

<b>COURSE CODE:</b>	<i>MCE 311</i>
<b>COURSE TITLE:</b>	<i>Materials Science for Engineers</i>
<b>NUMBER OF UNITS:</b>	<i>3 Units</i>
<b>COURSE DURATION:</b>	<i>Three hours per week</i>

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### **COURSE DETAILS:**

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<b>Office Location:</b>	<b>Room 02, MCE Dept., COLENG</b>
<b>Other Lecturers:</b>	<b>None</b>

### **COURSE CONTENT:**

Types of Engineering materials; physical properties of materials. Electrical properties of materials. Mechanical properties of materials; Thermal properties of materials; chemical properties of materials. Stability of materials in the service environment; Basic metallurgy; Non-metallic materials. Simple stress and strain: Bending and Torsion; Torsion, Deflection of beams: Complex stress and strain.

### **COURSE REQUIREMENTS:**

\*This is a compulsory course for all students in the Mechanical Engineering Department of the University. Students are expected to participate in all the course activities and have minimum of 75 % attendance to write the final examination. Class work and assignments given for practical understanding of students.

\*Continuous assessment test given at the middle of semester to test students understanding.

\*Both CAT and Assignments form about 30% of the examination.

\*Examination carries 70%.

### **READING LIST:**

1. Materials Science and Engineering, An Introduction, by Williams D. Callister Jr 1988
2. Engineering Metallurgy 1 by Higgins
3. Engineering Mechanics of Materials by Muvdi B.B and McNabb J.W 1980

## LECTURE NOTES

1.0 Materials Science is a discipline that involves investigating the relationships that exist between the structures and properties of materials. Materials engineering correlates structure with property of materials to produce a predetermined set of properties.

### 1.1 Types of Engineering Material

Three basic groups of Metals, ceramics and polymers. Other 3 importance of engineering materials are: composites, semiconductors and biomaterial.

**METALS:** normally combinations of metallic elements. Large number of non localized electrons(not bound to particular atoms). Good conductors of electricity and heat, not transparent to visible light, a polished metal surface has a lustrous appearance, quite strong and deformable which accounts for structural applications.

**CERAMICS:** compounds between metallic and non metallic elements. They are most frequent oxides, nitrides and carbides. Ceramics that are composed of clay materials, cement and glass; cannot conduct electricity and heat(insulators), more resistant to high temperature and harsh environments than metals and polymers. Ceramics are hard but very brittle.

**POLYMERS:** includes plastics and rubber materials. Organic compounds that are chemically based on carbon, hydrogen and other non-metallic elements, large molecular structures, low density and extremely flexible.

**COMPOSITES:** contains more than one material. Fiber glass is an example, glass and fiber embedded with a polymeric material, displays best characteristics of each component materials.

**SEMICONDUCTORS:** have electrical properties that are intermediate between the electrical conductors and insulators, have made possible the advent of integrated circuitry that has played major role in electronic and computer industries.

**BIOMATERIALS:** employed in components implanted into the human body for replacement of diseased or damaged body parts, not toxic and compatible with body issues; all other materials may be used, artificial replacement.

## 2.0 PHYSICAL PROPERTIES OF MATERIALS

General: Of the 106 elements, 76 are metals. Elements as Si, Ge, As, Se, and Te are intermediate between metals and non-metals.

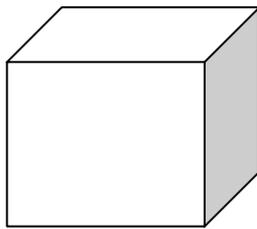
- 1) High thermal and electrical conductivity.
- 2) Positive temperature coefficient of electrical resistivity.
- 3) Thermionic emission, i.e the capacity for emitting electrons when heated.
- 4) Good reflection of light (metals are opaque and a specific metallic luster).
- 5) They can undergo plastic deformation.

## CRYSTAL STRUCTURES

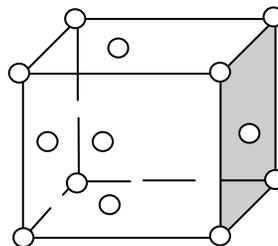
A crystalline material is one in which the atoms are situated in a repeating periodic array over large atomic distances. All metals, many ceramic materials and certain polymers form crystalline structures under normal solidification conditions. Others are non crystalline or amorphous materials.

LATTICE refers to three-dimensional array of points coinciding with atom positions.

UNIT CELLS are prisms having three sets of parallel faces.



(a) Simple Cubic



b) FCC

## THE FACE-CENTRED CUBIC CRYSTAL (FCC)

A unit cell of cubic geometry with atoms located at each of the corners and the centres of all the cube faces. Examples: copper, Al, Ag, and Au. The cube edge length  $a$  and the atomic radius  $R$ ,  
 $a=2R\sqrt{2}$

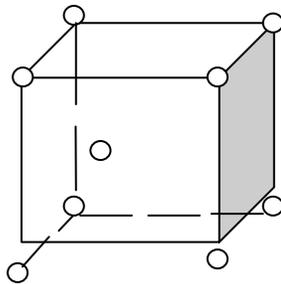
Coordination number and atomic packing factor (APF).

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

For FCC-APF= 0.74

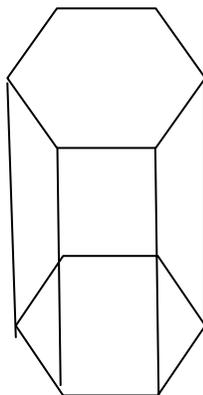
### BODY-CENTRED CUBIC (BCC)

$$a = \frac{4R}{\sqrt{3}} \quad \text{Ex: Cr, Fe, W}$$



### HEXAGONAL CLOSE-PACKED (HCP)

The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the centre.



## POLYMORPHISM AND ALLOTROPY

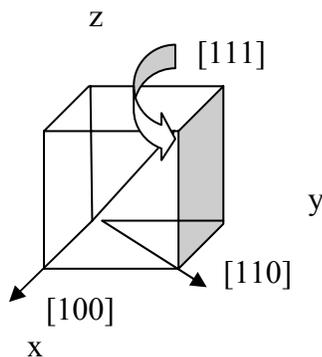
Some metals and non-metals have more than one crystal structure or allotropy. E.g, carbon, graphite. Diamond formed at high pressure.

Crystal system	Axial relations	Interaxial angles	Unit cell
1. Cubic	$a=b=c$	$\alpha=\beta=\gamma=90$	
2. Hexagonal	$a=b\neq c$	$\alpha=\beta=90, \gamma=120$	
3. Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90$	
4. Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90$	
5. Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90$	
6. Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90\neq \beta$	
7. Triclinic	$a\neq b\neq c$	$\alpha\neq \beta\neq \gamma\neq 90$	

## CRYSTALLOGRAPHIC DIRECTIONS

Definition: a vector or line between two points.

1. A vector of convenient length is positioned such that it passes through the origin of the coordinate system. Maintaining parallelism enables any vector to be translated throughout the crystal lattice without alteration.
2. The length of the vector projection on each of the three axes is determined in terms of the unit cell dimensions  $a$ ,  $b$  and  $c$ .
3. These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
4. The three indices, not separated by commas, are enclosed in square brackets,  $[UVW]$ - reduced projections along the  $x$ ,  $y$  and  $z$  axes respectively. Negative integers also possible e.g.  $[\bar{1}\bar{1}\bar{1}]$   $\therefore$  Y direction  $[\bar{1}\bar{1}0]$  opposite to  $[110]$ .  $[100]$ ,  $[110]$  and  $[111]$  directions are common ones.

