

Module-1

# Introduction

## Contents

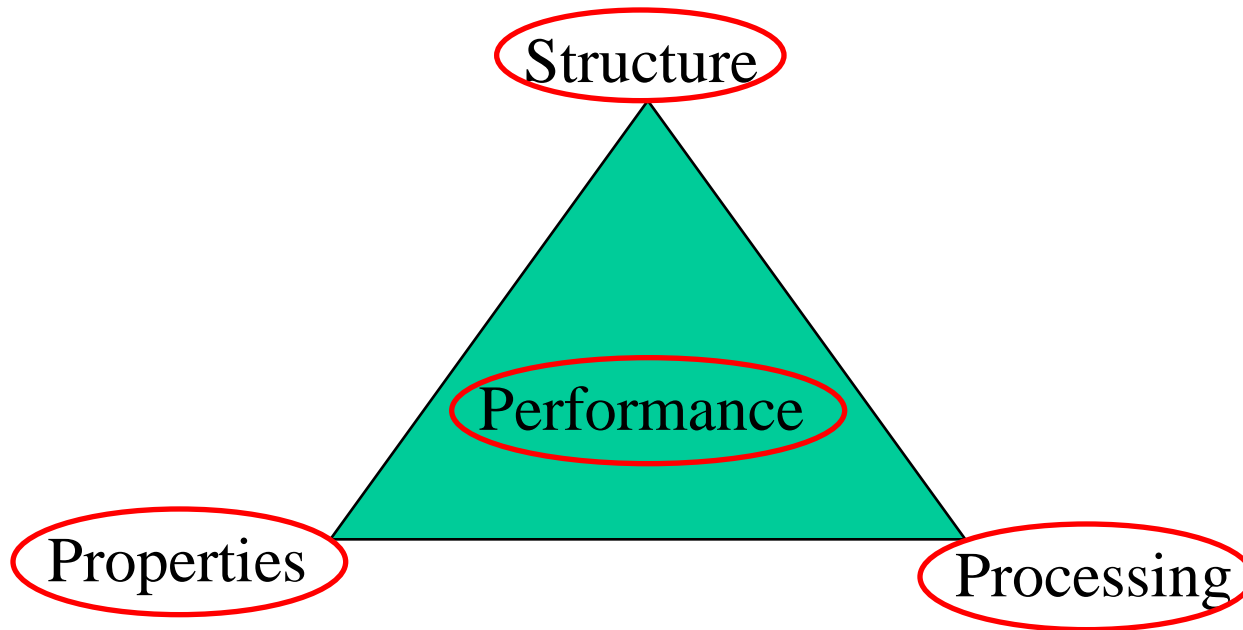
- 1) Historic perspective and Materials Science
- 2) Why study properties of materials,  
Classification of materials
- 3) Advanced materials, Future materials and  
Modern materials' needs

# 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 idle 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 luster. 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, ceramics 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.

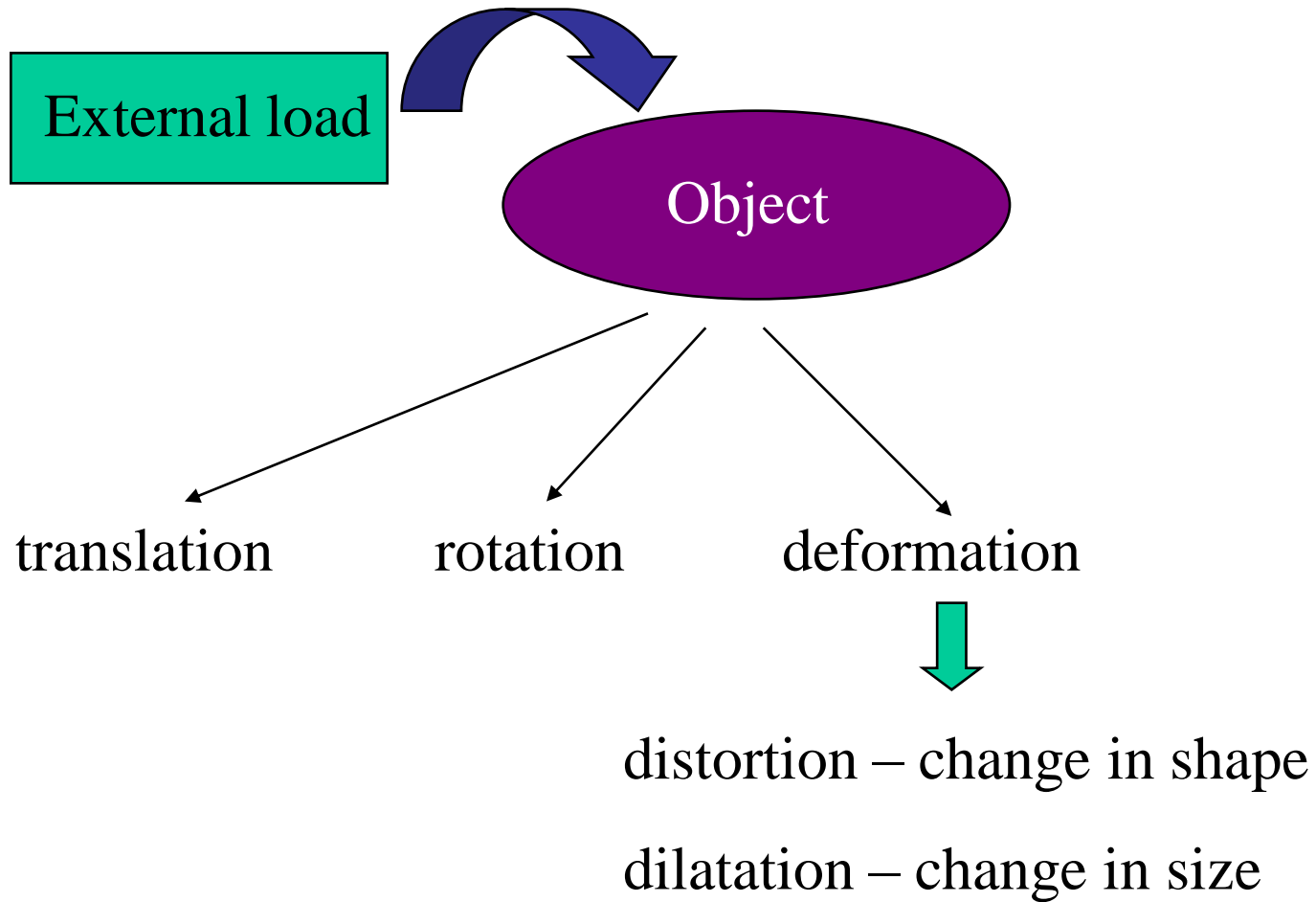
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# **Mechanical Properties of Metals**

## 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),

time dependent –

**creep** (under load),

**elastic aftereffect** (after removal of 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.

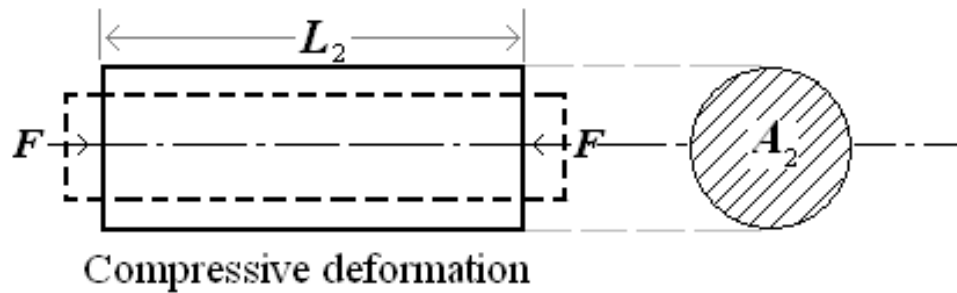
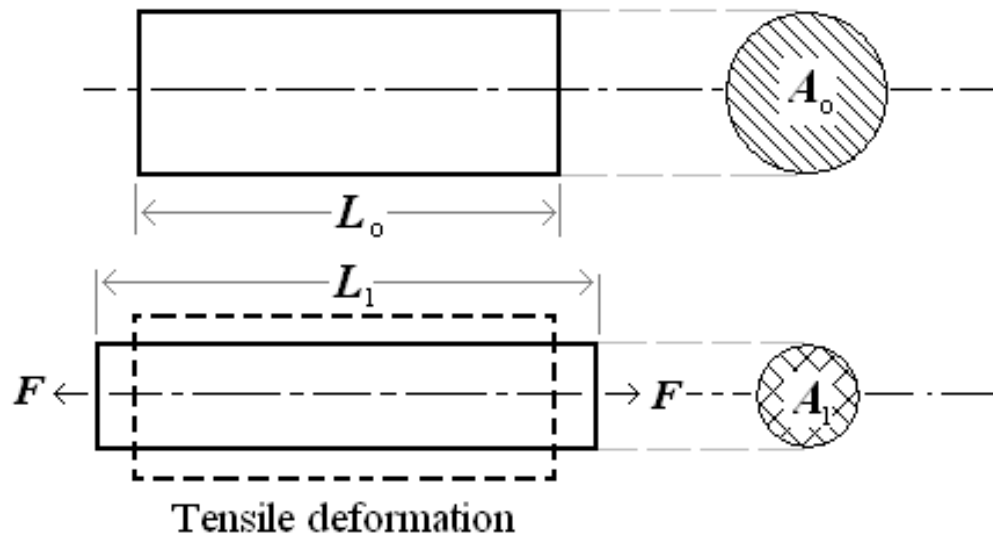
➤ True strain:

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

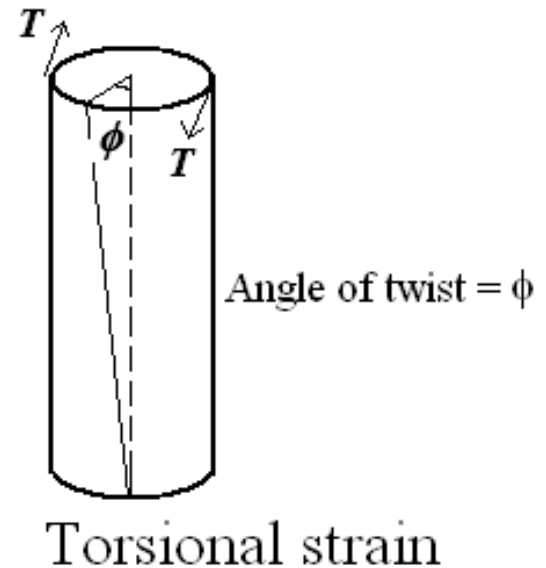
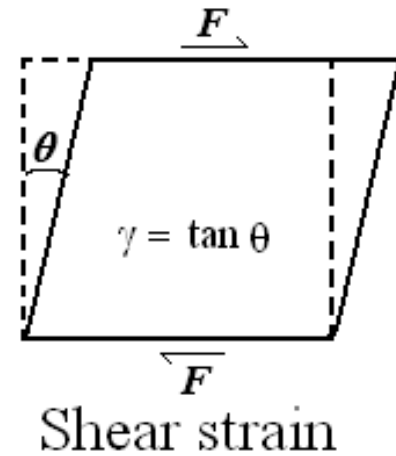
➤ True stress:

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

## Different loads – Strains



Linear strains



## 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*,  $E$ .

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

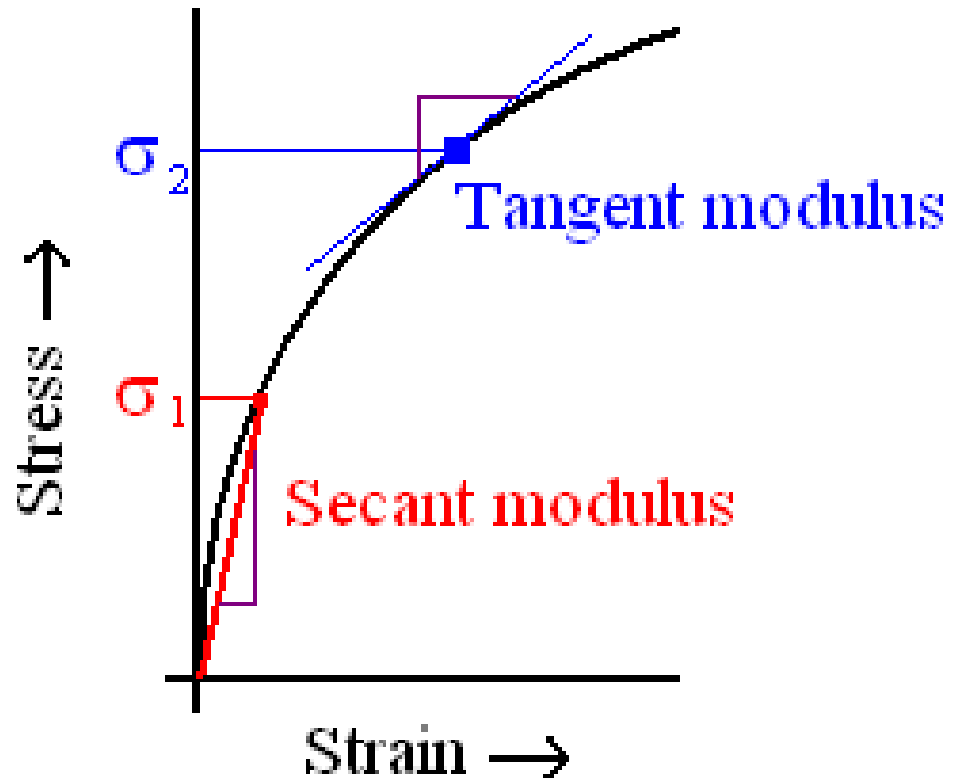
- Non-linear stress-strain relation is applicable for materials.  
E.g.: rubber.

## 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 moduli 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 moduli are not isotropic.
- For a polycrystalline material, it is considered as isotropic.
- Elastic moduli 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.

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

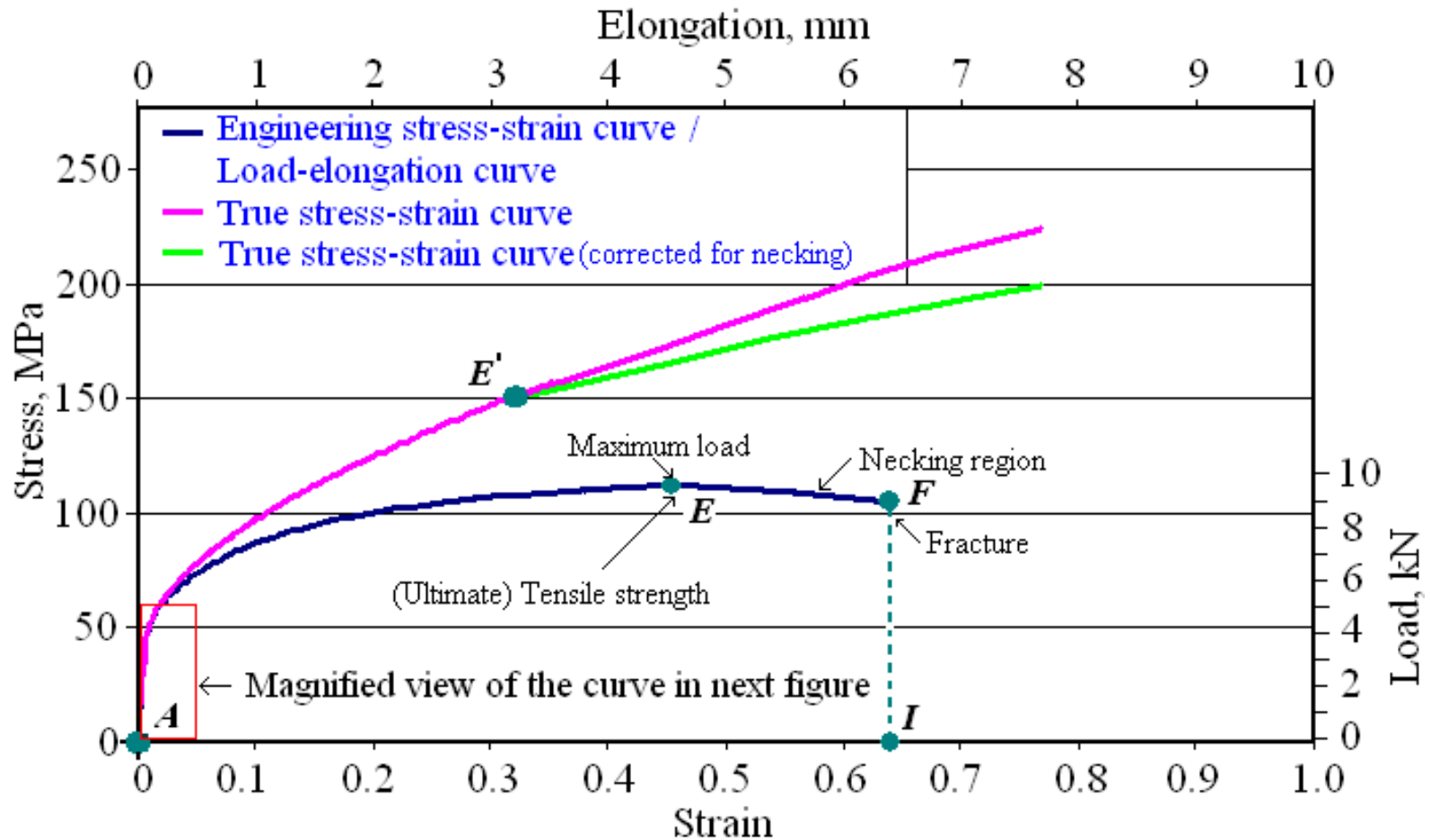
$$\sigma = K\varepsilon^n \quad \text{Strain hardening exponent, } n = 0.1-0.5$$

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

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

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

# Tensile stress-strain curve



A – Starting point

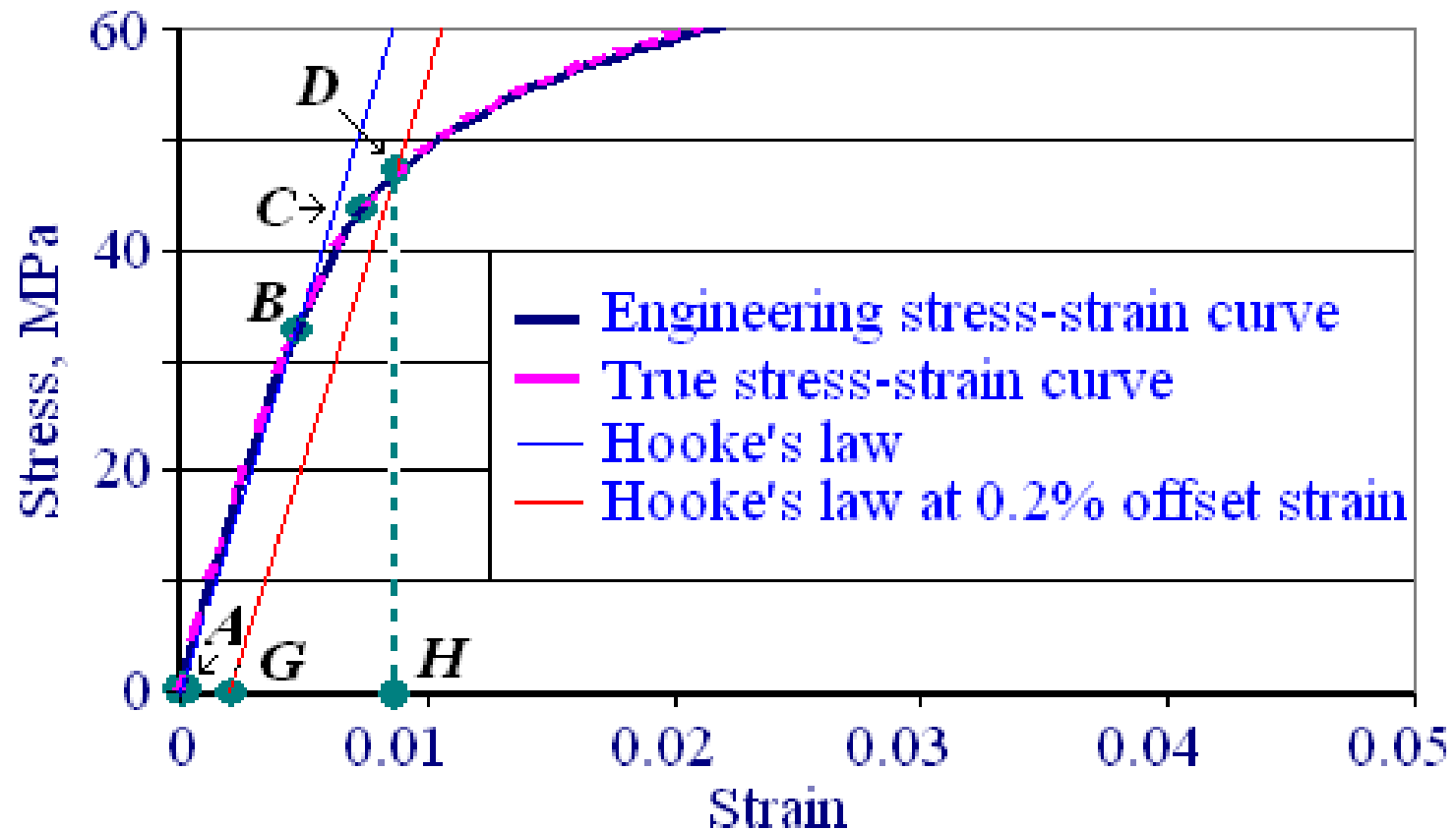
E – Tensile strength

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.

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

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

# 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.

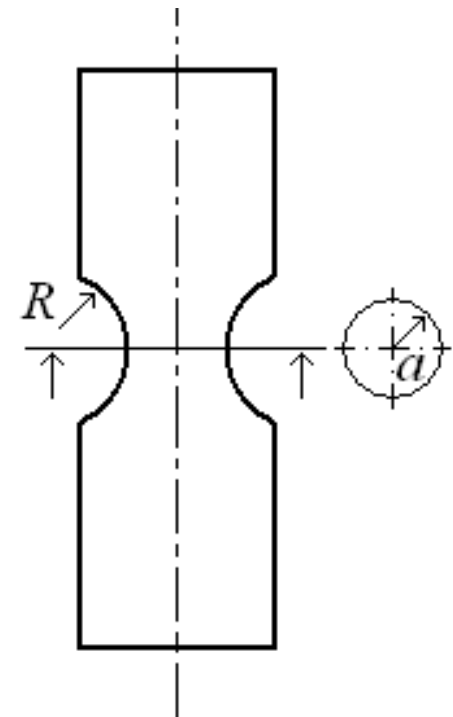
$$\sigma = \frac{(\sigma_x)_{avg}}{(1 + 2R/a) \ln(1 + a/2R)}$$

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  $\sigma_2 = \sigma_3 = 0$

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

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

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

## 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 ( $\sigma_1 = -\sigma_3 = k$ ,  $\sigma_2 = 0$ )

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

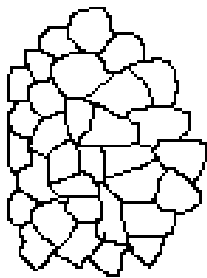
# Macroscopic aspects – Plastic deformation

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

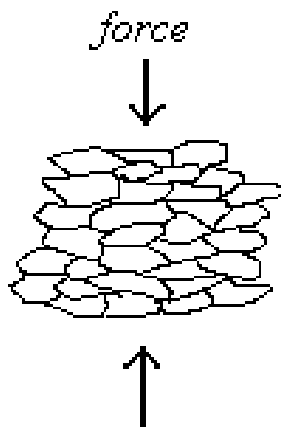
dimensional changes

change in grain shape

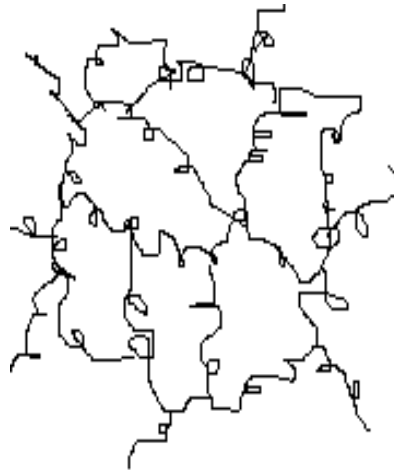
formation of cell structure in a grain



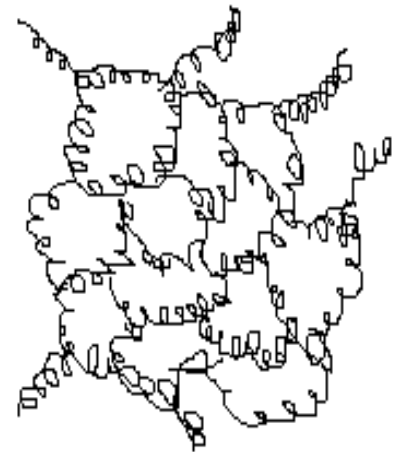
*equi-axed grains*



*deformed grains*



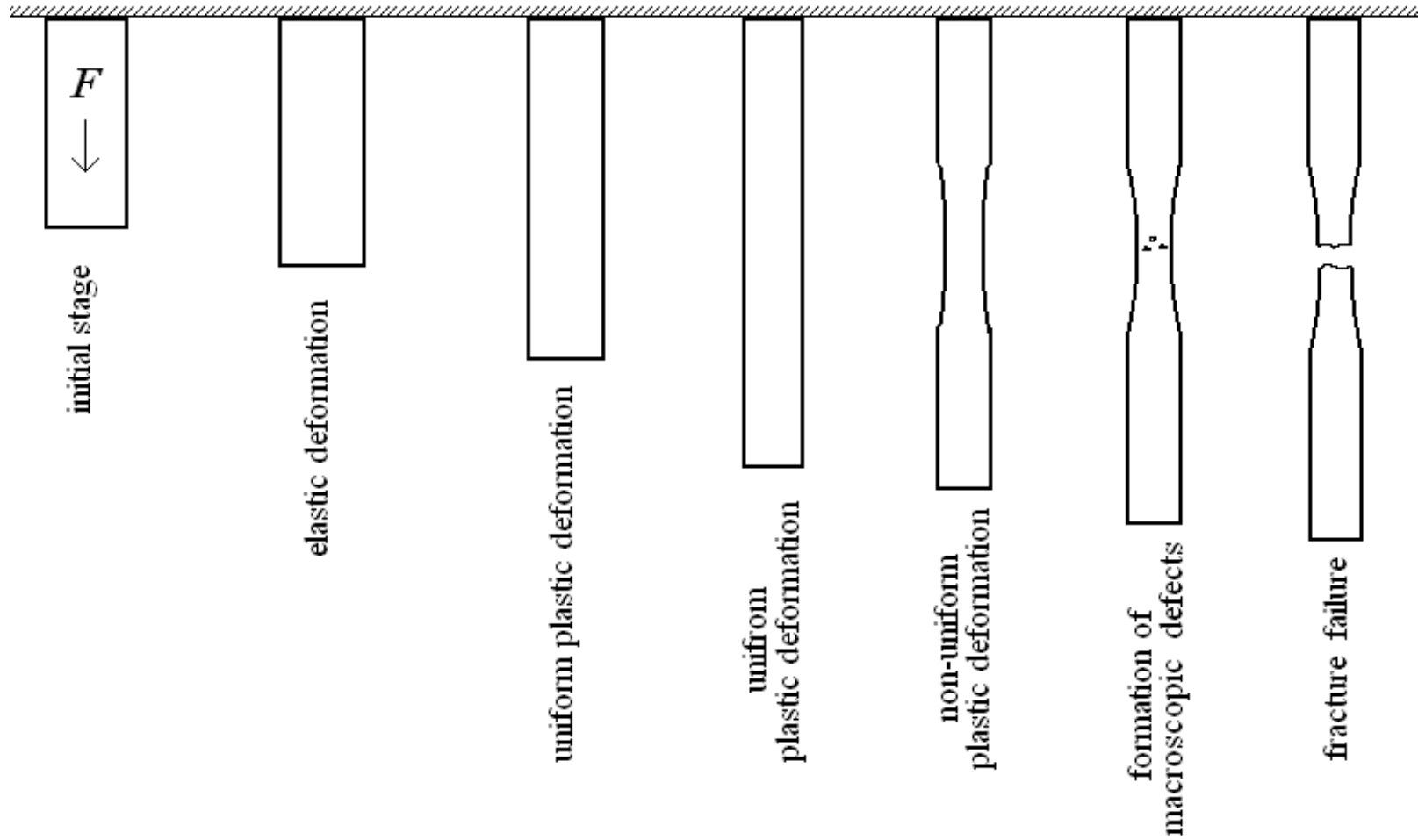
*initial cell structure*



*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.

## 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.
- 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  $\delta$  ( $\text{g}/\text{cm}^3$ )

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

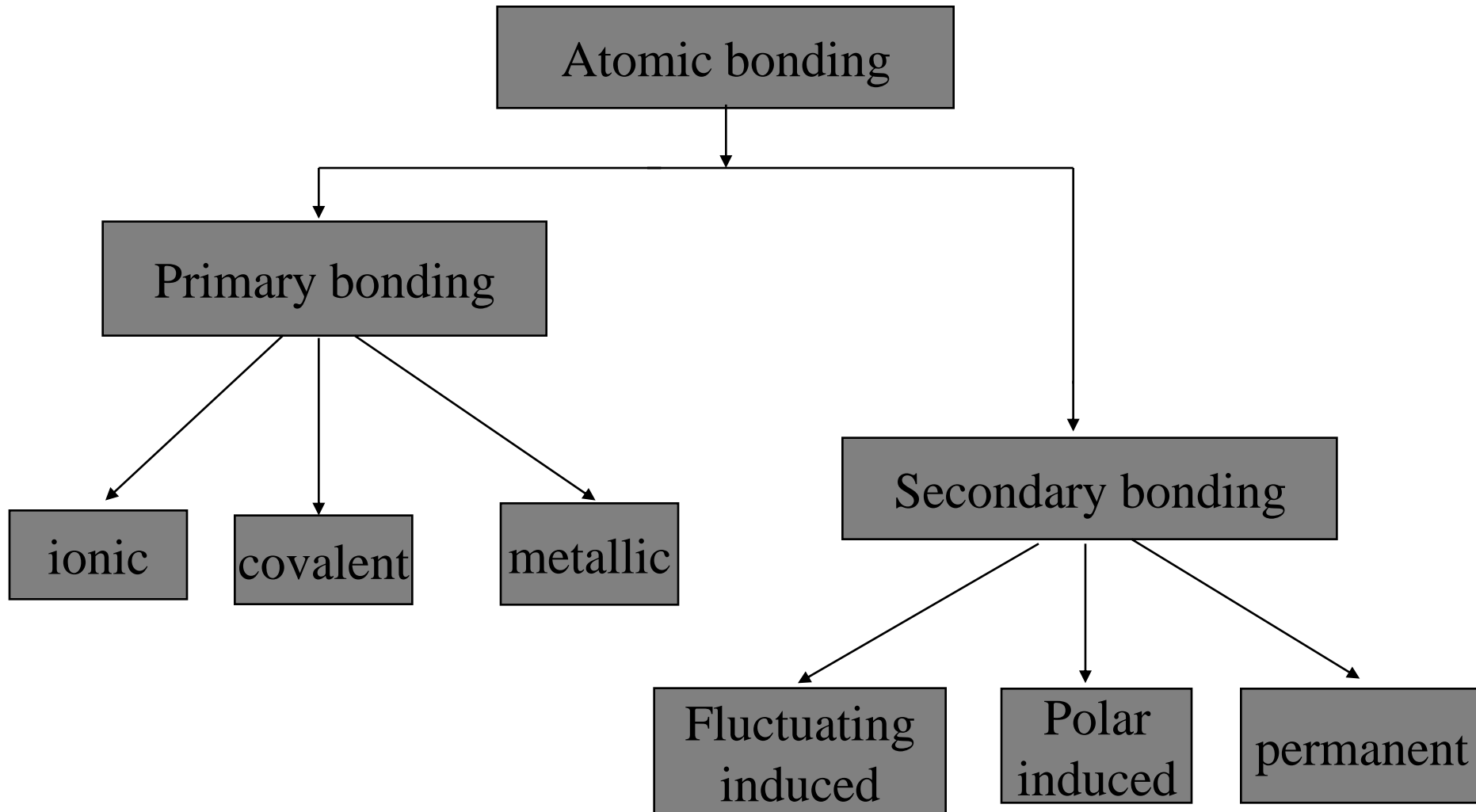
Thus, for graphite (carbon) with a density  $\delta = 1.8 \text{ g}/\text{cm}^3$  and  $M = 12$ ,  $n = 6.023 \times 10^{23} \text{ atoms/mol} \times (1.8 \text{ g}/\text{cm}^3 / 12 \text{ g/mol}) = 9 \times 10^{22} \text{ atoms}/\text{cm}^3$ .

- 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  $\text{Na}^+$ .

## 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.:**  $\text{H}_2$  molecule, where an electron from each of the atom shared by the other atom, thus producing the covalent bond.

# 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.

## 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



## 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 t 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:

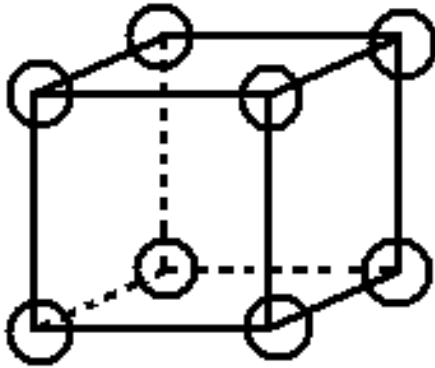
- Type of atom and their radii,  $R$
- Cell dimensions,  $a$  and  $c$  (for hexagonal structures)
- Number of atoms per unit cell,  $n$
- Coordination number ( $CN$ )— closest neighbors to an atom
- Atomic packing factor,  $APF$

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

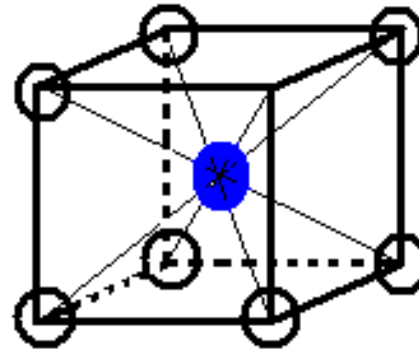
## Common Crystal Structures

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

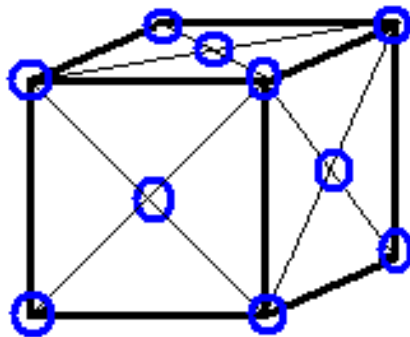
# Schematic Unit Cells



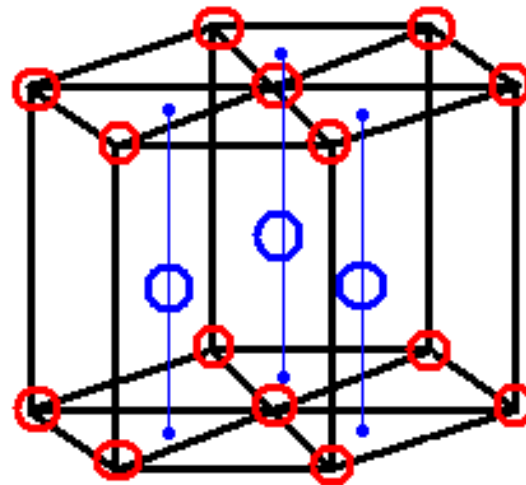
Simple Cubic



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

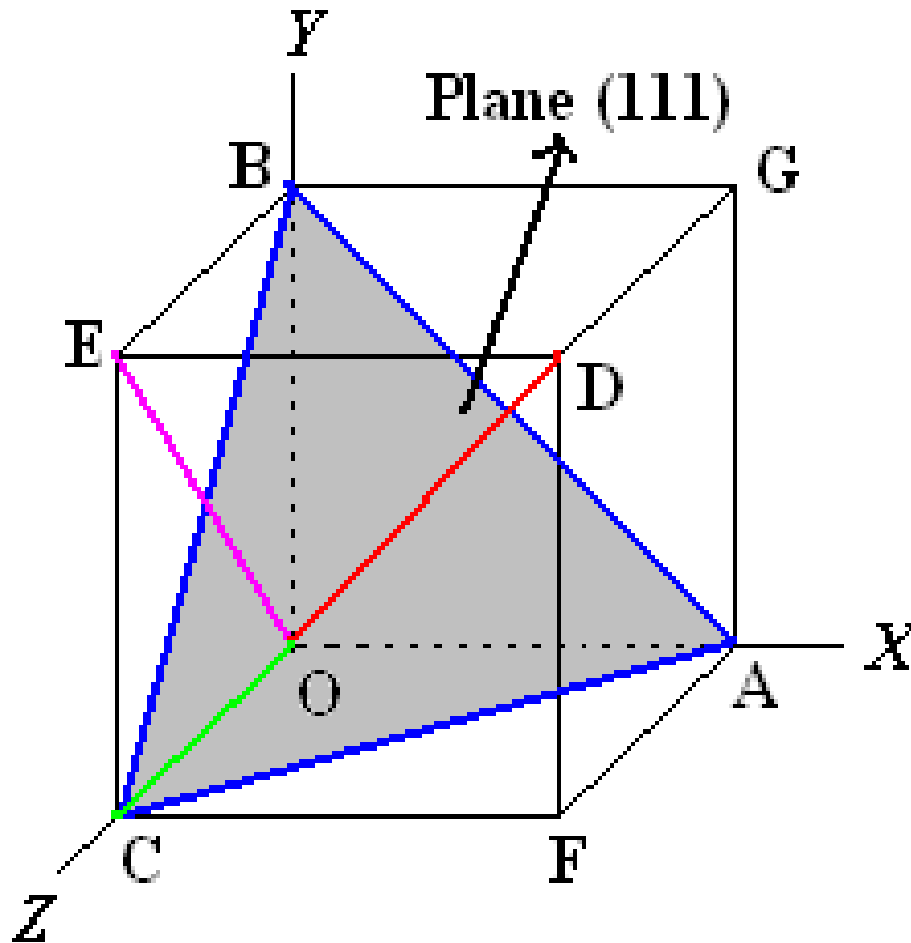
- A vector of convenient length is placed parallel to the required direction
- The length of the vector projection on each of three axes are measured *in terms of unit cell dimensions*
- These three numbers are made to smallest integer values, known as indices, by multiplying or dividing by a common 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° 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 10)

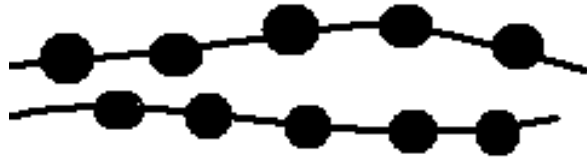
# Polymers - definition

- 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*

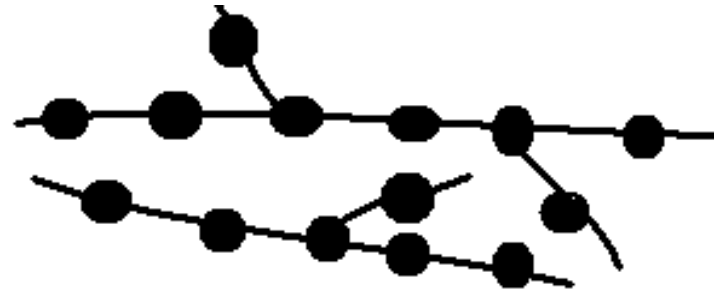
# Polymer structures

- 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
- 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.

