SCIENCE AND ENGINEERING OF MATERIALS

B.TECH, 3RD SEMESTER

LECTURES NOTE

BY

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BPUT SYLLABUS

Module-I

Bonding in Solids: Ionic, Covalent, and Metallic bonding, bonding forces and energy, secondary bonding.

Crystal Structure: Space lattices and Bravais lattices, Miller Indices of planes and directions, slip planes and slip directions, stereographic projections.

Selected crystal structures: Pure metals, Diamond and Graphite, coordination in ionic crystals, AB type compounds, Silica, Alumina, Complex Oxides, Silicates. Inorganic glass: Network structure in glasses. Polymeric structures: Thermo plastics, Elastomers, Thermosets, crystalinity in polymers.

Module-II

Principles of Alloy theory: Primary substitutional solid solution, Interstitial solid solution, types of intermediate phases, Ordered-Disordered phenomena. Hume Rothery Rules, Intermetallic compounds, Normal valency compounds, Electron compounds, Interstitial compounds.

Imperfections: Point defects, Vacancies, Interstialcies, Dislocations; Edge & Screw dislocations; Burgers vector. Crystallization from the melt: Freezing of a pure metal, plane front and dendritic solidification at a cooled surface, formation of cast structure, gas porosity and segregation, directional solidification.

Module-III

Binary Phase Diagrams: Isomorphous, Eutectic, Peritectic, Eutectoid, Monotectic and Syntectic systems, Phase rule and Lever rule. Iron-Cementite Equilibrium diagrams and its applications, Plain carbon and alloy steel, Industrial applications of steels.

Diffusion: Fick's First and Second law of diffusion, Atomic model of diffusion, Grain boundary, surface and thermal diffusion, Kirkendall Effect, Interstitial diffusion.

Nucleation: Homogeneous and Heterogeneous nucleation, Kinetics of nucleation, Growth and overall transformation kinetics.

Books for reference:

1. V. Raghavan, Materials Science and Engineering, Prentice-Hall of India Private Limited,2003.

2. W. F. Smith, Mc Graw Hill, Principles of Materials Science and Engineering, New York,1994.

3. R. E Reid Hill, Physical Metallurgy Principles, PWS-Kent Publishing,2004.

4. Vijendra Singh, Physical Metallurgy, Standard Publisher,2008.

5. C.Daniel Yesudian and D.G.Harris Samuel, Scitech Publication,India-2010

6. W. D. Callister, Materials Science & Engineering, An Introduction, John Wiley & Sons,2007.

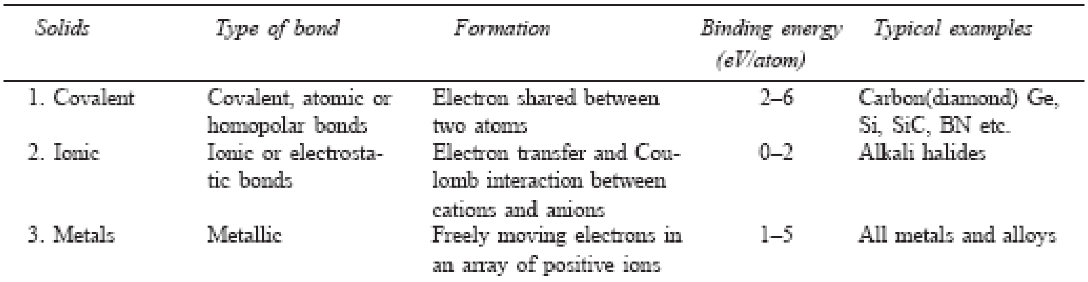
7. L. H. Van Vlack, Addison Wisley, Elements of Materials Science and Engineering, New York, 1985.

8. M.S.Vijaya and G.Rangarajan Mc Graw Hill Education(India)-2014

BONDING IN SOLIDS

In nature one comes across several types of solids. Solids are aggregates of atoms. The arrangement of atoms in any solid material is determined by the character, strength and directionality of the chemical binding forces, cohesive forces or chemical bonds. We call these binding forces as _atomic interaction_ forces. The atoms, molecules or ions in a solid state are more closely packed than in the gaseous and liquid states and are held together by strong mutual forces of attraction and repulsion. One can describe the atomic arrangement in elements and compounds on the basis of this.

The type of bond that appears between atoms in crystal is determined by the electronic structure of interacting atoms. Atoms in a crystal approach one another to certain distances at which the crystal is in the state of the highest thermodynamic stability. These distances depend on the interaction forces that appear in crystals. The attractive forces between atoms are basically electrostatic in origin. Its magnitude is proportional to some power of the interatomic distance r. The different types of bonding depend on the electronic structure of the atoms concerned and hence directly related to the periodic table. The type of bonding within a material plays a major role in determining the electrical, chemical and physical properties of the material. The repulsive forces which come into existence when the distance between the atoms is decreased to such an extent that they are very close to one another and increase more intensively than attractive forces do. The repulsion between positively charged nuclei also contributes to the repulsive forces. The magnitude of the total repulsive force is also proportional to some power of r. A state of equilibrium is reached when these attractive and repulsive forces balance and this happens when two atoms or molecules are at an equilibrium distance $r0$.



Solids	*Type of bond*	*Formation*	*Binding energy (eV/atom)*	*Typical examples*
1. Covalent	Covalent, atomic or homopolar bonds	Electron shared between two atoms	2–6	Carbon(diamond) Ge, Si, SiC, BN etc.
2. Ionic	Ionic or electrostatic bonds	Electron transfer and Coulomb interaction between cations and anions	0–2	Alkali halides
3. Metals	Metallic	Freely moving electrons in an array of positive ions	1–5	All metals and alloys

4.	Molecular (Vander waals)	Molecules between pairs	Weak attractive forces due to dipole-dipole interaction	0.002–0.1	Nobel gases
5.	Hydrogen bond	Hydrogen atom attracted between two other atoms	Electrostatic bond of H-atom with an electronegative atom	0.5	ice, organic compounds, biological materials

IONIC BONDING

Ionic bonding which is formed by the actual transfer of electrons from one atom to the other so that each atom acquires a stable configuration similar to the nearest inert gas atoms, is the simplest type of chemical bonding to visualize since it is almost totally electrostatic in nature.

Ionic bonding occurs between electropositive elements (metals, i.e., those elements on the left side of the periodic table) and the electronegative elements (non-metals; i.e. on the right hand of the periodic table). These bonds are formed mainly in inorganic compounds, e.g. sodium chloride (common salt NaCl), MgO, CuO, CrO2, and MoF_2. In MgO the ions are doubly ionized leading to a stronger interatomic bond and hence a higher melting point (~2800°C), compared to 800°C for NaCl. Examination of the formation of ionic bonds, e.g., cupric oxide, chromous oxide and molybdenum fluoride, reveals that the metallic element need not be from Group I or II but that any metal may get ionized by losing its valence electrons. The criterion for ionic bonding is the difference in *electronegativity* (the tendency to acquire electrons). An ionic bond is truly speaking the attractive force existing between a positive and negative ion when they are brought into close proximity. These ions, of course, are formed when the atoms involved lose or gain electrons in order to stabilise their outer shell electron configuration. The cohesive energy of ionic crystals is quite large; it is of the order of 5 to 10 eV. A good example of ionic crystals is the crystal of sodium chloride (NaCl). The electronic configurations of white soft metal Na and Cl atoms are as follows:

Na : $1s^2\ 2s^2\ 2p^6\ 3\ s^1$ [K (2) L (8) M (1)]

Cl : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ [K (2) L (8) M (7)]

Na atom has low ionisation energy and hence easily loses an electron; where as Cl atom has a high electron affinity and strongly tends to acquire an electron. The reaction can be represented by

$Na + Cl \rightarrow Na+ + Cl^- \rightarrow NaCl$.

Since chlorine exists as molecules, we can write the chemical

reaction as

$2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^- \rightarrow 2NaCl$.

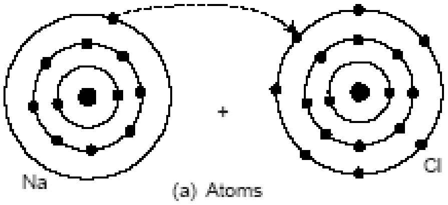
After the transfer of an electron from 3s orbital of Na to 3*p*

orbital of Cl, the electronic configurations become

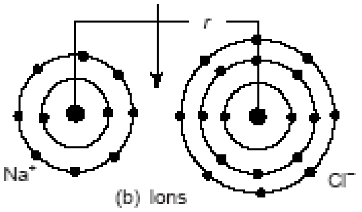
Na+ : 1*s*2 2*s*2 2*p*6 (same as Ne)

Cl– : 1*s*2 2*s*2 2*p*6 3*s*2 3*p*6 (same as Ar)

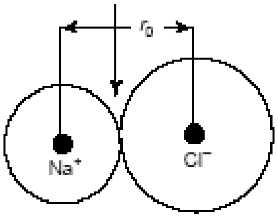
Schematic representation of the formation of an ionic molecule of sodium chloride is shown below.



(a) Atoms



(b) Ions



(c) Ionic molecule

Some other examples of ionic crystals are LiF, KCl, CsCl, Al_2O_3, etc.

Since ionic crystals have large binding energy, these are, in general, hard and exhibit high melting point and boiling points. At normal temperatures, ionic crystals are poor conductors of electricity but the conductivity increases with increase in temperature owing to the increased mobility of ions. Ionic crystals are generally transparent to visible light but exhibit characteristic absorption peaks in infrared region. Ionic crystals are also soluble in polar solvents, e.g. water. Ionic crystals have high melting and boiling points, high modulus of elasticity, and low coefficients of compressibility and linear expansion.

Characteristics of Ionic solids

(i) Ionic solids are generally rigid and crystalline in nature

(ii) The bond energy of ionic crystals is close in magnitude to that of covalent crystals and exceeds the bond energy of metallic and more so, of molecular crystals. For that reason, these have high melting and boiling points, high modulus of elasticity, and low coefficient of compressibility and linear expansion.

(iii) In ionic bonding, a metallic element loses from the outer electron shell of its atom a number of electrons equal to its valency (numerical). Obviously, an electrostatic attraction between positive and negative ions occurs.

(iv) In ionic crystal each positive ion attracts all neighbouring negative ions and vice versa, the bond itself is non-directional.

(v) Ionic solids are generally non-conductors of electricity.

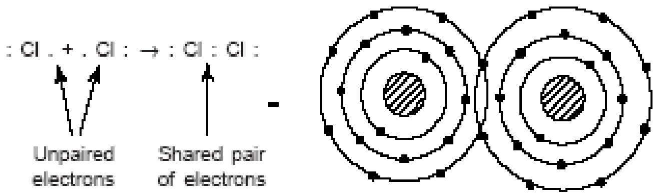
(vi) Ionic solids are highly soluble in water but insoluble in organic solvents.

(vii) In many ionic crystals, a fraction of covalent bond can also be present. Ions become polarized under the action of their electromagnetic fields and produce a combined ionic-covalent bond. Polarization deforms the electron zones, so that ions lose their spherical symmetry. With a change of the fraction of covalent bond, the properties of ionic crystals are changed. In crystals formed by elements of various groups, such as AI BVII, AII BVI, AIII BV, AIV BIV, the fraction of covalent bond increases from the first to the last. In compounds formed by elements of the fourth group (AIV BIV), the fraction of covalent bond is 90% and they are essentially covalent crystals. An increase of the fraction of the covalent bond increases the electric conductivity, so that AI BVII crystals are dielectrics and AIV BIV crystals, semiconductors.

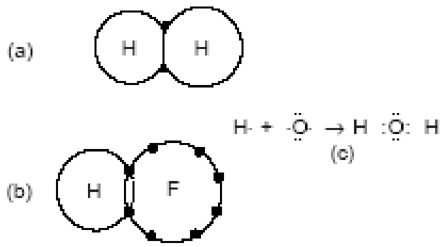
COVALENT BONDING

This type of bonding is formed by an equal sharing of electrons between two neighbouring atoms each having incomplete outermost shells. The atoms do so in order to acquire a stable electronic configuration in accordance with the octet rule. Unlike ionic bonding, the atoms participating in the covalent bond have such electronic configurations that they cannot complete their octets by the actual transfer of electrons from one atom to the other. Obviously, there is no charge associated with any atom of the crystal. The majority of solids incorporating covalent bonds are also bound by either ionic or Vander Waals bonds.

A covalent bond is formed between similar or dissimilar atoms each having a deficiency of an equal number of electrons. When two atoms, each having a deficiency of one electron, come so close that their electronic shells start overlapping, the original atomic charge distributions of atoms are distorted and each atom transfers its unpaired electron to the common space between the atoms. Obviously, the common space contains a pair of electrons which belongs equally to both the atoms and serves to complete the outermost shell of each atom. This is called *sharing of electrons*. The sharing is effective if the shared electrons have opposite spins. In such a case the atoms attract each other and a covalent bond is formed. As the participating atoms in the bond have the same valence state, this bond is also called the '*valence bond*'. An excellent example of covalent bonds is seen in the chlorine molecule. The outer shell of each chlorine atom possesses seven electrons. Obviously, each chlorine atom would like to gain an electron to form a stable octet. This can be achieved by sharing of two electrons between pairs. Chlorine atoms thereby producing stable diatomic molecules. The nature of sharing of the covalent bonds in molecules of hydrogen, hydrogen fluoride and water molecule are shown in Fig.



Covalent bond between two atoms of chlorine



Covalent bonds of H_2, HF and H_2O

Covalent bonds are formed by the elements of groups IV, V, and VI, subgroup *B*. They are electronegative due to a high ionization potential and, when interacting with elements of other groups, take up valence electrons to complete their valence zone; in interaction of these elements with each other, the valence electrons are shared by the neighbouring atoms so that the valence zone is completed.

Covalent crystals are formed by carbon, silicon, germanium, antimony, bismuth, and some other elements.

Characteristics of covalent compounds

(i) Covalent compounds are mostly gases and liquids.

(ii) They are usually electric insulators.

(iii) They are directional in nature.

(iv) They are insoluble in polar solvents like water but are soluble in non-polar solvents, e.g,, benzene, chloroform, alcohol, paraffins etc.

(v) Covalent compounds are homopolar, i.e. the valence electrons are bound to individual or pairs of atoms and electrons cannot move freely through the material as in the case of metallic bonds.

(vi) Covalent compounds are soft, rubbery elastomers, and form a variety of structural materials usually termed as plastics. The melting and boiling points of these compounds are low.

(vii) In the exceptional case of diamond covalent bonding is very strong due to the very large cohesive energy. Usually the binding energy ranges from 1 to 5 eV. The strong covalent bonding makes diamond very hard and with a high melting point.

METALLIC BONDING

Metallic bond is formed by the partial sharing of valence electrons by the neighbouring atoms. They are formed by the elements of all subgroups A and I-III, subgroups B. Unlike the case of covalent bond, the sharing in metallic bond is not localized. Hence metallic bond may also be considered as delocalized or unsaturated covalent bond. Metallic bonds are electropositive. When interacting with elements of other groups, atoms in a metallic crystal can easily give off their valence electrons and change into positive ions. When interacting with one another, the valence energy zones of atoms overlap and form a common zone with unoccupied sublevels. The valence electrons thus acquire the possibility to move freely with the zone.

Obviously, valence electrons are shared in the volume of a whole crystal. Thus the valence electrons in a metal cannot be considered lost or acquired by atoms. They are shared by atoms in the volume of a crystal, unlike covalent crystals where sharing of electrons is limited to a single pair of atoms. Due to delocalized nature of valence electrons, the metallic bond is much less directional than covalent bond. This results in a high coordination number and close packing of crystal structures of metals. High coordination numbers are typical of crystal structures with FCC and HCP lattices. A number of metals, e.g., Ni, Ag, Cu, Au, Fer, Pt, Al and Pb, have an FCC lattice. Many metals have an HCP lattice, but only Mg and Co among them have the axial ratio c/a = 1.633 corresponding to the spherical symmetry of atoms. Deviations of the c/a ratio from 1.633 can be explained by the presence of partial covalent bonds resulting in a non-spherical symmetry of atoms. In that case, the metallic interaction in the direction of atom stretching is supplemented by covalent interaction. If non-spherical atoms are arranged in a crystal so that their major axis is along the z-axis, the c/a ratio is greater than 1.633 (Zn and Cl). If however, their minor axis is arranged along the z-axis, the c/a ratio is less than 1.633 (Be, Ti and Zr).

The formation of crystal structures with a BCC lattice is also explained by partial covalent bonds and non-spherical symmetry of atoms. In these structures, atoms are not packed closely. Crystal structures with a BCC lattice are typical of Fe, Cr, Mo, W, V, Ta, Ti, Nb, Zr, and some other metals.

Many metals and some non-metals are polymorphous, i.e., may have different types of crystal structures in the solid state depending on temperature. Such crystal structures are called allotropic forms, or modifications.

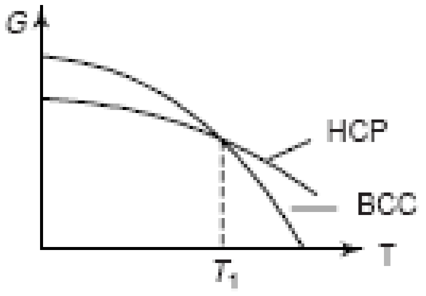
They are usually designated by Greek letters α, β, μ etc and so on, with 'α' denoting the form existing at the lowest temperature.

The stability of allotropic modifications at definite temperatures and pressures is determined by the thermodynamic potential (free energy)

$G = H – TS$ (5)

The modification having a lower algebraic value of thermodynamic potential is more stable at a given temperature, which can be achieved either by decreasing the enthalpy H or increasing the entropy S.

In metallic crystals, closed-packed structures: HCP (C = 12) and FCC (C = 12) [Fig. 4.9] have a lower enthalpy and thus are stable at low temperatures (upto T1).



The 'looser' BCC strucutre (C = 8) has a higher entropy and therefore is stable at elevated temperatures. This explains the stability of BCC structures at elevated temperatures in many metals: Ti, Zr, Fe, U.

The stability of the BCC lattice of iron at low temperatures is attributed to an increase of the electronic component of entropy. The stability of allotropic modifications may change due to changes in the type of bond. For example, the tin modification with diamond type lattice Sn α , is stable at low temperatures owing to the high energy of covalent bond, and therefore, low enthalpy. On heating, it changes to the Sn modification which has a weaker metallic bond. Around 30 metals, e.g. Titanium, Zirconium, Tin, Uranium, Iron, Cobalt etc. exhibit the phenomenon of temperature polymorphism. A high-temperature modification can be retained in a metal for a long time at 20-25°C by fast cooling, since the diffusion mobility of atoms at such temperatures is low and cannot cause rearrangement of the lattice.

Besides, some polymorphous transformations occur under the effect of pressure and temperature. For example, the graphite modification of carbon recrystallizes to diamond when heated to 2000°C under a pressure of about 1010 Pa. Under very high pressures, iron has a low-temperature modification with HCP lattice.

An increase of pressure at low temperatures can change less closely packed modifications into close packed structures. As has been observed for Ge, Si and Sn, application of a high pressure can change their covalent crystals with diamond type lattice (C = 4) into metallic crystals with a tetragonal body centered lattice (C = 8).

The entropy of metallic bond is somewhat lower than that of covalent bond, because of which most metals have lower melting and boiling points and lower elastic moduli, but higher temperature coefficients of linear expansion, compared to covalent crystals.

In most cases, an increase of bond energy increases the melting point, elastic modules, an activation energy of self diffusion, but, on the contrary, decreases the coefficient of linear expansion. These regularities have been observed experimentally and have a number of exceptions. In particular, the elastic modulus of beryllium is anomalously high, because of which beryllium alloys have an elevated stiffness.

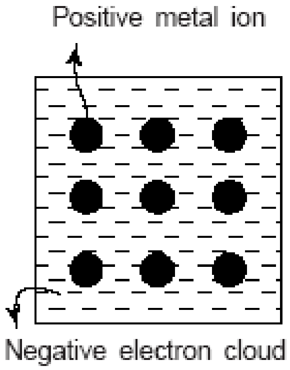
Ti and Zr exhibit too low values of elastic moduli and activation energy of self diffusion. The latter explains their low heat resistance.

By virtue of non-directivity of metallic bonds and close-packed structures, metallic crystals are more plastic and less hard than covalent crystals. Their high electric conductivity is due to the presence of free sublevels in valence energy zone.

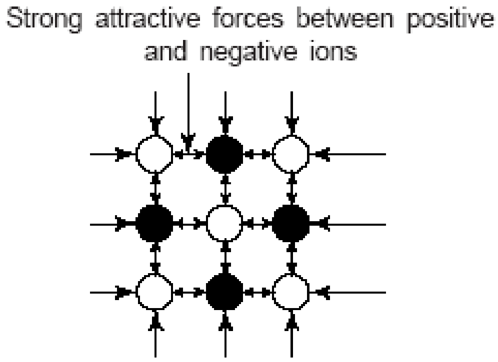
The temperature coefficient of electric resistance of metallic crystals is positive, i.e., the electric resistance increases on heating.

The metallic bond is weaker than ionic or covalent bond. The binding energy ranges from 1 to 5 eV per bond.

Quantum mechanically, it can be shown that the wave functions of valence electrons in metals are so spread out that these electrons can no longer belong to any one nucleus in the solid but are a property of the solid as a whole. This delocalization of the valence electrons leads to a decrease in both potential and kinetic energy which is responsible for metallic bonding.



(a)



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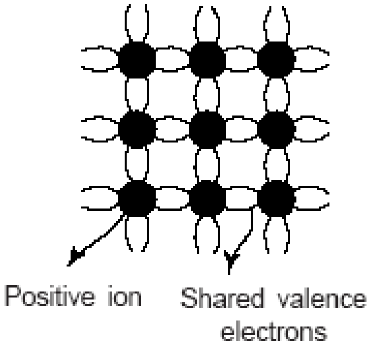
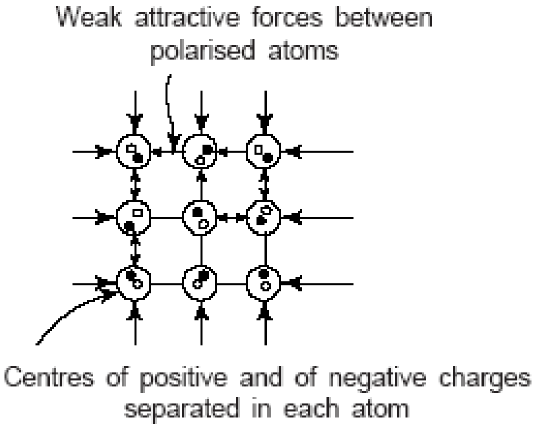




Properties	*Ionic bonds* (1)	*Covalent bonds* (2)	*Metallic bonds* (3)
Bonding force	Electrostatic attraction of oppositely charged ions	Mutual sharing of valence electrons between atoms	Attraction between the ion cores and conduction electron gas
Energy of bond kJ/k mol	(500–1000) 10^3	(60–700) 10^3	(100–350) 10^3
Character of bond	Non-directional	Directional	Non-directional
Bond formation condition	When one of the atoms has smaller number of valence electrons	When atomic orbitals of two atoms overlap	For elements having small number of valence electrons
Electrical conductivity	Low conductivity	Low electrical conductivity	Good conductivity
Lustre	Transparent or coloured, but not highly reflective.	Transparent to highly reflective	Highly reflective
Colour	Wide variety of goods colours	White to grey	Usually grey with a few exceptions
Density	Intermediate	Intermediate	High
Cleavage	Very good	Fairly good	Difficult except at low temperatures because of high ductility
Melting point	Intermediate (700–3300 K)	High (500–3700 K)	Intermediate (230–450)
Vapour state	Diatomic molecules or atoms	Atoms or occasionally small molecular aggregates	Atoms or occasionally small molecular aggregates.
Heat of vaporization *H* (kcal/mole)	121–242	85–405	26–94
Electrical resistivity (Ω-*m*)	10^{12}–10^{20}	10–10^{20}	10^{-3}–10^{-5}
Thermal Conductivity (W-m^{-1}-k^{-1}	2–20	4–600	40–400
Examples	NaCl, CsCl, LiF, $CaCl_2$, Mgo, etc.	Diamond, Germanium, Si, SiC, etc.	Al, Cu, Na, Fe, etc.

THE SPACE LATTICE

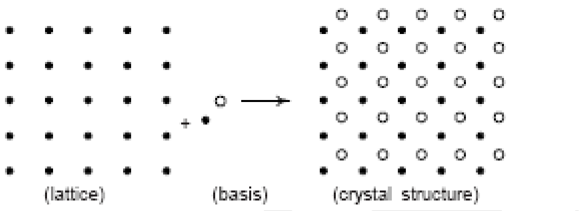
The space lattice has been defined as an array of imaginary points which are so arranged in space that each point has identical surroundings. We must note that the crystal structure is always described in terms of atoms rather than points. Thus in order to obtain a crystal structure, an atom or a group of atoms must be placed on each lattice point in a regular fashion. Such an atom or a group of atoms is called the *basis* and this acts as a building unit or a structural unit for the complete crystal structure. Obviously, a lattice combined with a basis generates the *crystal structure*. Mathematically, one can express it as

Space lattice + Basis = Crystal Structure

Thus, whereas a lattice is a mathematical concept, the crystal structure is a physical concept.

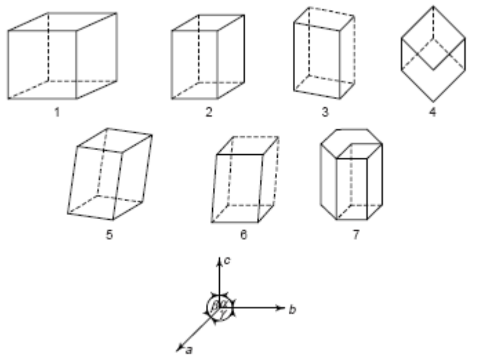
The generation of a crystal structure from a two-dimensional lattice is illustrated in Fig. The basis consists of two atoms, represented by and , having orientation as shown in Fig.. The crystal structure is obtained by placing the basis on each lattice point such that the centre of the basis coincides with the lattice point. We must note that the number of atoms in a basis may vary from one to several thousands, whereas the number of space lattices possible is only fourteen as described in a later section.

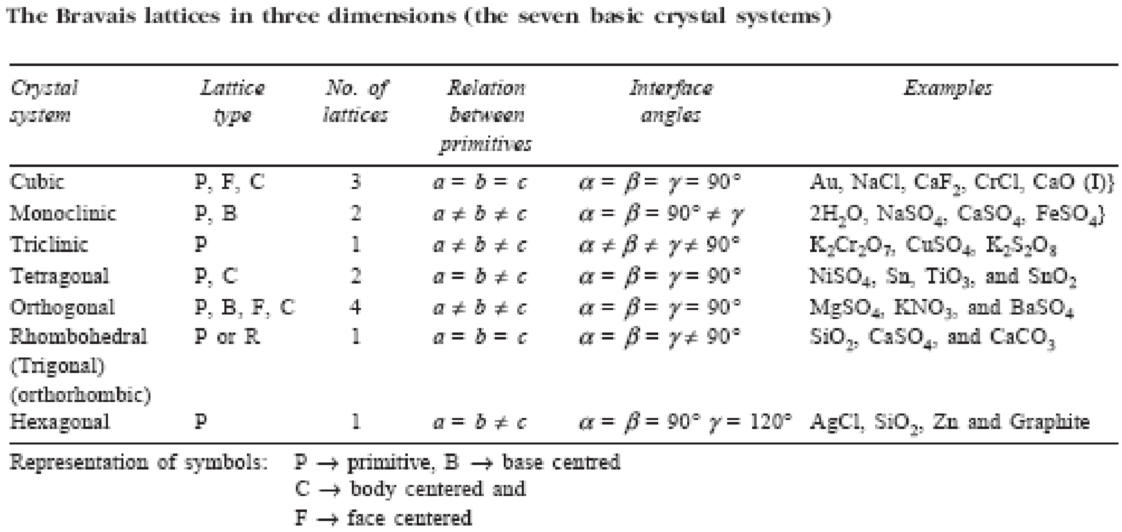
Obviously, one can obtain a large number of crystal structures from just fourteen space lattices simply because of the different types of basis available. If the basis consists of a single atom only, a monoatomic crystal structure is obtained. Copper is an example of monoatomic face-centred cubic structures. Examples of complex bases are found in biological materials.



CRYSTAL SYSTEMS

The seven basic crystal systems are shown in figure below.





The Bravais lattices in three dimensions (the seven basic crystal systems)

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

Representation of symbols: P → primitive, B → base centred
C → body centered and
F → face centered

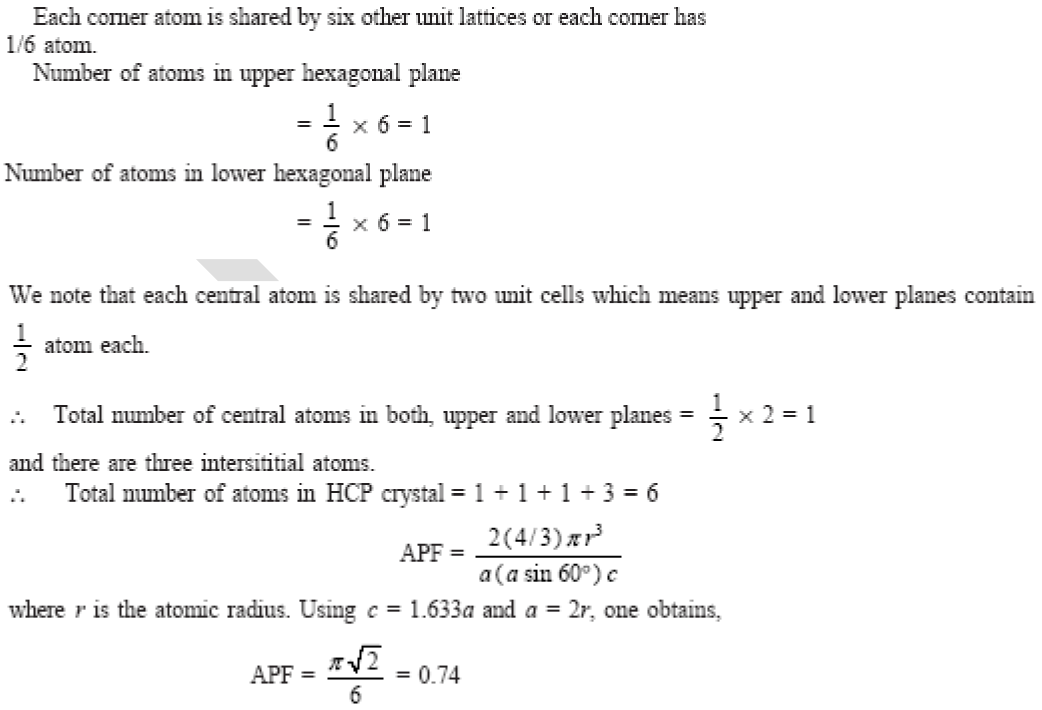
Atomic Packing Factor (APF): This is defined as the ratio of total volume of atoms in a unit cell to the total volume of the unit cell. This is also called relative density of packing (RDP).

Thus

APF = (No. of atoms volume of one atom/volume of unit cell)

Prove that APF of Simple cubic = 0.52, BCC = 0.68, FCC & HCP = 0.74

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



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

Number of atoms in upper hexagonal plane

$$= \frac{1}{6} \times 6 = 1$$

Number of atoms in lower hexagonal plane

$$= \frac{1}{6} \times 6 = 1$$

We note that each central atom is shared by two unit cells which means upper and lower planes contain $\frac{1}{2}$ atom each.

∴ Total number of central atoms in both, upper and lower planes = $\frac{1}{2} \times 2 = 1$

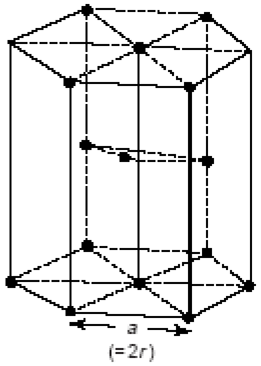
and there are three intersititial atoms.

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

$$\text{APF} = \frac{2(4/3)\pi r^3}{a(a \sin 60°)c}$$

where r is the atomic radius. Using $c = 1.633a$ and $a = 2r$, one obtains,

$$\text{APF} = \frac{\pi\sqrt{2}}{6} = 0.74$$



DENSITY OF CRYSTAL

This is defined as: Density of the crystal (ρ) = Mass of unit cell/Volume of unit cell

$$\text{Mass of unit cell} = \frac{\text{Atomic mass}}{\text{Avogadro number}} \times \text{Number of atoms per unit cell}$$

$$= \frac{M}{N_A} \times n$$

($n \rightarrow$ number of atoms per unit cell and $N_A \rightarrow$ Avogadro's number, $M \rightarrow$ the atomic weight, and $a \rightarrow$ side of a cubic unit cell).

$$= \frac{nM}{a^3 N_A}$$

(i) Linear density: This is defined as the number of atoms per unit length along a specific crystal direction.

(ii) Planar density: This is defined as the number of atoms per unit area on a crystal plane. This affect significantly the rate of plastic deformation.

Determination of Miller Indices:

(a) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes, i.e. x, y, z axes (Fig. 3.25)

x	y	z
$2a$	$3b$	c
pa	qb	rc

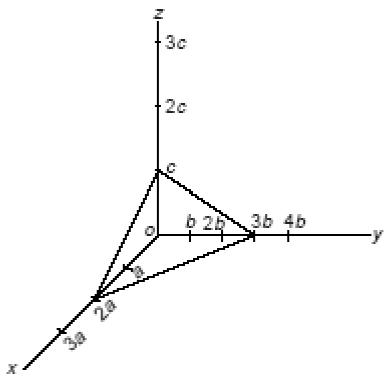
($p = 2$, $q = 3$, $r = 1$)

(b) Now, express the above intercepts as multiples of the unit cell dimensions, or lattice parameters along the axes, i.e.

axes	x	y	z
	$\frac{2a}{a}$	$\frac{3b}{b}$	$\frac{c}{c}$
Intercept	2	3	1

(c) Take the reciprocal of intercepts

$$\frac{1}{2} \quad \frac{1}{3} \quad \frac{1}{1}$$



(d) Now, reduce these reciprocals to the smallest set of integral numbers and enclose within a bracket

$$6 \times \frac{1}{2} \qquad 6 \times \frac{1}{3} \qquad 6 \times \frac{1}{1}$$

$$(3 \qquad 2 \qquad 6)$$

These integers within the bracket are Miller indices. In general it is denoted by (h, k, l). Thus, we note that

$$\frac{1}{p}:\frac{1}{q}:\frac{1}{r} = h : k : l$$

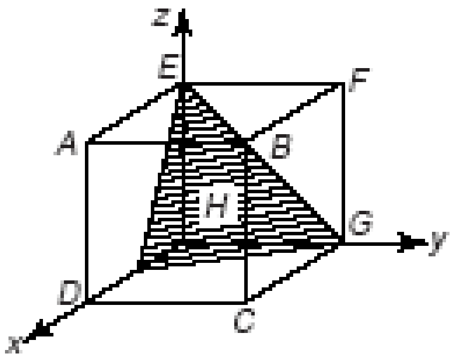
$$\frac{1}{2}:\frac{1}{3}:\frac{1}{1} = 3 : 2 : 6$$

Sketching the plane from miller indices:

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

(i) First, take the reciprocal of the given Miller indices. These reciprocals represent the intercepts in terms of the axial units along x-x, y-y and z-z axes respectively. For example, if the given Miller indices are (211), then its reciprocals or intercepts will be 1/2, 1/1 and 1/1 or 0.5, 1, 1 respectively.

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



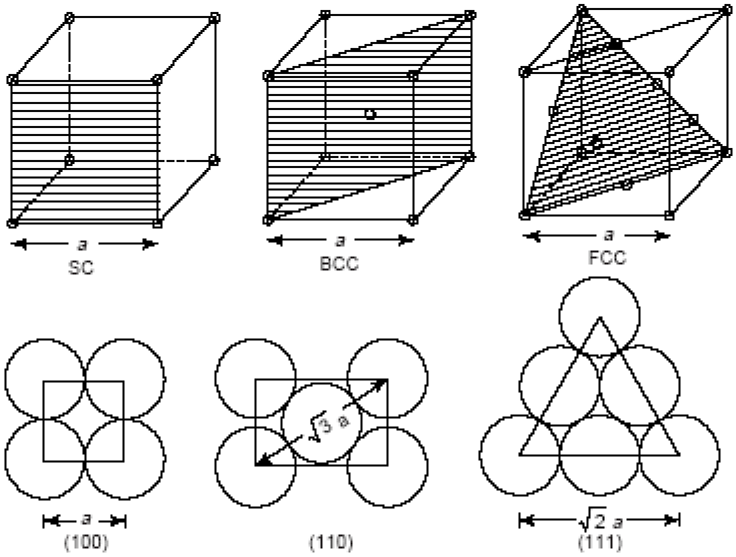
Example 1 *Determine the relationship between the lattice parameter a and the atomic radius r for monoatomic, SC, BCC and FCC structures*

Solution In simple cubic (SC) structure, the atoms touch one another along the cube edges,

$$\therefore \qquad a = 2r$$

In BCC, the atoms touch along the body diagonals,

$$\therefore \qquad \sqrt{3}\,a = 4r$$



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

In FCC structure, the atoms touch along the face diagonals,

∴ $$\sqrt{2}\,a = 4r$$

or $$a = 2\sqrt{2}\,r.$$

Example 2 *An atomic plane in a crystal lattice makes intercept of 3a, 4b and 6c with the crystallographic axes where a, b and c are the dimensions of the unit cell. Show that the Miller indices of the atomic plane are (432).*

Solution In terms of the lattice constants, the intercepts are 3, 4 and 6. Their reciprocals are 1/3, 1/4, 1/6. On reducing to a common denominator, they become 4/12, 3/12 and 2/12. Obviously, the Miller indices of the plane are (432).

Example 3 *In a single cubic crystal find the ratio of the intercepts on the three axes by (123) plane.*

Solution The reciprocals of Miller indices are 1/1, 1/2 and 1/3. On reducing to a common denominator they become 6, 3 and 2. Intercepts on the three axes are $6a$, $3b$ and $2c$, where a, b and c are the lattice constants along the three axes.

Example 4 *Draw (101) and (111) planes in a unit cubic cell. Find the Miller indices of the directions which are common to both the planes.*

Solution Intercepts of the plane (101) with the three axes are 1/1, 1/0 and 1/1 i.e. 1, ∞ and 1. Similarly, the intercepts of the (111) with the three axes are 1/1, 1/1 and 1/1, i.e. 1, 1 and 1.

Now, taking the point O as origin and lines OA, OB and OC as the axes a, b and c respectively, the plane with the intercepts 1, ∞ and 1 is the plane $ADGC$ and that with intercepts 1, 1 and 1 is plane ABC (Fig. 3.36). From figure, it is obvious that the line common to both the planes is the line AC. This line corresponds to two directions, i.e., AC and CA.

Projections of the direction AC on the axes are −1, 0 and 1. Projections of direction CA on the axes are 1, 0 and −1.

Thus the required indices are $[\bar{1}01]$ and $[10\bar{1}]$.

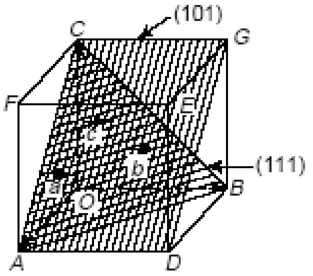
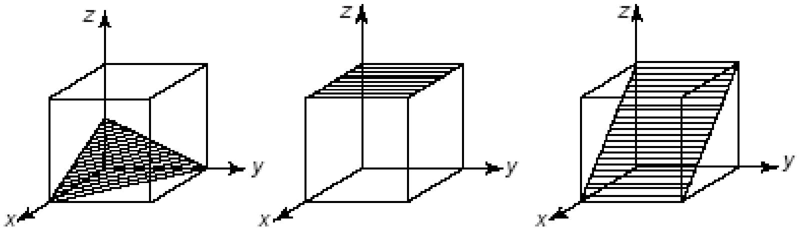


Fig. 3.36 Planes (101) and (111) in a simplecubiclattice

Example 5 *Draw the following planes and directions in the case of a FCC structure: (112), (001) and (101).*

Solution *(i) Plane and direction (112):* In this, we have $h = 1$, $k = 1$ and $l = 2$. The reciprocals of h, k and l are 1/1, 1/1, 1/2, i.e. 1, 1, 0.5.

Now, we can sketch the plane with intercepts 1, 1, 0.5 along x-x, y-y and z-z axes respectively (Fig. 3.37(a).



(a) Plane (112) (b) Plane (001) (c) Plane (101)

Fig. 3.37

(ii) Plane of (001): Here $h = 0$, $k = 0$, $l = 1$. The reciprocals are 1/0, 1/0, 1/1 i.e., ∞, ∞, 1. We obtain the sketch of the plane as shown in Fig. 3.37(b).

(iii) Plane of (101): Here $h = 1$, $k = 0$ and $l = 1$. The reciprocals are 1/1, 1/0 and 1/1, i.e. 1, ∞ and 1. We obtain the sketch as shown in Fig. 3.37(c).

Example 6 *A plane makes intercepts of 1, 2 and 0.5 Å on the crystallographic axes of an orthorhombic crystal with a : b : c = 3 : 2 : 1. Find the Miller indices of this plane.*

Solution Taking the lengths of the axes *OA*, *OB* and *OC* as 3, 2 and 1Å respectively, we obtain the plane with intercepts of 1, 2 and 0.5 Å on the axes is the plane *DBE* (Fig. 3.38). The intercepts of this plane relative to full lengths of the axes are: 1/3, 2/2 and 0.5/1 or 1/3, 1 and 1/2. Reciprocals are: 3, 1 and 2. Obviously, the Miller indices of the plane DBE are (312).

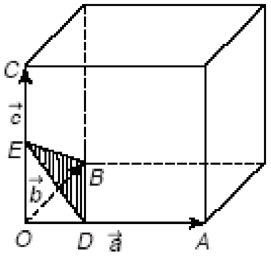


Fig. 3.38 **(312) plane in an orthorhombic lattice**

Example 7 *Sketch (111) plane of a unit cell of simple tetragonal crystal. Given c/a = 0.62.*

Solution Fig. 3.39 shows the plane (111). The plane cuts the three axes at unit distances. We note that the unit distance along *z*-axis is shorter than the unit distance of other two axes.

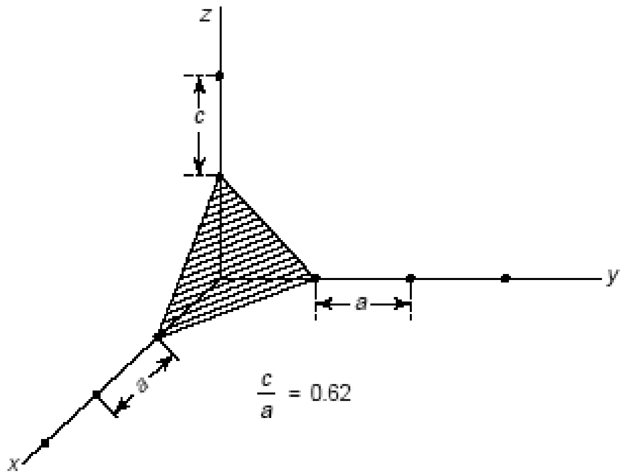


Fig. 3.39 **The plane (111) *z*-axis shorter**

Example 8 *Draw the planes (020), (120) and (220) in a FCC structure.*

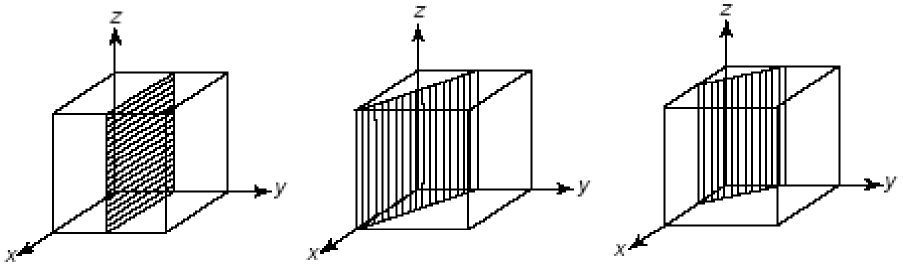
Solution *(i) Plane of (020):* Given $h = 0$, $k = 2$ and $l = 0$. The reciprocals are 1/0, 1/2, 1/0, i.e. ∞, 0.5, ∞.

Sketching the plane with intercepts ∞, 0.5, ∞ along *x-x*, *y-y* and *z-z* axes respectively, we obtain the plane (020) (Fig. 3.40(a)).

(ii) Plane of (120): Here $h = 1$, $k = 2$, and $l = 0$. The reciprocals of *h*, *k*, *l* are 1/1, 1/2, 1/0, i.e. 1, 0.5, ∞.

Sketching the plane, we obtain as shown in Fig. 3.40(b).

(iii) Plane of (220): Here $h = 2$, $k = 2$, and $l = 0$. The reciprocals of *h*, *k*, *l* are 1/2, 1/2, 1/0, i.e. 0.5, 0.5, ∞. The plane obtained is as shown in Fig. 3.40(c).



