

INTRODUCTION TO PHYSICAL METALLURGY AND ENGINEERING MATERIALS

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Syllabus

MODULE-I

Classification of Engineering Materials, Engineering properties of materials. Characteristic property of metals, bonding in solids, primary bonds like ionic, covalent, and metallic bond, crystal systems, common crystal structure of metals, representations of planes and directions in crystals, atomic packing in crystals, calculation of packing density, voids in common crystal structures and imperfections crystals.

MODULE-II

Concept of plastic deformation of metals, critical resolve shear stress, dislocation theory, deformation by slip and twin, plastic deformation in polycrystalline metals, yield point phenomenon and related effects, concept of cold working preferred orientation. Annealing ; recovery; recrystallization and grain growth; hot working.

Concept of alloy formation, types of alloys, solid solutions, factors governing solids solubility viz. size factor, valency factor, crystal structure factor and chemical affinity factor; order-disorder transformation.

MODULE-III

Binary phase diagrams (a) Isomorphism system, (b) Eutectic system, (c) Peritectic system, (d) Eutectoid system and (e) Peritectoid system. Allotropic transformation. Lever rule and its application, Interpretation of solidification behaviors and microstructure of different alloys belonging to those systems, Effect of non-equilibrium cooling, coring, and homogenization.

MODULE-IV

Iron-cementite and iron-graphite phase diagrams, microstructure and properties of different alloys (alloy steels; stainless steel, tool steel, HSS, high strength low alloy steel) types of cast iron, their microstructures and typical uses. Specification of steel.

T.T.T. diagram: concept of heat treatment of steels i.e. annealing, normalizing, hardening and tempering; microstructural effects brought about by these processes and their influences on mechanical properties; factor affecting hardenability.

MODULE-V

Optical properties of Materials: Scattering, Refraction, Theory of Refraction and absorption, Atomic Theory of optical properties. Lasers, Optical fibres- Principle, structure, application of optical fibres.

Plastic:- Thermosetting and thermoplastics.

Ceramics: Types, structure, Mechanical properties, application

Composite Materials: Agglomerated Materials: Cermets. Reinforced Materials: Reinforced Concrete. Fiber-reinforced plastics, Properties of composites, Metal matrix composites, manufacturing procedure for fiber reinforced composite.

LESSON PLAN

- Lesson 1:** Introduction to Engineering Materials
- Lesson 2:** Discuss the classification of engineering materials and their properties.
- Lesson 3:** Metals, alloys, ceramics, polymers, semiconductors, composites.
- Lesson 4:** Atomic Structure and Bonds
- Lesson 5:** Explore atomic bonding, crystal systems, and common crystal structures of metals.
- Lesson 6:** Ionic, covalent, metallic bonds; crystallography.
- Lesson 7:** Imperfections in crystals.
- Lesson 8:** Plastic Deformation
- Lesson 9:** Dislocation Theory
- Lesson 10:** Understand the concept of plastic deformation
- Lesson 11:** Critical Resolved Shear Stress and Dislocation Theory.
- Lesson 12:** Slip, twinning
- Lesson 13:** Yield Point Phenomenon, cold working, annealing.
- Lesson 14:** Alloy Formation and Phase Diagrams
- Lesson 15:** Learn about alloy formation, types of alloys, and binary phase diagrams.
- Lesson 16:** Solid solutions, solubility factors, isomorphous system, eutectic system.
- Lesson 17:** Analyze phase diagrams and predict microstructures of different alloys.
- Lesson 18:** Heat Treatment of Steels
- Lesson 19:** Study the iron-cementite
- Lesson 20:** Iron-graphite phase diagrams and heat treatment processes.
- Lesson 21:** TTT diagrams & CCT diagrams
- Lesson 22:** Annealing, normalizing, hardening, tempering.
- Lesson 23:** Optical Properties and Advanced Materials
- Lesson 24:** Discuss the optical properties of materials
- Lesson 25:** Discuss the application of lasers and optical fibers.
- Lesson 26:** Scattering, refraction, absorption
- Lesson 27:** Lasers, optical fibers.
- Lesson 28:** Analyze light refraction and laser pointers to understand optical properties.
- Lesson 29:** Plastic: Thermosetting and thermoplastics
- Lesson 30:** Ceramics: Types, structure, Mechanical properties, application
- Lesson 31:** Composite Materials: Agglomerated Materials: Cermet.
- Lesson 32:** Reinforced Materials: Reinforced Concrete.
- Lesson 33:** Fiber-reinforced plastics, Properties of composites, Metal matrix composites,
- Lesson 34:** Manufacturing procedure for fiber-reinforced composite.

MODULE-I

Classification Of Engineering Materials, And Their Properties:

Material classification:

There are different ways of classifying materials. One way is to describe five groups or families (Table 1-1):

TABLE 1-1 ■ *Representative examples, applications, and properties for each category of materials*

	Examples of Applications	Properties
Metals and Alloys		
Copper	Electrical conductor wire	High electrical conductivity, good formability
Gray cast iron	Automobile engine blocks	Castable, machinable, vibration-damping
Alloy steels	Wrenches, automobile chassis	Significantly strengthened by heat treatment
Ceramics and Glasses		
SiO ₂ -Na ₂ O-CaO	Window glass	Optically transparent, thermally insulating
Al ₂ O ₃ , MgO, SiO ₂	Refractories (i.e., heat-resistant lining of furnaces) for containing molten metal	Thermally insulating, withstand high temperatures, relatively inert to molten metal
Barium titanate	Capacitors for microelectronics	High ability to store charge
Silica	Optical fibers for information technology	Refractive Index, low optical losses
Polymers		
Polyethylene	Food packaging	Easily formed into thin, flexible, airtight film
Epoxy	Encapsulation of integrated circuits	Electrically insulating and moisture-resistant
Phenolics	Adhesives for joining plies in plywood	Strong, moisture resistant
Semiconductors		
Silicon	Transistors and integrated circuits	Unique electrical behavior
GaAs	Optoelectronic systems	Converts electrical signals to light, lasers, laser diodes, etc.
Composites		
Graphite-epoxy	Aircraft components	High strength-to-weight ratio
Tungsten carbide-cobalt (WC-Co)	Carbide cutting tools for machining	High hardness, yet good shock resistance
Titanium-clad steel	Reactor vessels	Low cost and high strength of steel with the corrosion resistance of titanium

Engineering Materials are classified into mainly;

1. Metals and alloy
2. Ceramics materials
3. Polymers materials
4. Composite materials

Metals and Alloys:

Metals and alloys include steels, aluminum, magnesium, zinc, cast iron, titanium, copper, and nickel. An alloy is a metal that contains additions of one or more metals or non-metals. In general, metals have good electrical and thermal conductivity. Metals and alloys have relatively high strength, high stiffness, ductility or formability, and shock resistance. They are particularly useful for structural or load-bearing applications. Although pure metals are occasionally used, alloys provide improvement in a particular desirable property or permit better combinations of properties.

Ceramics materials:

Ceramics can be defined as inorganic crystalline materials. Beach sand and rocks are examples of naturally occurring ceramics. Advanced ceramics are materials made by refining naturally occurring ceramics and other special processes. Advanced ceramics are used in substrates that house computer chips, sensors and capacitors, wireless communications, inductors, and electrical insulation. Some ceramics are used as barrier coatings to protect metallic substrates in turbine engines. Ceramics are also used in such consumer products as paints, and tires, and for industrial applications such as the tiles for the space shuttle. Traditional ceramics are used to make bricks, tableware, toilets, bathroom sinks, refractories (heat-resistant material), and abrasives. In general, due to the presence of porosity (small holes), ceramics do not conduct heat well; they must be heated to very high temperatures before melting. Ceramics are strong and hard, but also very brittle. We normally prepare fine powders of ceramics and convert these into different shapes. New processing techniques make ceramics sufficiently resistant to fracture that they can be used in load-bearing applications, such as impellers in turbine engines. Ceramics have exceptional strength under compression.

Polymers:

Polymers are typically organic materials. They are produced using a process known as polymerization. Polymeric materials include rubber (elastomers) and many types of adhesives. Polymers typically are good electrical and thermal insulators although there are exceptions such as the semiconducting polymers. Although they have lower strength, polymers have a very good strength-to-weight ratio. They are typically not suitable for use at high temperatures. Many polymers have very good resistance to corrosive chemicals. Polymers have thousands of applications ranging from bulletproof vests, compact disks, ropes, and liquid crystal displays (LCDs) to clothes and coffee cups. Thermoplastic polymers, in which the long molecular chains are not rigidly connected, have good ductility and formability; thermosetting polymers are stronger but more brittle because the molecular chains are tightly linked (Figure 1). Polymers are used in many applications, including electronic devices. Thermoplastics are made by shaping their molten form. Thermosets are typically cast into molds. Plastics contain additives that enhance the properties of polymers.

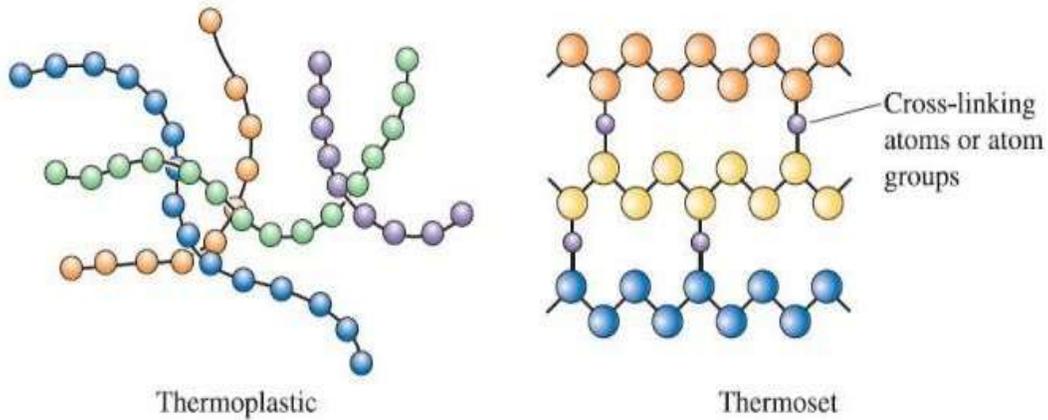


Figure. Polymerization occurs when small molecules, represented by the circles, combine to produce larger molecules or polymers. The polymer molecules can have a structure that consists of many chains that are entangled but not connected (thermoplastics)

Composite Materials:

The main idea in developing composites is to blend the properties of different materials. These are formed from two or more materials, producing properties not found in any single material. Concrete, plywood, and fiberglass are examples of composite materials. Fiberglass is made by dispersing glass fibers in a polymer matrix. The glass fibers make the polymer stiffer, without significantly increasing its density. With composites, we can produce lightweight, strong, ductile, temperature-resistant materials or we can produce hard, yet shock-resistant, cutting tools that would otherwise shatter. Advanced aircraft and aerospace vehicles rely heavily on composites such as carbon fiber-reinforced polymers (Figure 2). Sports equipment such as bicycles, golf clubs, tennis rackets, and the like also make use of different kinds of composite materials that are light and stiff.



Figure 1 The X-wing for advanced helicopters relies on a material composed of a carbon fiber reinforced polymer. (Courtesy of Sikorsky Aircraft Division – United Technologies Corporation).

Engineering Material properties:

So, what are these properties? Some, like density (mass per unit volume) and price (the cost per unit volume or weight), are familiar enough, but others are not, and getting them straight is essential. Think first of those that have to do with carrying load safely—the mechanical properties.

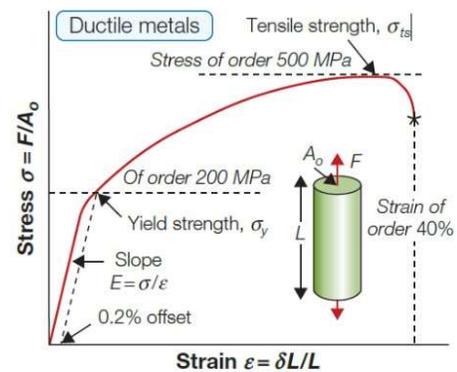
Mechanical properties

A steel ruler is easy to bend elastically ‘Elastic’ means that it springs back when released. Its elastic stiffness (here, resistance to bending) is set partly by its shape—thin strips are easy to bend—and partly by a property of the steel itself: their elastic moduli, E . Materials with high E , like steel, are intrinsically stiff; those with low E , like

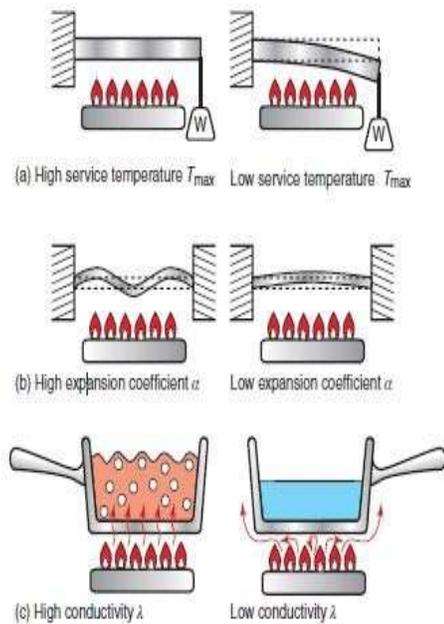
polyethylene, are not. The steel ruler bends elastically, but if it is a good one, it is hard to give it a permanent bend. Permanent deformation has to do with strength, not stiffness. The ease with which a ruler can be permanently bent depends, again, on its shape and a different property of the steel—its yield strength, σ_y . Materials with large σ_y , like titanium alloys, are hard to deform permanently even though their stiffness, coming from E , may not be high; those with low σ_y , like lead, can be deformed with ease.

When metals deform, they

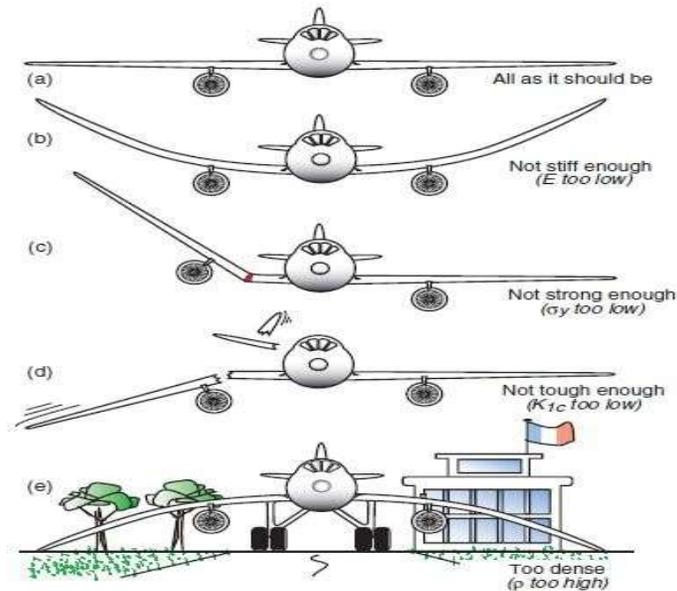
generally, get stronger (this is called ‘work hardening’), but there is an ultimate limit, called the tensile strength, σ_{ts} , beyond which the material fails (the amount it stretches before it breaks is called the ductility). So far so good. One more. If the ruler were made not of steel but of glass or of PMMA (Plexiglas, Perspex), as transparent rulers are, it is not possible to bend it permanently at all. The ruler will fracture suddenly, without warning, before it acquires a permanent bend. We think of materials that break in this way as brittle and materials that are not as tough. There is no permanent deformation here, so σ_y is not the right property. The resistance of materials to cracking and fracture is measured instead by the fracture toughness, K_{Ic} . Steels are tough—well, most are (steels can be made brittle)—they have a high K_{Ic} . Glass epitomizes brittleness; it has a very low K_{Ic} , suggesting consequences of inadequate fracture and toughness. We started with the material property density, mass per unit volume, symbol ρ . Density, in a ruler, is irrelevant. But for almost anything that moves, weight carries a fuel penalty, modest for automobiles, greater for trucks and



The stress-strain curve for a metal, showing the modulus, E , the 0.2% yield strength, σ_y , and the ultimate strength, σ_{ts} .



trains, greater still for aircraft, and enormous in space vehicles. Minimizing weight has much to do with clever design is equal to choosing of material. Aluminum has a low density, lead a high one. If our little aircraft were made of lead, it would never get off the ground at all. This is not the only mechanical properties, but they are the most important ones.



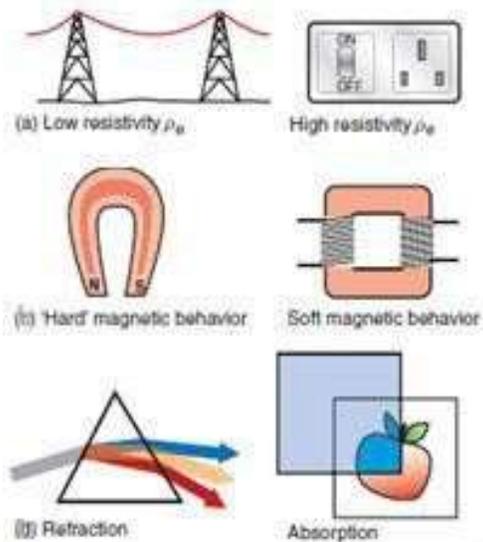
Thermal properties

The properties of a material change with temperature, usually for the worse. Its strength falls, it starts to ‘creep’ (to sag slowly over time), and it may oxidize, degrade, or decompose. This means that there is a limiting temperature called the maximum service temperature, T_{max} , above which its use is impractical. Stainless steel has a high T_{max} —it can be used up to 800°C ; most polymers have a low T_{max} and are seldom used above 150°C .

Most materials expand when they are heated but by differing amounts depending on their thermal expansion coefficient, α . The expansion is small, but its consequences can be large. If, for instance, a rod is constrained and then heated, expansion forces the rod against the constraints, causing it to buckle. Railroad track buckles in this way if provision is not made to cope with it. Some materials—metals, for instance—feel cold; others—like woods—feel warm. This feel has to do with two thermal properties of the material: thermal conductivity and heat capacity. The first, thermal conductivity, λ , measures the rate at which heat flows through the material when one side is hot and the other cold. Materials with high λ are what you want if you wish to conduct heat from one place to another, as in cooking pans, radiators, and heat exchangers; this suggests the consequences of high and low λ for the cooking vessel. But low λ is useful too—low λ materials insulate homes, reduce the energy consumption of refrigerators and freezers, and enable space vehicles to re-enter the earth’s atmosphere. These applications have to do with long-time, steady, heat flow. When time is limited, that other property—heat capacity, C_p —matters. It measures the amount of heat that it takes to make the temperature of the material rise by a given amount. High-heat capacity materials—copper, for instance—require a lot of heat to change their temperature; low-heat capacity materials, like polymer foams, take much less.

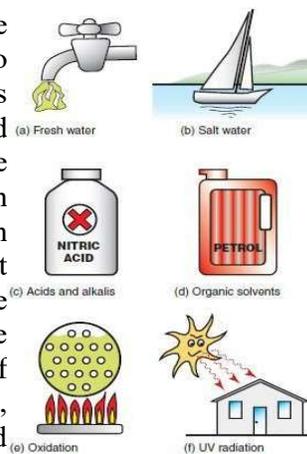
Electrical, magnetic and optical properties

We start with electrical conduction and insulation. Without electrical conduction, we would lack the easy access to light, heat, power, control, and communication that today we take for granted. Metals conduct well copper and aluminum are the best of those that are affordable. But conduction is not always a good thing. Fuse boxes, and switch casings, all require insulators. Here the property we want is resistivity, ρ_e , the inverse of electrical conductivity κ_e . Most plastics and glass have high resistivity they are used as insulators though, by special treatment, they can be made to conduct a little. Electricity and magnetism are closely linked. Electric currents induce magnetic fields; a moving magnet induces, in any nearby conductor, an electric current. The response of most materials to magnetic fields is too small to be of practical value. But a few called ferromagnets can trap a magnetic field permanently. These are called 'hard' magnetic materials because, once magnetized, they are hard to demagnetize. They are used as permanent magnets in headphones, motors, and dynamos. Here the key property is the remanence, a measure of the intensity of the retained magnetism. few others 'soft Magnet materials are easy to' magnetize and demagnetize. They are the materials of transformer cores. They can conduct a magnetic field, but not retain it permanently. For these, a key property is saturation magnetization, which measures how large a field the material can conduct. Materials respond to light as well as to electricity and magnetism—hardly surprising, since light itself is an electromagnetic wave. Opaque materials reflect light; those that are transparent refract it, and some can absorb some wavelengths (colors) while allowing others to pass freely.



Chemical properties

Products often have to function in hostile environments, exposed to corrosive fluids, to hot gases or to radiation. Damp air is corrosive, so is water; the sweat of your hand is particularly corrosive, and of course, there are far more aggressive environments than these. If the product is to survive for its design life it must be made of materials or at least coated with materials that can tolerate the surroundings in which they operate. Figure 2.6 illustrates some of the commonest of these: fresh and salt water, acids and alkalis, organic solvents, oxidizing flames and ultraviolet radiation. We regard the intrinsic resistance of a material to each of these as material properties, measured on a scale of 1 (very poor) to 5 (very good).



Chemical properties: resistance to water, acids, alkalis, organic solvents, oxidation and radiation.

Interatomic bonding in materials

Matter can exist in three states and as atoms change directly from either the gaseous state (desublimation) or the liquid state (solidification) to the usually denser solid state, the atoms form aggregates in three-dimensional space. Bonding forces develop as atoms are brought into proximity to each other. Sometimes these forces are spatially directed. The nature of the bonding forces has a direct effect on the type of solid structure that develops and therefore upon the physical properties of the material. The melting point provides a useful indication of the amount of thermal energy needed to sever these inter-atomic (or inter-ionic) bonds. Thus, some solids melt at relatively low temperatures (m.p. of tin is 232°C) whereas many ceramics melt at extremely high temperatures (m.p. of alumina exceeds 2000°C).

There are four principal types of bonding in materials follows: -

1. Metallic bonding
2. Ionic bonding
3. Covalent bonding
4. Van der Waals bonding.

However, in many solid materials, it is possible for bonding to be mixed, or even intermediate. We will first consider the general chemical features of each type of bonding. As we have seen, the elements with the most pronounced metallic characteristics are grouped on the left-hand side of the Periodic Table. In general, they have a few valence electrons, outside the outermost closed shell, which are relatively easy to detach. In a metal, each 'free' valency electron is shared among all atoms, rather than associated with an individual atom, and forms part of the so-called 'electron gas' which circulates at random among the regular array of positively-charged electron cores, or cation.

Application of an electric potential gradient will cause the 'gas' to drift through the structure with little hindrance, thus explaining the outstanding electrical conductivity of the metallic state. The metallic bond derives from the attraction between the cations and the free electrons and, as would be expected, repulsive components of force develop when cations are brought into proximity. However, the bonding forces in metallic structures are spatially non-directed and we can readily simulate the packing and space filling characteristics of the atoms with modeling systems based on equal-sized spheres (polystyrene balls, even soap bubbles).

Other properties such as ductility, thermal conductivity, and the transmittance of electromagnetic radiation are also directly influenced by the non-directionality and high electron mobility of the metallic bond.

The ionic bond develops when electron(s) are transferred from atoms of active metallic elements to atoms of active non-metallic elements, thereby enabling each of the resultant ions to attain a stable closed shell. For example, the ionic structure of magnesia (MgO), a ceramic oxide, forms when each magnesium atom

Z D 12 loses two electrons from its L-shell n D 2 and these electrons are acquired by an oxygen atom Z D 8, producing a stable octet configuration in its L-shell. Overall, the ionic charges balance and the structure is electrically neutral. Anions are usually larger than cations. Ionic bonding is unidirectional, essentially electrostatic, and can be extremely strong; for instance, magnesia is a very useful refractory oxide m.p. D 2930°C. At low to moderate temperatures, such structures are electrical insulators but, typically, become conductive at high temperatures when thermal agitation of the ions increases their mobility. The sharing of valence electrons is the key feature of the third type of strong primary bonding.

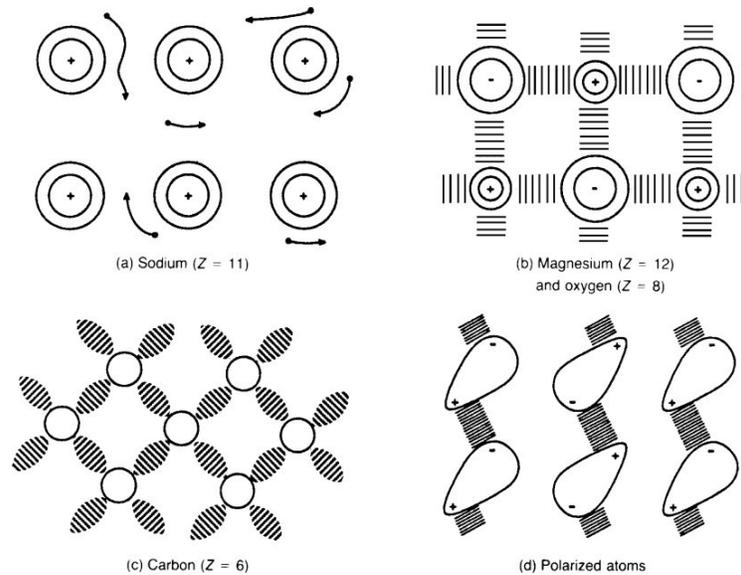


Figure. Schematic representation of (a) metallic bonding, (b) ionic bonding, (c) covalent bonding, and (d) van der Waals bonding.

Covalent bonds form when valence electrons of opposite spin from adjacent atoms can pair within overlapping spatially-directed orbitals, thereby enabling each atom to attain a stable electronic configuration. Being oriented in three-dimensional space, these localized bonds are unlike metallic and ionic bonds. Furthermore, the electrons participating in the bonds are tightly bound so that covalent solids, in general, have expansion and very high melting point 3300°C bear witness to the inherent strength of the covalent bond. First, using the $(8 - N)$ Rule, in which N is the Group Number¹ in the Periodic Table, we deduce that carbon ($Z = 6$) is tetravalent that is, four bond-forming electrons are available from the L-shell ($n = 2$). Following Hund's Rule, one of the two electrons in the $2s$ -state is promoted to a higher $2p$ -state to give a maximum spin condition, producing an overall configuration of $1s^2 2s^1 2p^3$ in the carbon atom. The outermost second shell accordingly paired. Thus, each carbon atom can establish electron sharing orbitals with four neighbors. For a given atom, these four bonds are of equal strength and are set at equal angles 109.50 to each other and therefore exhibit tetrahedral symmetry. This process by which s -orbitals and p -orbitals combine to form projecting hybrid sp -orbitals is known as hybridization. It is observed in elements other than carbon. For instance, trivalent boron ($Z = 5$) forms three coplanar sp^2 -orbitals. In general, a large degree of overlap of sp -orbitals and/or a high electron density within the overlap 'cloud' will lead to an increase in the strength of the covalent bond. As indicated earlier, it is possible for a material to possess more than one type of bonding.

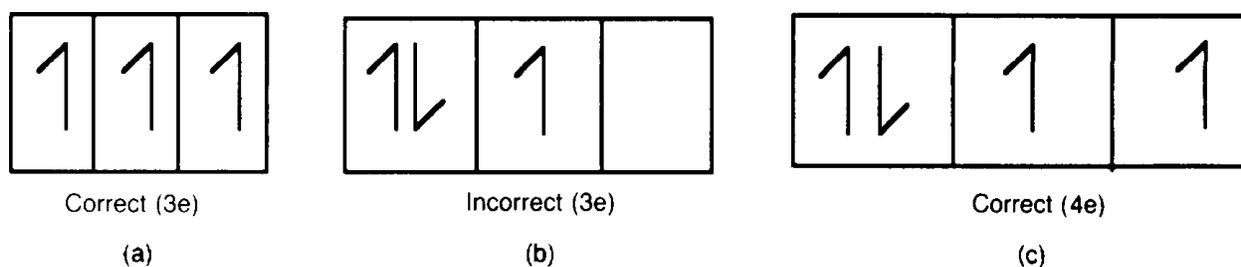
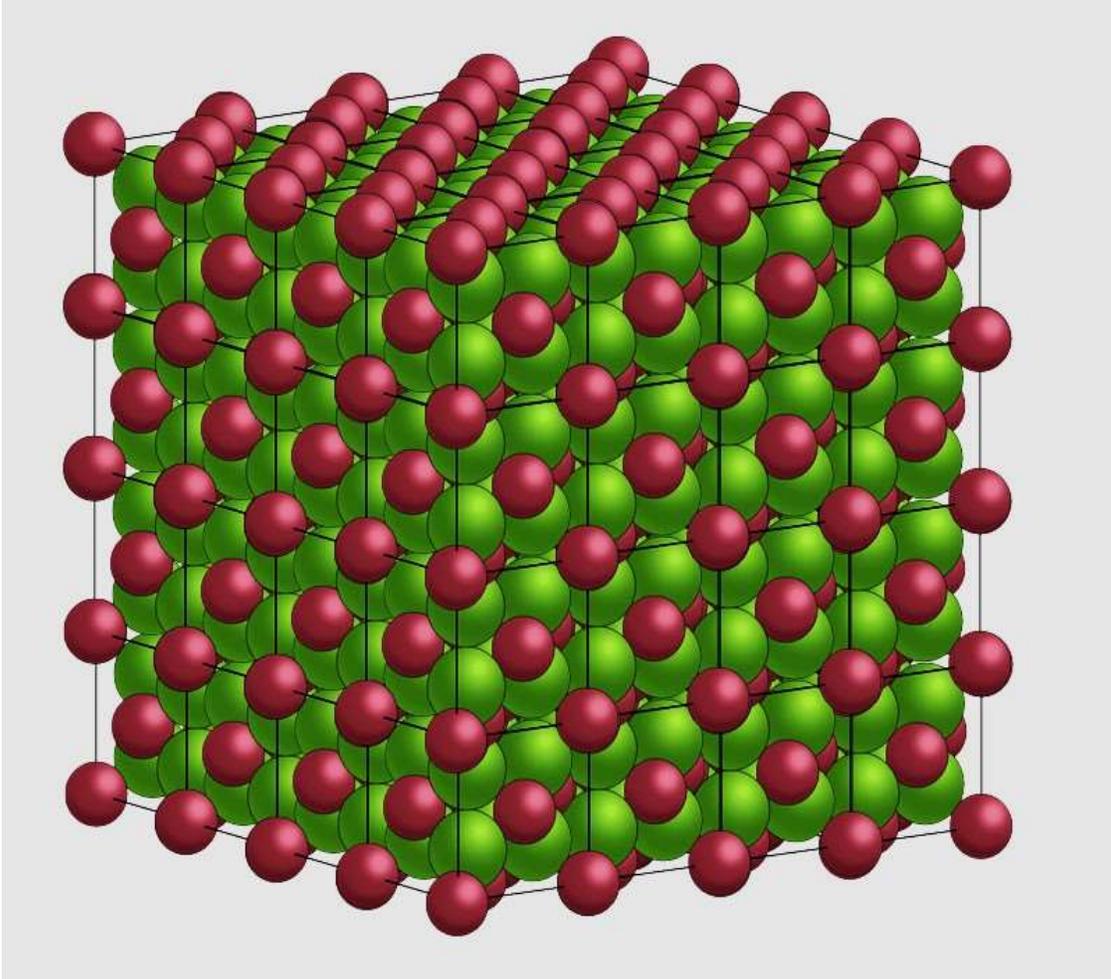


Figure. Application of Hund's multiplicity rule to the electron-filling of energy states.

The final type of bonding is attributed to the Vander Waals forces which develop when adjacent atoms, or groups of atoms, act as electric dipoles. Suppose that two atoms which differ greatly in size combine to form a molecule as a result of covalent bonding. The resultant electron 'cloud' for the whole molecule can be pictured as pear-shaped and will have an asymmetrical distribution of electron charge. An electric dipole has formed and it follows that weak directed forces of electrostatic attraction can exist in an aggregate of such molecules. There are no 'free' electrons hence electrical conduction is not favored. Although secondary bonding by Vander Waals forces is weak in comparison to the three forms of primary bonding, it has practical significance. In thermoplastic polymers, van der Waals forces of attraction exist between the extended covalently-bonded hydrocarbon chains; a combination of heat and applied shear stress will overcome these forces and cause the molecular chains to glide past each other. To quote a more general case, molecules of water vapor in the atmosphere each have an electric dipole and will accordingly tend to be adsorbed if they strike solid surfaces possessing attractive van der Waals forces (e.g. silica gel).

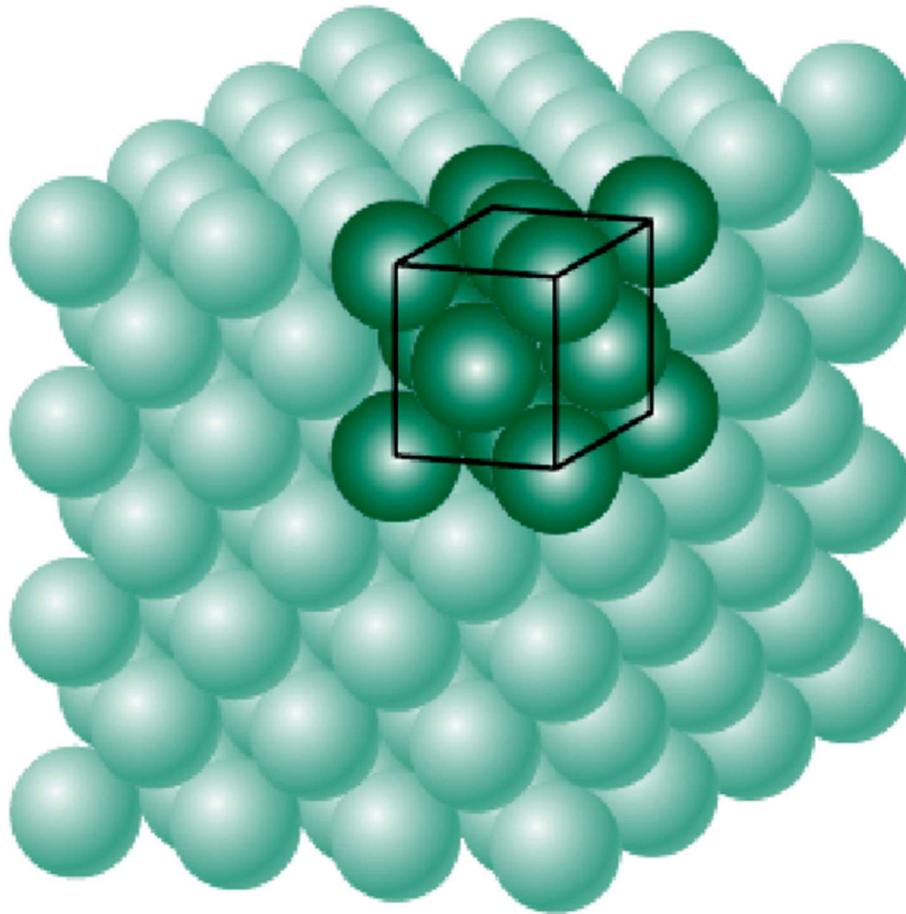
Crystal Structure of Metals



Introduction

Solid materials may be classified according to the regularity with which atoms or ions are arranged for one another. **A crystalline material:** is one in which the atoms are situated in a repeating or periodic array over large atomic distances; that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms. All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these **non-crystalline or amorphous materials.** For example (glass) and some of complex metallic materials. Some of the properties of crystalline solids depend on the **crystal structure** of the material lattice **Space and Unit Cell:** When describing crystalline structures, atoms (or ions) are thought

of as being solid spheres having well-defined diameters. This is termed the atomic hard sphere model in which spheres representing nearest-neighbor atoms touch one another. An example of the hard sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure. In this particular case, all the atoms are identical. Sometimes the term **lattice** is used in the context of crystal structures; in this sense “lattice” means a three-dimensional array of points coinciding with atom positions (or sphere centers). **The unit cell:** The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells**. It is the basic structural unit or building block of the crystal structure and defines the crystal structure by its geometry and the atom positions within. There are 14 types of crystal structures in various engineering materials as shown in the figure. The important crystal structures among all of them are the body-centered cubic structure (BCC). The face-centered cubic structure (FCC). Hexagonal close-packed structure (HCP).



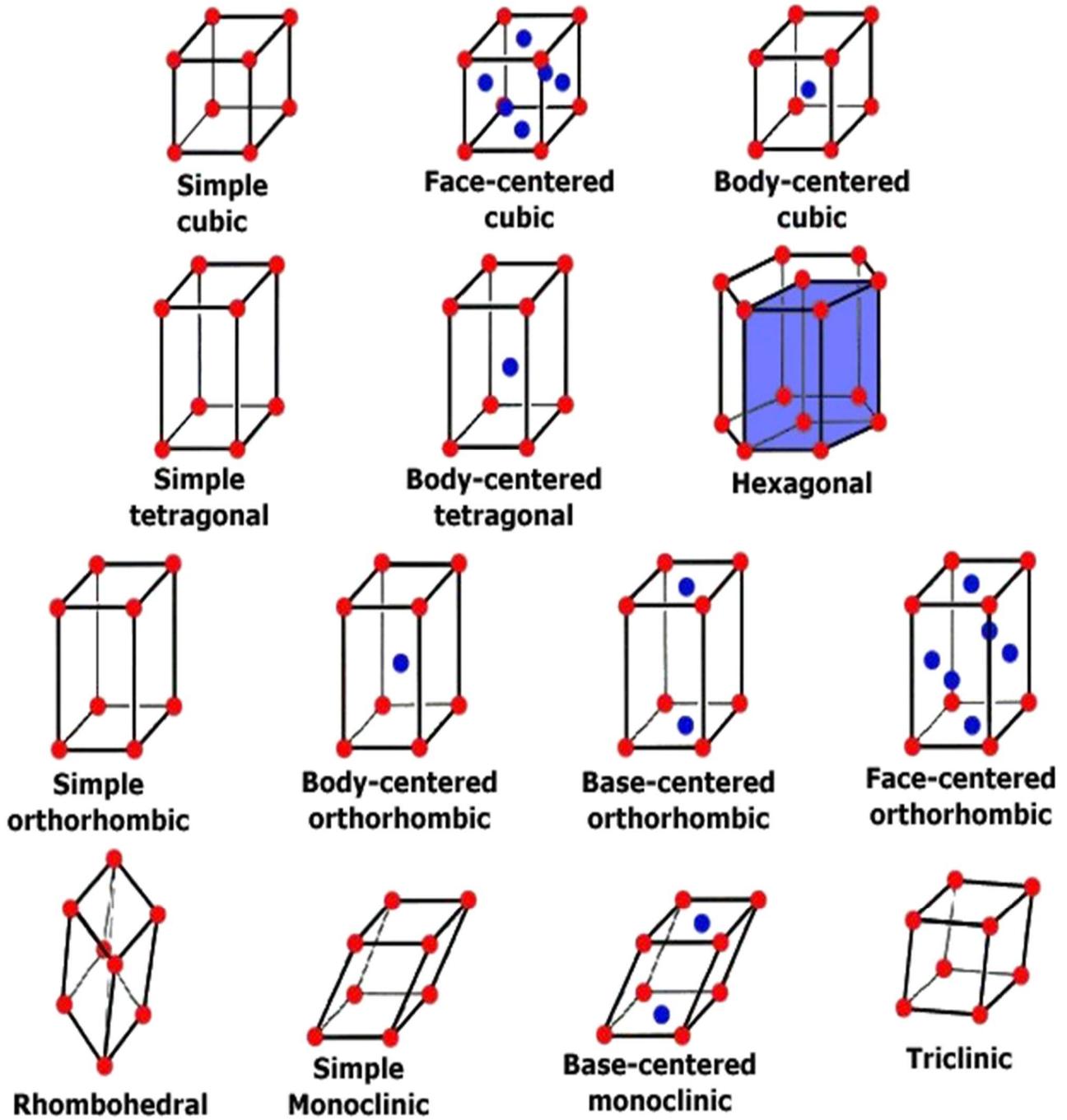


Figure: Types of Crystal structure of materials

The Face-Centered Cubic Crystal Structure

The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces. It is called the **face-centered cubic (FCC)** crystal structure. Some of the familiar metals having this crystal structure are copper, aluminum, silver, and gold. The mechanical properties of FCC are Low young modulus Low yield strength hardness good ductility and high ability for forming. Figure 2.3a shows a hard sphere model for the FCC unit cell, whereas in Figure 2.3b the atom centers are represented by small circles to provide a better perspective of atom positions. The aggregate of atoms in Figure 2.3c represents a section of crystal consisting of many FCC unit cells. These spheres or ion cores touch one another across a face diagonal; the cube edge length a and the atomic radius R are related through the FCC crystal structure, each corner atom is shared among eight-unit cells, whereas a face-centered atom belongs to only two. Therefore, one-eighth of each of the eight corner atoms and one-half of each of the six face atoms, or a total of four whole atoms, may be assigned to a given unit cell.

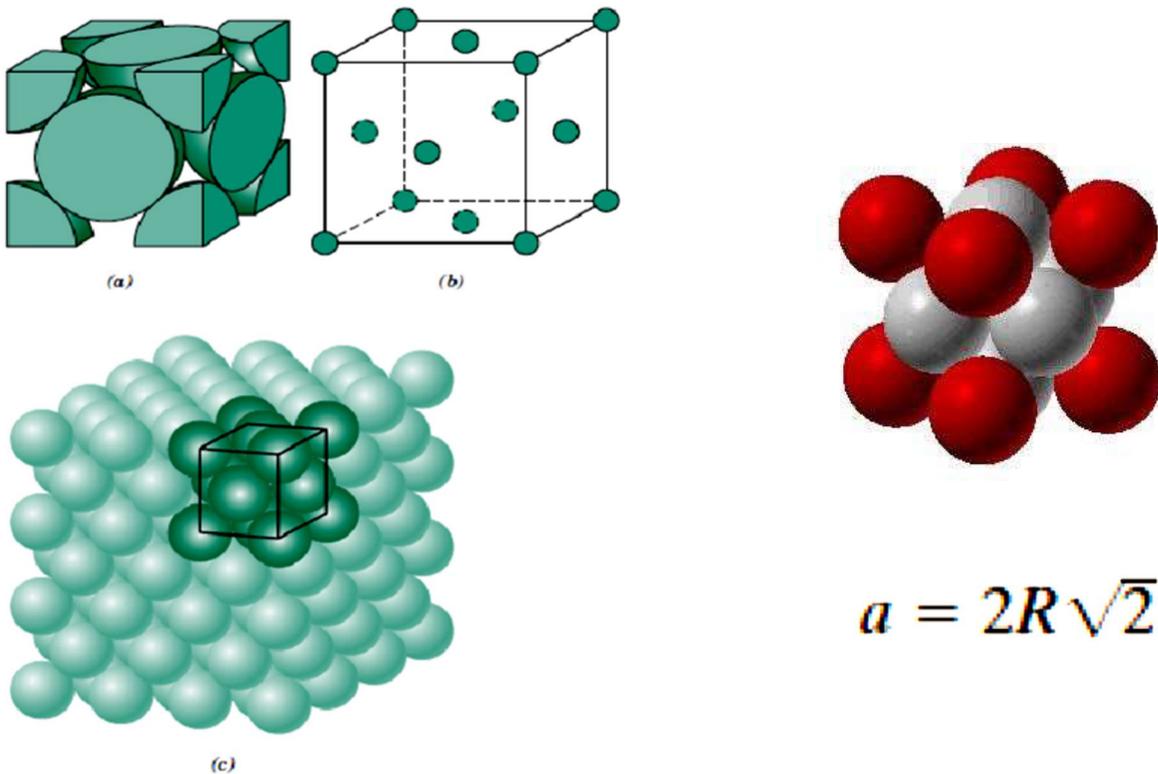
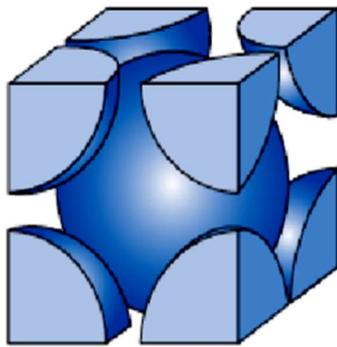


Figure: (a) Hard sphere model of FCC, (b) reduced sphere unit cell, and (c) crystal consists of many FCC unit cells.

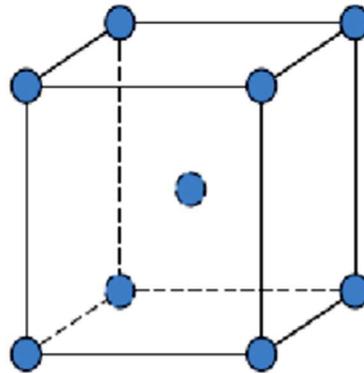
Two other important characteristics of a crystal structure are the **coordination number** and the **atomic packing factor (APF)**. For metals, each atom has the same number of nearest-neighbor or touching atoms, which is the coordination number. For face-centered cubic, **the coordination number is 12**. This may be confirmed by examination of Figure, the front face atom has four corner nearest-neighbor atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front, which is not shown. **The APF** is the sum of the sphere volumes of all atoms within a unit cell (assuming the atomic hard sphere model) divided by the unit cell volume—that is

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

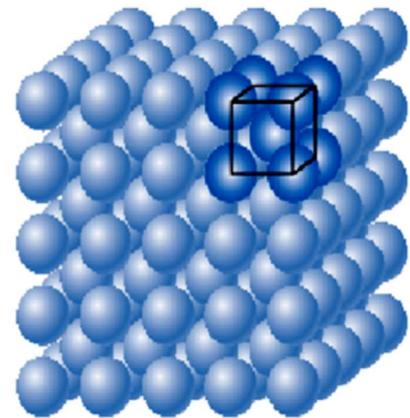
For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing for spheres all having the same: Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a body-centered cubic (BCC) crystal structure. A collection of spheres depicting this crystal structure is shown in Figure c, whereas Figures a and b are diagrams of BCC unit cells with the atoms represented by hard sphere and reduced-sphere models respectively. Chromium, iron, and tungsten are listed through BCC structure in Figure: a. Hard sphere model of BCC, b. reduced sphere unit cell, and c. crystal consists of many BCC unit cells. Center and corner atoms touch one another along cube diagonals, and unit cell length and atomic radius R are related through atoms associated with each BCC unit cell: the equivalent of one atom from the eight corners, each of which is shared among eight-unit cells, and the single center atom, which is wholly contained within its cell. The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms as shown in the figure below. Since the coordination number is less for BCC than FCC, so also is the atomic packing factor for BCC lower than 0.68 versus 0.74



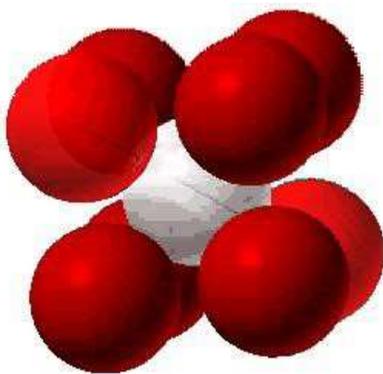
(a)



(b)



(c)



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

Hexagonal Close-Packed Crystal Structure Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a hexagonal unit cell. Figure 2.5a shows a reduced-sphere unit cell for this structure, which is termed hexagonal close-packed (HCP); an assemblage of several HCP unit cells is presented.

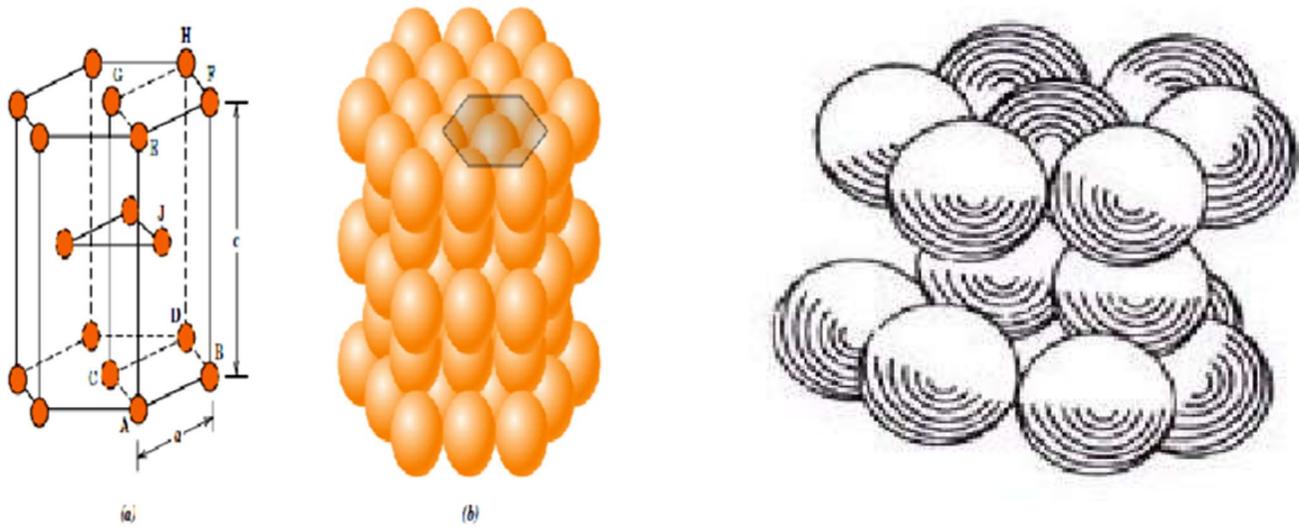


Figure: (a) reduced-sphere unit cell and (b) an aggregate of many atoms

The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 midplane interior atoms. **The coordination number and the atomic packing factor** for the hcp crystal structure are the same as for FCC: 12 and 0.74, respectively. see the figure below. unitcell length **a** and atomic radius **R** are related through HCP metals including cadmium,magnesium, titanium, and zinc.

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

DENSITY COMPUTATIONS

A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density through the relationship

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

Where:

N_A : Avogadro's number (6.023×10^{23} atoms/mol)

V_C : volume of the unit cell

A : atomic weight

n : number of atoms associated with each unit cell

Computation of the Atomic Packing Factor for FCC

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R . The volume for a sphere is $\frac{4}{3}\pi R^3$, and since there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

From Example Problem 3.1, the total unit cell volume is

$$V_C = 16R^3 \sqrt{2}$$

Therefore, the atomic packing factor is

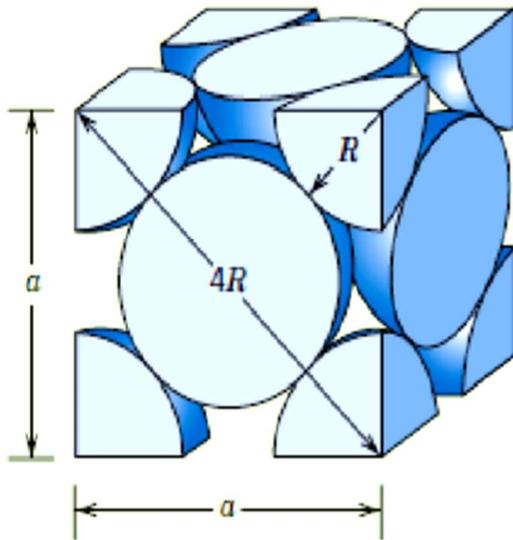
$$\text{APF} = \frac{V_S}{V_C} = \frac{(\frac{16}{3})\pi R^3}{16R^3 \sqrt{2}} = 0.74$$

Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R .

Solution

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Since the unit cell is a cube, its volume is a^3 , where a is the cell edge length. From the right triangle on the face,

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

or, solving for a ,

$$a = 2R\sqrt{2} \quad (3.1)$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \quad (3.4)$$

Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density and compare the answer with its measured density.

Solution

Equation 3.5 is employed in the solution of this problem. Since the crystal structure is FCC, n , the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R , the atomic radius, is 0.128 nm.

Substitution for the various parameters into Equation 3.5 yields

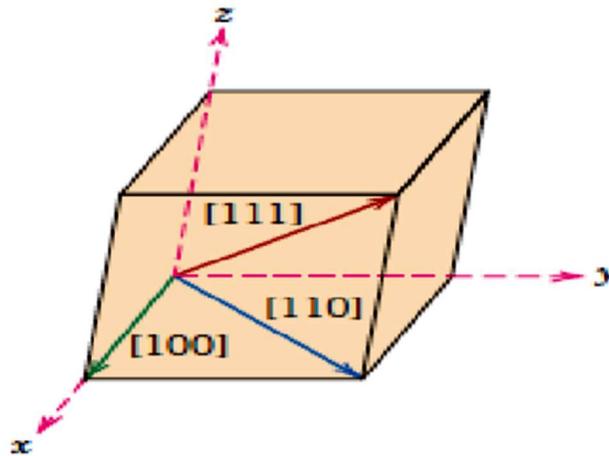
$$\begin{aligned}\rho &= \frac{nA_{\text{Cu}}}{V_C N_A} = \frac{nA_{\text{Cu}}}{(16R^3\sqrt{2})N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.023 \times 10^{23} \text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3\end{aligned}$$

The literature value for the density of copper is 8.94 g/cm^3 , which is in very close agreement with the foregoing result.

Crystallographic Directions:

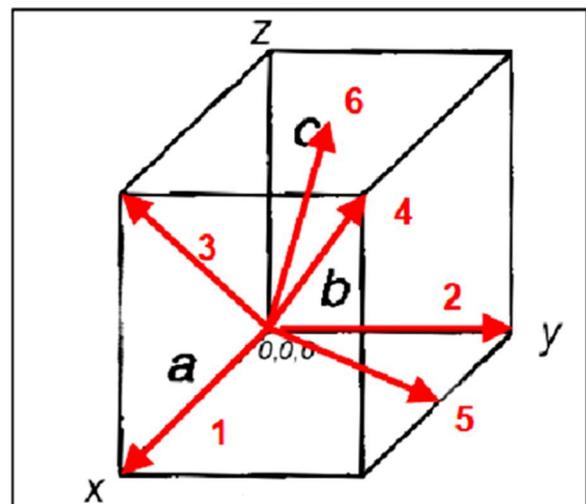
A crystallographic direction is defined a line between two points, or a vector.

