Preceramic polymer-derived ceramic foams with lamellar strut porosity

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Abstract. Open porous replica foams with additional lamellar strut pores were prepared by preceramic polymer processing combined with a freeze-drying process. Polymer foam templates were coated with an aqueous polymethylsilsequioxane system followed by freezing at -20 °C to generate hierarchical porosity within the foam struts. The cellular structure was preserved during freeze drying, cross-linking, template removal and pyrolysis, and additional strut porosity was formed. The size of the lamellar strut pores was found to depend on the solid load of the preceramic slurry and its pretreatment procedure. The cellular materials obtained in this work possess additional lamellar strut pore channels with a thickness of approximately 40 µm and a total foam porosity of >90 %.

1 Introduction
Open porous ceramic foams are frequently used as supports for heterogeneous catalysts, filters for liquid metal filtration, heat exchangers and other applications.[1–5] Within these applications the combination of mechanical strength and an increased surface area is advantageous and favored.[1]

With the freeze-casting technique a systematic positioning of pores into suspension-generated materials is possible. Typical for the production of porous ceramics are water based slurries primarily consisting of ceramic particles (in the nanometer to micrometer range), processing additives such as viscosity modifiers and deagglomerating agents and water.[6] Ceramic slurries based on other liquids than water are also suitable for freeze-drying processing. Specifically with regard to preceramic polymer systems, organic solvents such as cyclohexane, tert-butyl alcohol or camphene are used, as several preceramic polymers are not soluble in water.[7] During freeze casting/freeze drying processing the solvent solidifies, is removed by a freeze drying process (sublimation) and leaves behind pores instead of frozen material, within the sample.[8] Ice crystals from frozen water leave behind lamellar pore channels after sublimation within the structure, separated by ceramic lamellae. As the superior objective of this study was the accessibility of hollow struts in replica foam samples and to enlarge the foam surface, water was chosen as dispersant in this work; replica foams are typically manufactured by coating a polyurethane (PU) foam template with a ceramic slurry and subsequent thermal processing with a) template burnout and b) sintering or pyrolysis. The modification of lamellar pore channel structures was realized by varying the solid content or the freezing temperature. The pore channel formation is a result of nucleation and growth of ice crystals located in the suspension and has already been investigated extensively.[9–14]
Most research related to freeze drying was carried out with bulk ceramic materials [1, 3] or combined with direct foaming processes [7, 15].

The combination of the freeze drying process with the replica (impregnation of a polyurethane sponge as a template) method [16] was described in the literature [17] but its focus was on alumina based porous ceramics. Besides alumina, preceramic polymers may be used for the manufacturing of porous ceramics. In this context these are mostly Si-based oligomers [18] and they are suitable for the replica technique [19]. Due to a polymer–to–ceramic conversion, preceramic polymers can be transferred into Si-based ceramics with a high oxidation and creep resistance up to high temperatures [18].

The combination of freeze-drying and sponge replication technique with preceramic polymer based slurries is presented in this paper with a focus on the pretreatment of the starting preceramic polymer powders.

Characterization was carried out with respect to the coating process, the micro- and macrostructural features and the mechanical strength of the samples.

2 Experimental Section

The workflow of sample preparation is illustrated in Figure 1 showing the combination of the replica process and the freeze drying process.

![Figure 1](image.png)

**Figure 1.** Scheme of the workflow and basic processes: Replica technique combined with freeze drying: (a) Impregnation of a PU template with a ceramic slurry; (b) Freezing of coated PU foam; (c) growth of ice crystals; (d) Sublimation of ice crystals with reduced temperature and pressure; (e) PU template burnout and sintering of the ceramic foam with pores of freeze drying.

2.1 Powder processing

As a preceramic polymer powder commercially available polymethylsilesquioxane (SILRES®MK; d₅₀: 25 µm; information from the manufactures datasheet; Wacker Silicone AG, Munich, Germany) was used. The powder was grind with a ball mill (PM 400, Retsch GmbH, Haan, Germany). Two different milling process modifications were applied: dry milling, whereby the powder was placed in the Al₂O₃ ceramic containers with Si₃N₄ milling balls (d = 10 mm); and wet-milling, whereby water was added to the mixing containers. For the wetting of the hydrophobic polymer powder with water a surfactant was added (Alboclean n24-5, Albon-Chemie Dr. Ludwig-E. Gminder KG, Metzingen, Germany). Milling was performed for 30 min with 250 rpm. The preparation of the coating suspensions was performed with the grinded, dried and sieved (d₅₀ < 20 µm) SILRES®MK powders.

2.2 Slurry preparation

The preceramic polymer-processing route requires a crosslinking step to obtain a stable polymer network before pyrolysis. Therefore, aluminum acetylacetonate (Merck Schuchardt OHG, Germany) was added as crosslinking catalyst.
To increase the viscosity of the preceramic slurry, a suitable amount of methylcellulose (Carl Roth GmbH & Co. KG, 160 000 g mol\(^{-1}\), Karlsruhe, Germany) was added to distilled water before adding it to the mixing container (5.3 wt. % of water). Different solid contents of the preceramic powder (20, 30 and 40 vol. %) were used within this testing series. A planetary centrifugal mixer (THINKY Mixer ARE-250, THINKY Corp. Tokyo, Japan) was used for homogenization of the slurry (mixing mode: 15 min, 2000 rpm) and for degassing of the slurry (degassing mode: 10 min, 2200 rpm). The composition of the slurries with a different solid content is shown in Table 1.

