RIGA TECHNICAL UNIVERSITY
Faculty of Material Science and Applied Chemistry
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THE EFFECT OF MULLITE-FORMING ADDITIVES ON THE PROPERTIES OF POROUS ALUMINA CERAMICS

Summary of Doctoral Thesis

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REPRESENTATION

I hereby represent that I have independently written the present doctoral thesis, which has been submitted for review at the Riga Technical University for the award of a doctoral degree in engineering sciences. The thesis has not been submitted to any other university for the award of a scientific degree.

Ieva Zake-Tiluga ……………………………. (Signature)

Date: ………………………

The doctoral thesis is written in Latvian and comprises an introduction, three chapters (literature review, methodological part, experiment results and discussion), conclusions, a list of theses to be defended, and a list of publications by the author. The doctoral thesis has 149 pages, also containing 59 figures, 9 tables, 27 equations, 5 appendices, and a list of 245 sources used in research.

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OVERVIEW OF THE DOCTORAL THESIS

Relevance of the subject

Nowadays, there is an increasing demand for new materials with better performance and properties than the materials hitherto known. In the wide range of ceramic materials, highly porous materials (apparent porosity >50%) have a special importance, because the combination of thermal and chemical resistances characteristic to ceramics and the properties characteristic to porous structures (low bulk density, high specific surface area, high permeability of gases and liquids, low thermal conductivity, etc.) make it possible to use this kind of materials in cases where other material groups are unsuitable. However, porous ceramics have one major drawback – the presence of pores significantly decreases the mechanical strength of the material. This is the reason why material scientists for several decades have been looking for ways to improve the mechanical properties of these materials.

Alumina (Al_2O_3) ceramics is a widely used and studied material. A large number of studies have been devoted to dense alumina ceramics. At the same time, the interest in fabrication of highly porous Al_2O_3 ceramics and tailoring its properties (especially the thermal shock resistance) is growing due to increasing demand for porous materials with various applications (e.g., in thermal insulation, catalysts, and filters).

According to the information available in the literature, development of Al_2O_3 and mullite composite materials could improve the properties of highly porous Al_2O_3 ceramics. To date, there have been no comparative studies on the effect of different mullite-forming additives (MFAs) on the ceramic, mechanical, and thermal properties of porous Al_2O_3-mullite composite ceramics. The use of MFAs could be a promising way to improve the mechanical and thermal properties of alumina-based ceramics produced by chemical foaming.

The aim of doctoral thesis

The aim of the doctoral thesis was to evaluate the effect of different types of mullite-forming additives on the properties of porous alumina-based ceramics and to obtain highly porous (apparent porosity >50%) Al_2O_3-mullite composite ceramics with improved mechanical strength and thermal shock resistance by using slip casting and chemical foaming of the slurry.

Tasks to be carried out to actualise the aim of the doctoral thesis

- To summarise the information found in the scientific literature on the fabrication methods of porous ceramics and on alumina ceramics and tailoring of its properties (strength, thermal conductivity, thermal shock resistance, etc.);

- To evaluate the effect of MFAs (SiC, Si_3N_4, and Si_3N_4-Al_2O_3-Y_2O_3 nanopowders, micro-sized SiO_2, and micro-sized SiC) on the ceramic, mechanical, and thermal properties of Al_2O_3-mullite ceramics;
- To evaluate the effect of the microstructure of the studied materials on their mechanical and thermal properties;
- To evaluate the possibilities for tailoring the properties of porous Al_2O_3-mullite ceramics by choosing an appropriate type and amount of MFAs.

Scientific novelty

The novelty of this doctoral thesis is related to synthesising highly porous Al_2O_3-mullite ceramic materials and studying their properties, as the fabrication technology of porous ceramics by using the reaction between aluminium and water and the materials produced by this method have not been studied much so far. The results of this doctoral thesis provide new information about the effect of different MFAs (in terms of chemical composition and particle size) on the mechanical and thermal properties of highly porous Al_2O_3-mullite composite ceramics. An approach was found to improve the mechanical properties of alumina-based ceramics, at the same time retaining high apparent porosity. To the author’s knowledge, this is the first study on the thermal conductivity and its dependence on the temperature for Al_2O_3 and Al_2O_3-mullite ceramics produced by slip casting and chemical foaming.

Practical significance

The practical importance of this work is related to developing highly porous Al_2O_3-mullite composite materials, which could be used as aids for firing ceramic materials (e. g., as a base for placing green ceramic bodies in kilns), as filters for hot liquids, or as heat insulating ceramics with sufficient mechanical strength. During research, materials were developed which have improved mechanical strength, thermal shock resistance, and heat insulating properties in comparison with unmodified Al_2O_3 ceramics. The apparent porosity values of these materials were not less than 56%.

Approbation of the results

The scientific results of this work have been presented in 7 full text scientific articles (5 of them indexed in SCOPUS and/or Web of Science databases) and 11 international conferences.

THESES TO BE DEFENDED

1. It is possible to synthesise highly porous Al_2O_3-mullite ceramics with improved mechanical, thermal and heat insulating properties by slip casting, using chemical reaction as the pore-forming method.
2. Addition of nano-sized SiC improves the mechanical strength and thermal shock resistance of porous Al_2O_3 ceramics, whereas addition of micro-sized SiO_2 decreases the thermal conductivity of porous Al_2O_3 ceramics.
3. The amount of the glassy phase on the grain boundaries increases with increasing the added amount of mullite-forming additive, which results in decreased mechanical strength of the composite material of Al_2O_3-mullite ceramics.
4. Samples with smaller volume of pores with diameters in the range of ~3-30 μm determined by mercury intrusion porosimetry have higher mechanical strength.

LITERATURE REVIEW

The literature review of the doctoral thesis comprises the following topics: 1) uses of porous ceramics, 2) pore forming methods in porous ceramic materials, 3) aluminium oxide (Al_2O_3) and its main composite materials, 4) the Al_2O_3-SiO_2 system and its phase diagrams, and 5) possibilities of tailoring the mechanical and thermal properties of porous alumina-based ceramics.

There are many scientific papers devoted to the various fabrication methods of porous ceramics. The pore formation method is decisive in obtaining the desired pore size, pore size distribution, pore shape, and orientation, which determine the potential uses of the final material. Alumina and its composite ceramics have a special role in this material class, because these materials stand out for very good thermal and chemical resistance. It is possible to obtain ceramics with different microstructures and mechanical and thermal properties by applying various fabrication techniques of porous ceramics, different phase compositions, granulometric compositions, and other factors influencing the properties of the materials. This opens up possibilities for using these materials in various fields, for example, as thermal insulators, ceramic filters, membranes, or catalyst supports. There are a large number of studies on the fabrication methods of porous ceramics and their impact on the thermal, mechanical, and thermomechanical properties of the final material.

The Al_2O_3-SiO_2 system has been studied since the 1920s [1], and it is essential in the technology of refractory materials. Since the coefficients of linear thermal expansion of corundum (α-Al_2O_3) and mullite are relatively different and the formation of mullite is affected by the raw materials used, the properties of the materials synthesised in this system depend on the elements of the preceding synthesis, such as raw materials, formation method of the green body and thermal treatment regime [2]. Mullite formed by decomposition of kaolinite (the main mineral of kaolin clay) is called primary mullite, whereas mullite formed in a direct reaction between Al_2O_3 and SiO_2 – secondary mullite.

Most of the scientific papers are devoted to the thermal shock resistance of porous Al_2O_3-mullite, because these composite materials have better thermal shock resistance than pure Al_2O_3 ceramics. To the author's knowledge, the effect of mullite and mullite-forming raw materials on the mechanical properties of porous Al_2O_3-based ceramics has not been studied much.