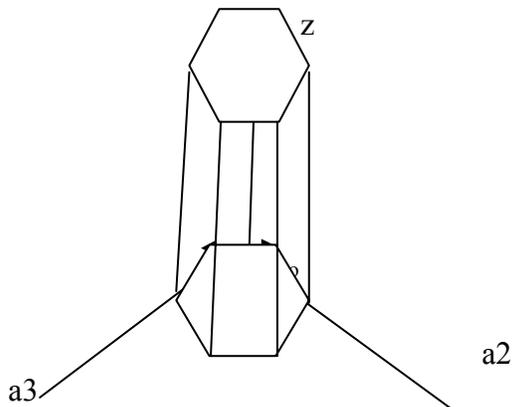


### HEXAGONAL CRYSTALS

Utilizing a four-axis or Miller-Bravais coordinate system.

$$[u'v'w'] \longrightarrow [uvw]$$

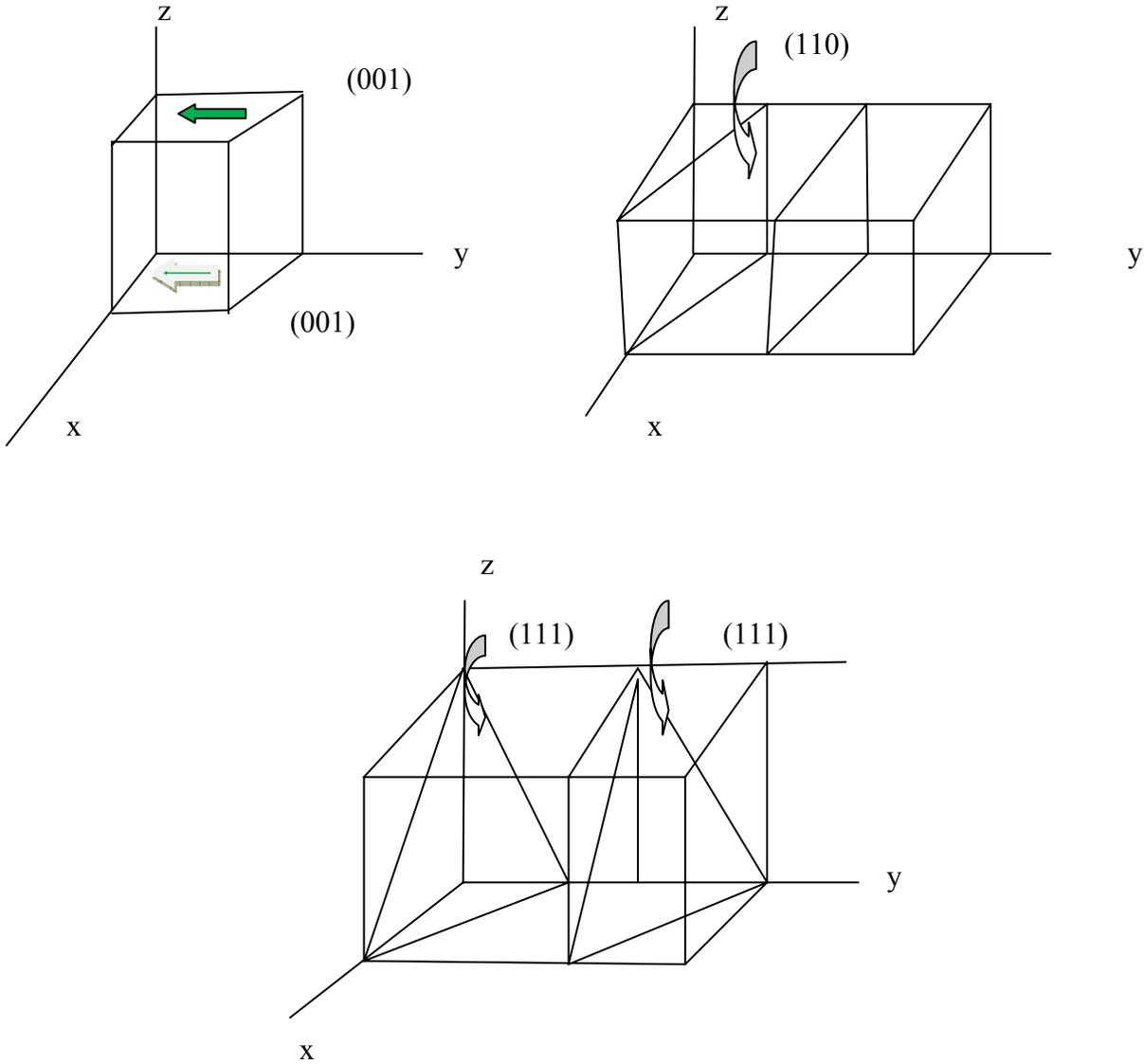
$$u = \frac{2}{3}(2u' - v') \quad v = \frac{2}{3}(2v' - u') \quad t = -(u+v) \quad w = nw'$$



### CRYSTALLOGRAPHIC PLANES

Orientations of planes for a crystal structure. Miller indices (hkl)

1. If the plane passes through the selected origin, either another parallel plane must be constructed within unit cell by appropriate translation.
2. Crystallographic plane either intersects or parallel to each of three axes.
3. Reciprocals of those numbers taken
4. These three numbers changed to set of smallest integers by  $\times$  or  $\div$  common factor.
5. (hkl) represents Miller indices.



### LINEAR AND PLANAR ATOMIC DENSITIES

linear density is the fraction of line length in a particular crystallographic direction that passes through atomic centers. Planar density is the fraction of total crystallographic plane area that is occupied by atoms.

Ex. Calculate the linear density of the [100] direction for BCC.

$$L_c = \frac{LC}{L_c} = \frac{2R}{\sqrt{3}} = 0.866$$

Ex 2. Calculate the planar density of the [110] plane for FCC.

The unit cell plane area,  $A_p$ , the rectangle length (AC) and width (AD) respectively.

$$AC = 4R \quad AD = 2R\sqrt{2}$$

$$\therefore A_p = (AC)(AD) = (4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$$

For total circle area, one fourth of each of atoms A, C, D and F and one half of atoms B and E reside within this rectangle to give a total of 2 equivalent circles. Total circle area  $A_c = (2)\pi R^2$ .

$$\text{Finally, the planar density, } PD = \frac{A_c}{A_p} = \frac{2\pi R^2}{8R^2\sqrt{2}} = 0.555$$

### CRYSTALLINE AND NON-CRYSTALLINE MATERIALS

Single crystal: formed when the periodic and repeated arrangement of atoms is perfect or extends throughout the entire specimen without interruption.

Poly crystalline: are composed of a collection of many small crystals or grains.

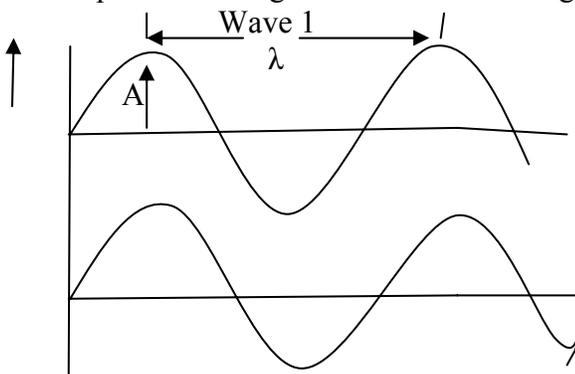
### ANISOTROPY

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. Example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] direction. This directionality of properties is termed ANISOTROPY, this is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are ISOTROPIC. The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure. The degree of anisotropy increases with decreasing structural symmetry. Trichis structures normally are highly anisotropic.

