SCH1102 MATERIAL SCIENCE AND ENGINEERING

Course Material

UNIT 1 NATURE OF MATERIALS

Selection process of engineering materials (General aspects), Chemical and physical properties of materials,chemical structure, Micro and macro structure, corrosion resistance, chemical reactivity. Mechanical properties, stress, strain, strength, hardness, malleability, ductility, elasticity, plasticity, toughness, thermal stability. Types of deformation: Plastic, viscous; plastic deformation of single crystal, poly crystalline metals, slip, twinning, dislocations, viscoelasticity, creeps in metals, amorphous materials.

The term **Material** is something that consists of matter. Anything that serves as a crude or raw material to be used or developed. Materials comprise a wide range of metals and nonmetals which must be operated to form the end product. The basics of the material properties plays a very important role in today's modern world. The ever increasing demands for materials of high strength, reliability, lightness, corrosion resistant, cost effective, heat resistance etc are tremendously increasing.

Materials Science forms the foundation for engineers in product development because the structures, components, and devices that engineers design are limited by the properties of the materials that are available and the techniques that can be used for fabrication. It investigates relationships existing between the structure of materials and their properties.

Factors affecting the selection of materials for engineering purposes

(1) Properties of Materials

The properties of a material define the specific characteristics of the particular material and forms a basis for predicting the behavior of the material under various conditions. It is a factor that influences qualitatively or quantitatively the response of a given material to the imposed stimuli.

Some of the important properties of materials are

1. Mechanical (Elasticity, Plasticity, Toughness, Tensile strength, Ductility, Brittleness , Hardness, Creep, Fatigue etc)
2. Thermal (Heat capacity, Specific Heat, Thermal Conductivity, Thermal shock Resistance etc)
3. Chemical (Corrosion)
4. Electrical (Resistivity, conductivity, dielectric strength etc)
5. Magnetic (Permeability, Superconductivity etc)
6. Optical (Reflectivity, Refractive Index, Absorptivity)

7. Physical (Colour, Density, Melting Point, Porosity, Structure etc)
8. Technological Properties (Castability, Machinability, Weldability etc)

(2) Performance Requirements

The material of which a part is composed must be capable of performing a parts function without failure.

(3) Materials reliability

Reliability can be defined as the degree of probability that a product, and the material of which it is made, will remain stable enough to function in service for the intended life of the product without failure.

(4) Safety

A material must perform its function in a safe manner. Otherwise, the failure of the product made out of it may lead to adverse effects.

(5) Availability

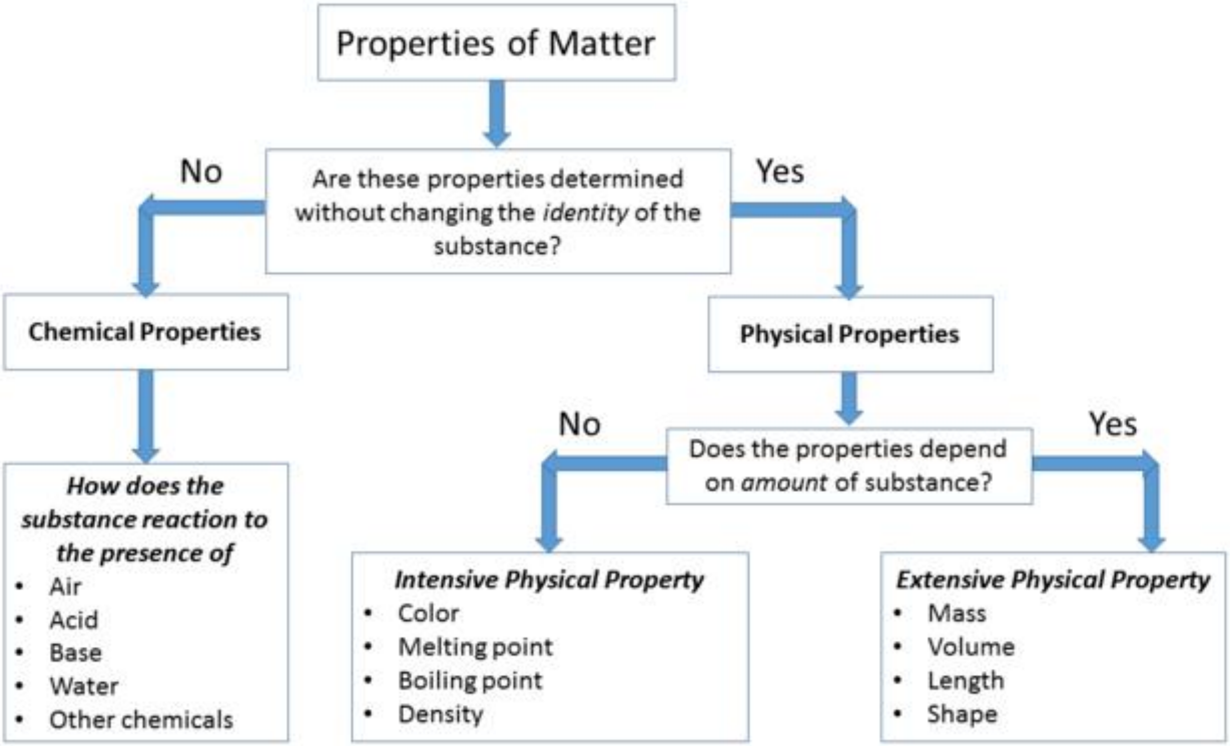
A material must be readily available, and in large quantities for intended application.

(6) Environmental Conditions

The environment in which the product operates strongly influences service performance. Humidity, water or chemicals may cause corrosion and subsequent material failure.

(7) Physical attributes

Physical attributes such as size, weight and appearance also serve functional requirements.



PHYSICAL PROPERTIES

Physical Properties include

(1) Colour
(2) Appearance
(3) Density
(4) Melting Point
(5) Dimensions
(6) Porosity
(7) Structure

(1) **Colour:** The **color of a material** is a physical property that in most cases comes from the excitation of electrons due to the absorption of energy performed by the material. It is that aspect of appearance of a material that depends on the spectral composition of the light reaching the eyes. The colour of a material depends on the wavelength of the light that a material can absorb. It plays a vital role in the identification of a material.

(2) **Density:** The **density**, or more precisely, the **volumetric mass density**, of a substance is its mass per unit volume. The symbol most often used for density is ρ Mathematically, density is defined as mass divided by volume

$$\rho = \frac{m}{V},$$

where $\rho$is the density, m is the mass, and V is the volume

Different metals possess different densities. Density helps differentiating between light and heavy metals.

Density depends to some extent on the

- Purity of the material
- Pore volume
- Treatment that the material has received.

(3) Appearance:

A **physical change** takes place without any changes in molecular composition. The same element or compound is present before and after the change. The same molecule is present throughout the changes.

Physical changes are related to physical properties since some measurements require that changes be made. The three main states of matter are: Solid, Liquid, and Gas.

- Solid is distinguished by a fixed structure. Its shape and volume do not change. In a solid, atoms are tightly packed together in a fixed arrangement.
- Liquid is distinguished by its malleable shape (is able to form into the shape of its container), but constant volume. In a liquid, atoms are close together but not in a fixed arrangement.
- Gas is made up of atoms that are separate. However, unlike solid & liquid, a gas has no fixed shape and volume.

Example 1: Physical Change

When liquid water (H_2O) freezes into a solid state (ice), it appears changed; however, this change is only physical as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass.

Mechanical Properties of Metals

STRESS-STRAIN DIAGRAMS

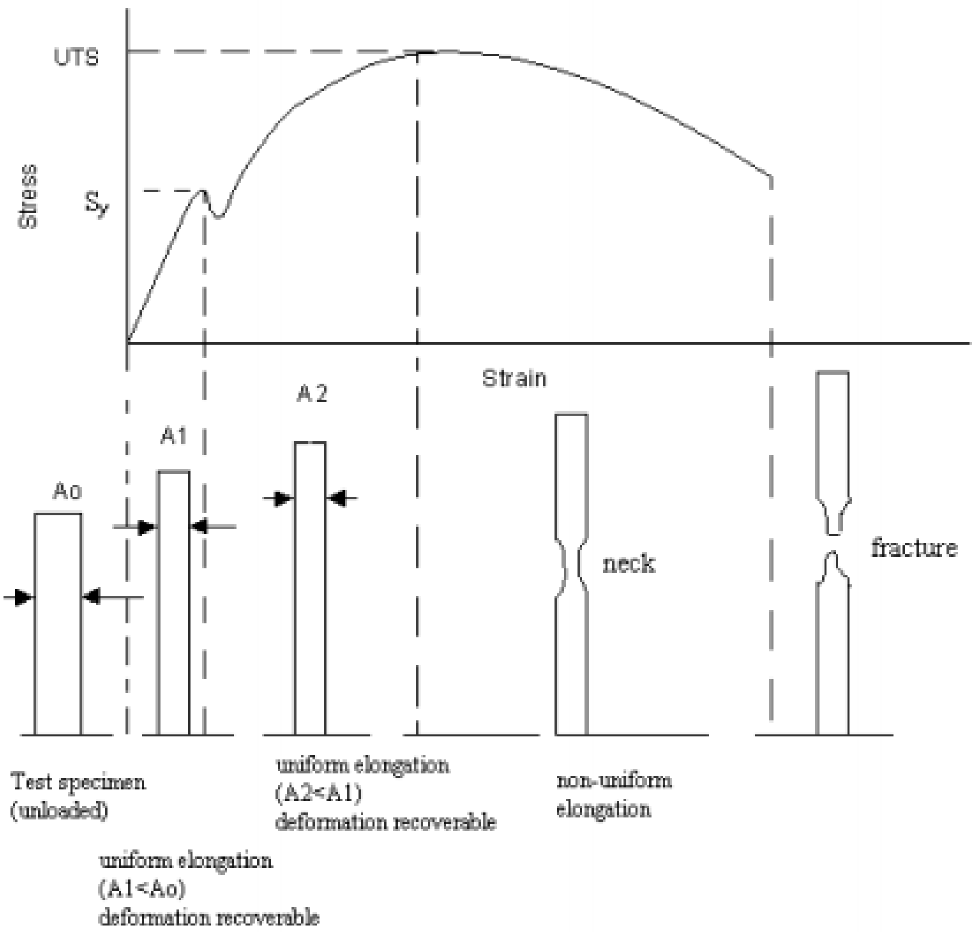
The internal resistance of the material to counteract the applied load is called stress, and the deformation as strain. There are three types of stresses:

Tensile stress: force acts to pull materials apart;

Compressive stress: the force squeezes material;

Shear stress: the force causes one part to slide on another part.

Stress-Strain curve (Mild Steel)



Tensile Properties

Yield point.

Hooke's law is not valid beyond the yield point. The stress at the yield point is called yield stress, and is an important measure of the mechanical properties of materials. In practice, the yield stress is chosen as that causing a permanent strain of 0.002. The yield stress measures the resistance to plastic deformation. The reason for plastic deformation, in normal materials, is not that the atomic bond is stretched beyond repair, but the motion of dislocations, which involves breaking and reforming bonds. Plastic deformation is caused by the motion of dislocations.

Tensile strength:

When stress continues in the plastic regime, the stress-strain passes through a maximum, called the tensile strength, and then falls as the material starts to develop a neck and it finally breaks at the fracture point.

For structural applications, the yield stress is usually a more important property than the tensile strength, since once it is passed, the structure has deformed beyond acceptable limits.

Ductility:

The ability to deform before braking. It is the opposite of brittleness. Ductility can be given either as percent maximum elongation åmax or maximum area reduction.

$$\%EL = \text{åmax} \times 100\ \%$$

$$\%AR = (A_0 - A_f)/A_0$$

These are measured after fracture (repositioning the two pieces back together).

Resilience:

Capacity to absorb energy elastically. The energy per unit volume is the area under the strain-stress curve in the elastic region.

Toughness:

Ability to absorb energy up to fracture. The energy per unit volume is the total area under the strain-stress curve. It is measured by an impact test.

Hardness

Hardness is closely related to strength. It is the ability of a material to resist scratching, abrasion, indentation, or penetration.

It is directly proportional to tensile strength and is measured on special hardness testing machines by measuring the resistance of the material against penetration of an indentor of special shape and material under a given load. The different scales of hardness are Brinell hardness, Rockwell hardness, Vicker's hardness, etc.

Hardness of a metal does not directly relate to the hardenability of the metal. Hardenability is indicative of the degree of hardness that the metal can acquire through the hardening process. i.e., heating or quenching.

True Stress and Strain:

When one applies a constant tensile force the material will break after reaching the tensile strength. The material starts necking (the transverse area decreases) but the stress cannot increase beyond tensile strength. The ratio of the force to the initial area, what we normally do, is called the engineering stress. If the ratio is to the actual area (that changes with stress) one obtains the true stress.

Elasticity

Elasticity of a material is its power of coming back to its original position after deformation when the stress or load is removed. Elasticity is a tensile property of its material.

The greatest stress that a material can endure without taking up some permanent set is called elastic limit (Point a).

Stiffness (Rigidity)

The resistance of a material to deflection is called stiffness or rigidity. Steel is stiffer or more rigid than aluminium.

Stiffness is measured by Young's modulus E. The higher the value of the Young's modulus, the stiffer the material. E is the ratio of stress over strain and is given by the slope of line 0-a. 1.3.4

Plasticity

The plasticity of a material is its ability to undergo some degree of permanent deformation without failure. Plastic deformation will take place only after the elastic range has been exceeded, beyond point b.

Plasticity is an important property and widely used in several mechanical processes like forming, shaping, extruding and many other hot and cold working processes. In general, plasticity increases with increasing temperature and is a favorable property of material for secondary forming processes.

Due to these properties various metals can be transformed into different products of required shape and size. This conversion into desired shape and size is effected either by the application of pressure, heat or both.

Ductility

Ductility of a material enables it to draw out into thin wire on application of the load. Mild steel is a ductile material. The wires of gold, silver, copper, aluminium, etc. are drawn by extrusion or by pulling through a hole in a die due to the ductile property. The ductility decreases with increase of temperature. The per cent elongation and the reduction in area in tension is often used as empirical measures of ductility.

Malleability

Malleability of a material is its ability to be flattened into thin sheets without cracking by hot or cold working. Aluminium, copper, tin, lead, steel, etc. are malleable metals. Lead can be readily rolled and hammered into thin sheets but can not be drawn into wire. Ductility is a tensile property, whereas malleability is a compressive property. Malleability increases with increase of temperature.

Brittleness

The brittleness of a material is the property of breaking without much permanent distortion. There are many materials, which break or fail before much deformation take place. Such materials are brittle e.g., glass, cast iron.

Elastic deformation:

When the stress is removed, the material returns to the dimension it had before the load was applied. Valid for small strains (except the case of rubbers).Deformation is reversible, non permanent.

Plastic deformation:

When the stress is removed, the material does not return to its previous dimension but there is a permanent, irreversible deformation. In tensile tests, if the deformation is elastic, the stress-strain relationship is called Hooke's law:

$$\sigma = E \epsilon$$

That is, E is the slope of the stress-strain curve. E is Young's modulus or modulus of elasticity. In some cases, the relationship is not linear so that E can be defined alternatively as the local slope:

$$E = d\sigma/d\epsilon$$

Shear stresses produce strains according to:

$$\tau = G \gamma$$

where G is the shear modulus. Elastic moduli measure the stiffness of the material. They are related to the second derivative of the interatomic potential, or the first derivative of the force vs. inter nuclear distance. By examining these curves we can tell which material has a higher modulus. Due to thermal vibrations the elastic modulus decreases with temperature. E is large for ceramics (stronger ionic bond) and small for polymers (weak covalent bond). Since the interatomic distances depend on direction in the crystal, E depends on direction (i.e., it is anisotropic) for single crystals. For randomly oriented policrystals, E is isotropic.