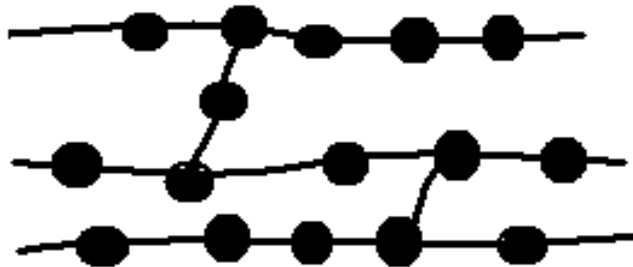
# Polymer structures



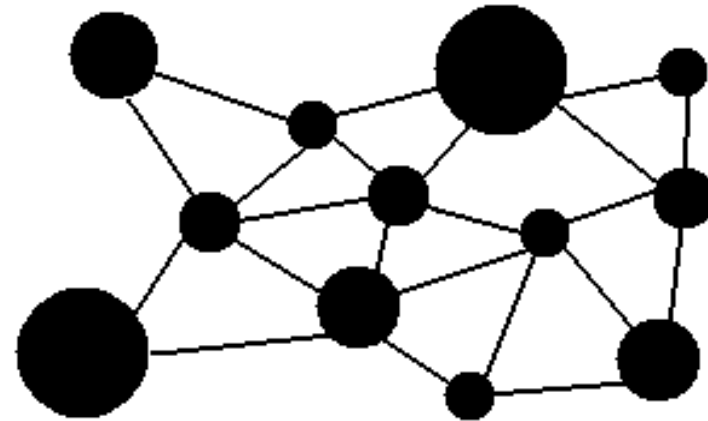
Linear



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 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

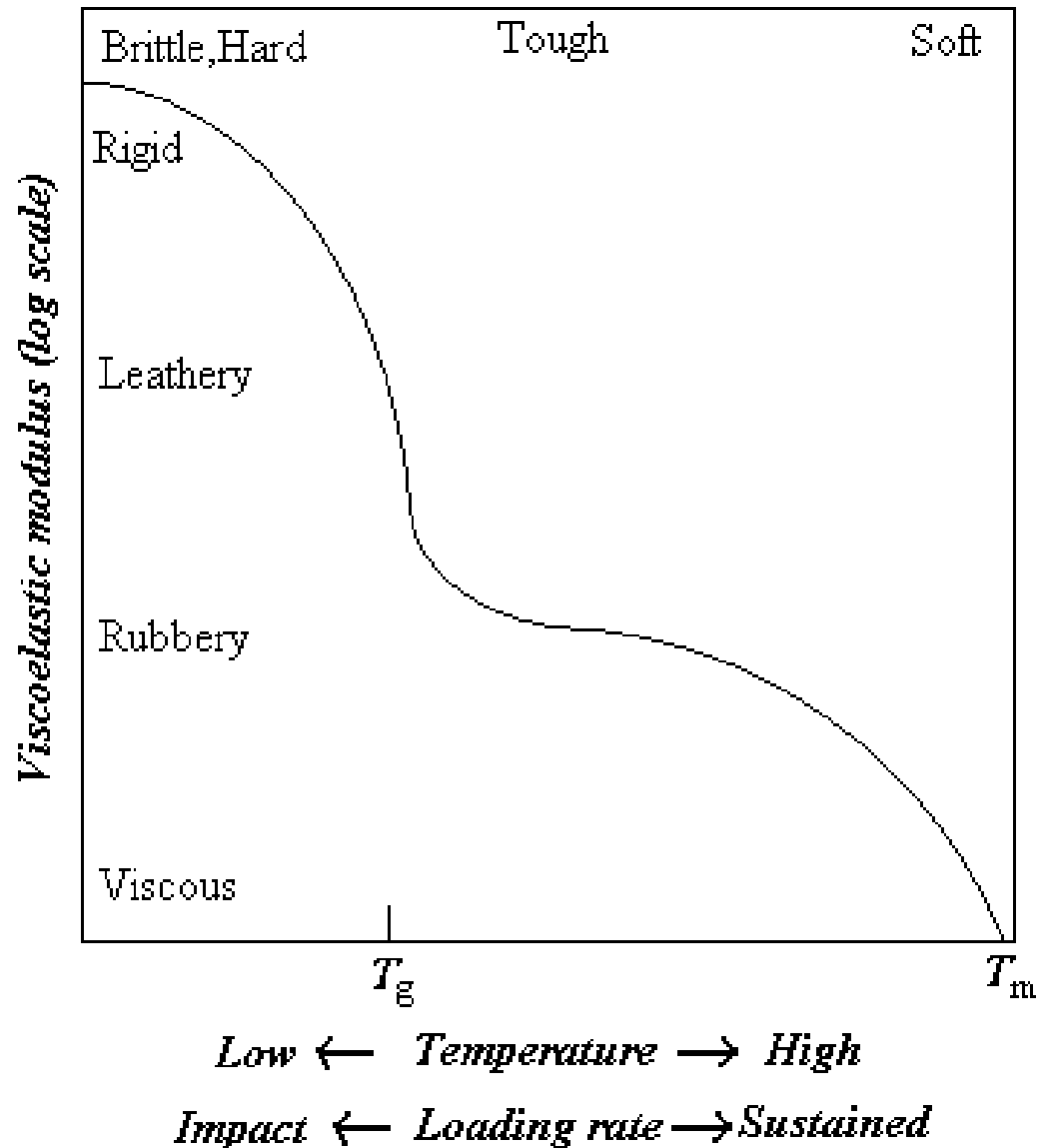


# Polymer crystallinity

- 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



# 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

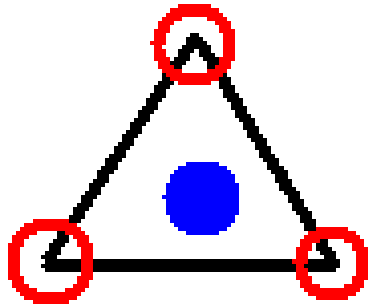
E.g.: Sand, Glass, Bricks, Marbles

# Ceramic structures

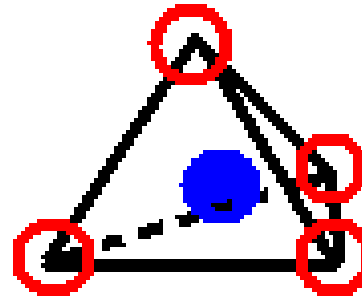
- Building criteria for ceramic structures:
  - maintain neutrality
  - closest packing
- Packing efficiency can be characterized by coordination number which depends on cation-anion radius ratio ( $r_c/r_a$ )

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

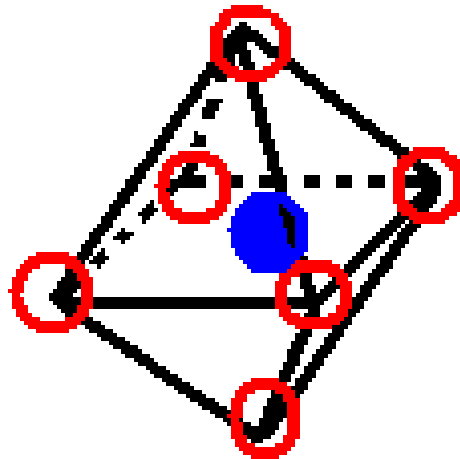
# Ion arrangement – Coordination numbers



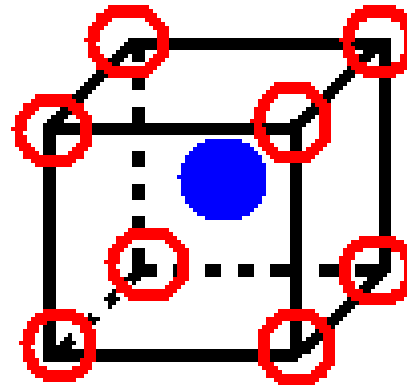
CN = 3



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.

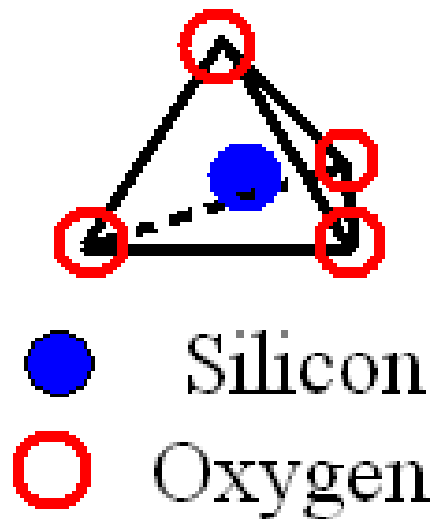
E.g.: CaF<sub>2</sub>, ThO<sub>2</sub>

- 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<sub>60</sub> - 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

Module-08

# 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

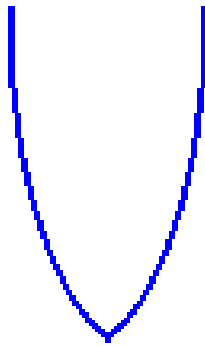
- Fracture *defined* as the separation or fragmentation of a solid body into two *or* more parts under the action of stress.
- Fracture is classified based on several characteristic features:

<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

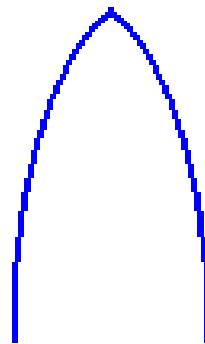


# Fracture modes

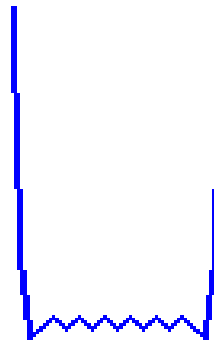
- Ductile and Brittle are relative terms.
- Most of the fractures belong to one of the following modes:  
(a) rupture, (b) cup-&-cone and (c) brittle.



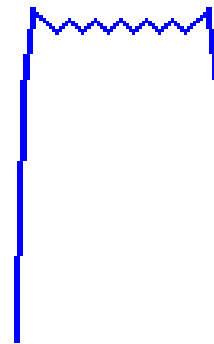
**Rupture**



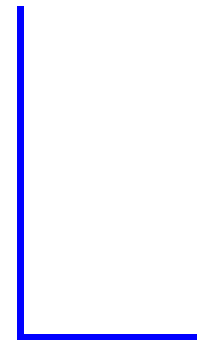
**(a)**



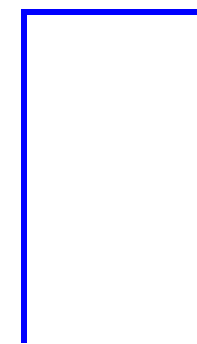
**Cup-&-Cone fracture**



**(b)**



**Brittle fracture**



**(c)**

## Ductile fracture Vs Brittle fracture

<i><b>Parameter</b></i>	<i><b>Ductile fracture</b></i>	<i><b>Brittle fracture</b></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

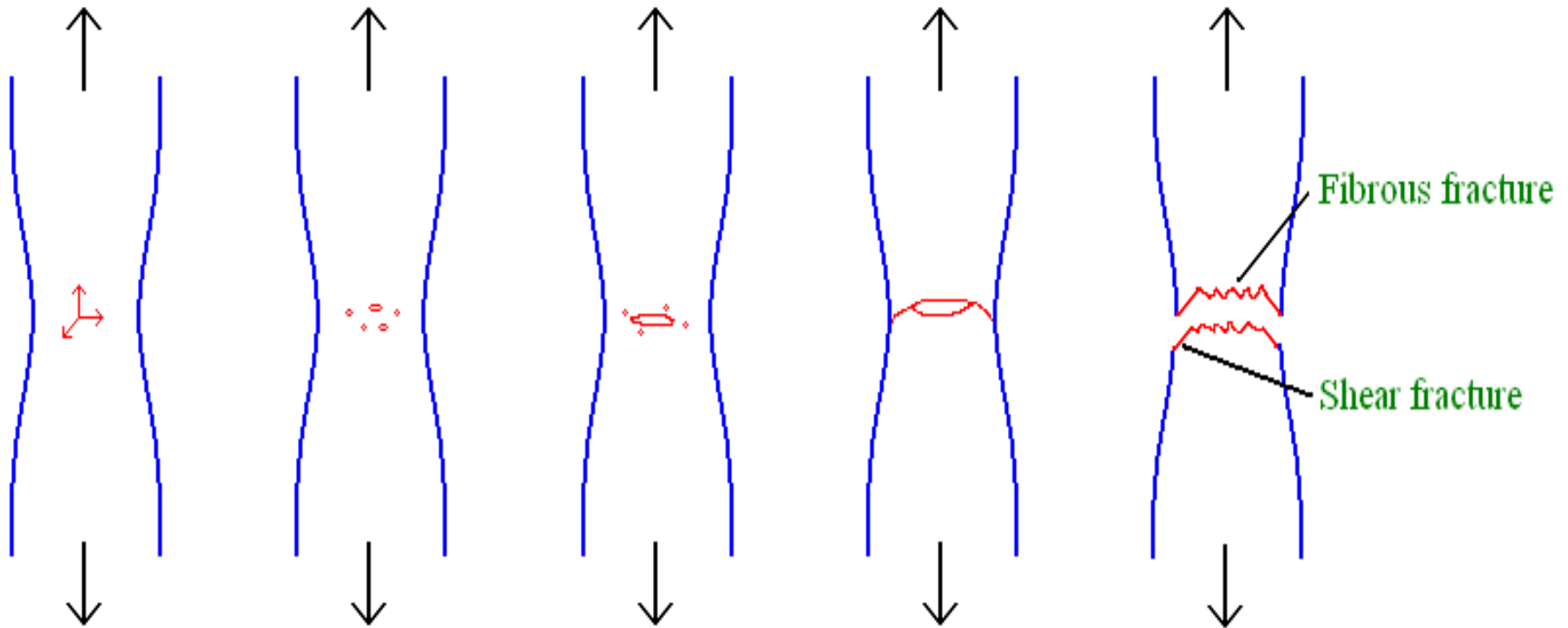
## Ductile fracture

- 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,  $\epsilon_f$ ,

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

## 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,  $K$ : 
$$K = \alpha \sigma \sqrt{c \pi}$$

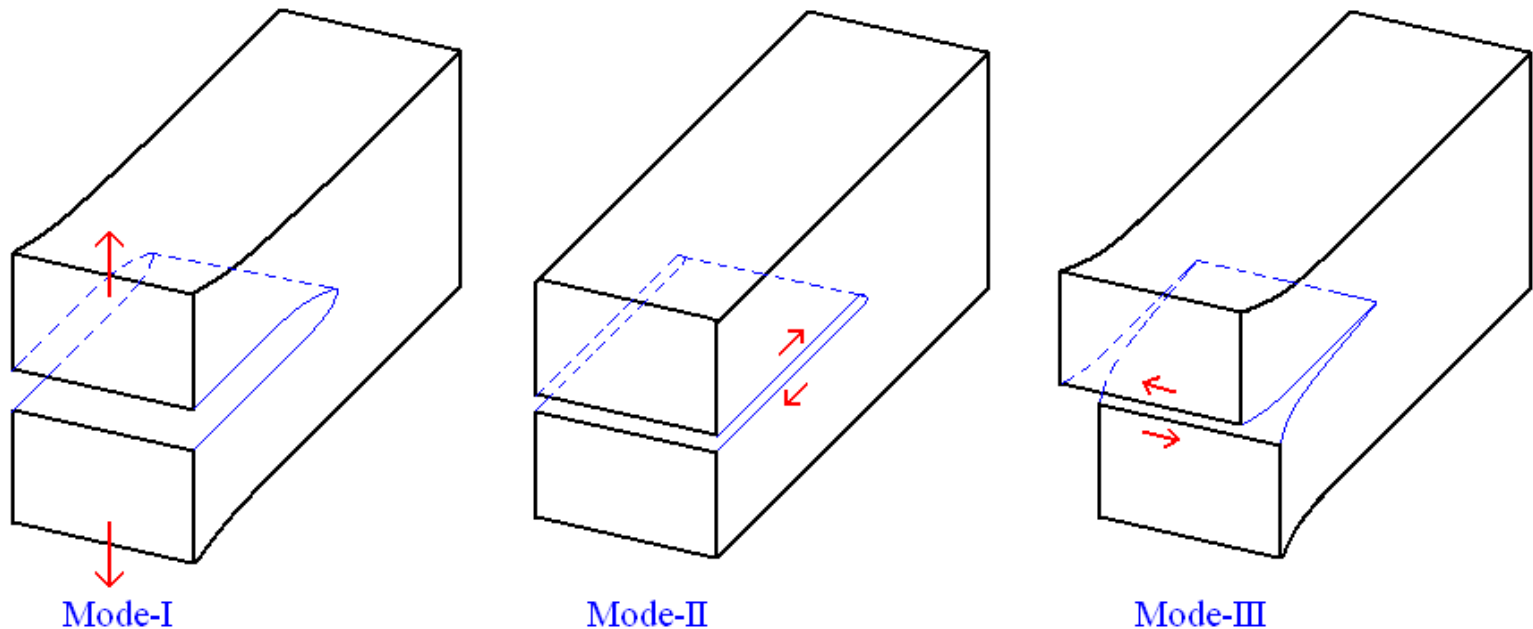
➤ Both parameters are related as:

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

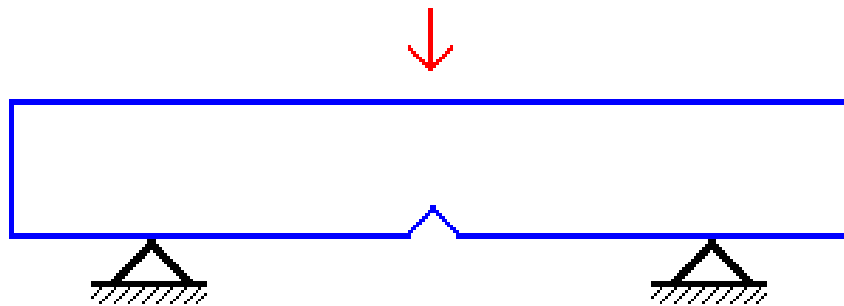


## Notch-impact testing

- 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.

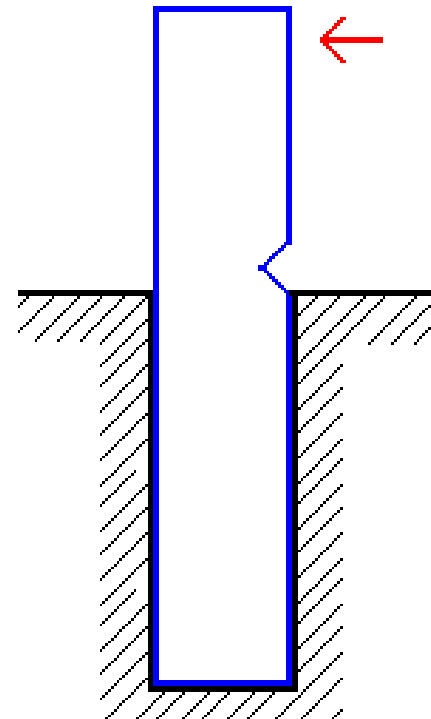
## Notch-impact testing (contd....)

- 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

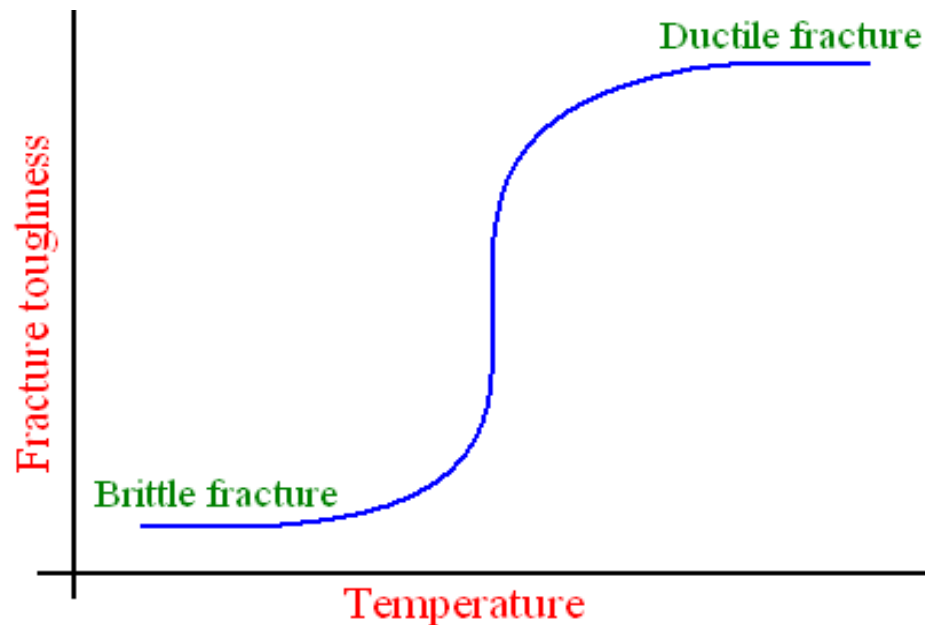
↑ Impact load direction



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.



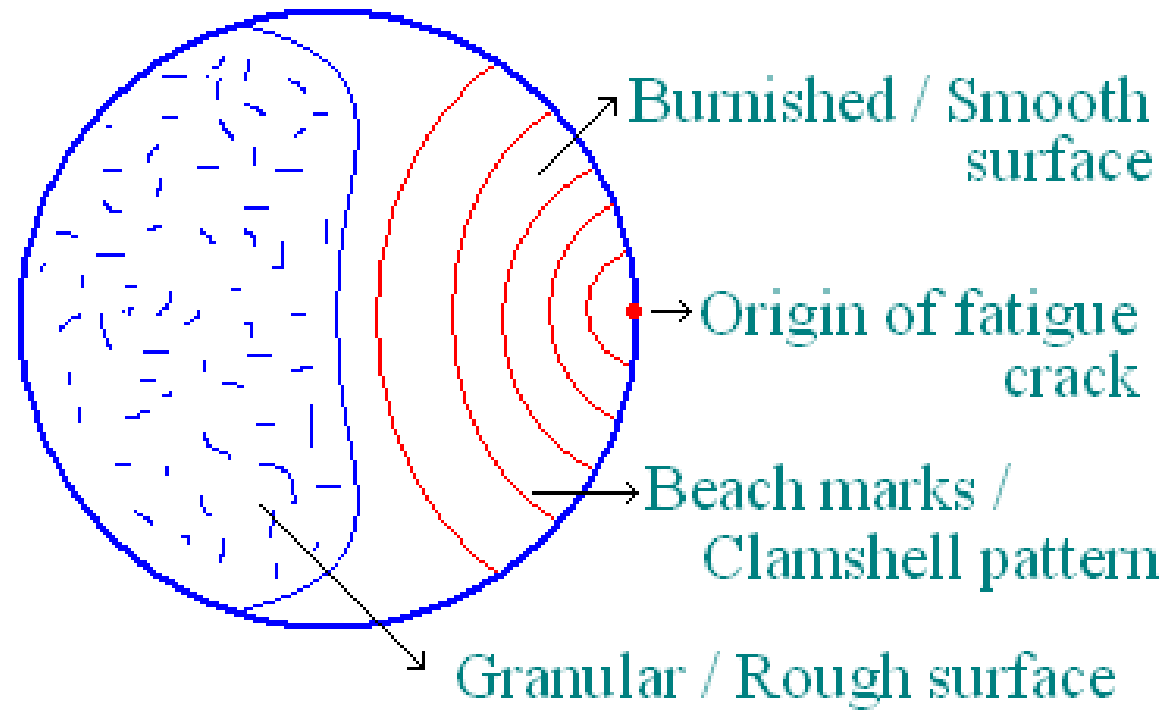
- In metals DBTT is around  $0.1-0.2 T_m$  while in ceramics it is about  $0.5-0.7 T_m$ , where  $T_m$  represents absolute melting temperature.

# 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,

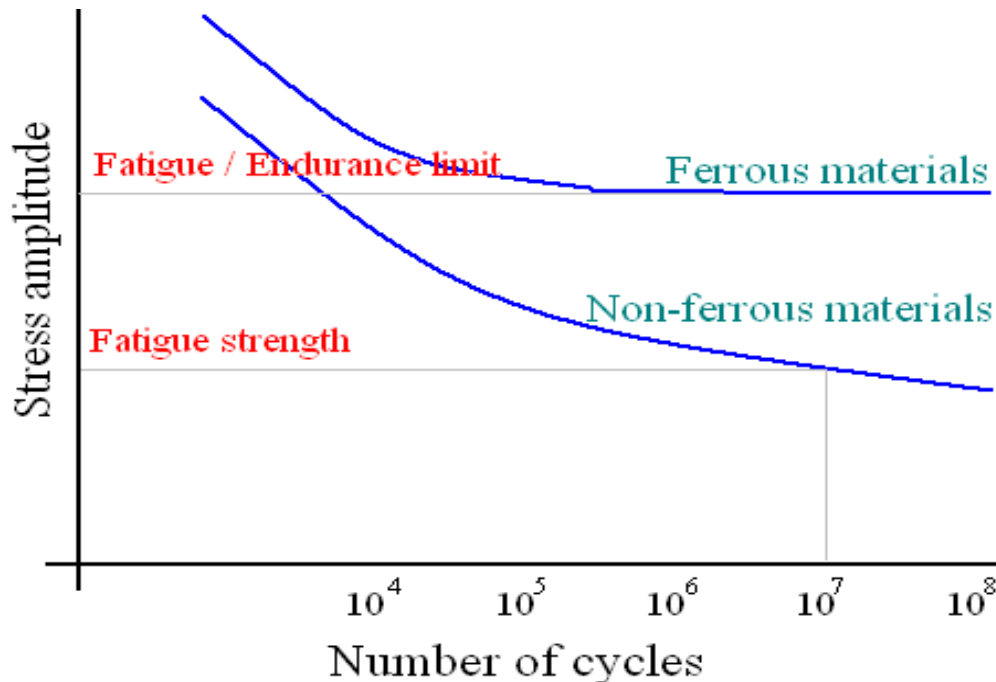
$$R = \sigma_{min} / \sigma_{max}$$

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:

$$N\sigma_a^p = C$$

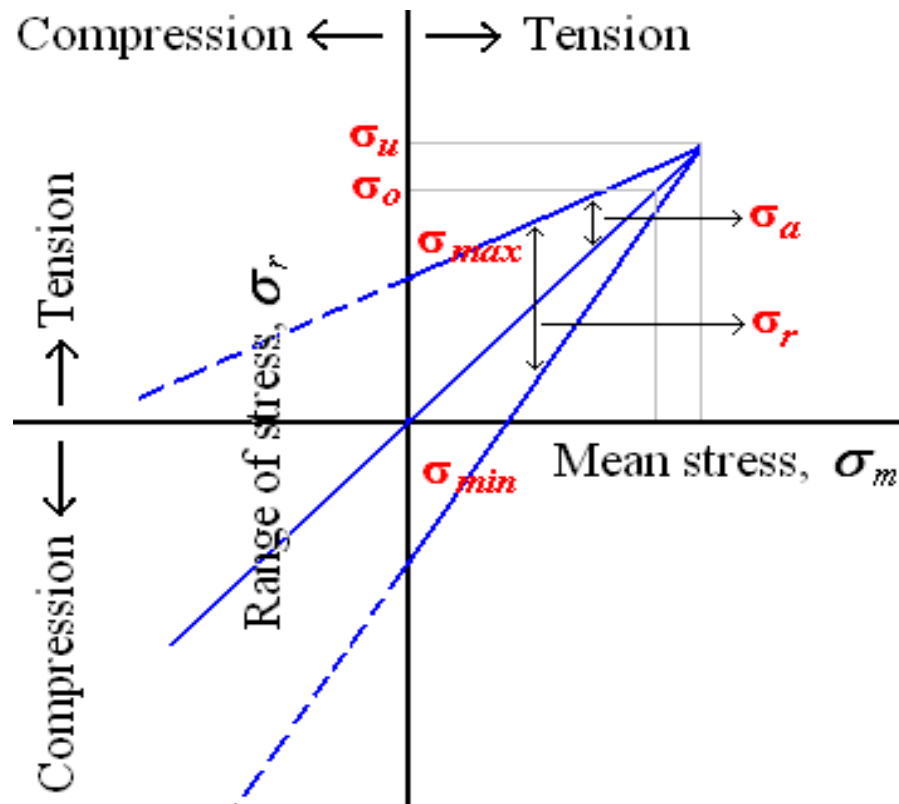
## Fatigue parameters

- 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.

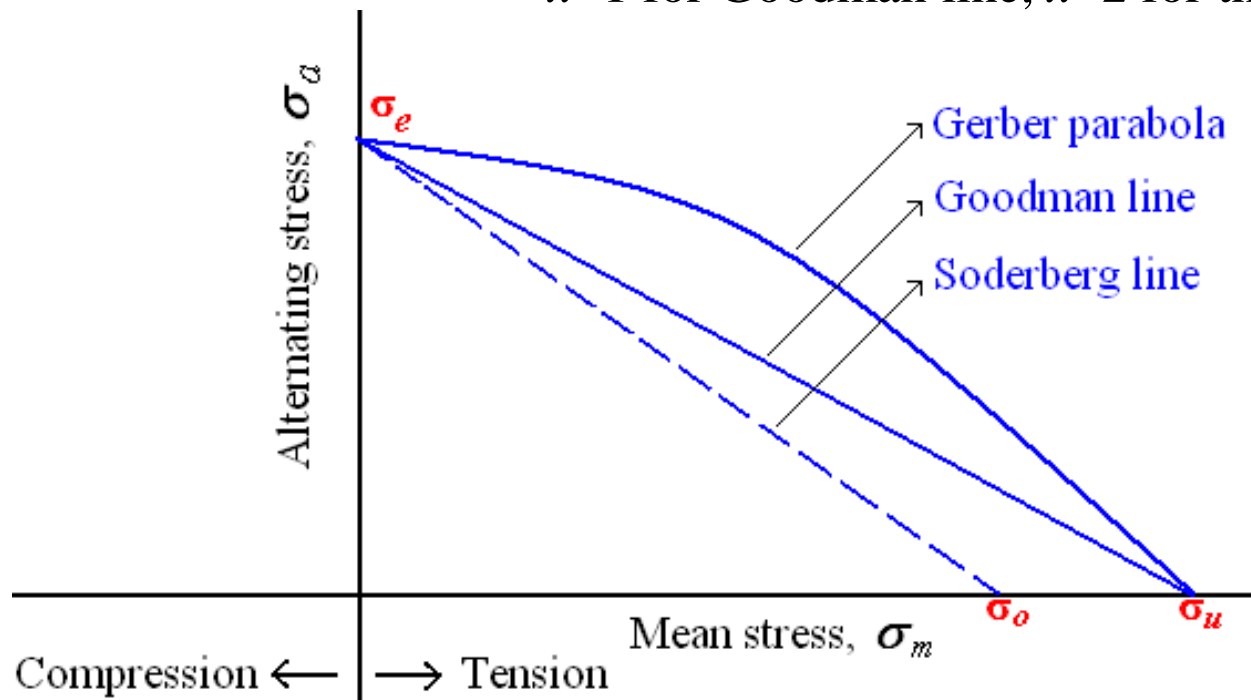


## Fatigue data presentation (contd....)

- 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.



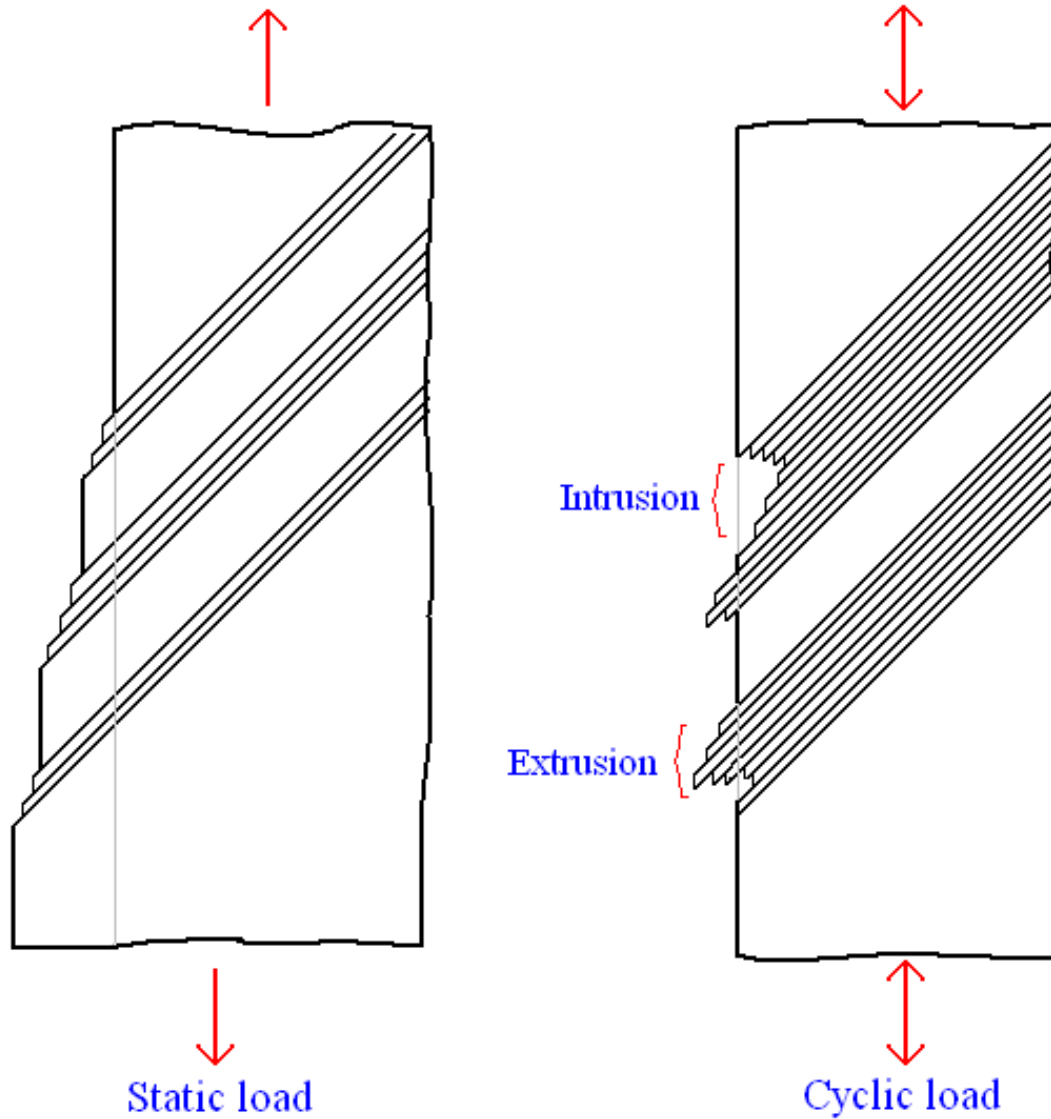
# Fatigue – Crack initiation & propagation

- 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

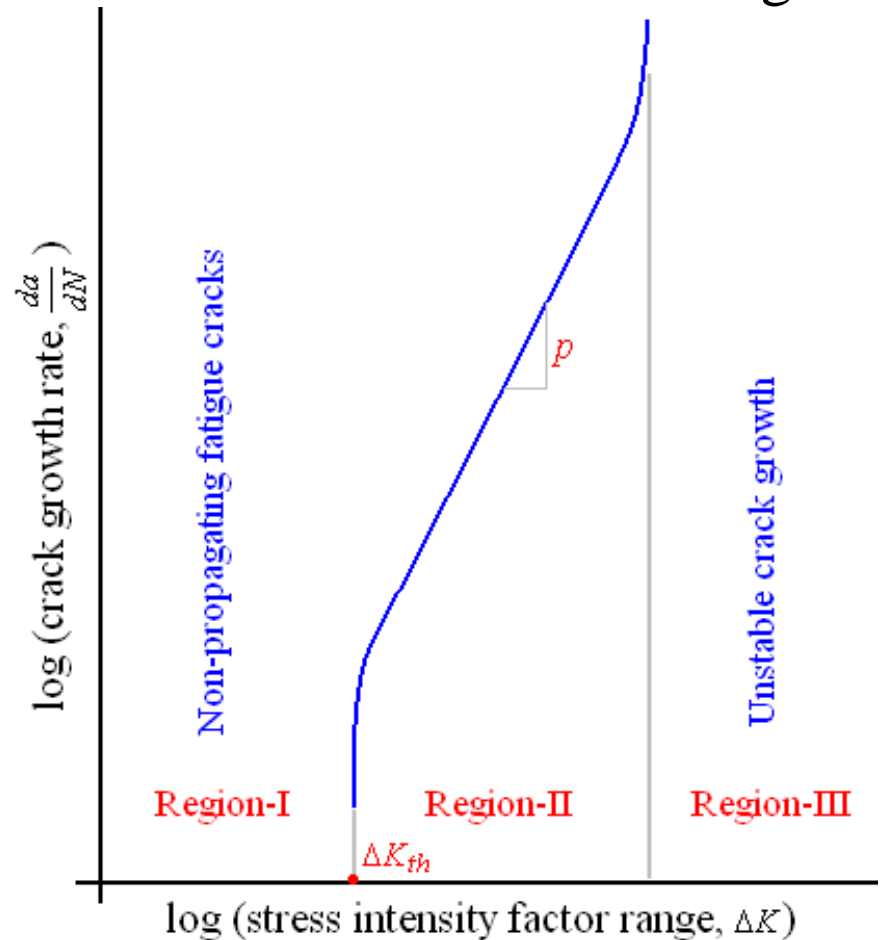
- Studies of fatigue crack propagation rate attained much importance because it can be used as fail-safe design consideration.

