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## 2- *Functional applications of alumina:*

- *Electricity and electronics:* Alumina ceramics are widely used by the electric and electronic industries. Spark plugs for automobiles illustrate the oldest application using materials on the borderline between aluminous ceramics and alumina, the compositions containing here  $\approx 94\%$   $\text{Al}_2\text{O}_3$ .

For electronics, the main product is the insulating substrate on which conducting or resistive, even capacitive or inductive, circuits are deposited. The advantage of alumina is its very high resistivity, but also its mechanical properties (hardness, mechanical strength), because it can never be stressed enough that functional materials must, and have a sufficient level of mechanical performance: spectacles with broken glasses cannot correct vision! Another advantage of alumina is that it lends itself to metallization by various techniques which require not only chemical compatibility, but also excellent surface quality. The alumina used very pure ( $\approx 99.7\%$ ) sintered close to the theoretical density. The three limitations of alumina for the manufacture of dielectric substrates are:

- i) A modest thermal conductivity ( $\approx 30 \text{ W m}^{-1} \text{ K}^{-1}$ ), which does not facilitate the dissipation of the heat produced by the Joule effect;
- ii) A coefficient of expansion doubles that of silicon, which generates stresses at the substrate (“chip” interfaces);
- iii) A marked permittivity ( $\epsilon \approx 10$ ), which induces capacitive couplings and decreases the transit times.

Aluminum nitride AlN is one of the competitors for the manufacture of high technology substrates, where it brings improvements with respect to the three drawbacks mentioned above, but its manufacture is expensive and delicate.

- *Optics:* The remarkable combination of optical and mechanical performances explains the uses of monocrystals (sapphire, possibly ruby). The main manufacturing method is the *Verneuil method*. It consists of melting the alumina powder in the flame of an oxyhydrogen blowpipe, and then solidifying the liquid

by making it drip on a monocrystal which turns around its axis. The monocrystals (called *balls*, although their form is elongated) can be large (diameter expressed in centimeters and length in tens of centimeters). Jewelry (jewels, scratch-proof glass for watches), laser matrices, and substrates for certain electronic circuits and waveguides are the primary applications of sapphire monocrystals, as well as abrasion-resistant optical windows: for military use, but also barcode readers in supermarkets. It is, however, at the polycrystal state that alumina has found its most widespread use: the internal, transparent tube of sodium vapor lamps used for street lighting.

The difficulties which had to be overcome and the methods adopted to succeed have made this application the academic case for the sintering of ceramics.

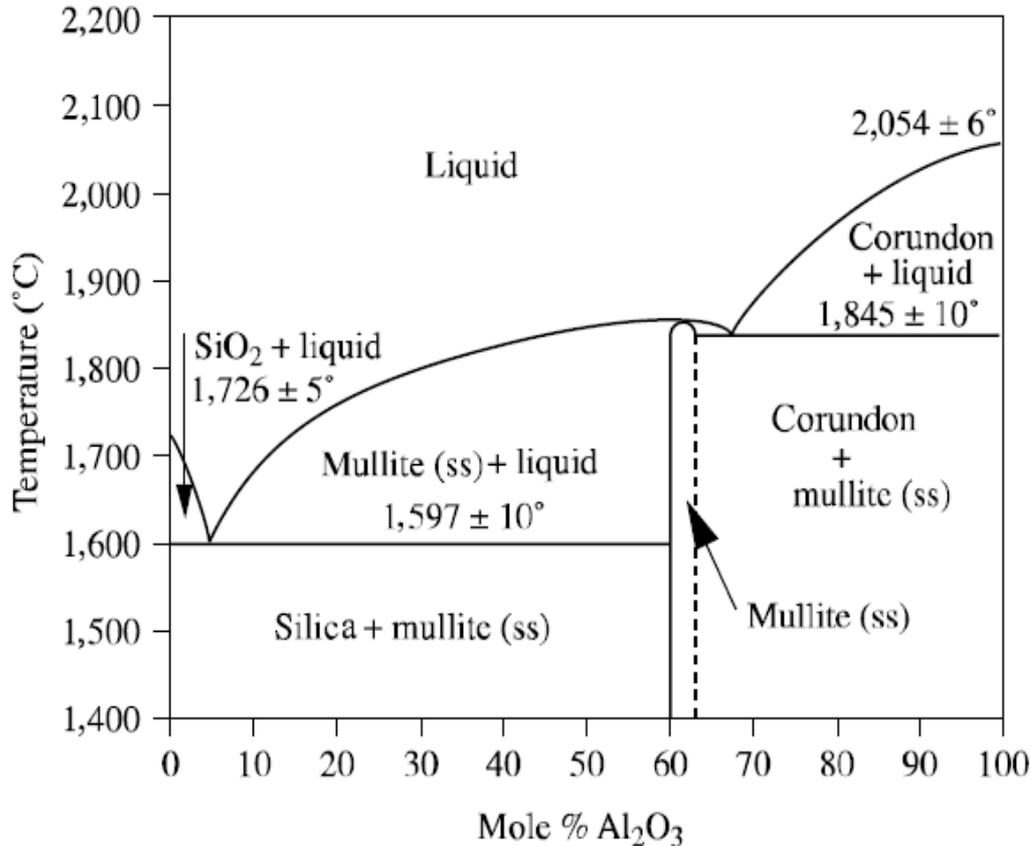
#### • *Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system mullite*