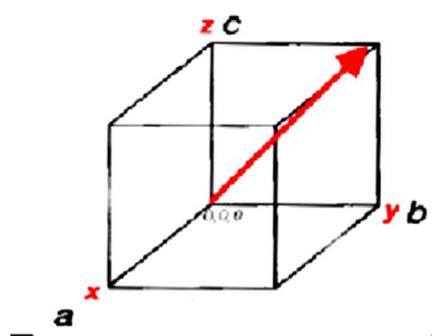
The following steps are utilized in the determination of the three directional indices: **1.** A vector of convenient length is positioned such that it passes through the origin of the coordinate system. Any vector may be translated throughout the crystal lattice without alteration if parallelism is maintained. **2.** The length of the vector projection on each of the three axes is determined; these are measured in terms of the unit cell dimensions a , b , and c . **3.** These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values. **4.** The three indices, not separated by commas, are enclosed in square brackets, thus: $[uvw]$. The u , v , and w integers correspond to the reduced projections along the x , y , and z axes, respectively. For each of the three axes, there will exist both positive and negative coordinates. Thus, negative indices are also possible, which are represented by a bar over the appropriate index. For example, the $[\bar{1}11]$ direction would have a component in the $(-y)$ direction. Also, changing the signs of all indices produces an antiparallel direction; that is, $[\bar{1}\bar{1}\bar{1}]$ is directly opposite to $[111]$. The $[100]$, $[110]$, and $[111]$ directions are common ones they are drawn in the unit cell shown in Figure



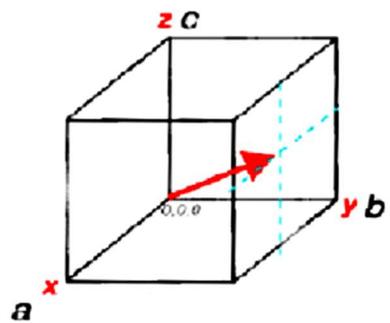
- **Direction 1** $1, 0, 0 = [100]$
- **Direction 2** $0, 1, 0 = [010]$
- **Direction 3** $1, 0, 1 = [101]$
- **Direction 4** $1, 1, 1 = [111]$
- **Direction 5** $\frac{1}{2}, 1, 0 = [120]$
- **Direction 6** $\frac{1}{2}, \frac{1}{2}, 1 = [112]$

-- Parallel directions have the same value





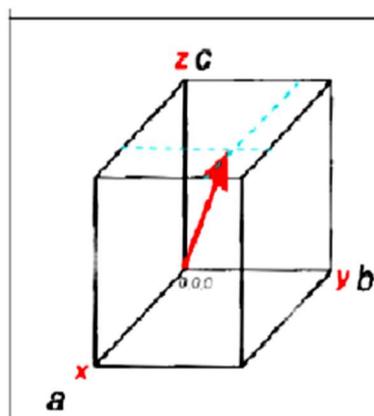
	x (a)	y (b)	z (c)
Point Coordinates	0	1	1
Clear Fractions	0	1	1
Crystal Direction	[011]		



	x (a)	y (b)	z (c)
Point Coordinates	$\frac{1}{2}$	1	$\frac{1}{2}$
Clear Fractions	1	2	1
Crystal Direction	[121]		

-- No Fractions, Convert to Integers [$\frac{1}{2}$ $\frac{1}{2}$ 1] = [112]

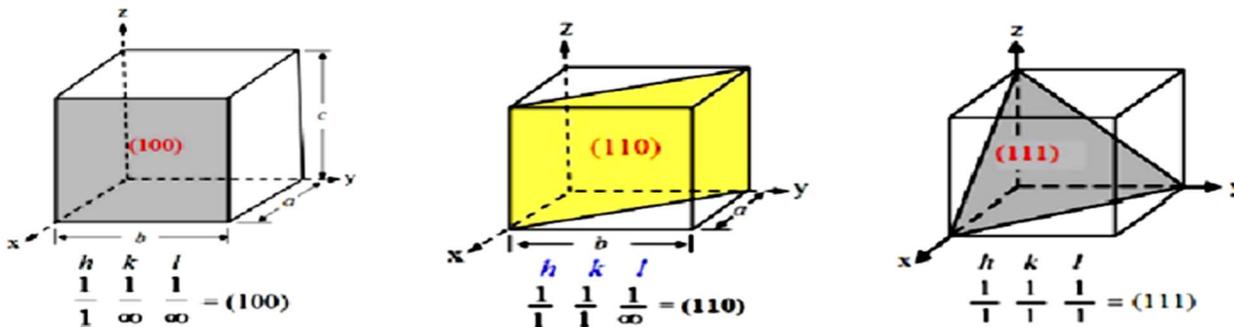
-- Negative Direction has a top bar on the hkl value $[\bar{1}\bar{1}\bar{1}]$



	x (a)	y (b)	z (c)
Point Coordinates	$\frac{3}{4}$	$\frac{3}{4}$	1
Clear Fractions	3	3	4
Crystal Direction	[334]		

Crystallographic Planes

The orientations of planes for a crystal structure are represented in a similar manner. **Miller indices** are specified by three **Miller indices** as (hkl). Any two planes parallel to each other are equivalent and have identical indices. The procedure employed in determination of the h, k, and l index numbers is as follows: **1.** The crystallographic plane either intersects or parallels each of the three axes; the length of the planar intercept for each axis is determined in terms of the lattice parameters a, b, and c. **2.** The reciprocals of these numbers are taken. A plane that parallels an axis may be considered to have an infinite intercept, and, therefore, a zero index. **3.** If necessary, these three numbers are changed to the set of smallest integers by multiplication or division by a common factor. **4.** Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl). An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index.:



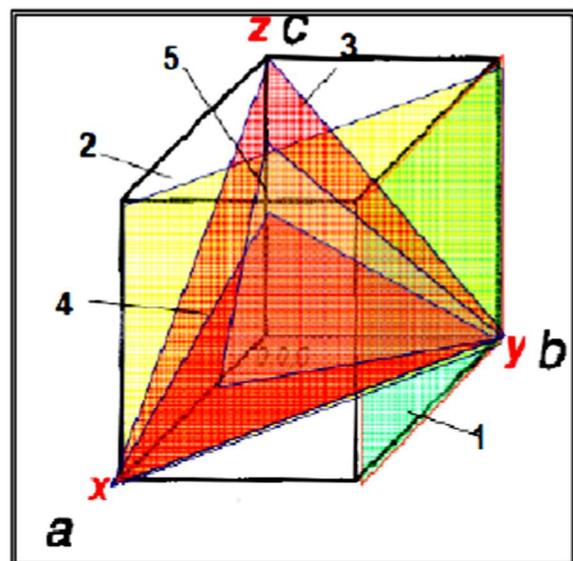
To find the Miller Indices of a plane, follow these steps:

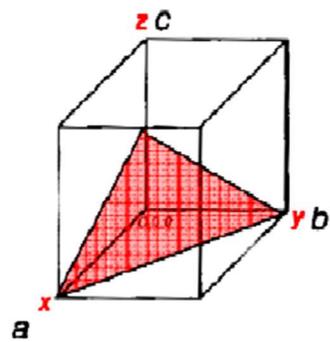
- Determine the intercepts of the plane along the crystal axes
- Take the reciprocals
- Clear fractions
- Reduce to lowest terms and enclose in brackets ()

Ex: Intercepts on a, b, c : $\frac{3}{4}, \frac{1}{2}, \frac{1}{4}$ (h k l) = $(\frac{4}{3}, 2, 4) = (2 \ 3 \ 6)$

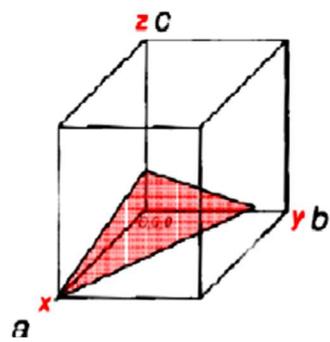
Miller Indices-- Based on reciprocal of the intersection of the plane with the cell axes, indicated with parenthesis (h, k, l)

- Plane 1 $1/\infty, 1/1, 1/\infty = (010)$
- Plane 2 $1/1, 1/1, 1/\infty = (110)$
- Plane 3 $1/1, 1/1, 1/1 = (111)$
- Plane 4 $1/1, 1/1, 1/(\frac{1}{2}) = (112)$
- Plane 5 $1/(\frac{1}{2}), 1/1, 1/(\frac{3}{4}) = (634)$

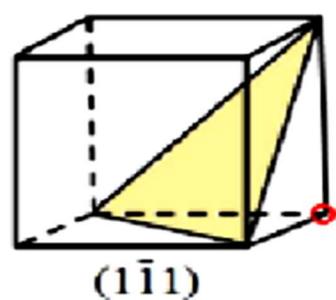
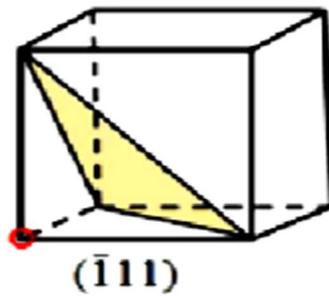
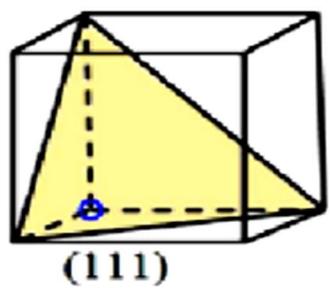
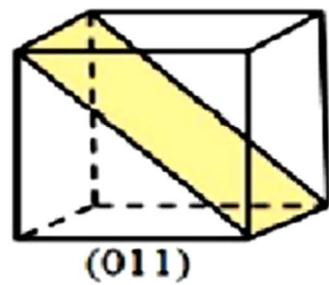
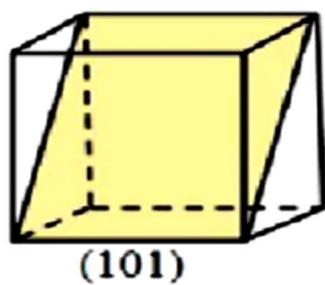
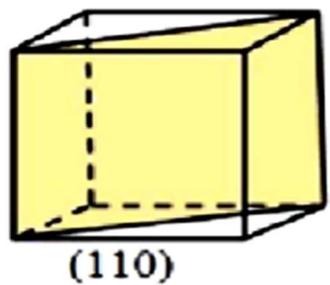
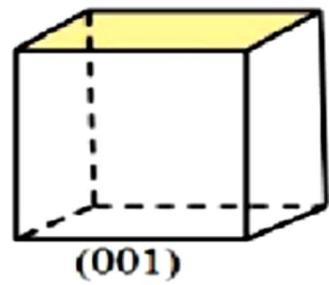
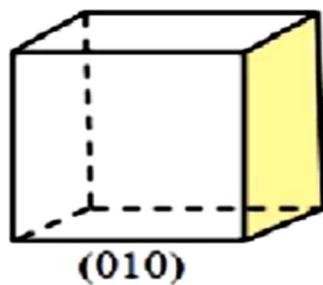
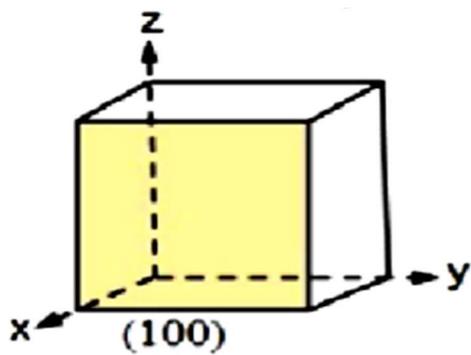




	x (a)	y (b)	z (c)
Intercept on axes	1	1	$\frac{1}{2}$
Reciprocal	1	1	2
Integer Clear	1	1	2
Miller Indices	(112)		



	x (a)	y (b)	z (c)
Intercept on axes	1	$\frac{3}{4}$	$\frac{1}{4}$
Reciprocal	1	$\frac{4}{3}$	4
Integer Clear	3	4	12
Miller Indices	(3 4 12)		



Liner and Planer Density

Linear density (LD): is defined as the number of atoms per unit length whose centers on the direction vector for a specific crystallographic direction; that is, Of course, the units of linear density are reciprocal length (e.g., nm^{-1} , m^{-1}).

Planar density (PD): is taken as the number of atoms per unit area that centered on particular crystallographic plan units for planar density are reciprocal area.

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

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

Example: Determine the liner and planer density of the [110] direction for the FCC crystalstructure.

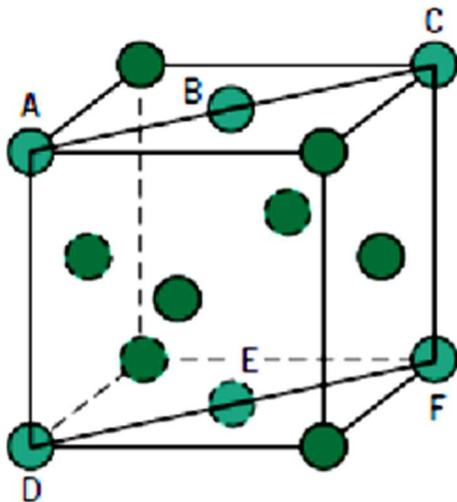
Solution:

There are 2 atoms through the vector [110] can be seen from figure (b) and the length of this vector is $4R$ so the linear density is:

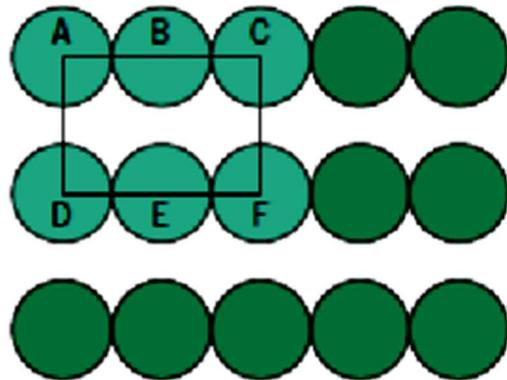
From the figure below:

consider the section of a (110) plane within an FCC unit cell as;

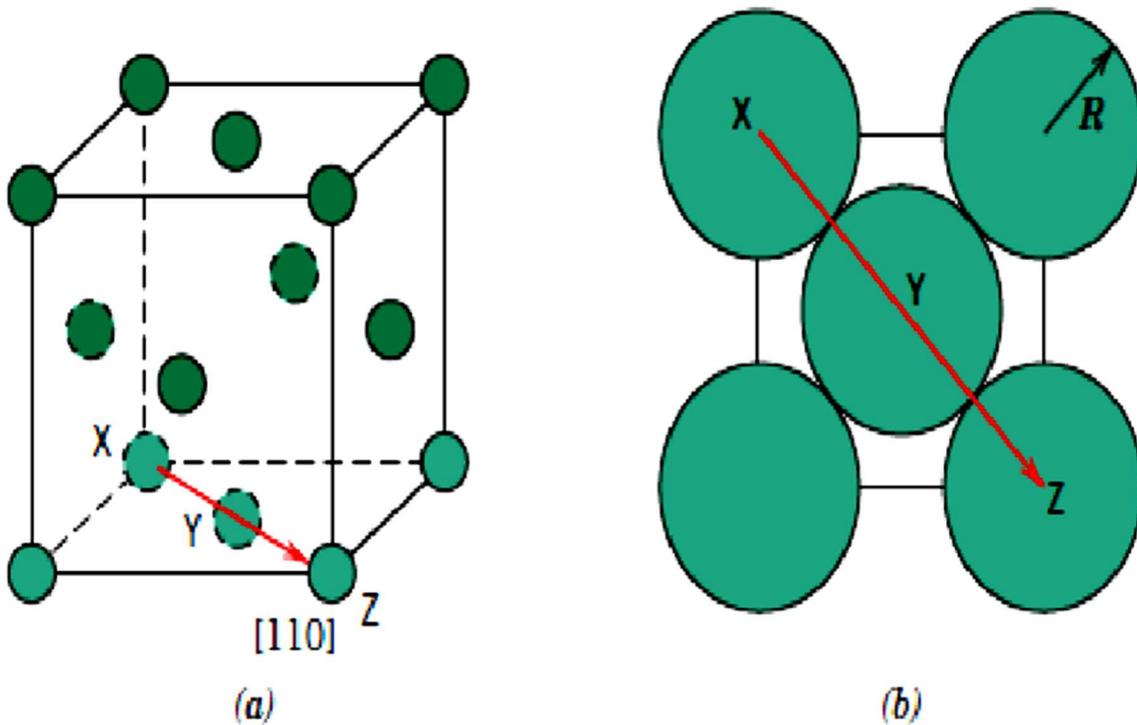
$$\text{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R} \quad (4R)(2R\sqrt{2}) = 8R^2\sqrt{2}, \quad \text{PD}_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}}$$



(a)



(b)



represented in Figures a and b. Although six atoms have centers that lie on this plane (Figure b), only one-quarter of each of atoms A, C, D, and F, and one-half of atoms B and E, for a total equivalence of just 2 atoms are on that plane. Furthermore, the area of this rectangular section is equal to the product of its length and width. From Figure b, the length (horizontal dimension) is equal to $4R$, whereas the width (vertical dimension) is equal to $2R\sqrt{2}$. Thus, the area of this planar region.

Planar density

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

$$\text{Planar Density} = \frac{\text{Number of atoms on a plane}}{\text{Area of plane}}$$

For example, there are 2 atoms ($1/4 \times 4$ corner atoms + $1/2 \times 2$ side atoms) in the $\{110\}$ planes in the FCC lattice. Planar density of $\{110\}$ planes in the FCC crystal

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

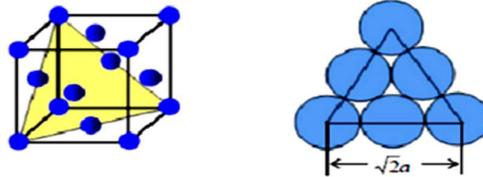


Planar density

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

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

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



Linear Density

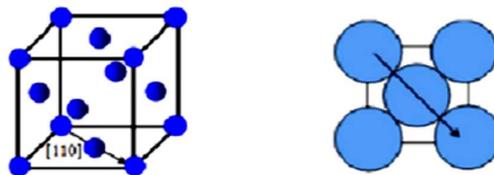
Linear density (LD) is the number of atoms per unit length along a particular direction

$$\text{Linear Density} = \frac{\text{Number of atoms on the direction vector}}{\text{Length of the direction vector}}$$

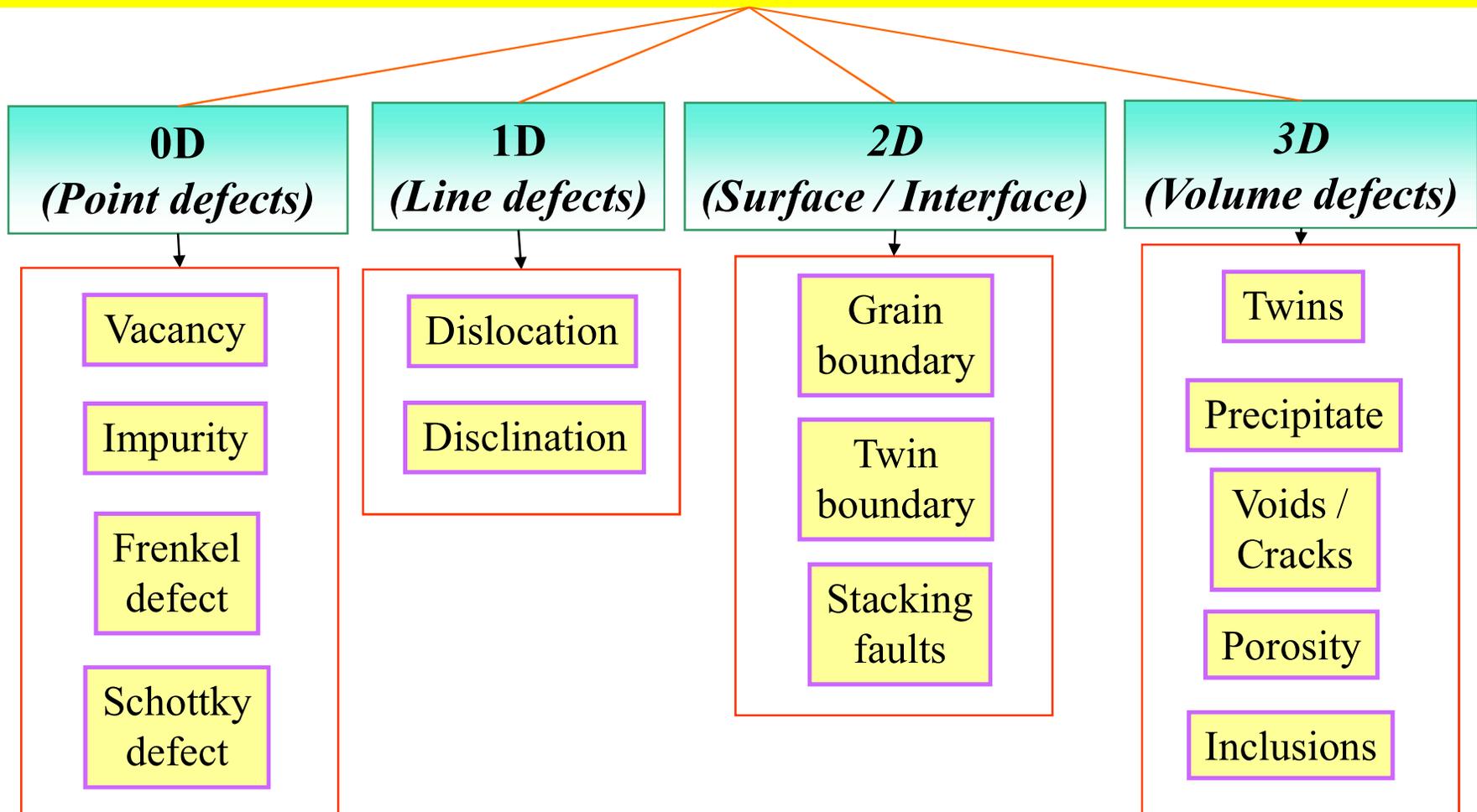
<110> directions in the FCC lattice have 2 atoms (1/2 x 2 corner atoms + 1 center atom) and the length is $\sqrt{2}a$

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

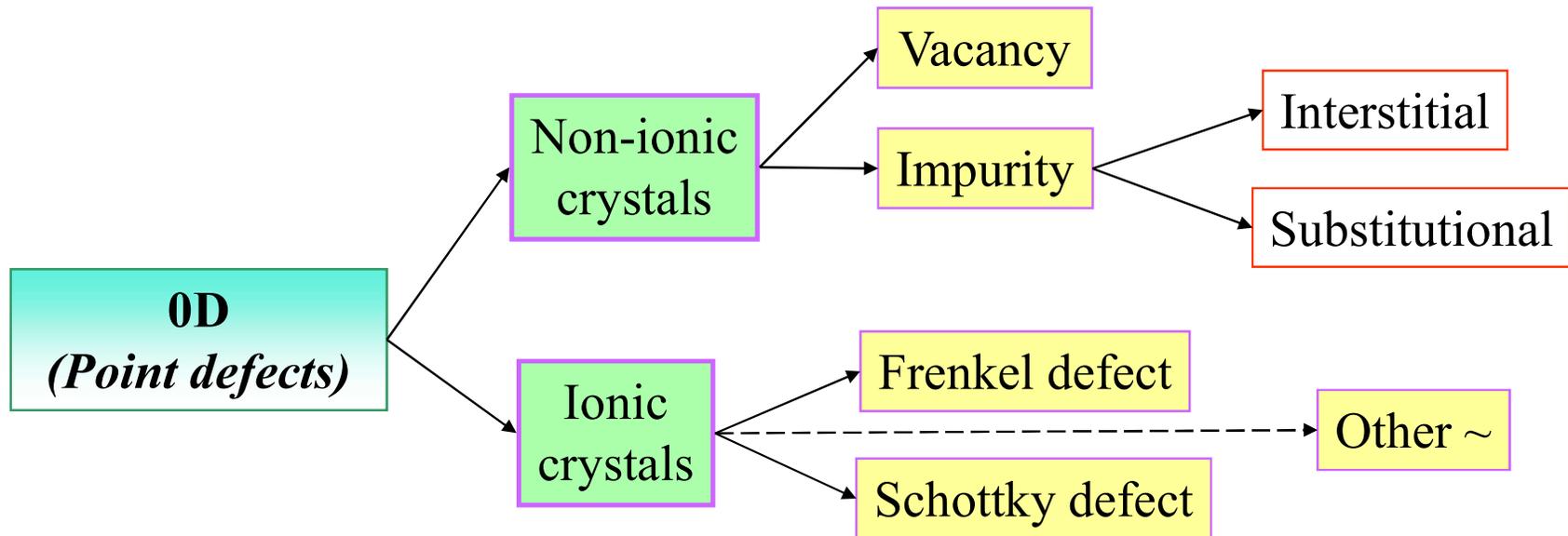
This is the most densely packed direction in the FCC lattice



CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY



Point Defects



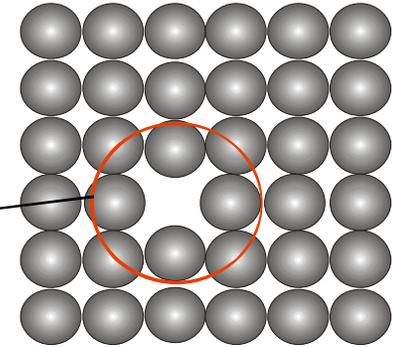
- ❑ Imperfect point-like regions in the crystal about the size of 1-2 atomic diameters

Point Defects : Non-ionic crystals

Vacancy

- ❑ Missing atom from an atomic site
- ❑ Atoms around the vacancy displaced
- ❑ Tensile stress field produced in the vicinity

Tensile Stress Fields ?



Impurity

Interstitial

Substitutional

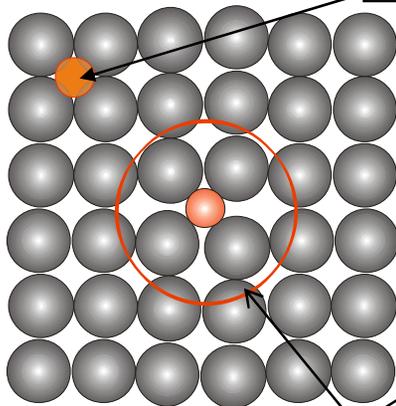
❑ Substitutional Impurity

- Foreign atom replacing the parent atom in the crystal
- E.g. **Cu** sitting in the lattice site of FCC-**Ni**

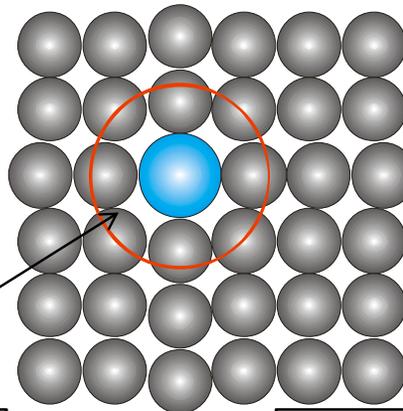
❑ Interstitial Impurity

- Foreign atom sitting in the void of a crystal
- E.g. **C** sitting in the octahedral void in HT FCC-**Fe**

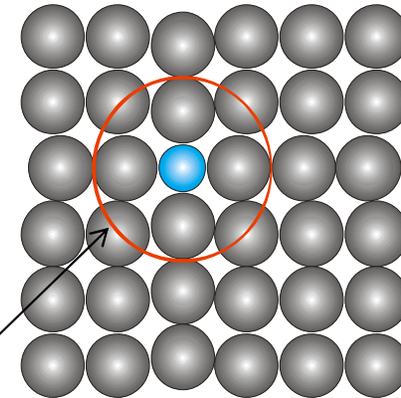
Relative size



Compressive Stress Fields



Tensile Stress Fields

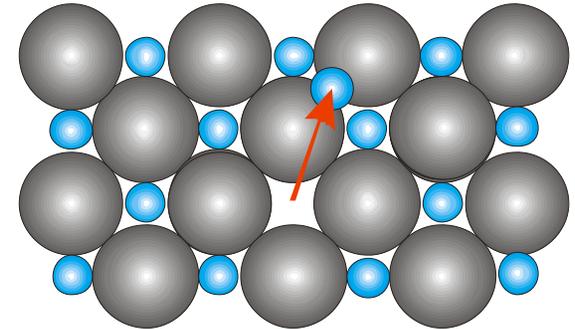


Point Defects : Ionic crystals

□ Overall electrical neutrality has to be maintained

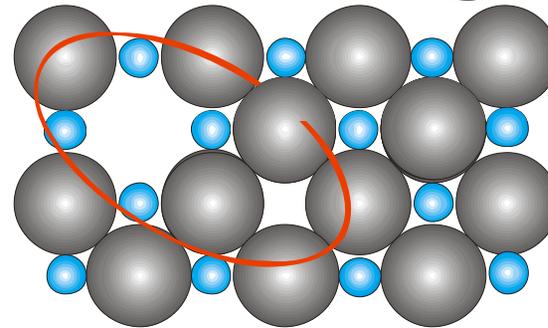
Frenkel defect

- Cation (being smaller get displaced to interstitial voids)
- E.g. AgI, CaF₂



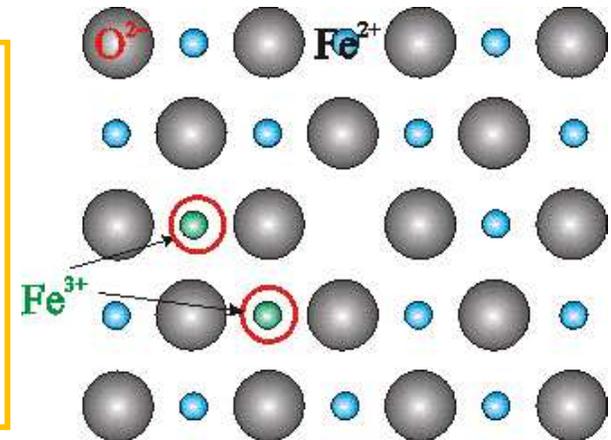
Schottky defect

- Pair of anion and cation vacancies
- E.g. Alkali halides



Other defects due to charge balance

- FeO heated in oxygen atmosphere → Fe_xO ($x < 1$)
- Vacant cation sites are present
- Charge is compensated by conversion of ferrous to ferric ion:
$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^{-}$$
- For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions → provides the 2 electrons required by excess oxygen



How many vacancies are present?

- The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, N_v , increases exponentially with the absolute temperature, T and can be estimated using the equation:

$$N_v = N_s \exp\left(\frac{-E_v}{K_B T}\right)$$

N_s = Number of regular lattice sites

K_B = Boltzman constant

E_v = Energy needed to form a vacant lattice site in a perfect crystal

- Using this simple equation we can estimate vacancy per 10^n lattice atoms.

Solved Example -1

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm³ respectively.

This problem may be solved by using following equations

It is first necessary, however, to determine the value of N_s , the number of atomic sites per cubic meter for copper,

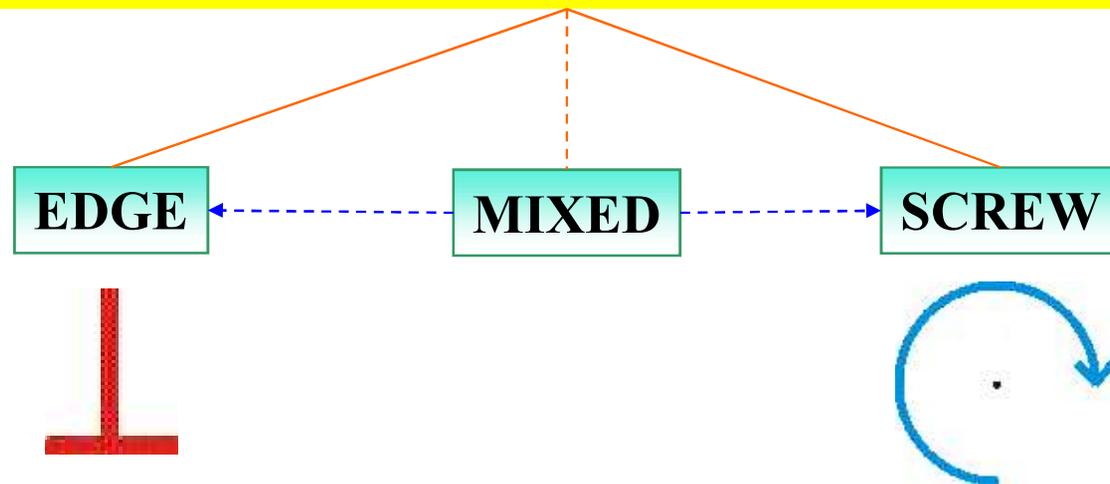
from its atomic weight A_{Cu} , its density ρ and Avogadro's number N_A , according to

$$\begin{aligned} N_s &= \frac{N_A \rho}{A_{Cu}} \\ &= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}} \\ &= 8.0 \times 10^{28} \text{ atoms/m}^3 \end{aligned}$$

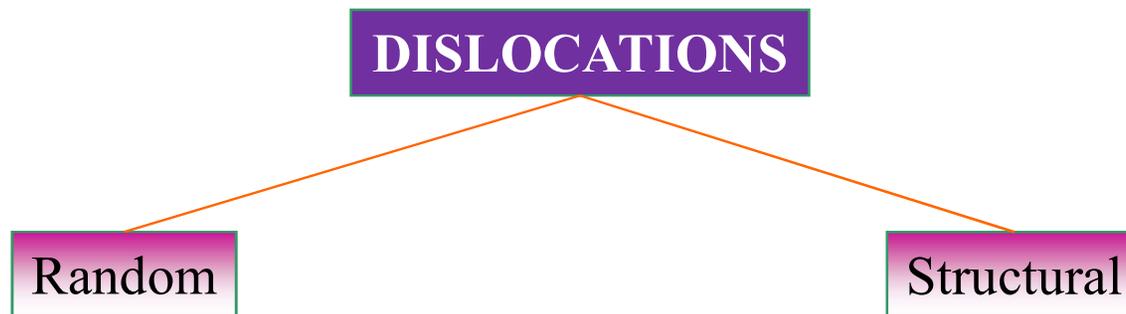
Thus the number of vacancies at 1000°C is equal to $N_v = N_s \exp\left(\frac{-E_v}{K_B T}\right)$

$$\begin{aligned} &= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[\frac{-0.9 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right] \\ &= 2.2 \times 10^{25} \text{ vacancies/m}^3 \end{aligned}$$

1D Defects : DISLOCATIONS

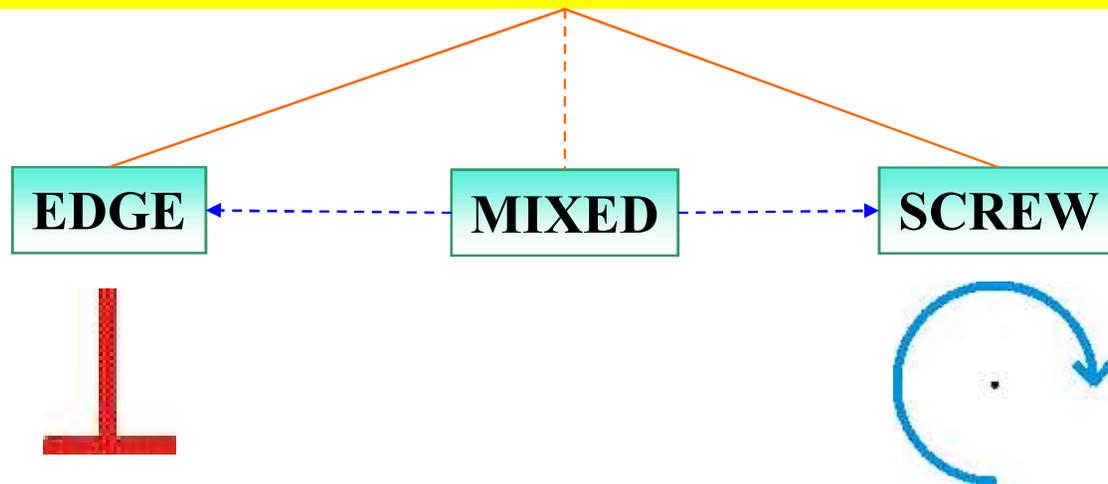


- Usually dislocations have a mixed character and *Edge* and *Screw* dislocations are the ideal extremes

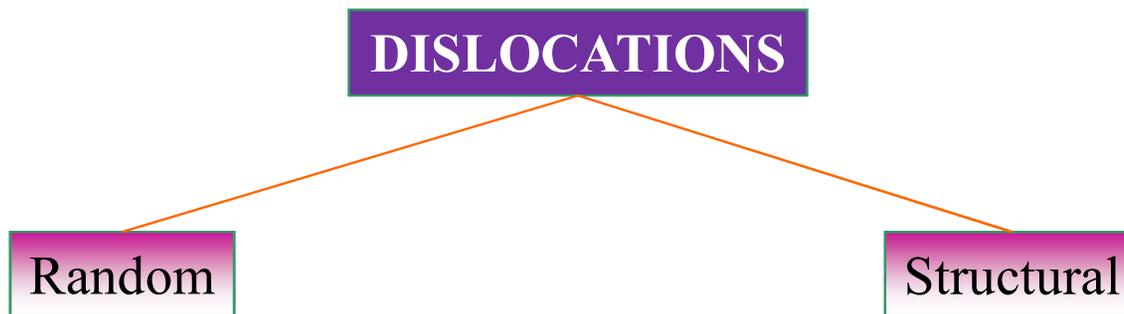


- Geometrically necessary dislocations

1D Defects : DISLOCATIONS



- Usually dislocations have a mixed character and *Edge* and *Screw* dislocations are the ideal extremes

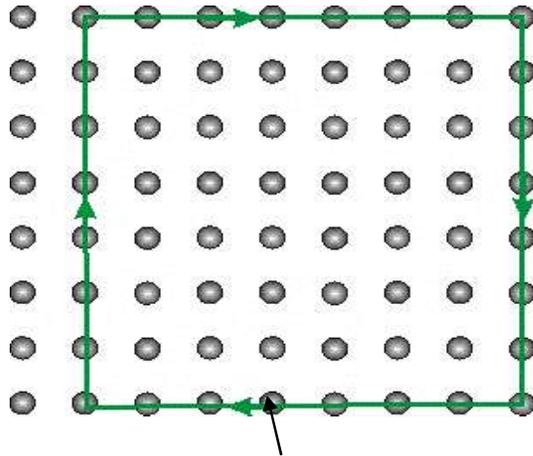


- Geometrically necessary dislocations

Introduction

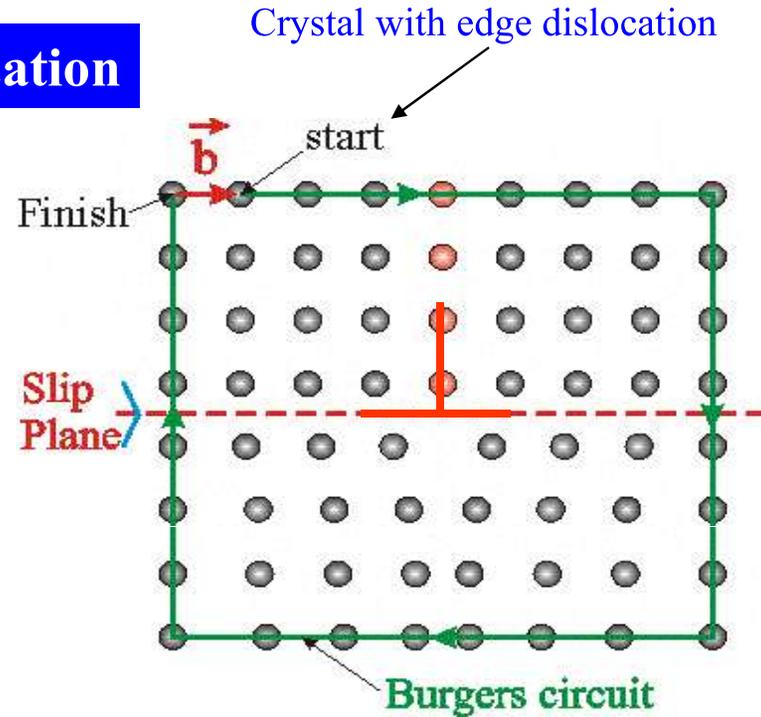
- ❑ Dislocation is a boundary between the slipped and the unslipped parts of the crystal lying over a slip plane
- ❑ The intersection of the extra half-plane of atoms with the slip plane defines the dislocation line (*for an edge dislocation*)
- ❑ Direction and magnitude of slip is characterized by the Burgers vector of the dislocation (*A dislocation is born with a Burgers vector and expresses it even in its death!*)
- ❑ The Burgers vector is determined by the Burgers Circuit
- ❑ Right hand screw (finish to start) convention is used for determining the direction of the Burgers vector
- ❑ As the periodic force field of a crystal requires that atoms must move from one equilibrium position to another \Rightarrow **b** must connect one lattice position to another (*for a full dislocation*)
- ❑ *Dislocations tend to have as small a Burgers vector as possible*
- ❑ The edge dislocation has compressive stress field above and tensile stress field below the slip plane.
- ❑ *Dislocations are non-equilibrium defects and would leave the crystal if given an opportunity*

Burgers Vector

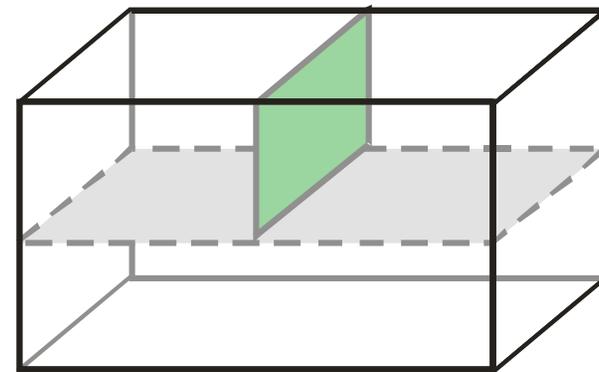
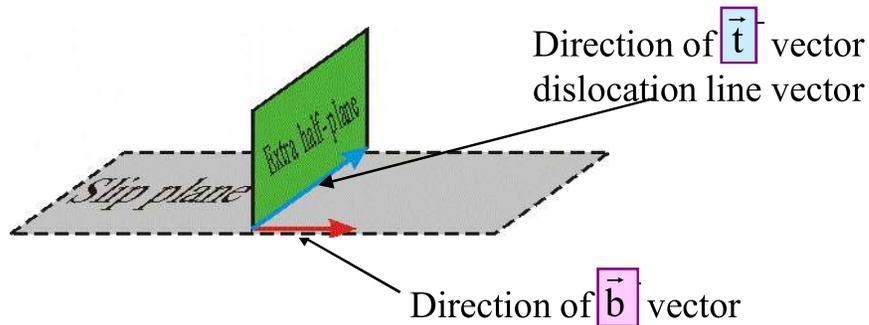


Perfect crystal

Edge dislocation



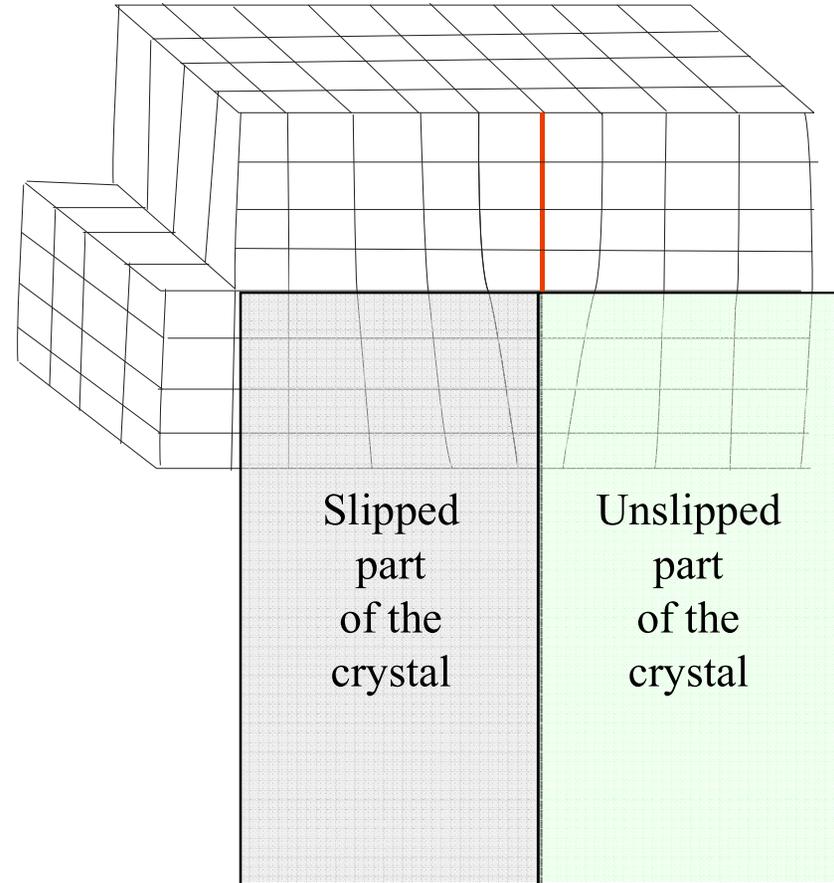
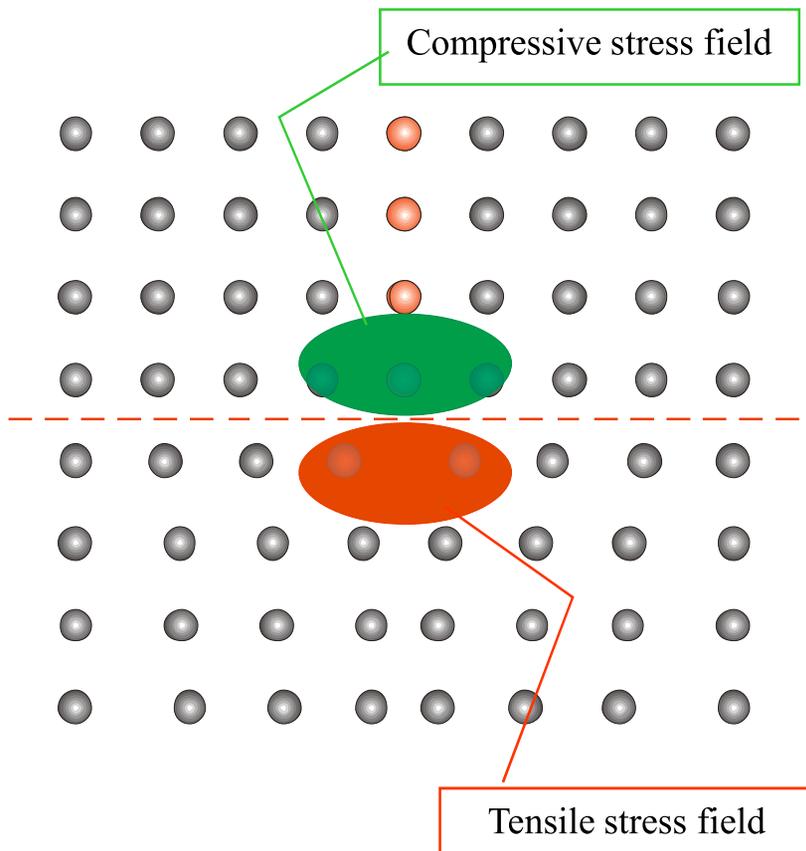
RHFS:
Right Hand Finish to Start convention



A dislocation has associated with it two vectors:

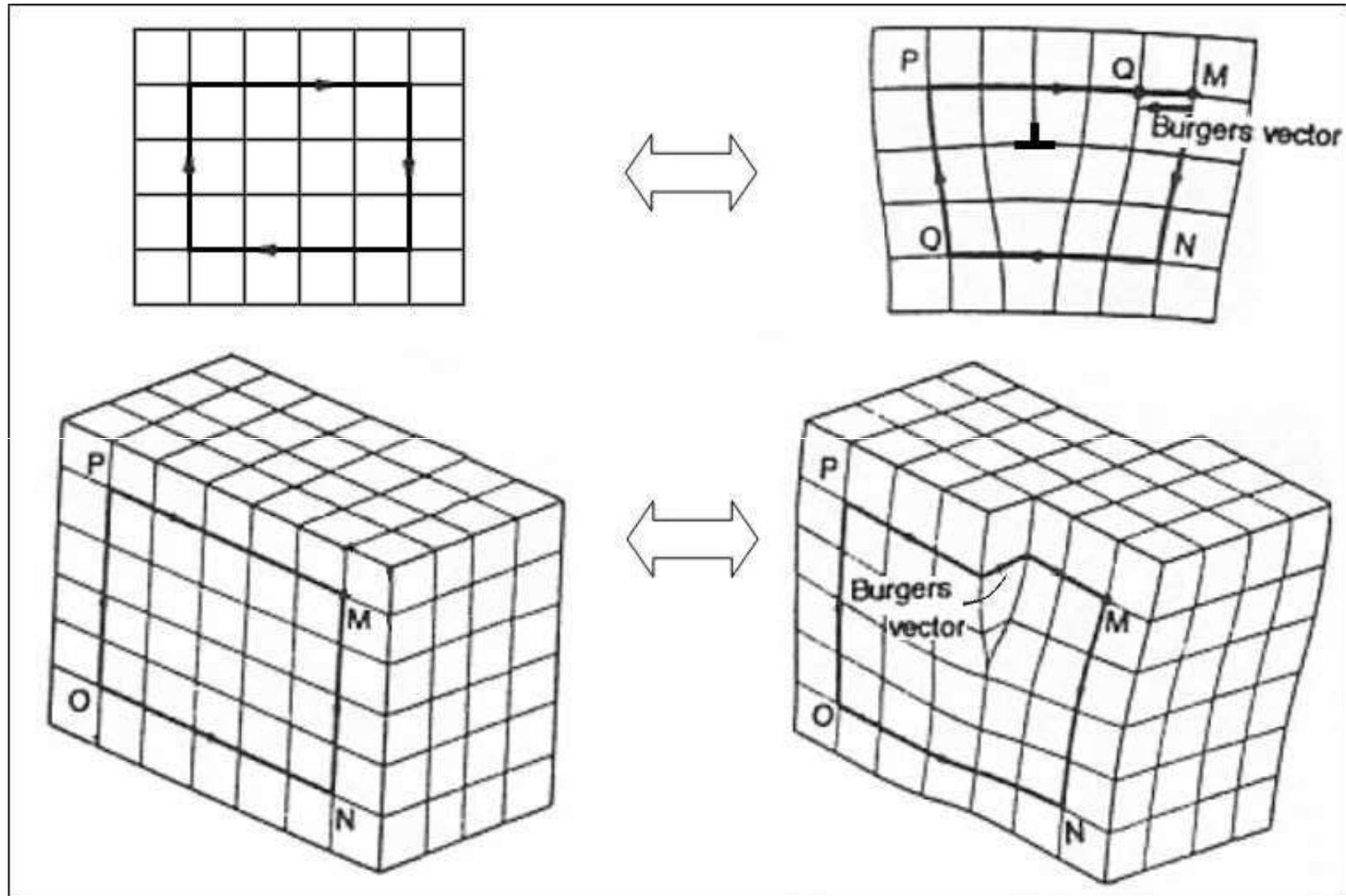
\vec{t} → A unit tangent vector along the dislocation line

\vec{b} → The Burgers vector



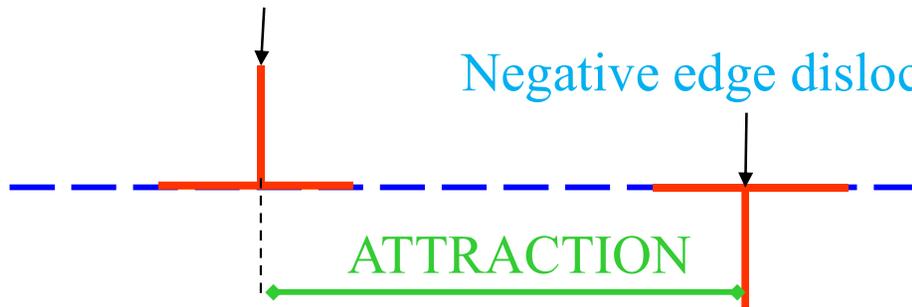
Dislocation is a boundary between the slipped and the unslipped parts of the crystal lying over a slip plane

Burgers Vector in Edge & Screw dislocations



+ve & -ve edge dislocations

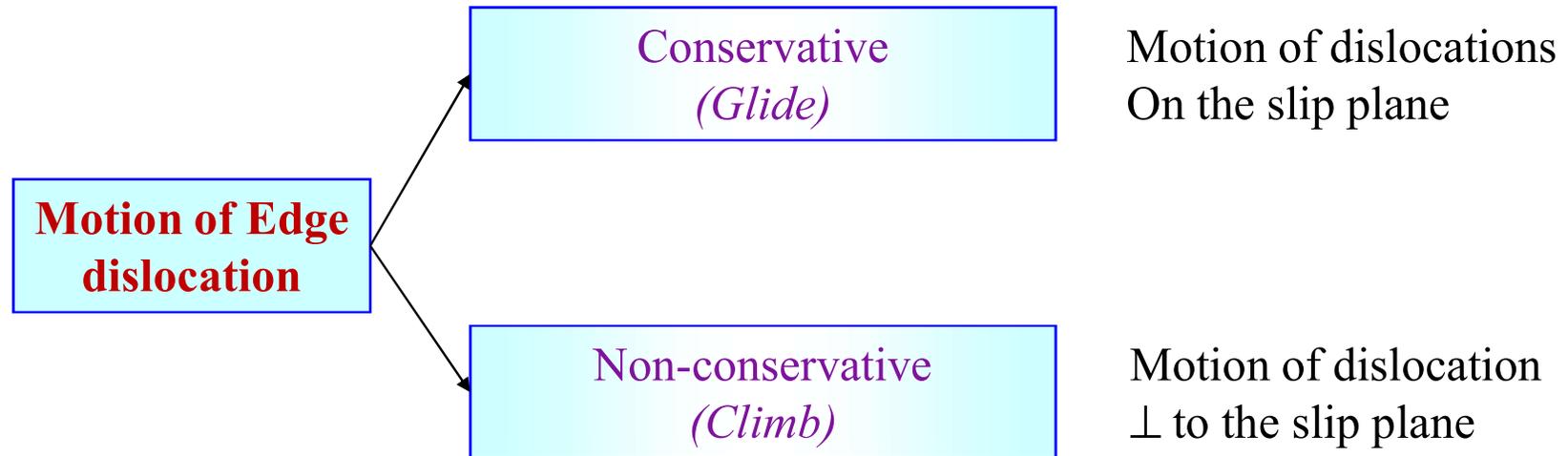
Positive edge dislocation



Can come together and cancel one another

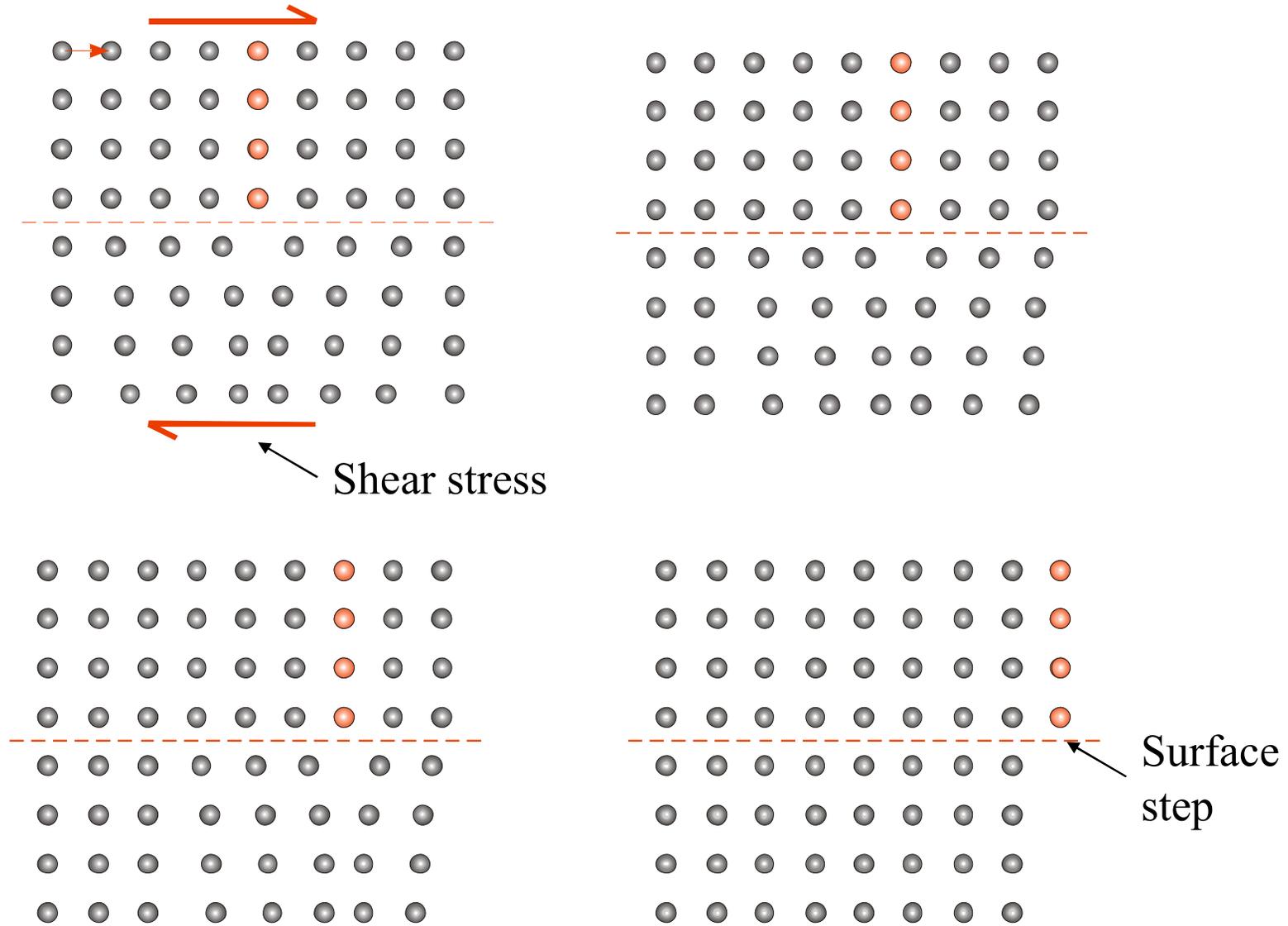


Motion of dislocations

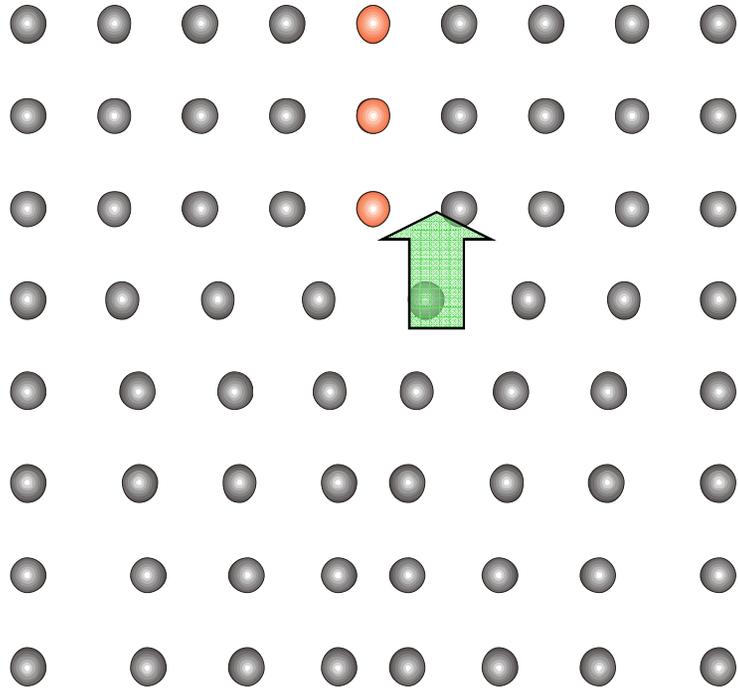


- ❑ For edge dislocation: as $\mathbf{b} \perp \mathbf{t} \rightarrow$ they define a plane \rightarrow *the slip plane*
- ❑ Climb involves addition or subtraction of a row of atoms below the half plane
 - ▶ +ve climb = climb up \rightarrow removal of a plane of atoms
 - ▶ -ve climb = climb down \rightarrow addition of a plane of atoms

