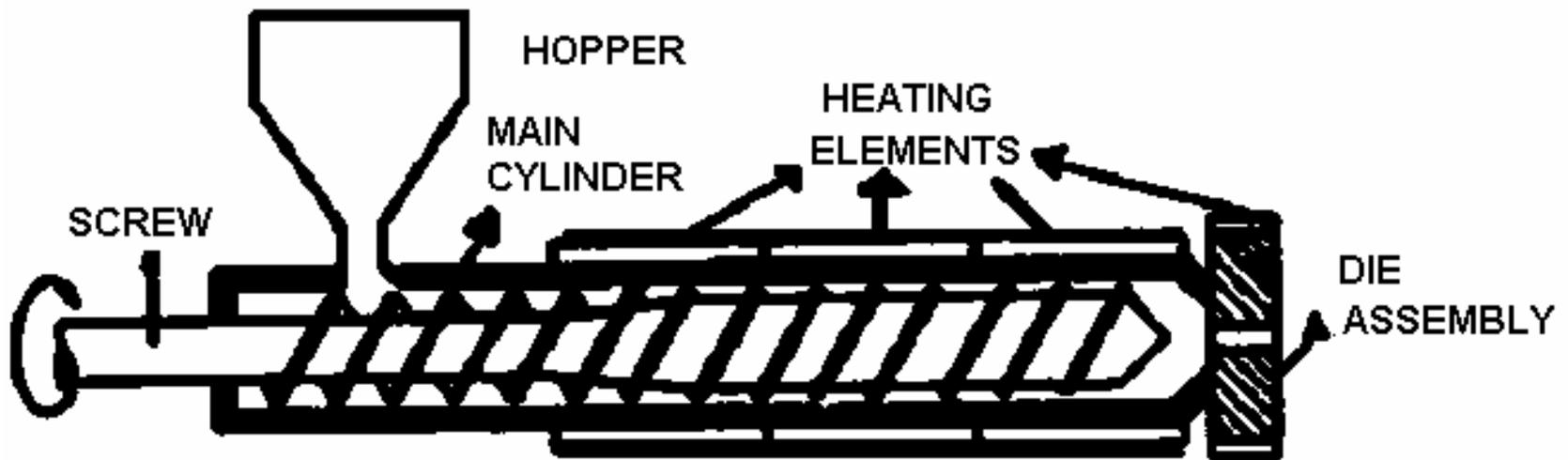
# Injection molding

- Palletized materials is fed with use of hopper into a cylinder where charge is pushed towards heating chamber where plastic material melts, and then molten plastic is impelled through nozzle into the enclosed mold cavity where product attains its shape.



# Extrusion

- Thermoplastic material is forced through a die orifice.
- This technique is especially adapted to produce continuous lengths with constant cross-section.



## Polymer forming mechanics

- Polymer forming involves melting, cooling upon which crystallization takes place. In addition, glass transition occurs in polymers.
- Crystallization rate depends on temperature and molecular weight. It decrease with increase in molecular weight.
- Polymer melting is different from that of metals as it takes place over a temperature range.
- Glass transition occurs in amorphous and semi-crystalline polymers. Upon cooling, this transformation corresponds to gradual change of liquid to rubbery material, and then rigid solid.

# Polymer forming mechanics

- Polymer melting and glass transition is heavily dependent on polymer morphology.
- Following factors has marked effect on these:
  - chain stiffness (e.g., single vs. double bonds)
  - size, shape of side groups
  - size of molecule
  - side branches, defects
  - cross-linking

# Mechanical behavior of polymers

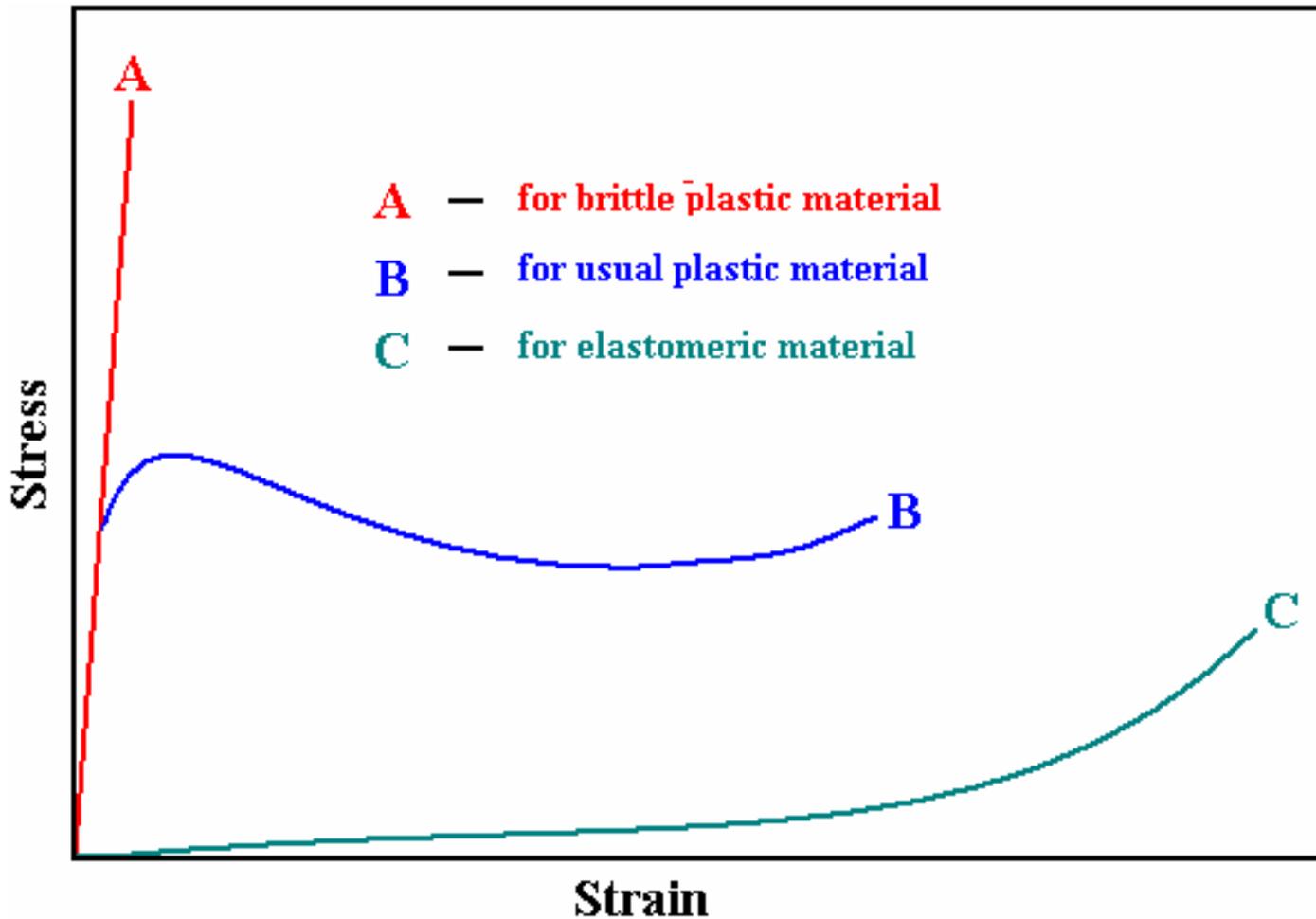
- To a large extent, mechanical behavior of polymers is similar to metals and ceramics.
- However, polymers are distinct in the sense that parameters namely temperature, strain rate, and morphology of polymers has strong influence on mechanical behavior of polymers.
- Mechanical properties of polymers change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures.

## Mechanical behavior of polymers

- Highly crystalline polymers behave in a brittle manner, whereas amorphous polymers can exhibit plastic deformation.
- Due to unique structures of cross-linked polymers, recoverable deformations up to very high strains / point of rupture are also observed with polymers (elastomers).
- Tensile modulus (modulus) and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 1000 % in some cases.

# Mechanical behavior of polymers

➤ Typical stress-strain diagram for polymers:



# Mechanisms of deformation in polymers

- Elastic deformation – bending and stretching of covalent bonds and slight adjustments of secondary van der Waals forces.
- Plastic deformation – NOT by dislocation movement, but either rotation, stretching, sliding or disentanglement of molecular chains, which may occur in several stages.
- Elastomers – simple uncoiling, and straightening of molecular chains that are highly twisted, kinked, and coiled in unstressed state. When an elastomer is stretched, causing decrease in entropy, in-turn causes the modulus of elasticity to increase with increasing temperature, which is opposite to the behavior of other materials.