Argillaceous minerals of the sillimanite group were used as early as in the first era of ceramics, but it is mullite  $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  that is the only stable crystallized compound in the binary phase diagram of the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ . However, mullite is very rare in the state of natural ore.

The phase diagram  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  has fuelled numerous debates; mullite exhibits a narrow field of solubility close to  $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  (Figure 1.2): this mullite is called 3:2, because of the alumina/silica ratio. It exhibits congruent melting, i.e. it melts to directly yield a liquid whose composition remains unchanged when the temperature continues to rise. This diagram accounted for most of the experiments; by showing that mullite exhibits incongruent melting at  $\approx 1,830^\circ\text{C}$ , with peritectic reaction  $\text{Al}_2\text{O}_3$ - $\alpha$  plus liquid, which forms this mullite with 52.3% in mass of  $\text{Al}_2\text{O}_3$ . However, the stable diagram often gives room to *metastable* extensions. For instance, a monocrystal that has grown in the absence of alumina germs does not have an alumina/silica ratio of 3:2 but 2:1, i.e. 77.2% in mass of  $\text{Al}_2\text{O}_3$ , and the solid solution can extend up to the composition 3:1, with 83.6% of  $\text{Al}_2\text{O}_3$ . A later fine-tuning of the diagram confirmed the incongruent melting and the metastable extensions, but by modifying some of the limits. It is now

admitted that when alumina germs are present, the peritectic reaction occurs and that there is incongruent melting, but for a homogeneous liquid free from these germs, the melting is congruent.

Mullite crystallizes in the orthorhombic system. Its complex structure accommodates stoichiometry variations (from  $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  to  $3\text{Al}_2\text{O}_3 \cdot i\text{O}_2$ ) thanks to the presence of oxygen vacancies.



**Figure 1.2  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  Diagram**

In comparison with alumina, mullite is slightly lighter ( $\rho \approx 3.2 \text{ g cm}^{-3}$ ) and has lower values of hardness ( $\text{HV} \approx 14 \text{ GPa}$ ), Young's modulus ( $E \approx 250 \text{ GPa}$ ), mechanical bending strength ( $\sigma_F \approx 250 \text{ MPa}$ ) and toughness ( $K_c \approx 2.5 \text{ MPa m}^{1/2}$ ). However, its thermal expansion is also less ( $\alpha_{20-1,000}^{\circ}\text{C} \approx 6 \cdot 10^{-6} \text{ K}^{-1}$ ), which improves resistance to thermal shocks, and its mechanical strength drops much less quickly when the temperature increases than in the case of alumina: at  $1,300^{\circ}\text{C}$ , most mullite ceramics have a mechanical strength close to the one at room temperature, and some mullite with vitreous segregations even have a peak mechanical strength at about  $1,300^{\circ}\text{C}$ . These characteristics make mullite a

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material of choice for refractory applications; particularly when it is necessary to consider attacks by silica or silicates, because then an alumina refractory would react to form mullite.

The manufacture of sintered mullite is not easy. On the one hand, mullite powders are not easily available. Furthermore, the diffusion phenomena are slow in this compound, a characteristic which justifies the good mechanical hot properties because less diffusion means less creep – but also more difficult sintering. The reactive sintering of a mixture of alumina and silica powders can be adopted with the use of a mixture of zircon ( $ZrSiO_4$ ) and alumina powders making the preparation of a mullite toughened by zirconia dispersions ( $ZrO_2$ ) possible. The difficulty is to avoid the presence of silica segregations along the grain boundaries, which would degrade creep resistance. The peak of mechanical strength at  $1,300^\circ C$  is due to such segregations, here beneficial, because they release the stress concentrations and thus attenuate the manifestations of brittleness.