

Principles of Metallurgy

INTRODUCTION

Metals make up a major part of the elements in the periodic table. Metals are divided into ferrous and non-ferrous. The ferrous metals group includes Fe, Mn, Cr and their alloys. All the rest are non-ferrous metals. Non-ferrous metals are of four types. (1) Heavy metals such as Cu, Pb, Sn and Ni. (2) Light metals such as Al, Mg, Ca, K and Na and often Ba, Be, Li and other alkaline earth metals are also included in this group. (3) Noble or precious metals such as Pt, Ir, Os, Pd, Ru, Rh and Ag. (4) Rare metals. (a) High melting metals such as tungsten, molybdenum, vanadium, tantalum, titanium, zirconium and niobium. Occasionally cobalt is also included in the group. (b) Light metals such as strontium, scandium, calcium, rubidium and others. (c) Scattered metals such as germanium, gallium, thallium, indium and rhenium. (d) Rare earth metals such as lanthanum, yttrium, hafnium, cerium, scandium and others. (e) Radioactive metals such as thorium, radium, actinium, polonium, uranium and the transuranium elements. The so called small metals (Sb, Hg and Bi) are often separated from the rare metals into a separate group.

Metals in the solid state are crystalline substances, whose atoms are arranged in a definite pattern and form a crystal lattice. The structure of a metal depends on the shape and respective location of the crystals in the crystal lattice. In metals, allotropic transformations often occur and a metal can have various crystal forms, depending on the conditions during crystallisation and cooling of the solid (polymerisation). Thermal treatment of metals such as annealing and tempering is based on their capability to undergo polymorphic transformation. The structure of a metal depends on the shape, size and respective location of the crystals in it.

Crystals (α -Fe, Cr, V, Mo, W, K and Na) have a body centred cubic structure with a co-ordination number of 8. Crystals of γ -Fe, Ni, Co, Cu, Al, Au, Ca etc have face centred cubic crystals with a co-ordination number of 12. Metals like Zn, Mg, Cd, Ti etc. have a hexagonal form, with the densest packing and a co-ordination number of 12.

CHARACTERISTICS OF METALS

109 elements are known at present. Oxygen is the most abundant element in the earth crust. About 80% of the known elements are metals, with the following important characteristics.

- (a) All metals, except mercury (which is liquid) are solids at room temperature.
- (b) They exhibit brilliant metallic lustre when freshly cut or polished. Some non-metals, like graphite, diamond, iodine also have lustre.
- (c) They are malleable as well as ductile. Malleability is the property of metals to be fabricated into sheets or foils, while ductility is the property of metals to be drawn into wires. These properties are related to the fact that the outer or valence electrons of metal atoms are loosely held and they can be easily removed or ionised. It is also easy to remove or ionise a valency electron from a metal atom than from a non metal atom.
- (d) They are usually hard, except alkali metals, which are soft enough to be cut with a knife.
- (e) They are very good conductors of heat and electricity.
- (f) Metals possess high electrical and thermal conductivities. The electrical conductivity of metals is even greater than that of electrolytes.
- (g) Normally metals possess relatively high densities, except a few metals, such as Li, Na, K, etc. which are exceptionally light.
- (h) Metals have a tendency to lose electrons, thereby acquiring the positive charge. Such elements have low ionisation potential as well as low electronegativity and electron affinity.

Energy is always required to remove one or more electrons from a neutral atom. Lesser the energy required for a metal atom to lose its valency electrons, the more reactive the metal will be and the more metallic character it will have. Because energy needed for removing the valence electrons from a metal atom varies considerably, the chemical reactivity of the metals also varies greatly. For example, sodium reacts very rapidly and violently with water, while copper and nickel do not react with water.

- (i) Because of their tendency to lose electrons, they are good reducing agents.

SLAGS AND FLUXES

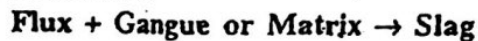
Metals and non-metals and some other components constitute what is known as slag. According to their chemical properties, these oxides may be classified into three groups:

(a) Basic Oxides, such as CaO , MgO , FeO , MnO , Na_2O and K_2O .

(b) Acidic Oxides, such as SiO_2 , P_2O_5 , TiO_2 , V_2O_5 etc.

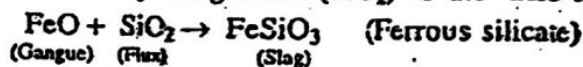
(c) Amphoteric Oxides, such as Al_2O_3 , V_2O_3 , Cr_2O_3 etc.

The gangue material in the ore is removed by adding another chemical substance, called flux. A substance added to convert the gangue or matrix into fusible mass is called flux. The fusible mass is known as slag. The flux reacts with gangue to form slag, which is generally obtained as an upper liquid layer over molten metal in the furnace.

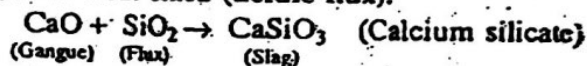


Fluxes are generally of two types.

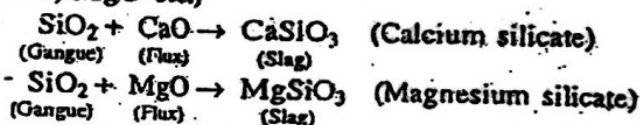
(a) Acidic Fluxes - When the ore is associated with basic impurities such as FeO , CaO , MgO etc, a suitable acid flux such as SiO_2 , P_2O_5 etc. is used. For example, in the extraction of copper, the ferrous oxide (FeO), a basic impurity is removed by using silica (SiO_2) as the acid flux.



Similarly, lime may be removed with silica (acidic flux).



(b) Basic Fluxes - If the ore is associated with acidic impurities such as SiO_2 , P_2O_5 etc., then the flux used must be basic (e.g. CaO , MgO etc.)



The fusible mass, known as slag is removed and used in road making as well as in the manufacture of cement and fertilizers. Thomas slag is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$.

METALS AND METALLIC CHARACTER

Metals have a tendency to lose electrons readily and tend to form positive ions such as Na^+ , Mg^{2+} , Al^{3+} etc, when they react with non-metals. We can associate metallic character with ionisation energy. Metallic character should decrease as we move across the periodic table and increase as we move down. The elements we commonly consider to be metals are : (a) All the elements in Groups IA and IIA. (b) The heavier elements in III A (Al , Ga , In , Tl), IVA (Sn , Pb), and VA (Bi). (c) All the transition-elements (B-subgroups). (d) All the lanthanides and actinides.