Braggs Law.

Non crystalline solids.

X-RAY DIFFRACTION: Diffraction occurs when a wave encounters a series of regularly spaced obstacles, that are 1) are capable of scattering the wave, and 2) have spacing that are comparable in magnitude to the wavelength.



Wave 2

### X-RAY DIFFRACTION AND BRAGG'S LAW

X-Rays are a form of electromagnetic radiation that have high energies and short wavelengths.

Or  $n\lambda = dhkl \sin \theta + dhkl \sin \theta = 2 dhkl \sin \theta$  -----Bragg's law, for crystal structures having

cubic symmetry,  $dhkl = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

### DIFFRACTION TECHNIQUES

The diffractometer is an apparatus used to determine the angles at which diffraction occurs for powdered specimens.

T= X-ray source; S= Specimen; C= Detector; O= The axis around specimen and detector rotate.

Ex1: For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866nm (2.886Å), also assume that monochromatic radiation having a wavelength of 0.1790nm (1.790 Å) is used and the order of refraction is 1.

### NON-CRYSTALLINE SOLIDS

These are solids that lack a systematic and regular arrangement of atoms over relatively large atomic distances. Also called amorphous (without form) or super cooled liquids in as much as their atomic structure resembles that of a liquid. E.g. comparison of the crystalline and non-crystalline compound (SiO<sub>2</sub>)

### 3.0 ELECTRICAL PROPERTIES OF MATERIALS

- Responses of materials to an applied electric field.

Electrical conduction by electrons and how the electron energy band structure of a material influence its ability to conduct. Extended to metals, semiconductors and insulators. Dielectric characteristics of insulating materials are ferroelectricity and piezoelectricity.

#### OHM'S LAW

$V=IR$ . R, resistance of materials through which current is passing. Volts ( $\frac{J}{C}$ ), amperes ( $\frac{C}{S}$ ) and ohms ( $\frac{V}{A}$ ).

The resistivity  $\rho$ , is independent of specimen geometry but related to R through the

expression,  $\rho = \frac{RA}{l}$  ----(2)  $l = \text{distance between two pts where voltage}$

A= cross-sectional area is measured, area perpendicular to direction of current.

$\rho$  = ohm meters ( $\Omega m$ ).

Ohm's Law:  $J = \alpha E$ , J= current density, E= electric field intensity or  $E = \frac{V}{l}$

3gps= conductors

Semiconductors

Insulators

#### ELECTRONIC AND IONIC CONDUCTION

An electric current results from the motion of electrically charged particles in response to forces that act on them from an externally applied electric field.

## ENERGY BAND STRUCTURES IN SOLIDS

Electronic conduction exists in most materials and the magnitude of the electrical conductivity is strongly dependent on the number of electrons available to participate in the conduction process. The number of electrons available for electrical conduction in a particular material is related to the arrangement of electron states or levels with respect to energy and then the manner in which these states are occupied by electrons.

Electrical configuration of atom-discrete energy levels that may be occupied by electrons, arranged into shells and subshells. Shells are designated by integers (1,2,3) and subshells by letters (s,p,d,f) for each of s, p, d and f subshell there exist one, three, five and seven states. Electrons fill the states having the lowest energy, two electrons of opposite spin per state, in accordance with the Pauli exclusion principle.

In crystalline materials, each atom is independent of all the others and will have the atomic energy levels and electron configuration as if isolated. However, as the atoms come within close proximity of one another, electrons are acted upon, or perturbed by the electron and nuclei of adjacent atom. Each distinct atomic state may split into a series of closely spaced electron states in the solid, to form electron energy band and begins with outermost electron shells.

The electrical properties of a solid material are a consequence of its electron band structure, i.e. the arrangement of the outermost electron bands and the way in which they are filled with electrons, the band containing the highest energy or valence electrons is termed the VALENCE BAND, the CONDUCTION band is the next higher energy band which is under most circumstances, virtually unoccupied by electron

In (a), the valence band is only partially filled with electrons. The energy corresponding to the highest filled state at 0K is called THE FERMI ENERGY,  $E_f$ , as indicated above. This energy band structure is typified by some metals, in particular those that have a single s valence electron (e.g copper). Each copper atom has one 4s electron; however for a solid comprised of N atoms, the 4s band is capable of accommodating 2N electrons. Only half the available electron positions within this 4s valence band are filled in (b), also found in metals, the valence band is full, but it overlaps the conduction band, otherwise empty magnesium has this band structure. Each isolated Mg atom has two 3s valence electrons. however, when a solid is formed, the 3s and 3p bands overlap. The Fermi energy is taken as that energy below which for N atoms, N states are filled, two electrons per state. The final two band structures are similar; all states in valence band are completely filled with electrons. no overlap and empty conduction band. (c)- insulator (d) semiconductor.

## CONDUCTION IN TERMS OF BAND AND ATOMIC BONDING MODELS

Electrons that participate in the conduction process are termed free electrons. charged electronic entity called a hole is found in semi conductors and insulators. Holes have energies less than  $E_f$  and also participate in electronic conduction. The electrical conductivity is a direct function of the numbers of free electrons and holes.

For a metal, occupancy of electron states (a) before and (b) after an electron excitation.

### METALS:

For an electron to become free, it must be excited or promoted into one of the empty and available energy states above  $E_f$ . Using structure shown above, there are vacant energy states adjacent to the highest filled state at  $E_f$ , thus, very little energy is required to promote electrons into the low lying empty states. Energy provide by an electric field is sufficient to excite large numbers of conduction electrons into these conducting states.

For metallic bonding mode, it was assumed that all valence electrons have freedom of motion and form an 'electron gas' which is uniformly distributed throughout the lattice of ion cores. Only a fraction are excited, which gives rise to a relatively large number of free electrons and consequently a high conductivity.

### INSULATORS AND SEMICONDUCTORS

Empty space adjacent to the top of the filled valence band are not available. To become free,  $e^-$  must be promoted across the energy band gap and into empty states at the bottom of the conduction band. It is possible only by supplying to an electron the difference in energy between these two states, which is approximately equal to the band gap energy e.g most often, the excitation energy is from a non electrical source like heat or light.

The number of  $e^-$ s excited thermally into the conduction band depends on the energy band gap width as well as temperature. At a given temperature, the larger the  $E_g$ , the lower the probability that a valence electron will be promoted into an energy stage within the conduction band resulting in fewer conduction  $e^-$ s i.e. the larger the band gap, the lower the electrical conductivity at a given temperature, the distinction between semi conductors and insulators lies in the width of the band gap; for semiconductors, it is narrow, whereas for insulating materials it is relatively wide.

Increasing the temp results in an increase in the thermal energy that is available for e-excitation , more  $e^-$ s are promoted into the conduction band, giving rise to an enhanced conductivity. The bonding in semiconductors is covalent and relatively weak valence electrons are more easily removed by thermal excitation than for insulators.