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

- **Paris law:**

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

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

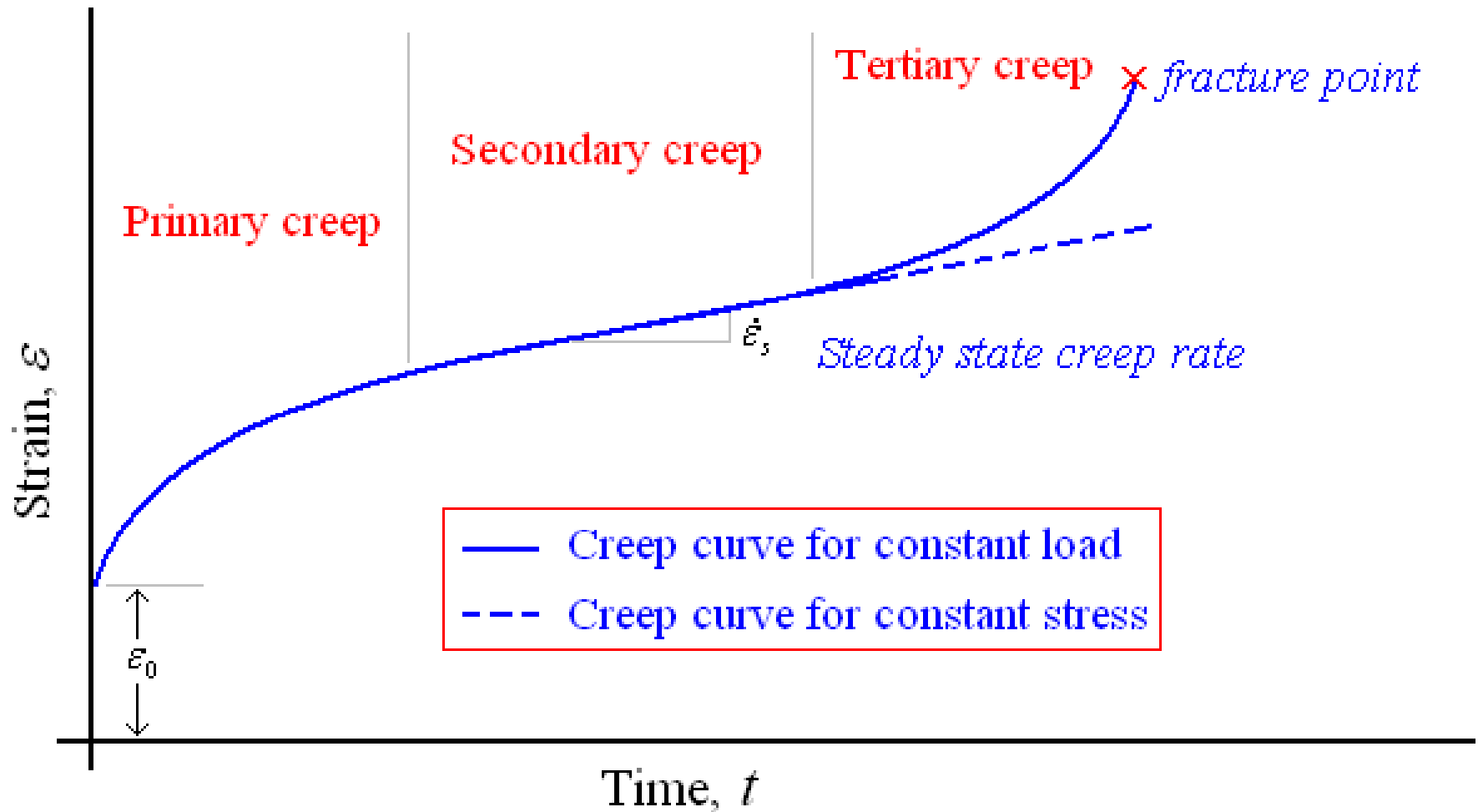


## Creep failure

- 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,  $\epsilon_0$ , 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:

$$\epsilon = \epsilon_0 (1 + \beta t^{1/3}) e^{kt}$$

- Garofalo creep equation:

$$\epsilon = \epsilon_0 + \epsilon_t (1 - e^{-rt}) + \dot{\epsilon}_s t$$

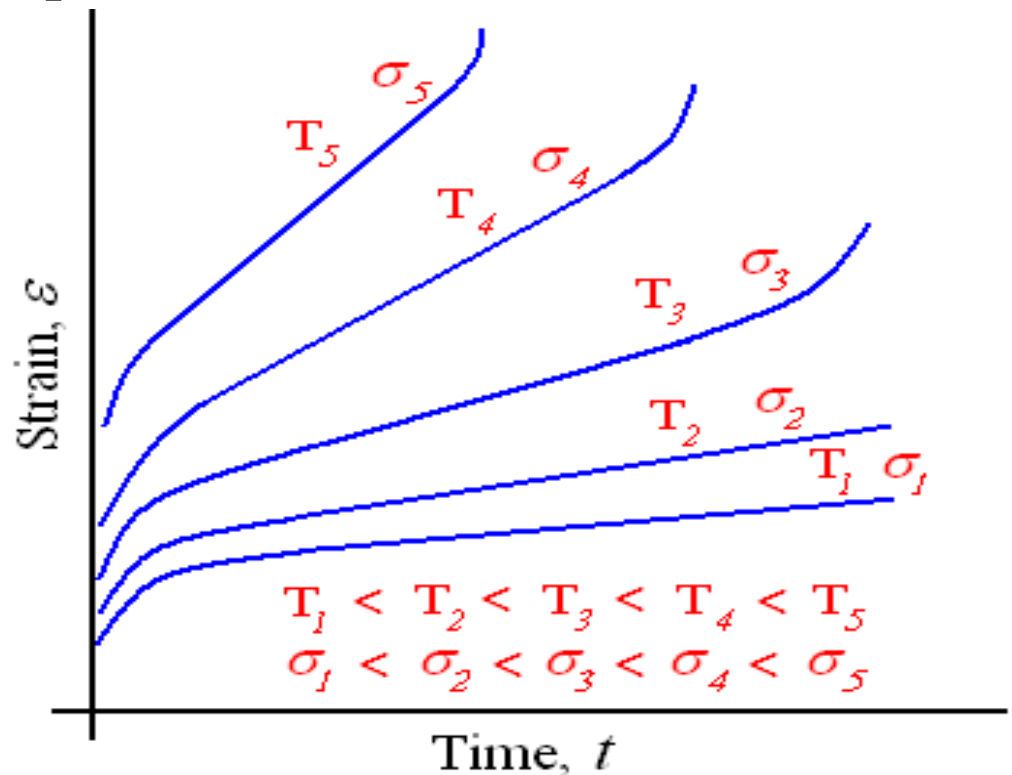
## Creep in different stages

- 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.

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



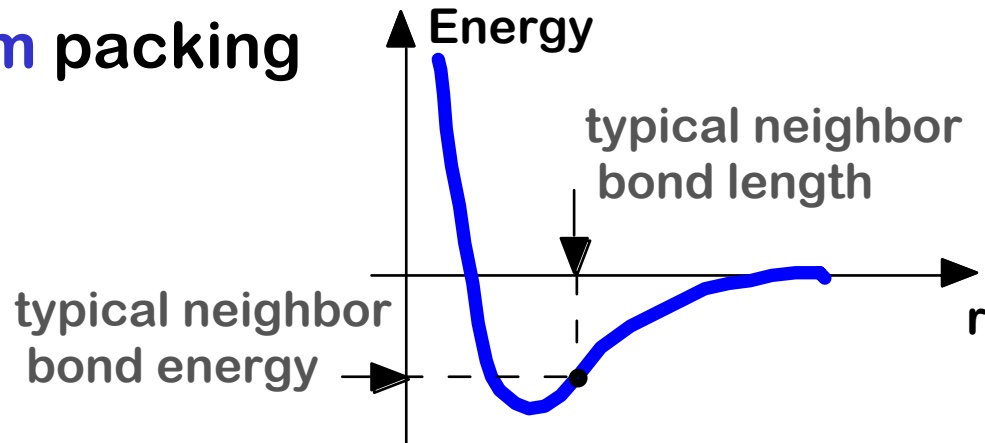
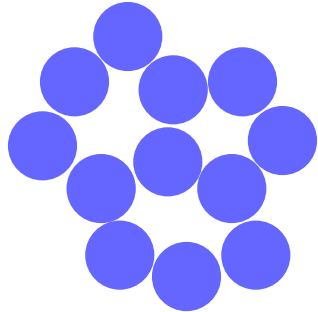
# Chapter 3

## Structure of Crystalline Solids

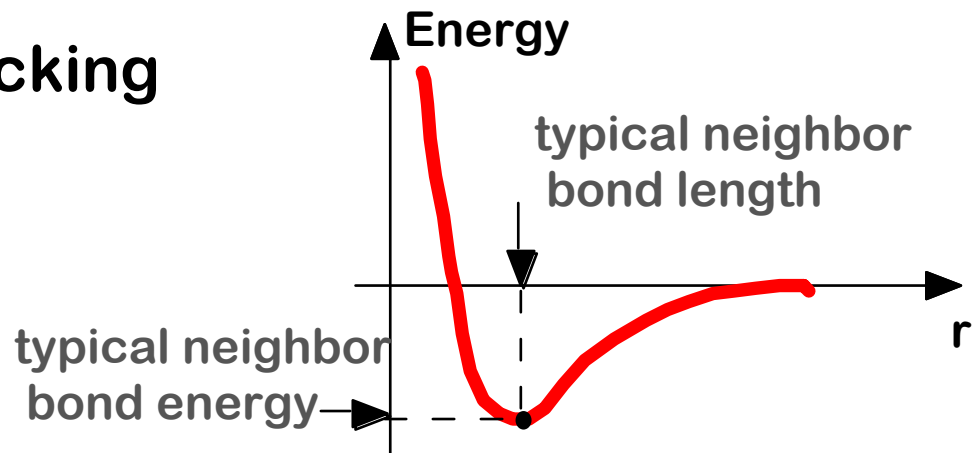
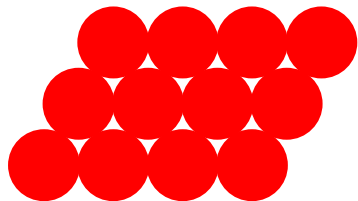
- Crystal Structures
- Points, Directions, and Planes
- Linear and Planar Densities
- X-ray Diffraction
  - How do atoms assemble into solid structures?  
(for now, focus on metals)
  - How does the density of a material depend on its structure?
  - When do material properties vary with the sample (i.e., part) orientation?

# Energy and Packing

- Non dense, **random** packing



- Dense, **regular** packing

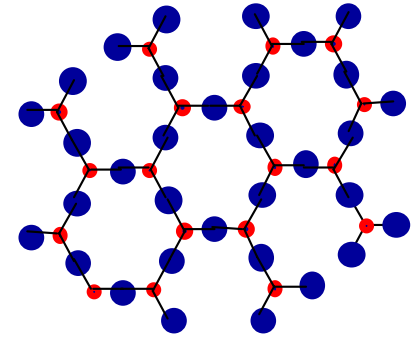


**Dense, regular-packed structures tend to have lower energy.**

# Materials and Packing

## Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals  
-many ceramics  
-some polymers

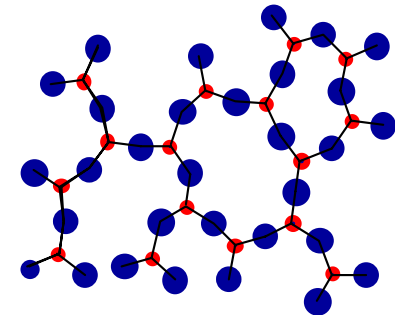


crystalline SiO<sub>2</sub>

## Noncrystalline materials...

- atoms have no periodic packing
- occurs for: -complex structures  
-rapid cooling

• Si      • Oxygen



noncrystalline SiO<sub>2</sub>

"Amorphous" = Noncrystalline

# Metallic Crystals

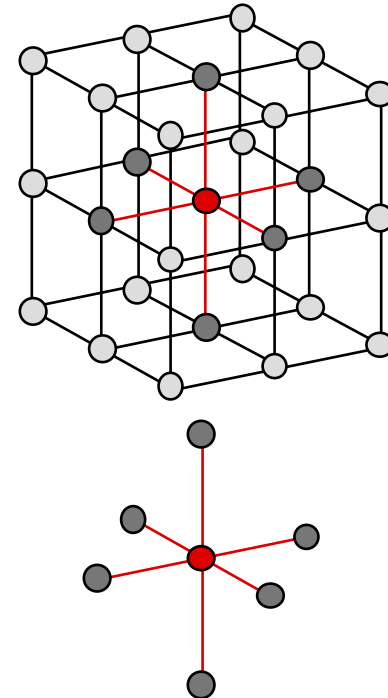
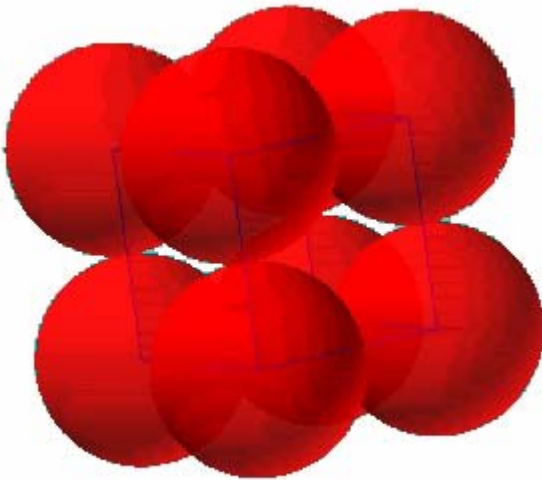
- **tend to be densely packed.**
- **have several reasons for dense packing:**
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
- **have the simplest crystal structures.**

**We will look at four such structures...**



# Simple Cubic Structure (SC)

- Unit Cell (small repeat entity)
- Rare due to poor packing (only Po has this structure)
- **Close-packed directions** are cube edges. **Coordination # = 6**  
(# nearest neighbors)

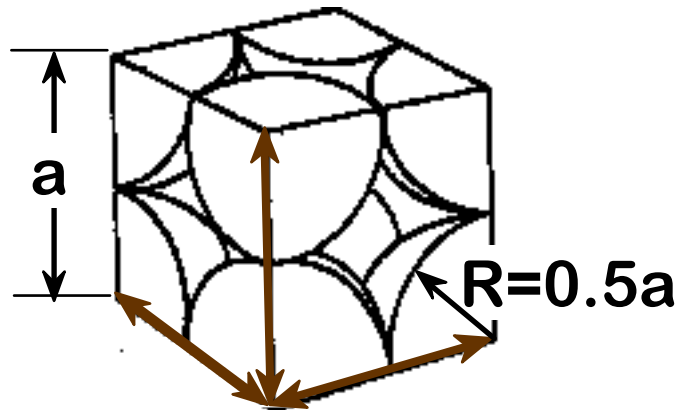


# Atomic Packing Factor (APF)

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

\*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

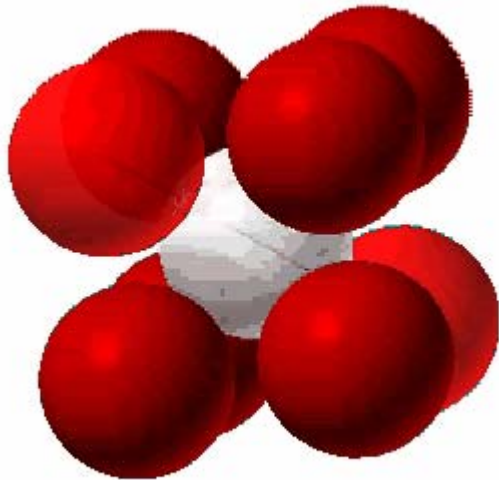
contains  $8 \times 1/8 =$

**1 atom/unit cell**

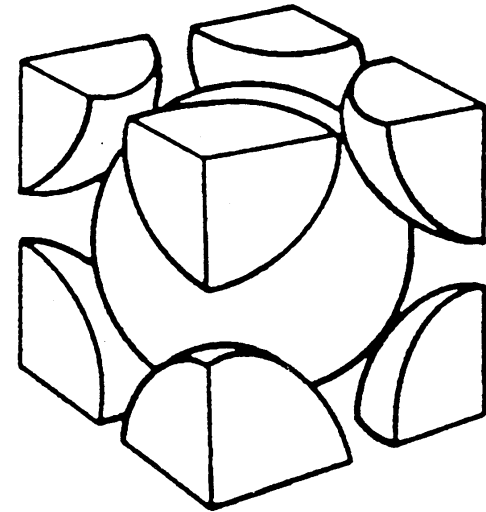
$$\text{APF} = \frac{\overbrace{1}^{\text{atoms}} \overbrace{\frac{4}{3} \pi (0.5a)^3}^{\text{volume atom}}}{\underbrace{a^3}_{\text{volume unit cell}}}$$

# Body Centered Cubic Structure (BCC)

- **Close packed directions are cube diagonals.**  
--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

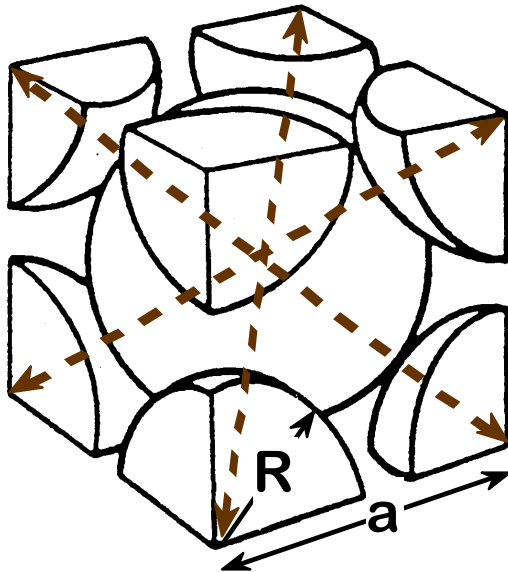


- **Coordination # = 8**



## APF of BCC

- APF for a body-centered cubic structure = 0.68



Close-packed directions:  
length =  $4R$   
 $= \sqrt{3} a$

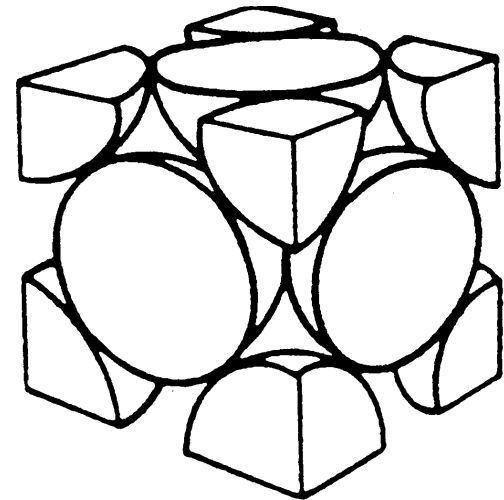
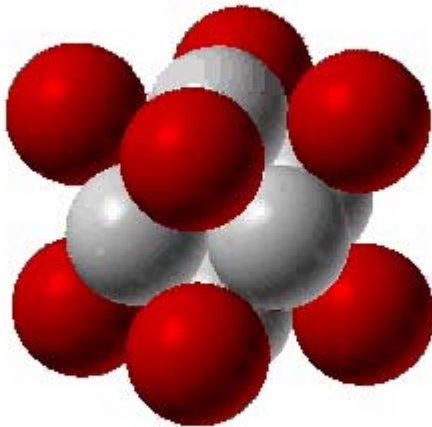
Unit cell contains:  
 $1 + 8 \times 1/8$   
 $= 2 \text{ atoms/unit cell}$

$$\text{APF} = \frac{\overbrace{2}^{\text{atoms}} \overbrace{\frac{4}{3} \pi (\sqrt{3}a/4)^3}^{\text{volume atom}}}{\underbrace{a^3}_{\text{volume unit cell}}}$$

# Face Centered Cubic Structure (FCC)

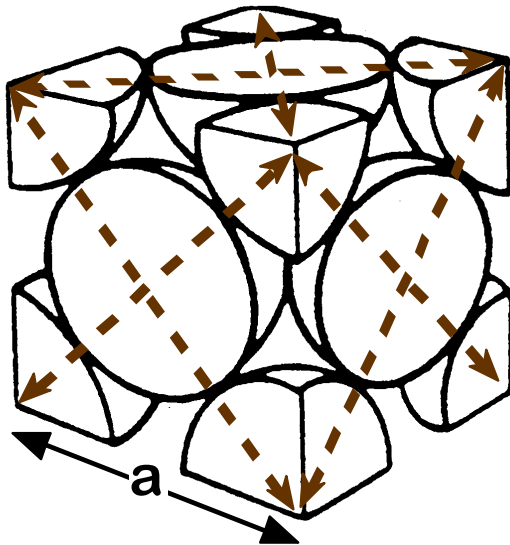
- **Close packed directions are face diagonals.**  
--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

- **Coordination # = 12**



## APF of FCC

- APF for a body-centered cubic structure = 0.74



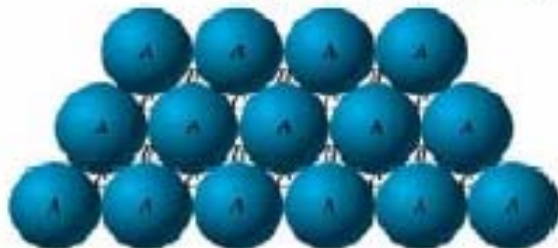
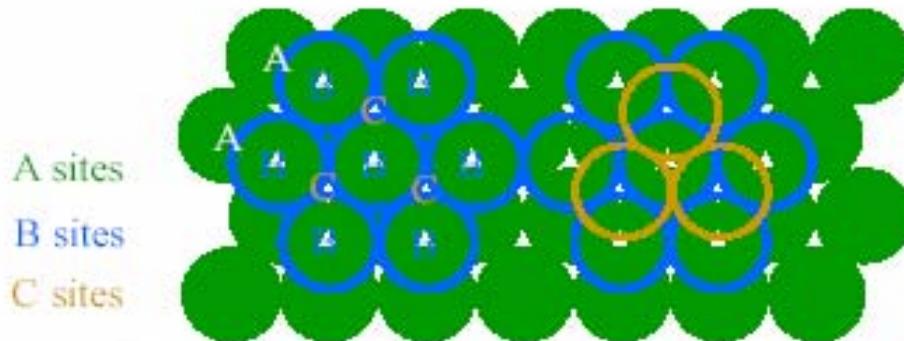
Close-packed directions:  
length =  $4R$   
 $= \sqrt{2} a$

Unit cell contains:  
 $6 \times 1/2 + 8 \times 1/8$   
 $= 4 \text{ atoms/unit cell}$

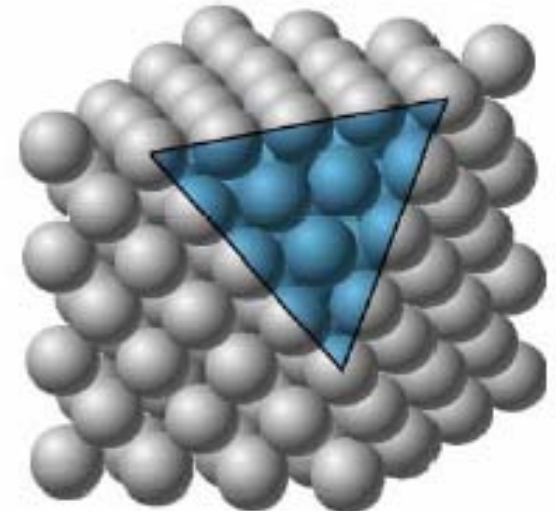
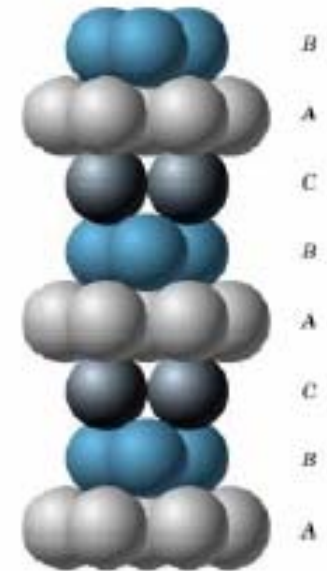
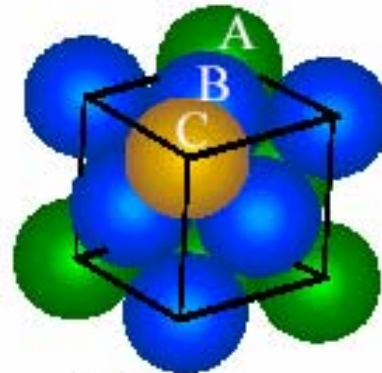
$$\text{APF} = \frac{\overbrace{4}^{\text{atoms}} \overbrace{\frac{4}{3} \pi (\sqrt{2}a/4)^3}^{\text{volume atom}}}{\underbrace{a^3}_{\text{volume unit cell}}}$$

## FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

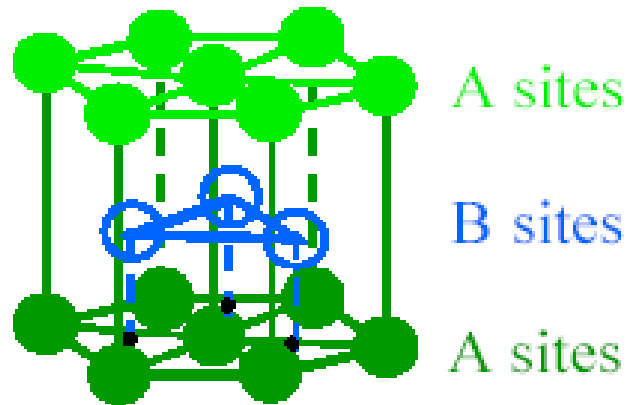


- FCC Unit Cell

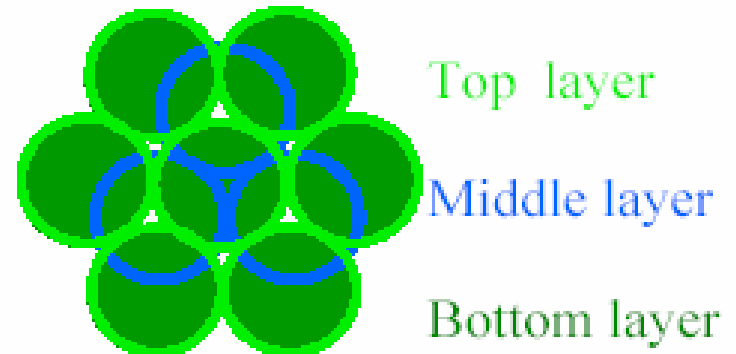


# Hexagonal Closed-Packed Structure (HCP)

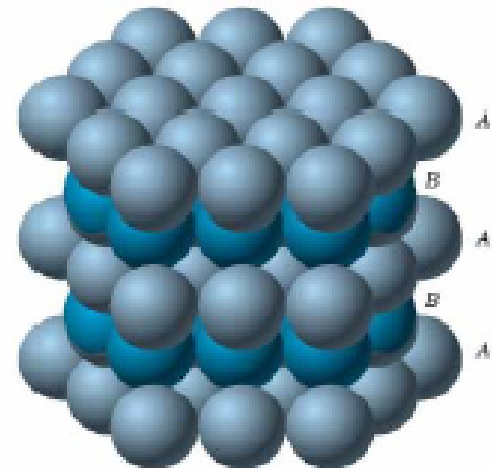
- ABAB... Stacking Sequence
- 3D Projection



- 2D Projection



- Coordination # = 12
- APF = 0.74





# Theoretical Density

$$\rho = \frac{n A}{V_c N_A}$$

# atoms/unit cell →  $n$  Atomic weight (g/mol) →  $A$

Volume/unit cell (cm<sup>3</sup>/unit cell) →  $V_c$  Avogadro's number (6.023 x 10<sup>23</sup> atoms/mol) →  $N_A$

## Example: Copper

Data from Table inside front cover of Callister (see next slide):

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius  $R = 0.128$  nm (1 nm = 10<sup>-7</sup> cm)

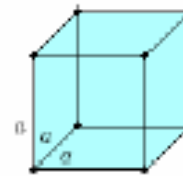
$$V_c = a^3 ; \text{ For FCC, } a = 4R\sqrt{2} ; V_c = 4.75 \times 10^{-23} \text{ cm}^3$$

Result: theoretical  $\rho_{\text{Cu}} = 8.89 \text{ g/cm}^3$

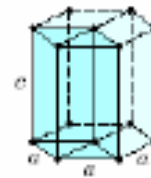
Compare to actual:  $\rho_{\text{Cu}} = 8.94 \text{ g/cm}^3$

# Seven Crystal Systems

Cubic  $a = b = c$   $\alpha = \beta = \gamma = 90^\circ$



Hexagonal  $a = b \neq c$   $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



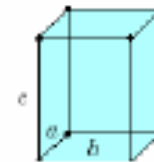
Tetragonal  $a = b \neq c$   $\alpha = \beta = \gamma = 90^\circ$



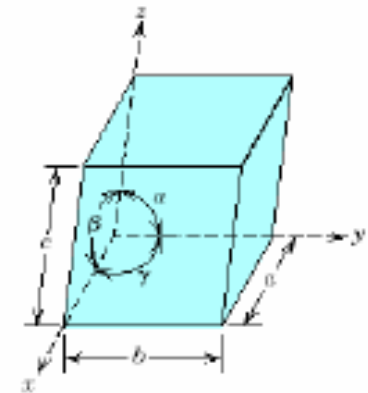
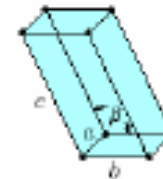
Rhombohedral  $a = b = c$   $\alpha = \beta = \gamma \neq 90^\circ$



Orthorhombic  $a \neq b \neq c$   $\alpha = \beta = \gamma = 90^\circ$

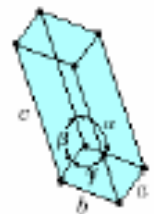


Monoclinic  $a \neq b \neq c$   $\alpha = \gamma = 90^\circ \neq \beta$



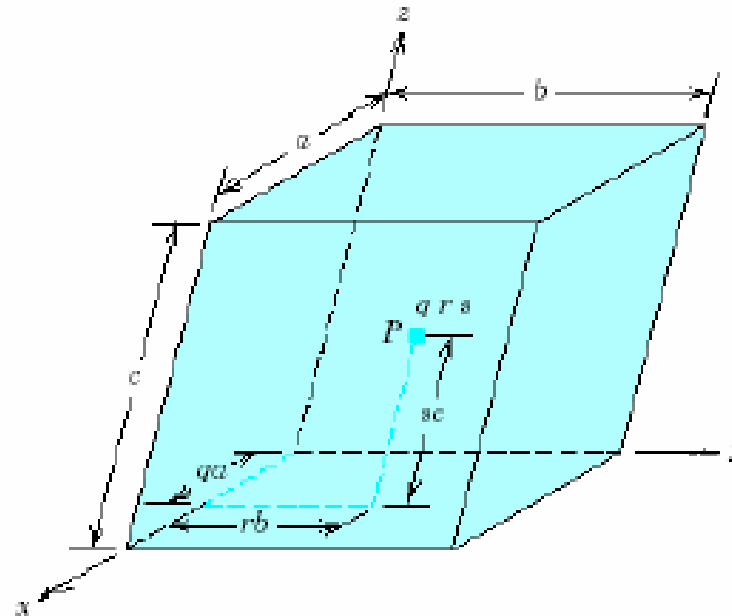
Triclinic

$a \neq b \neq c$   $\alpha \neq \beta \neq \gamma \neq 90^\circ$



# Crystallographic Points

- Be specified in terms of its coordinates
- Fractional multiples of the unit cell edge length



# Crystallographic Directions

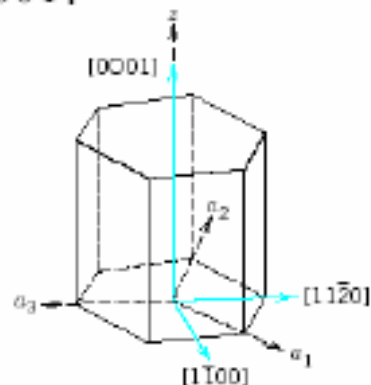
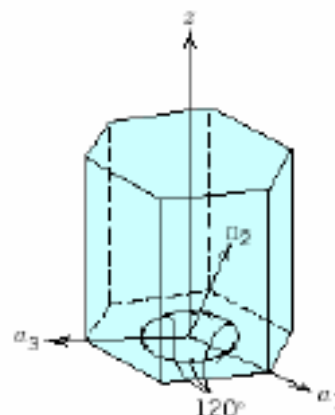
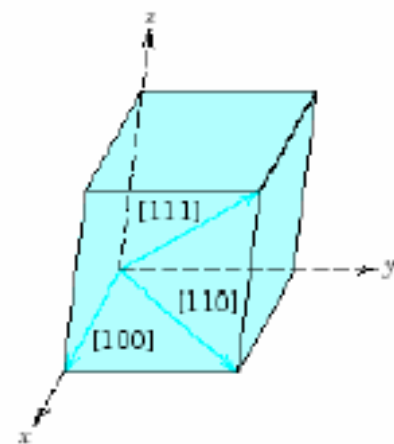
## Steps to determine the direction

- Let the vector pass origin
- Project to the axes
- Reduce the number to the smallest integer values
- Enclose in **Square Brackets**
- Use upper bar for negative value

Direction family: use **Angle Brackets**

$\langle 100 \rangle$ :  $[100]$ ,  $[\bar{1}00]$ ,  $[010]$ ,  $[0\bar{1}0]$ ,  $[001]$ ,  $[00\bar{1}]$

Four-axis system for hexagonal crystal



# Crystallographic Planes

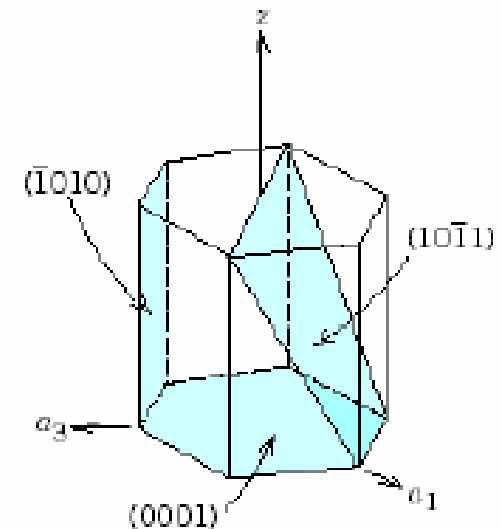
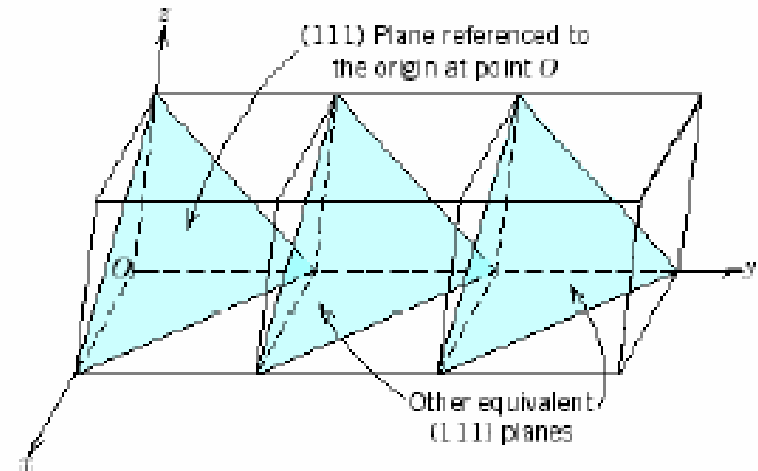
## Steps to determine the plane

- Choose right origin
- Intercept to the axes
- Take reciprocals
- Reduce the number to the smallest integer values
- Enclose in **Parentheses**
- Use upper bar for negative value

Plane family: use **Braces**

$\{111\}$ :  $(\bar{1}11)$ ,  $(1\bar{1}1)$ ,  $(11\bar{1})$ ,  $(111)$ .....

