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Microstructure and properties of mullite–ZrO_2 ceramics with silicon nitride additive prepared by spark plasma sintering

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Abstract

The process of densification and development of the microstructure of mullite–ZrO_2/Y_2O_3 ceramics from mixture of Al_2O_3, SiO_2, ZrO_2 and Y_2O_3 by gradually adding of α–β Si_3N_4 nanopowder from 1 to 5 wt% by traditional and spark plasma sintering were investigated by means of differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and some ceramic and mechanical properties. The processes of DTA for all samples are characterised by a low-pitched endo-effect, when gradual mullite formation and noticeable densification at temperatures of 1200–1400 °C is started. It is testified by shrinkage and density both for traditionally and by SPS-sintered samples. The influence of the Si_3N_4 additive on the density characteristics is insignificant for both sintering cases. For SPS samples, the density reaches up to 3.33 g/cm^3, while for traditionally sintered samples, the value is 2.55 g/cm^3, and the compressive strength for SPS grows with Si_3N_4 additives, reaching 600 N/mm^2. In the case of traditional sintering, it decreases to approximately 100 N/mm^2. The basic microstructure of ceramic samples sintered in a traditional way and by SPS is created from mullite (or pseudo-mullite) crystalline formations with the incorporation of ZrO_2 grains. The microstructure of ceramic samples sintered by SPS shows that mullite crystals are very densely arranged and they do not have the characteristic prismatic shape. The traditional sintering process causes the creation of voids in the microstructure, which, with an increasing amount of Si_3N_4 additive, are filled with mullite crystalline formations.

Keywords: A. SPS; B. Microstructure-final; C. Mechanical properties; D. Mullite; D. ZrO_2; D. Y_2O_3; D. Si_3N_4

1. Introduction

The wide use of mullite ceramics can be explained by their distinctive high-temperature properties such as high thermal and pressure stability in harsh oxidising environments, favourable thermal shock, as well as high chemical resistance both to alkali and acid media [1]. These properties can be achieved largely by complete densification in the process of sintering by using advanced sintering techniques such as spark plasma sintering, hot pressing inter alia [2,3]. One of the possible ways could be the modification of the primary composition of mullite–ZrO_2 ceramics by Si_3N_4 taking into account the fact that such an additive could promote the densification of the ceramic [4]. This phenomenon is based on the fact that during sintering the reaction with oxides (e.g., SiO_2) occuring on the surface of Si_3N_4 particles create a liquid phase (i.e. vitreous flux), thus promoting the diffusion processes and finally leading to densification of the product.

In the present work, a comparative study has be done to explore a Si_3N_4 additive effect on mullite-ZrO_2/Y_2O_3 ceramics structure, phase composition, and certain other properties of ceramics sintered by spark plasma (SPS) and compared to traditionally sintered ones.

2. Experimental procedure

For primary compositions, the chemically pure oxide components Al_2O_3, SiO_2, $ZrO_{2mon.}$, Y_2O_3 with the stoichiometric relations of Al_2O_3 and SiO_2 were taken, to form mullite with the gradual addition of α–β Si_3N_4 nanopowder from 1–5 wt%. Each oxide, ZrO_2 and Y_2O_3, additive was constant at 4.5 wt%.

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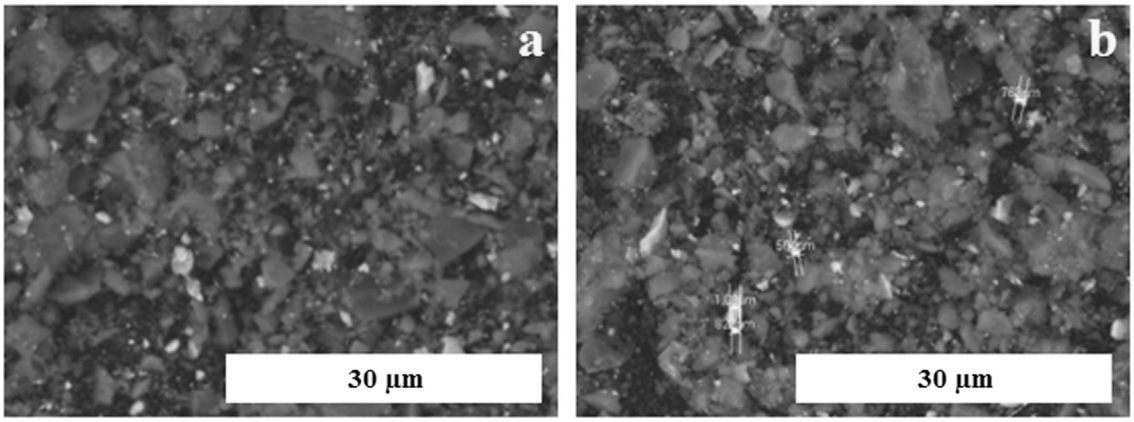

