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Thermal conductivity and microstructure characterisation of lightweight alumina and alumina–mullite ceramics

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ABSTRACT

The thermal conductivity of lightweight alumina and alumina–mullite ceramics produced by slip casting and chemical foaming has been measured as a function of temperature in the range from room temperature to 1100 °C by the laser flash technique. The microstructure of the studied materials was analysed by scanning mercury intrusion porosimetry, electron microscopy, and micro-computed tomography. Ceramics was fabricated by slip casting. Pores were formed by aluminium reacting with water. Micro-sized SiO_2 and plasma-synthesised SiC nanopowder were used as silica sources. The thermal conductivity of the investigated ceramics was in the range from 0.8 to 3.1 W/(m K), depending on the sintering temperature (1650 °C and 1750 °C) and amount of added SiO_2 source.

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1. Introduction

Highly porous alumina (Al_2O_3) ceramics (porosity > 50%) plays a significant role in various fields of engineering by virtue of its high thermal and chemical durability and unique properties owing to the high porosity, i.e. permeability of gases and liquids, good adsorption properties, and low thermal conductivity. Modification of Al_2O_3 with mullite allows to reduce the density of the material [1] and in some cases improves the mechanical properties and thermal shock resistance [2,3]. Porous Al_2O_3 and Al_2O_3-mullite ceramics have a potential application as high-temperature heat insulating materials. The effective thermal conductivity is an important property characterising the heat-insulating materials. The effective thermal conductivity of a polycrystalline material depends on three main factors: the intrinsic thermal conductivity, the thermal resistance due to interfaces called grain boundaries, and the presence of pores [4].

The effect of porosity on the thermal conductivity of lightweight corundum ceramics has been studied by Skidan and Borisov [5]. They examined lightweight corundum heat insulators of different total porosities (from 79.4 to 93%). It was established that materials of different porosity differ in absolute thermal conductivity while retaining similar temperature dependence.

Thermal conductivity of dense α-Al_2O_3 at 20 °C is ca. 30 W/m K [6]. The value of the thermal conductivity of porous Al_2O_3 and Al_2O_3-mullite composite ceramics is noticeably affected by the microstructure, porosity, pore shape and orientation, and pore size distribution, which can be adjusted by the fabrication method [7]. Delbrücke et al. fabricated porous Al_2O_3 ceramics with porosity of 40.7% and thermal conductivity of 1.63 W/(m K) by biotemplating cotton fibres. Samples were sintered at 1600 °C [8]. Skidan and Borisov reported about Al_2O_3 ceramics with thermal conductivity of ca. 0.3–1.0 W/(m K) at room temperature [5]. Nait-Ali and co-workers, using commercial Al_2O_3 and polymer as pore-forming agent, studied Al_2O_3 ceramics with a porosity of 40–75% and thermal conductivity in the range of 0.8–9 W/(m K). Samples were sintered at 1400 °C [9]. Zivcova and co-workers, using commercial Al_2O_3 and another polymer as a pore-forming agent, conducted a study on the thermal conductivity of Al_2O_3 with a porosity of 6.0 to 46.5%. The thermal conductivity of these ceramics was in the range of ~7–29 W/(m K) at room temperature. Samples were sintered at 1570 °C [10]. Shimizu et al. fabricated Al_2O_3 refractory bricks with 90–97.5% porosity by a slurry gelation and foaming method. Samples were sintered at 1500 °C. The thermal conductivity of these

materials was in the range of 0.1–0.4 W/(m K) at room temperature [11].

To our knowledge, there are only a few papers on the thermal conductivity of porous corundum–mullite ceramics. Thermal conductivities in the alumina–mullite system has been studied by Kingery and Shakhtin et al [12,13]. Kingery reported that the thermal conductivity of the composite material decreases with increasing the fraction of mullite up to 90 wt%. The decrease in the thermal conductivity is mostly related to the formation of flat grain-boundary cracks due to internal stresses which are caused by different linear expansion coefficients of alumina and mullite (between 20 °C and 1000 °C 8.6×10^{-6} °C^{-1} and 5.3×10^{-6} °C^{-1} respectively). It was suggested that the thermal conductivity in this system is dependent on previous fabrication history.