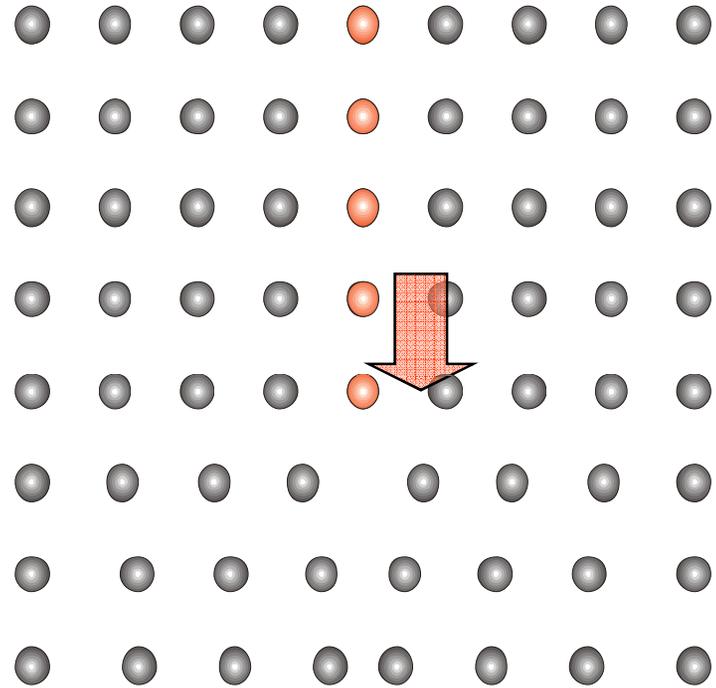
Edge Dislocation Glide



Edge Climb

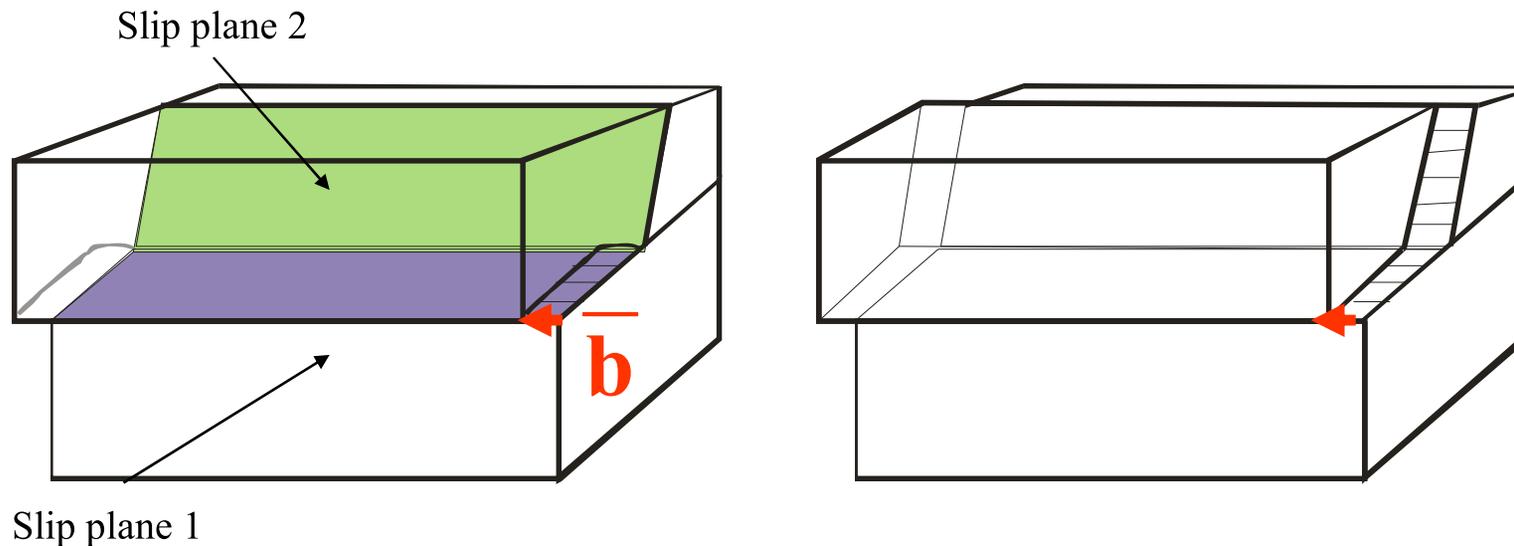


Positive climb
Removal of a row of atoms



Negative climb
Addition of a row of atoms

Screw dislocation cross-slip



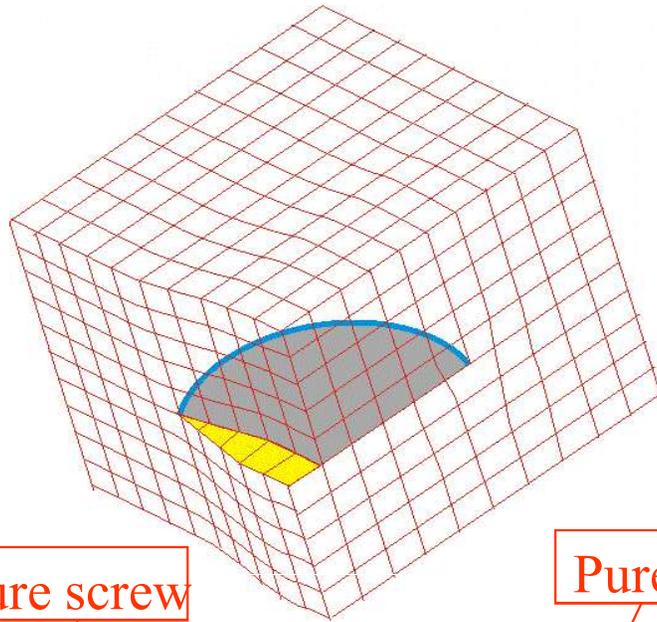
The dislocation is shown cross-slipping from the blue plane to the green plane

- The dislocation line ends on
 - ✓ The free surface of the crystal
 - ✓ Internal surface or interface
 - ✓ Closes on itself to form a loop
 - ✓ Ends in a node
- A node is the intersection point of more than two dislocations
- The vectoral sum of the Burgers vectors of dislocations meeting at a node = 0

Geometric properties of dislocations

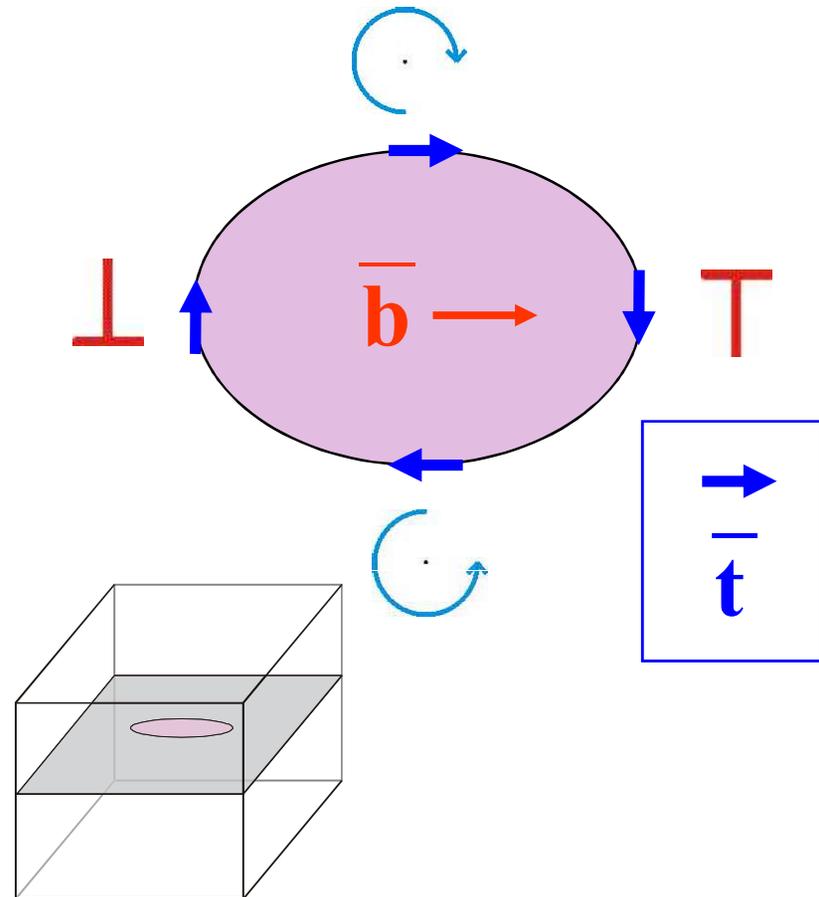
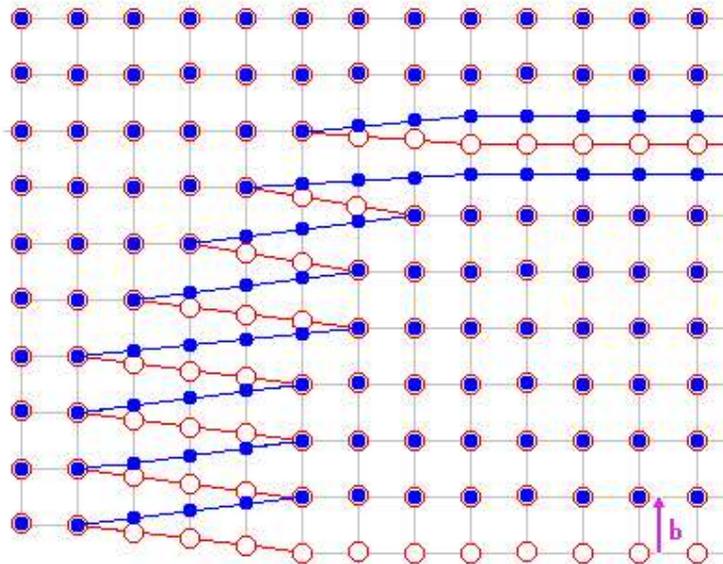
Dislocation Property	Type of dislocation	
	Edge	Screw
Relation between dislocation line (\mathbf{t}) and \mathbf{b}	\perp	\parallel
Slip direction	\parallel to \mathbf{b}	\parallel to \mathbf{b}
Direction of dislocation line movement relative to \mathbf{b}	\parallel	\perp
Process by which dislocation may leave slip plane	Glide/Climb	Cross-slip

Mixed dislocations



Pure screw

Pure Edge



We are looking at the plane of the cut (sort of a semicircle centered in the lower left corner). Blue circles denote atoms just below, red circles atoms just above the cut. Up on the right the dislocation is a pure edge dislocation on the lower left it is pure screw. In between it is mixed. In the link this dislocation is shown moving in an animated illustration.

Energy of dislocations

- ❑ Dislocations have distortion energy associated with them
- ❑ E per unit length
- ❑ Edge → Compressive and tensile stress fields
Screw → Shear strains

Energy of dislocation

Elastic

E

Non-elastic (*Core*)

~E/10

Energy of a dislocation / unit length

$$E \cong \frac{1}{2} G b^2$$

G → (μ) shear modulus
b → $|\mathbf{b}|$

Dislocations will have as small \mathbf{b} as possible

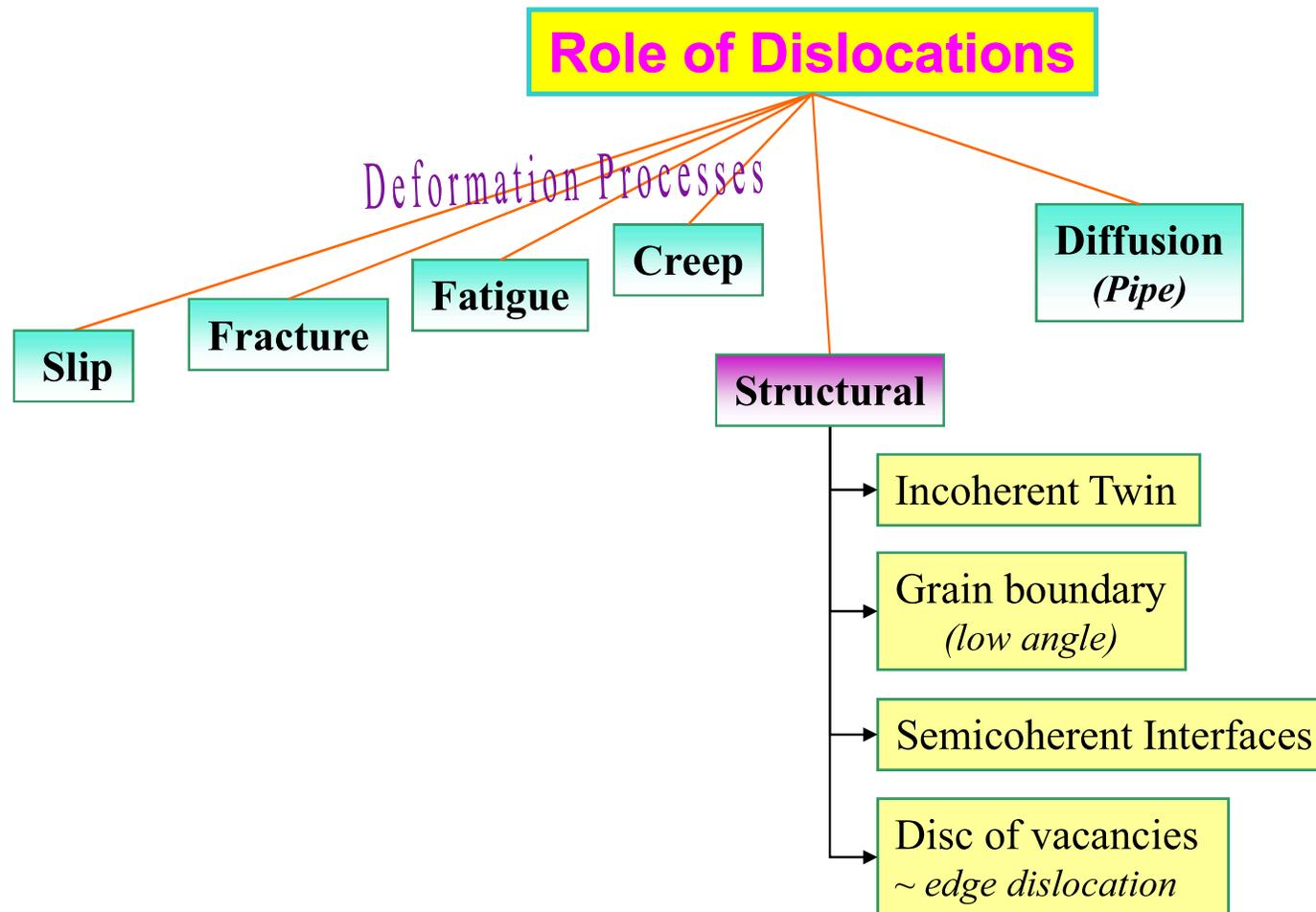
Dislocations
(in terms of lattice translation)

Full

\mathbf{b} → Full lattice translation

Partial

\mathbf{b} → Fraction of lattice translation

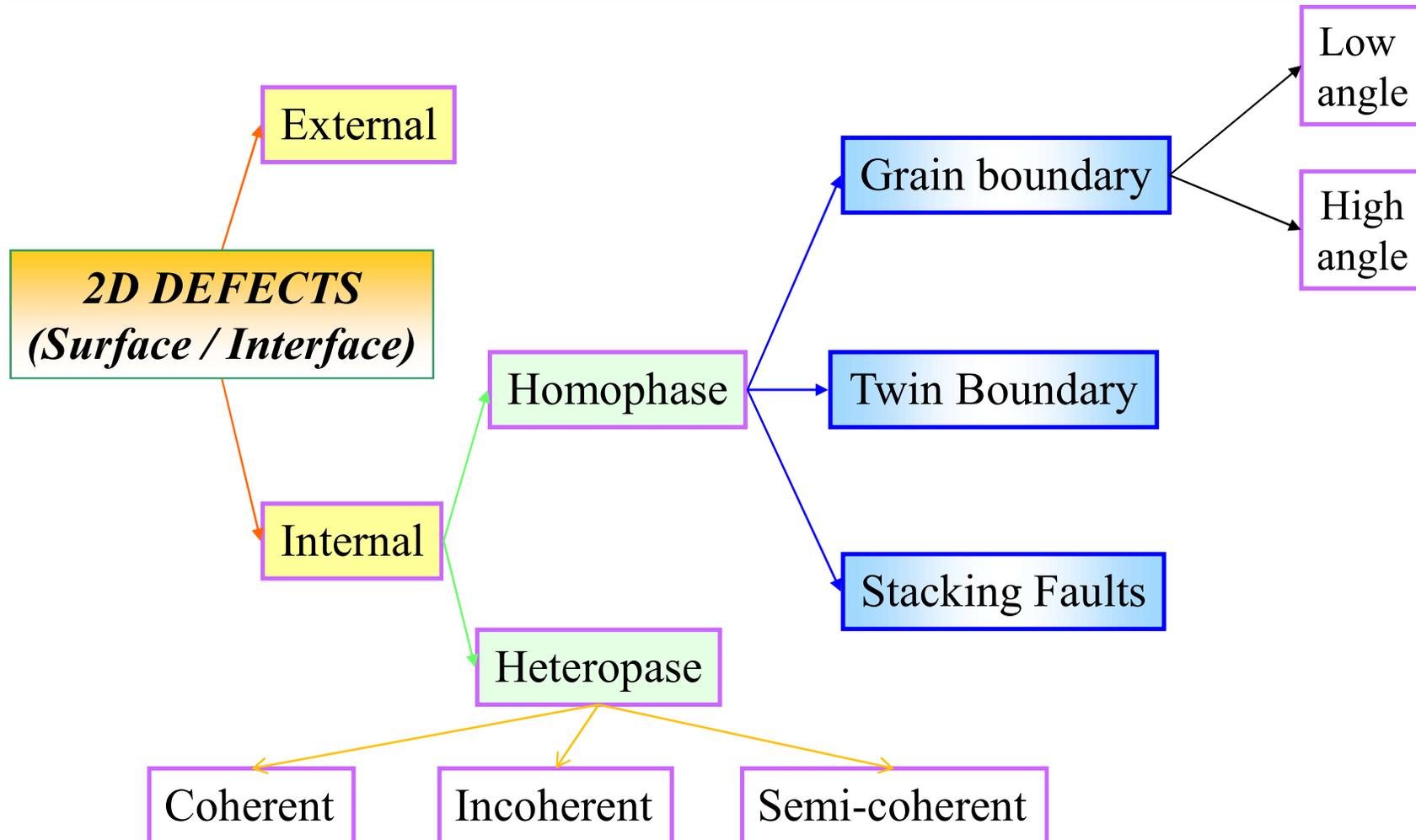


Formation of dislocations (in the bulk of the crystal)

- Due to accidents in crystal growth from the melt
- Mechanical deformation of the crystal

2D Defects : Surface defects

- ❑ 2D in a mathematical sense
- ❑ The region of distortion is \sim few atomic diameters in thickness

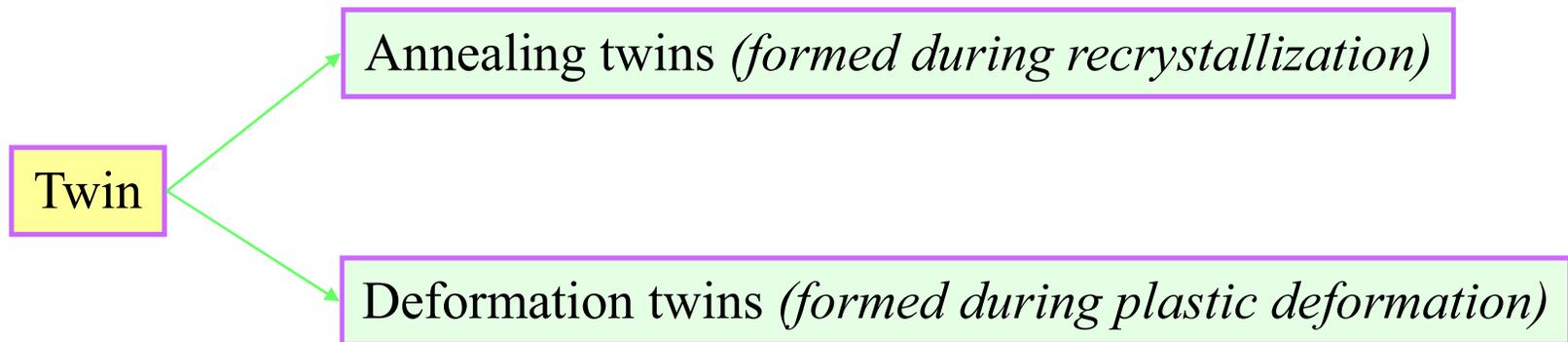


Grain Boundary

- ❑ The grain boundary region may be distorted with atoms belonging to neither crystal
- ❑ The thickness may be of the order of few atomic diameters
- ❑ The crystal orientation changes abruptly at the grain boundary
- ❑ In an low angle boundary the orientation difference is $< 15^\circ$
- ❑ In the low angle boundary the distortion is not so drastic as the high-angle boundary \rightarrow can be described as an array of dislocations
- ❑ Grain boundary energy is responsible for grain growth on heating $\sim (>0.5T_m)$
- ❑ Large grains grow at the expense of smaller ones
- ❑ The average no. of nearest neighbours for an atom in the grain boundary of a close packed crystal is 11

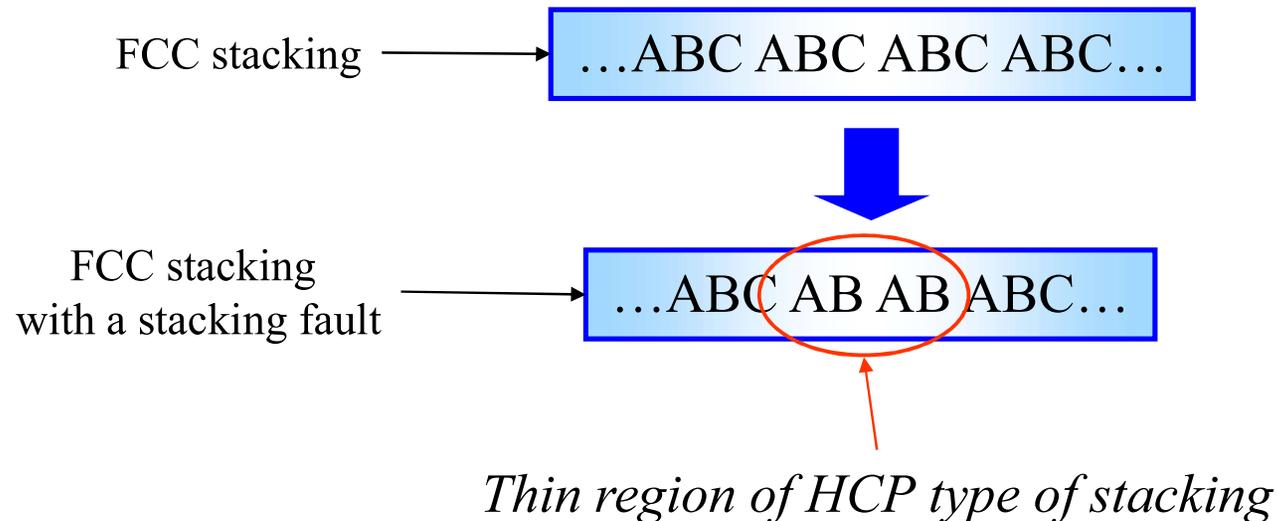
Twin Boundary

- ❑ The atomic arrangement on one side of the twin boundary is related to the other side by a symmetry operation (usually a mirror)
- ❑ Twin boundaries usually occur in pairs such that the orientation difference introduced by one is restored by the other
- ❑ The region between the regions is called the twinned region



Stacking Fault

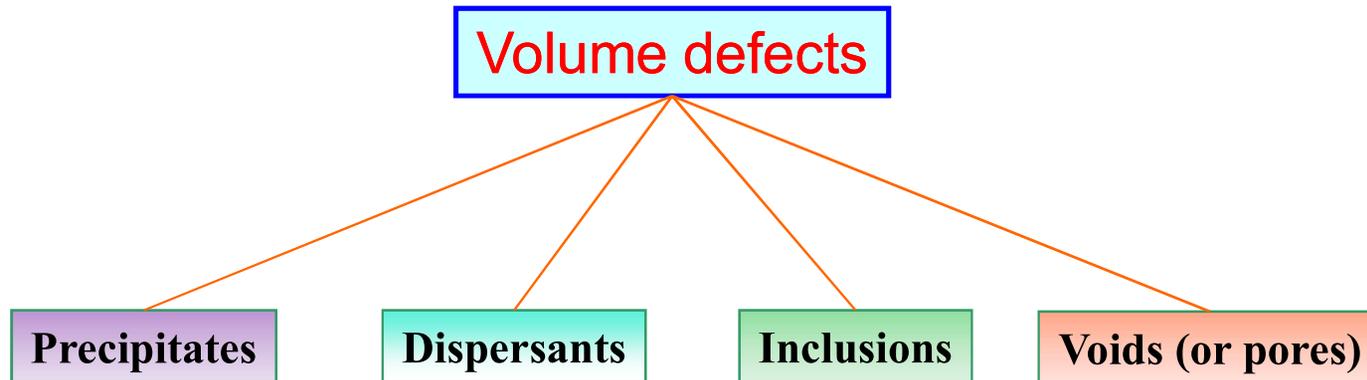
- ❑ Error in the sequence of stacking atomic planes → Stacking fault
- ❑ Defined by a shift vector



- ❑ In above the number of nearest neighbours remains the same but next-nearest neighbours are different than that in FCC
- ❑ Stacking fault energy $\sim 0.01 - 0.05 \text{ J/m}^2$
- ❑ Stacking fault in HCP can lead to thin region of FCC kind of stacking

3D Defects : volume defects

Volume defects in crystals are three dimensional aggregates of atoms or vacancies



PRECIPITATES

Precipitates are small particles that are introduced into the matrix by solid state reactions. While precipitates are used for several purposes, their most common purpose is to increase the strength of structural alloys by acting as obstacles to the motion of dislocations. Their efficiency in doing this depends on their size, their internal properties, and their distribution through the lattice. However, their role in the microstructure is to modify the behavior of the matrix rather than to act as separate phases in their own right.

3D Defects : volume defects

DISPERSANTS

Dispersants are larger particles that behave as a second phase as well as influencing the behavior of the primary phase. They may be large precipitates, grains, or polygranular particles distributed through the microstructure. When a microstructure contains dispersants such properties as mechanical strength and electrical conductivity are some average of the properties of the dispersant phase and the parent.

INCLUSIONS

Inclusions are foreign particles or large precipitate particles. They are usually undesirable constituents in the microstructure. For example, inclusions have a deleterious effect on the useful strength of structural alloys since they are preferential sites for failure. They are also often harmful in microelectronic devices since they disturb the geometry of the device by interfering in manufacturing, or alter its electrical properties by introducing undesirable properties of their own.

VOIDS (OR PORES)

Voids (or pores) are caused by gases that are trapped during solidification or by vacancy condensation in the solid state. They are almost always undesirable defects. Their principal effect is to decrease mechanical strength and promote fracture at small loads.

Plastic Deformation of Single Crystals

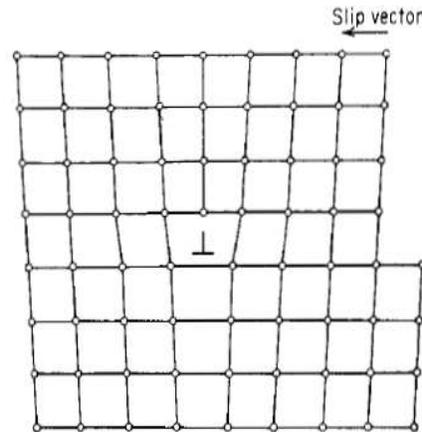


Figure Atomic arrangement in a plane normal to an edge dislocation

- Although the exact arrangement of atoms along AD is not known, it is generally agreed that Fig. closely represents the atomic arrangement in a plane normal to the edge dislocation AD.
- The plane of the paper in this figure corresponds to a (100) plane in a simple cubic lattice and is equivalent to any plane parallel to the front face of previous Figure.
- Note that the lattice is distorted in the region of the dislocation. There is one more vertical row of atoms above the slip plane than below it. The atomic arrangement results in a compressive stress above the slip plane and a tensile stress below the slip plane.
- An edge dislocation with the extra plane of atoms above the slip plane, as in Fig., by convention is called a positive edge dislocation and is frequently indicated by the symbol \perp . If the extra plane of atoms lies below the slip plane, the dislocation is a negative edge dislocation, \top .
- A pure edge dislocation can glide or slip in a direction perpendicular to its length. However, it may move vertically by a process known as climb, if diffusion of atoms or vacancies can take place at an appreciable rate.
- Consider Fig.. For the edge dislocation to move upward (positive direction of climb), it is necessary to remove the extra atom directly over the symbol \perp or to add a vacancy to this spot.
- One such atom would have to be removed for every atomic spacing; which the dislocation climbs. Conversely, if the dislocation moved down, atoms would have to be added. Atoms could be removed from the extra plane of atoms by the extra atom interacting with a lattice vacancy.
- Atoms are added to the extra plane for negative climb by the diffusion of an atom from the surrounding crystal, creating a vacancy. Since movement by climb is diffusion controlled, motion is much slower than in glide and less likely except at high temperatures.

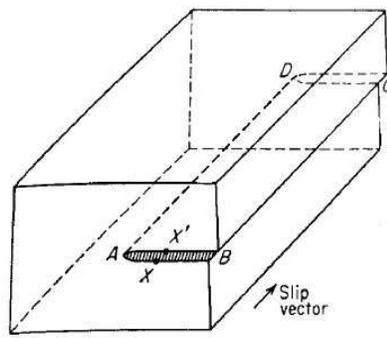


Figure Slip that produces a screw dislocation in a simple cubic lattice. Dislocation lies along AD, parallel to slip direction. Slip has occurred over the area ABCD.

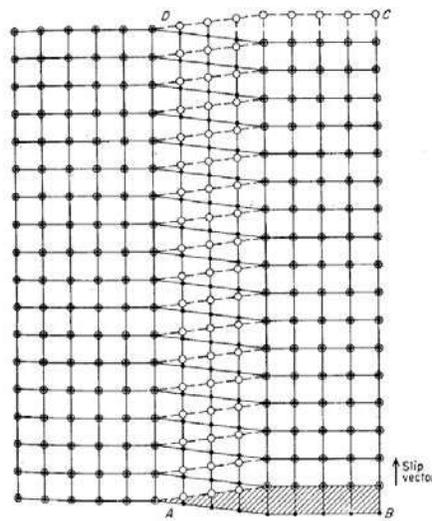


Figure Atomic arrangement around the screw dislocation shown in previous Fig.. The plane of the figure is parallel to the slip plane. A BCD is the slipped area, and AD is the screw dislocation. Open circles represent atoms in the atomic plane just above the slip plane, and the solid circles are atoms in the plane just below the slip plane.

- The second basic type of dislocation is the screw, or Burgers, dislocation. Figure shows a simple example of a screw dislocation. The upper part of the crystal to the right of AD has moved relative to the lower part in the direction of the slip vector. No slip has taken place to the left of AD, and therefore AD is a dislocation line.
- Thus, the dislocation line is parallel to its Burgers vector, or slip vector, and by definition this must be a screw dislocation. Consider the trace of a circuit around the dislocation line, on the front face of the crystal.
- Starting at X and completing a counterclockwise circuit, we arrive at X', one atomic plane behind that containing X. In making this circuit we have traced the path of a right-handed screw.
- Every time a circuit is made around the dislocation line, the end point is displaced one plane parallel to the slip plane in the lattice. Therefore, the atomic planes are arranged around the

dislocation in a spiral staircase or screw.

- The arrangement of atoms (in two dimensions) around a screw dislocation in a simple cubic lattice is shown in Fig.
- In this figure we are looking down on the slip plane in Fig.. The open circles represent atoms just above the slip plane, and the solid circles are atoms just below the slip plane. A screw dislocation does not have a preferred slip plane, as an edge dislocation has, and therefore the motion of a screw dislocation is less restricted than the motion of an edge dislocation. However, movement by climb is not possible with a screw dislocation.

DEFORMATION BY SLIP

- The usual method of plastic deformation in metals is by the sliding of blocks of the crystal over one another along definite crystallographic planes, called **slip planes**.
- As a very crude approximation, the slip, or glide of a crystal can be considered analogous to the distortion produced in a deck of cards when it is pushed from one end.

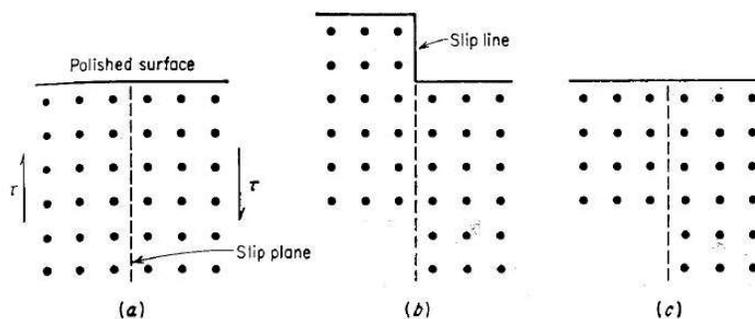


Figure 4-11 Schematic drawing of classical idea of slip.

- **Figure** illustrates this classical picture of slip.
- In Fig. 4- 11a, a shear stress is applied to a metal cube with a top polished surface. Slip occurs when the shear stress exceeds a critical value.
- The atoms move an integral number of atomic distances along the slip plane, and a step is produced in the polished surface (Fig. 4-11b).
- When we view the polished surface from above with a microscope, the step shows up as a line, which we call a slip line. If the surface is then repolished after slip has occurred, so that the step is removed, the slip line will disappear (Fig. 4-11c).
- Because of the translational symmetry of a crystal lattice, the crystal structure is perfectly restored after slip has taken place provided that the deformation was uniform.
- Note that slip lines are due to changes in surface elevation and that the surface must be suitably prepared for microscopic observation prior to deformation if the slip lines are to be observed. Figure 4-12 shows straight slip lines in copper.

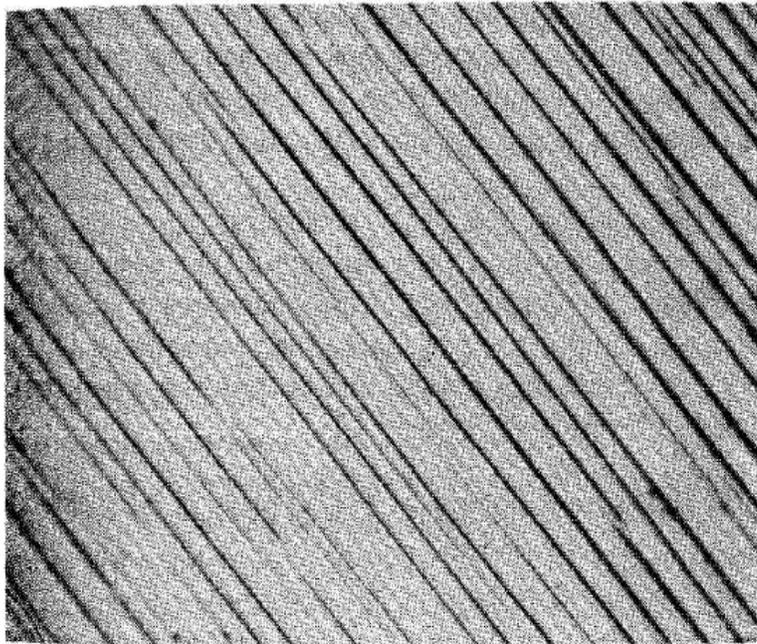


Figure 4-12 Straight slip lines in copper (500 ×). (Courtesy W. L. Phillips.)

The fine structure of slip lines has been studied at high magnification by means of the electron microscope. What appears as a line, or at best a narrow band at 1,500 diameters' magnification in the optical microscope can be resolved by the electron microscope as discrete slip lamellae at 20,000 diameters, shown schematically in Fig. 4-13.

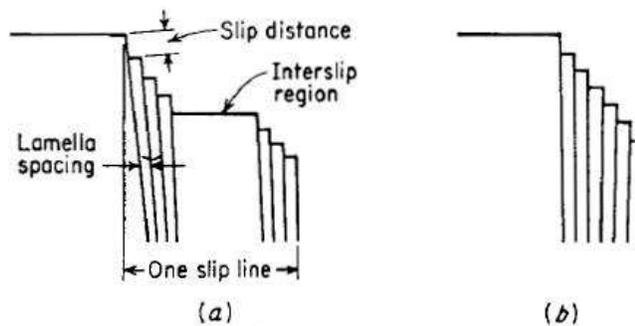


Figure Schematic drawing of the line structure of a slip band, (a) **Small deformation**; (b) **large deformation**

- Slip occurs most readily in specific directions on certain crystallographic planes.
- The **slip plane** together with the **slip direction** establishes the **slip system**

HCP System

- In the **hexagonal close-packed metals**, the only plane with high atomic density is the basal plane (0001). The axes $\langle 1120 \rangle$ are the close-packed directions.
- For zinc, cadmium, magnesium, and cobalt slip occurs on the (0001) plane in the $\langle 1120 \rangle$ directions.1 since there is only one basal plane per unit cell and three $\langle 1120 \rangle$ directions.
- The **hcp structure** possesses **three slip** systems.
- The **limited number of slip systems** is the reason for the **extreme orientation dependence and low ductility in hcp crystals**.
- **Zirconium** and **titanium**, which have low **c/a ratios**, slip primarily on the prism and pyramidal planes in the $\langle 1120 \rangle$ direction.

FCC System

- In the **face-centered cubic** structure, the **{111} octahedral planes** and the $\langle 110 \rangle$ directions are the close-packed systems.
- There are **eight {111} planes** in the fcc unit cell. However, the planes at opposite faces of the **octahedron are parallel** to each other, so that there are only **four sets of octahedral planes**.
- **Each {111} plane contains three $\langle 110 \rangle$ directions** (the reverse directions being neglected).
- Therefore, the **fcc lattice has 12 possible slip systems**.

BCC System

- The bcc structure is not a close-packed structure like the fcc or hcp structures.
- Accordingly, there is **no one plane of predominant atomic density**, as (111) in the fcc structure and (0001) in the hcp structure.
- The {110} planes have the **highest atomic density in the bcc structure**, but they are **not greatly superior** in this respect to several other planes.
- However, in the **bcc structure the (111) direction** is just as **close-packed** as the (110) and (1120) directions in the fcc and hcp structures.
- Therefore, the **bcc metals** obey the general rule that **the slip direction is the close-packed direction**, but they differ from most **other metals by not having a definite single slip plane**.
- Slip in bcc metals is found to occur on the **{110}, {112}, and {123} planes**, while the **slip direction is always the [111] direction**.
- There are **48 possible slip systems**, but since the planes are not **so close-packed** as in the fcc structure, higher shearing stresses are usually required to cause slip.
- Slip lines in bcc metals have a wavy appearance.
- This is due to the fact that **slip occurs on several planes, {110}, {112}, {123}** but always in the **close-packed (111) direction** which is common to each of these planes.

- Dislocations can readily **move from one type of plane to another by cross slip**, giving rise to **the irregular wavy slip bands**.

Slip in a perfect lattice

- If slip is assumed to occur by the translation of one plane of atoms over another, it is possible to make a reasonable estimate of the shear stress required for such a movement in a perfect lattice.
- Consider two planes of atoms subjected to a homogeneous shear stress (Fig. 4-14). The shear stress is
- assumed to act in the slip plane along the slip direction. The distance between atoms in the slip directions is **b**, and the spacing between adjacent lattice planes is **a**. The shear stress causes a displacement **x** in the slip direction between the pair of adjacent lattice planes.

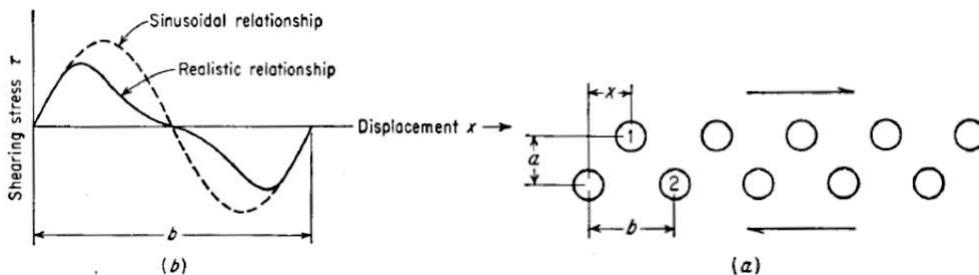


Figure (a) Shear displacement of one plane of atoms over another atomic plane; (b) variation of shearing stress with displacement in slip direction.

- The shearing stress is initially zero when the two planes are in coincidence, and it is also zero when the two planes have moved one identity distance b , so that point 1 in the top plane is over point 2 on the bottom plane.
- The shearing stress is also zero when the atoms of the top plane are midway between those of the bottom plane, since this is a symmetry position.
- Between these positions each atom is attracted toward the nearest atom of the other row, so that the shearing stress is a periodic function of the displacement.
- As a first approximation, the relationship between shear stress and displacement can be expressed by a sine function

$$\tau = \tau_m \sin \frac{2\pi x}{b}$$

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

➤ Where τ the amplitude of the sine wave and b is the period. At small values of displacement, Hooke's law should apply.

➤ For small values of x/b , Eq. (4-2) can be written

$$\tau \approx \tau_m \frac{2\pi x}{b}$$

➤ Combining Eqs. provides an expression for the maximum shear stress at which slip should occur.

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

➤ As a rough approximation, b can be taken equal to a , with the result that the theoretical **shear strength of a perfect crystal is approximately equal to the shear modulus divided by 2π** .

Slip by Dislocation Movement

- The concept of the dislocation was first introduced to explain the discrepancy between the observed and theoretical shear strengths of metals.
- For the dislocation concept to be valid it is necessary to show
- (1) that the motion of a dislocation through a crystal lattice requires a stress far smaller than the theoretical shear stress, and
- (2) That the movement of the dislocation produces a step, or slip band, at the free surface.
- In a perfect lattice all atoms above and below the slip plane are in minimum energy positions.
- When a shear stress is applied to the crystal, the same force opposing the movement acts on all the atoms. This is the model for slip presented in **Fig.**

- When there is a dislocation in the crystal, the atoms well away from the dislocation are still in the minimum energy positions but at the dislocation only a small movement of the atoms is required.
- Referring to Fig. 4-15a, the extra plane of atoms at the edge dislocation initially is at **4**.
- Under the action of the shear stress, a very small movement of atoms **to the right** will allow this **half plane** to line up with the **half plane 5'**, at the same time cutting the half plane 5 from its neighbors below the slip plane.

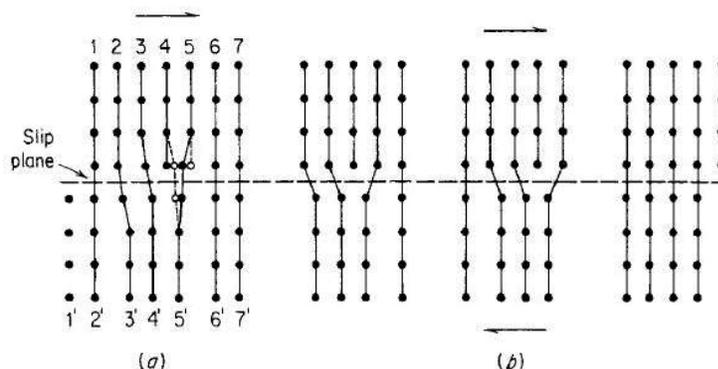


Figure (a) Atom movements near dislocation in slip; (b) movement of an edge dislocation.

- By this process the edge dislocation line has moved from its initial position between planes **4'** and **5'** to a new position between planes **5'** and **6'**.
- Since the atoms around the dislocations are symmetrically placed on opposite sides of the extra half plane, equal and opposite forces oppose and assist the motion.
- Thus, in a first approximation there is no net force on the dislocation and the stress required to move the dislocation is zero.
- The continuation of this process under the stresses shown in Fig. 4-15 moves the dislocation to the right.
- When the extra half plane of atoms reaches a free surface (Fig. 4-15b), it results in a slip step of one Burgers vector, or one atomic distance for the simple cubic lattice.

PEIERLS-NABARRO FORCE

- The dislocation width is important because it determines the force required to move a dislocation through the crystal lattice.
- This force is called the **Peierls - Nabarro force**. **The Peierls stress is the shear stress required to move a dislocation through a crystal lattice in a particular direction.**

$$\tau_p \approx \frac{2G}{1-\nu} e^{-2\pi w/b} \approx \frac{2G}{1-\nu} e^{-[2\pi a/(1-\nu)b]}$$

Where **a** is the distance between slip planes and **b** is the distance between atoms in the slip direction.

CRITICAL RESOLVED SHEAR STRESS FOR SLIP

The extent of slip in a single crystal depends on

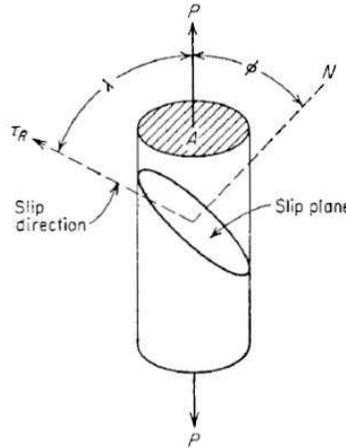
The magnitude of the shearing stress produced by external loads,

The geometry of the crystal structure,

and The orientation of the active slip planes with respect to the shearing stresses

- Slip begins when the shearing stress on the slip plane in the slip direction reaches a threshold value called the **critical resolved shear stress**.
- This value is really the single-crystal equivalent of the yield stress of an ordinary stress-strain curve.
- The value of the critical resolved shear stress depends mainly on composition and temperature.

- The fact that different tensile loads are required to produce slip in single crystals of different orientation can be rationalized by a critical resolved shear stress; this was first recognized by **Schmid**.
- To calculate the critical resolved shear stress from a single crystal tested in tension, it is necessary to know, from x-ray diffraction, the orientation with respect to the tensile axis of the plane on which slip first appears and the slip direction.



➤ **Figure Diagram for calculating critical resolved shear stress.**

- Consider a cylindrical single crystal with cross-sectional area **A**.
- The angle between the normal to the slip plane and the tensile axis is ϕ and the angle which the slip direction makes with the tensile axis is λ .
- The area of the slip plane inclined at the angle ϕ will be $A / \cos \phi$ and the component of the axial load acting in the slip plane in the slip direction is $P \cos \lambda$.
- Therefore, the critical resolved shear stress is given by:

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

- Equation (4-13) gives **the shear stress resolved on the slip plane in the slip direction**.
- If the tension axis is normal to the slip plane ($\lambda = 90^\circ$) or if it is parallel to the slip plane ($\phi = 90^\circ$), the resolved shear stress is zero.
- Slip will not occur for these extreme orientations since there is no shear stress on the slip plane.
- Crystals close to these orientations tend to fracture rather than slip.

Example:

Determine the tensile stress that is applied along the $[1\bar{1}0]$ axis of a silver crystal to cause slip on the $(1\bar{1}1)$ $[0\bar{1}1]$ system. The critical resolved shear stress is 6 MPa.

The angle between tensile axis $[1\bar{1}0]$ and normal to $(1\bar{1}1)$ is

The angle between $[1\bar{1}0]$ and slip direction $[0\bar{1}1]$ is

$$\cos \phi = \frac{(1)(1) + (-1)(-1) + (0)(-1)}{\sqrt{(1)^2 + (-1)^2 + (0)^2} \sqrt{(1)^2 + (-1)^2 + (-1)^2}} = \frac{2}{\sqrt{2}\sqrt{3}} = \frac{2}{\sqrt{6}}$$

tensile axis

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

From Eq. (4-13)

$$\sigma = \frac{P}{A} = \frac{\tau_R}{\cos \phi \cos \lambda} = \frac{6}{\frac{2}{\sqrt{6}} \times \frac{1}{2}} = 6\sqrt{6} = 14.7 \text{ MPa}$$

SCHMID LAW:

- The ratio of the resolved shear stress to the axial stress is called the Schmid factor m . For a single crystal loaded in tension or compression along its axis, $m = \cos \phi \cos \lambda$.
- It is observed experimentally that a single crystal will slip when the resolved shear stress on the slip plane reaches a critical value. This behavior, known as **Schmid's law**, is best demonstrated with hcp metals where the limited number of slip systems allows large differences in orientation between the slip plane and the tensile axis.

Deformation by Twinning

- The second important mechanism by which metals deform is the process known as twinning.
- Twinning results when a portion of the crystal takes up an orientation that is related to the orientation of the rest of the untwinned lattice in a definite, symmetrical way.

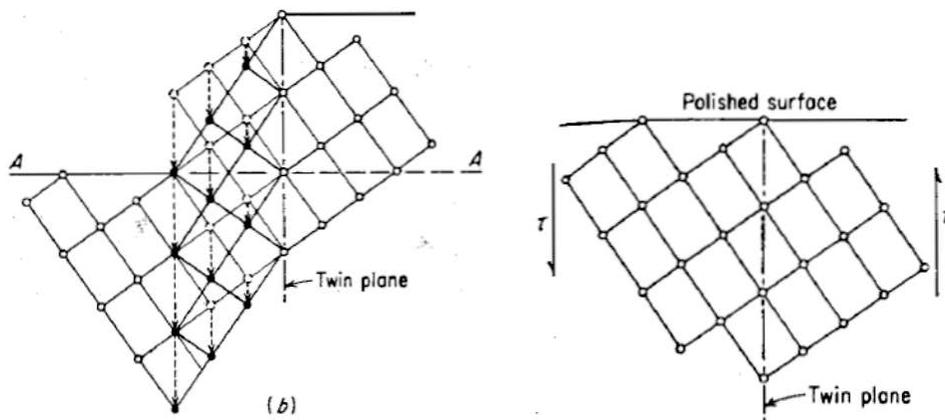


Figure Classical picture of twinning

- The twinned portion of the crystal is a mirror image of the parent crystal. The plane of symmetry between the two portions is called ***the twinning plane***.
- Figure 4-25 illustrates the classical atomic picture of twinning. Figure 4-25 a represents a section perpendicular to the surface in a cubic lattice with a low-index plane parallel to the paper and oriented at an angle to the plane of polish.
- The twinning plane is perpendicular to the paper.
- If a shear stress is applied, the crystal will twin about the twinning plane (Fig. 4-25b). The region to the right of the twinning plane is undeformed. To the left of this plane, the planes of atoms have sheared in such a way as to make the lattice a mirror image across the twin plane.
- In Fig. 4-25c, open circles represent atoms which have not moved, dashed circles indicate the original positions in the lattice of atoms which change position, and solid circles are the initial positions of these atoms in the twinned region.
- Note that the twin is visible on the polished surface because of the change in elevation produced by the deformation and because of the difference in crystallographic orientation between the deformed and undeformed regions.

Difference between Slip & Twinning

Slip	Twinning
<p>The orientation of the crystal above and below the slip plane is the same after deformation as before.</p> <p>Slip is usually considered to occur in discrete multiples of the atomic spacing</p> <p>Slip occurs on relatively widely spread planes</p> <p>Slip appears as thin lines</p> <p>There is very little change in lattice orientation and the steps are visible only on the surface of the crystal. If the steps are removed by polishing there will be no evidence that slip has taken place</p>	<p>While twinning results in an orientation difference across the twin plane. While in twinning the atom movements are much less than atomic distance. The twinned region of a crystal every atomic plane is involved in the deformation.</p> <p>While twinning appears as a board lines or bands</p> <p>In twinning, there is a different lattice orientation in the twinned region, removal of the steps by surface polishing will not destroy the evidence of twinning. Proper etching solutions, sensitive to the difference in orientation will reveal the twinned region</p>

DISLOCATION THEORY

Introduction

- A dislocation is the linear lattice defect that is responsible for nearly all aspects of the plastic deformation of metals.
- This chapter is intended to present a more complete treatment of dislocation theory. Techniques for observing dislocations in metals are discussed. The effect on dislocation behavior of considering real fcc, bcc, or hcp crystal structures are considered.
- The origin of dislocations and the mechanisms for their multiplication are discussed. Interaction of dislocations with other dislocations, vacancies, and foreign atoms is discussed in some detail.

Burgers vector and the dislocation loop

- The Burgers vector b is the vector which defines the magnitude and direction of slip. Therefore, it is the most characteristic feature of a dislocation.
- It has already been shown that for a pure edge dislocation the Burgers vector is perpendicular to the dislocation line, while for a pure screw dislocation the Burgers vector is parallel to the dislocation line.

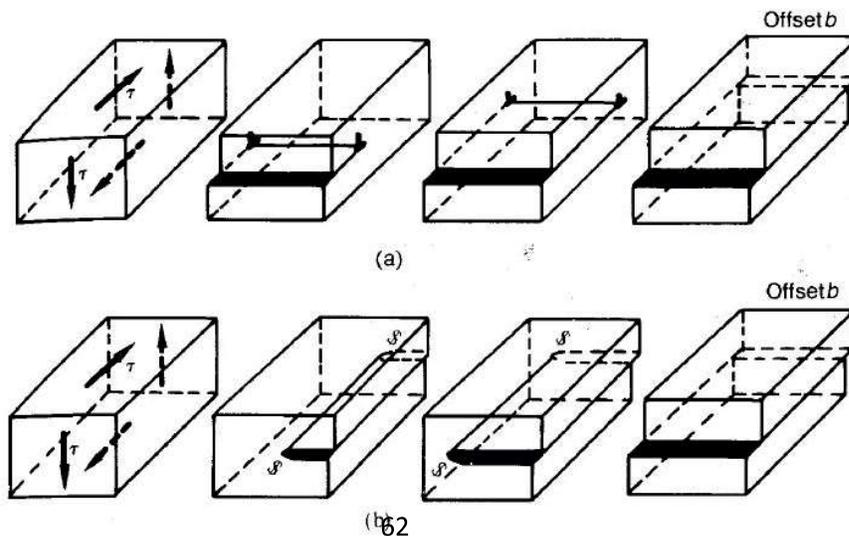


Figure 5-4 (a) Macroscopic deformation of a cube produced by glide of an edge dislocation. (b) Macroscopic deformation of a cube produced by glide of a screw dislocation. Note that the end result is identical for both situations.

- The macroscopic slip produced by the motion of an edge dislocation is shown in Fig. 5-4a and by a screw dislocation in Fig. 5-4b.
- an edge dislocation the dislocation line moves parallel to the slip direction while the screw dislocation moves at right angles to it.

