Polymer derived ceramic foams with additional strut porosity

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Ceramic foams with additional strut porosity were prepared by a self-foaming process of a polysilsesquioxane. The strut porosity was generated by adding sacrificial pore formers comprising of polymethylmethacrylate or of polyethylene to the self-foaming silicone. The polymer-inherent shrinkage was reduced by adding SiC particulate fillers to the silicone/pore-former mixture. Foaming was carried out on a preheated furnace at 270 °C, and subsequent pyrolysis was performed in argon atmosphere in the temperature range from 800 °C to 1200 °C in order to trigger the polymer-to-ceramic transformation of the polysilsesquioxane. The materials were characterized with respect to the pore size and the total porosity, the microstructure and the mechanical strength. The volumetric mean pore diameter of the strut ranged from 25 μm to 100 μm and the porosity was found to be 40% to 94%. The maximum compression strength exceeded 16 MPa.

Keywords: ceramic foams, preceramic polymers, self-foaming process, sacrificial pore formers

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1. Introduction

Due to their outstanding properties such as high porosity, low thermal conductivity, high permeability, high temperature stability, chemical inertness, excellent thermal shock resistance, low dielectric constant, etc., ceramic foams have gained increasing interest during the past fifteen years or so. Therefore, the foams are considered for a wide range of technological applications such as filters, membranes, absorbents, catalytic substrates, thermal insulation, gas burner media, refractory materials, lightweight structural panels, reinforcement for polymer or metal composites and biomedical devices [1–5]. Novel developments are dedicated to the manufacturing of high-transparent glass foams for optical applications such as biological cell support or support for photocatalysts [6, 7]. The most relevant processing routes for the fabrication of porous ceramics are (i) replica techniques [8–10], (ii) direct-foaming techniques [11–16] and (iii) sacrificial template methods [17–19].

In this work, SiC filled polymer derived ceramic foams with additional strut porosity were manufactured by the addition of polymethylmethacrylat (PMMA) or polyethylene (PE) as sacrificial pore formers to a polysilsesquioxane with structure terminating hydroxyl and ethoxy groups. When heat is applied in the temperature range between 220 °C and 300 °C condensation of the aforementioned functional groups occurs resulting in (i) the formation of water and ethanol, (ii) the formation of foam bubbles and (iii) the increase of the viscosity which actually prevents the foam from collapsing. As a result, a foamed thermoset silicone is obtained [12]. In contrast to previous work, in this work the foamed mixture comprises of the artificial burn-outs, additionally, which are more or less homogeneously distributed in the struts. The burn-out is intended to leave behind additional porosity in the struts.

2. Experimental procedure

Ceramic foam processing

A methyl phenyl poly (silsesquioxane) (general formula [(C$_6$H$_5$)$_{0.62}$(CH$_3$)$_{0.31}$(OR)$_{0.07}$SiO$_{1.5}$]$_n$ with $n{\sim}20$, Silres H44, Wacker Chemie, Burghausen, Germany) which contains additional cross-linking active groups R=[-OH] and [-OC$_2$H$_5$] was used as preceramic polymer [12, 13]. The polymer is solid at room temperature, has a melting interval at around 60 °C and exhibits a density of ~1 g/cm^3. The H44 was loaded with SiC (F800D, d$_{50}$ = 7,8–9,8 μm, ESK-SiC GmbH, Frechen, Germany). As sacrificial burn-out materials (strut-pore former) PMMA with a bead size of 50–150μm, an average molecular weight (M.W.) of 35,000 g/mol^{-1} and a density of ρ=1.2 g/cm^{-3} was used (Acros Organics, Geel, Belgium). The other pore former used in this work is ultra-high molecular weight polyethylene with three different particle size distributions (GUR®UHMW-PE,

GUR-X143 with d_{50}=20 μm, GUR-2126 with d_{50}= 30 μm and GUR-4150-3 with a particle size d_{50}=60 μm; density of all samples ρ=0.3 g/cm^{-3}; Ticona GmbH, Oberhausen, Germany).

