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Influence of ZrO_2 and WO_3 doping additives on the thermal properties of porous mullite ceramics

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ABSTRACT

Porous mullite-corundum refractory ceramics were produced by a patented slurry slip casting method from compositions based on commercially available α-Al_2O_3 and γ-Al_2O_3, fused SiO_2 and kaolin. Pores were formed as a result of a chemical reaction of aluminium with water. The influence of usage of raw materials and doping additives such as micro-size ZrO_2 and WO_3 on the sintering temperature, formation of crystalline phases, linear thermal expansion, thermal conductivity and thermal shock resistance of mullite-corundum ceramic was studied. The best thermal shock resistance and, simultaneously, lower thermal conductivity was achieved for the samples doped with WO_3. This was due to the influence of micro-sized WO_3 on the change in γ-Al_2O_3 modification to α-Al_2O_3 and on the structure of mullite ceramics.

1. Introduction

In the last few years, great attention has been devoted to increasing the efficiency of raw material usage for the production of porous mullite ceramics, the reduction of energy consumption, which results in a decrease in the ceramic sintering temperature and the reduction of heat loss due to the use of refractory insulating materials with lower coefficients of thermal conductivity [1–3]. A mullite and mullite-corundum ceramics have been used as a high-temperature thermal insulating ceramics. The ceramics have such disadvantage as relatively low thermal shock resistance. One of the ways to increase the resistance to the rapid temperature change of the dense mullite ceramics is the use the different additives such as Sm_2O_3 [4], La_2O_3 [5] and Na_2O [6]. However, the usage of these metal oxides is not suitable for porous mullite ceramics due to the formation of the liquid phase at the sintering time. Also, Li et al. [7] reported, that addition of aggregates with specific shape, such as alumina bubbles with hollow structure, can improve mullite castables. In this case, the thermal shock resistance and mechanical properties of such ceramics are improved, but the appropriate amount of alumina bubbles increases the bulk density and decreases the apparent porosity of ceramics. The increased bulk density and decreased porosity have the negative impact on the properties of porous lightweight mullite ceramics. Kong L.B. with colleagues [8] assumed that WO_3 additive acted as heterogeneous centres for mullite nucleation into the Al_2O_3 and SiO_2 system and influenced on the mullite whiskers morphology. The influence of WO_3 additive on the thermal properties of the porous mullite ceramics is not enough researched. In our previous research, attention was paid to the influence of kaolin as a raw material [9] and the use of MgO, ZrO_2 and WO_3 doping additives on the bulk density, shrinkage, porosity, bending strength and sintering temperature of mullite ceramics [10]. The results demonstrated that the use of kaolin reduces the amount of commercial α-Al_2O_3 and γ-Al_2O_3 which are necessary for the production of such materials. A relatively pure mullite phase was achieved by the use of 10–30 wt% of kaolin and sintering the samples at 1750 °C, due to the reactions between all components. Shrinkage and bulk density of the investigated mullite ceramic was increased, but porosity was decreased due to the increase of kaolin content from 10 to 30 wt% [9]. The use of 5 wt% metal oxides for doping of mullite ceramics obtained from raw materials mixed with 30 wt% kaolin allowed a decrease in the sintering temperature from 1700–1750°C to 1500°C (in the case of MgO and WO_3) and to 1650 °C for ZrO_2-doped samples. The highest porosity (42%) was achieved for the samples that were doped with WO_3. Compared with the undoped samples sintered at 1750 °C, the shrinkage and bulk density of the doped samples decreased after the use of WO_3 doping additive and sample sintering at 1500 °C, respectively from 24 ± 1% to approximately 5 ± 1% and from 1.70 ± 0.05 g/cm^3 to 1.29 ± 0.05 g/cm^3 [10].

The novelty of the present work is the investigation of the influence of WO_3 and ZrO_2 additives on the thermal expansion, thermal conductivity and thermal shock resistance of the porous mullite ceramics.

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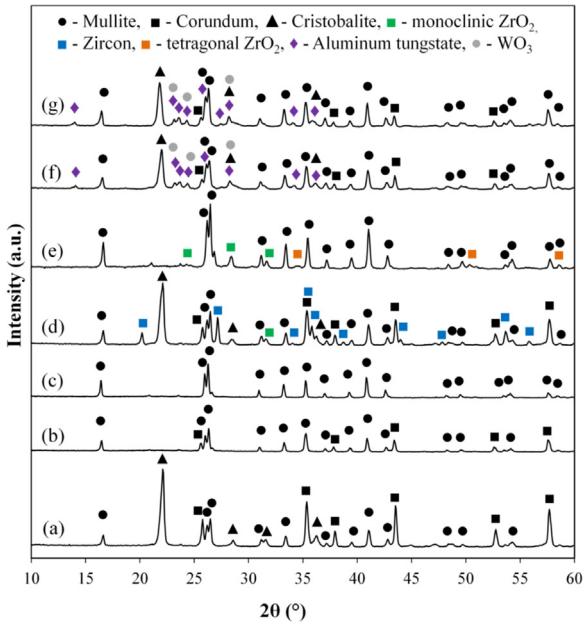

Fig. 1. XRD patterns of the undoped samples sintered at (a) 1500 °C, (b) 1650 °C, (c) 1750 °C; ZrO_2-doped samples sintered at (d) 1500 °C and (e) 1650 °C; WO_3-doped samples sintered at (f) 1400 °C and (g) 1500 °C.

