Lecture 2:

2- Oxide Ceramics: Structure, Technology, and Applications

2-1 Alumina

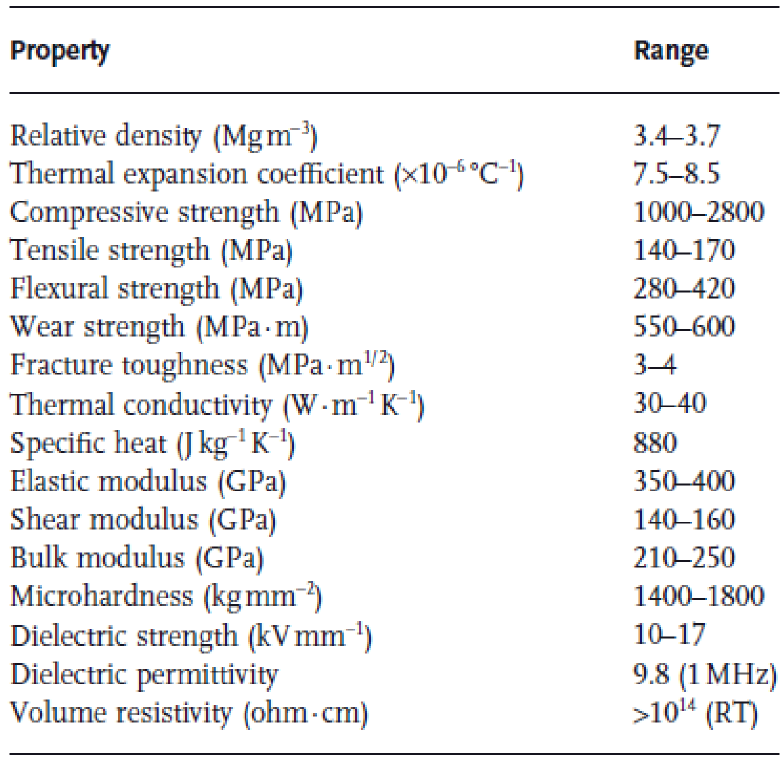
2-1-1 General Properties and Application

Alumina is the most cost - effective and widely used structural engineering material in the family of advanced ceramics. The raw materials from which this high - performance, technical grade ceramic is produced are readily available and reasonably priced, resulting in good value for the cost in fabricated alumina shapes. Hence, alumina (corundum, α-Al_2O_3) is considered the " workhorse material " of the structural ceramics industry. Its high hardness, abrasion resistance, and chemical inertness makes it an ideal material to perform well in a variety of aggressive environments, ranging from mining industry to chemical industry to metal manufacturing and processing, to ceramic armor and biomedical applications. Its electrically insulating nature, coupled with its moderate thermal conductivity, reasonably low dielectric permittivity, and low dielectric loss, offer a plethora of applications that include electronic substrates for integrated circuits (ICs) and automotive spark plugs.

However, these advantageous properties are partially offset by the material 's low tensile and flexural strengths and fracture toughness, and low thermal shock resistance (see Figure 6.1). Hence, the decision to include alumina - based wearing parts in engineering designs must be assessed judiciously so as to avoid catastrophic failure in service under harsh conditions. An overview of the important properties of alumina ceramics is provided in Table 7.1. The wide range of values attests to the fact that alumina ceramics depend on processing parameters, including the sintering temperature, sintering atmosphere, impurity content, grain size, and other extrinsic and intrinsic factors. For example, the extremely pure and fine - grained alumina specifications used in femoral heads for hip endoprostheses demonstrate noticeably higher strengths, toughness, and hardness characteristics. High - purity alumina parts and devices can be utilized in both oxidizing and reducing atmospheres to 1925 ° C. The mass loss in vacuum between 1700 ° and 2000 ° C ranges from 10^{-5} to 10^{-7} g $cm^{-2}.s^{-1}$. Alumina resists attack by all gases except for wet fluorine, and is resistant to all common reagents except for hydrofluoric and hot orthophosphoric acids. An elevated temperature corrosion occurs in the presence of alkali metal vapors, particularly at lower purity levels (< 90% Al_2O_3 content).

The additions of either chromium oxide or manganese oxide is known to improve the material's hardness and toughness. Other additions can be made to improve the ease and consistency of metal films fired to alumina ceramics for subsequently brazed and soldered assemblies.

