Aluminium

Occurrence

Aluminium is the most abundant (8.13 %) metallic element in the earth's crust and after oxygen and silicon, the third most abundant of all elements in the crust. Because of its strong affinity for oxygen, it is not found in nature in the elemental state but only in combined forms such as oxide or silicate. Aluminium occurs in igneous rocks chiefly as alumino-silicate in feldspar, feldspathoids, and mica; in the soil derived from them as clay and upon further weathering as bauxite and iron-rich laterite. Bauxite, a mixture of hydrated aluminium oxides, is the principal aluminium ore.

Extraction of aluminium

The extraction of aluminium is called electrometallurgy. It deals with the use of electricity for smelting or refining of metals. In electrometallurgy, the electrochemical effect of an electric current brings about the reduction of metallic compounds and thereby the extraction of metals from their ores (electro-winning) or the purification of the metals (electro-refining).

- The principal aluminium ore is bauxite Al_2O_3 . $2H_2O$. It is essentially an impure aluminium oxide. The major impurities include iron oxide, silicon dioxide and titanium dioxide.
- The extraction of aluminium, in principle , should be easy because the ore occurs in oxide form which can be reduced by a suitable reducing agent to give the metal.
- However, in practice, aluminium oxide can not be reduced that easily. Aluminium has great affinity for oxygen hence it can not be reduced by usual reducing agents.
- Aluminium is too high in the electrochemical series (it is a highly reactive element) so it can not be reduced by hydrogen or carbon. If at all reduced by carbon, the temperature required for the reduction is very high. This does not make the process economic. Hence aluminium is obtained by the electrolysis of pure alumina.

Purification of bauxite

- Bauxite contains iron oxide or silica as major impurity. The bauxite containing iron oxide as major impurity is called **red bauxite and the bauxite containing silica as major** impurity is called **white bauxite. Iron and silicon both make aluminium metal brittle and** liable for corrosion hence they must be eliminated. If bauxite contains iron oxide, Fe_2O_3 as the major impurity, it is purified by Baeyer's process or Hall's process. . If it contains silica , SiO_2 as the major impurity, it is purified by Serpek's process.

- (i) **Serpek's process – This process is used when bauxite ore contains appreciable** amount of silica (above 7 %) and low amount of Fe_2O_3 (less than 1 %) .Powdered bauxite is mixed with carbon and heated up to 1800^0C in a current of nitrogen .
- Aluminium from bauxite is converted to aluminium nitride while silica is reduced to silicon.
- Al_2O_3 .n H_2O + 3C + N2 → 2 AlN + 3 CO + n H_2O
- SiO_2 + 2C → Si ↑ + 2 CO ↑
- Silicon volatilizes at this temperature. Aluminium nitride is hydrolyzed with hot water. It precipitates aluminium hydroxide.

- $AlN + 3\ H_2O \rightarrow Al(OH)_3 \downarrow + NH$
- The precipitate of $Al(OH)_3$ is washed, dried and ignited at about 1500^0C to get pure alumina.
- $2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O \uparrow$

- b) **Baeyer's process – This process is used when bauxite ore contains appreciable** amount of Fe2O3 (7 to 10 %) and low amount of silica (less than 1 %). The ore is first calcined and then finely ground. It is then digested with a hot and strong solution of caustic soda (45 %)

- At this stage, aluminium oxide dissolves in NaOH to form sodium meta aluminate ($NaAlO_2$) while ferric oxide and titanium dioxide remain undissolved. They are then removed by filtration.
- $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
- Sodium meta aluminate (soluble)
- Silica dissolves in the form of silicate. After filtration, sodium meta aluminate solution

- is diluted with water, slowly cooled and then mixed with a little freshly precipitated aluminium hydroxide which acts as a nucleus for precipitation of aluminium hydroxide.(Alternatively CO_2 can be passed till the solution becomes acidic) It is then digested. Sodium meta aluminate, $NaAlO_2$ hydrolyses to give precipitate of aluminium hydroxide.

