

## **Lecture 3:**

### **2.1.4 Specific Properties and Applications**

#### **2.1.4.1 Duplex Al<sub>2</sub>O<sub>3</sub> – ZrO<sub>2</sub> Ceramics**

The addition of polycrystalline metastable tetragonal Y - partially stabilized zirconia (Y-PSZ) aggregates to a fine - grained alumina matrix results in so - called “duplex” structures (see Figure 7.32), with a high fracture strength  $> 700$  MPa and fracture toughness up to  $12 \text{ MPa}\cdot\text{m}^{1/2}$ . Since Y - PSZ has a lower elastic modulus (ca. 210 GPa) than alumina (350 – 400 GPa), cracks introduced by external loads tend to move towards the zirconia particle aggregates. The crack energy will then be

Dissipated by forcing the t - ZrO<sub>2</sub> to transform to m - ZrO<sub>2</sub>. This mechanism will be augmented by the compressive stress generated, that tends to counteract crack movement.

The considerably improved mechanical properties of such duplex ceramics are currently being exploited in novel developments in the field of femoral heads for hip endoprostheses that rely on high - purity alumina (BIOLOX R delta), with the addition of 17 vol% tetragonally stabilized zirconia and 1.4 vol% chromia particles. Whilst the former addition provides mechanical strengthening by transformation toughening (see Section 7.2.4), the latter addition acts as a reinforcement by dissipating crack energy via the deflection of crack paths. By applying these mechanisms, the four - point bending strength is increased three - to fourfold compared to that of unalloyed alumina (Table 7.1 ), to reach 1400 MPa, while the fracture toughness is increased to  $6.5 \text{ MPa}\cdot\text{m}^{1/2}$ .

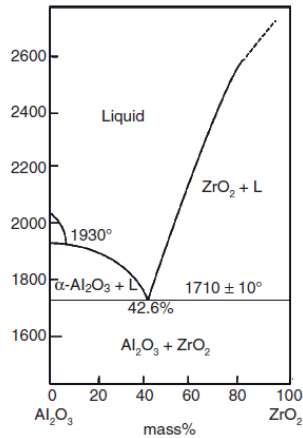


Figure 7.11 Binary phase diagram  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  (after Alper, 1967).

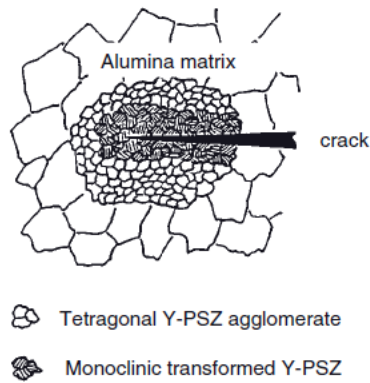


Figure 7.32 Reinforcement mechanism of an alumina–zirconia duplex ceramics with agglomerated Y-PSZ particles.

#### 2.1.4.2 Stuffed Alumina Ceramics

$\beta$  -  $\text{Al}_2\text{O}_3$  ( $\beta$  - alumina) is not an aluminum oxide, but rather a “stuffed” alumina compound,  $\text{MAl}_{11}\text{O}_{17}$ , where M is a monovalent ion such as Na, K, Rb, Ag, Te, or Li. Increasing amounts of M ions lead to related structures such as  $\beta'$  - alumina ( $\text{MAl}_7\text{O}_{11}$ ) and  $\beta''$  - alumina ( $\text{MAl}_5\text{O}_8$ ), with noticeably increased conductivities.  $\beta$  - alumina is thought to crystallize in the hexagonal system with  $a = 558$  pm and  $c = 2245$  pm.

Structurally,  $\beta$  - alumina is composed of spinel - like blocks of cubic close - packed oxygen ions with the stacking order ABC - ABC ... , in which the Al ions occupy both tetrahedral and octahedral interstices.