The preceramic polymer:SiC filler:burn-out materials were dry mixed in a weight ratio of 54:36:10 in an overhead mixer with grinding balls for 2 h. The mixture was then filled in aluminum tubes and foamed at 270 °C for 2 h in air in a preheated furnace. The next step was sintering in a tube furnace in argon atmosphere. The foams were fired at a heating rate of 3 K/min^{-1} to 500 °C and hold for 2 h. Subsequently, the foams were further heated at 5 K/min^{-1} to 800 °C, 1000 °C or 1200 °C with a holding time of 2 h. The cooling rate to room temperature was set to 5 K/min^{-1}. After pyrolysis, the foams were cut with a low-speed saw. The diameter of the samples was 20 mm and the height 25 mm. A processing scheme is given in *Fig. 1*.
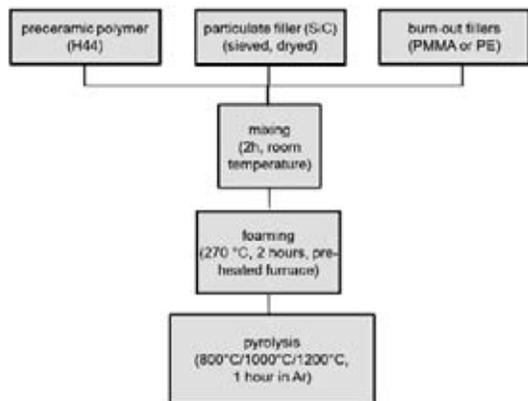

Fig.1. *Processing scheme of the manufacturing of polymer derived ceramic foams by a self-foaming process with additional burn-outs for strut porosity generation*
1. ábra *Polimer alapú kerámia habok előállításra szolgáló, a porozitás növelését célzó, járulékos kiégéssel kombinált önhabosodási eljárás folyamatsémája*

Characterization

Thermal analysis of the sacrificial templates as well of the samples was carried out with a STA 409 (NetzschGerätebau GmbH, Selb, Germany). The green material was heated with 5 K/min^{-1} to an end temperature of 1300 °C. The atmosphere was argon with a flow rate of 70 ml/min^{-1}. The foam morphology was characterized using scanning electron microscopy (SEM JSM-7000, EDX - JEOL Ltd. Tokyo, Japan). Prior to analysis the samples were sputter-coated with platinum.

Porosity and pore size distribution of the pyrolyzed foams was measured by Hg intrusion with a MicromeriticsAutoPore IV 9500 (Micromeritics Corporate Headquarters, Norcross, GA, USA). From selected samples microcomputertomography (μ-CT) was carried out to investigate the cell morphology of the macroscopic cells with a Skyscan 1172 (Skyscan, Kontich, Belgium).

The compressive strength was determined at room temperature with the cylindrical samples having a height of 25 mm and a diameter of 20 mm. A universal testing machine (Instron 4505, Instron, Norwood, MA, USA) was used with a constant crosshead speed of 1.5 mm/min^{-1}. From the maximum stress after elastic deformation the crushing strength of the foam was computed.

3. Results and discussion

Previous studies referring to synthesis parameters such as filler size, ratio of starting materials and foaming temperature showed a significant influence of these parameters on the effectiveness of the foaming process. The use of SiC filler particles with diameters of 0.6–0.9 μm, e.g., inhibits the foaming process. The obtained structures showed no macro porosity after the foaming procedure. To obtain foamed structures comparable to the unfilled system, filler particles with a particle size ranging from of 8 to 10 μm have been used. A preceramic polymer to filler ratio of 60:40 wt% showed good results in terms of foaming behavior. It was found that the maximum weight fraction of the sacrificial template should not exceed 10 wt% of the mixture. Especially in the case of PMMA a higher ratio led to an extremely high macro porosity with an inhomogeneous pore size distribution. Thus, foams were prepared with a polymer:SiC filler:burn-out template weight ratio of 54:36:10. X-ray diffraction analysis of foams pyrolysed up to 1200 °C showed no crystalline phases beside that of SiC which was introduced as filler particles to minimize shrinkage. Therefore the obtained silicon oxycarbide (SiOC) ceramic structures have been assumed to be amorphous. In accordance to results in the literature phase separation and crystallization occur at temperatures above 1200 °C [20].