### ELECTRON MOBILITY

When an electric field is applied, a force is brought to bear on the free electrons, as a consequence, they all experience an acceleration in a direction opposite to that of the field, by virtue of their negative charge. No interaction between an accelerating  $e^-$  and atoms in a perfect crystal lattice according to quantum mechanics. All the free  $e^-$  should accelerate as long as the electric field is applied which will give rise to a continuously increasing electric current with time. There is a frictional force which counter electron acceleration from the external field. These frictional forces result from the scattering of electrons by imperfections in the crystal lattice, including impurity atoms, vacancies, interstitial atoms, dislocations and even the thermal vibrations of the atoms themselves. Each scattering event causes an electron to lose kinetic energy and to change its direction of motion as shown above. There is some net electron motion in the direction opposite to the field and this flow of charge is the electric current.

The drift velocity  $V_d$  represents the average electron velocity in the direction of the force imposed by the applied field. It is directly proportional to the electric field.

$$V_d = \mu_e \epsilon \quad \mu_e = \text{electron mobility. Unit (m}^2/\text{v-s).}$$

The conductivity  $\sigma$  of most materials expressed as follows,  $\sigma = n/e/\lambda_e$ .  $n$  = no of free or conducting  $e^-$ s per unit volume (e.g. per cubic meter), and  $/e/-$ absolute magnitude of the electrical charge on an electron. ( $1.6 \times 10^{-19} \text{C}$ ).

### ELECTRICAL RESISTIVITY OF METALS

**Resistivity** is the reciprocal of **conductivity**. Total resistivity of a metal is the sum of the contributions from thermal vibrations, impurities and plastic deformation i.e. the scattering mechanisms act independently of one another.

$$\rho_{\text{total}} = \rho_t + \rho_i + \rho_d \quad (\text{a})$$

the above equation is known as **Mathiessen's rule**.

Room temperature electrical condition for nine common metals and alloys.

Metal	Electrical conduction [ $\Omega\text{m}$ ] <sup>-1</sup>
Ag	$6.8 \times 10^7$
Cu	$6.0 \times 10^7$
Au	$4.3 \times 10^7$
Al	$3.8 \times 10^7$
Iron	$1.0 \times 10^7$
Brass(70cu-30Zn)	$1.6 \times 10^7$
Platinum	$0.94 \times 10^7$
Plain carbon steel	$-0.6 \times 10^7$
Stainless steel	$-0.2 \times 10^7$

### INFLUENCE OF TEMPERATURE

For pure metal and all Cu-Ni alloys, the resistivity rises linearly with temperature above about -  $200^0\text{c}$ . This  $\rho_t = \rho_0 + aT$



Constant for particular metal.

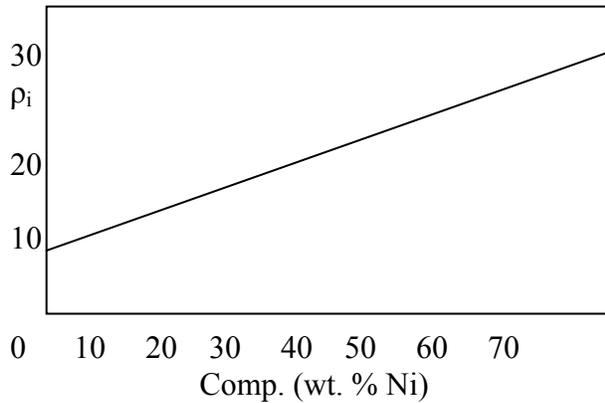
The dependence of the thermal resistivity component on temperature is due to the increase with temperature in thermal vibrations and other lattice irregularities (e.g. vacancies), which serve as electron-scattering centre.

### IMPURITIES

$\rho_i$  is related to the impurity concentration  $c_i$  in terms of the atom fraction(at 9/100) as follows:

$$\rho_i = \underline{A c_i (1 - c_i)}$$

constant function of impurity and lost metals



e.g. up to 50 wt. % Ni impurities in Copper.

For a two-phase alloy consisting of  $\alpha$  and  $\beta$  phases, a rule of mixtures expression may be utilized.

$\rho_i = \rho_{\alpha}V_{\alpha} + \rho_{\beta}V_{\beta}$  where the  $V$ 's and  $\rho$ 's rep. vol. fractions and individual resistivities.

### PLASTIC DEFORMATION

Raises the electrical resistance as a result of increased nos of  $e^-$  scattering dislocations.

### ELECTRICAL CHARACTERISTICS OF COMMERCIAL ALLOYS

Electrical and other properties of Cu render it the most widely used metallic conductor.  $O_2$ -free high-conductivity (OFHC) Cu, having extremely low  $O_2$  and other impurity contents, is produced for many electrical applications. Al has half conductivity of Cu and is frequently used as an electrical conductor, Ag has a higher conductivity than either Cu or Al; its use is restricted due to cost.

To improve the mechanical strength of a metal alloy without impairing significantly its electrical conductivity. Both solid solution alloying and cold working improve strength at the expense of conductivity, thus, a trade off must be made for these two properties. Strength may be enhanced by introducing a second phase that does not have adverse effect on conductivity e.g. Cu-Be alloys are precipitation hardened, conductivity reduced by factor of 5 over high-purity Cu.

For furnace heating element, a high electrical resistivity is desirable energy loss by  $e^-$ 's is dissipated as heat energy.

#### 4.0 CHEMICAL PROPERTIES OF MATERIALS

Most materials experience some type of interaction with a large number of diverse environments. Such interactions impair materials usefulness as a result of the deterioration of its mechanism properties (e.g. ductility and strength), other physical properties, or appearance.

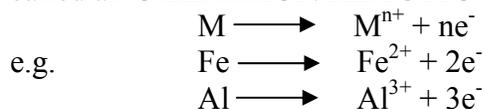
In metals, there are actual materials loss either by dissolution (corrosion) or by the formation of nonmetallic scale or film (oxidation) ceramic materials are resistant to deterioration, which usually occurs at elevated temperatures or in rather extreme environments called **CORROSION**, for polymers, degradation is often used. Polymers may dissolve when exposed to a liquid solvent or may absorb the solvent and swell, also, electromagnetic radiation (primarily ultraviolet) and heat may cause alterations in their molecular structure.

#### 4.1 CORROSION OF METALS

Corrosion is defined as the destructive and unintentional attack of a metal in the reaction with the environment. This problem is of significant importance in economic term. Approximately 5% of an industrialized nation's income is spent on corrosion prevention and the maintenance or replacement of products lost or contaminated as a result of corrosion reactions. Examples: rusting of automotive body panels and radiation and exhaust components.

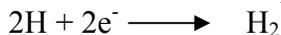
##### CORROSION REACTIONS

Corrosion process is electrochemical, that is, a chemical reaction in which there is transfer of electrons from one chemical species to another. Metal atoms lose or give up electrons which is called an **OXIDATION REACTION**.

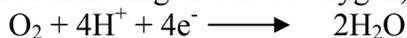


The site at which oxidation takes place is called the **ANODE**, thus oxidation is sometimes called an **ANODIC REACTION**.

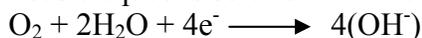
The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species which is termed a **REDUCTION REACTION**.



For an acid solution having dissolved oxygen, reduction occurs as follows:



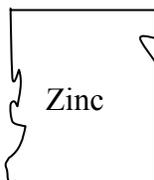
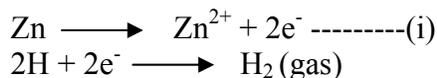
For a neutral or basic aqueous solution in which  $\text{O}_2$  is dissolved



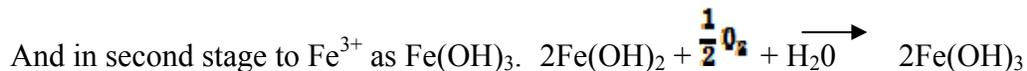
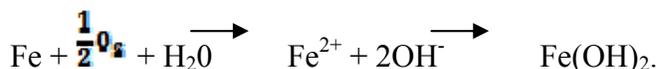
The location at which reduction occurs is called the **CATHODE**. In electrochemical reaction, the total rate of oxidation must equal the total rate of reduction, or all electrons generated through oxidation must be consumed by reduction.

e.g. Zn immersed in acid

Solution



Another example is the oxidation or rusting of iron in water, which contain dissolved oxygen.