Yield criteria and macroscopic aspects of plastic deformation

Gross plastic deformation of a polycrystalline specimen corresponds to the comparable distortion of the individual grains by means of slip. During deformation, mechanical integrity and coherency are maintained along the grain boundaries; that is, the grain boundaries are constrained, to some degree, in the shape it may assume by its neighboring grains. Before deformation the grains are equiaxed, or have approximately the same dimension in all directions. For this particular deformation, the grains become elongated along the directions. For this particular deformation, the grains become elongated along the direction in which the specimen was extended.

CREEP AND CREEP TESTING

The slow and continuous elongation of a material with time at constant stress and high temperature below elastic limit is called creep. At high temperatures, stresses even below the elastic limit can cause some permanent deformation on stress-strain diagram.

There are three stages of creep. In the first stage the material elongates rapidly but at a decreasing rate. In the second stage, the rate of elongation is constant. In third stage, the rate of elongation increases rapidly until the material fails. The stress for a specified rate of strain at a constant temperature is called creep strength.

Creep test is carried out at high temperature. A creep curve (Fig. 1.4) is a plot of elongation of a tensile specimen versus time, for a given temperature and under constant stress. Tests are carried out for a period of a few days to many years. The test can be carried out on Universal Testing Machine with special attachments.

Creep curve shows four stages of elongation:

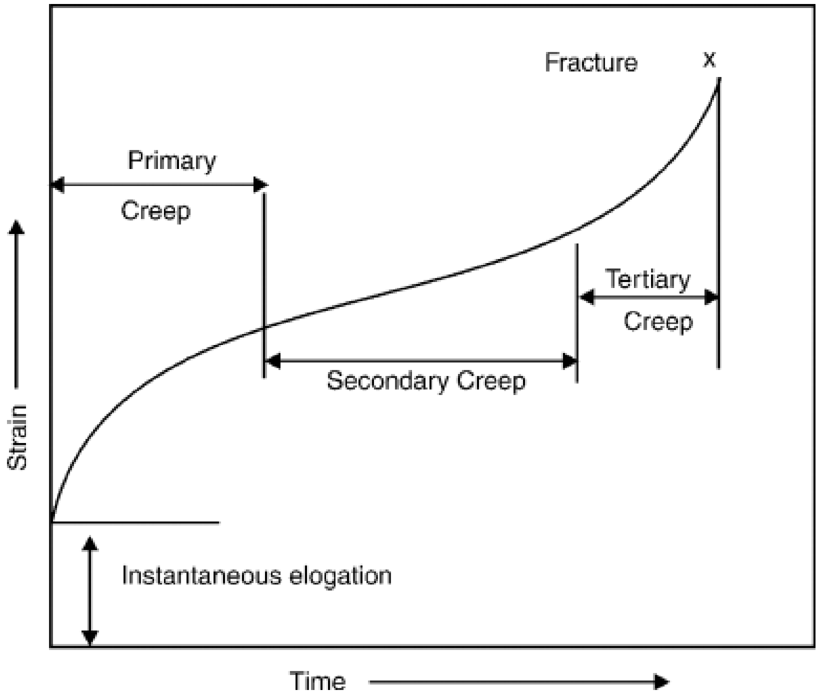
(a) Instantaneous elongation on application of load.

(b) Primary creep: Work hardening decreases and recovery is slow.

(c) Secondary creep: Rate of work hardening and recovery processes is equal.

(d) Tertiary Creep: Grain boundary cracks. Necking reduces the cross-sectional area of the test specimen.

The creep strength is used for the design of blades and other parts of steam and gas turbines working at high temperatures.



PLASTIC DEFORMATION IN SINGLE CRYSTALS

There are many mechanisms that can lead to plastic deformation in single crystals, but the most important is slip. The two things that we need to consider are the inherent resistance to the movement of dislocations provided by the periodicity of the lattice and the orientation of the crystal with respect to the applied stress.

***Lattice Resistance**

The stress, τ_f, needed to move a dislocation along the slip plane is known as the Peirels–Nabarro (or frictional) stress and is given by:

$$\tau_f = \mu \exp\left(-\frac{2\pi w}{b}\right)$$

The stress, which is clearly a function of the crystal structure and bonding, depends on *b* and *w*, that dislocation widths in covalent solids are quite narrow ($w \sim b$) compared with those in face centered cubic (fcc) metals ($w \sim 10b$).

- For metals $\tau_f \sim 10$ MPa $\sim 10^{-4}\mu$ these stresses are fairly small and dislocations can move freely. The yield stress is determined primarily by interactions between dislocations and other defects such as impurities.

- For simple ionic ceramics (e.g., NaCl and CaF_2) $\tau_f \sim 10$–100 MPa $\sim 10^{-4}\mu - 10^{-3}\mu$

- For complex ionic (e.g., Al_2O_3) and covalent ceramics (e.g., SiC) $\tau_f \sim 1000$ MPa $\sim 10^{-2}\mu$ Dislocations have low mobility and lattice resistance is the main obstacle.

***Orientation**

Plastic deformation depends not only on how easy it is for the dislocations to glide on their slip plane but also the orientation of the slip plane and the slip direction with the applied stress. If we consider a single crystal subject to uniaxial tension as the shear stress, τ_r, acting on the slip plane in the slip direction is

$$\tau_r = \sigma\cos\phi\ \cos\psi$$

For some structures it is possible to orient the crystal so that τ_r on all operative slip systems is zero. If this is the case, dislocation motion does not occur and the crystal will not plastically deform at stresses below the theoretical lattice strength.

The critical resolved shear stress, τ_{crss}, is the minimum shear stress required to initiate slip for a particular slip system defined when $\sigma = \sigma y$:

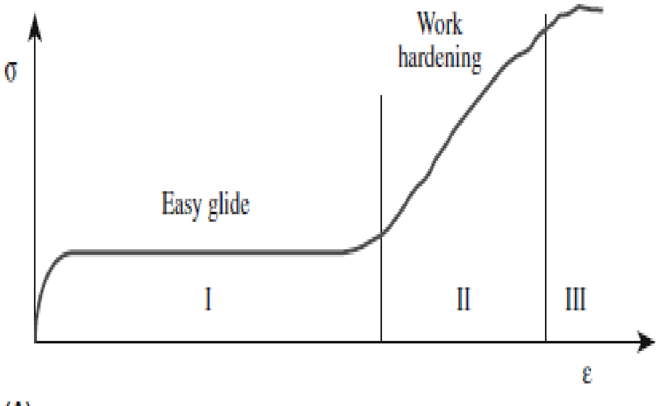
$$\tau_{crss} = \sigma y(\cos\phi\ \cos\psi$$

Figure 1.9 a shows the stress–strain behavior for a single crystal that is favorably oriented for plastic flow. This type of behavior is seen in MgO and other ceramics
with a rocksalt structure. There are three distinct stages:

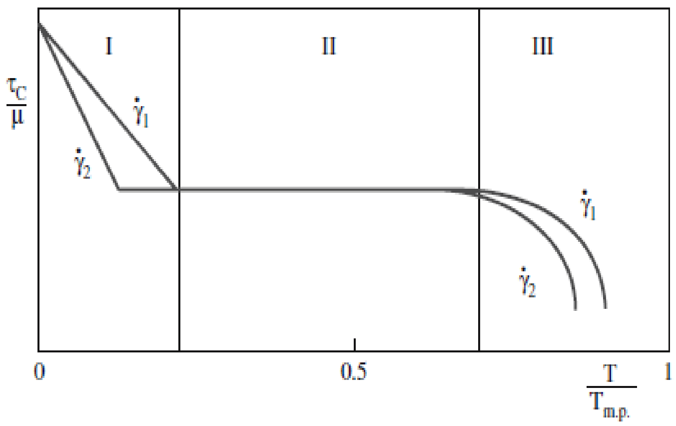
- Stage I: Easy glide of dislocations with the possibility of large strains (~20%)
- Stage II: Interaction of dislocations on intersecting slip planes resulting in work hardening
- Stage III: Cross-slip

The value of τ_{crss} depends on test conditions such as temperature and strain rate as shown schematically in Figure 1.9b. We can again identify three distinct behaviors:

- Region I: τ_{crss} decreases with increasing temperature and decreasing strain rate. Thermal fluctuations enhance dislocation motion.
- Region II: τ_{crss} is independent of temperature and strain rate. There is interaction between dislocations and between dislocations and other defects.
- Region III: τ_{crss} again decreases with increasing temperature and decreasing strain rate. At high temperatures diffusion processes can become important.



(A)



(B)

***FIGURE* (a) Stress–strain curve for a crystal suitably oriented for plastic flow. (b) Temperature dependence of the normalized critical resolved shear stress for two strain rates, where $\gamma_1 > \gamma_2$.**

1-2.5 PLASTIC DEFORMATION IN POLYCRYSTALS

Plastic deformation is more difficult in polycrystals than in single crystals because now we have to consider what happens at the grain boundaries. Grain boundaries act as barriers to dislocation motion and if adjacent grains are not favorably oriented for slip to continue, dislocations will pile up at the boundary.

A polycrystal needs five independent slip systems before it can undergo an arbitrary strain. This requirement is known as the von Mises criterion. A slip system is independent if the same strain cannot be produced from a combination of slip on other systems. For polycrystalline MgO the brittle-to-ductile transition occurs at ~1700°C as shown in Figure 1.10.

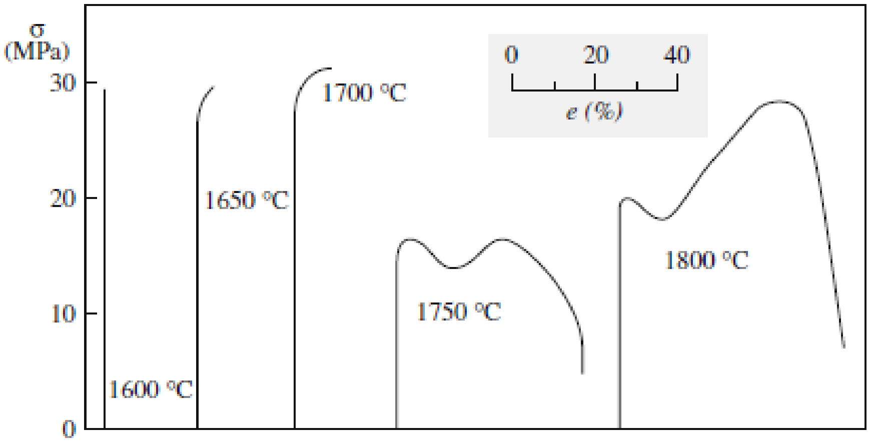


***FIGURE* Stress–strain curves for polycrystalline MgO as a function of temperature.**

Some cubic materials, e.g., TiC and $MgAl_2O_4$, do have enough independent slip systems, but the Peierls–Nabarro stress is high making dislocations immobile except at high temperature. The Hall–Petch relation:

$$\sigma_y = \sigma_0 + \frac{B}{d^{1/2}}$$

That indicates the effect of grain s required to make the dislocation move in a polycrystalline sample.

So the grain size of a polycrystalline ceramic is important in determining the yield strength and the fracture strength of ceramics.

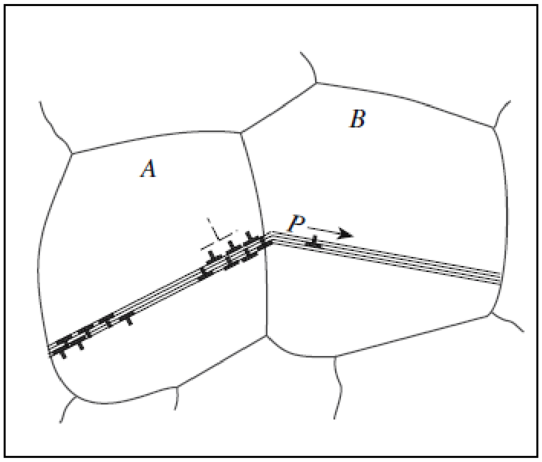


FIGURE **Illustration of slip propagation from grain A to grain B.**

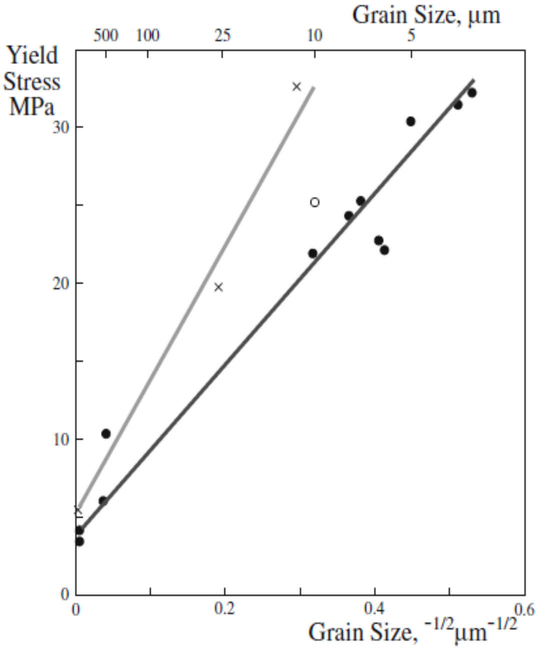


FIGURE **Grain size dependence of yield strength for KCl. The solid circles are for pure material with a <100> texture; the open circles are for pure material with a <111> texture. The crosses are for Sr-doped KCl.**

Figure illustrates the background to Eq. Slip starts in the most favorably oriented grains. If the material is to plastically deform then slip must propagate from one grain to the next. Stress concentrations are built up at the grain boundary at P and these are greater when the length of the slip band, or the grain size, is large. For deformation to continue the stress must be sufficient to start dislocation motion in an adjacent grain, which will be easier for large grained samples. The increase in strength of polycrystalline KCl as the grain size decreases (an illustration of the Hall–Petch phenomenon) is shown in Figure. In some cases the Hall–Petch equation appears to hold when the grain size is on the order of several nanometers. In these cases deformation cannot be due to dislocation glide and perhaps Eq. is best thought of as a scaling law.

UNIT II

Extractive Metallurgy: Hydro, pyro and electro metallurgy, refining of metals. Powder Metallurgy: methods of production of metal powder, mixing of metal powders, compaction of powders - applications. Extraction process of Iron: manufacture of pig iron, blast furnace operations, chemistry of reactions. Manufacture of cast iron, varieties of cast iron, effect of impurities. Production of steel, Bessemer process, open-hearth process, L D methods. Classification of steel, effect of impurities. Heat treatment process: annealing, hardening, tempering, normalizing and gas carburizing. Fe- Carbon phase diagram.

Metallurgy

The extraction of metals from their ores, heat treatments and the production of alloys.

Production of metals

- Mining
- Concentration
- Metal extraction

Mining

Five main types of mining:

- Open cast mining
- Underground mining
- Open pit mining
- Dredging
- Solution mining

Ore concentration

Also called **ore dressing**, the aim is to increase
The amount of metal in each tonne of ore. The
Ore is crushed then ground and concentrated,
The following methods may be used:

- Gravity concentration
- Flotation
- Magnetic separation
- Amalgamation

Metal extraction

The process of extracting metals from concentrates:

Pyrometallurgy – furnace heat is used with a reducing agent (iron uses coke) and a flux to produce metal and slag waste.

Hydrometallurgy – leaching dissolves ore in a solvent and then electrolysis is used to separate the metal.

Thermo-electrometallurgy- Aluminium can be extracted from salt or mineral mixtures by electrolysis. It uses a lot of electricity making it an expensive process. Blister copper is refined by electrolysis.

Extraction Metallurgy Part 2: Case studies

- Copper – Pyrometallurgy route and environmental concerns. The hydrometallurgical alternative.
- Hydrometallurgical processes – ion exchange processes, solvent extraction, and bacterial leaching.
- Iron – Pyrometallurgy and the blast furnace.
- Silicon – The electric arc furnace. Purification by the Czochralski process.
- Aluminium – Electrolytic reduction.
- The siderophiles – The extraction of Au and the Pt group metals and their purification.

Pyrometallurgy of copper Reminder: Pyrometallurgy is the use of heat to reduce the mineral to the free metal, and usually involves 4 main steps:

1.Calcination: thermal decomposition of the ore with associated elimination of a volatile product.

2.Roasting: a metallurgical treatment involving gas- solids reactions at elevated temperatures.