NON METALS

Clustered towards the upper right corner of the periodic table are 17 elements ordinarily known as non metals. The most important characteristics of non-metals is their tendency to gain electrons in chemical reactions. For example, oxygen and fluorine acquire electrons to form negative ions O^{2-} and F^- when they react with metals. The tendency of non-metal atoms to gain electrons readily is also reflected in their high electronegativities, which range from 2.1 to 4.0. All metals have electronegativities less than 2.0. Of the elements listed as non-metals, the so called noble gases are unique in two important respects: (a) Atoms of these elements have no tendency to combine with one another. All of these gases (He , Ne , Ar , Kr , Xe , Rn) are monoatomic. Most of the non metals form polyatomic molecules in the gaseous state (e.g. O_2 , N_2 , P_4 , S_8 , F_2 , Cl_2 , Br_2 , I_2). (b) Atoms of these elements have very little tendency to react with atoms of other elements. A few compounds of Kr , Xe and Rn have now been prepared, but no compound of He , Ne and Ar are known. Both of these characteristics are related to the unusual stability of the electronic configuration of noble gases which is ns^2np^6 .

METALLOIDS

Located along a diagonal line in the periodic table are several elements (B in III A, Si and Ge in IV A, As and Sb in VA, Te in VI A) that are known as metalloids, because they have properties

All the metals originally come from the natural deposits in the earth's crust and are called ores. Earth's crust refers to the outer siliceous shell of our globe - a shell of 10 miles thick (earth diameter is 8000 miles). Rocks of earth crust are classed as igneous, metamorphic and sedimentary rocks. Igneous rocks are probably the parent substances of all terrestrial matter, so the composition of earth's crust as a whole will not be very different from the composition of the igneous rocks.

Average analysis of igneous rocks

| | | |
|-----------------|-------------------|-------------------------|
| Oxygen 46.59 | Nickel 0.020 | Arsenic 0.000,n |
| Silicon 27.72 | Vanadium 0.017 | Tin 0.000,n |
| Aluminum 8.13 | Copper 0.010 | Antimony 0.000,0n |
| Iron 5.01 | Uranium 0.008 | Cadmium 0.000,0n |
| Calcium 3.63 | Tungsten 0.005 | Mercury 0.000,0n |
| Sodium 2.85 | Zinc 0.004 | Silver 0.000,00n |
| Potassium 2.60 | Lead 0.002 | Platinum 0.000,000,n |
| Magnesium 2.09 | Thorium 0.002 | Gold 0.000,000,n |
| Titanium 0.63 | Cobalt 0.001 | Iridium 0.000,000,0n |
| Manganese 0.10 | Beryllium 0.001 | Palladium 0.000,000,00n |
| Zirconium 0.026 | Molybdenum 0.000n | Radium 0.000,000,000n |

Letter 'n' used in some of the values indicates the position of the first significant figure and that its exact value is unknown.

The mining of metal bearing ores may be done by open pit or underground methods. There are fundamentally two types of mining. (1) Selective mining - In which relatively small veins or beds are removed in the form of high-grade ore.

(2) Bulk mining - In which large quantities of low-grade ore are mined without attempt to segregate the high-grade portions.

Metals It is defined as "an elementary substance whose hydroxide or oxide has basic rather than acid properties. This definition does not take into account the other and more valuable properties associated with metals. Metals have definite and characteristics properties - they are hard, strong, tough, lustrous, crystalline, have high M.P. and B.P., high density, high conductivity to heat and electricity, carry positive charge in electrolysis, are malleable and ductile.

Ore - Naturally occurring mineral or combination of minerals and gangue from which one or more metals can be extracted economically (at a profit)

Ore Minerals - Minerals are constituents of rocks. Naturally occurring homogeneous inorganic substance of definite chemical composition and with certain characteristic physical properties. Ore minerals are those minerals that contain the valuable metals in an ore.

Gangue Minerals – The valueless minerals found in ores are the gangue minerals.

Example- lead zinc ore may contain the minerals galena (Pbs), sphalerite (ZnS), pyrite (FeS₂) siderite (FeCO₃) and quartz (SiO₂)

Here galena and sphalerite are ore minerals and pyrite, siderite and quartz are the gangue minerals.

Remember- All ores are minerals but all minerals not ore.

For example – clay is the most common compound of Al, but has never been found possible to use it commercially as an ore of Al.

Criteria for the minerals to be an ore:

(i) *Percentage of the valuable metal(s)*

(ii) *Form in which the metals occurs (native, oxide, sulphide etc.)*

When copper occurs as a native metal in rocks (Michigan deposits), it can be easily recovered by smelting with a suitable flux, relatively pure Cu is obtained easily, quickly and cheaply, making the treatment economical even for low-grade ores. On the other hand, the Montana deposits are richer in Cu but require a complicated and expensive process because copper occurs with iron as sulphide and are also associated with minerals containing As, Sb, Au, and Ag.

(iii) *Nature of Impurities (gangue)*

Although an ore may contain an appreciable percentage of valuable metal it may be associated with others which are difficult or expensive to remove or are not removed and impart undesirable properties to the metal.

There was a fairly large and very high-grade deposit of silver ore in South America. The silver was combined with sulphur and therefore not amenable to amalgamation and was also associated with antimony which rendered its treatment by cyanidation unprofitable. For years the deposit lay unutilized (until froth floatation process was developed).

(iv) *Physical condition of the ore. (moisture, clay etc).*

It directly affects the workability and processing cost.

(v) *Location and nature of deposit. :*

Utah (U.S.A.) huge deposits of ore with 0.9 % Cu. Improved technology and efficiency of the process by Utah copper Co. have made the treatment of such a low grade ore very profitable.

On the other hand, a copper deposit containing well over 3 % Cu was found in Central America. Exploitation of this rich deposit was not regarded as a profitable venture since.

- (a) The deposit was small and erratic.
- (b) Heavy rainfall was rendered construction work difficult and expensive.
- (c) No railroad connecting this district with sea coast.

CLASSIFICATION OF ORES

Ore are classified in several ways.

(i) *Based on workability:*

- (a) Straight or simple ores: contain in only one kind of metal.
- (b) Free-milling ores: Ores of Ag or Au from which considerable percentage of the valuable metal can be extracted by the simple process of crushing and amalgamation.

2. Lowering the production cost of metals when recovered from furnace – reduction in flux and bulk of slag, energy, requirement size of furnace etc. ore dressing includes comminution and classification (concentration)

Comminution: Process of liberation mineral grains from gangue mineral is called comminution. Machines are used to reduce size of ores and minerals. The technique is known as crushing, grinding and size reduction. Crushing and grinding liberate the mineral particles and screening put in the condition best suited for a particular concentration process. Common machines employed for this purpose are crushers, grinders and screens.

