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Ceramics International 40 (2014) 3071–3077

CERAMICS INTERNATIONAL

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Highly porous corundum–mullite ceramics – Structure and properties

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Received 10 July 2013; received in revised form 30 September 2013; accepted 30 September 2013
Available online 7 October 2013

Abstract

The aim of this study was to improve the mechanical properties of porous corundum ceramics by adding various types of SiO_2 source (SiO_2, SiC and Si_3N_4), but at the same time retaining high porosity (at least 55%). Ceramics were fabricated by slip casting. Pores were formed using aluminium's reaction with water. It was found that the bending strength of the material can be improved and relatively high porosity retained by producing corundum–mullite composites. Addition of 3.7 equivalent wt% of SiO_2 source increased the bending strength by up to 250% in comparison with unmodified corundum ceramics. The apparent porosity decreased by up to ca. 8%. If the amount of SiO_2 source was increased from 3.7 equivalent wt% to 7.3 equivalent wt%, the bending strength decreased. The best mechanical properties were achieved with samples that were modified with SiC and Si_3N_4 nanopowders. This is due to better dispersion in Al_2O_3 matrix.

Keywords: C. Mechanical properties; D. Al_2O_3; D. Mullite

1. Introduction

Highly porous alumina (Al_2O_3) ceramics have a significant role in various fields of engineering due to high thermal and chemical durability of Al_2O_3, and unique properties, which are provided by the high porosity. These properties being permeability of gases and liquids, good adsorption, low thermal conductivity and decreased bulk density in comparison with dense ceramics. Alumina–mullite composites are of special interest due to their improved thermal and mechanical properties in comparison with pure corundum and mullite ceramics [1,2]. Alumina–mullite composites can be produced by using various raw materials – Al_2O_3, $Al(OH)_3$, aluminium salts (sol–gel technology), SiO_2, SiC, Si_3N_4, presynthesized mullite, kaolin and silicon organic compounds. Most of available studies focus on dense rather than highly porous alumina–mullite composites [2–7].

The aim of this study was to improve the mechanical properties of porous corundum ceramics at the same time retaining high porosity by adding various types of SiO_2 sources. The added or in situ formed SiO_2 reacts with Al_2O_3, and forms mullite ($3Al_2O_3 \cdot 2SiO_2$). Investigated materials were produced by chemical foaming of slurry. Method of slurry foaming is similar to aerated concrete technology and is described previously [8]. Pores form in the result of a chemical reaction between aluminium and water in an alkaline medium (pH > 9) during hydrogen gas evolution reaction, and solidification of the suspension.

2. Materials and methods

2.1. Raw materials and sample preparation

All investigated compositions contained a mixture of commercially available α-Al_2O_3 (d_{50}–3 μm, Nabalox NO 325, Nabaltec AG) and γ-Al_2O_3 (d_{50}–80 μm, Nabalox NO 201, Nabaltec AG) in the mass ratio of 1:3. Chemically pure amorphous SiO_2 (d_{50}–3.7 μm, Реахим), SiC (d_{50}–37 μm, Sigma-Aldrich), plasma synthesised nanopowders of SiC (d_{50}–80 nm, specific surface area 40 ± 3 m^2/g), Si_3N_4 (d_{50}–21 nm, specific surface area 70 m^2/g), and Si_3N_4–Al_2O_3-Y_2O_3 (91%-6%-3%, d_{50}–74 nm, specific surface area 87 ± 5 m^2/g) were used as SiO_2 sources. Nanopowders were provided by Plasma & Ceramic Technologies Ltd., Latvia. Pore forming agent was aluminium paste with solid content 70 ± 2%

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http://dx.doi.org/10.1016/j.ceramint.2013.09.139

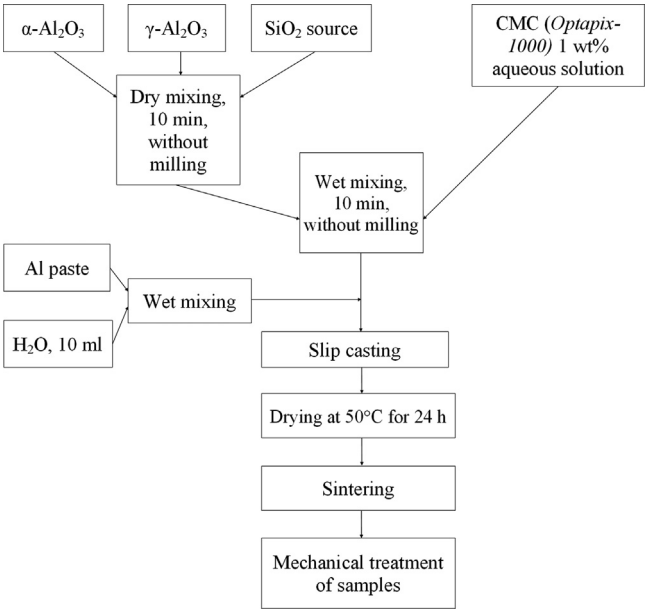

Fig. 1. Sample preparation process.