3.Smelting: a melting process which separates the chemical reaction products into 2 or more layers.

4.Refining: treatment of a crude metal product to improve its purity.

Cu ore usually associated with sulphide minerals.

Most common source of Cu ore is the mineral chalcopyrite ($CuFeS2$), which accounts for 50% of Cu production.

Other important ores include:

chalcocite [$Cu2S$],

Malachite [$CuCO3 \cdot Cu(OH)2$],

Azurite [$2CuCO3 \cdot Cu(OH)2$],

bornite ($3Cu2S \cdot Fe2S3$),

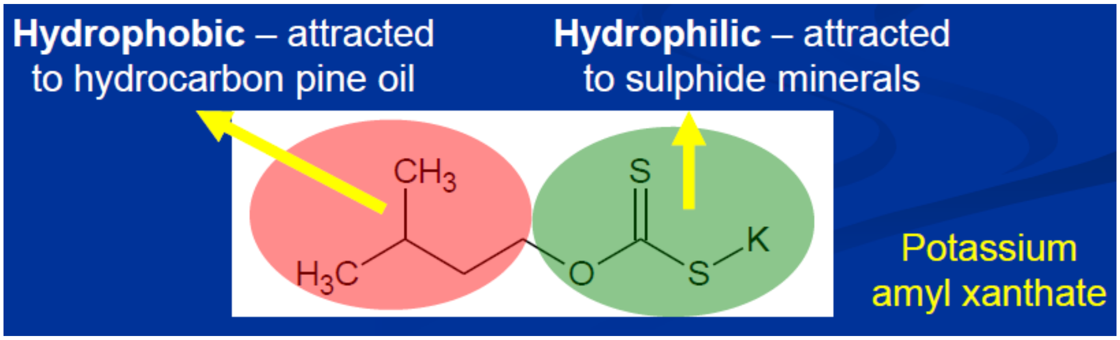
covellite (CuS).

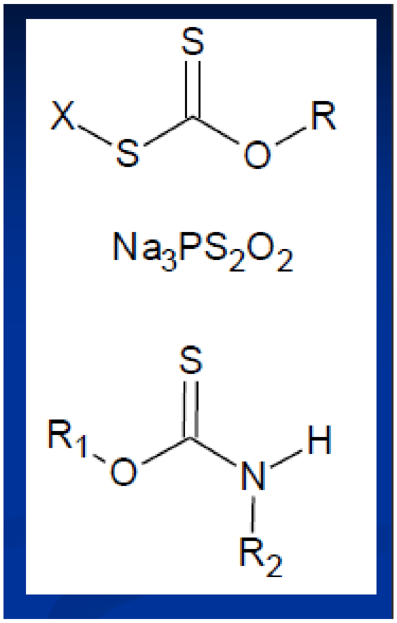
1. Concentration Only ~0.7% of the extracted ore contains Cu

Finely crushed ore concentrated by the froth-flotation process:

•Copper ore slurry mixed with: Lime water – to give basic pH Pine oil – to make bubbles An alcohol – to strengthen bubbles A chemical collector

Chemical collectors such as xanthates (salts & esters of xanthic acid), dithiophosphates, or thionocarbamates make the ore surface hydrophobic.





Raising the pH causes the polar ends to ionize more, thereby preferentially sticking to chalcopyrite (CuFeS2) and leaving pyrite (FeS2) alone.

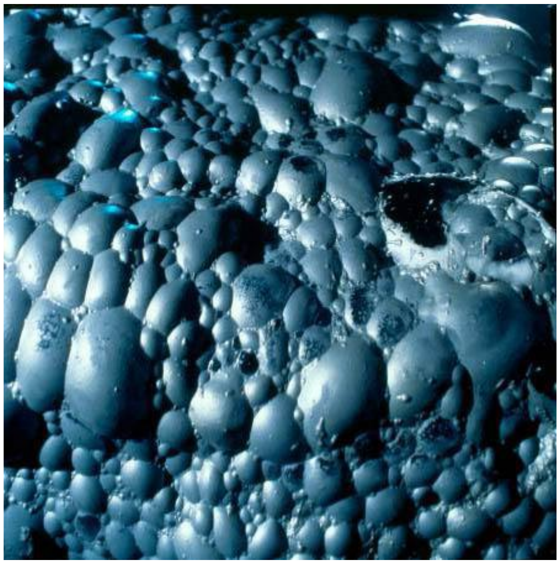
Air is bubbled through the suspension.

Finely divided hydrophobic ore particles latch on to the air bubbles and travel to the surface where a froth is formed.

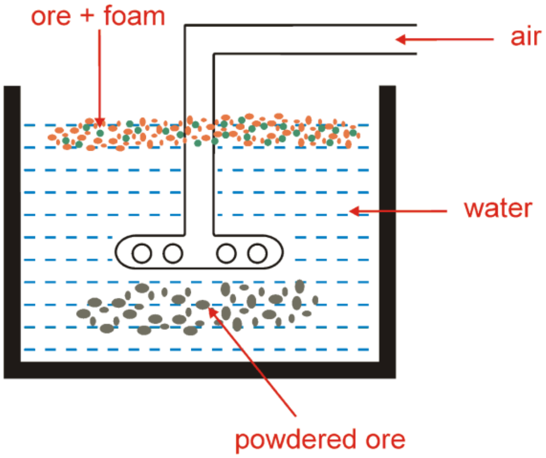
The froth containing the Cu ore is skimmed off and reprocessed.

In this manner, the ore is concentrated to an eventual value of over 28% Cu.

The remaining material (sand particles & other impurities) sink to the bottom & is discarded or reprocessed to extract other elements.



Froth-flotation



2. Roasting

Involves partial oxidation of the sulphide mineral with air at between 500C and 700C.

For chalcopyrite, the main reactions are:

$CuFeS_{2(s)} + 4O_{2(g)} \longrightarrow CuSO_{4(s)} + FeSO_{4(s)}$

$4CuFeS_{2(s)} + 13O_{2(g)} \longrightarrow 4CuO_{(s)} + 2Fe2O_{3(s)} + 8SO_{2(g)}$

Reactions are exothermic, roasting is an autogenous process requiring little or no additional fuel.

NB, not all the sulphides are oxidised, only around 1/3. Rest remain as sulphide minerals.

The gases produced contain around 5 – 15% SO2, which is used for sulphuric acid production.

Objectives of roasting: 1) Remove part of the sulphur. 2) Convert iron sulphides into iron oxide and iron sulphate to facilitate removal during smelting. 3) To pre-heat the concentrate to reduce amount of energy needed by the smelter.

3. Smelting

Smelting consists of melting the roasted concentrate to form 2 molten phases: 1) a sulphide "matte", which contains the iron-copper sulphide mixture. 2) an oxide slag, which is insoluble in the matte, and contains iron oxides, silicates, and other impurities.

Smelting is carried out at around 1200C, usually with a silica flux to make the slag more fluid.

The matte layer sinks to the bottom, and the slag layer floats on top of the matte & is tapped off & disposed of.

The main reaction is the reduction of copper oxides (formed during roasting) back into copper sulphide to ensure that they migrate into the matte phase:

$FeS(l) + 6CuO(l) \rightarrow 3Cu_2O(l) + FeO(l) + SO_2(g)$

$FeS(l) + Cu_2O(l) \rightarrow FeO(l) + Cu_2S(l)$

$Cu_2S(l) + FeS(l) \rightarrow Cu_2S \bullet FeS(l)$ (matte)

4. Conversion

After smelting, matte contains from between 30 to 80% Cu in the form of copper sulphide.

The sulphur is removed by selective oxidation of the matte with O_2 to produce SO_2 from S, but leave Cu metal.

Converting is carried out in two stages: 1) an iron removal stage, and 2) a copper-making stage.

Iron removal

A silica flux is added to keep the slag (see below) molten.

Air is blown into the converter to oxidize the iron sulphide according to the following reaction: $2Cu_2S \bullet FeS(l) + 3O_2(g) + SiO_2(l) \rightarrow 2FeO \bullet SiO_2(l) + 2SO_2(g) + Cu_2S(l)$

Si added to help form FeO slag.

The oxidized Fe and Si form a slag (insoluble in matte) that is skimmed off & disposed off.

Copper making

The sulphur in the Cu_2S can now be oxidized to leave behind metallic copper according to the following reaction: $Cu_2S(l) + O_2(g) \rightarrow 2Cu(l) + SO_2(g)$

Pyrometallurgy of copper 4. Conversion (*cont.*) The end product is around 98.5% pure & is known as blister copper because of the broken surface created by the escape of SO2 gas.

5. Refining

Almost all copper is refined by electrolysis.

The anodes (cast from blister copper) are placed into an aqueous CuSO4/H2SO4 solution.

Thin sheets of highly pure Cu serve as the cathodes.

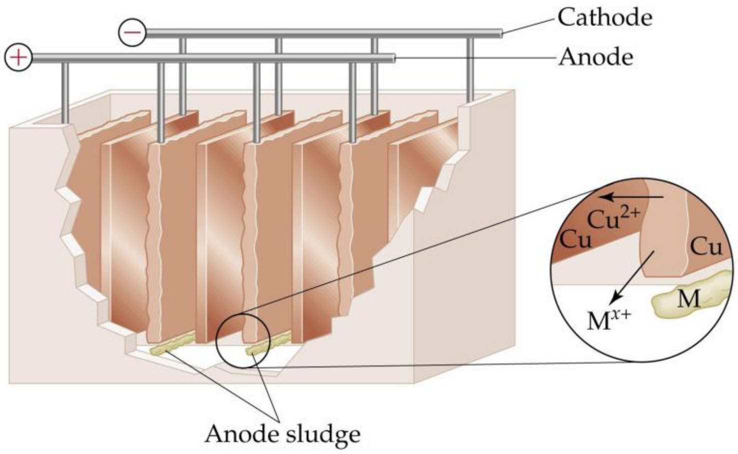
Application of a suitable voltage causes oxidation of Cu metal at the anode.

Cu2+ ions migrate through the electrolyte to the cathode, where Cu metal plates out.

Metallic impurities more active then Cu are oxidized at the anode, but don’t plate out at the cathode.

Less active metals are not oxidized at the anode, but collect at the bottom of the cell as a sludge.

The redox reactions are: Cu(*s*) Cu2+(*aq*) + 2e- Cu2+(*aq*) + 2e- Cu(*s*) Ered = -0.83V



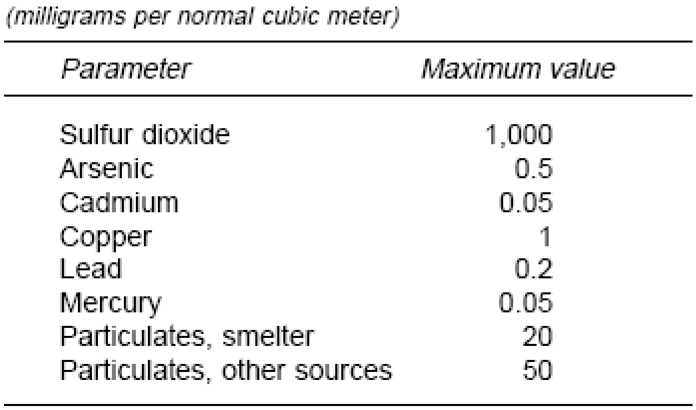
Environmental impact

Large amount of gases produced present air pollution problems, in particular SO2 gas acid rain.

Dust produced contains heavy metals such as mercury, lead, cadmium, zinc health problems.

Waste water contaminated with: Insoluble substances, mostly waste sludge (finely ground rock). Soluble substances (heavy metals, sulphates). Chemicals from flotation process.

Typical Air Emissions



(milligrams per normal cubic meter)

Parameter	*Maximum value*
Sulfur dioxide	1,000
Arsenic	0.5
Cadmium	0.05
Copper	1
Lead	0.2
Mercury	0.05
Particulates, smelter	20
Particulates, other sources	50

Hydrometallurgy of copper

Advantages

Much more environmentally friendly than pyrometallurgy.

Compared to pyrometallurgy, only a fraction of the gases liberated into the atmosphere.

Emissions of solid particles comparatively non-existent.

Disadvantages

Large amount of water used, greater potential for contamination.

Waste waters contain soluble metal compounds, chelating compounds & organic solvents.

The following steps are involved:

1.Ore preparation

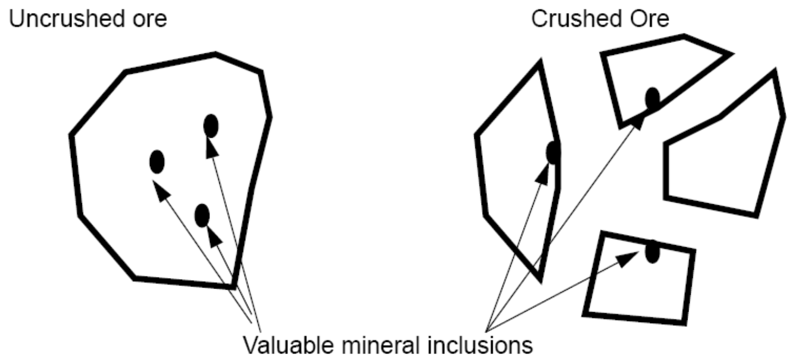
2.Leaching

3.Solution purification

4.Metal recovery

1. Ore preparation

Ore undergoes some degree of comminution (crushing & pulverisation) to expose the Cu oxides & sulphides to leaching solution.



Amount of comminution depends on quality of ore: Higher grade ore – more comminution. Lower grade ore – less comminution. (Why??)

If possible, ore is pre-concentrated; reject ore that contains very little Cu.

1. **Leaching**

   Definition : The dissolution of a mineral in a solvent, while leaving the gangue (rock or mineral matter of no value) behind as undissolved solids.

Cu is normally leached by one of three methods:

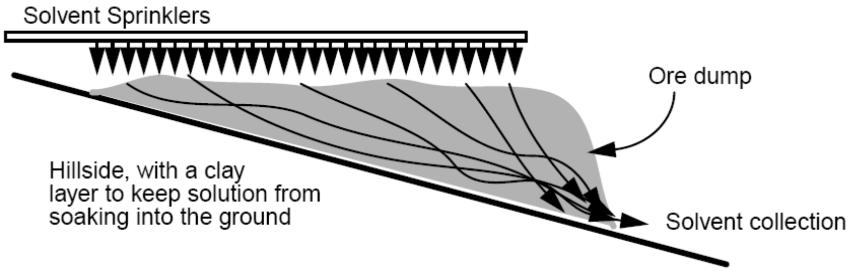
(a) Dump leaching (b) Heap leaching (c) Bacterial leaching

Leaching solution trickled over a dump.

Runoff solution collected & the Cu recovered from it.

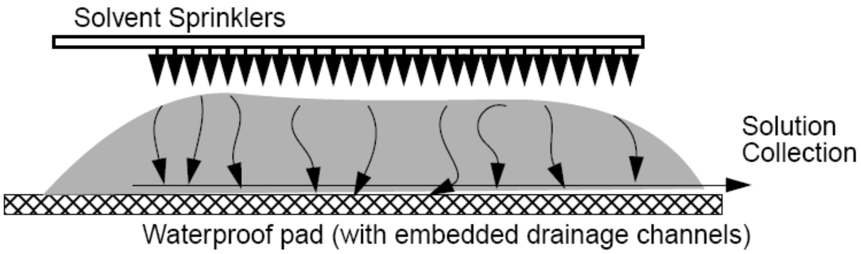
A slow process that takes months or years to complete.

Typically only around 60% of the Cu in the dump is recovered.



Similar to dump leaching except ore not simply dumped on a hillside, but is crushed to gravel size & piled onto an artificial pad.

After leaching (6 months to 1 year) gangue is removed from pad, disposed of & replaced with fresh ore.