Classification (concentration) - It refers to methods of separating mixtures of minerals into two or more products on the basis of difference in various properties of minerals.

1. Hand picking uses difference in color and luster.
2. Gravity method uses difference in densities.
3. Froth flotation method uses difference in surface properties.
4. Magnetic separation method uses difference in magnetic properties.

METALLURGY

Metallurgy may be defined as the art and science of extracting metals economically from their ores or concentrates and adapting these metals to human utilization. Thus the field of metallurgy may be divided into two parts.

1. Chemical metallurgy deals with the melting and refining of metals and known as extractive metallurgy.
2. Physical metallurgy deals with physical and chemical behavior of metals during different operations and known as adaptive metallurgy. It includes heat treatment methods, mechanical working, physical testing etc.

Extractive metallurgy is commonly divided into following fields.

1. **Pyrometallurgy** (fire metallurgy) – deals with chemical reaction at high temperatures. Furnaces are used for this purpose. All iron and steel, copper, tin, nickel, zinc, gold and many metals are won from their ores and concentrates by these methods. Fe, Cu, Pb, Zn, Ag and Sn.
2. **Hydrometallurgy** deals with leaching of ores and concentrates with aqueous solution to dissolve and recover valuable metals by electrolysis. Cu, Al, Ag, Au, Zn are recovered by it.
3. **Electrometallurgy** deals with metallurgical operations that require electric current for the chemical reduction. Al, Mg, Na, Ca, K are recovered by it.

FURNACES:

Shaft furnaces: Shaft furnaces are vertical furnaces with the charge entering at the top and discharging at the bottom. Air (or other gas) is blown near the bottom of the shaft and passes upward through the descending charge. The solid charge must consist of coarse material. The pieces should be large enough so that they will not be blown out by the escaping waste gases. The chemical reaction takes place between the flowing gas stream and the solid material of the charge. If fuel is used in a shaft furnace it is usually added as

a part of the charge- coke is one of the commonest fuels. The charge may be melted so that the liquid form and collect in the *crucible* at the bottom of shaft, or it may remain in the form of solid lumps and be removed in this form.

The charge fills the furnace completely and as it slowly descends, new material is added at the top; the charge must be open so that the uprising gases can pass freely through all parts of it.

Usually the hottest part of the furnaces is near the bottom of the shaft and sensible heat in the uprising gas is absorbed by the cold charge in upper portion; for this reason the shaft furnace has high thermal efficiency.

The iron blast furnace is the most important example of a shaft furnace.

Reverberatory furnaces: Reverberatory furnaces are made in many sizes and are employed in a large number of metallurgical process - two of the most important types are the open hearth steel furnaces and the large reverberatories employed in copper smelting. The reverberatory is essentially a smelting furnace; it consists of a shallow hearth upon which the charge rests, sidewalls and endwalls and a roof or arch. The furnaces are usually rectangular and are fired by means of burners set in the end wall. Long flame fuel is used on the hearth. The roof of reverberatory is exposed to the full radiation from the flame and erosion from the dusts carried in the hot gases.

There is little or no reaction between the fuel or products of combustion and the charge on hearth, the only function of the fuel is to provide heat which is radiated to the cold charge below. In shaft furnaces, on the other hand, the combustion gases usually react with the materials in the charge. Waste gases leave the furnace at very high temperature, hence the reverberatory furnace has a low thermal efficiency.

Muffle Furnaces: It is a furnace in which the charge must be kept separate from the fuel and combustion gases - the charge may be held in muffle, crucible, retort, or the other enclosure which is enveloped by the hot flame gases, and the heat must reach the charge by flowing through the walls of the container. This results in lower thermal efficiency.

Hearth furnaces: Furnaces like the multiple hearth roasting furnace and rotary kilns operate on the same basis as the reverberatory furnace although they do not resemble it. The charge rests on the hearth or kiln wall and is heated by hot gases passing over it.

Electric furnaces: Electric heat may be provided by resistance or by radiation from an electric arc. The resistance used may be a metal wire, silicon carbide, or the charge itself. In arc furnaces the arc is usually struck above the charge.

These furnaces differ from fuel furnaces in that they require no fuel supply nor do they need flues, stacks and other devices to handle the products of combustion. There is no standard type of electric furnace, however, shaft furnaces, reverberatories, muffles, retorts, etc. can all be heated by electrical means as well as by fuel.

There are three major steps involved in extractive metallurgy.

1. Preliminary treatment (comminution and concentration)
2. Smelting or reduction
3. Refining or purification.

Palletizing and Bricking: For some operations the finely divided concentrate is not suitable and the particles must be agglomerated. One such method is bricking or mechanically compressing the powder in small briquettes. Other method is palletizing in which finely divided material is rolled in a drum so that, particles cling together and roll up into spherical pellet. Material from palletizer is screened to separate and recycle small size. As a binding agent water is common. Sometimes-solid reagent or reducing agent is mixed with mineral powder.

Drying and Calcining -- Drying means removal of water or moisture from concentrate ore flux or other solids. It refers to removal of mechanically held water and not to chemically combined water. It is accomplished by converting water to vapor by thermal means. Drying is done in furnace or kiln where wet material is brought into contact with gases or air. Heat is supplied to dryer (i) to raise the temperature of liquid water (ii) to supply latent heat of vaporization

Calcination is process of heating a material to high temperature but below its fusing temperature to produce chemical decomposition. This originally meant the burning of limestone to make quick lime. Today it refers to any sort of reaction in which solid is heated to drive off volatile component, chemically combined water etc.

Examples - $\text{CaCO}_3 = \text{CaO} + \text{CO}_2 + 42.4 \text{ Kcal}$

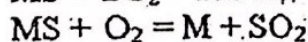
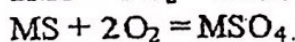
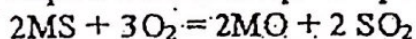
$\text{FeCO}_3 = \text{FeO} + \text{CO}_2 + 19.2 \text{ Kcal}$

$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 56.4 \text{ Kcal}$

Furnace used for calcination may be rotary kiln similar to those used for drying or roasting.

Roasting and Sintering:

Roasting may be defined as heating of ore or concentrate to an elevated temperature in contact with air or oxygen without fusion or at most incipient fusion. Principal objects of most roasting operation is to oxidize sulfide particles to oxides or sulfates which are required for subsequent operation. (Where M stands for Metal)



Other purposes of roasting are

1. Removal of impurities by the volatilization of certain oxides such as SO_2 , SO_3 , As_2O_3 , Sb_2O_3 etc.
2. Formation of chlorides by roasting in contact with chloridizing agent.
3. Formation of sulfates by controlling air supplied and temperature in oxidizing roast.
4. Reduction of certain metallic oxides by heating in contact with cold or other reducing agent
5. Alteration of physical condition of material (sintering)

Roasting is carried out in special furnaces and may require external source of heat or may be autogeneous, depending on exothermic nature of the reaction to provide necessary heat. In all roasting processes the temperature must be maintained at a high enough level to ignite the sulfides or other oxidisable constituents and to keep them above ignition point.

