

# Material Review: Alumina (Al<sub>2</sub>O<sub>3</sub>)

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## Abstract

Alumina (Al<sub>2</sub>O<sub>3</sub>) or Aluminum Oxide is the only oxide formed by the metal aluminum and occurs in nature as the minerals *corundum* (Al<sub>2</sub>O<sub>3</sub>); *diaspore* (Al<sub>2</sub>O<sub>3</sub>•H<sub>2</sub>O); *gibbsite* (Al<sub>2</sub>O<sub>3</sub>•3H<sub>2</sub>O); and most commonly as *bauxite*, which is an impure form of gibbsite. The precious stones *ruby* and *sapphire* are composed of corundum (and thus also natural forms of alumina)—getting their colors by small amounts of impurities.

The importance of alumina is two-fold; it is used as a starting material for the smelting of aluminum metal, and used as a raw material for a broad range of advanced ceramic products and as an active agent in chemical processing. (“Alumina” Britannica) Although the naturally occurring corundum, ruby and sapphire are sometimes also referred to as alumina, but the proper use of the term is limited to the material that is derived from bauxite and employed in the production of aluminum, industrial ceramics, and chemical processing.

In this paper, besides briefly covering the background information/ history of the material, we will describe its chemical and physical properties, its manufacturing process (the Bayer process) and its applications or uses.

**Key words:** Alumina, Material Review, Chemistry.

## Background Information: History of Alumina

The history of alumina is linked to that of alum from where it took its name. (“Historical Milestones”) Alum is a compound of Aluminum and potassium disulphate-(KAl(SO<sub>4</sub>)<sub>2</sub>, 12 H<sub>2</sub>O) – and it forms wherever schistose or clayey earth comes in contact with sulphuric acid as a result of sulphurated minerals or volcanic smoke and gas. (Ibid.)

Alum was known to the Sumerians, Egyptians, Greeks and Romans who used it for a wide variety of applications—as an astringent (medicine for stopping flow of blood), as mordant for wool dye, as tan for skins, as an anti-inflammatory product, as a healing substance, as an anti-perspirant, as an anti-diarrhoeal product, for embalming and fireproofing of wood. (Ibid.)

### *Initial Manufacture of Alumina*

Marggraf first isolated ‘alumina’ by extracting it from natural clay using sulphuric acid in 1754 and the

word “alumina” was first coined for the substance by Guyton de Morveau in 1761. This was followed by the discovery of earth rich in alumina near Les Baux (region of Arles- A medieval kingdom of eastern and southeast France) by Berthier who named it *Bauxite*.

Manufacturing of alumina was first started in 1860 in the South of France by using the Sainte-Claire Deville process that consisted of attacking bauxite by sodium carbonate followed by the precipitation of alumina hydrate.

### *Manufacture of Aluminum & the Bayer Process*

Other important developments in the history of the development of alumina were the perfection of the process of electrolyzing alumina into aluminum in 1886 by Héroult in France and Hall in the US. This process is still used today. The other important development was the perfection of the process of extracting alumina from bauxite by an Austrian named Bayer in 1888. The Bayer Process, named after its inventor, is still the most widely

used process in the manufacture of alumina all over the world. We will look at the process in greater detail later in this paper. (“Historical Milestones”)

### ***New Natural Forms of Alumina***

While progress was being made in the field of manufacturing of alumina, its new natural forms were also being discovered. Some of these are Corundum (discovered in 1799), Diaspore (1801), Gibbsite (1820), Boehmite (1924), Bayerite (1925), Nordstrandite (1956). Gibbsite was the first form of Alumina that replaced the use of alum in the paper industry and in the water treatment process.