(a) Plane (020) (b) Plane (120) (c) Plane (220)

Fig. 3.40

Example 9 *Draw the planes and directions of FCC structures (321), (102), (201) and (111).*

[B.E. 2001]

Solution *(i) Plane and Direction of (321):* Here $h = 3$, $k = 2$, and $l = 1$. The reciprocals are 1/3, 1/2, 1/1, i.e. 0.3, 0.5, 1. The sketch of the plane with intercepts 0.3, 0.5 and 1 is as shown in Fig. 3.41(a). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

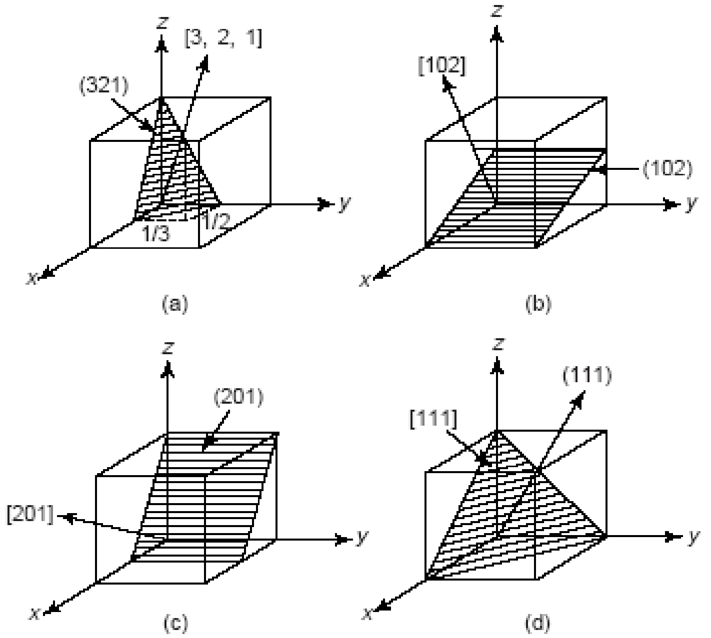


Fig. 3.41

(ii) Plane and Direction of (102): Here $h = 1$, $k = 0$, and $l = 2$. The reciprocals of these are: 1/1, 1/0 and 1/2, i.e. 1, ∞, 0.5. The sketch of the plane with these intercepts is as shown in Fig. 3.41(b). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

(iii) Plane and Direction of (011): Here $h = 0$, $k = 1$, and $l = 1$. The reciprocals of h and k, l are: 1/0, 1/1, 1/1, i.e. ∞, 1.1. The sketch of the plane with these intercepts is shown in Fig. 3.41(c). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

(iv) Plane and Direction of (001): Here $h = 0$, $k = 0$, and $l = 1$. The reciprocals of h, k and l are: 1/0, 1/0, 1/1, i.e. ∞, ∞, 1. The sketch of the plane with these intercepts is shown in Fig. 3.41(d). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

Example 10 *In a cubic unit cell, find the angle between normals to the planes (111) and (121).*

Solution Since the given crystal is cubic, the normals to the planes (111) and (121) are the directions [111] and [121] respectively. If θ be the angle between the normals, then

$$\cos\,\theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\left(h_1^2 + k_1^2 + l_1^2\right)^{1/2}\left(h_2^2 + k_2^2 + l_2^2\right)^{1/2}}$$

$$= \frac{1\times 1 + 1\times 2 + 1\times 1}{(1^2 + 1^2 + 1^2)^{1/2}\,(1^2 + 2^2 + 1^2)^{1/2}}$$

$$= 0.9428$$

$$\therefore \quad \theta = 19.47^\circ \quad \text{or} \quad 19^\circ\ 28'$$

Example11 *Determine the packing efficiency and density of sodium chloride from the following data: (i) radius of the sodium ion = 0.98 Å, (ii) radius of chlorine ion = 1.81 Å (iii) atomic mass of sodium = 22.99 amu and atomic mass of chlorine = 35.45 amu.*

Solution The unit cell structure of NaCl is shown in Fig. 3.18. We can see that the Na^+ and Cl^- ions touch along the cube edges.

$$\therefore \quad \text{Lattice parameter, } a = 2\,(\text{radius of Na}^+ + \text{radius of Cl}^-)$$

$$= 2(0.98 + 1.81) = 5.58\ \text{Å}$$

$$\text{Atomic Packing Fraction} = \frac{\text{Volume of ions present in the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{4(4/3)\pi r_{Na^+}^3 + 4\left(\frac{4}{3}\right)\pi r_{Cl^-}^3}{a^3}$$

$$= \frac{16\pi}{3}\left[\frac{(0.98)^3 + (1.81)^3}{(5.58)^3}\right]$$

$$= 0.663 \text{ or } 66.3\%$$

$$\text{Density} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{4(22.99 + 35.45)\times 1.66\times 10^{-27}}{(5.58\times 10^{-10})^3}\ \text{kg/m}^3$$

$$= 2234\ \text{kg/m}^3 \text{ or } 2.23\ \text{gm/cm}^3$$

Example 12 *Aluminium has FCC structure. Its density is 2700 kg/m³. Find the unit cell dimensions and atomic diameter. Given at. weight of Al = 26.98.* [Roorkee]

Solution

$$\text{Density} = \frac{nm}{a^3}\ \text{N}_A$$

$$= 2700\ \text{kg/m}^3 = 2.7\ \text{gm/cm}^3$$

$$= \frac{4\times 26.98}{a^3\times 6.023\times 10^{23}}$$

$$\therefore \quad a^3 = \frac{4\times 26.98}{2.7\times 6.023\times 10^{23}} = 6.6\times 10^{-23}/\text{cm}^3$$

$$\therefore \quad a = 4.048\times 10^{-10}\ \text{m} = 4.048\ \text{Å}$$

For FCP structure, $r = \dfrac{a}{2\times1.414} = \dfrac{4.048\,\text{Å}}{2\times1.414} = 1.43$ Å

$\therefore$ Diameter = $2r$ = 2.86 Å

Example 13 *Find the interplanar distance of (200) plane and (111) plane of Nickel crystal. The radius of Nickel atom is 1.245 Å.* [Jodhpur]

Solution Nickel has FCC structure. Given radius of Nickel = r = 1.245 Å

$$\text{Lattice constant} = a = \frac{4r}{\sqrt{2}} = \frac{4\times1.245}{\sqrt{2}} = 3.52\ \text{Å}$$

$$\therefore \quad d_{200} = \frac{3.52}{\sqrt{2^2+0^2+0^2)}} = 1.76\ \text{Å}$$

$$d_{111} = \frac{3.52}{\sqrt{1^2+1^2+1^2}} = 2.03\ \text{Å}$$

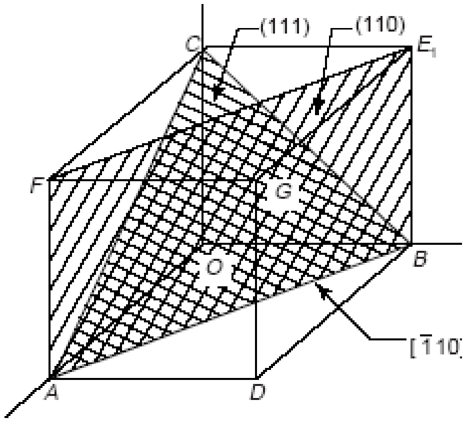


Fig. 3.42 **Plane in a unit cell of FCC Nickel**

Example 14 *The lattice constant of a unit cell of KCl crystal is 3.03 Å. Find the number of atoms/ mm² of planes (100), (110) and (111). KCl has simple cubic structure.* [B.E]

Solution a = 3.03 Å = 3.03×10^{-7} mm.

(100) plane The number of atoms in the (100) plane of a simple cubic structure

$$= \frac{1}{a^2} = \frac{1}{(3.03\times10^{-7})^2} = 10.9 \times 10^{12}$$

(110) plane The number of atoms in (110) plane of a simple cubic structure

$$= \frac{0.707}{a^2} = \frac{0.707}{(3.03\times10^{-7})^2} = 7.7 \times 10^{12}$$

(111) plane The number of atoms in (111) plane of a simple cubic structure

$$= \frac{0.58}{a^2} = \frac{0.58}{(3.03\times10^{-7})^2}$$

$$= 6.3 \times 10^{12}$$

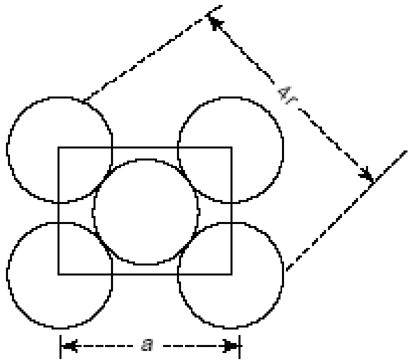


Fig. 3.43 **Interplanar distances in Ni crystal**

Example 15 *Determine the planar density of Ni (FCC structure) in (100) plane. Given, the radius of Ni atom = 1.245 Å.*

Solution From Fig. 3.43, we have

Number of atoms in (100) plane

$$= 1 + \frac{1}{4} \times 4 = 2$$

Area of plane = a^2,

$$= a = \frac{4r}{\sqrt{2}} = 3.52\ \text{Å}$$

$\therefore$ Planar density = $\dfrac{2}{(3.52\times10^{-7}\ \text{mm}^2)}$ = 16.1×10^{12} atoms/mm^2

Example 16 *Calculate the planar atomic densities of planes (100), (110) and (111) in FCC unit cell and apply your result for lead (FCC form).* [AMIE]

Solution (i) *Plane (100)*: Fig. 3.44(a) shows an FCC unit cell with planes (111) and (111). Figure 3.44(b) shows the plane (100) with atoms on it. Similarly Figs. 3.44(c) and (d) shows the planes (110) and (111) with atoms contained in them respectively.

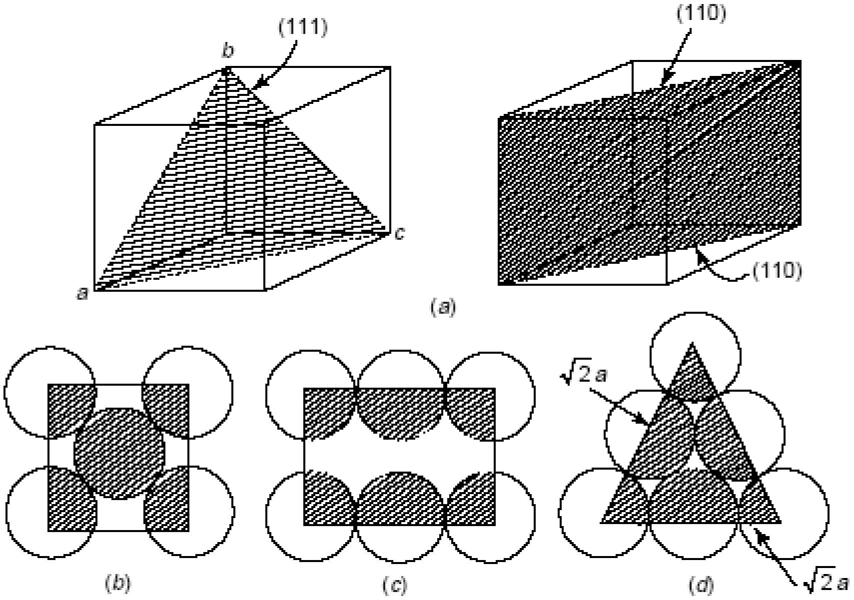


Fig. 3.44 Distribution of atoms in planes (100), (110) and (111) in FCC unit cell

Number of atoms contained in (100) plane is $4 \times \dfrac{1}{4} + 1 = 2$

Let a be the edge of the unit cell and r the radius of the atom, then

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

$\therefore$ Planar density of plane (100)

$$= \frac{2}{4\times 2r^2} = \frac{0.25}{r^2}$$

The radius of lead atom is 1.75 Å. The planar density of (100) plane of lead

$$= \frac{0.25}{(1.75\times10^{-7})^2} = 8.2 \times 10^{12}\ \text{atoms/mm}^2$$

$$= 8.2 \times 10^{18}\ \text{atoms/m}^2$$

(ii) Plane (110): From Fig. 3.44(c), we have the number of atoms contained in plane (110)

$$= 4 \times \frac{1}{4} + 2 \times \frac{1}{2} = 2$$

The top edge of the plane (110) is $4r$, whereas the vertical edge = a = $2\sqrt{2}\ r$. Thus the planar density of (110)

$$= \frac{2}{8\sqrt{2r^2}} = 0.177/r^2$$

In case of (110) plane in lead, we have planar density = $\frac{0.177}{(1.75 \times 10^{-2})^2}$

(iii) From Fig. 3.44(d), we have the number of atoms contained in the plane (111)

$$= 3 \times \frac{1}{6} + \frac{3}{2} = 2$$

Area of (111) plane = $\frac{1}{2}\sqrt{\frac{3}{2}}\,a\sqrt{2}\,a = 4\sqrt{3r^2}$

$\therefore$ Planar density of (111) = $\frac{2}{4\sqrt{3r^2}} = \frac{0.29}{r^2}$

For lead crystal, we obtain the value 9.5 × 10^{12} atoms/mm^2.

Example 17 *Determine the linear atomic density in the [110] and [111] directions of copper crystal lattice. Lattice constant of copper (FCC) is 3.61 × 10^{-10} m.* [AMIE]

Solution From Fig. 3.45 and earlier discussions. We note that the face diagonal along [110] direction intersects two half diameters and one full diameters. Thus the number of diameters of atom along [110] direction

$$= \frac{1}{2} + 1 + \frac{1}{2} = 2$$

Let a be the lattice constant, then the length of the face diagonal = $\sqrt{2}\ a$

$\therefore$ Linear density of [110] within unit cell

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

Since $a = 3.61 \times 10^{-10}$ m $= 3.61 \times 10^{-7}$ mm

$$\therefore \quad \rho_{110} = \frac{\sqrt{2}}{3.61 \times 10^{-7}} = 3.92 \times 10^{6} \text{ atoms/mm}$$

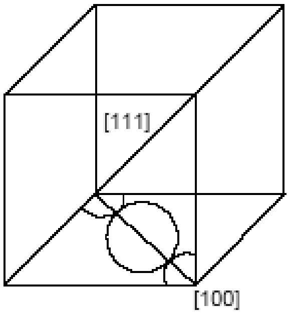


Fig. 3.45

The direction [111] is along the body diagonal. From Fig. 3.45, the length of the diagonal along [111]

$$= \sqrt{\left(\sqrt{2}a\right)^2 + a^2} = \sqrt{3}a$$

The number of atomic diameters intersected by diagonal along [111] is $\frac{1}{2} + \frac{1}{2}$ at two ends. Thus the linear density along [111] within the crystal unit cell

$$= \frac{1}{\sqrt{3}\,a} = \frac{1}{\sqrt{3} \times 3.61 \times 10^{-7}} = 1.6 \times 10^{6} \text{ atoms/mm}$$

Obviously, in FCC the linear density along [110] direction is greater than that along [111] direction.

Example 18 *The density of α – Fe is 7.87×10^3 kg/m^3. Atomic weight of Fe is 55.8. If α – Fe crystallizes in BCC space lattice, find lattice constant. Given Avogadro's number (N) = 6.02×10^{26}/kg/mole.*

[AMIE]

Solution Lattice constant (a) can be obtained from the relation,

$$a^3 = \frac{An}{N\rho} = \frac{55.8 \times 2}{6.02 \times 10^{26} \times 7.87 \times 10^3} = 2.355 \times 10^{-29}$$

$$\therefore \quad a = (2.355 \times 10^{-29})^{1/3} = 2.866 \times 10^{-10} \text{ m} = 2.866 \text{ Å}$$

Example 19 *Show that the number of atoms per unit cell of a metal having a lattice parameter of 2.9 Å and density of 7.87 gm/cc is 2. Given atomic weight of metal = 55.85 and N = 6.023×10^{23}*

Solution

$$a^3 = \frac{An}{N\rho}$$

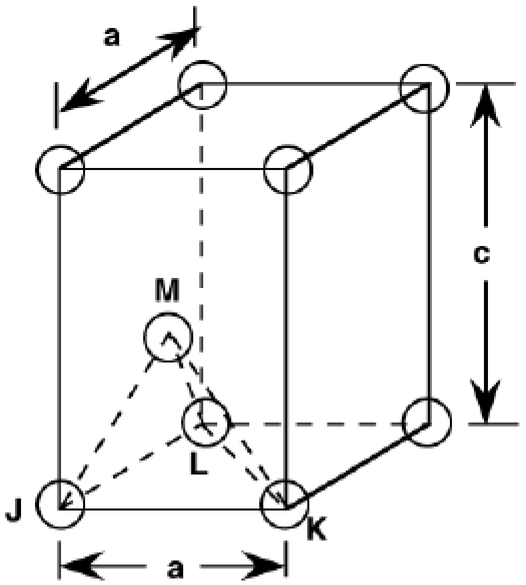
or

$$(2.9 \times 10^{-3})^3 = \frac{55.85\text{n}}{6.023 \times 10^{23} \times 7.87} = 1.18 \times 10^{-23} \text{ n}$$

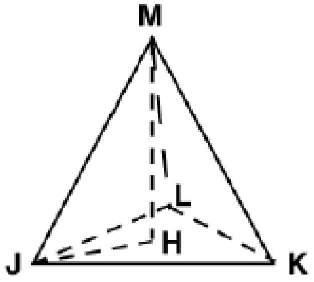
$$\therefore \quad n = \frac{(2.9 \times 10^{-8})^3}{1.18 \times 10^{-23}} = 2$$

Ex. 20. Prove that c/a ratio of HCP is 1.633

Solution: A sketch of one-third of an HCP unit cell is shown below.



Consider the tetrahedron labeled as **JKLM**, which is reconstructed as



The atom at point **M** is midway between the top and bottom faces of the unit cell--that is $\overline{\mathbf{MH}}$ = **c**/2. And, since atoms at points **J**, **K**, and **M**, all touch one another,

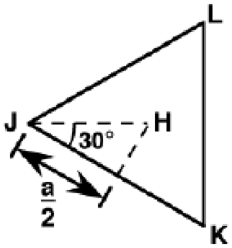
$$\overline{JM} = \overline{JK} = 2R = a$$

where **R** is the atomic radius. Furthermore, from triangle **JHM**,

$$(\overline{JM})^2 = (\overline{JH})^2 + (\overline{MH})^2, \text{ or}$$

$$a^2 = (\overline{JH})^2 + \left(\frac{c}{2}\right)^2$$

Now, we can determine the $\overline{\mathbf{JH}}$ length by consideration of triangle **JKL**, which is an equilateral triangle,



$$\cos 30° = \frac{a/2}{JH} = \frac{\sqrt{3}}{2}, \text{ and}$$

$$\overline{JH} = \frac{a}{\sqrt{3}}$$

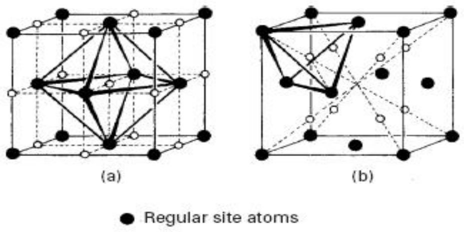
Substituting this value for $\overline{\mathbf{JH}}$ in the above expression yields

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

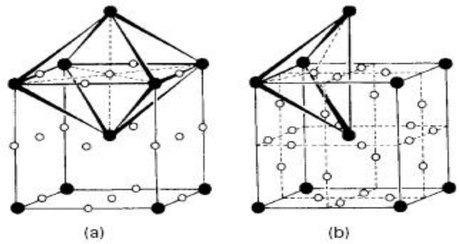
and, solving for **c**/**a**

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

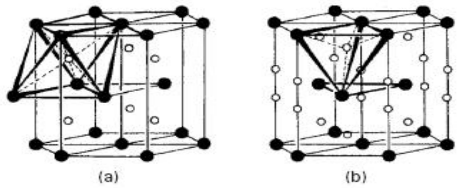
Voids



Interstices in FCC structure. (a) Octahedral void. (b) Tetrahedral void.



Interstices in the BCC structure. (a) Octahedral void. (b) Tetrahedral void.



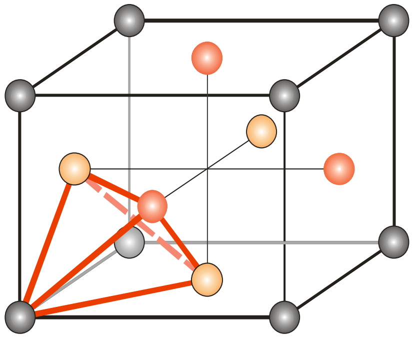
Interstices in the HCP structure. (a) Octahedral void. (b) Tetrahedral void.

FCC

VOIDS

TETRAHEDRAL

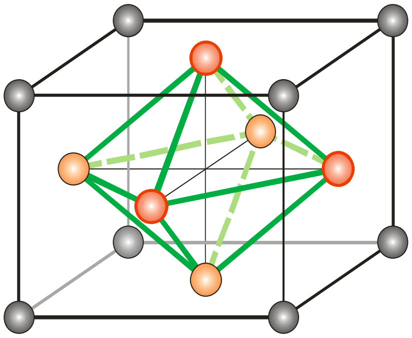
OCTAHEDRAL



¼ way along body diagonal
{¼, ¼, ¼}, {¾, ¾, ¾}
+ face centering translations

$$V_{tetrahedron} = \frac{1}{24} V_{cell}$$

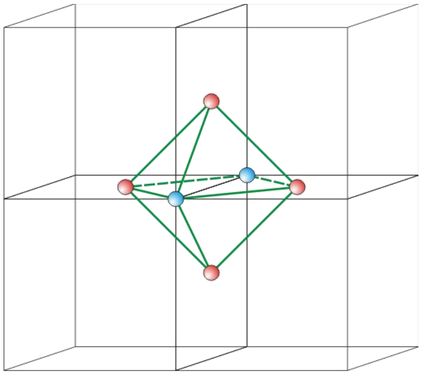
Note: Atoms are coloured differently but are the same

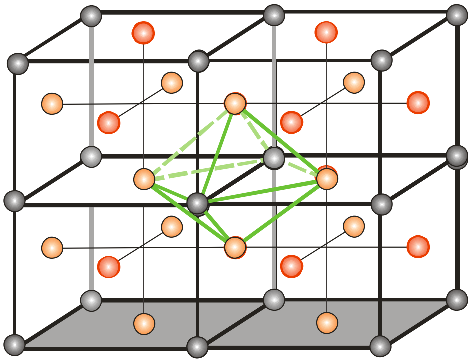


At body centre
{½, ½, ½}
+ face centering translations

$$V_{octahedron} = \frac{1}{6} V_{cell}$$

FCC- OCTAHEDRAL





Site for octahedral void

$\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\} + \{\frac{1}{2}, \frac{1}{2}, 0\} = \{1, 1, \frac{1}{2}\} \equiv \{0, 0, \frac{1}{2}\}$

Face centering translation

Equivalent site for an octahedral void

Note: Atoms are coloured differently but are the same

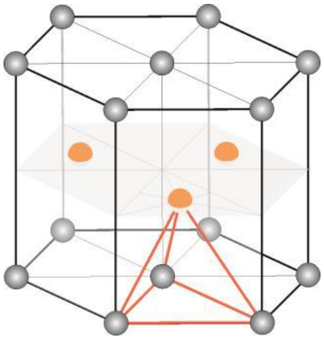
FCC voids	Position	Voids / cell	Voids / atom
Tetrahedral	¼ way from each vertex of the cube along body diagonal <111> → ((¼, ¼, ¼))	8	2
Octahedral	• Body centre: 1 → (½, ½, ½) • Edge centre: (12/4 = 3) → (½, 0, 0)	4	1

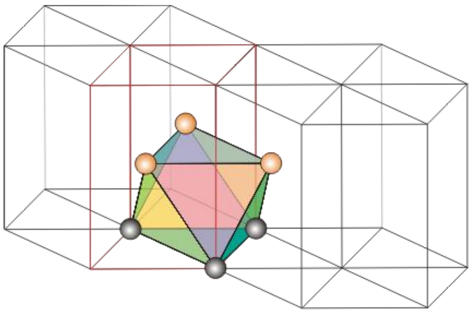
HCP

VOIDS

TETRAHEDRAL

OCTAHEDRAL





Coordinates : $(0,0,\frac{3}{8}),(0,0,\frac{5}{8}),(\frac{2}{3},\frac{1}{3},\frac{1}{8}),(\frac{2}{3},\frac{1}{3},\frac{7}{8})$

Coordinates: $(\frac{1}{3}\ \frac{2}{3},\frac{1}{4}), (\frac{1}{3},\frac{2}{3},\frac{3}{4})$

These voids are identical to the ones found in FCC

Note: Atoms are coloured differently but are the same

STEREOGRAPHIC PROJECTION

The stereographic projection is a useful metallurgical tool, for it permits the mapping in two dimensions of crystallographic planes and directions in a convenient and straightforward manner. The real value of the method is attained when it is possible to visualize crystallographic features directly in terms of their stereographic projections. The purpose of this IDEA is to concentrate on the geometrical correspondence between crystallographic planes and directions and their stereographic projections. In each case, a sketch of a certain crystallographic feature, in terms of its location in the unit cell, is compared with its corresponding stereographic projection. Several simple examples will be considered, but before this is done, attention will be called to several pertinent facts. The stereographic projection is a two-dimensional drawing of three-dimensional data. The geometry of all crystallographic planes and directions is accordingly reduced by one dimension. Planes are plotted as great circle lines, and directions are plotted as points. Also, the normal to a plane completely describes the orientation of a plane. As our first example, consider several of the more important planes of a cubic lattice: specifically the (100), (110), and (111) planes. All three planes are treated in the three parts of Fig. 1.20.

the stereographic projection of each plane can be represented either by a great circle or by a point showing the direction in space that is normal to the plane. Many crystallographic problems can be solved by considering the stereographic projections of planes and directions in a single hemisphere, that is, normally the one in front of the plane of the paper. The three examples given in Fig. 1.20 have all been plotted in this manner. If the need arises, the stereographic projections in the rear hemisphere can also be plotted in the same diagram. However, it is necessary that the projections in the two hemispheres be distinguishable from each other. This may be accomplished if the stereographic projections of planes and directions in the forward hemisphere are drawn as solid lines and dots, respectively, while those in the rear hemisphere are plotted as dotted lines and circled dots, respectively. As an illustration, consider Fig. 1.21, in which the projections in both hemispheres of a single plane are shown. The (120) plane of a cubic lattice is used in this example.

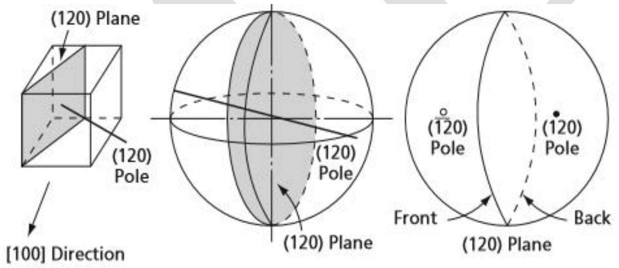


FIG. 1.21 Cubic system, the (120) plane, showing the stereographic projections from both hemispheres, line of sight the [100] direction

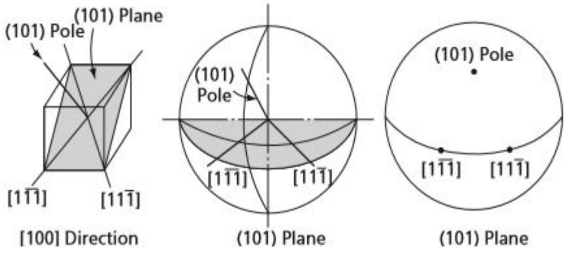


FIG. 1.22 Cubic system, the (101) plane and the two ⟨111⟩ directions that lie in this plane, line of sight [100]

SELECTED CRYSTAL STRUCTURES :

AX-Type Crystal Structures/AB type Compounds

Some of the common ceramic materials are those in which there are equal numbers of cations and anions. These are often referred to as AX compounds, where A denotes the cation and X the anion. There are several different crystal structures for AX compounds; each is normally named after a common material that assumes the particular structure

Rock Salt Structure

Perhaps the most common AX crystal structure is the *sodium chloride* (NaCl), or *rock salt,* type. The coordination number for both cations and anions is 6, and therefore the cation–anion radius ratio is between approximately 0.414 and 0.732. A unit cell for this crystal structure is generated from an FCC arrangement of anions with one cation situated at the cube center and one at the center of each of the 12 cube edges. An equivalent crystal structure results from a face-centered arrangement of cations. Thus, the rock salt crystal structure may be thought of as two interpenetrating FCC lattices, one composed of the cations, the other of anions. Some of the common ceramic materials that form with this crystal structure are NaCl, MgO, MnS, LiF, and FeO.

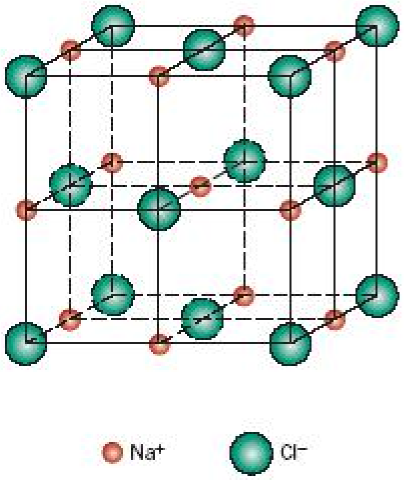
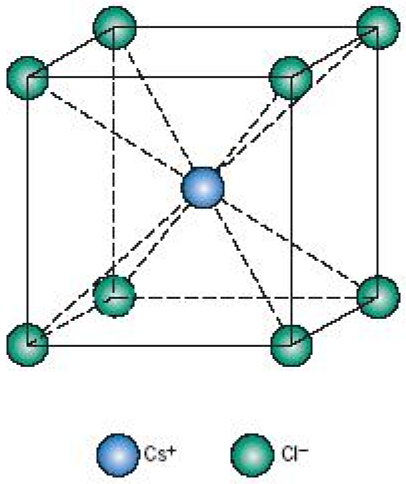
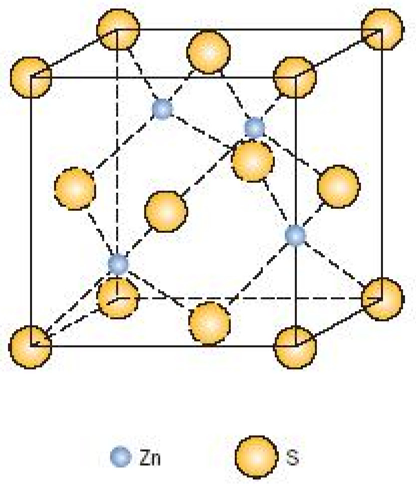


Figure shows a unit cell for the *cesium chloride* (CsCl) crystal structure; the coordination number is 8 for both ion types. The anions are located at each of the corners of a cube, whereas the cube center is a single cation. Interchange of anions with cations, and vice versa, produces the same crystal structure. This is *not* a BCC crystal structure because ions of two different kinds are involve.



A third AX structure is one in which the coordination number is 4; that is, all ions are tetrahedrally coordinated. This is called the *zinc blende,* or *sphalerite,* structure, after the mineralogical term for zinc sulfide (ZnS). A unit cell is presented in All corner and face positions of the cubic cell are occupied by S atoms, while the Zn atoms fill interior tetrahedral positions. An equivalent structure results if Zn and S atom positions are reversed. Thus, each Zn atom is bonded to four S atoms, and vice versa. Most often the atomic bonding is highly covalent in compounds exhibiting this crystal structure which include ZnS, ZnTe, and SiC.



GRAPHITE:

Graphite is a crystalline allotrope of carbon, a semimetal, a native element mineral, and a form of coal. Graphite is the most stable form of carbon under standard conditions. Therefore, it is used in thermochemistry as the standard state for defining the heat of formation of carbon compounds.

Graphite occurs in metamorphic rocks as a result of the reduction of sedimentary carbon compounds during metamorphism. It also occurs in igneous rocks and in meteorites.]Minerals associated with graphite include quartz, calcite, micas and tourmaline. In meteorites it occurs with troilite and silicate minerals. Small graphitic crystals in meteoritic iron are called cliftonite.

Structure

Graphite has a layered, planar structure. The individual layers are called graphene. In each layer, the carbon atoms are arranged in a honeycomb lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm.] Atoms in the plane are bonded covalently, with only three of the four potential bonding sites satisfied. The fourth electron is free to migrate in the plane, making graphite electrically conductive. However, it does not conduct in a direction at right angles to the plane. Bonding between layers is via weak van der Waals bonds, which allows layers of graphite to be easily separated, or to slide past each other.

The two known forms of graphite, alpha (hexagonal) and beta (rhombohedral), have very similar physical properties, except for that the graphene layers stack slightly differently.The alpha graphite may be either flat or buckled.] The alpha form can be converted to the beta form through mechanical treatment and the beta form reverts to the alpha form when it is heated above 1300 °C.

PROPERTIES

High strength

Good chemical stability at elevated temperature and in non oxidising atmosphere

High thermal conductivity

Good machinability

High temp refractories and insulation

Fig: graphite's unit cell

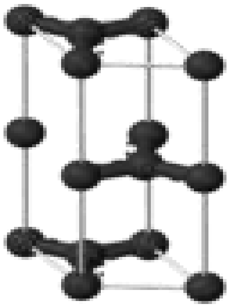


FIG: Side view of layer stacking

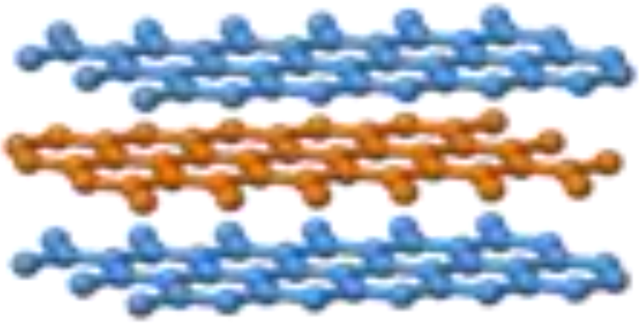
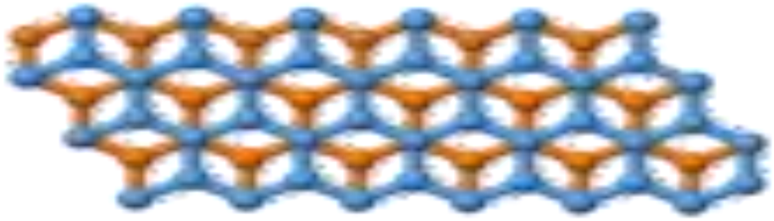
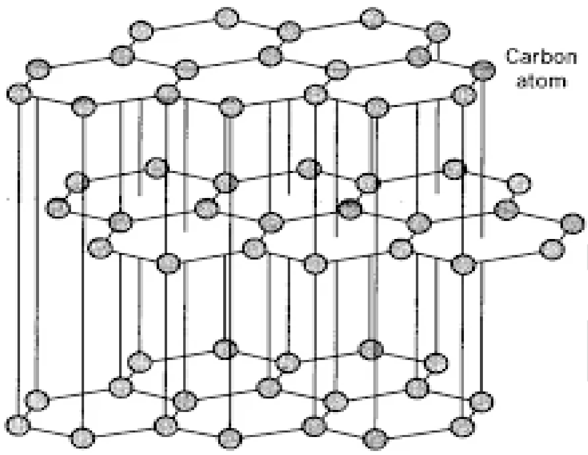


FIG: Plane view of layer stacking





DIAMOND:

The diamond cubic crystal structure is a repeating pattern of 8 atoms that certain materials may adopt as they solidify. While the first known example was diamond, other elements in group14 also adopt this structure, including α-tin, the semiconductors silicon and germanium, and silicon/germanium alloys in any proportion

Crystallographic structure

Diamond cubic follows the face-centered cubic Bravais lattice. The lattice describes the repeat pattern; for diamond cubic crystals this lattice is "decorated" with a motif of two tetrahedrally bonded atoms in each primitive cell, separated by 1/4 of the width of the unit cell in each dimension. The diamond lattice can be viewed as a pair of intersecting face-centered cubic lattices, with each separated by 1/4 of the width of the unit cell in each dimensions.

The atomic packing factor of the diamond cubic structure (the proportion of space that would be filled by spheres that are centered on the vertices of the structure and are as large as possible without overlapping) is $\pi\sqrt{3}/16 \approx 0.34$ significantly smaller (indicating a less dense structure) than the packing factors for the face-centered and body-centered cubic lattices.

Properties:

EXTREMELY HARD

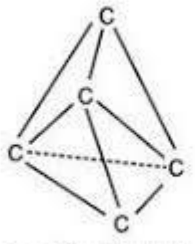
LOE ELECTRICAL CONDUCTIVITY

HIGH REFRACTIVE INDEX

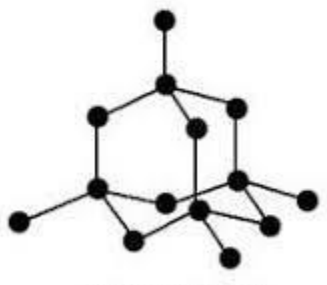
APPLICATION:

Industrialy diamonds are industrialy utilised to grind and cut other softer materials.

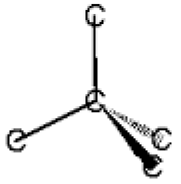
The surface of the drills, dies ,bearings,knives and other tools have been coated with diamond film to increase the surface hardness.



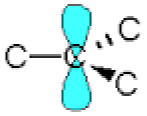
Basic Tetrahedral unit



Structure of Diamond



tetrahedral
carbon in
diamond

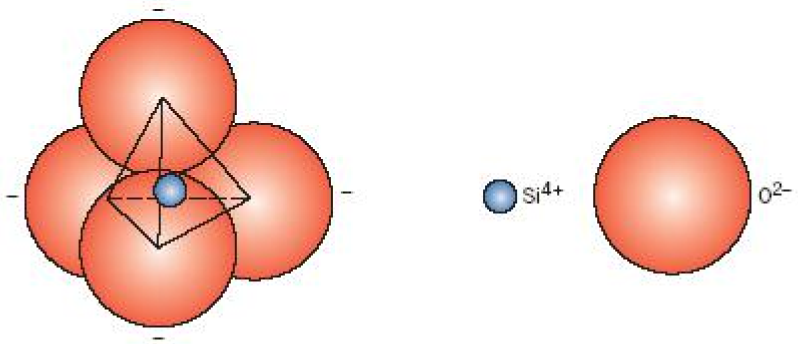


trigonal planar
carbon in graphite
with p orbital

Silicates

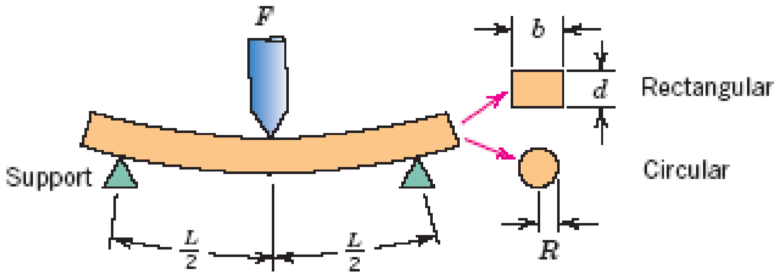
bulk of soils, rocks, clays, and sand come under the silicate classification.

Rather than characterizing the crystal structures of these materials in terms of unit cells, it is more convenient to use various arrangements of an tetrahedron SiO_4^{4-}.



The stress at fracture using this flexure test is known as the flexural strength, *modulus of rupture, fracture strength,* or the *bend strength,* an important mechanical parameter for brittle ceramics. For a rectangular cross section, the flexural strength is equal to

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$



$\sigma = \text{stress} = \frac{Mc}{I}$

where M = maximum bending moment
c = distance from center of specimen to outer fibers
I = moment of inertia of cross section
F = applied load

	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

Silicon dioxide

Silicon dioxide, also known as silica (from the Latin silex), is an oxide of silicon with the chemical formula SiO2, most commonly found in nature as quartz and in various living organisms.[5][6] In many parts of the world, silica is the major constituent of sand. Silica is one of the most complex and most abundant families of materials, existing as a compound of several minerals and as synthetic product. Notable examples include fused quartz, fumed silica, silica gel, and aerogels. It is used in structural materials, microelectronics, and as components in the food and pharmaceutical industries.

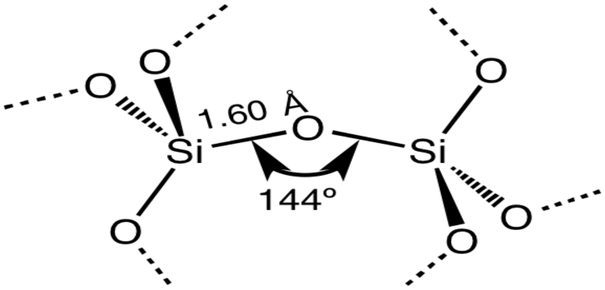
Inhaling finely divided crystalline silica is toxic and can lead to silicosis, bronchitis, lung cancer, and systemic autoimmune diseases, such as lupus and rheumatoid arthritis.

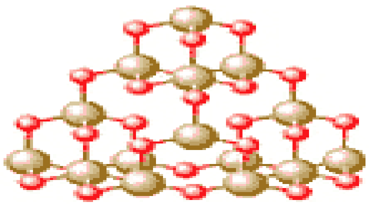
In the majority of silicates, the Si atom shows tetrahedral coordination, with four oxygen atoms surrounding a central Si atom. The most common example is seen in the quartzite polymorph.

For example, in the unit cell of α-quartz, the central tetrahedron shares all four of its corner O atoms, the two face-centered tetrahedra share two of their corner O atoms, and the four edge-centered tetrahedra share just one of their O atoms with other SiO4 tetrahedra. This leaves a net average of 12 out of 24 total vertices for that portion of the seven SiO4 tetrahedra that are considered to be a part of the unit cell for silica ..

SiO2 has a number of distinct crystalline forms (polymorphs) in addition to amorphous forms. With the exception of stishovite and fibrous silica, all of the crystalline forms involve tetrahedral SiO4 units linked together by shared vertices in different arrangements. Silicon–oxygen bond lengths vary between the different crystal forms; for example in α-quartz the bond length is 161 pm, whereas in α-tridymite it is in the range 154–171 pm. The Si-O-Si angle also varies between a low value of 140° in α-tridymite, up to 180° in β-tridymite. In α-quartz, the Si-O-Si angle is 144°.

The only stable form under normal conditions is alpha quartz, in which crystalline silicon dioxide is usually encountered. In nature, impurities in crystalline α-quartz can give rise to colors (see list). The high-temperature minerals, cristobalite and tridymite, have both lower densities and indices of refraction than quartz. Since the composition is identical, the reason for the discrepancies must be in the increased spacing in the high-temperature minerals. As is common with many substances, the higher the temperature, the farther apart the atoms are, due to the increased vibration energy.

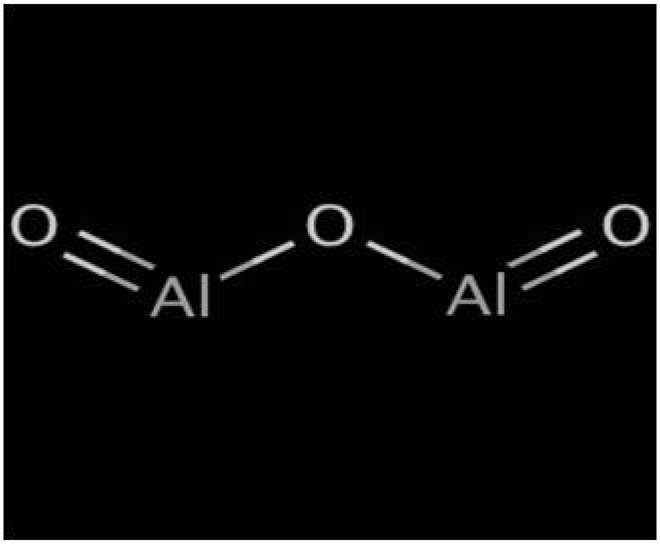




silica

ALUMINA:

Alumina is commonly termed as aluminum oxide which synthetically produces aluminum oxide. It is a chemical compound comprising of oxygen and aluminum. It is a colorless crystalline substance that is found naturally in the variety of forms namely sapphire and ruby. They are mostly used in a production of aluminum metal.



Aluminum Oxide is composed of bauxite. It is an aluminum oxide that is mixed with other elements and oxides of iron and silicon. It also comprises of clay. So bauxite can either be soft or hard as that of a rock. They are characterized with pink, white, red or combination of these.

Structure of Alumina

Aluminum Oxide occurs in several other forms. Among them the most common and naturally occurring crystalline form of alumina is Corundum. Example: Rubies and Sapphire. Rubies are dark red in color and sapphire consists of the particular amount of impurities namely titanium and iron are of different colors.

Oxygen atom forms a slightly distorted hexagonal slight packing in the lattice of corundum. It is found as a mineral in gneisses and some other marbles. They are also found in nepheline syenite intrusives.