Leaching reactions Nature of ore determines if leaching is non-oxidative or oxidative. **Non-oxidative leaching:** No change in oxidation state. *e.g.*

(1) dissolution of copper sulphate by water:

$CuSO_4(s) + H_2O(l)\ Cu^{2+}(aq) + SO_4^{2-}(aq)$

(2) dissolution of alkaline materials by acid:

$Cu_2(OH)_2 \cdot CO_3(s) + 2H_2SO_4(aq)$

$2CuSO_4(aq) + CO_2(g) + 3H_2O(l)$

Oxidative leaching: Many ores only soluble once oxidised. *e.g.* covellite (CuS) much more soluble if oxidised to $CuSO_4$ $CuS(s) + O_2(g)\ CuSO_4(aq)$

EXERCISE : work out which species is oxidised, and which is reduced, and write out the balanced half reactions for each.

SOLUTION: CuS Cu = +2, S = -2 O_2 O = 0

$CuSO_4$ Cu = +2, O_4 = -8, S = +6

$S^{-2}\ S^{+6} + 8e^-$ (oxidation) $2O_2 + 8e^-\ 4O^{2-}$ (reduction)

Several bacteria, especially *Thiobacilli*, are able to solubilise metal minerals by oxidising ferrous to ferric iron, as well as elemental sulphur, sulphide, and other sulphur compounds to sulphate or sulphuric acid.

20 to 25% of copper produced in the USA, and 5% of the worlds copper is obtained by bacterial leaching.

Very slow process; takes years for good recovery

But low investment and operating costs.

Thiobacilli

Are acidotolerant; some grow at pH's as low as 0.5

Are tolerant against heavy metal toxicity.

Are chemolithoautotrophs (C source is CO_2 & energy derived from chemical transformation of inorganic matter).

Mechanisms Generalised reaction : $M(II)S + 2O_2\ M^{2+} + SO_4^{2-}$

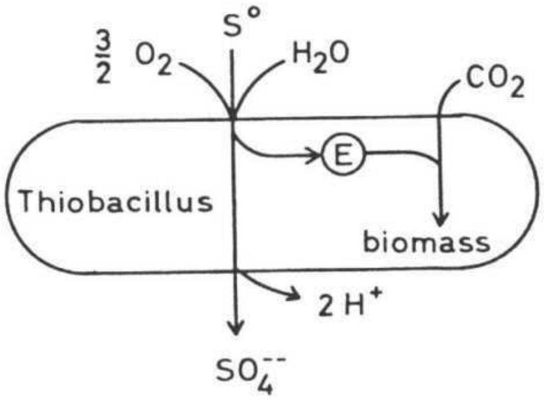
Two mechanisms: (a) indirect mechanism involving the ferric-ferrous cycle, and (b) direct mechanism involving physical contact of the organism with the sulphide mineral.

Mechanisms**: Indirect** First step: ferrous sulphate is converted into ferric sulphate by the action of *Acidithiobacillus ferrooxidans*: (c) Bacterial leaching $4FeSO_4 + O_2 + 2H_2SO_4$ $2Fe_2(SO_4)_3 + 2H_2O$ **CLASS EXERCISE : work out which is ferric- and which is ferrous sulphate, and write out the balanced half reactions for each.** $FeSO_4$ SO_4^{2-} Fe^{2+} (ferrous) $2Fe_2(SO_4)_3$ 3 SO_4^{2-} = -6, but 2 Fe Fe^{3+} (ferric)

Mechanisms**: Indirect** (c) Bacterial leaching $4Fe^{2+}$ $4Fe^{3+} + 4e^-$ (oxidation) $O_2 + 4e^-$ $2O^{2-}$ (reduction)
Ferric sulphate is a strong oxidising agent capable of dissolving a range of sulphide minerals.
In the case of chalcopyrite:

$CuFeS_2 + 2Fe_2(SO_4)_3$ $CuSO_4 + 5FeSO_4 + 2S$

Mechanisms**: Indirect** (c) Bacterial leaching
The elemental S produced by the indirect method can be converted to H_2SO_4 by *Acidithiobacillus ferrooxidans*:



The H_2SO_4 helps maintain the pH at levels favourable for bacterial growth.
Mechanisms**: Direct** (c) Bacterial leaching
Bacteria actually adheres to the mineral surface prior to enzymatic attack.
The mineral is oxidised with oxygen to sulphate and metal cations without any detectable intermediate occurring.
In the case of covellite:

$CuS + 2O_2 \; CuSO_4$

Compared to other extraction techniques: (c) Bacterial leaching

Traditional methods expensive (i.e. roasting + smelting) & require high concentrations of Cu in ore.

Bacteria can effectively deal with low [Cu] as they simply ignore surrounding waste materials.

Up to 90% extraction efficiency.

Compared to other extraction techniques: (c) Bacterial leaching

Economical: Simpler, cheaper, less infrastructure.

More environmentally friendly; no SO_2 emissions, less landscape damage.

ADVANTAGES:

Economical: Very slow compared to smelting; less profit. Delay in cash flow for new plants.

Environmental; Toxic chemicals sometimes produced. H_2SO_4 pollution. Precipitation of heavy ions (Fe, Zn, As) – pollution.

Leaching reactions not perfectly selective other elements in solution as well, not just Cu. These need to be removed.

After leaching, Cu in solution can be very dilute. need a way to concentrate it.

Both of these are generally done using ion exchange processes, the two most common being ion exchange chromatography, and solvent extraction.

2. **Solution Purification**

   Ion exchange chromatography

DEFINITION: a solution containing a mixture of metal ions is contacted with a resin that is insoluble in the metal-ion solution.

Ion-exchange resin consists of an inert solid phase to which labile functional groups are chemically bonded.

Functional groups can either be acidic (H^+) or basic ($OH^–$) groups that exchange with cations (M^+) or anions ($M^–$), respectively.

The ion-exchange process is reversible.

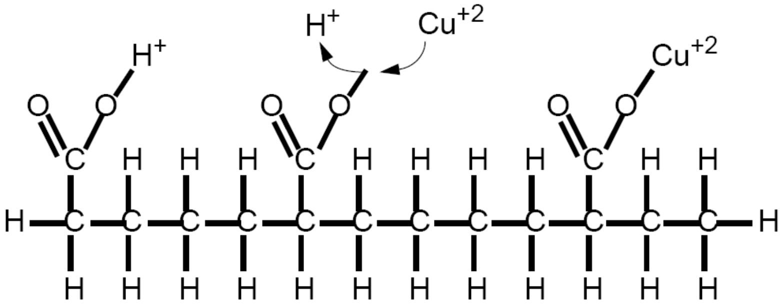
Ion exchange chromatography: Theory

Analyte molecules retained on a column (stationary phase) based on coulombic (ionic) interactions.

Stationary phase has ionic functional groups (R-X) that interact with analyte ions of opposite charge.

Two types: cation exchange chromatography: $R\text{-}X^-C^+ + \mathbf{M}^+B^- \; R\text{-}X^-\mathbf{M}^+ + C^+B^-$ anion exchange chromatography: $R\text{-}X^+A^- + M^+\mathbf{B}^- \; R\text{-}X^+\mathbf{B}^- + M^+A^-$

Cu Ion exchange chromatography



Carboxyl groups exchanges the ion it currently holds (H+) for a Cu2+ ion.

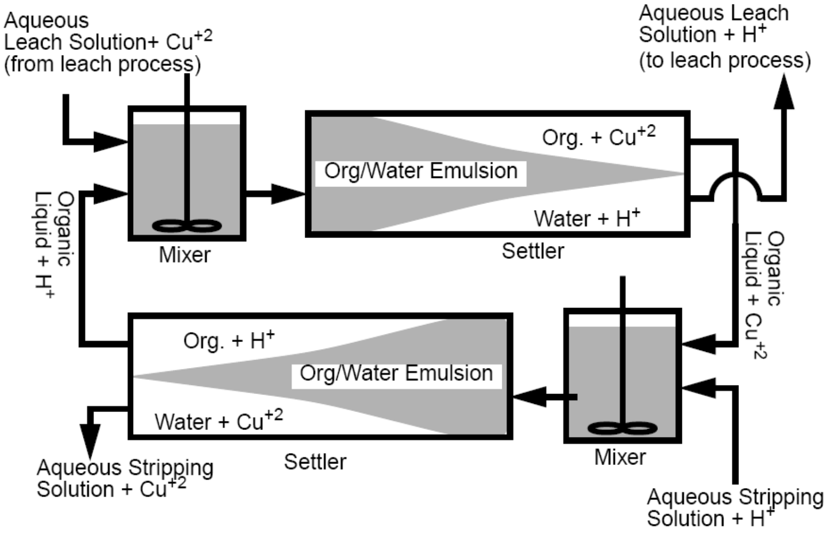
The Cu2+ is later released by contacting it with a stripping solution (very high H+ conc.).

Solvent extraction

DEFINITION: a method to separate compounds based on their relative solubilities in 2 different immiscible liquids.

In industry, this is usually set up as a continuous process.

Solvent extraction



4. Metal Recovery:

At this point, the metal needs to be recovered from solution in the solid form.

This is either achieved chemically, or electrochemically.

Basic Steps In Powder Metallurgy

Powder Production

Blending or Mixing

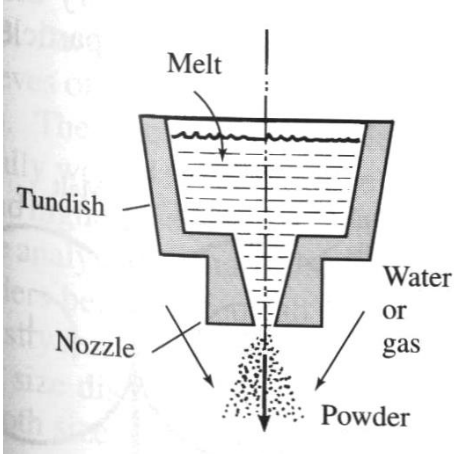
Compaction

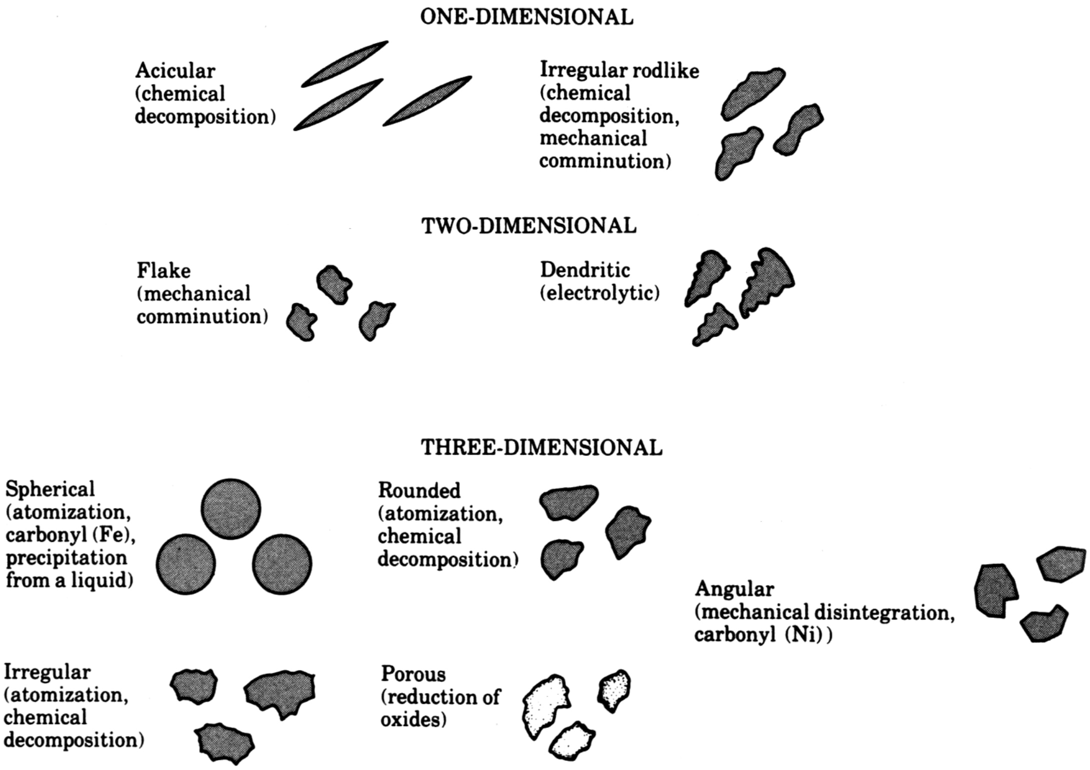
Sintering

Finishing

Powder Production

- Atomization the most common
- Others
    - Chemical reduction of oxides
    - Electrolytic deposition
- Different shapes produced
    - Will affect compaction process significantly



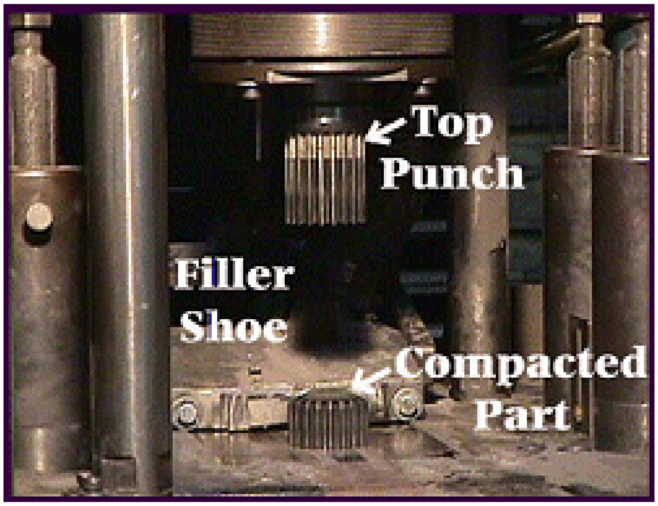


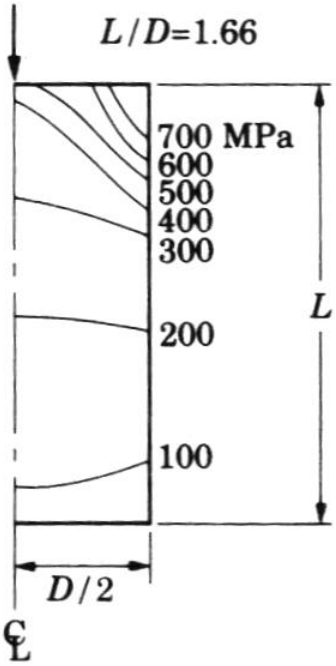
Blending or Mixing

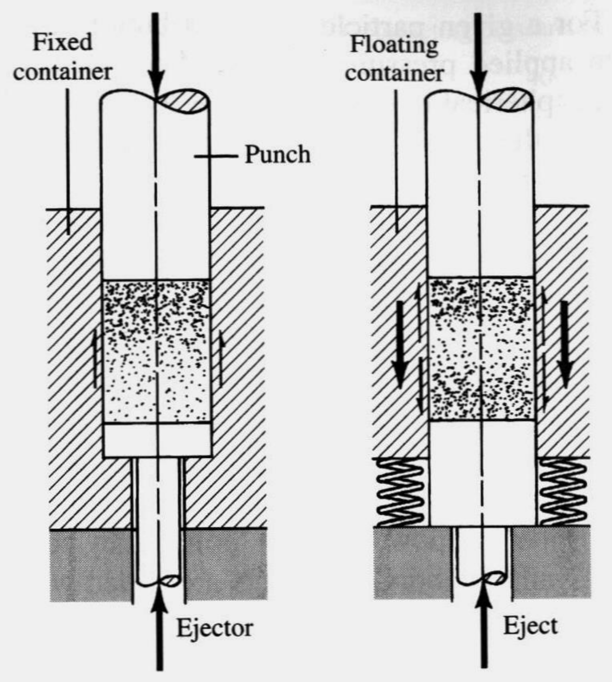
1. Can use master alloys, (most commonly) or elemental powders that are used to build up the alloys
    a. Master alloys are with the normal alloy ingredients
2. Elemental or pre-alloyed metal powders are first mixed with lubricants or other alloy additions to produce a homogeneous mixture of ingredients
3. The initial mixing may be done by either the metal powder producer or the P/M parts manufacturer
4. When the particles are blended:
    a. Desire to produce a homogenous blend
    b. Over-mixing will work-harden the particles and produce variability in the sintering process

Compaction

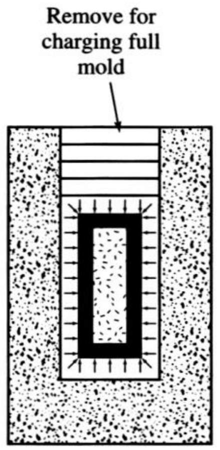
1. Usually gravity filled cavity at room temperature
2. Pressed at 60-100 ksi
3. Produces a “Green” compact
    a. Size and shape of finished part (almost)
    b. Not as strong as finished part – handling concern
4. Friction between particles is a major factor

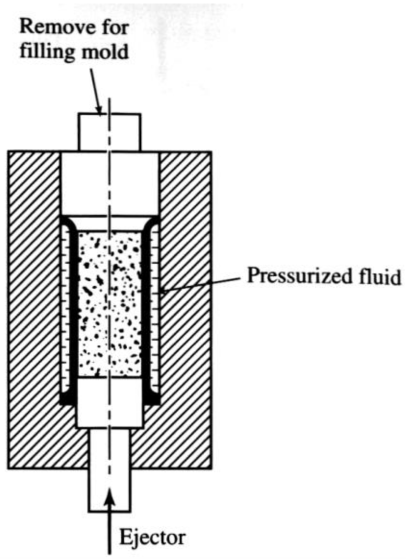






Isostatic Pressing





1. Because of friction between particles
    a. Apply pressure uniformly from all directions (in theory)
2. Wet bag (left)
3. Dry bag (right)

Sintering

1. Parts are heated to ~80% of melting temperature
2. Transforms compacted mechanical bonds to much stronger metal bonds
3. Many parts are done at this stage. Some will require additional processing

1. Final part properties drastically affected
2. Fully sintered is not always the goal
   a. Ie. Self lubricated bushings
3. Dimensions of part are affected

Die Design for P/M

1. Thin walls and projections create fragile tooling.
2. Holes in pressing direction can be round, square, D-shaped, keyed, splined or any straight-through shape.
3. Draft is generally not required.
4. Generous radii and fillets are desirable to extend tool life.
5. Chamfers, rather the radii, are necessary on part edges to prevent burring.
6. Flats are necessary on chamfers to eliminate feather-edges on tools, which break easily.