Fig. 1. SEM image of 10 h-milled primary powder of mullite–ZrO_2 composition without Si_3N_4 additive (a) and the same one (b) with 5 wt% Si_3N_4 additive.

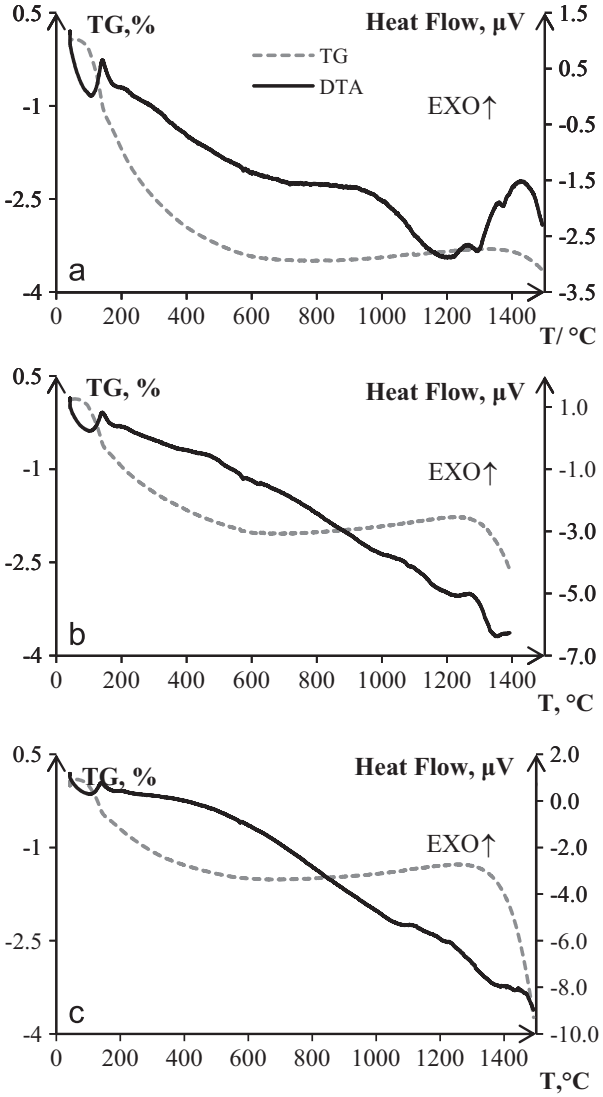

Fig. 2. DT–TG analysis curves for the samples with Si_3N_4 additive 0% (a) 1% (b) and 5% (c).

The primary composition mixtures of the powders were produced by ball-milling for 10 h in the planetary laboratory mill Retsch PM-100 with corundum balls and in alcohol media.

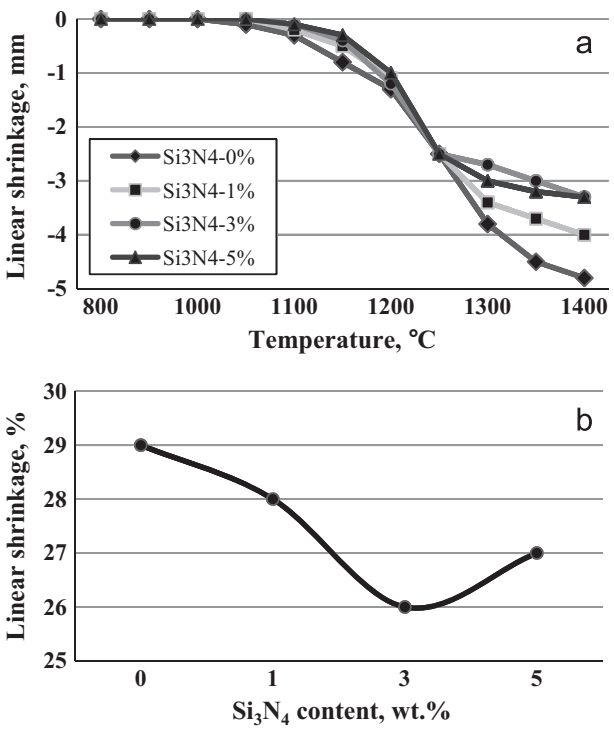

Fig. 3. Shrinkage kinetics of ceramic samples sintered at 1400 °C depending on the Si_3N_4 additive: (a) shrinkage for traditional sintering, (b) for SPS.