- $NaAlO_2 + 2\ H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$
- Aluminium hydroxide precipitate is then washed, dried and ignited to get pure alumina (Al_2O_3) .The filtrate containing caustic soda is concentrated and used again.
- $2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O \uparrow$

- c) **Hall's process - This process is used for low grade bauxite ores. In this process,** bauxite ore is fused with sodium carbonate, Na_2CO_3 to give water soluble sodium meta aluminate , $NaAlO_2$ leaving behind Fe_2O_3 and SiO_2.
- $Al_2O_3 + Na\ 2CO_3 \rightarrow 2\ NaAlO_2 + CO2 \uparrow$
- The fused mass of sodium meta silicate is extracted with water and filtered. The impurities Fe_2O_3 and SiO_2 remain on the filter paper. The filtrate containing $NaAlO_2$ is warmed and CO_2 is passed through it, when $Al(OH)_3$ is precipitated.
- $2\ NaAlO_2 + CO_2 + 3\ H_2O \rightarrow 2\ Al(OH)_3 \downarrow + Na_2CO_3$

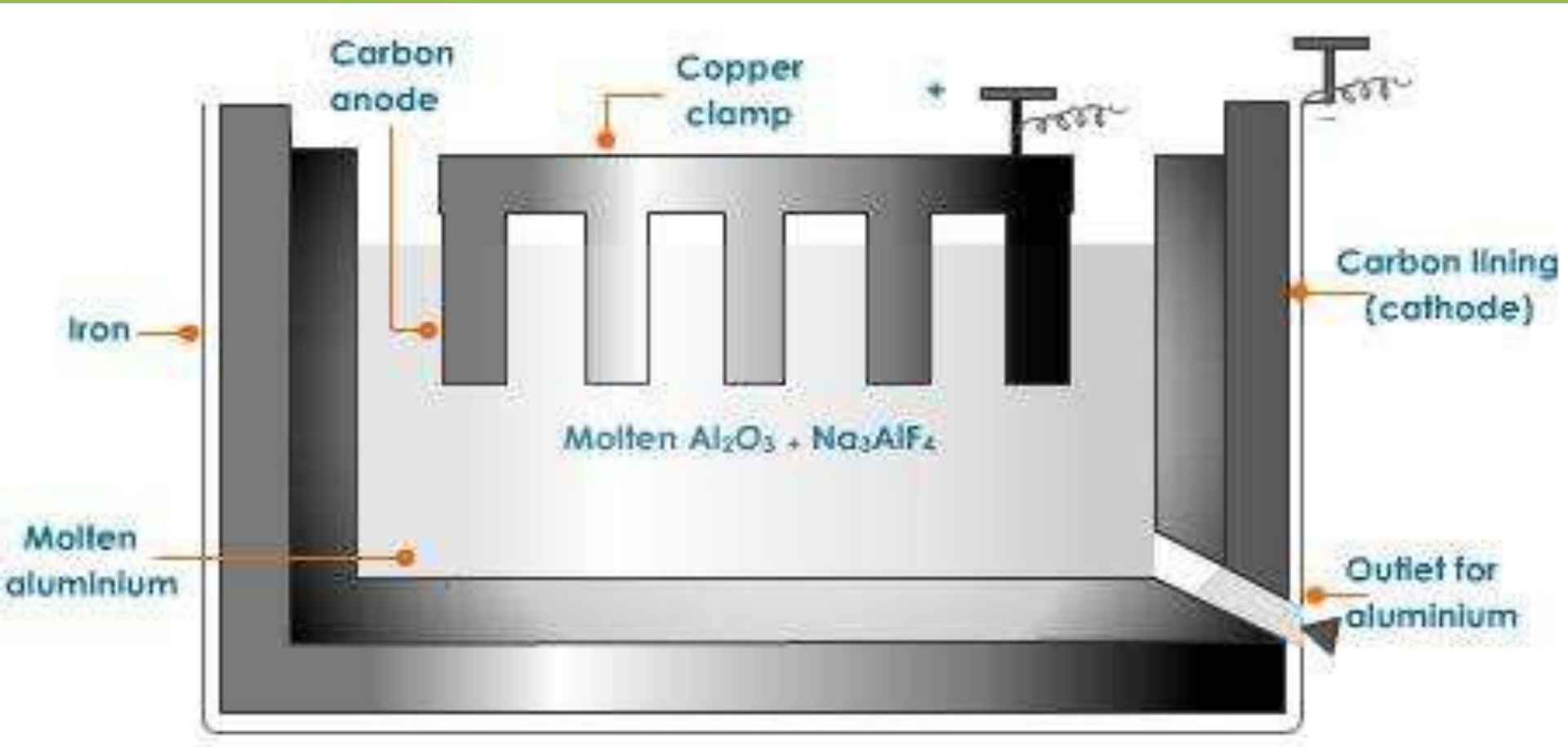
- The precipitate is filtered, washed and ignited to obtain pure alumina.
- $2\ Al(OH)3 \rightarrow Al2O3 + 3\ H2O \uparrow$
- Pure alumina