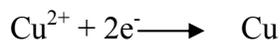


ELECTRODE POTENTIALS

Consider an electrochemical cell below. On the left hand side is a piece of pure iron immersed in a solution containing  $\text{Fe}^{2+}$  ions of 1M concentration. The other side of the cell consists of a pure copper electrode in a 1M solution of  $\text{Cu}^{2+}$  ions. The cell halves are separated by a membrane, which limits the mixing of the two solutions. If the iron and copper electrodes are connected electrically, reduction will occur for copper at the expense of the oxidation of iron, as follows,



Half cell reactions



Galvanic couple-two metals electrically connected in a liquid electrolyte wherein one metal becomes an anode and corrodes, while the other acts as a cathode. An electric potential or voltage exists between the two half cells, and its magnitude can be determined if a voltmeter is

connected in the external circuit. A potential of 0.780V results for a Cu-Fe galvanize cell when the temperature is 25°C (77°F).

Also, galvanic couple of iron and zinc immersed in a 1M solution of Zn<sup>2+</sup> ions. The zinc is the anode and corrodes, whereas the Fe now becomes the cathode. The electrochemical reaction is thus,

$Fe^{2+} + Zn \longrightarrow Fe + Zn^{2+}$ , the potential is 0.323V. A half-cell similar to above is termed a standard half-cell.

### THE STANDARD EMF SERIES

The standard hydrogen electrode consists of an inert platinum electrode in a 1M solution of H<sup>+</sup> ions, saturated with hydrogen gas that is bubbled through the solution at a pressure of 1atm and a temperature of 25°C. the platinum itself does not take part in the electrochemical reaction. It acts only as a surface on which hydrogen atoms may be oxidized or hydrogen ions may be reduced. The electromotive force (emf) serves is generated by coupling to the standard half-cells for various metals and ranking them according to measured voltage.

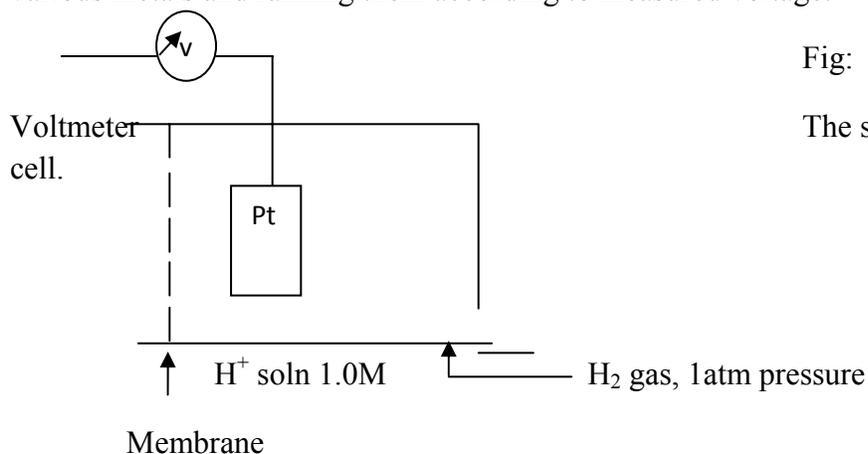


Fig:  
The standard H<sub>2</sub> reference half-

### The standard emf series

	Electrode Reaction	Std Electrode Potential
	$\longrightarrow$ $Au^{3+} + 3e^- \rightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$\longrightarrow$ $Pt^{2+} + 2e^- \rightarrow Pt$	+1.2
Inert(cathodic)	$Ag^+ + e^- \longrightarrow Ag$	+0.80

↑  
Increasingly

	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$		+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$		+0.401
	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$		+0.340
	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$		0.00
	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$		-0.126
	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$		-0.136
	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$		-0.250
	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$		-0.277
	$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$		-0.403
	$\text{Fe}^{2+} \rightarrow 2e^- + \text{Fe}$		-0.440
	$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$		-0.744
	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$		-0.763
	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$		-1.662
Increasingly	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$		-2.363
Active(anodic)	$\text{Na}^+ + e^- \rightarrow \text{Na}$		-2.714
	$\text{K}^+ + e^- \rightarrow \text{K}$		-2.924

From the table, gold and platinum are noble or chemically inert, while sodium and potassium have the highest reactivity's.

### INFLUENCE OF CONCENTRATION AND TEMP ON CELL POTENTIAL

The emf series applies to highly idealized electrochemical cells (i.e. pure metals in 1M solutions of their ions, at 25°C)

**Nernst equation:**  $\Delta V = (V_2 - V_1) - \frac{RT}{nF} \ln \frac{[m_1^{z+}]}{[m_2^{z+}]}$ , where R is the gas constant,

n –number of electrons either of half-cell, F – Faraday constant, 96500C/mol. The magnitude of charge per mole is  $6.023 \times 10^{23}$  At 25<sup>0</sup>C.

:  $\Delta V = (V_2 - V_1) - \frac{0.0592}{n} \log \frac{[m_1^{n+}]}{[m_2^{n+}]}$  to give  $\Delta V$  in volts. For reaction spontaneously,  $\Delta V$  must be positive. For 1M concentrations of both ion types.

Ex1: one half of an electrochemical cell consists of a pure nickel electrode in a solution on Ni<sup>2+</sup> ions. The other is a cadmium electrode immersed in a Cd<sup>2+</sup> solution.

(a) If the cell is a standard one, write the spontaneous overall reaction and calculate the voltage that is generated. (b) Compute the cell potential at 25<sup>0</sup>C if the Cd<sup>2+</sup> and Ni<sup>2+</sup> concentration are 0.5 and 10<sup>-3</sup>M respectively. Is the spontaneous reaction direction still the same as for the standard cell?

Solution:

(a) The cadmium electrode will be oxidized and nickel reduced because cadmium is lower in the emf series; thus, the spontaneous reactions will be  $Cd \rightarrow Cd^{2+} + 2e^-$ ,  $Ni^{2+} + 2e^- \rightarrow Ni$ ,  
 $Ni^{2+} + Cd \rightarrow Ni + Cd^{2+}$

Half-cell potentials for cadmium and nickel are respectively -0.403 and -0.250V.

$$\Delta V = V_{Ni} - V_{Cd} = -0.250V - (-0.403) = +0.153V$$

$$\rightarrow (b) Cd^{2+} + Ni \rightarrow Cd + Ni^{2+}, \text{ thus } \Delta V = (V_{Cd} - V_{Ni}) - \frac{RT}{nF} \ln \frac{[Ni^{2+}]}{[Cd^{2+}]}$$

$$= -0.403V - (-0.250V) - \frac{0.0592}{2} \log 10^{-3}$$

$$= -0.073V$$

Some  $\Delta V$  is negative the spontaneous reaction direction is opposite to.

## 5.0 STABILITY OF MATERIALS IN SERVICE ENVIRONMENT

The most common method of preventing corrosion is the selection of the proper material (metal or alloy or non-metal) for a particular service environment.