Four most common methods of roasting are

- (1) Hearth roasting
- (2) Fluidization roasting
- (3) Flash or suspension roasting
- (4) Blast roasting

Sintering is applied to any similar process that results in the agglomeration of fine particles. Sintering is not necessarily roasting. It is used to remove last traces of sulfur or and volatile impurities. The charge may be mixed with coal or other fuel and heated to high temperature in sintering machine.

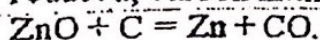
Smelting: The term smelting is often used to refer any metallurgical operation or combination of operation that produces liquid metal. Smelting is distinct from roasting, sintering, refining etc. It may be defined as, a process of reduction or concentration carried out at an elevated temperature in a furnace, in which major portion of valuable constituents of the ore is collected in the form of fused metal, matte (sulfide) where as worthless ones are removed by the added flux in the form of liquid slag. Roasting and calcination are usually carried out for the purpose of obtaining the metal in another form more suitable for smelting or to eliminate some impurities which might interfere with smelting process.

Characteristics of smelting:

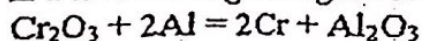
1. Material to be smelted is charged in solid state-
2. Necessary heat for smelting may be supplied from fuel or electricity
3. Smelting may be conducted in blast furnace reverberatory or electric furnace.
4. Product of smelting furnace are in liquid state.

Reduction smelting:

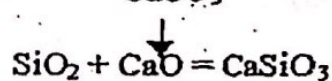
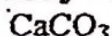
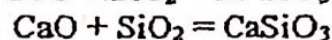
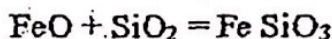
Oxide ores (and calcined carbonate and hydroxide ores which contain metal oxide) are reduced, carbon in the form of coke being most commonly used reducing agent e.g.



If a more energetic agent is required, a metal like Ca or Al is used as a reducing agent



Depending on the nature of the associated impurities a suitable flux. (Silica or limestone) is added which forms an easily fusible slag which being lighter floates on the liquid metal or matte.



CHAPTER XVII

NON-FERROUS METALS & ALLOYS

On the basis of weight the production of non-ferrous metals and alloys is very much less than that of the ferrous. Non-ferrous metals and alloys, however, are several times more expensive than the ferrous materials. They find applications because of certain very valuable properties like good corrosion-resistance, high electrical conductivity and in some cases, good strength combined with low specific gravity.

Some of the non-ferrous metals like aluminium, copper, zinc and lead are used in large quantities. Other metals like chromium, molybdenum, nickel, tungsten and vanadium are produced in much smaller quantities but are valuable alloying metals.

In India due to the abundance of aluminium ores and shortage of other non-ferrous metals attempts are being made to use aluminium as much as possible in place of other non-ferrous metals.

In some cases a pure metal is required, for example, copper used as an electric conductor must be very pure. In many cases few other materials, generally metals, are intentionally added to the metal in order to improve its properties. Such a combination is called an *alloy*. An alloy is defined as any combination of elements that results in a substance possessing metallic properties. The structures of alloys are complex. Their properties are significantly different from those of the constituent elements. For example, lead is a soft metal. Addition of 1 to 2% antimony makes it quite hard. Wood's metal is an alloy of Pb, Sn, Bi and Cd. Its melting point, 70.5° C, is much lower than that of any of its constituent metals.

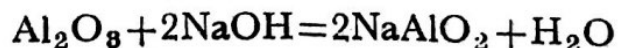
Aluminium

Extraction. Aluminium is more abundant in the earth's crust than iron but its production is much less. This is because rich ores of aluminium are fewer and chemical activity of aluminium is high which makes its extraction difficult. The principal ore of aluminium is bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. The chief deposits of bauxite are in Orissa and Andhra Pradesh, although it is found scattered in various other parts of India. 574 million tonnes of bauxite deposits have been proved and about 1450 million tonnes are inferred deposits.

Production of each tonne of aluminium requires 5 tonnes of

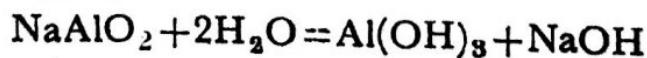
bauxite, 1.5 tonnes of coal, 0.7 tonne of carbon electrodes, 0.2 tonne of caustic soda, 0.2 tonne of pitch, 0.03 tonne of cryolite and 17,000 KWH of electric power. Cheap electric power and production of electrodes have been the chief hurdles in increasing the production of aluminium in India. The aluminium production has remained fairly constant at about 2 lakh tonnes per annum from the year 1976. The biggest plant is located at Renukoot (U. P.) with an installed capacity of 1,20,000 tonnes. Capacity of the plant at Belgaum (Maharashtra) is 80,000 tonnes. Other smaller plants are located at Hirakund (A. P.), Alwaye (Kerala) and Mettur (Tamil Nadu). Of the new plants the one located at Korba has a capacity of 1,00,000 tonnes. One of the largest plants is being constructed at Koraput (Orissa) with installed capacity of 2,18,000 tpa. It will have open cast mine 2 million tonnes per year. Total project is estimated to cost 2400 crores and is to be completed in the Sixth Plan. Capacities of some of the existing plants will be increased. Shortage of electricity is the main hurdle in the expansion work.

Most of the bauxite deposits contain 40-60% Al_2O_3 , with about 25% water. The chief impurities are silica, iron oxide and titanium oxide. The ore is thoroughly purified by Bayer process before extraction, because removal of impurities from the ore is easier than from the metal. The crushed ore is relieved of water and organic matter so that it becomes easier to grind. The ore is then finely ground and digested for 1 to 2 hours in a 20% caustic soda solution at 200 to 240° under 30-40 kg/cm² pressure. Alumina forms sodium aluminate and dissolves.



The ferric oxide, titanium oxide and most of the silica do not dissolve and remain behind as mud. Silica forms insoluble sodium aluminium silicate. In this way each part of silica present in bauxite ties up an equivalent weight of each of alumina and soda. This remains in the red mud. Therefore, if the ore contains more than 5% silica the Bayer process becomes uneconomical.

The solution is diluted, filtered and agitated with freshly precipitated aluminium hydroxide from a previous operation and in about 40 hours, sodium aluminate slowly hydrolyses, precipitating aluminium hydroxide.

