

# Aluminum

## HISTORY OF ALUMINUM

To the alchemists the term alum meant a group of substances, all of which had an astringent taste. Aluminum oxide was recognized as a distinct substance, related to alum, long before aluminum was isolated as a free element. Oersted (1825) and Wohler (1828) first prepared aluminum by reducing aluminum chloride with potassium ( $\text{AlCl}_3 + 3\text{K} \rightarrow \text{Al} + 3\text{KCl}$ ). The aluminum thus produced sold for \$150 per pound because the method was expensive. In 1854, Deville, in France, produced aluminum less expensively by substituting the cheaper sodium for potassium as the reducing agent. Improvements in technology also brought the cost of sodium down. By 1886 the price of aluminum had dropped to about \$4 per pound.

The metal is now produced by an electrolytic process discovered in 1886 by Charles M. Hall, who began work on the problem while he was a student at Oberlin College, and, independently a month or two later, by Heroult in France. The discovery made cheap aluminum possible and by the beginning of World War II in 1939, the price had dropped to 20 cents per pound. The current price (1962) is 25 cents per pound.

## OCCURRENCE AND METALLURGY OF ALUMINUM

Aluminum is the most abundant metal and the third most abundant element in the earth's crust. It is too active chemically to occur free in nature and is usually found combined with oxygen. The most important ore of aluminum is the hydrated oxide,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , which is called bauxite. The mineral cryolite,  $\text{Na}_3\text{AlF}_6$ , occurs in nature and is used in the metallurgy of aluminum, though it is not an ore of aluminum. Very large and widely distributed quantities of aluminum are found in complex aluminosilicate minerals, such as clays and feldspars. Anhydrous aluminum oxide occurs as corundum, ruby, and sapphire. Emery is a mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .

Aluminum can be produced from clays, which are largely hydrated aluminum silicates, but the higher cost involved in the preliminary treatment makes it impossible for aluminum from this source to compete with that produced from high grade bauxite at the present time. However, as the deposits of bauxite become depleted, our supplies of aluminum will probably come from clays, of which we have practically inexhaustible quantities. In March, 1962, the world's first commercial plant designed to obtain aluminum sulfate from coal shale by treatment with sulfuric acid was put into production at Powhatan, Ohio. The company intends later to make  $\text{Al}_2\text{O}_3$  from  $\text{Al}_2(\text{SO}_4)_3$ .

The first step in the production of metallic aluminum from bauxite involves the purification of the mineral. It is dried and pulverized and then digested with sodium hydroxide under steam pressure. The aluminum oxide is thereby converted to soluble sodium aluminate, while the iron oxide and silicates, both of which are present as impurities, remain undissolved.  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_4^-$  (aluminate ion)

After the insoluble iron oxide and silicates are filtered from the solution, the aluminum hydroxide is precipitated by hydrolysis of the aluminate. The hydrolysis is hastened by boiling and thoroughly aerating the solution. The precipitated aluminum hydroxide is ignited to the oxide, which is dissolved in fused cryolite,  $\text{Na}_3\text{AlF}_6$ . This solution is electrolyzed, whereupon aluminum metal is liberated at the cathode, and oxygen, carbon monoxide, and carbon dioxide are formed at the anode.

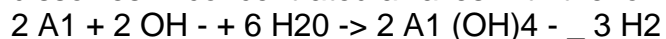
As the molten aluminum is drawn off, more aluminum oxide is added to the fused electrolyte. The carbon anodes are consumed, being converted to carbon monoxide and carbon dioxide.

In modern practice, an artificial mixture of fluorides sometimes replaces cryolite as the electrolyte. Typical is a mixture which approaches the composition  $2 \text{AlF}_3 \cdot 6 \text{NaF} \cdot 3 \text{CaF}_2$ . Aluminum prepared by electrolysis is about 99 per cent pure, the impurities being small amounts of copper, iron, silicon, and aluminum oxide.

If aluminum of exceptionally high purity (99.9%) is needed, it may be obtained by the Hoopes electrolytic process, which employs a fused bath consisting of three layers. The bottom layer is a fused alloy of copper and aluminum, the top layer is pure molten aluminum, and the middle layer (the electrolyte) consists of a fused mixture of the fluorides of barium, aluminum, and sodium, and nearly enough aluminum oxide to saturate it. The densities of the layers are such that their separation is maintained during electrolysis. The bottom layer serves as the anode and the top layer as the cathode. As electrolysis proceeds, the aluminum in the bottom layer passes into solution in the electrolyte as  $\text{Al}^{+++}$ , leaving the copper, iron, and silicon behind in the anode, for they are not oxidized under these conditions. The aluminum ion is reduced at the cathode. During electrolysis, purified aluminum is drawn off from the upper layer, and the impure metal is added to the lower layer through a carbon-lined funnel.

