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Highly porous corundum–mullite ceramics – Structure and properties

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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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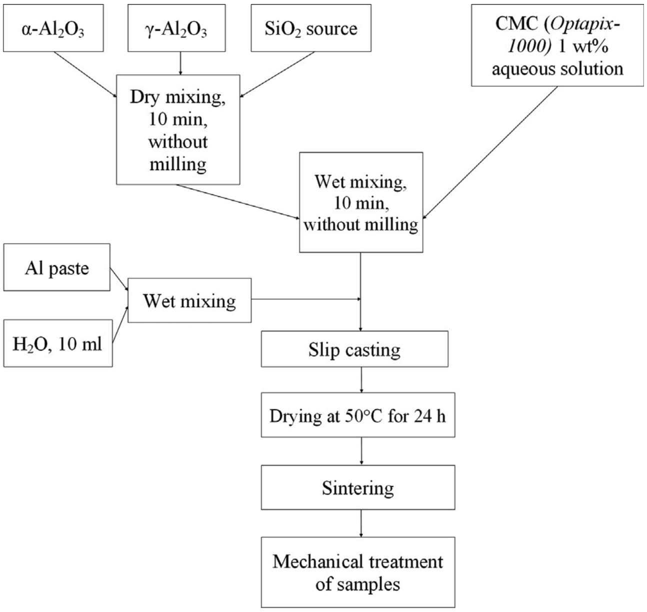


Fig. 1. Sample preparation process.

(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 × 20 × 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 2θ°, 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

Table 1
Compositions of the investigated samples before sintering.

Specimen	Ratio of α- and γ-Al_2O_3	SiO_2 source	Wt%	Equivalent amount of SiO_2 (wt%)
S0	1:3	–	0.0	0.0
C3.7		SiC micropowder	2.5	3.7
C7.3			5.0	7.3
S3.7		Amorphous SiO_2	3.7	3.7
S7.3			7.3	7.3
NC3.7		Plasma synthesised SiC	2.5	3.7
NC7.3			5.0	7.3
N3.7		Plasma synthesised Si_3N_4	2.9	3.7
N7.3			5.7	7.3
NY3.7		Plasma synthesised Si_3N_4–Al_2O_3–Y_2O_3 (91%–6%–3%)	3.2	3.7
NY7.3			6.3	7.3

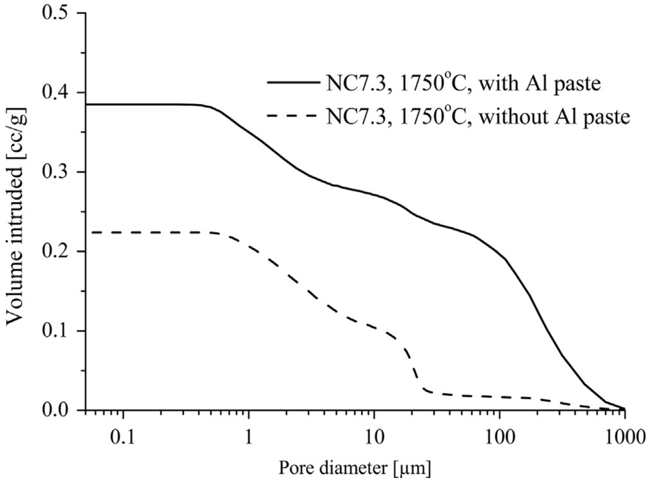


Fig. 2. The effect of the aluminium paste on the cumulative pore volume.

relative change of the bending strength of the materials is indicated.

Decreased amount of SiO_2 source acts as a sintering aid, but increased amount of added SiO_2 source can even deteriorate the mechanical properties of the material.