## Strengthening polymers

- Polymers' resistance to deformation – strength – is influenced by many parameters.
- For thermoplasts: average molecular mass, degree of crystallization, presence of side groups, presence of polar and other specific atoms, presence of phenyl rings in main chains and addition of reinforcements.
- For thermosets, its reinforcement methods.
- Every parameter that influence the strength can be used as means of strengthening the polymers.

## Reinforcements for polymers

- Reinforcement strengthening in polymers is an important mechanism, applicable to both thermoplasts and thermosets.
- Fibers used as reinforcements are made of either glass, carbon or aramid.
- Glass fibers are two varieties – E-glass and S-glass. The later variety is costlier but offers more strength than former.
- Aramid (aromatic polyamide) fibers – also known as Kevlar – are commercially highly successful fibers. They are used with plastics in many applications including protection from ballistics, ropes, aerospace, marine, and many other industrial applications.

# Examples – Thermo plastics

- Acrylonitrile-butadiene-styrene (ABS):
  - **Characteristics:** Outstanding strength and toughness, resistance to heat distortion; good electrical properties; flammable and soluble in some organic solvents.
  - **Application:** Refrigerator lining, lawn and garden equipment, toys, highway safety devices.
- Acrylics (poly-methyl-methacrylate)
  - **Characteristics:** Outstanding light transmission and resistance to weathering; only fair mechanical properties.
  - **Application:** Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs.
- Fluorocarbons (PTFE or TFE)
  - **Characteristics:** Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260° C; relatively weak and poor cold-flow properties.
  - **Application:** Anticorrosive seals, chemical pipes and valves, bearings, anti adhesive coatings, high temperature electronic parts.

# Examples – Thermo plastics

- Polyamides (nylons)
  - **Characteristics:** Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids.
  - **Application:** Bearings, gears, cams, bushings, handles, and jacketing for wires and cables
- Polycarbonates
  - **Characteristics:** Dimensionally stable: low water absorption; transparent; very good impact resistance and ductility.
  - **Application:** Safety helmets, lenses light globes, base for photographic film
- Polyethylene
  - **Characteristics:** Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering.
  - **Application:** Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials.

# Examples – Thermo plastics

- Polypropylene
  - **Characteristics:** Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light.
  - **Application:** Sterilizable bottles, packaging film, TV cabinets, luggage
- Polystyrene
  - **Characteristics:** Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive
  - **Application:** Wall tile, battery cases, toys, indoor lighting panels, appliance housings.
- Polyester (PET or PETE)
  - **Characteristics:** One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity acids, greases, oils and solvents
  - **Application:** Magnetic recording tapes, clothing, automotive tire cords, beverage containers.

# Examples – Thermo setting polymers

- Epoxies
  - **Characteristics:** Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties.
  - **Application:** Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates.
  
- Phenolics
  - **Characteristics:** Excellent thermal stability to over 150° C; may be compounded with a large number of resins, fillers, etc.; inexpensive.
  - **Application:** Motor housing, telephones, auto distributors, electrical fixtures.

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Module-12

# **Composites**

## Contents

- 1) Particle reinforced composites, fiber reinforced composites, structural composites

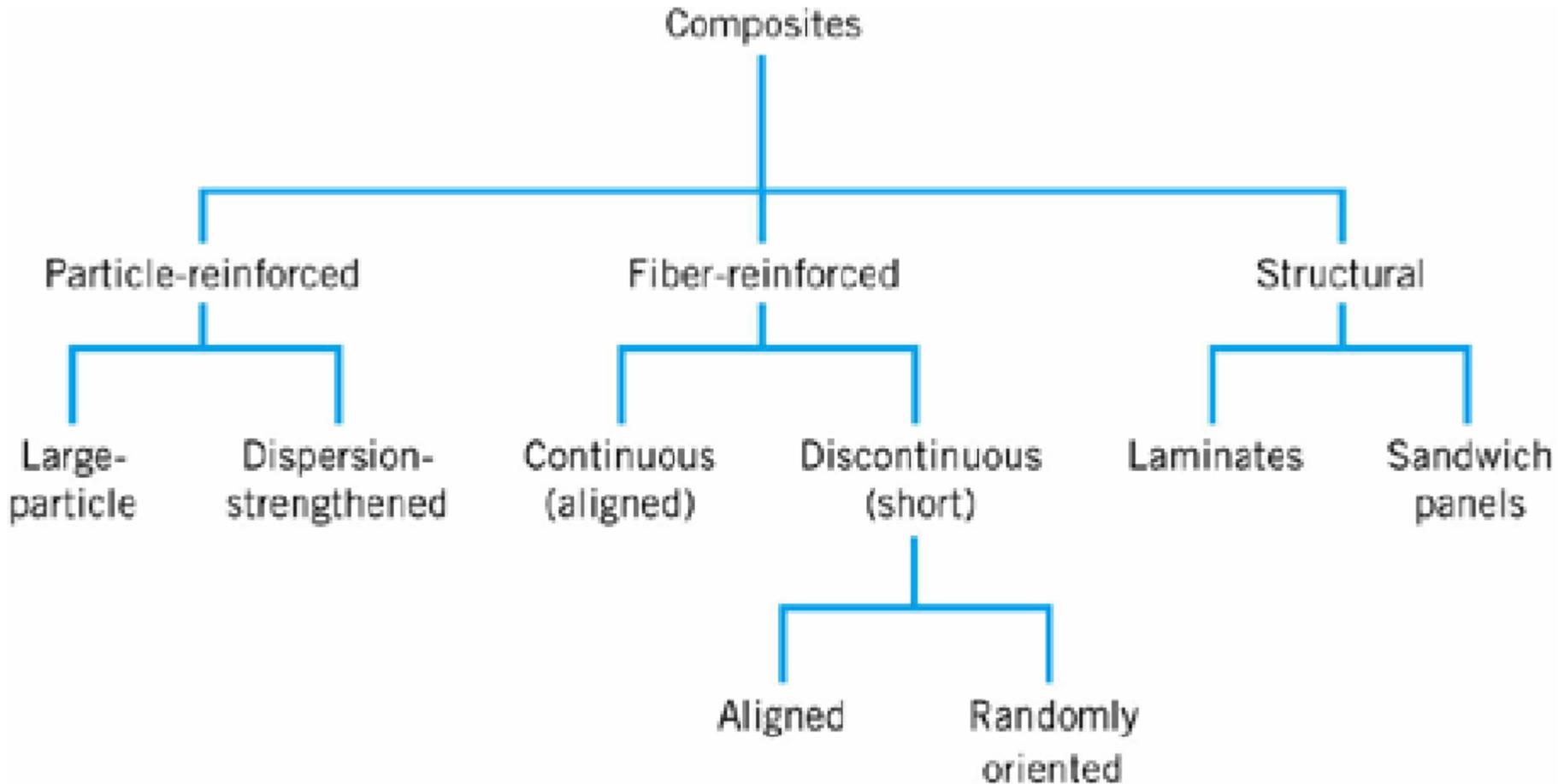
## Composite material- definition

- Conventional engineering materials are not able to serve some specific needs, especially of those related to new technologies.
- Need for materials with better properties, thus, growing.
- Combination of better properties can only be achieved with introduction of new materials.
- Composite material – can be defined as any multiphase material that is artificially made and exhibits a significant proportion of the properties of the constituent phases. The constituent phases of a composite are usually of macro sized portions, differ in form and chemical composition and essentially insoluble in each other.

# Classification of composites

- A composite is a material that consists of at least two distinct materials. Thus, number of composites are possible. For ease of recognition, they are classified based on two criteria.
- Based on type of matrix material as metal-matrix composites, polymer-matrix composites and ceramic-matrix composites.
- Based on size-and-shape dispersed phase as particle-reinforced composites, fiber-reinforced composites and structural composites.

# Classification of composites (contd...)



# Dispersion-strengthened composites

- In this composite, particles are of 0.01-0.1  $\mu\text{m}$  in size.
- Strengthening occurs as a result of dislocation motion hindrance. It is similar to that of precipitation hardening in metals.
- Matrix bears the major portion of the applied load, while dispersoids obstruct the motion of dislocations.

**E.g.:** thoria ( $\text{ThO}_2$ ) dispersed Ni-alloys (TD Ni-alloys) with high-temperature strength; SAP (sintered aluminium powder) – where aluminium matrix is dispersed with extremely small flakes of alumina ( $\text{Al}_2\text{O}_3$ ).

