



Mullite-based cellular ceramics obtained by a combination of direct foaming and reaction bonding

Thomas Konegger*, Ruth Felzmann, Birgit Achleitner, Dominik Brouczek

Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164-CT, 1060 Vienna, Austria

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Abstract

Mullite-based cellular ceramics were prepared *via* the polymer precursor route using poly(silsesquioxane) in combination with particulate alumina or alumina/aluminum mixtures. The multi-functional preceramic polymer was used as pore-forming agent by employing a self-foaming process during the polymer cross-linking step, as well as a precursor for reactive silica, one of the reagents in mullite formation. The size of filler particulates was found to strongly affect foaming of the polymer/filler mixtures, with coarser particles facilitating an improved foaming performance. Thermal conversion in air at 1600 °C resulted in the formation of cellular ceramics with high mullite contents. The partial substitution of alumina with aluminum in the initial mixtures resulted in improved mechanical properties at comparable porosities, resulting in compressive strengths of 0.3 MPa at total porosities of 93%. A correlation between thermal analysis data and crystalline phase development during the thermal treatment allowed for the clarification of processes taking place during heat treatment, yielding information for a future process optimization approaches.

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1. Introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is a structural ceramic material commonly used in high-temperature applications owing to its unique thermal and mechanical properties. A low coefficient of thermal expansion in combination with low thermal conductivity and high creep resistance as well as suitable mechanical properties at high temperatures have led to the use of mullite-based materials for a wide variety of both traditional and advanced ceramic applications [1,2].

As an alternative to conventional powder-based production techniques, the use of Si-based preceramic polymers in combination with Al_2O_3 or Al fillers has been suggested for the production of mullite-based ceramics [3–6]. A general, inherent advantage of the polymer route for the production of ceramics is the wide variety of forming techniques due to the polymer nature before thermal polymer-to-ceramic conversion [7]. Furthermore, a

thermo-oxidative degradation of the polymer compound yields highly reactive amorphous silica, thus effectively reducing the temperature necessary for mullite formation. Even lower mullite formation temperatures were achieved by using nano-scaled Al_2O_3 fillers [8].

In the past years, the polymer precursor route has been increasingly considered for the formation of cellular ceramic structures [9–11]. Cellular ceramics enable further improvement of properties relevant to applications at high temperatures, including improvement of the thermal shock behavior or thermal insulation [12]. The generation of cellular structures from polymer precursors can either be obtained by application of a blowing agent [13], by *in-situ* foaming of the precursor component [14], or by the use of sacrificial fillers within the polymer-containing initial mixture [15]. Following these concepts, a combination of polysiloxanes with Al_2O_3 and sacrificial fillers yielding cellular mullite has first been reported by Kim et al. [16].

In this contribution, we present the generation of cellular mullite employing Si-based polymer compounds with multi-functionality, acting as foaming agent, matrix material, and

*Corresponding author. Tel.: +43 1 58801 16161; fax: +43 1 58801 16199.
E-mail address: thomas.konegger@tuwien.ac.at (T. Konegger).

reagent in combination with particulate Al_2O_3 as well as an active Al filler within a single processing routine. Pore generation is accomplished by an *in-situ* foaming process, taking place during the cross-linking of the preceramic poly(silsesquioxane) polymer, a technique developed and extensively studied by Greil and co-workers [14,17–19]. By expanding on initial reports showing the formation of mullite when introducing particulate Al_2O_3 to this preceramic polymer [14,20], our investigations are focused on the identification of relevant parameters influencing the final product as a result of the strong correlation between foaming behavior and starting materials, aiming towards homogeneous pore structures and high mullite yields. Another closely related goal is the clarification of the thermal conversion process leading to the formation of mullite and, subsequently, the preservation of the structural and mechanical features established during the initial foaming step.

2. Materials and methods

2.1. Pore generation by direct foaming

Direct foaming was accomplished by using a phenyl methyl poly(silsesquioxane) (PMPS; *Silres H44*, Wacker Chemie, Germany) with a nominal elemental composition of $\text{SiO}_{1.51}\text{C}_{4.03}\text{H}_{4.06}$ [18]. PMPS is solid at room temperature, and starts to form a viscous melt at around 60 °C. During a thermally-induced cross-linking starting at around 200 °C, condensation reactions between small amounts of hydroxy and ethoxy functionalities within the PMPS compound lead to the formation of water or ethanol, effectively acting as *in-situ* foaming agents within the viscous polymer melt. Further cross-linking of the obtained cellular matrix leads to the formation of a stable, porous thermoset [17].