Advantages of P/M

1. Virtually unlimited choice of alloys, composites, and associated properties
   a. Refractory materials are popular by this process
2. Controlled porosity for self lubrication or filtration uses
3. Can be very economical at large run sizes (100,000 parts)
4. Long term reliability through close control of dimensions and physical properties
5. Wide latitude of shape and design

6. Very good material utilization

Disadvantages of P/M

1. Limited in size capability due to large forces
2. Specialty machines
3. Need to control the environment – corrosion concern
4. Will not typically produce part as strong as wrought product. (Can repress items to overcome that)
5. Cost of die – typical to that of forging, except that design can be more – specialty
6. Less well known process

Types of steels: Below are given some applications. Details can be looked into references given at the end of the lecture. Broadly we have either plain carbon (carbon is the principle alloying element) or alloy (in addition to carbon there are other alloying elements like Nb, V, W, Cr, Ni etc) steel. Plain carbon steels are the following types:

The alloy steels are classified as low (less than 5 weight% alloying elements), medium (in between 5 to 10 weight percent alloying elements) and high alloy steels (more than 10 weight percent alloying elements).

Effect of impurity elements on steel properties

Carbon imparts strength to iron. It reduces ductility and impact strength. But presence of carbon allows heat treatment procedures. Sulphur segregates during solidification (segregation coefficient is 0.02). Sulphur causes hot shortness due to formation of FeS formed during solidification of steel. Sulphide inclusions lower weldability and corrosion resistance. Presence of sulphur may also lead to development of tear and cracks on reheating the steel.

Phosphorus segregates during solidification (segregation coefficient is 0.02). Presence of phosphorus impairs plastic properties. Silicon and manganese: Silicon reduces the drawing capacity of steel. Manganese is beneficial; it increases strength without affecting ductility and sharply reduces hot shortness. Gases: Nitrogen impairs plastic properties and increases embrittlement at lower temperatures. Hydrogen causes defects such as flakes, fish-scale fracture. Inclusions: Presence of inclusions at the grain boundary weakens intra-granular bonds. Inclusions also act as stress concentrators. Some type of inclusions is brittle. Tramp elements: Tramp elements like copper, zinc, tin, antimony etc create problems during reheating of steels because their melting points are much lower than steel reheat temperature.

Heat Treatment

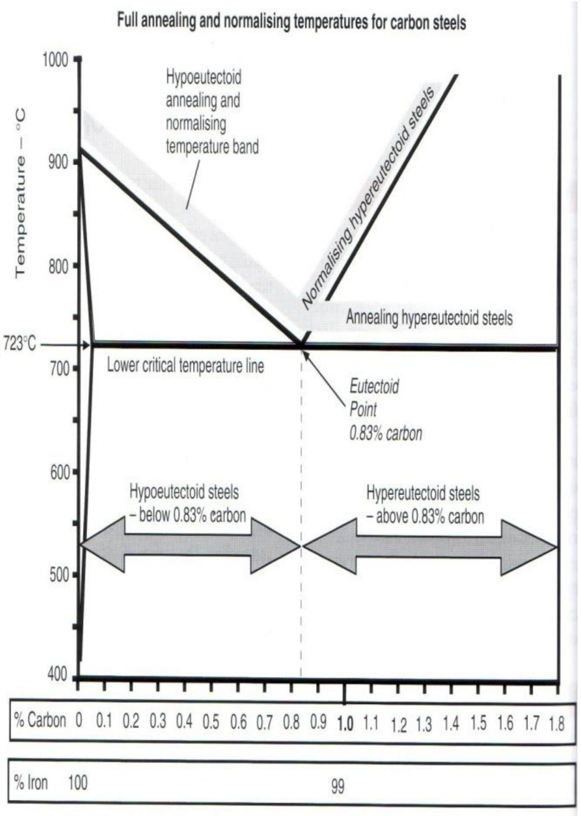
The amount of carbon present in plain carbon steel has a pronounced effect on the properties of a steel and on the selection of suitable heat treatments to attain certain desired properties. Below are some major types of heat treatment processes:

Types

1. *Annealing*
2. *Normalizing*
3. *Hardening*
4. Carburizing
5. *Tempering*

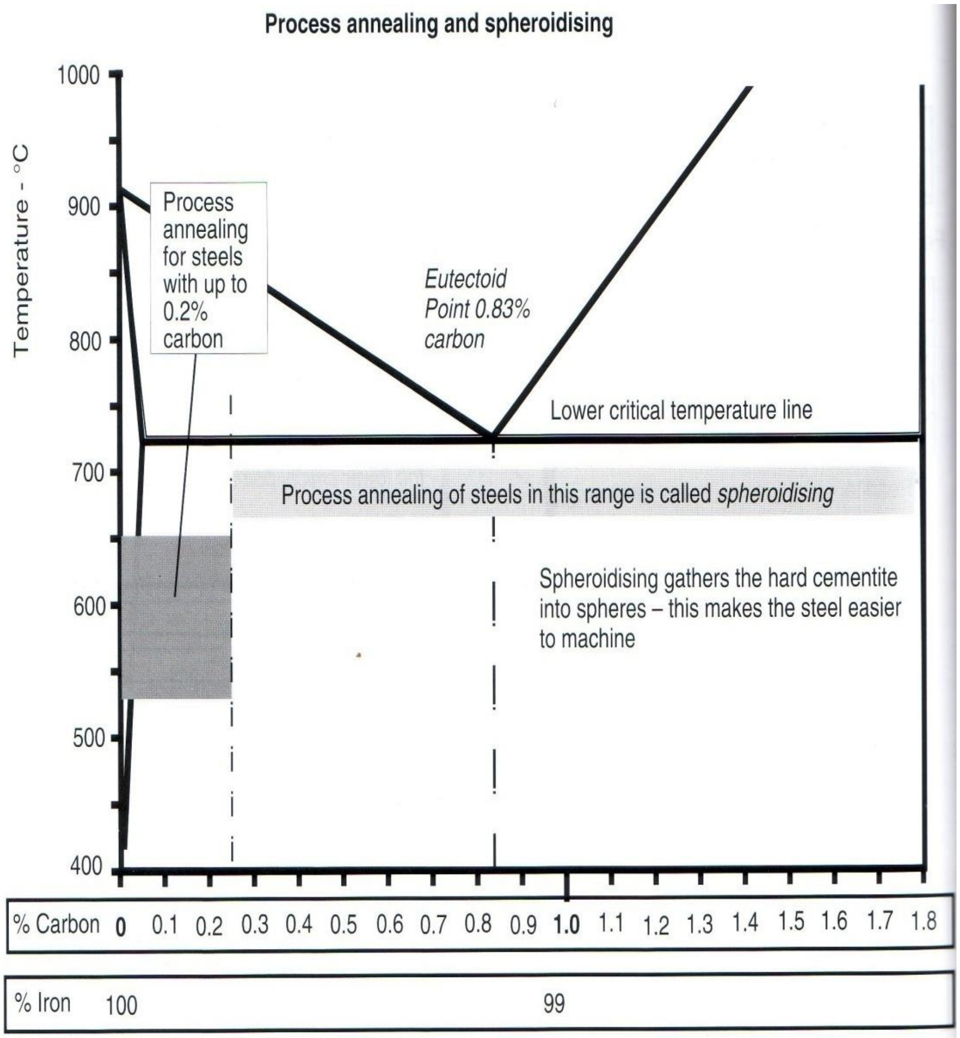
Annealing

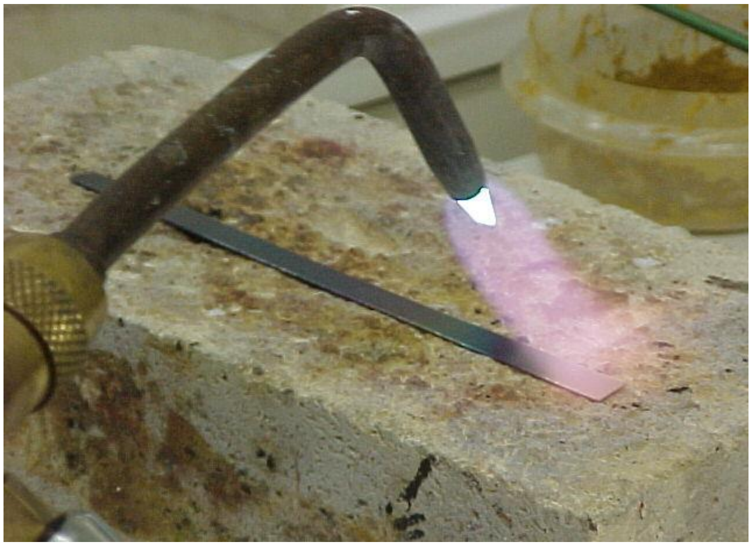
1. Makes a metal as soft as possible
2. Hypoeutectoid steels (less than 0.83% carbon) are heated above upper critical temp., soaked and cooled slowly.
3. Hypereutecoid (above 0.83%) are heated above lower critical temp., soaked and allowed to cool slowly.



Full annealing and normalising temperatures for carbon steels

1. Process Annealing. Low carbon steels may harden through cold working. They can be heated to around 100 degrees below lower critical temp., soaked and allowed to cool in air.
2. Spheroidising. High carbon steels may be annealed just below the lower critical temp. to improve machinability.





1. **Normalising**. Internal stresses caused by rolling and rolling or forging are removed. Steels are heated above upper critical temp., soaked and cooled in air. The cooling rate is faster than annealing giving a smaller grain structure.
2. **Stress relieving.** The component is reheated and held at temperature for a period of time and cooled slowly.

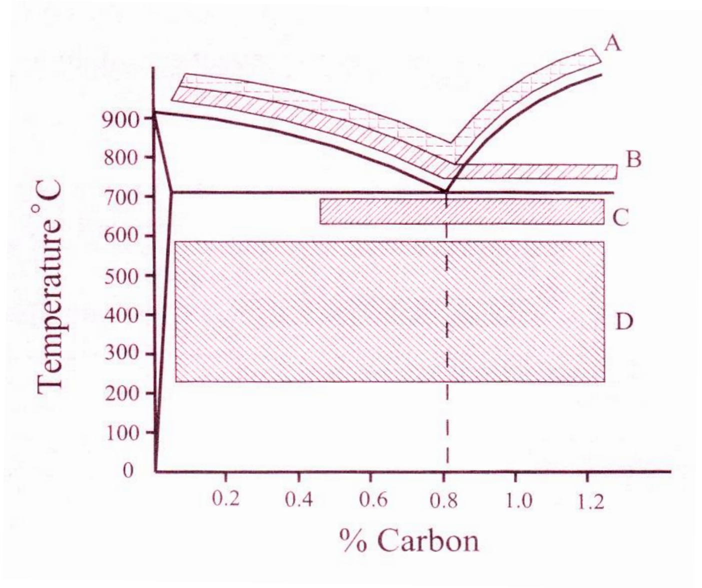
Hardening

Medium and High carbon steels (0.4 – 1.2%) can be heated until red hot and then quenched in water producing a very hard and brittle metal. At 723 degrees, the BCC ferrite changes into Austenite with a FCC structure.

Tempering

1. To remove some of the brittleness from hardened steels, tempering is used. The metal is heated to the range of 220-300 degrees and cooled.
2. Tempering colours are an indicator of temperature on polished metals. Colours range from yellow to brown to violet and blue.

Heat Treatments



A – Normalising

B – Annealing or Hardening

C – Spheroidising or Process Annealing

D - Tempering

Phase Diagrams

Metastable Iron-Carbon (Fe-C) Phase Diagram

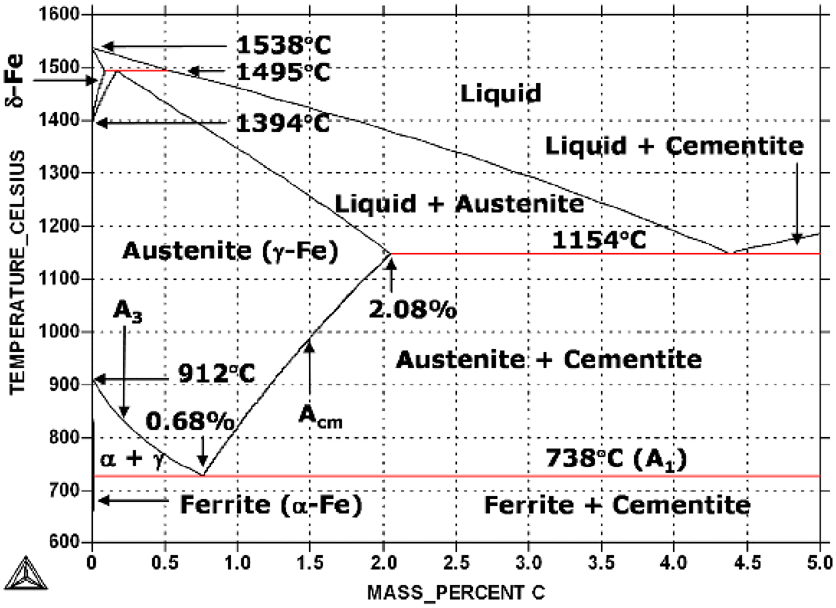


Figure The Fe-C phase diagram shows which phases are to be expected at metastable equilibrium for different combinations of carbon content and temperature.

At the low-carbon end of the metastable Fe-C phase diagram, we distinguish ferrite (alpha-iron), which can at most dissolve 0.028 wt. % C at 738 °C, and austenite (gamma-iron), which can dissolve 2.08 wt. % C at 1154 °C. The much larger phase field of gamma-iron (austenite) compared with that of alpha-iron (ferrite) indicates clearly the considerably grater solubility of carbon in gamma-iron (austenite), the maximum value being 2.08 wt. % at 1154 °C. The hardening of carbon steels, as well as many alloy steels, is based on this difference in the solubility of carbon in alpha-iron (ferrite) and gamma-iron (austenite).