The morphology and size of the particles in the primary powders were characterised by SEM (Hitachi TM3000). Phase transitions in the heating process were analysed by applying differential thermal analysis (DTA equipment Setaram, Setsys Evolution 1750) within the temperature range from room temperature to 1500 °C, at a heating rate of 10 °C/min.

Samples for traditional sintering were prepared as discs (Ø = 25 mm, h = 5 mm) and cylinders (Ø = 25 mm, h = 30 mm), by using the hydraulic press "Sprut". Traditional sintering was performed at maximum temperatures of 1400 °C with holding time 2 h. For the SPS the "Sumimoto, Model SPS-825.CE, Dr. Sinter, Japan" equipment was used The powders were pressed under pressure of 30 MPa as 25 mm × 20 mm cylindrical samples. The maximum temperature was 1400 °C, holding time ~40 min.,

heating rate 100 °C/min. The vacuum level of 6 Pa was maintained during the SPS process.

The sintering degree was characterised by the relative density, as well by the change of linear shrinkage. The Archimedes principle was used to measure the density of the sintered samples, with an accuracy of ±0.5% using distilled water.

The microstructure and phase compositions of the sintered samples were analysed using SEM (model NovaNano SEM 650, Netherlands) and XRD apparatus (model D8 Advance Bruker), with CuK$_\alpha$ radiation at a scanning interval from $2\theta = 10–60°$ and 4°/min, respectively.

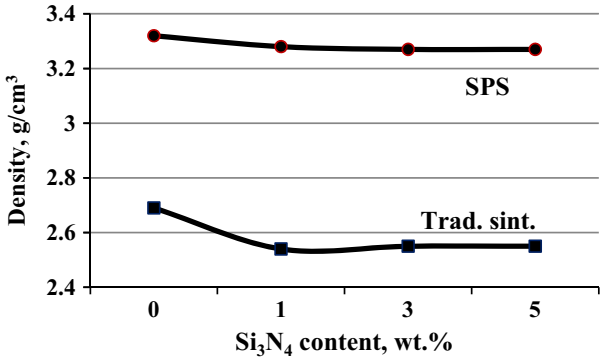

Fig. 4. Density of ceramic samples sintered at 1400 °C depending on the Si_3N_4 additive for traditional sintering and SPS.

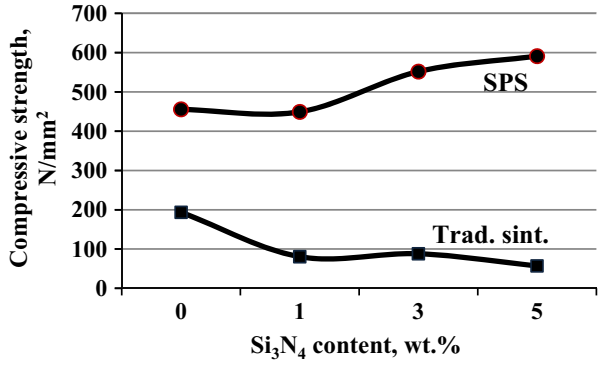

Fig. 5. The compressive strength of ceramic samples sintered by the traditional method and by SPS at 1400 °C depending on Si_3N_4 additive.

The compressive strength was determined by the Toni-Technic (Baustoffprüfung) model 2020 and calculated from 3 parallel measurements.

3. Results and discussion

3.1. Characterisation and thermal treatment of primary powder

SEM images of the powders milled for 10 h (Fig. 1) demonstrate particles (agglomerates) within the range of 3–10 μm. Particles are mainly irregular for the sample without the Si_3N_4 additive. Agglomerates appear rounded for the powder with added Si_3N_4 (Fig. 1a and b). We also found particles within the large nanometre range.