Electrolysis of pure alumina

- Aluminium can be obtained by electrolysis of pure alumina but it offers two problems.
- (i) Pure alumina is a poor conductor of electricity and melts at about 2000^0C.
- (ii) When fused alumina is electrolyzed at 2000^0C ,the metal formed vapourises as its boiling point is 1800^0C.
- Aluminium is usually prepared by **Hall- Heroult process. Alumina is fused with** cryolite Na_3AlF_6. Alumina dissolves in cryolite. Cryolite lowers the temperature of the mixture. Small amount of CaF_2 and AlF_3 are also added to lower the temperature of the mixture. Pure alumina melts at 2000^0 C while the mixture melts at about 950^0C. The charge consists of cryolite (85 %), CaF_2 (5 %), AlF_3 (5 %) and Al_2O_3(5 %)

- The electrolysis is carried out at temperature of 950^0C and with a voltage of 5.5 volts in a graphite lined steel tank which acts as a cathode. The anodes are made of graphite. The Al_2O_3 is added from feeder at the top. Some coke is thrown on the surface of charge to control the oxidation of the metal. The electrode reactions are complicated and their exact nature is not known . The simplified mechanism of electrode reactions is given below.
- $Na_3AlF_3 \rightarrow 3\ NaF + AlF_3$; $4\ AlF_3 \rightarrow 4Al^{3+} + 12\ F^-$
- At anode $\rightarrow 2\ Al_2O_3 + 12\ F^- \rightarrow 4\ AlF_3 + 3\ O_2 + 12\ e^-$; $4C + 3O_2 \rightarrow 2\ CO_2 + 2\ CO$
- At cathode $\rightarrow 4\ Al^{3+} + 12\ e^- \rightarrow 4\ Al$