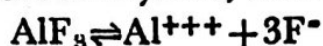


The liquor is evaporated to give concentrated caustic soda solution which is again used. The precipitate is washed, filtered, dried and calcined to give purified alumina.



Because of the high melting point of alumina it is dissolved in a fused mixture of cryolite ($\text{AlF}_3 \cdot 3\text{NaF}$) and fluorspar (CaF_2) at $940-970^\circ\text{C}$ and electrolysed. The cell for electrolysis is made of steel plates lined with firebricks covered with carbon blocks which act as a cathode. There is an opening for the removal of molten aluminium from the bottom. Anode consists of blocks of carbon. Electricity heats the cell as well as electrolyses alumina. See figure 17.1.

Cryolite and fluorspar are melted by passing electricity and alumina is added at intervals. It dissolves in the molten bath. The aluminium fluoride, present in cryolite, ionizes thus :



Aluminium is liberated at cathode and is tapped periodically. Fluorine reacts with alumina at the anode with the result that oxygen is liberated :

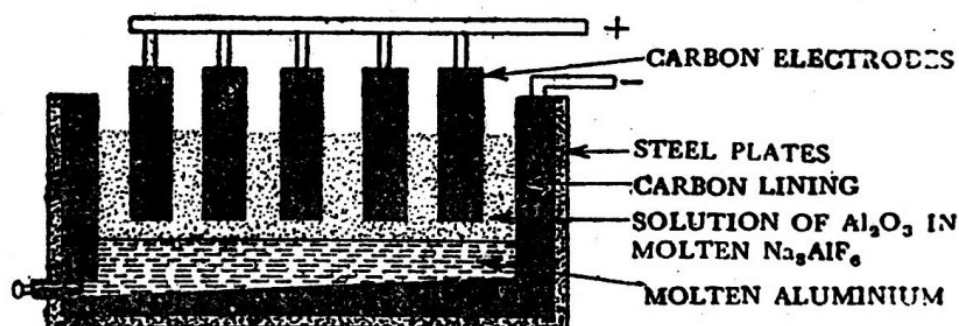
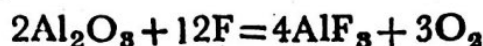


Fig. 17.1 Electrolysis cell for the extraction of aluminium.

As electrolysis proceeds the resistance of the cell increases and is indicated by a lamp placed in parallel which begins to glow, then more alumina is added. A crust of electrolyte and alumina is formed at the top and acts as insulator. Oxygen attacks the carbon anode with the result that the consumption of the anodes is high.

Purity of the metal so obtained is 99.6%. By using very pure alumina and electrodes, up to 99.85% pure aluminium is obtained. Generally, the metal is not purified. Only in some cases it is further purified by electrolysis in a cell having three layers of different materials. The bottom layer of molten impure aluminium acts as anode. Above it is the middle layer of fused electrolyte (mixture of cryolite, aluminium fluoride, barium fluoride and alumina) and its specific gravity is carefully adjusted. The pure aluminium acts as the cathode. On passing electricity aluminium dissolves in the electrolyte and the pure metal is liberated at the cathode.

Properties and Uses of Aluminium. Of the common metals aluminium and magnesium have very low specific gravities (2.7 and 1.7 respectively) as compared to those of zinc (7.2), steel (7.8), brass (8.4), copper (8.8) and lead (11.3). Hence the reason for the engineer's interest in these metals and their alloys is obvious.

Aluminium is ductile and highly malleable; it can be made into 0.002 mm thick sheets. It is a good conductor of heat and electricity. Its electrical conductivity is about 61% that of copper but due to its low specific gravity an aluminium bar has twice the conductivity of a copper bar of the same weight and length (due to its increased cross-section). Its coefficient of expansion is rather high, twice that of steel. The great disadvantage of aluminium is that it is mechanically weak, having a tensile strength of about 1,000 kg/sq. cm which is about one fourth of the strength of mild steel and about one tenth that of tool steels. This disadvantage can be overcome by alloying small amounts of other elements like Cu, Mg, Mn, Fe, Si, Zn, etc. thus retaining the advantage of low specific gravity, but adding strength and thereby making these alloys very suitable for making pistons, cylinders, crank cases, body, etc. for automobiles and aeroplanes and for use in a number of structures as well.

Pure aluminium has poor machining properties, for example, it tears badly, hence it is difficult to produce threads on aluminium parts. Due to the formation of a thin film of oxide on the surface, it has high resistance to atmospheric corrosion and to concentrated nitric acid. It has poor resistance to alkalis and common salt solution. The tendency to form oxide film on the surface easily makes soldering, welding and electro-plating of aluminium difficult. The corrosion-resistance of aluminium and its alloys can be greatly improved by anodizing. Anodizing is done by making the article an anode with a carbon cathode in a dilute sulphuric or chromic acid bath. The oxygen liberated at the anode forms a thin and adherent oxide film on the surface which is resistant to corrosion.

Aluminium melts at 660° , therefore the use of aluminium and its alloys at elevated temperatures is restricted. Use of aluminium in India is increasing because of the availability of its ore and scarcity of other non-ferrous metals.

Besides being used for making alloys, aluminium metal is rolled, pressed or cast into useful shapes. It is also used as aluminium foil. Extruded aluminium powder is used in making paints and explosives, in Thermite process of welding and in printing.

Alloys of Aluminium. Aluminium alloys are of two types: (1) casting alloys; and (2) wrought alloys.

(1) **Casting Aluminium Alloys.** In these alloys the chief alloying elements are copper and silicon. Zinc, magnesium, nickel and iron may also be present. These elements increase strength and hardness but reduce ductility. Alloys with copper have good machining properties and good mechanical strength after heat treatment, but have high contraction on solidification. When about 12% silicon is present in the aluminium alloy the contraction is small and corrosion-resistance is better. Aluminium-silicon alloys have high fluidity and are used for casting intricate designs. Ductility of aluminium-silicon alloys is increased by adding a trace (0.05%) of sodium or calcium.

Aluminium-magnesium alloys have good properties but are difficult to cast. Of all the aluminium casting alloys an alloy with 10% magnesium, after heat treatment, has the best combination of mechanical properties. They have good corrosion-resistance.

(2) **Wrought Aluminium Alloys.** Aluminium alloys of this type are more widely used than the cast alloys. Their shapes are changed by mechanical work which further improves their properties. They are divided into (a) non heat-treatable alloys; and (b) heat-treatable wrought alloys.