At the carbon-rich side of the metastable Fe-C phase diagram we find cementite (Fe_3C). Of less interest, except for highly alloyed steels, is the delta-ferrite at the highest temperatures.

The vast majority of steels rely on just two allotropes of iron

(1) **Alpha-iron**, which is body-centered cubic (BCC) ferrite, and

(2) **Gamma-iron**, which is face-centered cubic (FCC) austenite. At ambient pressure, BCC ferrite is stable from all temperatures up to 912 °C (the A_3 point), when it transforms into FCC austenite. It reverts to ferrite at 1394 °C (the A_4 point). This high-temperature ferrite is labeled

(3) **Delta-iron**, even though its crystal structure is identical to that of alpha-ferrite. The delta-ferrite remains stable until it melts at 1538 °C.

Regions with mixtures of two phases (such as ferrite + cementite, austenite + cementite, and ferrite + austenite) are found between the single-phase fields. At the highest temperatures, the liquid phase field can be found, and below this are the two-phase fields (liquid + austenite, liquid + cementite, and liquid + delta-ferrite). In heat treating of steels, the liquid phase is always avoided.

The steel portion of the Fe-C phase diagram covers the range between 0 and 2.08 wt. % C. The cast iron portion of the Fe-C phase diagram covers the range between 2.08 and 6.67 wt. % C.

The steel portion of the Fe-C phase diagram can be subdivided into three regions: hypoeutectoid ($0 <$ wt. % C < 0.68 wt. %), eutectoid (C = 0.68 wt. %), and hypereutectoid ($0.68 <$ wt. % C < 2.08 wt. %).

A very important phase change in the metastable Fe-C phase diagram occurs at 0.68 wt. % C. The transformation is eutectoid, and its product is called pearlite (ferrite + cementite):

gamma-iron (austenite) —> alpha-iron (ferrite) + Fe_3C (cementite).

Some important boundaries at single-phase fields have been given special names. These include:

A_1 — The so-called eutectoid temperature, which is the minimum temperature for austenite.

A_3 — The lower-temperature boundary of the austenite region at low carbon contents; i.e., the gamma / gamma + ferrite boundary.

A_{cm} — The counterpart boundary for high-carbon contents; i.e., the gamma / gamma + Fe_3C boundary. Sometimes the letters **c**, **e**, or **r** are included:

Ac_{cm} — In hypereutectoid steel, the temperature at which the solution of cementite in austenite is completed during heating.

Ac_1 — The temperature at which austenite begins to form during heating, with the **c** being derived from the French *chauffant*.

Ac_3 — The temperature at which transformation of ferrite to austenite is completed during heating.

Ae_{cm}, Ae_1, Ae_3 — The temperatures of phase changes at equilibrium.

Ar_{cm} — In hypereutectoid steel, the temperature at which precipitation of cementite starts during cooling, with the **r** being derived from the French *refroidissant*.

Ar_1 — The temperature at which transformation of austenite to ferrite or to ferrite plus cementite is completed during cooling.

Ar_3 — The temperature at which austenite begins to transform to ferrite during cooling.

Ar_4 — The temperature at which delta-ferrite transforms to austenite during cooling.

If alloying elements are added to an iron-carbon alloy (steel), the position of the A_1, A_3, and A_{cm} boundaries, as well as the eutectoid composition, are changed. In general, the austenite-stabilizing elements (e.g., nickel, manganese, nitrogen, copper, etc) decrease the A_1 temperature, whereas the ferrite-stabilizing elements (e.g., chromium, silicon, aluminum, titanium, vanadium, niobium, molybdenum, tungsten, etc) increase the A_1 temperature.

The carbon content at which the minimum austenite temperature is attained is called the eutectoid carbon content (0.68 wt. % C in case of the metastable Fe-C phase diagram). The ferrite-cementite phase mixture of this composition formed during slow cooling has a characteristic appearance and is called pearlite and can be treated as a microstructural entity or microconstituent. It is an aggregate of alternating ferrite and cementite lamellae that coarsens (or "spheroidizes") into cementite particles dispersed within a ferrite matrix after extended holding at a temperature close to A_1.

Finally, we have the martensite start temperature, M_s, and the martensite finish temperature, M_f:

M_s — The highest temperature at which transformation of austenite to martensite starts during rapid cooling.

M_f — The temperature at which martensite formation finishes during rapid cooling.

UNIT III COMPOSITES AND ADHESIVES

Composites consist of:

1) Combination of two or more materials – Composite = matrix + fiber (filler):

    Matrix:

    (i) material component that surrounds the fiber.
    (ii) Usually **a ductile, or tough, material w/ low density**
    (iii) **Strength usually = 1/10 (or less) than that of fiber**
    (iv) Examples include: thermoplastic or thermoset
        a. Thermoset most common (epoxy, pheneolic)
    (v) Serves to hold the fiber (filler) in a favorable orientation.

    Fiber aka reinforcing material aka Filler:

    (vi) **Materials that are strong with low densities**
    (vii) Examples include glass, carbon or particles.

2) Designed to display a combination of the best characteristics of each material i.e. fiberglass acquires strength from glass and flexibility from the polymer.
3) Matrix and filler bonded together (adhesive) or mechanically locked together!

Where are composites used??????

CFRP – carbon fiber reinforced composite.

GFRP – glass fiber reinforced composite

Advantages:

a) High strength to weight ratio (low density high tensile strength) or high specific strength ratio!
  i) 1020 HRS spec strength = 1 (E6 in)
  ii) Graphite/Epoxy, spec strength = 5 (E6 in)
b) High creep resistance
c) High tensile strength at elevated temperatures
d) High toughness
e) Generally perform better than steel or aluminum in applications where cyclic loads are encountered leading to potential fatigue failure (i.e. helicopter blades).
f) Impact loads or vibration – composites can be specially formulated with high toughness and high damping to reduce these load inputs.
g) Some composites can have much higher wear resistance than metals.
h) Corrosion resistance

- i) Dimensional changes due to temp changes can be much less.
- j) Anisotropic – bi-directional properties can be design advantage (i.e. helicopter blades)

Disadvantages (or limitations):

- a) Material costs
- b) Fabrication/ manufacturing difficulties
- c) Repair can be difficult
- d) Wider range of variability (statistical spread)
- e) Operating temperature can be an issue for polymeric matrix (i.e. 500 F). Less an issue for metal matrix (2,700 F).
- f) Properties non-isotropic makes design difficult!
  - i) Example – video test in line w/ fibers 10X stronger vs fibers oriented at an angle.
- g) Inspection and testing typically more complex.

Classification of Composite Materials by Matrix:

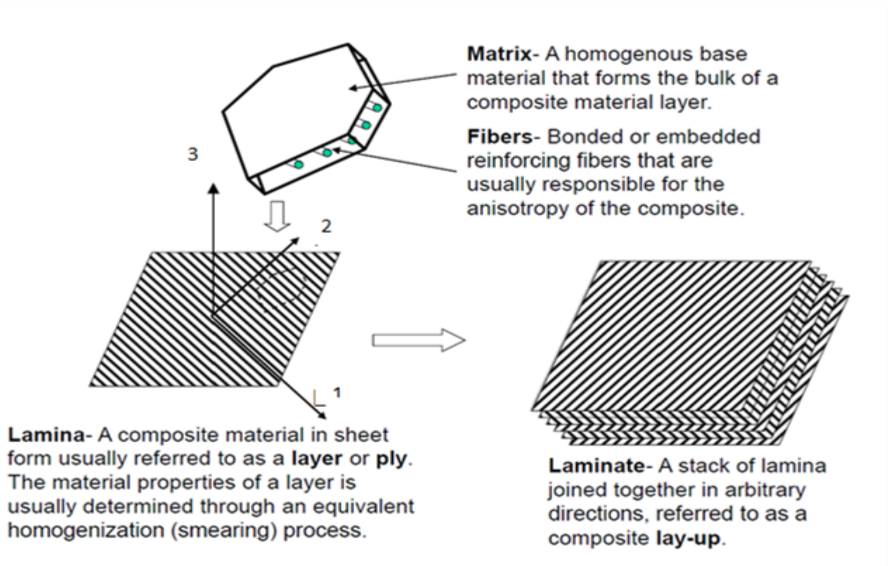
1. Metal matrix
2. Ceramic matrix
3. Polymer (Resin) matrix

Most common – also called fiber reinforced polymer

Classification of Composite Materials by Matrix:

1) Polymer matrix composites or Fiber Reinforced Polymer (FRP)
   - a) Fibers generally glass, carbon or kevlar
   - b) Matric can be:
     - i) Thermoplastics: PE, Nylon, PS, PP, PC, PVC
     - ii) Thermosets: Epoxy, polyester, phenolics
   - c) Have high strength and stiffness to weight ratio
   - d) Aerospace, sporting goods marine
   - e) Examples: GFRP aka fiberglass (polyester or epoxy and glass), CFRP (polyester or epoxy and carbon), KFRP (polyester or epoxy and Keflar)

Layered Composites



Ranking of Most Common Fibers for FRP

Property	Glass	Carbon	Kevlar
Strength	Worst	In - between	Best
Stiffness	Worst	Best	In – between
Cost	Best	Worst	In – between
Weight	Worst	Best	In-between

Classification of Composite Materials by Matrix:

Metal matrix composites (MMC):

a) Metal matrix: Al, Ti, Mg, Fe, Cu, Ni

b) Example: Al-SiC (silicon carbide)

c) Example: Al-Al_2O_3 (aluminum oxide)

High strength, high stiffness, abrasion resistance, dimensional stability, high temperature and toughness.

Ceramic matrix composites (CMC):

a) Silicon carbide-silicon carbide (SiC-SiC)

b) Same material both matrix and filler BUT filler different form such as whickers, chopped fibers or strands to achieve preferred properties.

The strength of the composite depends primarily on the amount, arrangement and type of fiber (or particle) reinforcement in the resin.

Typically, the higher the reinforcement content, the greater the strength. In some cases, glass fibers are combined with other fibers, such as carbon or aramid (Kevlar29 and Kevlar49), to create a "hybrid" composite that combines the properties of more than one reinforcing material.

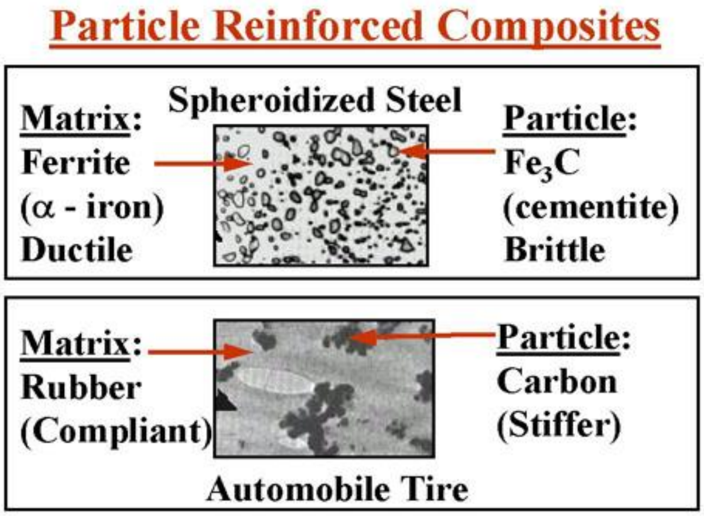
Classification of Composite by Filler Type:

- Particle-reinforced composites
- Fiber-reinforced composites
- Structural composites

Particle Reinforced Composites:

1) Particles used for reinforcing include:
    a) ceramics and glasses such as small mineral particles,
    b) metal particles such as aluminum,
    c) and amorphous materials, including polymers and carbon black.
2) Particles are used to increase the modulus of the matrix, to decrease the permeability of the matrix, or to decrease the ductility of the matrix.
3) Particle reinforced composites support higher tensile, compressive and shear stresses
4) Particles are also used to produce inexpensive composites.
5) Examples:
    a) automobile tire which has carbon black particles in a matrix of elastomeric polymer.
    b) spheroidized steel where cementite is transformed into a spherical shape which improves the machinability of the material.
    c) concrete where the aggregtes (sand and gravel) are the particles and cement is the matrix.

Figure Examples for particle-reinforced composites. (Spheroidized steel and automobile tire)



Fiber-reinforced Composites:

1) Reinforcing fibers can be made of metals, ceramics, glasses, or polymers that have been turned into graphite and known as carbon fibers. Fibers increase the modulus of the matrix material. The strong covalent bonds along the fiber's length gives them a very high modulus in this direction because to break or extend the fiber the bonds must also be broken or moved. Fibers are difficult to process into composites which makes fiber-reinforced composites relatively expensive. Fiber-reinforced composites are used in some of the most advanced, and therefore most expensive, sports equipment, such as a time-trial racing bicycle frame which consists of carbon fibers in a thermoset polymer matrix. Body parts of race cars and some automobiles are composites made of glass fibers (or fiberglass) in a thermoset matrix.
2) The arrangement or orientation of the fibers relative to one another, the fiber concentration, and the distribution all have a significant influence on the strength and other properties of fiber-reinforced composites. Applications involving totally multidirectional applied stresses normally use discontinuous fibers, which are randomly oriented in the matrix material. Consideration of orientation and fiber length for a particular composites depends on the level and nature of the applied stress as well as fabrication cost. Production rates for short-fiber composites (both aligned and randomly oriented) are rapid, and intricate shapes can be formed which are not possible with continuous fiber reinforcement.

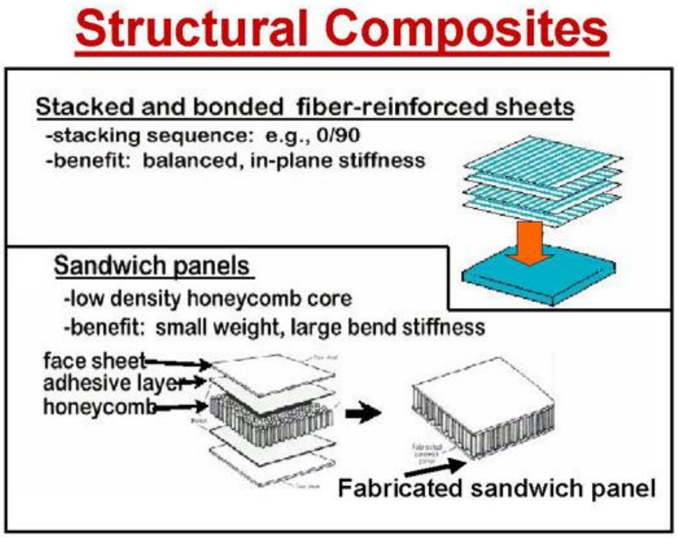
Structural Composites:

1) The properties of structural composites depend on:
   a) Constituents

b) Geometrical design

Common structural composite types are:

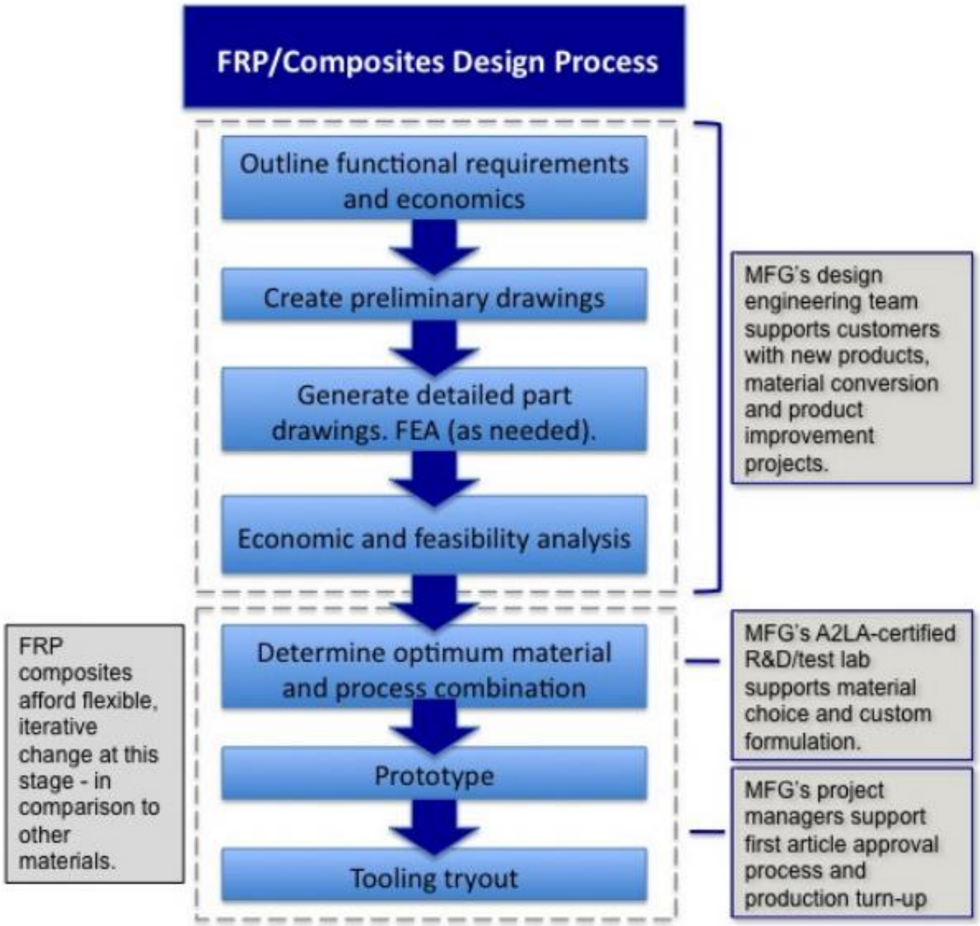
Sandwich Panels: Consist of two strong outer sheets which are called face sheets and may be made of aluminum alloys, fiber reinforced plastics, titanium alloys, steel. Face sheets carry most of the loading and stresses. Core may be a honeycomb structure which has less density than the face sheets and resists perpendicular stresses and provides shear rigidity. Sandwich panels can be used in variety of applications which include roofs, floors, walls of buildings and in aircraft, for wings, fuselage and tailplane skins.