In alloy selection, there are several “natural” metal-corrosion combination. These combinations of metal and corrosive usually represent the maximum amount of corrosion resistance for the least amount of money. Some of these combinations are listed below-

1. Stainless steels- nitric acid
2. Nickel and nickel alloys- caustic
3. Monel – hydrofluorine acid.
4. Hastelloys ( chlorinels) nos hydrochloric acid.
5. Lead- dilute sulphuric acid.
6. Aluminium-nonstaining atmospheric exposure.
7. Tin-distilled water.
8. Titanium-hot strong oxidizing solutions
9. Tantalium-ultimate resistance.
10. Steel-concentrated sulphuric acid.

Tantalum and glass are resistant to virtually all media except hydrofluoric acid and caustic solution. For reducing or oxidizing environments such as air free acids and aqueous solutions nickel, copper and their alloys are used.

For oxidizing solution-chromium containing alloys are used . For extremely powerful oxidizing conditions-titanium and its alloys show superior results.

NONMETALLIC; The five general classes are

1. rubbers, natural and synthetic
2. plastics
3. ceramics
4. carbon and graphite
5. wood.

In general rubbers and plastics are much weaker, softer, more resistant to chloride ions such as nitric, less resistant to solvent, have low temperature limitations (170 to 200°F). Ceramics possess excellent corrosion and high-temperature resistance but brittle and have low tensile strength.

Carbon-good corrosive resistance, electric and heat conductivity but fragile.

Wood-attacked by aggressive environment.

**6.0 BASIC METALLURGY:** is the applied science of the extraction of metals from their ores and subsequent refining of the crude metals produced. Shaping of metals by mechanical working processes together with simple heat treatment for steels. It is subdivided into

- a) Extraction Metallurgy: dealing with the winning of metals from the Earth's crust.
- b) Process Metallurgy : dealing with the alloying, shaping and subsequent heat-treatment of metals.
- c) Physical Metallurgy: dealing mainly with the crystal structure of metals and alloys and its effect on their physical and mechanical properties.

**6.1 PRODUCTION OF IRON AND STEEL:** iron occurs in the earth's crust in combination with other elements (mainly oxygen). The most important ores of iron are oxides.

Types of Iron Ore:

- a) Magnetite ( $\text{Fe}_3\text{O}_4$ ) which contains 72.4% iron when pure but rather less as mined. It is a magnetic mineral, a fact which proves useful in locating deposits.
- b) Hematite ( $\text{Fe}_2\text{O}_3$ ), which accounts for the bulk of ore mined in the world and occurs in a variety of forms –red, brown or black. It contains 40-65% iron.
- c) Limonite and other hydroxides types of ore, varying in composition from  $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  to  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and containing 20-55% iron.
- d) Siderite ( $\text{FeCO}_3$ ) and other types of carbonate ore; usually of rather low iron content.

**6.2 The Ore producing Region of the World:** they are

- a) The American Lake Superior deposits, which consist of high grade hematite and contain 30-65%

- b) The large deposits in the U.S.S.R, consisting mainly of hematite in the Ukraine and magnetite in Siberia.
- c) the low-grade or “lean” sedimentary deposits of Britain’s East Coast, which are mainly limonite and siderite containing 20-30% Fe.
- d) The Lorraine deposits of “minette” (hematite) in the north of France containing 26—50% Fe.
- e) The very high grade deposits of magnetite in Sweden’s “land of the midnight sun”. Kirimara is a mountain containing magnetite (60-68%Fe).
- f) Canadian deposits in Labrador, Quebec and New found land. High-grade hematite of the lake Superior type.
- g) Large reserves, mainly of hematite occurring in the Amazon basin of Brazil.
- h) Indian deposits of high-grade ore which are more than enough to satisfy home demands.
- i) Deposits in Venezuela of high-grade hematite (65%Fe).
- j) African deposits – Mauritania, Liberia, Algeria, Morocco, Sierra-Leone and Tunisia, Nigeria.
- k) Nigeria deposits- Itape, Ilesa.

**6.3 Pre-smelting Treatments of Ores:** after initial mining and crushing operations, an ore may undergo preliminary treatments before it is charged to the blast furnace. This is necessary to increase the efficiency of the smelting process.

Concentration: the removal of as much as possible of the earthy waste or gangue, which would otherwise take up useful space in the blast furnace. It is economical to concentrate ore at mine rather than to pay transport charges on the crude ore, containing large amount of useless gangue. Magnetites are concentrated in roasted to convert it to magnetite whilst hematite ores are treated by washing to remove lighter gangue.

Calcination: this is effected in a kiln of either the shaft or rotary type. It applies to ores containing large amount of moisture or  $\text{CO}_2$ . These substances may cause irregular working in the blast furnace and are best removed before the ore is smelted. Calcining also removes sulphur by oxidizing it to  $\text{SO}_2$ . Rotary kilns are fired at the lower end by either blast furnace gas or oil, and the temperature is high enough to expel water and  $\text{CO}_2$  from the ore, which is fed at the upper end so that it meets the rising hot gases. The calcined ore is ejected at lower end of the kiln.

## AGGLOMERATION

The dust produced by previous methods needs to be reclaimed as it is rich in iron.

(a) **Sintering**; the dust is mixed with a small amount of coke or breeze and fed to a sintering machine. Ignition of the coke, assisted by air drawn through the pallets, generates sufficient heat to frit together the particles of ore, producing a porous and easily reducible sinter.

(b) **Pelletising**: fine dust mixed with a little starch and water and rolled in a drum so that smallballs are formed. Coal dust is then added and the balls rolled on to the grate of a sintering machine where they are first dried and then baked at 1000<sup>0</sup>C to harden them.

(c) **Nodulising**: similar to pelletising except that a heated rotating technique is employed to produce the agglomerate.

The Smelting Operation: the treated ore is charged along with coke and limestone, to the blast furnace, where smelting takes place. Smelting is a two fold operation including:

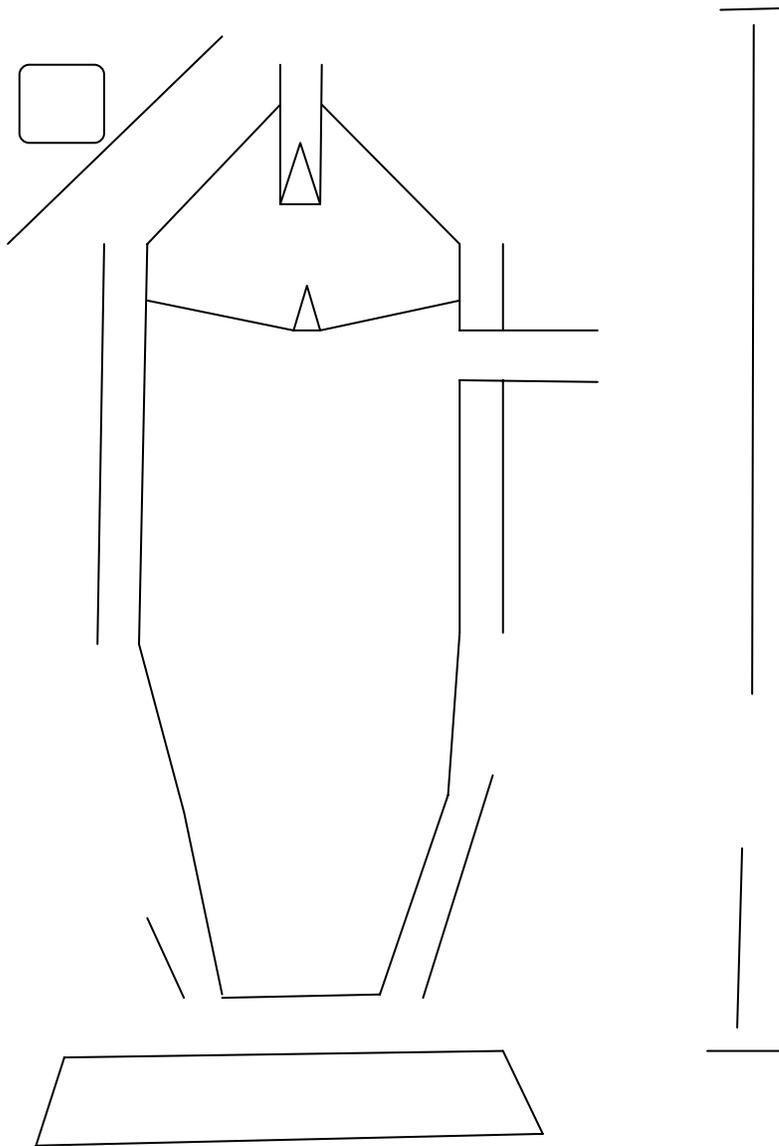
a) The chemical reduction of the iron oxide by the white-hot coke and the carbon monoxide gas arising therefrom.