The improvement of the bending strength was most pronounced by using 3.7 eqv.wt% of plasma synthesised nanopowders. When the coarser grained SiO_2 sources (amorphous SiO_2 and SiC) were used the increase of the bending strength was relatively insignificant in the samples sintered at 1650 °C, but in the samples sintered at 1750 °C it was even lower than the bending strength of pure corundum ceramics. When the added amount of SiO_2 source was increased from 3.7 eqv.wt% to 7.3 eqv.wt% the bending strength decreased no matter what type of SiO_2 source was used. Luthra and Park reported that they have detected formation of aluminosilicate glass in Al_2O_3–mullite matrix produced from Al_2O_3 and SiC at nonequilibrium conditions [9]. Formation of glassy phase between alumina and mullite grains could explain the decrease of bending strength, when the amount of SiO_2 source is increased from 3.7 to 7.3 eqv.wt%. Presence of glassy phase can

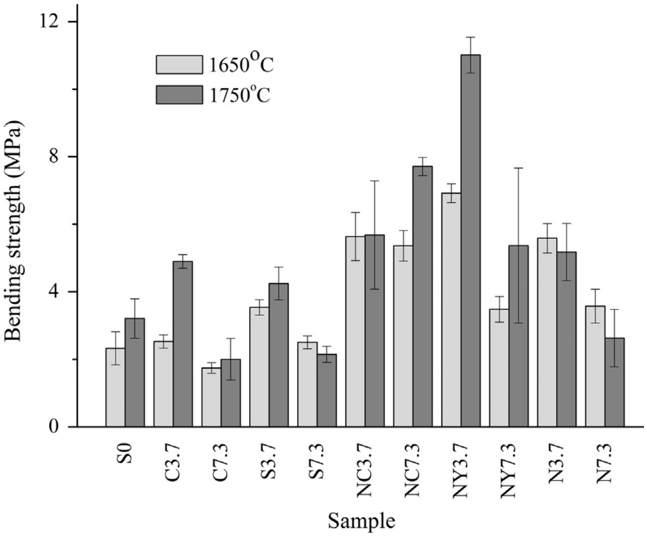


Fig. 3. Bending strength of the investigated materials. The error bars represent the standard deviation for each datum.

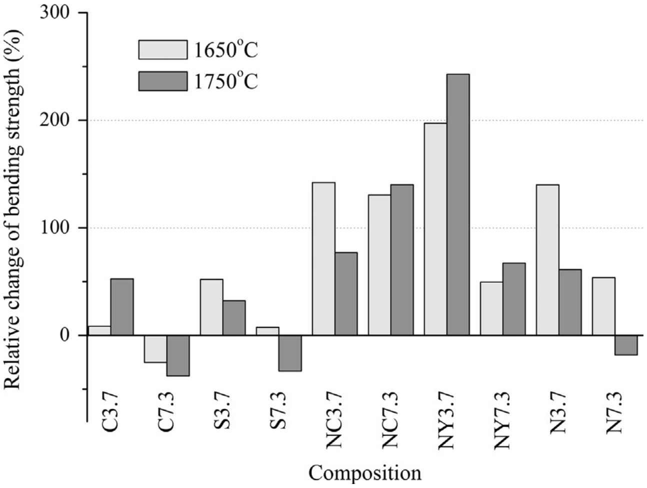


Fig. 4. The relative change of the bending strength of corundum–mullite composites in comparison with pure corundum samples.

negatively affect the creep resistance of the material at elevated temperatures.