As fillers, particulate Al_2O_3 with two distinct particle sizes (fine: *CT 3000 SG*, $d_{50}=0.7\ \mu\text{m}$; or coarse: *CT 1200 SG*, $d_{50}=1.3\ \mu\text{m}$; both from Almatix, Germany) and Al (*DG38*, $d_{50}=15\text{--}20\ \mu\text{m}$; Ecka Granules, Germany) were used.

For the preparation of cellular mullite from PMPS and Al_2O_3 , relative amounts of educts were chosen in order to yield stoichiometric mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) after total oxidation. Preliminary investigations of the thermal conversion of PMPS in air showed a SiO_2 yield of 51% after heating to 1000 °C. For the samples containing Al in addition to PMPS and Al_2O_3 , the ratio of PMPS to particulate fillers was slightly lower in order to account for the difference in PMPS volume fraction and to allow for a comparable foaming behavior. The compositions used are listed in Table 1.

The mixtures of PMPS and fillers were homogenized in a tumbler mixer for 1 h. For a typical sample, 50 g of the obtained powder was filled into an aluminum sleeve (diameter 50 mm, height 140 mm). After a thermal preconditioning to improve the foaming characteristics of two of the mixtures (4 h at 100 °C for PMPS/ Al_2O_3 -f, and 1 h at 200 °C for PMPS/ Al_2O_3 /Al), the container was put into a preheated furnace at 270 °C in air for a duration of 4 h in order to obtain the porous thermoset.

Information about the impact of the Al_2O_3 particle size on the cross-linking and foaming behavior of PMPS was gained by thermogravimetric investigations of the PMPS/filler mixtures up

Table 1
Sample compositions, in wt%.

	PMPS/ Al_2O_3 -f	PMPS/ Al_2O_3 -c	PMPS/ Al_2O_3 /Al
PMPS	43.5	43.5	47.2
Al_2O_3 ($d_{50}=0.7\ \mu\text{m}$)	56.5	–	–
Al_2O_3 ($d_{50}=1.3\ \mu\text{m}$)	–	56.5	34.5
Al ($d_{50}=15\text{--}20\ \mu\text{m}$)	–	–	18.3

to a temperature of 300 °C (10 K min^{-1} , flowing Ar; *TG 209 F3 Tarsus*, Netzsch, Germany).

2.2. Formation and characterization of cellular ceramic foams

The porous thermosets were cut into block-shaped specimens (typical dimensions: $35 \times 35 \times 25\ \text{mm}^3$) using a diamond cut-off wheel. Ceramization was conducted in a box furnace in air. The heat treatment involved an initial heating step to 1200 °C with a heating rate of 1 K min^{-1} and a 2 h hold. Subsequently, the system was heated to 1600 °C with a heating rate of 1 K min^{-1} and held at this temperature for 4 h before cooling.

After heat-treatment, the bulk density ρ was calculated from the weight-to-volume ratio of the block-shaped specimens. The porosity Φ of specimens was calculated following the relation $\Phi=1-(\rho/\rho_{th})$, assuming a theoretical density $\rho_{th}=3.2\ \text{g cm}^{-3}$, ρ_{th} being the density of mullite [2]. The microstructure was investigated by light-optical microscopy (*SteREO Discovery.V20*, Zeiss, Germany) as well as scanning electron microscopy (*Quanta 200*, FEI, the Netherlands).

The crystalline phase composition was determined by powder X-ray diffraction analysis (XRD) employing $\text{Cu K}\alpha$ radiation (*X'Pert Pro*, Philips, the Netherlands) after crushing the samples in a planetary ball mill. For selected samples, a quantitative estimation of the relative phase contents following Rietveld's method was carried out using the Topas software package (*Topas R 2.1*, Bruker, USA).

Al-containing specimens in cross-linked state were investigated by simultaneous thermal analysis including thermogravimetry and differential thermal analysis in flowing synthetic air up to 1600 °C (*STA 449C Jupiter*, Netzsch, Germany).

The compressive strength of block-shaped specimens (dimensions after ceramization: $30 \times 30 \times 15\ \text{mm}^3$) was determined with a universal testing machine (*Model 1474*, Zwick, Germany) with a cross-head speed of 0.5 mm min^{-1} . Before testing, the top and bottom sample surfaces were plane-parallelized by grinding with SiC paper.

3. Results and discussion

3.1. Influence of particulates on direct foaming process

In the PMPS system used, temperature-induced polycondensation reactions lead to the cross-linking of polymer chains and the evolution of gases responsible for foaming of the viscous

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