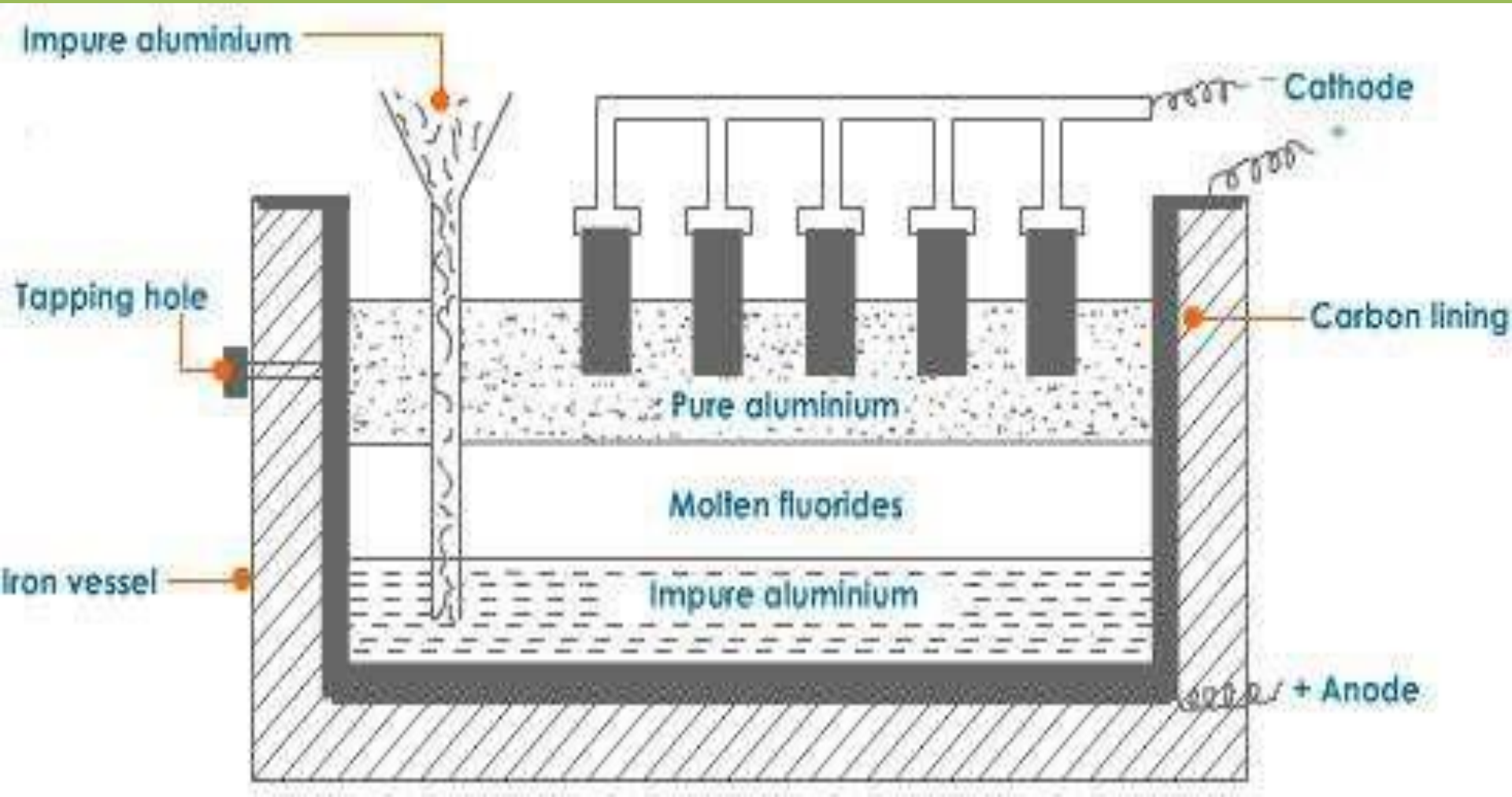
Electrolysis of alumina



Refining of aluminium metal

- Metal produced by Hall – Herouit's process is almost 99.9 percent aluminium and it contains small amounts of iron, silicon from the bath and some alumina and carbon. So Hoope's electrolytic refining process is used to refine the metal.
- **Hoope's process – In this process, fused salt electrolyte is used. The cell uses three** liquid layers of different densities.
- (i) The bottom anode layer consists of impure aluminium**.**
- (ii) The middle layer consists of cryolite , alumina and barium fluoride acting as electrolyte.
- (iii) The top cathode layer is of pure metal. This aluminium layer is connected with graphite electrode to the mains

Hoope's cell for refining aluminium



- The cell is made of iron box. It is lined from inside with carbon. The cell is shown in . On passing electric current, aluminium from the middle layer passes into the top layer and equivalent amount of aluminium passes from the bottom layer to the middle layer. From time to time , pure aluminium is removed from the top and aluminium of lower purity is added to the bottom layer. Thus, there is transfer of aluminium from the base to the top while impurities are left behind. Pure aluminium is tapped from the top.
- The refined aluminium has purity of 99.99 %.
- **Physical and Chemical Properties of Aluminium**
- (i) Aluminium is a white metal with a slight bluish tinge. In moist air, it becomes dull owing to the formation of superficial protective layer of its oxide.
- (ii) It is a light metal (sp. Gravity 2.7) which melts at 658^0 C and boils at 1800^0C.