3.4. Bulk density and apparent porosity

The bulk density of corundum ceramics sintered at 1650 °C and 1750 °C was 1.07 ± 0.01 g/cm^3 and 1.09 ± 0.02 g/cm^3 respectively. The effect that the modification of corundum matrix with SiO_2 source had on the materials' bulk density and apparent porosity (Figs. 5 and 6) depended on the type and amount of this source. Addition of coarse grained SiO_2 sources (microsized SiC and amorphous SiO_2) reduced the bulk density by up to ca. 10% in comparison with unmodified material. When SiC and Si_3N_4 nanopowders were used the bulk density of the samples sintered at 1650 °C was close to that of unmodified material, but increased up to 15% by increasing the sintering temperature to 1750 °C. This implies that in this range of temperature the addition of SiC and Si_3N_4 nanopowders intensifies densification; however, it was a common trend that the bulk density of the samples modified with higher amount of SiO_2 source was lower no matter what type of SiO_2 source was used. This tendency could be explained by the fact that the molecular volume of mullite is much higher than the molecular volume of corundum, which is 25.5 cm^3/mol and 140.5 cm^3/mol respectively [10]. If the intensity of densification is lower than the intensity of mullite formation, the bulk density decreases in comparison with unmodified corundum ceramics. The bulk density is decreased by up to ca. 10% if coarse grained SiO_2 or SiC is used.

The apparent porosity of corundum samples sintered at1650 °C and 1750 °C was 62 ± 1% and 61 ± 1% respectively. The apparent porosity of almost all modified samples sintered at a temperature of 1650 °C changed insignificantly (ca. ± 2.8%) in comparison with unmodified ceramics, considering that the standard deviation of the data is in the range of 0.6% to 1.2%. The effect of the initial composition on the apparent porosity was more pronounced, when the sintering temperature was increased from 1650 °C to 1750 °C (Fig. 6). Addition of SiC and Si_3N_4 nanopowders decreased the apparent porosity by up to 8.3%. However, it can be concluded that the fabrication of corundum–mullite composites allows to improve the mechanical strength of porous Al_2O_3 based ceramics at the same time retaining high porosity.

3.5. Mercury intrusion porosimetry results

Mercury intrusion analysis showed that the modification with the silica source affects the differential pore volume distribution in the pore diameter range from ca. 0.1 to ca. 10 μm (Fig. 7).

In the samples sintered at 1650 °C the maximum of pore volume distribution shifted to the direction of smaller pores without correlation to the used SiO_2 source; and the maximum of pore volume distribution curve increased up to 2 times, if the amount of added SiO_2 source was increased. The only exceptions were samples NY3.7 and NY7.3 sintered at both temperatures. In these samples the pore volume distribution maximums are noticeably lower and shifted in the direction of larger pores, which confirms pronounced densification of the matrix. This is related to the formation of liquid phase, which is triggered by Y_2O_3 in the plasma synthesised Si_3N_4–Al_2O_3–Y_2O_3 (91%–6%–3%) nanopowder. This effect of the presence of Y_2O_3 in the Al_2O_3 and SiO_2 systems has already been reported by other authors [11,12].

The pore volume noticeably decreased, if the sintering temperature was increased from 1650 °C to 1750 °C. The pore volume distribution maximum of the samples sintered at 1750 °C is up to ca. 4 times lower than that of samples sintered at 1650 °C. This change of pore volume distribution curves at an increased sintering temperature indicates that the densification of the investigated materials intensifies at temperatures higher than 1650 °C, and that the pore walls of the samples sintered at 1750 °C are denser. Compared to

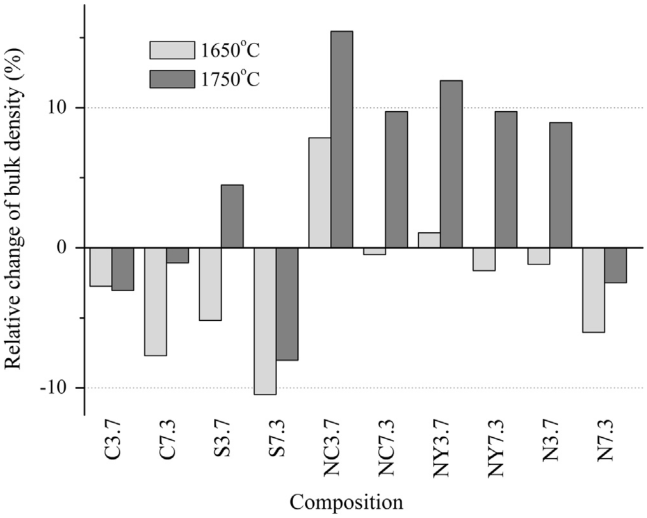


Fig. 5. The relative change of the bulk density of corundum–mullite composites in comparison with pure corundum samples.