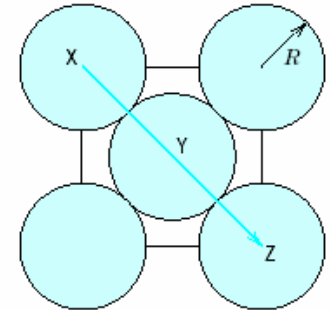
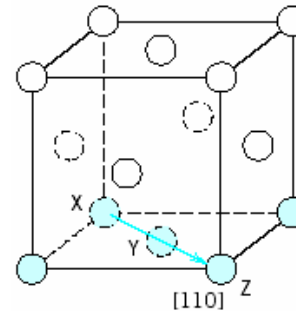
Four-axis system for hexagonal crystal



# Linear and Planar Densities

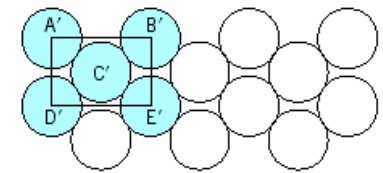
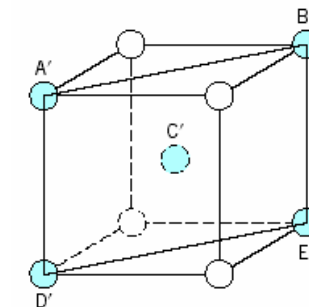
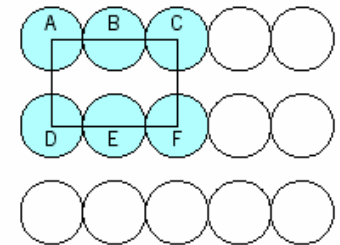
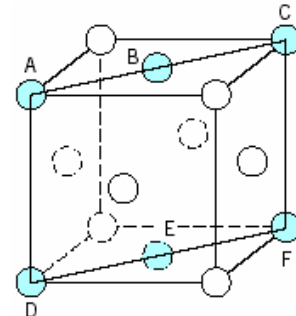
## • Linear Density

$$LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$



## • Planar Density

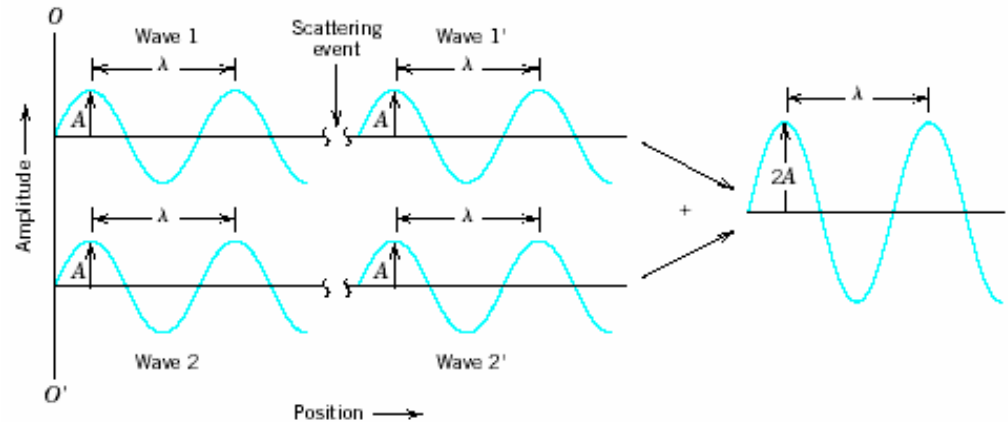
$$PD = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$



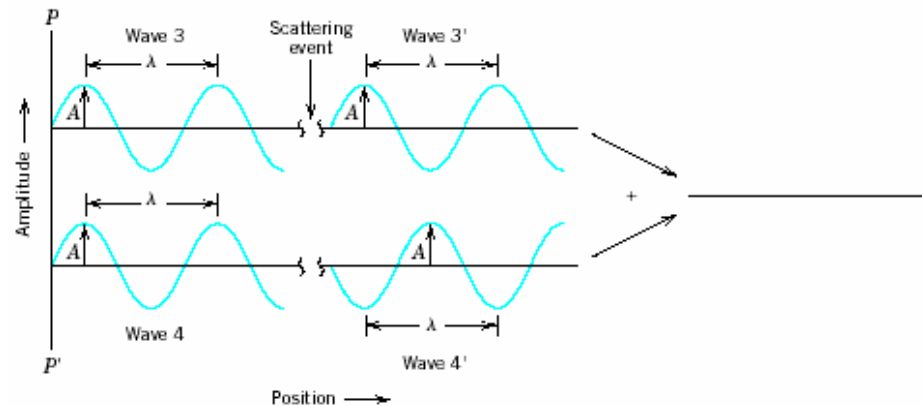
# X-ray Diffraction

## Diffraction Phenomenon

- A series regularly spaced obstacles
- Spacing  $\sim$  wavelength



- Constructive interference  
Path length difference  $\sim n \lambda$
- Destructive interference  
Path length difference  $\sim n/2 \lambda$



# Bragg's Law

Constructive interference:

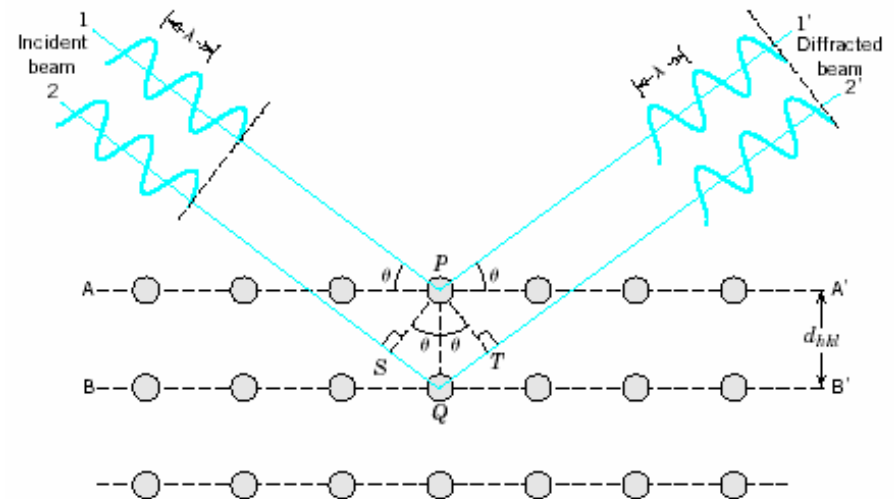
$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta$$

$$= 2d_{hkl} \sin \theta$$

For cubic system:

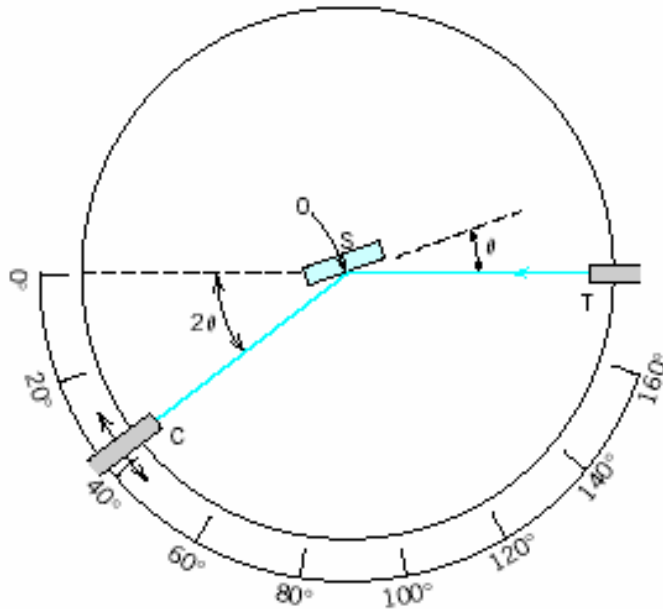
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



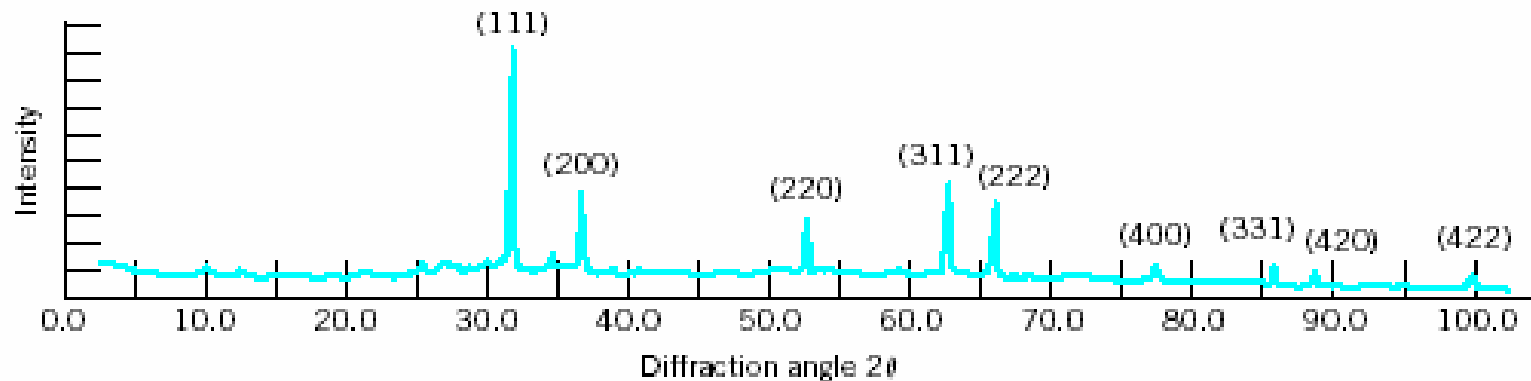
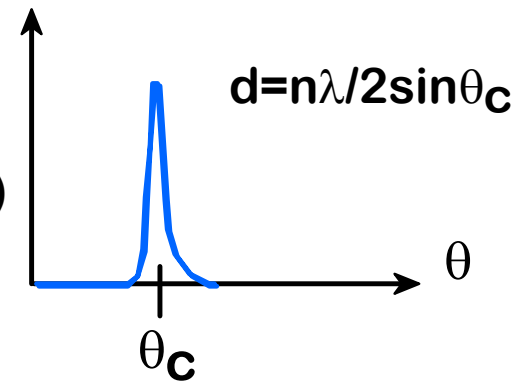


# Diffractometer

- Measurement of: Critical angles,  $\theta_c$ , for X-rays provide atomic spacing,  $d$ .



x-ray  
intensity  
(from  
detector)



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 an 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 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.

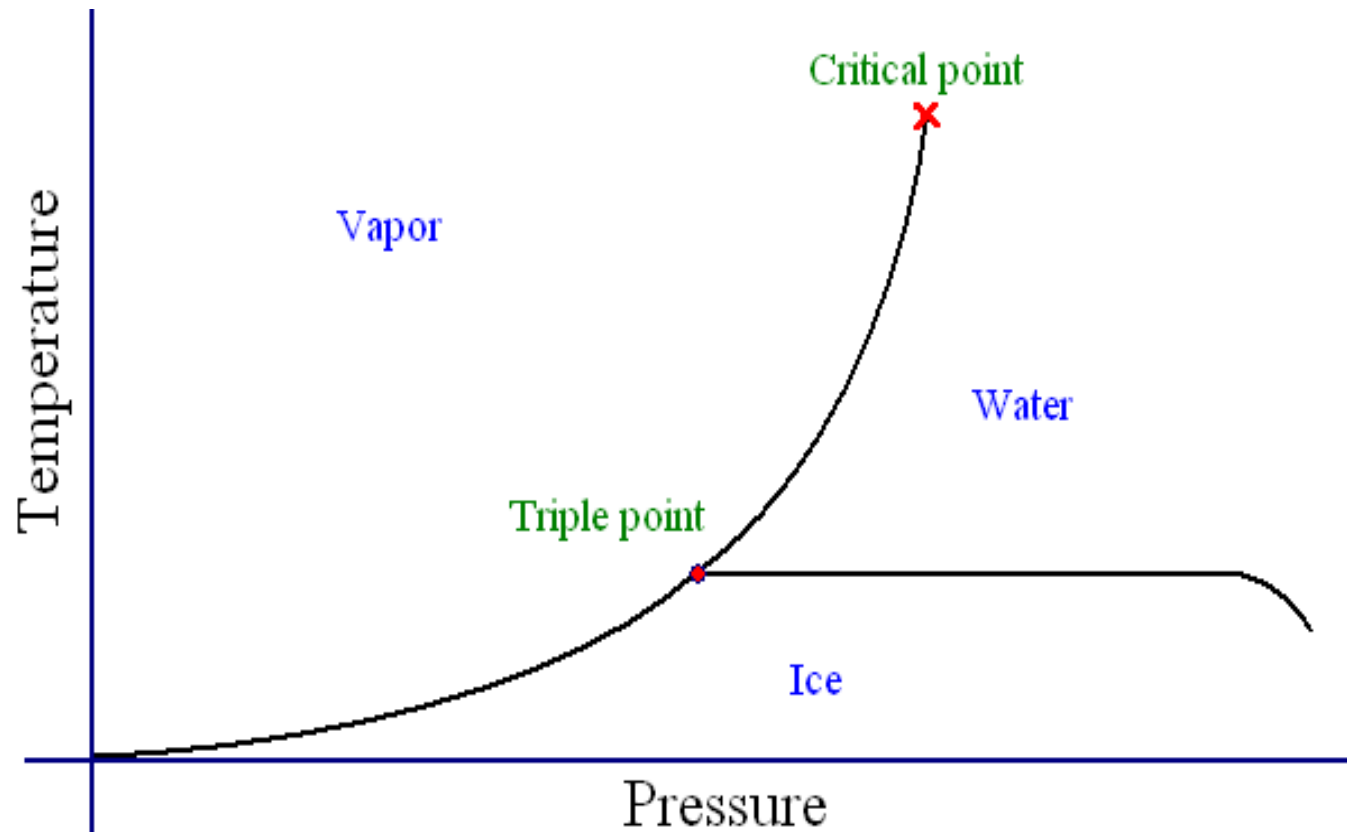
## Phase diagram – Useful information

- 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.



## Binary phase diagram

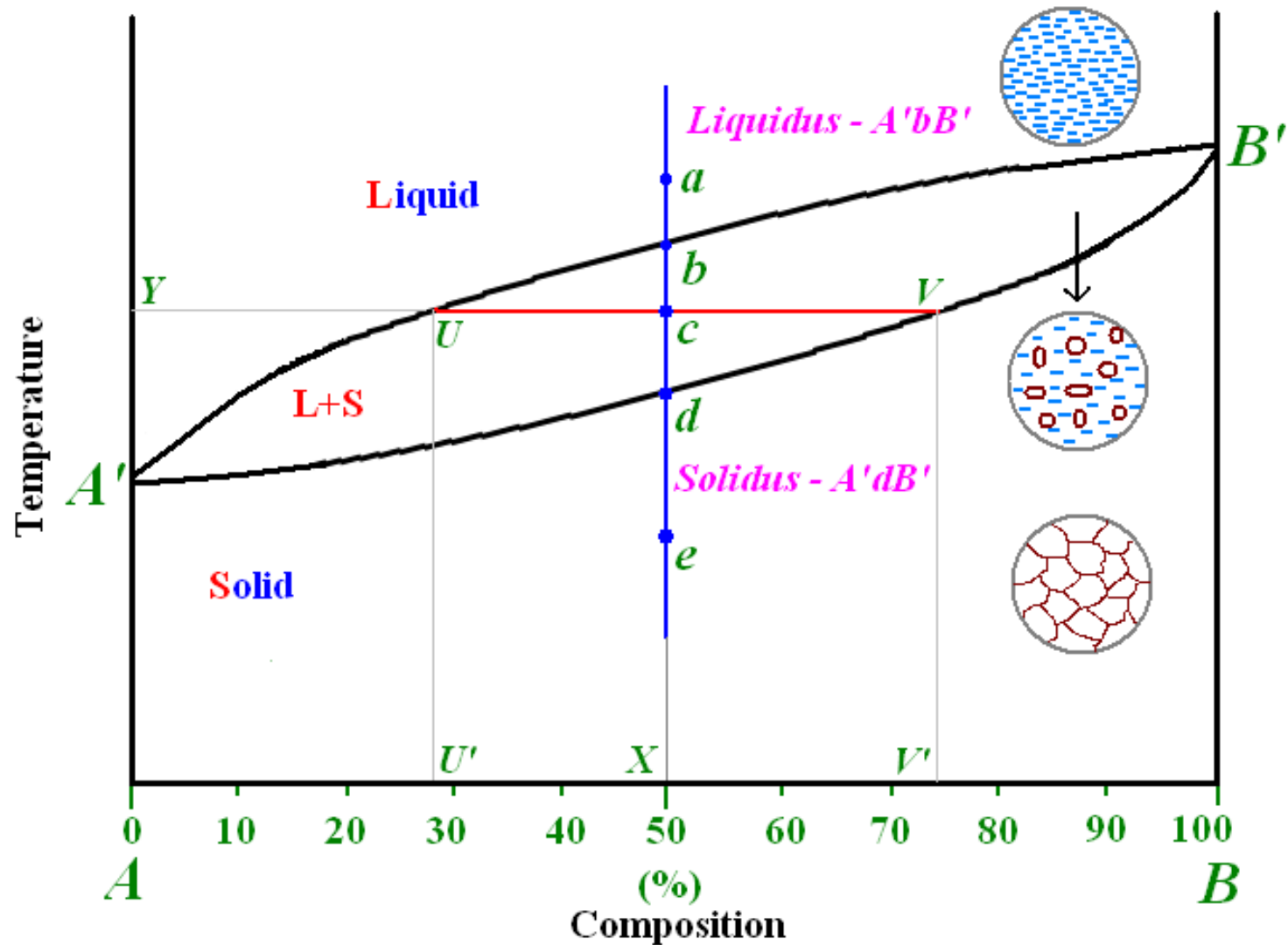
- If a system consists of two components, equilibrium of phases exist is depicted by *binary phase diagram*. For most systems, pressure is constant, thus independently variable parameters are – temperature and composition.
- Two components can be either two metals (Cu and Ni), or a metal and a compound (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>.

## 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.

## 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:

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

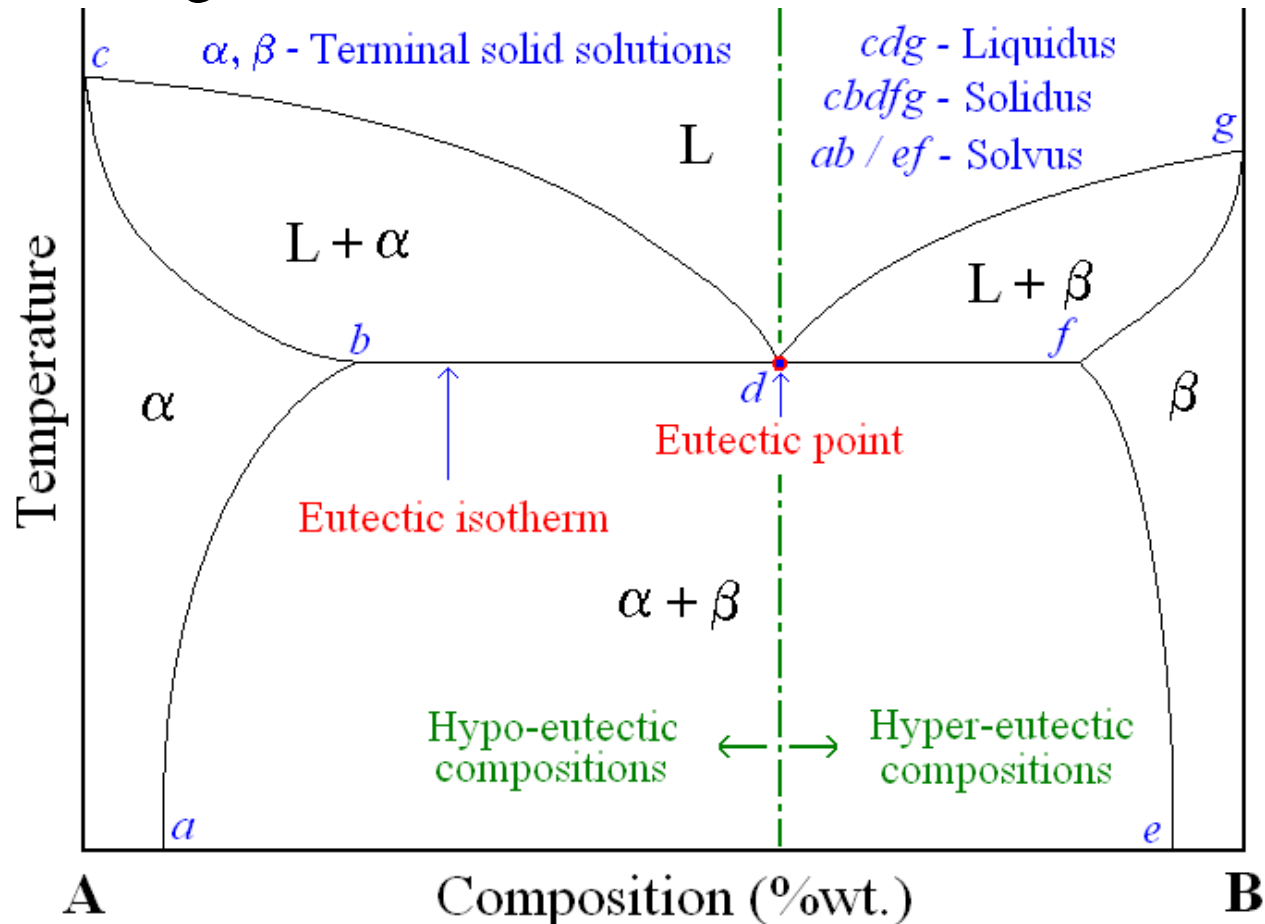
$$C_S = \frac{Uc}{UV}$$

$$C_L + C_S = 1$$

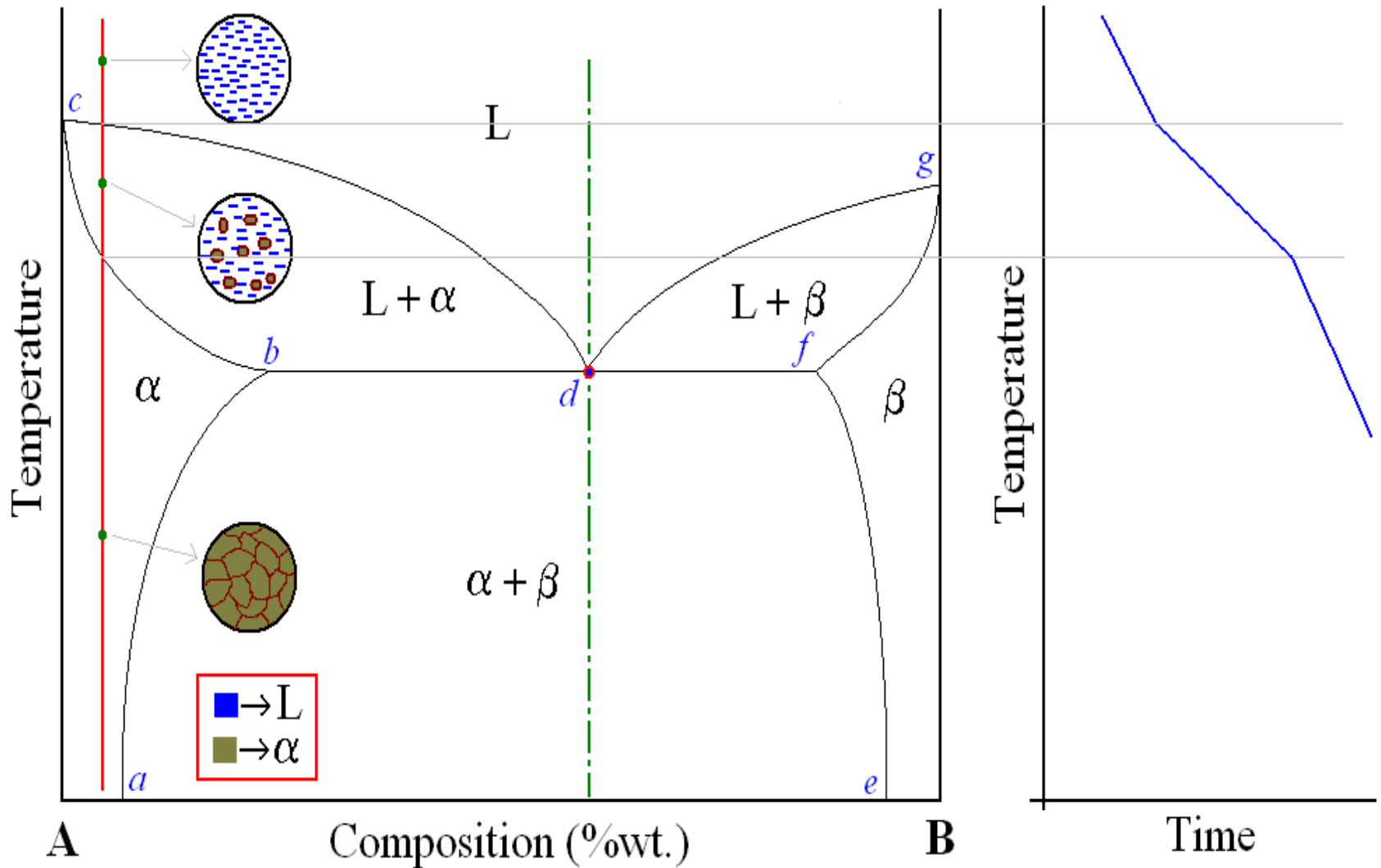
## Eutectic binary system

- 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

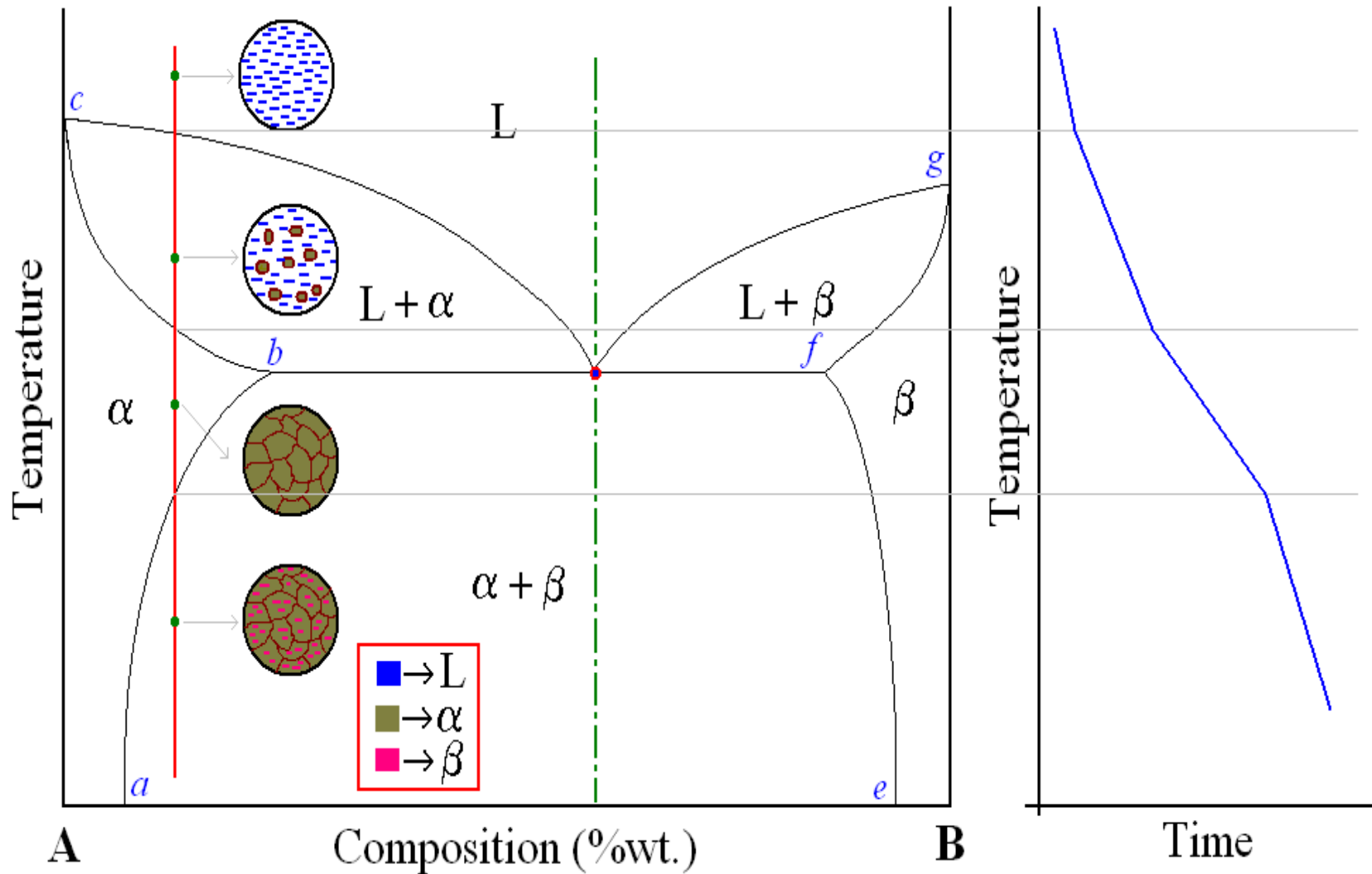


# Eutectic system – Cooling curve – Microstructure

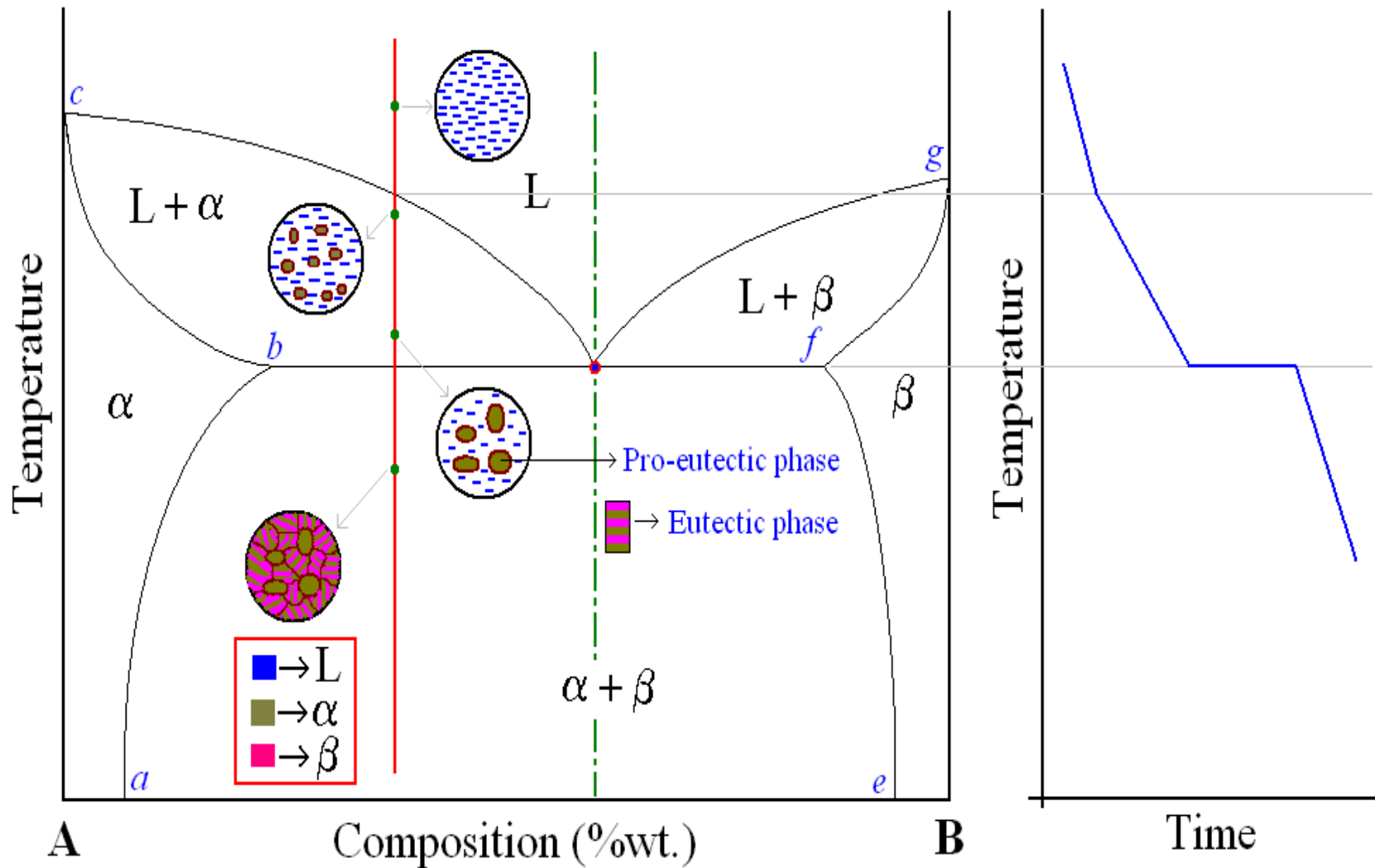




# Eutectic system – Cooling curve – Microstructure (contd....)

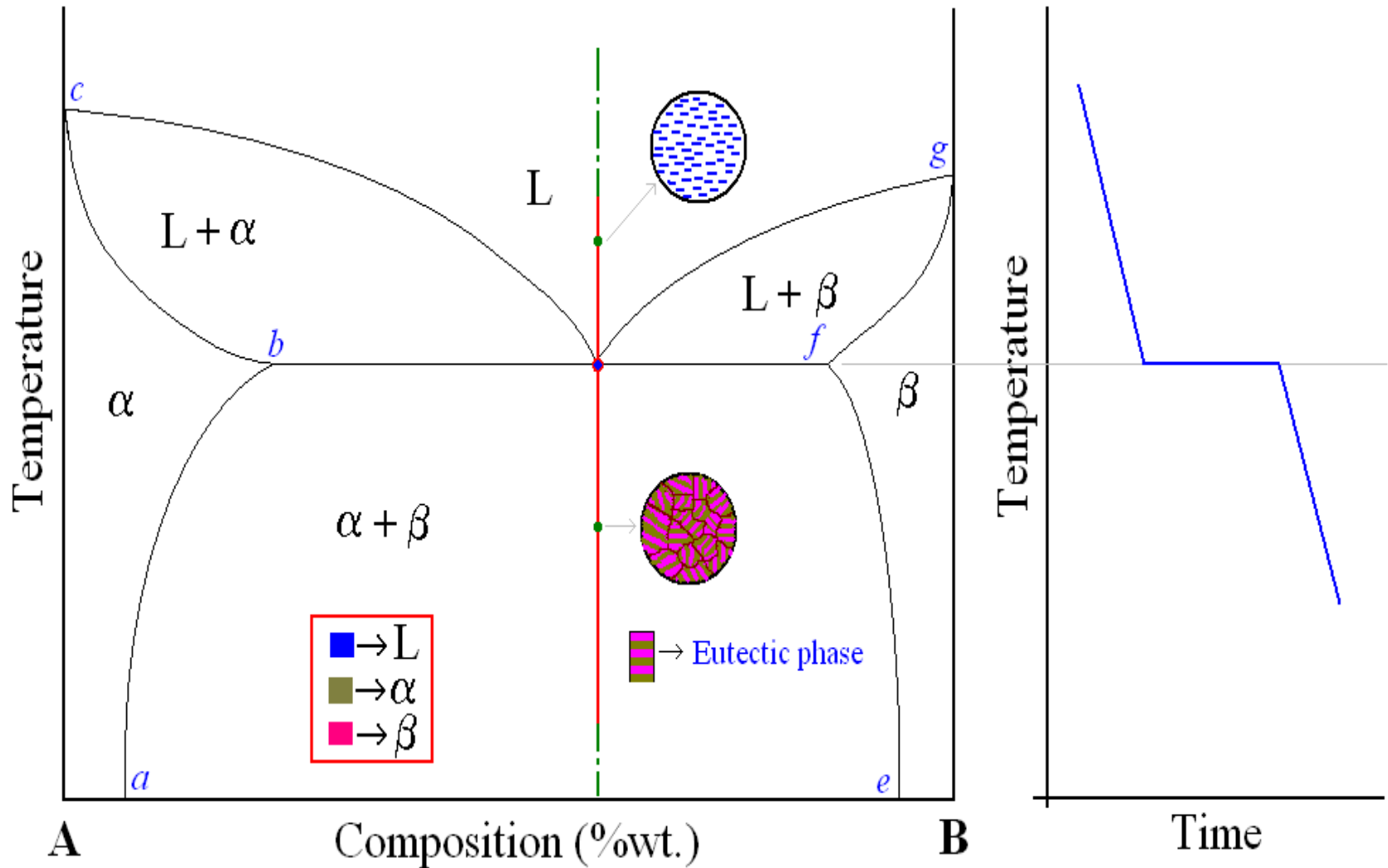


# Eutectic system – Cooling curve – Microstructure (contd....)



# Eutectic system – Cooling curve – Microstructure

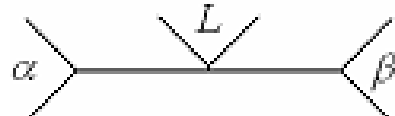


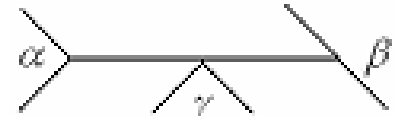


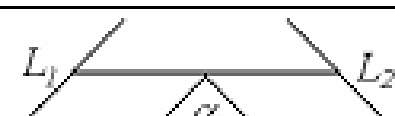
(contd....)



## 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, 1147 °C
Eutectoid	$\alpha \rightarrow \beta + \gamma$		Fe-C, 0.80% C, 723 °C
Peritectic	$L + \alpha \rightarrow \beta$		Fe-C, 0.16% C, 1495 °C
Peritectoid	$\alpha + \beta \rightarrow \gamma$		
Monotectic	$L_1 \rightarrow L_2 + \alpha$		Fe-C, 0.51% C, 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.:  $\text{Fe}_3\text{C}$  is metallic, whereas  $\text{MgO}$  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*.