Table 5-1 Geometric properties of dislocations

Dislocation property	Type of dislocation	
	Edge	Screw
Relationship between dislocation line and b	perpendicular	parallel
Slip direction	parallel to b	parallel to b
Direction of dislocation line movement relative to b (slip direction)	parallel	perpendicular
Process by which dislocation may leave slip plane	climb	cross-slip

- Actually, dislocations in real crystals are rarely straight lines and rarely lie in a single plane. In general, a dislocation will be partly edge and partly screw in character.
- example, in **Fig. 5-5**, the dislocation loop is pure screw at point A and pure edge at point B, while along most of its length it has mixed edge and screw components. Note, however, that the Burgers vector is the same along the entire dislocation loop.

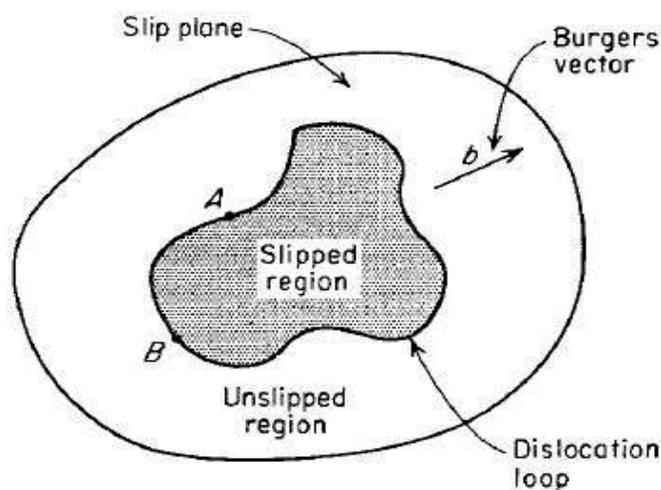


Figure 5-5 Dislocation loop lying in a slip plane (schematic).

- A convenient way of defining the **Burgers vector** of a **dislocation is with a Burgers circuit**. Consider the positive edge dislocation shown in Fig. 5-6a. If we **start at a lattice point and**

*Imagine a clockwise path traced from atom to atom an equal distance in each direction, we find that **at the finish of the path the circuit does not close.***

- *The closure failure from finish to start is the **Burgers vector b of the dislocation.** (If we had made the Burgers circuit around the dislocation in the anticlockwise direction, the direction of the Burgers vector would have been in the opposite sense.)*
- Moreover, if we traverse a **Burgers circuit about the screw dislocation** shown in Fig. 5-6b, we would find the closure error pointing out of the front face of the crystal. This is a right-handed screw dislocation since in traversing the circuit around the dislocation line; we advance the helix one atomic plane into the crystal.

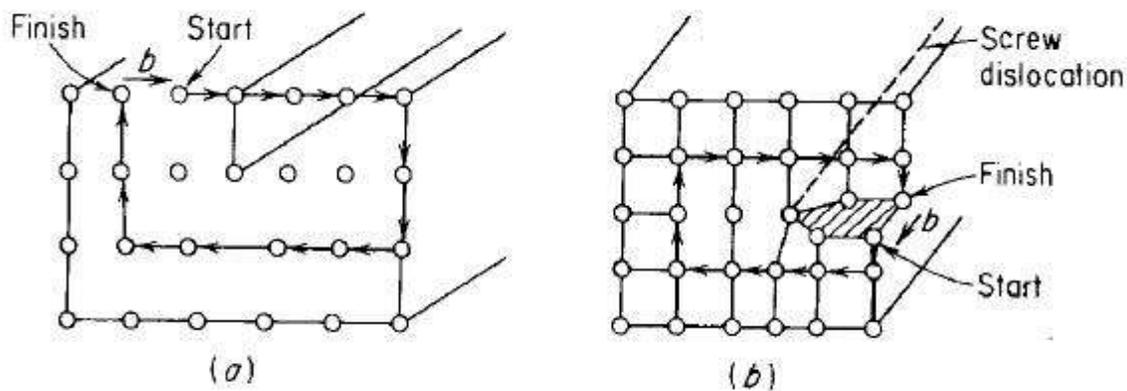


Figure 5-6 Burgers circuits, (a) **Around positive edge dislocation**, (b) **around a right-handed dislocation.**

- The process of **cross slip** illustrated in Fig. 5-7, will serve as an example of dislocation loops. In Fig. 5-7a a small loop of dislocation line with $b = a_0/2[101]$ is moving on a (111) plane in an fcc crystal.
- The dislocation loop is pure positive edge at w and pure negative edge at y. At x the dislocation is a right-handed screw while at z the dislocation loop is a pure left-handed screw dislocation. At some stage (Fig. 5-1b), the shear stress causing expansion of the loop tends to move the dislocation on the intersecting (111) plane.

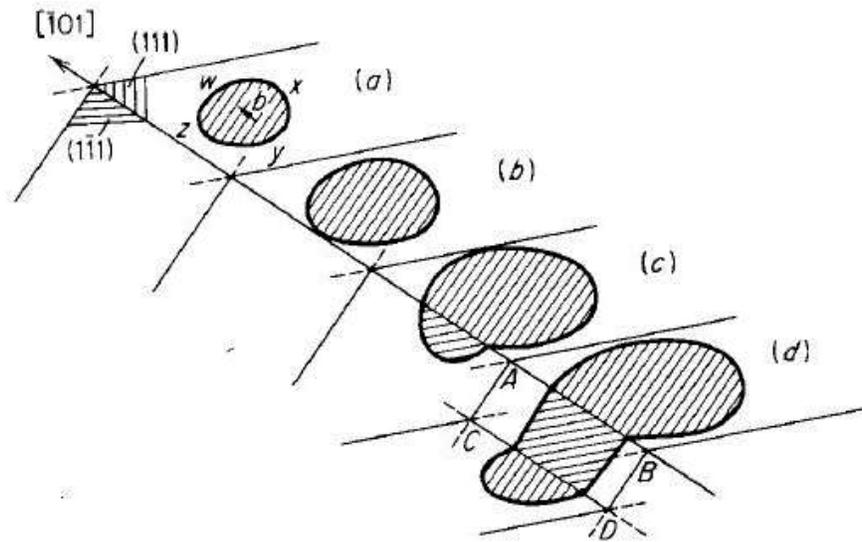


Figure 5-7 Cross slip in a face-centered cubic crystal

- Since the dislocation is pure screw at z , it is free to move on this plane. In Fig. 5-7c the loop has expanded on the second plane, while in Fig. 5-7d **double cross slip** has taken place as the loop glides back onto the original (111) plane.
- Note that during the glide of the dislocation on the cross-slip plane only the screw component of the loop has moved.

DISLOCATION CLIMB

- An edge dislocation can glide only in the slip plane containing the dislocation line and its Burgers vector. However, under certain conditions an edge dislocation can move out of the slip plane onto a parallel plane directly above or below the slip plane. This is the process of dislocation climb.
- This type of movement is termed nonconservative, as compared with conservative movement when a dislocation glides in its slip plane.

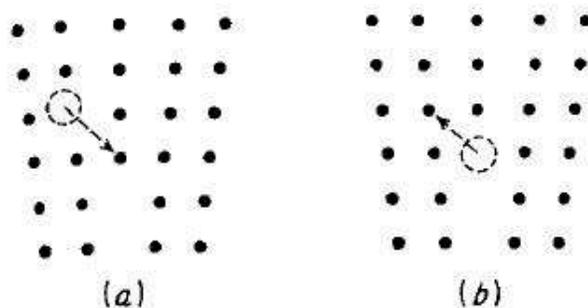


Figure 5-18 (a) Diffusion of vacancy to edge dislocation; (b) dislocation climbs up one lattice spacing.

- Dislocation climb occurs by the diffusion of vacancies or interstitials to or away from the site of the dislocation. Since climb is diffusion-controlled, it is thermally activated and occurs more readily at elevated temperature. In **positive climb** atoms are removed from the extra half plane of atoms at a positive edge dislocation so that this extra half plane moves up one atom spacing.
- In negative climb a row of atoms is added below the extra half plane so that the dislocation line moves down one atom spacing.

INTERSECTION OF DISLOCATIONS

- The intersection of two dislocations produces a sharp break, a few atom spacings in length, in the dislocation line. These breaks can be of two types.
- A **jog** is a sharp break in the dislocation moving it out of the slip plane.
- A **kink** is a sharp break in the dislocation line which remains in the slip plane.

MULTIPLICATION OF DISLOCATIONS

- One of the original stumbling blocks in the development of dislocation theory was the formulation of a reasonable mechanism by which sources originally present in the metal could produce new dislocations by the process of slip.
- Moreover, if there were no source generating dislocations, cold-work should decrease, rather than increase, the density of dislocations in a single crystal. Thus, there must be a method of generating dislocations or of multiplying the number initially present to produce the high dislocation density found in cold-worked metal. The scheme by which dislocations could be generated from existing dislocations was proposed by Frank and Read¹ and is commonly called a **Frank-Read source**.
- Consider a dislocation line DD' lying in a slip plane (Fig. 5-26(3)). The plane of the figure is the slip plane. The dislocation line leaves the slip plane at points D and D', so that it is immobilized at these points. This could occur if D and D' were nodes where the dislocation in the plane of the paper intersects dislocations in other slip planes, or the anchoring could be caused by impurity atoms
- The maximum value of shear stress is required when the dislocation bulge becomes a semicircle so that R has the minimum value $1/2$ (Fig. 5-26b).
- Beyond this point R will increase and the dislocation loop will continue to expand under a decreasing stress (Fig. 5-26c). When the loop reaches Fig. 5-26d, the segments at m and n will meet and annihilate each other to form a large loop and a new dislocation (Fig. 5-26e).

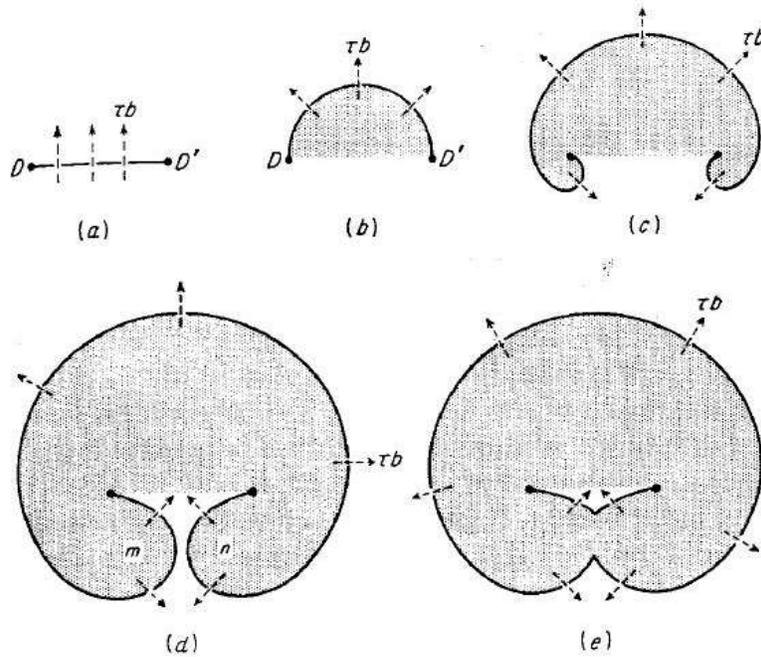


Figure 5-26 Schematic representation of the operation of a Frank-Read source.

- The stage shown in Fig. 5-26d can best be understood if we assume that the original pinned length DD' has a screw orientation. Then segments m and n are in edge orientation but of opposite sign, so that annihilation will occur. Once the loop moves into the stage shown in Fig. 5-26c, the loop can continue to expand under increased shear stress and the pinned segment DD' is in a position to repeat the process.
- This process can be repeated over and over again at a single source, each time producing a dislocation loop which produces slip of one Burgers vector along the slip plane.

YIELD-POINT PHENOMENON

- Many metals, particularly low-carbon steel, show a localized, heterogeneous type of transition from elastic to plastic deformation which produces a yield point in the stress-strain curve. Rather than having a flow curve with a gradual transition from elastic to plastic behavior, such as was shown in Fig. 3-1, metals with a yield point have a low curve or, what is equivalent, a load-elongation diagram similar Fig. 6-8.
- The load increases steadily with elastic strain, drops suddenly, fluctuates about some approximately constant value of load, and then rises with further strain. The load at which the

sudden drop occurs is called the **upper yield Point**. The constant load is called the **lower yield point**, and the elongation which occurs at constant load is called the yield-point elongation.

- The deformation occurring throughout the yield-point elongation is heterogeneous. At the upper yield point a discrete band of deformed metal, often readily visible with the eye, appears at a stress concentration such as a fillet, and coincident with the formation of the band the load drops to the lower yield point. The band then propagates along the length of the specimen, causing the yield-point elongation.
- In the usual case several bands will form at several points of stress concentration. These bands are generally at approximately 45° to the tensile axis. They are usually called **Luders bands, Hartmann lines, or stretcher strains**, and this type of deformation is sometimes referred to as the **Piobert effect**.
- The yield-point phenomenon was found originally in low-carbon steel. A pronounced upper and lower yield point and a yield-point elongation of over 10 percent can be obtained with this material under proper conditions.
- More recently the yield point has come to be accepted as a general phenomenon, since it has been observed in a number of other metals and alloys. In addition to iron and steel, yield points have been observed in polycrystalline molybdenum, titanium, and aluminum alloys and in single crystals of iron, cadmium, zinc, alpha and beta brass, and aluminum.
- Usually the yield point can be associated with small amounts of interstitial or substitutional impurities. For example, it has been shown¹ that almost complete removal of carbon and nitrogen from low carbon steel by wet-hydrogen treatment will remove the yield point. However, only about 0.001 percent of either of these elements is required for a reappearance of the yield point.
- A number of experimental factors affect the attainment of a sharp upper yield point. A sharp upper yield point is promoted by the use of an elastically rigid (hard) testing machine, very careful axial alignment of the specimen, the use of specimens free from stress concentrations, high rate of loading, and, frequently, testing at subambient temperatures.

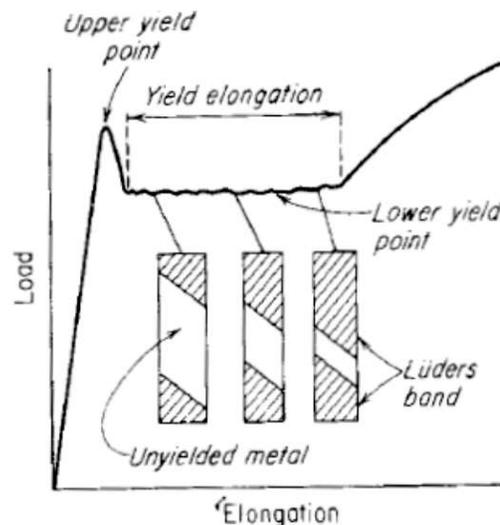


Figure 6-8 Typical yield-point behavior.

- If the stress to operate the sources is high, then the initial yield stress is high. The explanation of the yield-point phenomenon in terms of dislocation behavior arose originally from the idea that the dislocation sources were locked or pinned by solute atom interactions (Sec. 5-15).
- The explanation of this behavior was one of the early triumphs of dislocation theory. Carbon or nitrogen atoms in iron readily diffuse to the position of minimum energy just below the extra plane of atoms in a positive edge dislocation. The elastic interaction is so strong that the impurity atmosphere becomes completely saturated and condenses into a row of atoms along the core of the dislocation.
- Pinning can arise from the solute-dislocation interaction or by precipitation of fine carbides or nitrides along the dislocation. The yield point occurs as a result of unlocking the dislocations by a high stress, or for case of strong pinning, by creating new dislocations at the points of stress concentration.

ANNEALING OF COLD-WORKED METAL

- The cold-worked state is a condition of higher internal energy than the undeformed metal. Although the cold worked dislocation cell structure is mechanically stable, it is not thermodynamically stable.
- With increasing temperature the cold-worked state becomes more and more unstable. Eventually the metal softens and reverts to a strain-free condition.
- The overall process by which this occurs is known as annealing. Annealing is very important commercially because it restores the ductility to a metal that has been severely strain-hardened.
- Therefore, by interposing annealing operations after severe deformation it is possible to deform most metals to a very great extent.
- The process of annealing can be divided into three fairly distinct processes: recovery, recrystallization, and grain growth.
- Figure 6-30 will help to distinguish between these processes. Recovery is usually defined as the restoration of the physical properties of the cold-worked metal without any observable change in microstructure.

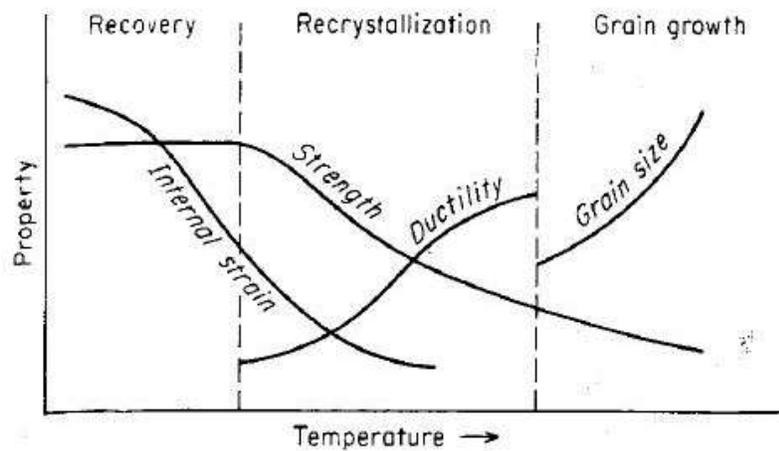
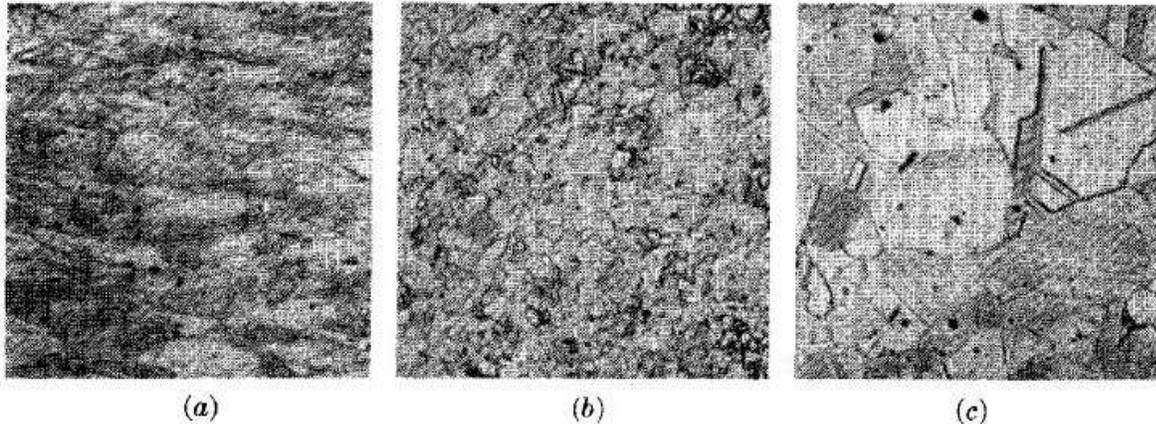


Figure 6-30 Schematic drawing indicating recovery, recrystallization, and grain growth and chief property changes in each, region.

- Electrical conductivity increases rapidly toward the annealed value during recovery, and lattice strain, as measured with x-rays, is appreciably reduced. The properties that are most affected by recovery are those which are sensitive to point defects.
- The strength properties, which are controlled by dislocations, are not affected at recovery temperatures. An exception to this is single crystals of hcp metals which have deformed on only one set of planes (easy glide)



- Figure 6-31 Changes in microstructure of cold-worked 70-30 brass with annealing, (a) Cold-worked 40 percent; (b) 440°C, 15 min; (c) 575°C, 15 min (150X)
- Recrystallization is the replacement of the cold-worked structure by a new set of strain-free grains.
- Recrystallization is readily detected by metallographic methods and is evidenced by a decrease in hardness or strength and an increase in ductility. The density of dislocations decreases considerably on recrystallization, and all effects of strain hardening are eliminated.
- The stored energy of cold-work is the driving force for both recovery and recrystallization. If the new strain-free grains are heated at a temperature greater than that required to cause re

crystallization, there will be a progressive increase in grain size.

- The driving force for grain growth is the decrease in free energy resulting from a decreased grain-boundary area due to an increase in grain size.
- Figure 6-31 shows the progression from a cold-worked microstructure to a fine recrystallized grain structure, and finally to a larger grain size by grain growth.
- **Six main variables influence recrystallization behavior. They are**
 - Amount of prior deformation,
 - Temperature,
 - Time,
 - Initial grain size,
 - Composition,
 - Amount of recovery or polygonization prior to the start of recrystallization.
- Because the temperature at which recrystallization occurs depends on the above variables, it is not a fixed temperature in the sense of a melting temperature.
- practical considerations a recrystallization temperature can be defined as the temperature at which a given alloy in a highly cold-worked state completely recrystallizes in 1 h.
- Because the driving force for grain growth is appreciably lower than the driving force for recrystallization, at a temperature at which recrystallization occurs readily grain growth will occur slowly. However, grain growth is strongly temperature-dependent, and a grain-coarsening region will soon be reached in which the grains increase in size very rapidly.

SR NO	HOT WORKING	COLD WORKING
1	Hot working is done above recrystallisation temperature	Cold working is done below recrystallisation temperature.
2	Refinement of grains takes place	Grain structure is distorted.
3	Impurities and porosity are removed from metals after hot working.	Impurities and porosities exist in metal after cold working.
4	Residual stresses are eliminated.	Residual stresses are not eliminated.
5	Rapid oxidation or scaling of surfaces occurs which results in poor surface finish.	No oxidation and hence good surface finish is obtained.
6	Close dimensional tolerances cannot be maintained.	Close dimensional tolerances can be obtained.
7	Toolling and handling costs are more.	Toolling and handling costs are less
8	Mecanical properties such as Toughness, ductility, elongation are improved.	Cold w2orking decreases elongation, reduction in area , hardness, tensile strength. Fatigue strength are improved.

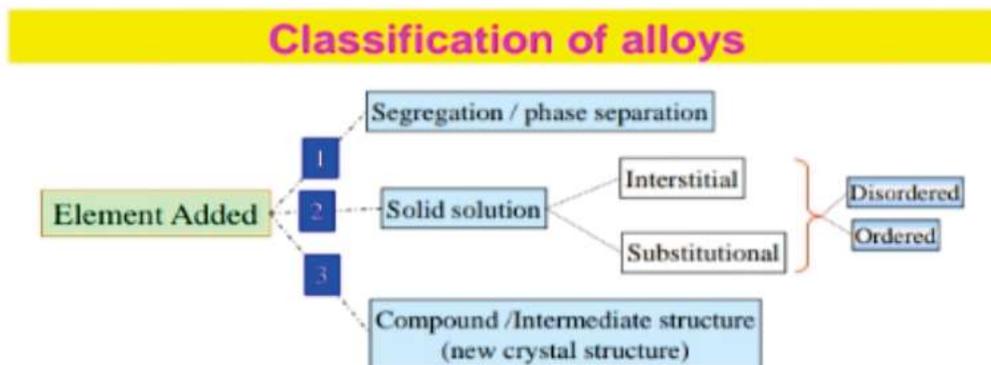
Solid Solution

Introduction

An alloy is a substance that has metallic properties and is composed of two or more chemical elements, of which at least one is a metal. An alloy system contains all the alloys that can be formed by several elements combined in all possible proportions. If the system is made up of two elements, it is called a binary alloy system; three elements, a ternary alloy system; etc. Taking only 45 of the most common metals, any combination of two gives 990 binary systems. Combinations of three give over 14,000 ternary systems. However, in each system, a large number of different alloys are possible. If the composition is varied by 1 percent, each binary system will yield 100 different alloys. Since commercial alloys often contain many elements, it is apparent that the number of possible alloys is almost infinite. Alloys may be homogeneous (uniform) or mixtures. If the alloy is homogeneous it will consist of a single phase, and if it is a mixture it will be a combination of several phases. The uniformity of an alloy phase is not determined on an atomic scale, such as the composition of each unit lattice cell, but rather on a much larger scale.

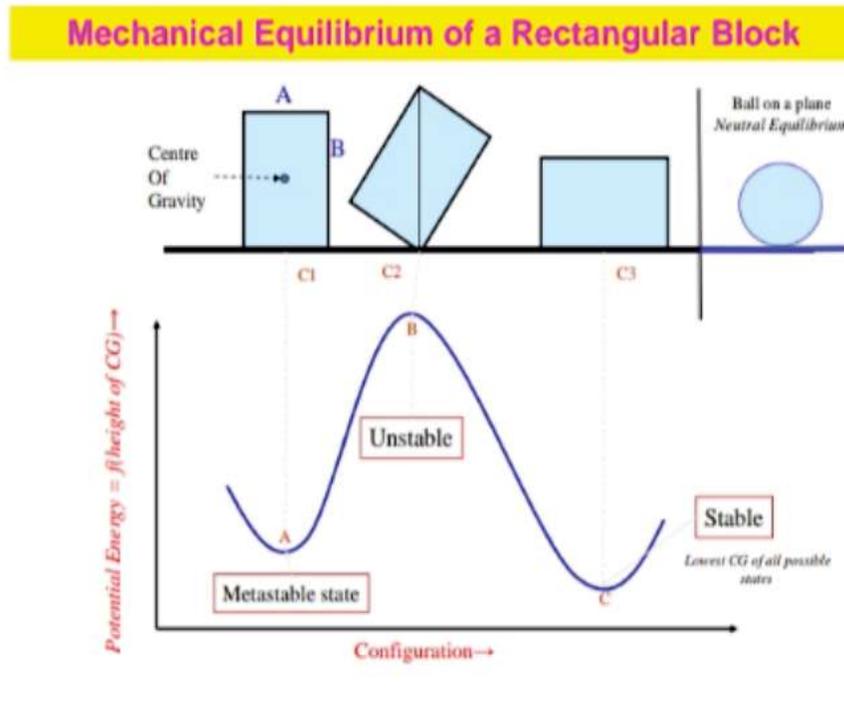
Phase

A phase is anything which is homogeneous and physically distinct. Any structure which is visible as physically distinct microscopically may be considered as a phase. For most pure elements the term phase is synonymous with state. There is, therefore, for pure elements, a gaseous, liquid, and solid phase. Some metals are allotropic in the solid state and will have different solid phases. When the metal undergoes a change in crystal structure, it undergoes a phase change since each type of crystal structure is physically distinct. In a pure material when other elements are added intentionally they are called alloying elements. Alloying elements are added to improve certain properties of the pure element. The alloying element can be accommodated in one of the three possibilities as shown in the figure below.



1. Segregation / phase separation

The added element does not dissolve* in the parent/matrix phase → in may form a separate phase** in a polycrystal it may go to the grain boundary in may segregate to other defects like dislocation cores etc. The solubility in the case of a substitutional solid solution is given by Hume-Rothery rules.



2 Solid Solutions

Temperature and pressure, it is said to be unsaturated. If it is dissolving the limiting amount of solute, it is saturated. If it is dissolving more of the solute than it should, under equilibrium conditions, the solution is supersaturated. The supersaturated condition is an unstable one, and given enough time or a little energy, the solution tends to become stable or saturated by rejecting or precipitating the excess solute. A solid solution is simply a solution in the solid state and consists of two kinds of atoms combined in one type of space lattice.

There are two types solid solutions, substitution

2.1 Substitutional solid solution

In this type of solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent. For example, silver atoms may substitute for gold atoms without losing the f.c.c structure of gold, and gold atoms may substitute for silver atoms in the f.c.c lattice structure of silver. All alloys in the silver-gold system consist of an f.c.c lattice with silver and gold atoms distributed at random through the lattice structure. This entire system consists of a continuous series of solid solutions. Several factors are now known, largely through the work of Hume-Rothery, that control the range of solubility in alloy systems. Empirical (precise) rules for the formation of substitutional solid solution are:

- The solute and solvent atoms do not differ by more than 15% in diameter
- The electro-negativity difference between the elements is small
- The valency and crystal structure of the elements is same

Additional rule

Element with higher valency is dissolved more in an element of lower valency rather than vice-versa

Hume Rothery Rules

CRYSTAL-STRUCTURE FACTOR : complete solid solubility of two elements is never attained unless the elements have the same type of crystal lattice structure.

RELATIVE-SIZE FACTOR : The size factor is favorable for solid solution formation when the difference in atomic radii is less than about 15%

VALENCY RULE : a metal will dissolve a metal of higher valency to greater extent than one of lower valency. The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.

ELECTRONEGATIVITY RULE : Electro negativity difference close to '0' gives maximum solubility. The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an inter metallic compound instead of a substitutional solid solution. The solute and the solvent should lie relatively close in the electrochemical series.

Hume Rothery Rules

Examples of pairs of elements satisfying Hume Rothery rules and forming complete solid solution in all proportions

System		Crystal structure	Radius of atoms (Å)	Valency	Electronegativity
Ag-Au	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	2.4
Cu-Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.8
Ge-Si	Ge	DC	1.22	4	1.8
	Si	DC	1.18	4	1.8

A continuous series of solid solutions may not form even if the above conditions are satisfied
e.g. Cu- γ Fe

2.2 Interstitial Solid Solutions

The second species added goes into the voids of the parent lattice E.g. Octahedral and tetrahedral voids in CCP, HCP (& BCC) crystals (E.g. of solvents: Fe, Mo, Cr etc.)

E.g.

B ($r = 0.97 \text{ \AA}$)

C ($r = 0.77 \text{ \AA}$),

N ($r = 0.71 \text{ \AA}$),

O ($r = 0.66 \text{ \AA}$),

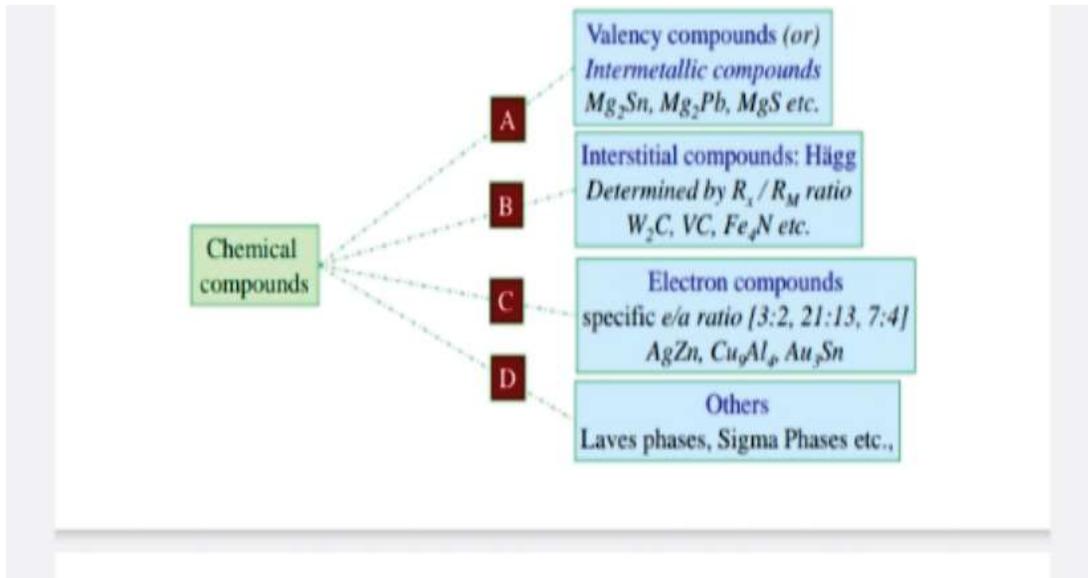
H ($r = 0.46 \text{ \AA}$)

If the solute atom has a diameter $< 0.59r$ then extensive solubility is expected (may or may not happen!) Solubility for interstitial atoms is more in transition elements (Fe, Ti, V, Zr, Ni, W, U, Mn, Cr) → due to electronic structure (incomplete inner shell) C is especially insoluble in most non-transition elements

3. Compound /Intermediate structure

Chemical compounds are combination of positive and negative valence elements. Intermetallic compounds can be very different from the normal chemical compounds (e.g. H₂O).

Most compounds like pure metals, the cooling curve for a compound is similar to that for a pure metal.



Substitutional solid solution

- Substitutional solid solutions can be of two types
 - 1. Ordered solid solution
 - 2. Disordered solid solution

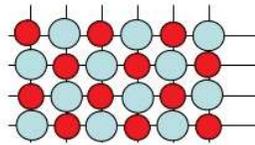
Ordered solid solution

- If the atoms of the solute occupy certain preferred sites in the lattice of the solvent, an ordered solid solution is formed. It may occur only at certain fixed ratios of the solute and solvent atoms.
- In Cu – Au system, Cu atoms occupying the face-centered sites and Au atoms occupying the corner sites of the FCC unit cell.

Ordered Substitutional solid solution

Ordered Substitutional solid solution

Substitutional
element replaces host atoms
in an orderly arrangement



e.g., Ni-Al, Al-(Li,Zr)

11

Disordered solid solution

- If the atoms of the solute are present randomly in the lattice of the solvent, it is known as disordered solid solution.
- Most of the solid solutions are disordered solid solutions

Gibbs Phase Rule

- ❑ The phase rule connects the Degrees of Freedom, the number of components in a system and the number of phases present in a system via a simple equation.
- ❑ To understand the phase rule one must understand the variables in the system along with the degrees of freedom.
- ❑ We start with a general definition of the phrase “degrees of freedom”.

Degrees of Freedom

The degree of freedom, F , are those externally controllable conditions of temperature, pressure, and composition, which are independently variable and which must be specified in order to completely define the equilibrium state of the system.

**For a system in
equilibrium**

$$F = C - P + 2$$

or

$$F - C + P = 2$$

F – Degrees of Freedom
 C – Number of Components
 P – Number of Phases

The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that can exist in equilibrium for a given system.

Gibbs Phase Rule

Variables in a phase diagram

- C – No. of components
- P – No. of phases
- F – No. of degrees of freedom
- Variables in the system = Composition variables + Thermodynamic variables
- Composition of a phase specified by $(C - 1)$ variables (*If the composition is expressed in %ages then the total is 100% → there is one equation connecting the composition variables and we need to specify only $(C - 1)$ composition variables*)
- No. of variables required to specify the composition of all phases: $P(C - 1)$ (*as there are P phases and each phase needs the specification of $(C - 1)$ variables*)
- Thermodynamic variables = $P + T$ (usually considered) = 2 (*at constant pressure (e.g. atmospheric pressure) the thermodynamic variable becomes 1*)
- Total no. of variables in the system = $P(C - 1) + 2$
- $F < \text{no. of variables} \rightarrow F < P(C - 1) + 2$

Gibbs Phase Rule

- For a system in equilibrium the chemical potential of each species is same in all the phases
 - ✓ If $\alpha, \beta, \gamma \dots$ are phases, then: $\mu_A(\alpha) = \mu_A(\beta) = \mu_A(\gamma) \dots$
 - ✓ Suppose there are 2 phases (α and β phases) and 3 components (A, B, C) in each phase then : $\mu_A(\alpha) = \mu_A(\beta), \mu_B(\alpha) = \mu_B(\beta), \mu_C(\alpha) = \mu_C(\beta) \rightarrow$ i.e. there are three equations. For each component there are $(P - 1)$ equations and for C components the total number of equations is $C(P - 1)$. In the above example the number of equations is $3(2 - 1) = 3$ equations.
 - ✓ $F = (\text{Total number of variables}) - (\text{number of relations between variables})$
 $= [P(C - 1) + 2] - [C(P - 1)] = C - P + 2$
 - ✓ In a single phase system $F = \text{Number of variables}$
 - ✓ $P \uparrow \rightarrow F \downarrow$ (For a system with fixed number of components as the number phases increases the degrees of freedom decreases.)

$$F = C - P + 2$$

It is worthwhile to clarify a few terms at this stage:

- Components 'can' go on to make a phase (*of course one can have single component phases as well e.g. BCC iron phase*)
- Phases 'can' go on to make a microconstituent.
- Microconstituents 'can' go on to make a microstructure (*of course phases can also directly go on to make a microstructure*)

Gibbs Phase Rule

A way of understanding the Gibbs Phase Rule : $P + F = C + 2$

The degrees of freedom can be thought of as the difference between *what you (can) control and what the system controls*

$$\begin{array}{c}
 \boxed{F} \\
 \uparrow \\
 \boxed{\text{Degrees of freedom}}
 \end{array}
 =
 \begin{array}{c}
 \boxed{C+2} \\
 \uparrow \\
 \boxed{\text{What you can control}} \\
 \text{Can control the no. of} \\
 \text{components added and P\&T}
 \end{array}
 -
 \begin{array}{c}
 \boxed{P} \\
 \uparrow \\
 \boxed{\text{What the system controls}} \\
 \text{System decided how many} \\
 \text{phases to produce given the} \\
 \text{conditions}
 \end{array}$$

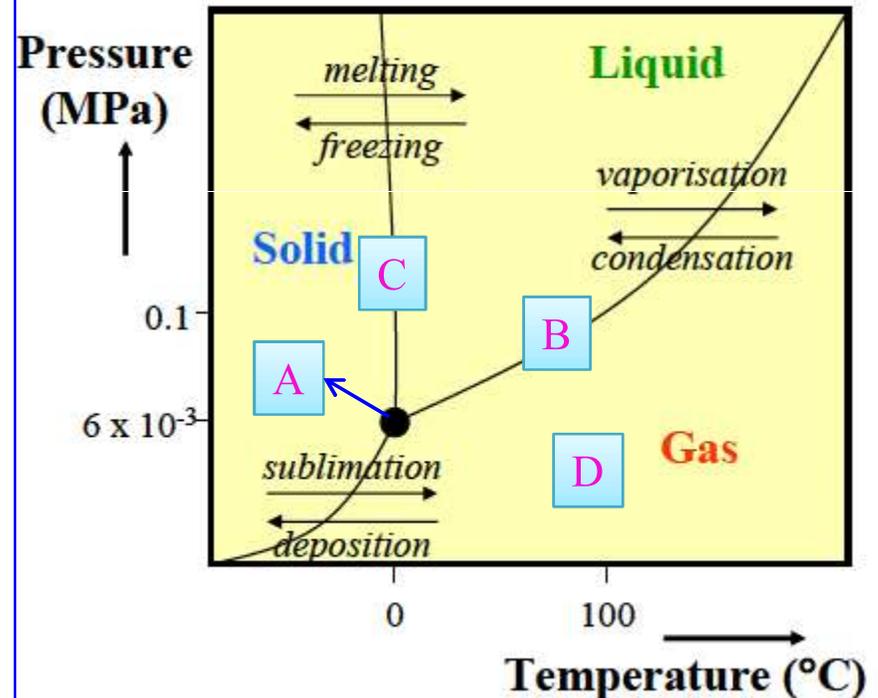
Variation of the number of degrees of freedom with number of components and number of phases

$C = 2$	No. of Phases	Total Variables $P(C-1)+2$	Degrees of freedom $C-P+2$	Degrees of freedom $C-P+1$
	1	3	3	2
2	4	2	1	
3	5	1	0	
4	6	0	<i>Not possible</i>	

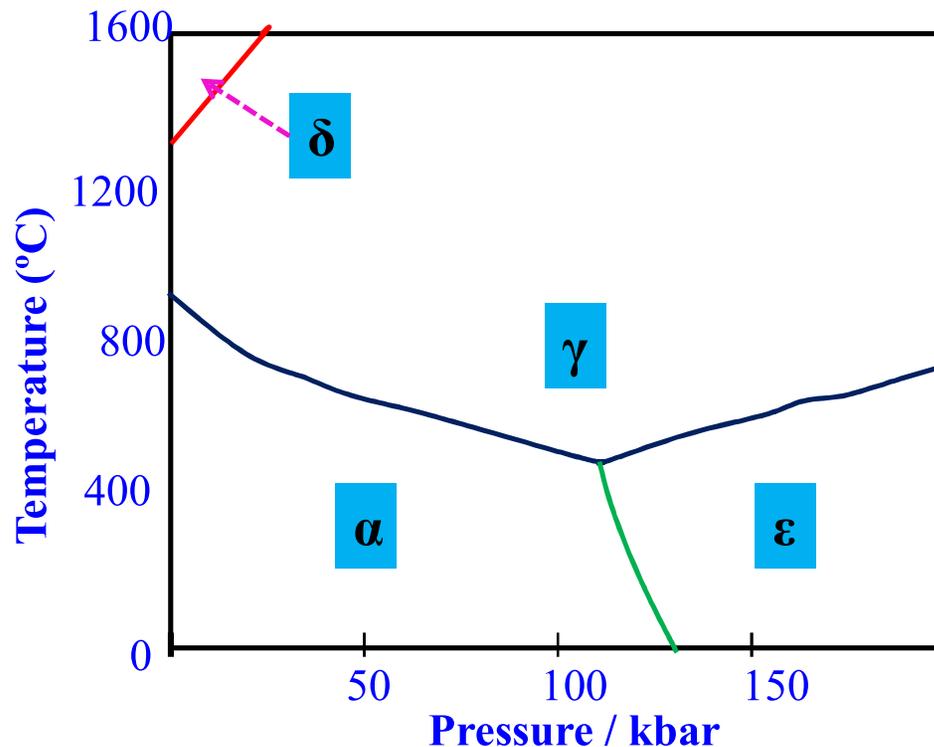
Unary Phase Diagram

- ❑ Let us start with the simplest system possible: the unary system wherein there is just one component.
- ❑ Though there are many possibilities even in unary phase diagram (in terms of the axis and phases), we shall only consider a T-P unary phase diagram.

- ❑ Let us consider the water (H_2O) unary phase diagram
- ❑ The Gibbs phase rule here is: $F=C-P+2$ (2 is for T&P) (no composition variables here)
- ❑ Along the 2 phase co-existence (at B & C) lines the degree of freedom (F) is 1 \rightarrow i.e. we can choose either T or P and the other will be automatically fixed.
- ❑ The 3 phase co-existence points (at A) are invariant points with $F=0$. (Invariant point implies they are fixed for a given system).
- ❑ The single phase region at point D, T and P can both be varied while still being in the single phase region with $F = 2$.



Unary Phase Diagram



The above figure represents the phase diagram for pure iron. The triple point temperature and pressure are 490°C and 110 kbars, respectively. α , γ and ϵ refer to ferrite, austenite and ϵ -iron, respectively. δ is simply the higher temperature designation of α .

Binary Phase Diagram

- ❑ Binary implies that there are two components.
- ❑ Pressure changes often have little effect on the equilibrium of solid phases (unless of course we apply 'huge' pressures).
- ❑ Hence, binary phase diagrams are usually drawn at 1 atmosphere pressure.
- ❑ The Gibbs phase rule is reduced to:
- ❑ Variables are reduced to : $F = C - P + 1$ (*1 is for T*).
- ❑ T & Composition (*these are the usual variables in materials phase diagrams*)

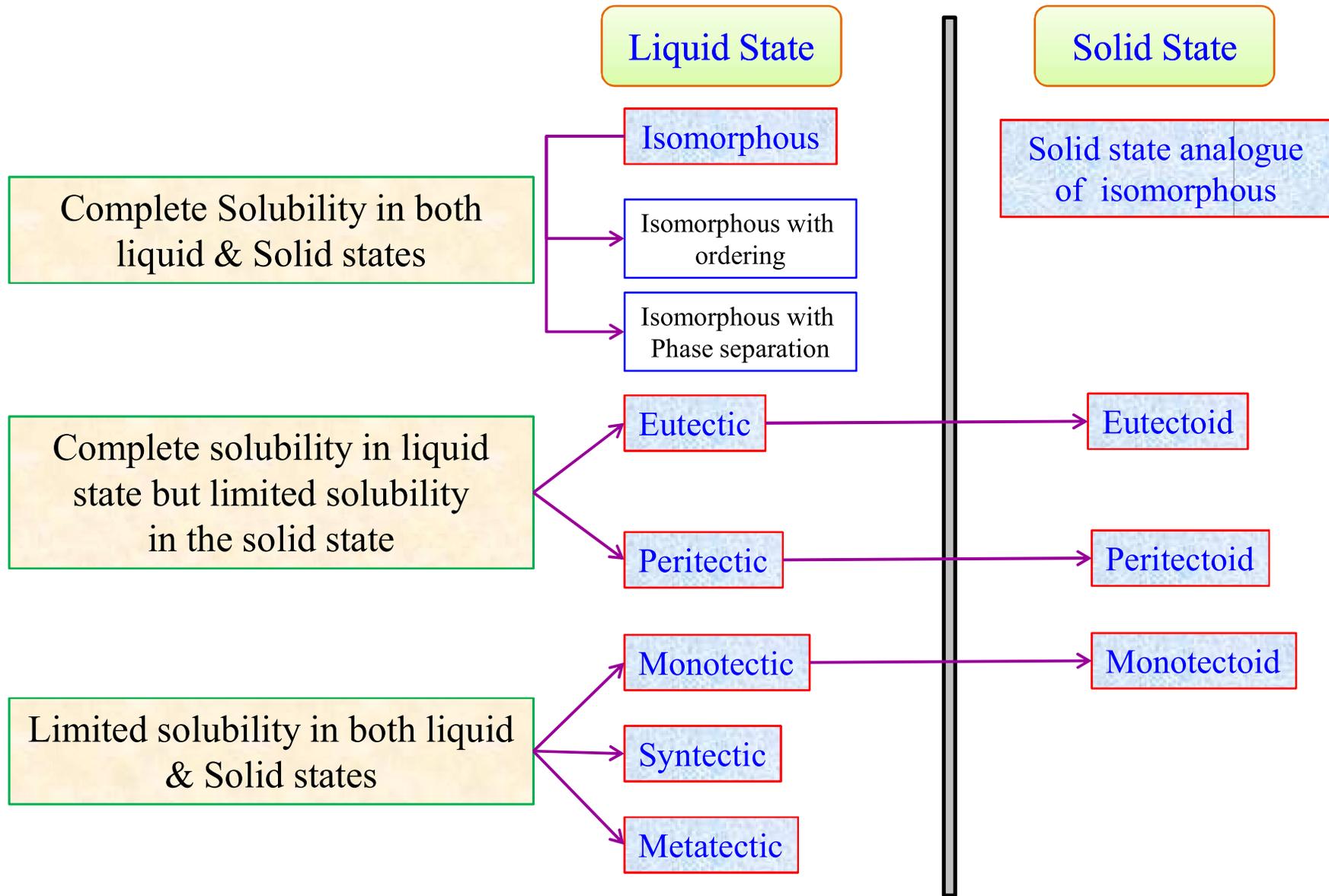
Phase rule for condensed phases

$$F = C - P + 1$$

For T

- ❑ In the next page we consider the possible binary phase diagrams. These have been classified based on:
 - ✓ Complete solubility in both liquid & solid states
 - ✓ Complete solubility in both liquid state, but limited solubility in the solid state
 - ✓ Limited solubility in both liquid & solid states

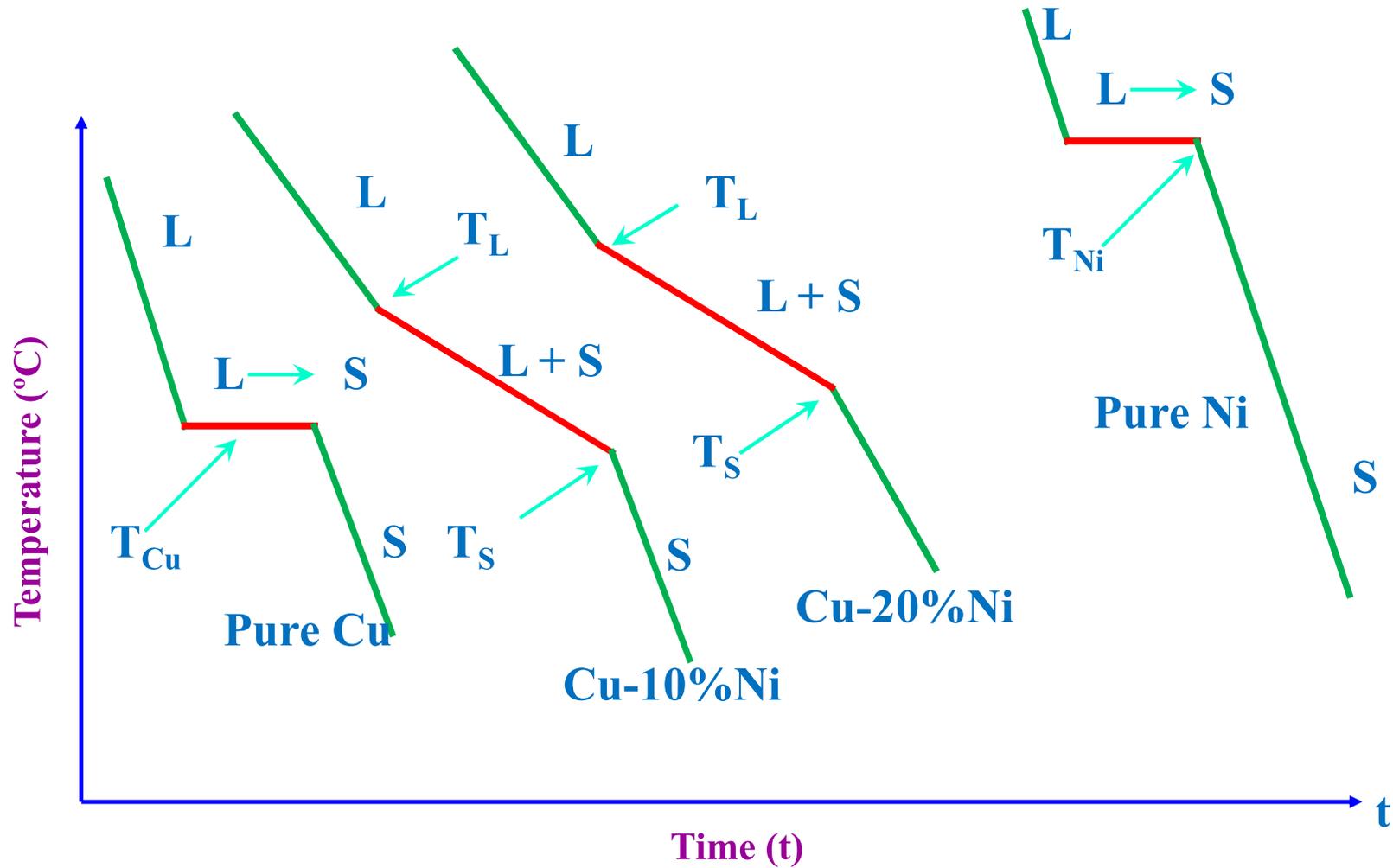
Overview of possible Binary Phase Diagram



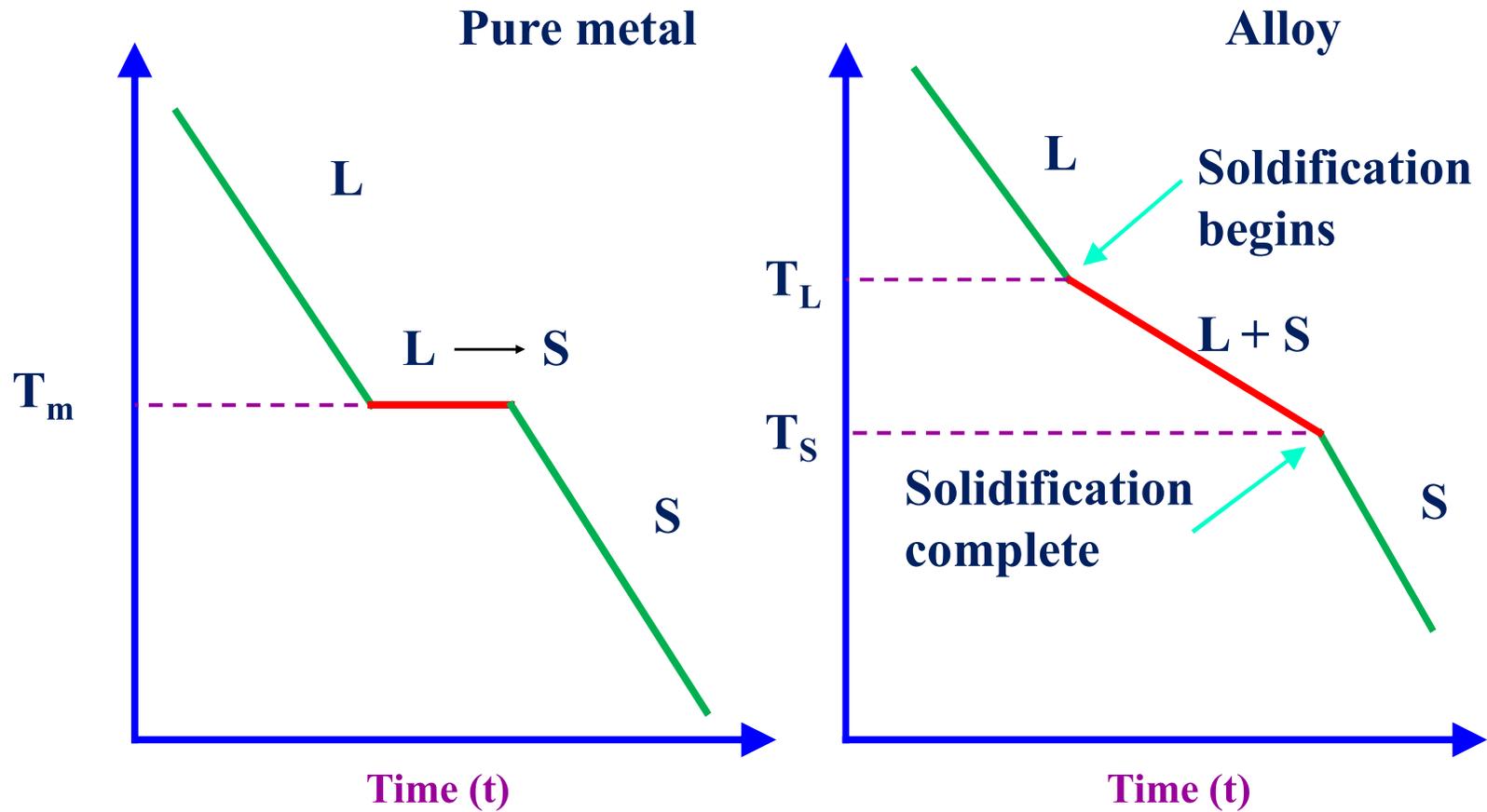
Isomorphous Phase Diagram

- ❑ Isomorphous phase diagrams form when there is complete solid and liquid solubility.
- ❑ Complete solid solubility implies that the crystal structure of the two components have to be same and Hume-Rothery rules to be followed.
- ❑ Examples of systems forming isomorphous systems: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3 - Cr_2O_3
- ❑ Both the liquid and solid contain the components A and B.
- ❑ In binary phase diagrams between two single phase regions there will be a two phase region → In the isomorphous diagram between the liquid and solid state there is the (Liquid + Solid) state.
- ❑ The Liquid + Solid state is NOT a semi-solid state → it is a solid of fixed composition and structure, in equilibrium with a liquid of fixed composition.
- ❑ In some systems (e.g. Au-Ni system) there might be phase separation in the solid state (i.e., the complete solid solubility criterion may not be followed) → these will be considered as a variation of the isomorphous system (with complete solubility in the solid and the liquid state).

cooling curves : Isomorphous system

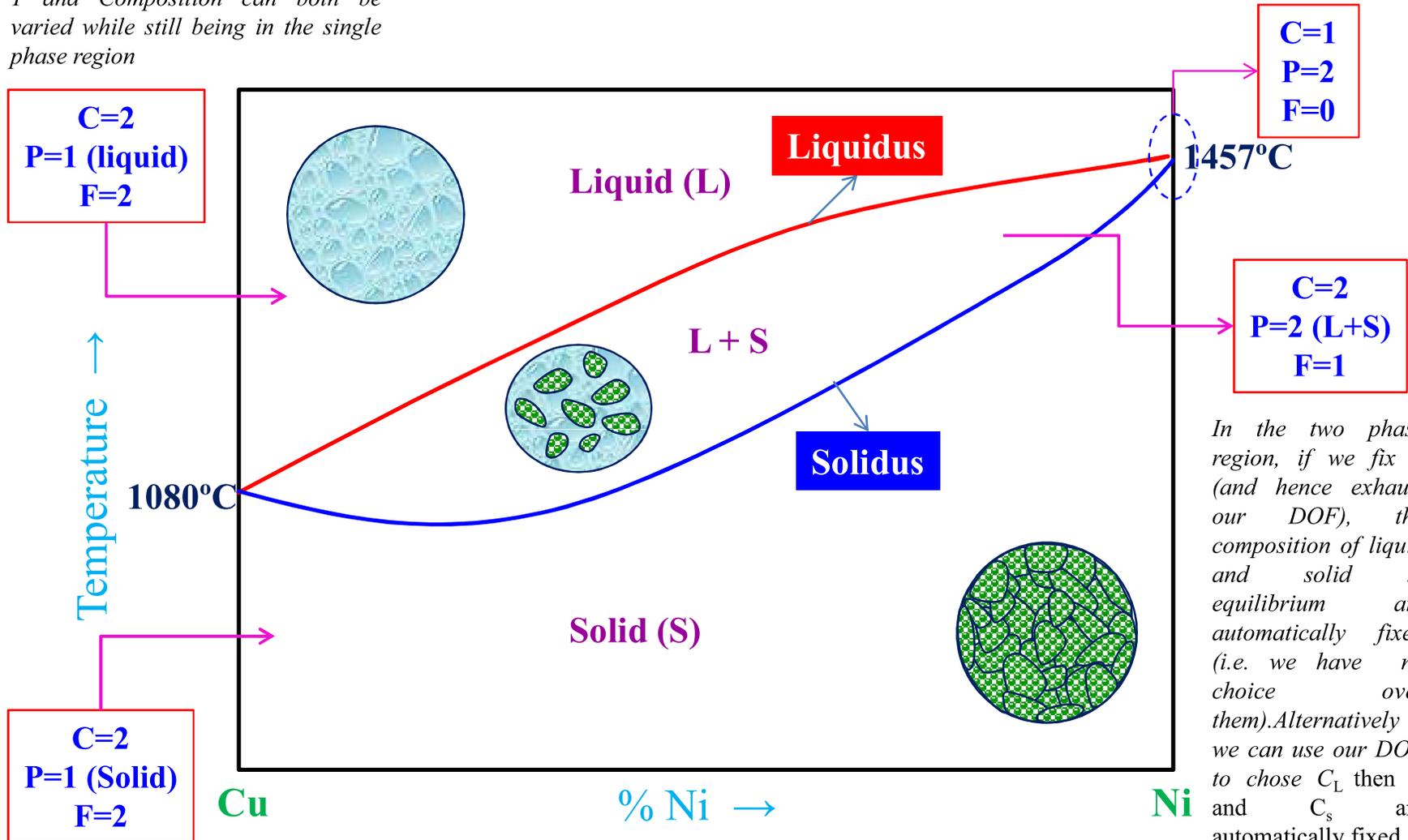


Revision : Solidification (cooling) curves



Isomorphous Phase Diagram

T and Composition can both be varied while still being in the single phase region



In the two phase region, if we fix T (and hence exhaust our DOF), the composition of liquid and solid in equilibrium are automatically fixed (i.e. we have no choice over them). Alternatively we can use our DOF to chose C_L then T and C_S are automatically fixed.