A large number of scientific papers focus on the improvement of mechanical properties (strength and fracture toughness) by using various forming methods, processing techniques of already sintered materials, and raw materials. Nanotechnologies have been playing an increasing role in both the raw material synthesis and materials processing, especially in dense ceramics.

The method of producing porous Al_2O_3 and Al_2O_3-mullite ceramics by using aluminium paste or powder as a pore-forming agent has not been studied extensively.

To the author's knowledge, there are no specific studies on how the mullite-forming additives (MFAs) with different chemical compositions and particle size distributions affect the strength, thermal conductivity, and thermal shock resistance of porous Al_2O_3-mullite ceramics. The thermal conductivity of porous Al_2O_3 and Al_2O_3-mullite ceramics fabricated by pore forming via chemical reaction in suspended raw materials has not been studied either. In the scientific literature, there is a lack of information on relatively simple and fast fabrication methods of porous ceramics. Usually, the described methods are time-consuming, allow producing only small-sized samples, and/or often are very expensive.

MATERIALS AND METHODS

The materials studied in this work were made by slip casting concentrated slurry, using the reaction between aluminium and water for pore forming. This reaction releases hydrogen, and the process can be described by the following equation:

$$2Al + 6H_2O \xrightarrow{pH \sim 9} 2Al(OH)_3 + 3H_2 \uparrow . \qquad (1)$$

The basic components are γ-Al_2O_3 (d_{50} = 80 μm, Nabalox NO 201, Nabaltec, Germany) and α-Al_2O_3 (d_{50} = 3 μm, Nabalox NO 325, Nabaltec, Germany). γ-Al_2O_3 had to be used, because this crystalline modification catalyses the reaction of aluminium and water. Chemically pure amorphous SiO_2 (SiO_2 content ≥ 98%, d_{50} = 3.7 μm, Reachim, Russia), micro-sized α-SiC (hexagonal structure) (d_{50} = 37 μm, Sigma-Aldrich), plasma synthesised crystalline β-SiC (cubic structure) nanopowder (d_{50} = 80 nm), plasma synthesised Si_3N_4 nanopowder (d_{50} = 21 nm), and plasma synthesised Si_3N_4-Al_2O_3-Y_2O_3 (91%-6%-3%) nanopowder (d_{50} = 74 nm) were used as MFAs. Nanopowders were provided by Plasma & Ceramic Technologies Ltd., Latvia. 1% solution of carboxymethyl cellulose sodium salt (CMC) (Optapix C 1000 G, Zschimmer & Schwarz GmbH & Co, Germany) was used as a binder. Aluminium paste with solid content 70±2% (d_{50} = 12 μm, Aquapor-9008, Schlenk Metallic Pigments GmbH, Germany) was the pore-forming agent. Aluminium paste was added to suspension after homogenisation (0.1 wt% of the total mass of dry raw materials). The total water content in the slurries varied from 32.6 to 35.3 wt%. Distilled water was added to have the initial viscosity of suspensions within the range of ca. 800 mPa·s. The heating rate was 2.3°C/min (140 °C/h), the dwelling time at the maximum sintering temperature – one and three[1] hours. The samples were sintered at 1650°C and 1750°C.

The diagrams of compositions and sintering temperatures are given in Fig. 1[2]. The initial compositions of the investigated samples and their denotations are given in Table 1. Numbers 1650 or 1750, when given after the denotations listed in the first column of Table 1 and also hereinafter in the text, indicate the sintering temperature of the samples.

The amounts of all MFAs are given in equivalent wt% (hereinafter in the text – eqv. wt%), which corresponds to theoretically calculated amount of SiO_2 in wt% that forms via passive mechanism by fully oxidising SiC or Si_3N_4 [4, 5].

The theoretically calculated amount of 3:2 mullite ($3Al_2O_3 \cdot 2SiO_2$) in the materials modified with 3.7 and 7.3 wt% SiO_2 after sintering was 13.0 wt% and 24.2 wt% respectively.

The sintered samples were cut into bars with thickness 1.5±0.1 cm, width 2.0±0.1 cm, and length 9.0±0.1 cm for further testing. Samples for the compression test were cut in cubic shapes with edge size 20.0±1.5 mm. The diagram of sample preparation is given in Fig. 2.

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[1] A dwelling time of three hours was set for the samples, which were used to determine the effect of dwelling time on the mechanical properties of the materials.

[2] The samples, which were prepared to evaluate the effect of dwelling time, were held at the maximum temperature for 1 and 3 hours, and this is not indicated in the diagram in Fig. 1.

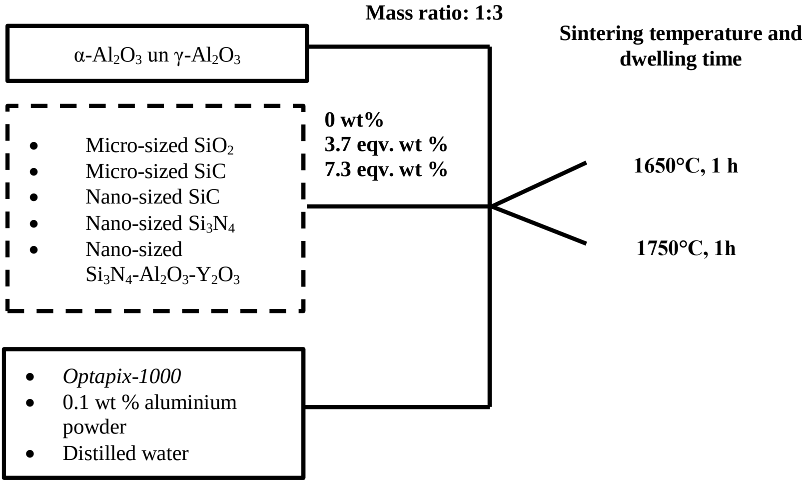


Fig. 1 Diagram of the investigated compositions and sintering temperatures (the variable components are indicated with a dotted line)

Table 1

The investigated compositions and their denotations

Denotation	Mass ratio of α- and γ-Al_2O_3	Mullite-forming additive	Mean particle size	Wt%	Equivalent amount of SiO_2, wt%
S0	1:3	-	-	0	0
C3.7		SiC	37 µm	2.5	3.7
C7.3				5.0	7.3
S3.7		Amorphous chemically pure SiO_2	3.7 µm	3.7	3.7
S7.3				7.3	7.3
NC3.7		Plasma-synthesised SiC	80 nm	2.5	3.7
NC7.3				5.0	7.3
N3.7		Plasma-synthesised Si_3N_4	21 nm	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%)	74 nm	3.2	3.7
NY7.3				6.3	7.3

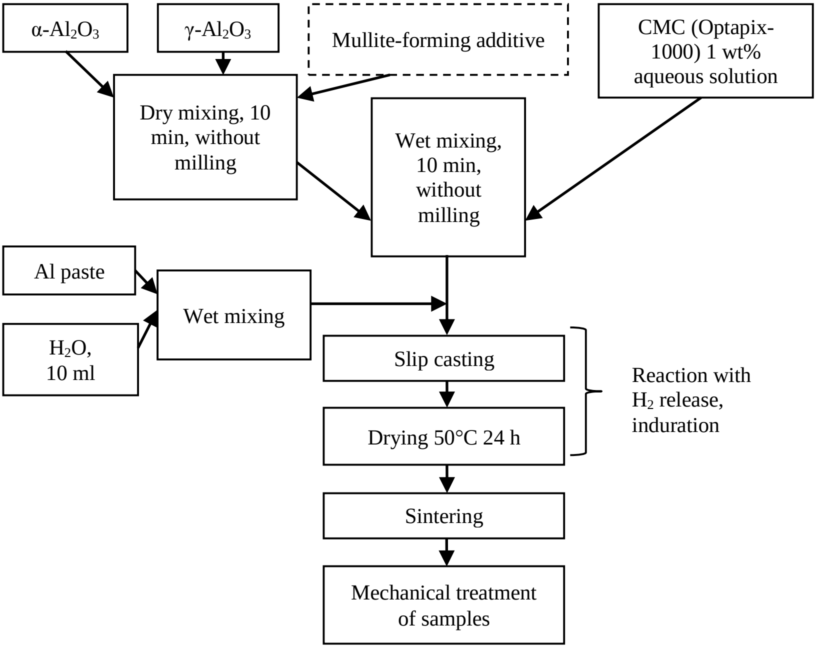


Fig. 2 Diagram of the sample preparation

The laser flash method was used to determine, via thermal diffusivity, the effective thermal conductivity (λ) of the samples. Thermal conductivity was measured as a function of temperature (from room temperature up to 1100ºC) using the laser flash method and corresponding standards. For these measurements, test pieces with 10×10×2 mm dimensions were cut out from each sample.