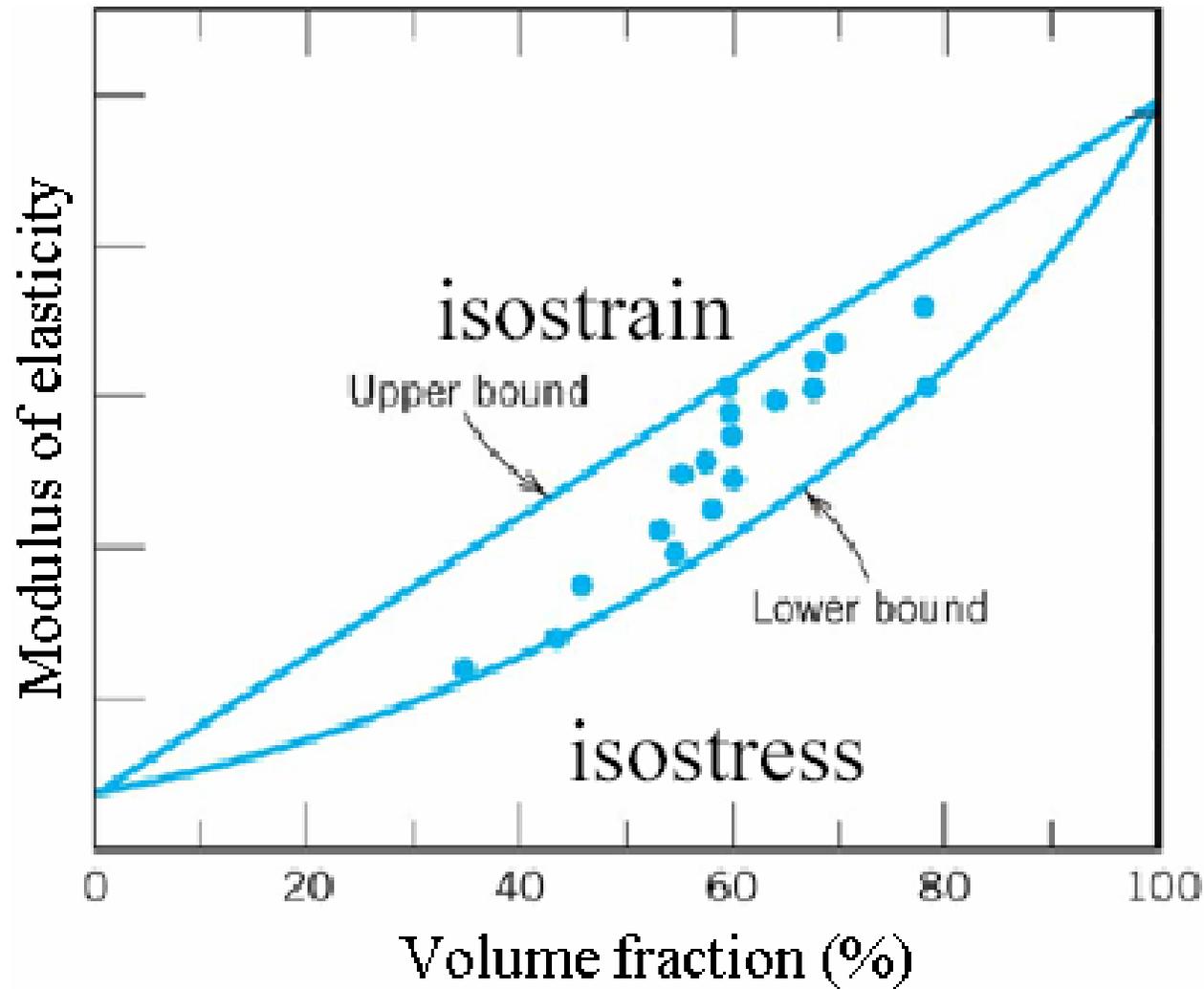
## Particulate composites

- These composites contain large number of coarse particles.
- These composites are designed to produce combination of properties rather than increase the strength.
- Mechanical properties are characterized by rule-of-mixtures.
- Elastic modulus of these composites is given by the following bounds, derived from rule-of-mixtures:

$$E_c(u) = E_m V_m + E_p V_p$$

$$E_c(l) = \frac{E_m E_p}{E_p V_m + E_m V_p}$$

## Particulate composites (contd...)



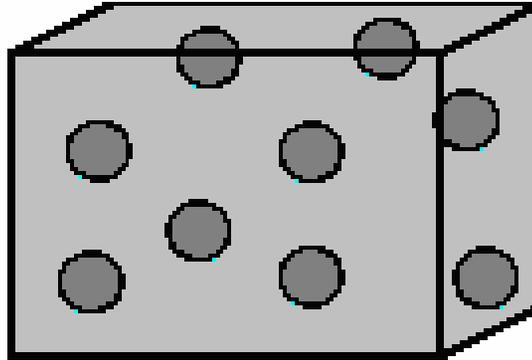


Figure 12.2. Particulate reinforced composite

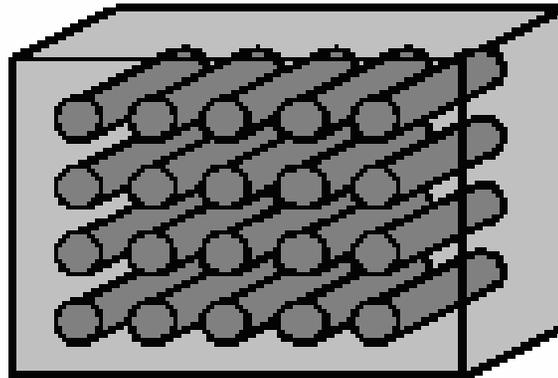


Figure 12.3 . Particulate reinforced composite

## Particulate composites (contd...)

- Particulate composites are usually made of all three conventional engineering materials, namely – metals, polymers and ceramics.

E.g.: tungsten carbide (WC) or titanium carbide (TiC) embedded cobalt or nickel based cutting tools.

Aluminium alloy castings containing dispersed SiC particles are widely used for automotive applications including pistons and brake applications.

Portland cement concrete where gravel and sand are particulates while the cement with water acts as binding matrix.

# Fiber-reinforced composites

- These composite constituents are, usually, soft matrix embedded with harder fibers.
- Matrix serves as medium to transfer applied load to fibers, which carry most of the applied load. It also protects fibers from external environment.
- Fibers are either continuous and discontinuous. Continuous fibers provide best efficiency, however discontinuous fibers are used when manufacturing economics dictate the use of a process where the fibers must be in this form.
- Properties of these composites depend on many parameters: properties of matrix and fibers, fiber length and volume fraction, their orientation, and interface bond strength.

## Fiber-reinforced composites (contd...)

- Effect of fiber length on composite strength:
- Some critical length ( $l_c$ ) is necessary for effective strengthening and stiffening of the composite material, defined:

$$l_c = \frac{\sigma_f^* d}{2\tau_c}$$

$\sigma_f^*$  – ultimate/tensile strength of the fiber,  $d$  – diameter of the fiber,  $\tau_c$  – interface bond strength.

- Fibers for which  $l \gg l_c$  (normally  $l > 15 l_c$ ) are termed as continuous, discontinuous or short fibers on the other hand.

## Fiber-reinforced composites (contd...)

- Effect of fiber orientation and length:
- For continuous fiber composites under longitudinal loading conditions: assuming isostrain conditions, strength and elastic modulus of the composite is given by

$$\sigma_c = \sigma_m \frac{A_m}{A_c} + \sigma_f \frac{A_f}{A_c}$$

$$\sigma_c = \sigma_m V_m + \sigma_f V_f$$

$$E_{cl} = E_m V_m + E_f V_f = E_m (1 - V_f) + E_f V_f$$

## Fiber-reinforced composites (contd...)

- Effect of fiber orientation and length:
- For continuous fiber composites under longitudinal loading conditions: assuming isostrain conditions, load sharing between matrix and fiber is given by

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m}$$

- For continuous fiber composites under transverse loading conditions: assuming isostress conditions, load sharing between matrix and fiber is given by

$$E_{ct} = \frac{E_m E_f}{E_f V_m + E_m V_f} = \frac{E_m E_f}{E_f (1 - V_f) + E_m V_f}$$

## Fiber-reinforced composites (contd...)

➤ Effect of fiber orientation and length:

- For continuous fiber composites, longitudinal strength is given by

$$\sigma_{cl}^* = \sigma_m' (1 - V_f) + \sigma_f^* V_f$$

- For discontinuous but aligned fiber composites, longitudinal strength is given by

when  $l > l_c$ ,

$$\sigma_{cd}^* = \sigma_f^* V_f \left(1 - \frac{l_c}{2l}\right) + \sigma_m' (1 - V_f)$$

when  $l < l_c$

$$\sigma_{cd'}^* = \frac{l\tau_c}{d} V_f + \sigma_m' (1 - V_f)$$

## Fiber-reinforced composites (contd...)

- Effect of fiber orientation and length:
- For discontinuous randomly orientated fiber composites, longitudinal strength is given by  
when  $K$  is fiber efficiency parameter.

$$E_{cl} = KE_m V_m + E_f V_f$$

# Structural composites

- Two classes of structural composites are – laminar composites and sandwich structures.
- Laminar composites – consists of layers of materials. Many laminar composites are designed to increase corrosion resistance while retaining low cost, high strength or light weight.  
*E.g.:* thin coatings, thicker protective coatings, claddings, bimetallics, laminates.
- Sandwich structures – consists of thin layers joined to core in between. Neither the filler material nor the facing material is strong or rigid, but the composite possesses both properties.