b) The liquefaction of the gangue by means of the flux (limestone) to form a fusible slag which will run from the furnace.

The blast furnace consists of a vertical steel shell lined with refractory materials and having a charging arrangement at the top and a means of running off the pig iron and slag at the bottom. Air is blown in near the bottom of the furnace and this forced draught increases the speed of combustion and maintains the necessary high temperature. The complete structure powers to 30m and often more.

During the production of pig iron large amounts of gas are evolved. This gas has a considerable calorific value due to the carbon monoxide which it contains and much of it is burned in brick work stoves in order to pre-heat the air blast to the furnace.

Pre heating the air blast will of course mean that less fuel is required. However, less sulphur will enter the pig iron since coke always contain sulphur.





Materials balance in blast furnace

Input/Charge (tonnes)	Output/Products(tonnes)
1. Ore (say, 50 % iron)-4,000	1. Pig iron..... 2000
2. Coke .....1800	2. Slag .....1600
3. Limestone .....800	3. B.F gas.....10,800
4. Air .....8000	4. Dust .....200
Total	14,600      Total      14,600

Pig iron is a complex alloy containing up to 10 % of other elements (carbon, silicon, manganese, phosphorus and sulphur).

**STEELS**

Steels are iron –carbon alloys that may contain appreciable concentrations of other alloying elements. The mechanical properties are sensitive to the content of carbon., which is normally less than 1.0 wt. % . They are classified into low, medium and high carbon types.

**LOW-CARBON STEELS**

They contain less than 0.25 wt. % C. They are greatly produced among steel type. Microstructure consist of ferrite and Pearlite constituents. These alloys are relatively soft and weak, but have outstanding ductility and toughness. They are machinable, weldable and least expensive to produce. Typical applications include automobile body components.Structural shapes (I beam,

channel and angle iron) and sheets used in pipelines, buildings, bridges and tin cans. They have yield strength of 275 Mpa, tensile strengths btw 415 and 550 Mpa and a ductility of 25% elongation. Another group of low-carbon alloys are the high strength low -alloy (HSLA) steels. They contain other alloying elements such as Copper, Vanadium, Nickel, and Molybdenum in combined concentrations as high as 10 wt.% and possesses higher strengths. They may be strengthened by heat treatment giving tensile strengths in excess of 480 Mpa. HSLA are more corrosion resistant and find applications in bridges, towers, support columns in higher buildings and pressure vessels.

### **MEDIUM-CARBON STEELS**

They have carbon concentrations between 0.25 and 0.60 wt %. These alloys may be heat treated by austenitizing, quenching, and then tempering to improve their mechanical properties. They have microstructures of tempered martensites. They have low hardenabilities. Applications include railway wheels and tracks, gears, crankshafts and other machine parts and high strength structural components of high strength, wear resistant and toughness.

### **HIGH-CARBON STEELS**

They have carbon content between 0.6 and 1.4 wt. %. They are the hardest, strongest and least ductile. They are used in a hardened and tempered condition. They are wear resistant and capable of holding a sharp cutting edge. The tool and die steels are high carbon alloys, usually containing chromium, vanadium, tungsten and molybdenum. These steels are utilized as cutting tools and dies for forming and shaping materials as well as in knives, razors, hacksaw blades, springs and high strength wires.

### **STAINLESS STEELS**

They are highly resistant to corrosion in a variety of environments especially the ambient atmosphere. The predominant alloying element is chromium. A concentration of at least 11 wt % Cr is required. Corrosion resistance may also be enhanced by nickel and molybdenum additions.

#### **Assignment**

1. Write brief note about Cast Iron. Distinguish between grey iron, ductile iron, white iron and malleable iron.

2. Write brief note about Nonferrous Alloys? Your note must include Copper and its alloys, Aluminium and its alloys, Titanium and its alloys and the Superalloys.

## NON METALLIC MATERIALS

These include ceramics, polymers, carbon, composites and biomaterials.

### CERAMIC MATERIALS

They are inorganic and non metallic materials. The term “ceramic” comes from the Greek word Keramikos, which means “burnt stuff” indicating that desirable properties of these materials are achieved through a high-temperature heat treatment process called **firing**.

The term “ceramic” has taken a broader meaning. To one degree or another, these new materials have a dramatic effect on our lives; electronic, computer, communication, aerospace and a host of other industries rely on their use.

### CERAMIC STRUCTURES

They are composed of at least two elements and often more their crystal structures are generally more complex than those for metals. The atomic bonding in these material ranges from purely ionic to totally covalent, many ceramics exhibit a combination of these two bonding types, the degree of ionic character being dependent on the electro negativities of the atoms.

Material	Percent Ionic character
CaF <sub>2</sub>	89
MgO	73
NaCl	67
Al <sub>2</sub> O <sub>3</sub>	63
SiO <sub>2</sub>	51
Si <sub>3</sub> N <sub>4</sub>	30

ZnS	18
SiC	12

### **CRYSTAL STRUCTURES**

For ceramic materials whose atomic bonding is predominantly ionic, the crystal structures would contain electrically charged ions instead of atoms. The metallic ions or cations are positively charged because they have given up their valence electrons to the non metallic ions or anions which are negatively charged. Two characteristics of the component ions in crystalline ceramic materials influence the crystal structure, the magnitude of the electrical charge on each of the component ions and the relative sizes of the cations and anions. With regard to the first characteristic, the crystal must be electrically neutral i.e all the cation positive charges must be balanced by an equal number of anion negative charges.  $\text{CaF}_2$ :  $\text{Ca}^{2+}(\text{F}^-)_2$ . The second criterion involves the sizes or ionic radii of the cations and anions,  $r_c$  and  $r_A$  respectively, because the metallic elements give up electrons when ionized, cations are ordinarily smaller than anions and consequently the ratio  $r_c/r_A$  is less than unity.

Stable ceramic crystal structures form when those anions surrounding a cation are all in contact with that cation as illustrated below. The coordination number (i.e number of anion nearest neighbors for a cation) is related to the cation-anion radius ratio. For a specific coordination number, there is a critical of minimum  $r_c/r_A$  ratio for which this cation-anion contact is established which ratio may be determined from pure geometrical considerations.

