

Microstructure–stress relationships in liquid-phase sintered alumina modified by the addition of 5 wt.% of calcia–silica additives

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Abstract

Hot-pressed alumina samples, with 5 wt.% additions of CaO:SiO₂ possessing molar ratios ranging between 1:5 and 10:1 were studied by electron microscopy. Marked differences in microstructure (e.g. grain size, secondary crystalline phases and grain boundary film thickness) were observed, which depended on the composition of sintering additives. The compositions of glassy phases in triple pockets and in grain boundaries varied markedly depending on sintering additives, but also within individual specimens. High residual compressive stresses were measured in alumina grains of samples which contained low thermal expansion crystalline phases such as anorthite and grossite, while gehlenite-containing samples were correspondingly less stressed.

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1. Introduction

Using sintering additives accelerates the overall sintering process, lowers sintering temperatures and also affects the mechanical properties of ceramic materials. It has been found that small additions of silica influence the sintering, grain growth and wear resistance of polycrystalline alumina [1]. Also different amounts of magnesium and calcium silicates [2–5] are often used to modify mechanical properties, including the wear behaviour, of polycrystalline aluminas.

The low thermal expansivity of glasses and of secondary crystalline phases formed during the course of cooling from the sintering temperature by the presence of sintering additives in both triple pockets and at two grain boundaries

between alumina grains are believed to generate significant compressive hoop stresses that lead to a strengthening of the grain boundaries because of the mismatch in thermal expansion coefficients between alumina and the aluminosilicate glass, and/or crystalline secondary crystalline phases [2]. It is expected that high-silica glass films (low thermal expansivity) could generate a high compressive hoop stress in polycrystalline alumina grain boundaries, with similar effects on wear resistance as has been found for magnesium aluminosilicate glass additions [2]. A high calcia glass film with thermal expansion coefficient nearly equal to that of crystalline alumina is expected to yield a virtually stress-free material (apart from stresses generated as a result of the intrinsic anisotropy in the thermal expansion coefficients of alumina crystals) [6]. Secondary crystalline phases such as anorthite ($\alpha(\text{linear}) = 5.33 \times 10^{-6} \text{ K}^{-1}$) [7], gehlenite ($\alpha(\text{linear}) = 8.33 \times 10^{-6} \text{ K}^{-1}$) [7] and grossite ($\alpha(\text{linear}) = 4.1 \times 10^{-6} \text{ K}^{-1}$) [8–11] all have a lower thermal expansivity compared to pure α -alumina ($\alpha(\text{linear}) = 8.93 \times 10^{-6} \text{ K}^{-1}$)

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[12]. In particular, grossite has a low thermal expansivity, and is remarkable in that it has a negative thermal expansivity along one crystallographic axis below 900 °C [10,11]. Internal stresses caused by mismatches in thermal expansivity can be measured by a Raman optical microprobe [2,13] via analysis of the Cr^{3+} photoluminescence spectra and the influence of stresses on microstructure can be directly observed as strain contrast in transmission electron microscopy (TEM) images [2,13,14].

Alumina–alumina two-grain boundaries were recently studied by molecular dynamics simulations where the gap between two alumina grains was filled with silica glass. Simulations indicated that cage-like structures formed at the interface between the alumina grain and the amorphous silica phase, which can, in principle, accommodate metal cations such as calcium or magnesium [15]. Up to a concentration of 12 at.% calcium cations prefer to segregate to these cage-like structures and this segregation lowers the glass/grain interfacial energy, as was revealed by subsequent simulations of calcium silicate intergranular films [16–18]. Fracture simulations for a calcia content <12 at.% showed fracture propagation only through glassy film/alumina grain interface plane. As the content of calcia grows beyond 12 at.% this is increasingly accommodated in the glassy phase, disrupting siloxane bonding and allowing fracture to occur through the interior of the glassy film, leading to a corresponding decrease in the overall fracture strength. Another effect is observed if the intergranular silicate film contains at least 30 mol% of calcia and has a thickness of at least 1.5 nm. This leads to negative interfacial energies, which would be expected to trigger abnormal grain growth during sintering [17].

