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Liquid/glass immiscibility in yttria doped mullite ceramics

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ABSTRACT

5 wt.% yttria doped mullite ceramics were sintered using nanocomposite powders which consisted of a Y_2O_3–SiO_2 core coated with pseudoboehmite. Firstly, the powders were heated up to 1300 °C; mullite began to form at 1050 °C which is ~150 °C lower than in previous diphasic precursors. Then, the powders were sintered at 1550 °C for 0.5, 5 and 48 h, and characterized using XRD, SEM and TEM with EDS.

The phases present were mullite and two intergranular glasses comprising silica-rich droplets embedded in a Y–Si–Al–O glassy matrix, providing direct evidence of liquid-liquid phase separation at the grain boundaries during sintering. This liquid-liquid separation is facilitated by the prior existence of yttrium disilicate which moves the overall sintering liquid compositions toward the two immiscible liquids region of the Y_2O_3–Al_2O_3–SiO_2 phase diagram. The presence of the silica-rich phase in the grain boundaries will effectively increase their viscosity and thus the resistance of the Y_2O_3 densified mullite to creep.

1. Introduction

Glass phase separation or liquid immiscibility is a common phenomenon observed in rare-earth silicate glasses [1,2]. In the Y_2O_3–Al_2O_3–SiO_2 ternary phase diagram, an immiscibility region of two liquids has been reported near the yttria-silica binary system with up to 8 wt.% Al_2O_3 [3]. When Y_2O_3 is used as a sintering additive to accelerate sintering of mullite ($3Al_2O_3{\cdot}2SiO_2$) ceramics, the Y_2O_3–Al_2O_3–SiO_2 system can be applied to explain the formation of yttrium silicates and also residual glassy phase [4,5]. While phase separation readily occurs in yttrium silicate based glasses and extends into the Y_2O_3–Al_2O_3–SiO_2 system [1–3,6,7], this phenomenon has not been reported at grain boundaries of yttria doped mullite ceramics [8–17].

High density mullite ceramics are often fabricated by reaction sintering at 1600–1700 °C of mixed alumina and silica phases because mullite powder compacts have poor solid state sinterability as a result of low interdiffusion rates of Si^{4+} and Al^{3+} ions within the mullite lattice. Y_2O_3 has been extensively used as a dopant [4,5,8–14] to reduce the sintering temperature of mullite to 1400 °C. It has been proposed that the mass transport of the diffusing species is enhanced via a low viscosity transient yttrium aluminosilicate liquid (~1371 ± 5 °C) [4,5,7,12], which is later decomposed into yttrium silicates and α-Al_2O_3 [4,5,8–17]. Several secondary phases in Y_2O_3-doped mullite ceramics have been detected according to the different processing routes. Fang and Hwang [9] studied the sintering of mullite using 2–10 wt.% of Y_2O_3 at 1500 °C and found $Y_2Si_2O_7$ and α-Al_2O_3 as secondary phases. It was also found that the secondary phases were dependent on the amount of Y_2O_3 added. For instance, with 5 wt.% Y_2O_3, α-$Y_2Si_2O_7$ was observed and with 10 wt.% Y_2O_3, β-$Y_2Si_2O_7$ was observed. In the reaction bonding process proposed by Mechnich et al. [4] using Al_2O_3, metallic Si and Y_2O_3 as starting materials, the formation of a low viscosity transient Al–O–Y–Si liquid which aids sintering was proposed. The residual phases were identified as crystalline $Y_2Si_2O_7$ and α-Al_2O_3 after sintering at 1350 °C for 5 h. Arellano-López et al. [10] studied the creep resistance of 5 and 9 wt.% Y_2O_3 doped mullite at high temperature. They observed a partially crystallized $Y_2Si_2O_7$ at 1550 °C and proposed a relationship between $Y_2Si_2O_7$ crystallization and the annealing temperature. She et al. [5] observed the nucleation and growth of mullite grains in a low viscosity Y–Al–Si–O liquid which later decomposes to form $Y_2Si_2O_7$ and α-Al_2O_3. Using reaction sintering between SiO_2, Al_2O_3 and Y_2O_3, Kong et al. [11] observed that diverse crystalline phases of yttrium silicates are found at different temperatures, from triclinic $Y_2Si_2O_7$ below 1200 °C to monoclinic $Y_2Si_2O_7$ above 1350 °C. However, in all of the previously described processes, glass phase separation was not observed.