2. Materials and methods

2.1. Raw materials and sample preparation

Commercially available α-Al_2O_3 (d_{50} = 2 μm, Nabalox NO 725, Nabaltec AG) and γ-Al_2O_3 (d_{50} = 80 μm, Nabalox NO 201, Nabaltec AG) and chemically pure amorphous SiO_2 (d_{50} = 6.9 μm, Реахим) and kaolin (d_{50} = 1.5 μm, Al_2O_3 = 31.5wt% and SiO_2 = 56.2wt% MEKA, Amberger Kaolinwerke) were used as the raw materials. In all compositions the ratio of commercial Al_2O_3 to SiO_2 was 2.57:1, which corresponded to the mullite stoichiometric composition $3Al_2O_3{\cdot}2SiO_2$. The ratio of γ-Al_2O_3 to α-Al_2O_3 was 3:1. The basic composition of undoped ceramics was selected from previous works [9,10] and contained 30 wt % kaolin. Metal oxides such as ZrO_2 partially stabilized by 10 wt% of MgO (d_{50} = 0.9 μm, Raushert, written in the text below as ZrO_2) and WO_3 (d_{50} = 7 μm, Реахим) were used as doping additives in the amount of 5 wt%. Aluminium paste (0.18 wt%) with a solid content of 70 ± 2% (Aquapor-9008, Schlenk Metallic Pigments GmbH) (mean particle diameter, 12 μm) was used to prepare porous ceramic. Water content was 38–40 wt%. The prepared samples were sintered at the corresponding temperatures for the investigation of the properties of these ceramics: undoped samples at 1500 °C, 1650 °C and 1750 °C; ZrO_2-doped samples at 1500 °C and 1650 °C and WO_3-doped samples at 1400 °C and 1500 °C.

Porous mullite ceramics were formed by slip casting a concentrated slurry of raw materials. The porosity of the samples obtained was due to hydrogen gas evolution as a result of the reaction between aluminium paste and water. The patented method includes six main stages: 1. the dry mixing of raw materials; 2. the preparation of the homogenised suspension of raw materials with distilled water; 3. the mixing of the dispersed aluminium paste with the homogenised suspension of raw materials; 4. the slip casting of homogenised suspension into polyurethane moulds; 5. the slow drying and solidification (T = 50 °C for 24 h); 6. the sintering of the samples (heating rate, 250 °C/h (4.2 °C/min); holding time at a maximum temperature, 1 h). The sintered materials were cut into bars (150 × 20 × 20 mm) for further testing. The method and process of sample preparation was described in more detail in previous articles [9–11].

2.2. Characterisation

The phase composition of the obtained samples was characterised by X-ray diffraction (XRD, Rigaku Ultima + , Japan) with Cu K_a radiation and a goniometer scanning speed of 2°/min. The voltage on the Cu anode was 30 kV, the current intensity was 20 mA and the range of measurement angle was 5–60 2θ°. The microstructure of samples was observed by scanning electron microscopy (SEM; Hitachi TM3000, Japan) and high-resolution SEM (FEI Nova NanoSEM 650, Netherlands). The cross-sections of samples with dimension of 1 cm × 1 cm were analysed in all SEM investigations. The preparation of the samples for the SEM investigation involved the specimen mechanical cutting from material volume and blowing by air to remove possible small material particles that could appear during cutting. The metal sputtering was not carried out. The elemental composition of samples was measured using energy-dispersive X-ray spectroscopy (EDX) with an X-ray fluorescence spectrometer (Apollo X SDD) created by TEAM™ Integrated EDX. The linear thermal expansion coefficients of the samples were determined by a horizontal dilatometer L76/1600D in the temperature range from 20 °C to 1300 °C. The determination of apparent porosity was based on the Archimedes principle according to the European standard EN 623-2. A mercury porosimeter (Quantachrome, Pore Master 33, USA) was used to determine the pore size distribution. The thermal conductivity of the mullite ceramics was determined by the laser flash contactless method using the universal

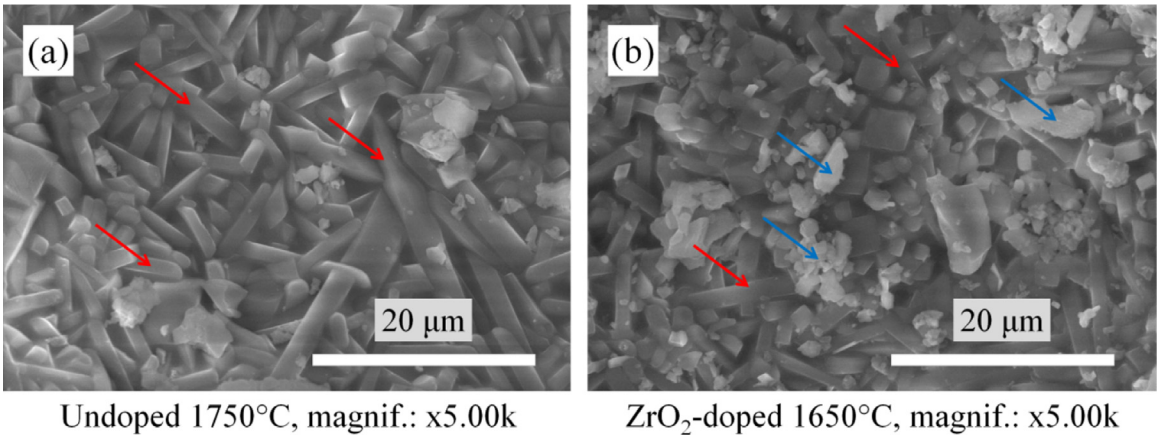

Fig. 2. SEM micrographs of the microstructure of the sintered samples cross-section: (a) undoped sample sintered at 1750 °C; (b) ZrO_2-doped sample sintered at 1650 °C; red arrows denote mullite crystals, blue arrows denote ZrO_2 crystals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).