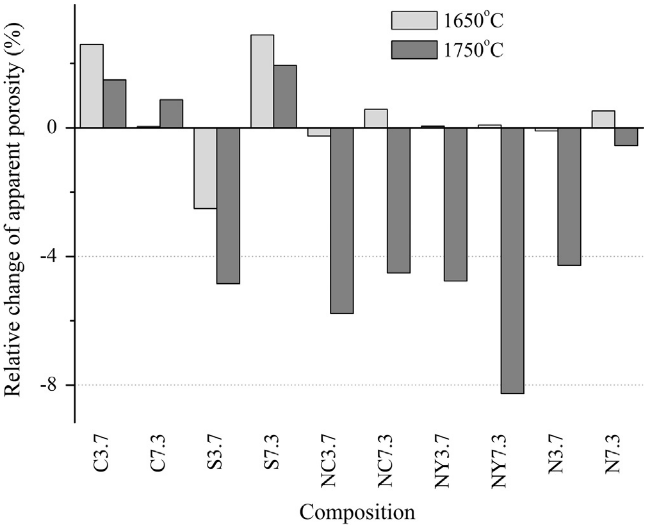


Fig. 6. The relative change of the apparent porosity of corundum–mullite composites in comparison with pure corundum samples.

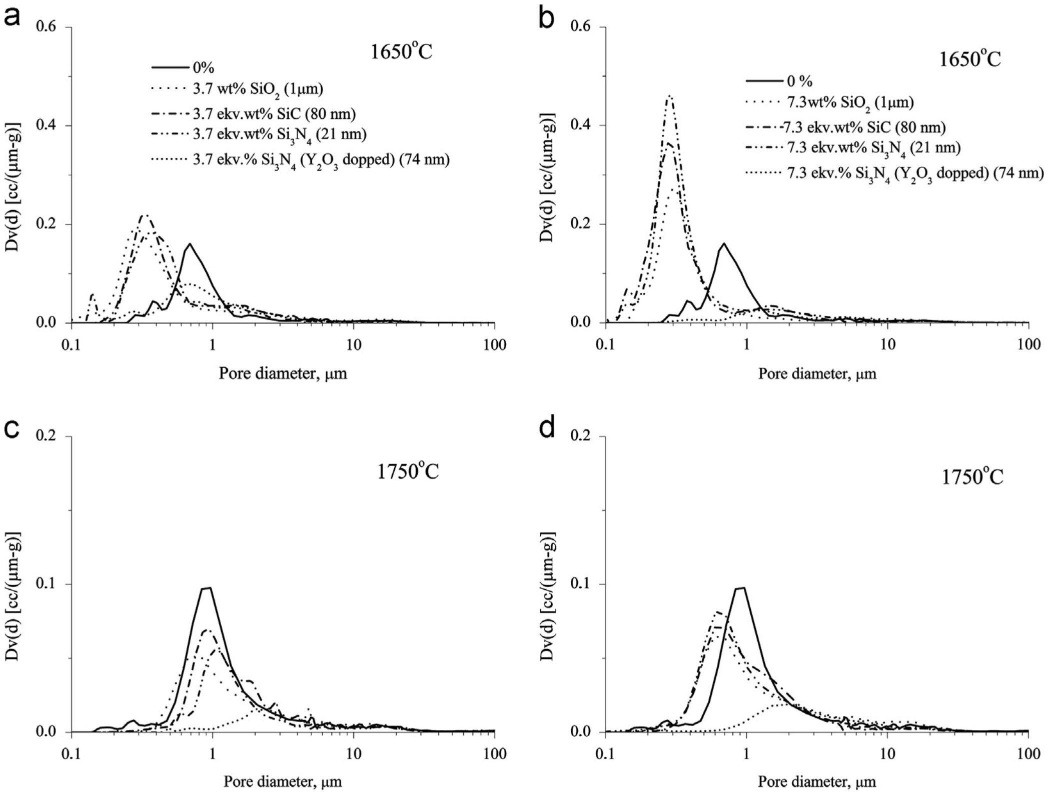


Fig. 7. The comparison of the differential pore volume distributions of the investigated samples.