T and Composition can both be varied while still being in the single phase region

Tie line and Lever rule

Chemical Composition of Phases

Tie Line Rule

- ❑ To determine the actual chemical composition of the phases of an alloy, in equilibrium at any specified temperature in a two phase region, draw a horizontal temperature line, called a *tie line*, to the boundaries of the field. These points of intersection are dropped to the base line, and the composition is read directly.

Relative Amounts of Each Phase

Lever Rule

- ❑ To determine the relative amounts of the two phases in equilibrium at any specified temperature in a two phase region, draw a vertical line representing the alloy and a horizontal temperature line to the boundaries of the field.
- ❑ The vertical line will divide the horizontal line into two parts whose lengths are inversely proportional to the amount of the phases present. This is also known as *Lever rule*.
- ❑ The point where the vertical line intersects the horizontal line may be considered as the *fulcrum* of a lever system.
- ❑ The relative lengths of the lever arms multiplied by the amounts of the phases present must balance.

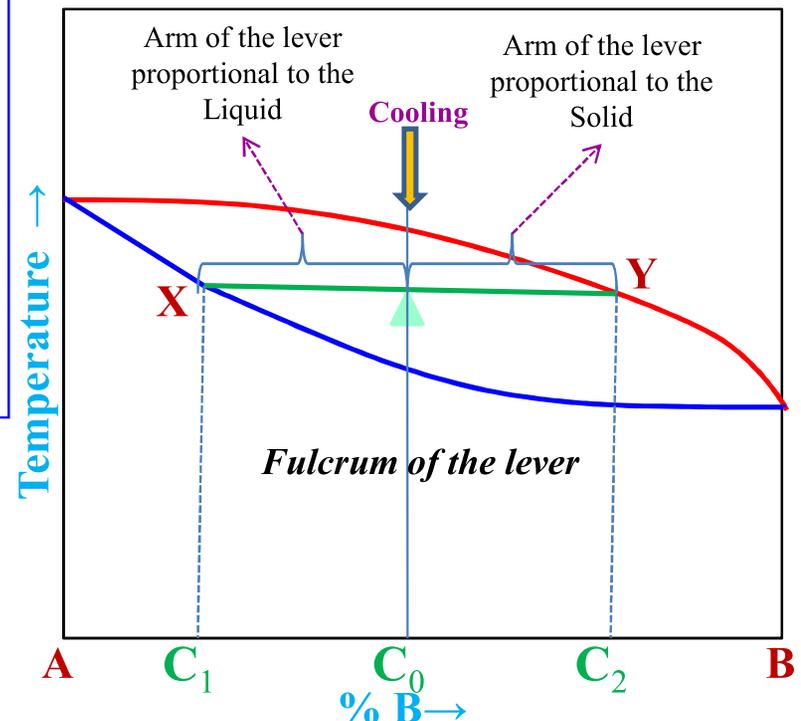
Tie line and Lever rule

- ❑ We draw a horizontal line (called the Tie Line) at the temperature of interest (say T_0). Let Tie line is XY.
- ❑ Solid (crystal) of composition C_1 coexists with liquid of composition C_2
- ❑ Note that tie lines can be drawn only in the two phase coexistence regions (fields). Though they may be extended to mark the temperature.
- ❑ To find the fractions of solid and liquid we use the lever rule.

- ❑ The portion of the horizontal line in the two phase region is akin to 'lever' with the fulcrum at the nominal composition (C_0)
- ❑ The opposite arms of the lever are proportional to the fraction of the solid and liquid phase present (this is lever rule)

$$f_{liquid} = \frac{C_0 - C_1}{C_2 - C_1}$$

$$f_{Solid} = \frac{C_2 - C_0}{C_2 - C_1}$$



Tie line and Lever rule

Example

At $C_0 = 35 \text{ wt\% Ni}$

At T_A : Only Liquid (L)

$$W_{\text{liquid}} = 100 \text{ wt\%}, W_{\text{solid}} = 0$$

At T_D : Only Solid (S)

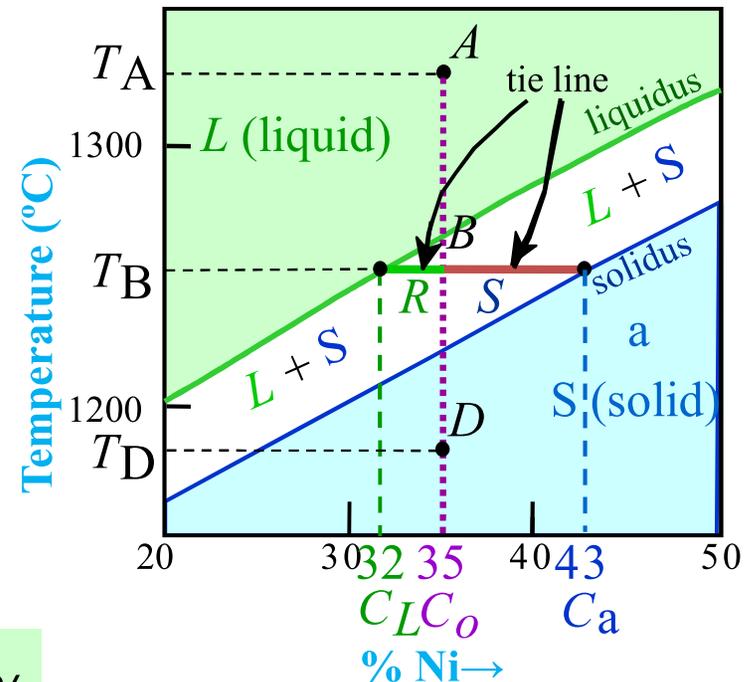
$$W_L = 0, W_{\text{solid}} = 100 \text{ wt\%}$$

At T_B : Both S and L

$$W_L = \frac{S}{R + S} = \frac{43 - 35}{43 - 32} = 73 \text{ wt\%}$$

$$W_S = \frac{R}{R + S} = 27 \text{ wt\%}$$

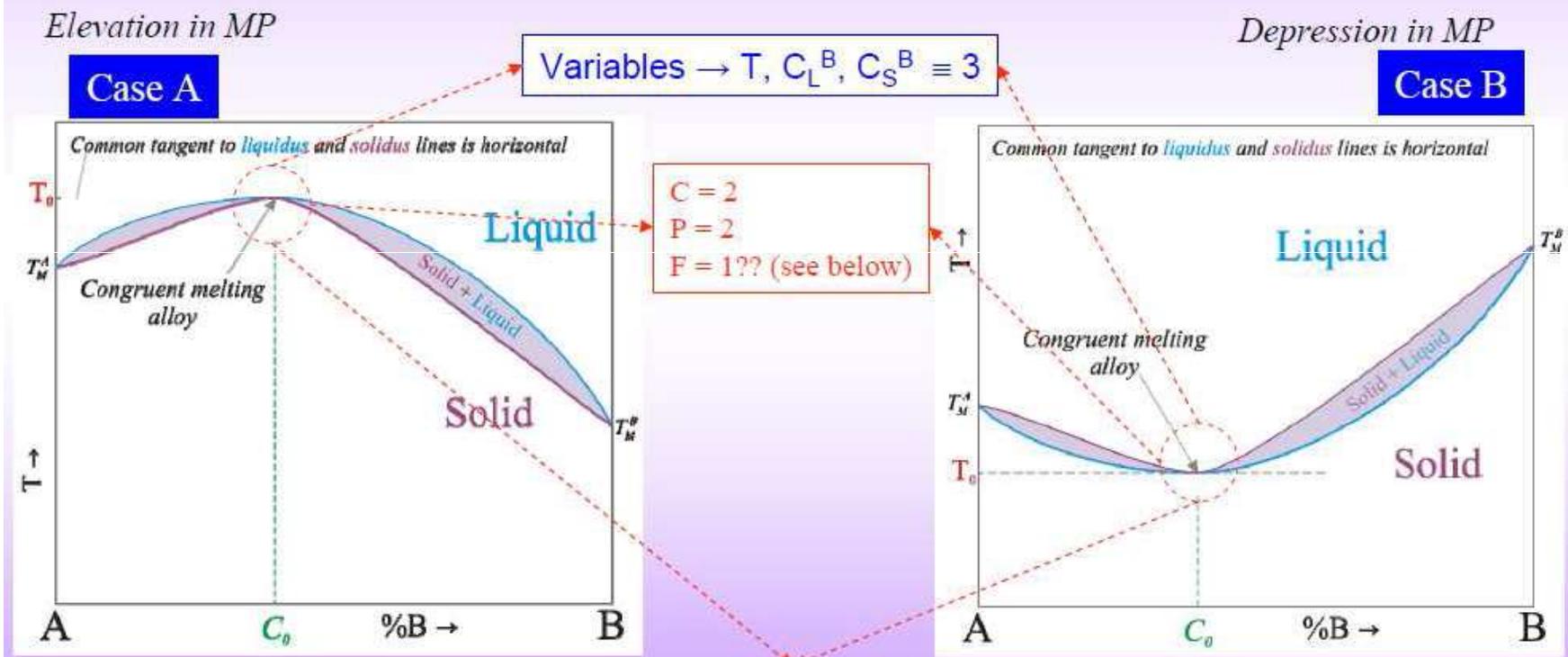
Cu - Ni System



Notice: as in a lever “the opposite leg” controls with a balance (fulcrum) at the ‘base composition’ and $R+S$ = tie line length = difference in composition limiting phase boundary, at the temp of interest

Variations of Isomorphous System

An alloy typically melts over a range of temperatures. However, there are special compositions which can melt at a single temperature like a pure metal. There is no difference in the liquid and solid composition. It begins and ends solidification at a constant temperature with no change in composition, and its cooling curve will show a horizontal line. Such alloys are known as a **congruent-melting alloys**, sometimes known as a **pseudo-eutectic alloy**. Ex: Cu-Au, Ni-Pd.



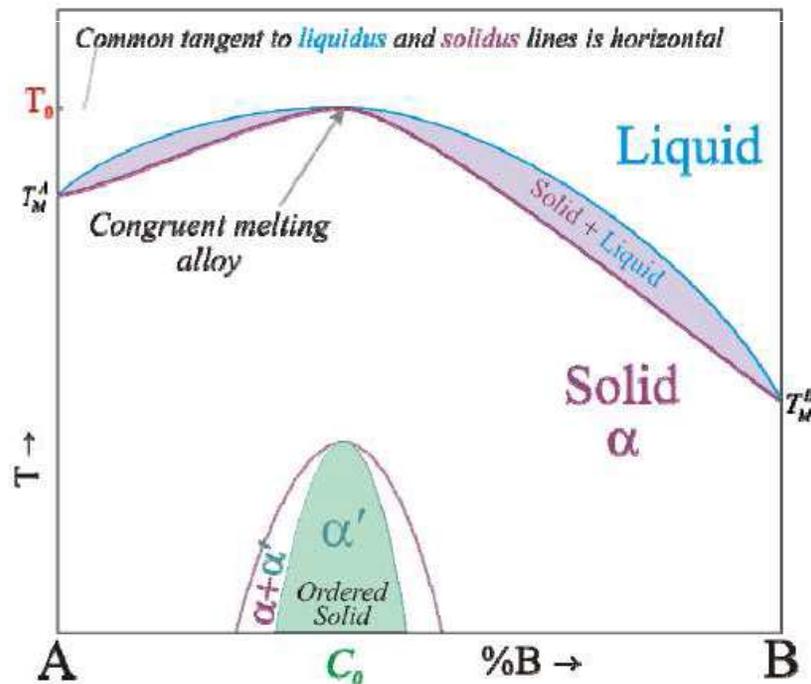
- Congruently melting alloys \rightarrow just like a pure metal
- Is the DOF 1? No: in requiring that $C_L^B = C_S^B$ we have exhausted the degree of freedom. Hence T is automatically fixed \rightarrow DOF is actually Zero..!

Variations of Isomorphous System

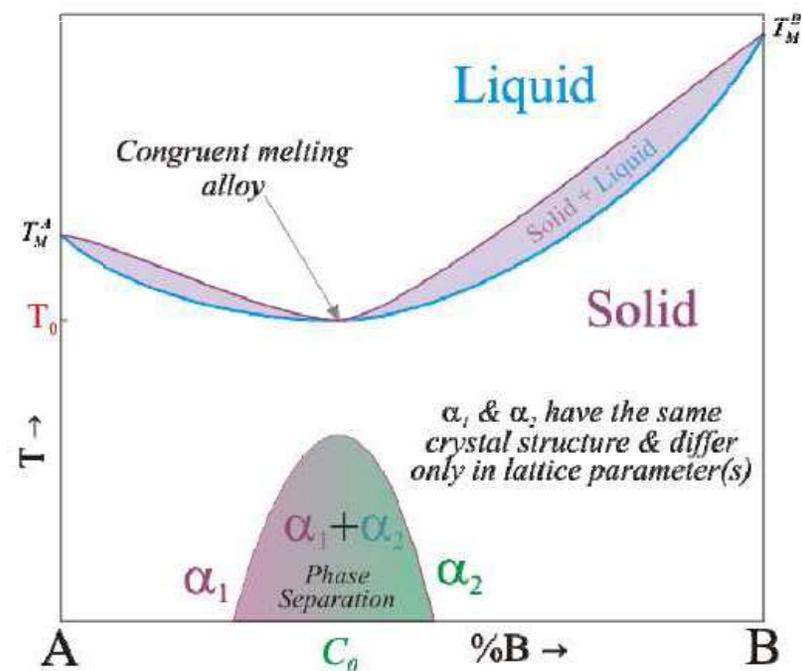
- ❑ Elevation in the MP means that the solid state is 'more stable' (*crudely speaking the ordered state is more stable*) → ordering reaction is seen at low T.
- ❑ Depression in MP 'means' the liquid state (disordered) is more stable → phase separation is seen at low T. (*phase separation can be thought of as the opposite of ordering. Ordering (compound formation) occurs for -ve values for ΔH_{mix}*).

- A – B bonds stronger than A – A and B – B bonds
- Solid Stabilized → Ordered Solid Formation
- A – A and B – B bonds stronger than A-B bonds
- Liquid Stabilized → Phase separation in the solid

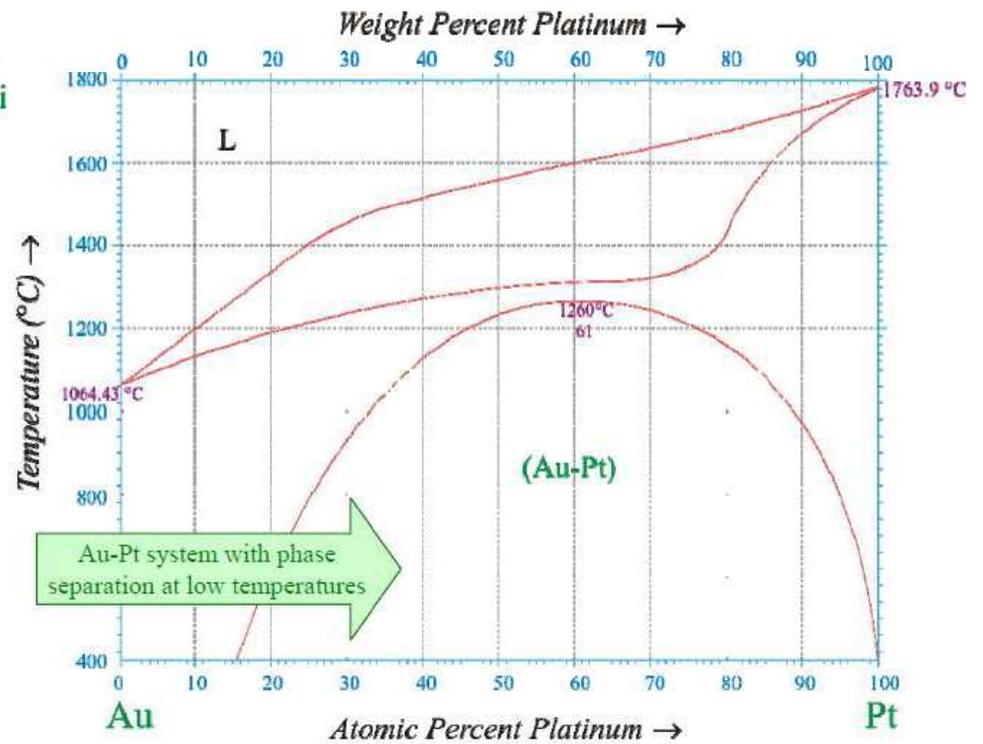
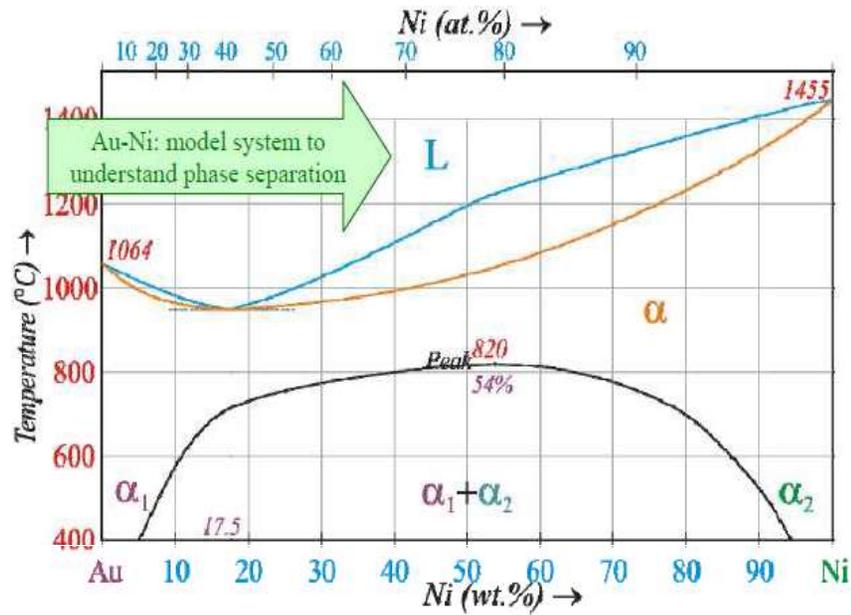
Case 1



Case 2



Examples of Isomorphous System with phase separation



Equilibrium Cooling

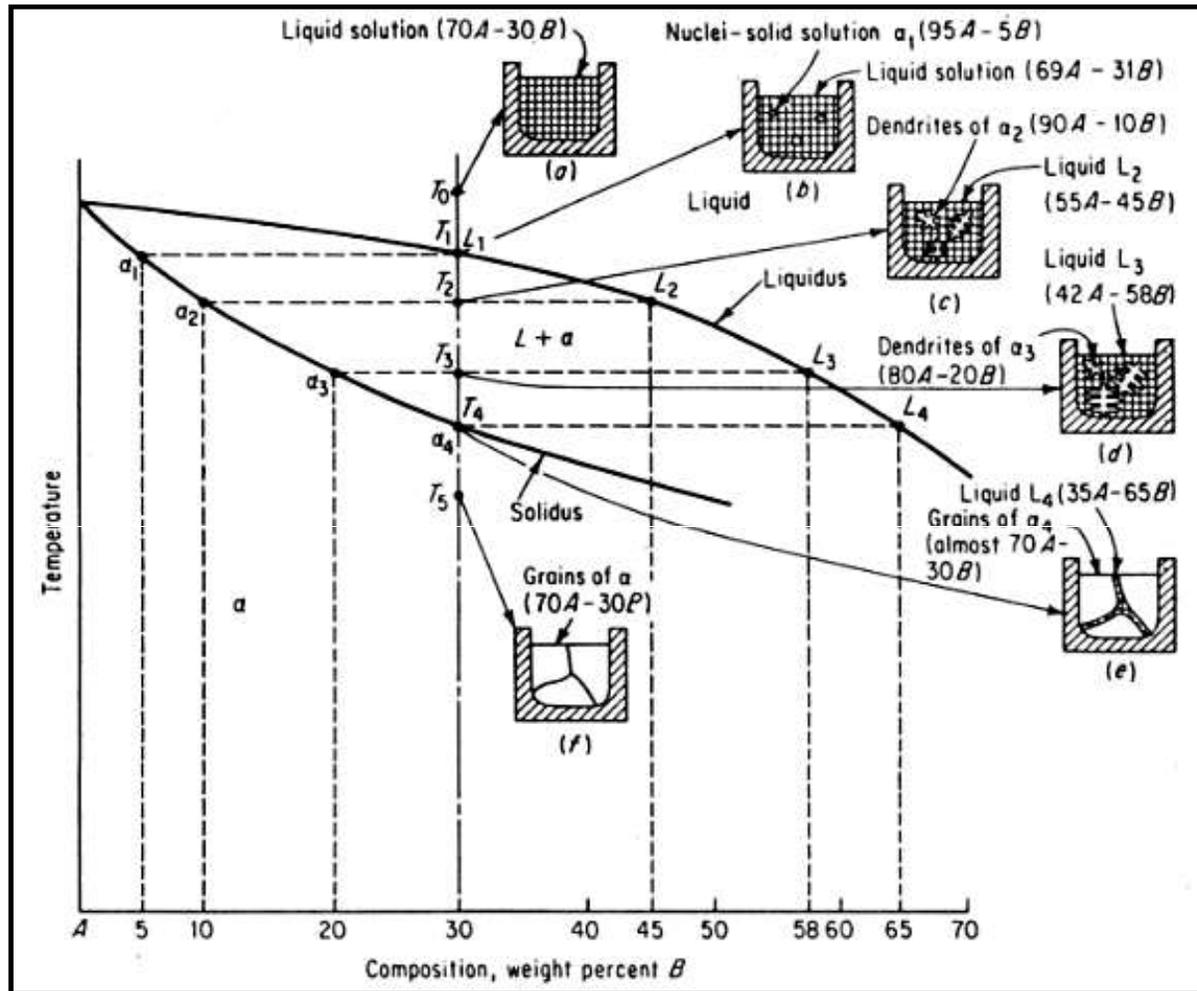
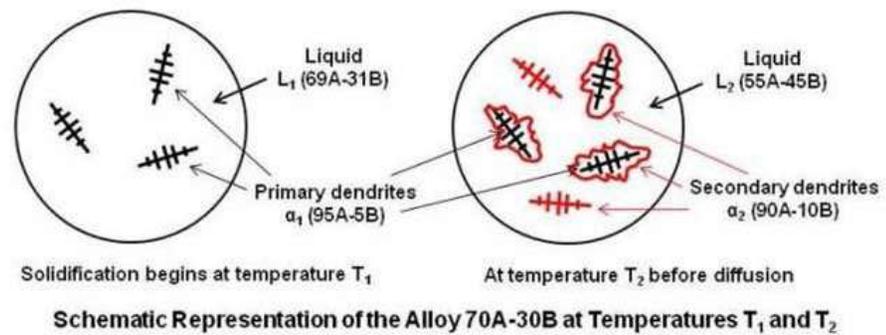


Figure: The above figure represents the very slow cooling , under equilibrium conditions, of a particular alloy 70A-30B will now be studied to observe the phase changes that occur .

Equilibrium Cooling

- ❑ This alloy at temperature T_0 is a homogeneous single-phase liquid solution (*a*) and remains so until temperature T_1 is reached. Since T_1 is on the liquidus line, freezing or solidification now begins.
- ❑ The first nuclei of solid solution to form α_1 will be very rich in the higher melting point metal A and will be composed of 95A-5B (*by tie line rule*). Since the solid solution in forming takes material very rich in A from the liquid, the liquid must get richer in B. Just after the start of solidification, the composition of the liquid is approximated as 69A-31B (*b*).
- ❑ When the lower temperature T_2 is reached, the liquid composition is at L_2 . The only solid solution in equilibrium with L_2 and therefore the only solid solution forming at T_2 is α_2 . Applying tie line rule, α_2 is composed of 10B. Hence, as the temperature is decreased, not only does the liquid composition become richer in B but also the solid solution.
- ❑ At T_2 , crystals of α_2 are formed surrounding the α_1 composition cores and also separate dendrites of α_2 (*see figure in below*).



Equilibrium Cooling

- ❑ In order for equilibrium to be established at T_2 , the entire solid phase must be a composition α_2 . This requires diffusion of B atoms to the A-rich core not only from the solid just formed but also from the liquid. This is possible in crystal growth (c).
- ❑ The composition of the solid solution follows the solidus line while the composition of liquid follows the liquidus line, and both phases are becoming richer in B.
- ❑ At T_3 (d), the solid solution will make up approximately three-fourths of all the material present.
- ❑ Finally, the solidus line is reached at T_4 , and the last liquid L_4 , very rich in B, solidifies primarily at the grain boundaries (e).
- ❑ However, diffusion will take place and all the solid solution will be of uniform composition $\alpha(70A-30B)$, which is the overall composition of the alloy (f).
- ❑ There are only grains and grain boundaries. There is no evidence of any difference in chemical composition inside the grains, indicating that diffusion has made the grain homogeneous.

Equilibrium Cooling

□ The very slow cooling, under equilibrium conditions, of particular alloy 65Cu - 35Ni will now be studied.

A – Homogeneous single phase (Liquid)

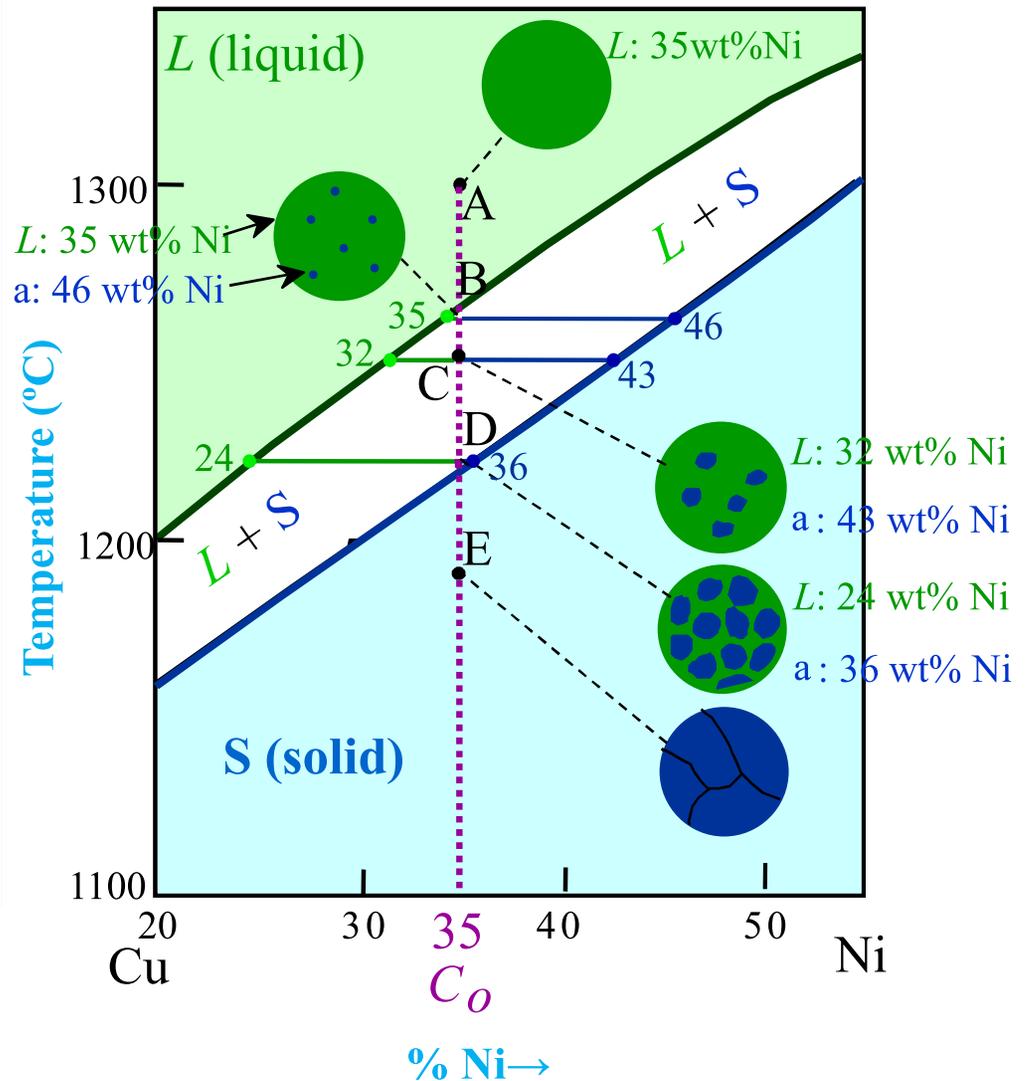
B - 'B' is on the liquidus line, solidification now begins.

C – Solid surrounded by liquid crystals.

D – 'D' is on the solidus line, solidification now ends.

E – Homogeneous single phase (Solid)

Cu-Ni Phase Diagram

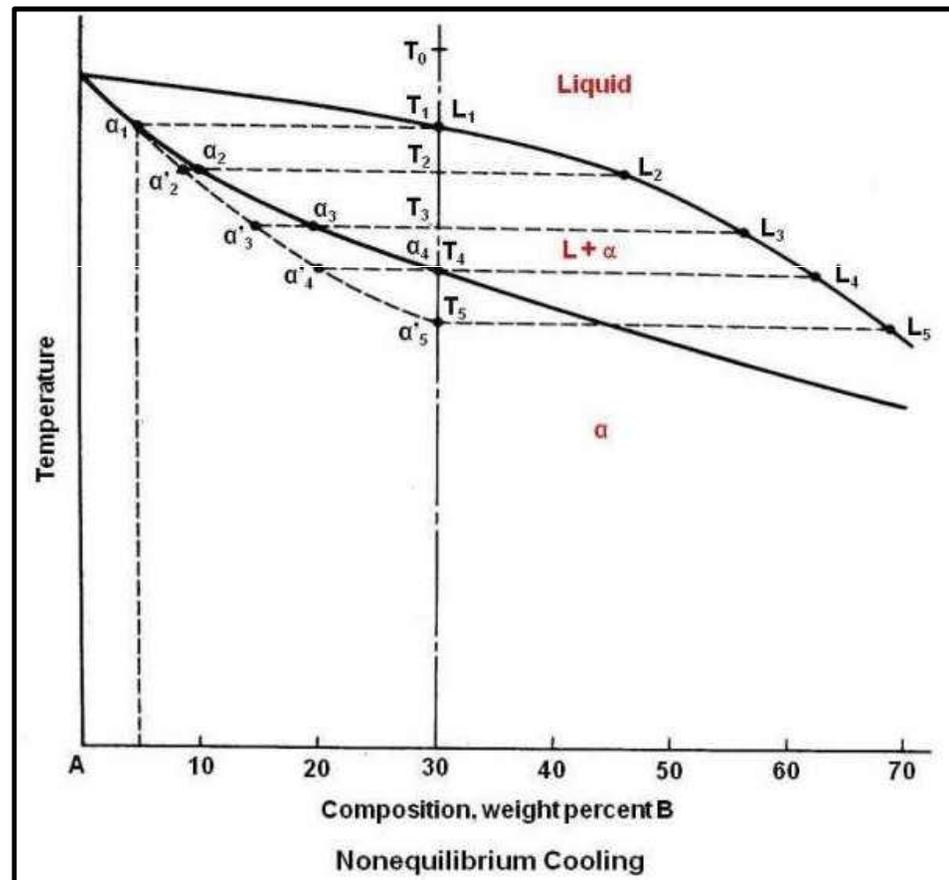


Non Equilibrium Cooling - Coring

□ In actual practice it is extremely difficult to cool under equilibrium conditions. Since diffusion in the solid state takes place at a very slow rate, it is expected that with ordinary cooling rates there will be some difference in the conditions as indicated by the equilibrium diagram.

□ Consider again 70A-30B alloy, solidification starts at T_1 forming a solid solution of composition α_1 .

□ At T_2 the liquid is L_2 and the solid solution now forming is of composition α_2 . Since diffusion is too slow to keep pace with crystal growth, not enough time will be allowed to achieve uniformity in the solid, and the average composition will be between α_1 and α_2 , say α'_2 .



Non Equilibrium Cooling - Coring

- ❑ As the temperature drops, the average composition of the solid solution will depart still further from equilibrium conditions. It seems that the composition of the solid solution is following a “nonequilibrium” solidus line α_1 to α'_5 , shown dotted lines in figure.
- ❑ The liquid, on the other hand, has essentially the composition given by the liquidus line, since diffusion is relatively rapid in liquid. At T_3 the average solid solution will be of composition α'_3 instead of α_3 .
- ❑ Under equilibrium cooling, solidification should be complete at T_4 ; however, since the average composition of the solid solution α'_4 has not reached the composition of the alloy, some liquid must still remain. Applying lever rule at T_4 gives $\alpha'_4 = 75\%$ and $L_4 = 25\%$.
- ❑ Therefore, solidification will continue until T_5 is reached. At this temperature the composition of the solid solution α'_5 coincides with the alloy composition, and solidification is complete. The last liquid to solidify, L_5 , is richer in B than the last liquid to solidify under equilibrium conditions.

Non Equilibrium Cooling - Coring

- ❑ *The more rapidly the alloy is cooled the greater will be the composition range in the solidified alloy. Since the rate of chemical attack varies with composition, proper etching will reveal the dendritic structure microscopically (see below figure). The final solid consists of a “cored” structure with a higher-melting central portion surrounded by the lower-melting, last-to-solidify shell. The above condition is referred to as coring or dendritic segregation.*



- ❑ To summarize, nonequilibrium cooling results in an increased temperature range over which liquid and solid are present; Since diffusion has not kept pace with crystal growth, there will be a difference in chemical composition from the center to the outside of the grains. The faster the rate of cooling, the greater will be the above effects.

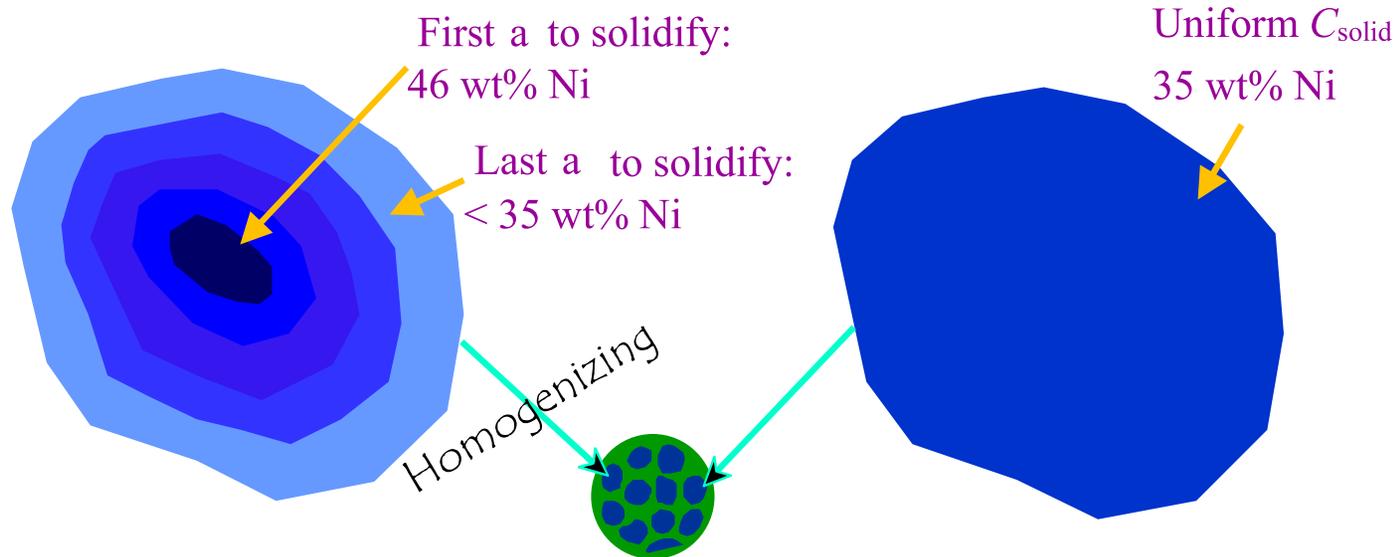
Cored vs. Equilibrium Phases

Consider Cu-Ni phase diagram case

First a to solidify has $C_{solid} = 46 \text{ wt\% Ni}$.
Last a to solidify has $C_{solid} = 35 \text{ wt\% Ni}$.

On Fast rate of cooling
Cored structure

On Slow rate of cooling
Equilibrium structure



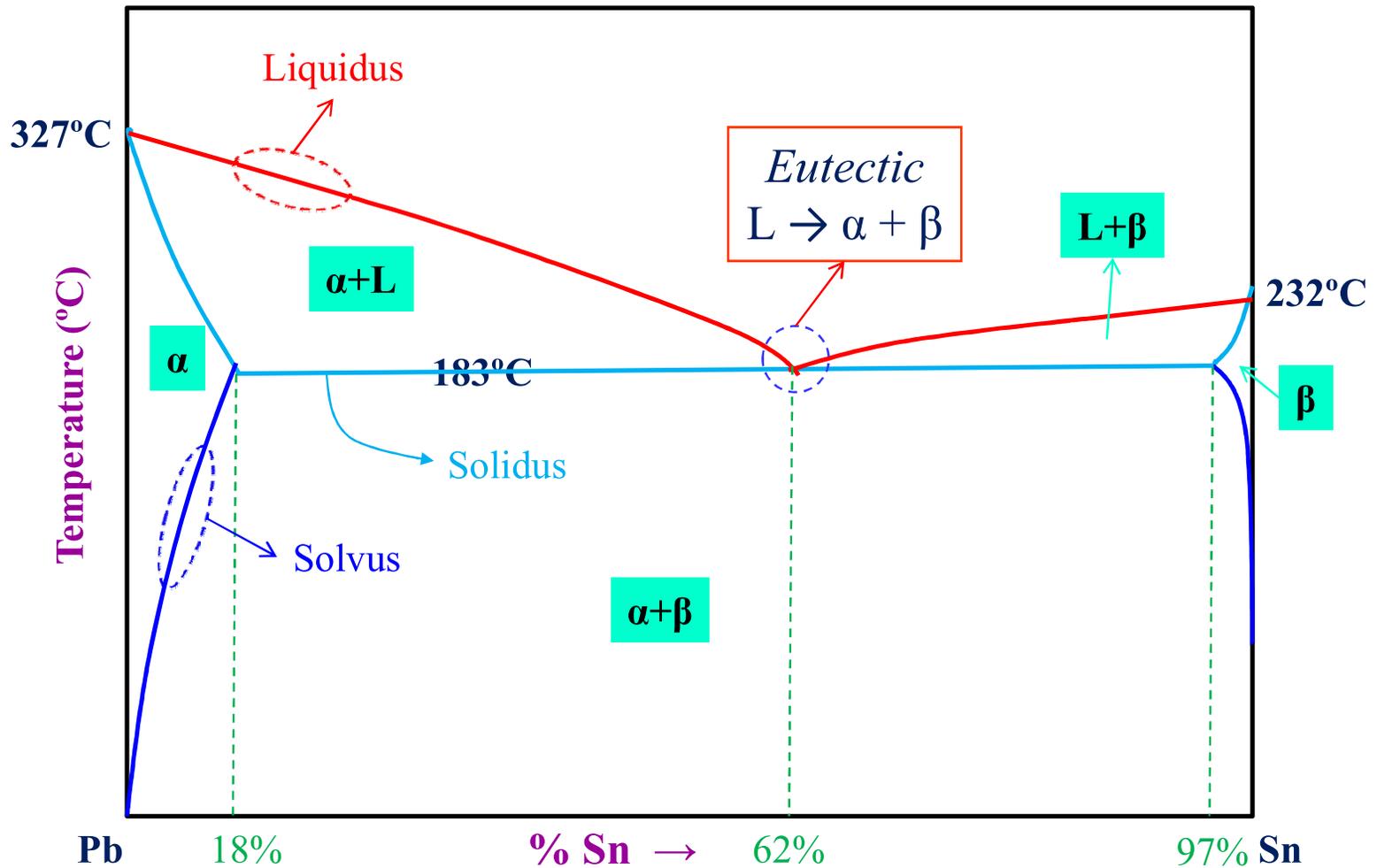
Homogenization

- ❑ Cored structures are most common in as-cast metals. From the earlier discussion of the origin of a cored structure, it is apparent that the last solid formed along the grain boundaries and in the inter-dendritic spaces is very rich in the lower-melting-point metal.
- ❑ Depending upon the properties of the lower-melting-point metal, the grain boundaries may act as a plane of weakness. It will also result in a serious lack of uniformity in mechanical and physical properties and, in some cases, increased susceptibility to intergranular corrosion because of preferential attack by corrosive medium. Therefore, for some applications a cored structure is objectionable.
- ❑ There are two methods for solving the problem of coring. One is to prevent its formation by slow freezing from the liquid, but this result in large grain size and requires a very long time. The preferred method industrially is to achieve equalization of composition or homogenization of the cored structure by diffusion in the solid state.
- ❑ At room temperature, for most metals, the diffusion rate is very slow; but if the alloy is reheated to a temperature below the solidus line, diffusion will be more rapid and homogenization will occur in a relatively short time.

Eutectic Phase Diagram

- ❑ Very few systems exhibit an isomorphous phase diagram (usually the solid solubility of one component in another is limited).
- ❑ Often the solid solubility is severely limited – through the solid solubility is never zero (due to entropic reasons).
- ❑ In a Simple eutectic system (binary), there is one composition at which the liquid freezes at a single temperature. This is in some sense similar to a pure solid which freezes at a single temperature (unlike a pure substance the freezing produces a two solid phases both of which contain both the components).
- ❑ The term **Eutectic** means easy melting → The alloy of eutectic composition freezes at a lower temperature than the melting points of the constituent components.
- ❑ *This has important implications → e.g. the Pb-Sn eutectic alloy melts at 183°C, which is lower than the melting points of both Pb (327°C) and Sn (232°C) → Can be used for soldering purposes (as we want to input least amount of heat to solder two materials).*
- ❑ In the next page we consider the Pb-Sn eutectic phase diagram.

Eutectic Phase Diagram



Eutectic reaction at 183°C

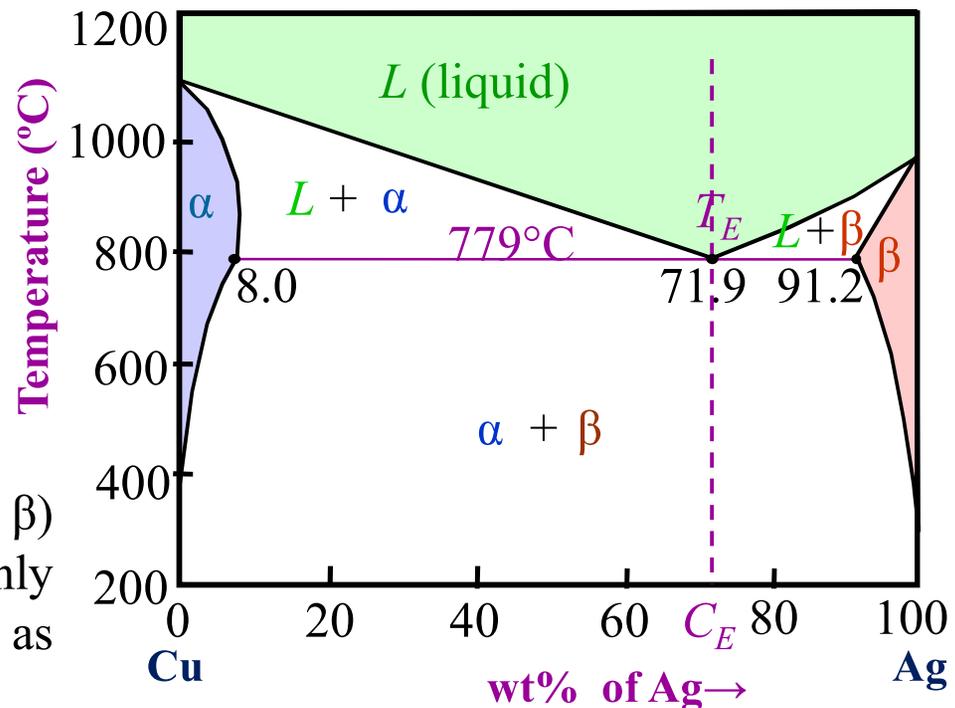
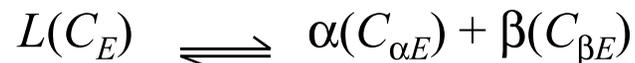


Example : Cu-Ag Eutectic System

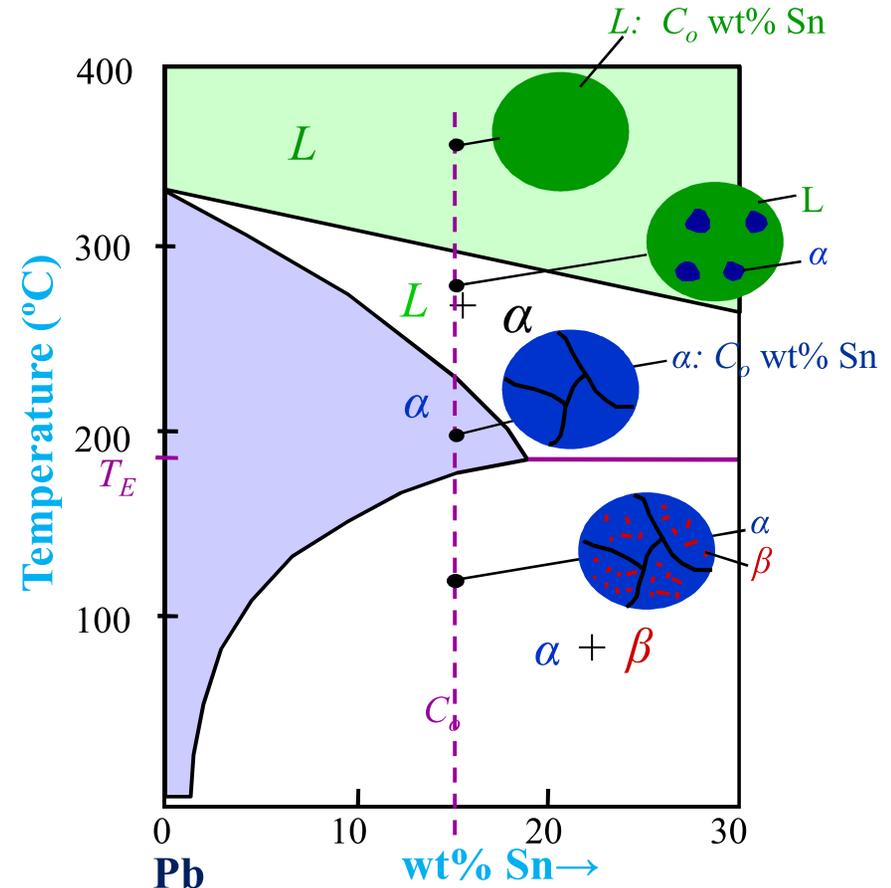
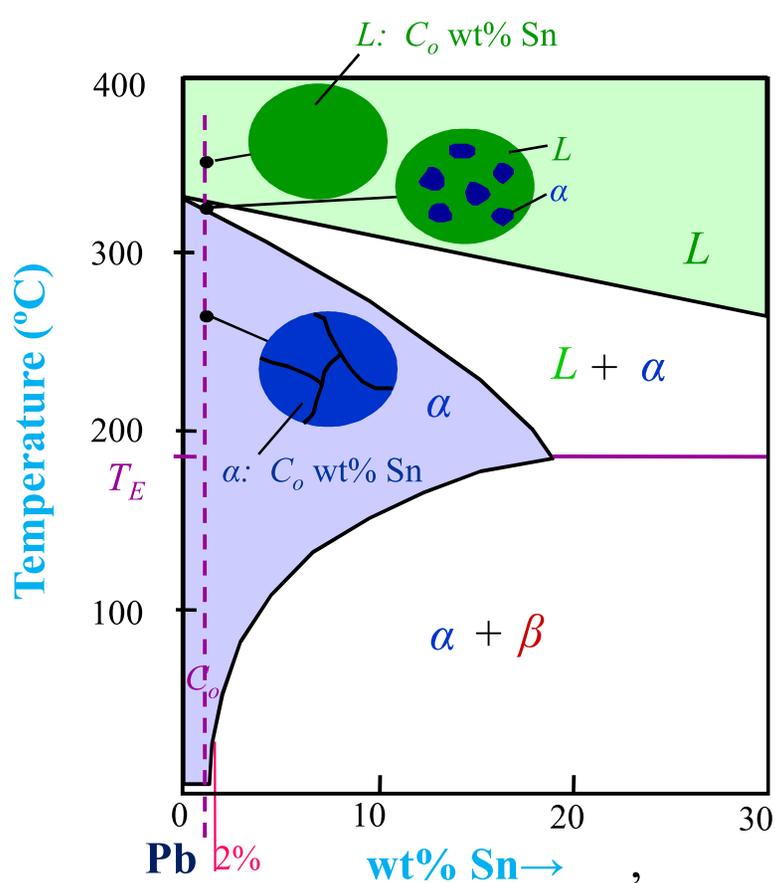
□ Raoult's law states that the freezing point of a pure substance will be lowered by the addition of a second substance provided the latter is soluble in the pure substance when liquid and insoluble when solidified. The amount of lowering of the freezing point is proportional to the molecular weight of the solute.

- Limited solubility:
 - α : mostly Cu
 - β : mostly Ag
- T_E : No liquid below T_E
- C_E : Min. melting T_E

Three single phase regions – (L, α , β) exist at 71.9% Ag at 779°C commonly known as Eutectic. The reaction is as follows...!



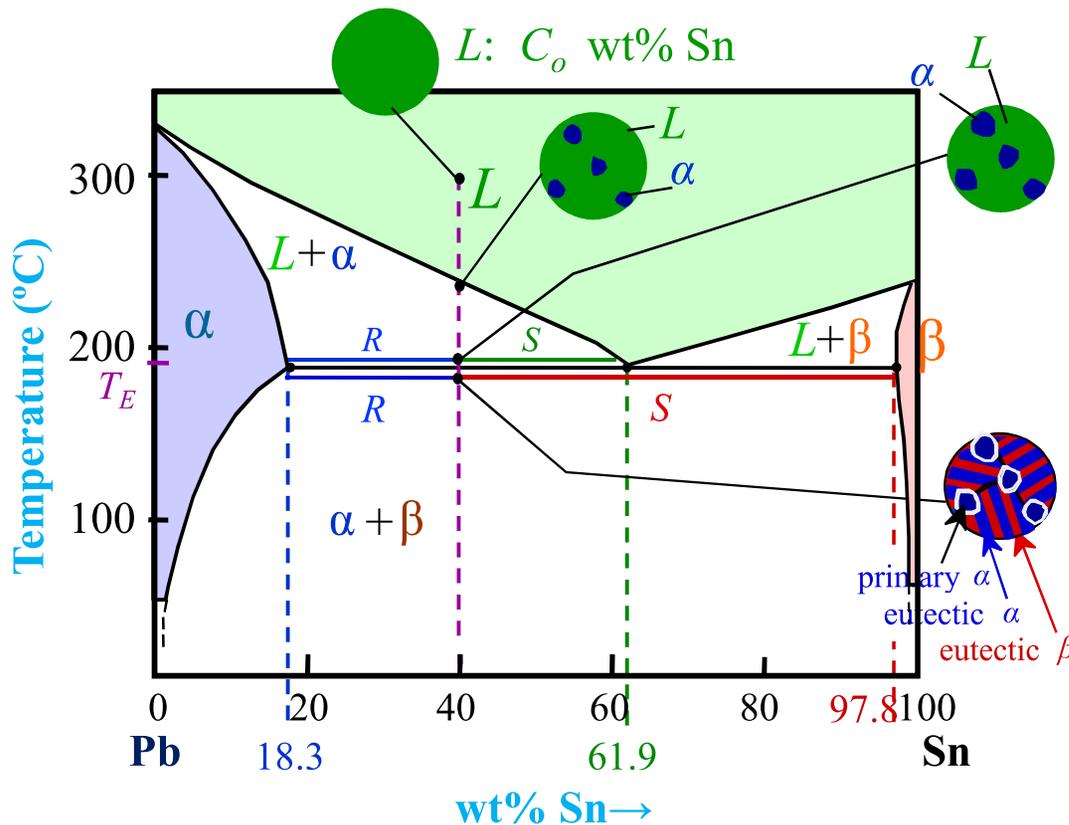
Microstructural Characteristics of Eutectic System



- To reiterate an important point: Phase diagram do not contain microstructural information (i.e. they cannot tell you what is the microstructures produced by cooling. Often microstructural information is overlaid on phase diagram for convenience. Hence, strictly cooling is not in the domain of phase diagram – but we can overlay such information keeping in view the assumptions involved.