This could result in a change in the wear behaviour, as the grain size was reported to be an important factor, which significantly influences the wear properties of brittle polycrystalline materials [3,19]. Polycrystalline aluminas with a mean grain size less than 1 μm wear tribochemically, whereas materials with larger mean grain size wear mechanically by grain detachment. When comparing materials which wear only by grain detachment, a material with a bigger grain size will wear faster due to the larger volume of alumina removed per detachment process.

The aim of this work is to examine the micro- and nano-structural features of a series of hot-pressed liquid-phase sintered polycrystalline aluminas modified by the addition of 5 wt.% of liquid phase-forming sintering additives of composition $x\text{CaO} \cdot y\text{SiO}_2$ (x varies between 1 and 10 and y ranges from 1 to 5), and to reveal the influence of chemical composition of the additives on microstructure, grain boundary structure and crystallization of secondary phases in polycrystalline alumina ceramics.

2. Experimental

The alumina powders containing sintering additives (CaO and SiO_2) were prepared by ball milling of Al_2O_3

powder (Martoxid CS400M, mean particle size 400 nm, Martinswerk GmbH, Bergheim, Germany) in isopropyl alcohol together with calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AnalaR grade, BDH Ltd., Poole, UK), and tetraethylorthosilicate (TEOS), (AnalaR grade, BDH Ltd., Poole, UK), in a polyethylene jar. The amounts of additive components were adjusted to be equivalent to 5 wt.% of calcium silicate with $\text{CaO}:\text{SiO}_2$ molar ratios of 1:5 (CS5), 4:5 (CSp), 1:1 (CS), 2:1 (C2S), 3:1 (C3S) or 10:1 (C10S). After 2 h of homogenization, an aqueous solution of ammonium hydroxide was added in order to precipitate calcium hydroxide, and to hydrolyze the TEOS. A further 1 h of mixing at room temperature was used in order to finish the hydrolysis and the suspension was then dried under an infrared lamp. Dry powders were calcined for 30 min at 750 °C and passed through a 100 μm mesh nylon sieve to provide reasonably free-flowing powders. The powders were hot-pressed in graphite die for 10 min at 1450 °C at a pressure of 20 MPa.

Four bulk glasses with $\text{CaO}:\text{SiO}_2$ molar ratios identical or close to the calcia-to-silica molar ratios of sintering aids from the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiC}$ were prepared by melting batches of appropriate amounts of CaCO_3 , β -quartz and α - Al_2O_3 powders hand mixed in a glass beaker. The batches were melted in a Pt–Rh10 crucible in an electric furnace, with a dwell time of 1 h at maximum temperature. The glass melt was then poured onto a steel plate and conditioned for 0.5 h at 700 °C. The compositions of glasses and the melting temperatures are listed in Table 1. Each glass was then cut into rectangular bars with dimensions 5 × 5 × 20 mm and the thermal expansion coefficient was measured in the range 200–600 °C using a thermal mechanical analyser (NETZSCH TMA 402, Netzsch Gerätebau GmbH, Germany) equipped with a quartz measuring rod. The expansion coefficient was calculated from the slope of the cooling part of the dilatation curve; heating and cooling rates of 10 °C min^{-1} were applied.

For scanning electron microscopy (SEM) examination, sintered specimens were cut, polished and thermally etched (1400 °C for 30 min), or alternatively, in some cases, chemically etched using boiling phosphoric acid, to reveal the grain boundaries. Finally, the samples were carbon coated to achieve an electrically conductive surface to avoid charging and SEM (CamScan IV, Cambridge Instruments) examination was used in order to determine the mean grain sizes, measurements being made from digital micrographs using standard image analysis software (Kontron, KS 400, Kontron Electronic GmbH, Germany).

For TEM examination specimens were core drilled and sliced to prepare 3 mm diameter discs of 500 μm thickness. The discs were further ground, polished, dimpled and ion-milled (Gatan Precision Ion Polishing System model 691; low-angle ion beam thinner) until transparent to the electron beam. Specimens were examined using a field emission TEM instrument (Philips CM200 FEG TEM) fitted with a scanning (STEM) unit, ultrathin-window energy dispersive X-ray analysis (EDX) detector (Oxford Instrument UTW

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