Properties of Alumina

- Alumina possesses good thermal conductivity. At elevated temperature, it can withstand alkali attacks and a strong acid.
- It consists of excellent dielectric properties. It is a wear resistant.
- Metallic Aluminium is highly reactive with atmospheric oxygen.
- It exhibits high stiffness and strength.
- It is available at a purity range from 94%.

Applications of Aluminium Oxides

- They are widely used in Electronic Substrates, Thread and Wire Guides, Seal Rings, Ballistic armor, Thermometry Sensors, Grinding Media, Furnace Liner Tubes, High Voltage Insulators, Laboratory Instrumentary Tubes.
- Various formulation of glass consists of aluminum oxide as an ingredient. It is used in purification that is the removal of water from gas streams. They are employed in high-performance applications.

- It is a favored filler for plastic. It is sometimes present in cosmetics such as nail polish, lipstick and blush.
- They are broadly used as an abrasive. Various sandpaper makes use of aluminum oxide crystals.
- They are employed in the manufacturing of titles where they are attached inside the pulverized fuel lines to protect high wearing areas.

GLASS STRUCTURE:

Glass is an amorphous or non-crystalline solid that is brittle in nature and the structure is obtained by melt-quenching process. The glass structure (Figure 1(b)) is also obtained by using sol-gel and vapor deposition technique. Glass is weak in tension because of its non-crystalline molecular structure. When load is applied beyond the strength limit, glass breaks without any prior warning, unlike steel and aluminium where plastic deformation occurs. Therefore, the atomic structure of the glass is different from the structure of the crystalline materials (Figure 1(a).

The main constituent of glass is silica sand. Almost, all glass contains at least 50% silica. The structure of the glass is formed by bonding silicon and oxygen ions. Network modifiers (or intermediates) and network formers such as sodium (Figure 1(c)), may interrupt the continuity or contribute to the network structure of glass. There are two main differences between crystalline and amorphous solids; crystalline solids are formed by repeating geometric arrangement of atoms whereas; amorphous solids have random atomic arrangement. The second difference is their phase transformation behavior (Figure 2) when they are heated. For example, the transformation phases of crystalline and amorphous solids can be understand by examining silica (SiO2) which can exist in either state. When silica is in crystal form and is heated at a temperature Tm (freezing or melting point), it becomes liquid. It is observed that at melting point the specific volume of crystalline solids changes abruptly which causes sharp changes in physical properties. Whereas the amorphous structure of silica softens gradually (start softening at temperature Tg) when those are heated because there is a wide temperature range between the solid and liquid state. The temperature Tg is the glass transition temperature of the solids.

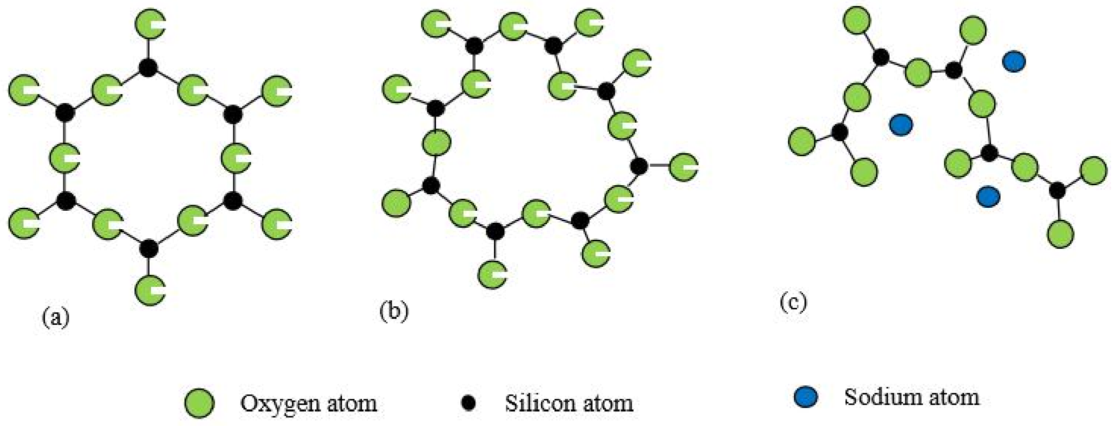


Figure 1. Two-dimensional demonstration of: (a) crystalline structure of silica; (b) amorpho structure of silica glass; (c) soda silica glass.

Polymeric structure:

Naturally occurring polymers—those derived from plants and animals—have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers such as proteins, enzymes, starches, and cellulose are important in biological and physiological processes in plants and animals. Modern scientific research tools have made possible the determination of the molecular structures of this group of materials, and the development of numerous polymers, which are synthesized from small organic molecules. Many of our useful plastics,rubbers,and fiber materials are synthetic polymers.In fact,since the conclusion of World War II, the field of materials has been virtually revolutionized by the advent of synthetic polymers. The synthetics can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts. In some applications metal and wood parts have been replaced by plastics,which have satisfactory properties and may be produced at a lower cost. As with metals and ceramics ,the properties of polymers are intricately related to the structural elements of the material.

WHY WE STUDY Polymer Structures?

A relatively large number of chemical and structural characteristics affect the properties and behaviors of polymeric materials. Some of these influences are as follows:

1. Degree of crystallinity of semi crystalline polymers— on density, stiffness, strength, and ductility.
2. Degree of crosslinking—on the stiffness of rubberlike materials
3. Polymer chemistry—on melting and glass-transition temperatures.

MOLECULAR STRUCTURE:

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network, in addition to various isomeric configurations.

Linear polymers:

Linear polymers are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti , as represented schematically in Figure 14.7a, where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

Branched Polymers:

Polymers may be synthesized in which side-branch chains are connected to the main ones, as indicated schematically in Figure 14.7b; these are fittingly called branched polymers. The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches ,which results in a lowering of the polymer density. Those polymers that form linear structures may also be branched. For example, high density polyethylene (HDPE) is primarily a linear polymer, while low density polyethylene (LDPE) contains short chain branches.

Crosslinked Polymers

In crosslinked polymers, adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure 14.7c. The process of crosslinking is achieved either during synthesis or by a nonreversible chemical reaction. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization.

Network Polymers :

Multifunctional monomers forming three or more active covalent bonds, make three-dimensional networks (Figure 14.7d) and are termed network polymers. Actually , a polymer that is highly crosslinked may also be classified as a network polymer. These materials have distinctive mechanical and thermal properties; the epoxies, polyurethanes, and phenol-formaldehyde belong to this group.

Polymers are not usually of only one distinctive structural type. For example , a predominantly linear polymer might have limited branching and crosslinking.

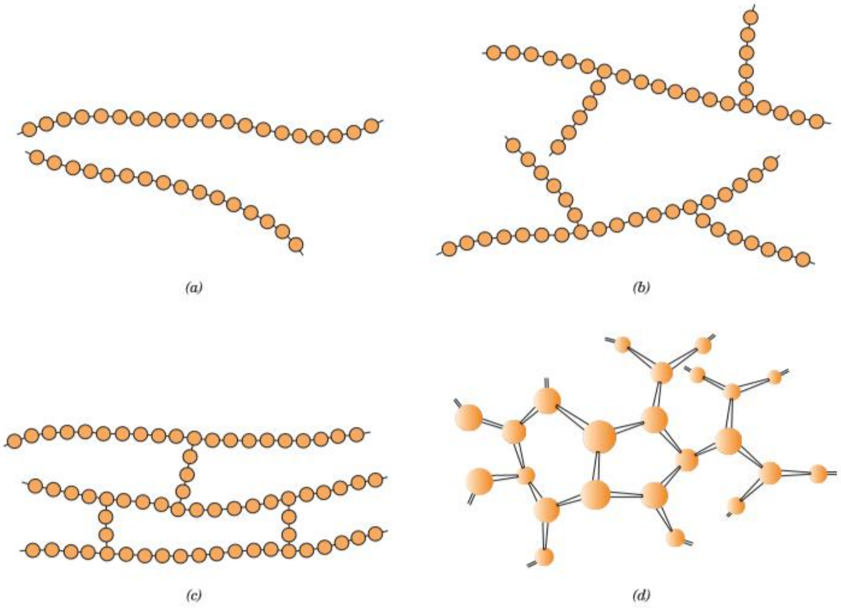


Figure 14.7 Schematic representations of (*a*) linear, (*b*) branched, (*c*) crosslinked, and (*d*) network (three-dimensional) molecular structures. Circles designate individual repeat units.

Based on the magnitude of intermolecular forces polymers are divided into 4 groups:

1.ELASTOMERS

2. THERMOPLASTICS

3.THERMOSETTING

4. FIBERS

1.ELASTOMERS:

One of the most fascinating properties of the elastomeric material is the rubber like elasticity i.e they have the ability to be deformed to quite large deformations and then elastically spring back to their original form.

This results cross links in polymers , which provides a force to restore the change to their undeformed conformations.

The process of crosslinking is achieved during synthesis or by nonreversible chemical reaction.

In an unstressed condition an elastomer will be amorphous and composed of crosslinked molecular chain that are highly twisted, kink and coiled.

Part of the driving force for the elastic deformation is a thermodynamic parameter called entropy which is a measure of degree of disorder within a system.

Entropy increases with increasing disorder , as the elastomer is stretched , the chain straightened and becomes more aligned and the system becomes more ordered.

From this state, the entropy increases if the chains return to their original kinked and coiled contours. Two intriguing phenomena result from this entropic effect. First, when stretched, an elastomer experiences a rise in temperature; second, the modulus of elasticity increases with increasing temperature, which is opposite to the behavior found in other materials .

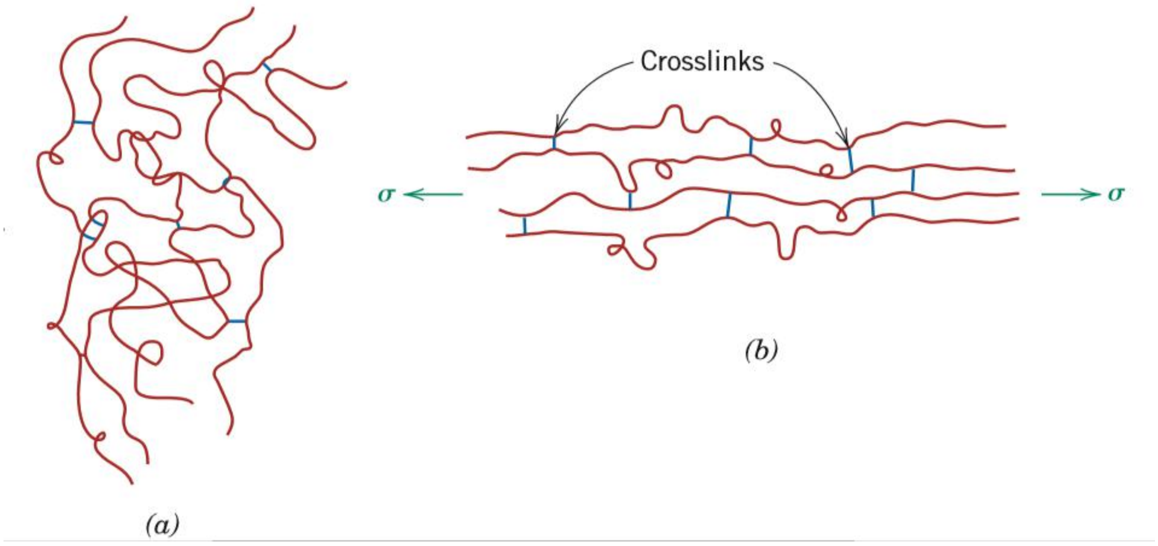
CRITERIA FOR A POLYMER TO BE ELASTOMER:

-it must be easily crystalised.

- for the elastomer to explain relatively large deformations , the onset of plastic deformation must be delayed.

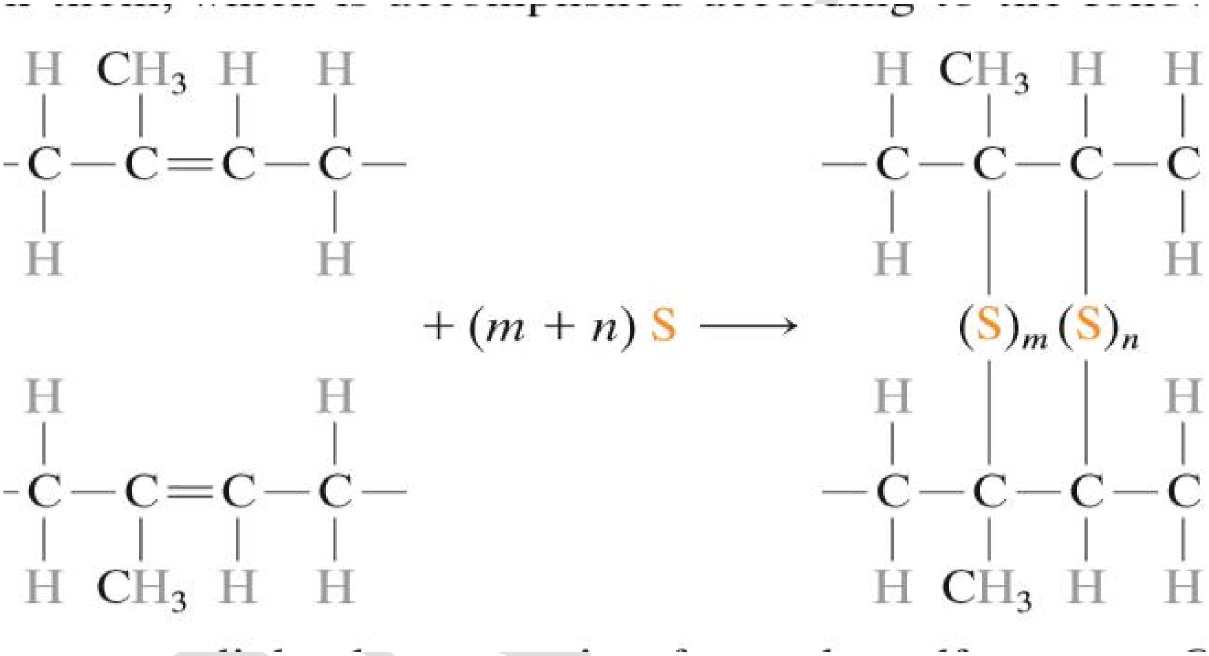
-the elastomer must be above its glass transition temperature.

The temp at which the polymer experience the transition from rubbery state to rigid state is known as glass transition temperature, below this temperature the material is brittle in nature .

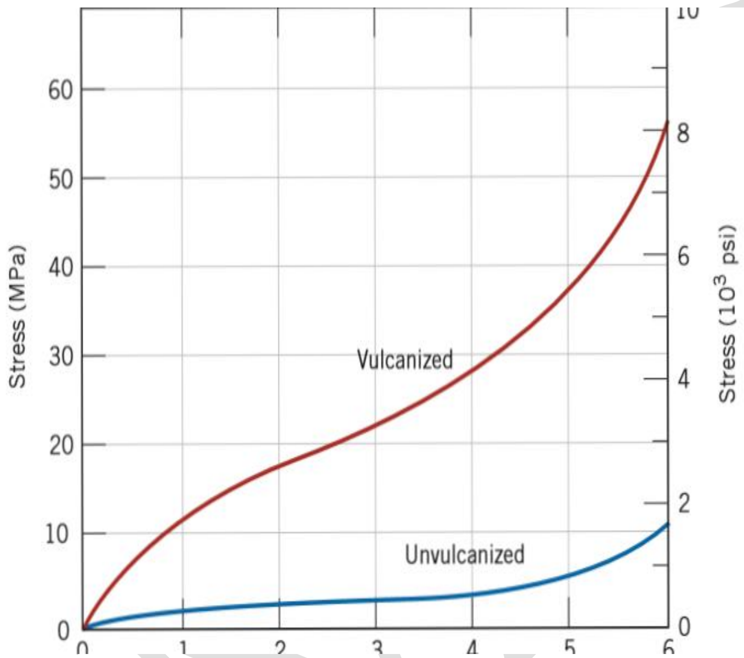


VULCANIZATION:

The crosslinking process in elastomers is called vulcanization, which is achieved by a nonreversible chemical reaction, ordinarily carried out at an elevated temperature. In most vulcanizing reactions, sulfur compounds are added to the heated elastomer; chains of sulfur atoms bond with adjacent polymer backbone chains and crosslink them, which is accomplished according to the following reaction:



in which the two crosslinks shown consist of m and n sulfur atoms. Crosslink main chain sites are carbon atoms that were doubly bonded before vulcanization but, after vulcanization, have become singly bonded. Unvulcanized rubber, which contains very few crosslinks, is soft and tacky and has poor resistance to abrasion. Modulus of elasticity, tensile strength, and resistance to degradation by oxidation are all enhanced by vulcanization.The magnitude of the modulus of elasticity is directly proportional to the density of thecrosslinks. Stress–strain curves for vulcanized and unvulcanized natural rubber are presented in Figure 15.16.To produce a rubber that is capable of large extensions without rupture of the primary chain bonds,there must be relatively few crosslinks, and these must be widely separated. Useful rubbers result when about 1 to 5 parts (by weight) of sulfur are added to 100 parts of rubber.This corresponds to about one crosslink for every 10 to 20 repeat units. Increasing the sulfur content further hardens the rubber and also reduces its extensibility.Also,since they are crosslinked, elastomeric materials are thermosetting in nature.



THERMOPLASTIC AND THERMOSETTING POLYMERS:

The response of a polymer to mechanical forces at elevated temperatures is related to its dominant molecular structure. In fact, one classification scheme for these materials is according to behavior with rising temperature. Thermoplastics (or thermoplastic polymers) and thermosets (or thermosetting polymers) are the two subdivisions.

Thermoplastics soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated. On a molecular level, as the temperature is raised, secondary bonding forces are diminished (by increased molecular motion) so that the relative movement of adjacent chains is facilitated when a stress is applied. Irreversible degradation results when a molten thermoplastic polymer is raised to too high of a temperature. In addition,thermoplastics are relatively soft.Most linear polymers and those having some branched structures with flexible chains are thermoplastic.These materials are normally fabricated by the simultaneous application of heat and pressure .Most linear polymers are thermoplastics.Examples of common thermoplastic polymers include polyethylene, polystyrene, poly(ethylene terephthalate), and poly(vinyl chloride). Thermosetting polymers are network polymers.They become permanently hard during their formation,and do not soften upon heating.Network polymers have covalent crosslinks between adjacent molecular chains.During heat treatments,these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures.Thus,the materials do not soften when heated.Crosslinking is usually extensive,in that 10 to 50% of the chain repeat units are crosslinked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, and some polyester resins, are thermosetting.

POLYMER CRYSTALLINITY:

The crystalline state may exist in polymeric materials.However,since it involves molecules instead of just atoms or ions,as with metals and ceramics,the atomic arrangements will be more complex for polymers.We think of polymer crystallinity as the packing of molecular chains to produce an ordered atomic array. Crystal structures may be specified in terms of unit cells,which are often quite complex.

Molecular substances having small molecules (e.g.,water and methane) are normally either totally crystalline (as solids) or totally amorphous (as liquids). As a consequence of their size and often complexity, polymer molecules are often only partially crystalline (or semicrystalline),having crystalline regions dispersed within the remaining amorphous material.Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common, since twisting, kinking, and coiling of the chains prevent the strict ordering of every segment of every chain. Other structural effects are also influential in determining the extent of crystallinity, as discussed below. The degree of crystallinity may range from completely amorphous to almost entirely (up to about 95%) crystalline; in contrast, metal specimens are almost always entirely crystalline,whereas many ceramics are either totally crystalline or totally noncrystalline.Semicrystalline polymers are,in a sense,analogous to two-phase metal alloys, discussed previously. The density of a crystalline polymer will be greater than an amorphous one of the same material and molecular weight, since the chains are more closely packed together for the crystalline structure.The degree of crystallinity by weight may be determined from accurate density measurements, according to:

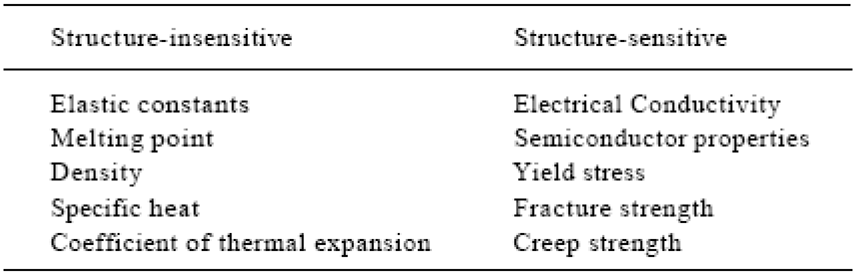
$$\%\,\text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

MODULE II

IMPERFECTIONS:

LATTICE DEFECTS/ IMPERFECTIONS

Real crystals deviate from the perfect periodicity that should exist in a perfect crystal. While the concept of the perfect lattice is adequate for explaining the *structure-insensitive* properties of metals, for a better understanding of the *structure-sensitive* properties it has been necessary to consider a number of types of lattice defects. The description of the structure-sensitive properties then reduces itself largely to describing the behavior of these defects.



Structure-insensitive	Structure-sensitive
Elastic constants	Electrical Conductivity
Melting point	Semiconductor properties
Density	Yield stress
Specific heat	Fracture strength
Coefficient of thermal expansion	Creep strength

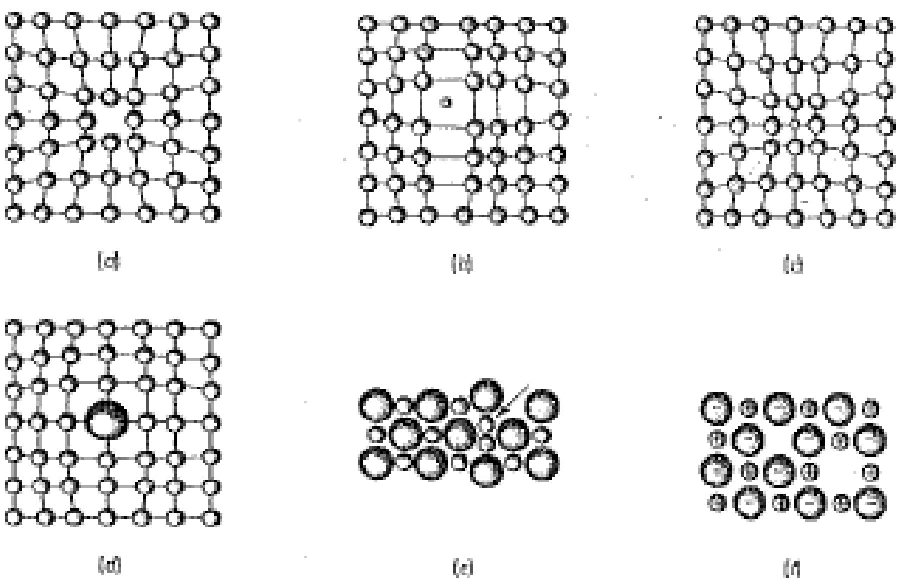
As is suggested by the above brief tabulation above, practically all the mechanical properties are structure-sensitive properties. Only since the realization of this fact, in relatively recent times, have really important advances been made in understanding the mechanical behavior of materials.

The term *defect,* or *imperfection,* is generally used to describe any deviation from an orderly array of lattice points. When the deviation from the periodic arrangement of the lattice is localized to the vicinity of only a few atoms it is called a *point defect,* or *point imperfection.*

However, if the defect extends through microscopic regions of the crystal, it is called a *lattice imperfection.* Lattice imperfections may be divided into *line defects* and *surface,* or *plane, defects.*

Point Defects

Point Defects

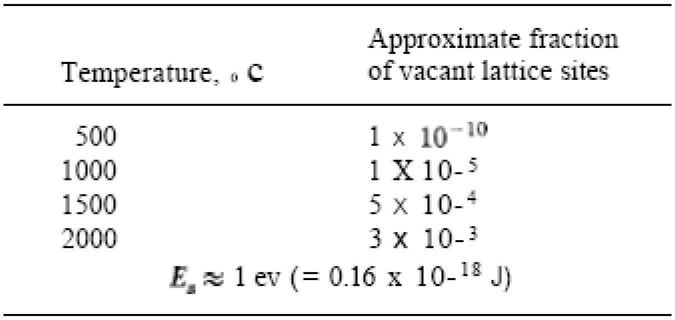


(a) Vacancy (b) Interstitial (c) Small substitutional (d) Large substitutional (e) Frenkel (f) Schottky

A *vacancy,* or vacant lattice site exists when an atom is missing from a normal lattice position *(a).* In pure metals, small numbers of vacancies are created by thermal excitation, and these are thermodynamically stable at temperatures greater than absolute zero. At equilibrium, the fraction of lattices that are vacant at a given temperature is given approximately by the equation

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

where *n* is the number of vacant sites in *N* sites and *Es* is the energy required to move an atom from the interior of a crystal to its surface. Table below illustrates how the fraction of vacant lattice sites in a metal increases rapidly with temperature.



Temperature, $_{o}$C	Approximate fraction of vacant lattice sites
500	1 x 10^{-10}
1000	1 X 10^{-5}
1500	5 x 10^{-4}
2000	3 x 10^{-3}

$E_s \approx 1$ ev (= 0.16 x 10^{-18} J)

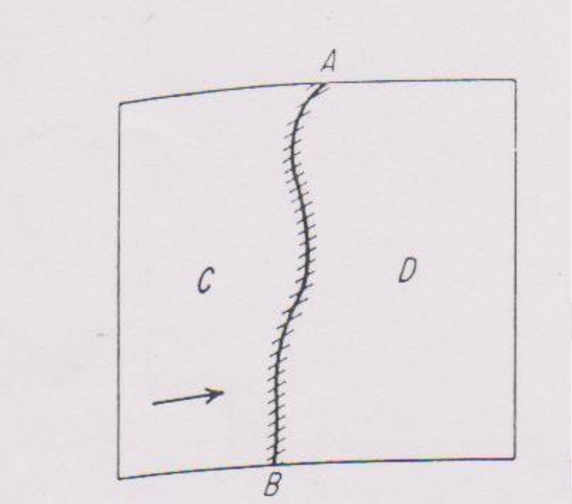
By rapid quenching from close to the melting point, it is possible to trap in a greater than equilibrium number of vacancies at room temperature.

An atom that is trapped inside the crystal at a point intermediate between normal lattice positions is called an *interstitial atom,* or interstitialcy (b).

Line defects obtain their name because they propagate as lines or as a two-dimensional net in the crystal. The edge and screw dislocations that are discussed in this section are the common line defects encountered in metals.

Line Defects-Dislocations

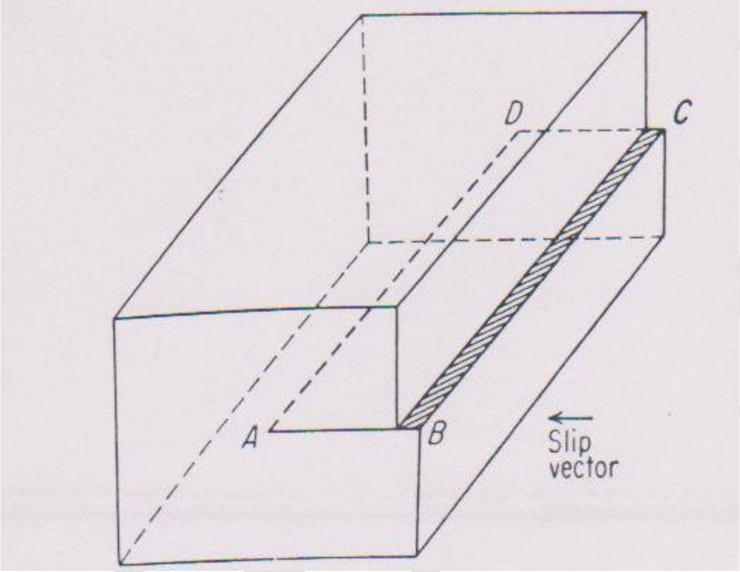
The most important two-dimensional, or line, defect is the *dislocation.* The dislocation is the defect responsible for the phenomenon of slip, by which most metals deform plastically. Therefore, one way of thinking about a dislocation is to consider that it is the region of localized lattice disturbance separating the slipped and unslipped regions of a crystal.



.

In above figure, *AB* represents a dislocation lying in the slip plane, which is the plane of the paper. It is assumed that slip is advancing to the right. All the atoms above area C have been displaced one atomic distance in the slip direction; the atoms above *D* have not yet slipped. *AB* is then the boundary between the slipped and unslipped regions. It is shown shaded to indicate that for a few atomic distances on each side of the dislocation line there is a region of atomic disorder in which the slip distance is between zero and one atomic spacing. As the dislocation moves, slip occurs in the area over which it moves. In the absence of obstacles, a dislocation can move easily on 'the application of only a small force; this helps explain why real crystals deform much more readily than would be expected for a crystal with a perfect lattice. Not only are dislocations important for explaining the slip of crystals, but they are also intimately connected with nearly all other mechanical phenomena such as strain hardening, the yield point, creep, fatigue, and brittle fracture.

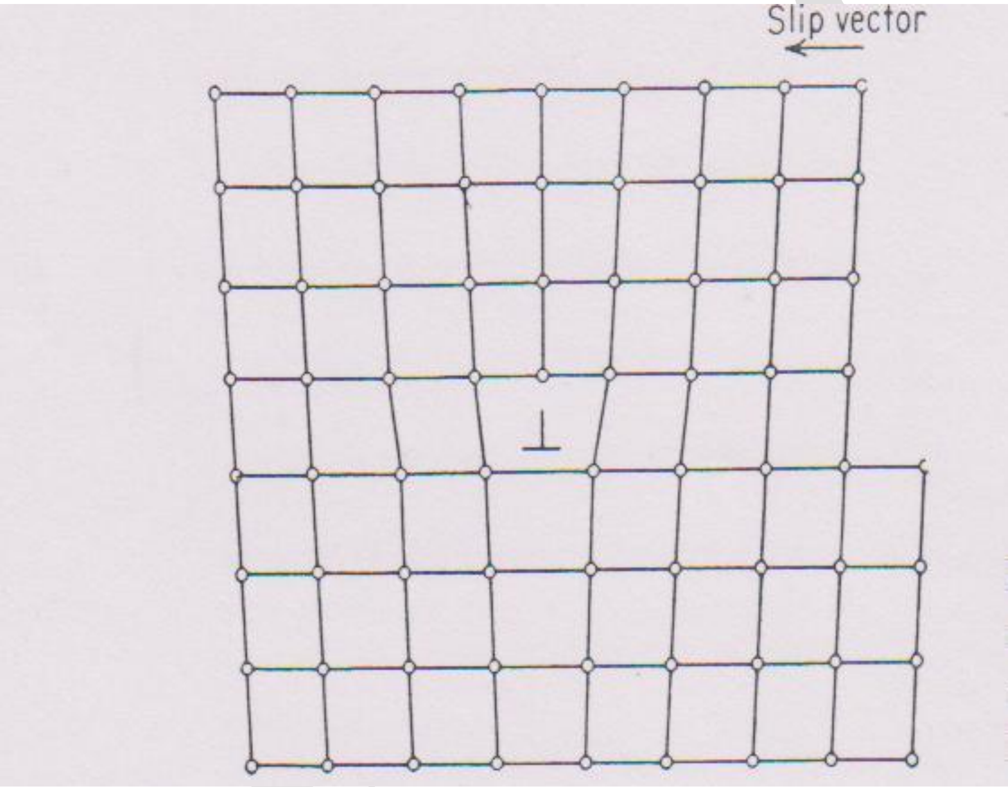
The two basic types of dislocations are the edge dislocation and the screw dislocation. The simplest type of dislocation, which was originally suggested by Orowan, Polanyi, and Taylor, is called the *edge dislocation,* or Taylor-Orowan dislocation. Figure below shows the slip that produces an edge dislocation for an element of crystal having a simple cubic lattice.



Edge dislocation produced by slip in a simple occurred over area *ABCD* cubic lattice. Dislocation lies along *AD,* perpendicular to slip direction. Slip has occurred over area *ABCD*

Slip has occurred in the direction of the slip vector over the area *ABCD.* The boundary between the right-hand slipped part of the crystal and the left-hand part which has not yet slipped is the line *AD,* the edge dislocation. Note that the parts of the crystal above the slip plane have been displaced, in the direction of slip, with respect to the part of the crystal below the slip plane by an amount indicated by the shaded area. All points in the crystal which were originally coincident across the slip plane have been displaced relative to each other by this same amount. The amount of displacement is equal to the *Burgers vector* b of the dislocation. A defining characteristic of an edge dislocation is that its Burgers vector is always perpendicular to the dislocation line.

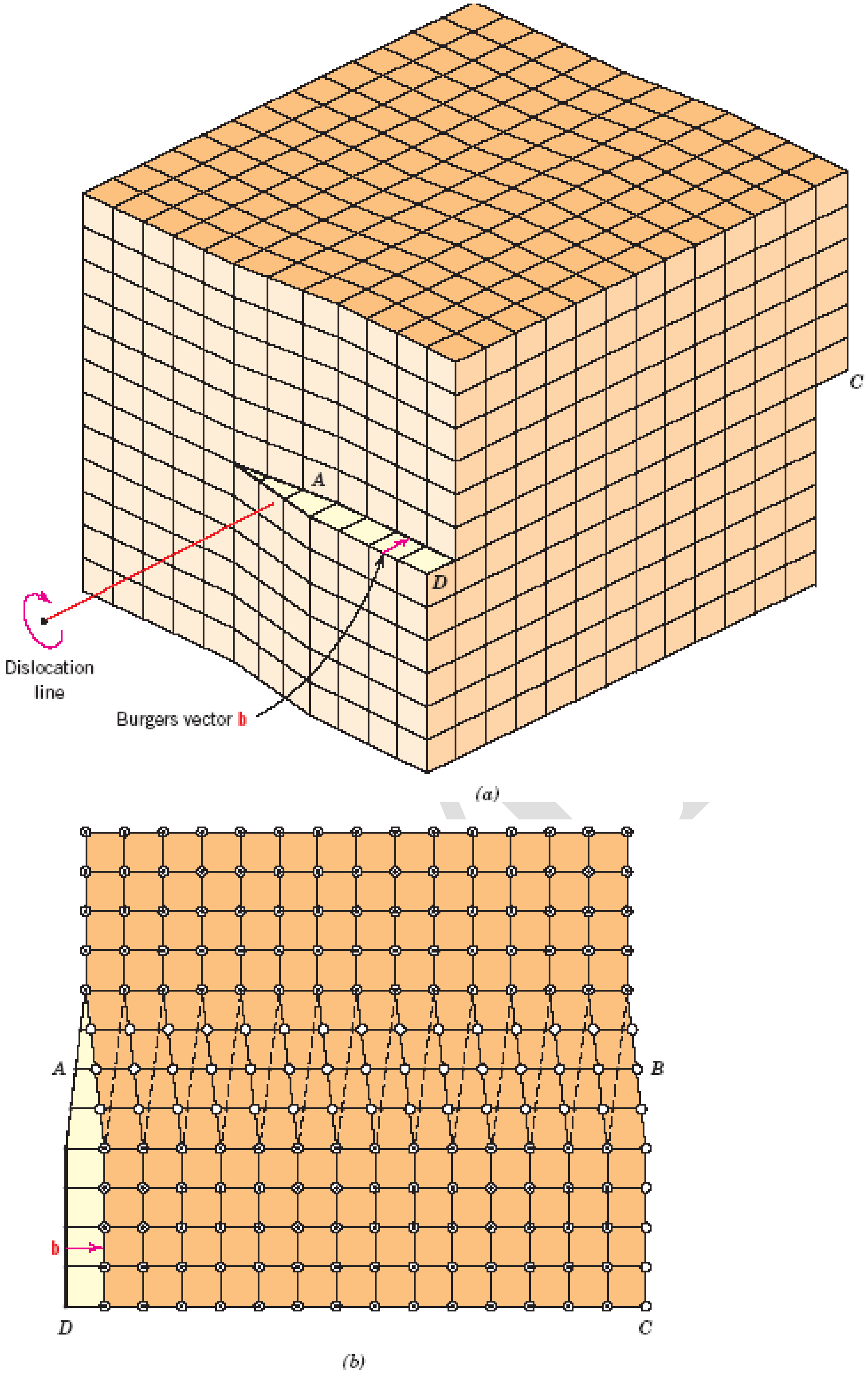
Although the exact arrangement of atoms along *AD* is not known, it is generally agreed that Fig. below closely represents the atomic arrangement in a plane normal to the edge dislocation *AD.*



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. 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 above figure, by convention is called a *positive edge dislocation* and is frequently indicated by the symbol.⊥. If the extra plane of atoms lies below the slip plane, the dislocation is a negative edge dislocation, T 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.

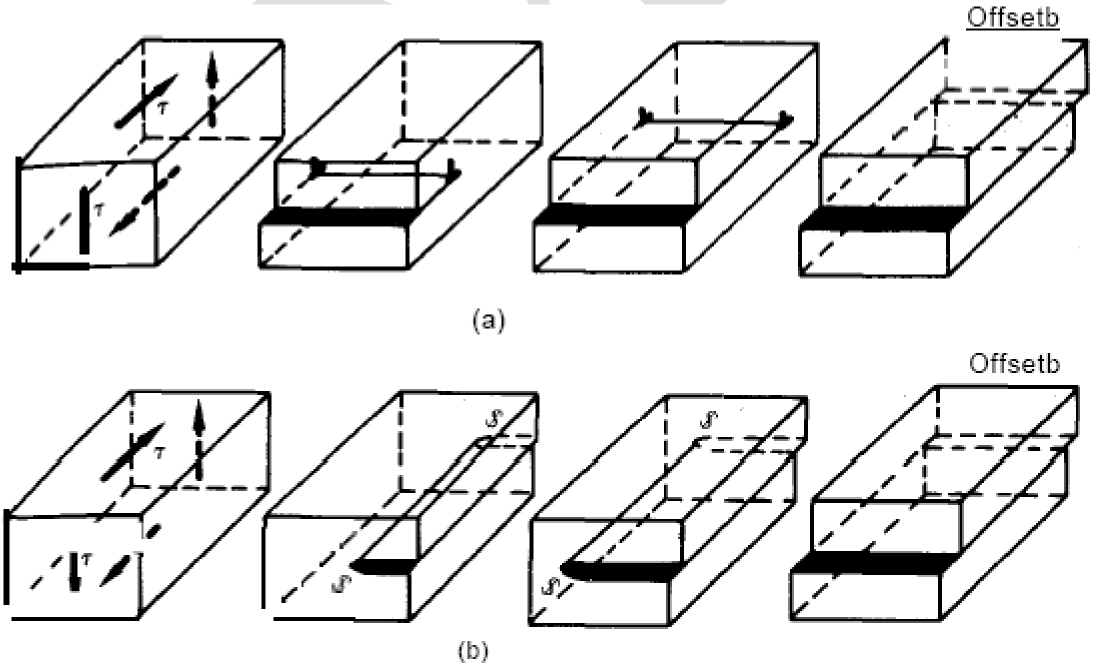
Consider above figure, for the edge dislocation to move upward (positive direction of climb), it is.necessary to remove the extra atom directly over the symbol ⊥ or to add a vacancy to this spot. One such atom would have to be removed for every atomic spacing that the dislocation climbs. Conversely, 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.

The second basic type of dislocation is the *screw,* or Burgers, dislocation. Figure below shows a simple example of a screw dislocation.



The upper part of the crystal to the right of *AB* has moved relative to the lower part in the direction of the slip vector. No slip has taken place to the left of *AB,* and therefore *AB* 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 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 dimension) around a screw dislocation in a simple cubic lattice is shown in above figure. In this figure we are looking down on the slip plane. 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.

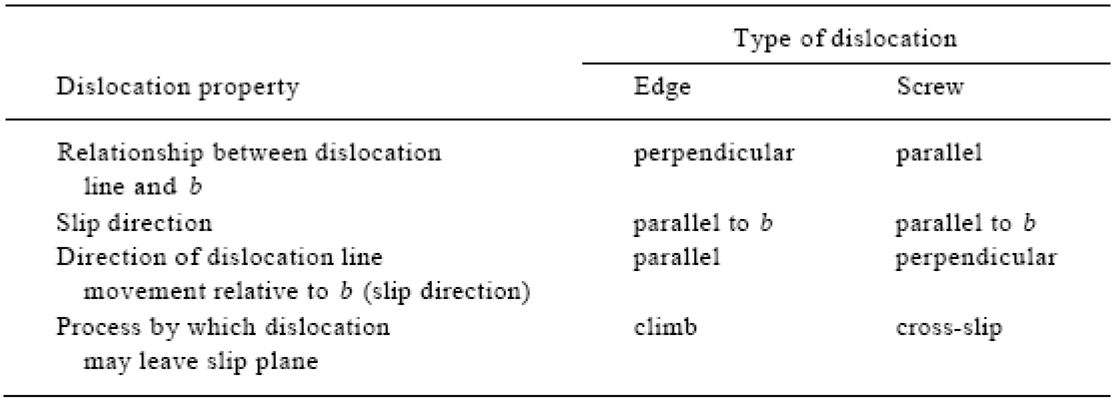


(a)

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

Comparison of Edge and Screw Dislocation



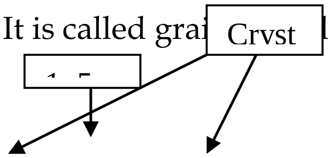
Dislocation property	Type of dislocation Edge	 Screw
Relationship between dislocation line and *b*	perpendicular	parallel
Slip direction	parallel to *b*	parallel to *b*
Direction of dislocation line movement relative to *b* (slip direction)	parallel	perpendicular
Process by which dislocation may leave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

Surface defects arise from the clustering of line defects into a plane. Low-angle boundaries and grain boundaries are surface defects. The *stacking fault* between two close-packed regions of the crystal that have alternate stacking sequences and twinned region of a crystal are other examples of surface defects. It is important to note that even at the places where the long-range periodicity of the crystal structure breaks down, as at dislocations and stacking faults, it does so only in certain well-defined ways. Thus, the defects in crystals have regular and reproducible structures and properties.

Surface defects

1. Grain Boundaries
2. Tilt boundaries
3. Twin Boundaries
4. Stacking faults

Engineering materials may be either polycrystalline or single crystal type. A polycrystalline alloy contains an enormous quantity of fine grains. Grain boundary imperfections are those surface imperfections which separate crystals or grains of different orientation in a polycrystalline aggregation during nucleation or crystallization. The shape of a grain is usually influenced by the presence of surrounding grains. The lattices of adjacent grains are oriented at random and differently and a boundary between any two grains is essentially a transition layer of thickness of 1–5 nm. This layer may have a disordered arrangement of atoms, dislocation of clusters, and an elevated concentration of impurities. In grain boundaries the atomic packing is imperfect and between two adjacent grains, there is a transition zone that is not aligned with either grain. It is called grai lary.



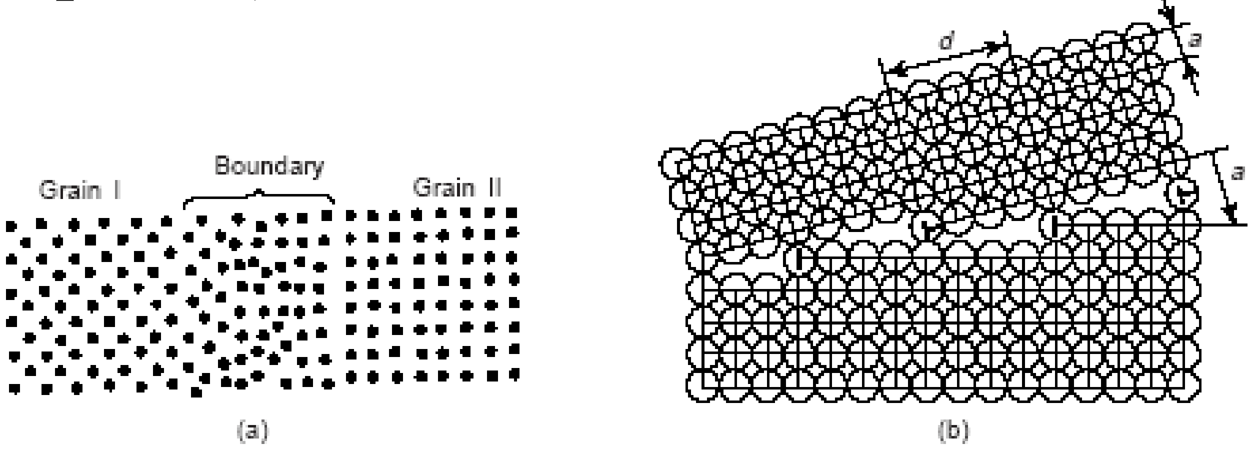
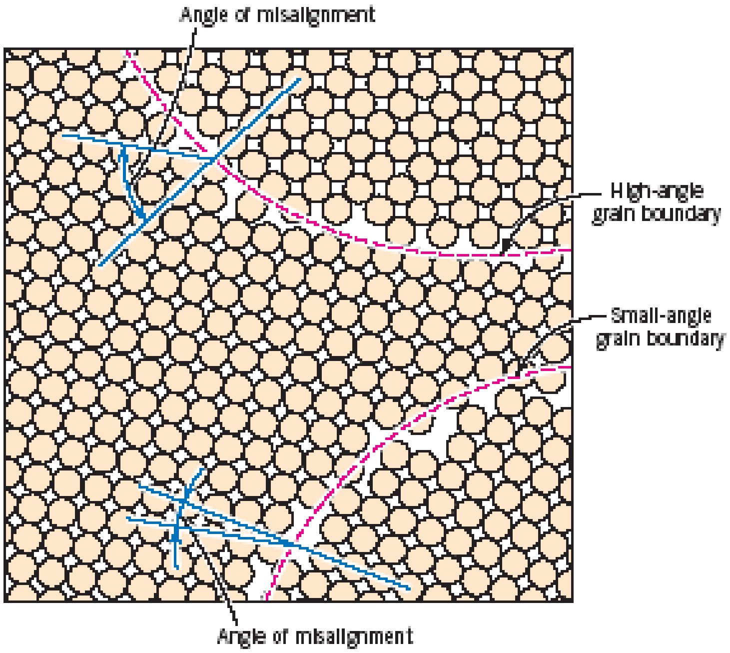


Fig. 3.54 Schemes of (a) high angle and (b) low-angle boundaries



As a result, we note that boundary atoms in such cases cannot have a perfect complement of surrounding atoms. The mismatch with orientation of the adjacent grain produces a less efficient packing of atoms along the boundary. Thus, the atoms along the boundary have a higher energy than those within the grains. The higher energy of the boundary atoms is also important for the nucleation of polymorphic phase changes. The boundary between two crystals which have different crystalline arrangements or different compositions, is called an *interphase* boundary or commonly called an *interface.*

The lower atomic packing along the boundary favours atomic diffusion. When the orientation difference between neighbouring grains is more than 10°–15°, boundaries are called *high angle grain boundaries* (Fig. 3.54(a)). Each grain in turn consists of *subgrains or blocks*. A subgrain is a portion of a crystal of a relatively regular structure. Subgrain boundaries are formed by walls of dislocations which divide a grain into a number of subgrains or blocks [Fig. 3.54(b)]. Angle of misorientation between adjacent subgrains are not large (not more than 5°), so that their boundaries are termed 'low angle'. Low angle boundaries can also serve as places of accumulation of impurity.