Microstructural Characteristics of Eutectic System

- ❑ $18.3 \text{ wt\% Sn} < C_o < 61.9 \text{ wt\% Sn}$
- ❑ Microstructure consists a crystals and a eutectic microstructure



→ Just above T_E :

$$C_\alpha = 18.3 \text{ wt\% Sn}$$

$$C_L = 61.9 \text{ wt\% Sn}$$

$$W_\alpha = \frac{S}{R + S} = 50 \text{ wt\%}$$

$$W_L = (1 - W_\alpha) = 50 \text{ wt\%}$$

→ Just below T_E :

$$C_\alpha = 18.3 \text{ wt\% Sn}$$

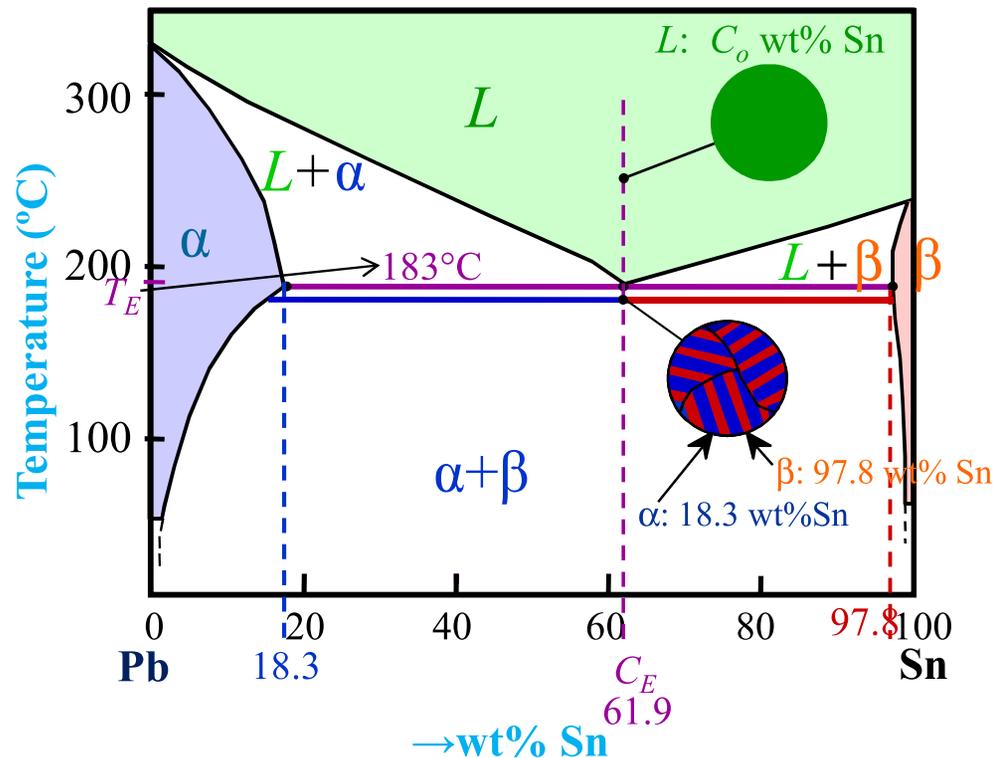
$$C_\beta = 97.8 \text{ wt\% Sn}$$

$$W_\alpha = \frac{S}{R + S} = 72.6 \text{ wt\%}$$

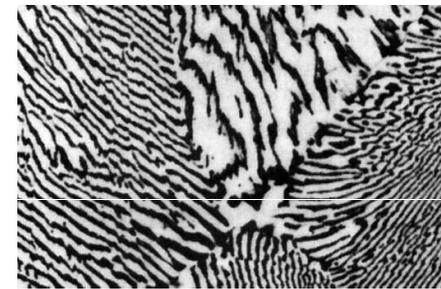
$$W_\beta = 27.4 \text{ wt\%}$$

Microstructural Characteristics of Eutectic System

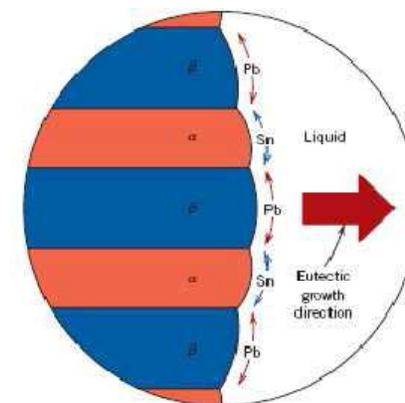
- $C_o = C_E$
- Microstructure represents Eutectic microstructure (lamellar structure) alternating layers (lamellae) of a and b crystals.



Pb-Sn Eutectic Microstructure

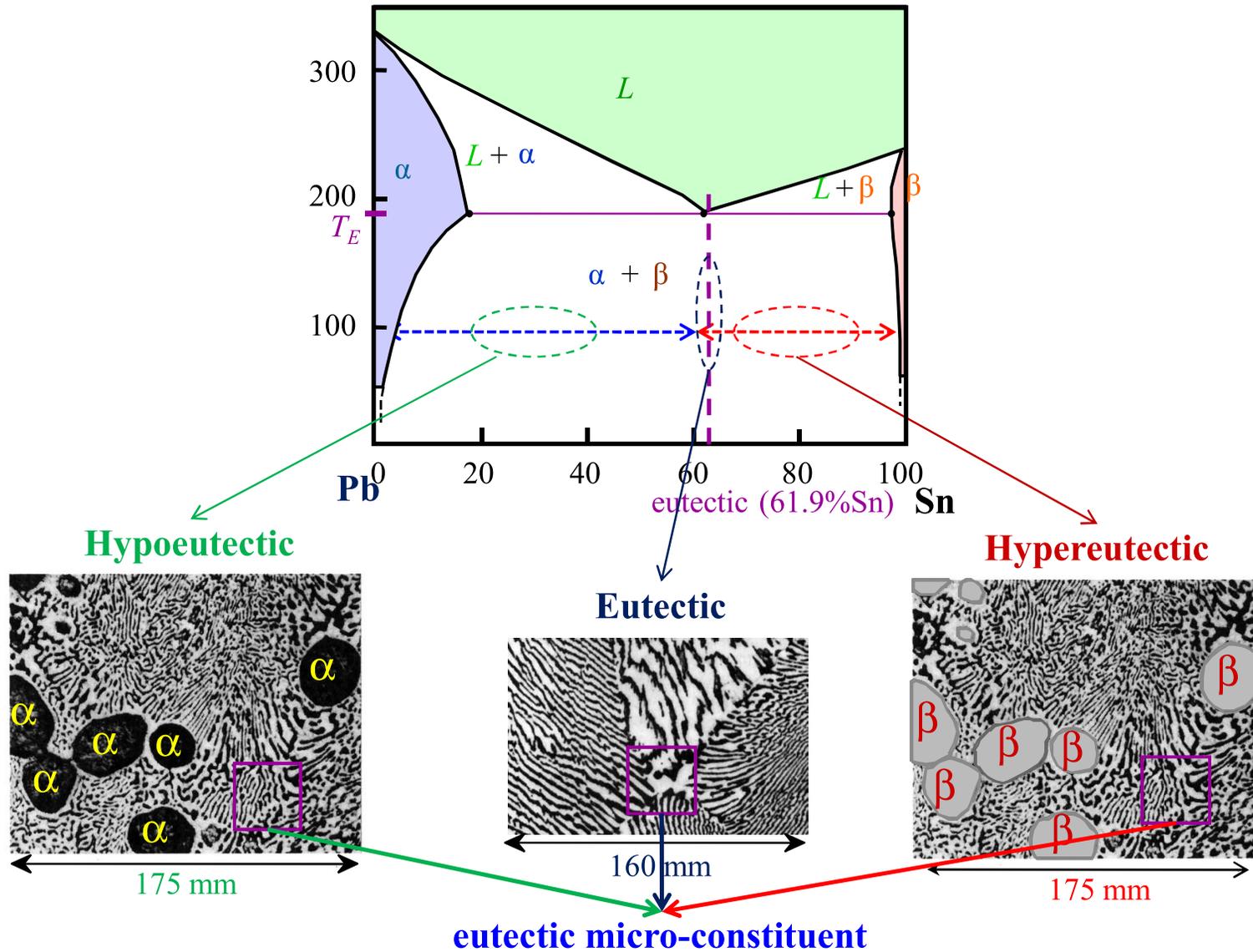


160 μ m



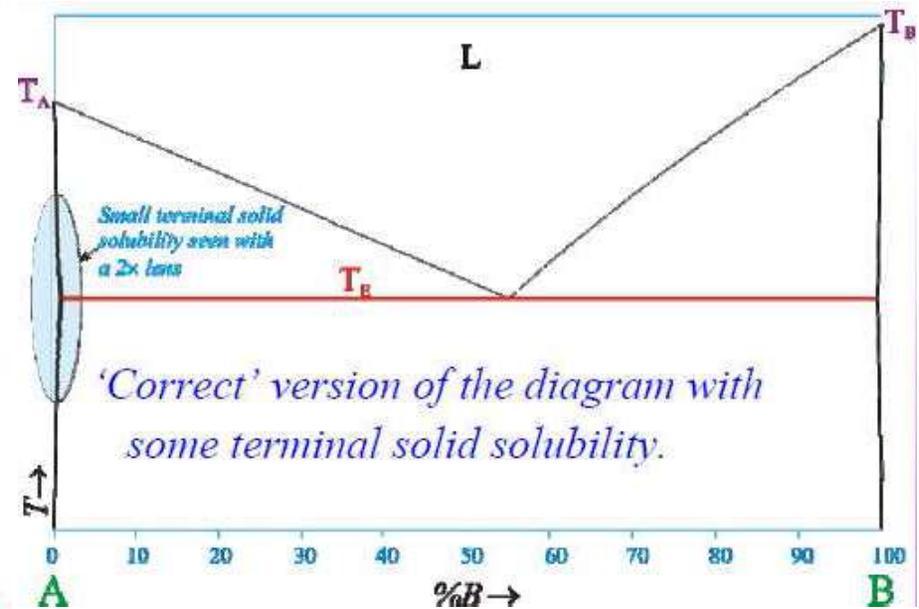
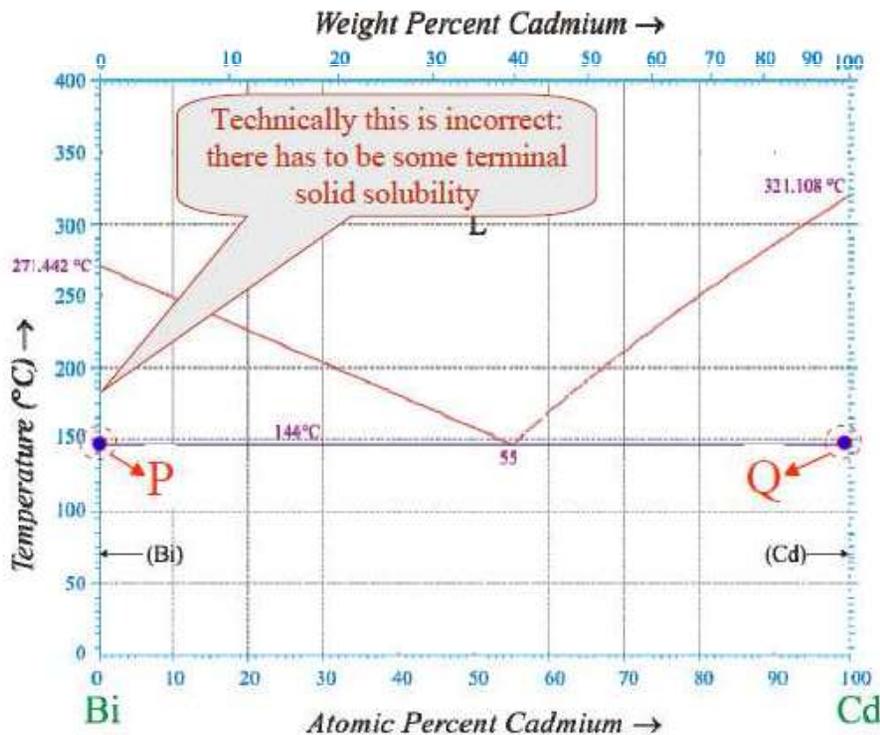
45.1% α and 54.8% β

Hypo Eutectic – Eutectic – Hyper Eutectic

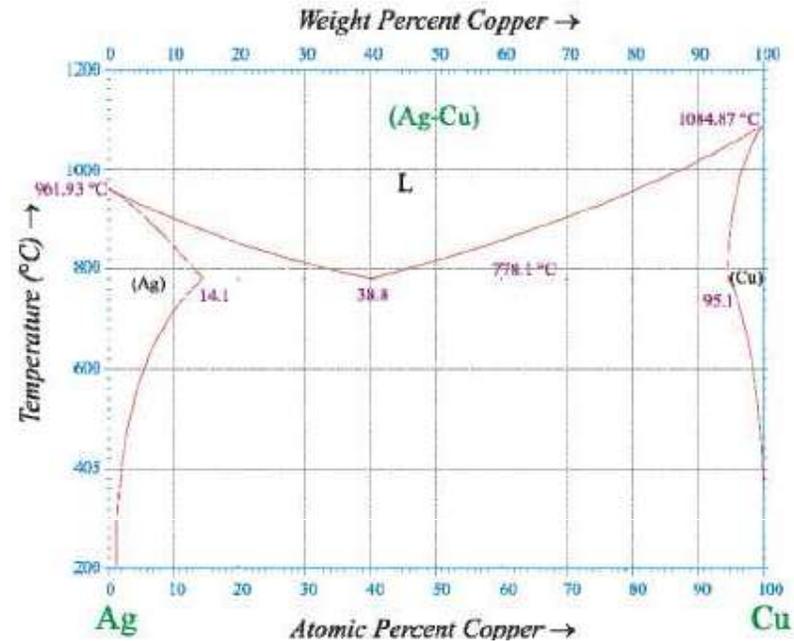
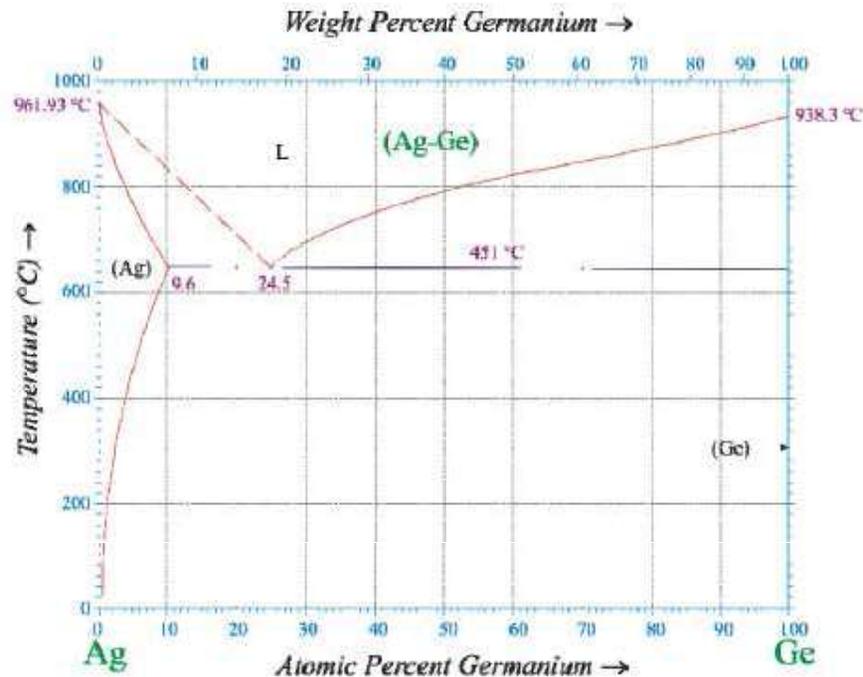


Special Eutectic Systems

- ❑ Consider the eutectic system *without terminal solid solubility* : **Bi-Cd**
- ❑ Technically it is incorrect to draw eutectic phase diagrams with zero solid solubility.
- ❑ This would imply that a pure component (say Bi in the example considered) melts over a range of temperatures (from 'p' to 271 °C) → which is wrong.
- ❑ Also let us consider an example of a point 'p' (which lies on the 'eutectic line' PQ). At 'p' the phase rule becomes : $F = C - P + 1 = 1 - 3 + 1 = -1$!!!



Special Eutectic Systems



- ❑ Note that the above is an alternate way of arriving at the obvious contradiction that at ‘P’ on one hand we are saying that there is a pure component and on the other hand we are considering a three phase equilibrium (which can happen only for Bi-Cd alloys).
- ❑ In Eutectic systems, at Eutectic point E → 3 phases co-exist : L, α & β
- ❑ The number of components in a binary phase diagram is 2 → the number of DOF $F=0$
- ❑ This implies that the Eutectic point is an **Invariant Point** → For a given system it occurs at a fixed composition and temperature.

Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find the phases present: α and β , Composition of phases

$$C_o = 40 \text{ wt\% Sn}$$

$$C_a = 11 \text{ wt\% Sn}$$

$$C_b = 99 \text{ wt\% Sn}$$

The relative amount of each phase by using lever rule

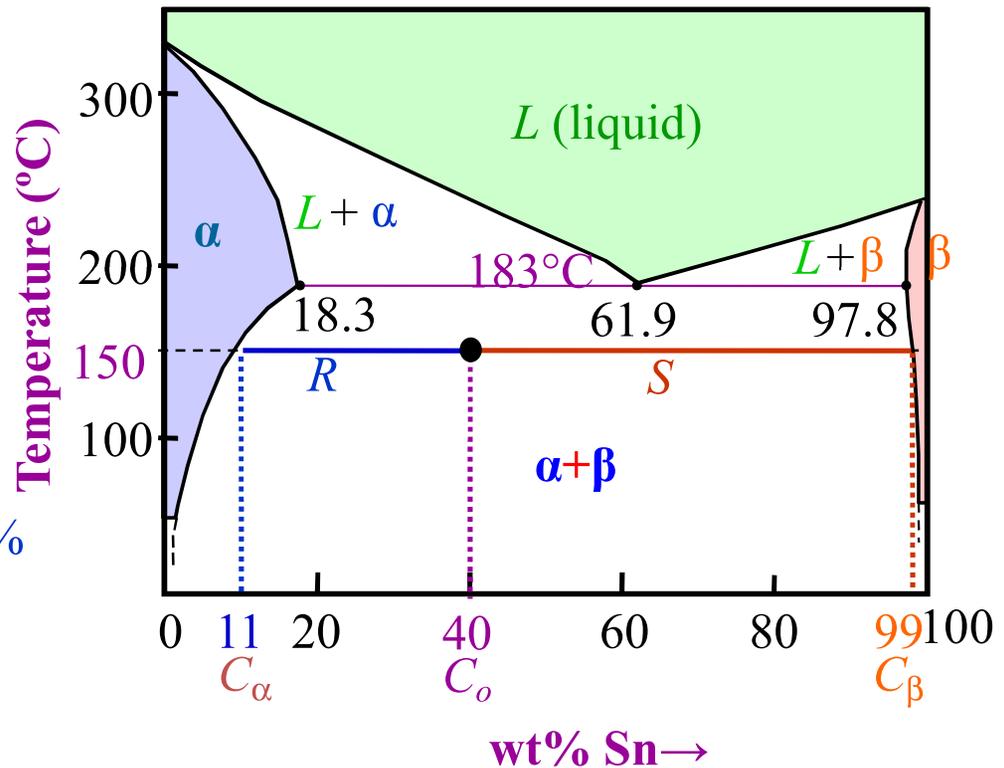
$$W_a = \frac{S}{R+S} = \frac{C_\beta - C_o}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

$$W_\beta = \frac{R}{R+S} = \frac{C_o - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$

Pb-Sn Phase Diagram



Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find the phases present: α and Liquid, Composition of phases

$$C_O = 40 \text{ wt\% Sn}$$

$$C_a = 17 \text{ wt\% Sn}$$

$$C_L = 46 \text{ wt\% Sn}$$

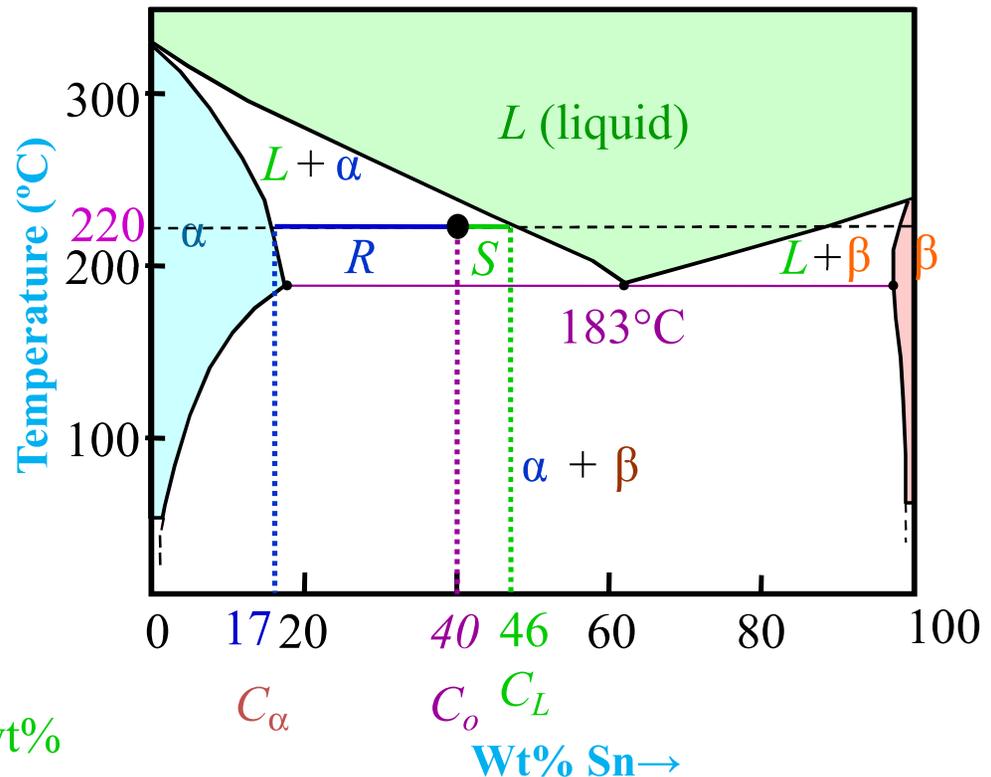
The relative amount of each phase by using lever rule

$$W_a = \frac{C_L - C_O}{C_L - C_a} = \frac{46 - 40}{46 - 17}$$

$$= \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_a}{C_L - C_a} = \frac{23}{29} = 79 \text{ wt\%}$$

Pb-Sn Phase Diagram



Solved Example

During the solidification of a off eutectic (Pb-Sn) composition (C_0), 90 vol.% of the solid consisted of the eutectic mixture and 10vol.% of the proeutectic β phase. What is the value of C_0 ?

Density data for β and α

$$\rho_\alpha = 10300 \text{ Kg/m}^3$$

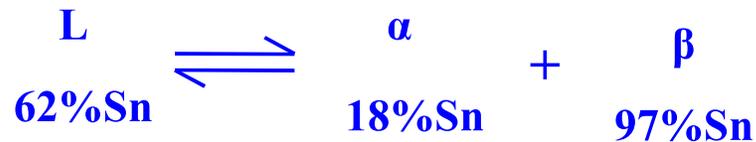
$$\rho_\beta = 7300 \text{ Kg/m}^3$$

Eutectic Data

183 °C

62 wt% Sn

Let us start with some observations: ♦Pb is heavier than Sn and hence the density of α is more than that of β ♦Since the proeutectic phase is β → the composition is hypereutectic (towards the Sn side) ♦ The volume fraction (in %) are usually calculated by taking the area fractions by doing metallography (microstructure) and then converting it into volume fractions (usually volume fraction is assumed to be equal to area fraction



Using the fact that there is 10 Vol% β phase :

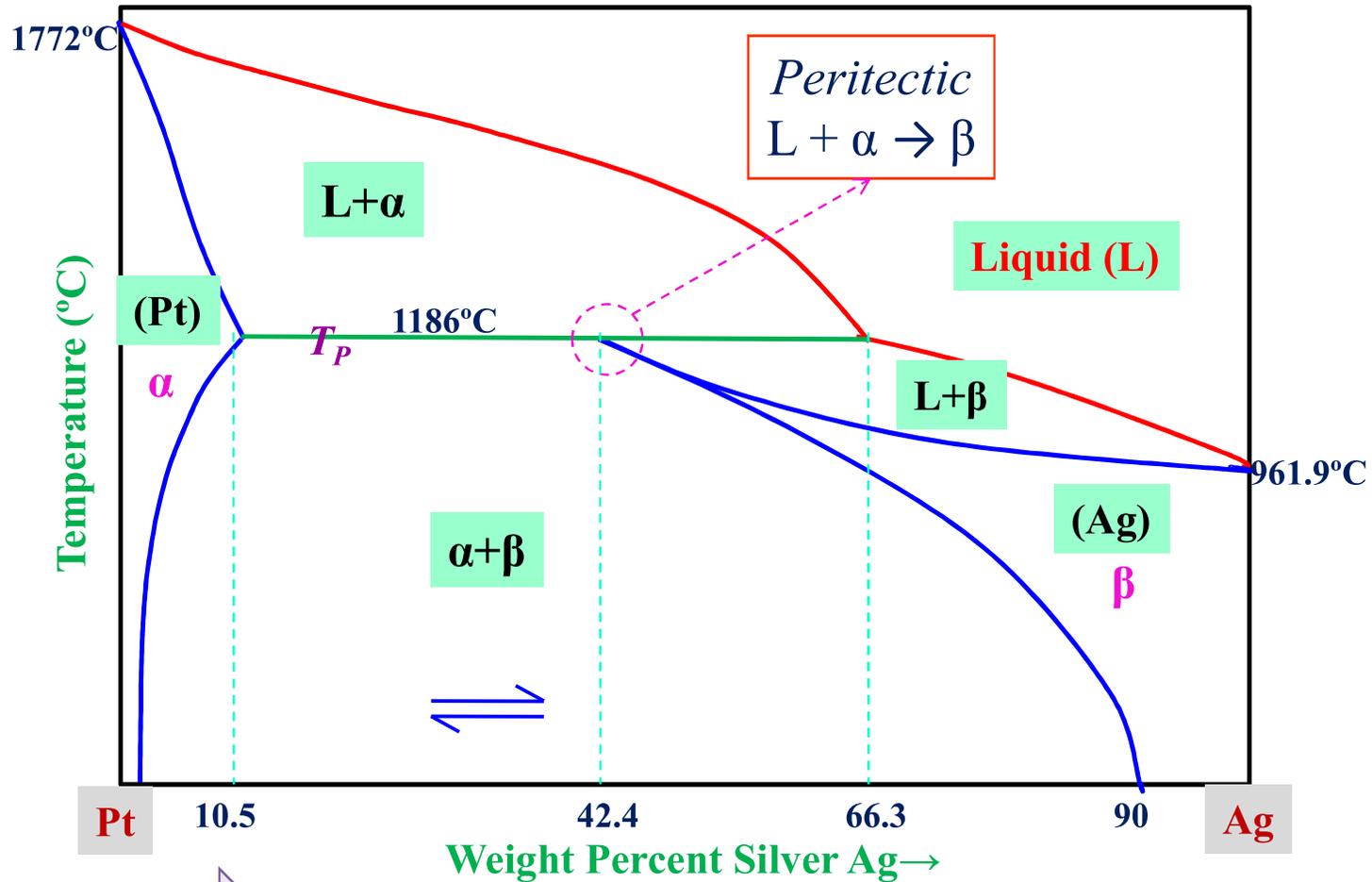
$$\text{Wt. fraction of proeutectic } \beta = \left[\frac{\text{Wt. of } \beta}{\text{Wt. of the alloy}} \right] = \frac{0.1 \times 7300}{(0.1 \times 7300) + (0.9 \times \rho_{\text{eutectic mix}})}$$

$$\text{Where, } \rho_{\text{eutectic mix}} = 10300 \left(\frac{97-62}{97-18} \right) + 7300 \left(\frac{62-18}{97-18} \right) = 4563 + 4066 = 8629 \text{ Kg/m}^3$$

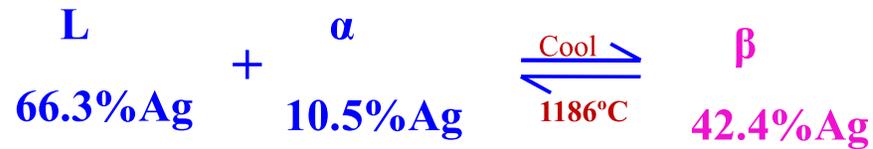
Substituting in equation (1): Wt. fraction of proeutectic $\beta = 0.086$

$$\text{U sin gleverrule : } 0.086 = \frac{C_0 - 0.62}{0.97 - 0.62}, C_0 = 0.650 = 65.0\%$$

Peritectic Phase Diagram

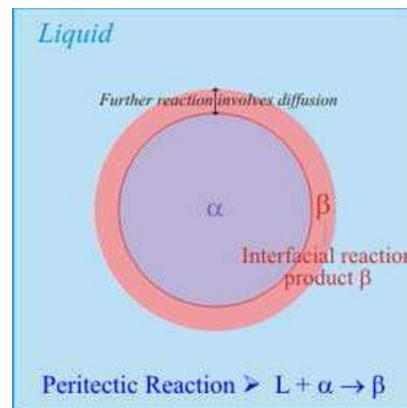


Peritectic Reaction



Peritectic Phase Diagram

- ❑ Like the eutectic system, the Peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.
- ❑ In the Peritectic reaction the liquid (L) reacts with one solid (α) to produce another solid (β). $L + \alpha \rightarrow \beta$
- ❑ Since the solid β forms at the interface between the L and the α , further reaction is dependent on solid state diffusion. Needless to say this becomes the rate limiting step and hence it is difficult to 'equilibrate' peritectic reactions (as compared to say eutectic reactions).

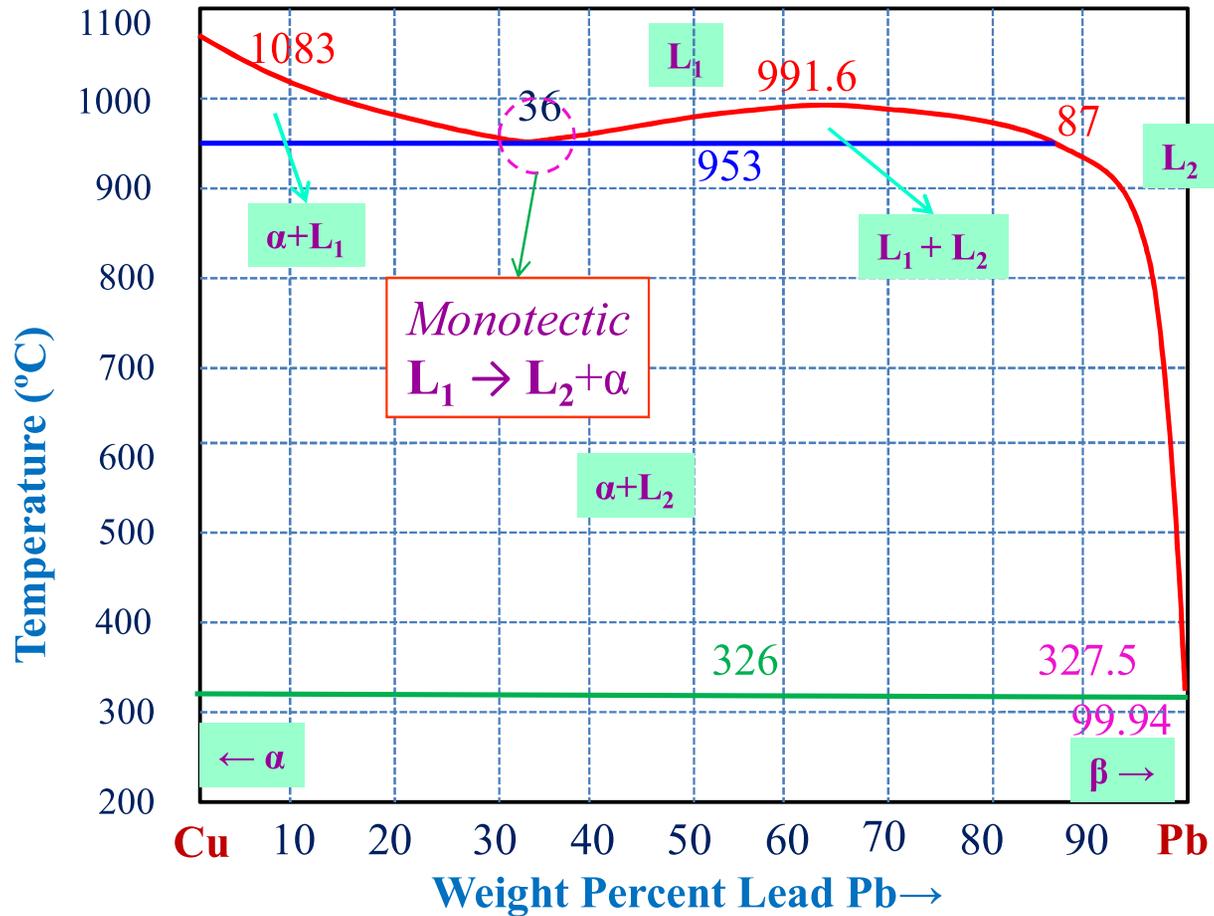


- ❑ In some Peritectic reactions (e.g. the Pt-Ag system – previous page). The (pure) β phase is not stable below the Peritectic temperature ($T_P = 1186$ °C for Pt- Ag system) and splits into a mixture of ($\alpha + \beta$) just below T_P .

Monotectic Phase Diagram

- ❑ In all the types discussed previously, it was assumed that there was complete solubility in the liquid state. It is quite possible, however, that over a certain composition range two liquid solutions are formed that are not soluble in each other.
- ❑ Another term for solubility is miscibility. Substances that are not soluble in each other, such as oil and water, are said to be immiscible. Substances that are partly soluble in each other are said to show a miscibility gap, and this is related to Monotectic Systems.
- ❑ When one liquid forms another liquid, plus a solid, on cooling, it is known as a *Monotectic Reaction*.
- ❑ It should be apparent that the Monotectic reaction resembles the eutectic reaction, the only difference being that one of the products is a liquid phase instead of a solid phase.
- ❑ An example of an alloy system showing a Monotectic reaction is that between *copper and lead* given in next page. Notice that in this case the $L_1 + L_2$ is closed.
- ❑ Also, although the terminal solids are indicated as α and β , the solubility is actually so small that they are practically the pure metals, copper and lead.

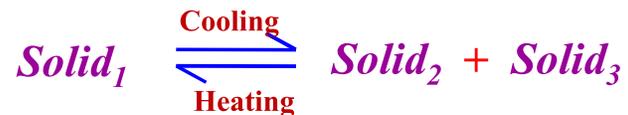
Monotectic Phase Diagram



In Cu-Zn Phase diagram the eutectoid reaction occurs
At 560 °C with 75% Zn

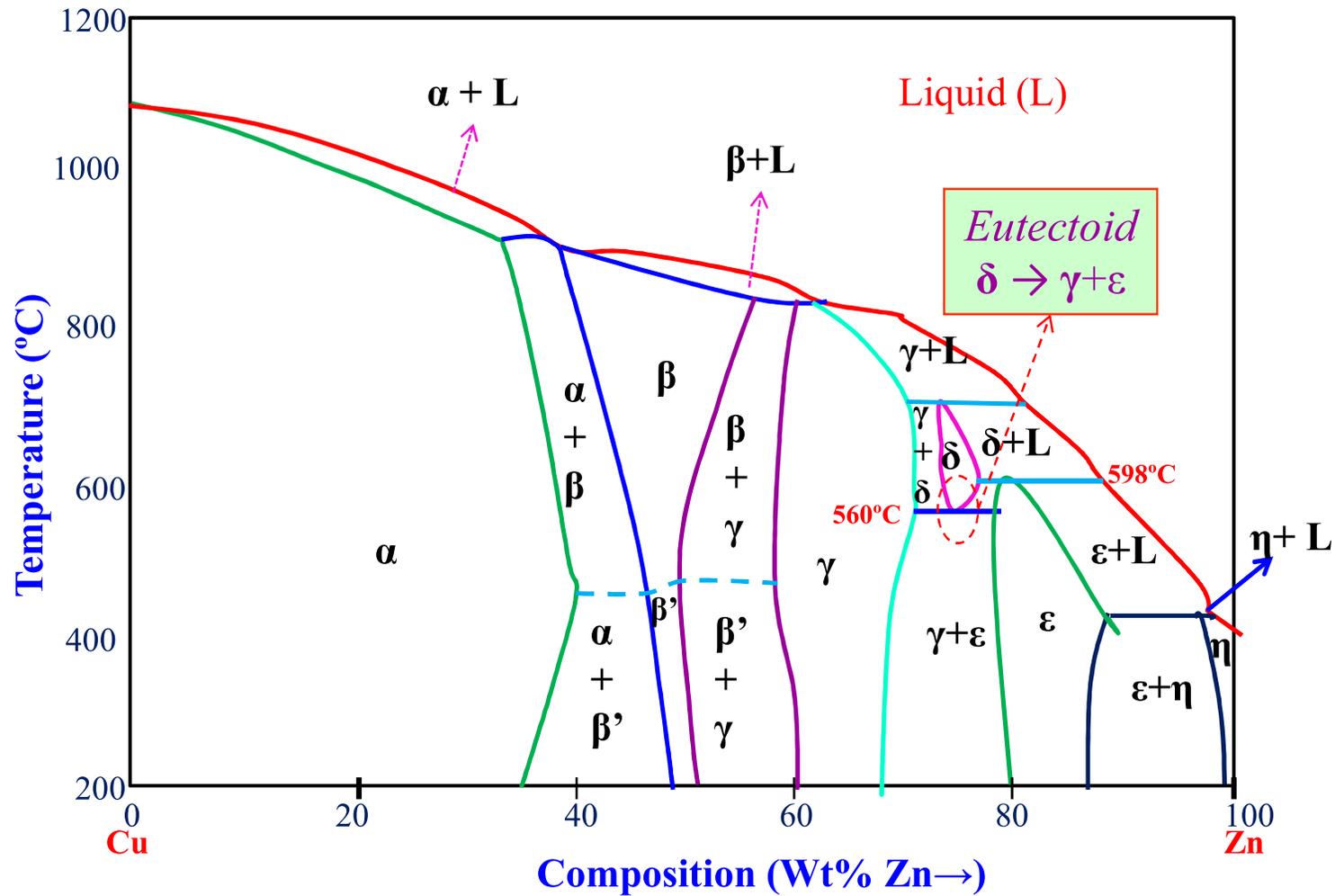
The Eutectoid Reaction

- ❑ This is a common reaction in the solid state. It is very similar to the eutectic reaction but does not involve the liquid. In this case, a solid phase transforms on cooling into two new solid phases. The general equation may be written as..!



- ❑ The resultant Eutectoid mixture is extremely fine, just like the eutectic mixture. Under the microscope both mixtures generally appear the same, and it is not possible to determine microscopically whether the mixture resulted from a eutectic reaction or eutectoid reaction.
- ❑ An **equilibrium diagram of Cu-Zn**, illustrating the eutectoid reaction is shown in figure (*see in next page*).
- ❑ In copper (Cu) – Zinc (Zn) system contains two terminal solid solutions i.e. these are extreme ends of phase diagram α and η , with four intermediate phases called β , γ , δ and ϵ . The β' phase is termed an ordered solid solution, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell.

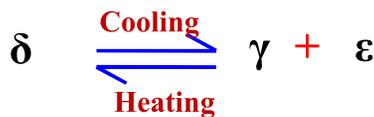
Cu-Zn Phase Diagram - Eutectoid Reaction



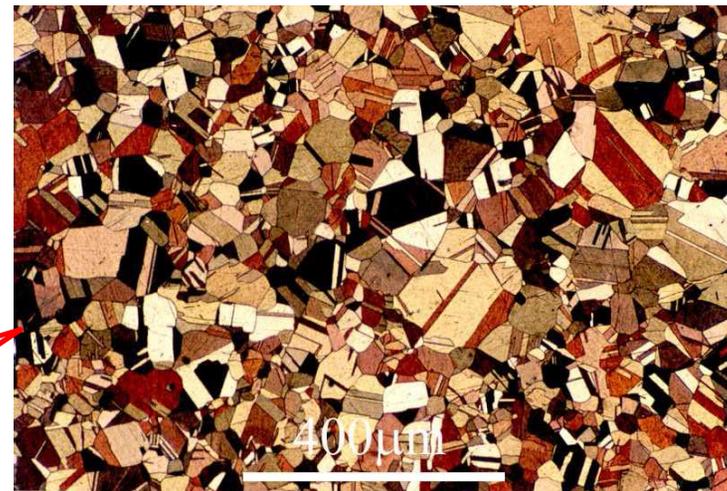
Cu-Zn Phase Diagram - Eutectoid Reaction

- ❑ In the diagram, some phase boundary lines near the bottom are dashed to indicate that their positions have not been exactly determined. The reason for this is that at low temperatures, diffusion rates are very slow and inordinately long times are required for the attainment of equilibrium.
- ❑ Again only single- and two- phase regions are found on the diagram, and the same and we can utilize the lever rule for computing phase compositions and relative amounts.
- ❑ The commercial material brasses are copper-rich copper-zinc alloys: for example, cartridge brass has a composition of 70 wt% Cu-30 wt% Zn and a microstructure consisting of a single α phase.

In Cu-Zn Phase diagram the eutectoid reaction occurs at 560 °C with 75% Zn



Cu 70, Zn 30 (wt%),
recrystallized
annealing twins



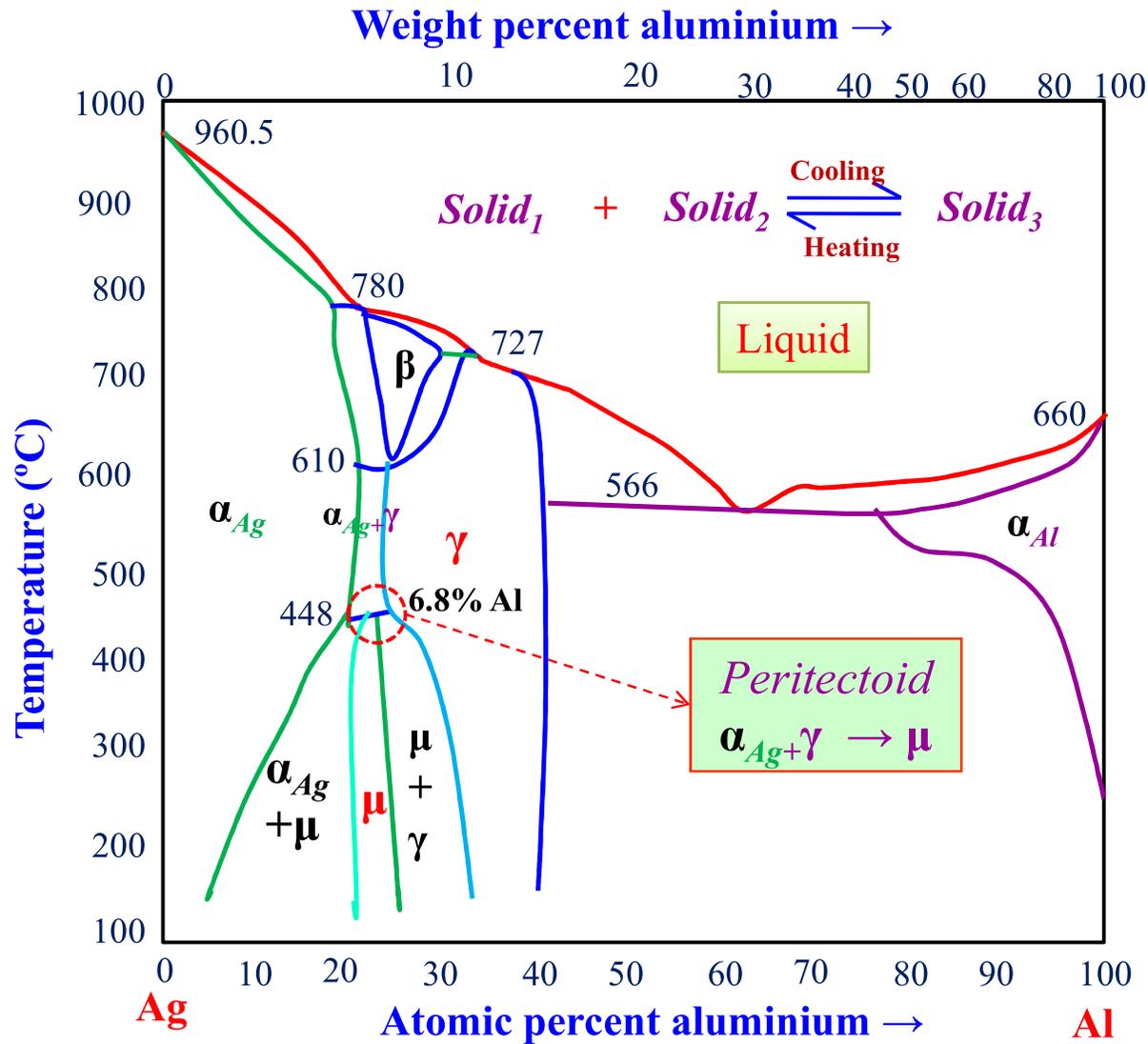
The Peritectoid Reaction

- ❑ This is a fairly common reaction in the solid state and appears in many alloy systems. The peritectoid reaction may be written as

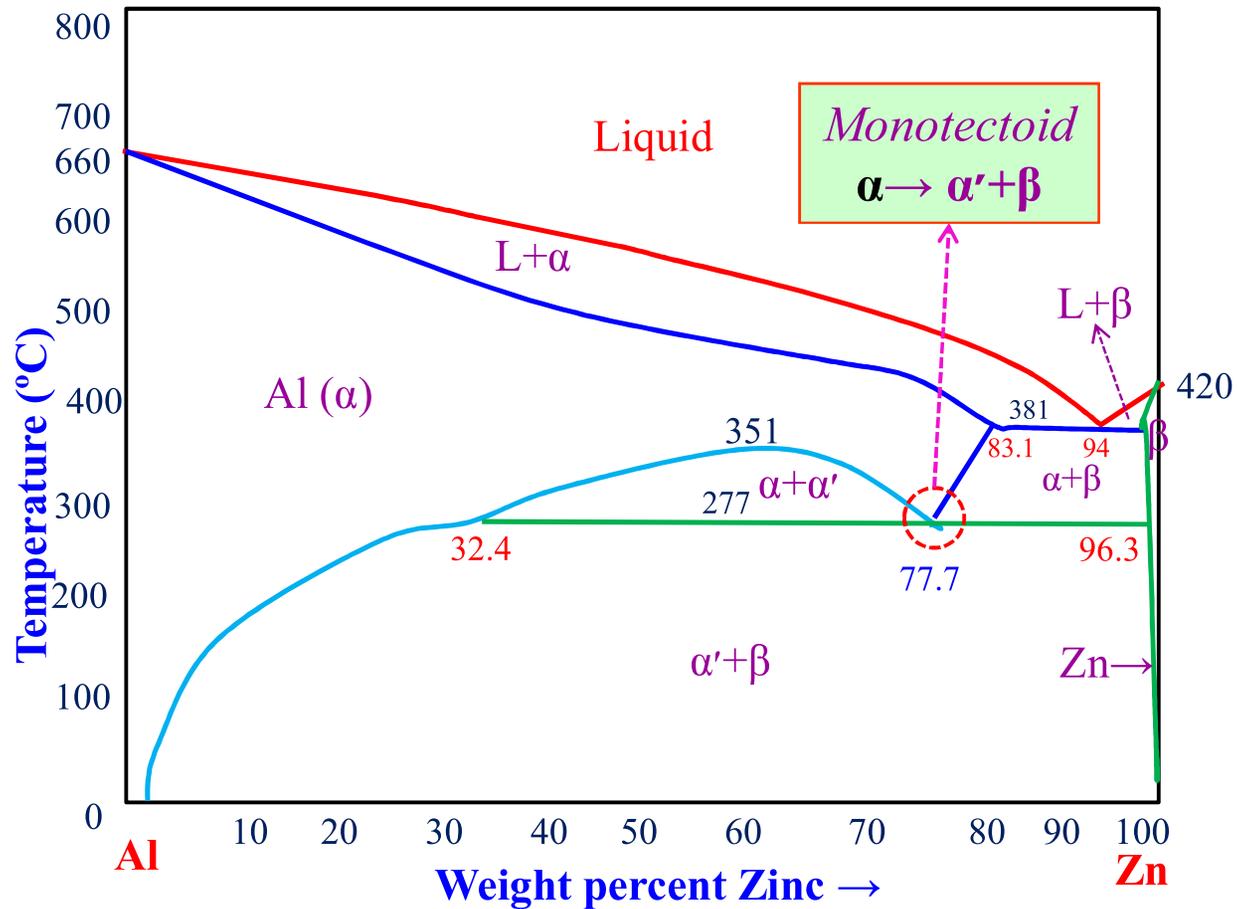


- ❑ The new solid phase is usually an intermediate alloy, but it may also be a solid solution. The peritectoid reaction has the same relationship to the peritectic reaction as the eutectoid has to the eutectic. Essentially, it is the replacement of a liquid by a solid.
- ❑ The peritectoid reaction occurs entirely in the solid state and usually at lower temperatures than the peritectic reaction, the diffusion rate will be slower and there is less likelihood that equilibrium structures will be reached.
- ❑ Consider Silver (Ag) – Aluminium (Al) phase diagram (*in next page*) containing a peritectoid reaction.
- ❑ If a 7% Al alloy is rapidly cooled from the two phase area just above the peritectoid temperature the two phases will be retained, and the microstructure will show a matrix of γ with just a few particles of α . When we cool at below the peritectoid temperature by holding we get single phase μ .

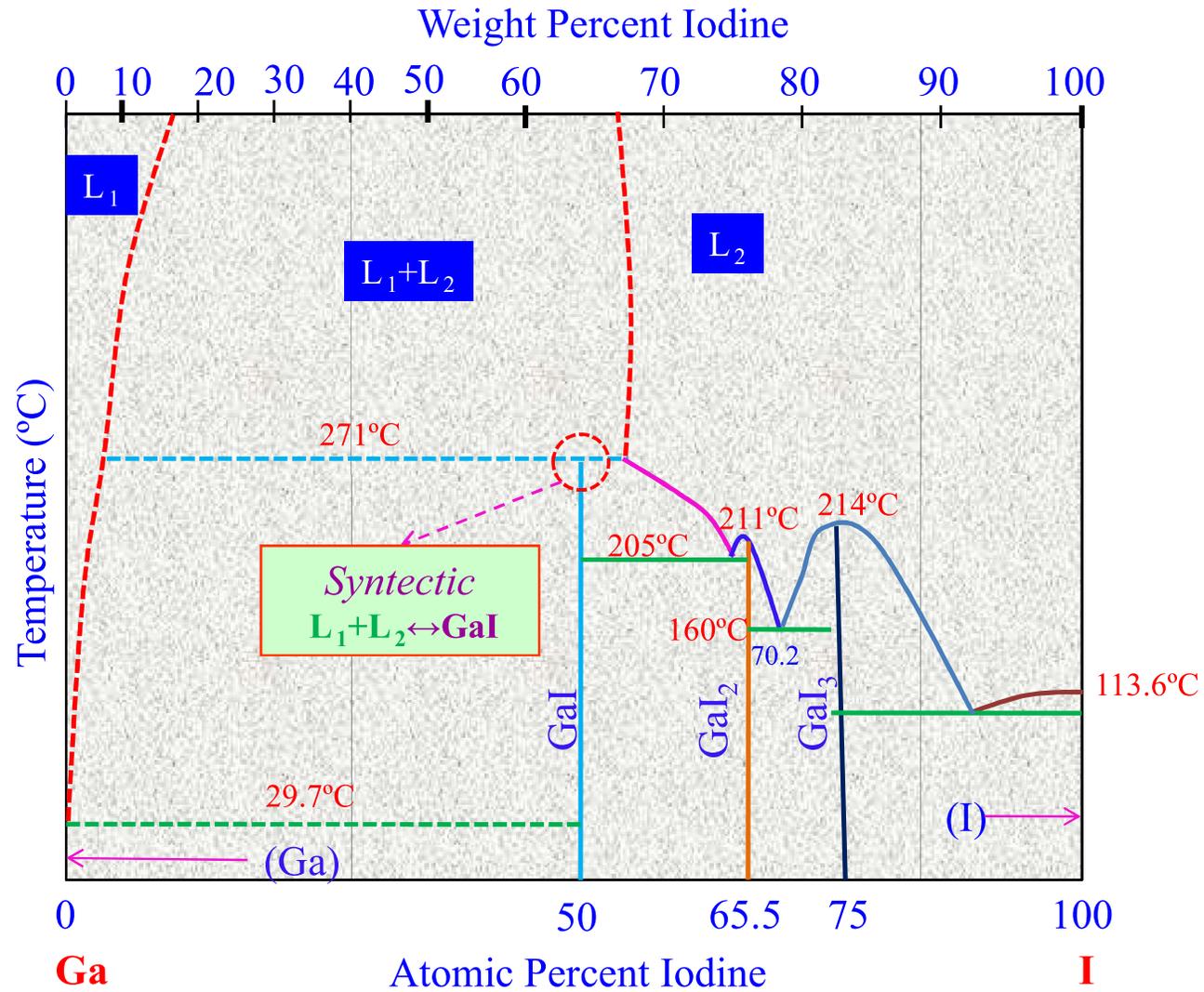
Peritectoid Reaction : Ag-Al Phase Diagram



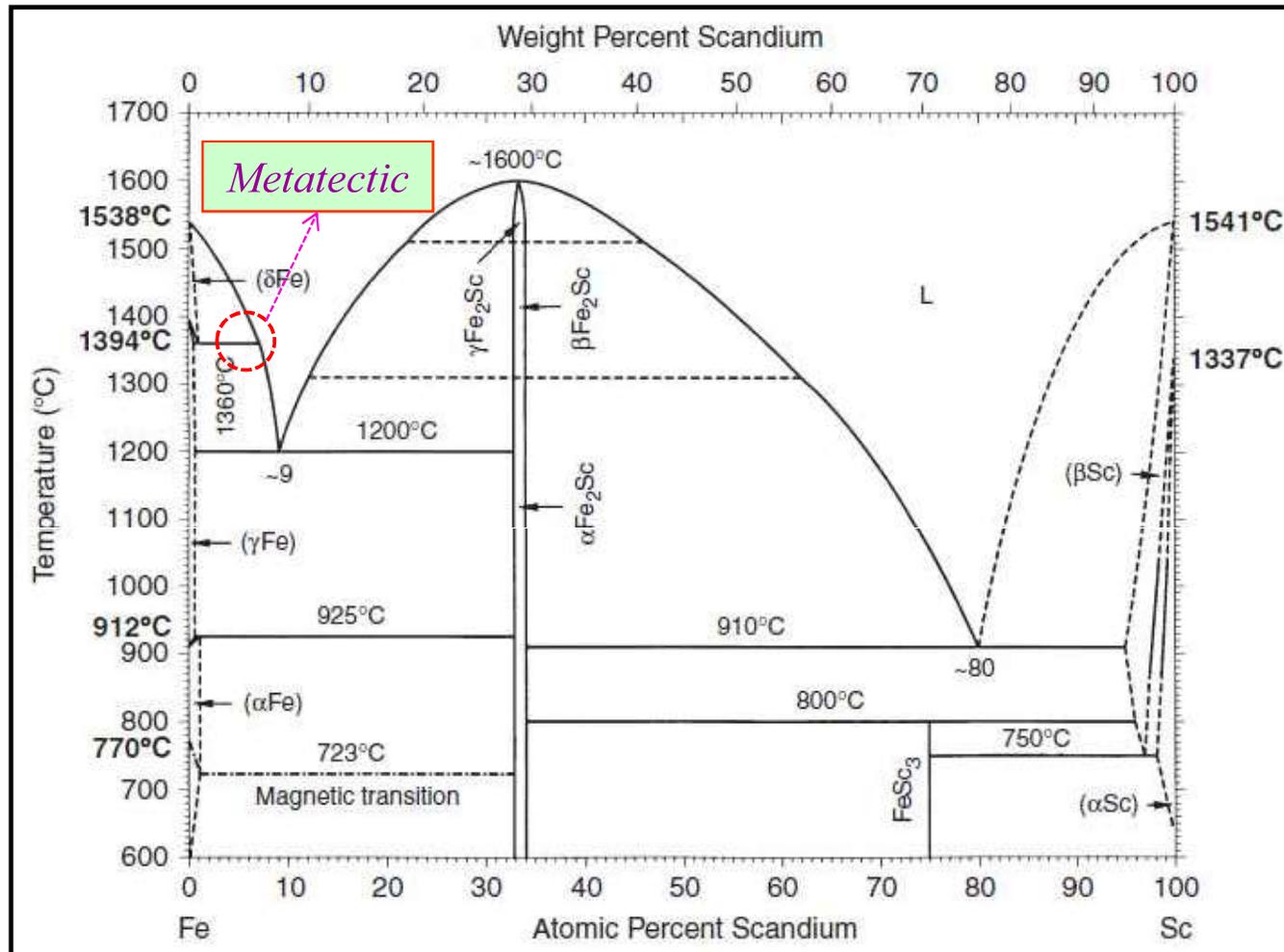
Monotectoid Reaction : Al-Zn Phase Diagram



Syntectic Reaction : Ga – I Phase Diagram



Metatectic Reaction : Fe - Sc Phase Diagram



□ In the above Fe-Sc system represents a Metatectic reaction,



Summary of Invariant reactions

Name of reaction	Phase equilibrium	Schematic representation
Eutectic	$L \leftrightarrow S_1 + S_2$	
Peritectic	$S_1 + L \leftrightarrow S_2$	
Monotectic	$L_1 \leftrightarrow S_1 + L_2$	
Eutectoid	$S_1 \leftrightarrow S_2 + S_3$	
Peritectoid	$S_1 + S_2 \leftrightarrow S_3$	
Monotectoid	$S_{1a} \leftrightarrow S_{1b} + S_2$	
Metatectic	$S_1 \leftrightarrow S_2 + L$	
Syntectic	$L_1 + L_2 \leftrightarrow S$	

Solidification of pure iron:

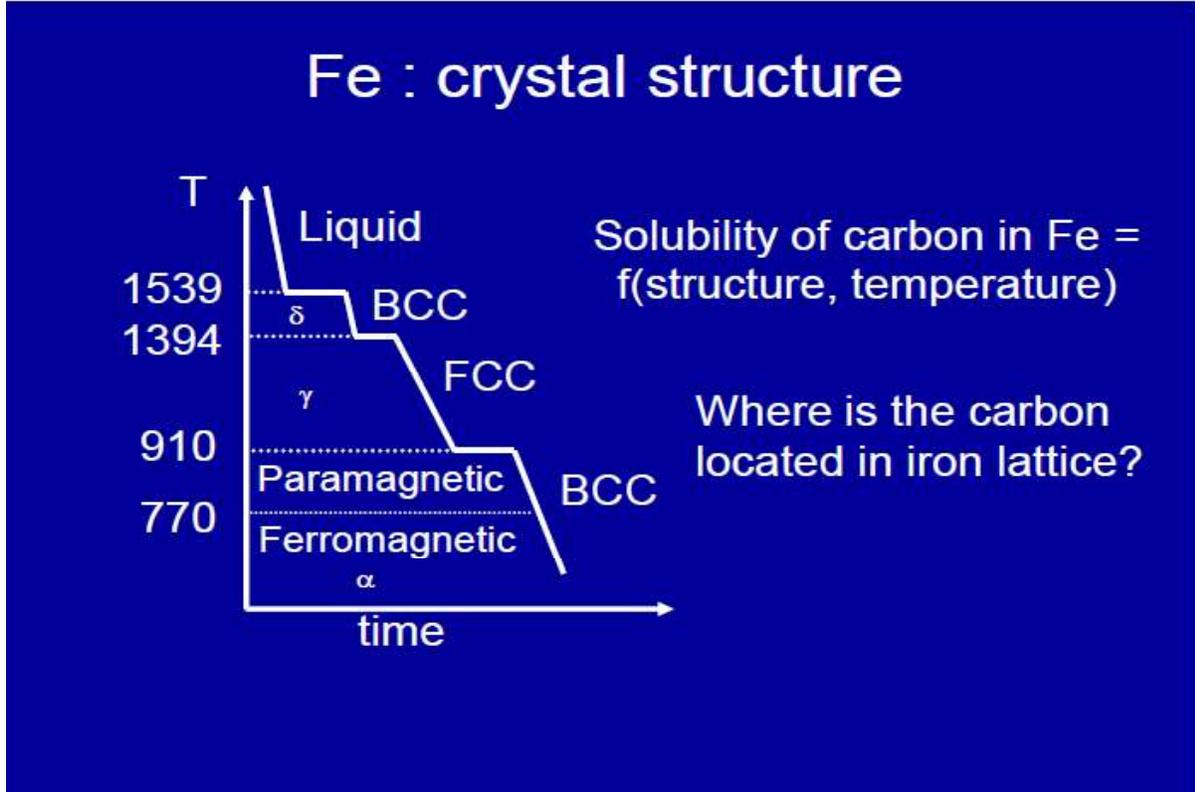


Fig.2.17: Solidification of pure Iron

Fig.2.17 is a typical cooling curve of pure iron. Solidification begins with nucleation and growth of crystals of iron at 1539°C. It is BCC (body centered cubic). At 1394°C it transforms into FCC (face centered cubic) structure. This is stable till 910°C where it again transforms into BCC. Each of these transformations appears as steps on the cooling curve. Apart from this there is another transformation which may not get detected by thermal analysis. This is the transformation from paramagnetic to ferromagnetic state. It occurs at 770°C. This is known as its Curie temperature. The property which is most sensitive to detect it, is magnetic permeability. The three different forms of iron are known as ferrite (α), stable until 910°C, austenite (γ), stable from 910°-1394°C and ferrite (δ), stable from 1394°-1539°C. Note that the BCC form of iron is known as ferrite. Therefore in order to distinguish between the two, the high temperature form is termed as delta ferrite. If carbon atoms are introduced into iron these are likely to occupy the interstitial sites because the atoms carbon are much smaller than those of iron atoms. The interstitial sites in BCC and FCC are shown in Fig 2.18 The solubility of carbon in iron is a function of temperature and crystal structure.