(a) *Non-heat-treatable wrought aluminium alloys* have manganese and magnesium as the chief alloying elements. These alloys are not so expensive and can be easily formed and welded. They have low strength but high ductility and corrosion resistance. Their strength can be increased by cold work. Addition of manganese (1.5%) increases the strength (from 1,000 kg/cm² to 1,700 kg/cm²). Magnesium increases the strength as well as resistance to attack by sea water.

(b) *Heat-treatable wrought aluminium alloys* can be strengthened by heat treatment as well as by cold work. They exhibit a property known as "age-hardening". The process consists of first heating the alloy to about 500° when a homogeneous solid solution is obtained. It is then rapidly cooled by quenching in water or oil. Thus the high temperature structure is retained, but this is not a stable state. The result is that in the course of several days inter-metallic compounds are precipitated which give hardness and strength to the alloy. The latter process, known as *aging*, can be hastened by heating the alloy for a shorter period. This mechanism of hardening gives an engineering advantage. After quenching, the

alloy is soft and can easily be given the desired shape which in course of time hardens. Sometimes, after quenching, the alloy is kept in a refrigerator so as to delay hardening and later made into the required shape which gets hardened in course of time.

Duralumin is one of the best known alloys of this group. It contains about 4% Cu, 0.5% Mn, 0.5% Mg and small amounts of Fe and Si.

After age hardening, its tensile strength (4,000 kg/sq. cm) approaches that of mild steel whereas its specific gravity is only one third. *Duralumin* has been superseded by 'Super duralumin', which has slightly higher percentages of the alloying elements. This has a still higher tensile strength (5,000 kg/sq. cm) which is equal to that of mild steel. *Duralumin* type alloys have very good mechanical properties, but their corrosion-resistance is lower than that of aluminium. This difficulty is overcome by 'cladding'. This is done by rolling a thin sheet of aluminium on both the sides of the alloy sheet, thus forming a protective coating. Due to their strength and low specific gravity, they are widely used for making various parts of aircraft and automobiles.

Y-alloy is similar to *duralumin* but has also about 2% nickel. It is mostly used as a casting but can be hot worked. It is superior to *duralumin* in corrosion-resistance and in mechanical properties above 200°.

Messrs. Rolls-Royce Ltd. have developed a series of alloys known as *R. R. alloys* which have better properties than *duralumin*. These have smaller percentages of copper but have some iron and titanium. A typical, average composition is 2% Cu, 0.1% Ti and about 1% each of Ni, Mg, Fe and Si, the rest being Al. Some *R. R.* alloys have higher strength to weight ratios than other alloys.

Copper

India's position in respect to copper production is not very satisfactory. Demand for copper in 1973-74 was about 83,000 tonnes and it rose to 1,05,000 tonnes by the end of the Fifth Plan. The Hindustan Copper Corporation is developing the main deposits of the country, which are at Rekha in Bihar, Khetri in Rajasthan and Malanjkhand in Madhya Pradesh, as well as minor deposits found at Dariba and Chandmari (Rajasthan) and Agnigundala (Andhra Pradesh). The copper smelter at Ghatshila (Bihar) has a capacity of 25,000 tonnes per annum whereas, due to the shortage of the ore, the production in 1979-80 was 22,500 tonnes as compared to

8,400 tonnes in 1971-72. Khetri copper complex is being developed to produce 31,000 tonnes of copper using ores from Khetri and Kolihan. It will produce super phosphate fertiliser using sulphuric acid obtained as a by-product from the oxidation of the sulphide ore. Known deposits of copper are estimated at about 450 million tonnes with a total metal content of about 5.6 mt. It is planned to import concentrated ores and produce copper metal in the country in addition to importing the metal itself.

Extraction. Native copper is found in several parts of the world but about 90% of the metal is obtained from sulphide ores. The principal sulphide ores are chalcocite or copper glance, Cu_2S , and chalcopyrites, CuFeS_2 . Of the oxidized copper ores malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and cuprite, Cu_2O , are important. Most of the ores being worked at present contain less than 2% copper. Before smelting, the ores are concentrated by the flotation process and the copper content is raised to about 25%. Extraction of copper is complicated and consists of the following five steps, principles of which have been discussed in the chapter on Extraction of Metals :

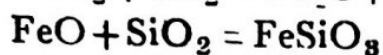
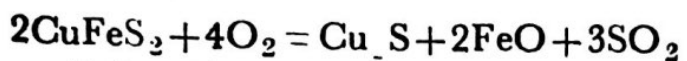
1. Concentration of ore by froth flotation.
2. Roasting of ore (to eliminate part of the sulphur).
3. Smelting (to eliminate gangue and to produce matte).
4. Conversion of matte to blister copper.
5. Electrolytic refining of copper.

1. Concentration. The ore is crushed and then powdered in ball mills and mixed with creosote oil or pine oil and xanthates, which act as frother and collector, and is finely ground with water. It is then transferred to a flotation machine into which air is blown. The oil-coated sulphide particles collect at the top in the froth and are removed.

2. Roasting. The object of roasting is to oxidize a part of the sulphur so that the matte produced later contains about 40% copper. The ore is roasted in a vertical furnace in an oxidizing atmosphere. The ore is charged at the top and is gradually moved down by a rotating rake. Arsenic and antimony volatilize and part of the iron sulphide is oxidized to iron oxide. Sulphur dioxide is produced and used for making sulphuric acid.

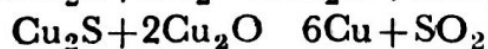
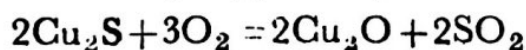
3. Smelting. By smelting, slag and matte are produced. Slag contains the gangue. Matte is a molten mixture of sulphides of iron and copper. It is essentially a simple melting operation. Noble metals present in traces also go with the matte. Formerly a blast furnace

was used for smelting but as the ores are now obtained in a powdered state, due to flotation process, they are heated on the sloping bed of a reverberatory furnace. Some silica is mixed with the ore, if not already present. Care is taken that copper sulphide is not oxidized at this stage. Iron oxide forms slag with silica and is removed. The molten, heavy, sulphide layer is called matte and contains about 40% copper. Oxidation to a small extent only takes place according to the following reaction :



4. Converting, The molten matte, with calculated amount of silica, is transferred to a converter similar to the Bessemer converter for steel, the essential difference being that in the converter for copper air is blown from the side and not from the bottom. This is necessary because the copper produced is heavier than the matte and sinks below the tuyeres and escapes oxidation. The converter for copper is much larger in size and cold air is blown for several hours. This is because in the case of copper smelting a much larger amount of impurities are oxidized. Horizontal converters (shaped like the common barrels or drums) which are up to 10 m long and 4 m in diameter are being used to a greater extent than the Bessemer type converters.