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In this article, direct evidence is presented of liquid-liquid phase separation at the grain boundaries in yttria doped mullite ceramics prepared using a doped nanocomposite precursor. Since the final properties of dense ceramics – mechanical, electrical or thermal – can be affected by the chemistry at grain boundaries it is crucial to characterise the intergranular phases.

2. Experimental

2.1. Precursor powder preparation

The fabrication of core and shell nanocomposite powders used in this study followed the *Homogeneous Precipitation Technique* developed by Sugita and Contreras-Soto [18] where aluminium sulphate $Al_2(SO_4)_3{\cdot}18H_2O$ (Alfa & Omega Chemical S.A. De C.V, Irapuato, Mexico) was first dissolved in distilled water. SiO_2 nanoparticles (Aerosil@200: Degussa Ag, Frankfurt, Germany) and the 5 wt.% of Y_2O_3 nanoparticles (Yttrium Oxide nanopowder < 50 nm: Sigma Aldrich, Co., St. Louis, MO., USA) were suspended in distilled water. This suspension and the aluminium sulphate solution were individually agitated by magnetic stirring for 1 h and then were mixed together and similarly agitated for another 30 min. This mixture was then placed in an ultrasonic bath for 20 min in order to break up any agglomerates. To promote the precipitation reaction, the solution was heated up to 80 °C and ammonium bisulphite (NH_3HSO_3) was added as a precipitating agent. The pH was kept lower than 4 during the precipitation process to ensure that attractive forces were maintained between the SiO_2 and Y_2O_3 particles, allowing the formation of the yttria–silica nanoparticulate nucleus. The precipitated powders consisted of a finely mixed Y_2O_3 and SiO_2 core covered by basic aluminium sulphate ($Al_x(OH)_y(SO_4)_z$) in which the Al:Si ratio = 6:2 with the alumina to silica ratio = 3:2 consistent with stoichiometric mullite, $Al_6Si_2O_{13}$. The powders obtained were then neutralized in an ammonia solution at 70 °C to extract the remaining sulphate ions on particulate surfaces, and produce an external coating of pseudo-boehmite. The final powders were filtered, dried and hand milled.

2.2. Mullite transformation and sintering of ceramics

In order to study the ease of formation of mullite from the nanopowder doped with yttria, powder samples were heated in a Lindberg/blue – 1700 °C box type electric furnace at various temperatures (500, 900, 1050, 1100, 1150, 1200 and 1300 °C for 2 h), increasing the temperature at a rate of 5 °C per min in a mullite crucible. Samples were then cooled down to room temperature, decreasing by 10 °C per min. These powders were then subjected to X-ray diffraction to determine the phases present.

For sintering, pseudoboehmite-SiO_2–Y_2O_3 nanocomposite powders were first heat treated at 5 °C per min up to 1300 °C in an electric furnace to ensure complete reaction to mullite. After this heat treatment the mullite powders were aqueous ball milled for 24 h using Tiron as a dispersing agent (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate: Sigma Aldrich, Co., St. Louis, MO., USA). The slip thus formed was cast into green compacts using alumina molds. Yttria doped compacts were then sintered in air in a mullite crucible at 1550 °C for 0.5, 5 and 48 h in a Carbolite 1700 °C electric furnace at a heating rate of 5 °C per min.