The thermal shock resistance of the materials was evaluated by comparing the elastic modulus E before and after the thermal shock cycles ($\Delta T = 980°C$). The elastic modulus was measured by the non-destructive impulse excitation technique. Five specimens of each composition were subject to thermal shock. 15×20×100 mm size bars at room temperature were put into a furnace heated up to 1000°C. After one hour, the samples were taken out and quenched in air at room temperature (20°C). The samples were kept in an air flow generated by a fan until they cooled completely. Quenching was repeated twelve times. The elastic modulus was determined from the frequency and from the shape, size, and mass of the sample as per ASTM E1876/C1259. The Poisson's ratio (μ) for all samples was assumed to be 0.2.

The total shrinkage of the studied materials and also their bulk density and apparent porosity were measured by means of hydrostatic weighing in water. The phase compositions were detected by X-ray diffraction (XRD). The samples with compositions S3.7, S7.3, NC3.7 and NC7.3 sintered at 1750°C were analysed by semi-quantitative XRD to approximately evaluate the quantitative crystalline phase ratios in the materials after sintering. Green samples were analysed by the differential thermal analysis (DTA) and thermogravimetric analysis. The series of the most prospective compositions were analysed by a horizontal dilatometer to evaluate their thermal expansion (see Table 2). The pore size distribution and specific surface area distribution were determined by means of mercury intrusion porosimetry. The mechanical strength was evaluated by means of a three-point bending test and a compression test. The microstructural features of the materials were studied in various magnifications on non-sputtered cut surfaces and on cut surfaces sputtered with Cr. The energy-dispersive X-ray spectroscopy was used to evaluate the dispersion of the mullite phase in the Al_2O_3 matrix. The samples, which were tested for thermal conductivity, were also analysed by X-ray micro-computed tomography (μCT) to evaluate the cell size and strut size.

A list of the studied samples and characterisation methods are given in Table 2.

Table 2

Characterisation methods of the studied materials

<table>
<tr><th>Composition</th><th colspan="5">Methods of analysis</th></tr>
<tr><td>S0</td><td rowspan="11">XRD;
DTA, TGA;
determination of total shrinkage by geometrical measurements;
determination of bulk density and apparent porosity by geometrical measurements and the Archimedes method;
mercury intrusion porosimetry;
three-point bending test;
SEM</td><td rowspan="7">Compression test;
dilatometry</td><td rowspan="5">Laser flash method;
evaluation of thermal shock resistance by means of the impulse excitation method</td><td rowspan="4">μCT</td><td></td></tr>
<tr><td>S3.7</td><td rowspan="4">EDS</td></tr>
<tr><td>S7.3</td></tr>
<tr><td>NC3.7</td></tr>
<tr><td>NC7.3</td><td></td></tr>
<tr><td>C3.7</td><td></td><td></td><td></td></tr>
<tr><td>C7.3</td><td></td><td></td><td></td></tr>
<tr><td>N3.7</td><td></td><td></td><td></td><td></td></tr>
<tr><td>N7.3</td><td></td><td></td><td></td><td></td></tr>
<tr><td>NY3.7</td><td></td><td></td><td></td><td></td></tr>
<tr><td>NY7.3</td><td></td><td></td><td></td><td></td></tr>
</table>

The properties of the NC series samples were studied thoroughly, because these materials had an optimal combination of mechanical strength and apparent porosity. The samples of S series had high apparent porosity and were also interesting from the point of view of comparison, because they were different in terms of chemical and granulometrical compositions.

RESULTS AND DISCUSSION

Phase composition and thermochemical processes during sintering

Porous Al_2O_3-mullite composite ceramics was sintered by adding different (in terms of chemical composition and particle size) MFAs in the amounts of 3.7 and 7.3 eqv. wt% to the mixture of α and γ-Al_2O_3. In the samples sintered at 1650°C and 1750°C, SiO_2, which was added in the amorphous micro-sized form or formed via oxidation of SiC or Si_3N_4, reacted with Al_2O_3 and formed porous Al_2O_3-mullite composite. During sintering, γ-Al_2O_3 transformed into thermodynamically more stable α-Al_2O_3 (corundum). According to semi-quantitative XRD results, a small amount (<2%) of quartz also was formed, and, in the samples modified with 3.7 and 7.3 eqv. wt% of MFAs, the content of mullite was in an approximate range of 11 to 13 wt% and 31 to 36 wt% respectively.

The results of DTA and TGA showed that the increase in mass related to the oxidation process in the samples modified with micro-sized SiC and with nano-sized SiC and Si_3N_4 started at ca. 520°C, whereas the endothermic effect started already at ca. 300°C.

The effect of mullite-forming additives on shrinkage, bulk density, and apparent porosity

The total shrinkage (TS) of materials modified with various MFAs is shown in Fig. 3. When manufacturing ceramic products, it is desirable that their TS be as low as possible. The TS of unmodified corundum ceramics sintered at 1650°C and 1750°C was 8.3±0.7% and 11.6±0.4% respectively. Analysis of the effect of MFAs on the TS of porous Al_2O_3-mullite ceramics showed the lowest shrinkage in the samples with compositions containing micro-sized SiO_2 and micro-sized SiC. The TS of these samples decreased by 18-37% in comparison with the TS of unmodified corundum ceramics. The MFAs decreased the TS in the samples sintered at 1750° more than in the samples sintered at 1650°C. The addition of nano-sized Si_3N_4 or Si_3N_4-Al_2O_3-Y_2O_3 increased the TS of corundum ceramics. The highest TS was found in the samples with Si_3N_4-Al_2O_3-Y_2O_3 nanopowder added (by 25-38% higher than the TS of unmodified Al_2O_3 ceramics), because the presence of Y_2O_3 promoted the formation of liquid phase during sintering. The TS decreased with increasing the amount of added MFA from 3.7 to 7.3 eqv. wt% (except in case of Si_3N_4-Al_2O_3-Y_2O_3). The S7.3-1650 sample had the lowest TS (6.6±0.9%), and NY7.3-1750– the highest (15.4±1.6%).

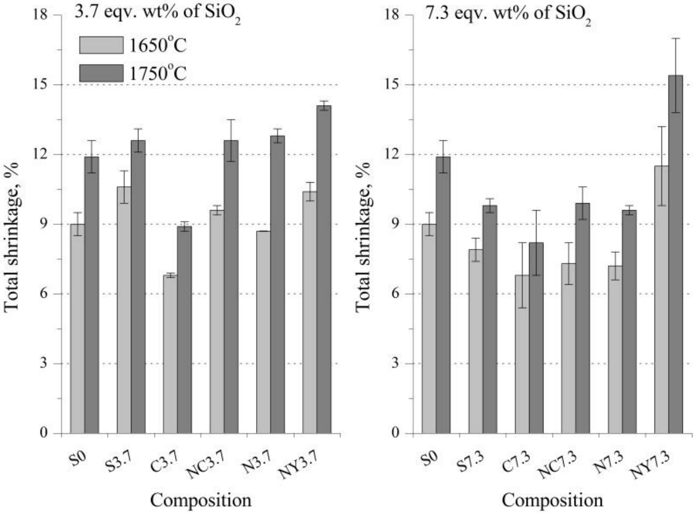


Fig. 3 Total shrinkage of the studied Al_2O_3 and Al_2O_3-mullite ceramics

The effect of dwelling time on TS was also evaluated in the study. In this step of research, samples with compositions S0, S3.7, S7.3, NC3.7, and NC7.3 were analysed. The TS increased negligibly with increasing the dwelling time at the maximum sintering temperature.