Copper gets separated from iron because of the fact that FeS is oxidized more easily than Cu_2S is. Oxidation of iron sulphide is a highly exothermic reaction and supplies heat for keeping the charge in a molten state. On blowing air, iron sulphide is oxidized and forms slag with silica. Some copper sulphide is also oxidized which oxidizes the remaining copper sulphide.



The molten copper sinks below the tuyere level and escapes oxidation. After the completion of the reactions the slag is poured out and molten copper is cast into blocks. The escaping sulphur dioxide from the molten copper gives a blister-like appearance to the solidified metal, hence it is called blister copper. It is about 99% pure.

5. Refining. There are two methods of refining copper, fire refining and electrolytic refining. In fire refining blister copper is melted on the bed of a reverberatory furnace in an oxidizing atmosphere when sulphur and arsenic oxidize and are removed. Baser

metals, like iron, oxidize and a layer of oxide forms on the molten metal and is removed and the surface of the metal is again exposed to oxygen. Some cuprous oxide is formed which, besides the loss of copper, makes copper weak and brittle. At this stage the molten metal is covered with charcoal and stirred with poles of green wood from which reducing gases, like the hydro-carbons, evolve and reduce cuprous oxide. The metal is then cast into blocks. This gives commercially pure copper, (99.5%) and is called 'tough pitch' copper.

Since even traces of impurities adversely affect the properties of copper, the metal obtained by fire refining is subjected to further refining by electrolytic process. Anodes are made of fire refined copper and thin sheets of pure copper serve as cathodes. These are alternately suspended in a solution containing about 10% copper sulphate and 20% sulphuric acid. When electric current is passed, anodes dissolve and pure copper is deposited at the cathodes. The current is so adjusted that the metals baser than copper remain in solution and the nobler metals deposit under the anodes giving anode mud. This anode mud contains noble metals like gold and silver. The concentration of soluble metals like iron, zinc, etc. tend to increase in the electrolyte and reduce the efficiency of the process. Therefore, it is desirable to eliminate them as far as possible from blister copper by fire refining and then to electrolyse for final purification. The purity of electrolytic copper is 99.96 to 99.99%.

Properties and Uses of Copper. Next to iron and aluminium, copper is the most widely used metal. Its wide applications are due to several important engineering properties. Its electrical and thermal conductivities are next to silver. The electrical conductivity falls even if traces of impurities are present. For example, 0.1% of phosphorus (or 0.5% of arsenic) reduce its electrical conductivity to about 50%. Copper has high thermal conductivity which also falls with alloying. Another reason for its wide use is that copper has resistance to atmospheric corrosion because of the formation of a uniform layer of oxide on the surface of the metal. It is resistant to most acids and alkalis except strong mineral acids and ammonia. Copper has good mechanical properties. The cast metal has a tensile strength of about 1,600 kg/cm² which increases to 2,400 kg/cm² on hot working and the strength becomes three times as great when the section is reduced to 90% by cold work. Copper also has good malleability and formability which makes fabrication easy. It can be easily welded and soldered. Melting point of copper is quite

alpha phase, hence beta brasses cannot be cold worked to any appreciable extent. Its softening begins at 470° and at 800° it becomes softer than the alpha phase. Consequently, the beta brasses are more suitable for hot work.

Among the alpha brasses the most widely used is 70/80 brass (70% Cu, 30% Zn). This is also called *cartridge brass*. It has a very good combination of ductility and strength. It can be easily rolled, pressed and spun and is used for making cartridge cases, condensers and other shapes by drawing or stamping. In highly worked alpha brasses some internal stresses are produced due to which they suddenly crack in service. This is known as 'season cracking' and the defect can be removed by heating around 300° for about half an hour when the stresses are removed without loss of strength or hardness.

60/40 brass (60% Cu and 40% Zn) is known as *munz metal* and contains varying proportions of alpha and beta phases depending upon the rate of cooling from the liquid state. It is harder and stronger than cartridge brass and has to be hot worked.

The properties of the brasses, especially corrosion-resistance, can be improved by the addition of about 1% tin. Addition of 1% tin to 70/30 brass gives *admiralty brass*, which is resistant to sea water corrosion. Similarly 1% tin in 60/40 brass gives *naval brass* which is used for marine and engineering castings. Addition of up to 3% of lead to 60/40 brass improves its machining property and is known as *leaded brass*. It is used for hot stamping and for hot extrusion into rods. On these rods threads are cut on lathes to make screws, nuts, etc. When in a brass a part of the zinc is replaced by nickel the resulting alloy is known as '*nickel silver*' or '*German silver*'. It has very good mechanical properties and corrosion-resistance. Because of its white colour and moderate cost nickel silver has found wide use in making household utensils. This use is now being replaced

Lead

Extraction. Lead metal has been in use since the early days because it can be easily produced from the ore and it has a low melting point. It is almost exclusively extracted from galena, PbS . It also occurs as carbonate and sulphate.

Lead and zinc ores are mined from the Zawar Mines, Udaipur Dist., Rajasthan. The total reserves of lead-zinc ores are estimated at 350 mt. About 5,000 tonnes of lead ore concentrates and about 3,000 tonnes of lead are produced annually in India.

Galena is almost always associated with zinc sulphide, therefore, the powdered ore is concentrated by differential flotation, as explained in the chapter on Extraction of Metals. The concentrated ore is then roasted in air when the sulphide is oxidized to oxide and partly to sulphate. Arsenic and antimony oxide volatilize but iron and copper oxides remain behind. The oxides mixed with coke are smelted in a blast furnace when crude lead is obtained. The crude metal is heated in a reverberatory furnace in an oxidizing atmosphere when some of the impurities oxidize and the oxide layer floating above the molten metal is skimmed off. This process is known as softening of lead. Lead so obtained contains traces of

precious metals like silver and gold which are removed by Parkes's process. It depends on the fact that the noble metals are more soluble in molten zinc than in molten lead. The metal is melted and zinc is added and mixed. Zinc carrying noble metals floats at the top and solidifies. The solid metal is removed, and zinc is distilled leaving behind the noble metals. If necessary, lead which forms the lower layer is further purified by electrolytic process.

Properties and Uses. Lead metal is used because of its corrosion-resistance, malleability, plasticity and high density. It has very poor ductility due to which it cannot be drawn into thin wires. Due to high malleability, it can be rolled into sheets and foils. Lead has good casting properties. It has low tensile strength (100 kg/cm^2). Due to its low melting-point (328°), it cannot be used at elevated temperatures. On exposure to air a thin layer of oxide is formed on the surface which protects the metal underneath.

Nearly one third of the lead produced is used in storage batteries. Other principal uses are cable-sheathing, alloys for bearings solder and type metals, chemicals and pigments, tetra ethyl lead and building materials.