Template	d_{50} of burn-out template in μm (manufacturers data)
PMMA	50 – 150 (bead size)
PE GUR-4150-3	60
PE GUR-2126	30
PE GUR-X143	20

Table 1. *Template sizes used to create additional strut porosity*
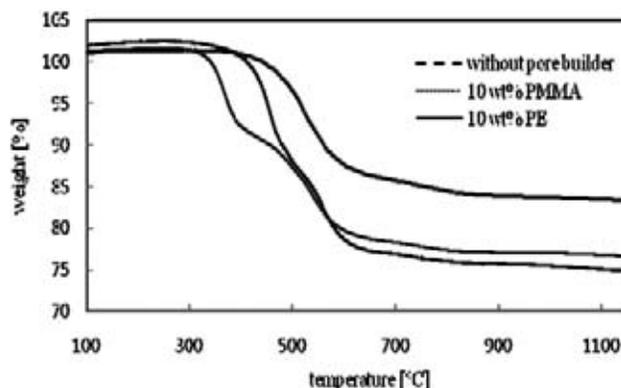*1. táblázat* *A növelt porozitás kialakításhoz használt sablonok*

Fig. 2. *Thermal gravimetric analysis of the as-synthesized foams*
2. ábra *Az eredetileg előállított habok termogravimetriás elemzése*

Foams with additional strut porosity were prepared by using distinct pore formers made up of polymethylmethacrylate (PMMA) microbeads or ultra-high molecular weight polyethylene grains (PE), respectively. In the latter case, three different particle sizes were used (see *Table 1*). Thermal gravimetric analysis in argon revealed a total weight loss > 98 wt% for both types of raw materials. The decomposition of PMMA

was found to start at about 280 °C and was completed at 440 °C, whereas all PE types decomposed identically in a temperature range from about 440 to 500 °C. *Fig. 2.* shows a comparison in weight loss for foams prepared with and without pore former materials pyrolysed in argon up to 1200 °C. The heating rates were set in correspondence to the sintering process. The weight loss of the pore former-free foam was about 17 wt%. Due to the removal of additional sacrificial templates, a higher weight loss of about 24% of the foam prepared with PMMA was found, whereas the total weight loss of PE containing foams was approximately 26 wt%. Presumably, this small difference occurs due to incipient burn-out of PMMA during the foaming process in combination with decomposition at lower temperatures as compared to PE burn-outs. In general, the weight loss for PMMA and PE containing samples is in good agreement with theoretical values taking into account the nearly complete decomposition of the burn-out materials.

The different foams prepared with and without the addition of the sacrificial templates were imaged after sintering in argon at 1000 °C using scanning electron microscopy. For the template-free approach (cf. *Fig. 3a.*), apart from the occurrence of cracks, large cells with dense struts were observed. As shown exemplarily in *Fig. 3b.* and *3c.*, the addition of pore formers led to an increased porosity in the struts. Detailed micrographs of the porous struts revealed that pore size and shape depend on the morphology of the sacrificial template. Large pores (i.e. spherical in shape) with diameters ranging from 40–150 μm are formed when PMMA microspheres were employed (see

Fig. 4a.). However, further observations within the pores depict small spheres of about 1–10 μm after burn out of the PMMA and sintering (cf. *Fig. 4b.*). EDX analysis revealed no difference in elemental distribution compared to the surrounding SiOC amorphous ceramic structure.

We assume that low-molecular weight components from the preceramic polymer have interacted with PMMA during the low-temperature thermal processing prior to foaming, and spheres have been formed during condensation and crosslinking resulting in the SiOC spheres as found in these samples. However, for a deeper understanding further investigations are necessary.

In comparison, the addition of smaller PE particles such as GUR-2126 resulted in an increased number of irregular formed strut pores with diameters varying from 8–35 μm (see *Fig. 4c.*). SEM analysis of pure GUR-2126 showed strongly aggregated and irregular formed particles in a similar size range as well. In general, after sintering the generated pore sizes are slightly smaller due to the shrinkage during polymer-to-ceramic conversion during pyrolysis.