2.3. Characterization of powders and sintered materials

The heat treated powder samples were characterized using a field emission scanning electron microscope (SEM) (JSM–7600 F) and the phases present indentified by X-ray Diffraction (XRD) using CuKα radiation (Bruker D-8 Advance).

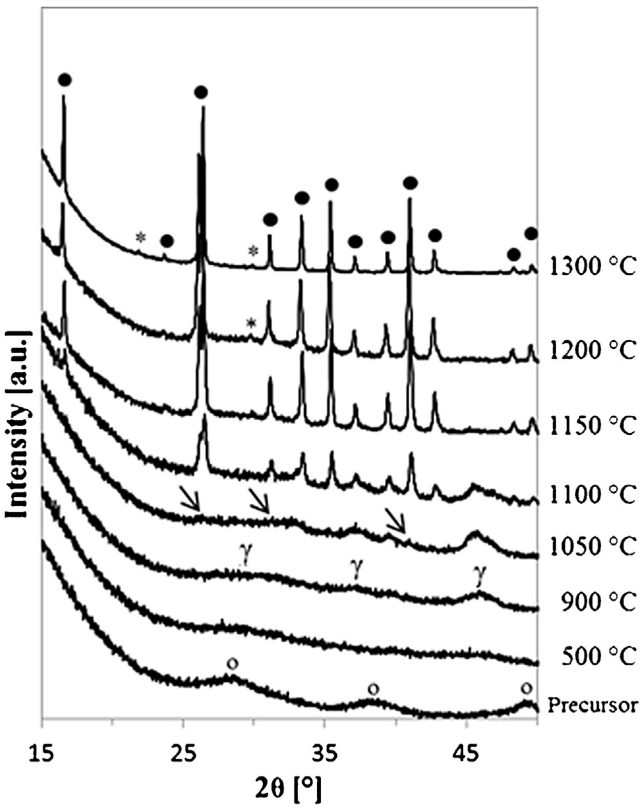

Fig. 1. XRD patterns of 5 wt.% yttria mullite nanocomposite heat treated at different temperatures showing the thermal evolution up to 1300 °C. Arrows indicate the first signals of mullite.: ● mullite, *: α- $Y_2Si_2O_7$, γ: γ-Al_2O_3 and o: pseudoboehmite.

The density of sintered materials was measured using the Archimedes method. The microstructures of the sintered materials, after grinding and polishing to a 1 μm diamond finish, were examined using a Hitachi Su-70 Schottky SEM. Comparisons in local chemistry were made using the backscattered imaging mode. TEM samples from the sintered bodies were prepared by first cutting them from the bulk using an ultrasonic cutter (Gatan Model 601) into 2 mm discs. These samples were then glued inside a copper ring with an inner diameter of 2 mm and outer diameter of 3 mm to reduce the possibility of cracking during the thinning and polishing process. The 3 mm samples were then mechanically ground and polished on both sides down to about 50–60 μm in thickness. A mechanical dimpler (Gatan model 656) was utilized to grind and polish the center of the thin disk before final milling using a Gatan Model 691 Precision Ion Polishing System (PIPS). The TEM samples were examined using a JEOL 2100 F transmission electron microscope (TEM) operated at 200 kV using a Field Emission Electron Gun equipped with a Gatan Ultrascan Digital Camera and an EDAX Genesis XM 4 system to analyse chemical compositions.

3. Results

3.1. Formation of mullite from 5 wt. % Y_2O_3 nanocomposite precursor powders

XRD patterns showing the phase evolution of the 5 wt.% Y_2O_3 nanocomposite with heat treatment temperature are presented in Fig. 1. The starting compound contains the characteristic peaks of pseudoboehmite near 28, 38 and 49° 2θ. The presence of Y_2O_3 is not detected. At 500 °C, the peaks of pseudoboehmite have disappeared due to dehydration and transformation into, presumably, a low crystalline form of γ-Al_2O_3. On further heating to 900 °C,