The aim of the present work was to investigate the effect of the silica source (micro-sized SiO_2 and nano-sized SiC) on the thermal conductivity of porous alumina–mullite ceramics in comparison with porous Al_2O_3 ceramics fabricated by chemical foaming of slurry. The added or in situ formed SiO_2 reacted with Al_2O_3, forming mullite ($3Al_2O_3 \cdot 2SiO_2$) as a result. The investigated materials were produced by chemical foaming of slurry, which is similar to the aerated concrete technology and has been described previously [14]. Pores form as a 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, Germany) and γ-Al_2O_3 (d_{50} = 80 μm, Nabalox NO 201, Nabaltec AG, Germany) in the mass ratio of 1:3. Chemically pure amorphous SiO_2 (d_{50} = 3.7 μm, Reachim, Russia) and crystalline plasma-synthesised SiC nanopowder (d_{50} = 80 nm, Plasma & Ceramic Technologies Ltd. Latvia) were used as SiO_2 sources. The pore-forming agent was aluminium paste with solid content 70 ± 2% (d_{50} = 12 μm, Aquapor-9008, Schlenk Metallic Pigments GmbH, Germany). The 1% solution of carboxymethyl cellulose sodium salt (CMC) (Optapix C 1000 G, Zschimmer & Schwarz GmbH & Co. Germany) was used as a binder. SiO_2 source was added in the amount equivalent to 3.7 and 7.3 wt% of SiO_2 (hereinafter in the text—eqv. wt%). Mass of SiC was calculated assuming that SiC fully oxidizes into SiO_2 via the passive oxidation mechanism [15].

The scheme and details of the sample preparation are described elsewhere [3]. 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 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.

2.2. Determination of the total linear shrinkage, bulk density, open porosity, mercury intrusion porosity, specific surface area, pore volume distribution, strut size, cell size, and 3D microstructure

The total linear shrinkage was determined by the equation $100\% \times (l_0 - l)/l_0$, where l_0—length of the inner dimension of the mould, l—length of the corresponding outer dimension of the sintered sample. The bulk density was determined by dividing a geometrically measured volume of the sample with its mass. The open porosity was tested using the water immersion method based on the Archimedes law. The total porosity and closed porosity were calculated from the bulk density, true density, and water absorption data. The true density of the materials was evaluated by means of a water pycnometry according to ASTM C135–96(2015). Mercury intrusion porosimeter (PoreMaster 33, Quantachrome Instruments, USA) was used to determine the mercury intrusion porosity, specific surface area, and pore volume distribution.

The samples were scanned by a high resolution micro-computed tomograph (μCT) using a Skyscan 1172 (Skyscan B.V., Kontich, Belgium) with an 11 Megapixel detector. The X-ray tungsten tube was operated at a voltage of 80 kV and a current of 100 μA using an Al 0.5 mm source filtering. The scan was performed with a rotation step of 0.25° over 360° with a resolution of 4.47 μm/voxel. The measured raw data sinograms were reconstructed with the tomographic reconstruction software (NRecon Client and Server 1.6.9.3 with GPU support, Skyscan, Kontich, Belgium), which calculates the two-dimensional (2D) cross-sections after adjusting grey value levels. The 3D visual images were generated using the imaging software (Amira 5.5.0, Visage Imaging, Berlin, Germany) after labelling with a global threshold and using a 26-side growing algorithm on all layers. Cell size and strut thickness was calculated by a CT-Analyser (1.1.13, Skyscan B.V., Kontich, Belgium) using a volume-based approach. The mean cell and mean strut sizes were calculated from the cell and strut size distribution derived from the μCT measurements averaged on the quantity of struts and cells belonging to one size range. In determining the cell and strut distribution, the first step was the binarisation of μCT images based on a given threshold. After the skeletonisation step, the cell and strut size distribution was determined by spheres fitting along the distance path.

The microstructure of the samples was additionally analysed by a Schottky Field Emission scanning electron microscope (Nova NanoSEM 650, FEI Company, Eindhoven, The Netherlands) on cut surfaces sputtered with Cr.

2.3. Determination of the phase composition

The phase compositions of the fabricated materials were characterised by X-ray diffraction (XRD; Rigaku Ultima+, Japan) with Cu Kα radiation. Voltage on Cu anode −40 kV, current intensity −20 mA, range of measurement angle −6 to 60 2θ degrees, goniometer speed −2°/min. The semi-quantitative XRD analysis was done by the Rietveld method [16]. using the EVA 3.0 software (Bruker AXS GmbH, Karlsruhe, Germany) and the fundamental parameter approach [17].

Table 1
Compositions of the investigated samples before sintering.

Denotation	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
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