The bulk density (BD) of the studied materials was in the range from 0.95±0.01 g/cm^3 (sample S7.3-1650) to 1.26±0.01 g/cm^3 (sample NC3.7-1750) (Fig. 4), and the apparent porosity (AP) – in the range from 56.0±0.8% (sample NY7.3-1750) to 64.0±0.8% (sample S7.3-1650) (Fig. 5). The BD and AP were affected by the sintering temperature, MFA and its amount.

In comparison with unmodified corundum ceramics, BD slightly increased by modifying it with 3.7 eqv. wt% of MFA and slightly decreased by adding 7.3 eqv. wt% of MFA. The BD decreased with increasing the amount of added MFA from 3.7 to 7.3 eqv. wt%, which is related to the volume expansion caused by the formation of mullite [6]. Increase of the sintering temperature increased the BD in all cases. The BD increased with increasing the sintering temperature mostly in the samples modified with nanopowders, because the small particle size and high specific surface area intensified the densification.

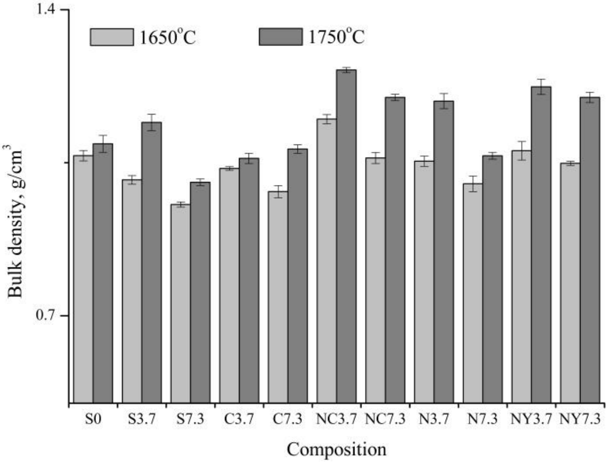


Fig. 4 Bulk densities of the investigated materials

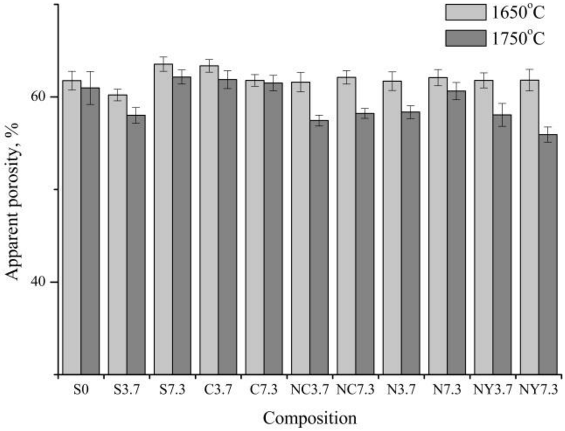


Fig. 5 Apparent porosities of the studied materials

Increase of the sintering temperature decreased the AP. Increase in the sintering temperature mainly affected the samples modified with nano-sized MFAs. In this case, the AP decreased more than in the samples with micro-sized MFAs, because nano-sized MFAs significantly promote sintering and densification at such temperature. The AP was slightly increased (by 1.5-2.9%) by addition of micro-sized SiC and SiO_2.

The effect of mullite-forming additives on the mechanical properties of porous Al_2O_3 ceramics

One of the most important parameters characterising ceramics is its mechanical strength. Therefore, the effect of various MFAs on the bending and compressive strength of porous, alumina-based ceramics was evaluated. The study succeeded in improving the bending and compressive strength of this ceramics, while retaining the AP at a level not less than 56% (sample NY7.3-1750). The bending strength (σ_B) of the studied materials is shown in Fig. 6. In unmodified Al_2O_3 ceramics sintered at 1650°C and 1750°C, it was 2.3±0.5 MPa and 3.2±0.6 MPa respectively. It was found that the strength of the studied materials was noticeably affected by the added MFA and its amount, whereas increase in the sintering temperature from 1650°C to 1750°C had a lesser effect.

The samples modified with plasma-synthesised SiC and Si_3N_4-Al_2O_3-Y_2O_3 nanopowders manifested the most notable improvement of the bending strength in comparison with unmodified Al_2O_3 ceramics. The highest increase in the bending strength occurred in samples NY3.7-1750 (increase of σ_B by 243%, retaining 58±1% AP), NY3.7-1650 (increase of σ_B by 197%, retaining 62%±1 AP), and NC3.7-1750 (increase of σ_B by 190%, retaining 58±1% AP).

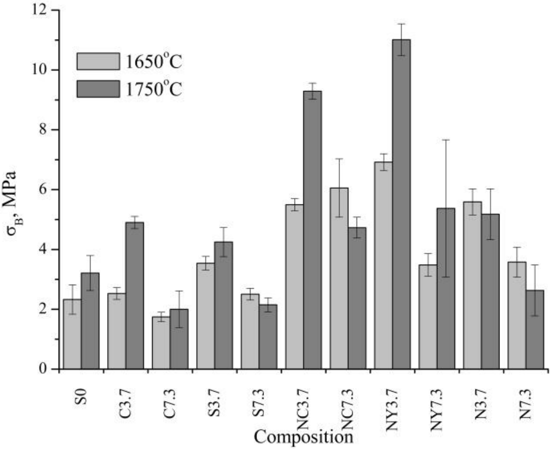


Fig. 6 The bending strength of the studied materials

The bending and compressive strengths of the studied materials decreased with increasing the amount of added MFA from 3.7 to 7.3 eqv. wt%. When 7.3 eqv. wt% of micro-sized SiO_2 or SiC were added, the strength of the Al_2O_3-mullite composite system was even lower than that of Al_2O_3 ceramics. At the same time, a positive fact to be noted is that the AP of the samples with improved mechanical strength was relatively high – not lower than 56%.

Luthra and Park reported that aluminosilicate glass was found in an Al_2O_3-mullite matrix sintered from Al_2O_3 and SiC [7]. The formation of a glassy phase on the grain boundaries of Al_2O_3 and mullite could be the reason why the mechanical strength of the studied materials decreased with increasing the added amount of MFA from 3.7 to 7.3 eqv. wt%. The presence of a glassy phase was confirmed by SEM (see chapter "Structure of the studied materials", pages 22-23). Another reason for the deterioration of mechanical properties could be increase in the structural micro-heterogeneities (for example, agglomerates which were detected by the SEM analysis) when the amount of MFA was increased.

Compositions with Si_3N_4 and Si_3N_4-Al_2O_3-Y_2O_3 nanopowders were not further examined, because the samples with these compositions had nonhomogeneous distribution of large pores (>0.5 mm) in the samples' bulk (pore size gradient along the samples' height).

The study also evaluates the effect of dwelling time on the compressive strength by testing the samples of S0, S3.7, S7.3, NC3.7, and N7.3 series held at the maximum sintering temperature for 1 and 3 hours. The compressive strength was measured in two directions – parallel and perpendicular to the bottom of the sample. This was done so, because the pores formed by the hydrogen release reaction (with pore size in the range from ~200 μm to 1.3 mm) in all of the samples had an elongated shape in the direction parallel to the bottom of the sample (Fig. 7).