## **Properties of Alumina**

Fused alumina (the substance produced after being melted and re-crystallized) is identical in chemical and physical properties with natural corundum. It is a very hard material and its hardness is exceeded only by diamond and a few synthetic substances such as *carborundum*, and *silicon carbide*. This property of alumina lends itself for use as an abrasive material. Another useful property of the material is its high melting point, i.e., above 2000°C (3632°F), which makes it useful as a refractory and as linings of special furnaces. (“Alumina” Britannica) The mechanical, chemical, and electrical properties of Alumina (99.7% purity) often used in the ceramic industry are depicted in the following tables:

### *Mechanical Properties*

Properties	Conditions	Units	values
Bulk Density	20°C	g/cm <sup>3</sup>	3.96
Tensile Strength	20°C	Mpa	220
Flexural (Bending) Strength	20°C	> Mpa	410
Elastic Modulus	20°C	Gpa	375
Hardness	20°C	kg/mm <sup>2</sup>	14
Fracture Toughness	20°C	Mpa·m <sup>1/2</sup>	4-5
Porosity	20°C	%	0

### *Thermal Properties*

Max. working temp	-	°C	1700
Coef. Thermal Expansion	25-300°C	10 <sup>-6</sup> /°C	7.8
Coef. Thermal Expansion	25-1000°C	10 <sup>-6</sup> /°C	8.1
Thermal Conductivity	20°C	W/m°K	28

### *Electrical Properties*

Dielectric Strength	2.5mm tk	ac-kv/mm	10
Dielectric Constant	1 MHz	-	9.7
Volume Resistivity	20°C	Ohm-cm	>10 <sup>14</sup>
Volume Resistivity	300°C	Ohm-cm	10 <sup>10</sup>
Volume Resistivity	1000°C	Ohm-cm	10 <sup>6</sup>
Loss Factor	1 MHz	-	0.009
Dissipation Factor	1 MHz	-	0.0001

Source: Aluminum Oxide (Alumina) Ceramics & Properties-Marketech International Inc.

## Structure of Crystalline Alumina

The basic unit cell structure of corundum (the naturally occurring alumina) is *hexagonal*. In a hexagonal unit cell, the sides that provide depth and width to the cell (sides “a” and “b”) are equal, and are at an angle of 120 degrees to each other. Side “c” (the side which provides height) is not equal to “a” and “b,” and is at angles of 90 degrees to sides “a” and “b.” (“Sundahl and Durfey”)

The crystal lattice of the hexagonal structure is made up of three unit cells. The planes and directions in the crystal lattice are denoted by *Miller-Bravais* Lattices, which provide a four-numbered description of location within the crystal. (Ibid.)

### *Alumina (Aluminum Oxide) Structure*

The structure of Aluminum Oxide has two types of sites, *hexagonal* and *octahedral* in which it holds the atoms. Hexagonal sites are the corner atoms in the cell while the octahedral sites are present between two layers of vertical stacking. Aluminum cations are in 2/3 of the octahedral sites, and oxygen anions are in 1/3 of the octahedral sites. Each oxygen is shared between four octahedra. The oxygen presence in octahedral sites permits strong bonding and, therefore, gives rise to the characteristics of the properties of alumina.

### *Structure of Liquid Alumina*

Although scientists have known the crystalline structure of Alumina for some time, the structure of liquid alumina has been determined only recently, i.e., in 2001. The study of the structure is significant as alumina, having a very high-melting point (over 2000 degrees C), is the hottest liquid whose placement of atoms has been found. (“Structure of Liquid Alumina Determined..”) The studies show that, in liquid alumina, each aluminum atom has just 4 neighboring oxygen atoms and each oxygen just 3 aluminum atoms. This makes the structure of liquid alumina significantly different from the structure of crystalline alumina. The distribution of the different atomic configurations in the liquid state explains the 30% drop in density (from 3.8 g/cm<sup>3</sup> to 2.8 g/cm<sup>3</sup>) when alumina melts and the shrinkage seen when alumina ceramics are fabricated. (Ibid.) The discovery of the structure of alumina in its molten state will help scientists to understand better the properties of alumina

and to incorporate that knowledge in the development of ceramics and glasses for the future.

## Applications of Alumina

More than 90% of alumina produced worldwide is utilized in the production of Aluminum. This is because converting the naturally occurring bauxite into alumina is the necessary first step before it can be converted into Aluminum. The figure, however, does not detract from the usefulness and application of the material as an industrial material on its own. It is estimated that over 4 million tons of alumina is used in material applications worldwide (excluding the alumina used for aluminum production). (“The World of Alumina” *Using Alumina*) The varied applications of alumina are due to its abundance and its multiple forms as well as its properties of stability, purity, refractoriness, and chemical inertia (Ibid.) The applications of Alumina are too many to be covered in this paper. Some of these are described briefly below:

### **1. Ceramics**

The most important and wide-ranging use of alumina is in the field of ceramics.