The processes occurring as a result of heating the primary powders with different Si_3N_4 additives within temperature range from room temperature to 1500 °C demonstrate the DT- and TG- analysis curves for 3 samples: without the Si_3N_4 additive (sample MN0), with 1 wt% (sample MN1) and 5 wt% (sample MN5) of the additive (Fig. 2). The main process for all samples (Fig. 2a–c) is related to the transformation of the initial components. They are characterised by low-pitched endo-effects until the temperature reaches 1200–1400 °C, i.e., almost the maximum temperature of sintering. The small pronounced exo-effect at temperatures up to 1000 °C for the sample without the Si_3N_4 additive is obviously connected with the ZrO_2 transformation to a tetragonal modification. This effect is shifted to higher temperatures when the Si_3N_4 additive is used. Mullite crystallisation, beginning on the DTA-curve, is only observed for the sample without Si_3N_4 additives (Fig. 2a). For two other samples with Si_3N_4 additive 1 and 5 wt% (Fig. 2b and c) this effect is somewhat shifted to temperatures up to 1500 °C or a little higher, and obviously could be formed after full decomposition of Si_3N_4.

3.2. Densification of samples

As seen from the DTA-curves (Fig. 2) the formation of new phases associated with the densification process can start at

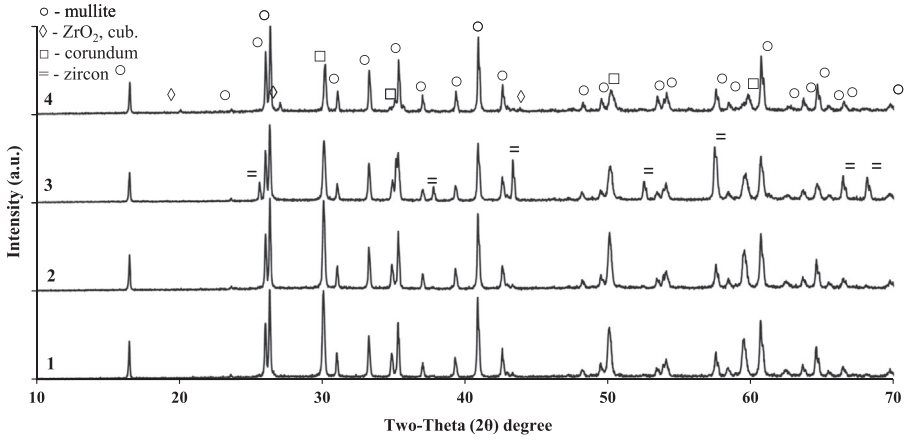

Fig. 6. XRD patterns of mullite–ZrO_2 ceramics sintered traditionally with different Si_3N_4 additives: 1–0%; 2–1%; 3–3%; 4–5%.