Structural Composites

Stacked and bonded fiber-reinforced sheets
-stacking sequence: e.g., 0/90
-benefit: balanced, in-plane stiffness

Sandwich panels
-low density honeycomb core
-benefit: small weight, large bend stiffness


FRP/Composites Design Process
Outline functional requirements and economics
Create preliminary drawings
Generate detailed part drawings. FEA (as needed).
Economic and feasibility analysis
Determine optimum material and process combination
Prototype
Tooling tryout
MFG's design engineering team supports customers with new products, material conversion and product improvement projects.
MFG's A2LA-certified R&D/test lab supports material choice and custom formulation.
MFG's project managers support first article approval process and production turn-up
FRP composites afford flexible, iterative change at this stage - in comparison to other materials.

UNIT IV BIOMATERIALS

Biomaterials

Biomaterials are used to make devices to replace a part or a function of the body in safe, reliably economically, and physiologically acceptable manner. A variety of devices and materials are used in the treatment of disease or injury. Commonplace examples include suture needles, plates, teeth fillings, etc.

Biomaterial: A synthetic material used to make devices to replace part of a living system or to function in intimate contact with living tissue.

Biological Material: A material that is produced by a biological system.

Bio-compatibility: Acceptance of an artificial implant by the surrounding tissues and by the body as a whole.

1) Polymeric biomaterials
2) Bioceramics
3) Metallic biomaterials
4) Biocomposite
5) Biologically based (derived) biomaterials

Polymerization

a) Condensation: A reaction occurs between two molecules to form a larger molecule with the elimination of a smaller molecule.
b) Addition: A reaction occurs between two molecules to form a larger molecule without the elimination of a smaller molecule.

Bioceramics

1) Alumina
2) Zirconia (partially stabilized)
3) Silicate glass
4) Calcium phosphate (apatite)
5) Calcium carbonate

Metallic biomaterials

1) Stainless steel (316L)
2) Co-Cr alloys
3) Ti_6Al_4V

4) Au-Ag-Cu-Pd alloys
5) Amalgam (AgSnCuZnHg)
6) Ni-Ti
7) Titanium

Surface modification (treatment)

Physical and mechanical treatment

Chemical treatment

Biological treatment

Surface Properties of Materials

1) Contact angle (Hydrophilic & Hydrophobic)
2) ESCA & SIMS (surface chemical analysis)
3) SEM (Surface morphology)

Deterioration of Biomaterials

1) Corrossion
2) Degradation
3) Calcification
4) Mechanical loading
5) Combined

General Criteria for materials selection

1) Mechanical and chemicals properties
2) No undersirable biological effects
   a) carcinogenic, toxic, allergenic or immunogenic
3) Possible to process, fabricate and sterilize with a godd reproducibility
4) Acceptable cost/benefit ratio

Cell/tissue reaction to implant

1) Soft tissue
2) Hard tissue
3) Blood cells

METALLIC IMPLANT MATERIALS

1) Stainless steel
2) Cobalt-chromium alloys

3) Titanium alloys

a) Must be corrosion resistant
b) Good fatigue properties
c) Other compatible issues

Metallic implants are used for two primary purposes.

To replace a portion of the body such as joints, long bones and skull plates.

Fixation devices are used to stabilize broken bones

a) less chromium content should be utilized (because Cr is a highly reactive metal)
b) Make use of austenite type steel (less magnetic properties)
c) Lowered carbon content
d) Inclusion of molybdenum helps corrosion resistance
e) Electroplating technique (increases corrosion resistance)

COBALT CHROMIUM ALLOYS

Cobalt based alloys are used in one of three forms

a) Cast; as prepared
b) Wrought (fine structure with low carbon contents ; pure forms)
c) Forged

Cobalt based alloys are better than stainless steel devices because of low corrosion resistance

Polymers

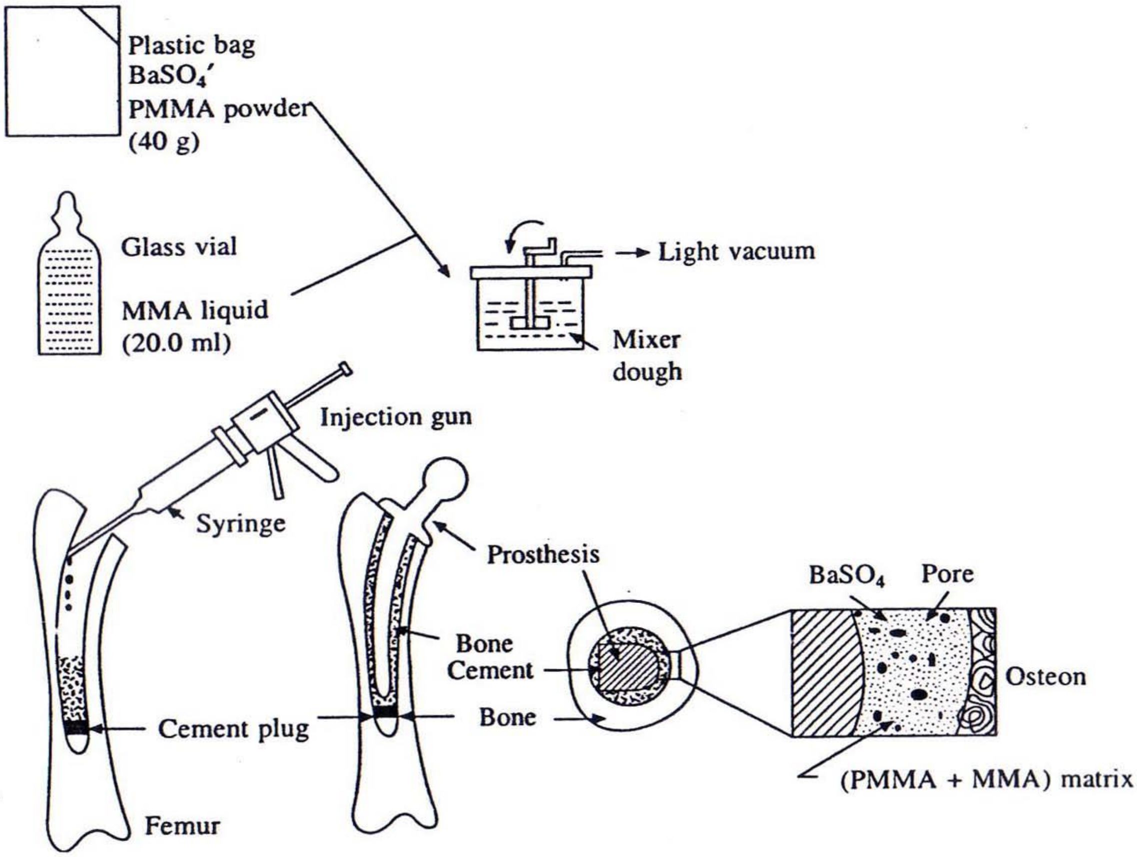
Polyethylene and Polypropylene

a) Suture materials of monofilament polypropylene (Prolene are used clinically.
b) Compared with metal wire, catgut, silk, and polyglycolic acid sutures, propylene product exhibits least fibroblastic response and silk the most in the nerve tissues of rabbits.

ACRYLIC RESINS

a) Simple acrylates have relatively high toughness and strength.
b) The most widely used polyacrylate is poly(methyl methacrylate,PMMA).
c) The features of acrylic polymers are brittle in comparison with other polymers
d) excellent light transparency
e) high index of refraction.

BONE CEMENT MIXING AND INJECTION



HYDROGELS

a) Hydrogels find their name from their affinity for water and incorporation of water into their structure.

b) The concentration of water in the hydrogel can affect the interfacial free energy of the hydrogel,as well as the biocompatibility.

c) Hydrogels have inherently weak mechanical properties.

d) Hence for some applications they are often attached to tougher materials such as silicone rubber, polyurethane or PMMA.

POLYAMIDES

a) Since the hydrogen bonds play a major role in determining properties, the number and distribution of amide bonds are important factors.

b) Nylon tubes find applications in catheters.

c) The coated nylon sutures find wide biomedical applications.

d) Nylon is also utilized fabrication of hypodermic syringes

Soft Tissue Implants

a) Attempts have been made to replace or augment most of the soft tissues in the body
   a) Connective tissues: skin, ligament, tendon, cartilage
   b) Vascular tissue: blood vessels, heart valves
   c) Organs: heart, pancreas, kidney
   d) Other: eye, ear, breast

b) Most soft tissue implants are constructed from synthetic polymers
   a) Possible to choose and control the physical and mechanical properties
   b) Flexibility in manufacturing

c) "Soft tissue implants" can also be designed for soft tissue repair

Sutures

a) Used to repair incisions and lacerations
b) **Important characteristics for sutures::**
c) Tensile strength
d) Flexibility
e) Non-irritating

Tissue Adhesives

a) Used for repair of fragile, non-suturable tissues
   a) Examples: Liver, kidney, lung

b) The bond strength for adhesive closed tissues is not as strong after 14 days as for suture closed tissues

Percutaneous Implants

a) Refers to implants that cross the skin barrier
   a) In contact with both the outside environment and the biological environment

b) Used for connection of the vascular system to external "organs"
   a) Dialysis
   b) Artifical heart
   c) Cardiac bypass

c) Also used for long term delivery of medication or nutrition (IV)

d) Main Problems:
   a) Attachment of skin (dermis) to implant difficult to maintain through ingrowth due to rapid turnover of cells

  b) Implant can be extruded or invaginated due to growth of skin around the implant
  c) Openings can also allow for the entrance of bacteria, which may lead to infection

Artifical Skin

a) Is actually a percutaneous implant -- contacts both external and biological environments
b) No current materials available for permanent skin replacement
c) Design ideas:
  a) Graft should be flexible enough to conform to wound bed and move with body
  b) Should not be so fluid-permeable as to allow the underlying tissue to become dehydrated but should not retain so much moisture that edema (fluid accumulation) develops under the graft
d) Polymeric or collagen-based membrane
  a) Some are too brittle and toxic for use in burn victims
  b) Flexibility, moisture flux rate, and porosity can be controlled
e) Fabrics and sponges designed to promote tissue ingrowth
  a) Have not been successful
f) Immersion of patients in fluid bath or silicone fluid to prevent early fluid loss, minimize breakdown of remaining skin, and reduce pain
g) Culturing cells *in vitro* and using these to create a living skin graft
  a) Does not require removal of significant portions of skin

Maxillofacial implants

a) Designed to replace or enhance hard or soft tissue in the jaw and face
b) Intraoral prosthetics (implanted) are used to reconstruct areas that are missing or defective due to surgical intervention, trauma, or congenital condition
c) Must meet all biocompatibility requirements
d) Metals such as tantalum, titanium, and Co-Cr alloys can be used to replace bony defects
e) Polymers are generally used for soft tissue augmentation
  a) Gums, chin, cheeks, lips, etc.
f) Injectable silicone had been examined for use in correcting facial deformities; however, it has been found to cause severe tissue reactions in some patients and can migrate
g) Extraoral prosthetics (external attachment) should:
  a) Match the patients skin in color and texture
  b) Be chemically and mechanically stable

  c) Not creep, change colors, or irritate skin
  d) Be easily fabricated
h) Have been fabricated out of numerous polymers

Biomaterials for organ replacement

Artificial limb

An artificial limb is a type of prosthesis that replaces a missing extremity, such as arms or legs. The type of artificial limb used is determined largely by the extent of an amputation or loss and location of the missing extremity. Artificial limbs may be needed for a variety of reasons, including disease, accidents, and congenital defects.

Design challenges of heart valve prostheses

a) A replaceable model of Cardiac Biological Valve Prosthesis.
b) Thrombogenesis / haemocompatibility
  a) Mechanisms:
    i) Forward and backward flow shear
    ii) Static leakage shear
    iii) Presence of foreign material (i.e. intrinsic coagulation cascade)
    iv) Cellular maceration
c) Valve-tissue interaction
d) Wear
e) Blockage
f) Getting stuck
g) Dynamic responsiveness
h) Failure safety
i) Valve orifice to anatomical orifice ratio
j) Trans-valvular pressure gradient
k) Minimal leakages
l) Replaceable Models of Biological Valves

Lower Limb Prosthesis

a) Components of the Prosthesis

b) Socket- Forms the connection between the residual limb and the prosthesis.

c) Sleeve- Provides suction suspension for prosthesis.

d) Shank (pylon)- Transfers weight from socket to the foot-ankle.

e) Foot-ankle- Absorbs shock and impact and provides stability.