Table 7.1 Mechanical, thermal, elastic and electrical properties of high-alumina ceramics.



Property	Range
Relative density ($Mg\,m^{-3}$)	3.4–3.7
Thermal expansion coefficient ($\times10^{-6}\,°C^{-1}$)	7.5–8.5
Compressive strength (MPa)	1000–2800
Tensile strength (MPa)	140–170
Flexural strength (MPa)	280–420
Wear strength (MPa·m)	550–600
Fracture toughness ($MPa\cdot m^{1/2}$)	3–4
Thermal conductivity ($W\cdot m^{-1}K^{-1}$)	30–40
Specific heat ($J\,kg^{-1}K^{-1}$)	880
Elastic modulus (GPa)	350–400
Shear modulus (GPa)	140–160
Bulk modulus (GPa)	210–250
Microhardness ($kg\,mm^{-2}$)	1400–1800
Dielectric strength ($kV\,mm^{-1}$)	10–17
Dielectric permittivity	9.8 (1 MHz)
Volume resistivity (ohm·cm)	$>10^{14}$ (RT)

RT = room temperature.

2-1-2 Processing of Alumina

The process of producing pure alumina from bauxite ore (Bayer process) has changed very little since its inception in 1893, and can be divided into three stages of extraction, precipitation, and calcination.

2.1.2.1 **Extraction**

The aluminum hydroxide (gibbsite, γ - $Al(OH)_3$) and oxyhydroxide (boehmite, γ - AlOOH; diaspore α-AlOOH) minerals) in bauxite ore are selectively extracted from the insoluble components (mostly quartz, clay minerals, and iron and titanium oxides) by dissolving the ore in a solution of sodium hydroxide (caustic soda) according to:

$$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$$

The ore is washed, crushed and milled (Figure 7.1 , step A) to reduce the particle size and make the minerals more available for extraction. It is then combined with the process caustic liquor and sent as slurry to a heated pressure digester for extraction (step B).

The concentration, temperature and pressure within the digester are set according to the properties of the bauxite ore. Ores with a high gibbsite content can be processed at 140 °C, whereas the processing of boehmite requires temperatures between 200 and 240 °C. The steam pressure at 240 °C is approximately 3.5 MPa.

Although the application of higher temperatures would, in theory, be advantageous, there are several disadvantages that include corrosion problems and the possibility of oxides other than the alumina dissolving into the caustic liquor.

Following the extraction stage, the insoluble oxide residue must be separated from the aluminum - containing liquor by a process known as *settling* (step C). Here, the liquor is purified by filtering before being transferred to the precipitators. The insoluble, so - called “ red mud ” from the first settling stage is thickened and washed to recover the caustic soda, which is then recycled back into the main process.