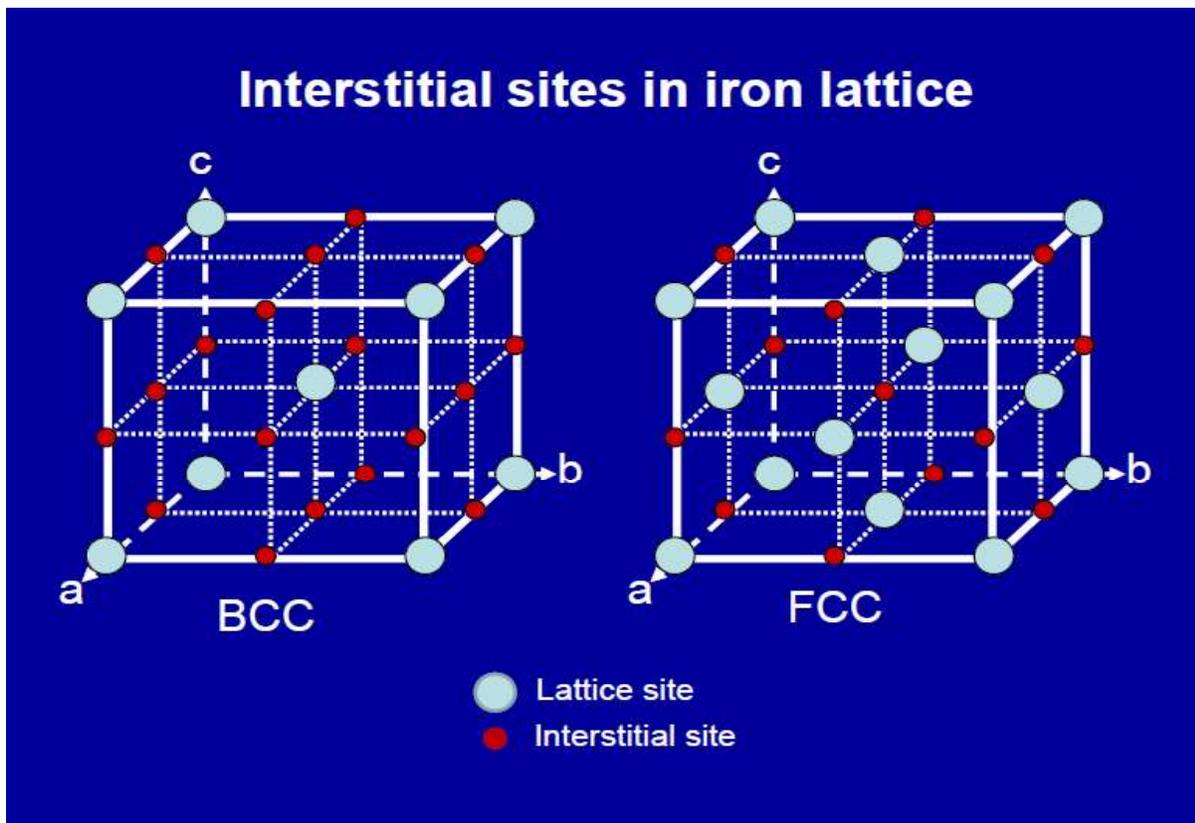


Fig.2.18: shows the lattice sites occupied by iron atoms

Fig.2.18 shows the lattice sites occupied by iron atoms and possible interstitial sites for carbon atoms in both BCC & FCC structures. The interstitial sites shown here are known as octahedral sites. The sketches in Fig.2.18 show only the positions of iron atoms and the interstitial sites in one unit cell. The sites located within the cell belong exclusively to a unit cell but those lying on the faces, the edges or the corners are shared by the neighboring unit cells as well. BCC has eight corner sites for iron atoms. Each of these is shared by 8 neighboring unit cells. The contribution of corner site is thus $1/8$. The atom at the centre

belongs exclusively to this unit cell. Therefore the number of iron atoms / unit cell = $8 \times (1/8) + 1 = 2$. Let us use the same approach to estimate the number of interstitial sites /unit cell for BCC structure. The sketch in Fig.2.18 shows the locations of interstitial sites. There are 6 sites at the centers of 6 faces. Each face is shared by two unit cells. There are 12 sites at each of the 12 edges. Each of these is shared by 4 neighboring cells. Therefore the number of interstitial sites /

unit cell in BCC crystal = $12 \times (1/4) + 6 \times (1/2) = 6$. Note that it is 3 times the number of Fe atoms in a unit cell. Look at the sketch for FCC unit cell in Fig.2.18. Count the number of lattice sites. Follow the same approach to show that the number of Fe atoms / unit cell = $6 \times (1/2) + 8 \times (1/8) = 4$. In the same way the number of interstitial sites / unit cell in FCC structure = $1 + 12 \times (1/4) = 4$. Note that in FCC structure the ratio of the number of interstitial site to the number of lattice sites = 1.

Phases in iron – carbon binary system:

Iron can exist in three different crystalline forms each having limited solubility of carbon. The stability of these depends on temperature and composition. The two high temperature forms of iron are δ ferrite which is BCC (stable above 1394°C) and austenite (γ stable above 910°C) which is FCC. The room temperature form of iron is α ferrite which is BCC. The solubility of carbon in ferrite is limited. The maximum solubility is around 0.025wt% as against this the solubility of carbon in austenite is a little more. It is about 2wt%. Apart from this iron carbon system may have iron carbide (Fe_3C) called cementite. It has 6.67% carbon. It is considered as an inter-metallic compound having relatively more complex crystal structure than those of ferrite and austenite. It is a meta-stable phase. It may exist for indefinite periods of time at room temperature. However on prolonged thermal exposure at 600°C or beyond it transforms into ferrite and graphite. Therefore iron carbon alloys of commercial importance may be considered as a binary alloy of iron and cementite. Let us first look at its phase diagram. It is also known as iron cementite meta-stable phase diagram. Although it is a binary system there are 5 different phases including the liquid. This is likely to have more than one invariant reaction involving 3 phases.

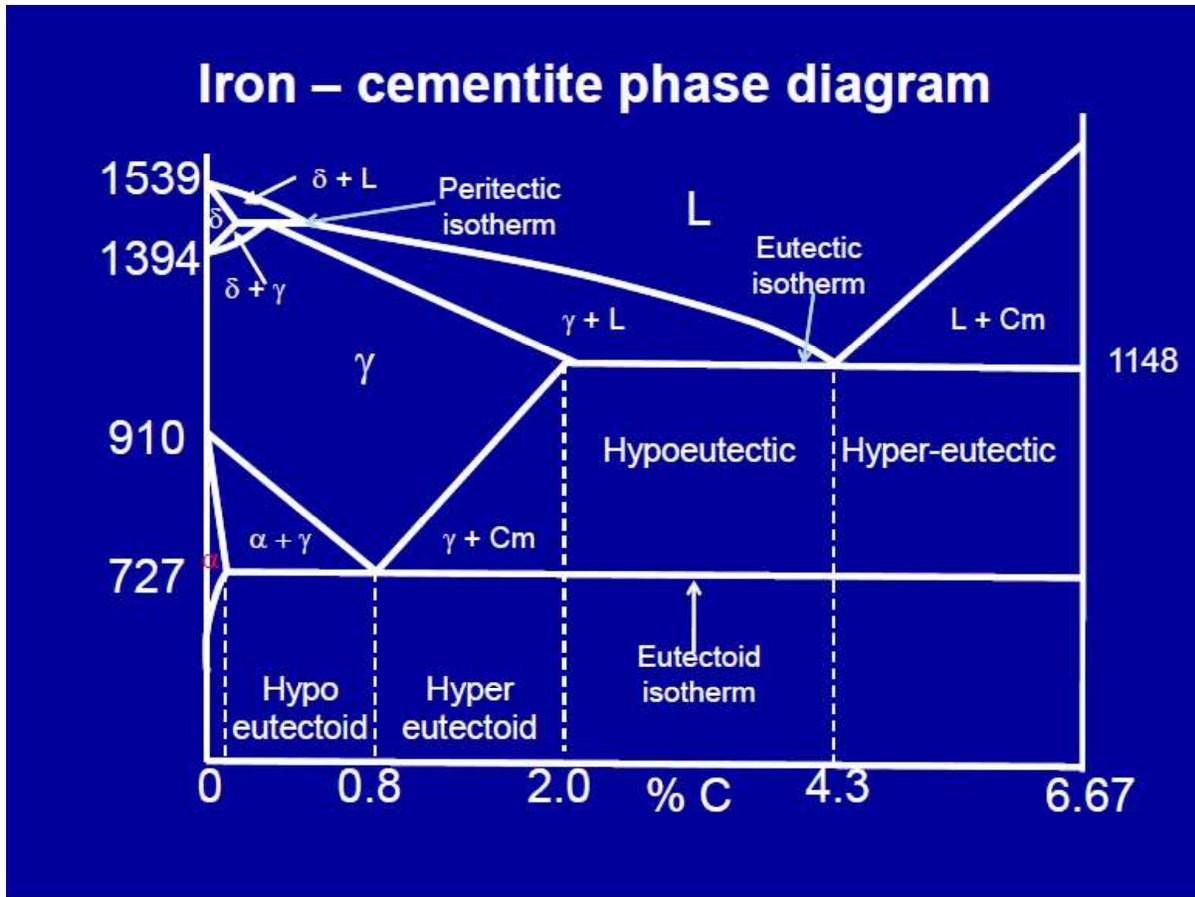
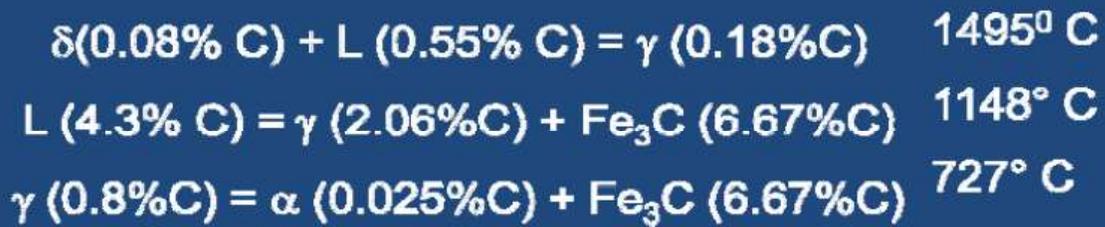


Fig.2.19: shows the Iron-Cementite phase diagram

Fig.2.19 shows a schematic Fe-Fe₃C phase diagram. It has 3 invariant reactions (transformation). These are given below. The one occurring at 1495°C is the peritectic reaction. The delta ferrite reacts with liquid to form austenite. The one at 1148°C is known as the eutectic reaction where the liquid transforms into a mixture of austenite and cementite. The eutectic is known as Ledeburite. The one at 727°C is known as eutectoid transformation where austenite decomposes into a mixture of ferrite and cementite. This is known as Pearlite. On the basis of this diagram iron – carbon alloys having less than 2.0% carbon are known as steel, whereas those having more than 2.0% carbon are known as cast iron. This classification is based on their ability to undergo large plastic deformation. Steel is ductile but cast iron is brittle.



Steel:

It is an iron carbon alloy where most of the carbon is present as meta-stable iron carbide called cementite. The upper limit of carbon content is 2%. Phase diagram helps us guess the structure of alloys and their properties. Let us look at what kinds of structure steel could have depending on its composition. We would only consider the structure that develops under equilibrium rate of cooling. The steel on solidification is expected to have fully austenitic structure. It may be assumed to be homogeneous since the rate of cooling is considered to be slow. Depending on its composition we may have 3 types of structures.

- (i) % carbon < 0.02 (ii) 0.02 < % carbon < 0.8 (iii) 0.8 < % Carbon < 2.0.

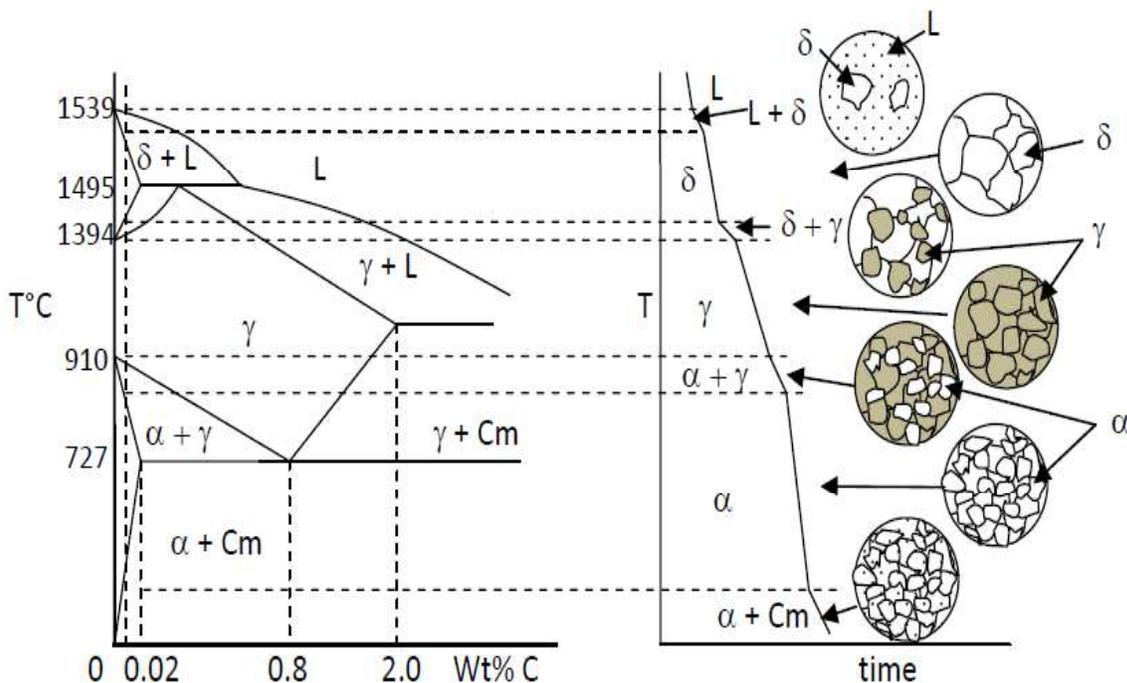


Fig.2.20: Shows the solidification behavior of steel having less than 0.02% carbon

(i) Fig.2.20 explains the solidification behavior of steel having less than 0.02% carbon with the help of a set of schematic diagrams. The sketch on the left shows a part of the equilibrium diagram (Fe-Fe₃C) with the location of the alloy by a vertical dotted line. It intersects the liquidus, solidus, and a set of solvus curves. These are projected on to the cooling curve shown on the right with the help of a set of horizontal lines. The cooling curve exhibits inflection points at each of these intersections. Solidification begins with precipitation of a few grains of δ ferrite. The top most microstructure corresponds to this stage. The solidification takes place by nucleation and growth. The composition of the liquid and the solid keeps changing during this stage. When solidification is complete the entire liquid is replaced by δ ferrite having the same composition as that of the alloy. This is shown by the second schematic structure from the top in Fig.2.20. The structure remains unchanged until the temperature crosses the boundary between $\delta / \delta+v$ phase fields. Thereafter austenite precipitates from δ ferrite. The grain corners and boundaries are the preferred sites where grains of austenite nucleate. The third microstructure from the top in Fig.2.20 represents its main features. It consists of grains of δ (white) and a few grains of v (grey). There is partition of carbon between these two phases. Bulk of the carbon goes into austenite. The composition of the two keeps changing as the temperature drops. The volume fraction of v increases at the cost of δ . When the %carbon in austenite becomes equal to that of the steel δ ferrite disappears. The structure now consists of 100% austenite. Note the main features of the fourth microstructure from the top in Fig.2.20. The grain size is finer than that of 100% δ ferrite. The structure remains as 100% austenite until the temperature drops below the line representing the boundary between v and $\alpha+v$ phase fields of the equilibrium diagram. This is where α ferrite starts precipitating from austenite. The grain boundaries and the grain corners are the preferred sites for precipitation. The fifth sketch from the top of Fig.2.20 is a typical representation of its microstructure at this stage. Ferrite grains are shown as white and austenite grains are shown as grey. This continues through nucleation of new grains and growth of the existing ones until the temperature drops below the line between $\alpha+v$ and α phase fields of the phase diagram. At this stage the structure is 100% ferrite (α). The 6th sketch in Fig.2.20 is a typical representation of the microstructure. This remains unchanged till the temperature drops below the solvus. At this stage excess carbon precipitates as cementite. The last sketch in Fig.2.20 is a

typical representation of its microstructure. The amount of cementite keeps increasing as the room temperature drops. It can be estimated by lever rule. From the phase diagram it is evident that the steel at room temperature would consist of ferrite with a few specks of cementite. If % carbon in the steel is 0.01 the amount of cementite is given by $(0.01/6.67) \times 100 = 0.15\%$. The grains are relatively finer than that after solidification.

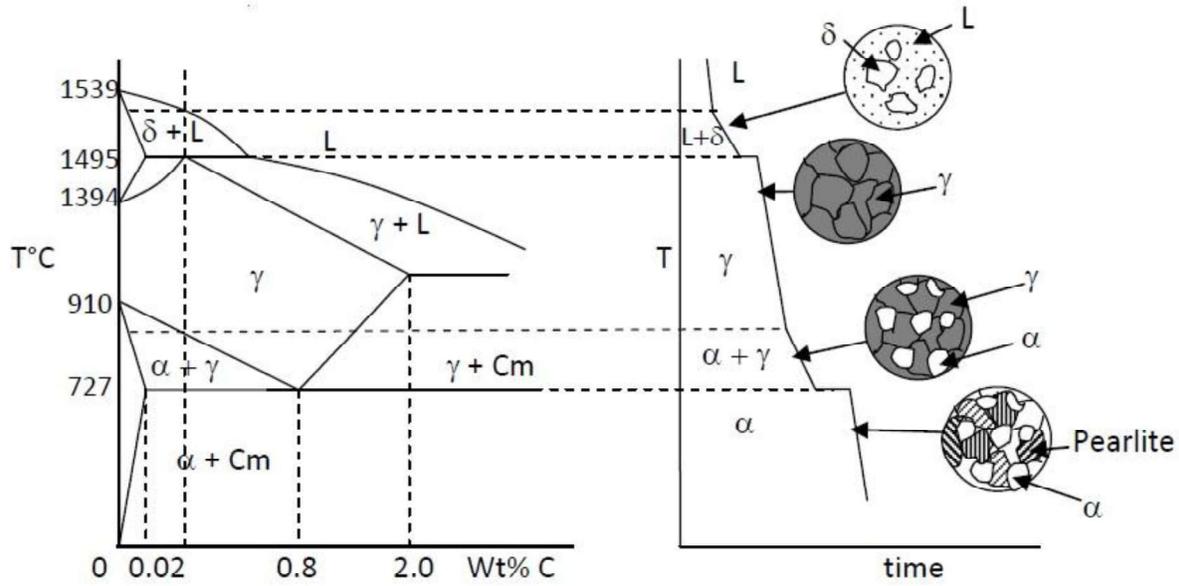


Fig.2.21: Shows the solidification behavior of steel having greater than 0.02% carbon but less than 0.8% carbon

(ii) Fig.2.21 explains the solidification behavior of steel having greater than 0.02% carbon but less than 0.8% carbon with the help of a set of schematic diagrams. The sketch on the left shows a part of the equilibrium diagram (Fe-Fe₃C) with the location of the alloy by a vertical dotted line. It has around 0.18% carbon. It intersects the liquidus and a set of lines denoting either phase field boundaries or isotherms representing 3 phase equilibrium. These are projected on to the cooling curve shown on the right with the help of a set of horizontal lines. The cooling curve exhibits inflection points or steps (discontinuity) at each of these intersections. Solidification begins with the precipitation of a few grains of δ ferrite. The first microstructure from the top corresponds to this stage. Solidification takes place by the nucleation of new grains and the growth of the existing ones. The composition of the liquid and the solid keeps changing during this stage. When the temperature reaches 1495°C peritectic reaction sets in. This is an invariant reaction. The liquid having 0.55% carbon reacts with δ ferrite having 0.08% carbon to form austenite (γ) having 0.18% carbon. The amount of δ is just enough to

consume the remaining liquid. The alloy on solidification consists of austenite (γ) having 0.18% carbon. This is shown by the second schematic structure from the top in Fig.2.21. The structure remains unchanged until the temperature crosses the boundary between $\gamma / \alpha + \gamma$ phase fields. Thereafter ferrite (α) precipitates from (γ) austenite. The grain corners and boundaries are the preferred sites where grains of ferrite nucleate. The ferrite precipitating from austenite is known as pro-eutectoid ferrite. The third microstructure from the top in Fig.2.21 represents its main features. It consists of grains of pro-eutectoid α (white) and a few grains of γ (grey). There is partition of carbon between these two phases. Bulk of the carbon goes into austenite. The composition of the two keeps changing as the temperature drops. The volume fraction of α increases at the cost of γ . When % carbon in austenite reaches 0.8% eutectoid reaction sets in. This is an invariant reaction. As long as it continues the temperature remains constant. During this stage both cementite and ferrite start precipitating from austenite at the same time. The product is an intimate mixture of two phases. It is known as pearlite. It consists of parallel layers (plates) of ferrite and cementite. Fig.2.22 gives a series of sketches showing various stages involved in the formation of pearlite. When a cementite plate nucleates as in (Fig.2.22 (a)) at an austenite boundary it takes carbon from its neighboring area. This results in a change in local carbon profile as shown in the sketch. Just beside cementite % C = 0.02 whereas at a distance far from this it approaches 0.8 % C (this is the composition of the eutectoid). When this becomes low enough a ferrite plate nucleates. Fig.2.22 (b) illustrates this. Note the change in carbon concentration as a function of distance. Fig.2.22 (c) shows the arrangement of ferrite cementite plates in a colony of pearlite. The width of the two is approximately proportional to % ferrite and % cementite in eutectoid steel having 0.8% carbon. Using lever rule % cementite in pearlite = $100 \times (0.8 - 0.025) / (6.67 - 0.025) = 12\%$ (approximately). Therefore % ferrite = 88%. The ratio of the two is approximately equal to 1:7. This means the width of the ferrite plate will be seven times the width of cementite plate. On completion of the eutectoid reaction the structure consists of pro-eutectoid ferrite and pearlite. Note the main features of the fourth microstructure from the top in Fig 2.21. When the temperature drops below the eutectoid temperature, excess carbon from ferrite (α) precipitates as cementite. This is known as tertiary cementite (Why this is called tertiary will be clear from subsequent part of this module). However the change in structure below the eutectoid temperature is too little to detect. Steels having carbon within 0.02 – 0.8 consist of ferrite and pearlite. They are known as hypo-eutectoid steel.

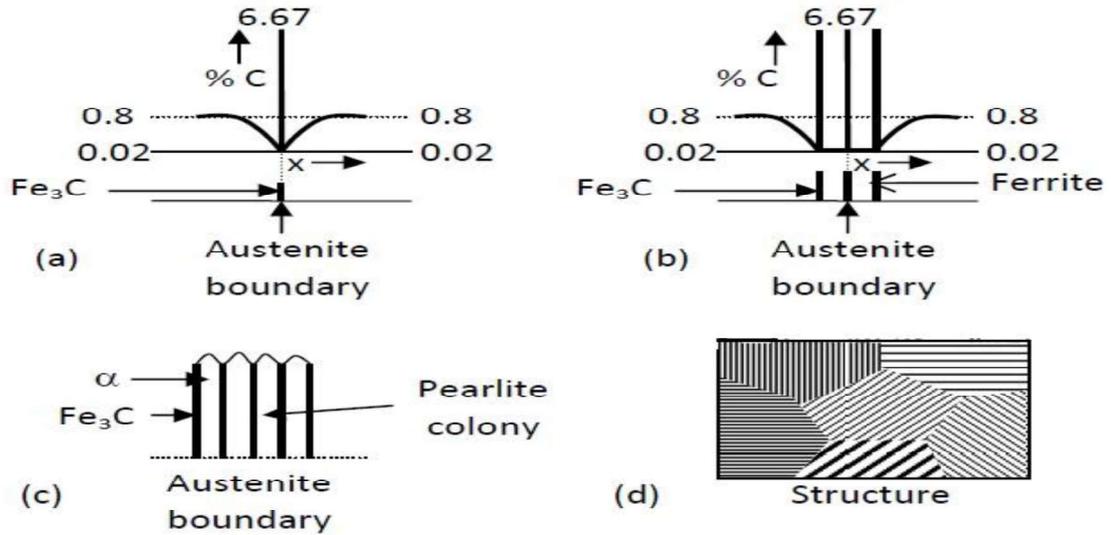


Fig.2.22: Shows a series of sketches showing various stages involved in the formation of pearlite

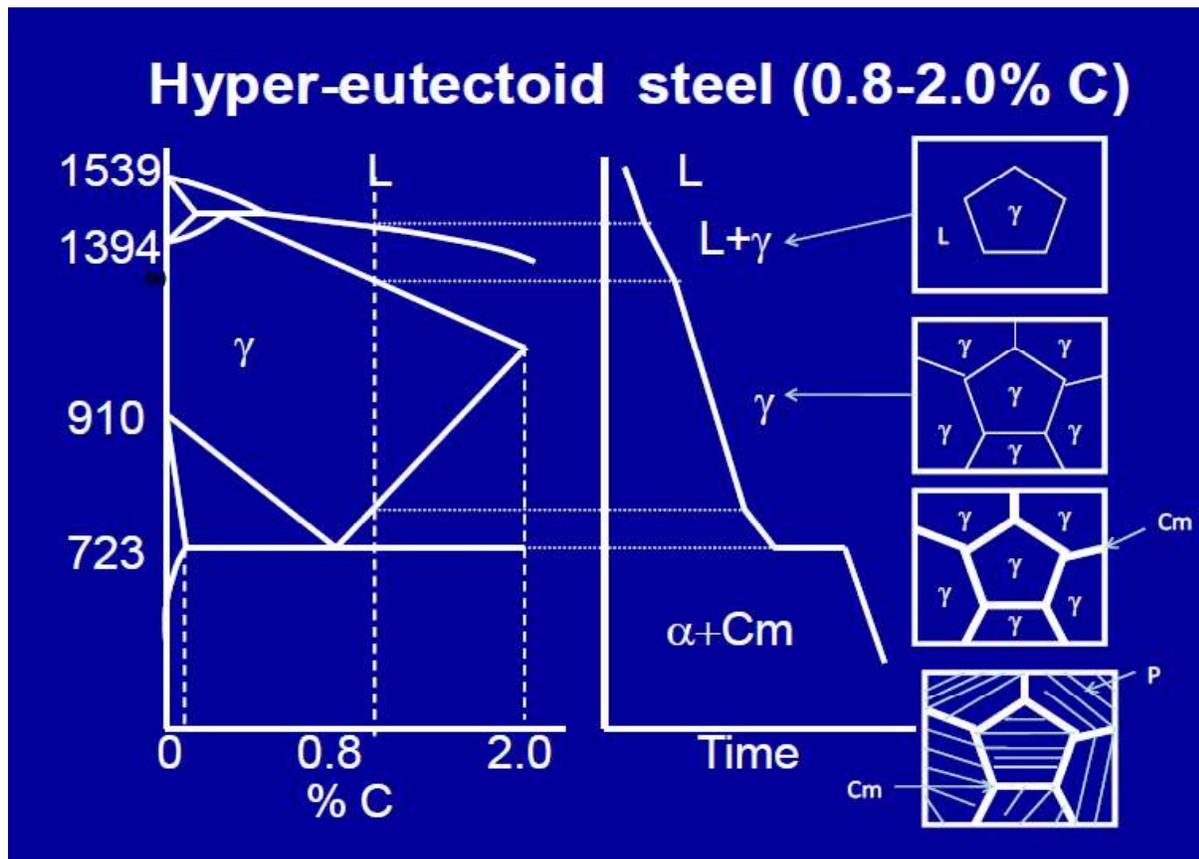


Fig.2.23: Shows solidification behavior of steel having greater than 0.8% carbon but less

than 2.0% carbon

(iii) Fig.2.23 explains the solidification behavior of steel having greater than 0.8% carbon but less than 2.0% carbon with the help of a set of schematic diagrams. Such steels are known as hyper-eutectoid steel. The sketch on the left shows a part of the equilibrium diagram (Fe-Fe₃C) with the location of the alloy as a vertical dotted line. It has around 1.0% carbon. It intersects the liquidus, solidus, solvus and the eutectoid reaction isotherm representing 3 phase equilibrium. These are projected on to the cooling curve shown on the right with the help of a set of horizontal lines. The cooling curve exhibits inflection points or a step (discontinuity) at each of these intersections. Solidification begins with precipitation of a few grains of γ austenite. The top most microstructure corresponds to this stage. The solidification takes place by nucleation of new grains and growth of the existing ones. The composition of the liquid and the solid keeps changing during this stage. When the temperature reaches that of the solidus the composition of the solid becomes equal to that of the steel. The alloy on solidification consists of 100% austenite (γ) having 1.0% carbon (say). This is shown by the second schematic structure from the top in Fig.2.23. The structure remains unchanged until the temperature crosses the solvus, the boundary between $\gamma/\gamma + \text{Cementite}$ phase fields. At this stage cementite starts precipitating from austenite. It grows at the cost of austenite. The % carbon in austenite keeps decreasing as the amount of cementite increases. The grain boundary is the most favored site for precipitation. The fourth structure from the top in Fig.2.23 gives a typical structure of steel at this stage. When % carbon in austenite decreases to 0.8% eutectoid reaction sets in. This is an invariant reaction. As long as it continues the temperature remains constant. During this stage both cementite and ferrite start precipitating from austenite at the same time. The product is an intimate mixture of two phases. It is known as pearlite. The details about the pearlitic structure are shown in Fig 2.22. Cementite is a hard and brittle phase. The presence of a continuous network of cementite makes steel extremely brittle. There are methods to avoid the formation of such a network to make it suitable for engineering applications. We shall learn about in one of the subsequent modules.

Estimation of the amount of micro-constituents in steel from phase Diagram:

The micro-constituents in steel are ferrite, austenite, cementite and pearlite. Out of these austenite is not stable at room temperature. When we look at microstructures of steel we get an

idea about the distribution of various constituents. If the composition or % carbon in steel is known we can estimate the volume fraction (weight fraction) of each the likely constituents.

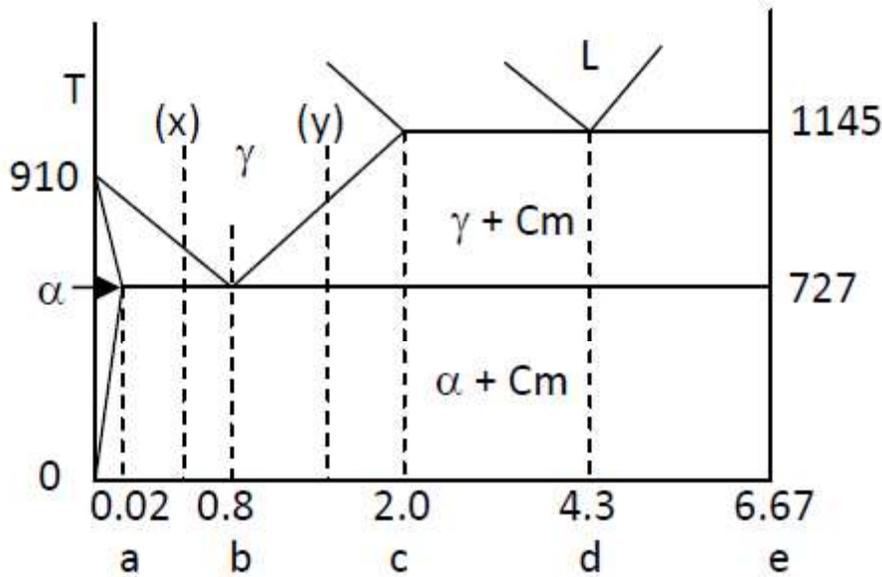


Fig 2.24: Shows how to estimate the amounts of micro-constituents in steel at room temperature.

Fig.2.24 gives the relevant part of Fe-Fe₃C phase diagram. For practical purpose we may assume that the solubility of carbon in ferrite is negligible. The general expressions for the amount of Pearlite (P),Cementite (Cm), Pro- eutectoid Ferrite & Total ferrite (α) in a hypo-eutectoid steel having x% C are as follows.

$$\%Pearlite = \frac{x-a}{b-a} \times 100 \approx \frac{x}{0.8} \times 100$$

$$\%Pro - eutectoid ferrite = \frac{b-x}{b-a} \times 100 \approx \frac{0.8-x}{0.8} \times 100$$

$$\%Cementite = \frac{x-a}{e-a} \times 100 \approx \frac{x}{6.67} \times 100$$

$$\%Total ferrite = \frac{6.67-x}{e-a} \times 100 \approx \frac{6.67-x}{6.67} \times 100$$

This truly gives weight % of various constituents. When you look at the microstructure you get an estimate of volume %. However if the density of the phases are known weight % can be converted to volume %. In the case of steel the density of ferrite is 7.87 g/cc and that of cementite is 7.662. Although the difference is not much the amount of Cm seen in a microstructure (volume fraction) will be a little more than weight fraction obtained from the lever rule.

Cast iron:

If % carbon is greater than 2.0 but less than 6.67 the Fe-Fe₃C alloy is known as white cast iron. Such an alloy can be easily cast into various shapes but it has poor ductility. The fracture surface has silvery white luster. This is why it is known as white cast iron. On the basis of its microstructure there are two types of white cast iron. These are (i) hypoeutectic white cast iron (2.0 < % C < 4.3) and (ii) hypereutectic white cast iron (4.3 < %C < 6.67). Cementite (Fe₃C) is the hardest constituent in the Fe – Fe₃C system. Its hardness is of the order of 1000HV (Vickers Hardness Number). This is why it has excellent wear resistance. Recall that the % carbide in eutectic is around 60%. Hard materials are known to be brittle.

There is no wonder that white cast iron has poor ductility. Let us look at the evolution of microstructure in hypo & hyper eutectic white cast iron. This has been explained with the help of a set of sketches given in Fig 2.25 – 2.26.

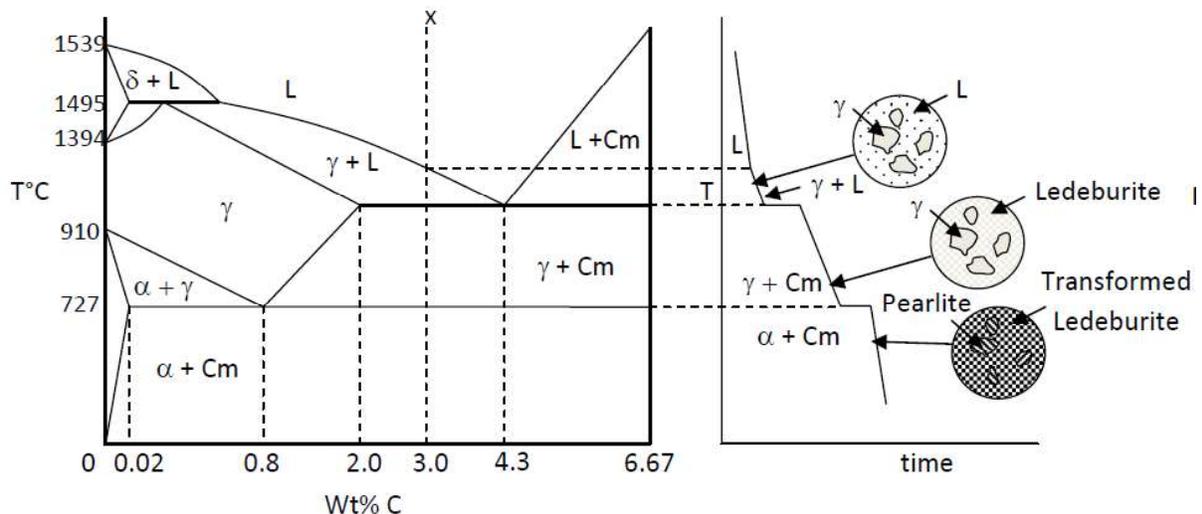


Fig 2.25: Shows the evolution of the microstructure in a hypoeutectic cast iron

Fig.2.25 describes the evolution of the microstructure in a hypoeutectic cast iron. The vertical dotted line marked x is the location of the alloy with respect to the Fe-Fe₃C phase diagram. The sketch on the right gives its cooling curve. Solidification begins with nucleation and growth of austenite grains. As it cools the amount of austenite increases at the cost the liquid. The composition of the austenite and the liquid keep changing. At the eutectic temperature the composition of liquid is 4.3 whereas that of the austenite is 2.0. If %C in the cast iron is 3.0, % austenite at this temperature = $100 \times (4.3-3.0)/(4.3-2.0) = 57\%$. The balance 43% is liquid. On cooling this it solidifies as a mixture of austenite and cementite. The eutectic is known as ledeburite. The austenite that forms before eutectic transformation is called proeutectic austenite or primary austenite. On subsequent cooling, the volume fraction of cementite increases at the cost of austenite. At the eutectoid temperature the primary austenite and the austenite in the eutectic transform into pearlite. The final structure would consist of relatively large nodule of pearlite (originating from primary austenite) and a fine dispersion of tiny nodules of pearlite (originating from the austenite in the eutectic) in a matrix of cementite.

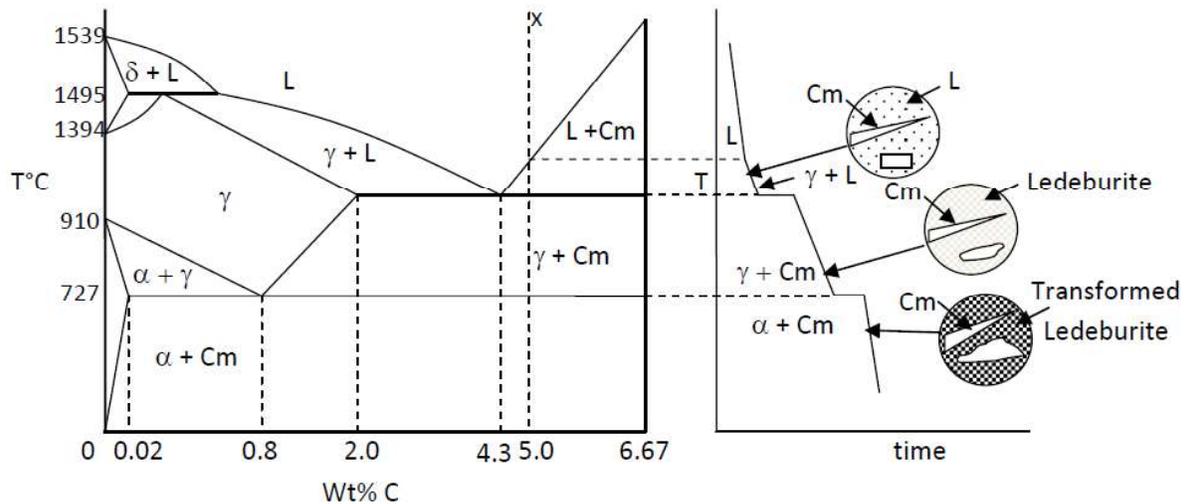


Fig 2.26: Shows the evolution of the microstructure in a hyper-eutectic white cast iron

Fig 2.26 describes the evolution of the microstructure in a hyper-eutectic white cast iron. The vertical dotted line marked x is the location of the alloy with respect to the Fe-Fe₃C phase diagram. The sketch on the right gives its cooling curve. Solidification begins with nucleation and growth of primary (proeutectic) grains of cementite. As it cools the amount of cementite increases at the cost the liquid. Note that cementite has a fixed composition. However the composition of the liquid keeps changing. At the eutectic temperature the composition of liquid

is 4.3. If %C in the cast iron is 5.0, %liquid at this temperature = $100 \times (6.67-5.0)/(6.67-4.3) = 70\%$. On further cooling it solidifies as a mixture of austenite and cementite. The eutectic is known as ledeburite. The cementite that forms before eutectic transformation is called pro-eutectic cementite or primary cementite. On subsequent cooling, the volume fraction of cementite increases at the cost of austenite within the eutectic. The cementite that forms during this stage is called secondary cementite. At the eutectoid temperature the austenite in the eutectic transforms into pearlite. The final structure consists of relatively large primary cementite and a fine dispersion of tiny nodules of pearlite (originating from the austenite in the eutectic) in a matrix of cementite. The eutectic in cast iron at room temperature is known as transformed ledeburite. The cementite present in iron carbon system has several distinct morphologies. In hyper-eutectic white cast iron has all of these. Cementite precipitating from the liquid is called primary cementite, that precipitating from austenite is called secondary cementite, and those precipitating from ferrite below eutectoid temperature is called tertiary cementite. Apart from these cementite is also present as thin plates within nodules of pearlite.

Iron – carbon system

In the previous section we looked at Fe-Fe₃C meta-stable phase diagram. It was mentioned that iron carbide is not a stable phase although it can exist in this form at room temperature for indefinite periods. However on prolonged exposure to high temperature (around 600°C) it can decompose into ferrite and graphite. We would therefore look at iron graphite phase diagram and learn about alloys where carbon is present as graphite.

Iron Carbon (Graphite) Phase Diagram:

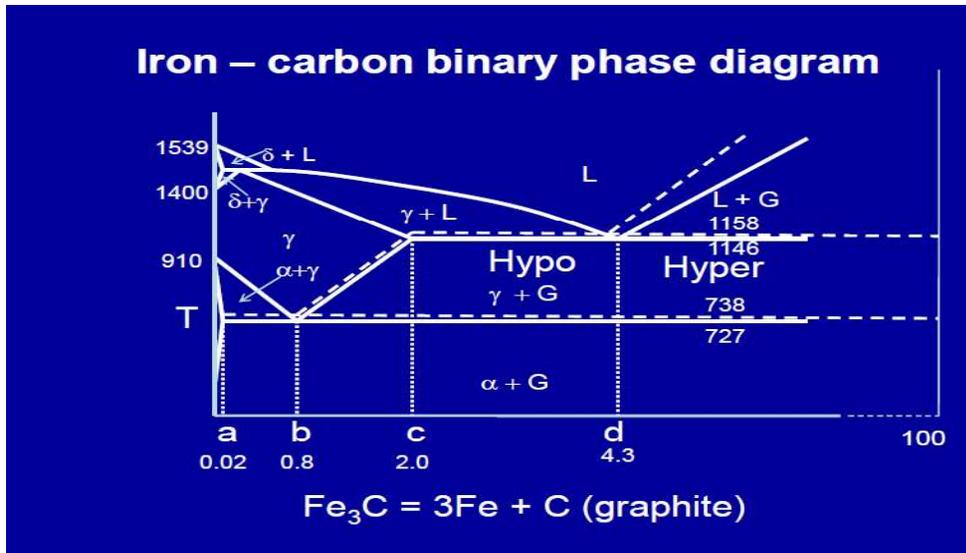


Fig.2.27: Iron-Carbon (graphite) phase diagram

The Fe-Fe₃C phase diagram and the iron graphite phase diagram is very similar. Solubility of carbon in the two forms of ferrite is still the same. There is a minor change in the upper limit of the solubility of carbon in austenite and in liquid. The broken (dashed) lines are the boundaries between various phase fields in the case of Fe-C phase diagram. Note that the compositions of the critical points marked as a, b, c, & d are nearly the same as those in Fe-Fe₃C phase diagram. The eutectoid and the eutectic temperatures are a little higher. The diagram extends till 100% C. Fe₃C is not a stable phase. It decomposes into Fe and C. There are several grades of cast iron having graphite as one of the constituents. However graphite is rarely present in steel. The density of graphite is 2.2 gm/cc whereas that of iron is 7.87gm/cc. This is why iron carbon alloys where carbon is present as graphite expands on solidification. They are easy to cast as there is no problem associated with shrinkage during solidification. Fig.2.28 shows different morphologies of graphite in cast iron.

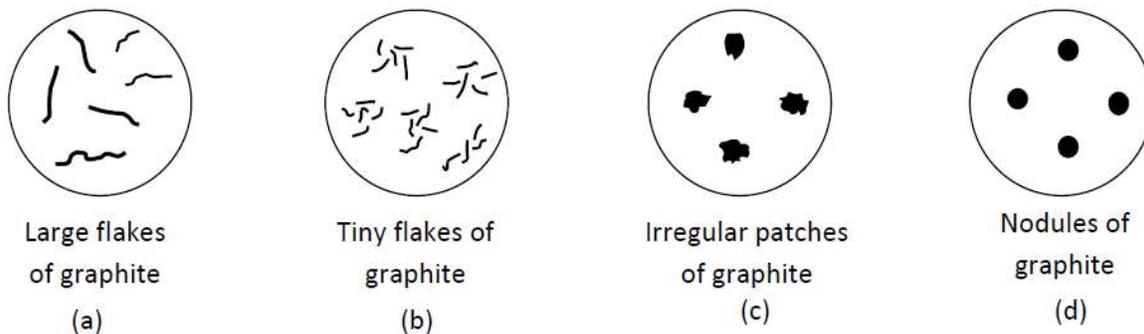


Fig 2.28: Shows a few common shapes of graphite present in cast iron

The most common forms of graphite present in cast iron are flakes of various sizes and shapes. Fig.2.28 (a) and (b) are the two common morphology. It is visible under microscope in even if the specimen is not etched. Flakes act like stress raisers. Therefore cast irons having flakes of graphite are brittle. The appearance of its fracture surface is grey. This is why it is known as grey cast iron. Long flakes usually develop as primary phase during solidification. This is possible only in hyper-eutectic cast iron. In hypo-eutectic grey cast iron the primary phase that forms during solidification is austenite. The last liquid to solidify is the eutectic which is a mixture of austenite and graphite. The graphite flakes that form during this stage are much smaller. Its appearance may look like that in Fig.2.28 (b). % graphite in eutectic can be estimated from the phase diagram using lever rule. This is approximately equal to $100 \times (4.3 - 2.0)/(100 - 2.0) = 2.4$. The balance is austenite. The excess carbon from austenite can precipitate as graphite as it cools. This continues till the composition of austenite reaches that of the eutectoid point. On further cooling it may transform into pearlite if the cooling rate is not slow enough. If the cooling rate is extremely slow it should transform into a mixture of ferrite and graphite. Under such a condition grey cast iron would consist of ferrite grains and graphite flakes. The matrix of such cast iron can vary from 100% ferrite to 100% pearlite. The morphology of graphite shown in Fig.2.28 (c) develops when white cast iron is held at around 950°C for long hours. This shape is usually known as temper carbon. White cast iron is extremely brittle. However such treatment results in substantial improvement in its ductility. Cast iron having such a structure is known as malleable cast iron. Flakes of graphite behave as long cracks. This makes grey cast iron brittle. Temper carbons appear as collections of irregular shaped patches of graphite in a microstructure. Unlike flakes such a form of carbon does not act as notches or stress raisers. Therefore cast iron where graphite exists in this form is ductile. The morphology shown in Fig.2.28 (d) can be obtained by special treatment during solidification. If molten iron having high superheat is inoculated with magnesium, graphite nucleates in nodular shapes. This too has good ductility. It is known as SG (Spheroidal Graphite) or nodular iron. Like grey cast iron both nodular and malleable cast iron can have a matrix of 100 % ferrite or 100% pearlite or a mixture of the two. Commercial cast iron has significant amount of silicon. Truly cast iron is not a binary alloy. It is often considered as a ternary alloy of Fe-C-Si.

Cast iron- It is an alloy of iron, carbon and silicon and it is hard and brittle. Carbon content may be within 1.7% to 3% and carbon may be present as free carbon or iron carbide Fe₃C. In general

the types of cast iron are (a) grey cast iron and (b) white cast iron (c) malleable cast iron (d) spheroidal or nodular cast iron.

(a) **Grey cast iron**- Carbon here is mainly in the form of graphite. This type of cast iron is inexpensive and has high compressive strength. Graphite is an excellent solid lubricant and this makes it easily machinable but brittle. Some examples of this type of cast iron are FG₂₀, FG₃₅ or FG₃₅Si₁₅. The numbers indicate ultimate tensile strength in MPa and 15 indicates 0.15% silicon.

(b) **White cast iron**- In these cast irons carbon is present in the form of iron carbide (Fe₃C) which is hard and brittle. The presence of iron carbide increases hardness and makes it difficult to machine. Consequently these cast irons are abrasion resistant.

(c) **Malleable cast iron**- These are white cast irons rendered malleable by annealing. These are tougher than grey cast iron and they can be twisted or bent without fracture. They have excellent machining properties and are inexpensive. Malleable cast iron are used for making parts where forging is expensive such as hubs for wagon wheels, brake supports. Depending on the method of processing they may be designated as black heart BM32, BM30 or white heart WM42, WM35 etc.

(d) **Spheroidal or nodular graphite cast iron**- In these cast irons graphite is present in the form of spheres or nodules. They have high tensile strength and good elongation properties. They are designated as, for example, SG50/7, SG80/2 etc where the first number gives the tensile strength in MPa and the second number indicates percentage elongation.