#### 2.1.4.3 Selected Applications of Alumina Ceramics

Of the approximately 6 million tons of non - metallurgical alumina produced worldwide in 2006, about 50% was used to produce refractory and wear ceramics, 20% abrasives, 15% whiteware and spark plugs, and 15% other technical ceramics. Owing to its favorable mechanical, electrical and chemical properties, the typical uses of polycrystalline  $\alpha$  - alumina ceramics include:

- Wear pads

- Sealing rings and washers (e.g., for hot water mixing batteries and automotive water pumps)
- High - temperature electrical insulators
- High - voltage insulators, as in spark plugs
- Surge arrester sleeves
- Rectifier housings for thyristors
- Gas laser tubes
- Sheaths for high - voltage sodium vapor lamps (Lucalox <sup>TM</sup> )
- Furnace liner tubes
- Thread and wire guides
- Abrasion - and erosion - resistant pipe and elbow liners
- Liners for Venturi nozzles
- Filters for molten metals
- Cutting tool bits
- Grinding media
- Ballistic armor
- Electronic substrates
- Nose cones and radomes for missiles, infrared detector windows for short - range attack missiles

Applications of single - crystal corundum include:

- Laser crystals
- Dental roots
- Bone screws (only in Japan)
- Optical windows for high - temperature – high pressure reactors
- Scratch - proof watch glasses
- Ruby bearings for watches

- Artificial gemstones

Single crystals of pure and doped alumina can be grown using well – established techniques such as flame fusion (Verneuil process), crystal pulling, and top - seeded solution growth ( TSSG ), as well as under hydrothermal conditions and from the vapor phase.

**Alumina - Lined Pipes** Extraordinary amounts of coal are burned worldwide, not only in conventional coal - fired power plants but also in modern developments, including cogeneration power plants. The burners of these units must be fed with pulverized coal or coal slurry that is transported pneumatically to the burner nozzles at high velocity and throughput. However, as most coals contain a percentage of highly abrasive quartz grains, severe wear problems of the feeder pipes may ensue. Currently, alumina is being applied successfully not only to combat mechanical wear and erosion of the coal powder transport piping, but also for the handling of abrasive fly and bottom ash, for example, as liners for ash slurry lines.

**Filters for Molten Metal** Inclusions in molten metals, such as oxide skins, mold sand particles, inoculation reaction by products or furnace slags, can be efficiently removed by filtering through pressed cellular, extruded cellular, or foam ceramic filters manufactured from high - temperature - resistant, chemically inert alumina, and also mullite, silicon carbide, and stabilized zirconia. Alumina is particularly useful when filtering liquid aluminum alloys in the range of 750 – 850 °C, and copper - based alloys at 1000 – 1200 ° C. These ceramic filters are designed for use in either “batch” or “ in - mold ” filtration:

- In *batch filtration*, large quantities of molten metal may be filtered while being transferred from the melting kiln to the holding furnace, or from the holding furnace to the casting ladle.

- For *in - mold filtration*, the ceramic filter is placed across one of the channels of the mold. Since, in this design, the melt is filtered immediately before solidifying inside the mold, the cleaning efficiency is very high.

**Spark Plugs** Spark plug insulators, which typically contain 88 – 95% alumina, were first developed during World War II, as the then - existing mullite insulators (with a high silica content) were particularly susceptible to corrosive attack from the lead tetraethyl contained in the vehicles ' fuel, and also from additives in the lubricants. Alumina provides to the spark plug insulators not only chemical inertness but also a wide range of temperature stability (from subzero to over 1000 ° C), a reasonably high thermal conductivity required to avoid pre ignition, a high mechanical strength, and an ability to withstand voltages of the order of 20 kV at high temperatures.

**Cutting Tool Bits** The way in which the cutting speed of metal milling has been increased over time as a response to the development of hard tool and specialty steels requiring tool materials with ever - increasing hardness, toughness, and wear resistance. Today, alumina is alloyed with other ceramics such as zirconia, silicon nitride, and titanium carbide ( “ black ” alumina) and nitride, so as to increase the cutting speed beyond 2000 m min<sup>-1</sup> .

The key to producing functional and long lasting alumina cutting tools is to maximize the impact strength and to minimize not only the abrasive, adhesive, and solution wear but also the plastic deformation. Apart from normal wear and tear, ceramic cutting tools undergo a special type of wear caused by solid – state welding reactions between the tool material and the metal turnings. This leads to a zone of intense shear within the turning, to high local temperatures exceeding 1000 ° C, and to chemical reactions between the tool materials and the milled metal.

This leads in turn to: (i) abrasive wear of the metal surface, caused by hard particles being broken off the cutting tool; (ii) adhesive wear among tools and turned or milled metals; (iii) diffusional or solution wear by chemical reactions occurring between

the ceramic and the metal; and (iv) a general plastic deformation by the combined action of stress and temperature and, in turn, induced fracture processes. The typical counter measures taken to overcome this situation include:

(i) increasing the abrasive hardness of the cutting tool material; (ii) improving the cohesive bonding within the polycrystalline cutting tool so as to prevent strong adhesive bonding to the turnings; and (iii) selecting ceramic materials with a low solubility in the metal, or coating them with TiC or TiN.