Fig 7.1.2: stable and unstable anion-cation coordination configurations

### **MECHANICAL PROPERTIES OF METALS**

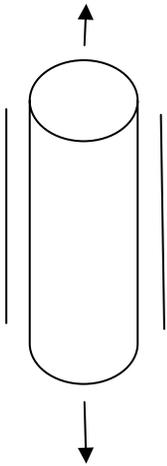
The mechanical behaviour of a material reflects the relationship between its response or deformation to an applied load or force. Important properties are strength, hardness, ductility and stiffness. Mechanical properties are of concern to a variety of parties ( e.g producers and consumers of materials, research organizations, government agencies) that have differing interests, son.

The role of structural engineers is to determine stresses and stress distributions within members that are subjected to well-defined loads. These topics are covered in stress analysis and strength

of materials. Materials engineers are concerned with producing and fabricating materials to meet service requirements as predicted by those stress analyses. Materials are chosen for structural applications because they have desirable combinations of mechanical characteristics.

### Concepts of Stress and Strain

Loading is applied in tension, compression, shear and torsion.



$\sigma$

### TENSION TESTS

$$\sigma = \frac{F}{A_0} \text{----- (1)}$$

F- instantaneous load applied perpendicular to the specimen cross section F(N) and  $A^0(m^2)$

$\sigma$  - mPa,  $1\text{mPa} = 10^6 \text{ N/m}^2$

$$E = \frac{l_1 - l_0}{l_0} = \frac{\Delta l}{l_0}$$

$L_0$  is original length before any load is applied and  $l_1$  is the instantaneous length.

Compression Tests: similar to tensile test except that the force is compressive and the specimen contracts along the direction of the stress.

### **SHEAR AND TORSIONAL TESTS**

$T = \frac{F}{A_0}$  F is the load or force imposed parallel to the upper and lower faces, each of which has an area of  $A_0$ . The shear strain  $\lambda$  is the tangent of the strain angle  $\theta$ . Torsion is a variation of pure shear, wherein a structural member is twisted in the above.

$\sigma = E \epsilon$ , E is the modulus of elasticity or Young's modulus (GPa)

This is known as **Hooke's Law**, and the constant of proportionality E (GPa or Psi) is the **modulus of elasticity or Young's modulus**

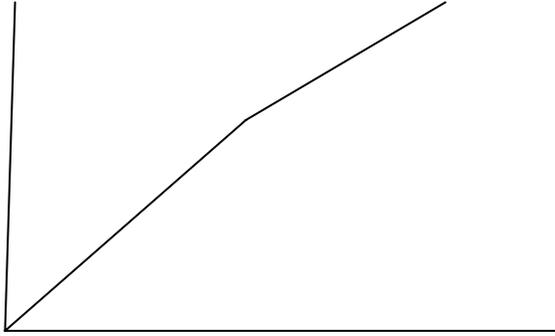
Deformation in which stress and strain are proportional is called elastic deformation

$$1 \text{ GPa} = 10^9 \text{ N/m}^2 = 10^3 \text{ MPa},$$

E is resistance of elastic deformation. The greater the modulus, the stiffer the material or the smaller the elastic strain that results from the application of a given stress. For some materials (e.g. grey cast iron, concrete, and many polymers) this initial elastic portion of the stress-strain curve is not linear, hence no modulus of elasticity. For this non-linear behavior either tangent or secant modulus is normally used.

Tangent modulus=slope of stress-strain curve at some specified level of stress. While secant modulus represents the slope of a secant drawn from origin to some given point of the  $\sigma$ - $\epsilon$  curve.

$$\tau = G \gamma$$



### SHEAR STRESS

The maximum shear stress is related to the applied torque T as

$$\tau_{\max} = \frac{Tr}{J}$$

where  $J = \pi r^4/2$  is polar second moment of area of the cross section.

The maximum point on a torque-trust diagram corresponding to a point u is

$T_u, S_{su} = Tur/J$ , defines the modulus of rupture for the torsion test.

#### Example 1

A piece of Copper 305 mm long is pulled in tension with a stress of 276 MPa. If the deformation is entirely elastic, What will be the resultant elongation?

Solution  $\sigma = E\varepsilon = (\Delta l/l_o)E$

$$\Delta l = \sigma l_o/E = (276 \text{ MPa} \times 305 \text{ mm})/(110 \times 10^3 \text{ MPa})$$

$$= 0.77 \text{ mm}$$

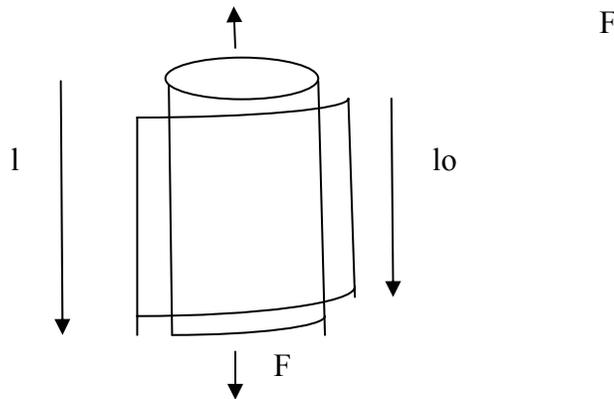
Poisson's ratio  $\nu$  is the ratio of the lateral and axial strains or

$$\nu = -\epsilon_x/\epsilon_z = -\epsilon_y/\epsilon_z$$

-ve sign means,  $\nu$  is always +ve. Shear and elastic moduli are related to each other and to **Poisson's ratio**.  $E = 2G(1+\nu)$ , in most metals,  $G = 0.4E$

**Ex2:** A tensile stress is to be applied along the long axis of a cylindrical brass rod that has a diameter of 10mm. Determine the magnitude of the load required to produce a  $2.5 \times 10^{-3}$  mm change in diameter if the deformation is elastic.

Solution



$$\Delta d = 2.5 \times 10^{-3} \text{ mm.}$$

$$\epsilon_x = \frac{\Delta d}{d_0} = \frac{-2.5 \times 10^{-3}}{10} = -2.5 \times 10^{-4}$$

$$\epsilon_z = \frac{-\epsilon_x}{\nu} = -\frac{(-2.5 \times 10^{-4})}{0.34} = 7.35 \times 10^{-4}$$

$$\sigma = \epsilon_z E = (7.35 \times 10^{-4})(97 \times 10^3 \text{ mPa}) = 71.3 \text{ mPa}$$

$$F = \sigma A_0 = \sigma \left( \frac{d_0}{2} \right)^2 \pi = 5600 \text{ N}$$

**RESILIENCE** is the capacity of a material to absorb energy when it is deformed elastically and then upon unloading to have the energy recovered.  $U_r$  is the strain energy per unit volume required to stress a material from an unloaded state up to the point of yielding.

$$U_r = \int_0^{\epsilon_y} \sigma d\epsilon$$

For linear elastic region,

$$U_r = 1/2 \sigma_y \epsilon_y = 1/2 \sigma_y \sigma_{y/E} = \sigma_y^2 / 2E$$

### **DUCTILITY**

It is a measure of the degree of plastic deformation that has been sustained at fracture. Brittle material has little or no plastic deformation.

$$\text{Percent elongation or percent area reduction, \% EL} = \left( \frac{l_f - l_o}{l_o} \right) \times 100$$

$l_f$  = fracture length,  $l_o$  = original gauge length

$$\%AR = \left( \frac{A_o - A_f}{A_o} \right) \times 100$$