#### a. As an Insulating Material

The dielectric and excellent thermal shock properties of Alumina make it an excellent choice as an insulating material. For applications in very high frequencies (UHF), high purity dense alumina, fired at temperatures above 1600°C, is generally used. Examples are applications for television or satellite transmitter tubes or for microwave generators for heating, or for powerful lasers. (The World of Alumina” *The Application of dielectric ceramics*)

#### b. Electronics

Alumina is widely used in the electronics industry for passive components such as interconnection, resistances, and capacitors and is specifically employed in applications such as substrates for hybrid circuits, multi-layer interconnection circuits, materials for type II condensers, and hyper frequency resonators (mobile phones). (Ibid. *Use of Electronic Ceramics*)

### c. Mechanical Ceramics

Due to their excellent mechanical properties, alumina-based ceramics are being increasingly used as a substitute material for several applications. These include the use of ceramic for abrasive and cutting tools.

Alumina-based ceramics are also used for making extrusion and sanding nozzles and for parts of machinery (particularly in the mining industry) where wear resistant qualities are critical. They are also used for making ice-skate blades and some friction parts such as wear-resistant seals in piston engines. (Ibid. *Mechanical Ceramics*)

### d. Military Uses

The shock-resisting quality of alumina-ceramics makes them useful as armor plating for protection of tanks and helicopters as well as for bullet-proof jackets and in aeronautics for protection of hydraulic parts. (Ibid.)

### e. Bio Medical

Alumina is also an inert substance, and at room temperature, it is insoluble in all ordinary chemical reagents. It also has excellent wear resistance and can be polished to high surface finish. These qualities make it useful as a biomaterial. For example, alumina is used for artificial joint replacements; porous alumina is used as a 'bone spacer' and for teeth implants. ("Alumina as a bio material")

In the biomedical field, alumina is also used for cochlear implants (hearing aids for the deaf). In the more general field of medical instruments, ceramics are also used to manufacture medical tubes and other scientific, medical products.

### f. Chemical Ceramics

Alumina-based Ceramic filters are chemically inert and can be manufactured with fine porosity. Due to their resistance to a wide-range of chemical attacks, the material is also used for chemical storage and

transportation of aggressive products. ("The World of Alumina" *Use of Chemical ceramics*)

### g. Enameling

Enameling is the coating given to the surface of insulators and other ceramic materials like tiles. Alumina contributes to adherence to metal or ceramic, opacity and resistance to corrosion and to scratching in the enameling process. Enameling is also used to make decorative items. (Ibid. *Applications for Enamels, glazes*)

## **2. Refractory Uses**

Another major use of alumina is in the manufacturing of refractories. Refractories are required to resist compression, erosion, creeping, thermal shock, chemical attack, vitreous dissolution and heat loss at ever higher temperatures. These requirements have necessitated the use of greater quantities of alumina as a constituent in refractories. As a result, a quarter of all alumina production (less that used in Aluminum production) goes into refractories. (Ibid. *Refractory Products*)

## **3. Chemical Industry**

Alumina is used for coating titanium-oxide that is an important pigment for paints, paper and plastics to inhibit its catalytic properties. It is also used for water treatment and paper manufacturing. (Ibid. *Chemical Industries*)

## **4. Catalysts, Fillers, and the Glass industry**

Catalysts can be supports or active principles. Some catalysts are aluminas, others, such as sodium desilication solid products (Zeolite) are aluminous compounds. Hydrated or calcined aluminas are used as fillers in several fields of application such as welding (it is used as a welding flux) brake linings, and as a fire retardant. Alumina and silica are the main components of glass. Pure alumina, produced in the Bayer process, contains very few impurities and is used in the production of special glass. (Ibid. *Catalysts, Fillers, & the Glass Industry*)