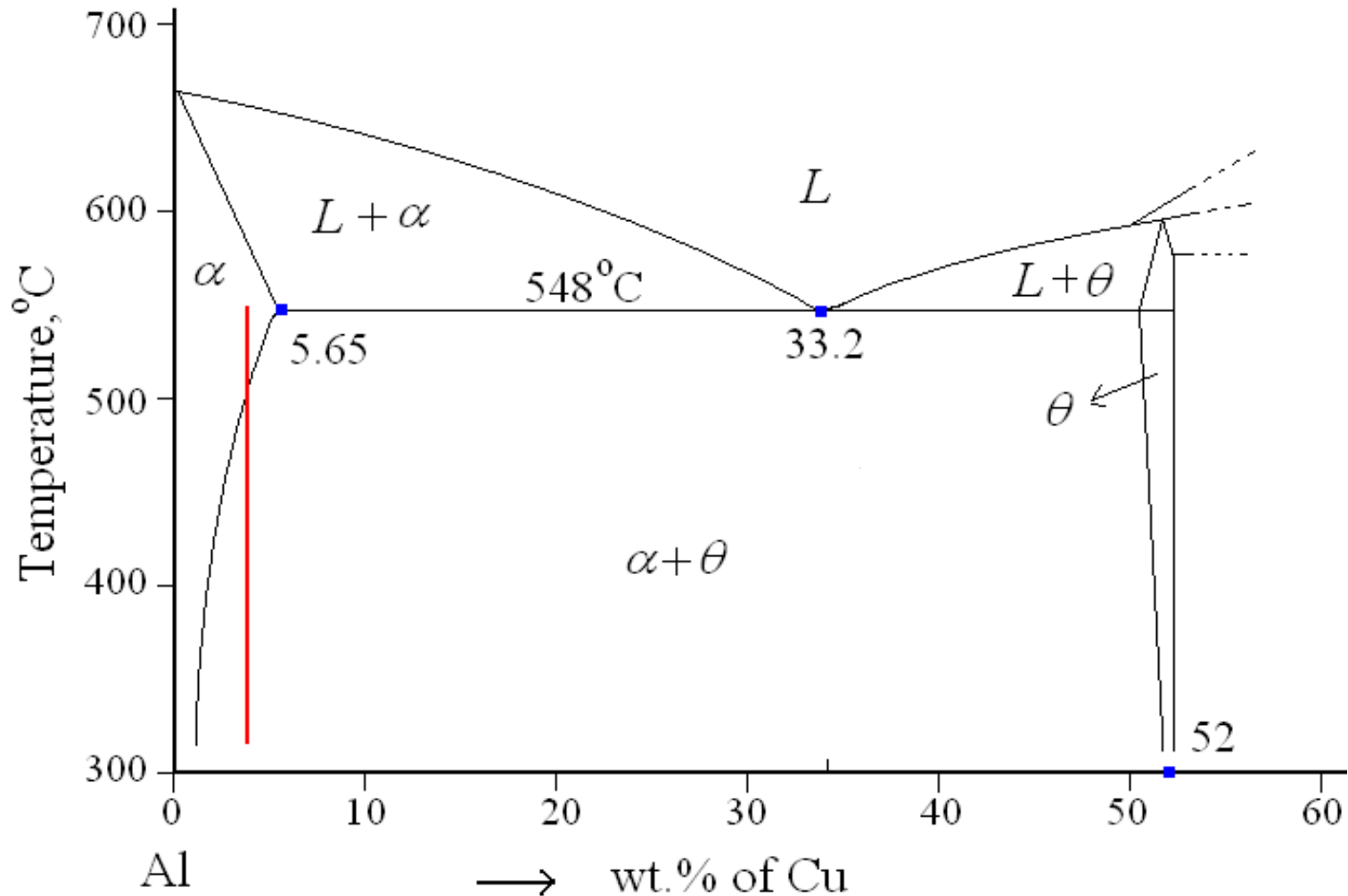


# Precipitation – Strengthening – Reactions (contd....)

- 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.

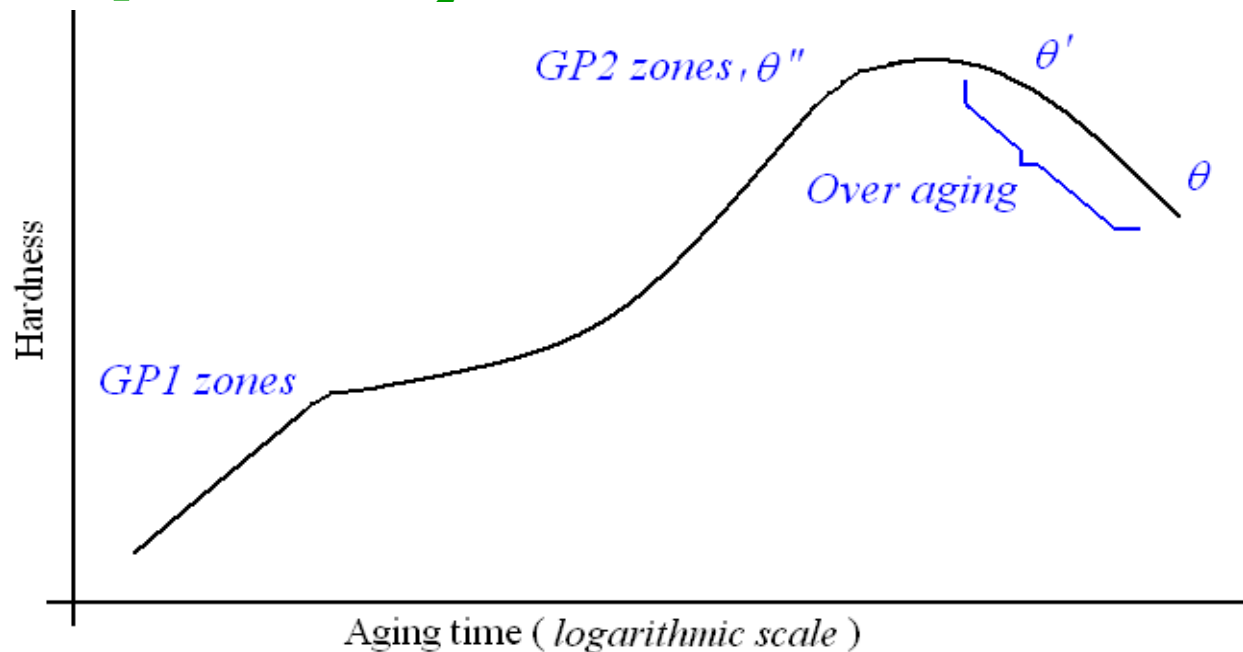
## Precipitation – Strengthening – Reactions (contd....)

- 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

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

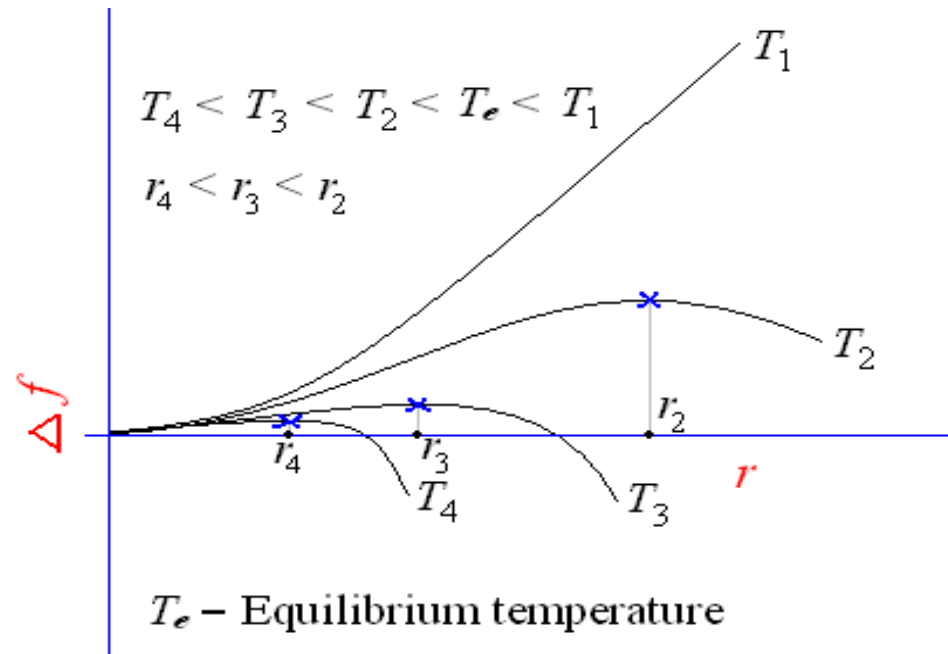
where  $r$  is the radius of the particle,  $\Delta g$  is the Gibbs free energy change per unit volume and  $\gamma$  is the surface energy of the interface.

# 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

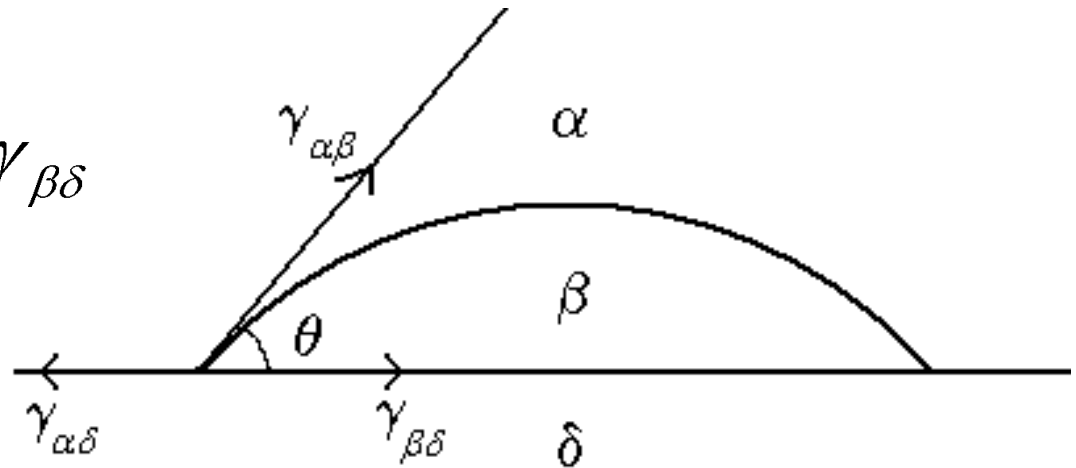
- In heterogeneous nucleation, the probability of nucleation occurring at certain preferred sites is much greater than that at other sites.

**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.  $\theta = 180$ , 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.  $\theta = 0$ , there is no barrier for heterogeneous nucleation  $\rightarrow$

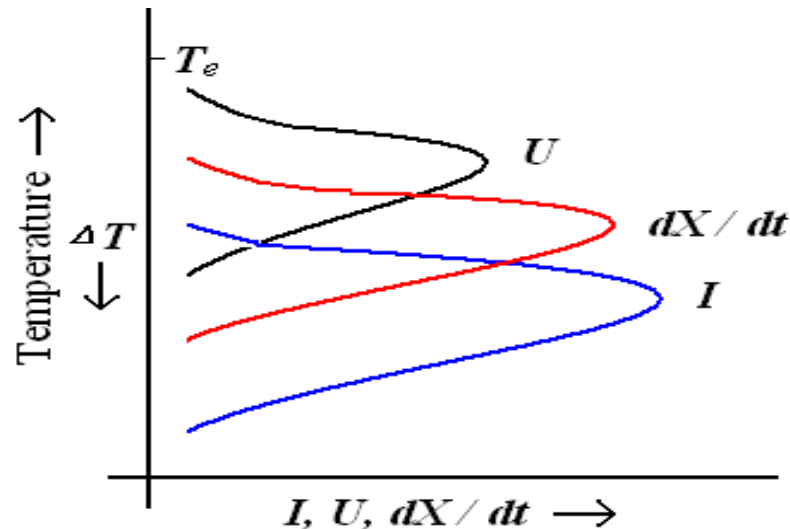
$$\Delta f_{het}^* = 0$$

- In intermediate conditions such as where the product particle attains hemispherical shape,  $\theta = 90 \rightarrow \Delta f_{het}^* = \frac{1}{2} \Delta f_{hom}^*$



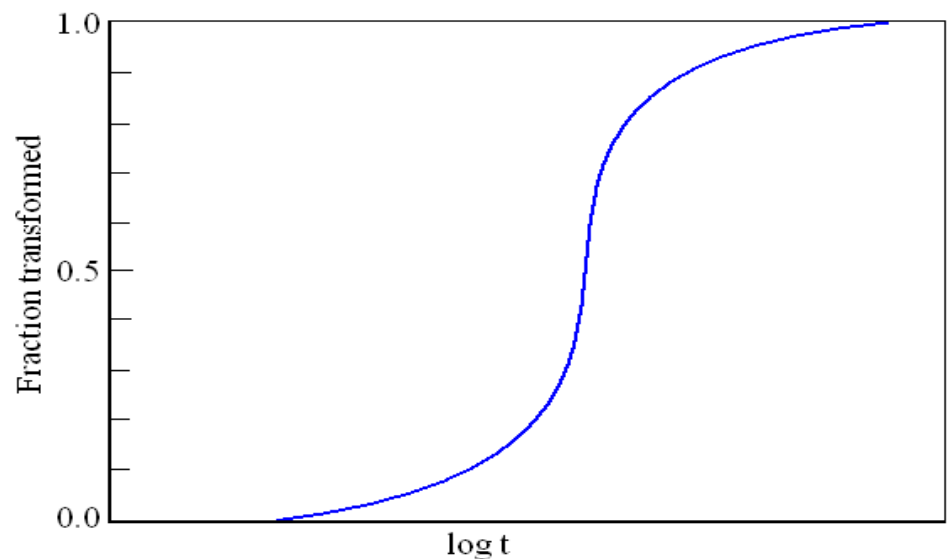
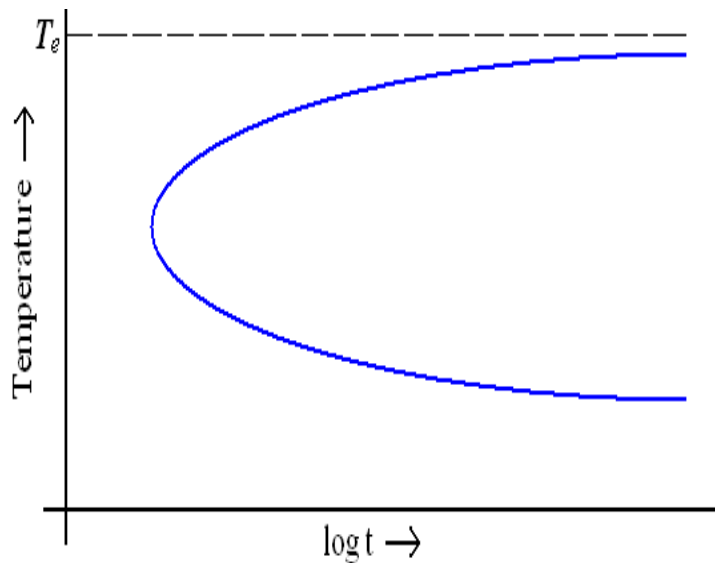
## Growth kinetics

- 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.  $dX/dt = f_n(U, I)$ :



## Growth kinetics (contd....)

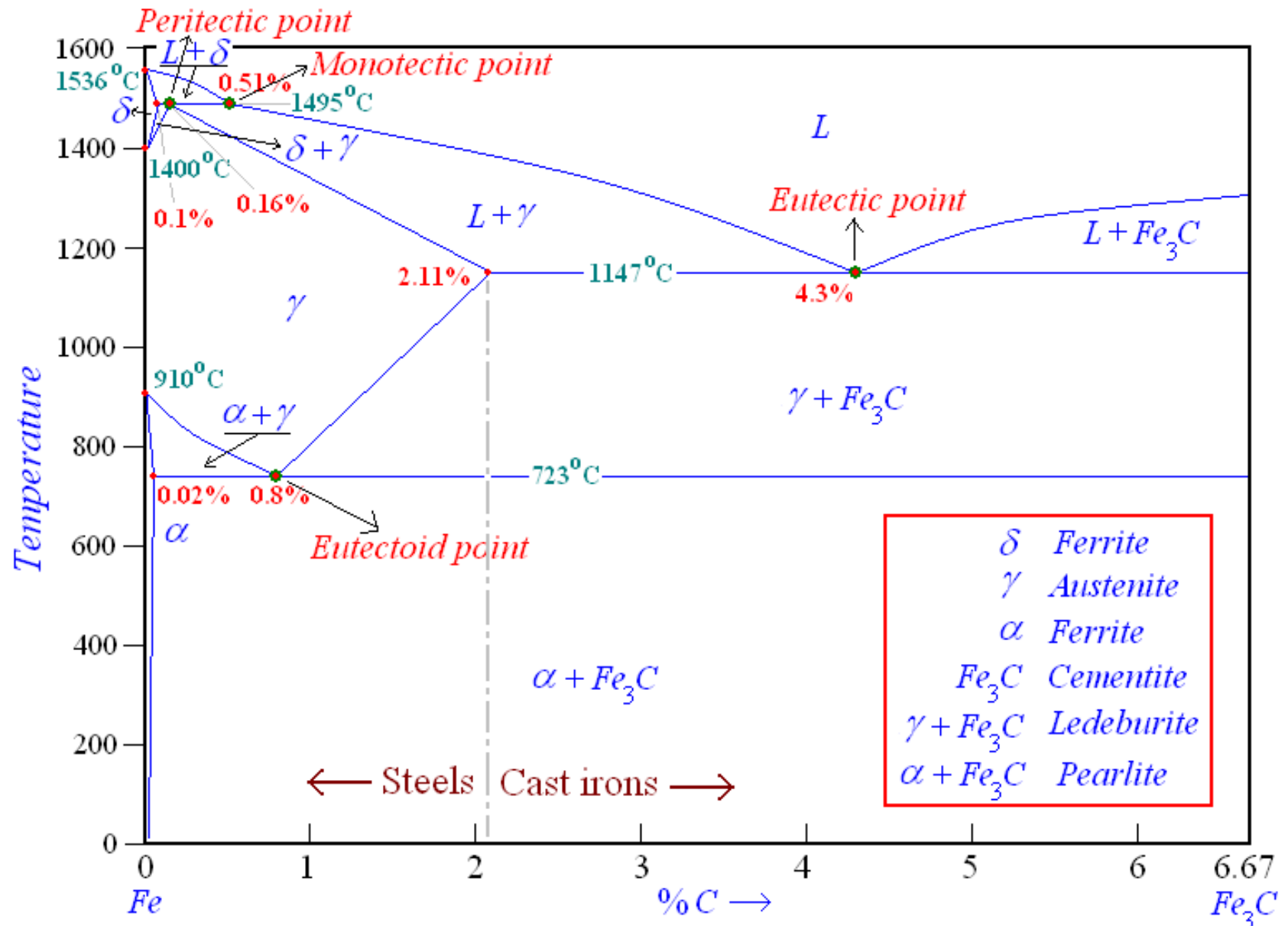
- Time required for a transformation to completion has a reciprocal relationship to the overall transformation rate, C-curve (time-temperature-transformation *or* TTT diagram).
- Transformation data are plotted as characteristic *S-curve*.
- At small degrees of supercooling, where slow nucleation and 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]

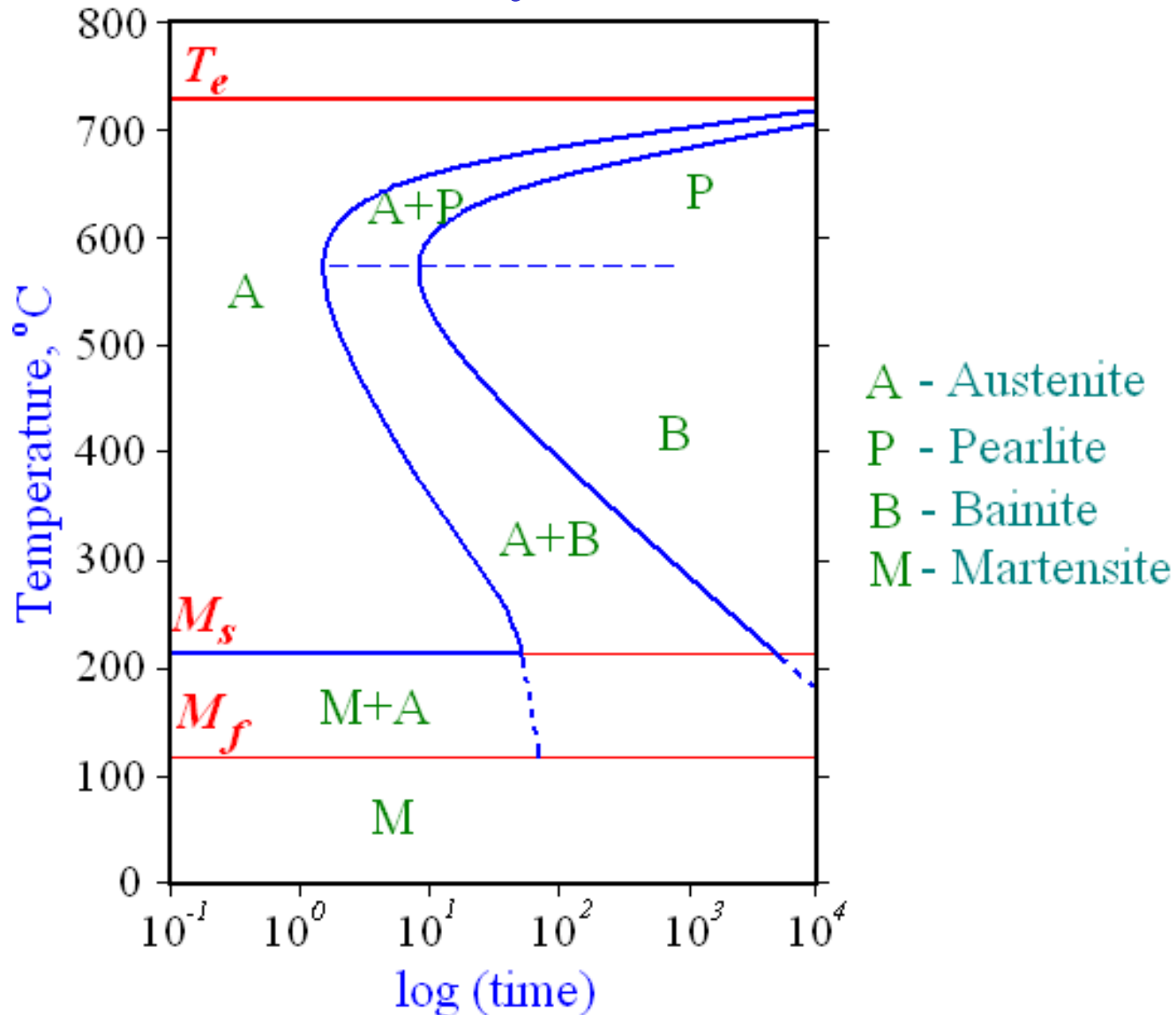
## Fe-C alloy classification

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

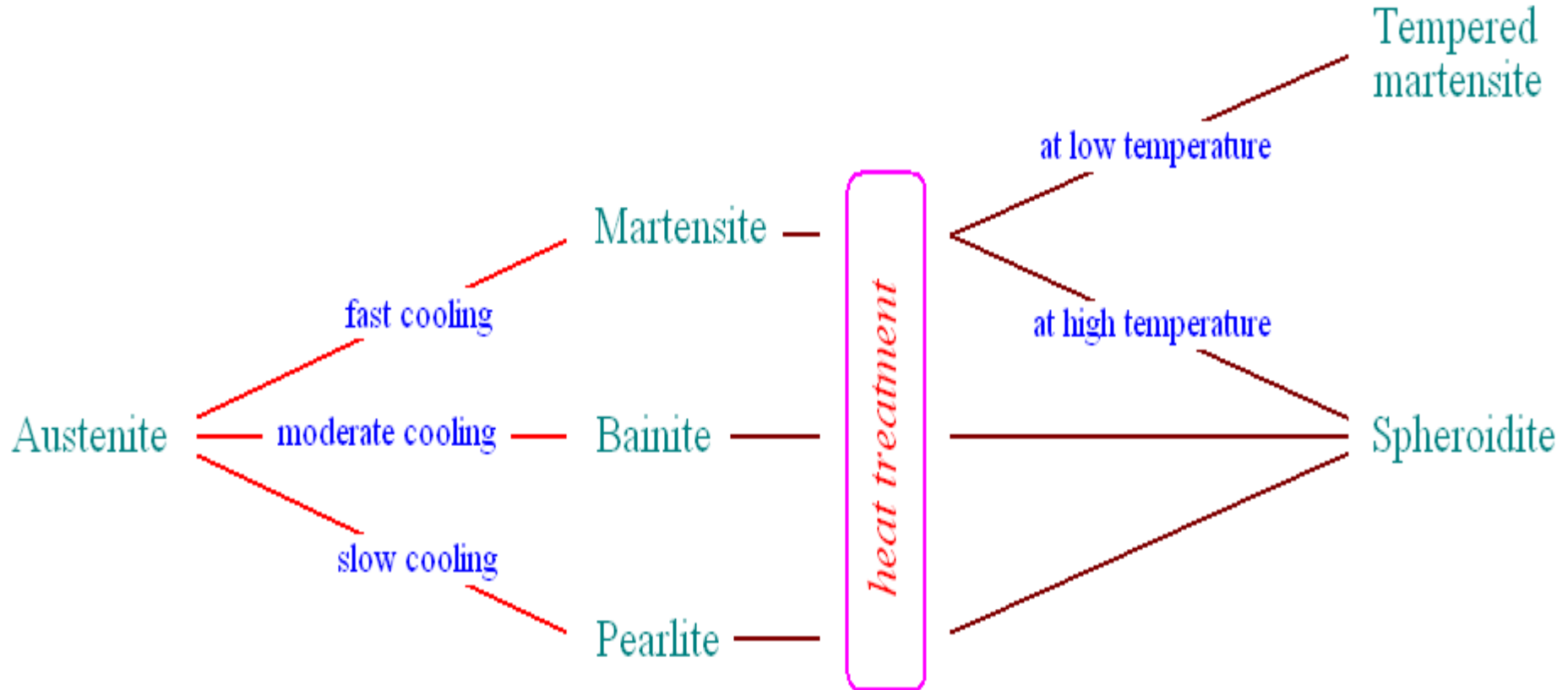
Commercial pure irons	% C < 0.008
Low-carbon/mild steels	0.008 - %C - 0.3
Medium carbon steels	0.3 - %C - 0.8
High-carbon steels	0.8- %C - 2.11
Cast irons	2.11 < %C

- 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

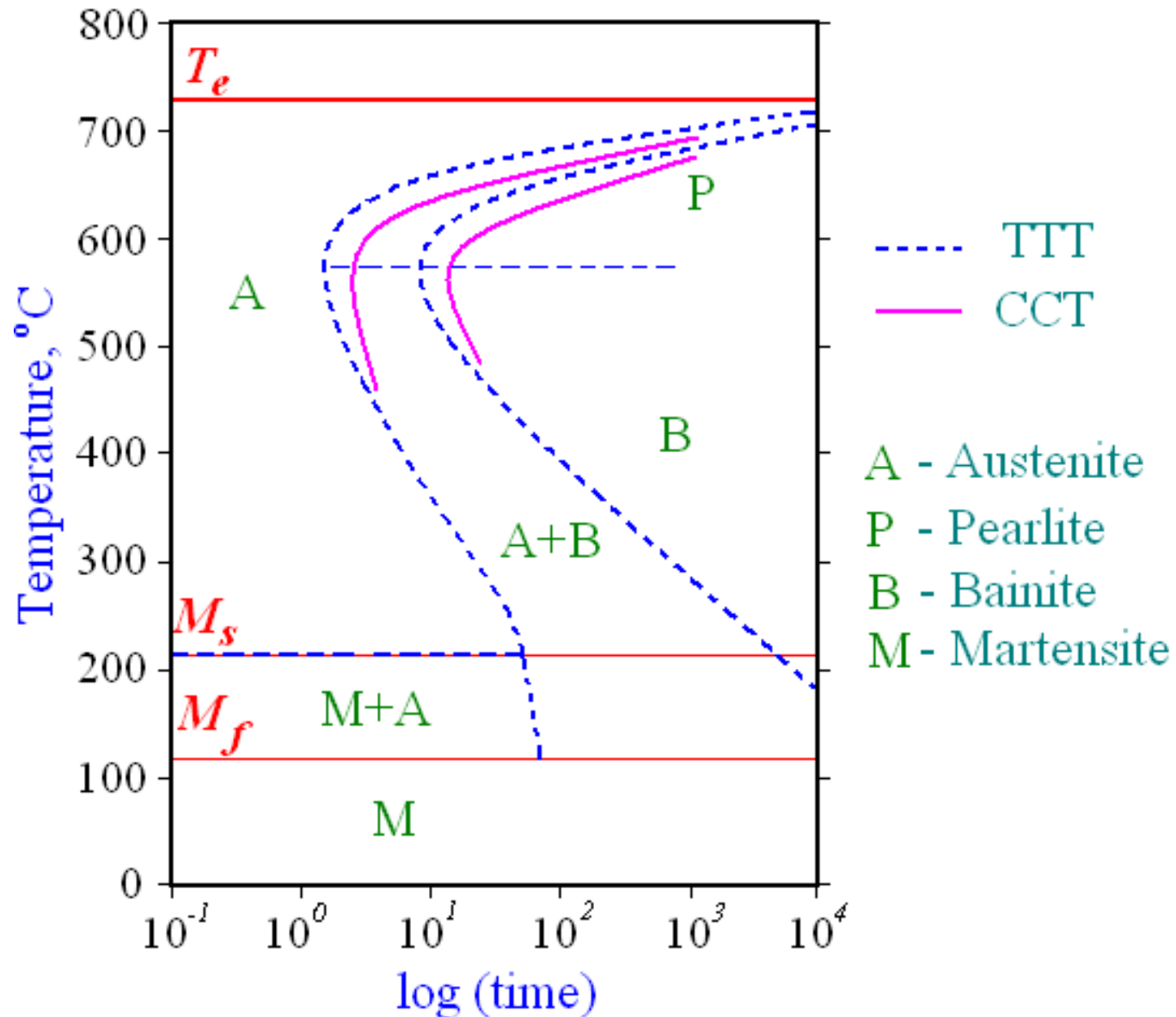




## CCT diagram for Fe-C system

- 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....)



# Materials Science

Jane Blackford

4 lectures “Metals”

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Room: S141, Sanderson Building

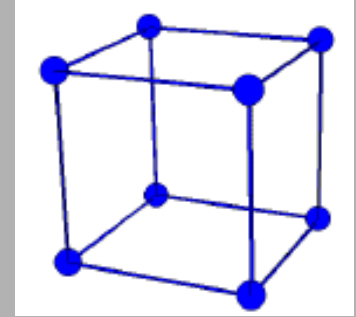
# Outline

- Introduction
- Strengthening mechanisms
- Classification of metals  
ferrous (e.g. steel, cast iron) & non ferrous (e.g. Al, Ni)
- Applications  $\leftrightarrow$  properties
- Ferrous Metallurgy  
bcc  $\leftrightarrow$  fcc; Fe-C phase diagram  
microstructure  $\leftrightarrow$  properties  
effects of %C and heat treatment
- Specific types of steels - tool, stainless, cast iron
- Non-ferrous metals

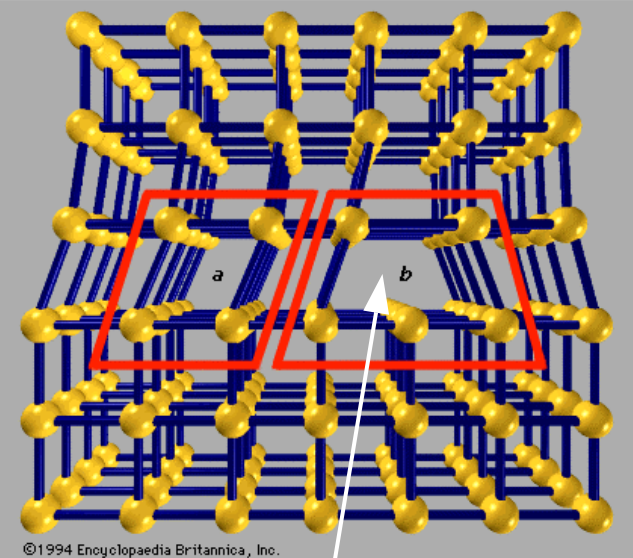
# Introduction - metals

- Extraction metallurgy - obtaining metals from ores
- Physical metallurgy - how to get the metal into the most useful condition of hardness, strength and toughness

# Metals are crystalline



- in reality they are not perfect
  - they contain dislocations



dislocation

A pure metal is very soft and weak

- Because dislocations move easily (plastic deformation)
- Physical metallurgy aims to restrict movement of dislocations →  
    ↑ strength and hardness

*[shorthand  $\perp$  = dislocation]*

# Strengthening mechanisms in metals

- Grain boundaries
- Solid solution hardening
- Work hardening
- Precipitation hardening
- These mechanisms influence the microstructure which in turn influences the material properties



# Grain boundaries

act as barriers to  $\perp$  movement

$\therefore \downarrow$  grain size  $\rightarrow \uparrow$  strength

Hall Petch  $\sigma_y = \sigma_o + k (1/\sqrt{d})$

$\sigma_y = \text{yield stress}$

$\sigma_o$  and  $k = \text{material constants}$

$d = \text{grain size}$

see Callister 7.8

# Solid solution hardening

- lattice strain interactions between impurity atoms and dislocations increase strength
- see Callister 7.9

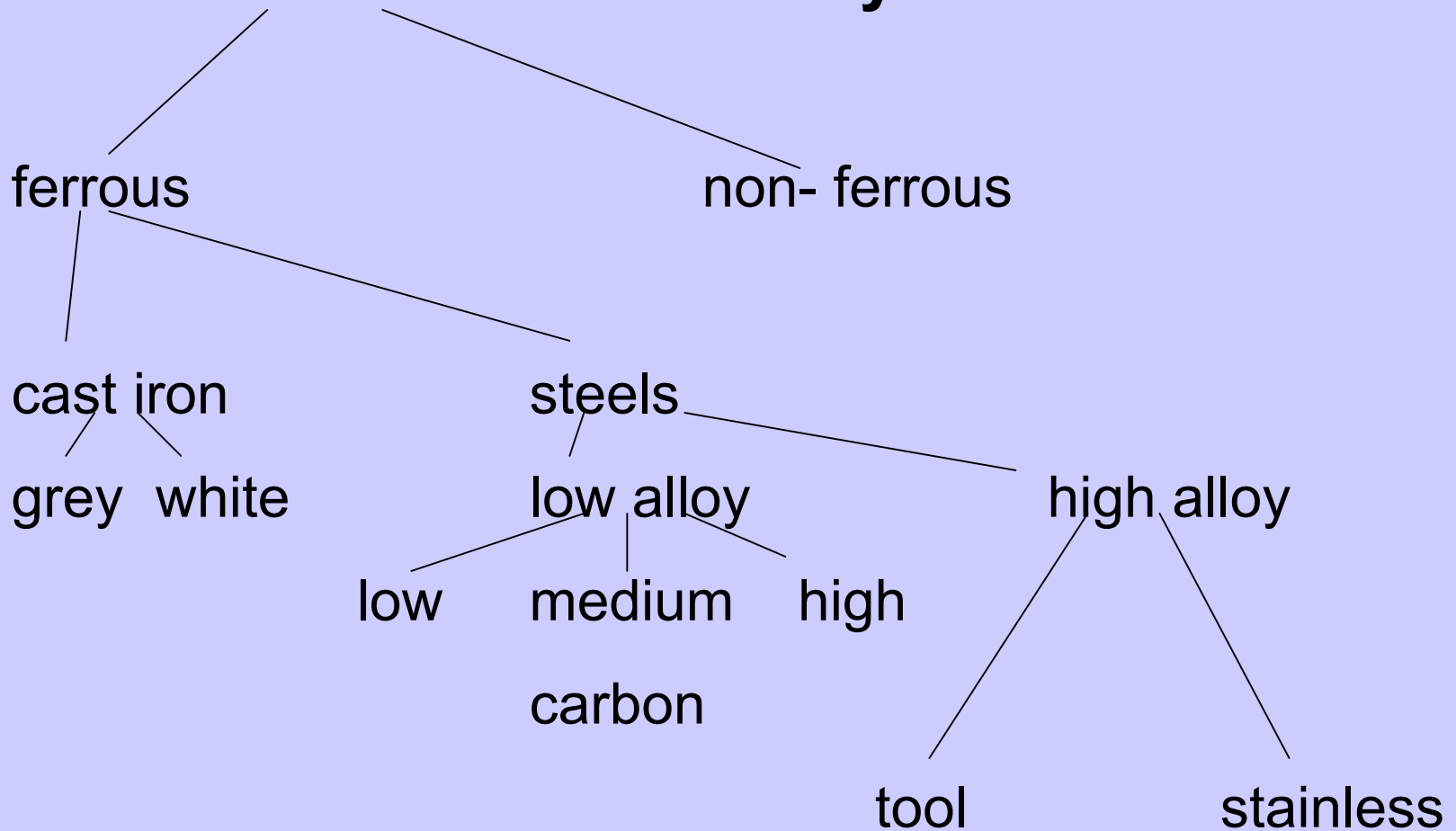
# Work hardening

- Work hardening = strain hardening  
(~ cold work)
- plastic deformation  $\rightarrow$   $\uparrow$  in  $\perp$  density  
 $\therefore$   $\uparrow$  repulsive  $\perp$  -  $\perp$  strain field interactions
- strength  $\uparrow$  with  $\uparrow$  plastic deformation
- *example paper clip*
- see Callister 7.10

# Precipitation hardening

- Formation of a uniform distribution of very small particles  $\rightarrow$   $\uparrow$  in resistance to  $\perp$  motion because of lattice strains near particles
- important in many alloy systems e.g. tempered martensite, Al alloys
- see Callister 11.7, 11.8

# Classification of metal alloys



# Steel

- Advantages
  - Low cost
  - high strength
  - relatively high toughness
  - weldable
- Disadvantages
  - heavy (high density)
  - poor corrosion resistance

# Applications

see table of properties and  
applications on handout

# Ferrous metallurgy

- Definition : Steel = iron with  $\leq 1.7$  wt % carbon (C)
- Iron is allotropic/polymorphic i.e. has different crystal structures in the solid state

912°C

1495 ° C

1538 ° C

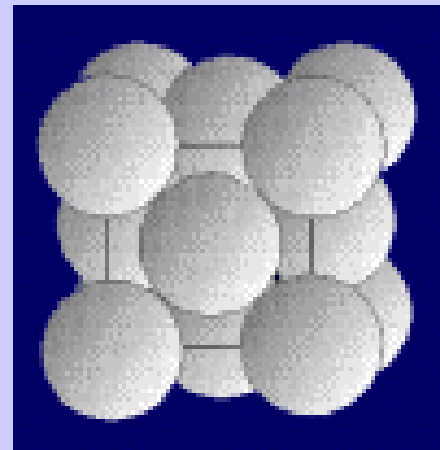
- bcc  $\leftrightarrow$  fcc  $\leftrightarrow$  bcc  $\leftrightarrow$  liquid
- solubility of carbon in bcc ( $\alpha$ ) = 0.02 wt %  
and in fcc ( $\gamma$ ) = 2.1 wt %
- Iron carbon phase diagram (useful for slow cooling and predicting microstructures).
- See handout and Callister Chapt 9.