Dental implant

A dental implant is an artificial tooth root replacement and is used in prosthetic dentistry to support restorations that resemble a tooth or group of teeth. There are several types of dental implants. The major classifications are divided into osseointegrated implant and the fibrointegrated implant. Earlier implants, such as the subperiosteal implant and the blade implant were usually fibrointegrated

Biosensors

a) Promising approach to medical diagnostics by patients or in doctors offices
b) Other important applications: pathogens, disease biomarkers, DNA, peroxide, etc.
c) Method of choice for blood glucose in diabetics
d) Rapid diagnostics may lead to more timely and effective treatment

UNIT V MODERN ENGINEERING MATERIALS

Shape Memory Alloys

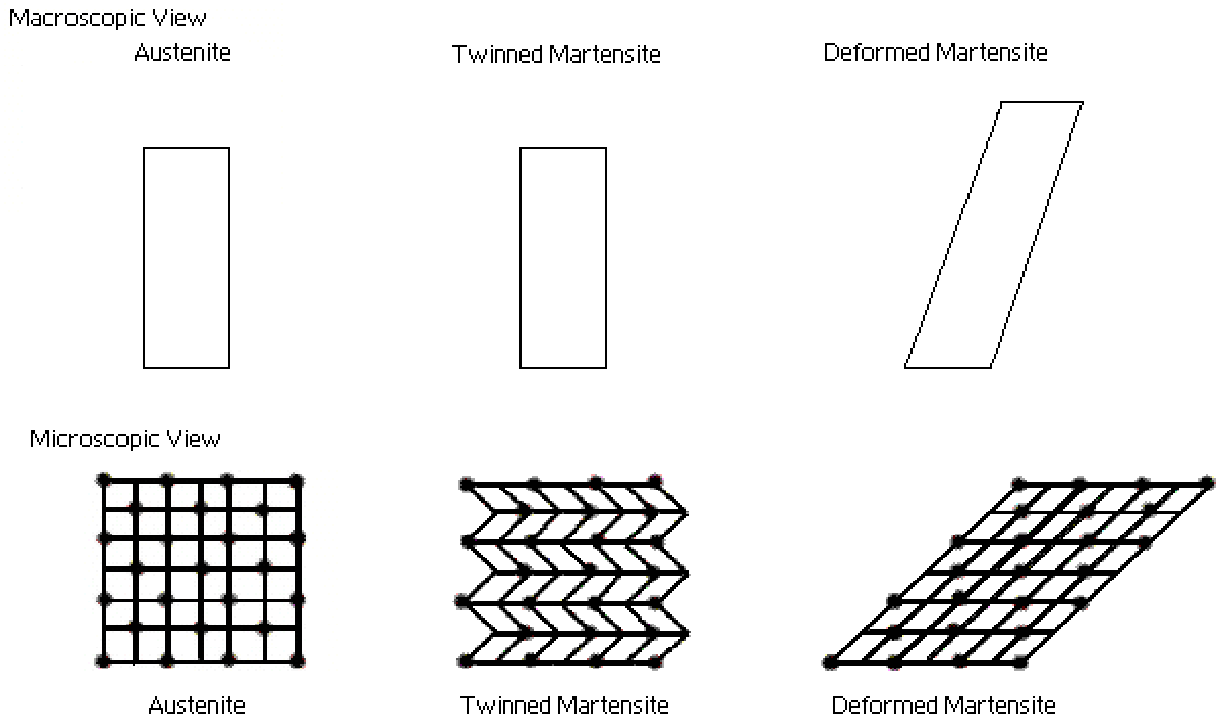
Two Phases

a) Austenite
    a) Hard, firm
    b) Inelastic
    c) Resembles titanium
    d) Simple FCC structure
b) Martensite
    a) Soft
    b) Elastic
    c) Complex structure

Shape Memory Alloy Qualities

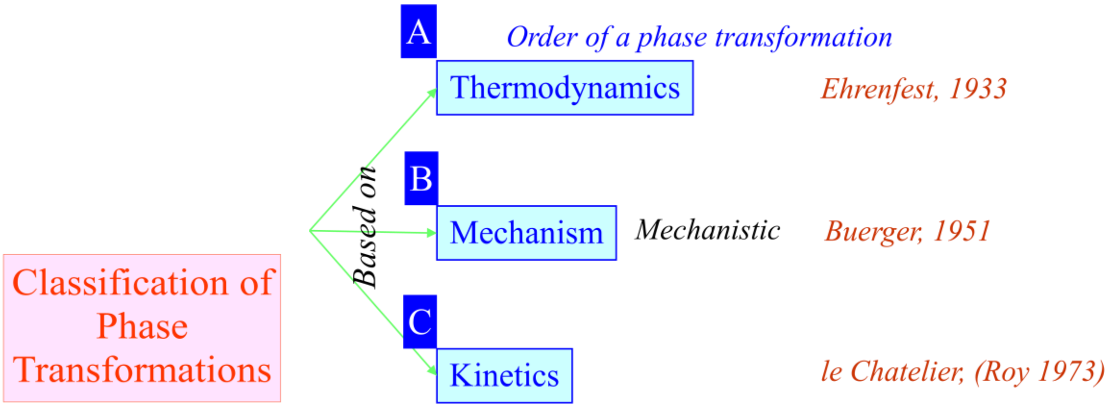
a) Ability to “remember” its austenite phase
    a) As the metal is cooled to the martensite phase, it can be easily deformed. When the temperature is raised to the austenite phase, it reforms to the original shape of the material.
b) Pseudoelasticity
    a) When the metal is changed to the martensite phase simply by strain. The metal becomes pliable and can withstand strains of up to 8%.
c) A mix of roughly 50% nickel and 50% titanium is the most common SMA. Also CuZnAl and CuAlNi are widely used.

Shape Memory



Biological Applications

a) Bone Plates
   a) Memory effect pulls bones together to promote healing.
b) Surgical Anchor
   a) As healing progresses, muscles grow around the wire. This prevents tissue damage that could be caused by staples or screws.
c) Clot Filter
   a) Does not interfere with MRI from non-ferromagnetic properties.
d) Catheters
e) Retainers
f) Eyeglasses



Magnetic Shape Memory Alloys

Shape Memory Alloys

-General Description of how they work

-Twinning

Combinatorial Approach

-Cantilever Fabrication

-Deposition

-Rapid Analysis

Magnetic Shape Memory Alloys

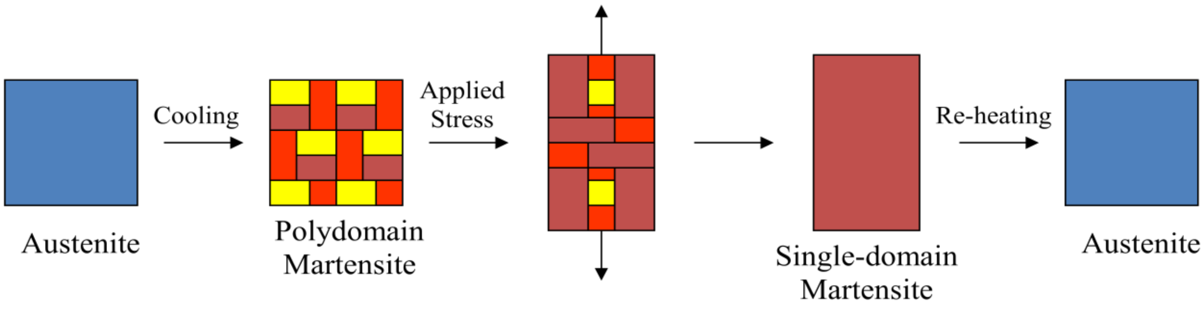
-Similar functionality to SMA

-Magnetostriction

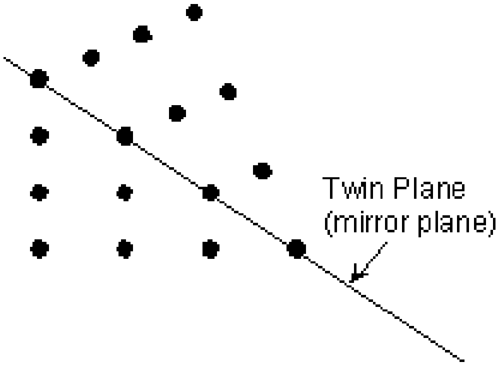
-Applications and downfalls

Shape Memory Alloys (NiTi, NiMnGa) are used in switches, actuators, airplane components, and other applications.

-Austenite-Martensite Transformation



Twinning- Formation of symmetrical, inter-grown crystals



Magnetic Shape Memory Alloys: What are they?

-An alloy that demonstrates the Austenite to Martensite phase transformation (Shape Memory Effect)

-An alloy that is ferromagnetic (possibly a need for Iron, Cobalt, or Nickel in the alloy)

-The most well known “MSMA” is NiMnGa

-Nickel Manganese Gallium has an L_{21} crystal structure

Magnetostriction

Definition: Spontaneous deformation of a solid in response to its magnetization (James and Wuttig)

-Discovered in 1842 by James Joule while experimenting with nickel (a ferromagnetic material)

-examples: Terfenol-D, Alloys including Iron, Cobalt, or Nickel, PZT, etc…

-If martensitic material is ferromagnetic there is a possibility that application of a magnetic field will rearrange the martensite variants! This results in strains one order of magnitude or higher than that of Giant Magnetostrictive materials.

-Switches and Actuators that are both more responsive and more cost-efficient.

-Microwrapper – used for controlling micro-organisms and even tumor removal in the medical industry

-Metal MSMA more responsive and less brittle than Terfenol-D

-MSMA’s exist due to their ferromagnetic and phase transformation characteristics

-Metal Alloys such as NiMnGa exhibit strains on the order of 6% as compared to the .2% exhibited by Terfenol-D

-Actuation by application of a magnetic field is inexpensive, very sensitive, and requires less time than the heating required for general SMA’s

-Very few MSMA’s well known at this point paving the way for Combinatorial Discovery

Actuator and Sensor Materials Chromic materials

This group of materials refers to those which change their colour in response to a change in their environment, leading to the suffix chromic. A variety of chromic materials exist and they are described in terms of the stimuli which initiate a change, thus:

Thermochromic materials change with temperature;

Photochromic materials change with the light level;

Piezochromic materials change with applied pressure;

In the case of electrochromic, solvatechromic and carsolchromic materials the stimulus is either an electrical potential, a liquid or an electron beam respectively.

Thermochromic, photochromic and piezochromic materials are the most popular with the first two groups finding everyday applications. How do thermochromic materials work? There are two types of thermochromic systems: those based on liquid crystals and those which rely on molecular.

Electrorheological fluids

The rheology of electrorheological fluids With electrorheological fluids' rheology, the electric field must be taken into the calculations. For example, with the shear stress from Equation (2), the force needed to separate the particles from each other, when an electric field is present, can be calculated through the polarization contribution. The shear resistance of an ER fluid reflects the combined action of polarization and viscous forces, giving for the flow stress

$$\tau\tau\ \eta = +\ \gamma \bullet\ E\ s = \tau\ \tau\ E\ V\ +$$

where τ E is the polarization contribution, called the Bingham yield strength, ηs is the dynamic viscosity of the suspension at zero electric field and γ is the shear strain rate [32]. Bingham materials are plastic masses that have a flow index. For Bingham plastic fluids, the Newtonian model is:

$$\tau\tau\ \eta = + \cdot\ V\ du\ dy\ ,\ \text{if}\ \tau\ \tau > y$$

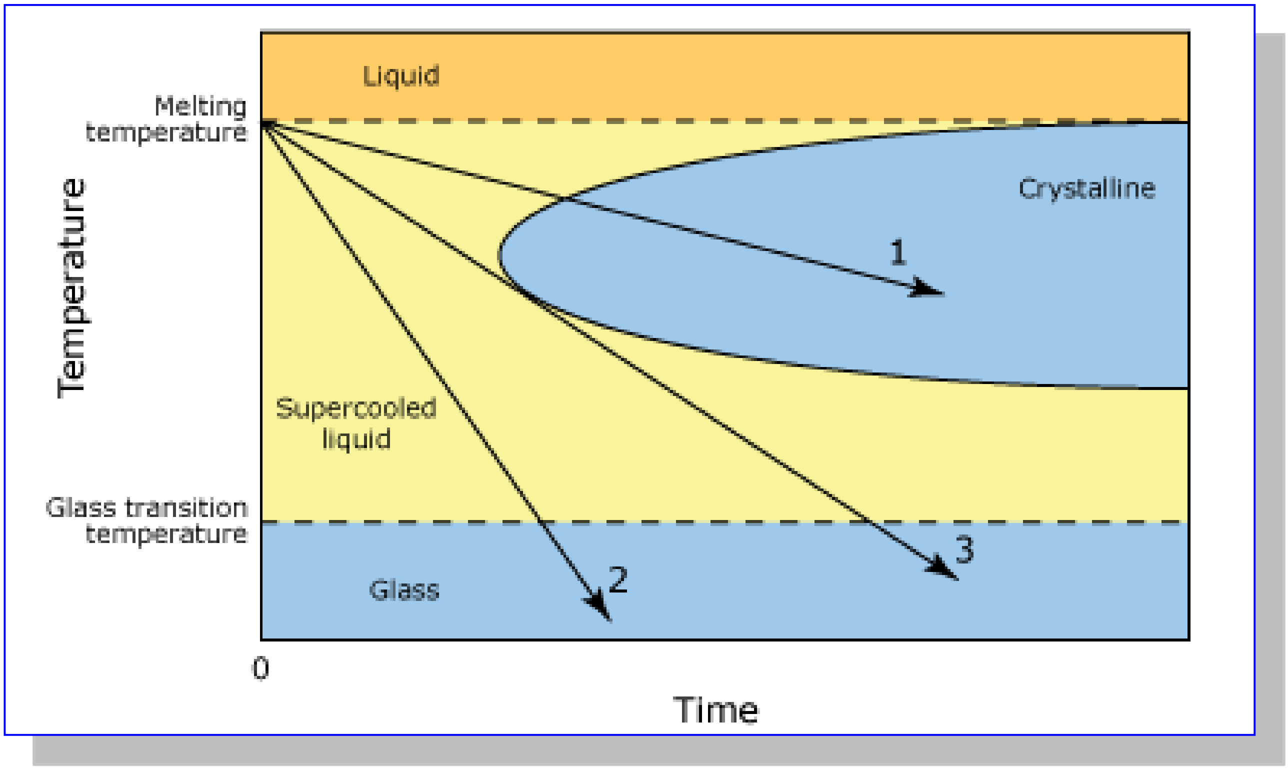
where τ y is the limiting yield stress and du/dy is the shear rate's speed gradient. Over this index their rheological behaviour is Newtonian and under it nonNewtonian. Equation (1) expresses the plastic flow of a Bingham material. It can be developed to give the following equation for the relative viscosity ηηr s of an ER fluid in terms of the Mason number (Mn), which indicates the relation between viscous force and polarization force.

PROCESSING OF METALLIC GLASSES

Virtually any liquid can be turned into a glass if it is cooled quickly enough to avoid crystallization. The question is, how fast does the cooling need to be?

Common oxide glasses (such as ordinary window glass) are quite resistant to crystallization, so they can be formed even if the liquid is cooled very slowly. For instance, the mirror for the 200" telescope at the Palomar Observatory weighed 20 tons and was cooled over a period of eight months, but did not crystallize.

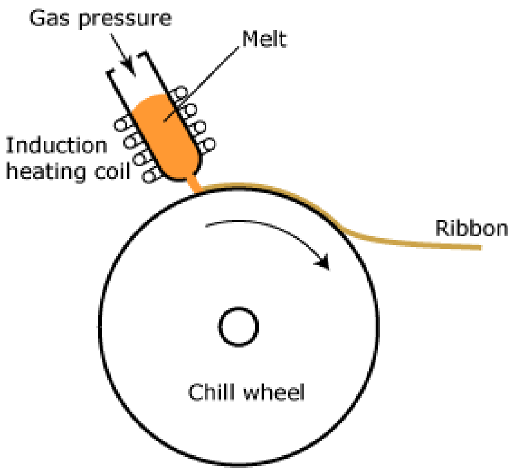
Many polymer liquids can also be turned into glasses; in fact, many polymers cannot be crystallized at all. For both oxides and polymers, the key to glass formation is that the liquid structure cannot be rearranged to the more ordered crystalline structure in the time available.



Metallic glasses are another story. Because the structural units are individual atoms (as opposed to polymer chains or the network structure of an oxide), in most alloys it is relatively easy for crystals to nucleate and grow. As a result, the earliest metallic glasses (which were discovered at Caltech in the late1950s) required very rapid cooling - around one million degrees Celsius per second - to avoid crystallization. One way to do it is by single-roller melt spinning, as shown here:

SINGLE-ROLLER MELT SPINNING

In this process, the alloy is melted (typically in a quartz tube) by induction heating, and then forced out through a narrow nozzle onto the edge of a rapidly rotating chill wheel (typically made of copper). The melt spreads to form a thin ribbon, which cools rapidly because it is in contact with the copper wheel.



SUCTION CASTING

An ingot in the upper chamber under an inert atmosphere is melted with an electric arc (much like in arc welding) and then sucked into a mold when the lower chamber is opened to vacuum. One of the potentially useful properties of metallic glasses is that they do not melt abruptly at a fixed temperature. Instead, like ordinary oxide glasses, they gradually soften and flow over a range of temperatures. By careful control of temperature, the viscosity of the softened glass can be precisely controlled. This ability can be used to form metallic glasses into complex shapes by techniques similar to those used for molding polymers.