## The Bayer Process<sup>1</sup>

As noted earlier, the Bayer process for extracting alumina from bauxite was first developed in 1888, just one year after the manufacture of Aluminum from Alumina through the electrolytic process. The Bayer Process is carried out in 5 stages:

### 1. Grinding of Bauxite

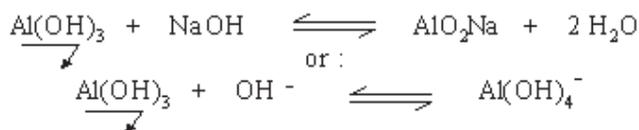
Bauxite is crushed to form grains with a diameter of less than 30 mm in hammer crushers; then mixed with the recycled liquor downstream from the process and ground more finely.

This grinding is necessary to increase the contact surface between the liquor and the bauxite and to improve the yield of the digestion. The recycled liquor is enriched in soda (NaOH) and lime (CaO) before grinding to make it more 'aggressive' towards the bauxite.

### 2. Digestion of Bauxite

The bauxite- liquor mixture (slurry) obtained after the grinding is preheated and put into digesters for several hours. The temperature and the pressure of the slurry digesters depend on the type of bauxite being processed, e.g., a gibbsitic bauxite can be digested at atmospheric pressure while diasporic bauxite is heated to over 200°C and put under high pressure to make alumina. During the digestion stage of the Bayer process, the alumina contained in the bauxite gets dissolved and the compounds are deposited in the form of insoluble scale.

The main equation of the Bayer Process is as follows:



### 3. Settling and washing of Residues

In this stage of the process, the mud and the liquor that make up the slurry are separated by settling. The liquor that is separated contains sodium aluminate, while

the mud that settles at the bottom of the settling tank is removed since alumina has been extracted from it. The floating liquor is filtered and then sent to be precipitated. In the 'mud washing' process, the sodium aluminate is recovered to be used again in the Bayer cycle, while the mud is cleansed to be stored in a natural environment.

### 4. Crystallization of Hydrates

Dissolved alumina is recovered from the liquor by precipitation of crystals as the trihydrate Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O in a reaction which is the reverse of the digestion of trihydrate, as follows:



The crystallization of the alumina hydrate (in the form of gibbsite) is actually a complex process involving nucleation, growth and agglomeration. The conditions such as the temperature, soda concentration and the gibbsite seed determine the particle size, and impurities of the gibbsite and the calcined alumina produced. The crystalline structures obtained also depend on the technique used in the process. The "European Technique" leads to a growth mechanism while the American Technique, provokes strong agglomeration apart from growth.

### 5. Calcination of Hydrate

In this last stage of the Bayer Process, alumina is formed by calcination of the wet hydrate (Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O) in inclined rotary kilns. The massive water vapor release at between 250 and 400°C fluidizes the alumina that begins to flow like liquid in kiln. At around 1000-1250°C the exothermic transformation into alpha alumina occurs which makes the temperature rise further. For the gibbsite to be completely transformed into alpha alumina it must remain at the transformation temperature for about 1 hour. "Mineralizers" are used to catalyze the transformation. The characteristics of calcined alumina vary a great deal and depend on the conditions of calcination. Soda is the main impurity of the alumina produced in the Bayer process and is not a desirable impurity. It is removed by hydrate washing or by the use of silica. Calcined alumina, the final product

<sup>1</sup>This section has been summarized from "The BAYER Process"-The World of Alumina & "Alumina Process" [both available online]

of the Bayer Process, is produced in the form of alpha alumina crystallite agglomerates the size of which typically varies from 0.5 to 10  $\mu\text{m}$ .

## Conclusion

We have seen in this research paper that the history of alumina dates back to the earliest days of human civilization when a close relative of alumina (alum) was used for a variety of applications including medicinal purposes. Its industrial and commercial use in the modern times, however, took off after the development of the Bayer process that has made the wide-scale production of the material possible at low cost. Apart from Alumina's importance as a 'stepping stone' in the production of Aluminum, its usefulness as a 'stand alone' material has grown over the years as reflected in the wide range of its applications. These applications are likely to proliferate rather than diminish in the foreseeable future.

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