A fine-grained material (one that has small grains) is harder and stronger than one that is coarse grained, since the former has a greater total grain boundary area to impede dislocation motion. For many materials, the yield strength varies with grain size according to

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

In this expression, termed the *Hall-Petch equation, d* is the average grain diameter and other factors are constant for a particular material.

Tilt boundaries

This is another type of surface defect called low-angle boundary as the orientation difference between two neighbouring crystals is less than 10°. This is why the disruption in the boundary is not so drastic as in the high angle boundary. This type of boundary is associated with relatively little energy and is composed of edge dislocations lying one above the other. In general, one can describe low-angle boundaries by suitable arrays of dislocation.

The angle or tilt, $\theta = \frac{b}{D}$

where *b* is the magnitude of Burgers vector and *B* is the average vertical distance between dislocations.

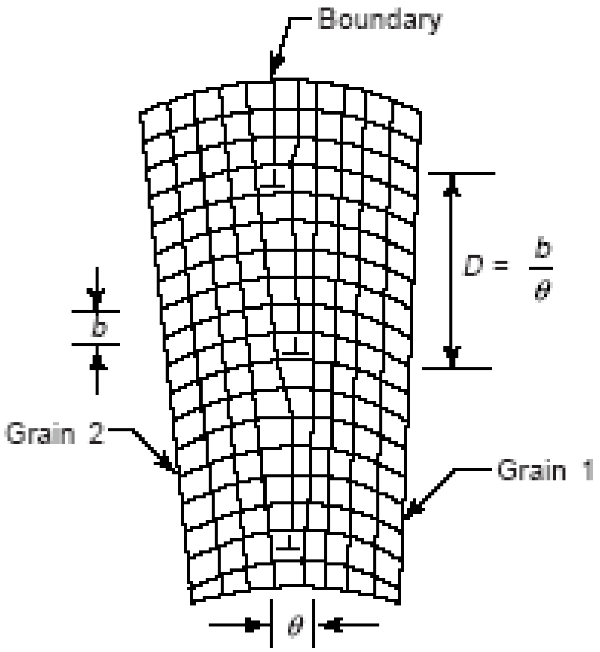


Fig. 3.55(a) Tilt boundary

Twin Boundary

This is another planar surface imperfection. The atomic arrangement on one side of a twin boundary is a mirror reflection of the arrangement on the other side. Twinning may result during crystal growth or deformation of materials. Twin boundaries occur in pairs, such that the orientation change introduced by one boundary is restored by the other. The region between the pair of boundaries is termed as the *twinned region*. One can easily identify twin boundaries under an optical microscope. Twins which form during the process of recrystallization, i.e., in the process of mechanical working are known as mechanical twins, whereas twins formed as a result of annealing after plastic deformation are known as annealing twins (Fig. 3.56).

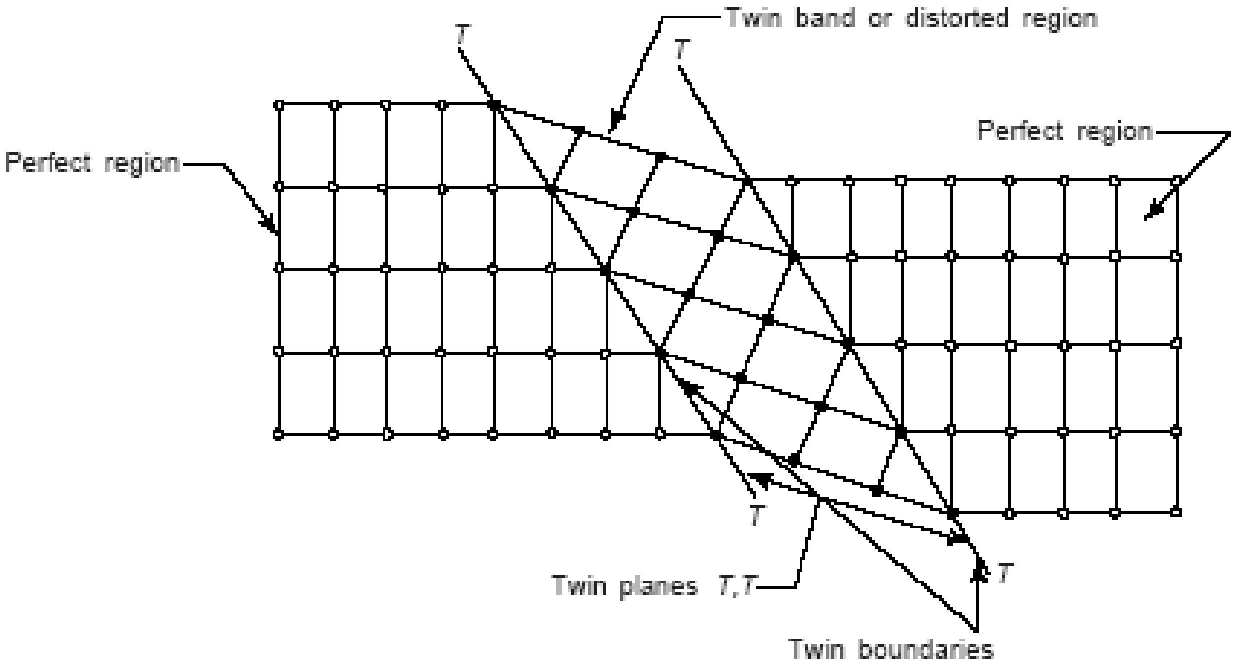


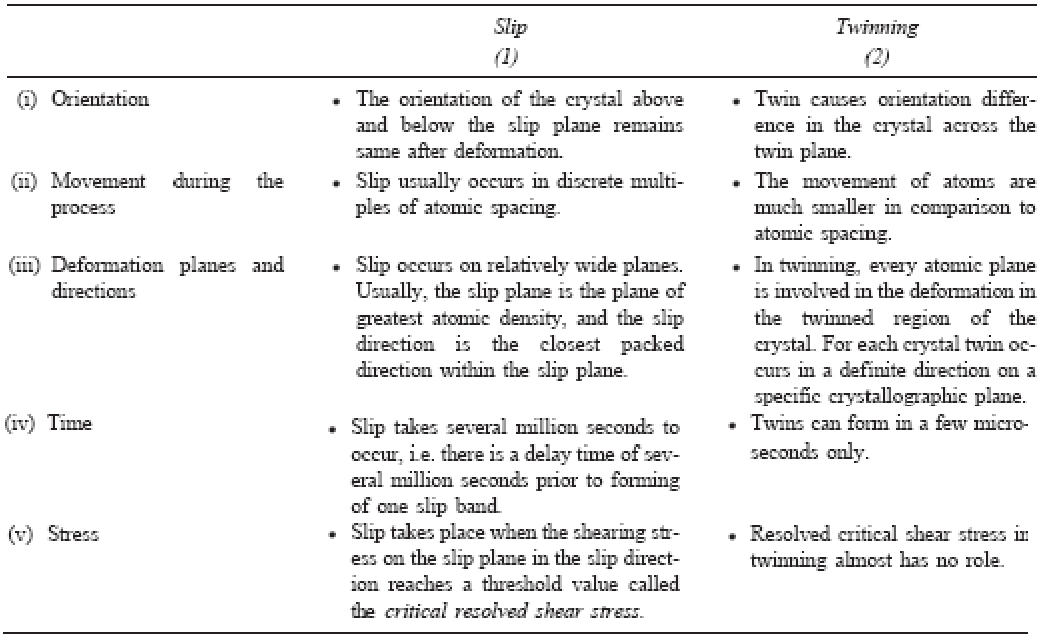
Fig. 3.56 Twin boundaries

Slip vs. Twinning:

It should be noted that twinning differs from slip in several specific respects. In slip, the orientation of the crystal above and below the slip plane is the same after deformation as before, while twinning results in an orientation difference..across the twin plane. Slip is usually considered to occur in discrete multiples of the atomic spacing, while in twinning the atom movements are much less than an atomic distance. Slip occurs on relatively widely spread planes, but in the twinned region of a crystal every atomic plane is involved in the deformation.

	Slip	Twinning
Atomic movement	Atoms move a whole number of atomic spacing.	Atoms move fractional atomic spacing.

Microscopic appearance	Thin lines	Wide bands or broad lines
Lattice orientation	No change in lattice orientation. The steps are only visible on the surface of the crystal and can be removed by polishing. After polishing there is no evidence of slip.	Orientation changes
Plane involvement	Occurs in wide spread closely packed planes	In the twinned region of a crystal every atomic plane is involved in deformation



	Slip *(1)*	*Twinning* *(2)*
(i) Orientation	• The orientation of the crystal above and below the slip plane remains same after deformation.	• Twin causes orientation difference in the crystal across the twin plane.
(ii) Movement during the process	• Slip usually occurs in discrete multiples of atomic spacing.	• The movement of atoms are much smaller in comparison to atomic spacing.
(iii) Deformation planes and directions	• Slip occurs on relatively wide planes. Usually, the slip plane is the plane of greatest atomic density, and the slip direction is the closest packed direction within the slip plane.	• In twinning, every atomic plane is involved in the deformation in the twinned region of the crystal. For each crystal twin occurs in a definite direction on a specific crystallographic plane.
(iv) Time	• Slip takes several million seconds to occur, i.e. there is a delay time of several million seconds prior to forming of one slip band.	• Twins can form in a few microseconds only.
(v) Stress	• Slip takes place when the shearing stress on the slip plane in the slip direction reaches a threshold value called the *critical resolved shear stress*.	• Resolved critical shear stress in twinning almost has no role.

Stacking Faults

This is a part of an atomic plane confined between dislocations and in which the regular order of alternation of atomic layers is disturbed. This type of fault arise from the stacking of one atomic plane out of sequence on another while the lattice on either side of the fault is perfect. For instance, in FCC lattice alloys, close packed atomic layers are normally in an alternation $ABC\ ABC\ AB$ …. On passing through a stacking fault, their alternation may change, for instance, to $ABC\ BCA\ BC$ …. The BCBC alternation is typical of an HCP lattice, and therefore the stacking fault in the case considered represents, as it were, a thin plate of an HCP lattice in the structure of an FCC lattice. Figure 3.57 shows the faults in the structure of an FCC crystal.

Here the stacking sequence of an ideal FCC crystal is described as $ABC\ ABC$ . . . and the stacking fault may change the sequence $ABC\ ACAB$.

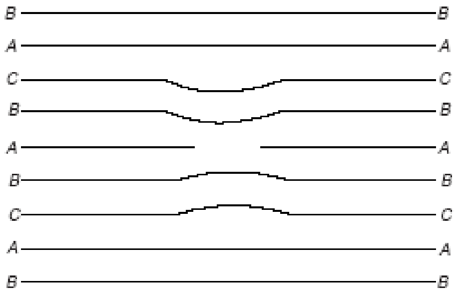
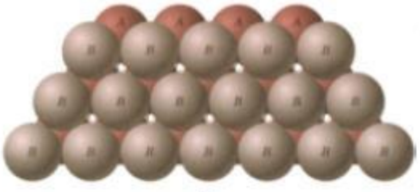
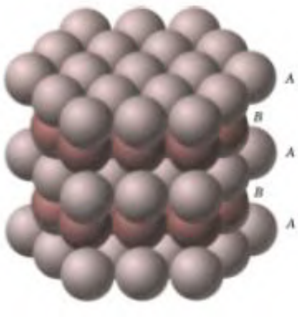
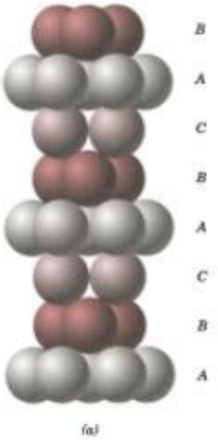


Fig. 3.57 Fault in stacking sequence in FCC crystal







Concept of alloy formation

Pure metals are very soft indeed, and have a high ductility. This is what, for centuries, has made them so attractive at first for jewellery and weapons, and then for other implements and structures: they were used by working to the shape that we wanted them..

But present scenario demanded materials with different physical and mechanical properties e.g. strength. Properties of materials are found to vary significantly if one element combines several elements. This gave rise to the concept of alloying. This concept led to the development of alloys. Alloys are homogeneous mixture of two or more metals or a metal and a non-metal when fused together at a certain temperature forms a new metal after solidification.

Metallic objects in actual commercial use are almost exclusively alloys, and not pure metals, because it is possible for the design engineer to get the desired physical and mechanical properties in the product by varying the metallic composition of the alloy.

The alloying elements are added to improve one or more of the following properties: (a) tensile strength, hardness and toughness (b) corrosive and oxidation resistance, (c) machinability, (d) elasticity (e) hardenability (f) creep strength and (g) fatigue resistance, etc.

The alloy is usually more corrosion resistant and less affected by atmospheric conditions. The conductivity of an alloy varies with the degree of order of the alloy and the hardness varies with the particular heat treatment. The basic knowledge of structural properties of alloys is still in large part empirical, and indeed, it will probably never be possible to derive formulas which will predict which metals to mix in a certain proportion and with a certain heat treatment to yield a specified property or set of properties. However, a set of rules exists which describes the qualitative behaviour of certain group of alloys. These rules are statements concerning the relative sizes of constituent atoms for alloy formation, and concerning what kinds of phases to expect in terms of the valence of the constituent atoms. The rules were discovered in a strictly empirical way, and for the most part, the present theoretical understanding of alloys consists of rudiomentary theories which describe how the rules arise from the basic principles of physics.

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

(i) As a solid solution

(ii) As an intermediate phase or intermediate chemical compound

(iii) As a finely divided mechanical mixture of solid solution

(iv) As a finely divided mechanical mixture of the metals

(v) As a finely divided mechanical mixture of chemical compounds of metals, the individual metals and solid solutions.

Alloys are classified according to components. Components are the substances, either chemical elements or chemical compounds,

Binary alloys:- composed of two components; i,e. consists of two elements,

Ternary alloys:- composed of three components i,e. consists of three elements,

Multicomponent alloys:- More components

Most commercial alloys are multicomponent.

The composition of an alloy is described by giving the percentage (either by weight or by atoms) of each element in it. Metal alloys by virtue of composition, are often grouped into two classes: (i) ferrous and non-ferrous. Ferrous alloys are those in which iron is the principal constituent, include steels and cast irons. The nonferrous alloys are all alloys that are not iron based.

The characteristic of any series of alloys can be easily studied by using alloy phase diagrams. A phase diagram is a graphical description of the kinds and amounts of the phases that can be expected in an alloy as a function of its composition, temperature, and pressure, when it has reached thermodynamic equilibrium.

The phases may be liquid, vapour or solid with various ordered and disordered crystal structures.

The following terms are frequently used in the study of solid phases and phase diagrams:

(i) System: It is the selected portion under study. A system may be composed of solids, liquids, gases or their combinations and may have metals and non-metals separately or in any combination. It is explained as the whole complex of phases of one or several components at different pressures and compositions. A system is so isolated from its surroundings that it is unaffected by solids, liquids, gases or their combinations and is subjected to the change in the overall composition, temperature, pressure or total volume, only to the extent permitted by the investigator.

(ii) Components: These are the substances, either chemical elements or chemical compounds, whose presence is essential and sufficient to make a system. A pure metal is called a one-component system; an alloy of two metals is called a binary or two component system, etc.

(iii) Phase: It is a homogeneous portion of a system that has uniform physical and chemical characteristics. The gaseous phase is a single phase, as atoms in the gaseous phase are mixed in the atomic level, A liquid solution (e.g. salt solutiond) is a single phase but a liquid mixture of water and oil forms separate phases because. they are not mixed at the atomic level.

(iv) Phase diagram: A graphical representation of the relationships between environmental constraints (e.g. temperature and sometimes pressure), composition, and regions of phase stability, ordinarily under conditions of equilibrium.

Most phase diagrams are prepared by using slow cooling conditions whereby phases are in equilibrium.

One can get following important information from the phase diagrams

(a) Phases at different composition and temperature

(b) Solubility of one element or compound in another element.

(c) Melting points of different phases in an alloy.

(d) Temperature of solidification or range of solidification of an alloy.

(v) Phase Equilibrium: The state of a system where the phase characteristics remain constant over indefinite time periods. At equilibrium the free energy is a minimum In an equilibrium diagram, liquid is one phase and solid solution is another phase.

(vi) Phase Transformation: A change in the number and/or character of the phases that constitute the microstructure of an alloy.

Types of Alloys

There are two types of alloys.

1. Solid solution
2. Intermediate phases

Solid solution

When two metals are melted together and cooled to crystallize (solidify), a single crystal structure may form. In the unit cell of the crystal both the metal atoms are present according to their concentration or proportion. This structure is called solid solution. The crystal structure is maintained, and no new structures are formed. In other words, When the two components of a binary alloy remain completely mixed in each other both in liquid and solid state, the two components are said to be soluble in each other and a different type of solution may be formed. It is called a solid solution.

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

There are three types of solid solutions

a. Substitutional solid solution
b. Random substitutional solid solution
c. Ordered substitutional solid solution
d. Interstitial solid solution

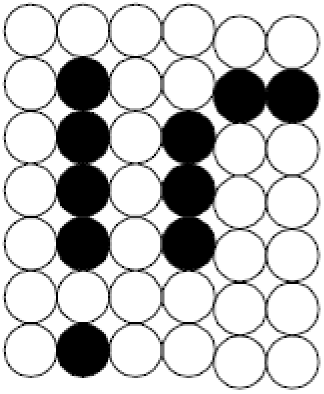
Substitutional solid solution

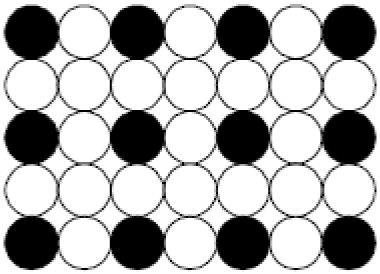
When the two metals in solid solution form a single face centered cubic lattice, i.e., in general solute or impurity atoms replace or substitute for the host atoms, is called assubstitutional solid solution. Size and electronic structure and solvent. The lattice parameter changes and it causes distortion of the alloy. It impedes the motion of dislocation and strength increases,

Random substitutional solid solution

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

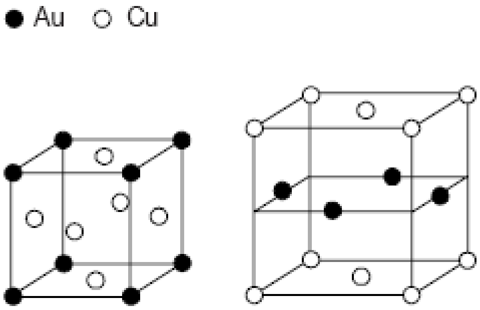
Many substitutional solid solutions can be in an ordered state at relatively low temperatures, i.e. unlike atoms of two elements are distributed between the sites of the space lattice not statistically, but in a perfectly definite order. Such solid solutions are called *ordered*; the term '*superstructure*'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





Random substitutional Ordered substitutional solid solution

In ordered solid solutions atoms arrange themselves in a preferred manner. It retains the same crystal structure of the solvent metal. So it is different from chemical compound where the crystal structure changes completely. Ordered solid solutions can be found in systems with either substantial or unlimited solubility in the solid state; in that case complete ordering can occur with concentrations of the solid solution elements corresponding to simple atomic ratios of the components of the type, say *AB* or *AB*3. Partial ordering may be observed in systems with concentration ratios close to the indicated ones. The arrangement of atoms in ordered solid solutions of two Cu and Au alloys of the corresponding to AuCu3 and AuCu.are shown below.



AuCu AuCu3

The appearance and disappearance of an order in the arrangement of atoms in solid solutions is associated with changes in the properties of an alloy.

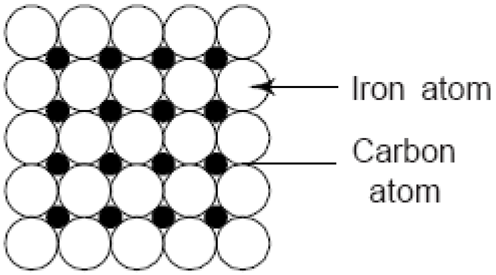
Ordering increases the electrical conductivity, temperature coefficient of electric resistance, hardness, and strength, but decreases the ductility of an alloy. In ferromagnetic alloys, it changes magnetic properties; for instance, the magnetic permeability of perm alloys (magnetic iron-nickel alloys) can drop on ordering to a small fraction of the original value. Some alloys are paramagnetic in disordered state, but become ferromagnetic after ordering, such as Heusler (Mn-Cu-Al) alloys.

Interstitial solid solution

The possibility of obtaining an interstitial solution is mainly determined by the size factor; i.e., the size of a solute atom must be equal to or slightly smaller than the size of an interstitial void. Interstitial solid solutions always have a limited solubility and form preferably in solvents having an HCP or FCC lattice because of their large interstices with a radius of 0.41 *R*, where *R* is the radius of a solvent atom.

In BCC lattices, the solubility is low, since the size of interstices does not exceed 0.29 *R*. Examples of interstitial solid solutions of commercial application are solid solution of carbon in α-Fe and γ-Fe, which has an FCC lattice, can dissolve upto 2.14% (by mass) of carbon; α-Fe (BCC lattice) does not practically dissolve carbon, the maximum solubility being around 0.02 (by mass).

*Other elements like:*nitrogen for maintaining stainless steel in austenitic condition for nitriding condition and hydrogen when introduced into steels during welding operations, acid cleaning and plating results in hydrogen embrittlement and causes a sharp decrease in ductility. Lattice distortions appearing on the formation of interstitial solid solutions are stronger than those in the substitutional solid solutions, because of which the properties of alloys can be changed more drastically. As the concentration of a solute in a solid solution increases, this increases noticeably the electric resistance, coercive force, hardness and strength, but decreases the ductility and toughness. Interstitial solid solutions usually have very limited solubility and are normally considered of secondary importance.



Intermediate phases

Crystals formed by various elements and having their own type of crystal lattice which differs from the crystal lattices of the component elements are called intermediate phases.

Fe_3C (iron carbide), a common constituent of steels, is an example of intermediate phase. It has a complex crystal structure referred to an orthorhombic lattice which differs from crystal structure of both Fe and C and is hard and brittle.

Intermediate phases may have any type of bond which depends on their components and determines largely the properties of the crystals, in particular, electric properties.

The arrangement of atoms (or ions) in the lattice may be disordered or partially or completely ordered. As in solid solutions, ordering sharply changes the properties, in particular, bring about the effect of super conductivity.

Like solid solutions, intermediate phases are crystals whose composition varies within a certain, sometimes very narrow, range of concentrations. Their variable composition can be explained by either the presence of interstitial 'extra' atoms (or ions) in the crystal lattice of intermediate phases or deficiency of atoms in the lattice site.

Numerous and diverse intermediate phases have not been classified properly yet. The structure of an intermediate phase is noticed to depend on three factors: *(i)* relative size of atoms, *(ii)* valencies, and *(iii)* positions of elements in the Periodic Table of elements which determine their electronic structure.

The intermediate phases of fixed composition which obey the normal rules of valency are called *intermetallic compounds*. Examples are NaCl, CaF2, Mg2Si, Cu2S. The properties are different from properties of their elements.

The intermediate phases of variable composition which do not obey the valency law are called *electron phases* or *electron compounds*.Hume Rothery has shown that electron phases occur at certain definite value of free electron to atom ratio in the alloy such as 3 : 2, 21 : 13 and 7 : 4. Few typical examples of electron phases are CuZn (3 : 2), Cu5Zn8 (12 : 13) and CuZn3 (7 : 4).

Order-disorder transformation.

A substitutional solid solution can be one of two types, either ordered in which the A and B atoms are arranged in a regular pattern, or disordered in which the distribution of the A and B atoms is random. From the previous section it is clear that the necessary condition for the formation of a superlattice, i.e. an ordered solid solution, is that dissimilar atoms must attract each other more than similar atoms.

In addition, the alloy must exist at or near a composition which can be expressed by a simple formula, such as AB, A3B orAB3. The following are common structures:

1. *CuZn*. While the disordered solution is bcc with equal probabilities of having copper or zinc atoms at each lattice point, the ordered lattice has copper atoms and zinc atoms

segregated to cube corners (0, 0, 0) and centers (½, ½, ½) respectively. The superlattice in the β-phase therefore takes up the CsCl (also described as B2 or L20) structure, as illustrated in Figure a. Other examples of the same type, which may be considered as being made up of two interpenetrating simple cubic lattices, are AgMg, Zn or Cd), AuNi, NiAl, FeAl and FeCo.

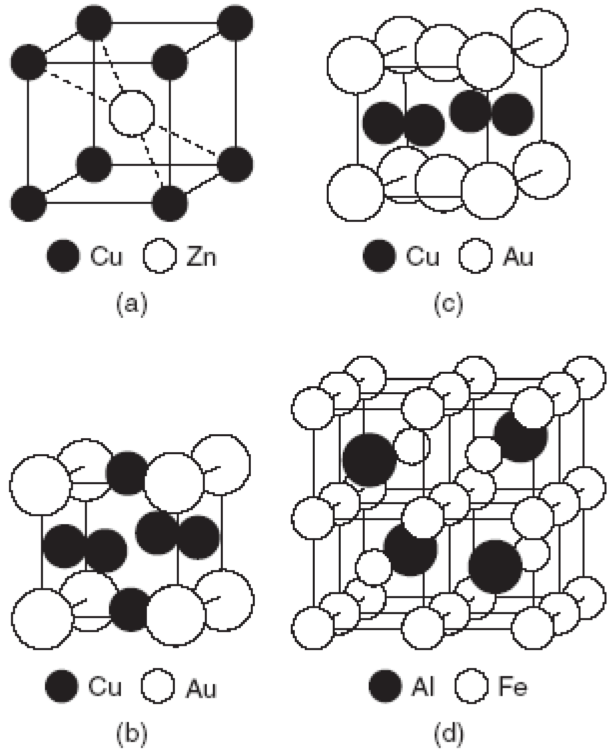
2. *Cu3Au*. This structure, which occurs less frequently than the β-brass type, is based on the fcc structure with copper atoms at the centers of the faces (0, ½. ½,), and gold atoms at the corners (0, 0, 0), as shown in Figure b. Other examples of the structure include Ni3Al, Ni3Ti, Ni3Si, Pt3Al, Fe3Ge, Zr3Al.

3. *AuCu*. The AuCu structure shown in Figure c is also based on the fcc lattice, but in this case alternate (0 0 1) layers are made up of copper and gold atoms, respectively. Hence, because the atomic sizes of copper and gold differ, the lattice is distorted into a tetragonal structure having an axial ratio c/a=0.93. Other examples of the L10 include CoPt, FePt and TiAl.

4. *Fe3Al*. Like FeAl, the Fe3Al structure is based on the bcc lattice but, as shown in Figure d, eight simple cells are necessary to describe the complete ordered arrangement. In this structure any individual atom is surrounded by the maximum number of unlike atoms and the aluminum atoms are arranged tetrahedrally in the cell. Other examples of the D03 include Fe3Si and Cu3Al.

5. *Mg3Cd*. This ordered structure is based on the cph lattice. Other examples of the D019 structure are Ti3Al, MgCd3 and Ni3Sn.

Another important structure which occurs in certain intermetallics is the defect lattice. In the compound NiAl, as the composition deviates from stoichiometry towards pure aluminum, the electron-to-atom ratio becomes greater than 32 , but to prevent the compound becoming unstable the lattice takes up a certain proportion of vacancies to maintain the number of electrons per unit cell at a constant value of 3. Such defects obviously increase the entropy of the alloy, but the fact that these phases are stable at low temperatures, where the entropy factor is unimportant, demonstrates that their stability is due to a lowering of internal energy. Such defects produce an anomalous decrease in both the lattice parameter and the density above 50 at.% Al.



(a) CuZn, (b) Cu3Au, (c) CuAu, (d)Fe3Al

Hume-Rothery's rules (factors governing solids solubility viz. size factor, valency factor, crystal structure factor and chemical affinity factor)

While developing an alloy, it is frequently desirable to increase the strength of the alloy by adding a metal that will form a solid solution.

Hume-Rothery has framed empirical rules that govern the choice of alloying elements in the formation of substitutional solutions. We may note that if an alloying element is chosen at random, it is likely to form an undesired intermediate phase instead of a solid solution.

Extensive solid solubility by substitution occurs, when

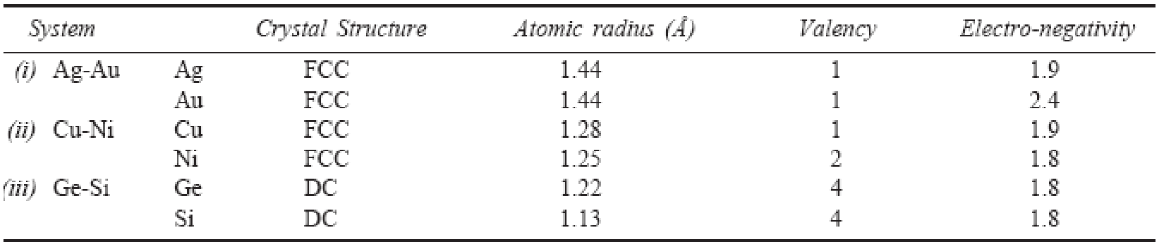
(i) the solute and solvent atoms must be less than 15% in size, i.e. diameter. within this limit of size factor, each of the metals will be able to dissolve appreciably (to the order of 10%) in the other metal. However, if the atomic size factor is greater than 15%, solid solution formation tends to be severely limited and is usually only a fraction of one percent. If the size difference is more, then the stress field is more. The stress field increases the potential energy of the crystal. So the solubility becomes limited as the size difference increases.

(ii) the electronegativity difference between the elements is small. If the chemical affinity of two metals is greater, then the solid solubility will be more restricted. When the chemical affinity of two metals is great, they tend to form an intermediate phase rather than a solid solution.

(iii) the valency and the crystal structures of the elements are the same. If the alloying element has a different valence from that of the base metal, the number of valence electrons per atom (called the electron ratio), will be changed by alloying. We may note that the crystal structures are more sensitive to a decrease in the electron ratio than to an increase. An excess of electrons is readily tolerated rather than a deficiency of bonding electrons. Obviously, a metal of high valence can dissolve only a small amount of lower valence metal; whereas the lower valence metal may have good solubility for a higher valence metal. Moreover, only metals that have the same type of lattice (for example FCC) can form a complete series of solid solutions. For complete solubility, it is found that the size factor must usually be less than 8%. Examples of binary and ternary systems exhibiting complete solid solubility are Cu-Ni and Ag-Au-Pt respectively.

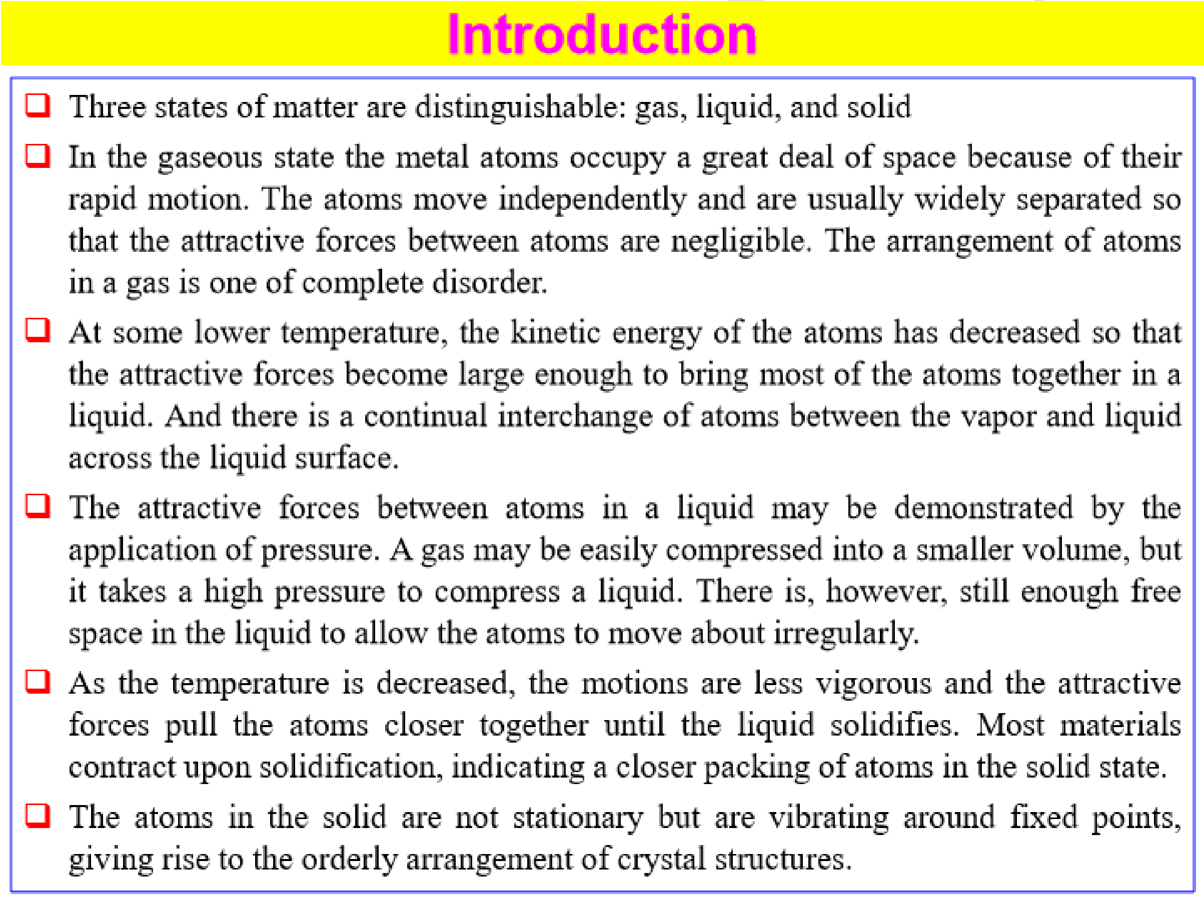
Ag-Au, Cu-Ni and Ge-Si are the systems which satisfy Hume Rothery conditions very well .

Obviously, these systems form complete solid solutions, i.e. the elements mix in each other in all proportions.



System		*Crystal Structure*	*Atomic radius (Å)*	*Valency*	*Electro-negativity*
(i) Ag-Au	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	2.4
(ii) Cu-Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.8
(iii) Ge-Si	Ge	DC	1.22	4	1.8
	Si	DC	1.13	4	1.8

CRYSTALLIZATION FROM THE MELT:

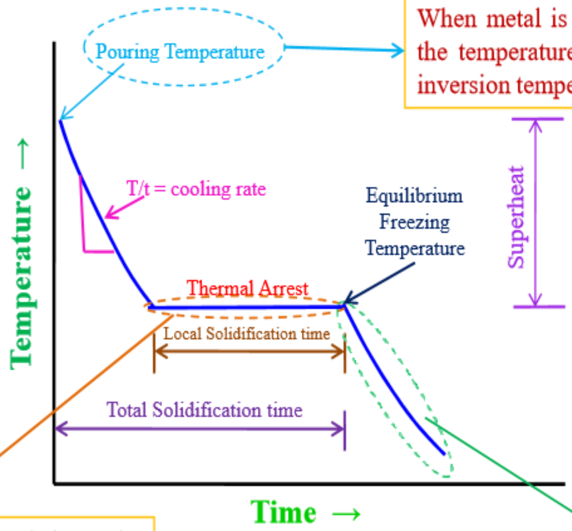


Introduction

- Three states of matter are distinguishable: gas, liquid, and solid
- In the gaseous state the metal atoms occupy a great deal of space because of their rapid motion. The atoms move independently and are usually widely separated so that the attractive forces between atoms are negligible. The arrangement of atoms in a gas is one of complete disorder.
- At some lower temperature, the kinetic energy of the atoms has decreased so that the attractive forces become large enough to bring most of the atoms together in a liquid. And there is a continual interchange of atoms between the vapor and liquid across the liquid surface.
- The attractive forces between atoms in a liquid may be demonstrated by the application of pressure. A gas may be easily compressed into a smaller volume, but it takes a high pressure to compress a liquid. There is, however, still enough free space in the liquid to allow the atoms to move about irregularly.
- As the temperature is decreased, the motions are less vigorous and the attractive forces pull the atoms closer together until the liquid solidifies. Most materials contract upon solidification, indicating a closer packing of atoms in the solid state.
- The atoms in the solid are not stationary but are vibrating around fixed points, giving rise to the orderly arrangement of crystal structures.

Mechanism of Crystallization

- Crystallization is the transition from the liquid to the solid state and occurs in two stages:
  - Nuclei formation
  - Crystal Growth
- Although the atoms in the liquid state do not have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified.
- These chance aggregates or groups are not permanent but continually break up and reform at other points.
- The higher the temperature, the greater the kinetic energy of the atoms and the shorter the life of the group. When the temperature, of the liquid is decreased, the atom movement decreases, lengthening the life of the group, and more groups will be present at the same time.
- Atoms in a material have both kinetic and potential energy. *Kinetic energy is related to the speed at which the atoms move and is strictly a function of temperature.* The higher the temperature, the more active are the atoms and the greater is their kinetic energy. *Potential energy*, on the other hand, *is related to the distance between atoms*. The greater the average distance between atoms, the greater is their potential energy.



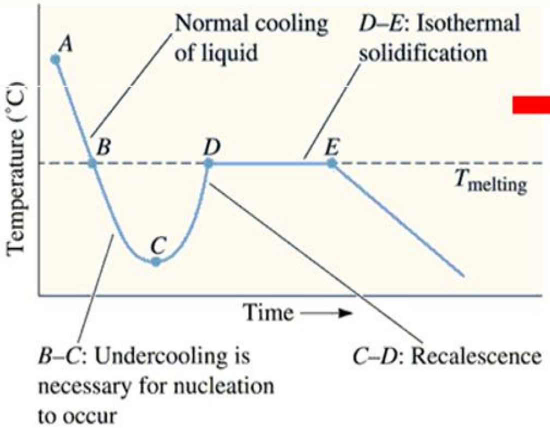
When metal is poured into the mould, the temperature will be as high as its inversion temperature.

It gets cooled when poured into the mould and molten metal in the liquid form will solidify. This time is called local solidification time

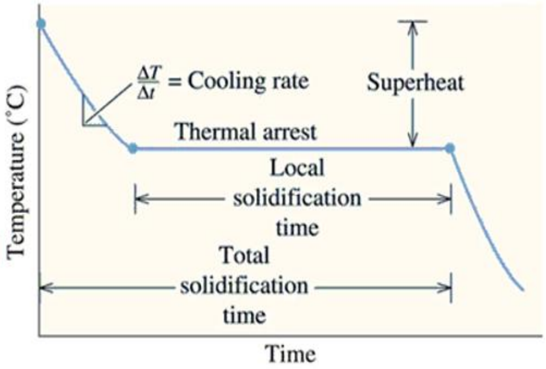
The solidified metal in the mould (called casting) gets cooled in the mould to the temperature of the surroundings

Cooling Curves

- Recalescence : The increase in temperature of an undercooled liquid metal as a result of the liberation of heat during nucleation.
- Thermal Arrest : A plateau on the cooling curve during the solidification of a material caused by the evolution of the latent heat of fusion during solidification.
- Total Solidification Time : The time required for the casting to solidify completely after the casting has been poured.
- Local Solidification Time : The time required for a particular location in a casting to solidify once nucleation has begun.



Cooling curve for a pure metal that has not been well inoculated. Liquid cools as specific heat is removed (betweens points *A* and *B*). Undercooling is thus necessary (between points *B* and *C*). As the nucleation begins (point *C*), latent heat of fusion is released causing an increase in the temperature of the liquid. This process is known as recalescence (point *C* to point *D*). Metal continues to solidify at a constant temperature (T melting). At point *E*, solidification is complete. Solid casting continues to cool from the point.

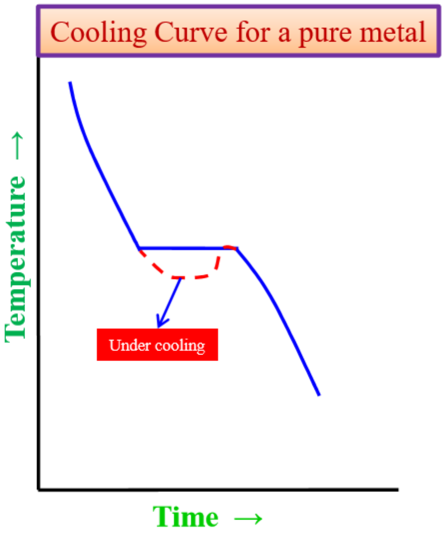


Cooling curve for a well inoculated, but otherwise pure metal. No undercooling is needed. Recalescence is not observed. Solidification begins at the melting temperature

Solidification of pure metal : Super cooling

- In a pure metal at its freezing point where both the liquid and solid states are at the same temperature. The kinetic energy of the atoms in the liquid and the solid must be the same, but there is a significant difference in potential energy.
- The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in potential energy between the liquid and solid states is known as the *latent heat of fusion.*

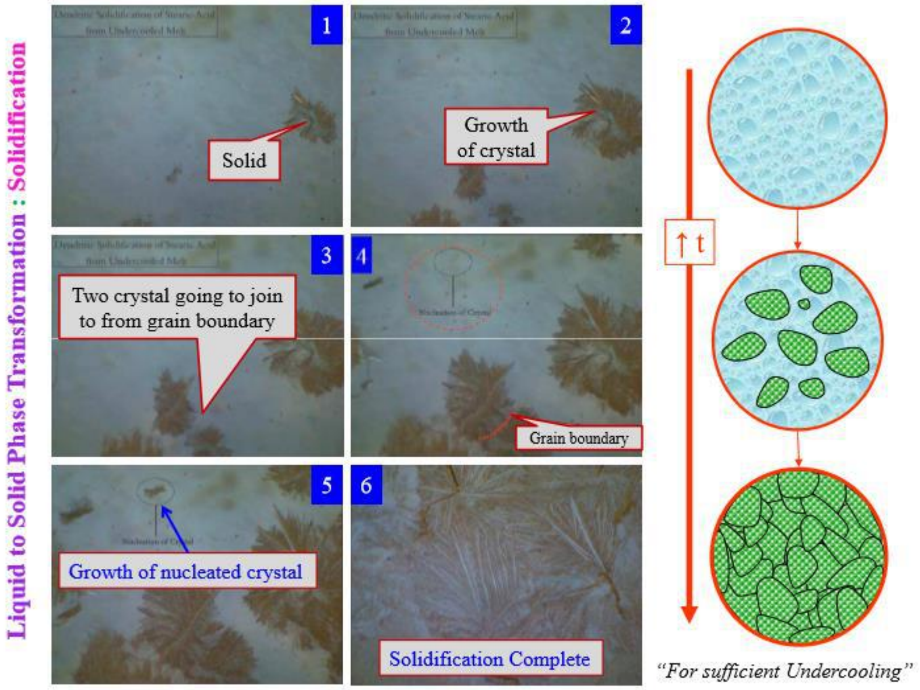
- However, energy is required to establish a surface between the liquid and solid. In pure materials at the freezing point insufficient energy is released by the heat of fusion to create a stable boundary, and some under cooling is always necessary to form stable nuclei.
- Subsequent release of the heat of fusion will raise the temperature to the freezing point. The amount of undercooling required may be reduced by the presence of solid impurities which reduce the amount of surface energy required.