- (iii) It is malleable and ductile especially between 100^0C and 150^0C. Near about its
- melting point, it becomes brittle and can be ground to powder.
- (iv) It is an excellent conductor of heat and electricity.
- (v) It is tough and has a moderate tensile strength.
- (vi) Finely divided aluminium or thin aluminium foil burns readily in air or oxygen when heated, forming aluminium oxide (with little nitride AlN also) liberating much heat.
- $4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$ + Heat
- (vii) **Action of acids - Aluminium is above hydrogen in the activity series and it**
- displaces hydrogen from non-oxidising acids like HCl and dilute H_2SO_4.
- $2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2$
- $2Al + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2$
- But hot concentrated H_2SO_4 gives SO_2
- $2\ Al + 6\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ SO_2 + 6\ H_2O$

- Concentrated HNO_3 makes aluminium passive and with dilute HNO3, it produces ammonium nitrate but no gas is evolved.
- $8\ Al + 30\ HNO_3 \rightarrow 8\ Al(NO_3)_3 + 3\ NH_4NO_3 + 9\ H_2O$
- (viii) **Action of alkalies - Aluminium is an amphoteric metal so it reacts with acids as** well as alkalies. (The reaction with acids are given above)
- $2\ Al + 2\ NaOH + 2\ H_2O \rightarrow 2\ NaAlO_2 + 3\ H_2$
- (ix) **Action of non-metals - Heated aluminium directly combines with halogens, carbon** nitrogen and sulphur.
- a) $2Al + 3\ Cl_2 \rightarrow 2\ AlCl_3$ b) $4\ Al + 3\ C \rightarrow Al_4C_3$
- c) $2\ Al + N_2 \rightarrow 2\ AlN$ d) $2\ Al + 3\ S \rightarrow Al_2S_3$
- (x) **Reducing action - At high temperature, aluminium has a strong affinity for oxygen** and hence it reduces oxides of iron, manganese etc.
- $Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe + Heat$

Areas of application of aluminium

- (i) Since it is lighter and has high tensile strength, aluminium is used in making body of air-ships and motor cars.
- (ii) On account of its good electrical conductivity, it is used for making electrical transmission cables.
- (iii) On account of its good thermal conductivity, it is used in making cooking utensils.
- (iv) Since it resists corrosion, it is used in aluminium paints.
- (v) Aluminium foils are used in wrapping cigaretts, confectionary items etc.
- (vi) Aluminium is used as a deoxidizer and for removing blow holes in metallurgy.
- (vii) It is used in thermite welding and in the aluminothermic process.
- (viii) Salts of aluminium such as alum are used as mordants in dyeing industries

Alloys of aluminium

- Alloy Composition Properties Uses-
- 1) Magnalium 98 % Al, 2 % Mg Hard, tough, light, For making balance beams, articles, Can be excellently, light worked on lathe instruments,
- -2) Duralium 95 % Al, 4 % Mn, 0.5 % Mg corrosion, Resistance to For making airships, highly aeroplanes etc. ductile, light
- 3) Aluminium 10 t0 12 % Al, Bronze 88 to 90 % Cu, Resistance to corrosion, For making, readily jewellery, decorative utensils, fusible, strong articles , coins
- 4) Nickeloy 95 % Al, 4% Cu, Extremely light, 1 % Ni great mechanical strength, For making airships
- 5) Alnico 50% steel, 20%Al, - 20% Ni, 10% Cu For making permanent magnets.