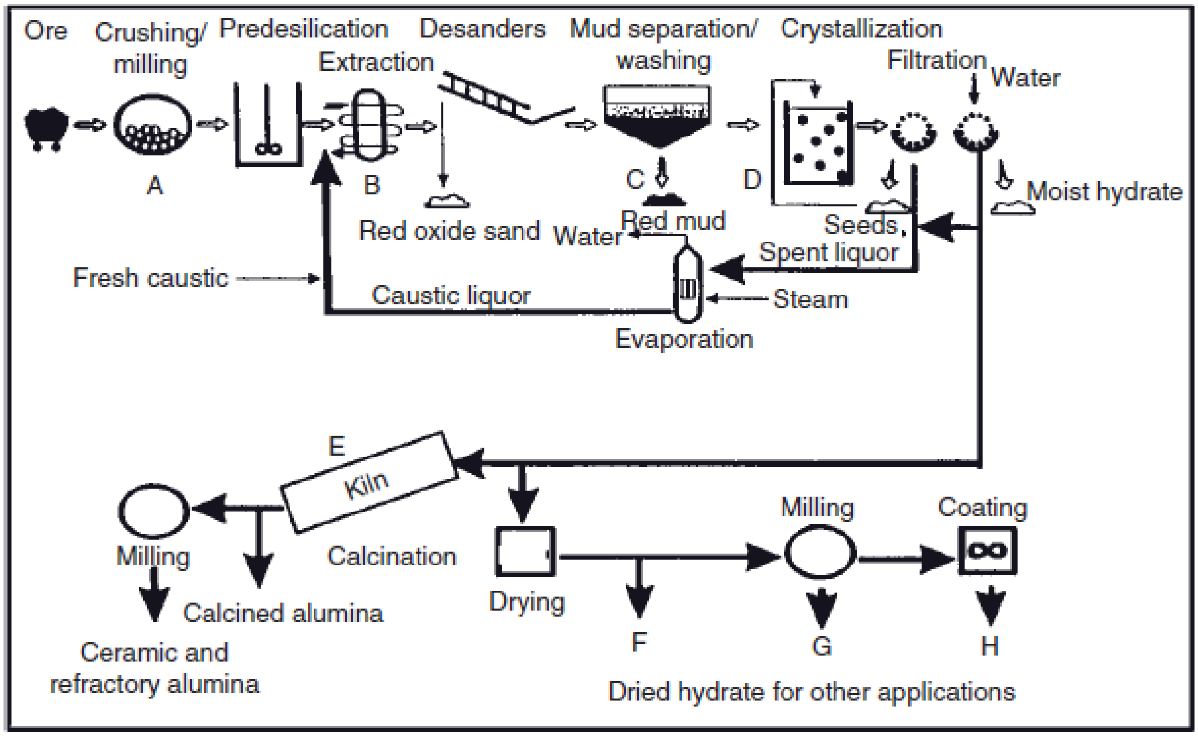


Figure 7.1 Process flow sheet of the Bayer process. Modified after Evans (1996).

2.1.2.2 **Precipitation**

Crystalline pure aluminum hydroxide (gibbsite) is then precipitated from the digestion liquor after cooling and diluting, and adding seed crystals (step D) according to:

$$[\mathrm{Al(OH)_4}]^- \rightarrow \mathrm{Al(OH)_3} + \mathrm{OH}^-$$

This is essentially the reverse of the extraction process, except that the product ’s nature is carefully controlled by the plant conditions, including seeding or selective nucleation, precipitation temperature, and the cooling rate. The gibbsite crystals are then classified into size fractions and fed into a rotary or fluidized - bed calcination kiln (step E). Undersized particles are fed back into the precipitation stage.

2.1.2.3 **Calcination**

The gibbsite crystals are calcined (step E) to form high - purity alumina (α -Al_2O_3) as the precursor material for a variety of alumina ceramics according to:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

The calcination process must be carefully controlled since it dictates the properties of the final product. A secondary process stream containing dried gibbsite can be separated to produce aluminates, zeolites, filler materials for toothpaste, fire retardants, and others (steps F – H). As will be shown below, the stepwise removal of water and OH groups, respectively, leads to a plethora of transitional alumina polytypic structures that eventually will determine the performance of the end products.

The stability of aluminum hydroxides shows also a pronounced pH dependence. Hydroxides precipitated from an aqueous solution of AlCl 3 show the structures of gibbsite at pH 5 – 7, bayerite at pH 7 – 11, and nordstrandite at pH 11 – 13. This means that the controlled dehydration of aluminum hydroxides can lead to alumina products with tailored properties for a large variety of industrial applications. In particular, the size and morphology of the crystalline alumina particles can be adjusted in such a way that, on subsequent sintering, ceramics with predetermined and reproducible properties can be obtained (see also Figure 7.1 , steps F to H).

The worldwide production of alumina was estimated to be 62.4 million tons in 2006, an increase from the 1995 value of 38 million tons (Evans, 1996), with Australia (17.7 million tons), China (8.6 million tons), Brazil (5.3 million tons) and USA (5.2 million tons) as the leading producers (Source: USGS Mineral Resources Program). While 90% of the alumina is used to extract metallic aluminum by electrolysis, approximately 10% of the total is non - metallurgical alumina used for advanced ceramic allocations.

2.1.3 **Structure of Alumina Polymorphs**

2.1.3.1 **Stable Alumina Polymorphs**

Under ambient conditions, only two stable modifications of Al_2O_3 exist. The thermodynamically stable polymorph between room temperature and the melting point at 2050 °C is α-Al_2O_3 (corundum), which forms a lattice of hexagonally close - packed oxygen atoms with stacking order AB - AB … , in which two - thirds of the octahedral sites are occupied by Al cations (Figure 7.2). The oxygen octahedral share edges to form six - membered rings that are linked into gibbsite – like sheets parallel (0001). The sheets are stacked into a framework structure by sharing the faces and corners of octahedra. In the hexagonal cell (a = 475 pm, c = 1298 pm).