## Structural composites (contd...)

- The faces bear most of the in-plane loading and also any transverse bending stresses.
- Typical face materials include Al-alloys, fiber-reinforced plastics, titanium, steel and plywood.
- The core serves two functions – it separates the faces and resists deformations perpendicular to the face plane; provides a certain degree of shear rigidity along planes that are perpendicular to the faces.
- Typical materials for core are: foamed polymers, synthetic rubbers, inorganic cements, balsa wood.
- Sandwich structures are found in many applications like roofs, floors, walls of buildings, and in aircraft for wings, fuselage and tailplane skins.



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Module-13

**Corrosion and Degradation  
of materials**

## Contents

- 1) Corrosion of metals
- 2) Corrosion of ceramics
- 3) Degradation of polymers

# Deterioration of materials

- Conventional engineering materials are not able to serve at their full potential for long periods of time i.e. they get deteriorated during the service.
- There are many reasons for deterioration of engineering materials, like physical, chemical, mechanical, weather, etc.
- Chemical deterioration is most common in metals, and also observed to some extent in ceramics. It is known as corrosion.
- Physiochemical deterioration of polymers is known as degradation of polymers.

# Corrosion of metals

- Corrosion of metals is mainly due to electrochemical reactions.
- It is also most influenced by temperature and concentration gradients.
- Relative tendency of a metal to get corroded is presented in terms of its electro-motive force (EMF).
- Standard EMF series is suitable for easy recognition of basic elements for their relative tendency towards corrosion.
- Another usefulness of the series is to pick material for cathodic protection.

## Corrosion of metals (contd...)

- Effect of concentration on EMF is given by Nernst equation:

$$E = E_0 + \frac{0.0592}{n} \log(C_{ion})$$

where  $E_0$  – standard potential at 1M,  $n$  – valence,  $C_{ion}$  – concentration.

- Corrosion rate is presented in form of Faraday's equation:

$$w = \frac{ItM}{nF}$$

where  $I$  – current (A),  $M$  – atomic mass of the metal,  $n$  – valence of the metal ion,  $t$  – the time (secs), and  $F$  – Faraday's constant (96,500 C).

# Standard EMF series w.r.t Hydrogen

|                       | Metal   | Electrode potential, $E_0$ (V) |
|-----------------------|---|--------------------------------|
| Increasingly inert ↑  | $\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$                        | +1.420                         |
|                       | $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$    | +1.229                         |
|                       | $\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$                        | +1.200                         |
|                       | $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$                            | +0.800                         |
|                       | $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$                    | +0.771                         |
|                       | $4(\text{OH})^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ | +0.401                         |
|                       | $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$                        | +0.340                         |
|                       | $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$                          | 0.000                          |
|                       | $\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$                        | -0.126                         |
|                       | $\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$                        | -0.136                         |
| Increasingly active ↓ | $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$                        | -0.250                         |
|                       | $\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$                        | -0.277                         |
|                       | $\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$                        | -0.403                         |
|                       | $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$                        | -0.440                         |
|                       | $\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$                        | -0.744                         |
|                       | $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$                        | -0.763                         |
|                       | $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$                        | -1.662                         |
|                       | $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$                        | -2.363                         |
|                       | $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$                            | -2.714                         |
|                       | $\text{K} \rightarrow \text{K}^+ + \text{e}^-$                              | -2.924                         |
|                       | $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$                            | -3.050                         |

# Galvanic Series

## Anodic or Least Noble end

Magnesium

Magnesium Alloys

Zinc

Aluminum 5052, 3004, 3003, 1100, 6053

Cadmium

Aluminum 2117, 2017, 2024

Mild Steel (1018), Wrought Iron

Cast Iron, Low Alloy High Strength Steel

Chrome Iron (Active)

Stainless Steel, 430 Series (Active)

302, 303, 321, 347, 410, 416, Stainless Steel (Active)

Ni - Resist

316, 317, Stainless Steel (Active)

Carpenter 20cb-3 Stainless (Active)

Aluminum Bronze (Ca 687)

Hastelloy C (Active) Inconel 625 (Active) Titanium (Active)

Lead - Tin Solders

Lead

Tin

Inconel 600 (Active)

Nickel (Active)

60 Ni-15 Cr (Active)

80 Ni-20 Cr (Active)

Hastelloy B (Active)

Brasses

## Cathode Or Most Noble end

# Galvanic Series

## Anodic or Least Noble end

Copper (Ca102)  
Manganese Bronze (Ca 675), Tin Bronze (Ca903, 905)  
Silicone Bronze  
Nickel Silver  
Copper - Nickel Alloy 90-10  
Copper - Nickel Alloy 80-20  
430 Stainless Steel  
Nickel, Aluminum, Bronze (Ca 630, 632)  
Monel 400, K500  
Silver Solder  
Nickel (Passive)  
60 Ni- 15 Cr (Passive)  
Inconel 600 (Passive)  
80 Ni- 20 Cr (Passive)  
Chrome Iron (Passive)  
302, 303, 304, 321, 347, Stainless Steel (Passive)  
316, 317, Stainless Steel (Passive)  
Carpenter 20 Cb-3 Stainless (Passive), Incoloy 825nickel - Molybdeum - Chromium -  
Iron Alloy (Passive)  
Silver  
Titanium (Pass.) Hastelloy C & C276 (Passive), Inconel 625(Pass.)  
Graphite  
Zirconium  
Gold  
Platinum

## Cathode Or Most Noble end

## Forms of metal corrosion

- Corrosion of metals is classified based on the manner in which it is manifest into eight forms.
- Uniform corrosion: As name suggests, corrosion occurs over entire exposed surface. Less of detrimental. Easy to monitor and control. Is it also most common form. Painting is best counter measure for it.
- Galvanic corrosion: Occurs when two metal with different EMF are electrically connected, of which one gets corroded. Counter measures include: insulation; pairing metals with less difference between their EMF; altering the corrosive environment; tailoring the design of components *w.r.t.* their EMF.

## Forms of metal corrosion (contd...)

- Crevice corrosion: This occurs as a result of concentration gradient within a component. Corrosion occurs at the site of lower concentration. Counter measures include: welding instead of riveting; removing scales, etc.
- Pitting: Other localized corrosion. Difficult monitor and very dangerous. Material removal is minimal, but occurs in normal to surfaces. Counter measures: polishing of surface, and other common methods.
- Inter-granular corrosion: This is due to concentration difference at micro-level. Grain boundaries are inferior to grains, and more prone to corrosion. Counter measures: suitable heat treatment; addition of alloying elements; low %C in steels.



Uniform Corrosion



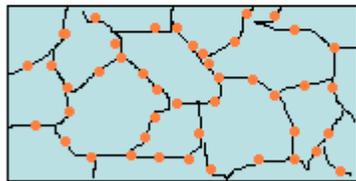
Galvanic corrosion



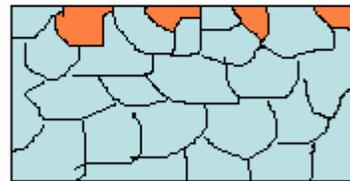
Crevice corrosion



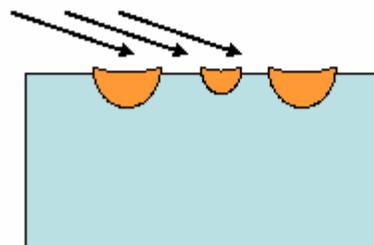
Pitting Corrosion



Inter-granular corrosion



Selective leaching



Erosion-corrosion



Stress corrosion

## Forms of metal corrosion (contd...)

- Selective leaching: Occurs in selective metals. It is selective removal of a particular metal from the component. Example – dezincification of brass. Counter measures: change of material; cathodic protection.
- Erosion-Corrosion: It is acceleration of corrosion due to mechanical actions. All metals and alloys are prone to this form of corrosion. More damaging in case of metals with passive scales. Counter measures: change of component design; clearing the fluids for particulates.
- Stress concentration: Also known as stress corrosion cracking (SCC). Result of combined action of tensile stresses and corrosive environment. Counter measures: change of environment; cathodic protection; addition of inhibitors.