- bcc = body centre cubic



- fcc = face centre cubic

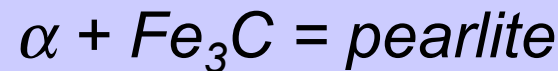


- **Properties of steels depend on their microstructure**
- Now consider how different microstructures can be formed by :

1. Slow cooling from  $\gamma$  to room temperature

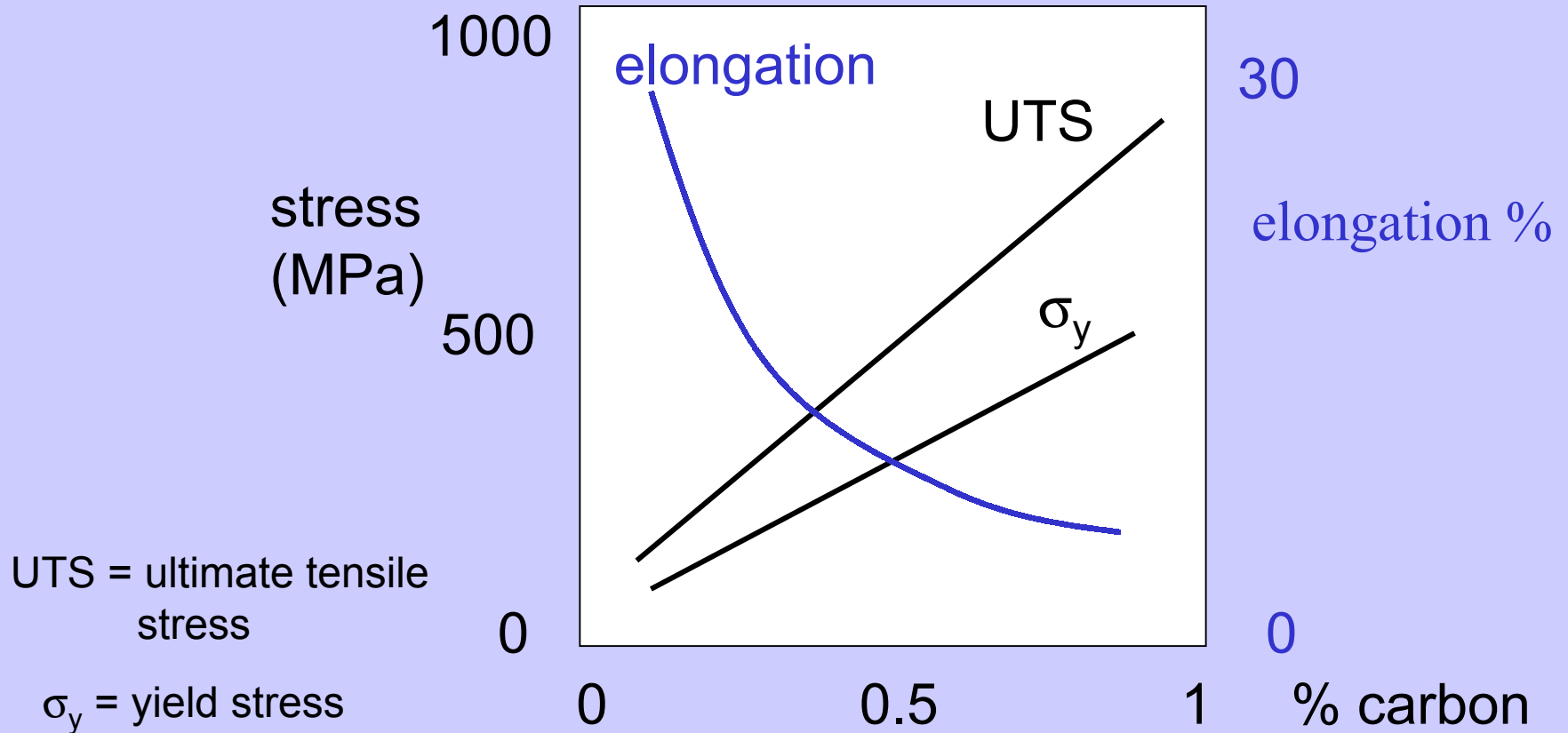
2. Fast cooling from  $\gamma$  to room temperature

1. slow cooling:



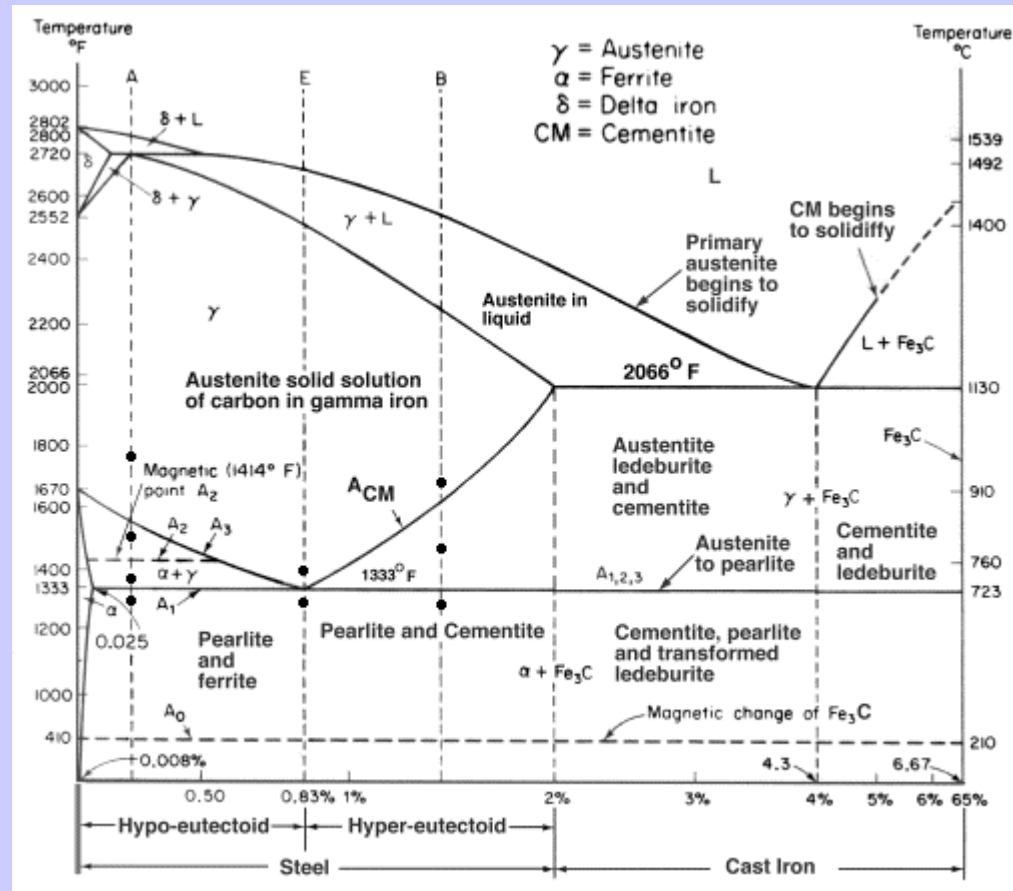
As  $\uparrow \text{C} \rightarrow \uparrow \text{Fe}_3\text{C} \rightarrow \uparrow \text{strength} \uparrow \text{hardness} \downarrow \text{ductility}$

# Mechanical properties of SLOW cooled carbon steels



- relate properties to microstructures
- NB can obtain very different properties by fast cooling
- see Callister Chapt. 10

# Iron-carbon phase diagram



- see handout including constituents, symbols and description [Callister Chapt. 9]

# Formation of pearlite

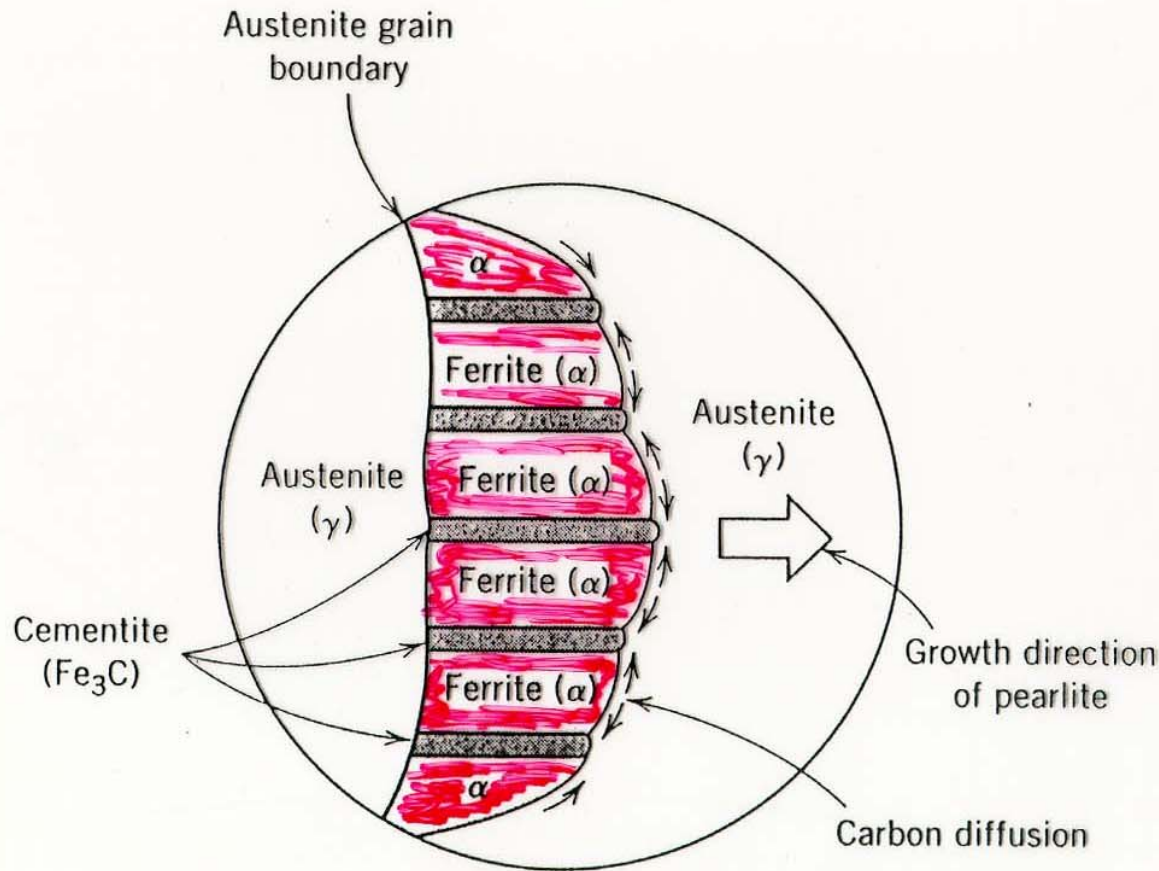
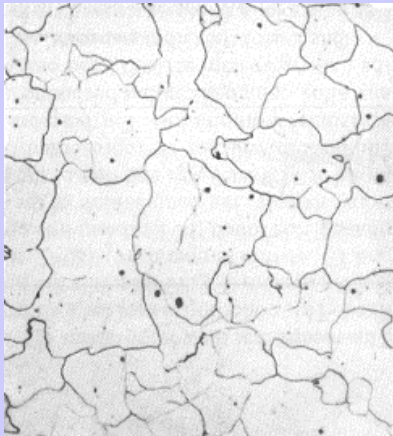


FIGURE 9.26 Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows.

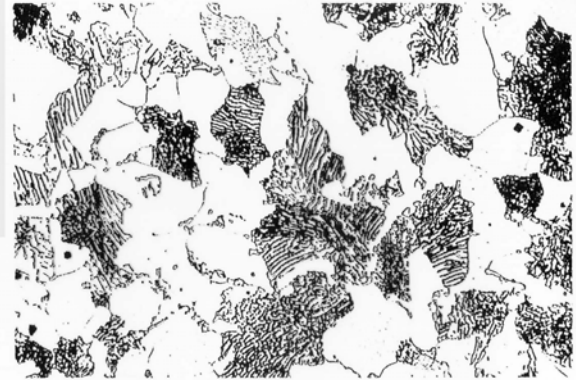
# Microstructures in slow cooled steels



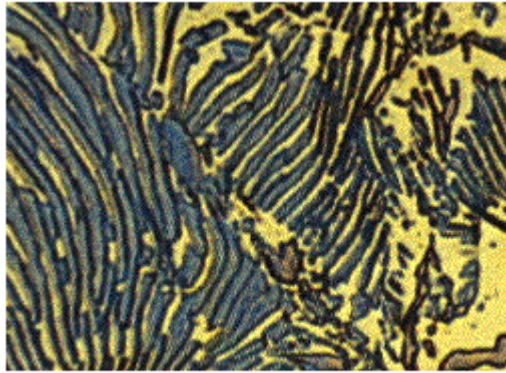
0% carbon - pure ferrite

0.4% C ferrite + pearlite

FIGURE 9.28  
Photomicrograph of  
a 0.38 wt% C steel  
having a micro-  
structure consisting of  
pearlite and  
proeutectoid ferrite.  
635 $\times$ .  
(Photomicrograph  
courtesy of Republic  
Steel Corporation.)



1.4% C ferrite + cementite



20 μm

Two-dimensional morphology of pearlite, apparently consisting of alternating layers of cementite and ferrite.



Three-dimensional analogy to the morphology of pearlite, i.e. the cabbage represents a single crystal of pearlite, and the water in the bucket the single crystal of ferrite.

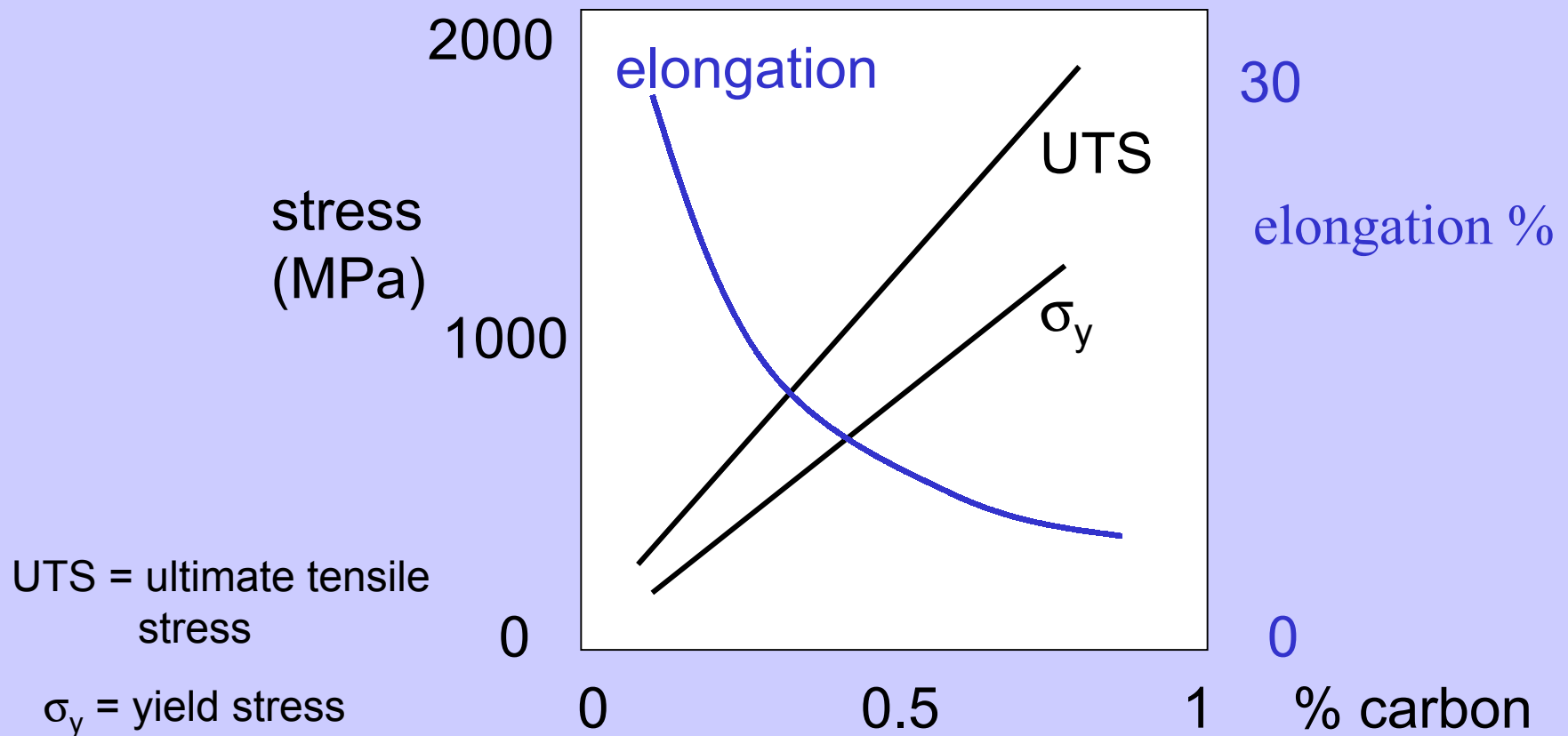
# Properties of steels depend on their microstructure

Now consider how different microstructures can be formed by :

1. Slow cooling from  $\gamma$  to room temperature
2. Fast cooling from  $\gamma$  to room temperature



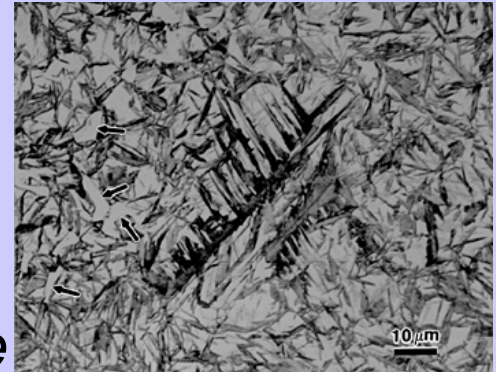
# Mechanical properties of RAPIDLY cooled carbon steels



# Rapidly cooled carbon steels - martensite

- Fast cooling from  $\gamma$  to room temperature  
 $\gamma$  (austenite)  $\rightarrow$   $\alpha'$  (martensite)

*very hard and brittle*



Cooling rates required :

- Pure Fe  $10^5$  °C/s
- Fe-0.8%C 200 °C/s

critical  
cooling  
rates

so  $\alpha'$  difficult to achieve in thick sections

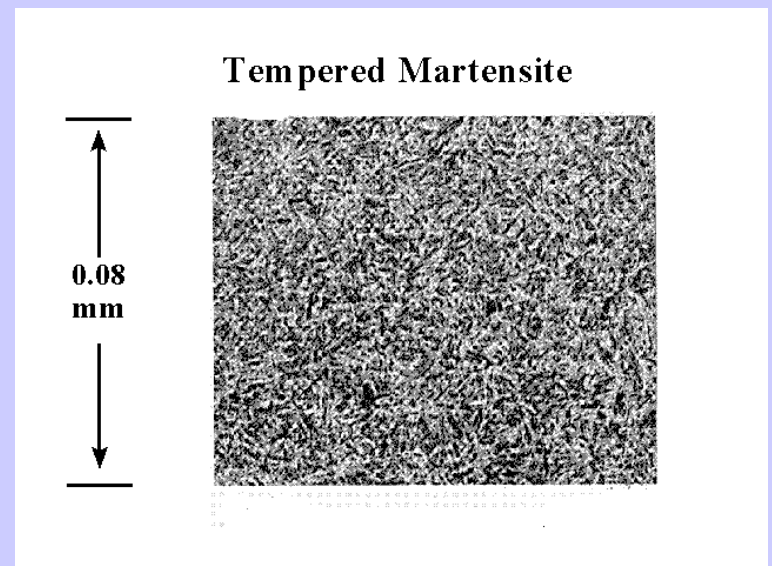
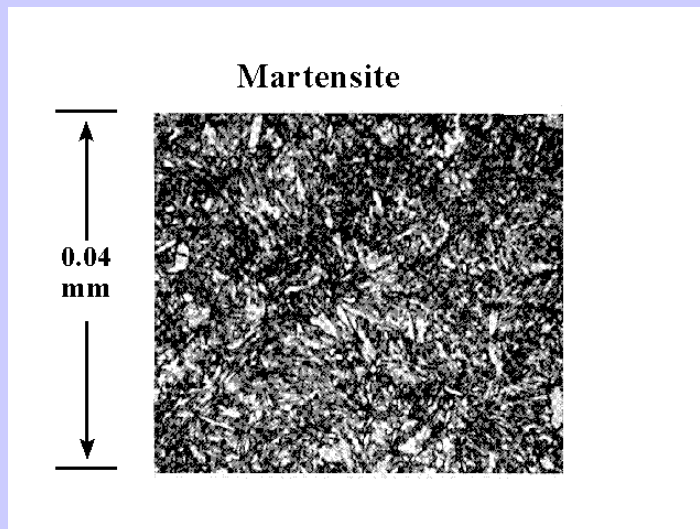
and may  $\rightarrow$  component distortion [Callister chpt 10]

## Martensite...

- Adding Mo, Mn, Cr, Ni, C decreases the critical cooling rate required for  $\alpha'$  formation
- Steels containing 2-7% of these elements = *low alloy steels*. They have high hardenability i.e. form  $\alpha'$  readily .
- Also these elements increase strength by solid solution strengthening
- USES: crankshafts, spanners, high tensile bolts

# Martensite

- But for most uses  $\alpha'$  is too brittle
- So it is tempered by heat treatment at 200-600°C
- $\alpha' \rightarrow \alpha$  (ferrite) +  $\text{Fe}_3\text{C}$  (as fine particles)
- $\text{Fe}_3\text{C}$  fine particles increase strength by precipitation hardening
- These steels are known as *quench and tempered* steels



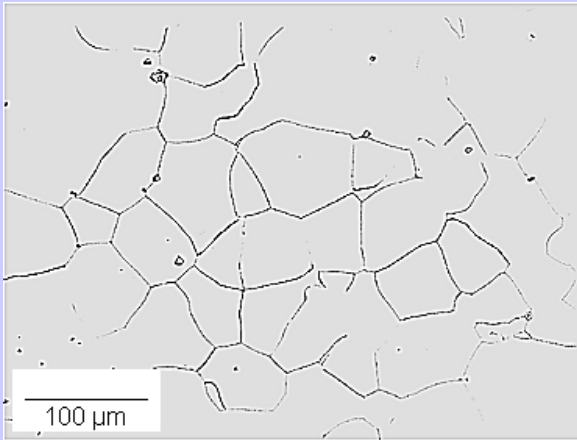
# Stainless steel

- Plain carbon steels rust and oxidise if heated in air
- Adding Cr  $\rightarrow$   $\text{Cr}_2\text{O}_3$  formation, an oxide which protects the underlying alloy
- Definition:

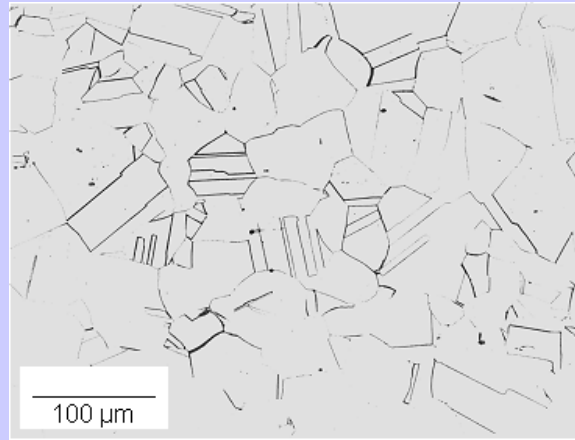
Fe with  $>11$  wt% Cr = stainless steel

# Classification of stainless steel

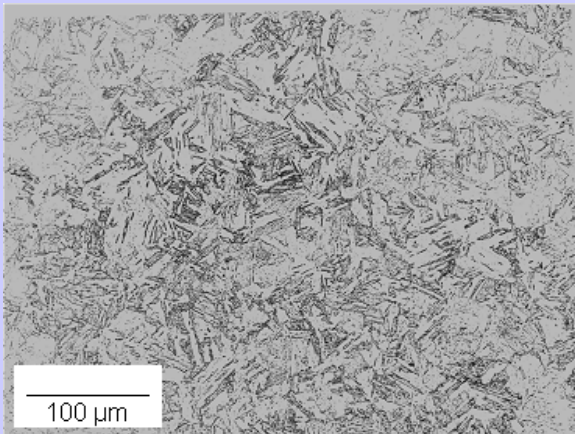
## Ferritic



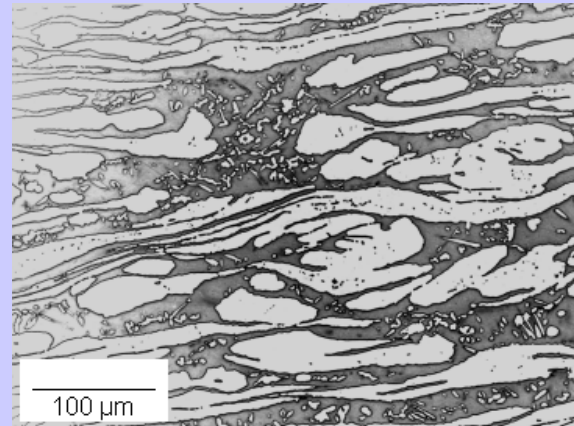
## Austenitic



## Martensitic



## Duplex



# Ferritic stainless steel

- bcc structure
- Typical alloy Fe-15Cr-0.6C, used in quench and tempered condition
- strengthened by carbide precipitation
- Uses rust-free ball bearings, scalpels, knives

# Austenitic stainless steel

- fcc structure (stabilised by adding Ni)
- Typical alloy Fe-18Cr-8Ni-1Mn-0.1C
- Disadvantage work harden rapidly so more difficult to shape and machine
- Advantages of ALL fcc metals and alloys
  - ↑ toughness
  - ↑ ductility
  - ↑ creep resistance



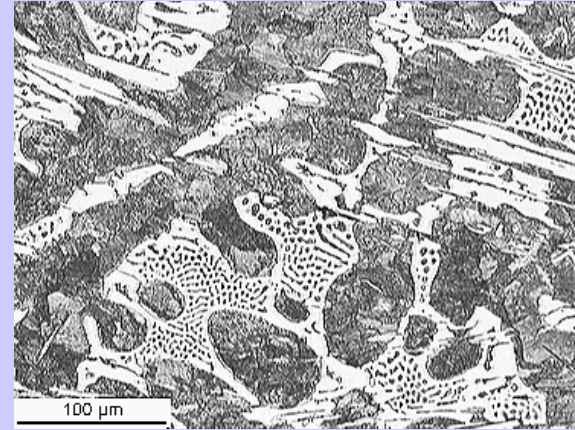
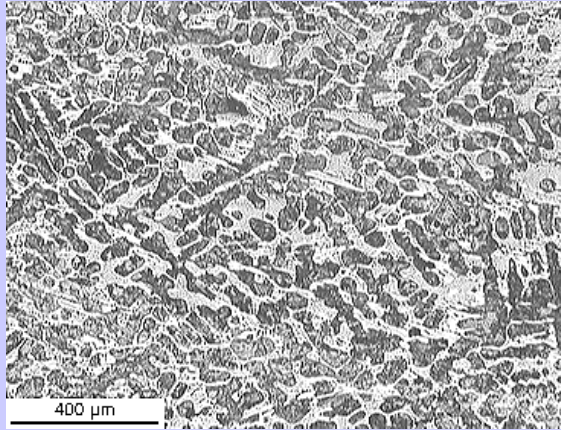
# Cast Iron

- Steel can be cast but tends not to be as it's technically difficult (due to high melting temperature), and high cost
- Definition: Fe with  $>1.7\text{wt}\%$  C = cast iron
- Advantages can be sand cast to intricate shapes using basic technology
- Disadvantage BRITTLE so can't be used for high stress or shock loading

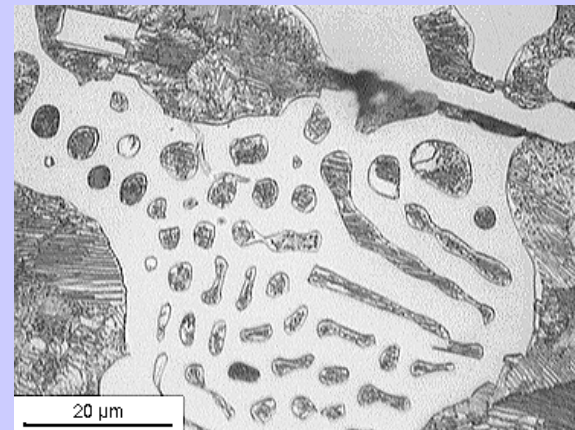
# Classification of Cast Iron

- WHITE
  - microstructure based on Fe + Fe<sub>3</sub>C
- GREY
  - Silicon (Si) added e.g. Fe-2%Si-C
  - Si stabilises the Fe-C system, rather than Fe-Fe<sub>3</sub>C
  - so microstructure based on Fe + C (free graphite)
  - the properties of grey cast iron are strongly dependant on the shape of the graphite flakes:
    - flakes
    - spheroids - relatively high toughness and ductility; formed by adding Ce or Mg

## Fe-2.8wt%C-1.8wt%Si (White cast iron)



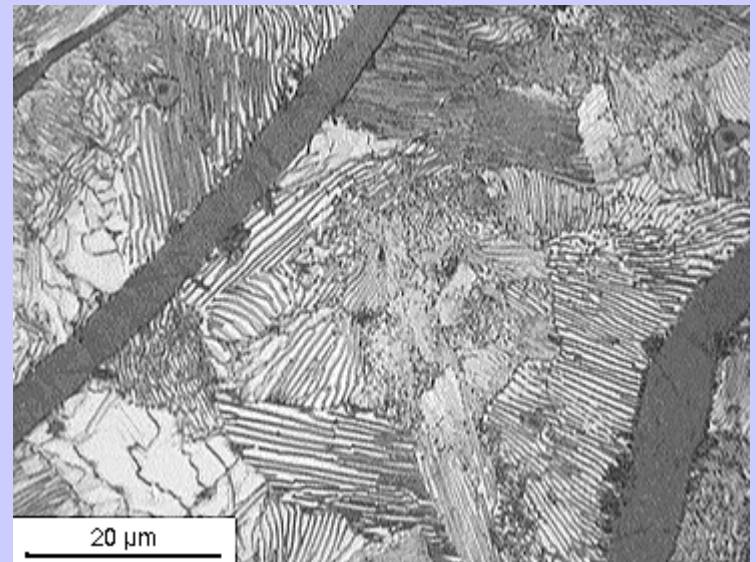
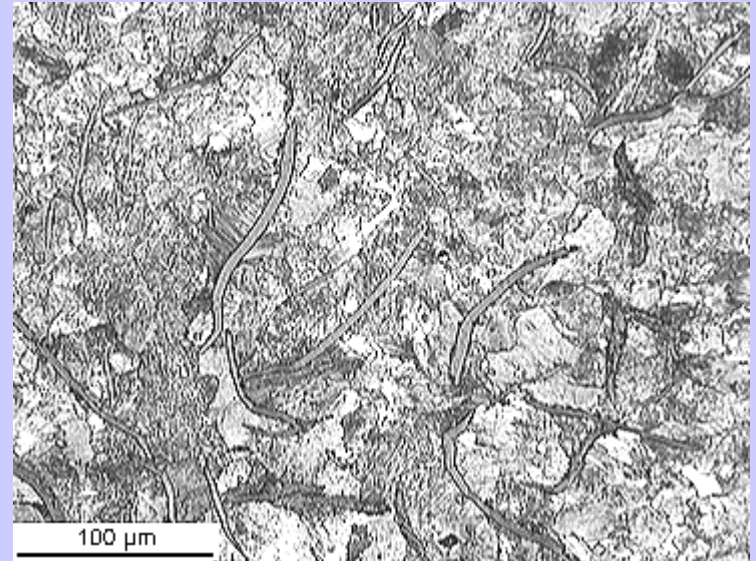
The cementite makes white cast iron very hard and abrasion resistant. It is commonly used for rollers and wear resistant surfaces. It is brittle and almost impossible to machine.



# Fe 3.4wt%C 2.5wt%Si 0.01wt%P (Low P, high grade cast Iron) pearlitic grey cast iron

Grey cast irons have good mechanical properties in compression, and are particularly effective in damping vibration. They are commonly used for the bases of heavy machinery for this reason.

Grey cast irons also have low cost, good wear resistance and high fluidity with low shrinkage during casting.

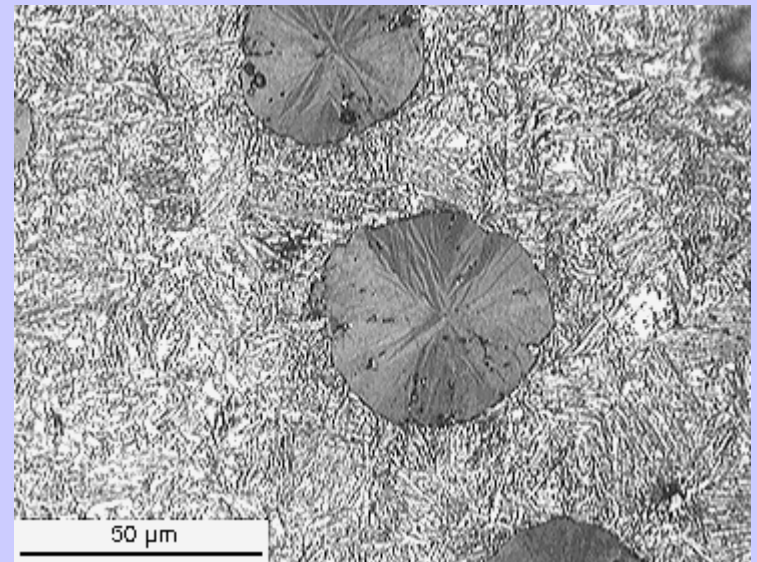
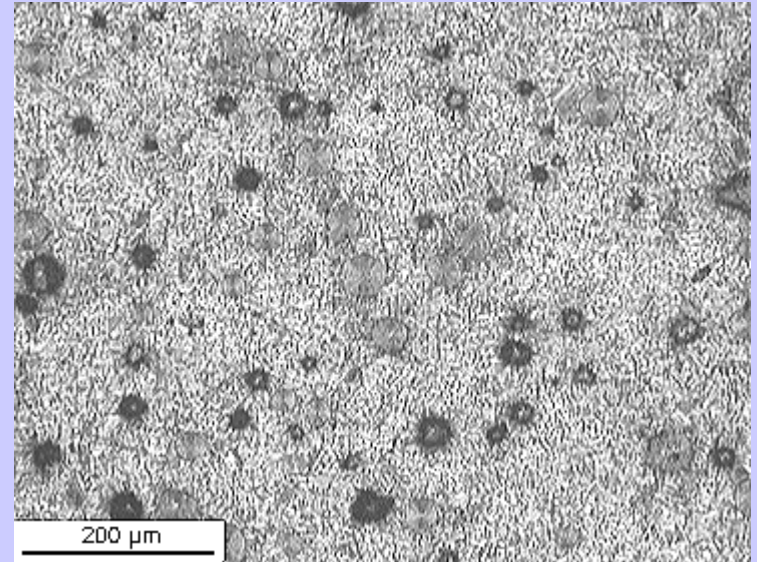




Fe 3.4wt%C 2.5wt%Si 0.01wt%P 0.03wt%Mg  
pearlitic ductile or nodular iron

Removing the graphite flakes improves the tensile strength, ductility and toughness.

Typical applications include gears, valves and camshafts.