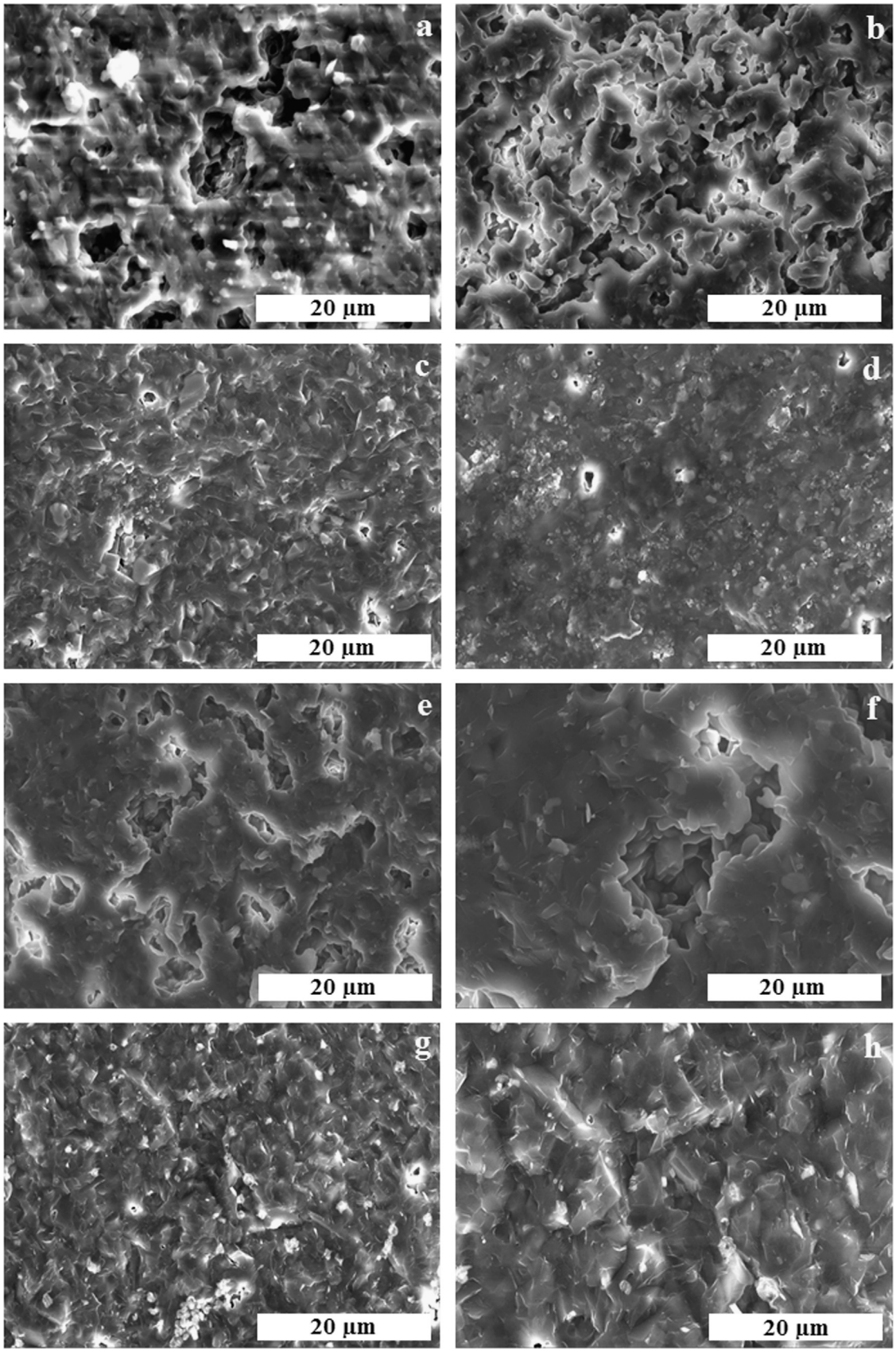

Fig. 7. SEM micrographs of mullite–ZrO_2/Y_2O_3–Si_3N_4 ceramics samples sintered by the traditional method and by SPS at the temperature 1400 °C: (a) – Si_3N_4–0%, traditional; (b) – Si_3N_4–1%, traditional; (c) – Si_3N_4–0%, SPS; (d) – Si_3N_4–1%, SPS; (e) – Si_3N_4–5%, traditional; (f) – Si_3N_4–5%, traditional; (g) – Si_3N_4–5%, SPS; (h) – Si_3N_4–5%, SPS.

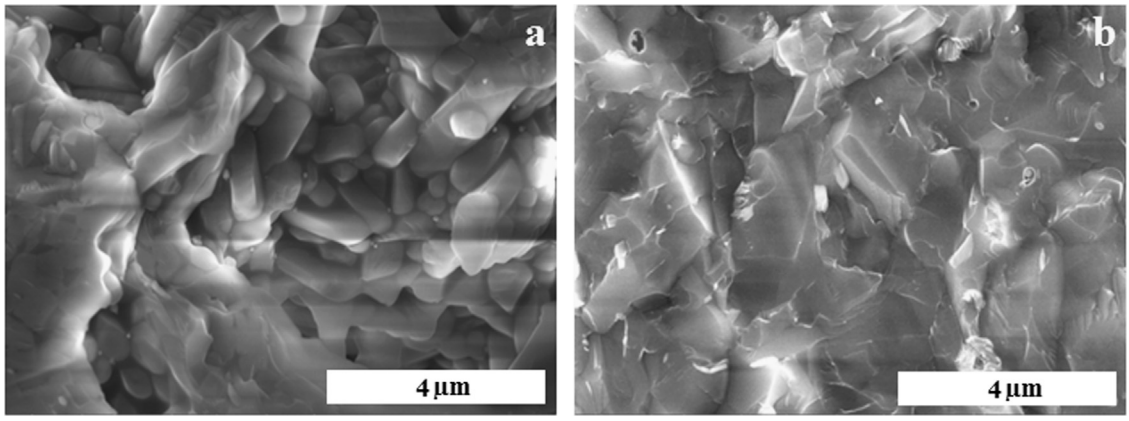

Fig. 8. SEM micrographs of ceramics samples with Si_3N_4 5% additive, sintered by the traditional method (a) and by SPS (b) at a temperature of 1400 °C.