unmodified corundum ceramics, the pore volume distribution maximum slightly decreased if SiO_2 source was added.

The pore volume distribution curves of the samples modified with coarse and fine grained SiO_2 sources at both sintering temperatures were similar. The most noticeable difference was observed in the samples modified with 7.3 eqv.wt% of SiO_2 source, but these differences diminished during densification, when the sintering temperature was increased from 1650 °C to 1750 °C.

3.6. *Results of scanning electron microscopy*

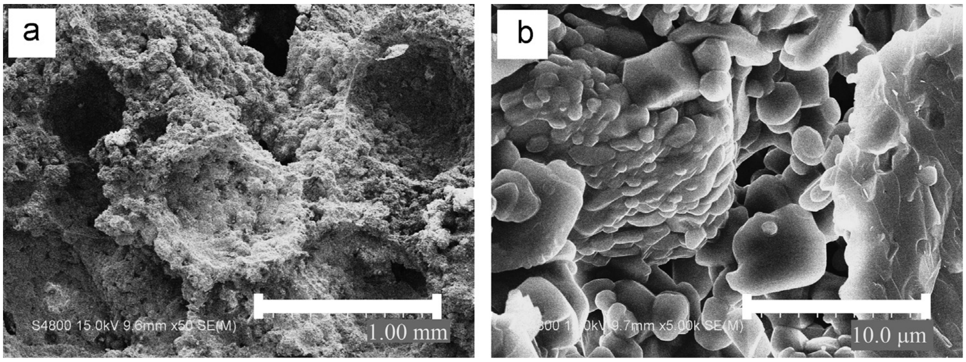
In low magnifications the microstructure of investigated materials slightly reminds broccoli or cauliflower (Fig. 8a). The reason for this is that ceramics were produced from coarse γ-Al_2O_3 grains (mean particle diameter is 80 μm), which were surrounded by relatively fine α-Al_2O_3 grains (mean particle diameter is 3 μm) (Fig. 8b).

Pore size range in these materials was very wide – from millimetre sized pores (Fig. 8a) to micron sized pores formed by hydrogen gas (Fig. 8a and c) or voids between alumina grains (Fig. 8d,e,f).

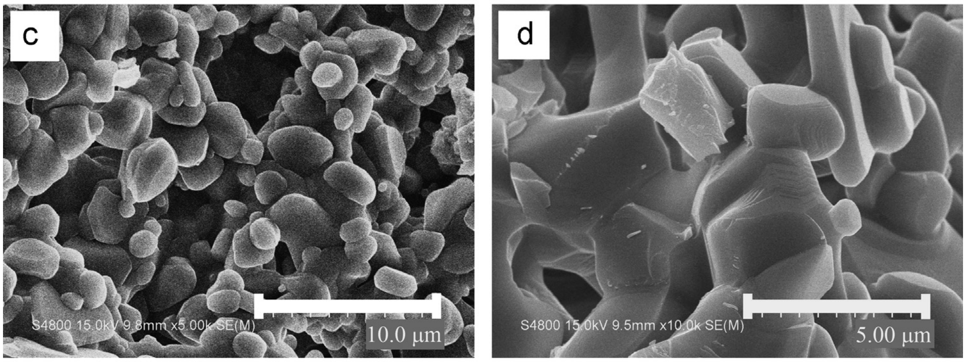
The microstructure of samples modified with nanopowders seems to be denser than that of pure corundum ceramics, especially in the samples modified with Si_3N_4 doped with Y_2O_3 (Fig. 8d). The microstructure of the samples produced from Y_2O_3 comprising raw materials implies on the formation of the liquid phase and pronounced densification during sintering process. This agrees with the obtained bulk density, bending strength and mercury intrusion porosimetry results. In the samples modified with SiO_2 source, the contacts between particles are better developed than in unmodified corundum samples; however, it was not possible to observe noticeable differences between the microstructure of the samples modified with different amounts of SiO_2 source. However, it was possible to detect some differences between microstructures of the samples modified with nanopowders and coarse grained SiO_2 sources. In the microstructure of the samples modified with SiC and Si_3N_4 nanopowders formations as shown in Fig. 9a–d were observed. These could be related to agglomeration of the nanopowder. However, despite the presence of these agglomerates, the mechanical properties of the samples modified with nanopowders were better. The main reason could be the fact that nanopowders were better dispersed and had increased surface area with Al_2O_3 grains.