TTT DIAGRAM

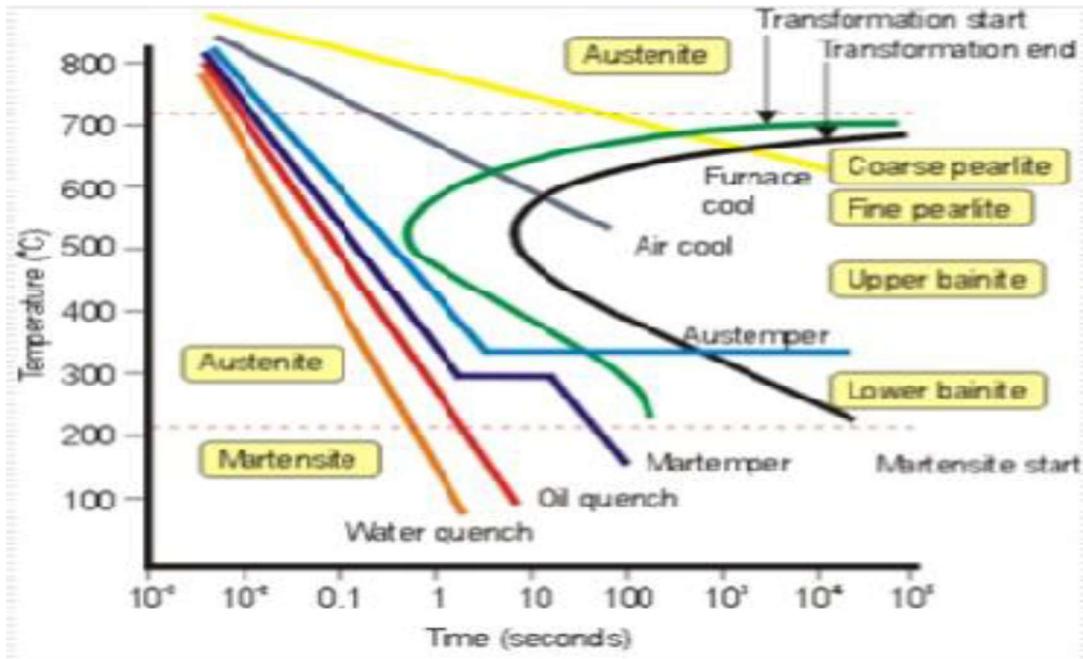


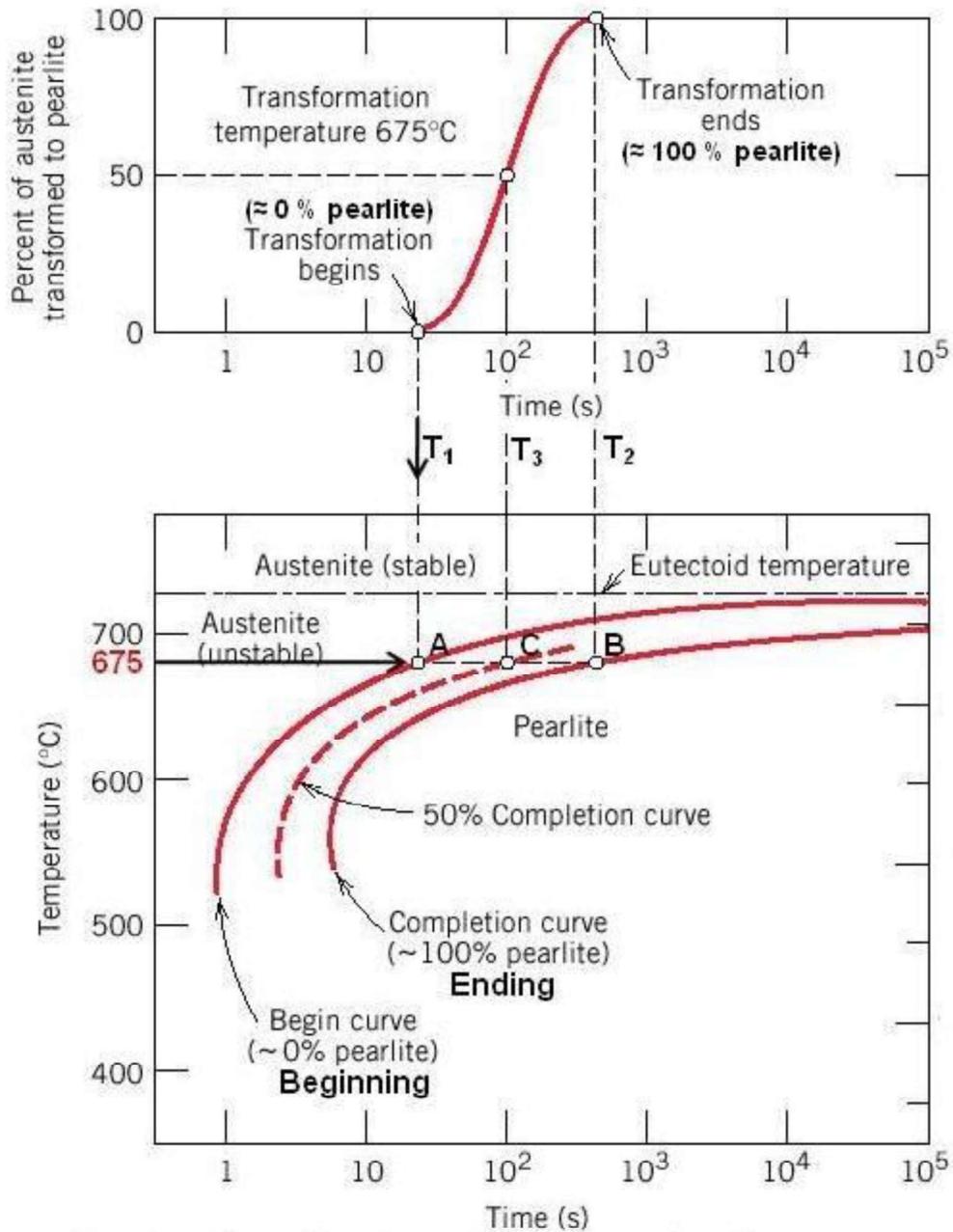
Figure-3.1(a)

The diagram that illustrates the transformation of austenite as a function of time at a constant temperature is a TTT or Isothermal Transformation diagram. A number of small samples are taken from the same steel. These samples are heated to a predetermined austenitizing temperature and are held at this temperature for a sufficient long period so as to obtain a homogeneous austenite. These austenitized samples are transferred quickly to another bath maintained at a constant temperature below eutectoid temperature, selected for the study of kinetic of transformation. These samples are taken out one by one from the sub-critical temperature bath after different time intervals and are quenched immediately.

The quenching of samples results in the formation of martensite from the untransformed austenite. By this technique, the amount of transformation austenite can be determined as a function of time at constant temperature. The amount of transformed austenite will increase by allowing samples to remain in constant temperature bath for longer time.

Transformation of austenite to ferrite-cementite mixture occurs after a definite time. This time during which transformation does not proceed is known as incubation period corresponds to

lesser stability of austenite. TTT diagram is an extension of isothermal transformation of austenite diagram.



Construction of Isothermal Transformation Diagram

Figure-3.1(b)

Silent Features of TTT diagram:-

- The minimum incubation period of TTT diagram of 0.8%C steel is maximum at pearlite nose.
- As the carbon percentage is decreased below 0.8%C the TTT diagram shifted towards left and the minimum incubation period goes on decreasing.
- And eventually of 0.2%C steel the TTT diagram shifted so much towards the left and it is truncated by the Y-axis.
- Further as the carbon content is increased beyond or above 0.8%C the corresponding TTT diagram also shift towards left.

Factors affecting TTT diagram

- Composition of steel-

(a) carbon wt%:-

Carbon increases the stability of austenite and the amount of free ferrite decreases as the carbon content increases up to 0.77%. As the ferrite is the nucleating phase for pearlite in hypoeutectoid steels, the nose of the s-curve becomes more and more right hand side, as the carbon increases to 0.77%, but shift towards left hand side as carbon increases more than 0.77% in hypereutectoid range, because of the presence of increasing amount of free cementite in them, as cementite act as the nuclei for pearlite transformation in hypereutectoid steels.

(b) alloying element wt%:-

All alloying elements (except Co) shift the s-curve to the right in both pearlite and bainitic regions. Elements like Mn, Ni, etc, the austenite stabilisers, just like carbon, stabilise the austenite and thus shift the s-curve to the right.

- Grain size of austenite:-

All the decomposition products of austenite nucleate heterogeneously preferentially at the grain boundaries. As a fine grained steel has larger grain boundary area than a coarse grained steel, thus there are more potential sites for the nucleation of ferrite, pearlite,

bainite, cementite. It reduces the incubation period, i.e., s-curve of the fine grained steel is more towards left, significantly in the pearlitic range.

- For 1.1%C steel the TTT diagram also truncated by the Y-axis.

Concept of Heat Treatment of Steels:-

Temperature band for heat treatment (like annealing, normalizing, hardening) of various grades of steel is shown in the Fe-Fe₃C equilibrium diagram. For Hypoeutectoid steel the temperature band for heating is 50°C above the Ac₃ temperature. On the other hand for hypereutectoid steel the temperature band for heating is 50°C above Ac₁ (723°C) and not above 50°C above Ac_m, because the slope of Ac_m curve is much steeper than the Ac₃ curve. If we use 50°C above Ac_m temperature for hypereutectoid steel, then the austenite is formed will be very high grain size and upon quenching this will result;

- Formation of quench cracks
- The overall strength of the product will be poor because of the larger martensite needle.

However for the hypo-eutectoid steel we can use 50°C above Ac₃ temperature, with the result;

- No quench cracks
- Strength of the martensite will be higher because of the smaller size of martensite needle.

ANNEALING:-

Annealing in general involves heating to a predetermined temperature, holding at this temperature and finally cooling at a very slow rate, i.e., inside the furnace. The temperature to which steel is heated and the holding time are determined by various factors such as the chemical composition of the steel, size and shape of the steel component and final properties desired. The various purposes of this treatment are to;

- Relieve internal stresses developed during solidification, machining, forging, rolling or welding.
- Improve ductility and toughness
- Enhance machinability
- Eliminate chemical non-uniformity
- Refine grain size
- Reduce the gaseous contents in steel.

The microstructure of the annealing treatment of steel is coarse pearlite (less in number of pearlite colonies but bigger in size).

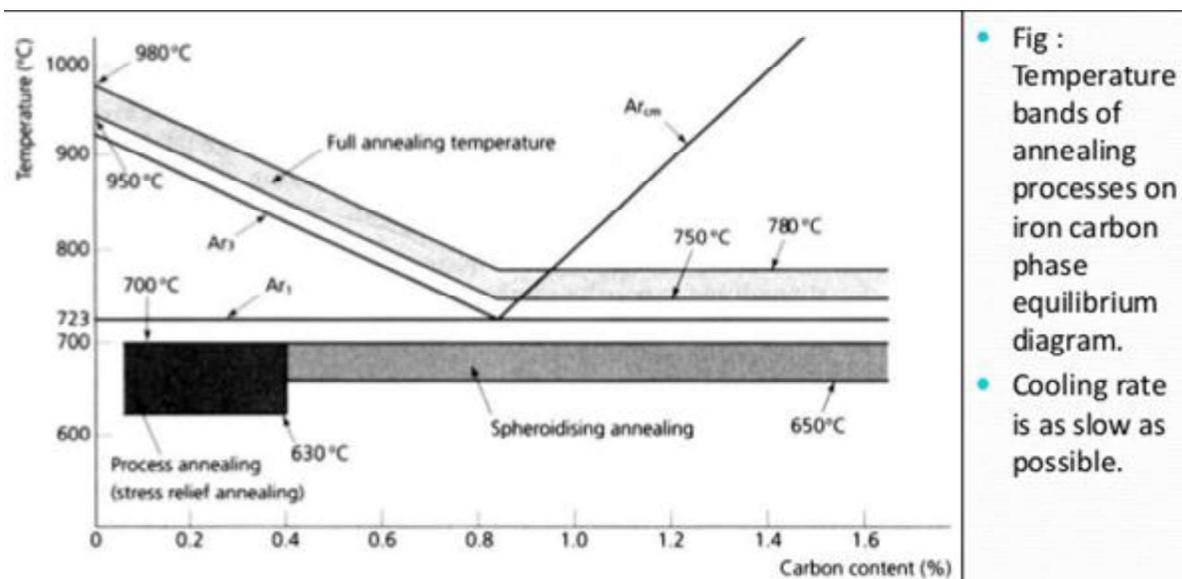


Figure-3.2(a)

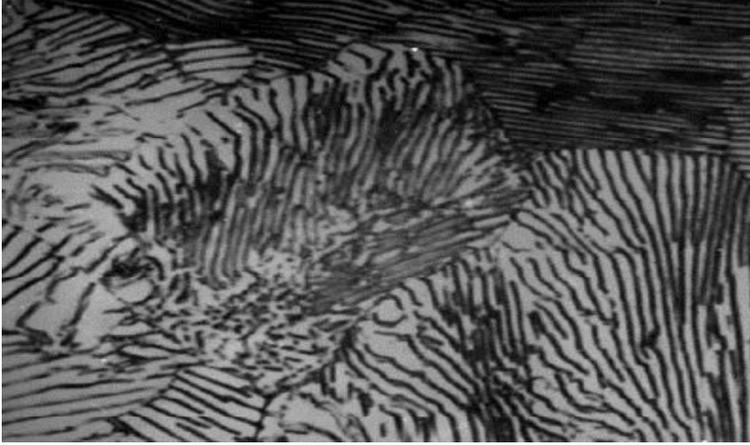


Figure-3.2(b)

Annealing treatment can be classified into groups based on;

- 1) Temperature of treatment**
 - Full annealing
 - Partial annealing
 - Sub-critical annealing
- 2) Phase transformation that takes place during treatment**
 - First order annealing
 - Second order annealing
- 3) The purpose of the treatment**
 - Diffusion annealing
 - Spherodizing annealing
 - Recrystallization annealing

NORMALIZING:-

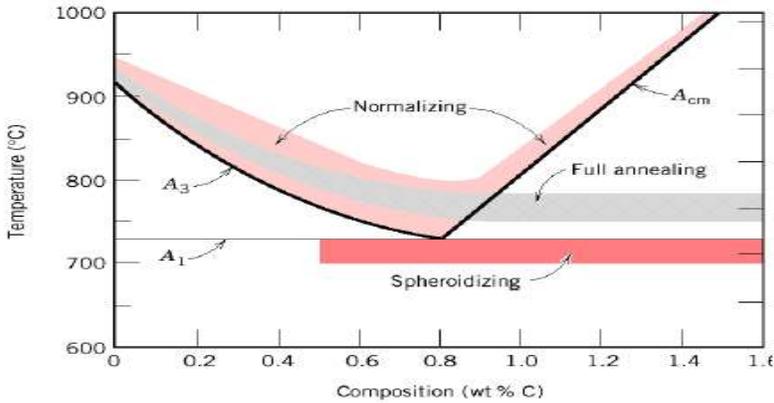


Figure-3.3(a)

It is the process of heating steel to above 40-50°C above upper critical temperature (A_{c3} or A_{cm}), holding for proper time and then cooling in air to room temperature. After normalizing the resultant microstructure should be fine pearlite (more number of pearlite colonies but small in size). The grain size is finer in normalized structure than in annealed structure. Normalized steels are generally stronger and harder than full annealed steels. The machinability of steel shows an improvement on normalizing.

By normalizing an optimum combination of strength and softness is achieved. This method of improving machinability is specially applicable to hypo-eutectoid steel. Normalizing treatment is frequently applied to steels in order to achieve any one or more of the objectives;

- Grain refinement
- Improvement in machinability
- Enhanced mechanical properties such as hardness, strength and toughness.

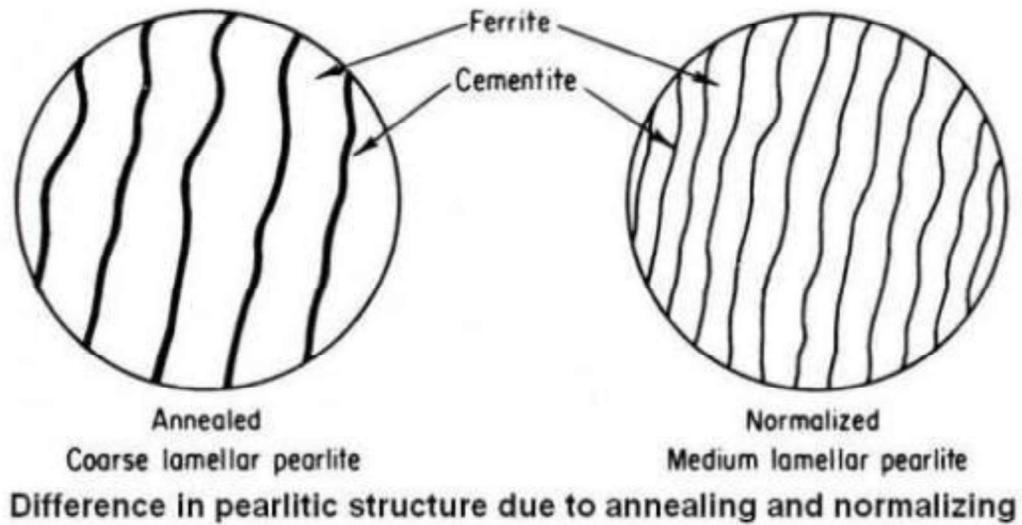


Figure-3.3(b)

HARDENING:-

High tensile strength and hardness values can be obtained by a process known as hardening. It is the process of heating the steel to proper austenitising temperature, holding at this temperature and then cooling with rapid cooling such as quenching in water, oil or salt bath. Rapid cooling results in the transformation of austenite at considerably low temperature into non-equilibrium product. The product of low temperature transformation of austenite is martensite which is a hard micro-constituents of steel. Martensite having BCT structure which is hard and brittle. Hardness of the martensite mainly depends on the carbon content of the steel.



Martensite (Quenching)

X 700

Figure-3.4(a)

The hardening temperature depends on chemical composition and for plain C-steels, it depends on carbon content alone. Hypoeutectoid steels are heated about 30-50°C above the upper critical temperature, whereas eutectoid and hyper-eutectoid steels are heated to about 30-50°C above the lower critical temperature. Normally the C-steels are quenched in water & alloy steels in oil.

If hypoeutectoid steel is heated to a hardening temperature equivalent to that for hypereutectoid steel, then the structure will consist of ferrite and austenite. This will transform to ferrite and martensite on quenching. Ferrite is a very soft phase and lowers the hardness of hardened steel considerably. This is known as incomplete hardening.

Heating of hyper-eutectoid steel above the upper critical temperature (A_{c_m}) for hardening is detrimental because such a high temperature will result in coarsening of austenite grains and decarburize at the surface. Coarse austenite will transform to coarse acicular martensite which has poor mechanical properties. Quenching from such a high temperature will introduce several internal stresses into the hardened steel.

Purpose of hardening:-

- a. To develop high hardness.
- b. Improves tensile strength, yield strength and wear resistance.

Factors affecting hardening process:-

- i. Chemical composition of steel
- ii. Size, shape and the surface condition of the steel part
- iii. Quenching medium
- iv. Homogeneity & the grain size of austenite
- v. Hardening cycle (i.e., heating rate, hardening temperature, holding time and the cooling rate)

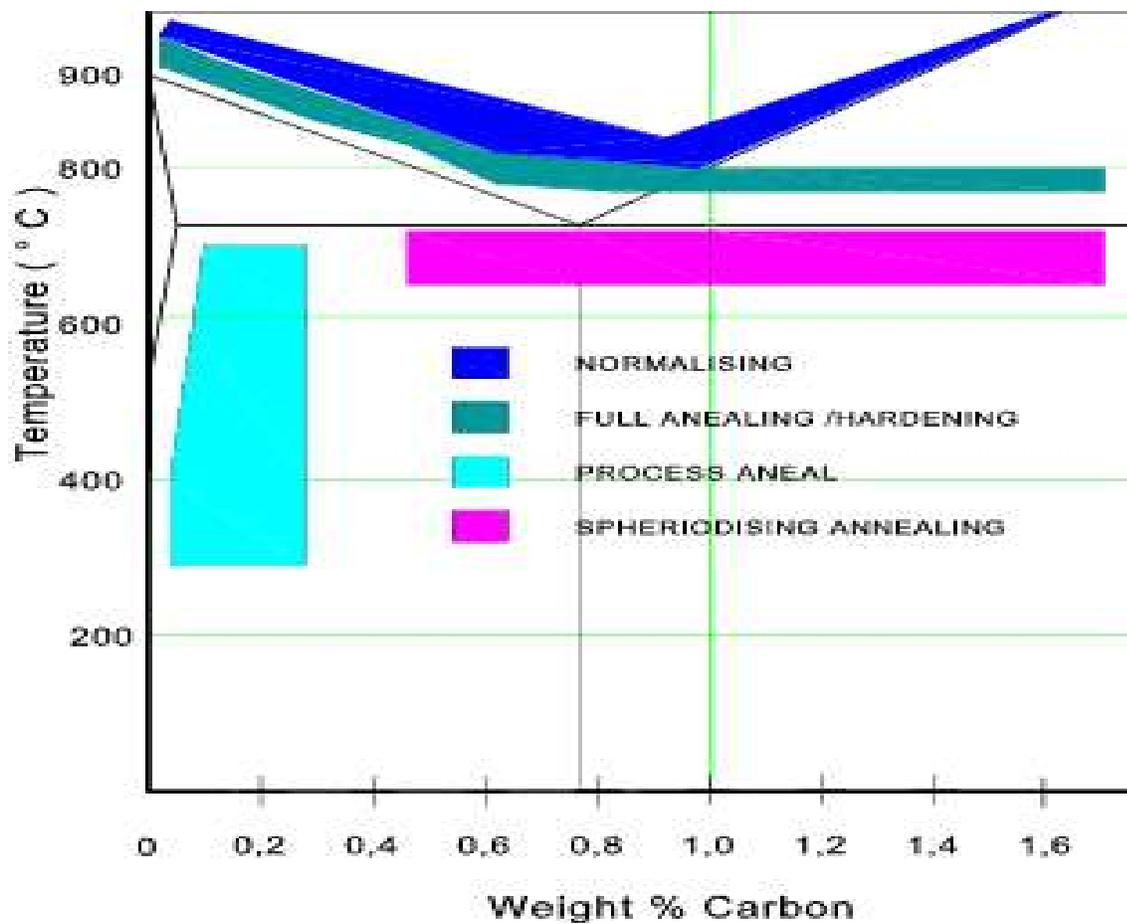


Figure-3.4(b)

TEMPERING:-

Tempering is the process of heating hardened steel to a temperature below the lower critical temperature (A_{c1}). It is done after the steel is quenched. There are two products obtained on quenching;

1. Martensite
2. Retained austenite

Both these products are unstable in nature, even at room temperature these phases can decompose. As a result there can be dimensional instability. The advantages gained by tempering are;

- Relieving internal stresses
- Restoration of ductility & toughness
- Transformation of retained austenite

The higher the tempering temperature, the more is the restored ductility & tougher the steel.

CONVENTIONAL QUENCHING AND TEMPERING

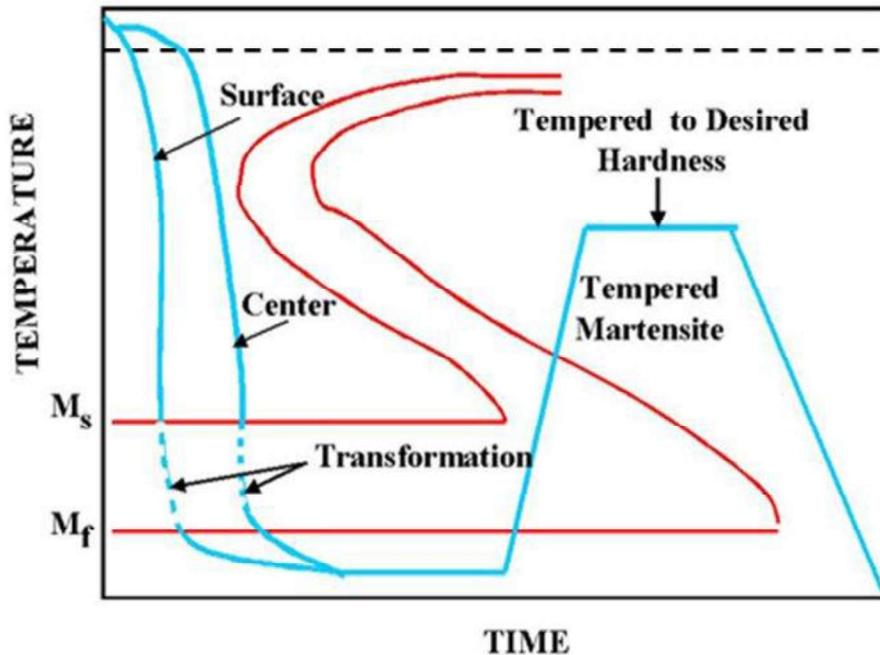


Figure-3.5(a)

Stages of tempering:-

Depending on the range of tempering temperature, the treatment proceeds to various stages.

1st stage:- (up to 200⁰C)

The 1st stage of tempering also referred to as low temperature tempering. The maximum temperature to which steel is heated is restricted to about 200⁰C at this stage. Precipitation of ϵ -carbide carried out due to decrease of tetragonality of martensite. Such a structure is called tempered martensite. Decrease in tetragonality decrease the hardness but precipitation of ϵ -carbide increases the hardness of the steel.

2nd stage:- (200-300⁰C)

(Decomposition of retained austenite), During this stage retained austenite transforms to lower bainite. There takes place slightly increase in volume of the steel. When the carbon content

of the steel is high, the amount of retained austenite being larger transforms to more hard lower bainite in large proportions.

3rd stage:- (200-350⁰C)

Formation of rods of cementite, complete loss of tetragonality of martensite and dissolution of ϵ - carbide occur. Hardness decreases continuously & sharply. Structure is ferrite & small particles of cementite.

4th stage:- (350-700⁰C)

Coarsening and spherodisation of cementite along with recovery & recrystallisation of ferrite occur. The growth of cementite starts at around 300⁰C, but spherodisation occurs above 400⁰C. Above 600⁰C equiaxed grains of ferrite form having coarse globule of cementite. It is spherodised or globular pearlite, which is softest with highest ductility & best machinability.

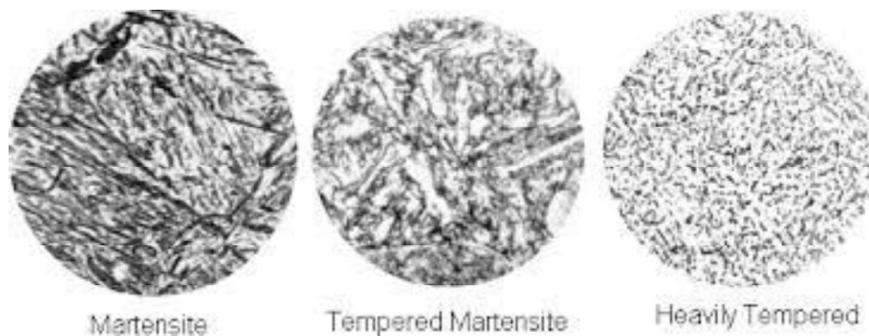


Figure-3.5(b)

HARDENABILITY:-

Hardenability refers to the depth up to which a material is hardened after putting through a heat treatment process. The unit of hardenability is the same as of length. It is an indication of how deep into the material a certain hardness can be achieved. It should not be confused with hardness, which is a measure of a sample's resistance to indentation or scratching. It is an important property for welding, since it is inversely proportional to weldability, that is, the ease of welding a material.

Or **Hardenability**-the susceptibility to hardening-by rapid cooling is defined as the property of steel which determine the depth and distribution of hardness produced by quenching. A steel quenched to 100% martensite up to its centre may have lower surface hardness (as its carbon content is low), but still has higher hardenability as compare to a steel having higher surface hardness due to 100% martensite there but lower hardenability.

The different methods for measuring hardenability;

1. Easy detection of 50% martensite

2. Grossman's method of measuring hardenability

- In Grossman's method, we use round bars of different diameters.
- These bars are quenched in a suitable quenchant.
- Further, we determine the critical diameter (d_c) which is the maximum diameter of the rod which produced 50% martensite on quenching.
- The ideal diameter (D_I) is then determined from the curve.
- This type of experiment requires multiple austenitization and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.

3. Jominy End-Quench Test

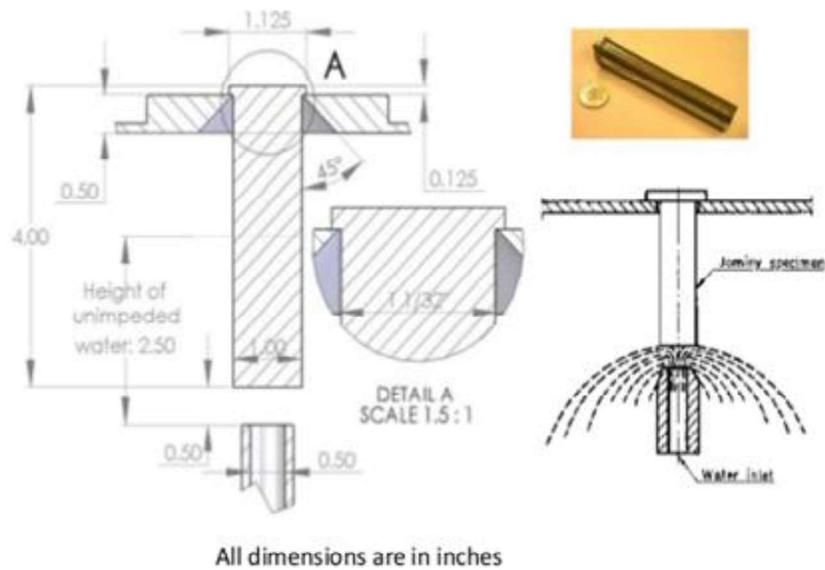


Figure-3.6

Factors Affecting Hardenability:-

a) Grain size:-

Grain boundaries are preferential nucleation sites for ferrite & pearlite. If the austenite grain size is large, the grain boundary area is less, the probability of nucleation to ferrite and pearlite decreases. Thus the hardenability of the steel increases as the grain size increases as the 'S' curve of the steel more towards right. But this method of increasing hardenability is avoided as coarse grains have other bad effects like increased brittleness, more tendency to quench cracks, etc.

b) Carbon content:-

Carbon fixes the maximum attainable surface hardness on quenching. It also increases hardenability as it stabilises austenite and thus shift the TTT or CCT curve to the right as its content increases up to 0.77%C (eutectoid point), but beyond that hardenability decreases, because the undissolved proeutectoid cementite as a nuclei for the pearlite transformation and the CCT or TTT curve shift towards left.

c) Alloying Elements:-

Most alloying elements (except Co) shift the TTT or CCT curve towards right to increase the hardenability of steel, if the alloying elements are dissolved in austenite . The

presence of undissolved alloy carbides, not only depletes the austenite of the alloying elements as well as carbon, which would have increased the hardenability, but helps to nucleate pearlite to decrease the hardenability. Presence of carbides decreases the grain growth. Had the grain growth occurred, the hardenability would have increased. Co increases the nucleation and growth of pearlite to shift the curve towards left to decrease the hardenability. Mn is very effective in increasing the hardenability. Boron (0.003-0.005%) is most effective in increasing the hardenability.

d) Severity of quenching:-

The hardenability increases as the severity of quenching increases. Thus the coolant is made constant to study the effect of other factors on hardenability.

e) Mass Effect:-

It has been observed that the maximum hardness is obtain on the surface of the bar of small diameters, and decreases as diameter increases. The centre hardness continues to drop as the diameter of the bar increases. To standardise this factor, the hardenability is measured in terms of depth of penetration of hardness.

COMMON ALLOY STEELS:-

Alloy steel is steel that is alloyed with a variety of elements in total amounts between 1.0% and 50% by weight to improve its mechanical properties. Alloy steels are broken down into two groups: **low-alloy steels** and **high-alloy steels**. Every steel is an alloy, but not all steels are called "alloy steels". The simplest steels are iron (Fe) alloyed with carbon (C) (about 0.1% to 1%, depending on type). However, the term "alloy steel" is the standard term referring to steels with *other* alloying elements *in addition to* the carbon. Common alloyants include manganese (the most common one), nickel, chromium, molybdenum, vanadium, silicon, and boron. Less common alloyants include aluminium, cobalt, copper, cerium, niobium, titanium, tungsten, tin, zinc, lead, and zirconium. The following is a range of improved properties in alloy steels (as compared to carbon steels): strength, hardness, toughness, wear resistance, corrosion resistance, hardenability, and hot hardness. To achieve some of these improved properties the metal may require heat treating. Some of these find uses in exotic and highly-demanding applications, such as in the turbine blades of jet engines, in spacecraft, and in nuclear reactors. Because of the

ferromagnetic properties of iron, some steel alloys find important applications where their responses to magnetism are very important, including in electric motors and in transformers.

Principal effects of major alloying elements for steel		
Element	Percentage	Primary function
<u>Aluminium</u>	0.95–1.30	Alloying element in <u>nitriding</u> steels
<u>Bismuth</u>	-	Improves machinability
<u>Boron</u>	0.001–0.003	A powerful hardenability agent
<u>Chromium</u>	0.5–2	Increases hardenability
	4–18	Increases corrosion resistance
<u>Copper</u>	0.1–0.4	Corrosion resistance
<u>Lead</u>	-	Improved machinability
<u>Manganese</u>	0.25–0.40	Combines with <u>sulphur</u> and with <u>phosphorus</u> to reduce the brittleness. Also helps to remove excess oxygen from molten steel.
	>1	Increases hardenability by lowering transformation points and causing transformations to be sluggish
<u>Molybdenum</u>	0.2–5	Stable <u>carbides</u> ; inhibits grain growth. Increases the toughness of steel, thus making molybdenum a very valuable alloy metal for making the cutting parts of <u>machine tools</u> and also the <u>turbine</u> blades of <u>turbojet engines</u> . Also used in <u>rocket motors</u> .
<u>Nickel</u>	2–5	Toughened

Plastic:

(i)- Plastic are materials comes under polymers materials.

(II)-plastic are materials that have some structural rigidity under load and are used in general purpose application .

(iii)- polythene , polypropylene , pvc, polyster and fluorocarbon, epoxies phenolics, polyester, may all be classified as plastic.

(IV)- wide variety of combination of properties , some plastics are rigid and brittle , some are flexible having exhibiting both elastic and plastic deformation when stressed and sometimes experiencing considerable defoemation before fracture.

(V)- polymer falling under this type of classification may have any degree of crystallinity and all molecular structure and configuration (linera , branched , isotectic, etc) can be possible.

Classification of plastic material :

1- Thermoplastic

2- Theromosetting

The primary physical difference is that thermoplastics can be remelted back into a liquid, whereas plastics always remain in a permanent solid state. Think of thermoplastics as butter – butter can be melted and cooled multiple times to form various shapes.

Ceramics

(I)-ceramics are inorganic and non metallic materials

(II)-ceramics are composed of at least two elements and often more, their crystalline structure are generally more complex than those for metals.

(III)-the atomic bonding in these metals are range from pure ionic to totally covalent. Many ceramics exhibits a combination of these two bonding types.the degree of ionic character being dependent on the electronegativities of atoms.

Properties of Ceramic Materials:

(A)-High hardness, electrical and thermal insulating, chemical stability, and high melting temperatures

(B)-Brittle, virtually no ductility - can cause problems in both processing and performance of ceramic products

(C)-Some ceramics are translucent, window glass (based on silica) being the clearest example

Three Basic Categories of Ceramics:

1. Traditional ceramics - clay products such as pottery and bricks, common abrasives, and cement
2. New ceramics - more recently developed ceramics based on oxides, carbides, etc., and generally possessing mechanical or physical properties superior or unique compared to traditional ceramics
3. Glasses - based primarily on silica and distinguished by their noncrystalline structure
In addition, glass ceramics - glasses transformed into a largely crystalline structure by heat treatment

Application of ceramics :

- Window glass •Containers –cups, jars, bottles •Light bulbs •Laboratory glassware –flasks, beakers, glass tubing •Glass fibers –insulation, fiber optics •Optical glasses – lenses.
- Abrasives (grinding wheel grit) •Bioceramics (artificial bones and teeth) •Electrical insulators and electronic components •Refractory brick •Cutting tool inserts •Spark plug barrels •Engineering component

Composite

(i)-multiphase material that is artificially made.as opposed to one that occurs or forms naturally . In addition , the constituent phase must be chemically dissimilar and separated by a distinct

interface.

(ii)- most composite has been created to improve combination of mechanical characteristic such as stiffness , toughness,and ambient and high temperature strength.

(iii)- many composite material are composed of two just phase that is Matrix phase:which is continuous and surrounds the other phase called Dispersed phase.

(iv)- the properties of composite material is afunction of the properties of the constituent phases, their relative amount,and the geometry of the dispersed phase.

Here dispersed phase geometry means the shape of the particles, the particles size, distribution and orientation.

Classification of composite material.

It is classified into three types.

1-particle reinforced

2-fiber reinforce

3-structural

1- Large particle is further divide into

(A)-large particle

(B)-dispersion strengthening

2- Fiber reinforced

(A)-continuous aligned

(B)-discontinuous short (aligned and discontinuous)

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3- structural is further divided into

(A)-laminates

(B)- sandwich panel

(I)-the dispersed phase for particle reinforced composite is equiaxed particle dimension are same in all direction. For fiber reinforced composite the dispersed phase has a geometry of fibre (large length to diameter ratio). Structural composite are combination of composite and homogeneous material.

Particle reinforced composite:

large-particle and dispersion-strengthened composites are the two subclassifications of particle-reinforced composites. The distinction between these is based upon reinforcement or strengthening mechanism. The term "large" is used to indicate that particle-matrix interactions cannot be treated on the atomic or molecular level; rather, continuum mechanics is used. For most of these composites, the particulate phase is harder and stiffer than the matrix. These reinforcing particles tend to restrain movement of the matrix phase in the vicinity of each particle. In essence, the matrix

transfers some of the applied stress to the particles, which bear a fraction of the load. The degree of reinforcement or improvement of mechanical behavior depends on strong bonding at the matrix–particle interface. For dispersion-strengthened composites, particles are normally much smaller, with diameters between 0.01 and 0.1 μm (10 and 100 nm). Particle–matrix interactions that lead to strengthening occur on the atomic or molecular level. The mechanism of strengthening is similar to that for precipitation hardening discussed in Section 11.9. Whereas the matrix bears the major portion of an applied load, the small dispersed particles hinder or impede the motion of dislocations. Thus, plastic deformation is restricted such that yield and tensile strengths, as well as hardness, improve.

Fibre reinforced composite

Technologically, the most important composites are those in which the dispersed phase is in the form of a fiber. Design goals of fiber-reinforced composites often include high strength and/or stiffness on a weight basis. These characteristics are expressed in terms of specific strength and specific modulus parameters, which correspond, respectively, to the ratios of tensile strength to specific gravity and modulus of elasticity to specific gravity. Fiber-reinforced composites with exceptionally high specific strengths and moduli have been produced that utilize low-density fiber and matrix materials.

fiber-reinforced composites are subclassified by fiber length. For short fiber, the fibers are too short to produce a significant improvement in strength.

Structural composite

A structural composite is normally composed of both homogeneous and composite materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Laminar composites and sandwich panels are two of the most common structural composites; only a relatively superficial examination is offered here for them

Laminar composite :

A laminar composite is composed of two-dimensional sheets or panels that have a preferred high-strength direction such as is found in wood and continuous and aligned fiber-reinforced plastics. The layers are stacked and subsequently cemented together such that the orientation of the high-strength direction varies with each successive layer

Sandwich panel :

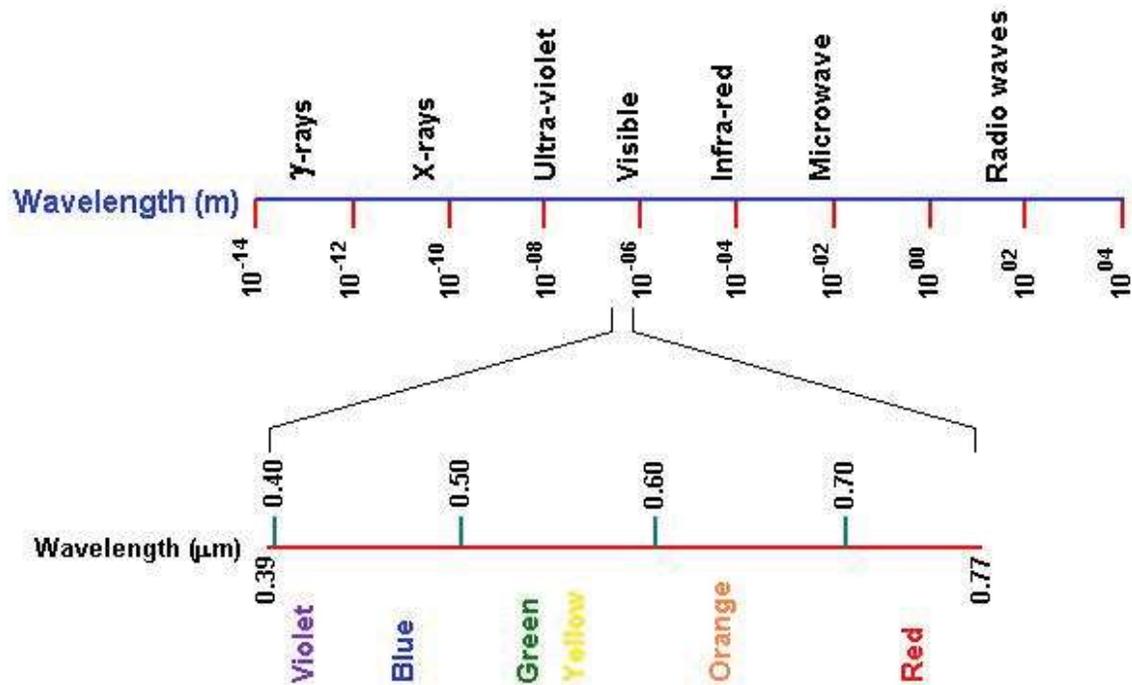
Sandwich panels, considered to be a class of structural composites, are designed to be light-weight beams or panels having relatively high stiffnesses and strengths. A sandwich panel consists of two outer sheets, or faces, that are separated by and adhesively bonded to a thicker core

Optical properties

Introduction

- Engineering materials are important in everyday life because of their versatile structural properties.
- than these properties, they do play an important role because of their physical properties.
- physical properties of materials include: electrical properties; thermal properties; magnetic properties; and **optical properties**.
- optical properties of engineering materials are useful in different applications. ∴ domestic, medicine, astronomy, manufacturing.
- property of a material is defined as its interaction with electro-magnetic radiation in the visible.
- spectrum of radiation spans the wide range from γ-rays with wavelength as 10^{-12} m, through x-rays, ultraviolet, visible, infrared, and finally radio waves with wavelengths as long as 10^9 m.
- light is one form of electromagnetic radiation with wavelengths ranging from 0.39 to 0.77 μm. can be considered as having waves and consisting of particles called photons.

$$E = h\nu = \frac{hc}{\lambda}$$



Material – Light interaction

- Interaction of photons with the electronic or crystal structure of a material leads to a number of phenomena.
- The photons may give their energy to the material (absorption); photons give their energy, but photons of identical energy are immediately emitted by the material (reflection); photons may not interact with the material structure (transmission); or during transmission photons are changes in velocity (refraction).
- At any instance of light interaction with a material, the total intensity of the incident light striking a surface is equal to sum of the absorbed, reflected, and transmitted intensities i.e.

$$I_0 = I_A + I_R + I_T$$

Optical materials

- Materials are classified on the basis of their interaction with visible light into three categories. that are capable of transmitting light with relatively little absorption and reflection are called *transparent materials* i.e. we can see through them.
- *Translucent materials* are those through which light is transmitted diffusely i.e. objects are not clearly distinguishable when viewed through.
- Those materials that are impervious to the transmission of visible light are termed as *opaque materials*. These materials absorb all the energy from the light photons.

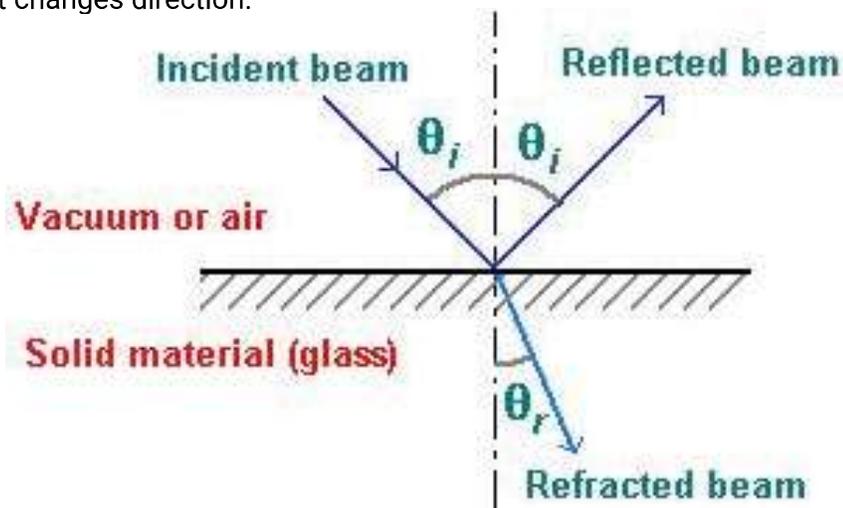
Optical properties - Metals

- Metals consist partially filled high-energy conduction bands.
- When photons are directed at metals, their energy is used to excite electrons into unoccupied states. Thus metals are opaque to the visible light.

- Metals are, however, transparent to high end frequencies i.e. x-rays and γ-rays.
- Absorption of takes place in very thin outer layer. Thus, metallic films thinner than 0.1 μm can transmit the light.
- The absorbed radiation is emitted from the metallic surface in the form of visible light of the same wavelength as reflected light. The reflectivity of metals is about 0.95.

Optical properties – Non-metals

- Non-metallic materials consist of various energy band structures. Thus, all four optical phenomena are important.
- Refraction: when light photons are transmitted through a material, they causes polarization of the electrons and in-turn the speed of light is reduced and the beam of light changes direction.



- Refraction
- Speed of light can be related to its electrical and magnetic
-
- Since most materials are only slightly magnetic:

$$n \cong \sqrt{\epsilon_r}$$

➤ Snell's law of light refraction:

- $n = \frac{\sin \theta'}{\sin \theta}$
- $n' \sin \theta$

Refractive index

<i>Material</i>	<i>Refractive index</i>	<i>Material</i>	<i>Refractive index</i>
Air	1.00	Epoxy	1.50
Ice	1.309	Polystyrene	1.49
Water	1.33	Spinel, MgAl ₂ O ₃	1.72
Teflon	1.35	Sapphire, Al ₂ O ₃	1.76
Silica glass	1.458	Rutile, TiO ₂	2.41
Polymethyl methacrylate	1.49	Diamond	2.42
Silicate glass	1.50	Silicon	3.42
Polyethylene	1.52	Gallium arsenide	3.4
Salt, NaCl	1.54	Germanium	4.0

Reflection

- Reflectivity is defined as fraction of light reflected at an interface.
- _____
- If the material is in other material with refractive index n_i
- Materials with a high index of refraction have a higher reflectivity than materials with a low index. Because the index of refraction varies with the wavelength of the photons, so does the reflectivity.
- In metals, the reflectivity is typically on the order of 0.90-0.95, whereas for glasses it is close to 0.05. The high reflectivity of metals is one reason that they are opaque. High reflectivity is desired in many applications including mirrors, coatings on glasses, etc.

Absorption

- When a light beam is impinged on a material surface, portion of the incident beam that is not reflected by the material is either absorbed or transmitted through the material.
- *Bouguer's law*: The fraction of beam that is absorbed is related to the thickness of the materials and the manner in which the photons interact with the material's structure
 $I = I_0 \exp(-\alpha \cdot x)$
- Absorption occurs by two mechanisms: Rayleigh scattering and Compton scattering.

Absorption mechanisms

- Rayleigh scattering: where photon interacts with the electrons, it is deflected without any change in its energy. This is significant for high atomic number atoms and low photon energies. **Ex.:** Blue color in the sunlight gets scattered more than other colors in the visible spectrum and

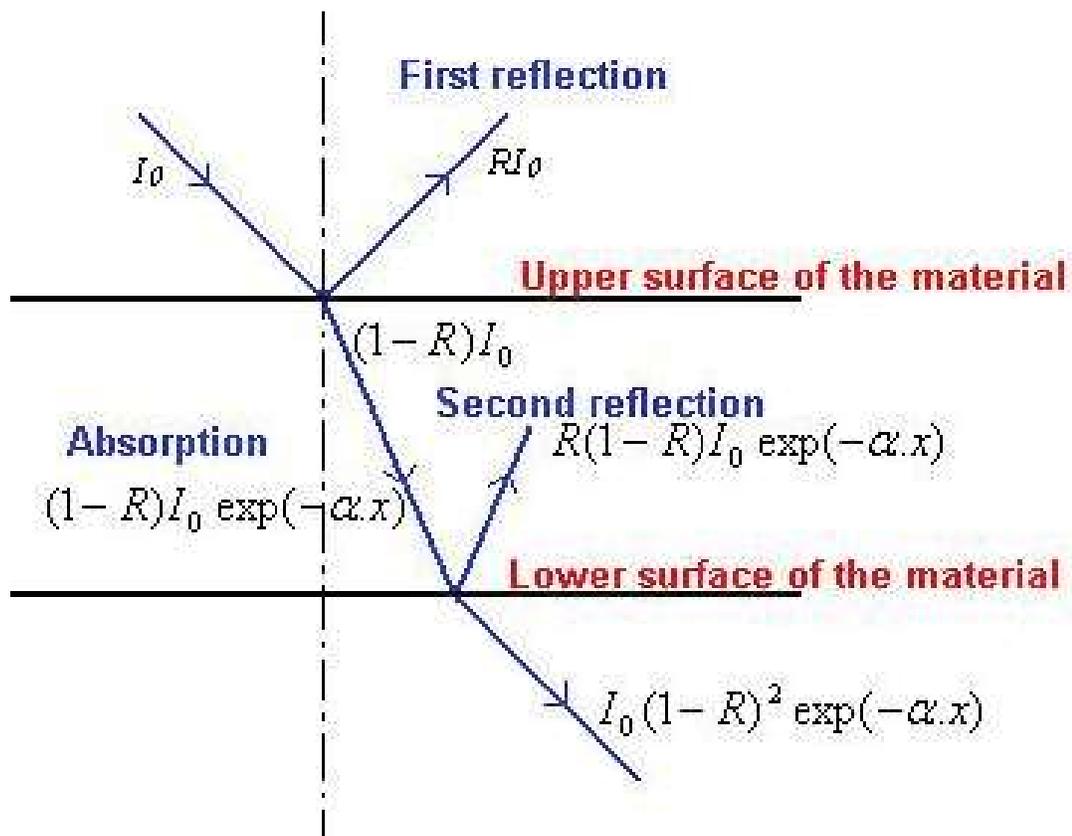
thus making sky look blue.

- *Tyndall effect* is where scattering occurs from particles much larger than the wavelength of light. **Ex.:** Clouds look white.
- Compton scattering – interacting photon knocks out an electron losing some of its energy during the process. This is also significant for high atomic number atoms and low photon energies.
- *Photoelectric effect* occurs when photon energy is consumed to release an electron from atom nucleus. This effect arises from the fact that the potential energy barrier for electrons is finite at the surface of the metal. **Ex.:** Solar cells.

Transmission

- Fraction of light beam that is not reflected or absorbed is transmitted through the material.

$$I_t = I_0 (1 - R)^2 \exp(-\alpha.x)$$



Optical applications

- Light interacts with a material in many ways.
- Depending on the material, its crystal-/micro-structure, and also on the characteristics of incident light, there are many peculiar phenomena occurs, which are known as *optical phenomena*. These include:
 - luminescence lasers
 - thermal emission
 - photo-conductivity
 - optical fibers
- All these find quite many applications in technology for every day life

Luminescence

- It is the process where a material absorbs energy and then immediately emits visible or near-visible radiation. It consists of electron excitation and then dropping down to lower energy states.
- If the emission of radiation occurs within 10^{-8} sec.s after excitation, the luminescence is called *fluorescence*, and if it takes longer than 10^{-8} sec.s, it is known as *phosphorescence*.
- Ordinarily pure materials do not display this phenomenon. Special materials called *phosphors* have the capability of absorbing high-energy radiation and spontaneously emitting lower-energy radiation. **Ex.:** some sulfides, oxides, tungstates, and few organic materials.

Photo-luminescence

- Based on source for electron excitation, luminescence is three types: photo-luminescence, cathode-luminescence, and electro-luminescence.

- *Photo-luminescence* occurs in fluorescent lamps.
- Here ultra-violet radiation from low-pressure mercury arc is converted to visible light by calcium halo-phosphate phosphor ($\text{Ca}_{10}\text{F}_2\text{P}_6\text{O}_{24}$).
- In commercial lamps, about 20% of F^- ions are replaced with Cl^- ions.
- Antimony, Sb^{3+} , ions provide a blue emission while manganese, Mn^{2+} , ions provide an orange-red emission band.

Cathode-luminescence

- *Cathode-luminescence* is produced by an energized cathode which generates a beam of high-energy bombarding electrons.
 - **Ex.:** Applications of this include electron microscope; cathode-ray oscilloscope; color television screens.
- The modern televisions have very narrow, about 0.25 mm wide, vertical stripes of red-, green-, and blue- emitting phosphors deposited on the inner surface of the screens.
- Commercial phosphors for different colors are: red – yttrium oxy-sulfide ($\text{Y}_2\text{O}_2\text{S}$) with 3% europium (Eu); green (Zn,Cd)S with a Cu^+ acceptor and Al^{3+} donor; blue – zinc sulfide (ZnS) with Ag^+ acceptor and Cl^- donor

Electro-luminescence

- *Electro-luminescence* occurs in devices with p-n rectifying junctions which are stimulated by an externally applied voltage.
- When a forward biased voltage is applied across the device, electrons and holes recombine at the junction and emit photons in the visible range (mono-chromatic light i.e. single

color). These diodes are called *light emitting diodes* (LEDs).

- LEDs emit light of many colors, from red to violet, depending on the composition of the semiconductor material used.
 - o Ex.: GaAs, GaP, GaAlAs, and GaAsP are typical materials for LEDs.

Materials for colored LEDs

Wave length (nm)	Color	Material
-	Infra-red	GaAs
660	Red	$\text{GaP}_{0.40}\text{As}_{0.60}$ or $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$
635	Orange	$\text{GaP}_{0.65}\text{As}_{0.35}$
578	Yellow	$\text{GaP}_{0.85}\text{As}_{0.15}$
556	Green	GaP ($\text{GaP}_{1.00}\text{As}_{0.00}$)
-	Blue	$\text{Ga}_{0.94}\text{In}_{0.06}$

Lasers

- Laser is an acronym for *light amplification by stimulated emission of radiation*. It is in fact special application of luminescence.

- Unlike most radiation processes, such as luminescence, which produce incoherent light, the light produced by laser emission is coherent.
- This is based on the fact that in certain materials, electrons excited by a stimulus produce photons which in turn excite additional photons of identical wavelength.
- Lasers are useful in many applications such as welding, metal cutting, heat treatment, surgery, mapping, reading compact disks, etc. **Ex.:** Ruby, single crystal of Al_2O_3 doped with little amount of Cr_2O_3 ; yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$ – YAG) doped with neodymium, Nd; CO_2 gas; He-Ne gas; some semi-conductors like GaAs and InGaAsP

Thermal emission

- When a material is heated, electrons are excited to higher energy levels, particularly in the outer energy levels where the electrons are less strongly bound to the nucleus.
- These excited electrons, upon dropping back to the ground state, release photons in process what is called *thermal emission*.
- During thermal emission a continuous spectrum of radiation is emitted with a minimum wavelength and the intensity distribution is dependent on the temperature.
- Higher the temperature, wider will be the range of wavelengths emitted. By measuring the intensity of a narrow band of the emitted wavelengths with a pyrometer, material's temperature can be estimated.

Photo-conductivity

- Bombardment of semiconductors by photons, with energy equal to greater than the band gap, may result in creation of electron-hole pairs that can be used to generate current. This process is called *photo-conductivity*.
- It is different from photo-electric effect in the sense that an electron-hole pair is generated whose energy is related to

the band gap energy instead of free electron alone whose energy is related to the Fermi level.

- The current produced in photo-conductivity is directly related to the incident light intensity.
- This phenomenon is utilized in photographic light meters. Cadmium sulfide (CdS) is commonly used for the detection of visible light, as in light meters.
- Photo-conductivity is also the underlying principle of the photo-voltaic cell, known to common man as *solar cell*, used for conversion of solar energy into electricity.

Optical fibers

- Optical fibers have revolutionized the communication industry.
- It primarily consists of core, cladding and coating. The core transmits the signals, while the cladding constrains the light beam to the core; outer coating protects the core and cladding from the external environment.
- Typically both the core and cladding are made of special types of glass with carefully controlled indices of refraction.
- The indices of refraction are selected such that $n_{cladding} < n_{core}$
- Once the light enters the core from the source, it is reflected internally and propagates along the length of the fiber.
- Internal reflection is accomplished by varying the index of refraction of the core and cladding glass materials. Usually two designs are employed in this regard.

Types of optical fibers

- In step-index optical fiber, there is a sharp change in refractive index between the core and cladding. In this design output pulse will be broader than the input one. It is because light rays traveling in different trajectories have a variety of path lengths.
- It is possible to avoid pulse broadening by using *graded-*

index fiber. This results in a helical path for the light rays, as opposed to zig-zag path in a step-index fiber.

- Here impurities such as boron oxide (B_2O_3) or germanium dioxide (GeO_2) are added to the silica glass such that the index of refraction varied gradually in parabolic manner across the cross section. This enables light to travel faster while close to the periphery than at the center. This avoids pulse broadening.
- Both step- and graded- index fibers are termed as multi-mode fibers. Third type optical fiber is called single-mode fiber in which light travels largely parallel to the fiber axis with little distortion of the digital light pulse. These are used for long transmission lines.

Optical fiber properties

- Core and cladding materials are selected not only on the basis of their refractive indices, but also on basis of ease of manufacturability, light loss, mechanical strength properties and dispersion properties.
- However, density (ρ) and refractive index (n) are critical. These two parameters are related approximately as
 - $n = (\rho + 10.4)/8.6$
- High-purity silica-based glasses are used as fiber material, with fiber diameter ranging from 5 to 100 μm .
- The fibers are carefully fabricated to be virtually free from flaws.