## **PROPERTIES AND USES OF ALUMINUM**

When freshly cut, aluminum has a silvery appearance, but it soon becomes superficially oxidized and assumes a dull white luster. The metal is very light and possesses high tensile strength. Weight for weight, it is twice as good as a conductor of electricity as copper. Although aluminum is a relatively reactive metal, the tenacious coating of the oxide which forms on it prevents further atmospheric corrosion. When heated in the air, finely divided aluminum burns with a brilliant light. Because of the formation of a protective coat of oxide, aluminum does not decompose water. It is readily dissolved by hydrochloric acid and sulfuric acid, but is rendered passive by nitric acid. Aluminum dissolves in concentrated alkalis with the formation of aluminates and hydrogen.



This behavior is in accord with the amphoteric character of aluminum hydroxide. When heated, aluminum combines directly with the halogens, nitrogen, carbon, and sulfur.

The fact that aluminum is an excellent conductor of heat, together with its light weight and resistance to corrosion, accounts for its use in the manufacture of cooking utensils. The most important uses of aluminum are in the airplane and other transportation industries. Here the lightness, toughness, and high tensile strength of the metal are important. The average 1962 automobile contains 66.5 pounds of aluminum, compared to only six pounds in each 1948 automobile. Aluminum is also used in the manufacture of electrical transmission wire, as a paint pigment, and, in the form of foil, as a wrapping material.

Aluminum is one of the best reflectors of heat and light, including the wave lengths in the ultraviolet. For this reason it is used as an insulating material, and as a mirror in reflecting telescopes. The 200-inch mirror in the world's largest telescope at Mount Palomar, California, is coated with aluminum.

About half of the aluminum produced in this country is converted to alloys for special uses. Duralumin is an alloy containing aluminum, copper, manganese, and magnesium. It is light and nearly as strong as steel, so it is useful in the construction of aircraft. Aluminum bronzes contain copper, and occasionally some silicon, manganese, iron, nickel, and zinc. These light-weight alloys have high tensile strength and great resistance to corrosion, so they are used extensively in the manufacture of crankcases and connecting rods for gasoline motors. Alnico is a magnetic alloy containing 50 per cent iron, 20 per cent aluminum, 20 per cent nickel, and 10 percent cobalt; it will lift more than 4000 times its own weight of iron. It is made by pressing together the constituent metals in powder form and heating the mixture just below the melting point. This is an example of powder metallurgy - a branch of science which is growing rapidly in importance.

When powdered aluminum and iron (III) oxide are mixed and ignited by means of a magnesium fuse a vigorous and highly exothermic reaction occurs.

$$2 \text{ Al} + \text{Fe}_2\text{O}_3 \rightarrow 2 \text{ Fe} + \text{Al}_2\text{O}_3 +$$

This is an example of the thermite or Goldschmidt reaction. The temperature of the reaction mixture rises to about 3000° so the iron and aluminum oxide become liquid. The process is frequently used in welding large pieces of iron or steel. Thermite bombs were used for incendiary purposes during World War II because of the high temperature generated by the thermite reaction and because the reaction is not readily quenched by water. The thermite reaction of metallic oxides, such as MnO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>, which do not give pure metal when reduced by carbon. The reaction is also of particular value when carbon-free alloys, such as ferrotitanium, are desired.

## **ALUMINUM OXIDE**

The oxide, Al<sub>2</sub>O<sub>3</sub>, occurs in nature in pure form as the mineral corundum, a very hard substance which is used as an abrasive for grinding and polishing. Emery is aluminum oxide mixed with Fe<sub>3</sub>O<sub>4</sub>; it is also used as an abrasive. Artificial corundum, sold under the name alundum, is produced by fusing bauxite in an electric furnace. It is used as an abrasive, refractory, and as a filtering medium for corrosive liquids. Several precious stones are composed of aluminum oxide. These stones are colored by impurities; ruby

(red, by chromium compounds); sapphire (blue, by compounds of cobalt, chromium, and titanium); oriental amethyst (violet, by manganese compounds); and oriental topaz (yellow, by iron). Artificial rubies and sapphires are now manufactured by melting aluminum oxide (m.p. 2050°) with small amounts of oxides to produce the desired color, and cooling the melt so as to produce large crystals. The gems are indistinguishable from natural stones, except for microscopic, rounded air bubbles in the synthetic ones and flattened ones in the natural stones. These are used not only as jewelry, but as bearings ("jewels") in watches and other instruments, and as dies through which wires are drawn. Very finely divided aluminum oxide, called "activated alumina," is used as a dehydrating agent and as a catalyst.

Various aluminum articles, such as drinking tumblers, are given a wear resistant coating of oxide by anodic oxidation in a bath of chromic, sulfuric, oxalic acid. This surface readily absorbs dyes and pigments which give a pleasing decorative effect to the article.