Specific routes to realize improvements include: (i) the use of a smaller grain size by adding magnesia so as to suppress grain growth during sintering; (ii) alloying with zirconia; and (iii) adding TiC to reduce attrition wear at the tool flanks and also to increase the thermal conductivity and hence improve the thermal shock resistance. This involves the incorporation of SiC whiskers and the addition of TiN, BN, or SiAlON.

**Grinding Materials** Owing to its high abrasion hardness, alumina has been used since antiquity in the form of (emery) to cut and polish less - resistive materials, including rocks, steel, nonferrous metals and jewelry.

**Electronic Substrates** High - quality alumina substrates are used ubiquitously in IC devices as a substrate onto which the electronic components (i.e., the source, gate and drain) of a transistor for modern very large - scale integration ( VLSI ) applications can be built. It can also be used as a thermal management ceramic in radiofrequency ( RF ) power transistors, when the substantial waste heat generated by the electronic switching processes must be dissipated both rapidly and efficiently. The manufacture of alumina substrates begins with the mixing of ultrapure alumina powder with additives and organic binders, and the formation of a “ green sheet ” into which holes are drilled. After having applied a conducting line network by screen printing, the green sheets are laminated into thicker sheets. The organic binder

is then removed by heating at low temperature, after which the sheets are sintered at temperatures  $> 1500\text{ }^{\circ}\text{C}$  in a hydrogen atmosphere.

**High - Temperature Sodium – Sulfur Battery** This battery employs the ionic conductivity of  $\beta$  - alumina, that acts as a diaphragm containing liquid sodium which serves as the negative pole of the battery (Figure 7.12 ).

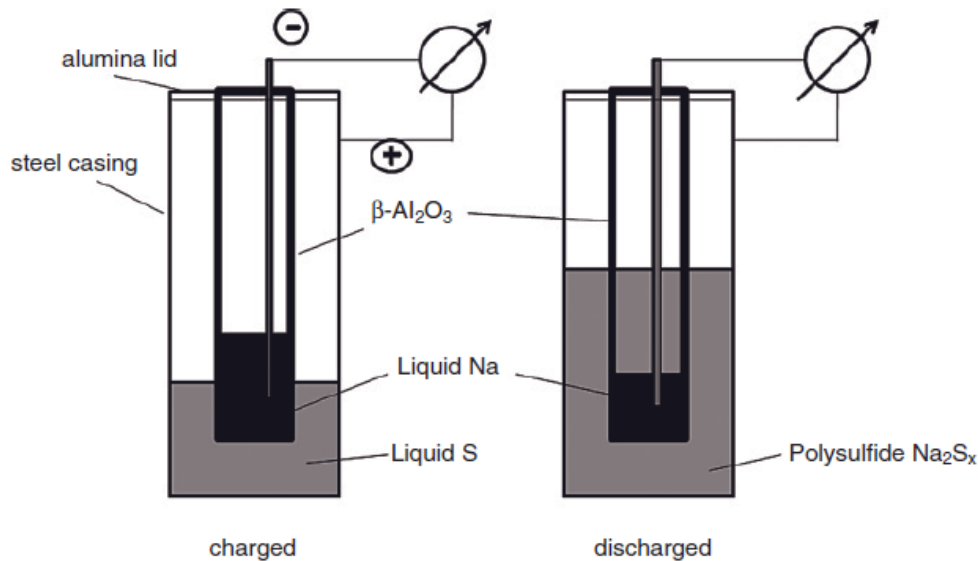


Figure 7.12 Schematic representation of a high-temperature, sodium-sulfur battery.

**Activated Alumina** Historically, all transitional polymorphs of alumina obtained by dehydroxylation of aluminum hydroxide below  $1000\text{ }^{\circ}\text{C}$  were termed “ active ” or “ activated ” alumina, since they served as an important carrier for catalysts. For example, catalysts used in the oxychlorination of ethylene (Degussa, 1999 ), and noble metal (Pt, Pd) catalysts used in the purification of exhaust gases (ICT, 2002 ), rely on porous, reactive support materials that can be provided by  $\gamma / \eta$  – alumina surfaces.