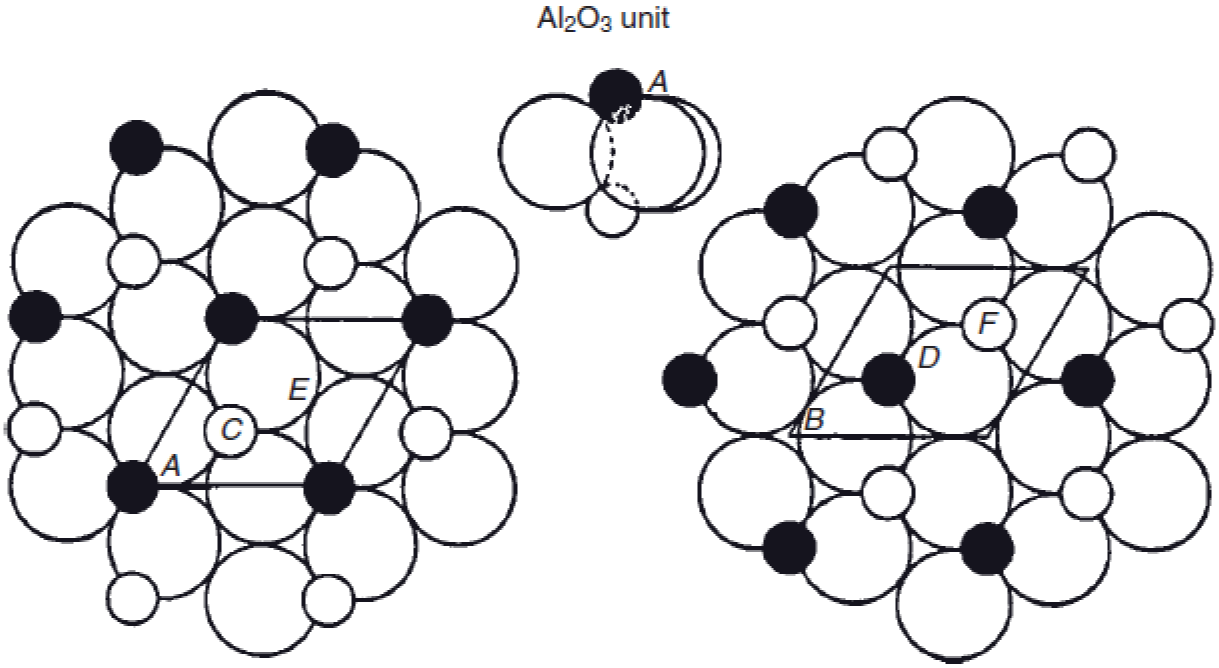


Figure 7.2 Structure of α-Al_2O_3. The framework is composed of AB-AB...-stacked gibbsite-like sheets of oxygen octahedra.

2.1.3.2 **Transitional Alumina Polymorphs**

The kinetics and structural relationships of the dehydration of gibbsite, and boehmite occurring as the main minerals in bauxite ore are quite complex, and in several aspects remain controversial. Depending on the grain size, heating rate and water partial pressure, three main pathways of dehydration have been described (Wefers and Misra, 1987 ; Ingram - Jones *et al.* , 1996). The general structural principle of these dehydration sequences is that the stacking order of oxygen atoms is maintained during transformation within the series of the transitional aluminas (i.e., gibbsite → boehmite → χ → γ → δ → θ), all of which have a cubic close - packed ABC - ABC … stacking sequence. On the other hand, rapid quenching during the chemical vapor deposition (CVD) of alumina for coatings of cemented carbide cutting tools leads to the sequence κ → α , with hexagonal close - packed layers of oxygen atoms (Prengel *et al.* , 1994). All metastable alumina structures are ordered or partially ordered cation arrays at the interstitial sites of either cubic f.c.c. (γ - , η - , θ - , and δ - alumina) or hexagonally close - packed (χ - , κ - , and α - alumina) oxygen atoms (Levin and Brandon, 1998).