Cooling Curve for a pure metal

Solidification of pure metal

- When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appear spontaneously at various points in the liquid. These nuclei, which have now solidified, act as centers for further crystallization.
- As cooling continues, more atoms tend to freeze, and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice.
- Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of the crystal this gives rise to a characteristic treelike structure which is called a dendrite.

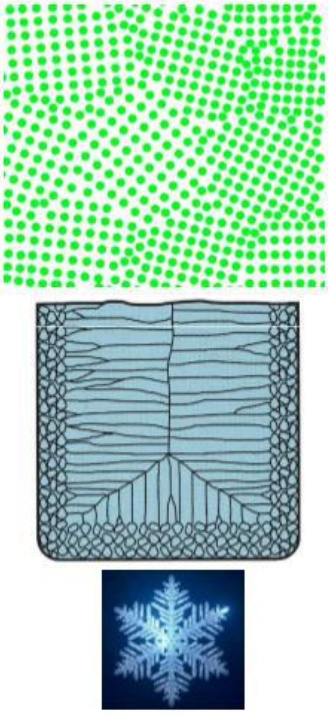
- Since each nucleus is formed by chance, the crystal axes are pointed at random and the dendrites growing from them will grow in different directions in each crystal. Finally, as the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbors. This leads to a very irregular external shape.
- The crystals found in all commercial metals are commonly called grains because of this variation in external shape. The area along which crystals meet, known as the grain boundary, is a region of mismatch.



"For sufficient Undercooling"

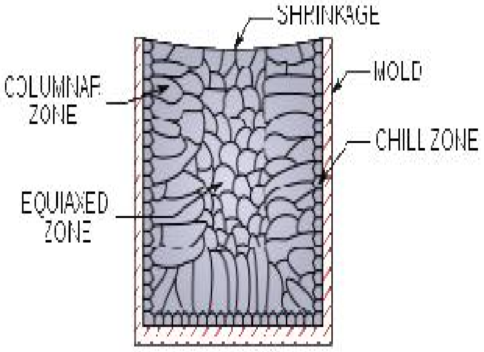
Solidification of pure metal

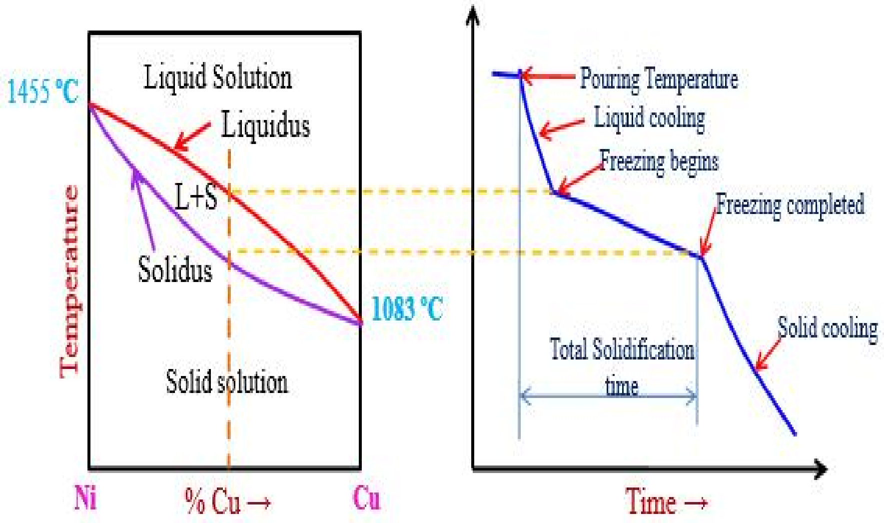
- ❑ This mismatch leads to a noncrystalline (amorphous) structure at the grain boundary with the atoms irregularly spaced.
- ❑ Since the last liquid to solidify is generally along the grain boundaries, there tends to be higher concentration of impurity atoms in that area. Figure (previous page) shows schematically the process of crystallization from nuclei to the final grains.
- ❑ Due to chilling action of mold wall, a thin skin of solid metal is formed at the wall surface immediately after pouring.
- ❑ Grain structure in a casting of a pure metal, showing randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting.



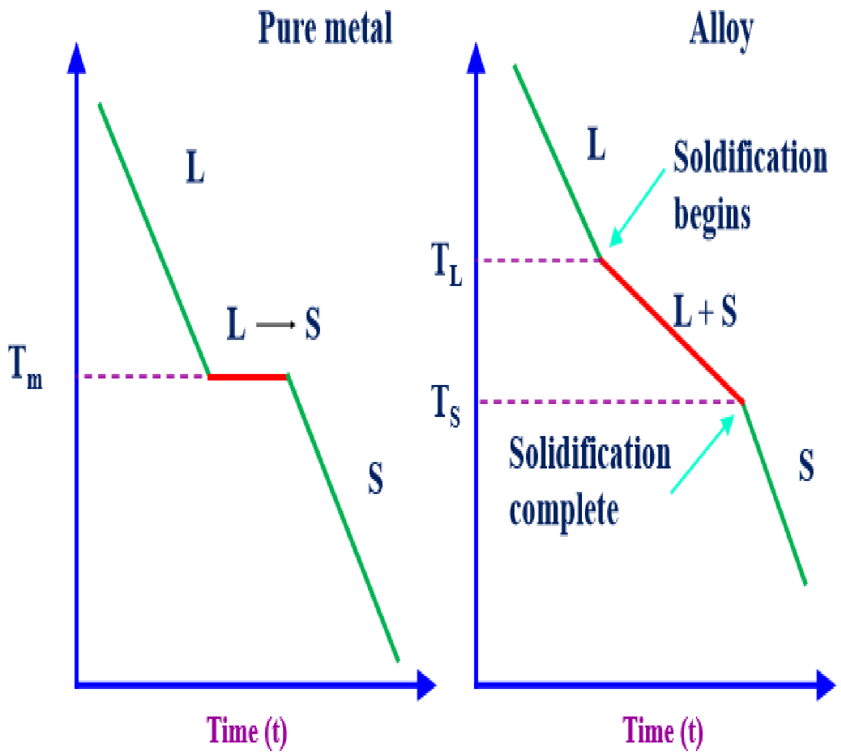
Solidification of Alloys

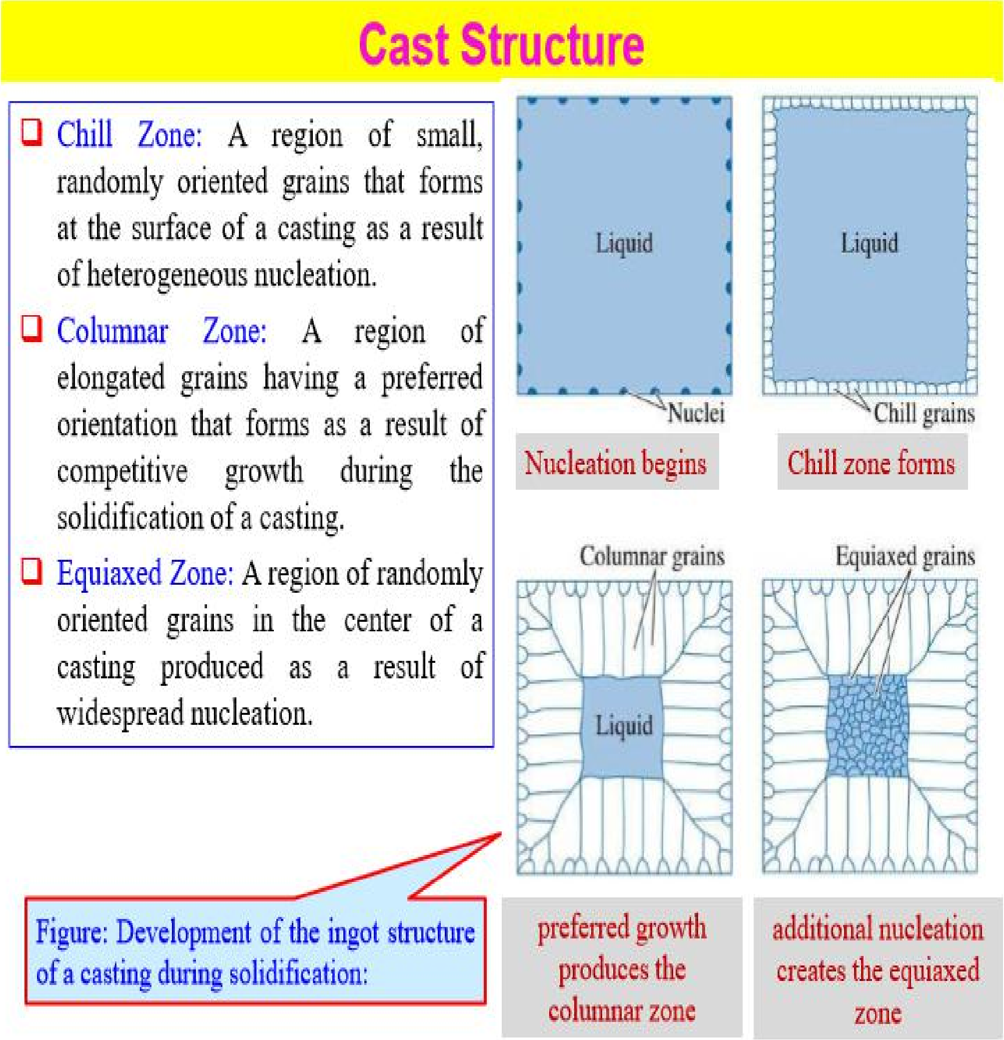
- ❑ Most alloys freeze over a temperature range
- ❑ Phase diagram for a Cu-Ni alloy system and cooling curve for different alloy systems.
- ❑ Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting.





Comparison of cooling curves





Cast Structure

- ❑ **Chill Zone:** A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- ❑ **Columnar Zone:** A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.
- ❑ **Equiaxed Zone:** A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.

Nucleation begins

Chill zone forms

preferred growth produces the columnar zone

additional nucleation creates the equiaxed zone

Figure: Development of the ingot structure of a casting during solidification:

Directional solidification

How the heat is extracted from the molten pool of metal is of considerable importance in determining the structure of the solid. When liquid metal is poured into a mould (sometime preheated) the heat flows from the liquid through the mould wall to the surrounding environment. Heat flows from higher to lower temperature. The rate is proportional to thermal gradient. It also depends on the effective heat transfer coefficient of the entire system consisting of the liquid, solidified layer, the mould and the region surrounding the mould. Figure 13 illustrates a case where heat is being extracted in one direction from the liquid metal through solid metal and the mould. Note that the solid liquid interface is flat in this case. The liquid to solid transformation is accompanied by evolution of heat at the interface. This can only be extracted down the temperature gradient. Figure 14 shows a sketch why any unevenness is likely to disappear.

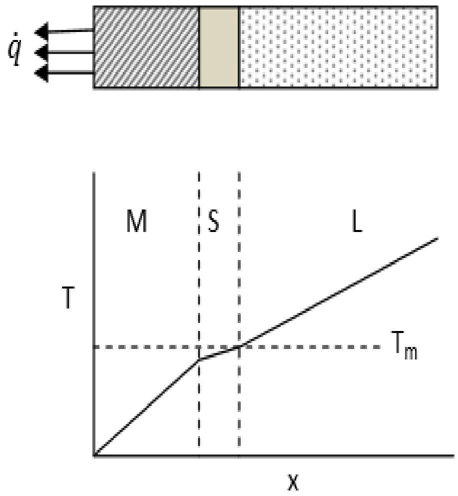


Fig 13: Sketch showing the direction of heat flow from the liquid metal through the solid and the mould. It also gives the temperature as a function of distance. The S/L interface is likely to be flat. The rate at which it moves would depend on how fast the heat can be extracted.

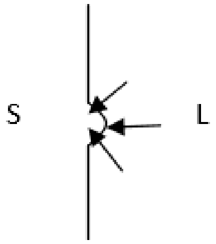


Fig 14: Sketch showing a bulge in the S/L interface. The arrow denotes the direction of heat flow. This makes it unstable as the heat flowing into the bulge would melt it again.

Segregation

The liquids that are frozen to form industrial alloys usually contain, in addition to solute elements added intentionally for their beneficial effects, many impurity elements that find their way into the liquid metal by a number of different routes. Thus, impurity elements, present in the ores from which the basic metals were obtained, are frequently only partly eliminated during the smelting and refining operations. The refractory brick linings of furnaces used in melting or refining (purifying) and the gases in the furnace atmospheres may be other sources. In the latter case, elements enter the liquid metal in the form of dissolved gases. The various elements dissolved in commercial liquid metals can and often do react with each other to form compounds (oxides, silicates, sulfides, etc.). In many cases, the latter may be less dense than the liquid, and rise to the surface and join the slag which floats on top of the liquid metal. On the other hand, it is quite possible for small impurity particles (compounds) to exist in the liquid. Certain of the latter undoubtedly form nucleation centers for heterogeneous nucleation. This fact has been used to some extent to control the grain size of castings by inoculating liquid metals with elements that combine to form nucleation catalysts. Increasing the number of nucleation centers will, of course, produce a finer grain size in the solidified casting. When an alloy is frozen, a more or less general rule which applies is that solute elements, whether present as alloying elements or as impurities, are more soluble in the liquid state than in the solid state. This fact usually leads to a segregation of the solute elements in the finished casting. There are two basic ways of looking at the resulting nonuniformity of the solute. First, because the liquid becomes progressively richer in the solute as freezing progresses, the solute concentrations in a casting tend to rise in those regions that solidify last (center of the ingot). This and similar long-range composition fluctuations fall in the classification of macrosegregation. In general, macrosegregation refers to the change in the average composition of the metal as one moves from place to place in an ingot. Segregation of this form is not always caused by the selective freezing out of high-melting-point constituents. Gravitational effects are often a factor in producing macrosegregation, especially during the formation of the central equiaxed zone. The crystals that form freely in the liquid often have a different density from that of the liquid. As a result, they may either rise toward the surface of the casting, or settle toward the bottom. An extreme example44 of gravity-induced segregation occurs in an alloy system somewhat different from the solidsolution alloys presently being considered. Thus, in the lead-antimony system, an eutectic forms at 11.1 percent Sb and 252°C. When alloys containing more than 11.1 percent Sb (say 20 percent) are frozen, crystals of almost pure antimony form from the liquid until the composition of the latter reaches the eutectic composition, at which time the eutectic mixture begins to freeze. Since antimony crystals have a lower density than the liquid from which they originate, they tend to rise toward the surface. Slow cooling of this alloy, therefore, results in a structure whose lower fraction is composed almost entirely of eutectic solid, with an upper portion containing the primary-alpha antimony crystals with some eutectic solid filling in the gaps between the primary crystals. In castings not only do we find composition variations (macrosegregation) over large distances, but it is also possible to have localized composition variations on a scale smaller than the crystal size. This is called microsegregation and one form has already been described; the composition segregation associated with the cellular structure resulting from the combined movement of the liquid-solid interface and a very narrow zone of constitutional supercooling. A much more frequent form of microsegregation, commonly known as coring, is caused by dendritic freezing in alloys. The original dendrite arms, which shoot out into the liquid metal, freeze as relatively pure metal. The liquid surrounding these arms is, accordingly, enriched in solutes and normally, when this liquid solidifies, the spaces between the arms become regions high in solute concentration.

Dendritic segregation, or coring, is very common in alloy castings solidified under normal conditions. It can occur with a solute concentration as low as 0.01 percent under the proper conditions. Rapid solidification, however, can drastically reduce segregation and in some cases lead to its total elimination.

When a casting is sectioned and the surface prepared for metallographic examination, the exposed surface will usually be a planar section cutting through the forest of dendrite arms. Since the composition at the center of an arm differs from that at points midway between arms, the dendrite arms can be revealed by etching with a suitable metallographic etch. Dendritic segregation in a copper-tin alloy is shown in Fig. 14.34.

FIG. 14.34 Coring, or dendritic segregation, in a copper-tin alloy. Several different grains are shown. Note that the dendrite arms have different orientations in each crystal. 200X

INVERSE SEGREATION:

Dendritic freezing in the columnar zone of ingots may sometimes lead to a phenomenon known as inverse segregation. In the normal freezing of ingots, the center and top portions of the ingot, which freeze last, become richer in solutes than the outer portions of the ingot, which freeze first. In some alloys, however, the dendrite arms may extend for long distances before the spaces between them are filled in by the freezing operation. Under the proper conditons, channels between the dendrite arms offer a path by which liquid from the center of the casting can work its way back toward the surface. The latter phenomenon is promoted by the fact that as solidification progresses, the casting as a whole can shrink away from the mold walls, causing a suction that pulls the liquid toward the surface. Other important factors are the internal pressure that develops in an ingot due to gas evolution during freezing and convective currents developed in the liquid. “Tin sweat,” which occurs in tin bronzes (copper-tin alloys), is an example. When the liquid contains a relatively large concentration of dissolved hydrogen, the release of this gas near the end of freezing forces the liquid enriched in tin through interdendritic pores to the surface, where it coats the normally yellow-bronzecolored surface with a fine layer of white alloy.

POROSITY:

Other than shrinkage cracks resulting from unequal cooling rates in different sections of castings, there are two basic causes for porosity in cast metals: gas evolution during freezing, and the shrinkage in volume that accompanies the solidification of most metals. Gases differ from other solutes in that their solubility in metals depends markedly on the applied pressure. Many gases with which metals come in contact are diatomic: O2, N2, H2, etc. Providing that the solubility is small, it is often possible to express the relationship between the pressure and the solubility of diatomic gases in a simple form, known as Sievert's law.

$$c_g = k\sqrt{p}$$

cg is the solubility of the dissolved gas, p is the gas pressure, and k is a constant. Some experimental data corresponding to hydrogen dissolved in pure magnesium are shown in Fig. 14.40. The melting point of pure magnesium is 650°C (923 K). Notice that the data plots well as straight lines (on cg and coordinates) both above and below the melting point. This signifies that Sievert's law is probably valid for the solution of hydrogen in both liquid and solid magnesium.

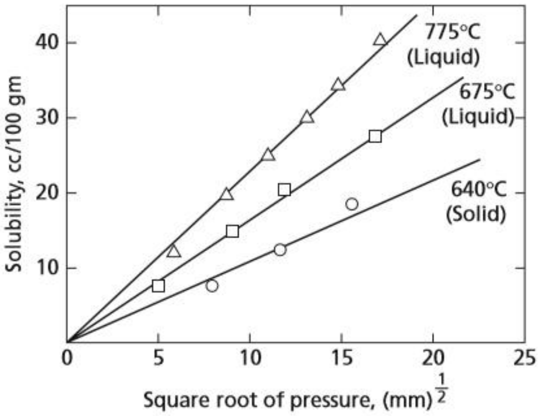


FIG. 14.40 Solubility of hydrogen in both liquid and solid magnesium as a function of the partial pressure of hydrogen. (From Koene, J., and Metcalfe, A.G., *Trans. ASM*, **51** 1072 [1959] Reprinted with permission of ASM International (R). All rights reserved. www.asminternational.org)

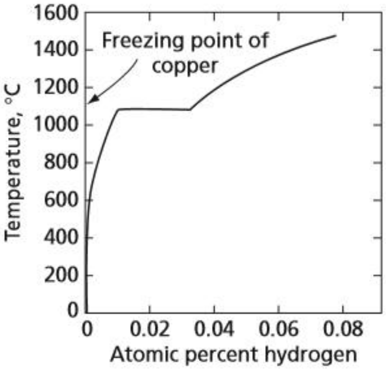


FIG. 14.41 Solubility of hydrogen in copper at one atmosphere pressure. (From *Constitution of Binary Alloys*, by Hansen, M., and Anderko, K. Copyright, 1958. McGraw-Hill Book Co., Inc., New York, p. 587. Used by permission.)

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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,

The Gibbs Phase Rule

Phase rule derived by Josiah Willard Gibbs provides an interesting way to analyze not only one-component three-phase systems, but systems containing an arbitrary number of components and phases. This rule connects the number of degrees of freedom (F) in a system to the number of components (C) and phases (P), as

$P+F= C + 2$

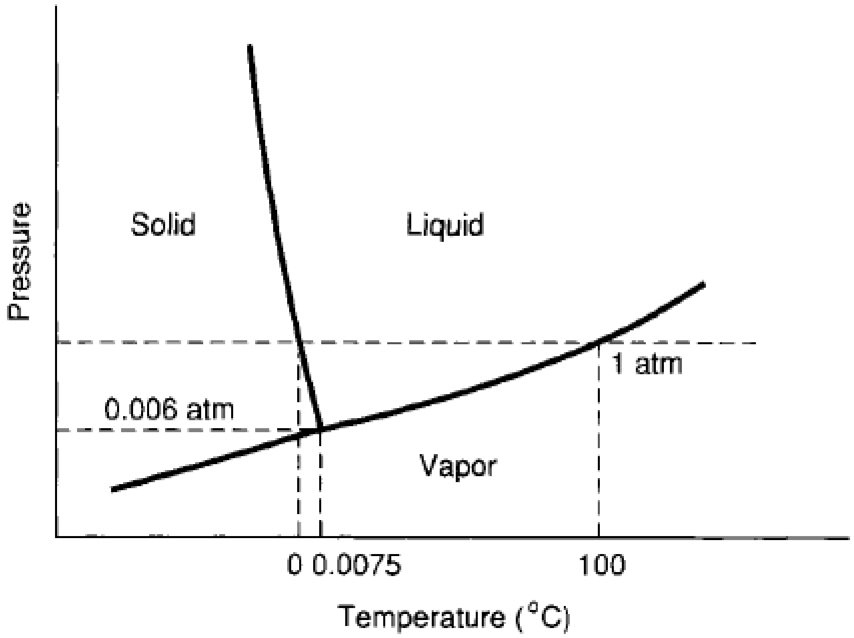
By degrees of freedom or variance, we mean the number of variables (here T and P) that can be independently varied without altering the phases of the system. Thus, water ($C = 1$) will remain a liquid ($P = 1$) even though both temperature and pressure ($F = 2$) can be independently raised or lowered over a reasonable range of values.

Water (lquid) and steam (vapor) coexist at 100°C and 1 atm, $P = 2$ and $F = 1$. Now assume that P is increased independently, (e.g. pressure cooker). The temperature then must rise in a specific, dependent fashion along the vaporization line to continue to preserve the water-steam equilibrium. Finally, at the critical triple point, $P =3$ and $F = 0$. Any change in either temperature or pressure will destroy the very precarious three-phase equilibrium and push the system into one of the single-phase fields.

Most frequently we are interested in systems at atmospheric pressure. Under such conditions one variable is fixed by the equation P = 1 atm. Pressure changes often produce no significant effect on equlibirium, specially in metallic systems e.g melting point doesn't change whether you measure it in hill top or bottom of a hill. The variance is thus reduced by one so that the Gibbs phase rule now reads

$P+F= C + 1$

Thus, for one component (C = 1) at the melting point, both liquid and solid are present P = 2), so that F = 0, called *invariant point*. This is why melting occurs at a fixed temperature i.e. invariant.



Pressure-temperature phase diagram for H2O

In binary (i.e two components) systems, we are simply interested in knowing what is happening when two elements, of initially known proportions, are mixed and brought to temperatures of interest where they come to thermodynamic equilibrium. To simplify matters, only fixed pressure {P = 1 atm) is considered so that the Gibbs phase rule (P+F=C+2) becomes (P+F=C+1, the variable pressure remains constant). So F = 3 — P when C = 2. Because it is impossible for F to be negative, three phases, at most, can coexist in equilibrium at fixed pressure. Whatever phases are present, however, can have differing melting temperatures, chemical compositions, and solubilities. Therefore, a graphic representation, that is, a binary phase diagram,that reflects this information would be very handy. The different types of binary phase diagrams are described

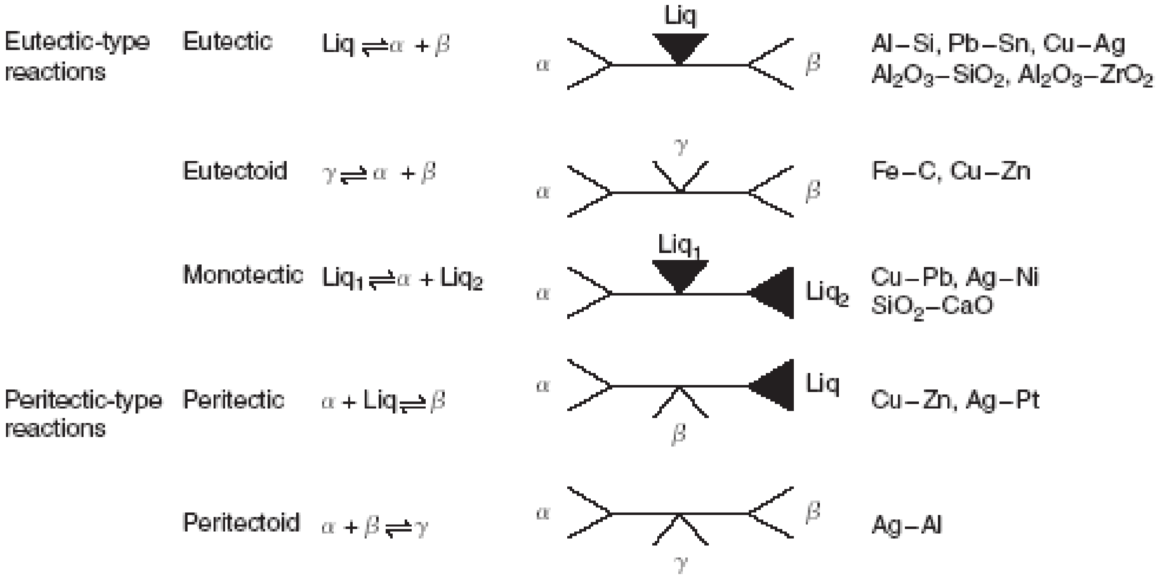
a) Isomorphism system,

(b) Eutectic system,

(c) Peritectic system,

(d)Eutectoid system

and (e) Peritectoid system



a)

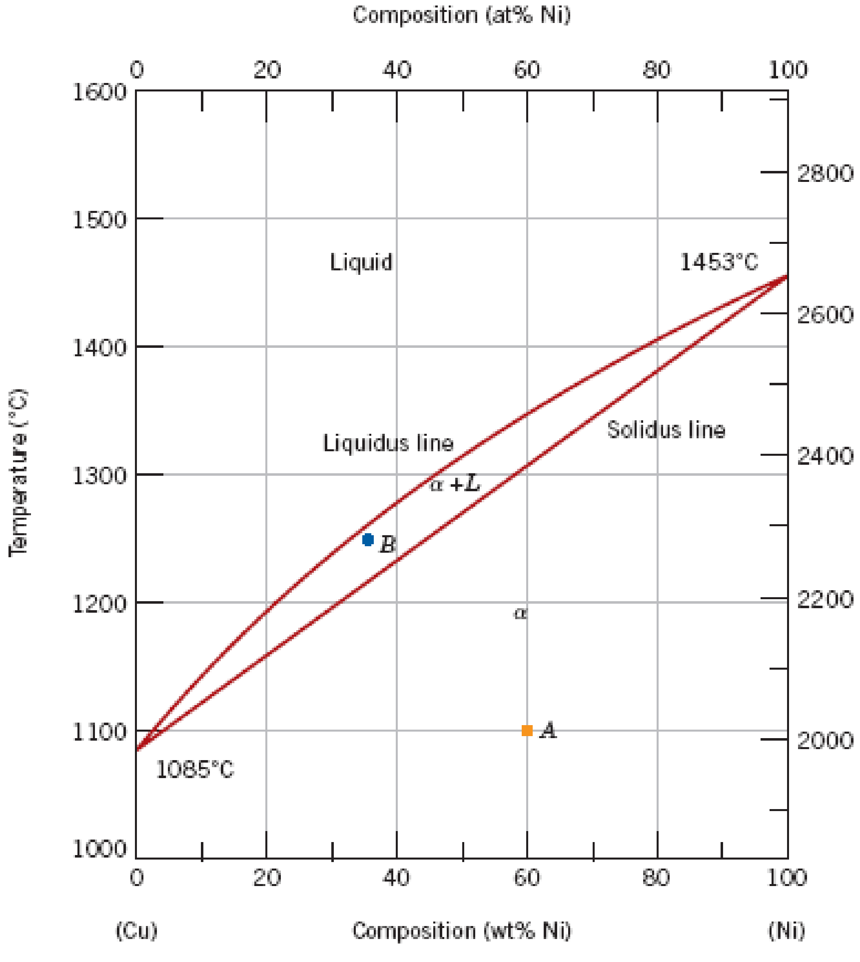
Isomorphism system

The system is called isomorphous (iso-same, morphous-structure) because the components have same structure and are completely soluble in liquid as well as solid state. Example:- Cu-Ni system (shown below). The example is shown below.

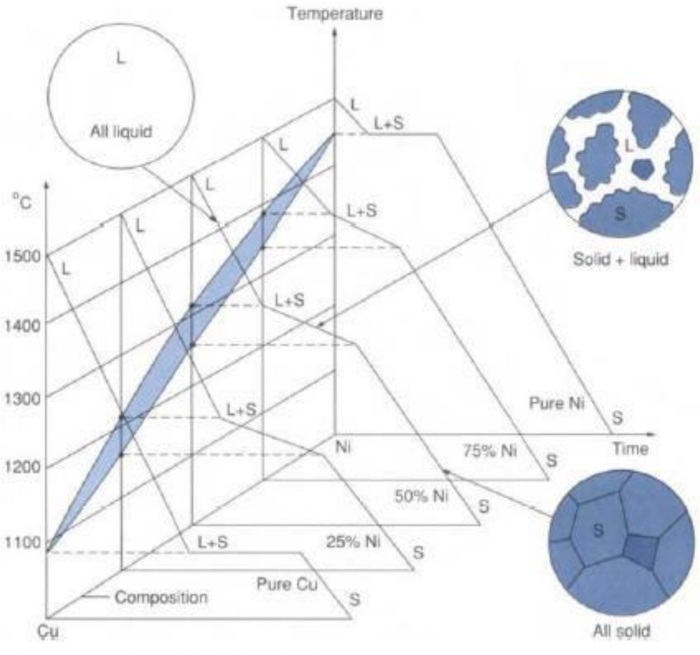
They satisfy hume-ruthery rules for extensive solid solubility and so exhibit complete solubility. This complete solubility is explained by the fact that both Cu and Ni have the same crystal structure (FCC), nearly identical atomic radii and electronegativities, and similar valences.

The phase diagram is shown in figure below. Temperature is plotted along the y-axis and the x-axis represents the composition of the alloy, in weight percent (bottom) and atom percent (top) of nickel. The composition ranges from 0 wt% Ni (100 wt% Cu, pure Cu) on the left horizontal extremity to 100 wt% Ni (0 wt% Cu) on the right. Three different phase regions, or fields, appear on the diagram, an alpha (α) field, a liquid (*L*) field, and a two-phase field (α + L). Each region is defined by the phase or phases that exist over the range of temperatures and compositions delimited by the phase boundary lines. The liquid *L* is a homogeneous liquid solution composed of both copper and nickel.

The phase α is a substitutional solid solution consisting of both Cu and Ni atoms, and having an FCC crystal structure.



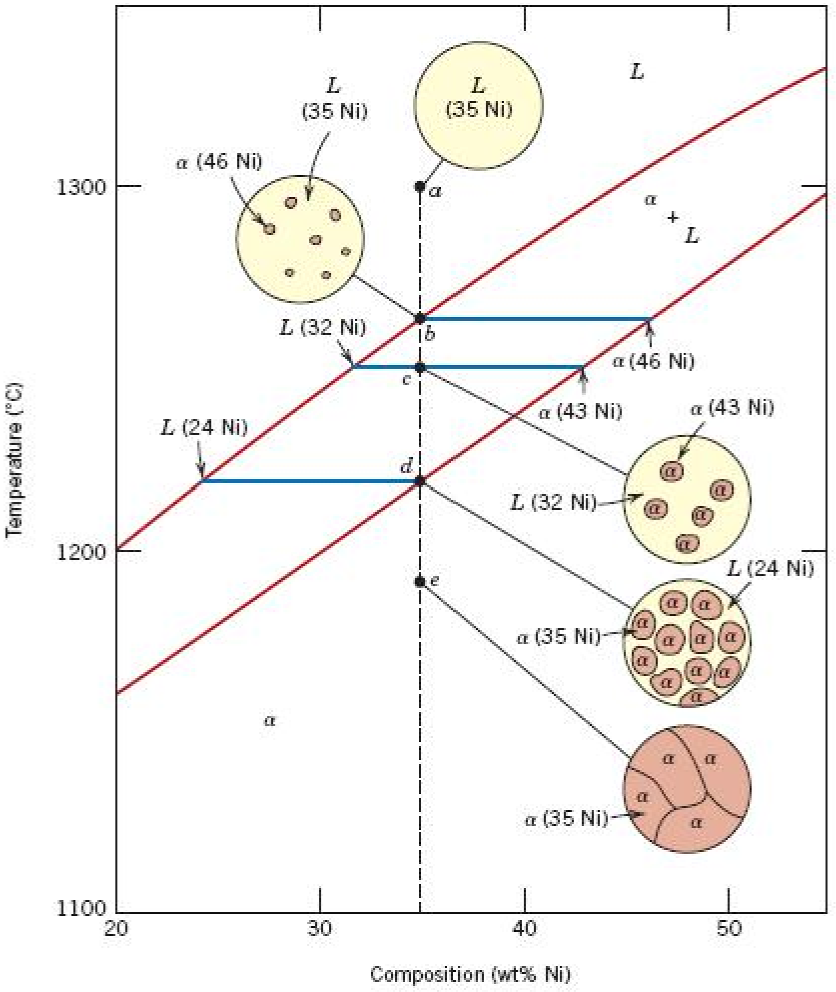
(a)



Temperature–time cooling curves for a series of Cu–Ni alloys.

A couple of comments should be remembered regarding analysis of phase diagrams. First, for metallic alloys, solid solutions are commonly designated by lowercase Greek letters (α, β, γ etc.). Furthermore, with regard to phase boundaries, the line separating the *L* and hase fields is termed the *liquidus line* (everything is liquid at all temperatures and compositions above this line). The *solidus line* is the line below which only the solid phase exists. Solvus line is the line separating two solid phase regions.

Interpretation of solidification behaviors and microstructure



Equilibrium Cooling (Slow cooling)

Microstructure has a significant effect on the properties of alloys.

At this point we will examine the development of microstructure that occurs for isomorphous alloys during solidification. We first treat the situation in which the cooling occurs very slowly, in that phase equilibrium is continuously maintained. By slow cooling, we are providing sufficient time for atomic diffusion required to maintain equlibirium and to get a uniform composition. So uniformity of composition is maintained. So coring (explained later) doesn't occur by slow cooling i.e. by equlibirium cooling.

Let us consider the copper–nickel system (Figure above), specifically an alloy of composition 35 wt% Ni–65 wt% Cu as it is cooled from. The region of the Cu–Ni phase diagram in the vicinity of this composition is shown in Figure above. Cooling of an alloy of the above composition corresponds to moving down the vertical dashed line.

At point *a*, the alloy is completely liquid (of composition 35 wt% Ni–65 wt% Cu) and has the microstructure represented by the circle inset in the figure. As cooling begins, no microstructural or compositional changes will be realized until we reach the liquidus line (point *b*,).

At this point, the first solid begins to form, which has a composition dictated by the tie line drawn at this temperature [i.e., 46 wt% Ni–54 wt% Cu, noted as (46 Ni)]; the composition of liquid is still approximately 35 wt% Ni–65 wt% Cu [*L*(35 Ni)], which is different from that of the solid .With continued cooling, both compositions and relative amounts of each of the phases will change. The compositions of the liquid and phases will follow the liquidus and solidus lines, respectively. Furthermore, the fraction of the phase will increase with continued cooling. Note that the overall alloy composition (35 wt% Ni–65 wt% Cu) remains unchanged during cooling even though there is a redistribution of copper and nickel between the phases.

At point *c* in Figure above, the compositions of the liquid and phases are 32 wt% Ni–68 wt% Cu [*L*(32 Ni)] and 43 wt% Ni–57 wt% Cu [(43 Ni)], respectively.

The solidification process is virtually complete at about point *d*; the composition of the solid is approximately 35 wt% Ni–65 wt% Cu (the overall alloy composition) while that of the last remaining liquid is 24 wt% Ni–76 wt% Cu. Upon crossing the solidus line, this remaining liquid solidifies; the final product then is a polycrystalline α-phase solid solution that has a uniform 35 wt% Ni–65 wt% Cu composition (point *e*, Figure above). Subsequent cooling will produce no microstructural or compositional alterations.

For a binary system (two component system) of known composition, at least three kinds of information are available from phase diagram at:

(1) The phases that are present,

(2) The compositions of these phases (tie line rule),

and

(3) The percentages or fractions of the phases (lever rule).

1. Phases Present

To know what phases are present, locate the temperature–composition point on the diagram and note the phase(s) with which the corresponding phase field is labeled.

2. Tie line rule

It is a horizontal line drawn at a particular temperature in a phase diagram in a two phase region. These tie lines extend across the two-phase region and terminate at the phase boundary lines on either side. The steps are

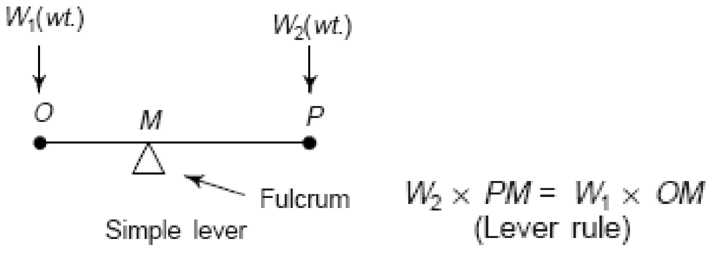
1. A tie line is constructed across the two-phase region at the temperature of interest.
2. The intersections of the tie line and the phase boundaries on either side are noted.
3. Perpendiculars are dropped from these intersections to the horizontal composition axis, from which the composition of respective phases are noted.

3. Lever rule

The tie line must be utilized in conjunction with a procedure that is often called the lever rule (or the *inverse lever rule*), which is applied as follows:

1. The tie line is constructed across the two-phase region at the temperature of interest.
2. The overall alloy composition is located on the tie line.
3. The lever rule is so named because the fraction of a phase multiplied by its "lever arm" is equal to the product of *fraction of other phase* and other phase’s lever arm. The fraction of one phase is computed by taking the length of tie line from the overall alloy composition to the phase boundary for the *other* phase, and divided by the total tie line length.

Let us prove it.



We know that $W_1+W_2=1$, where W_1 and W_2 are the weight fractions of phases

Suppose OM=x, MP=y, OP=x+y

Applying lever rule $W_1*x = W_2*y$

But $W_2 = 1-W_1$

Putting in above equation, we get $W_1*x = (1 – W_1)*y$

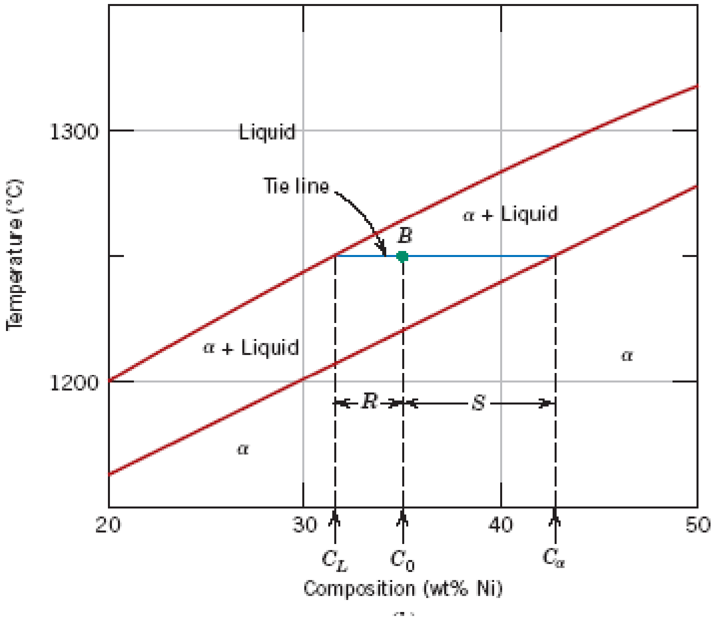
solving, we get $W_1 = y/(x+y)$ or MP/OP

and $W_2 = OM/OP$

4. The fraction of the other phase is determined in the same manner.

5. If phase percentages are desired, each phase fraction is multiplied by 100. When the composition axis is scaled in weight percent, the phase fractions computed using the lever rule are mass fractions—the mass (or weight) of a specific phase divided by the total alloy mass (or weight). The mass of each phase is computed from the product of each phase fraction and the total alloy mass.

Consider the phase diagram for copper and nickel and apply the lever rule.



A portion of the copper–nickel phase diagram

By applying lever rule, we get

$W_L = S/(R+S) = (C\alpha - C_0)/(C\alpha - C_L)$

$W\alpha = R/(R+S) = (C_0 - C_L)/(C_\alpha – C_L)$

When applied to our 65 wt% Ni—35 wt% Cu alloy at 1340°C, the fraction of solid and liquid are

fs = 40-35/40-27 = 0.385.

f_L= (35-27)/ (40-27) = 0.615

Let us derive the lever rule from phase diagram through two conservation of- mass expressions.

With the first, since only two phases are present, the sum of their mass fractions must be equal to unity; that is

$W\alpha + W_L = 1$

For the second, the mass of one of the components (either Cu or Ni) that is present in both of the phases must be equal to the mass of that component in the total alloy, or

$W\alpha C\alpha + W_L C_L = C_0$

Simultaneous solution of these two equations leads to the lever rule expressions for this particular situation, Solving above equations give

W_L _= ($C\alpha$ - C_0)/($C\alpha$ - C_L))

$W\alpha$ = (C_0 - C_L)/($C\alpha$ - C_L)

.It is easy to confuse the foregoing procedures for the determination of phase compositions and fractional phase amounts; thus, a brief summary is warranted. *Compositions* of phases are expressed in terms of weight percents of the components (e.g., wt% Cu, wt% Ni).

For any alloy consisting of a single phase, the composition of that phase is the same as the total alloy composition.

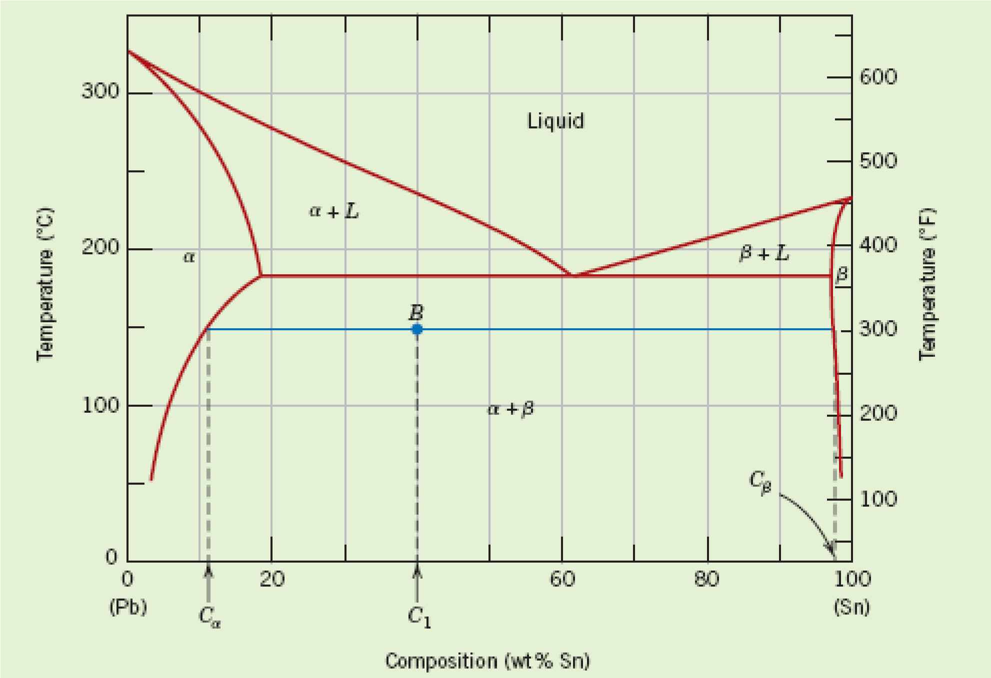
If two phases are present, the tie line must be employed, the extremities of which determine the compositions of the respective phases. The lever rule is utilized to find out phase amounts.

Assignment

Q.1. A hypothetical A–B alloy of composition 40 wt% B–60 wt% A at some temperature is found to consist of mass fractions of 0.66 and 0.34 for the α and β phases, respectively.

If the composition of the α phase is 13 wt% B–87 wt% A, what is the composition of the β phase?

Q.2. For a 40 wt% Sn–60 wt% Pb alloy at 150 ^{0}C (phase diagram shown below),



(a) What phase(s) is (are) present?

(b) What is (are) the composition(s) of the phase(s)?