Results from mercury intrusion porometry are shown in *Fig. 5.* Sintered samples formerly containing PMMA microbeads possess a volumic median pore diameter of about 100 μm, and a pore diameter of 9 μm was found in foams containing GUR-2126. Strut porosities of sintered foams derived from the PE types GUR-X143 and GUR-4150-3 were estimated to possess volumetric median pore diameters of 25 μm and 81 μm, respectively.
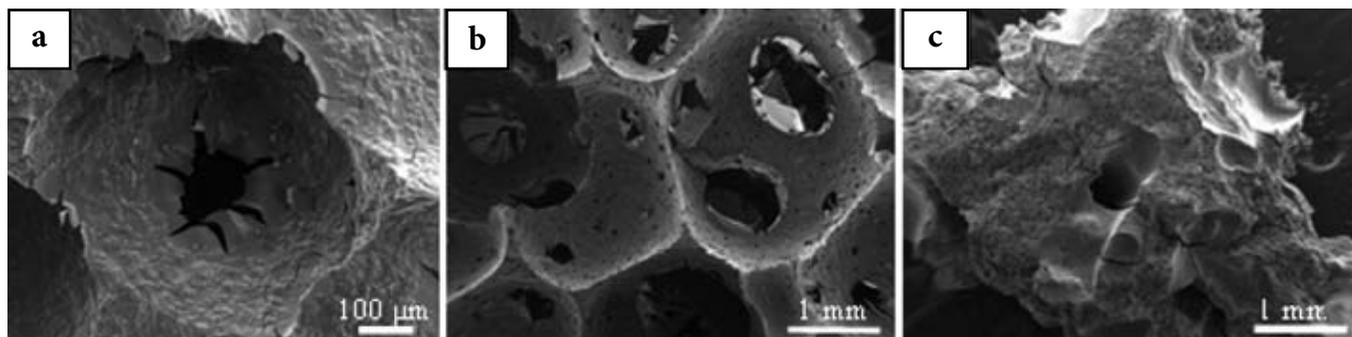

Fig. 3.   SEM micrographs of the foam obtained after pyrolysis in argon at 1000 °C. a) no additional pore builder, b) with PMMA, and c) with PE-GUR-2126
3. ábra   Az argonban, 1000 °C-on végzett pirolízissel készült habok SEM felvételei (a) további pórusképző nélkül, (b) PMMA-val és (c) PE-GUR-2126-tal
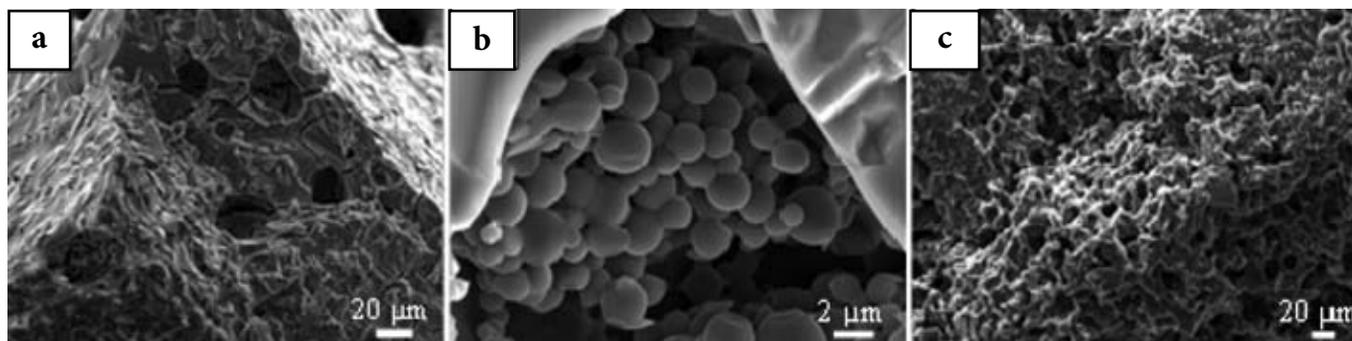