4. Conclusions

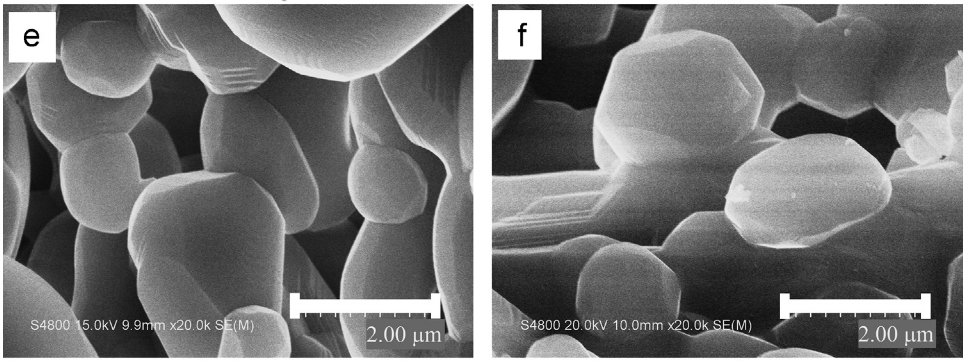
In this study was evaluated the effect of various types of SiO_2 source on the bending strength of porous corundum-mullite ceramics. It was found that it is possible to increase mechanical properties of porous corundum ceramics and retain relatively high apparent porosity (in the range of 56 ± 1% to 62 ± 1%) by adding plasma synthesised SiC, Si_3N_4, and Si_3N_4–Al_2O_3–Y_2O_3 nanopowders (mean particle size 80 nm, 21 nm, and 74 nm respectively). The apparent porosity of the samples modified with microsized SiO_2 and SiC (mean particle size 3.7 μm and 37 μm respectively) was in the range of 58–64 ± 1%; however,



NY7.3 1750°C, magnif.: x50 S3.7 1750°C, magnif.: x5.00k



S7.3 1750°C, magnif.: x5.00k NY3.7 1750°C, magnif.: x10.00k



S0 1750°C, magnif.: x20.00k NC3.7 1750°C, magnif.: x20.00k

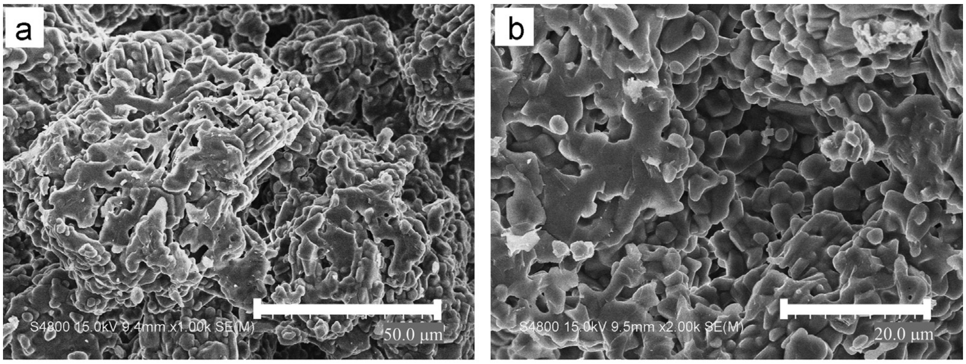
Fig. 8. SEM micrographs illustrating the microstructure of the investigated samples sintered at 1750 °C

