

Calcium and (alpha)- Alumina

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Ca and Si are probably the most common two impurities in commercial alumina. They found use in liquid phase sintered ceramics, but are also blamed for many shortcomings of alumina: Low creep resistance, hard-to-control microstructural evolution, abnormal grain growth (AGG), low fracture toughness et c. The effects of various impurities and their combinations such as Ca, Si, Mg and Y on the microstructure of Al₂O₃ and related properties have been documented in the literature. Calcium and silica are regarded as the main cause of abnormal grain growth in the ceramic either acting synergetically or alone.

The effect of calcium, like most of the other impurities in alumina, is closely related to its segregation to the grain boundaries and consequent reactions of it with the host during supersaturation-precipitation transition (Fig. 1).

Studying (i) formation of various calcium aluminate phases (CaAl₂O₄ [CA], CaAl₄O₇ [CA₂], and CaAl₁₂O₁₉ [CA₆]) from amorphous precursors at low homologous temperatures^{1,2}, (ii) the interface reactions in the calcium aluminate-sapphire model system^{2,3}, (iii) microstructural evolution of calcium doped alpha alumina⁴, and (iv) atomic and electronic structure as well as the chemistry of Ca-segregated interfaces⁵, an attempt to understand the role of calcium in alumina ceramics has been made.

Investigations of Ca-doped amorphous alumina indicated that large quantities of Ca can be accommodated in crystalline gamma-alumina before calciumhexaaluminate (CA₆) forms (Fig. 2). High resolution electron imaging and spectroscopy revealed that the reactions between calciumdialuminate (CA₂) and sapphire also proceeds through formation of Ca-containing gamma alumina (Fig. 3). Calciumhexaaluminate is the end station of this reaction. In light of these and other observations in the literature, a model is proposed for the segregation, super-saturation, and precipitation behaviour in Ca-doped alumina. The model tries to bring an explanation to the formation and rapid growth of CA₆ precipitates within the fine grained alumina matrix.

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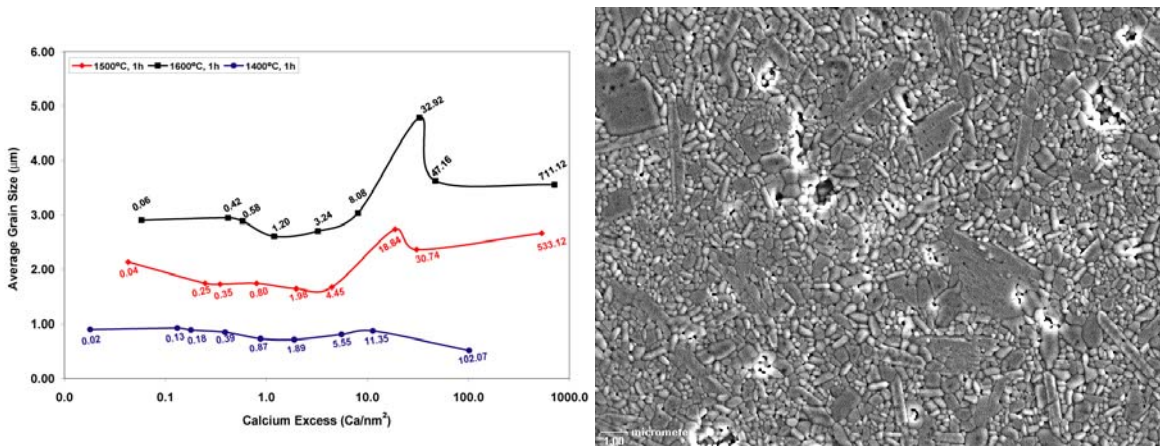


Figure 1. Variation of grain sizes in Ca-doped alumina versus calculated GB-excess of Ca (indicated on curves), and microstructure of Ca-doped alumina sintered at 1400°C. Large grains are primarily calcium hexa aluminate (CA₆) precipitates.

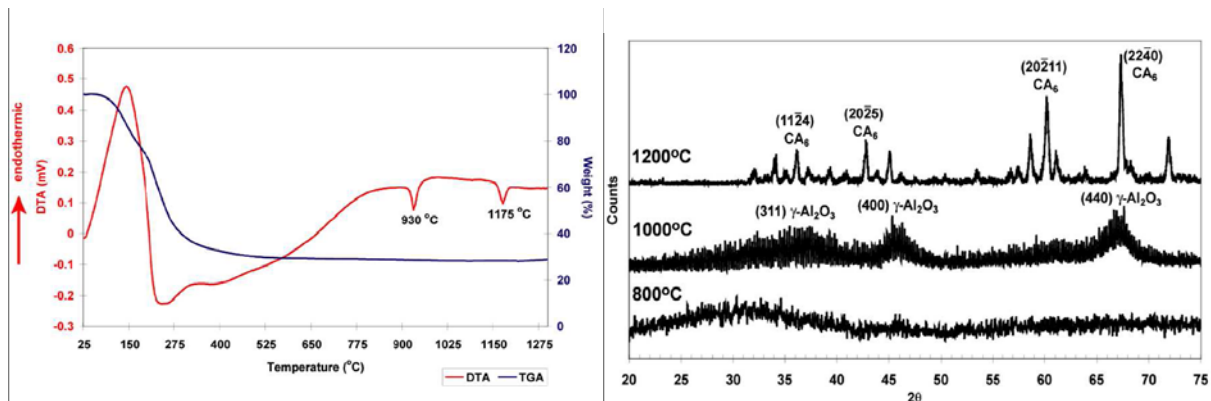


Figure 2. Thermal analysis and x-ray diffraction investigations of amorphous precursors with a nominal composition of CaAl₁₂O₁₉ illustrating formation of Ca-doped gamma-alumina prior to formation of calcium hexa aluminate (CA₆).

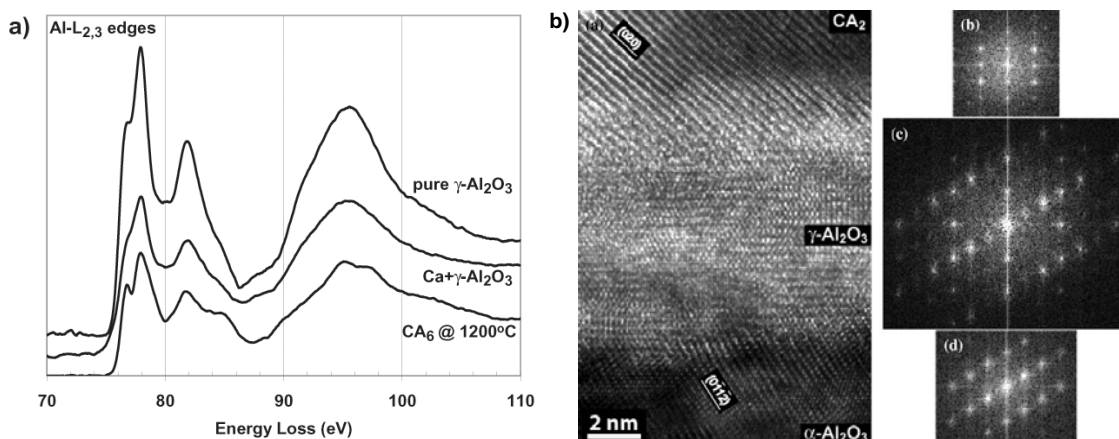


Figure 3. a) Al-L_{2,3} Near edge structures for pure or Ca-doped gamma-alumina and calcium hexa aluminate (CA₆). b) HREM and SADPs of the interface between CA₂ and (0001) oriented sapphire.