Fig. 4.   SEM micrographs detailed view of structures obtained after burn-out of template and pyrolyzed in argon at 1000 °C. a) Strut pores generated by PMMA, b) detailed view within a pore generated by PMMA c) porous strut generated by PE-GUR 2126
4. ábra   A sablon kiégése és az argonban, 1000 °C-on végzett pirolízis után kapott termékek mikroszerkezetét mutató SEM felvételek (a) a PMMA-val kialakított pórusok, (b) a PPMA-val kialakított pórusok részletes képe és (c) a PE-GUR-2126-tal kialakított pórusszerkezet
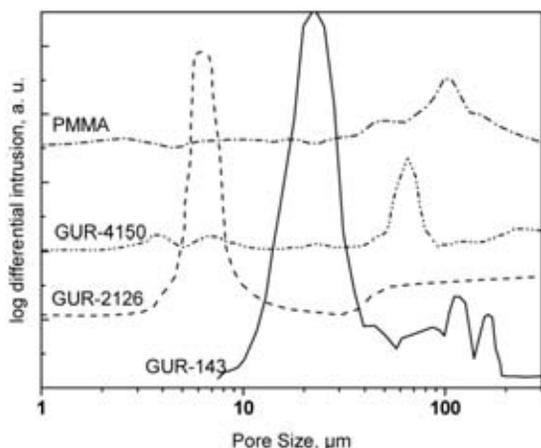
Fig. 5.   *Results of mercury intrusion for pore size distribution characterization of foams after pyrolysisat 1200 °C*

5. ábra   *Az 1200 °C-on végzett pirolízis után higanypenetrációs módszerrel meghatározott pórusméret eloszlás*

The influence of added sacrificial material on cell size distribution and total foam porosity was determined by Micro-CT-analysis (μ-CT). Since obtained cell sizes were inhomogeneously distributed within the macrostructure, the samples were taken from a central part of the foam where a better degree of homogeneity was obvious. *Fig. 6a–6c.* show 2D images of μ-CT layers of sintered foams prepared with PMMA microbeads and two selected PE types. The addition of large PMMA microbeads led to a low number of relatively large pores. A total foam porosity of 51% was calculated. A 3D reconstruction in two different resolutions is shown in *Fig. 6d, e.*
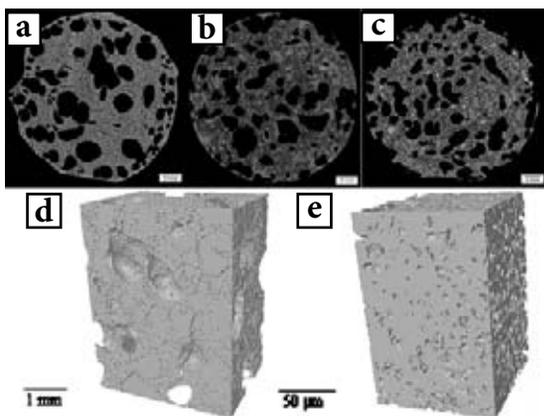
Fig. 6.   *2D μ-CT images of sintered foams. a) PMMA microbeads, b) PE GUR-4150-3, c) PE GUR-2126; d) 3D reconstruction foams cells with GUR-2126-generated strut porosity, e) 3D reconstruction of a porous strut in higher resolution*

6. ábra   *A szinterelt habok 2D μ-CT módszerrel felvett képei. a) PMMA mikrogyöngyök, b) PE-GUR-4150-3, c) PE-GUR-2126; d) PE-GUR-2126-tal kialakított pórusszerkezet 3D rekonstruált képe, e) a pórusos szerkezet 3D rekonstruált képe nagyobb felbontásban*

Regarding the PE templates, a decrease of the PE particle size resulted in a lower total foam porosity accompanied by the occurrence of smaller cell sizes. GUR-4150-3 derived foams showed a total porosity of 54%, whereas a porosity of 40% was measured using the PE template GUR-143-3 with the smallest particle sizes.

Compression tests of the different foams sintered in argon at temperatures from 800 to 1200 °C showed a stepwise crushing

behavior typical for ceramic foams. *Fig. 7.* shows exemplarily the stress-strain diagram for sintered foams prepared using the PMMA burn-outs. Compressive strength values of up to 12 MPa were obtained. This is in good agreement with data from literature [13]. In comparison, the compressive strength for foams prepared with PE increased with increasing burn-out grain sizes of the template up to values of 16 MPa using GUR-4150-3. However, an influence of the sintering temperature on the compressive strength was not detectable. Further investigations of template effects on formation of the macrostructure and total porosity are necessary.
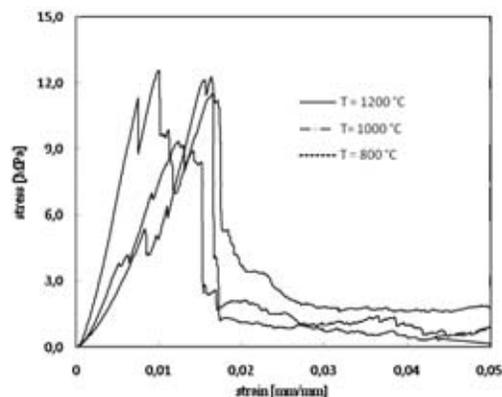