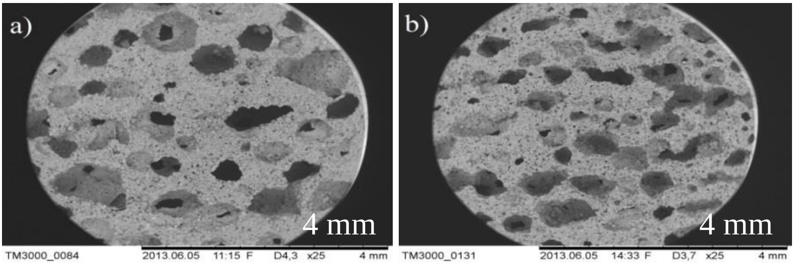
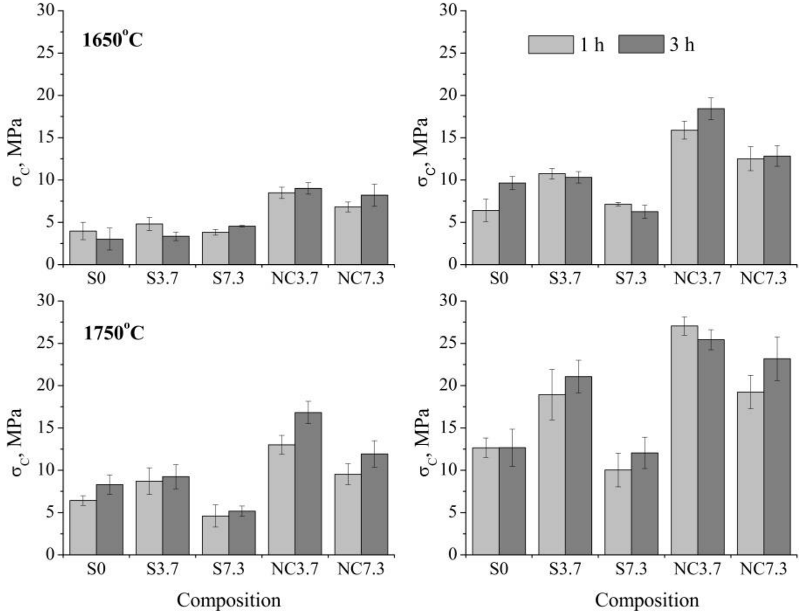


Fig. 7 Examples of the pore shape of the samples: a) S0-1650; b) NC3.7-1650

The compressive strength (σ_C) of the studied samples depending on the composition, sintering temperature, dwelling time, and loading direction is shown in Fig. 8. The effect of the initial composition on the compressive strength is similar to the effect on the bending strength. This confirms the fact that the mechanical strength of porous Al_2O_3-mullite ceramics decreases with increasing the amount of added MFA from 3.7 to 7.3 eqv. wt%, irrespectively of the type of MFA used.



Loading direction perpendicular to the bottom of the sample

Loading direction parallel to the bottom of the sample

Fig. 8 The compressive strength of the studied materials depending on the composition, sintering temperature, dwelling time and loading direction

The compressive strength in the direction parallel to the bottom of the sample was 1.6 to 2.2 times higher than in the perpendicular direction (6.4±1.3 to 27.0±1.1 MPa and 3.8±0.3 to 13.0±1.1 MPa respectively). This result is related to different cross-section areas of the solid material in both directions. The compressive strength in the direction perpendicular to the bottom of the sample is lower, because the pore area in the plane parallel to the base of the sample is larger, and therefore the cross-section area of the load-bearing pore walls is smaller.

The impact of dwelling time on the mechanical strength in the chosen time range was ambiguous. It was expected that an increase in the dwelling time from 1h to 3h would increase the mechanical strength to some extent; however, the experimental results did not fully confirm this assumption. This result implies that the increase of the dwelling time from 1h to 3h in some cases does not compensate for the decrease of the mechanical strength due to various micro-heterogeneities, for example, due to internal microcracks. A more efficient way to increase the mechanical strength of such materials is selection of an appropriate MFA and increase of the sintering temperature.

Structure of the studied materials

The structure of the studied materials was based on the Al_2O_3 matrix formed by sintering a mixture of fine α-Al_2O_3 powder (d_{50} – 3 μm) and coarse γ-Al_2O_3 powder (d_{50} – 80 μm) in the mass ratio of 1:3.

According to the SEM analysis and mercury intrusion porosimetry (MIP) results, the hydrogen release reaction produces pores with diameters in the range from ~20 to 1300 μm, whereas the initial composition determined the pore size distribution in the diameter range from ~0.1 to 20.0 μm.

Increase in the sintering temperature intensified the densification, and the MIP results clearly indicated that the increase most affected the densification degree of the samples modified with MFAs, because the volume of small pores in these samples decreased more than in corundum ceramics without additives (Fig. 9).

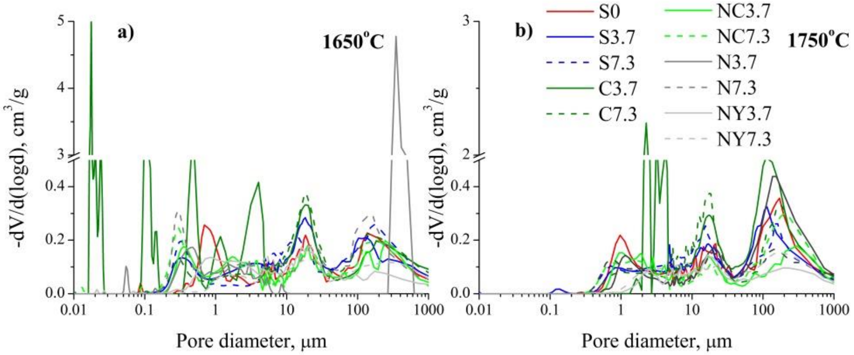
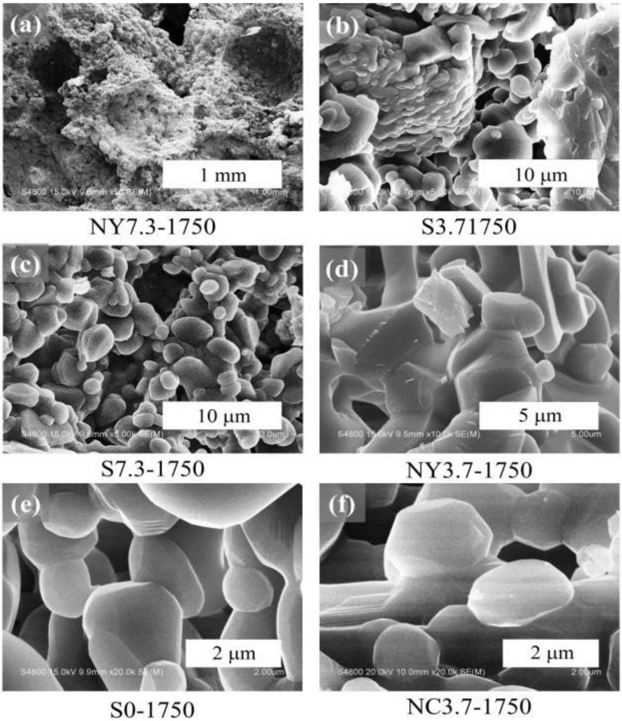


Fig. 9 Logarithmic pore size distribution of the samples sintered at 1650°C (a) and 1750°C (b)

The studied materials had a trimodal pore size distribution (Fig. 9). The distribution pattern remained similar with increasing the sintering temperature from 1650°C to 1750°C, whereas the volume of pores with a diameter <0.3 μm decreased. Exceptions were samples C3.7-1650, YN3.7-1650, and C3.7-1750, where significant deviations from the trimodal pore size distribution were observed, indicating the presence of voids and/or pores atypical to the other samples. This may be due to the crack/void formation during the suspension thickening or during the oxidation of SiC and Si_3N_4 particles.