# Chapter Outline: Characteristics, Applications, and Processing of Polymers

- Mechanical properties
  - Stress-Strain Behavior
  - Deformation of Semicrystalline Polymers
- Crystallization, Melting, Glass Transition
- Thermoplastic and Thermosetting Polymers
- Viscoelasticity
- Deformation and Elastomers
- Fracture of Polymers
- Polymerization
- Elastomers

*Optional reading: 15.6, 15.17-15.19, 15.21-15.24*

## **“The Graduate” 1967:**

Mr. McGuire: *I want to say one word to you. Just one word.*

Benjamin: *Yes, sir.*

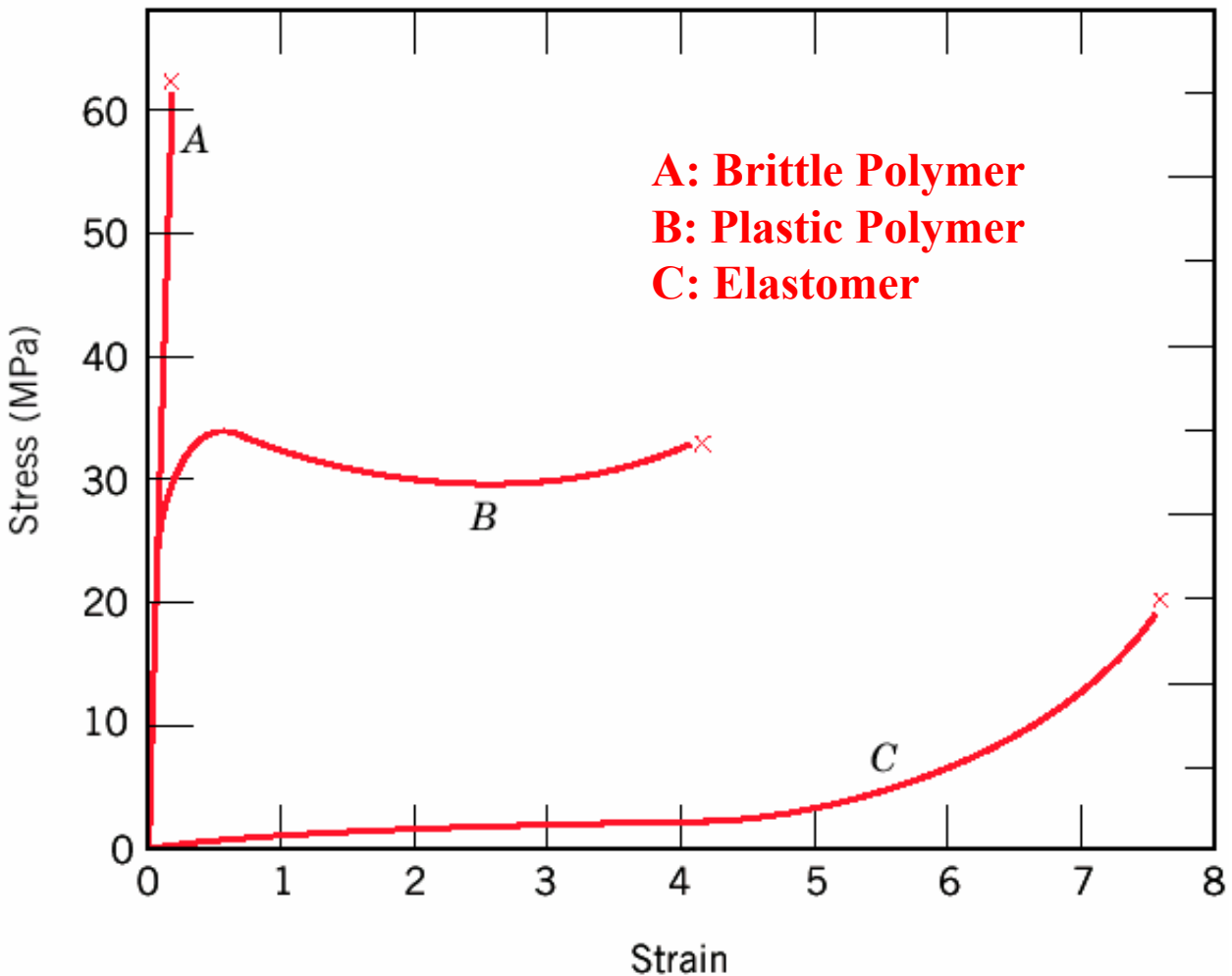
Mr. McGuire: *Are you listening?*

Benjamin: *Yes, I am.*

Mr. McGuire: *Plastics.*

## Stress – Strain Behavior (I)

- The description of stress-strain behavior is similar to that of metals

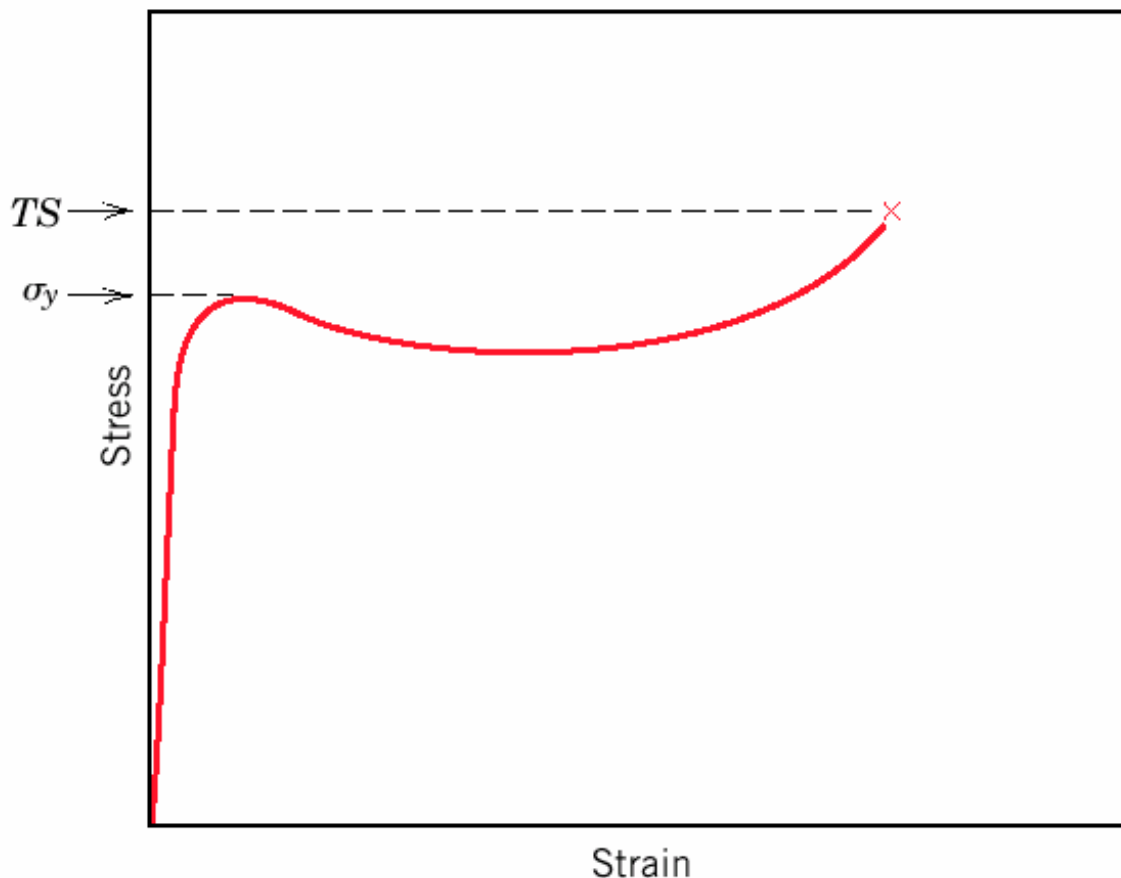


Polymers can be brittle (**A**), plastic (**B**), or highly elastic (**C**). Deformation shown by curve **C** is totally elastic (rubber-like elasticity, large recoverable strain at low stress levels). This class of polymers - **elastomers**

## Stress – Strain Behavior (II)

Characteristics of stress-strain behavior:

- **Modulus of elasticity** – defined as for metals
- **Ductility** (%EL) – defined as for metals
- **Yield strength** - For plastic polymers (B), yield strength is defined by the maximum on curve just after the elastic region (different from metals)
- **Tensile strength** is defined at the fracture point and can be lower than the yield strength (different from metals)





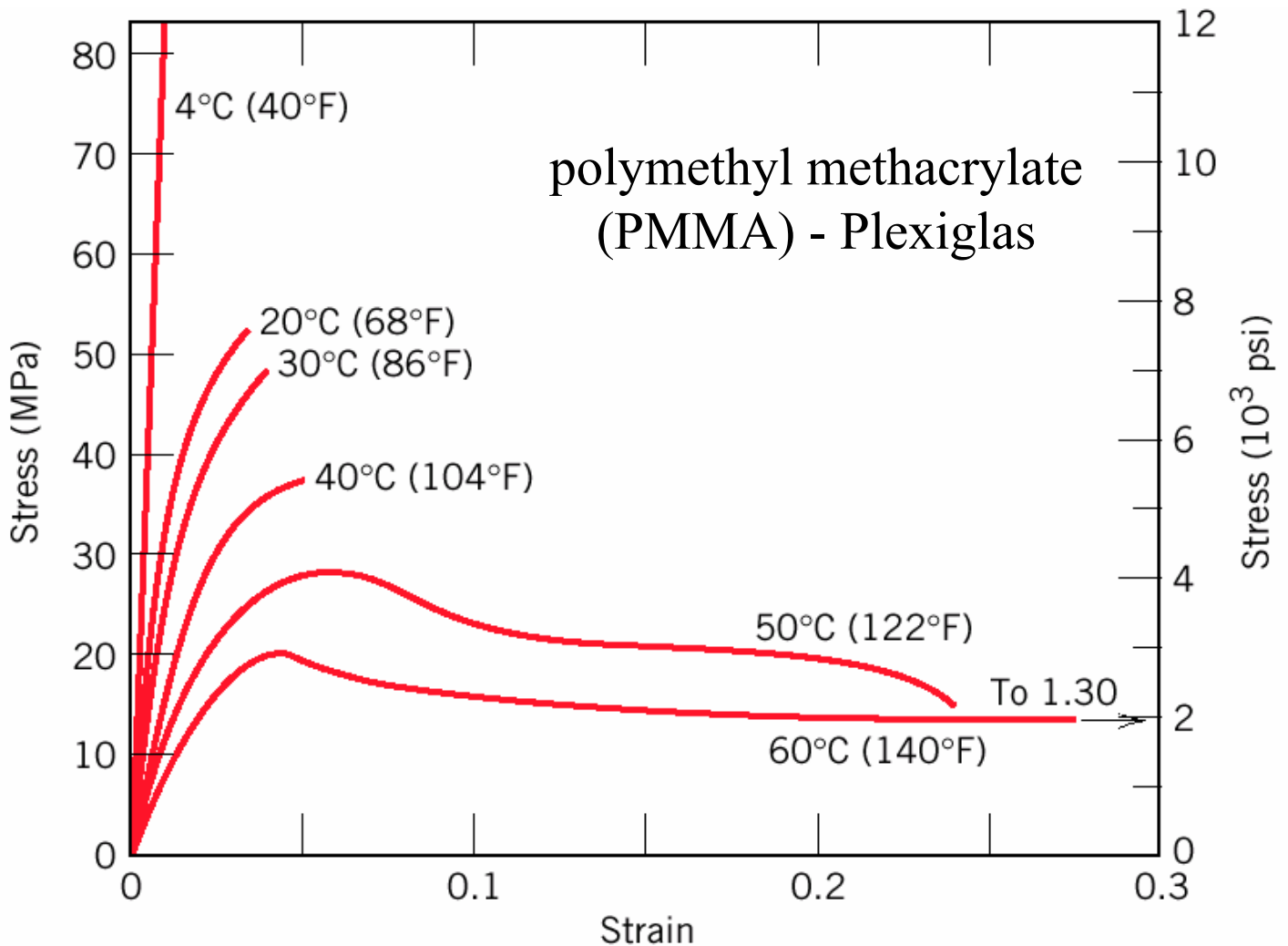
## Stress – Strain Behavior (III)

- Moduli of elasticity for polymers are  $\sim 10 \text{ MPa} - 4 \text{ GPa}$  (compare to metals  $\sim 50 - 400 \text{ GPa}$ )
  - Tensile strengths are  $\sim 10 - 100 \text{ MPa}$  (compare to metals, hundreds of MPa to several GPa)
  - Elongation can be up to 1000 % in some cases ( $< 100\%$  for metals)
- 
- 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.
  - Polymers are also very sensitive to the rate of deformation (strain rate). Decreasing rate of deformation has the same effect as increasing T.

## Stress – Strain Behavior (IV)

Temperature increase leads to:

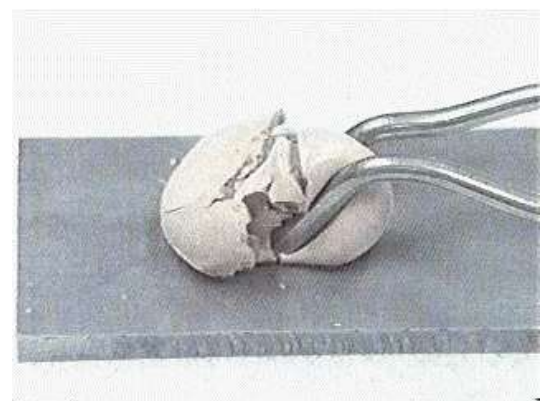
- ✓ Decrease in elastic modulus
- ✓ Reduction in tensile strength
- ✓ Increase in ductility



The **glass transition temperature** ( $T_g$ ) of PMMA ranges from 85 to 165 °C – all of the above curves are for temperatures below  $T_g$ .

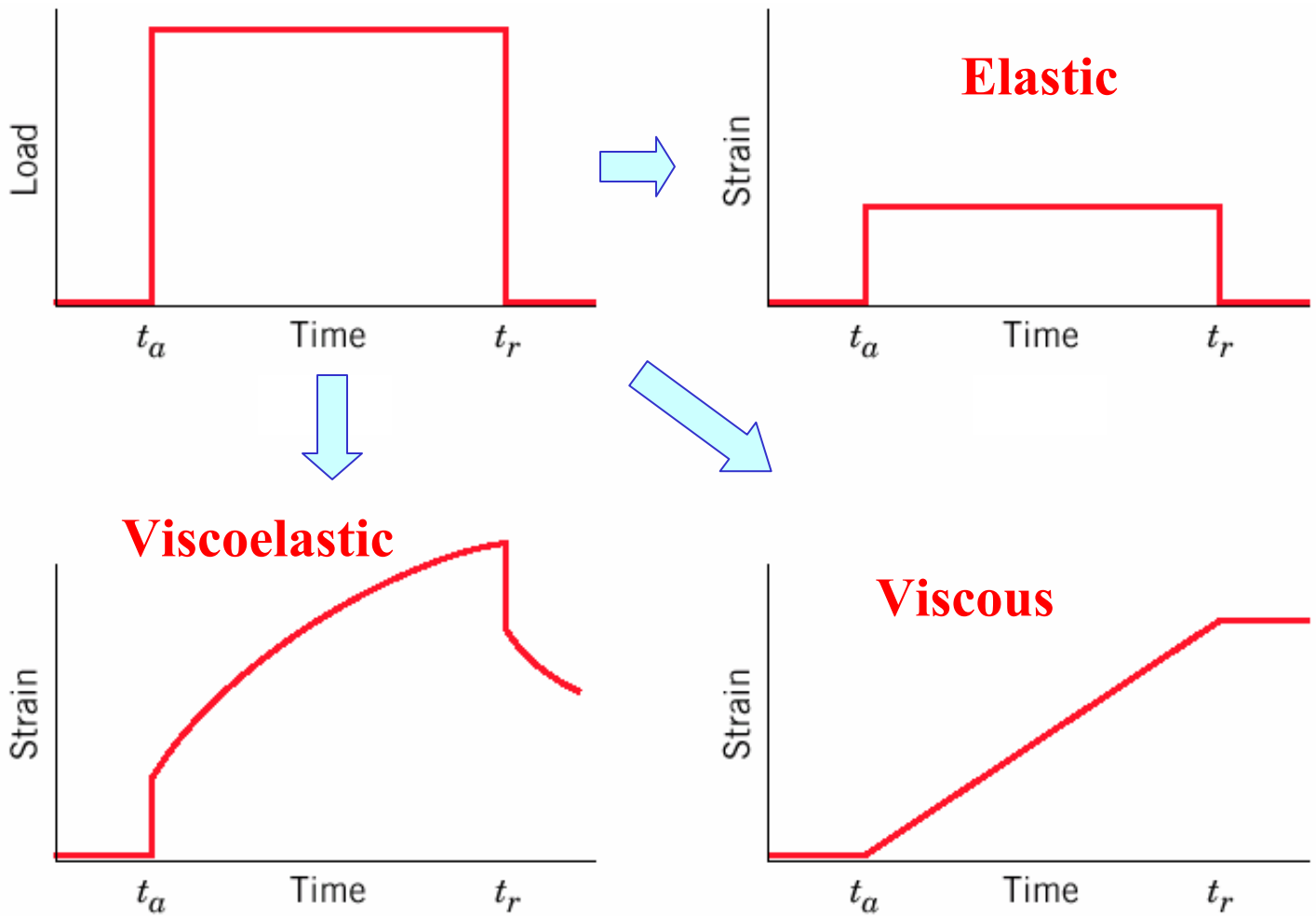
## Viscoelasticity (I)

- Amorphous polymer: glass at low temperatures, rubber at intermediate temperatures, viscous liquid at high T.
- Low temperatures: **elastic** deformation at small strains ( $\sigma = E\varepsilon$ ). Deformation is instantaneous when load is applied. Deformation is reversible.
- High temperatures: **viscous** behavior. Deformation is time dependent and not reversible.
- Intermediate temperatures: **viscoelastic** behavior. Instantaneous elastic strain followed by viscous time dependent strain.
- Viscoelastic behavior is determined by rate of strain (elastic for rapidly applied stress, viscous for slowly applied stress)



Rate dependence of viscoelastic properties in a silicone polymer (Silly Putty). Picture by Geon Corp.

## Viscoelasticity (II)



Load is applied at  $t_a$  and released at  $t_r$

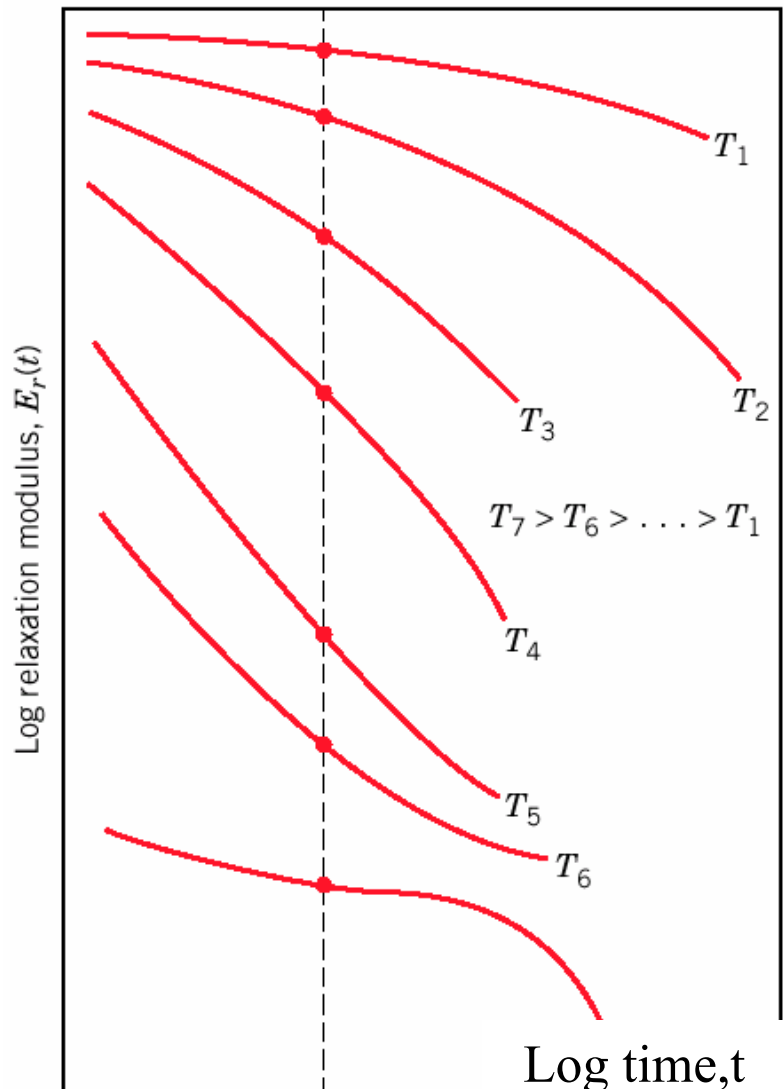
## Viscoelasticity (III)

Viscoelasticity can be characterized by the **viscoelastic relaxation modulus**:

- Sample is strained rapidly to pre-determined strain
- Stress required to maintain this strain  $\epsilon_0$  over time is measured at constant T
- Stress decreases with time due to molecular relaxation processes
- Relaxation modulus can be defined as

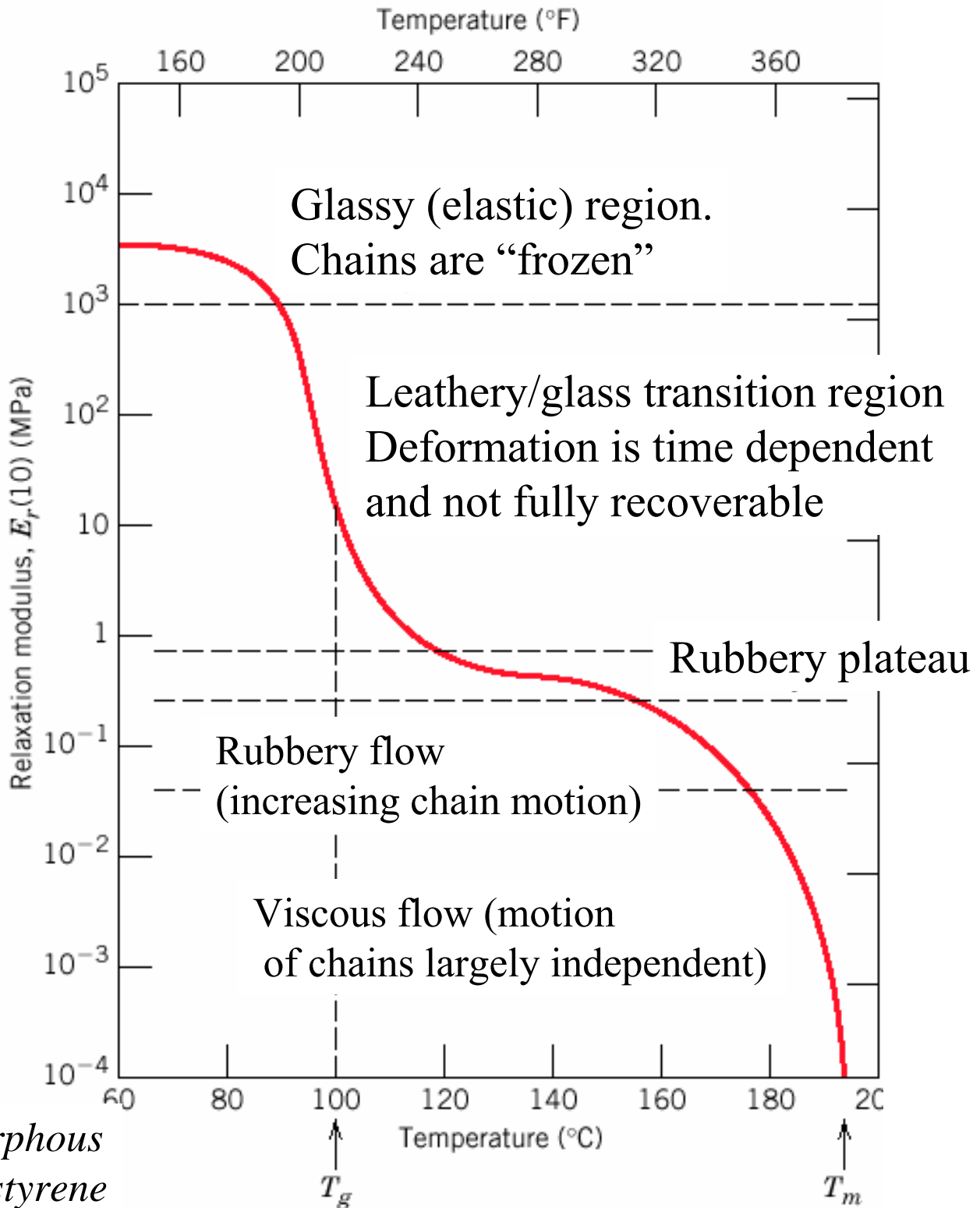
$$E_r(t) = \sigma(t)/\epsilon_0$$

- $E_r(t)$  is also a function of temperature



## Viscoelasticity (IV)

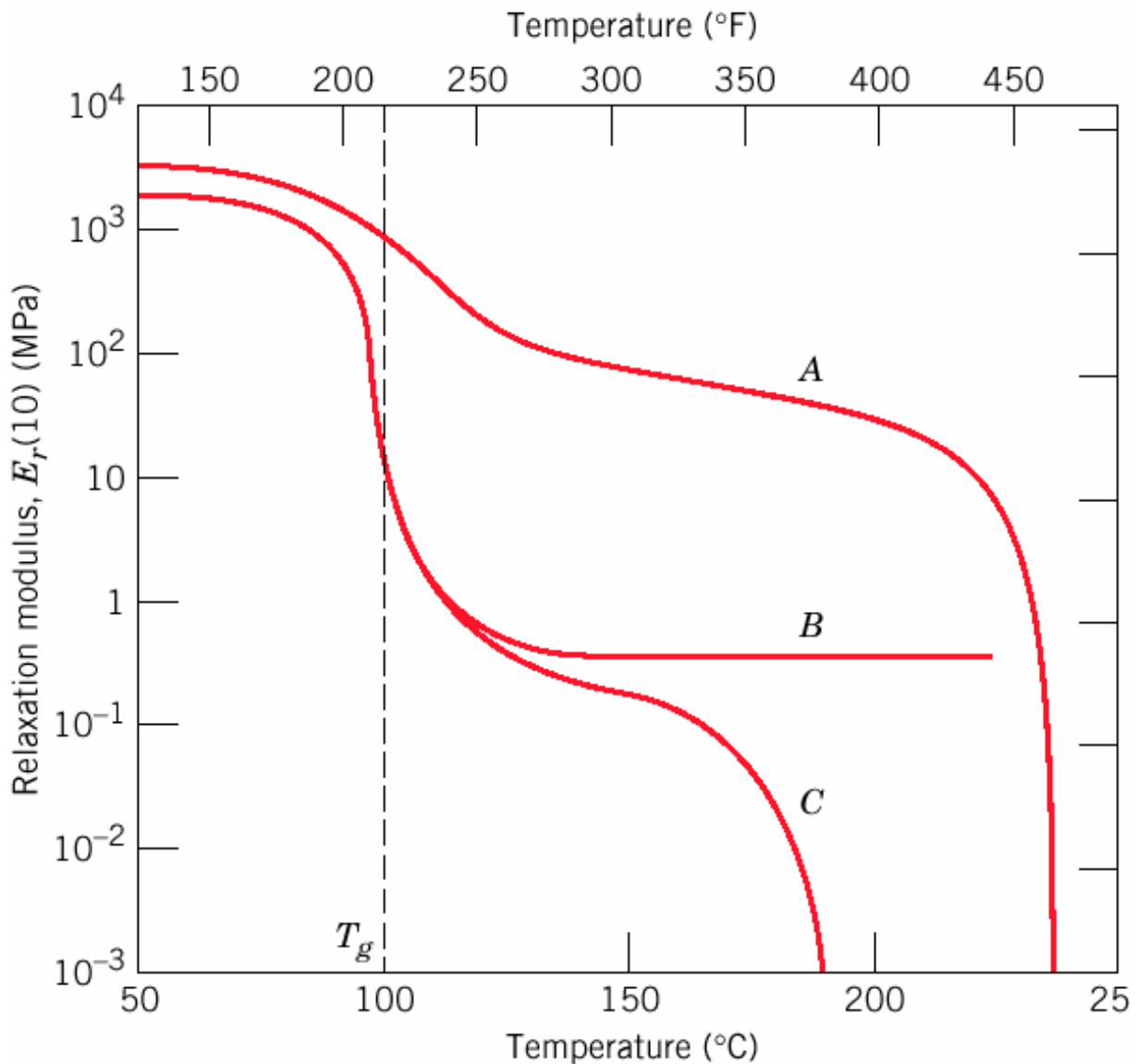
To show the influence of temperature, the relaxation modulus can be plotted at a fixed time for different T:



*amorphous  
polystyrene*

## Viscoelasticity (V)

Temperature dependence for different **polymer structures**



A : Largely crystalline isotactic polystyrene. Glass transition region limited – small amount of amorphous material

B: Lightly cross-linked atactic polystyrene - leathery region extends to decomposition temperature: no melting

C: Amorphous polystyrene

## Viscoelastic Creep

Many polymers susceptible to time-dependent deformation under constant load – viscoelastic creep

Creep may be significant even at room temperature and under moderately low stresses (below yield strength)

Results of creep tests are described by time dependent creep modulus:

$$E_c(t) = \sigma_0 / \epsilon(t)$$

Amount of creep decreases as crystallinity increases

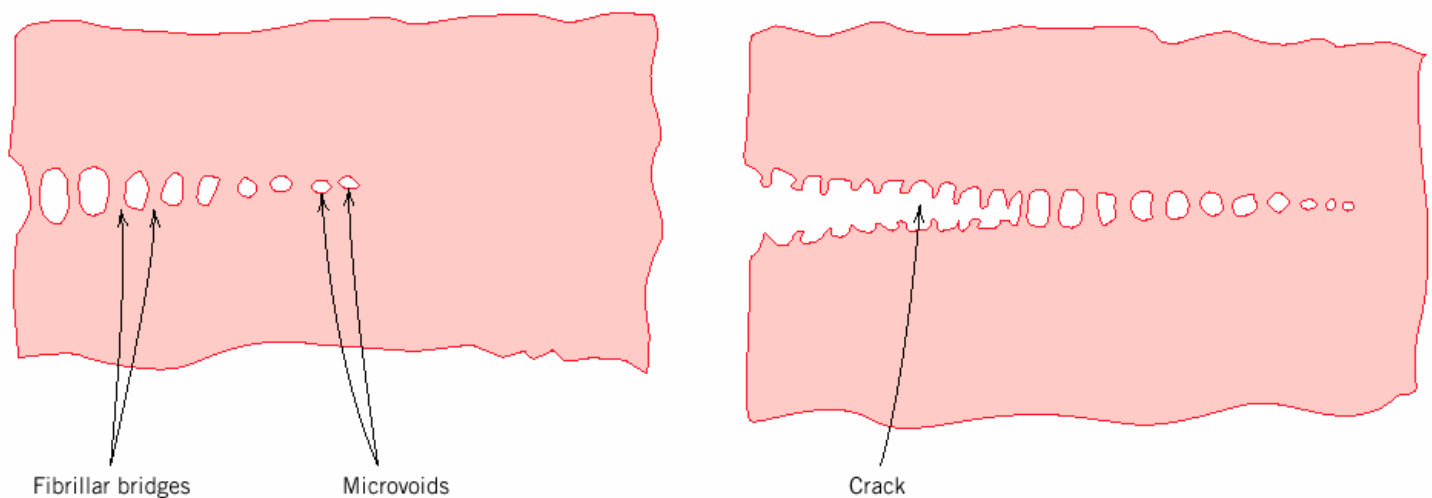


## Fracture of Polymers

- Fracture strengths of polymers are low compared to metals and ceramics
- Brittle fracture occurs in thermosetting polymers. Fracture is initiated at stress concentrators (scratches, notches, etc). Covalent bonds are severed during fracture
- In thermoplastic polymers, both ductile and brittle fracture are possible. Brittle fracture is favored at lower temperatures, higher strain rates, and at stress concentrators
- Brittle to ductile transition often occurs with increasing temperature

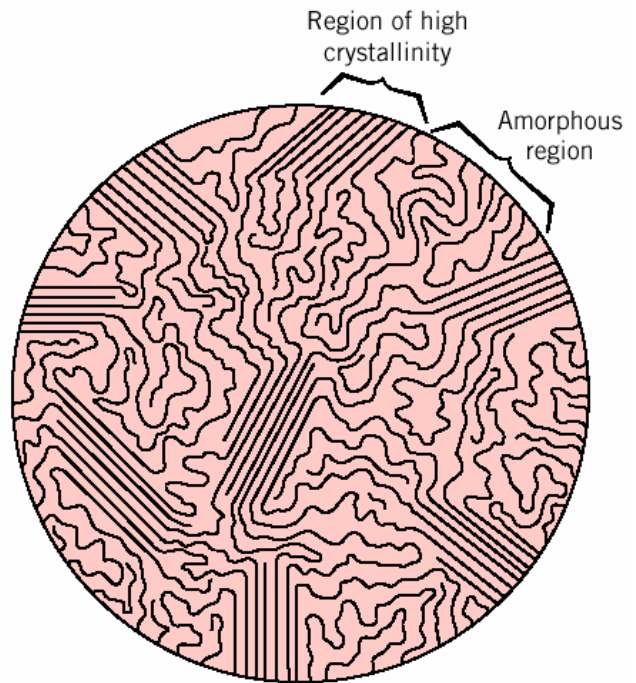
# Fracture of Polymers: Crazing

- Fracture of glassy thermoplastic polymers often proceeds through crazing. Crazing occurs when localized regions yield, forming an interconnected array of microvoids. Fibrillar bridges of oriented molecular chains form between voids.
- At high enough tensile loads, these bridges elongate and break, enabling crack propagation
- Crazing absorbs fracture energy and increases fracture toughness



# Deformation of Semicrystalline Polymers

Semi-crystalline polymers: crystalline regions separated by amorphous material (Chapter 14)



## Elastic deformation:

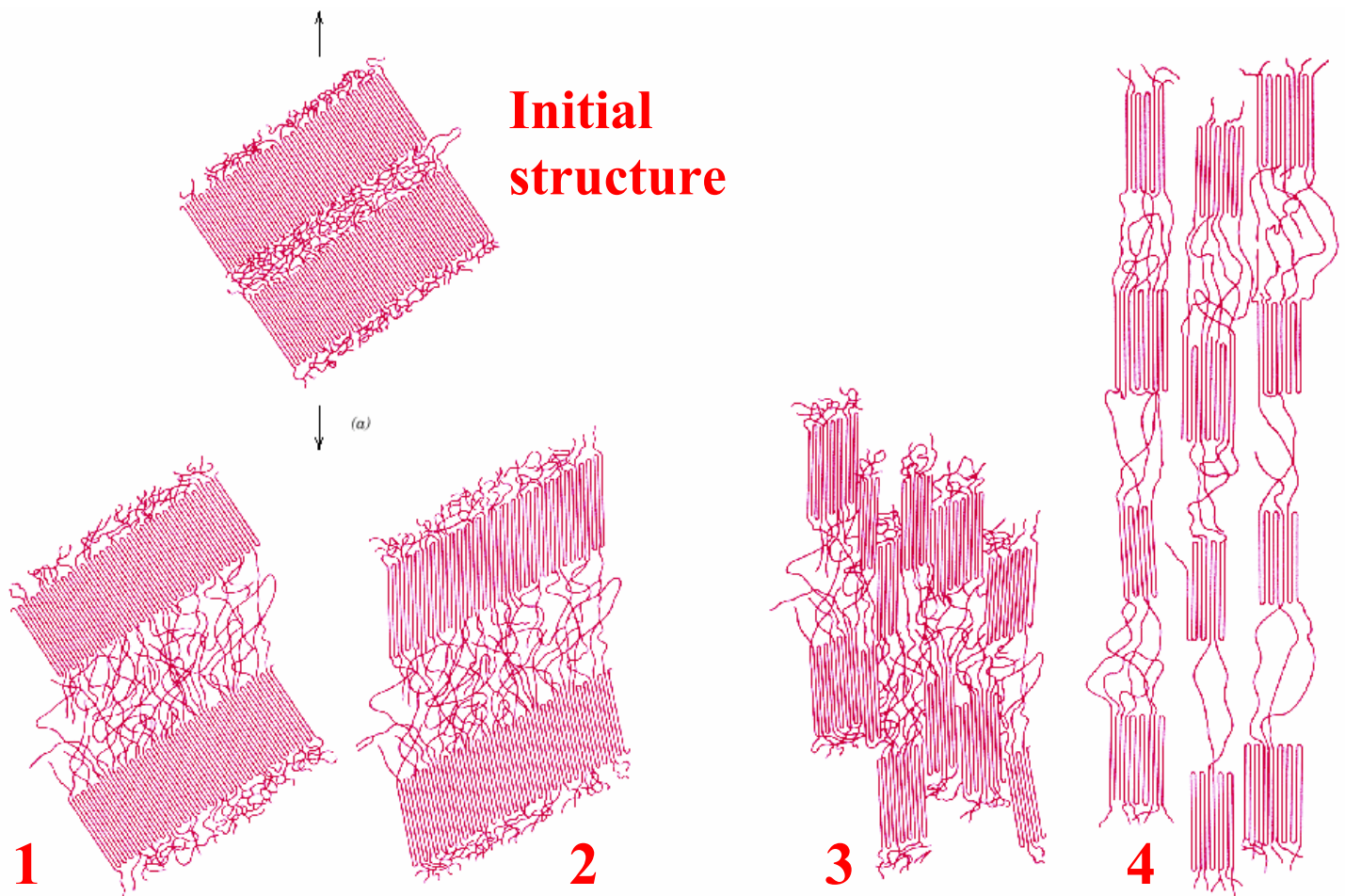
Basic mechanism of elastic deformation is elongation (straightening) of chain molecules in the direction of the applied stress. Elastic modulus is defined by elastic properties of amorphous and crystalline regions and by the microstructure.

# Plastic Deformation of Semicrystalline Polymers

Plastic deformation is defined by the interaction between crystalline and amorphous regions and is **partially reversible**.

Stages of plastic deformation:

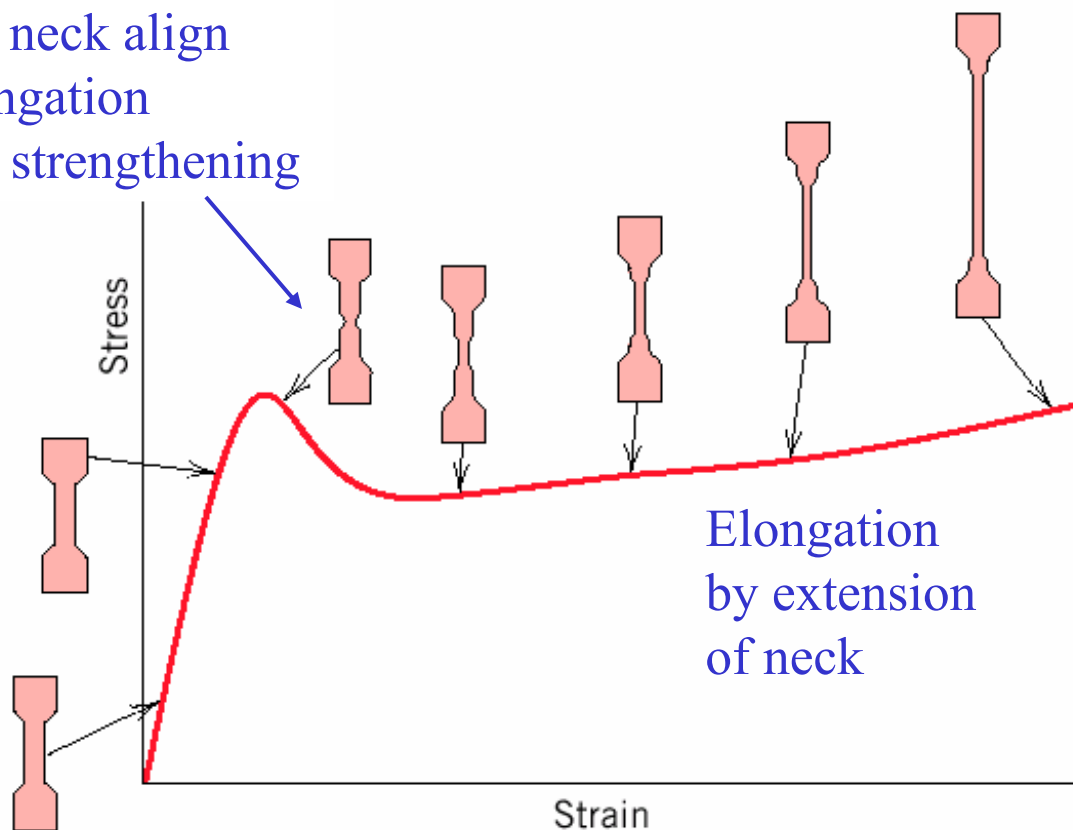
1. elongation of amorphous tie chains
2. tilting of lamellar crystallites towards the tensile axis
3. separation of crystalline block segments
4. stretching of crystallites and amorphous regions along tensile axis



# Plastic Deformation of Semicrystalline Polymers

The macroscopic deformation involves necking. Neck gets stronger since the deformation aligns the chains and increases local strength in the neck region (up to 2-5 times)  $\Rightarrow$  neck is expanding along the specimen.