(c) Calculate the relative amount of each phase present in terms of

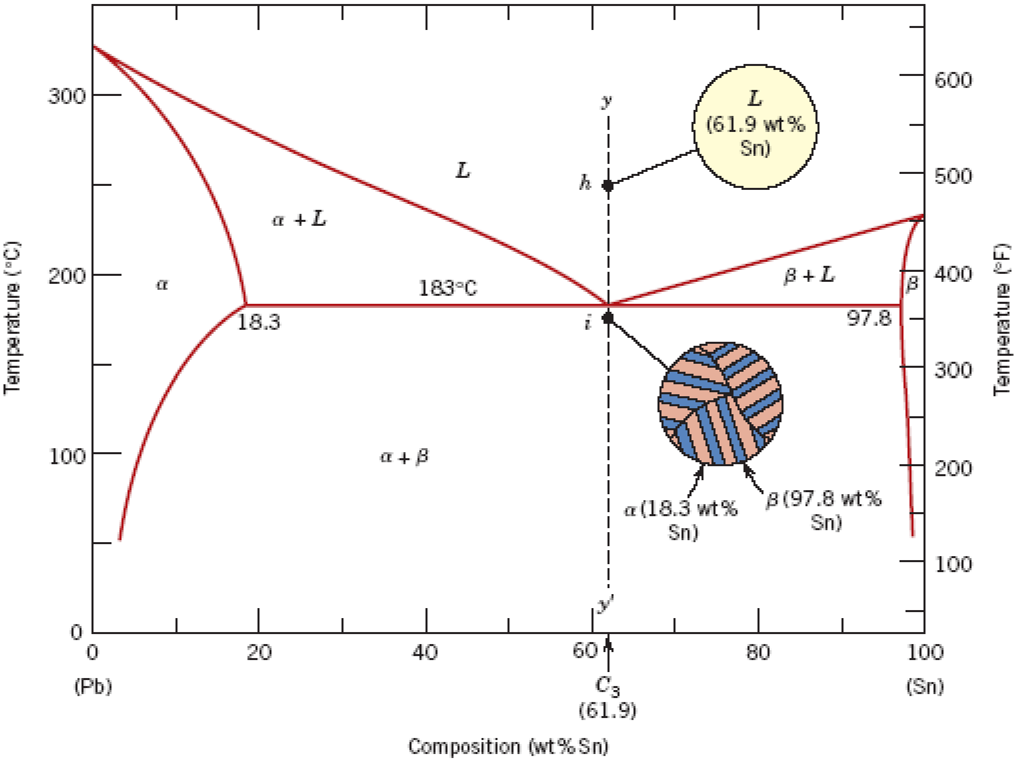
(a) mass fraction and

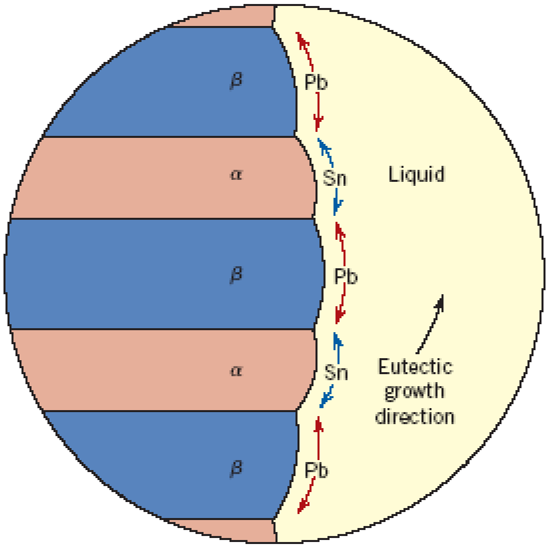
(b) volume fraction. At 150 ^{0}C take the densities of Pb and Sn to be 11.23 and 7.24 g/cm3, respectively.

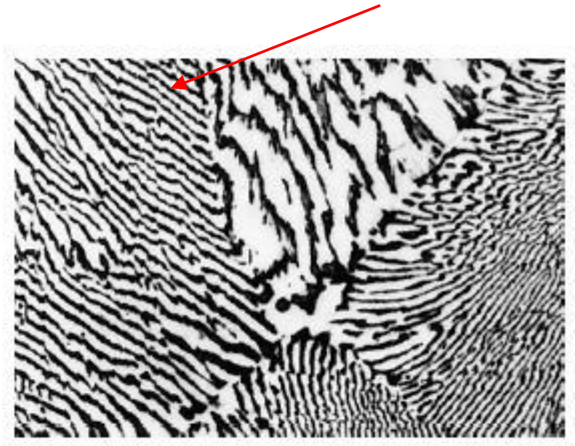
Q.3. Find out the relation between volume percentage, weight percentage and atmic percentage in a binary alloy.

(b) Eutectic system

Eutectic







Solidification of the eutectic composition, 61.9 wt% Sn shown above. Consider an alloy having this composition that is cooled from a temperature within the liquid-phase region down the vertical line yy'.

As the temperature is lowered from liquid region, no changes occur until we reach the liquidus i.e. eutectic temperature. Upon crossing the eutectic, the liquid transforms to two solid phases, α phase and β phase.

This is represented by the reaction

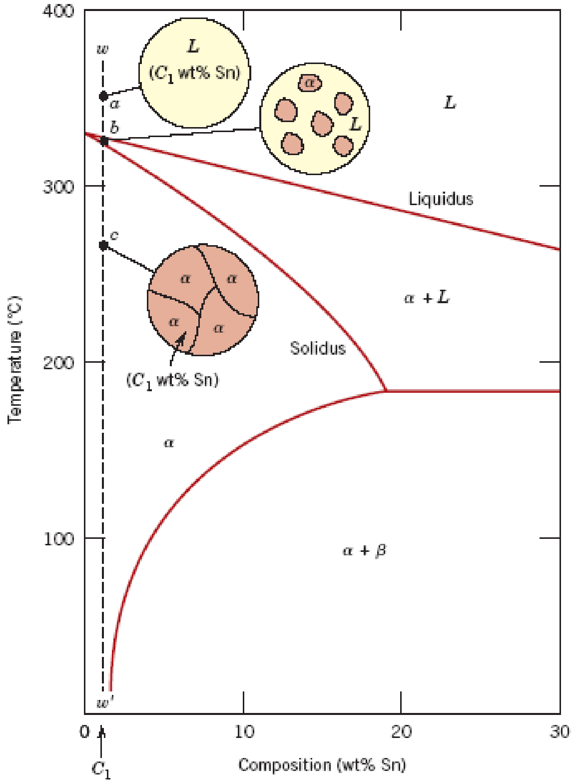
L (61.9 wt% Sn) → α (18.3 wt% Sn)+ β (97.8 wt% Sn) at eutectic temperature

The α- and β-phase compositions are dictated by the eutectic line end points. α-phase is lead-rich (18.3 wt% –81.7 wt% Pb); β-phase is tin-rich (97.8 wt% –2.2 wt% Pb)

The microstructure of the alloy will consist of alternating layers of α and β. This is also called lammelar structure or eutectic structure.

The microstructural change during solidification at eutectic is shown in Figure above; The layered solid eutectic (α+β) growing into and replacing the liquid phase. The process of the redistribution of lead and tin occurs by diffusion in the liquid just ahead of the eutectic–liquid interface. The arrows indicate the directions of diffusion of lead and tin atoms; lead atoms diffuse toward the α-phase layers since this phase is lead-rich (18.3 wt% –81.7 wt% Pb); conversely, the direction of diffusion of tin is in the direction of the tin-rich (97.8 wt% –2.2 wt% Pb) layers.

Hypo-Eutectic

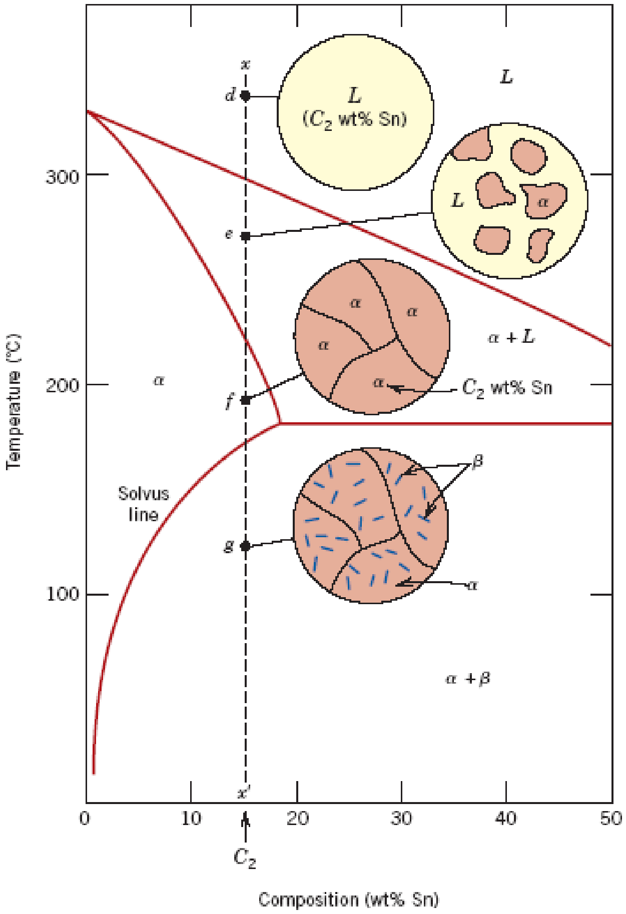


An alloy of C_1 composition is slowly cooled from the liquid-phase region (shown by dotted line),

The alloy remains totally liquid until the liquidus line. After crossing liquidus, the solid phase begins to form. It enters the two phase region (α+L).

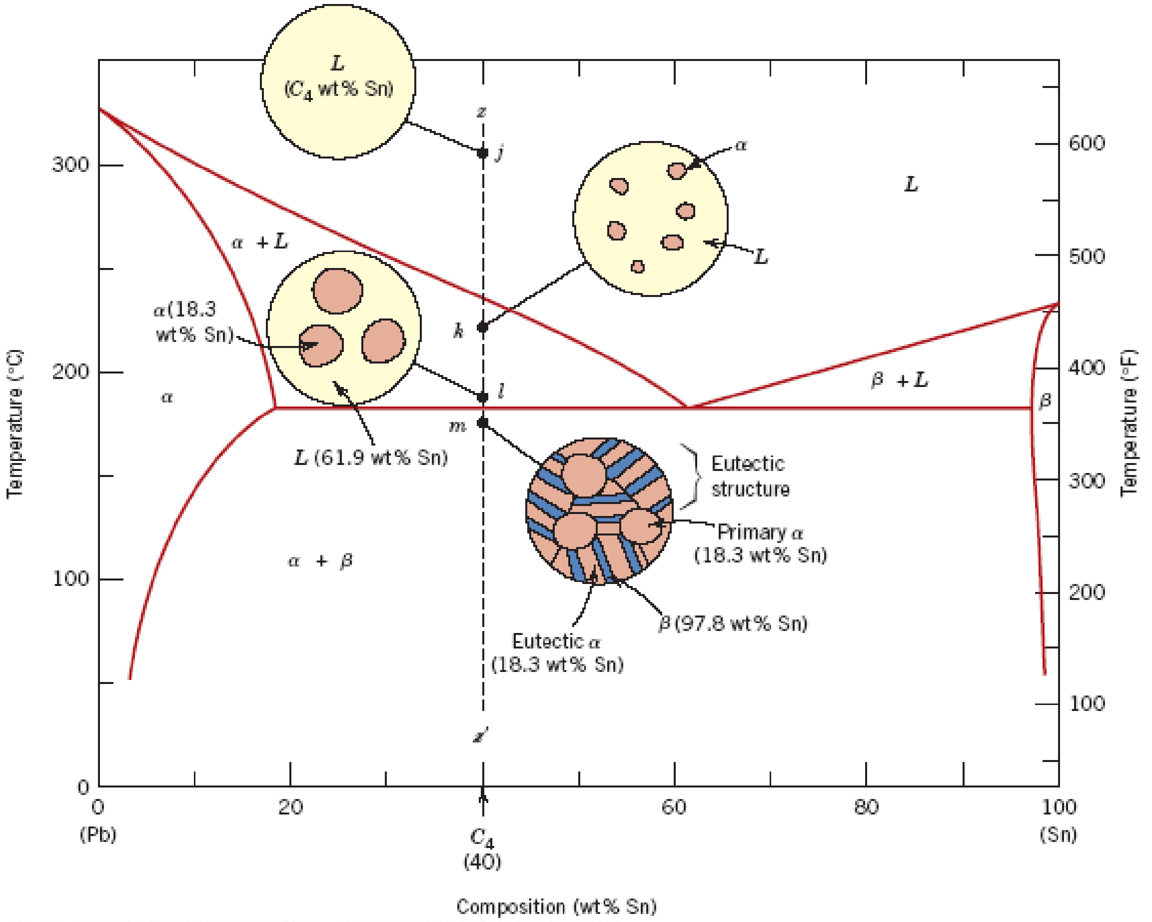
While passing through this narrow two phase region (α+L), solidification proceeds. With continued cooling more of the solid α forms. Liquid- and solid-phase compositions are different and follow along the liquidus and solidus phase boundaries, respectively. Solidification reaches completion at the point where it crosses the solidus line.

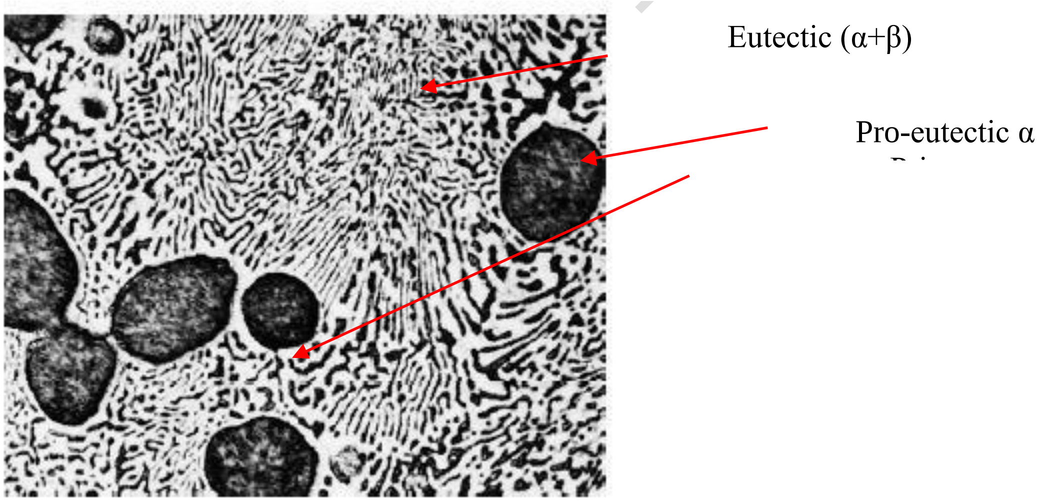
The resulting alloy consists of α-grains with a uniform composition of C_1, and no subsequent changes will occur upon cooling to room temperature. This microstructure is represented schematically by the inset at point c in above Figure.



Let us examine an alloy of composition as it is cooled along the vertical line xx′ at C2 composition. Cooling from liquid to point f can be explained as explained for composition C_1. Just above the solvus intersection, point *f*, the microstructure consists of grains of α of composition C_1. Upon crossing the solvus line, the solid solubility is exceeded, which results in the formation of small β-phase particles; these are indicated in the microstructure inset at point g. With continued cooling, these particles will grow in size because the mass fraction of the phase increases slightly with decreasing temperature

Hypo-Eutectic



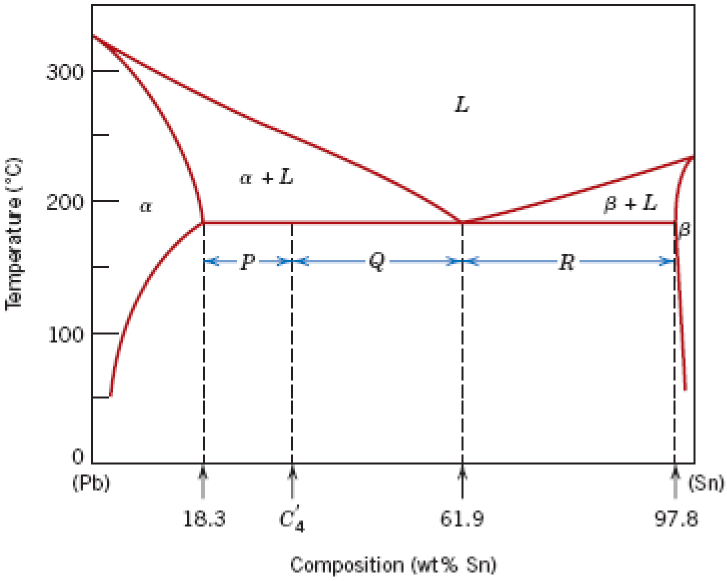


The microstructural development between points *j* and *l* is similar to that for the above case.

Just before eutectic (point *l*), the α and liquid phases are present having compositions of approximately 18.3 and 61.9 wt% respectively, as determined from the appropriate tie line.

As the temperature is lowered to just below the eutectic, the liquid phase, which is of the eutectic composition, will transform to the eutectic structure (i.e., alternating and lamellae); insignificant changes will occur with the phase that formed during cooling through the region. This microstructure is represented schematically by the inset at point *m* in Figure.Thus, the α phase will be present both in the eutectic structure and also as the phase that formed while cooling through the phase field. To distinguish one from the other, that which resides in the eutectic structure is called eutectic while the other that formed prior to crossing the eutectic isotherm is termed primary both are labeled in Figure below. The photomicrograph in Figure is of a lead–tin alloy in which both primary and eutectic structures are shown.

Application of Lever rule to eutectic systems



$$\boxed{W_e = W_L = \frac{P}{P + Q}}$$

$$= \frac{C_4' - 18.3}{61.9 - 18.3} = \frac{C_4' - 18.3}{43.6}$$

The fraction of the eutectic microconstituent W_e s just the same as the fraction of liquid from which it forms W_L

$$W_{\alpha'} = \frac{Q}{P+Q}$$

$$= \frac{61.9 - C_4'}{61.9 - 18.3} = \frac{61.9 - C_4'}{43.6}$$

Furthermore, the fraction of primary α is Wα just the fraction of the phase that existed prior to the eutectic transformation

$$W_{\alpha} = \frac{Q+R}{P+Q+R}$$

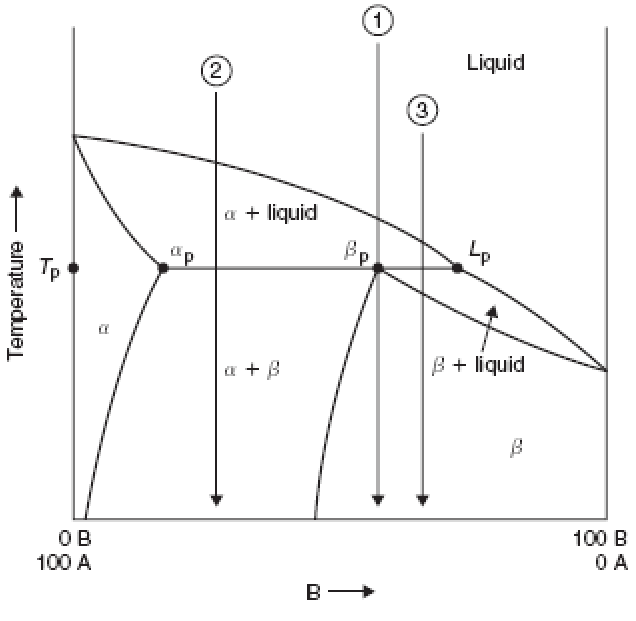
$$= \frac{97.8 - C_4'}{97.8 - 18.3} = \frac{97.8 - C_4'}{79.5}$$

$$W_{\beta} = \frac{P}{P+Q+R}$$

$$= \frac{C_4' - 18.3}{97.8 - 18.3} = \frac{C_4' - 18.3}{79.5}$$

The fractions of *total a* (both eutectic and primary), and also of total β are determined by use of the lever rule and a tie line that extends *entirely across the phase field*.

Peritectic System



When the melting points of the two components are fairly similar, eutectic systems often occur. But when the components have a large difference in melting points .,the peritectic reaction, is often found.

Examples are Cu–Zn (1083 & 419 0C), Nickel-rhenium (1455 & 3186) Ag–Pt systems

A simple form of peritectic system is shown in Figure above.

The peritectic line links three critical phase compositions; that is, ap, βp and liquid Lp. A peritectic reaction occurs if the average composition of the alloy crosses this line during either slow heating or cooling.

It can be represented by the equation $ap + Lp \rightarrow \beta p$.

Binary alloys containing less of component B than the point ap will behave in the same manner as previously described for eutectic α solid solutions.

Alloy 1, which is of peritectic composition, will freeze over a range of temperature, depositing crystals of primary a-phase. The melt composition will move down the liquidus, becoming richer in component B. At the peritectic temperature Tp, liquid of composition Lp will react with these primary αp crystals, transforming them completely into a new phase, β, of different crystal structure in accordance with the equation ap +Lp→βp. In the system shown, β remains stable during further cooling.

Alloy 2 will also deposit primary a, but the reaction at temperature Tp will not consume all these crystals and the final solid will consist of β formed by peritectic reaction and residual a.

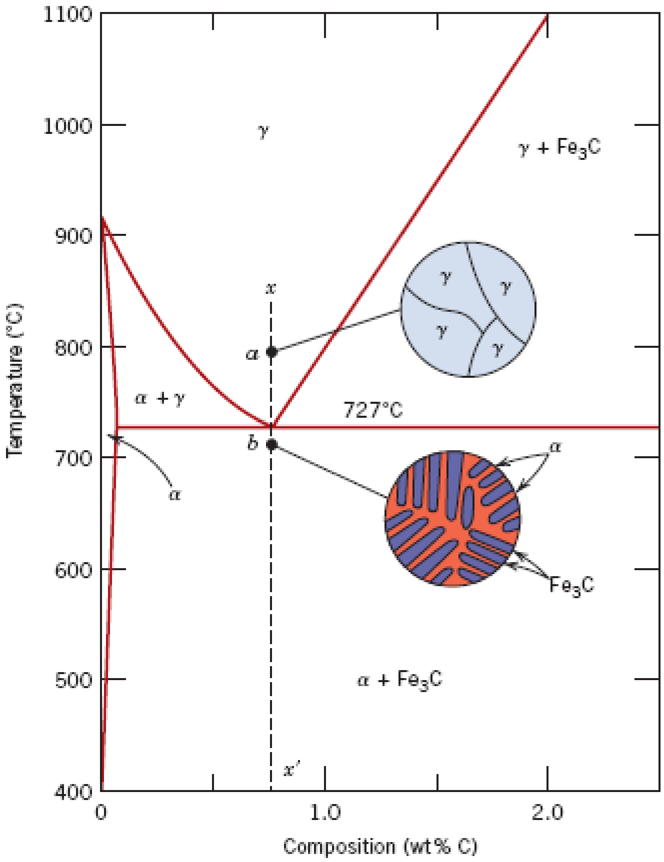
Alloy 3, fewer primary crystals of a form: later, they are completely destroyed by the peritectic reaction. The amount of β in the resultant mixture of β and liquid increases until the liquid disappears and an entire structure of β is produced.

The above descriptions assume that equilibrium is attained at each stage of cooling.

Eutectoid and peritectoid

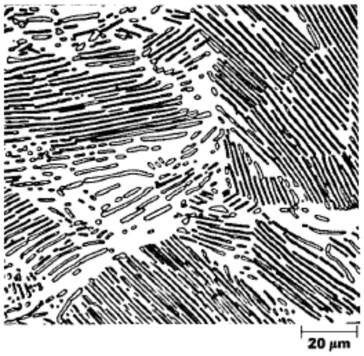
Eutectoid and peritectoid reactions occur wholly in the solid state.

The eutectoid reaction γ↔α+Fe3C is the basis of the heat treatment of steels. So it is important to understand it.

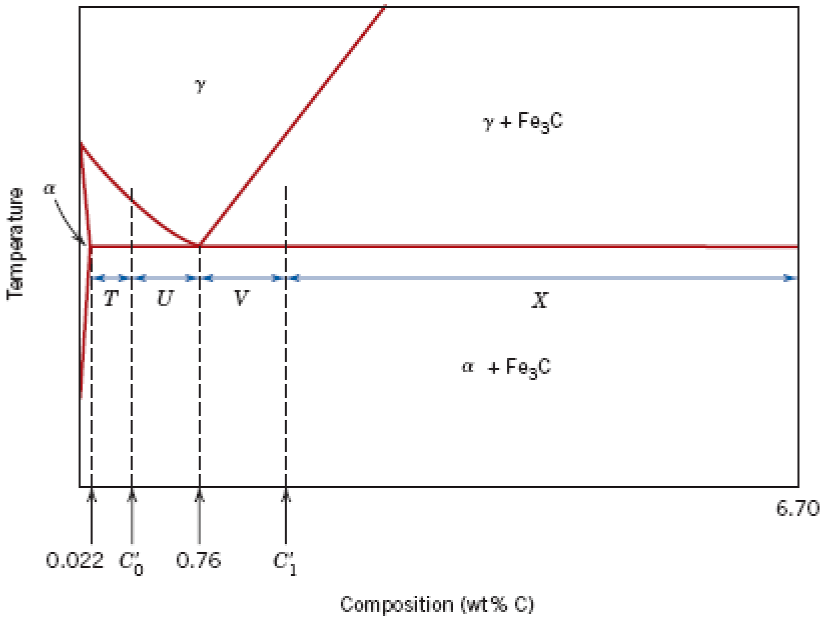


$$\gamma(0.76\text{ wt\% C}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(0.022\text{ wt\% C}) + Fe_3C\,(6.7\text{ wt\% C})$$

The microstructure for this eutectoid steel that is slowly cooled through the eutectoid temperature consists of alternating layers or lamellae of the two phases (α and Fe3C) that form simultaneously during the transformation. It is shown below.



P toid steel showing the pearlite microstructure consisting of
a α (the light phase) and Fe3C (thin layers most of which
a
A o hypo-eutectoid (< 0.77 wt% C, i.e eutectoid) and hyper-
e C)



$$W_{p} = \frac{T}{T + U}$$

$$= \frac{C'_0 - 0.022}{0.76 - 0.022} = \frac{C'_0 - 0.022}{0.74}$$

Fraction of proeutectoid is computed as follows:

$$W_{\alpha'} = \frac{U}{T + U}$$

$$= \frac{0.76 - C'_0}{0.76 - 0.022} = \frac{0.76 - C'_0}{0.74}$$

$$W_{p} = \frac{X}{V + X} = \frac{6.70 - C'_1}{6.70 - 0.76} = \frac{6.70 - C'_1}{5.94}$$

$$W_{\mathrm{Fe_3C'}} = \frac{V}{V + X} = \frac{C'_1 - 0.76}{6.70 - 0.76} = \frac{C'_1 - 0.76}{5.94}$$

Phase mass fraction to phase volume fraction

Volume fraction of phase α, Vα, is defined by

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta}$$

where vα and vα are the volumes of the respective phases in the alloy. Furthermore, the density of each phase is equal to the ratio of its mass and volume, or upon rearrangement

$$v_\alpha = \frac{m_\alpha}{\rho_\alpha}$$

$$v_\beta = \frac{m_\beta}{\rho_\beta}$$

Substitution of these expressions

$$V_\alpha = \frac{\dfrac{m_\alpha}{\rho_\alpha}}{\dfrac{m_\alpha}{\rho_\alpha} + \dfrac{m_\beta}{\rho_\beta}}$$

Phase volume fraction to phase mass fraction.

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta}$$

We know that density=mass/volume or mass=volume*density

$$m_\alpha = v_\alpha \rho_\alpha$$

$$m_\beta = v_\beta \rho_\beta$$

Substituting, gives

$$W_\alpha = \frac{V_\alpha \rho_\alpha}{V_\alpha \rho_\alpha + V_\beta \rho_\beta}$$

Determination of Relative Amounts of Ferrite, Cementite, and Pearlite Microconstituents

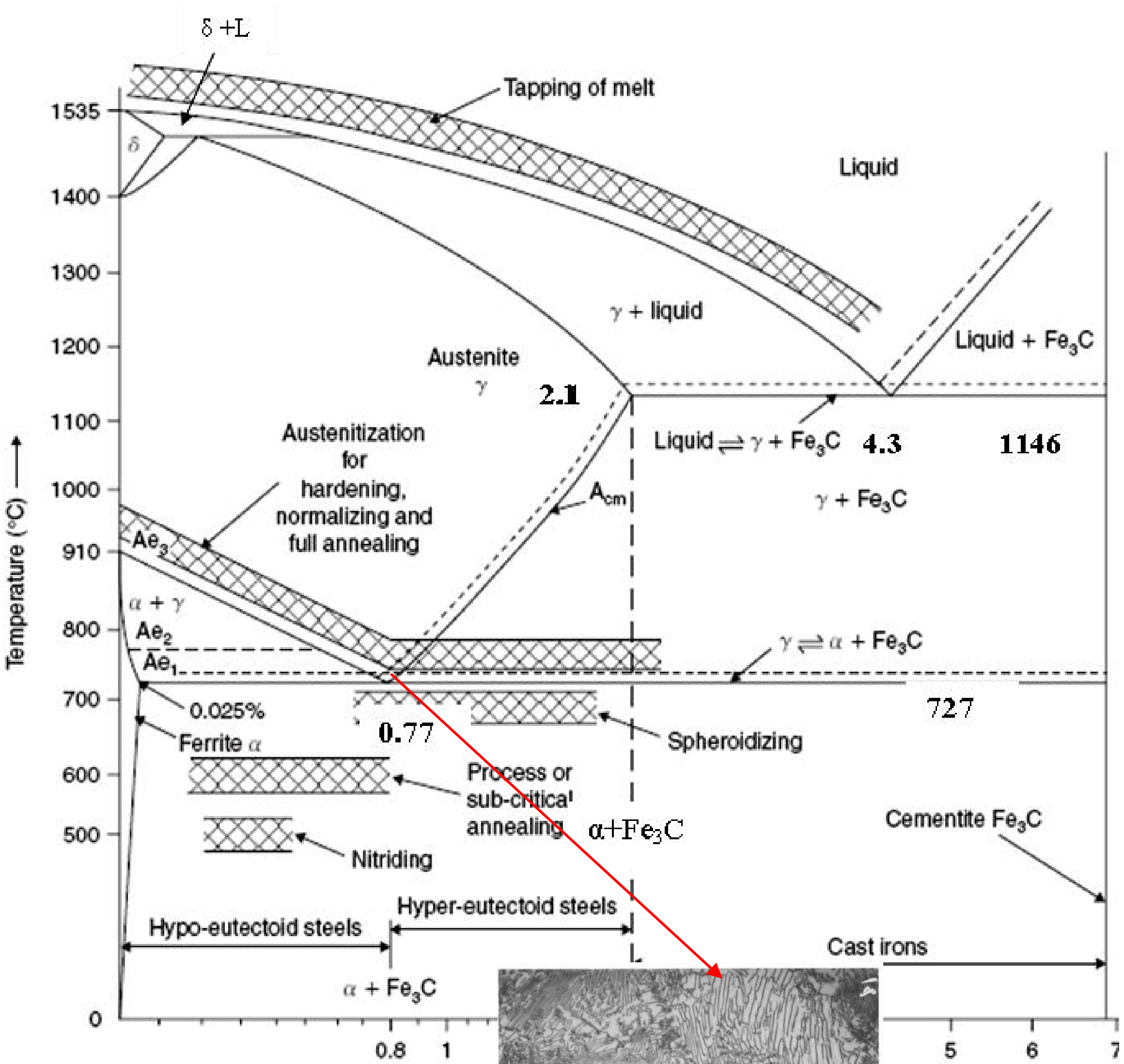
For a 99.65 wt% Fe–0.35 wt% C alloy at a temperature just below the eutectoid, determine the following:

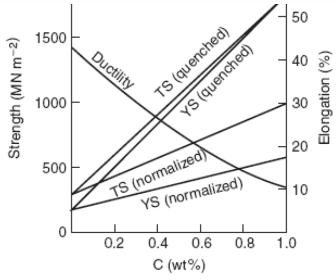
(a) The fractions of total ferrite and cementite phases

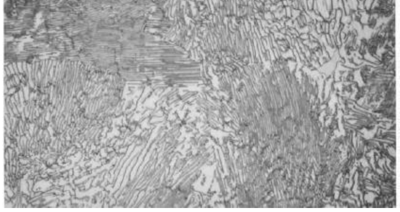
(b) The fractions of the proeutectoid ferrite and pearlite

(c) The fraction of eutectoid ferrite

Iron-cementite and iron-graphite phase diagrams

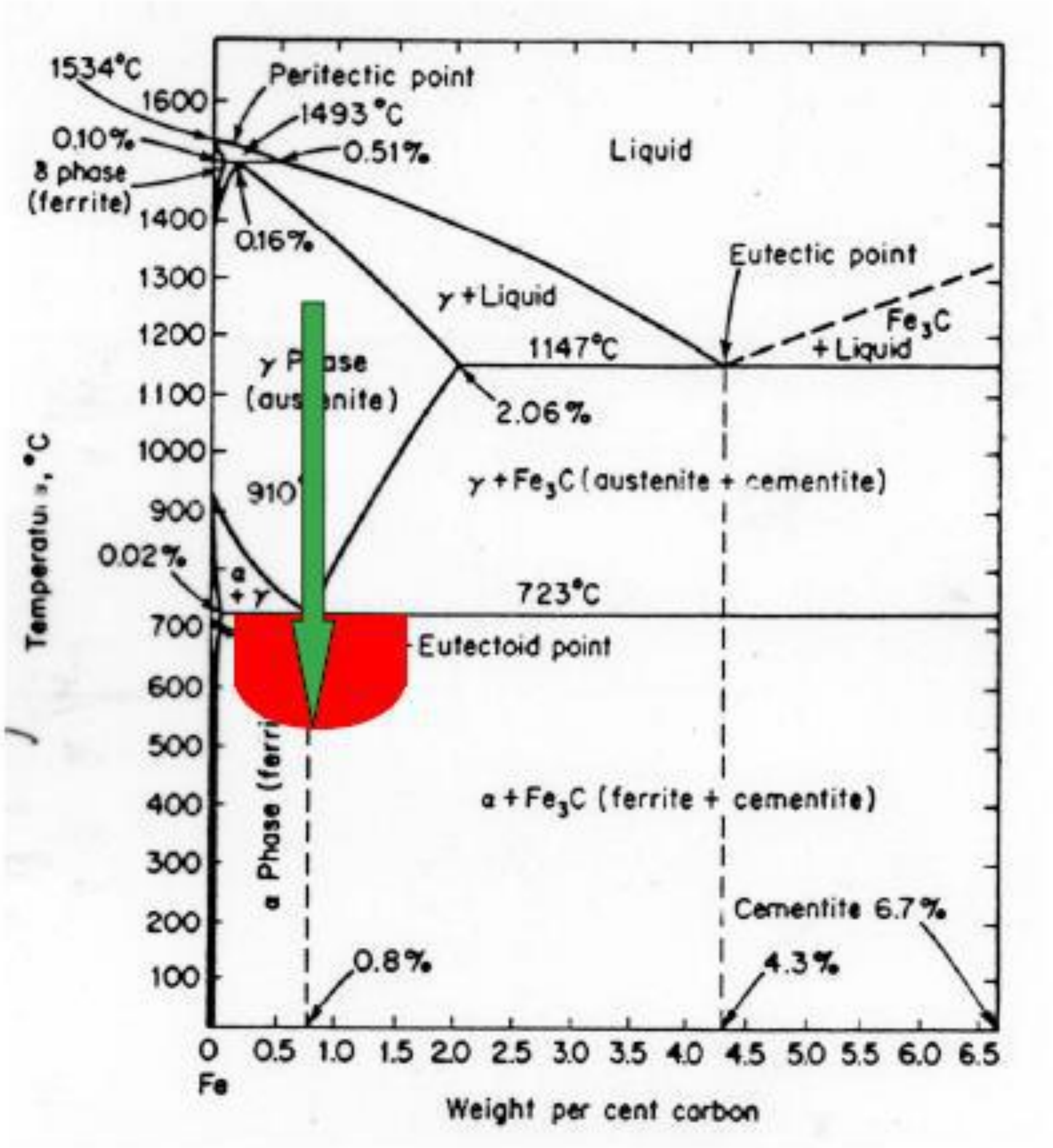


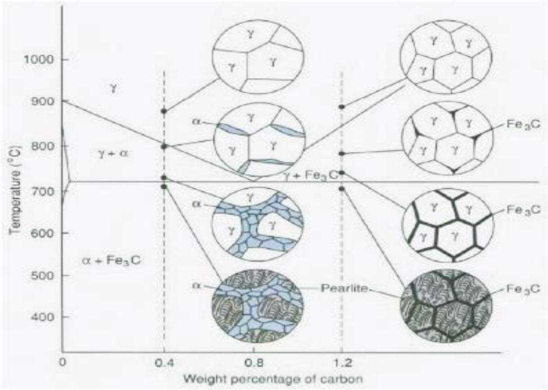




Pearlite

(Alternative Lamellae of Ferrite and Cementite)


1534°C
Peritectic point
1493°C
0.10%
0.51%
δ phase (ferrite)
0.16%
Liquid
Eutectic point
γ + Liquid
Fe3C + Liquid
1147°C
γ Phase (austenite)
2.06%
910°
γ + Fe3C (austenite + cementite)
0.02%
α + γ
723°C
Eutectoid point
α Phase (ferrite)
α + Fe3C (ferrite + cementite)
Cementite 6.7%
0.8%
4.3%
Temperature, °C
1600
1400
1300
1200
1100
1000
900
700
600
500
400
300
200
100
0
Fe
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
Weight per cent carbon



Equilibrium phase transformations in hypoeutectoid and hypereutectoid steels together with schematic microstructures.

The difference between iron-cementite and iron-graphite diagram

Iron cementite microstructures consists of α-phase and cementite. Cementite (Fe3C) is a metastable compound, and under some circumstances it can be made to dissociate or decompose to form ferrite and graphite, according to the reaction

Fe3C → 3Fe(α)+ C (graphite)

This tendency to form graphite is controlled by the composition and rate of cooling. Graphite formation is promoted by the presence of silicon in concentrations greater than about 1 wt%. Also, slower cooling rates during solidification favor graphitization (the formation of graphite).

Eutectic and eutectoid temperatures for the Fe–Fe3C system are 1147 ^{0}C and 727 ^{0}C respectively, as compared to 1153 ^{0}C and 740 ^{0}C for Fe–C); however, iron-graphite diagram extends to 100 wt% carbon such that graphite is the carbon rich phase, instead of cementite at 6.7 wt% C in iron-cementite diagram

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.

Alloy steels

The principal objectives in adding alloying elements to steel are:

(i) to improve and extend the existing properties of plain carbon steels;

(ii) to introduce new properties not available in plain carbon steels.

Thus the addition of small quantities of nickel and chromium will produce a general improvement in the basic mechanical properties of strength and toughness, whilst larger amounts of these elements will introduce new phenomena such as the stabilisation of austenite at ambient temperatures, a very high resistance to corrosion. The alloying elements added may either simply dissolve in the ferrite or they may combine with some of the carbon, forming carbides.

The principal effects which alloying elements have on the microstructure and properties of an alloy steel can be classified as follows:

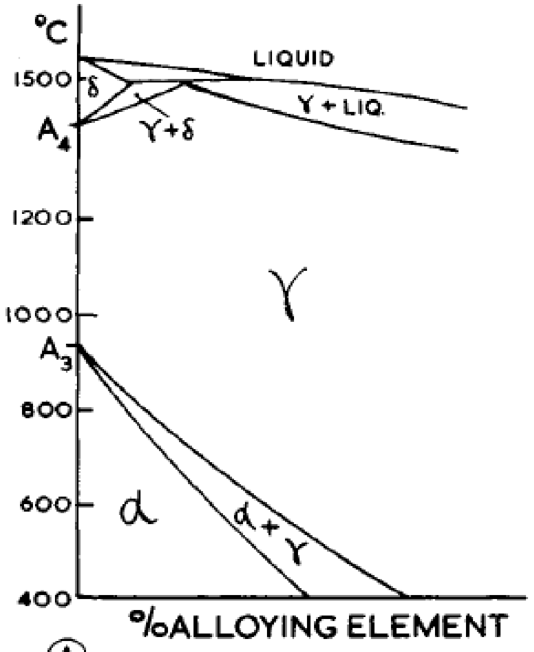
The Effect on the Polymorphic Transformation Temperatures

The polymorphic transformation temperatures which concern us here are those at 910 ^{0}C where the α→ γ transformation occurs; and at 1400 ^{0}C where the $\gamma \rightarrow \delta$ change takes place. That is, when BCC (α) iron is heated above 910 0C it transforms to FCC (γ) iron and if heated further to 1400 0C it changes again to BCC (δ) iron. These transformations are reversible on cooling. The temperatures 9100C and 14000C are designated *A3* and *A4* respectively (Fig. below).

Some elements (having FCC structure), notably nickel, manganese, cobalt and copper, raise the *A4* temperature and lower *A3* as shown in Fig. A. Therefore these elements, when added to a carbon steel tend to stabilise austenite (γ) still further and increase the range of temperature over which austenite can exist as a stable phase.

Other elements(having BCC structure), the most important of which include chromium, tungsten, vanadium, molybdenum, aluminium and silicon, have the reverse effect, in that they tend to stabilise ferrite (a) by raising the *A3* temperature and lowering the *A4*, as indicated in Fig. B. Such elements restrict the field over which austenite may exist, and thus form what is commonly called a 'gamma (y) loop'. Many of the elements of the austenite-stabilising group have a FCC crystal structure like that of austenite. They therefore dissolve substitutionally with ease in austenite and consequently resist and retard the transformation of austenite to ferrite. Carbon itself has the same effect on the transformation of austenite to ferrite, as indicated in the iron-carbon diagram, because it dissolves interstitially in FCC iron but not significantly in BCC iron. This group of elements retards the precipitation of carbides and this also has the effect of stabilising austenite over a wider range of temperature.