The pore size range in the studied materials was wide. Both millimetre-sized pores (Fig. 10 a) and micrometre-sized pores (Fig. 10 a, c) were formed during the hydrogen release reaction. A part of the micrometre-sized pores were voids between particles (Fig. 10 d, e, f). According to the μCT results, the pore and strut sizes were more affected by the added MFA, whereas the effect of the sintering temperature was less notable. The struts in the samples modified with micro-sized SiO_2 were slightly thicker than in the samples with compositions S0 and NC3.7 (45-47 μm and 35-40 μm respectively).



NY7.3-1750
S3.71750
S7.3-1750
NY3.7-1750
S0-1750
NC3.7-1750

Fig. 10 Examples of the microstructures of the samples sintered at 1750°C

The pore size distribution of the samples modified with Si_3N_4-Al_2O_3-Y_2O_3 nanopowder indicates a denser microstructure than in other compositions. This is related to the presence of a glassy phase, which was also confirmed by SEM (Fig. 10d). The formation of the liquid phase during sintering was promoted by Y_2O_3 present in the Si_3N_4-Al_2O_3-Y_2O_3 (91%-6%-3%) nanopowder. Such an effect of the presence of Y_2O_3 has already been reported by other authors [8, 9].

The specific surface area (SSA) of the samples sintered at 1650°C did not exceed ~1.3 m^2/g. The SSA significantly decreased with increasing the sintering temperature up to 1750°C and was in the range from ~0.3 to 0.6 m^2/g. An exception was sample C3.7-1650, the SSA of which was significantly higher (~55 m^2/g) – probably due to increase of the SSA during oxidation of the micro-sized SiC grains or formation of microcracks during sintering.

In the materials sintered at 1650°C, the SSA was slightly increased by the crystallisation of mullite on the surface of corundum grains when the raw materials did not contain Y_2O_3. At a sintering temperature of 1750°C, such an effect was not observed, which can be explained by a higher densification degree when increasing the sintering temperature.

A comparison of the bending and compressive strength data and the MIP results showed a relation between the bending and compressive strengths and the volume of pores in the diameter range from ~3 to 30 μm. Samples with higher strength had a lower pore volume in this diameter range.

A hypothesis was that the mechanical strength of the materials decreases with increasing the amount of MFA from 3.7 to 7.3 eqv. wt% due to an increased amount of the glassy phase on the grain boundaries. The presence of a glassy phase was confirmed by the SEM results (Fig. 11). However, it was not possible to evaluate the amount of the glassy phase by the available characterisation methods. Another possible reason of the deterioration of the mechanical properties is that increase in the amount of MFA increases the amount of agglomerates in the porous matrix, thereby reducing the positive effect of the presence of mullite on the mechanical strength. This assumption was partly confirmed by the SEM analysis, because agglomerates of various sizes and shapes were observed in the samples modified with micro-sized SiO_2 and nano-sized SiC, Si_3N_4, and Si_3N_4-Al_2O_3-Y_2O_3 powders (Fig. 12). Presumably, the agglomerates formed because no specific dispersion methods (e.g., ultrasound) were applied. Despite the presence of agglomerates, the mechanical properties of the samples modified with nano-disperse MFAs were better. This is because nanopowders were more evenly distributed among Al_2O_3 grains and the contact area between particles was larger than in the case of micro-sized SiO_2 sources.

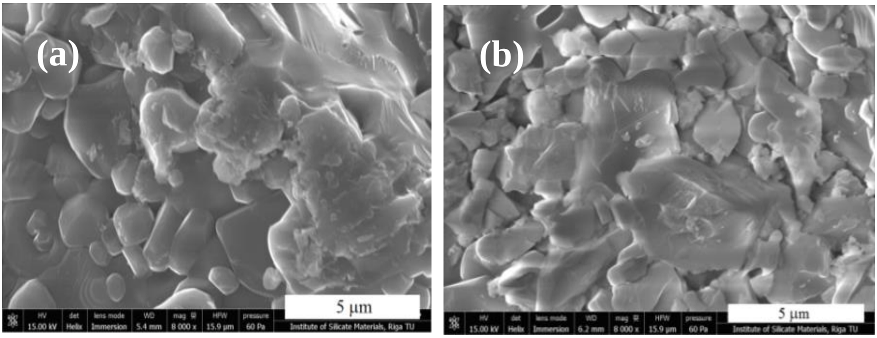
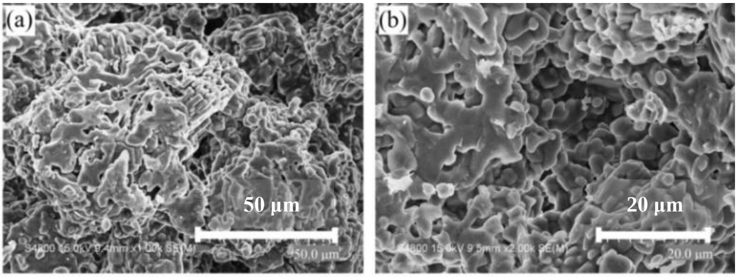
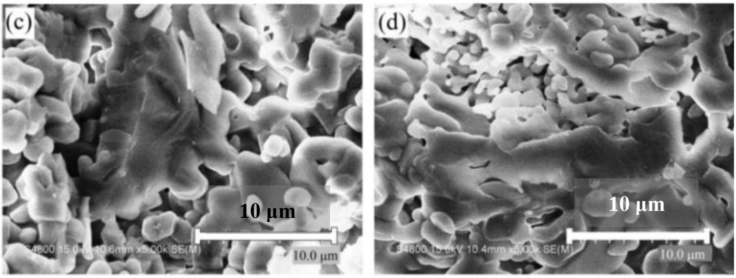


Fig. 11 Glassy phase in samples S7.3-1750 (a) and NC7.3-1750 (b)



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



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

Fig. 12 SEM micrographs of Al_2O_3 ceramics modified with SiC and Si_3N_4-Al_2O_3-Y_2O_3 nanopowders

Energy-dispersive X-ray spectroscopy (EDS) was used to evaluate approximately the distribution of mullite phase in the Al_2O_3 matrix. EDS mapping was performed on samples S7.3-1750 (composition with 7.3 wt% of SiO_2) and NC7.3-1750 (composition with 7.3 eqv. wt% of nano-sized SiC) to compare how the phase which contains silicon (Si) atoms is distributed into the Al_2O_3 matrix. During the EDS analysis, areas were searched from where it would be possible to detect signals corresponding to Si atoms. According to the EDS mapping results, the mullite phase in the material modified with micro-sized SiO_2 is distributed more unevenly than in the material where mullite is formed in the reaction of nano-sized SiC with Al_2O_3 (Fig. 14).

It was not possible to determine unambiguously the morphology of the mullite phase by the SEM microphotographs and EDS maps; therefore, signals corresponding to Si atoms were searched for in different microstructural elements, such as agglomerates or grains of various shapes and sizes. However, an unambiguous relation between the grain shape and size and the density of Si signals was not found.

The analysis of MIP, SEM, total shrinkage, and bulk density data allows to conclude that different MFAs differently affect the densification degree and microstructure of the materials, including grain size, necks between particles, porosity of the matrix, and pore size distribution. This in turn explains the effect of MFAs on the mechanical properties of the studied ceramics.