these additives improved the bending strength negligibly or even decreased it. These differences are related with more homogeneous dispersion of nanopowders and increased contact surface between components before sintering. It is provided by smaller particle size of nanopowders in comparison with microsized SiO_2 sources.

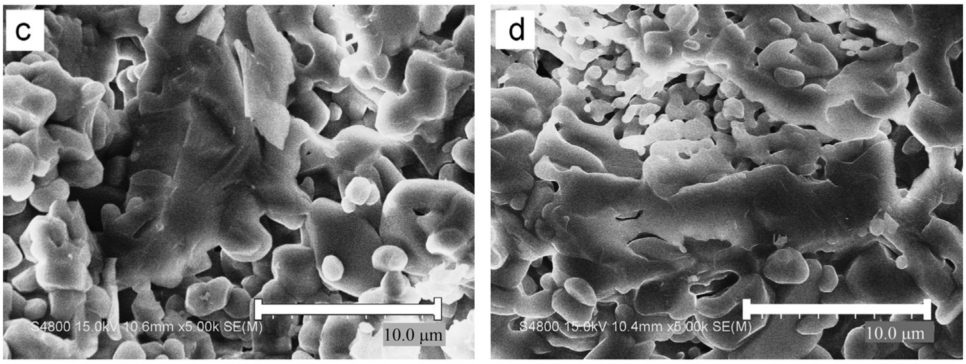
The highest bending strength was achieved by adding 3.7 eqv. wt% of plasma synthesised Si_3N_4-Al_2O_3-Y_2O_3 nanopowder and sintering the samples at 1750 °C. The bending strength increased from 3.2 ± 0.6 MPa of unmodified material to 11.0 ± 0.5 MPa of modified material, but the apparent porosity decreased from $61 \pm 2\%$ to $58 \pm 1\%$ respectively. The results showed that in this case a significant contribution to the improvement of the mechanical properties gives the glassy phase which forms intensively in the presence of raw materials containing Y_2O_3.

It was found that the bending strength and bulk density of the samples sintered both at 1650 °C and 1750 °C decrease by increasing the added amount of the SiO_2 source from 3.7 eqv. wt% to 7.3 eqv.wt% regardless of the particle size of the SiO_2 source. This implies that the material's properties are more affected by mullite formation than by the densification process if the amount of SiO_2 source is increased from 3.7 eqv.wt% to 7.3 eqv.wt%. Addition of 3.7 eqv.wt% of SiO_2 source increased the bending strength of the corundum matrix; however, increase of the added amount of SiO_2 from 3.7 eqv.wt% to 7.3 eqv.wt% led to increased heterogeneity of the system and weakened contact between Al_2O_3 grains which negatively affected the strength of the material.

The results showed that the apparent porosity decreases and the bulk density increases more rapidly by increasing the sintering



NY7.3 1750°C, magnif.: x1.00k NY3.7 1750°C, magnif.: x2.00k



NC7.3 1750°C, magnif.: x5.00k NC3.7 1750°C, magnif.: x5.00k

Fig. 9. SEM micrographs of Al_2O_3 ceramics modified with SiC and Si_3N_4-Al_2O_3-Y_2O_3 nanopowders.

temperature from 1650 °C to 1750 °C if samples are modified by plasma synthesised nanopowders. This implies that use of the nanopowders provides more intense densification than when using microsized SiO_2 sources.

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