Alloys of Lead. As pure lead does not have good mechanical properties, it is mostly used after adding some alloying elements. These add hardness and strength to the metal and also lower the melting point. Most of the lead alloys contain antimony. The alloys are of two types, the high-lead alloys and low-lead alloys.

Grid Metal. The largest single use of lead is in making grid metal which is used in storage batteries. It contains about 10% antimony and less than 1% of tin and traces of arsenic and copper. These elements improve hardness and casting properties. The alloy is cast into perforated plates or grids for storage batteries.

Quantitatively next in importance comes *cable-sheathing metal*. It has a smaller amount of antimony than the grid metal. It has 95 to 98% lead and 5 to 2% antimony. Much smaller amounts of other metals are also incorporated in the alloy.

Solders. For joining two metals an alloy whose melting point is lower than the melting points of the metals to be joined is used. The process is known as *soldering* or *brazing*. The distinction between these two is not sharp. When the alloy used has lower m. p. the process is known as soldering and with a high m. p. alloy the same process is called brazing. In welding the metal being joined is melted.

The most common solders are *tinman's solder* (2 parts Sn and 1 part Pb) and *plumber's solder* (1 part Sn and 2 parts Pb). Tinman's solder contains almost an eutectic mixture and melts at 180° and is very convenient for ordinary joining of metals. The plumber's solder begins to solidify at 240° and passing through a pasty stage solidifies at 180° . This range of solidification enables the plumber to make his 'wiped' joint.

In brazing alloys of copper and zinc are used. These alloys have higher melting points and the joint has better mechanical properties.

Type metal should certainly be low melting but more important requirements are strength and hardness, ability to cast well and make good impressions. These are attained by adding antimony and tin to lead (12%, 3% and 85%). Antimony not only contributes to strength and hardness but, as it expands on cooling, it fills the mould and an accurate shape is obtained. Here, mention may be made of lead shots which contain 1% arsenic. Lead shots for long range use need to be hard, and therefore contain 2 to 6 per cent of antimony.

Bearing Metals have still different requirements. These alloys have two constituents one of which is hard and resists wear, but is not so hard as to cause wear of the journal. Its particles are embedded in a soft matrix. The hard particles support the load but the soft matrix provides plasticity and ductility and thus enables the harder particles to adjust themselves to the differing surface requirements. This latter property becomes necessary as it is very difficult in actual practice to make perfect alignment of a journal and a bearing. The most important group of alloys for the purpose are known as *Babbit metals*. These contain tin, antimony, copper and also lead. The compositions of these alloys differ widely. They include alloys with 90% or more tin without lead, to 5% tin with 80% lead. A composition commonly used contains 91% Sn, 4.5% Sb and 4.5% Cu.

Tin being expensive, cheaper substitute of Babbit metals have been made, e. g. using about 65% Cu, 30% Pb and 5% Sn. These have a structure opposite to that of a Babbit metal, i. e. there is a soft constituent in hard matrix. These alloys; known as *lead bronzes*, are inferior as they are not so plastic and do not adjust so well to the load.

Magnesium

Extraction. Magnesium is obtained either by electrolysis of fused magnesium chloride or by reduction of the oxide by carbon at

high temperatures.

Magnesia, MgO , is mixed with carbon and heated in a current of chlorine when magnesium chloride is produced. Large quantities of it are being obtained from sea water. Sea water is treated with slaked lime when magnesium hydroxide is precipitated which is dissolved in hydrochloric acid and the solution is concentrated. Magnesium chloride, mixed with sodium chloride and potassium chloride, is electrolysed at 70° in a cell using a graphite anode and steel cathode. Chlorine is liberated at the anode and is used to produce hydrochloric acid. Magnesium collects at the cathode under the surface of a thin layer of electrolyte and is periodically removed.

Another method of production is by the reduction of magnesium oxide by carbon at $2,000^\circ$. Magnesium volatilizes and is immediately cooled so that it may not oxidize. The metal is purified by distillation in vacuum.

Alloys of Magnesium. Of all the metallic materials used by the engineers, magnesium (sp. gr. 1.74) is the lightest and its alloys, which have good engineering properties, also have low specific gravity (1.8). Although on a weight basis, it has good mechanical properties, it is not used in the pure condition for engineering purposes, because on alloying, its properties are greatly improved without losing the advantage of lightness. Importance of low specific gravity in engineering uses is so obvious that it need not be emphasised.

After heat treatment and mechanical working the strength of magnesium alloys may be as high as 3000 kg/cm^2 . Thus their strength-weight ratio is far superior to that of steel and is better than even duralumin. A great engineering drawback of magnesium alloys is low modulus of elasticity. They also do not have good high temperature properties. Their corrosion-resistance to acids and to salt water is poor, hence they do not give satisfactory service near a sea coast unless protective coatings are used. Just like duralumin they can be cast or wrought and also heat treated. Machining properties are also good.

The chief use of magnesium alloys lies where a saving in weight is required. Hence, they are widely used in aircraft construction for crank cases, undercarriage parts, wheels, housings, engine parts interior fittings, etc.

Dow metal (61% Al, 3% Zn and 0.5% Mn with Mg) is a widely used alloy of magnesium. After heating to 350° it is quenched in air and then age-hardened.

Nickel

Extraction, Properties and Uses. Nickel is commonly extracted from sulphide ores which also contain sulphides of iron and copper. The roasted ore is smelted when matte containing sulphides of nickel, iron and copper is produced. On Bessemerization iron is removed. The molten matte is also used for giving a mixture of metallic copper and nickel which are used for making some alloys. The matte containing sulphides of copper and nickel is heated with sodium sulphate and coke when sodium sulphide is produced which dissolves copper sulphide and floats on the nickel sulphide layer. Nickel sulphide is roasted to give the oxide which is reduced by coke, and nickel is obtained.

Pure nickel is obtained by heating the oxide in producer gas at 50° to 80° when nickel carbonyl, $\text{Ni}(\text{CO})_4$, volatilizes. It is then heated to 180° when it decomposes to give pure nickel and carbon monoxide.

Tensile strength of nickel is $3,000 \text{ kg/cm}^2$ and on cold working is increased to $10,000 \text{ kg/cm}^2$. Thus it is stronger than other common metals. It is hard, ductile and malleable. It is ferro-magnetic. Many of the uses of nickel are due to its high corrosion-resistance, therefore, it is used for nickel plating.

Alloys of Nickel. Because of high resistance to corrosion and good mechanical properties, nickel finds important applications in making ferrous and non-ferrous alloys. These alloys have been described under 'Ferrous Alloys' and 'Alloys of Copper'.