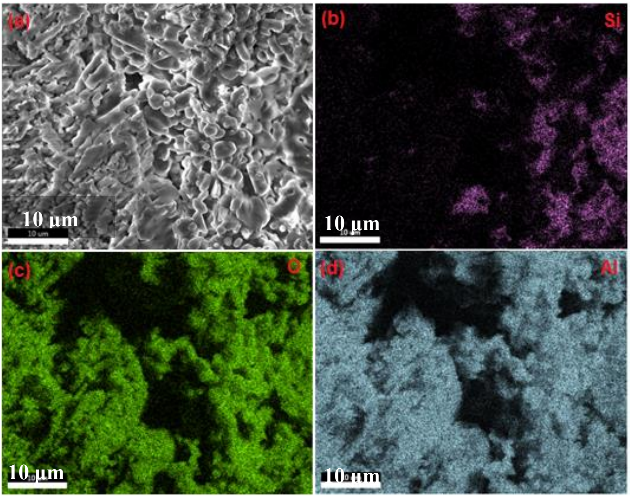


Fig. 13 SEM image (a) and EDS maps for silicon (b), oxygen (c) and aluminium (d) of sample S7.3-1750 (scale bar corresponds to 10 µm)

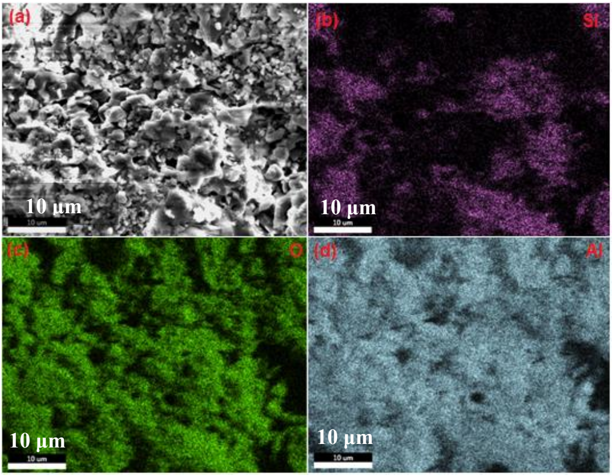


Fig. 14 SEM image (a) and EDS maps for silicon (b), oxygen (c) and aluminium (d) of sample NC7.3-1750 (scale bar corresponds to 10 µm)

Thermal conductivity

Thermal conductivity (TC) is an important property characterising heat insulation materials. Due to the porous structure of the studied ceramics, the investigated materials have heat-insulating properties. This study compared TCs and their dependence on temperature in Al_2O_3 and Al_2O_3-mullite ceramics. In the studied samples, micro-sized SiO_2 and nano-sized SiC were used for mullite synthesis.

In terms of TC, the studied materials are competitive with other porous Al_2O_3-based materials described in the literature. At room temperature, the TCs of Al_2O_3 and Al_2O_3-mullite ceramics sintered at 1650°C and 1750°C were 0.77-2.23 W/(m·K) and 1.23-3.07 W/(m·K) respectively (Fig. 15).

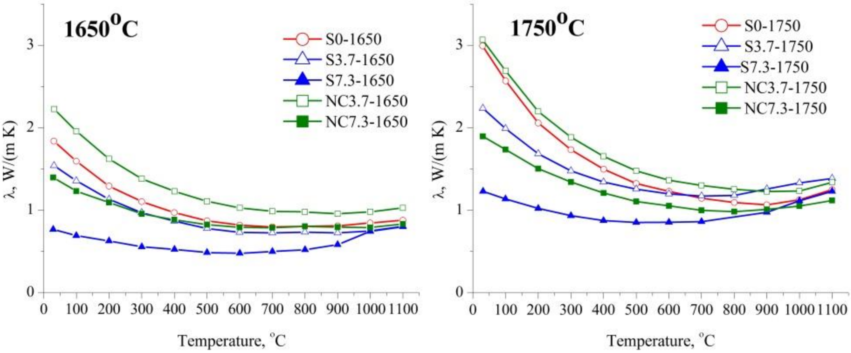


Fig. 15 Thermal conductivity of the investigated samples

The effective TC of the materials depends on the porosity, the TC of the individual components, and the amount and distribution of the Al_2O_3, mullite and glassy phases. Considering that mullite has a lower TC than corundum, it was expected that addition of a MFA would decrease the TC of porous Al_2O_3-based ceramics. This assumption was confirmed only partly. In almost all cases, addition of micro-sized SiO_2 or nano-sized SiC reduced the TC of the material. The samples with S7.3 composition had the lowest TCs at both sintering temperatures. Exceptions were samples NC3.7-1650 and NC3.7-1750, where TC was higher than in samples S0-1650 and S0-1750. The presence of mullite did not compensate for the increase in TC caused by the microstructural differences between modified and unmodified Al_2O_3 ceramics.

According to the MIP results, the samples with S0, NC3.7 and NC7.3 compositions had the lowest pore volumes in the pore diameter range from 2 to 20 μm at both sintering temperatures. The pore size distribution in this diameter range mostly depended on the initial composition and was less affected by the sintering temperature. The SEM results likewise indicated that samples without MFAs and samples with nano-sized SiC additives had denser microstructures in comparison to samples with micro-sized SiO_2 added.

TCs of the studied materials slightly increased with increasing sintering temperature. Sintering at 1750°C increased the porous matrix densification, which was confirmed by the results of MIP, showing slight shrinkage at a higher sintering temperature. Sintering at 1750°C mainly decreased the volume of pores with a diameter smaller than 2 μm. These results explain why the samples sintered at 1750°C had higher TC.

The influence of composition on TC is more pronounced at lower temperatures. Differences between the thermal conductivity values of the materials with different compositions diminished with increasing TC measurement temperature. The TC decreased with increasing the measurement temperature up to 500°C–900°C (depending on the composition and sintering temperature), after which it started to slowly increase. This increase is associated with increased contribution of the radiation component of TC [10, 11].

Thermal shock resistance

The study evaluated the thermal shock resistance (TSR) of compositions S0, S3.7, S7.3, NC3.7, and NC7 sintered at 1750°C. The NC series (modified with SiC nanopowder) was chosen, because sample NC3.7-1750 had the optimal combination of mechanical strength and apparent porosity. For comparison, the author chose the samples modified with amorphous micro-sized SiO_2, because these materials had lower TCs than the materials of NC series. The TSRs of the investigated materials were compared by means of the relative elastic modulus:

$$E_{relat} = \frac{E_i}{E_0} \cdot 100\%, \qquad (2)$$

where E_i stands for an acoustically determined elastic modulus after the *i*th thermal shock cycle and E_0 – for an acoustically determined elastic modulus before the thermal shock.

The elastic moduli of the samples modified with plasma-synthesised SiC (NC3.7-1750 and NC7.3-1750) was least affected by the thermal shock. In the case of NC7.3-1750, the elastic modulus even slightly increased after the first thermal shock cycle (Fig. 16). The relative elastic modulus of samples S0-1750, S3.7-1750 and S7.3-1750 after the first thermal shock cycle decreased by 2.9-4.4 percentage points (pp) and continued decreasing steadily with further thermal shock cycles. Taking into account the ±1 standard deviation, the highest decrease after the first thermal shock cycle was 3.4-8.4 pp. After the twelfth cycle, no elastic modulus of any sample decreased by more than 6 pp (10 pp taking into account the ±1 standard deviation) in comparison with its value before the thermal shock.

Implicit information about the TSRs of the studied materials can be obtained by comparing the standard deviations of the relative elastic modulus. The highest standard deviation of the relative elastic modulus was detected in samples S7.3-1750 and S3.7-1750; the lowest – in S0-1750, NC7.3-1750, and NC3.7-1750. This is related to different quantities of cracks formed during the thermal shock. According to the results shown in Fig. 16, the level of damage in samples S0-1750, S3.7-1750, S7.3-1750, and NC3.7-1750 remained relatively constant. Supposedly, the porous microstructure hindered further propagation of cracks. The standard deviation of the elastic modulus of NC7.3-1750 slightly increased after four thermal shock cycles and remained almost constant up to the twelfth cycle, which indicates the formation of cracks and stabilisation of their propagation.