(Aquapor-9008, Schlenk Metallic Pigments GmbH) (mean particle diameter 12 μm). The 1% solution of carboxymethyl cellulose sodium salt (CMC) (Optapix C 1000G, Zschimmer & Schwarz GmbH & Co) was used as a binder. SiO_2 source was added in the amount equivalent to 3.7 and 7.3 wt% of SiO_2 (further in text eqv. wt%). Mass of silica source was calculated assuming that SiC and Si_3N_4 fully oxidises into SiO_2.

The scheme of the sample preparation steps is given in Fig. 1.

The initial viscosity of the suspensions was controlled by a rotation viscometer (VT550 Thermo Haake Electron Corp., sensor MV-DIN). Rotation speed – 68.3 rpm. Distilled water was added to have the initial viscosity of the suspensions in the value of ca. 800 mPa s. Aluminium paste dispersed in 10 ml of distilled water was added to suspension after homogenisation. Total water content in the slurries varied from 32.6 to 35.3 wt %. Slurries were poured into polypropylene moulds. The initial thickness of slurry layer in a mould was 30 ± 2 mm. After slip casting the samples were put into drying chamber at 50 °C to speed up the reaction between aluminium paste and water. During the hydrogen gas evolution reaction the sample thickness increased approximately 1.5 times.

Dried samples were sintered at 1650 °C and 1750 °C. Heating rate – 140°/h (2.3°/min), holding time at a maximum temperature – 1 h. The sintered samples were cut into bars with dimensions $15 \times 20 \times 100$ mm for further testing.

The initial compositions of the investigated samples and their denotations are given in Table 1.

2.2. Characterisation

The bulk density was determined by dividing a geometrically measured volume of the sample with its mass. Archimedes' method with water as the medium was used to determine the apparent porosity. The phase compositions of the fabricated materials were characterised by X-ray diffraction (XRD; Rigaku Ultima+, Japan) with Cu K_α radiation. Voltage on Cu anode – 40 kV, current intensity – 20 μA, range of measurement angle – 6–60 $2\theta^\circ$, speed of goniometer – 2°/min. The microstructure of the fracture surface of the samples was characterised by scanning electron microscopy (Oxford Instrument, UK). The bending strength of each of the sample series was determined by using the three-point bending test (Zwick BDO-FB020TN, Germany, crosshead speed 1 mm/min). At least six samples of each series were tested to obtain the average value of the bending strength, apparent porosity and bulk density. Mercury intrusion porosimetry (Quantachrome, PoreMaster, USA) was used to determine the pore volume distribution.

The relative change of the bending strength of the materials was calculated by the following equation:

$$\Delta = 100\%(\sigma_{cm} - \sigma_c)/\sigma_c,$$

where σ_c is bending strength of unmodified corundum ceramics, and σ_{cm} is bending strength of corundum–mullite composite ceramics. The relative change of the bulk density and apparent porosity was calculated the same way.

3. Results and discussion

3.1. X-ray diffraction results

After sintering in the compositions that initially contained SiO_2, SiC, or Si_3N_4 only two crystalline phases were detected – corundum and mullite. This shows that the added or in situ formed SiO_2 has reacted with Al_2O_3 and formed mullite.

3.2. Macrostructure

The shape and size of millimetre-scale pores were affected by viscosity of the slurry of the raw materials. In this study the suspensions were prepared with equal viscosity; therefore, the shape and orientation of millimetre scale pores were similar. In the investigated samples the millimetre-scale pores had an elongated shape in the direction parallel to the base of the mould. The most anisotropic pore shape was found in the samples modified with nanopowders, because the viscosity of these slurries increased slightly faster during solidification stage compared to that of slurries containing only alumina or alumina together with coarse SiC and SiO_2.

The addition of the aluminium paste formed pores in the range of ca. 25-1000 μm and increased the overall volume of the open pores (Fig. 2).

3.3. Bending strength

Addition of SiO_2 source noticeably affected the mechanical properties of the material. The bending strength of corundum ceramics without mullite phase, and sintered at 1650 °C and 1750 °C was 2.3 ± 0.5 MPa and 3.2 ± 0.6 MPa respectively. The bending strength of the samples changed depending on the type and amount of the added SiO_2 source (Fig. 3). To better illustrate the effect of adding SiO_2 source, please see Fig. 4, where the