temperatures of around 1250 °C for the sample without the Si_3N_4 additive and at higher temperatures for the samples with the Si_3N_4 additive, when a liquid phase is formed. This process is accompanied by the main reaction, i.e., gradual mullite formation and noticeable densification, characterised by shrinkage and an increase of density. The values of linear shrinkage both for traditional and spark plasma sintered samples at the temperature 1400 °C, depending on the Si_3N_4 additive, are shown in Fig. 3a and b.

Fig. 4 shows density changes of samples sintered traditionally and by SPS. A marked difference can be observed for the density values of the ceramic samples sintered by both methods. The influence of the Si_3N_4 additive is insignificant for this characteristic. As it can be seen, traditionally sintered samples are characterised by a significant shrinkage, which demonstrates a tendency to decrease with the Si_3N_4 additive, until the value of 3%, after which is observed increase in shrinkage. Obviously, in this case the formation of the small amounts of gaseous phase and sequentially of voids (closed pores) in the microstructure is the reason for the increase in shrinkage.

Density correlates with compressive strength values both for traditional and SP-sintered samples (Fig. 5) to a certain extent.

3.3. Phase composition and microstructure

As a result of traditional sintering at 1400 °C, the samples consist mainly of the mullite phase and other phases, such as corundum and ZrO_2 cub. $ZrSiO_4$ is also observed for samples with a 5% Si_3N_4 additive (Fig. 6).

With respect to the crystalline phase composition, the difference between traditional and SPS-sintered samples is negligible. The formation of zircon $ZrSiO_4$ is not observed in the case of SPS. At the same time, in the case of SPS, for the samples with 3 wt% and 5 wt% Si_3N_4 additive, the presence of $ZrO_{2mon.}$ is also observed. This can be explained through our prior experience [3]: ZrO_{2mon} transformation to $ZrO_{2tetr./cub.}$ is largely dependent on the sintering regime, and has a direct relation to the holding time at maximum temperature.

Fig. 7 presents the SEM micrographs of fractured surfaces of mullite–ZrO_2/Y_2O_3–Si_3N_4 ceramics sintered at 1400 °C, traditionally and by SPS. All specimens in both cases consisted of mullite and a pseudo mullite formation with ZrO_2 grain inclusions, as expected.

The micro-structural peculiarity is that, by traditional sintering, voids are formed where secondary mullite crystallisation may occur (Fig. 7a and b). The backfilling of mullite crystalline structures in voids grows with the increase of the Si_3N_4 additive (Fig. 7e and f). The microstructure is significantly denser for SPS (Fig. 7c, d, g and h) than for the traditionally sintered samples: mullite crystals are very densely arranged and do not show the characteristic elongated prismatic shape of mullite (Fig. 8a and b).

4. Conclusions

The reactive sintering of dense, Si_3N_4 reinforced mullite–ZrO_2–Y_2O_3 ceramics from a powder mixture of pure oxide components was achieved by SPS and compared to traditionally synthesised ceramics.

We demonstrated that in the traditional sintering process the compressive strength in the case of the Si_3N_4 additives decreases to approximately 100 N/mm^2. On the other hand, for the ceramic samples processed by spark plasma sintering, these values with the Si_3N_4 additives increase, reaching 600 N/mm^2. These results correlate with density values and microstructural observations.

SEM micrograph analysis reveals that the microstructure of ceramic samples sintered traditionally, and by SPS, consists of mullite (or pseudo-mullite) crystalline formations, incorporating ZrO_2 grains. This microstructure is dense in the ceramic samples sintered by SPS: mullite crystals are very tightly packed, and do not have a characteristic prismatic shape.

The main difference between the microstructures formed by the two sintering methods is that voids are only observed in traditionally sintered ceramic samples.

Acknowledgements

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