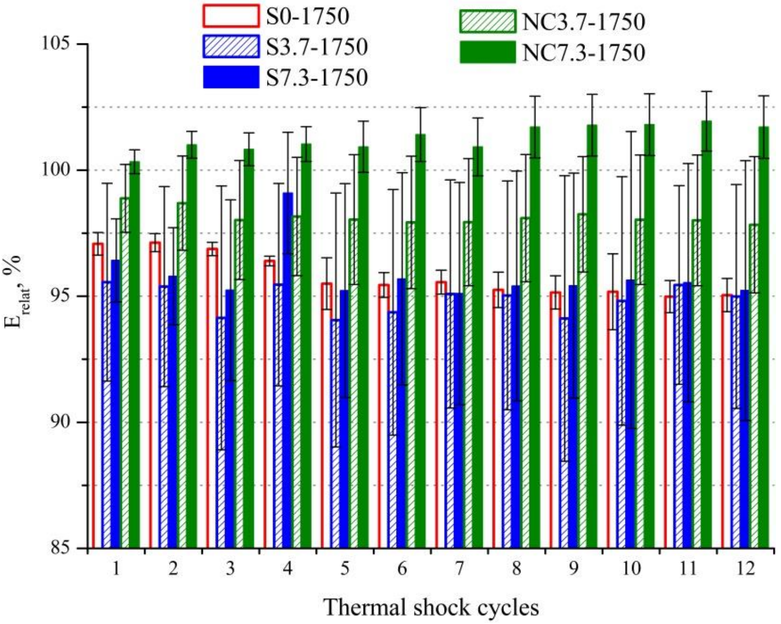


Fig. 16 Relative elastic moduli of the investigated samples after thermal shock cycles (error bars represent the ±1 standard deviation)

Specimens of samples S0-1750, S7.3-1750, and NC7.3-1750 after twelve thermal shock cycles were analysed by SEM. There were no obvious changes in the microstructure after the twelve cycles, with the exception of presence of some cracks. After the thermal shock, mainly transgranular cracks were observed in sample S7.3. There were fewer cracks in the specimens with the S0 and NC7.3 compositions than in sample S7.3, and it was relatively difficult to notice them. This is consistent with the standard deviation data (Fig. 16). The TSRs of the investigated materials were more affected by their microstructure (dependent on the MFA used) than by the presence of mullite, which, according to the literature [6, 12], improves the TSR of Al_2O_3 ceramics. The decrease in the elastic modulus after the thermal shock and the standard deviations of the relative elastic moduli of S3.7-1750 and S7.3-1750 were much higher than those of S0-1750, NC3.7-1750, and NC7.3-1750.

The improved TSRs of the samples modified with nano-sized SiC in comparison with the samples modified with micro-sized SiO_2 can be explained by a more homogeneously distributed mullite phase in the SiC sample series. This thesis was validated by the EDS results. The EDS mapping showed that the areas containing silicon (Si) atoms (and thus the mullite phase) in sample S7.3-1750 were more unevenly distributed than in sample NC7.3-1750 (see Fig. 13 and Fig. 14 on page 24). The materials modified with SiC nanopowder had a slightly higher bending strength and lower linear thermal expansion coefficient (α) compared to corundum ceramics without addition of MFAs (see Table 3). This, in accordance with the TSR parameter R' introduced by Hasselman [13], explains why the compositions of the NC series had better TSRs than that of sample S0-1750. This parameter defines the critical temperature difference at which the tensile stress imposed on the surface of the material is equal to the fracture stress (σ_f):

$$R' = \Delta T_C = \frac{\sigma_f(1-\nu)}{E\alpha}\lambda, \tag{3}$$

where ν is the Poisson's ratio, λ – thermal conductivity, E – the elastic modulus, and α – the linear thermal expansion coefficient.

Table 3

Bending strength, linear thermal expansion coefficients, and thermal conductivity of the samples tested for thermal shock resistance

Sample	**σ_B, MPa**	**α, $10^6 \cdot °C^{-1}$**	**$\lambda_{30°C}$ ($\lambda_{1000°C}$), W/(m·K)**
S0-1750	3.2±0.6	9.4	2.99 (1.13)
S3.7-1750	4.2±0.5	9.7	2.24 (1.33)
S7.3-1750	2.1±0.2	9.4	1.23 (1.12)
NC3.7-1750	9.3±0.3	9.2	3.07 (1.23)
NC7.3-1750	4.7±0.4	8.4	1.90 (1.05)

Porosity has a significant impact on the TSR of porous ceramics. Pores hinder crack propagation, and therefore the ceramic material does not collapse so fast even despite the micro-heterogeneities formed during the production of the material or because of sharp temperature fluctuations. Although the fracture toughness of the studied materials was not determined, it was presumed that their structure (presence of pores and particles of various sizes, shapes, and orientations) impedes crack propagation, thus hindering the collapse of the materials as a result of the thermal shock.

CONCLUSIONS

1. Highly porous Al_2O_3 and Al_2O_3-mullite ceramics with improved mechanical and thermal properties were produced by using pore formation via chemical reaction in the mix of suspended raw materials.
2. Crystallisation of secondary mullite occurs on the corundum grain surface during thermal treatment when a definite amount of mullite-forming additive (amorphous micro-size SiO_2, nano-sized SiC, Si_3N_4 or Si_3N_4-Al_2O_3-Y_2O_3) is added to the mixture of γ and α-Al_2O_3.
3. Crystallisation of mullite on the corundum grain surface slightly increases the specific surface area of the studied Al_2O_3-mullite ceramics sintered at 1650°C.
4. The mechanical properties of porous Al_2O_3 ceramics are improved most effectively by addition of 3.7 eqv. wt% of nano-sized SiC, Si_3N_4, and Si_3N_4-Al_2O_3-Y_2O_3. The positive effect decreases with increasing the amount of additive up to 7.3 eqv. wt%, because of increase in the amount of a glassy phase on the grain boundaries.
5. Formation of mullite increases the bending and compressive strengths of the material compared with unmodified corundum ceramics. The highest increase of the bending strength is manifest in samples with addition of 3.7 eqv. wt% of nano-sized Si_3N_4-Al_2O_3-Y_2O_3 (increase of the bending strength by 197-243%) and 3.7 and 7.3 eqv. wt% of nano-sized SiC (increase of the bending strength by 136-190%).
6. Results of the bending and compression tests and mercury intrusion porosimetry indicate that samples with a smaller volume of pores with diameter in the range of ~3-30 μm have higher mechanical strength.
7. Presence of Y_2O_3 in the additives used for production of highly porous Al_2O_3-mullite ceramics is not recommendable, because it increases the density and decreases the porosity of the material.
8. Crystallisation of secondary mullite decreases the thermal conductivity of the studied materials in comparison with unmodified ceramics; however, the influence of the initial composition decreases with increasing the thermal conductivity measurement temperature. The S7.3-1650 samples modified with 7.3 wt% of amorphous micro-sized SiO_2 (0.77 W/(m·K) at room temperature had the lowest thermal conductivity.
9. Thermal shock resistance of the studied materials is affected by their microstructure and the presence of mullite phase and its distribution in the corundum matrix, which, in turn, is affected by the mullite-forming additive used. Al_2O_3 ceramics modified with addition of 7.3 eqv. wt% of nano-sized SiC and sintered at 1750°C retained the initial mechanical strength after twelve thermal shock cycles.

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