# H-embrittlement and Passivity

- Hydrogen embrittlement is form of failure than corrosion, but occurs as a result of hydrogen produced during corrosion. Atomic hydrogen diffuses into crystals and inhibits dislocation motion, causing failure. Counter measures: heat treatment; removal of hydrogen source.
- Passivity: It is form protection against corrosion. It results from thin, strong adherent oxide layer formed over the surface. Usually observed in Al, Cr, Fe, Ni, Ti and their alloys. Passive layers may get damaged during mechanical vibrations, and so these metals are prone to erosion-corrosion.

# Corrosion of ceramics

- As ceramics are made of metals and non-metals, they can be considered as already corroded!
- Ceramics do get deteriorated during their service under extreme temperatures and external loads.
- Factors effecting life of ceramic components include: temperature, external loads, vibrations, environment, etc.
- Life span of ceramics can be increased by controlling the environment they are exposed to; operational loads and temperatures; altering the component design.

# Degradation of polymers

- As other engineering materials, polymers also deteriorated during their service. However, in contrast to electrochemical nature of metal corrosion, polymer degradation is of physiochemical in nature.
- As polymer structures are complex, so are the mechanisms involved in their deterioration.
- Many factors involved in degradation of polymers, like – temperature, radiation, environment, moisture, bacteria or external loads/stress.
- Polymers degrade mainly in three forms – swelling and dissolution, bond rupture, and weathering.

# Forms of polymer degradation

- Swelling and Dissolution: When exposed to humid environment, polymers get swelling due to diffused and absorbed moisture. It may also involve dissolution of polymers, hence swelling is considered as partial dissolution. Dissolution involves complete solution of polymer in solvent.
- Weathering: When exposed to outdoor weather for long periods of time, polymer may get decolorized, distort from their original shape. This may be due to many actions including radiation of the sun, oxidation, etc.

## Forms of polymer degradation (contd...)

- Bond rupture: This is main form of polymer failure. Bond rupture, also known as scission, may occur due to effects like radiation, heat energy, or chemical reactions. When polymers are exposed to certain types of radiation, which may result in broken bonds and rearrangement of atoms leads to degradation of polymers. At elevated temperatures, bonds in polymers may get weakened, leading to deterioration of polymers. Some chemical elements like oxygen, ozone can alter the chain scission rate as a result of chemical reactions. This is especially pronounced in vulcanized rubbers.

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## **Electrical properties**

## Contents

- 1) Electrical conduction
- 2) Semi conductivity - Super conductivity
- 3) Electrical conduction in ionic ceramics and polymers
- 4) Dielectric behavior
- 5) Ferroelectricity - Piezoelectricity

# Introduction

- 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.
- The electrical behaviors of engineering materials are diverse, and so are their uses in electrical applications.

# Electrical conduction

- Materials are classified based on their electrical properties as conductors, semiconductors and insulators. New to this group is super conductors.
- Electrical conductivity of a material is defined in terms of ease of charge flow through it.
- Charge that flows comprised of either electrons, ions, charged holes, and their combinations.
- Ohm's law relates the current and applied voltage:

$$V = IR$$

where      V – applied voltage (volts)

              I – current (amperes)

              R – resistance (ohms)

## Electrical conduction (contd...)

- Material's electric resistance is NOT an intrinsic-property i.e. it depends on object geometry.
- Electrical resistivity, defined as follows, is an intrinsic property, inverse of which called conductivity.

$$\rho = \frac{RA}{l}$$

A – cross sectional area

l – length of the object

$$\sigma = \frac{1}{\rho} = \frac{l}{RA}$$

- Either conductivity / resistivity can be used to classify materials.

# Classification – Electrical conductivity

- Conductivity of solid engineering material is observed to vary over 27 orders of power.
- Based on their conductivity, materials are classified as: conductors, semiconductors, and insulators.

Conductors  $> 10^7 (\Omega\text{-m})^{-1}$

Semiconductors  $10^{-6} - 10^4 (\Omega\text{-m})^{-1}$

Insulators  $< 10^{-10}(\Omega\text{-m})^{-1}$

## Conduction – Flow of charge

- Power loss due to conduction is given by

$$P = VI = I^2R$$

- When this is combined with conductivity equation,

$$\frac{I}{A} = \sigma \frac{V}{l} \Rightarrow J = \sigma E$$

- It ( $J$  – *current density*) is also expressed as

$$J = n.q.\bar{v}$$

It results in

$$\sigma = n.q.\mu$$

# Charge carriers - Conductivity

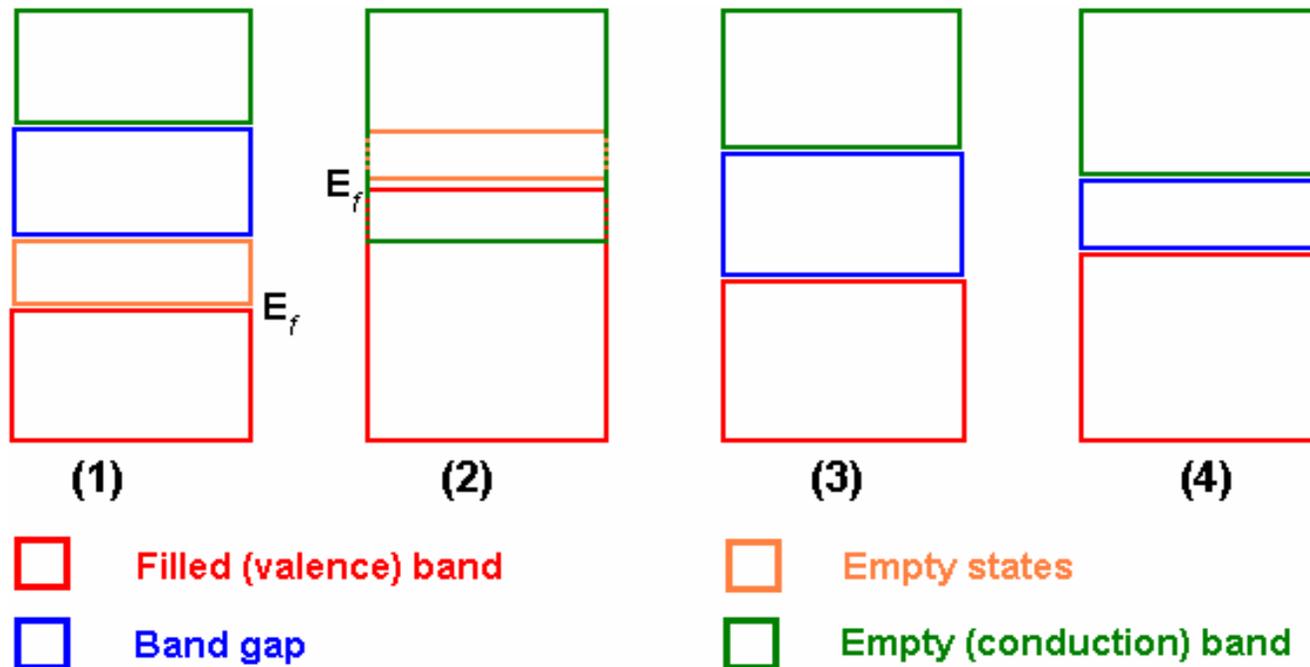
- From the last equation, electrical conductivity of a material can be controlled by (i) controlling number of charge carriers,  $n$  or (ii) controlling the mobility of the carriers,  $\mu$ .
- Mobility is important for metals or electrical conductors, whereas number of carriers is important for semi-conductors and insulators.
- for metals :  $\sigma = n_e \cdot q_e \cdot \mu_e$
- for semiconductors :  $\sigma = n \cdot q \cdot \mu_n + n \cdot q \cdot \mu_p$
- for ionic materials :  $\sigma_{total} = \sigma_{electronic} + \sigma_{ionic}$

# Genesis of electrical conduction

- It is known that electrons are prime charge carriers.
- Electrons in metals are arranged into shells and sub-shells in accordance with Pauli exclusion principle with distinct energy state/level.
- In metals many electrons will have same energy state, leading to formation of energy bands.
- The electrons not involved in bonding remain in what is called the core band, whereas the valence electrons that form the electron gas enter into the valence band. The remaining un-filled orbitals form higher-energy bands, called conduction band. It is the conduction band that gives metals and alloys the ability to freely conduct electrons.

# Energy band structures

- The energy corresponding to the highest filled state at 0 K is called the Fermi energy,  $E_f$ .
- Four types of band structures are possible at 0 K as shown in the following figure.



## Energy band structures (contd...)

- Band structures (1) and (2) are found in metals / conductors. Band structures (3) and (4) are distinguished by the size of energy band gap.
- Narrower energy band gap i.e. size  $< 2$  eV, is found in semiconductors, while the broader energy band gap i.e. size  $> 4$  eV, is found in insulators.
- Fermi energy for the last two band structures lies within the band gap near its center.
- Metals have high conductivities because of the large number of free electrons that have been excited into empty states above the Fermi energy.