The ferrite-stabilising elements are principally those which, like α-iron have a BCC crystal structure. They will therefore dissolve substitutionally more readily in α-iron than in γ-iron, thus stabilising ferrite (α) over a wider temperature range. As shown in Fig. progressive increase in one or more of the stabilising elements will cause a point to be reached, beyond the confines of the γloop, where the γ-phase cannot exist at any temperature. Thus the addition of more than 30% chromium to a steel containing 0.4% carbon would lead to the complete suppression of the polymorphic transformations, and such a steel would no longer be amenable to normal heat-treatment



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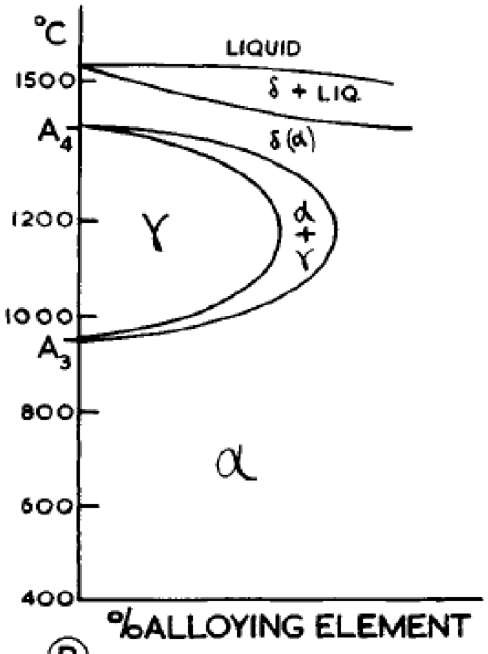

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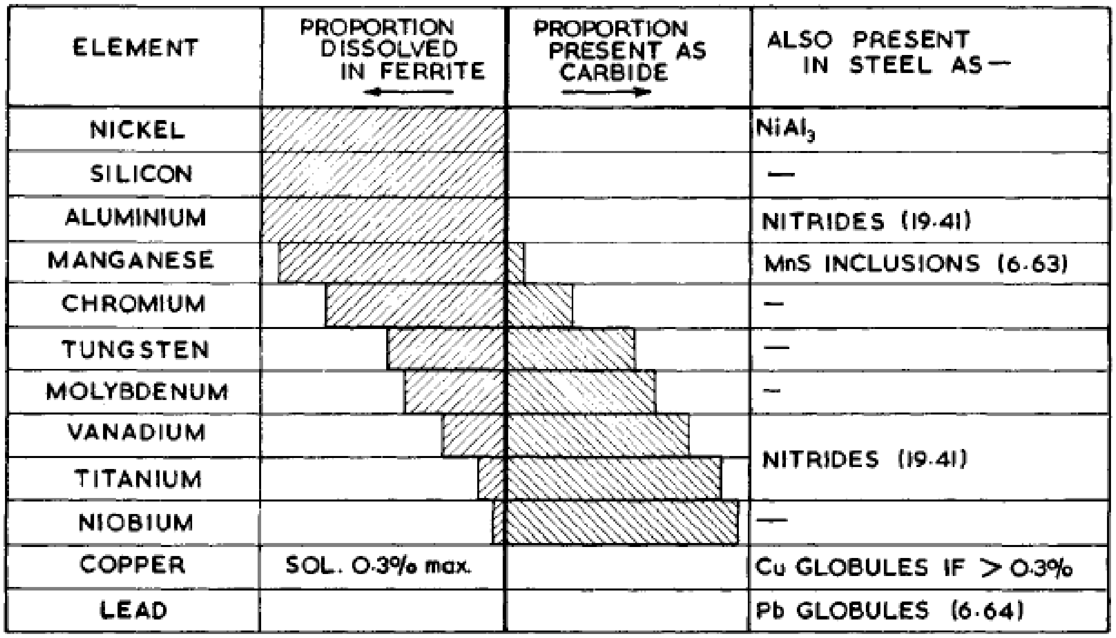
Relative effects of the addition of an alloying element on the polymorphic transformation temperatures at A3 and A4 (A) Tending to stablise γ and (B) tending to stabilise α

The Effect on the Formation and Stability of Carbides

Some alloying elements form very stable carbides when added to steel (Fig. below). This generally hardens the steel, particularly when the carbides formed are harder than iron carbide itself. Such elements include chromium, tungsten, vanadium, molybdenum, titanium and niobium, often forming interstitial compounds. eg Cr23C_6, W2C, Mo2C, VC



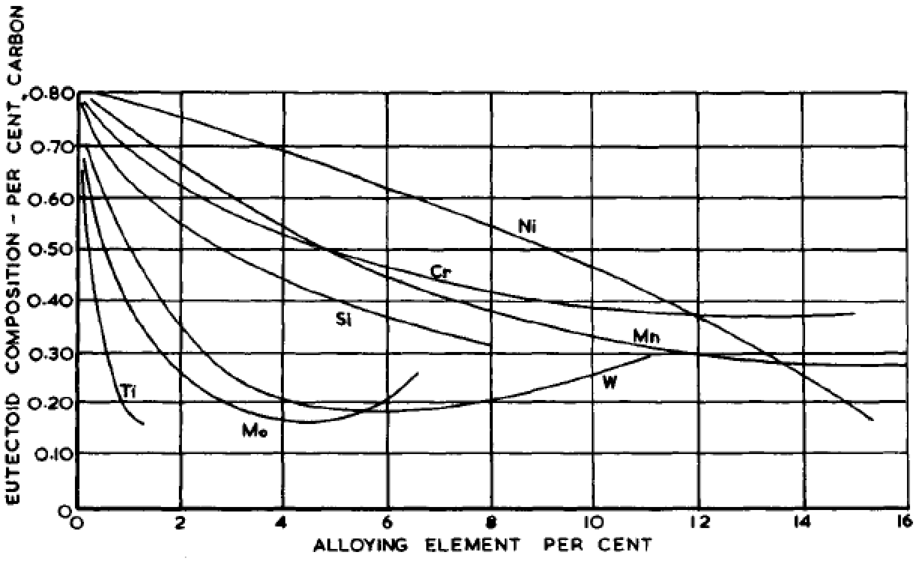
ELEMENT	PROPORTION DISSOLVED IN FERRITE ←	PROPORTION PRESENT AS CARBIDE →	ALSO PRESENT IN STEEL AS—
NICKEL			$NiAl_3$
SILICON			—
ALUMINIUM			NITRIDES (19·41)
MANGANESE			MnS INCLUSIONS (6·63)
CHROMIUM			—
TUNGSTEN			—
MOLYBDENUM			—
VANADIUM			NITRIDES (19·41)
TITANIUM			
NIOBIUM			—
COPPER	SOL. 0·3% max.		Cu GLOBULES IF > 0·3%
LEAD			Pb GLOBULES (6·64)

The physical states in which the principle alloying elements exist when in steel.

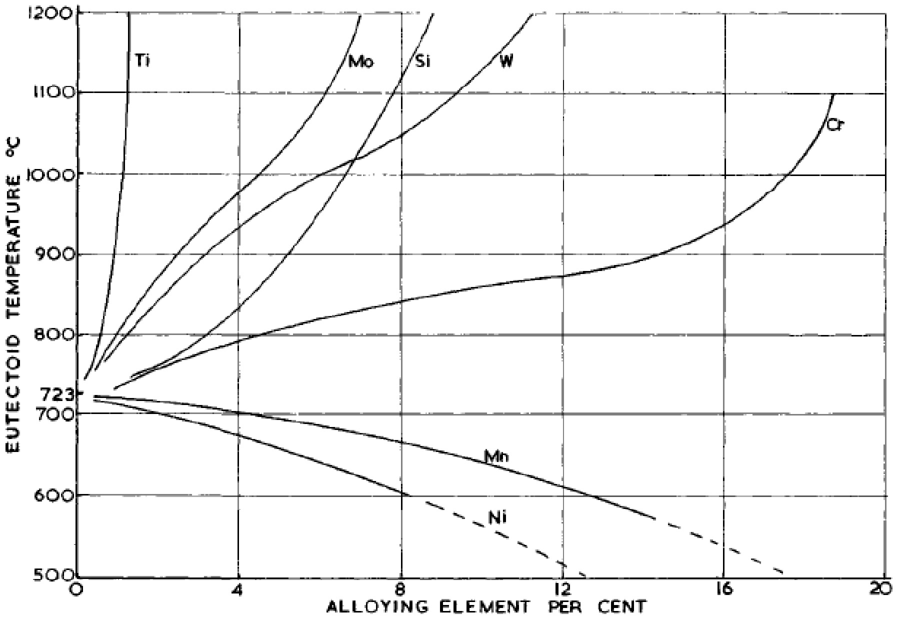
The Effect on Grain Growth The rate of crystal growth is accelerated, particularly at high temperatures, by the presence of some elements, notably chromium. Fortunately, grain growth is retarded by other elements notably vanadium, titanium, niobium, aluminium and to a small extent, nickel. Steels containing these elements are less sensitive to the temperature conditions of heat-treatment. Vanadium is possibly the most potent grain-refining element. As little as 0.1% will inhibit grain-growth by forming finely dispersed carbides and nitrides which, being relatively insoluble at high temperatures, act as barriers to grain-growth. Titanium and niobium behave in a similar manner, whilst in high-alloy tool steels the carbides of tungsten and molybdenum reduce grain growth at the necessarily high heat-treatment temperatures.

The Displacement of the Eutectoid Point The addition of any alloying element to carbon steel diminishes the solubility of carbon in austenite and so results in a displacement of the eutectoid point towards the left of the equilibrium diagram. That is, an alloy steel will be completely pearlitic even though it contains less than 0.8% carbon (Fig. 13.3). This explains why low-alloy steels contain less carbon than plain carbon steels of similar characteristics and uses. At the same time the *Ai* (or eutectoid) temperature is altered by alloying. The ferrite-stabilisers (chromium, tungsten, molybdenum, titanium, etc.) raise the eutectoid temperature in the same way that they

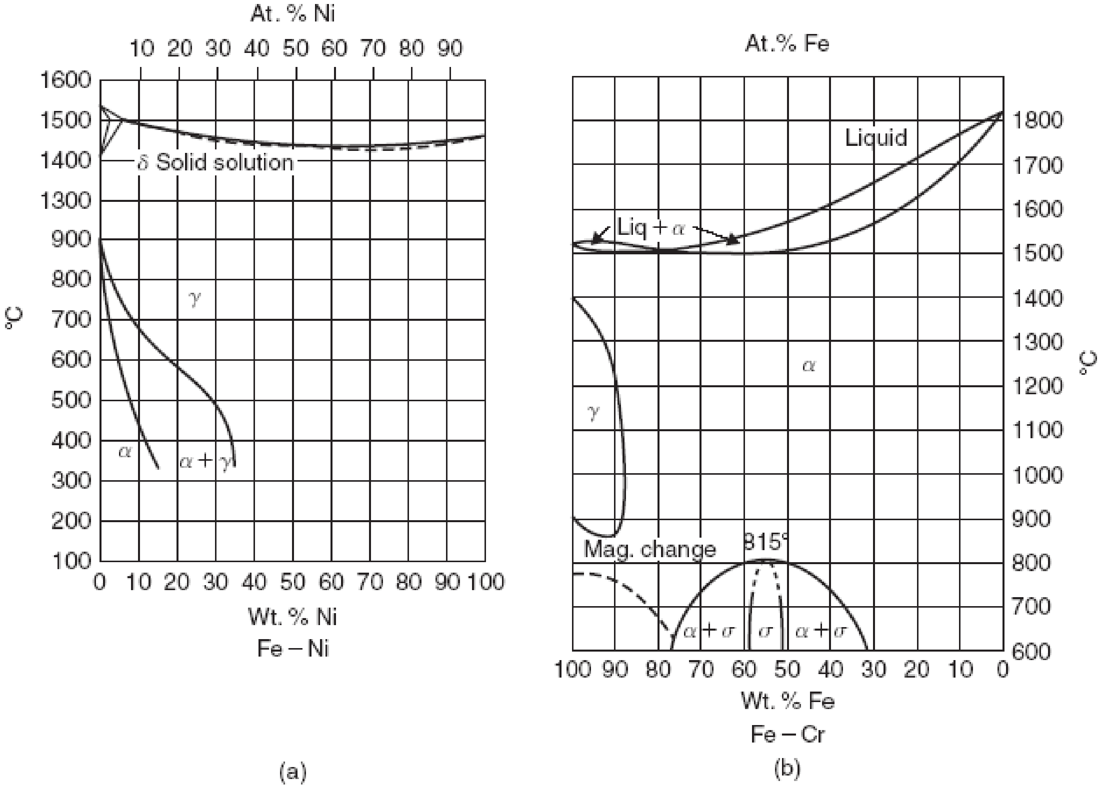
raise *A3;* whilst the austenite-stabilisers (nickel and manganese) lower the eutectoid temperature (Fig. 13.4). Thus the addition of 2.5% manganese to a steel containing 0.65% carbon will give it a completely pearlitic structure in the normalised condition, along with a reduction in the eutectoid temperature to about 7000C



The effect of alloying elements on the eutectoid composition.



The effect of alloying elements on the eutectoid temperature.



Effect of Ni (a) and Cr (b) on γ-field (from Smithells, 1967).

STAINLESS STEELS

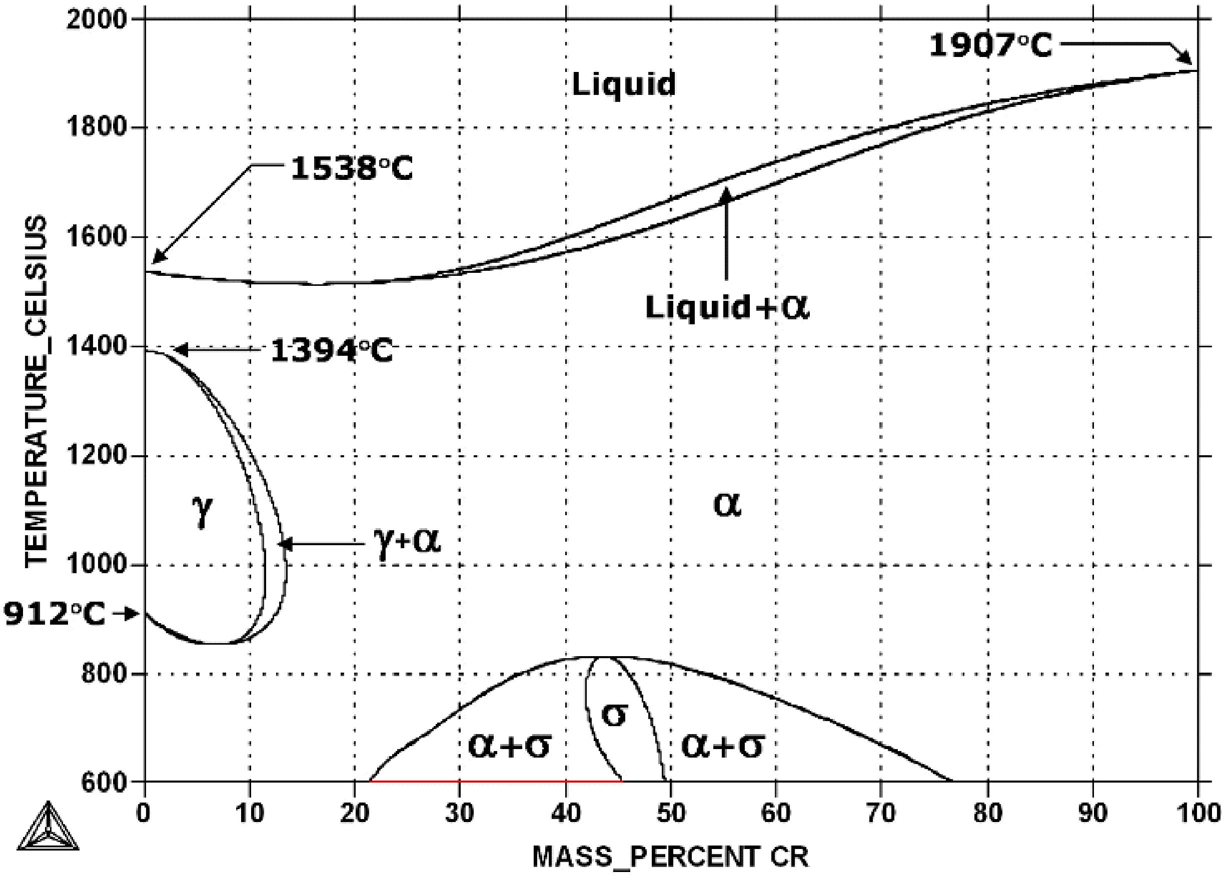
The stainless steels are highly resistant to corrosion (rusting) in a variety of environments, especially the ambient atmosphere. Their predominant alloying element is chromium; a concentration of at least 11 wt% Cr is required.

Stainless steel differs from carbon steel by the amount of chromium present. Carbon steel rusts when exposed to air and moisture. This iron oxide film (the rust) is active and accelerates corrosion by forming more iron oxide. Stainless steels contain sufficient chromium to form a passive film of chromium oxide Cr2O3, which prevents further surface corrosion and blocks corrosion from spreading into the metal's internal structure. Corrosion resistance may also be enhanced by nickel and molybdenum additions.

Stainless steels are divided into three classes on the basis of the predominant phase constituent of the microstructure—martensitic, ferritic, or austenitic. A wide range of mechanical properties combined with excellent resistance to corrosion make stainless steels very versatile in their applicability.

Martensitic stainless steels are capable of being heat treated in such a way that martensite is the prime microconstituent. Additions of alloying elements in significant concentrations produce dramatic alterations in the iron–iron carbide phase diagram). For austenitic stainless steels, the austenite (γ) phase field is extended to room temperature. Ferritic stainless steels are composed of the ferrite (BCC) phase.Austenitic and ferritic stainless steels are hardened and strengthened by cold work because they are not heat treatable. The austenitic stainless steels are the most corrosion resistant because of the high chromium contents and also the nickel additions; and they are produced in the largest quantities. Both martensitic and ferritic stainless steels are magnetic; the austenitic stainlesses are not. Some stainless steels are frequently used at elevated temperatures and in severe environments because they resist oxidation and maintain their mechanical integrity under oxidizing atmospheres. Equipment employing these steels includes gas turbines, high-temperature steam boilers, heat-treating furnaces, aircraft, missiles, and nuclear power generating units.

Stainless steels are generally chosen for service conditions where corrosion and oxidation resistance is important. In addition, they often have good creep strength, as cross-slip of screw dislocations is difficult due to the low stacking fault energy. They contain not less than 10-12%Cr and often Ni in addition. Chromium forms a protective passive film on the steel surface. Referring to the Fe-Cr phase diagram, Fig. 2.13, we note that, for Cr>12.7%, the ferrite phase becomes stable over the entire temperature range up to the melting point. In the presence of carbon, to produce an all-ferrite microstructure, we need (Cr- 17 X%C)>12.7. If this is less than 12.7%, we have the martensitic stainless steel, as martensite froms on cooling the high temperature austenite to room temperature. In austenitic stainless steels, the gamma stabilizres such as Ni and Mn are present in sufficient amounts to make austenite stable at room temperature.



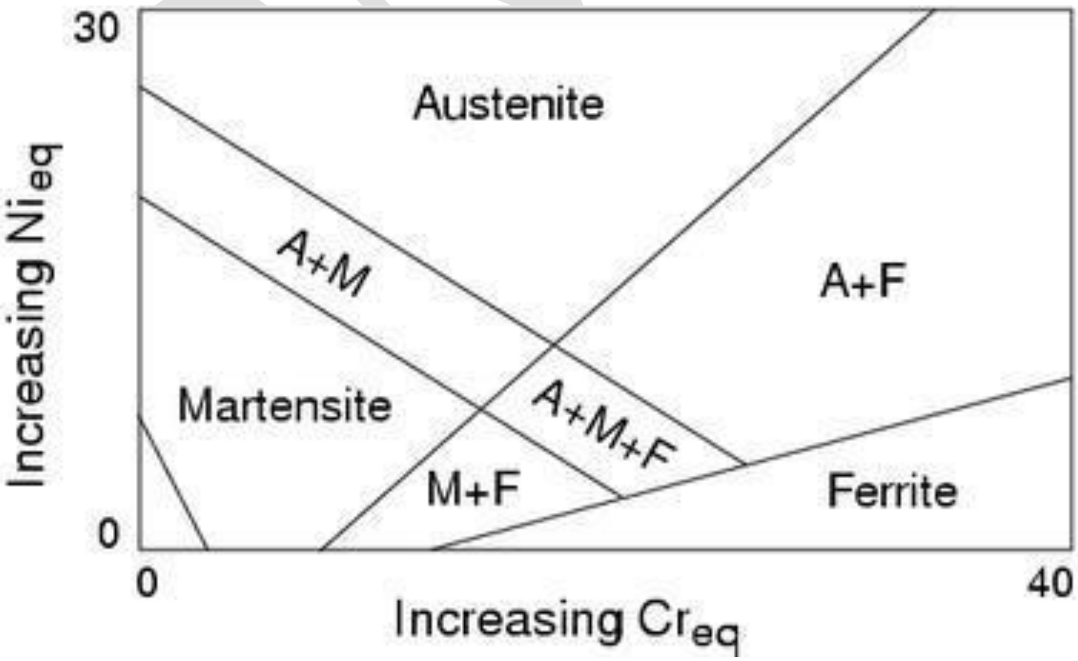
The effect of other elements present in Cr-Ni steels can be expressed as nickel equivalent if they stabilize the austenite and as chromium equivalent if they stabilize ferrite:

Ni equivalent = Ni +Co + 0.5Mn + 0.3Cu + 30C + 25N

Cr equivalent = Cr + 2Si + 1.5Mo + 5V + 5.5Al + 1.7Nb + 1.5Ti + 0.75W

The Schaeffler diagram (Fig. above) depicts the phases present in an alloy as a function of nickel and chromium equivalents. More recent thermodynamic calculations by this author indicate that the Ni and Cr equivalents are also a function of the annealing temperature.

In discussing the various stainless steels, we can follow the AISI classification, as it is widely understood. Three digits are used in this classification. The AISI 500 series steels contain 4-6%Cr and so are not true stainless steels. However, they are 5-10 times more resistant to sulphide corrosion that a carbon steel and 3 times more oxidation resistant. Typical uses are in the petroleum refining industry for valve bodies and cracking still tubes.



Ferritic stainless steels When (%Cr – 17 X %C) > 12.7, the stainless steel is in the ferrite state and cannot be heat treated, as austenite does not form at any temperature. The strength can be increased only by cold working. Grain refinement is done by recrystallization following cold work. AISI 430 with 16%Cr and 012%C max. and AISI 446 with 25%Cr and 0.20%C max. are typical examples. By virtue of the high chromium content, these steels possess excellent corrosion and oxidation resistance. Typical mechanical properties of 430 in the annealed condition are:

Y.S., MPa	T.S., MPa	% Elongation	Izod impact, J
350	550	30	75

The formability of ferritic stainless steels is poorer than that of the austenitic steels. In recent years, the formability has been improved considerably, by lowering the level of the interstitial carbon and nitrogen to 100 ppm (0.01%) by special processing techniques. Addition of 2%Mo to the basic compositions of 18%Cr and 25%Cr improves the resistance to pitting corrosion. By virtue of their lower cost (expensive nickel is not present!), the ferritic stainless steels with improved properties are competing with austenitic stainless steels in house – hold and transportation uses.

Martensitic stainless steels AISI 410 and 416 are typical of the low carbon martensitic varieties, with 12 – 14%Cr and 0.15%C max. Here (%Cr – 17 X %C) < 12.7. They respond to heat treatment, but due to the low carbon, the martensite is not brittle. Typical as-quenched properties are:

Hardness, R_C	Y.S., M Pa	T.S.,NPa	% Elongation

42	1200	1300
5		

The cutlery grade AISI 440B is typical of high carbon martensitic stainless steels, with 17%Cr and).75%C. The as – quenched hardness is 60 R_C. This grade is used for cutlery items, surgical instruments and high quality ball bearings.

Austenitic stainless steels: Austenitic stainless steels of the 300 series contain nickel as the austenite stabilizing element. When nickel is partly or fully replaced by the cheaper manganese, we have the 200 series.

In the 300 series, the most commonly used type is 304, with 18%Cr, 8%Ni, and 0.08%C max. The significance of the carbon content in relation to intergranular corrosion was discussed in sec. 6.8. The low carbon variety with 0.03%C max. is much les susceptible to intergranular corrosion. Addition of 2%Mo gives the 316 variety, which has better resistance to pitting and sulphuric acid.

The formability of the 18/8 austenitic stainless steels is excellent. The work hardening rate is high and is attributed to the very low stacking fault energy of 0.002J M^{-2} . The uniform elongation is also large. Typical tensile properties of 304 stainless steel are:

Y.S., MPa	T.S., MPa	% Elongation
240	600	65

By moderate working, the yield strength can be increased up to 1000 MPa. It is used in a very wide variety of applications in the chemical industry and for household and sanitary fittings.

Precipitation-hardened or controlled-transformation stainless steels contain, in addition to the basic compositon, Mo, Nb, Ti, or Al. Precipitates such s Ni_3Ti form on ageing and increase the strength. 17-7PH grade, for example, contains 1.15%Al in addition to 17%Cr and 7%Ni.

Tool Steels

Classification and property requirements: The production pf almost every object in industry requires tools. In addition to the familiar *hand tools*, there is a wide variety of *machine tools* used by7 industry. Tools play a vital role in industrial advancement. Most tools have been developed on the basis of shop floor experience. Nevertheless, the structure-property relationships in tool steels are better understood today, due to increasing availability of new data on phase relationships and T-T-T diagram.

Tools can be classified into the following types:

1. Cutting tools such as those used on a lathe,
2. *Shearing tools*: shears and blanking dies,
3. *Battering tools*: chisels, rail track tools and punches, and
4. *Forming tools*: forging dies, piercing tools, extrusion dies, die-casting dies and cold forming dies.

The general properties required of a tool are:

1. Wear and abrasion resistance, a property that is met by the presence of hard alloy carbides,
2. Toughness that is obtained with lower carbon contents,
3. red hardness is the ability to retain hardness at elevated temperatures, a property that is imparted by secondary hardening during tempering,
4. Nondeforming property is the resistance to distortion or dimensional changes during heat treatment, a property that is achieved by a high hardenability that permits air cooling hardening, and
5. Minimum cost, the steel should be no more expensive than is needed to meet the particular requirements.

Tool steel refers to a variety of carbon and alloy steels that are particularly well-suited to be made into tools. Their suitability comes from their distinctive hardness, resistance to abrasion, their ability to hold a cutting edge, and/or their resistance to deformation at elevated temperatures (red-hardness). Tool steel is generally used in a heat-treated state.

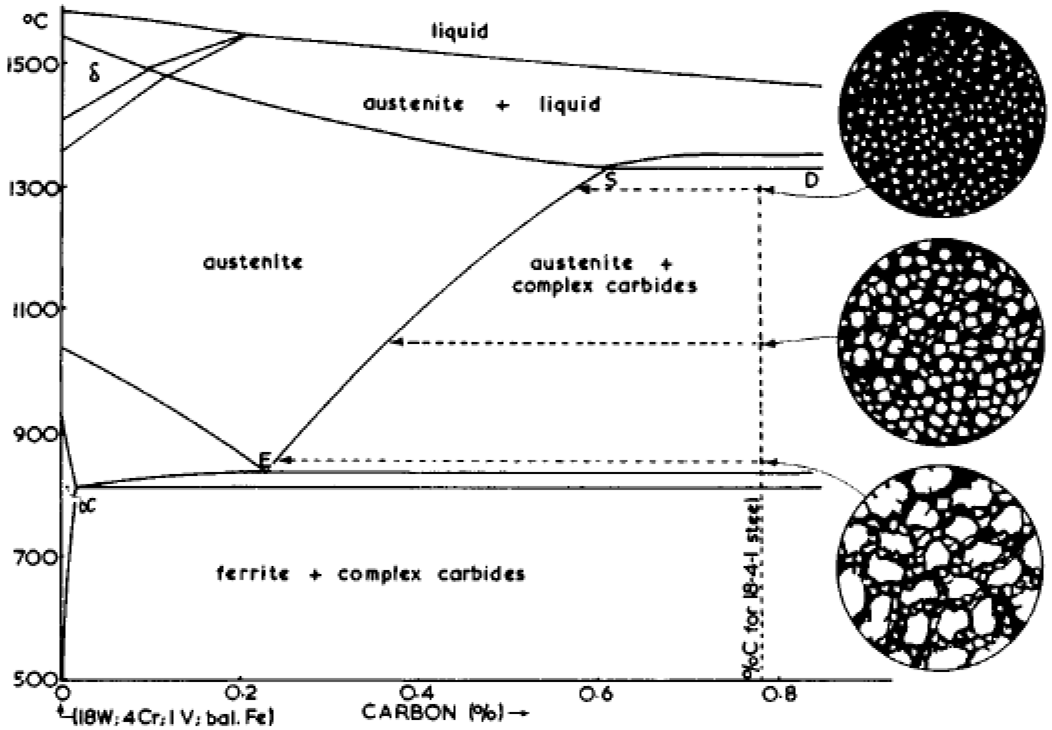
With a carbon content between 0.7% and 1.5%, tool steels are manufactured under carefully controlled conditions to produce the required quality. The manganese content is often kept low to minimize the possibility of cracking during water quenching. However, proper heat treating of these steels is important for adequate performance, and there are many suppliers who provide tooling blanks intended for oil quenching.

HSS

The term `high speed steel' was derived from the fact that it is capable of cutting metal at a much higher rate than carbon tool steel and continues to cut and retain its hardness even when the point of the tool is heated to a low red temperature. Tungsten is the major alloying element but it is also combined with molybdenum, vanadium and cobalt in varying amounts. Although replaced by cemented carbides for many applications it is still widely used for the manufacture of taps, dies, twist drills, reamers, saw blades and other cutting tools. 18-4-1 is an example. It contains 18%W, 4%Cr, 1%V, 0.7%C,.

The main features of a high-speed steel are its great hardness in the heat-treated condition, and its ability to resist softening at relatively high working temperatures. Thus, high-speed steel tools can be used at cutting speeds far in excess of those possible with ordinary steel tools, since high-speed steel resists the tempering effect of the heat generated. In high-speed steels ordinary cementite, Fe3C, is replaced by single or double carbides of three different groups based on the general formulae M6C; M23C6 and MC, where 'M' represents the total metallic atoms. Thus

M6C is represented by Fe4WiC and Fe4Mo2C, whilst M23C6 is present as $Cr_{23}C6$ and MC as WC and VC. Vanadium Carbide is very abrasion resistant and so improves cutting efficiency with abrasive materials. Since vanadium is also an important grain-refiner, this effect is very useful in high-speed steels because of the very high heat-treatment temperatures involved. It also increases the tendency towards air hardening by retarding transformation rates. Vanadium tends to stabilise the 6-ferrite phase (13.11) at high temperatures and this leads to carbide precipitation so that high-vanadium steels may be somewhat brittle. Nevertheless vanadium is now added in amounts up to 5.0% to modern high-speed steels. Up to 12.0% cobalt is also added to 'super' high-speed steels. Not being a carbide former it goes into solid solution and raises the solidus temperature, thus allowing higher heat-treatment temperatures to be used with a consequent increase in the solution of carbides and, hence, hardenability and wear-resistance. Since cobalt promotes excellent red-hardness these super-high-speed steels are useful for very heavy work at high speeds. As mentioned above, high-speed steels containing greater proportions of molybdenum are now widely used. Generally these alloys require greater care during heat-treatment, being more susceptible to decarburization than the tungsten varieties. With modern heat-treatment plant, however, this is not an unsurmountable difficulty. Molybdenum high-speed steels are considerably tougher than the corresponding tungsten types and are widely used for drills, taps and reamers. All of the metallic carbides mentioned above are harder than ordinary cementite, Fe3C, but the most important feature of high-speed steel is its ability to resist softening influences once it has been successfully hardened. This 'red' hardness, or resistance to softening at temperatures approaching red-heat, is due to tungsten, molybdenum, cobalt, etc being taken into solid solution in the austenite along with carbon before the steel is quenched. Further transformations in the resultant martensite are very sluggish as a result of the large quantities of alloying elements in solid solution, so that the steel can be raised to quite high temperatures before softening sets in due to carbide precipitation



A 'pseudo-binary' diagram representing the structure of 18-4-1 high-speed steel.

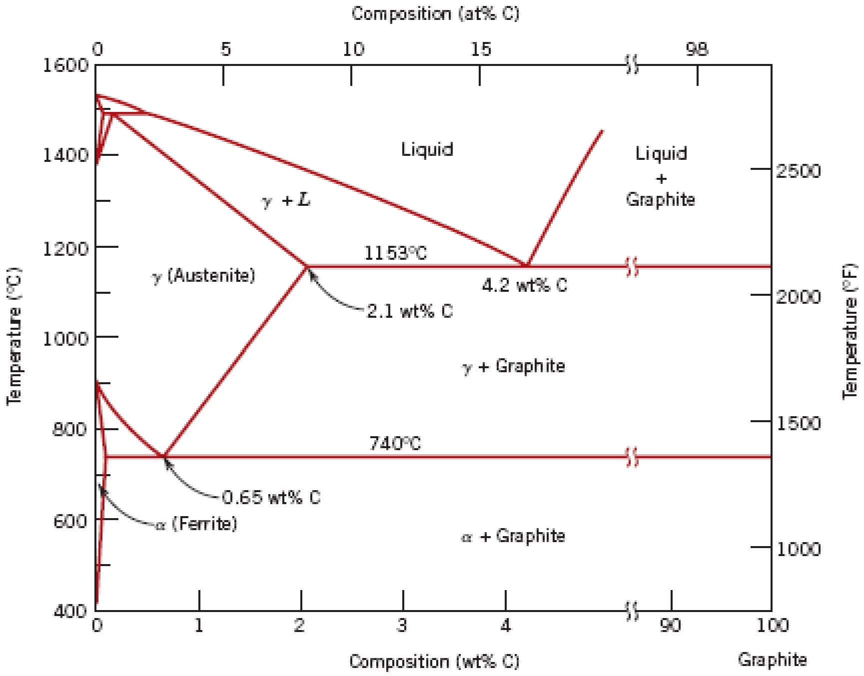
High-strength low-alloy (HSLA) steels

The requirement for structural steels to be welded satisfactorily has led to steels with lower C (<0.1%) content. Unfortunately, lowering the C content reduces the strength and this has to be compensated for by refining the grain size. This is difficult to achieve with plain C-steels rolled in the austenite range, but the addition of small amounts of strong carbide-forming elements (e.g. <0.1% Nb) causes the austenite boundaries to be pinned by second-phase particles and fine grain sizes (<10μm) to be produced by controlled rolling. Nitrides and carbonitrides as well as carbides, predominantly fcc and mutually soluble in each other, may feature as suitable grain refiners in HSLA steels; examples include AlN, Nb(CN), V(CN), (NbV)CN, TiC and Ti(CN). The solubility of these particles in the austenite decreases in the order VC, TiC, NbC while the nitrides, with generally lower solubility, decrease in solubility in the order VN, AlN, TiN and NbN. Because of the low solubility of NbC, Nb is perhaps the most effective grain size controller. However, Al,V andTi are effective in high-nitrogen steels, Al because it forms only a nitride, V and Ti by forming V(CN) and Ti(CN), which are less soluble in austenite than either VC or TiC.

The major strengthening mechanism in HSLA steels is grain refinement, but the required strength level is usually obtained by additional precipitation strengthening in the ferrite. VC, for example, is more soluble in austenite than NbC, so if V and Nb are used in combination, then on transformation of the austenite to ferrite, NbC provides the grain refinement and VC precipitation strengthening;

Solid-solution strengthening of the ferrite is also possible. Phosphorus is normally regarded as deleterious due to grain boundary segregation, but it is a powerful strengthener, second only to carbon. In car construction, where the design pressure is for lighter bodies and energy saving, HSLAsteels, rephosphorized and bake-hardened to increase the strength further, have allowed sheet gauges to be reduced by 10–15% while maintaining dent resistance. The bake hardening arises from the locking of dislocations with interstitials, as discussed in Chapter 6, during the time at the temperature of the paint-baking stage of manufacture.

Fe-Fe3C and presented in figure below.

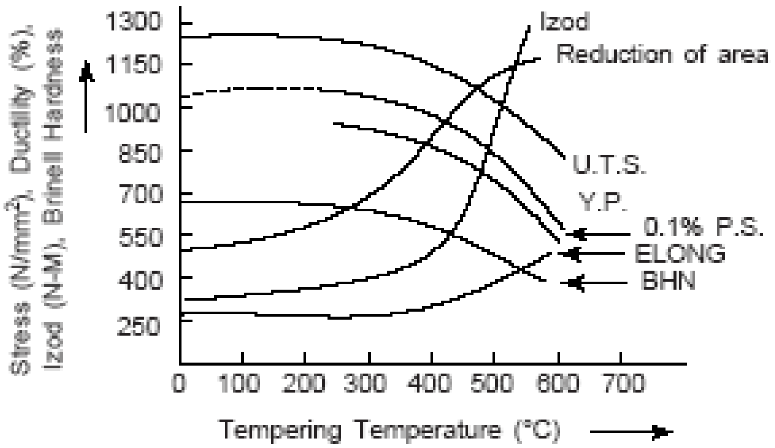


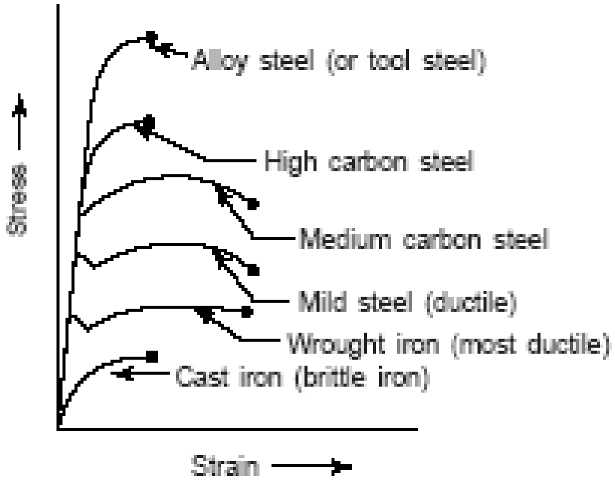
Steel Specifications

A widely used system for designating carbon and alloy steel grades has been developed by the American Iron and Steel Institute (AISI) and the Society of Automotive Engineers (SAE). Because AISI does not write specifications, currently only SAE designations are used

The SAE system consists of a four-digit AISI/SAE numbering system for the various chemical grades of carbon and alloy steels. The first two digits specify the major alloying elements, and if none are present, as for plain carbon steels, the first two digits are 10. The second two digits specify nominal carbon contents in hundredths of a percent. Tempering improves the ductility and toughness of quenched steel while decreases hardness. Figure 10.9

shows how these properties are affected by tempering. The tempering temperature is so chosen that it results





DIFFUSION

Diffusion is the process by which atoms move in a material. Many reactions in solids and liquids are diffusion dependent. Structural control in a solid to achieve the optimum properties is also dependent on the rate of diffusion.

Atoms are able to move throughout solids because they are not stationary but execute rapid, small-amplitude vibrations about their equilibrium positions. Such vibrations increase with temperature and at any temperature a very small fraction of atoms has sufficient amplitude to move from one atomic position to an adjacent one. The fraction of atoms possessing this amplitude increases markedly with rising temperature. In jumping from one equilibrium position to another, an atom passes through a higher energy state since atomic bonds are distorted and broken, and the increase in energy is supplied by thermal vibrations. As might be expected defects, especially vacancies, are quite instrumental in affecting the diffusion process on the type and number of defects that are present, as well as the thermal vibrations of atoms.

Diffusion can be defined as the mass flow process in which atoms change their positions relative to neighbors in a given phase under the influence of thermal and a gradient. The gradient can be a compositional gradient, an electric or magnetic gradient, or stress gradient. In this chapter we discuss diffusion because of concentration gradient only.

Diffusion mechanisms

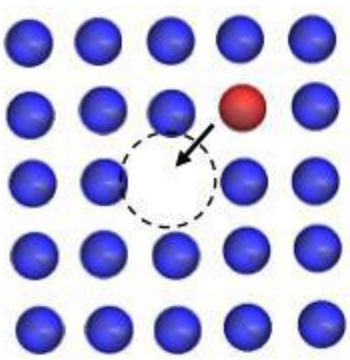
In pure metals self-diffusion occurs where there is no net mass transport, but atoms migrate in a random manner throughout the crystal. In alloys inter-diffusion takes place where the mass transport almost always occurs so as to minimize compositional differences. Various atomic mechanisms for self-diffusion and inter-diffusion have been proposed. presents schematic view of different atomic diffusion mechanisms.

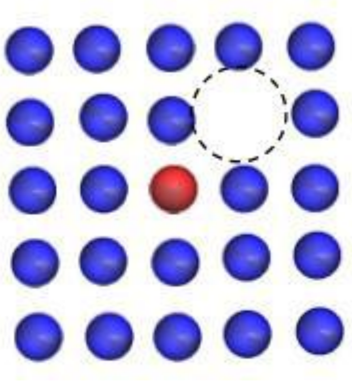
The most energetically favorable process involves an interchange of places by an atom and a neighboring vacancy – vacancy diffusion. This process demands not only the motion of vacancies, but also the presence of vacancies. The unit step in vacancy diffusion is an atom breaks its bonds and jumps into neighboring vacant site. In interstitial diffusion, solute atoms which are small enough to occupy interstitial sites diffuse by jumping from one interstitial site to another. The unit step here involves jump of the diffusing atom from one interstitial site to a neighboring site. Hydrogen, Carbon, Nitrogen and Oxygen diffuse interstitially in most metals, and the activation energy for diffusion is only that associated with motion since the number of occupied, adjacent interstitial sites usually is large. Substitutional diffusion generally proceeds by the vacancy mechanism. Thus interstitial diffusion is faster than substitutional diffusion by the vacancy mechanism. During self-diffusion or ring mechanism or direct-exchange mechanism, three or four atoms in the form of a ring move simultaneously round the ring, thereby interchanging their positions. This mechanism is untenable because exceptionally high activation energy would be required. A self-interstitial is more mobile than a vacancy as only small activation energy is required for self-interstitial atom to move to an equilibrium atomic position and simultaneously displace the neighboring atom into an interstitial site. However, the equilibrium number of self-interstitial atoms present at any temperature is negligible in comparison to the number of vacancies. This is because the energy to form a self-interstitial is extremely large.

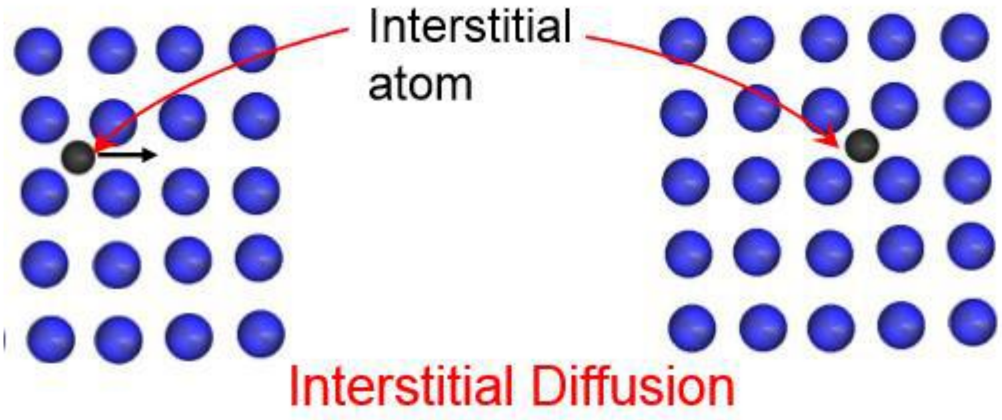
Diffusion in most ionic solids occurs by a vacancy mechanism. In ionic crystals, Schottky and Frankel defects assist the diffusion process. When Frenkel defects (pair of vacancyinterstial) dominate in an ionic crystal, the cation interstitial of the Frenkel defect carries the diffusion flux. If Schottky defects (pair of vacant sites) dominate, the cation vacancy carries the diffusion flux. In thermal equilibrium, in addition to above defects, ionic crystal may have defects generated by impurities and by deviation from stochiometry. Thus imperfections in ionic materials that influence diffusion arise in two ways: (1) intrinsic point defects such as Frenkel and schottky defects whose number depends on temperature, and (2) extrinsic point defects whose presence is due to impurity ions of different valance than the host ions. The former is responsible for temperature dependence of diffusion similar to that for self-diffusion in metals, while the latter result in a temperature dependence of diffusion which is similar to that for interstitial solute diffusion in metals.

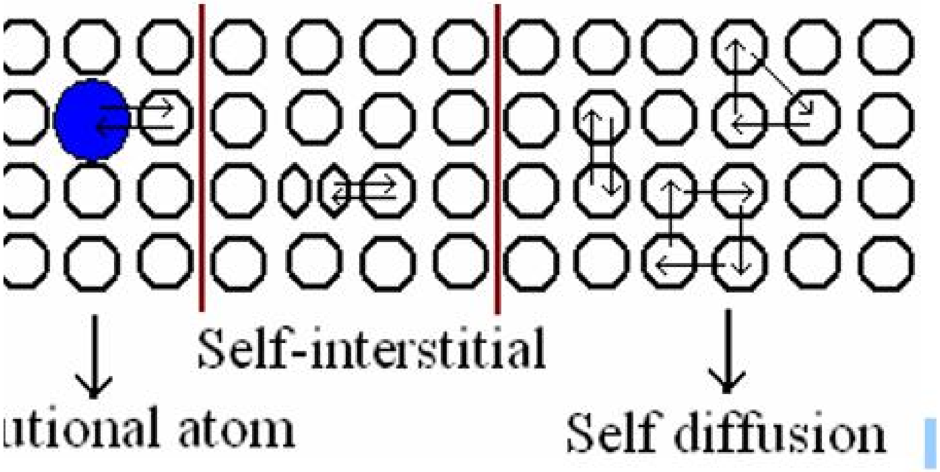
For example: Cd+2 cation in NaCl crystal will results in a cation vacancy. As Schottky defects form easily in NaCl crystal and thus cation vacancies carry the diffusion flux, even small fraction of Cd+2 increases the diffusivity of NaCl by several orders. Excess Zn+2 interstitials present in a non-stoichiometric ZnO compound increase the diffusivity of Zn+2 ions significantly. It is same with non-stoichiometric FeO.

In addition to diffusion through the bulk of a solid (volume diffusion), atoms may migrate along external or internal paths that afford lower energy barriers to motion. Thus diffusion can occur along dislocations, grain boundaries or external surfaces. The rates of diffusion along such short-circuit paths are significantly higher than for volume diffusion. However, most cases of mass transport are due to volume diffusion because the effective cross-sectional areas available for short-circuit processes are much smaller than those for volume diffusion.









Ficks laws of diffusion:

There is a difference between diffusion and net diffusion. In a homogeneous material, atoms also diffuse but this motion is hard to detect. This is because atoms move randomly and there will be an equal number of atoms moving in one direction than in another. In inhomogeneous materials, the effect of diffusion is readily seen by a change in concentration with time. In this case there is a net diffusion. Net diffusion occurs because, although all atoms are moving randomly, there are more atoms moving away from regions where their concentration is higher.

Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux. It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time. A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes

Fick'sLaw

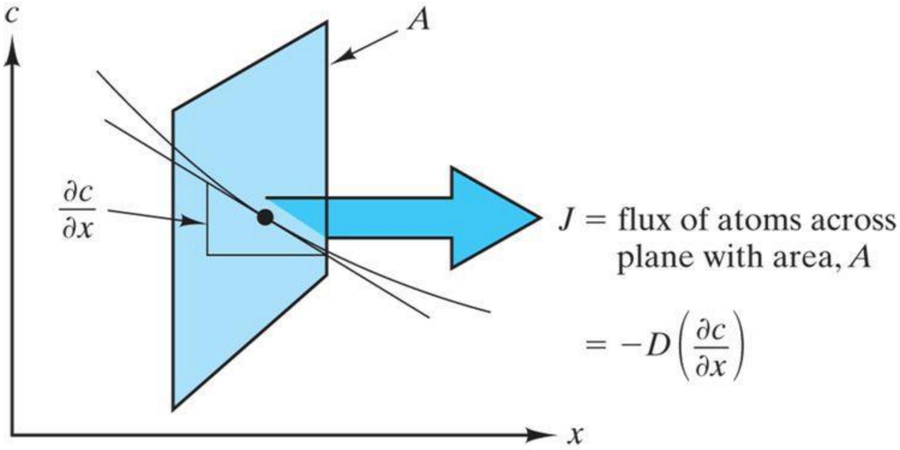
Steady-state diffusion

Steady-state diffusion is the situation when the diffusion flux is independent of time (e.g. diffusion of a gas through solid medium where concentration/pressure of the gas is kept constant at both the end). Fick's first law describes steady-state diffusion and is given by

$J= -D\ dc/dx$

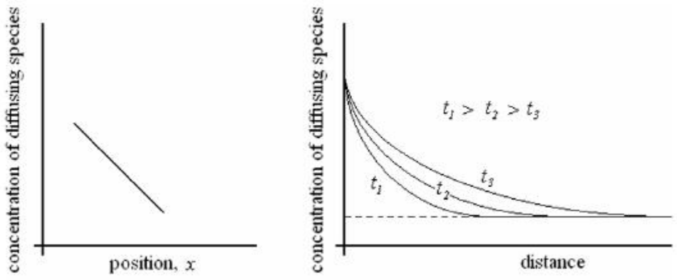
Where, Jis the diffusion flux or the mass transported per unit time per unit area and dC/dxis the concentration gradient. D is known as the diffusion coefficient.

Quantifying Diffusion: Fick's First Law (Equation 5.8) is a statement of Material Flux across a 'Barrier'



$$J \equiv \text{Flux} \equiv \frac{\text{moles (or mass) diffusing}}{(\text{surface area})(\text{time})} = \frac{\text{mol}}{\text{cm}^2\text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2\text{s}}$$

We will consider this model as a Steady State Diffusion system



Steady-state diffusion Non-steady-state diffusion

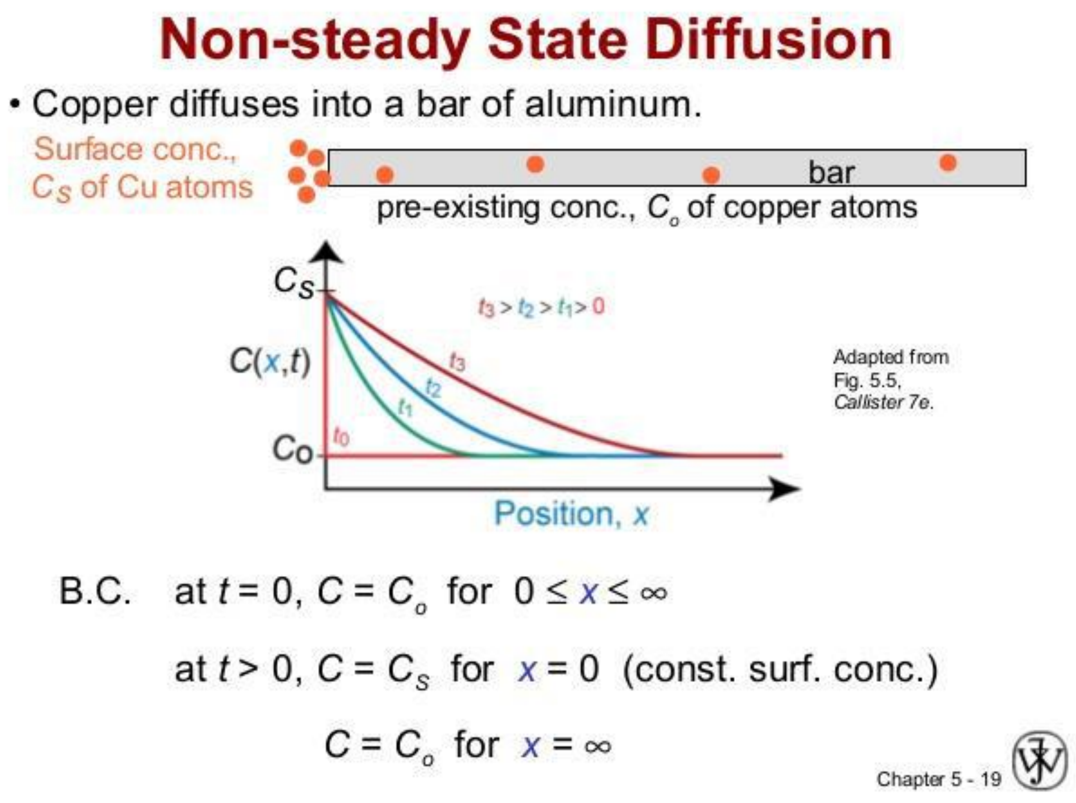
Figure-5.2: *Steady-state and Non-steady-state diffusion processes.*

Fick's Second Law

In most practical situations, diffusion is non-steady state i.e. diffusion flux and concentration gradient varies with time.

This is described by Fick's second law:

$dc/dt = D\, dc^2/d2x$



Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Adapted from Fig. 5.5, *Callister 7e.*

B.C. at $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (const. surf. conc.)

$C = C_o$ for $x = \infty$

Chapter 5 - 19

Influencing factors for diffusion

Diffusing species: Interstitial atoms diffuse easily than substitutional atoms. Again substitutional atoms with small difference in atomic radius with parent atoms diffuse with ease than atoms with larger diameter.

Temperature: It is the most influencing factor. Their relations can be given by the following Arrhenius equation

$D = D0 \exp(-Q/RT)$

where D0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature.

Lattice structure: Diffusivity is high for open lattice structure and in open lattice directions.

Presence of defects: The other important influencing factor of diffusivity is presence of defects. Many atomic/volume diffusion processes are influenced by point defects like vacancies, interstitials.

Apart from these, dislocations and grain boundaries, i.e. short-circuit paths as they famously known, greatly enhances the diffusivity.

Kirkendall Effect

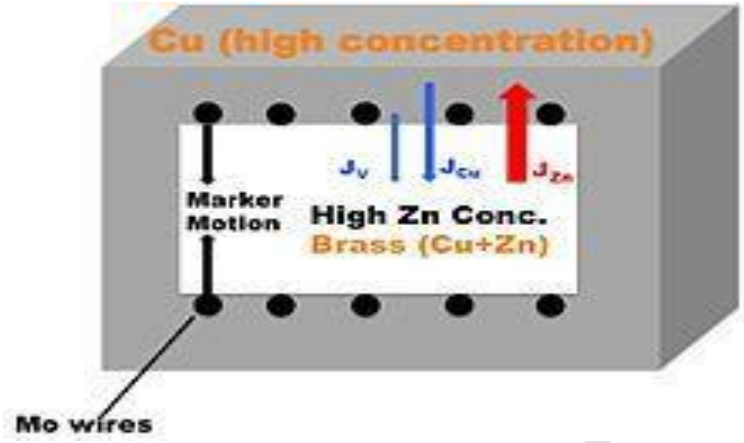
If the diffusion rates of two metals A and B in to each other are different, the boundary between them shifts and moves towards the faster diffusing metal as shown in the figure

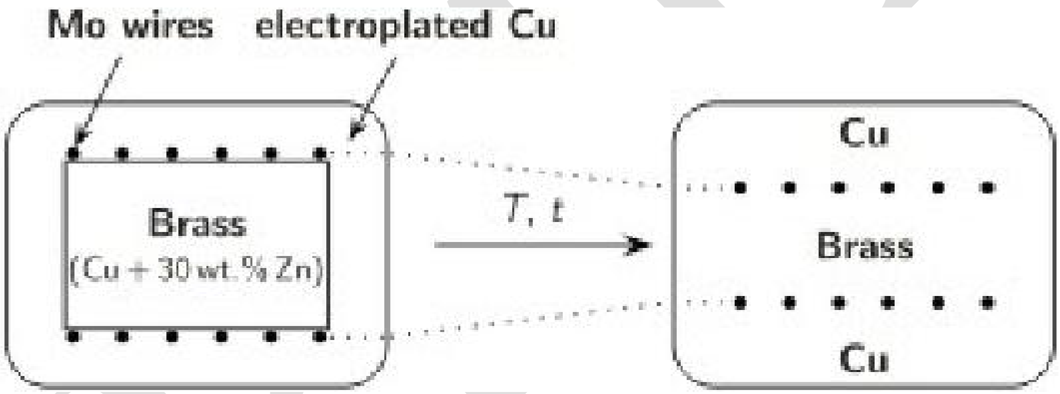
This is known as Kirkendall effect. Named after the inventor Ernest Kirkendall (1914 – 2005).

It can be demonstrated experimentally by placing an inert marker at the interface. This is a direct evidence of the vacancy mechanism of diffusion as the other mechanisms do not permit the flux of diffusing species to be different.

Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (Brass).

Same will happen in a Cu-Ni couple as Cu diffuses faster in Ni than vice versa. Since this takes place by vacancy mechanism, pores will form in Cu (of the Cu-Ni couple) as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.

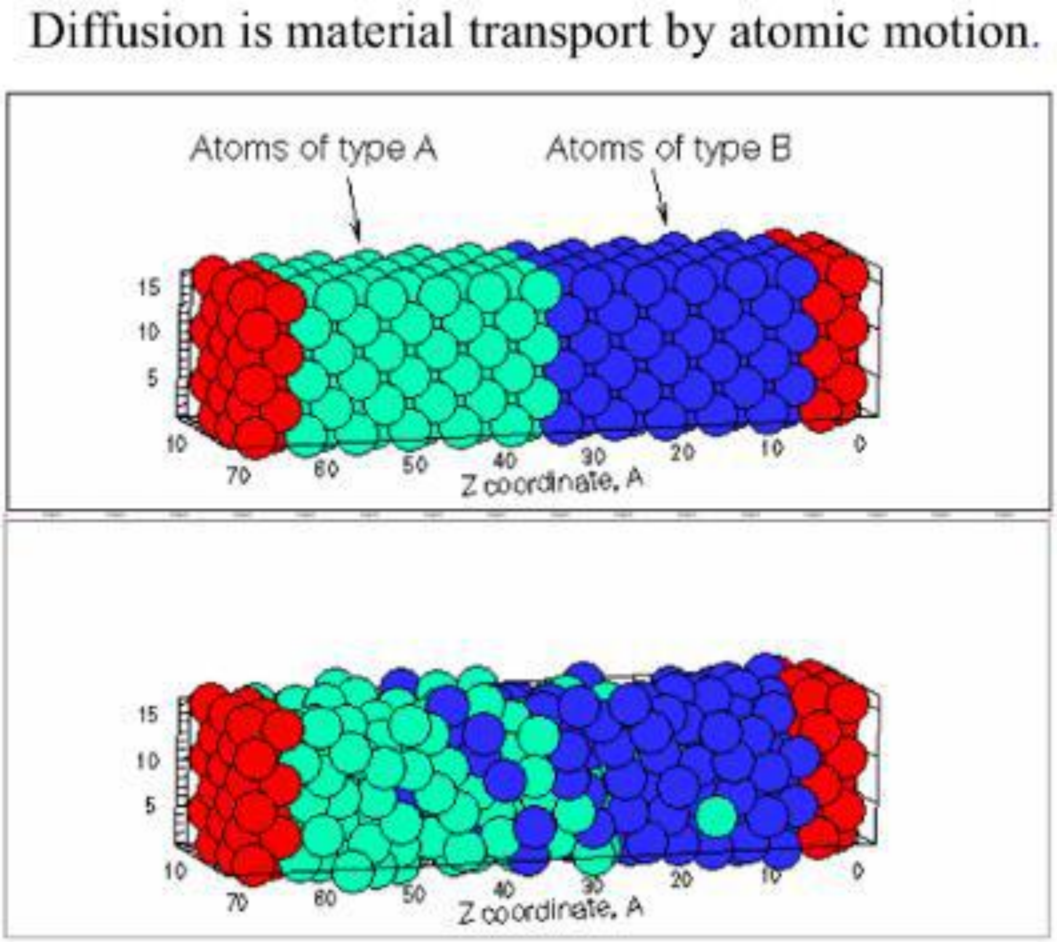




Surface diffusion:

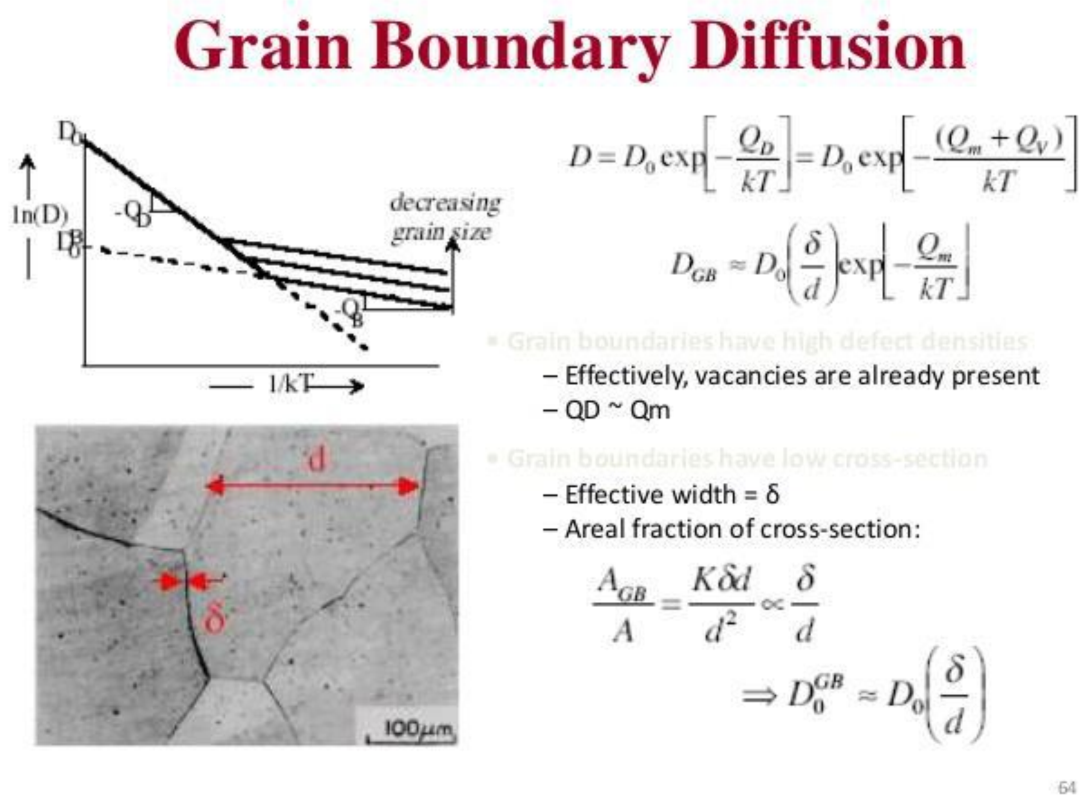
Surface diffusion is a general process involving the motion of adatoms, molecules, and atomic clusters (adparticles) at solid material surfaces.[1] The process can generally be thought of in terms of particles jumping between adjacent adsorption sites on a surface, as in Just as in bulk diffusion, this motion is typically a thermally promoted process with rates increasing with increasing temperature. Many systems display diffusion behavior that deviates from the conventional model of nearest-neighbor jumps. Tunneling diffusion is a particularly interesting example of an unconventional mechanism wherein hydrogen has been shown to diffuse on clean metal surfaces via the quantum tunneling effect.

Surface diffusion rates and mechanisms are affected by a variety of factors including the strength of the surface-adparticle bond, orientation of the surface lattice, attraction and repulsion between surface species and chemical potential gradients. It is an important concept in surface phase formation, epitaxial growth, heterogeneous catalysis, and other topics in surface science. As such, the principles of surface diffusion are critical for the chemical production and semiconductor industries. Real-world applications relying heavily on these phenomena include catalytic converters, integrated circuits used in electronic devices, and silver halide salts used in photographic film.



GRAIN BOUNDARY DIFFUSION:

The grain boundary diffusion coefficient is the diffusion coefficient (during atomicdiffusion) of a diffusant along a grain boundary in a polycrystalline solid. At lower temperatures in metals and metal alloys, this diffusion term may dominate the effective diffusion rate.



Grain Boundary Diffusion

$$D = D_0 \exp\left[-\frac{Q_D}{kT}\right] = D_0 \exp\left[-\frac{(Q_m + Q_V)}{kT}\right]$$

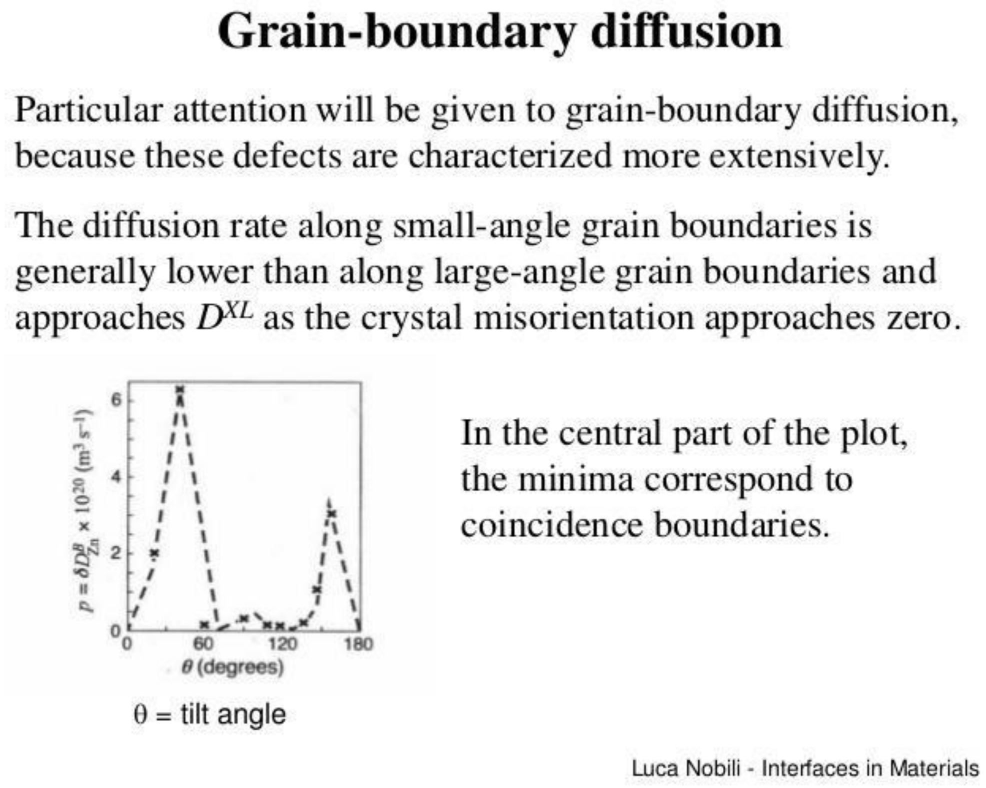
$$D_{GB} \approx D_0\left(\frac{\delta}{d}\right)\exp\left[-\frac{Q_m}{kT}\right]$$

- Grain boundaries have high defect densities
  - Effectively, vacancies are already present
  - QD ~ Qm
- Grain boundaries have low cross-section
  - Effective width = δ
  - Areal fraction of cross-section:

$$\frac{A_{GB}}{A} = \frac{K\delta d}{d^2} \propto \frac{\delta}{d}$$

$$\Rightarrow D_0^{GB} \approx D_0\left(\frac{\delta}{d}\right)$$

64



Grain-boundary diffusion

Particular attention will be given to grain-boundary diffusion, because these defects are characterized more extensively.

The diffusion rate along small-angle grain boundaries is generally lower than along large-angle grain boundaries and approaches D^{XL} as the crystal misorientation approaches zero.

In the central part of the plot, the minima correspond to coincidence boundaries.

θ = tilt angle

Luca Nobili - Interfaces in Materials

NUCLEATION:

If a pure material is kept at its freezing point, there will be no solidification. It needs some undercooling for the liquid to solid transformation to take place. More importantly, there is a critical undercooling above which there is almost no nuclei that form and below which there is an explosion in the number of nuclei that form.

HOMOGENOUS NUCLEATION:

Consider a pure melt which is cooled below its melting temperature. Such a liquid is known as undercooled. Let a small volume V_s of the liquid turn into solid. If G_s is the free energy per unit volume of the solid, and G_l that of the liquid, if A_{ls} is the solid-liquid interfacial area, and if γ_{sl} is the interfacial free energy, then, the total free energy of the system is given by

$$G_f = V_s G_s + V_l G_l + \gamma_{ls} A_{ls} \qquad (11)$$

Before the small volume of solid formed, the free energy of the system is given by

$$G_i = (V_s + V_l) G_l \qquad (12)$$

Thus, the total free energy change associated with the transformation of a small volume of liquid $V_s$insto solid is given by

$$\delta G = G_f - G_i = V_s(G_s - G_l) + \gamma_{ls} A_{ls}, \qquad (13)$$

If $\Delta G = G_s - G_l$

$$\delta G = V_s \Delta G + \gamma_{ls} A_{ls} \qquad (14)$$

since ΔG is negative in sign and γ_{ls} positive in sign, as expected, the r_c is a positive quantity.

In other words, there is a critical radius for which the overall free energy change is zero; any particle above this size will reduce the overall free energy and any particle below this size will increase the overall free energy. In the nucleation literature, particles which are smaller in size than the critical radius are known as embryos.

One can calculate the δG at r_c as follows:

$$[\delta G]_c = \frac{4}{3}\pi r_c^3 \Delta G + 4\pi r_c^2 \gamma_{ls} = -\frac{32}{3}\pi \frac{\gamma_{ls}^3}{(\Delta G)^2} + 16\pi \frac{\gamma_{ls}^3}{(\Delta G)^2} \qquad (18)$$

$$[\delta G]_c = \frac{16\pi \gamma_{ls}^3}{3(\Delta G)^2} \qquad (19)$$

It is possible to relate the undercooling of the melt to the radius of the critical nucleus and the free energy change associated with the critical nucleus

Critical undercooling

Consider any liquid. Inside the liquid, due to thermal fluctuations, clusters of various sizes keep forming. The probability of finding a cluster of given radius r is given by the Boltzmann distribution:

$$n = n_0 \exp\left(\frac{\delta G}{k_B T}\right) \qquad (20)$$

where n_0 is the total number of atoms, k_B is the Boltzmann constant, and δG is the free energy change associated with the formation of a solid of size r (and is given by Eq. 15).

Above the melting temperature of the solid, any such cluster that forms also breaks down immediately. However, below melting point, that is, in an undercooled melt, if the radius of the cluster formed is greater than r_c, then, that cluster becomes part of a solid and the given equation is no longer valid.

Using the above equation for thermal fluctuations, it is also possible to calculate the size of the biggest cluster (of radius, say, r_{max}) that has a reasonable probability of occurence. In Figure 10, we show the variation of this cluster size as a function of undercooling ΔT. In the same plot, we have also shown the variation of γ_s with undercooling. From this plot, it is clear that there is a critical undercooling at which these two curves intersect; in other words, due to thermal fluctuations, there is a reasonable probability to form a cluster of size equal to the critical nucleus size. Thus, when this undercooling is reached, one expects that homogeneous nucleation will take place in the undercooled melt.

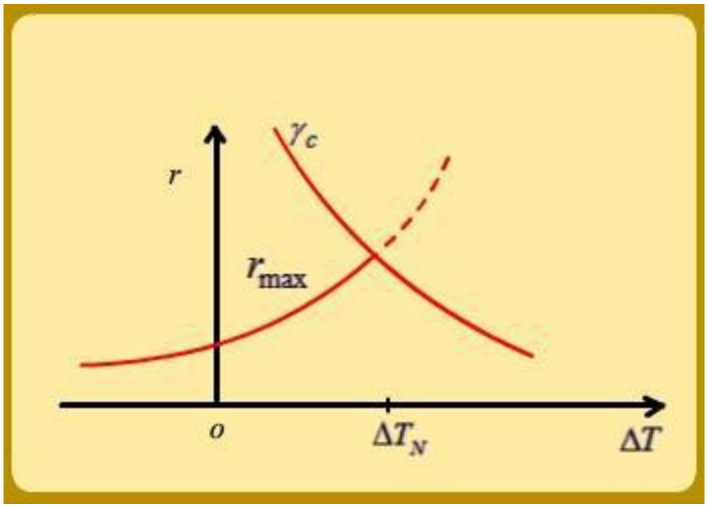


Figure 10: Thermal fluctuation versus critical nucleus size: need for critical undercooling.

Heterogeneous nucleation:

During solidification, unless special care is taken (for example, by keeping the liquid in air using electromagnetic levitation), the nucleation is always heterogeneous; that is, the liquid nucleates on another solid (mold walls, for example) and grows into the undercooled liquid.

We can understand the ubiquity of heterogeneous nucleation by considering the heterogeneous nucleation of a spherical cap on a flat mold wall as shown in Figure 12. In such a case, the excess free energy associated with the formation of a solid in the undercooled liquid is given by

$$\Delta G_{het} = V_s \Delta G + \gamma_{ls} A_{ls} + \gamma_{ms} A_{ms} - \gamma_{lm} A_{ms}$$

where V_s is the volume of the spherical cap, A_{ms} and A_{ls} are the areas of the mold wall/solid and liquid-solid interfaces, and the γ_{ls},γ_{ms} and γ_{lm} , are, respectively, the interfacial energies of the liquid-solid, mold-solid and liquid-mold interfaces, respectively.

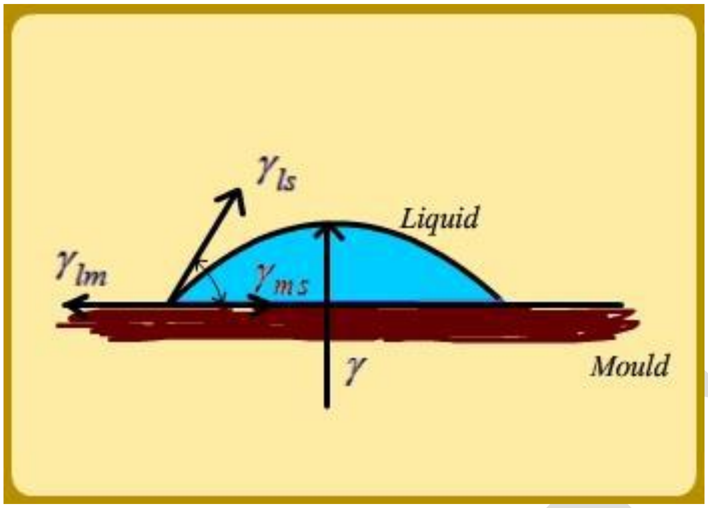


Figure 12: Heterogeneous nucleation on mould walls.

In terms of the wetting angle , it can be shown that

$$\Delta G_{het} = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}\left[\frac{1}{3}\pi r^3 \Delta G + 4\pi r^2 \gamma_{ls}\right]$$

In otherwords, except for the $S(\theta) = 0.25(2+\cos\theta)(1-\cos\theta)^2$ term, the expression is identical to that obtained in the homogeneous solidification case above.

Hence, one obtains the following relationships:

$$r_c^{het} = -\frac{2\gamma_{ls}}{\Delta G}$$

$$[\delta G]_c^{het} = [\Delta G]_c^{hom} S(\theta)$$

In other words, while the critical nucleus size for heteogeneous nucleation is only dependent on the undercooling, the activation energy barrier is smaller than that of homogeneous nucleation by a factor of $S(\theta)$; hence, one can expect the critical undercooling also to be smaller as shown in Fig. 13.

that the interfacial energy is always positive. Hence the contribution from the second term is always positive. However, depending on whether the liquid is above or below the melting temperature, ΔG is positive or negative. Hence, in an undercooled liquid, where ΔG is negative, the system will try to minimize the shape in such a way that the overall interfacial energy is reduced so that the maximum reduction in free energy can be achieved.

If we assume interfacial energy to be isotropic, then the volume transformed is a sphere of radius r(since the maximum volume is enclosed for the minimal surface area for a sphere), we get

$$\delta G = \frac{4}{3}\pi r^3 \Delta G + 4\pi r^2 \gamma_{ls}$$

In Figure 9, we show the variation of the volume free energy, interfacial energy and the overall free energy change as a function of r. Since the interfacial contribution goes as r^2 and that of bulk free energy as r^3, at smaller r, interfacial energy always dominates, and being a positive energy, it actually suppresses the formation of solid. Unless the size of the solid is above some size wherein the (negative) bulk free energy change can more than compensate for the (positive) interfacial energy, the solid will not be stable (even if it forms). Thus, one can identify the critical radius of the solid that is stable when formed in the undercooled liquid by minimizing δG with respect to r:

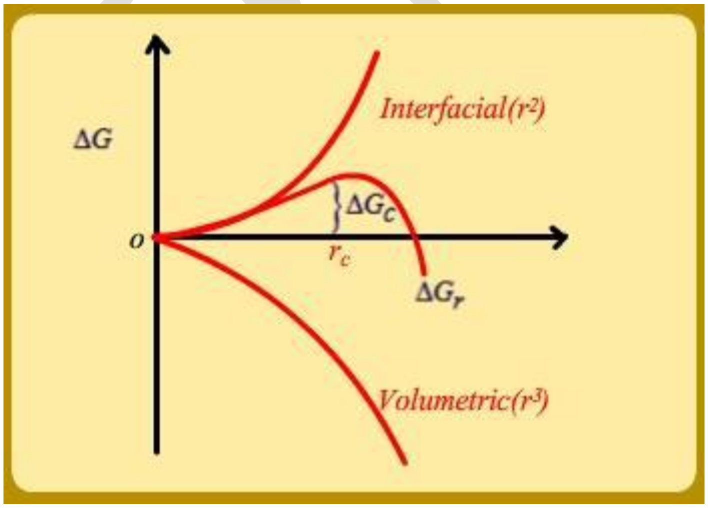


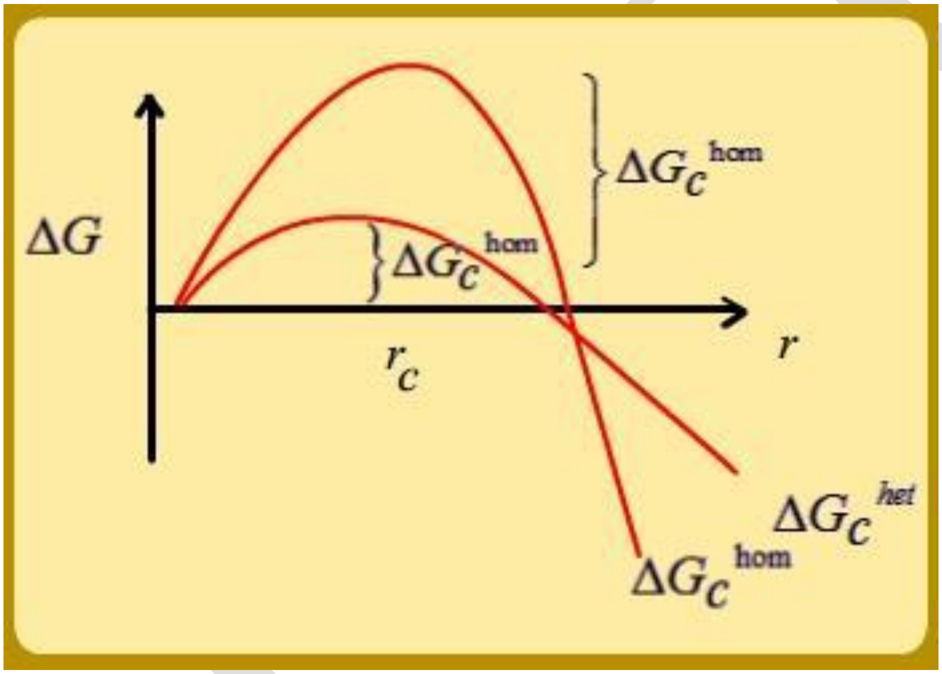
Figure 9: Energetics of homogeneous nucleation of a solid from its melt.

$$\left[\frac{d\delta G}{dr}\right]_{r=r_c} = 0 = 4\pi r_c^2 \Delta G + 8\pi r_c \gamma_{ls} \qquad (16)$$

This implies,

$$r_c = -\frac{2\gamma_{ls}}{\Delta G} \qquad (17)$$

In other words, while the critical nucleus size for heteogeneous nucleation is only dependent on the undercooling, the activation energy barrier is smaller than that of homogeneous nucleation by a factor of $S(\theta)$; hence, one can expect the critical undercooling also to be smaller as shown in Fig. 13.



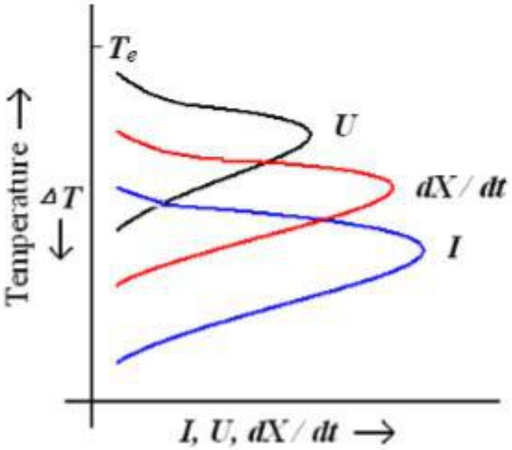
While it is possible to undercool a melt below melting temperature without freezing, it is not possible to heat a solid above melting temperature without melting setting in. Why?

. ANS: It is generally found that the vapour-solid, liquid-solid, and vapour-liquid free energies are such that $\gamma_{ls} + \gamma_{vl} < \gamma_{vs}$. Hence, the wetting angle θ is zero, and there is no need for superheating for the nucleation of liquid to take place. Hence, melting starts at the melting temperature when a solid is heated

GROWTH KINETICS:

After formation of stable nuclei, growth of it occurs

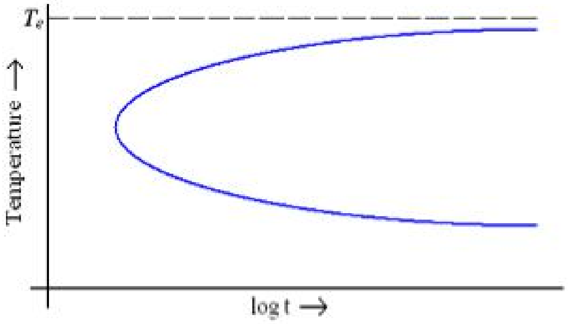
Growth occurs in two methods –thermal activated diffusion controlled individual atom movement, or a thermal collective movement of atoms. First one is more common than the other. Temperature dependence of nucleation rate (U), growth rate (I) and overall transformation rate (dX/dt) that is a function of both nucleation rate and growth rate i.e. dX/dt= fn (U, I):

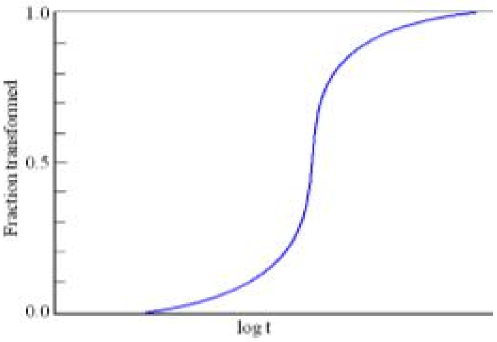


Time required for a transformation to completion has a reciprocal relationship to the overall transformation rate, C-curve (time-temperaturetransformation or TTT diagram).

Transformation data are plotted as characteristic S-curve.

At small degrees of supercooling, where slow nucleation and rapid growth prevail, relatively coarse particles appear; at larger degrees of supercooling, relatively fine particles result .


T_e
Temperature →
log t →


1.0
0.5
0.0
Fraction transformed
log t

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Total Number of Pages: 03

B.TECH
PMT3I101

3rd Semester Regular Examination 2016-17
SCIENCE AND ENGINEERING OF MATERIALS
BRANCH(S): METTA, MME
Time: 3 Hours
Max Marks: 100
Q.CODE:Y504

Answer Part-A which is compulsory and any four from Part-B.
The figures in the right hand margin indicate marks.

Part – A (Answer all the questions)

Q1 **Answer the following questions:** **(2 x 10)**

a) A 0.2 wt. % plain carbon steel sheet is heated and equilibrated in the inter-critical region followed by instant water quenching. The microstructure of the quenched steel sheet consists of
[✓ (A)] Fully martensite (B) proeutectoid ferrite + martensite (C) martensite + pearlite (D) martensite + austenite.

b) The atomic packing fraction of diamond cubic structure is ________

c) A unit cell of an element has maximum linear density along the [110] direction. The packing density of its (100) plane is
(A) 0.68 [✓ (B)] 0.74 (C) 0.79 (D) 0.91

d) Which one of the following is an equilibrium defect?
(A)Vacancies(B)Dislocations[✓ (C)] Stacking faults (D) Grain boundaries

e) If the radius of an atom in a simple cubic crystal is r, the body diagonal of the unit cell is
(A) r√3 [✓ (B)] 2r√3 (C) 4r/√3 (D) 3r/4

f) The number of members in the family <123> in a cubic crystal are
(A) 8 (B) 12 [✓ (C)] 24 (D) 48

g) The packing efficiency of a simple cubic crystal with an interstitial atom exactly fitting at the body centre is
[✓ (A)] 0.52 (B) 0.68 (C) 0.73 (D) 0.91

h) The number of tetrahedral voids in HCP unit cell is
(A) 4 (B) 6 [✓ (C)] 8 (D) 12

i) If the vacancy concentration in a crystal doubles itself between 25°C and 31°C, the enthalpy of formation of vacancies (kJ/mole) is
(A) 138 (B) 87 (C) 51 (D) 0.7

j) The fraction of pearlite in a 0.55% steel is
(A) 0.55 (B) 0.31 [✓ (C)] 0.69 (D) 0

Q2 **Answer the following questions:** **(2 x 10)**

a) Distinguish between homogeneous and heterogeneous nucleation.

b) How much proeutectoid ferrite is there in a slowly cooled 0.6% C steel? How much eutectoid ferrite is there in the same steel?

c) Explain the phenomenon of diffusion with the help of a diffusion couple.

d) What is Kirkendall effect?

e) Explain the Snoek effect in interstitial diffusion.

f) Give the stacking sequence in HCP and FCC structures and also give the different types of stacking faults that occur in FCC structures.

g) Calculate the number of atoms in 100g of aluminium. Atomic weight of aluminium is 26.98 g/mol and Avogadro's number is 6.023 x 1023 mol^{-1}

h) Draw a (111) plane and a (222) plane in the unit cell of a cubic lattice with lattice parameter a. Determine their distances from a parallel plane through the origin.

i) In the Pb-Sn system, determine the fraction of β phase in an alloy of 80% Sn at 184^0C and 182^0C.

j) What is solid solution? Write the different types of solid solutions with examples.

Part – B (Answer any four questions)

Q3 a) 0.20 wt. % C and 1.0 wt. % steels are cooled slowly from austenite region to room temperature. (i) Draw cooling curves for the two steels. (ii) Draw schematic microstructures and identify different phases that occur at room temperature. **(10)**

What is the difference between the eutectic and the eutectoid reaction? Give examples for each reaction. How can we modify the mechanical properties of materials having these structures?

A binary alloy of the eutectic composition 70 wt % B solidifies into α and β phases of compositions - α of 10 wt% B and β of 85 wt% B, respectively. Determine the relative amounts of α and β phases just below the eutectic temperature, T_e, at equilibrium.

b) What are dual phase steels? How are these produced? And in what way are they superior to conventional low carbon steels? **(5)**

Q4 a) Sketch the following planes and directions within each cubic unit cell: **(10)**

$(10\bar{1}),(012),(211),(3\bar{1}\bar{2}),[\bar{1}1\bar{1}],[0\bar{1}2],[11\bar{2}],[\bar{1}01]$

Determine the number of vacancies needed for a BCC iron lattice to have a density of 7.87 g/cm^3. The lattice parameter of the iron is 2.866 x 10^{-8} cm.

b) What is homogeneous nucleation? Derive the expression for the free energy change accompanying the formation of a spherical new phase particle. **(5)**

Q5 a) Draw the Iron-cementite phase diagram. Label the important phase fields, temperatures and compositions. Give the important invariant reactions occurring in the system. **(10)**

A 0.2 wt. % steel is cooled slowly from austenitic region to room temperature. Calculate the proportions of the different phases at room temperature and draw the microstructure.

b) Compare the mechanical properties of low carbon, microalloyed, and dual phase steels with the help of engineering stress – strain curves. **(5)**

Q6 a) Consider one alloy that initially has a uniform carbon concentrationof 0.25 wt% and is to be treated at 950^0 C (1750^0 F). If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt%, how long will it take to achieve a carbon content of 0.80 wt% at a **(10)**

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position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is 1.6×10^{-11} m^2/s; assume that the steel piece is semi-infinite.

b) The diffusion coefficients for nickel in iron are given at two temperatures: **(5)**

T(K)	$D(m^2/s)$
1473	2.2×10^{-15}
1673	4.8×10^{-14}

Determine the values of D_0 and the activation energy Q_d. What is the magnitude of D at 1300^0C (1573 K)?

Q7 a) Give the schematic plot of the variation of the nucleation rate with temperature and explain the shape of the curve. Estimate the (i) magnitude of critical radius, r*, (ii) critical free energy of nucleation, Δf^* and (iii) the number of atoms in the critical embryo of solid silver in super cooled liquid silver at 735 °C. For silver ΔH (fusion) = 12 kJ/mole. T_m = 960.8 °C. Density of solid silver, ρ = 10.6 g/cm^3. The interfacial surface free energy between solid and liquid silver, $\gamma_{s/L} = 126 \times 10^{-7}$ J/cm^2. Atomic weight of silver = 107.87 Avogadro's number = 6.023×10^{23} mol^{-1}. **(10)**

b) Explain the dendritic growth in pure metals with suitable diagrams. **(5)**

Q8 a) Melting point of an element A is 1500 °C while that of element B is 1800 °C. The α solid solution containing 30 wt.% B, the β solid solution containing 80 wt.% B and the liquid containing 50 wt.% B are in equilibrium at 1200 °C. At room temperature, the maximum solubility of B in the α phase is 20 wt.% and the maximum solubility of A in the β phase is 10 wt.%. **(10)**

Sketch the phase diagram and label different regions.

What are the weight fractions of phases present in the A-70wt. %B alloy

(i) at a temperature just above 1200 °C
(ii) at a temperature just below 1200 °C
(iii) at room temperature

b) What is the difference between the eutectic and the eutectoid reaction? Give examples of each reaction. How can we modify the mechanical properties of materials having these structures? **(5)**

Q9 a) Name the seven crystal systems. And give the geometrical relationships of the edge lengths and the interaxial angles of the unit cells of the seven crystal systems with neat sketches. What is a Bravais space lattice? Name and draw the fourteen Bravais space lattices with spatial arrangement of the atom positions in the unit cells. Find the Miller indices of a plane that makes an intercept of 1 on a-axis and 2 on b-axis and is parallel to c-axis. **(10)**

b) State the Hume-Rothery conditions that govern the formation of substitutional solid solutions having unlimited solubility. Draw the cooling curves of a pure metal with and without undercooling, an isomorphous alloy, a eutectic alloy, and a hypoeutectic alloy and label them. **(5)**

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B. Tech
PCMT 4201

Third Semester Regular Examination – 2014

INTRODUCTION TO PHYSICAL METALLURGY

BRANCH : MM, MME

QUESTION CODE : H 401

Full Marks – 70

Time : 3 Hours

Answer Question No. ***1*** *which is compulsory and any* ***five*** *from the rest.*
The figures in the right-hand margin indicate marks.

1. Answer the following questions : 2 × 10

   (a) Define Unit cell.

   (b) What is coordination number in crystal structure ?

   (c) What is hot working of metal ?

   (d) What is the significance of a phase diagram ?

   (e) Define eutectic reaction.

   (f) What is burger's vector ?

   (g) Why tempering is done ?

   (h) Draw the planes (020) and (120) in a cubic structure.

   (i) What is the maximum solubility of carbon in austenite phase ?

   (j) What is meant by yield point phenomena ?

2. (a) What are engineering materials and classify them ? 5

   (b) Derive the expression for critical resolved shear stress of a single crystal. 5

3. (a) Schematically draw T T T diagram of eutectoid steel and label it. 5

P.T.O.

(b) Consider 2.5 kg of austenite containing 0.65 wt% C, cooled to Below the eutectoid temperature. 5

   (i) What is the proeutectoid phase ?

   (ii) How many kilograms each of total ferrite and cementite form ?

   (iii) How many kilograms each of pearlite and the proeutectoid phase form ?

   (iv) Schematically sketch and label the resulting microstructure ?

4. Briefly explain about the defect in the crystal. 10

5. (a) Explain from Hume Rothery's rule for complete solid solutions in which elements mix in each other. 5

   (b) Differentiate between annealing and normalizing. 5

6. (a) Define slip system. Do all metals have the same slip system ? Give reasons. 5

   (b) Define the term heat treatment. Why the steels are heat treated ? 5

7. (a) Aluminium has FCC structure, its density is 2700kg/m^3. Calculate the unit cell dimension and atomic diameter. Atomic weight of aluminium is 26.98. 5

   (b) Explain how a cored structure is produced in a 70%Cu-30% Ni alloy. 5

8. Write short notes on any two of the following : 5 × 2

   (a) Toughness

   (b) Gibbs phase rule

   (c) Hardness and hardenability

   (d) Strain Hardening.