Chains in neck align  
along elongation  
direction: strengthening



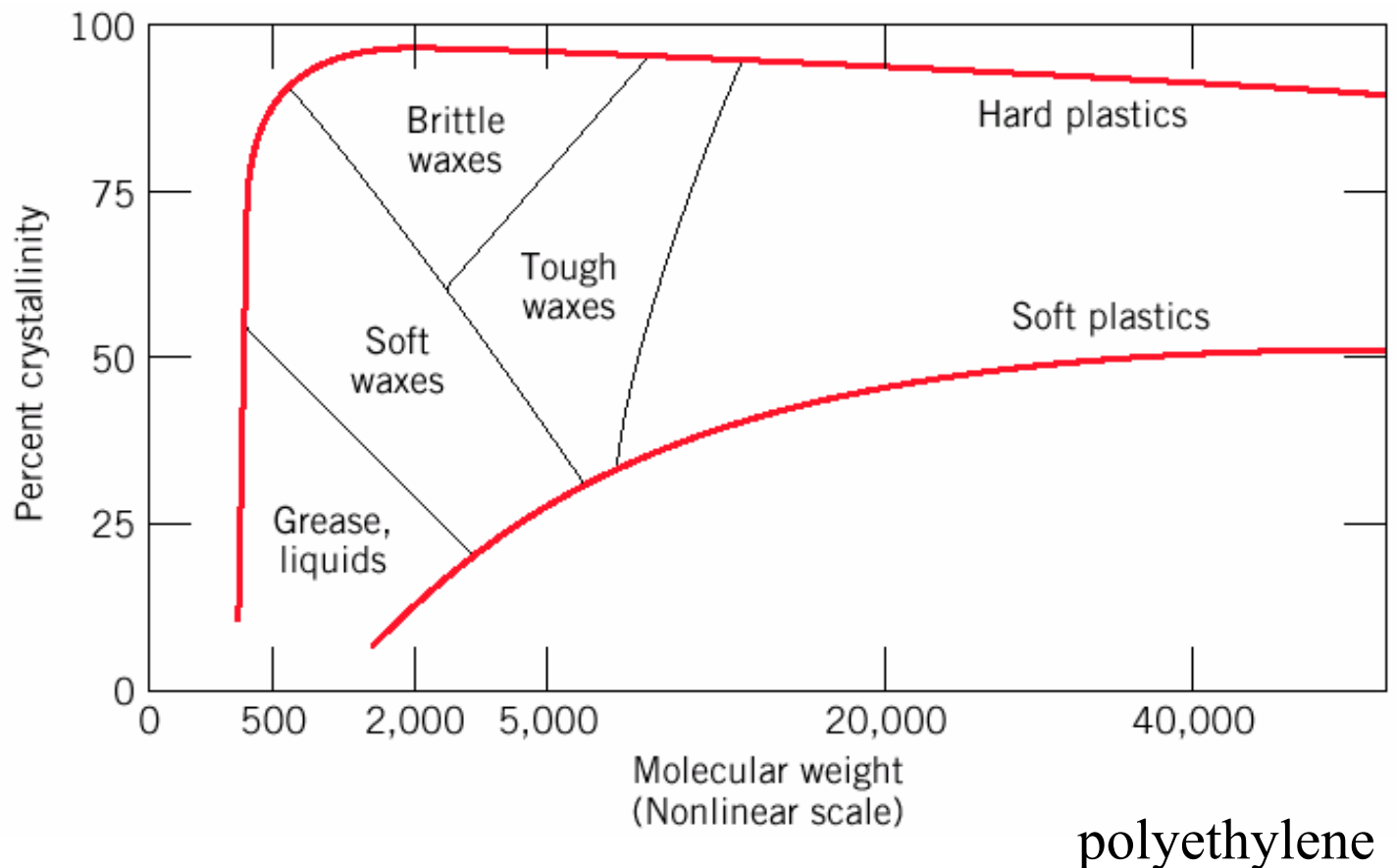
Different from ductile metals where the deformation is confined in the initial neck region.

## Factors that Influence Mechanical properties (I)

- **Temperature and strain rate** (already discussed)
- **Chain entanglement, strong intermolecular bonding** (van der Waals, cross-links) increase strength
- **Drawing**, analog of work hardening in metals, corresponds to the neck extension. Is used in production of fibers and films. Molecular chains become highly oriented  $\Rightarrow$  properties of drawn material are **anisotropic** (perpendicular to the chain alignment direction strength is reduced)
- **Heat treatment** - changes in crystallite size and order
  - **undrawn material**: Increasing annealing temperature leads to
    - ✓ increase in elastic modulus
    - ✓ increase in yield/tensile strength
    - ✓ decrease in ductility
  - Note that these changes are opposite from metals
  - **drawn material**: opposite changes (due to recrystallization and loss of chain orientation)

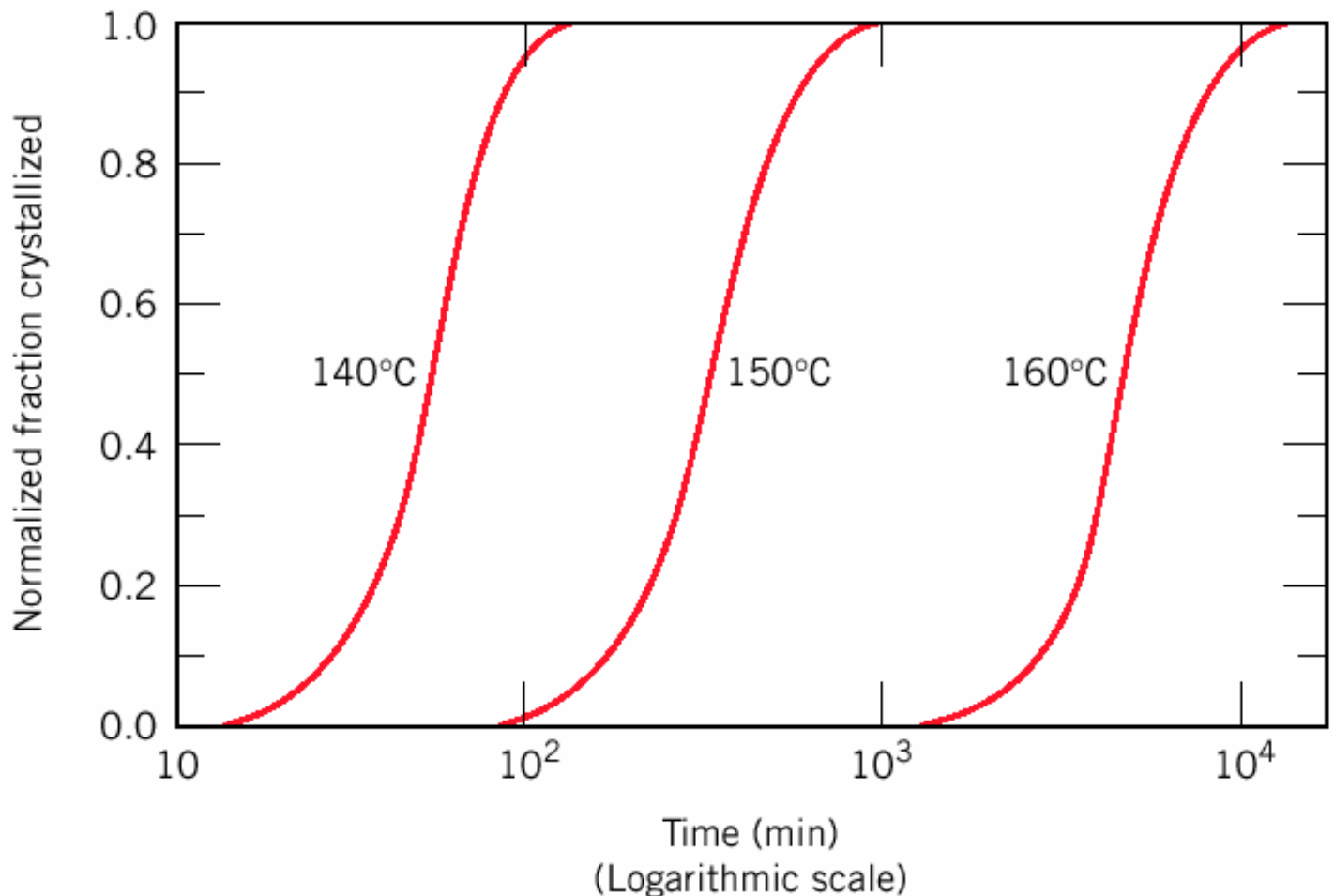
## Factors that Influence Mechanical properties (II)

- Tensile strength increases with **molecular weight** – effect of entanglement
- Higher **degree of crystallinity** – stronger secondary bonding - stronger and more brittle material



# Crystallization, Melting, Glass Transition (I)

**Crystallization:** crystalline nuclei form and grow, chains align and order. Crystallization rates can be defined from the same type of S-curves we saw for metals - can be described by the same Avrami equation:  $y = 1 - \exp(-k t^n)$

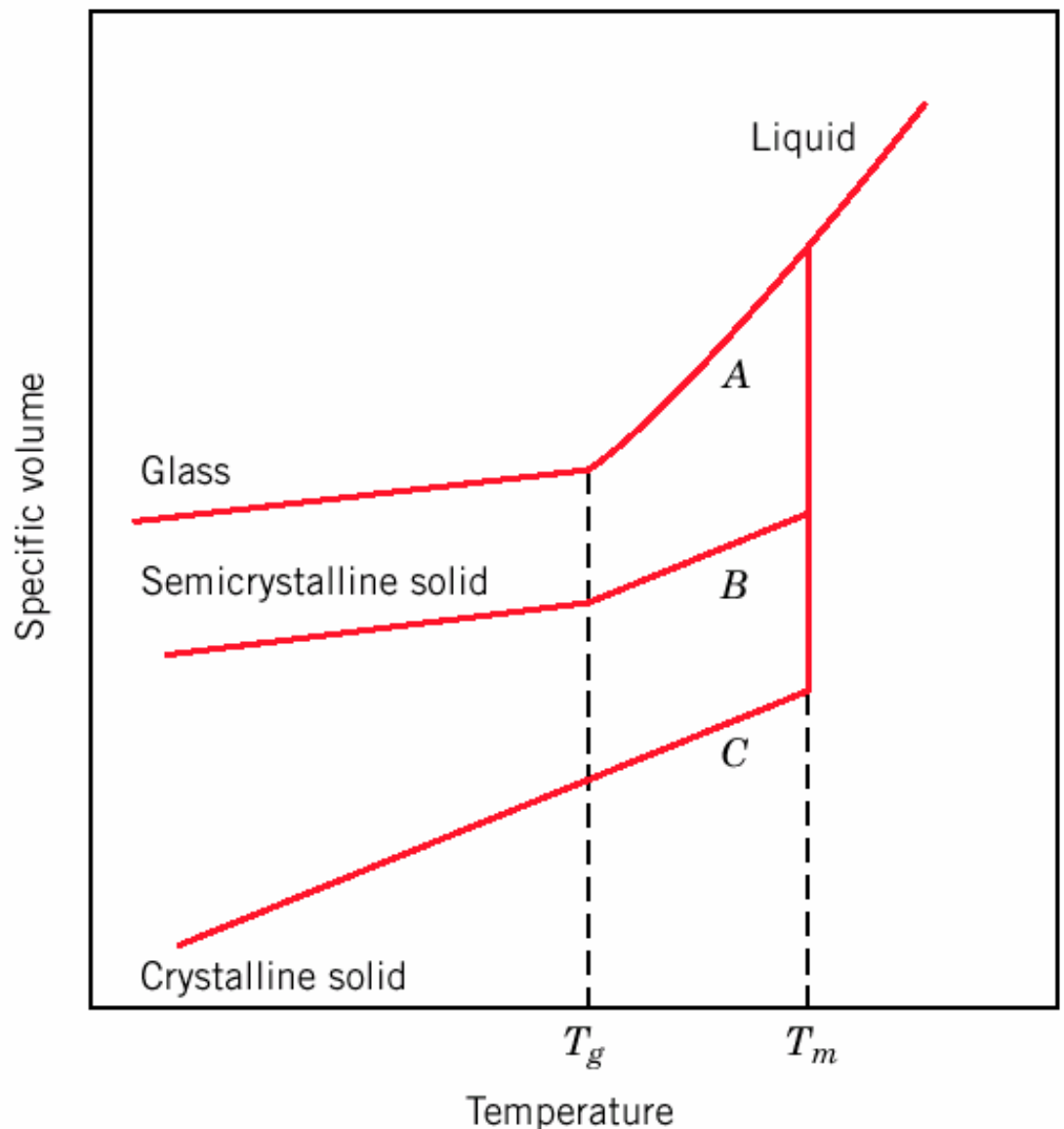


**Glass transition:** polymer become rigid solids (viscosity is increasing) upon cooling yet retain the disordered molecular structure characteristic for liquids



## Crystallization, Melting, Glass Transition (II)

**Melting** behavior of semicrystalline polymers is intermediate between that of crystalline materials (sharp density change at a melting temperature) and that of a pure amorphous material (melting can be only defined from changes in viscosity).



The glass transition temperature is between 0.5 and 0.8 of the melting temperature.

## Crystallization, Melting, Glass Transition (III)

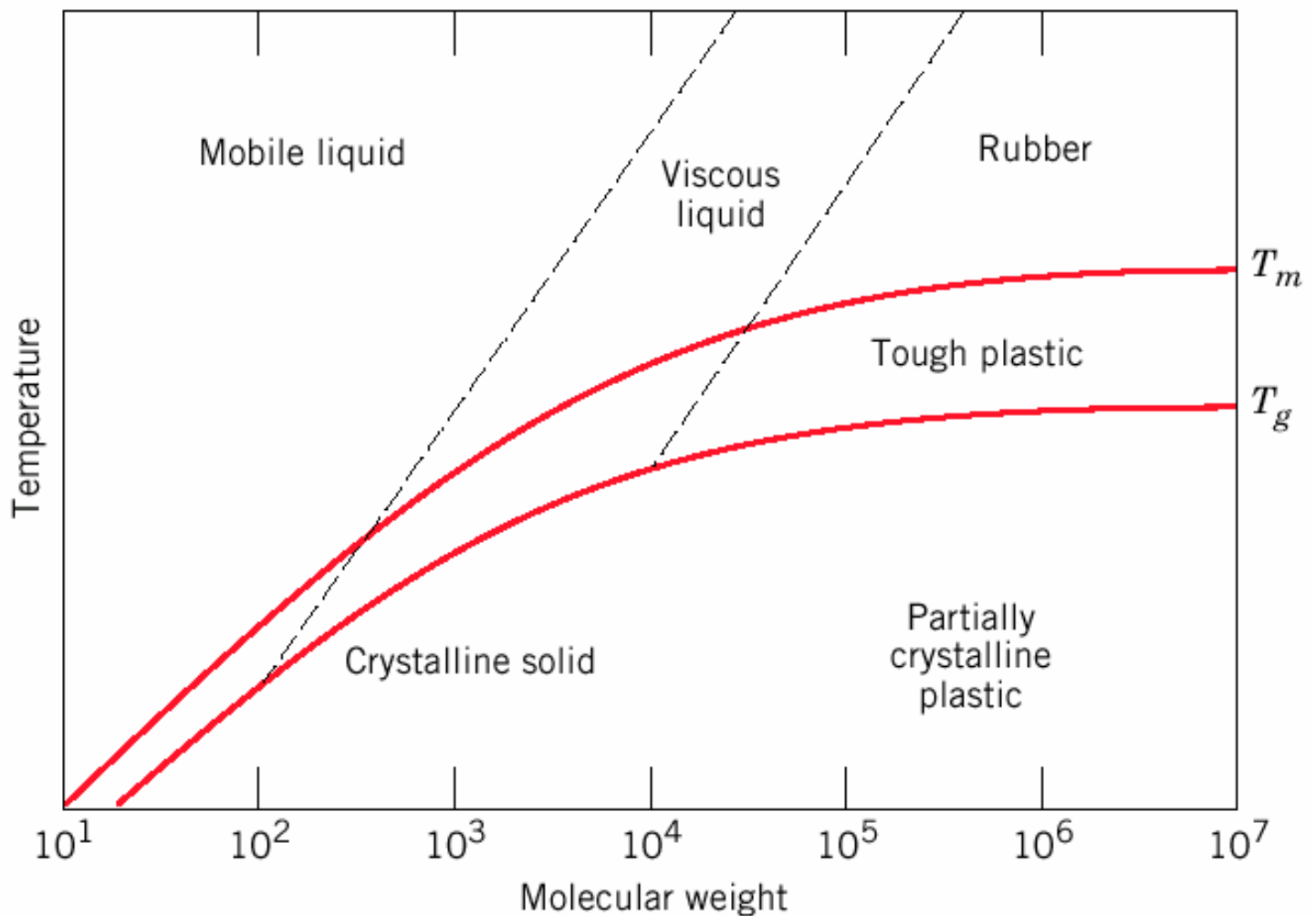
The melting temperature increases with the rate of heating, thickness of the chain-folded crystalline lamellae, and depends on history of material, especially crystallization temperature.

Melting involves breaking of the inter-chain bonds, therefore the glass and melting temperatures depend on:

- chain stiffness (e.g., single vs. double bonds) - rigid chains have higher melting temperatures
- size/weight of molecule - increasing molecular weight increases  $T_m$  (range of  $M$  produces range of  $T_m$ )
- size, shape of side groups, side branches, cross-linking, defects, etc.

Essentially the same molecular characteristics rise and lower both melting and glass transition temperatures.

## Crystallization, Melting, Glass Transition (IV)



Dependence of melting and glass transition temperatures and polymer properties on molecular weight

# Thermoplastic and Thermosetting Polymers

**Thermoplastic polymers (thermoplastics):** soften *reversibly* when heated (harden when cooled)

At elevated temperatures inter-chain bonding is weakened allowing deformation at low stresses. Most thermoplastics are linear polymers and some branched structures

**Thermosetting polymers (thermosets):** harden *permanently* when heated.

Covalent crosslinks ( $\sim 10 - 50\%$  of mers) formed during heating. Cross-linking hinder bending and rotations. Thermosets are harder, more dimensionally stable, and more brittle than thermoplastics. Examples: vulcanized rubber, epoxies, resins.

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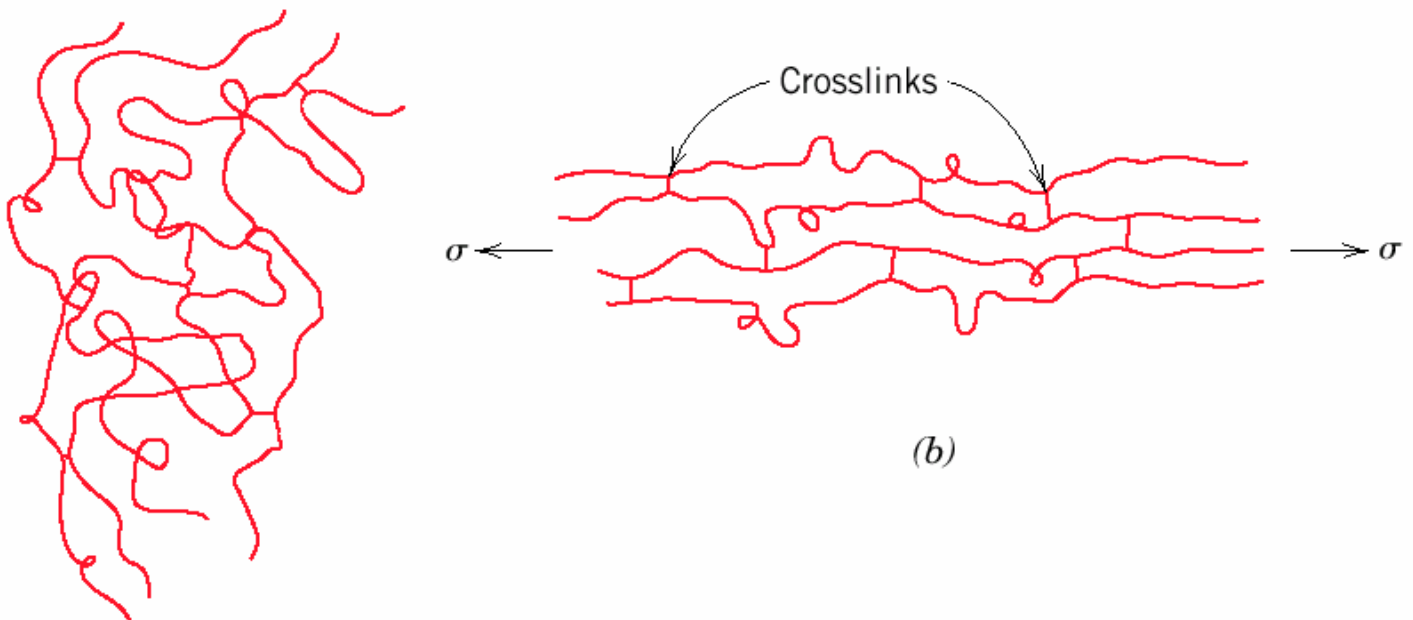
**Classification by the end use in applications**  
(plastics, elastomers, fibers, etc.)

**Plastics** – a broad class of polymeric materials that exhibit some structural rigidity under mechanical loading and are used in general-purpose applications.

# Elastomers

Elastomers can be deformed to **very large strains** and then spring back elastically to the original length, a behavior first observed in natural rubber. To be elastomeric, the polymer needs to meet several criteria:

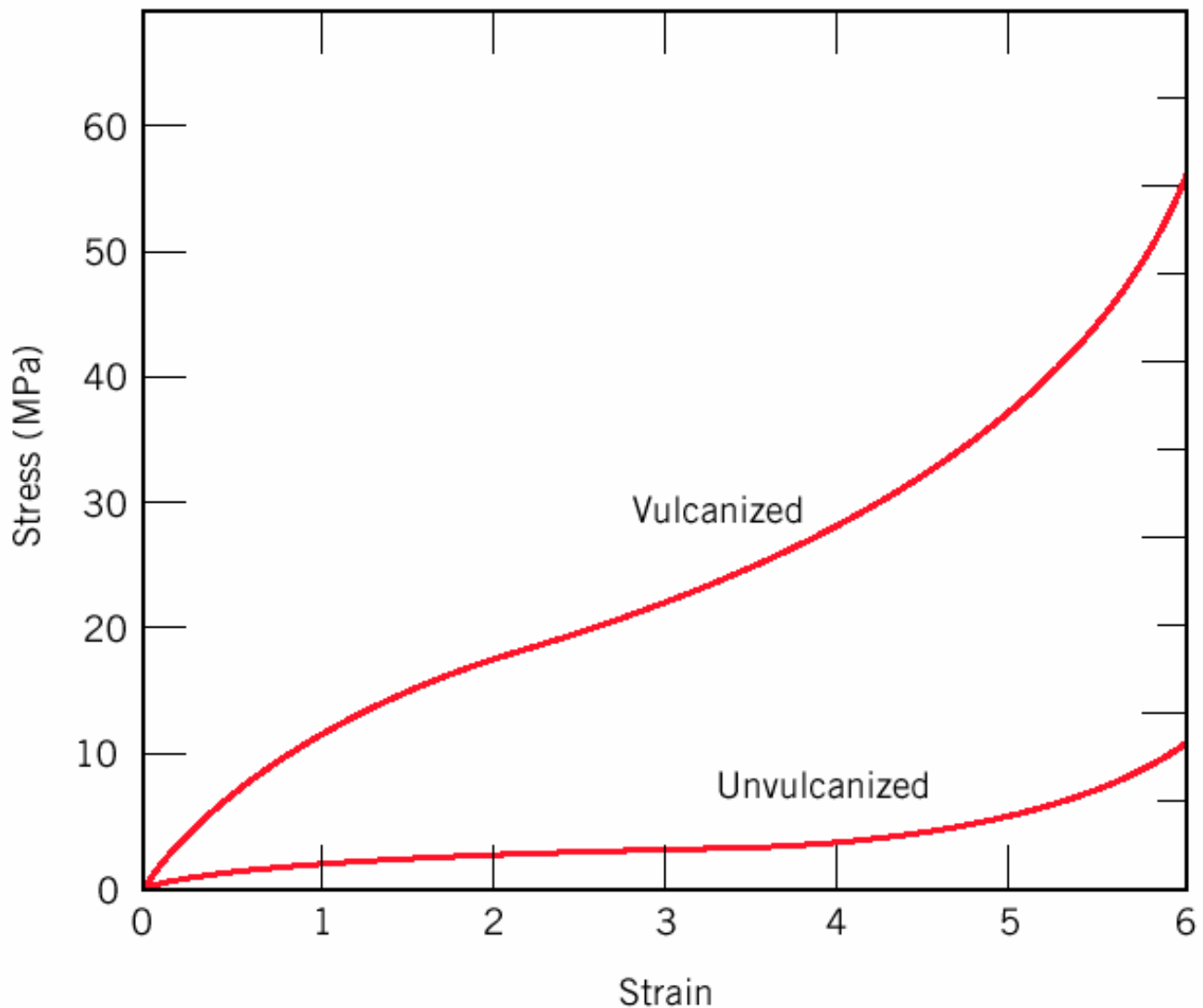
- Resistance to crystallization (elastomers are amorphous)
- Relatively free chain rotations (unstressed elastomers have coiled/twisted structure – uncoil during deformation)
- Certain degree of cross-linking (achieved by vulcanization) that increases resistance to plastic deformation
- Temperature is above the glass transition temperature (below  $T_g$  elastomer becomes brittle)



# Elastomers: Vulcanization (I)

## Elastomers: Vulcanization (II)

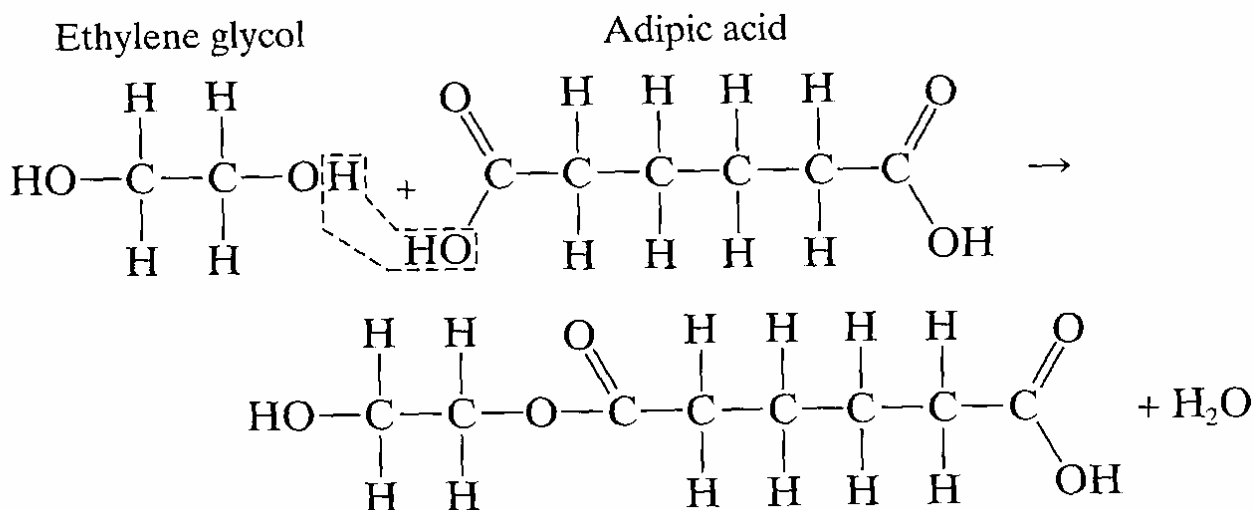
- Because they are cross-linked, elastomeric materials are **thermosetting polymers**
- Elastic modulus, tensile strength, oxidation resistance increased by vulcanization - magnitude of  $E$  proportional to number of cross-links. Too many cross-links reduces extensibility



# Polymerization

Polymerization is the synthesis of high polymers from raw materials like oil or coal. It may occur by:

1. **Addition (chain-reaction) polymerization**, where monomer units are attached one at a time (discussed in Chapter 14). Has three distinct stages: initiation, propagation, and termination.
2. **Condensation (step reaction) polymerization**, by stepwise intermolecular chemical reactions that produce the mer units.
  - Usually there is small by-product that is then eliminated
  - Significantly slower than addition polymerization
  - Often form trifunctional molecules that can form cross-linked and network polymers





## Summary

Make sure you understand language and concepts:

- Addition polymerization
- Condensation polymerization
- Crazing
- Creep modulus
- Deformation of semicrystalline polymers
- Effect of molecular weight, crosslinks, drawing, degree of crystallinity on mechanical properties
- Elastomer
- Fracture of polymers
- Glass transition temperature
- Plastics
- Relaxation modulus
- Thermoplastic polymer
- Thermosetting polymer
- Viscoelasticity
- Vulcanization

Module-12

# Composites

## Contents

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

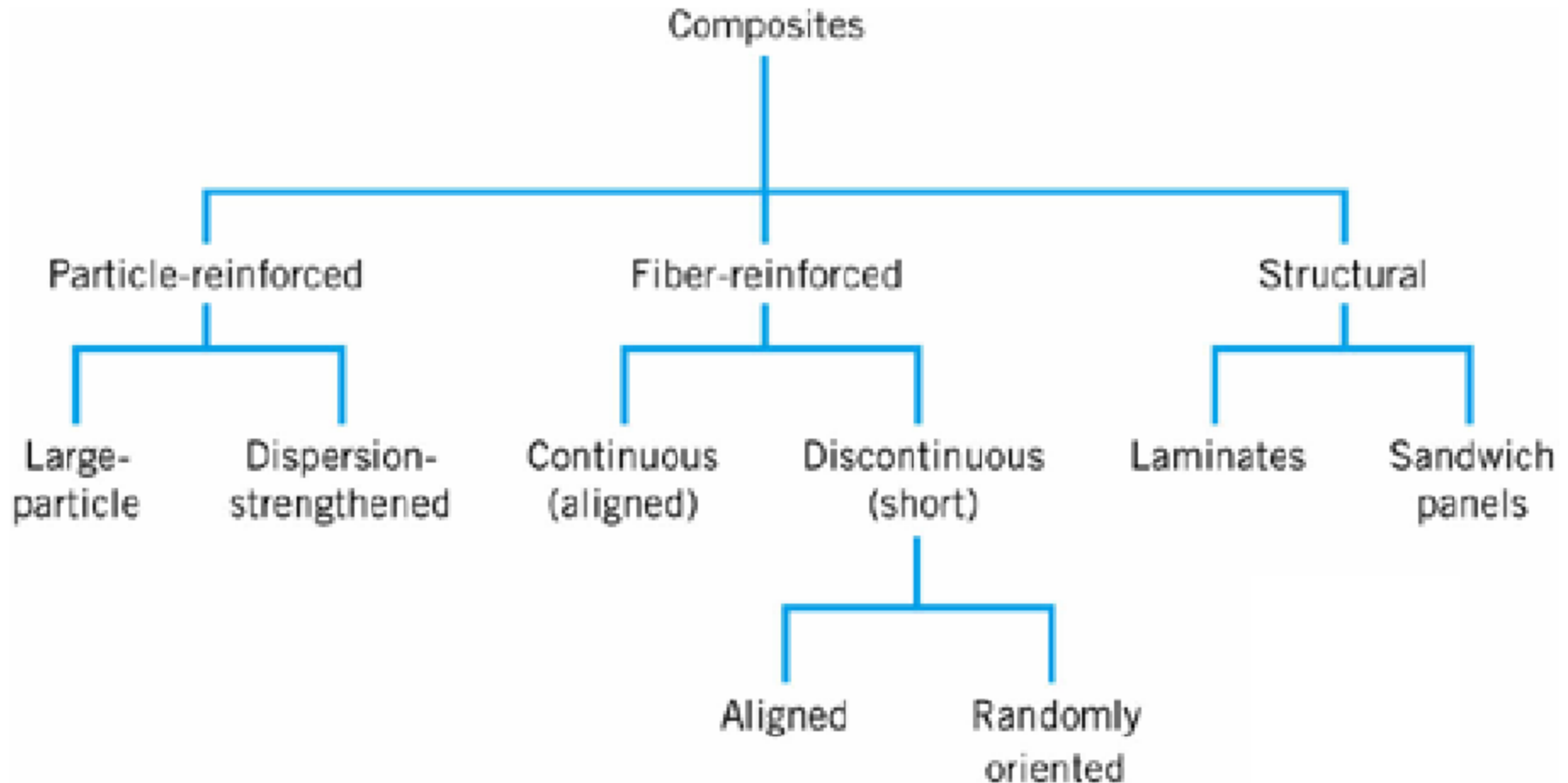
## Composite material- definition

- 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

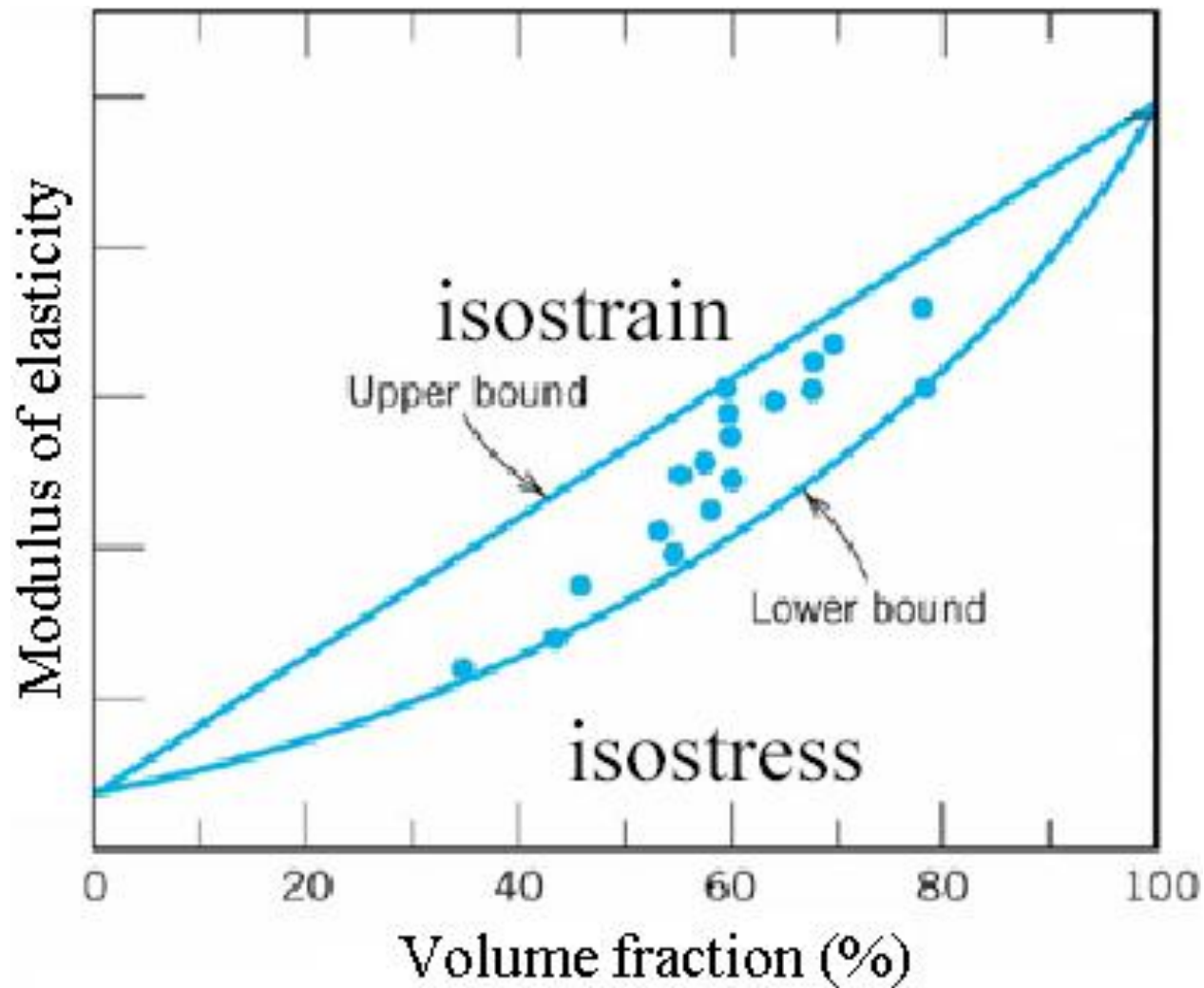
- These composites contain large number of coarse particles.
- These composites are designed to produce combination of properties rather than increase the strength.
- Mechanical properties are characterized by rule-of-mixtures.
- Elastic modulus of these composites is given by the following bounds, derived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



## 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.



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.

## 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.
- 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 & Injection molding

- 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.
- 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 leads to coalescence of particles, and eventual mechanical integrity.



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

## 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.



## 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 decolored, 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.