## Mathiessens rule - Resistivity

- Lattice vibrations and phonon scattering play a role in disrupting the mean free path of electrons. In addition, crystalline defects and impurity atoms affect the conductivity. These scattering mechanisms act independently on one another. Thus the effective resistivity of metals can be represented as follows:

$$\rho = \rho_{thermal} + \rho_{residual}$$

- With increase of temperature, thermal vibrations increase so the resistivity, and vice versa. In the same manner, with increase of either defects or impurities, resistivity increases.
- For pure metals, the resistivity approaches zero at absolute zero temperature.

# Superconductivity

- Some metals lose all resistivity abruptly and completely at some low temperatures, above 0 K. - phenomenon is called *superconductivity*, and the materials that exhibit it are called *superconductors*.
- The temperature at which the resistivity vanishes is called the *critical transition temperature,  $T_c$* .
- Many metals, solid-solution alloys, some ceramics and intermetallic compounds exhibit superconductivity.  
*Ex.:* Ti, V, Zn, W, Al, Hg, NbTi, Nb<sub>3</sub>Sn, MgB<sub>2</sub>, La-Sr-Cu oxide, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, carbon nanotubes, etc.
- BCS (Bardeen, Cooper and Schrieffer) theory explains that the super conductivity is caused by electron-lattice interaction and that the superconducting electrons consist of paired ordinary electrons called a *Cooper pair*.

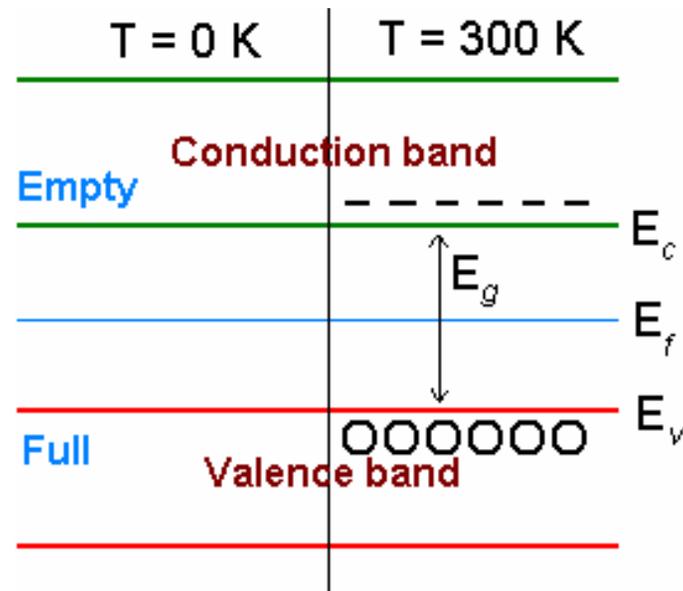
# Semiconductivity

- Electrical properties of semiconductors are unique, in the sense that their electrical properties are extremely sensitive to even minute concentrations of impurities.
- Two kinds of semiconductors – *intrinsic* and *extrinsic*.
- For intrinsic semiconductors, their electrical behavior is based on inherent electronic structure of the pure material.
- On the other hand, if the electrical properties are dominated by impurities, they are called extrinsic semiconductors.
- In semiconductors, the valence and conduction bands do not overlap as in metals, but they possess enough electrons in the valence band those can be promoted to the conduction band at a certain temperature.

# Intrinsic semiconduction

- Conduction is due to promoted electrons, and charged hole left behind by these electrons.
- This occurs at elevated temperatures. At still higher temperatures, the concentration of thermally excited electrons in the conduction band becomes so high that the semiconductor behaves more like a metal.

Ex.: Si, Ge, Sn, Pb, etc.



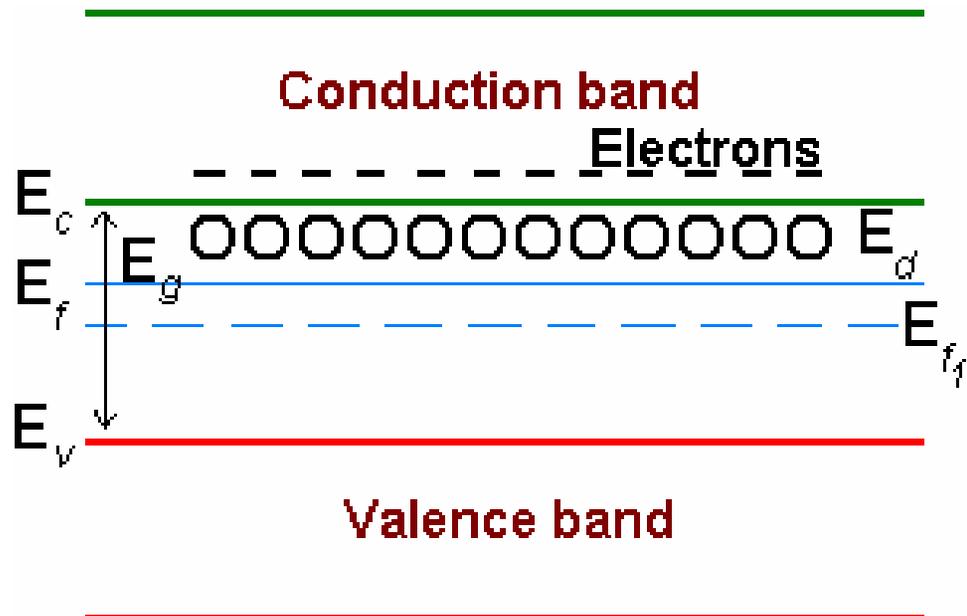
## Extrinsic semiconduction

- The charge carrier density can also be increased by adding impurities of either higher or lower valence to intrinsic semiconductors. This addition of impurities is known as doping, and impure atoms in the element are called donor atoms.
- *n*-type semiconductor uses higher valence elements as donors, while *p*-type semiconductors uses lower valence elements.
- Donor atoms increases number of charge carriers in form negatively charged electrons (*n*-type) *or* positively charged holes (*p*-type).
- Doping also results in altering the Fermi energy level, and its exact position ( $E_f$ ) is a function of both temperature and donor concentration.

## *n*-type semiconduction

- Fermi level ( $E_f$ ) of *n*-type extrinsic semiconductor is higher than that of intrinsic semiconductor ( $E_{fi}$ ) i.e. it shifted upward in the band gap, to within the vicinity of the donor state.

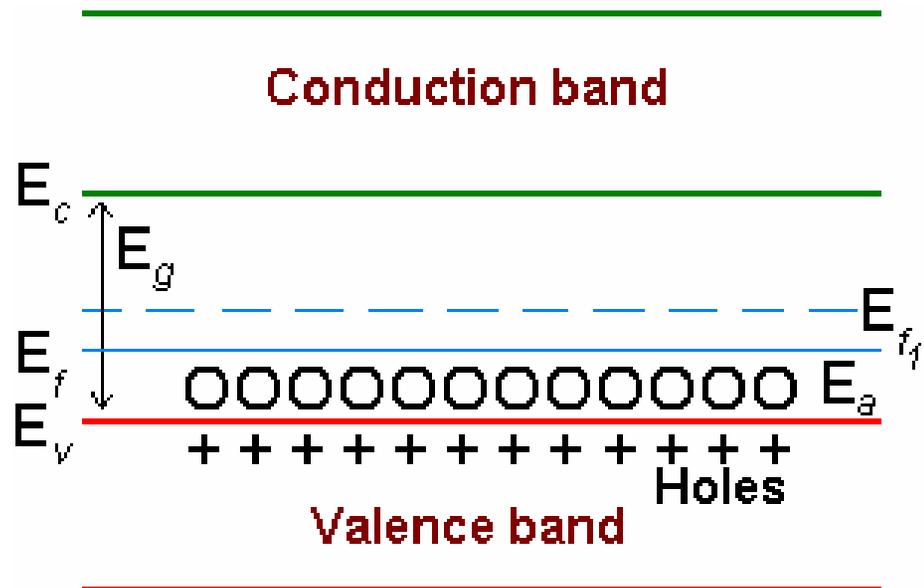
**Ex.:** Pentavalent substitutional atoms like P, As, or Sb are used as donors.



## *p*-type semiconduction

- Fermi level ( $E_f$ ) of *p*-type extrinsic semiconductor is lower than that of intrinsic semiconductor ( $E_{f1}$ ) i.e. it shifted downward in the band gap, to within the vicinity of the donor state.