Fig. 7.   *Stress-strain diagram obtained from foams prepared with PMMA template and pyrolysis in argon at different temperatures*

7. ábra   *PMMA sablonnal, és argonban, különböző hőmérsékleteken végzett pirolízissel készült habok terhelés-feszültség görbéi*

Finally it should be noticed that the obtained total porosities of < 55% derived from foams prepared in small aluminum tubes are rather low. When foaming is carried out in large containment the coalescence rate of the foamed material is significantly lower resulting in a higher porosity, typically between 80 and 95%.

Fig. 8a. and *8b.* show 2D images of μ-CT of sintered foams produced in an aluminum tray of 10 by 15 cm in size without additional pore builder and with PMMA microbeads, respectively. Micro-CT calculations revealed a high total porosity of 90–94 % for both. Samples prepared with PMMA showed a better pore distribution within the macrostructure with struts equally distributed compared to samples prepared without additional pore builders.
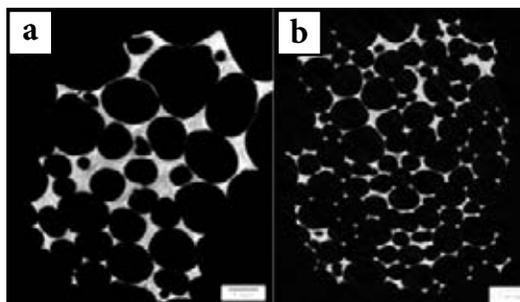

Fig. 8.   *2D μ-CT images of pyrolyzed foams prepared in an aluminum tray. a) without sacrificial template – 94% porosity; b) with PMMA microbeads sacrificial burn-outs – 90% porosity*

8. ábra   *Alumínium vályúban pirolizált habok 2D μ-CT módszerrel felvett képei a) sablon nélkül, 94% porozitással, b) PMMA mikrogyöngyök kiégésekor, 90% porozitással*

4. Conclusions

Polymer derived ceramic foams with additional strut porosity were successfully fabricated by a direct foaming approach with a self-foaming polysiloxane and additional sacrificial burn-outs comprising of PMMA or PE. The size and shape of the resulting pores in the struts can be controlled by altering the morphology of the sacrificial templates used in this approach. The polymer derived ceramic foams possessed total porosities ranging from 40% to 95%, and compressive strength exceeded 16 MPa, depending on nature and size of the template, and on foaming containment, respectively.

Acknowledgements

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Polimer alapú, növelt porozitású kerámia habok

Növelt porozitású kerámia habokat állítottunk elő poliszil-szeszkvioxán önhabosodási folyamatával. A porozitást az önhabzó szilikonhoz további póruszképzőt, nevezetesen poli(metil-metakrilátot) vagy polietilént adagolva növeltük meg. A polimer saját belső zsugorodását úgy csökkentettük, hogy a kiindulási szilikon-polimer elegybe SiC részecskéket tartalmazó töltő-anyagot kevertünk. A habosítást 270 °C-ra előmelegített kemencében végeztük. Ezt követően az anyagot argon atmosz-férában, 800–1200 °C közötti hőmérsékleten pirolizáltuk a poliszilszeszkvioxán kerámiai anyaggá történő átalakítása céljából. Meghatároztuk a termékek pórusméretét és teljes porozitását, vizsgáltuk mikroszerkezetüket és mechanikai szilárdságukat. A termékek térfogat szerinti átlagos pórusmérete 25 és 100 μm között, porozitása 40 és 94% között változott. A legnagyobb mért nyomószilárdság 16 MPa felett volt.

Kulcsszavak: kerámia habok, prekerámia polimerek, önhabosodási folyamat, növelt hatású póruszképzők