**Ex.:** Trivalent substitutional atoms like B, Al, Ga, In, Th are used as donors.



# Electrical conduction in ionic ceramics

- Charge can also be conducted via ions - called ionic conduction. This may occur either in conjunction with or separately from electronic conduction.
- Several types of compounds show exceptionally high ionic conductivity.
- Such phases fall into three broad categories: halide and chalcogenides of silver and copper; oxides with  $\beta$ -alumina structure; and oxides of fluorite structure.  
**Ex.:**  $\text{La}_2\text{CuO}_4$  ( $T_c = 30$  K), YBC compounds – yttrium doped perovskite structure,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 92$  K).
- By properly engineering the point defects, it is possible to convert ceramics into semiconductors. **Ex.:** Indium tin oxide (ITO).

# Electrical conduction in polymers

- Polymers are, in general, insulators. They can be made conductors in two ways: (1) introducing an additive to the polymer to improve conductivity, and (2) creating polymers with inherent conductivity.
- (1) Adding ionic compound *or* Introducing conductive fillers such as carbon black.
- (2) Inherent conductivity by doping.  
*Ex.:* polyparaphynylene, polypyrrole, polyaniline, acetal polymers.
- Some other polymers such as polyphthaocyanine can be cross-linked by special curing processes to raise its conductivity.

# Dielectric behavior concept

➤ Dielectric is a material separating two charged bodies. For a material to be a good dielectric, it must be an electrical insulator. Dielectric materials are used in capacitors, devices used to store the electric energy.

➤ Energy stored,  $Q$ , between two plates having area,  $A$ , charged by voltage,  $V$ , separated at a distance,  $l$ , in vacuum is given by

$$Q = CV \quad C = \epsilon_0 \frac{A}{l}$$

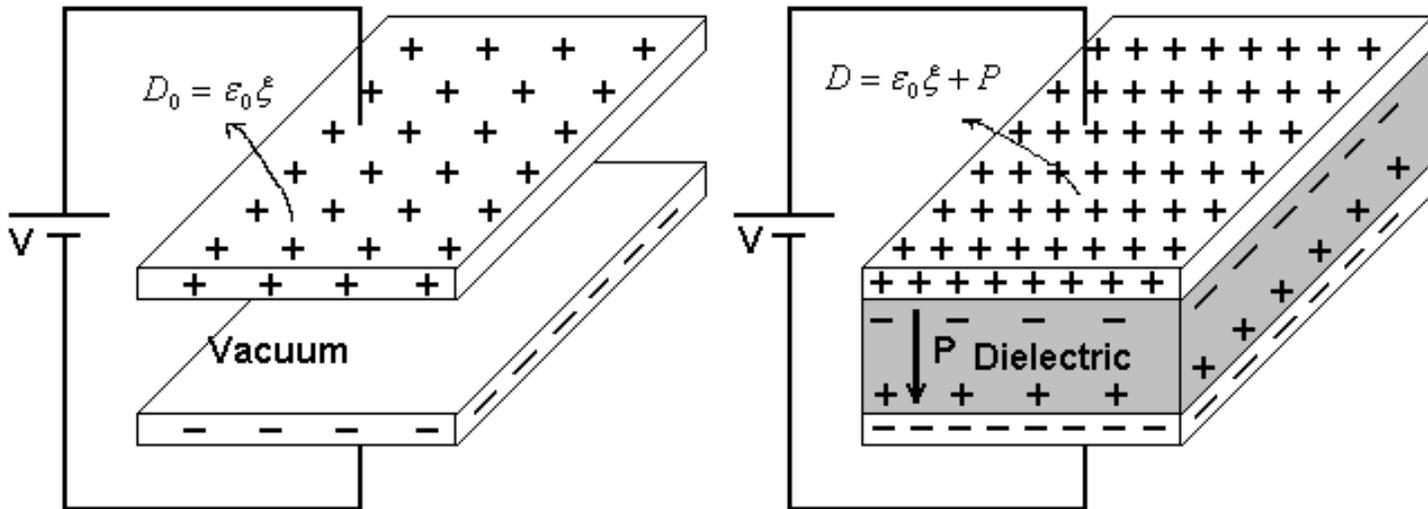
where  $\epsilon_0$  – permittivity of vacuum ( $8.85 \times 10^{-12}$  F/m)

➤ For a dielectric material,  $\epsilon = \epsilon_r \epsilon_0$

➤  $\epsilon_r$  value is always greater than '1', as a result of polarization.

# Capacitor concept

- Polarization ( $P$ ) is orientation of permanent *or* induced dipoles under externally applied electric field.
- It results in charge density increase above that for a vacuum because of the presence of the dielectric material.
- Surface charge density for a capacitor  $D = \epsilon\xi = \epsilon_0\xi + P$



# Polarization

- Four types of polarization: electronic, ionic (atomic), orientation, and space charge (interfacial).
- Electronic polarization arises because the center of the electron cloud around a nucleus is displaced under an applied electric field.
- Ionic polarization occurs in ionic materials because an applied field acts to displace cations in the direction of the applied field while displacing anions in a direction opposite to the applied field.
- Orientation polarization can occur in materials that possess permanent electric dipole moments. These permanent dipoles tend to become aligned with the applied electric field, but entropy and thermal effects tend to counter this alignment, thus it is highly temperature dependent.
- Space charge polarization results from the accumulation of charge at structural interfaces in heterogeneous materials. Such polarization occurs when one of the phases has a much higher resistivity than the other.

## Power loss

- During the use, polarization subjected to an alternating electric field depends upon the ease with which the permanent or induced dipoles can reverse their alignment.
- The time required for dipole reversal is called the *relaxation time*, and its reciprocal is called the *relaxation frequency*.
- As the frequency of the applied electric field approached the relaxation frequency, the polarization response increasingly lags behind the applied field. The reorientation of each type of dipole is opposed by internal friction, which leads to heating in the sample and power loss.
- The power loss depends on the degree to which the polarization lags behind the electric field. This is also called *dielectric loss*, and a low dielectric loss is desired at the frequency of utilization.

# Dielectric strength

- At high enough frequencies, the dielectric will experience electrical breakdown initiated by the field-induced excitation of a number of electrons into the conduction band, and the insulator become a conductor. The magnitude of the electric field required to cause dielectric breakdown is called the *dielectric strength* or *breakdown strength*.
- Many ceramics and polymers are utilized as insulators and in capacitors. For example: glass, porcelain, stealite, mica. These have dielectric constants within the range of 6-10. Typical applications: electrical insulation, switch bases, light receptacles.
- Dielectric constant for most polymers lies in the range of 2-5, less than that for ceramics, since the later exhibit greater dipole moments. Typical applications: insulation for wires, cables, motors, generators, some capacitors.

# Ferro-electricity

- Ferro-electricity is defined as the spontaneous alignment of electric dipoles by their mutual interaction in the absence of an applied electric field.
- It arises from the fact that the local field increases in proportion to the polarization. Thus, ferro-electric materials must possess permanent dipoles.  
**Ex.:** BaTiO<sub>3</sub>, Rochelle salt (NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.4H<sub>2</sub>O), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), potassium niobate (KNbO<sub>3</sub>).
- These materials have extremely high dielectric constants at relatively low applied field frequencies. Thus, capacitors made from ferro-electric materials are smaller than capacitors made of other dielectric materials.

# Piezo-electricity

- Piezo-electricity, *or* pressure electricity, is defined as polarization induced by the application of external force.
  - Thus by reversing the direction of external force, direction of the field can be reversed i.e. the application of an external electric field alters the net dipole length and causes a dimensional change.
  - Hence piezo-electric materials are useful as transducers – devices that convert mechanical stress into electrical energy and vice versa.
  - Application for these materials includes microphones, ultrasonic generators, sonar detectors, and mechanical strain gauges.
- Ex.:** Barium titanate, lead titanate, lead zirconate ( $\text{PbZrO}_3$ ), ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), and quartz.

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## **Thermal properties**

## Contents

- 1) Heat capacity
- 2) Thermal expansion
- 3) Thermal conductivity
- 4) Thermal stresses

# Introduction

- 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.
- The thermal properties of engineering materials are diverse, and so are their uses in different applications.

# Heat capacity

- A solid material's potential energy is stored as its heat energy.
- Temperature of a solid is a measure its potential energy.
- External energy required to increase temperature of a solid mass is known as the material's *heat capacity*. it is defined as its ability to absorb heat energy.

$$C = \frac{dQ}{dT}$$

- Heat capacity has units as J/mol-K *or* Cal/mol-K.
- Heat capacity is not an intrinsic property i.e. it changes with material volume/mass.

## Specific heat

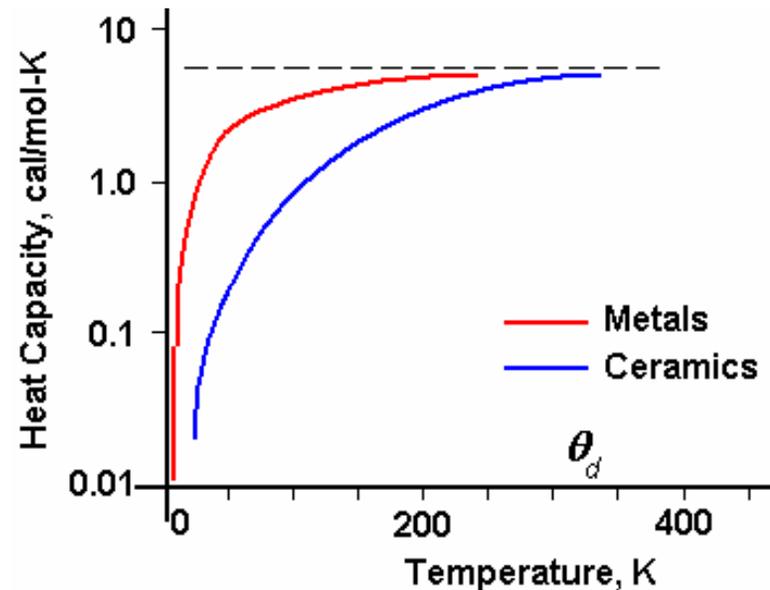
- For comparison of different materials, heat capacity has been rationalized.
- *Specific heat* is heat capacity per unit mass. It has units as J/kg-K or Cal/kg-K.
- With increase of heat energy, dimensional changes may occur. Hence, two heat capacities are usually defined.
- Heat capacity at constant pressure,  $C_p$ , is always higher than heat capacity at constant volume,  $C_v$ .
- $C_p$  is ONLY marginally higher than  $C_v$ .
- Heat is absorbed through different mechanisms: lattice vibrations and electronic contribution.

# Heat capacity

- At low temperatures, vibrational heat contribution of heat capacity varies with temperature as follows:

$$C_v = AT^3$$

- The above relation is not valid above a specific temperature known as *Debye temperature*. The saturation value is approximately equal to  $3R$ .



# Thermal expansion

- Increase in temperature may cause dimensional changes.
- Linear *coefficient of thermal expansion* ( $\alpha$ ) defined as the change in the dimensions of the material per unit length.

$$\alpha = \frac{l_f - l_0}{l_0(T_f - T_0)} = \frac{\Delta l}{l_0 \Delta T} = \frac{\varepsilon}{\Delta T}$$

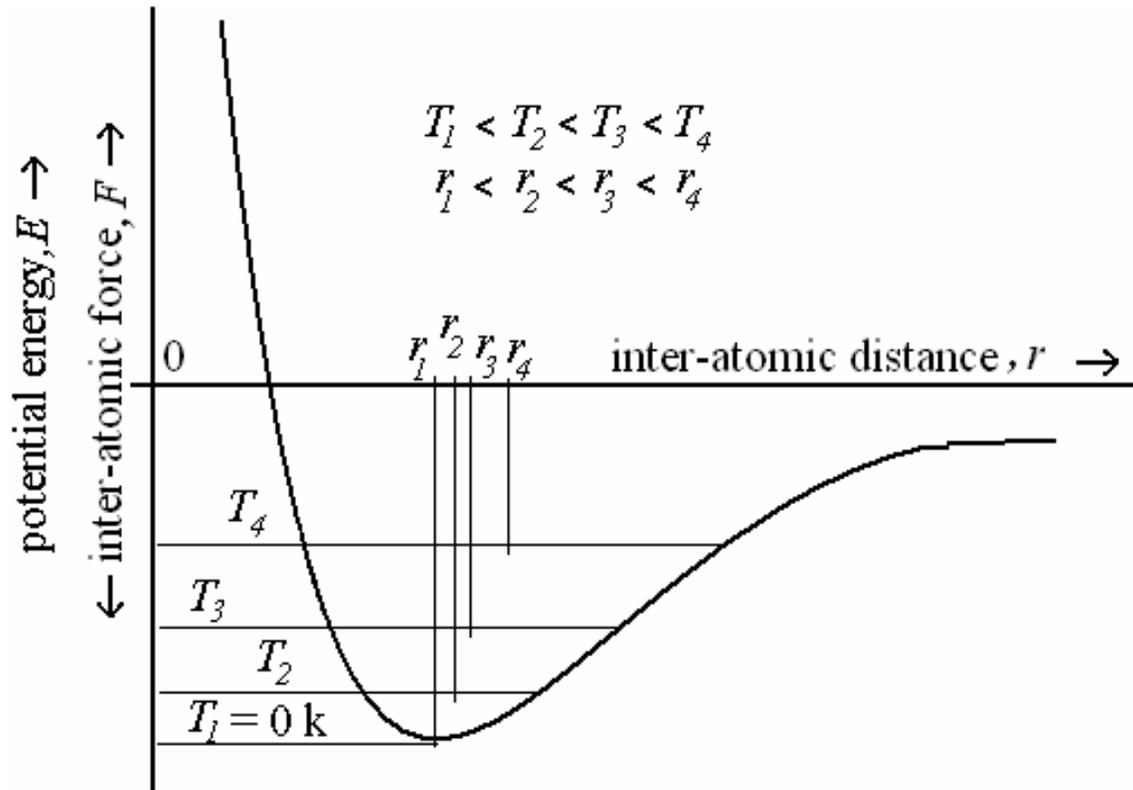
- $\alpha$  has units as  $(^\circ\text{C})^{-1}$ .

- $\alpha$  values:

|              |                         |
|--------------|-------------------------|
| for metals   | $5-25 \times 10^{-6}$   |
| for ceramics | $0.5-15 \times 10^{-6}$ |
| for polymers | $50-400 \times 10^{-6}$ |

# Thermal expansion (contd...)

- Changes in dimensions with temperature are due to change in inter-atomic distance, rather than increase in vibrational amplitude.



## Thermal shock

- If the dimensional changes in a material are not uniform, that may lead to fracture of brittle materials like ceramics. It is known as *thermal shock*.
- The capacity of a material to withstand thermal shock is defined as *thermal shock resistance*, TRS.

$$TSR \cong \frac{\sigma_f k}{E \alpha}$$

- Thermal shock behavior is affected by several factors: thermal expansion coefficient – a low value is desired; thermal conductivity – a high value is desired; elastic modulus – low value is desired; fracture strength – high value is desired; phase transformations.

## Thermal shock (contd...)

- Thermal shock may be prevented by altering external conditions to the degree that cooling or heating rates are reduced and temperature gradients across the material are minimized.
- Thermal shock is usually not a problem in most metals because metals normally have sufficient ductility to permit deformation rather than fracture.
- However, it is more of a problem in ceramics and glass materials. It is often necessary to remove thermal stresses in ceramics to improve their mechanical strength. This is usually accomplished by an annealing treatment.

# Thermal conductivity

- *Thermal conductivity* is ability of a material to transport heat energy through it from high temperature region to low temperature region.
- Heat energy transported through a body with thermal conductivity  $k$  is

$$Q = kA \frac{\Delta T}{\Delta l}$$

- It is a microstructure sensitive property.
- It has units as W/m.K.
- Its value range
  - for metals 20-400
  - for ceramics 2-50
  - for polymers order of 0.3

# Mechanisms - Thermal conductivity

- Heat is transported in two ways – electronic contribution, vibrational (phonon) contribution.
- In metals, electronic contribution is very high. Thus metals have higher thermal conductivities. It is same as electrical conduction. Both conductivities are related through Wiedemann-Franz law:

$$\frac{k}{\sigma T} = L$$

where L – Lorentz constant ( $5.5 \times 10^{-9}$  cal.ohm/sec.K<sup>2</sup>)

- As different contributions to conduction varies with temperature, the above relation is valid to a limited extension for many metals.

## Mechanisms - Thermal conductivity (contd...)

- With increase in temperature, both number of carrier electrons and contribution of lattice vibrations increase. Thus thermal conductivity of a metal is expected to increase.
- However, because of greater lattice vibrations, electron mobility decreases.
- The combined effect of these factors leads to very different behavior for different metals.

**Eg.:** thermal conductivity of iron initially decreases then increases slightly; thermal conductivity decreases with increase in temperature for aluminium; while it increases for platinum

## Thermal stresses

- Stresses due to change in temperature or due to temperature gradient are termed as *thermal stresses*.

$$\sigma_{thermal} = \alpha E \Delta T$$

- Thermal stresses in a constrained body will be of compressive nature if it is heated, and vice versa.
- Engineering materials can be tailored using multi-phase constituents so that the overall material can show a zero thermal expansion coefficient.

**Eg.:** Zerodur – a glass-ceramic material that consists of 70-80% crystalline quartz, and the remaining as glassy phase.

Sodium-zirconium-phosphate (NZP) have a near-zero thermal expansion coefficient.