Table 1. Composition of investigated slurries.

| Component/Share | 20 vol. % solid (g) | 30 vol. % solid (g) | 40 vol. % solid (g) |
|-----------------|----------------------|---------------------|---------------------|
| SILRES®MK       | 18.1                 | 8.7                 | 27.3                |
| Water+Cellulose | 81.7                 | 36.1                | 72.3                |
| Tenside         | 0.2                  | 0.1                 | 0.3                 |
| Catalyst        | 0.1                  | 0.1                 | 0.1                 |

2.3 Coating of the PU templates

Open cell polyurethane foam templates (S30P20R, Koepp-Schaum GmbH, Oestrich Winkel, Germany) with a volume of (15*15*20) mm³ and a pore count of 20 ppi (pores per linear inch) were squeezed and immersed into the suspension, withdrawn and excess suspension was removed manually by facile squeezing. Coated foams were weighed to ensure almost the same load of all templates (~1.5 g per foam piece). After coating of approximately 10 foam pieces they were put into the freezing compartment of a laboratory fridge at approximately -20 °C and kept there for at least 24 hours to ensure complete freezing of all samples.

2.4 Freeze drying and heat treatment

After the freezing process was completed, the samples were put into a freeze dryer (Gefriertrockenschrank BETA 1-16 LMC 2, Martin Christ Gefriertrocknungsanlagen GmbH, Osterode, Germany) at -50 °C and 0.1 mbar for 24 hours. The last step of sample processing was the heat treatment consisting of crosslinking and pyrolysis. Crosslinking of the dried preceramic polymer slurry was performed with a heating rate of 1 K min\(^{-1}\) at a maximum temperature of 180 °C with a dwelling time of 3 hours in air (KU 40/04/A, THERMCONCEPT Dr. Fischer GmbH, Bremen, Germany). In this temperature range the PU template is still intact, so it is pyrolyzed together with the preceramic polymer in the next heating step. Pyrolysis took place in a tube furnace (THERMCONCEPT Dr. Fischer GmbH, Bremen, Germany) with a heating rate of 2 K min\(^{-1}\) in nitrogen (nitrogen flow rate set to 15 l min\(^{-1}\)) for 3 hours at a maximum temperature of 800 °C.

3 Characterization

The measurement of particle size distribution was performed with dried, sieved powders after ball-milling (wet- and dry-milled) in air with the light scattering method using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, United Kingdom). For the determination of the particle size the Fraunhofer model [20] was used for particle sizes distribution analysis for a particle size range from 10 μm to 20 μm for the wet-milled powders and of 100 μm for the dry-milled powders. The particle size of the unmilled SILRES®MK powder was extracted from the supplier’s data sheet.

For the characterization of the rheological behavior of the slurries a viscometer (Anton Paar GmbH, Graz, Austria) with plate-plate configuration (d\(_{\text{plate}}\) = 50 mm) was used and the distance between the parallel plates was set to 1 mm. The shear rate was varied between 0.1 s\(^{-1}\) and 100 s\(^{-1}\), the corresponding shear stress values were recorded with the software package Rheoplus V. 3.40 (Anton Paar GmbH, Graz, Austria). During each measurement 31 data points were recorded, the measuring duration for each point was logarithmically reduced from 60 s to 1 s. The rheological data – shear stress \(\tau\) as a function of the
shear rate $\gamma$ were fitted with the Power-Law model (equation 1) as a shear thinning flow behavior was observed for these slurries:[21, 22]

$$ \tau = K\gamma^n. $$

(1)

The parameter $K$ is defined as consistency coefficient of the slurry and the parameter $n$ defines the variation to Newtonian flow behavior of the fluid. For $n$ equal to 1 the fluid possesses Newtonian flow behavior (shear stress is proportional to the shear rate), $n < 1$ describes a shear-thinning flow (the shear stress reduces significantly for increased shear rates) and $n > 1$ means a shear-thickening behavior (the shear stress increases strongly with an increase of the shear rate).[21]

To determine the bulk density of the strut material after the heat treatment, the volume of the solid was measured with a helium pycnometer (AccuPyc 1330, Micromeritics GmbH, Unterschleißheim, Germany). For this, pieces of pyrolyzed foams were ball-milled with a planetary ball mill (Retsch PM400, Haan, Germany). The powder was filled into the cylindrical measuring chamber of the pycnometer. The measuring program was carried out for five times. After determination of the sample weight (Cubis, Sartorius, Göttingen, Germany) the density was calculated using equation (2):

$$ \rho_{\text{bulk}} = \frac{m}{V}. $$

(2)

Scanning electron micrographs were taken from sample pieces mounted on the SEM sample carriers with electrical and electrically conductive glue (Plano Leit C, Plano GmbH, Wetzlar, Germany). The samples were sputtered in a vacuum-chamber with gold to guarantee electric conductivity of the samples. The accelerating voltage of in the SEM (SEM, XL30 ESEM-FEG, FEI Company, Hillsboro, OR, USA) was set to 10 kV, specifically to avoid melting of the preceramic polymer before pyrolysis, when green foams were analyzed.

Cell size and porosity measurements were carried out with a microcomputer tomograph Nanotom S (GE Sensing & Inspection Technologies, Wunstorf, Germany). For the determination of the pore size distributions generated with freeze drying the incremental pore volumes were plotted against the mean pore diameter and their maxima were determined with a Gaussian curve fit. For scanning in a µ-CT, pieces of reticulated foams after pyrolysis (to determine the lamellar thickness of the strut pores small pieces of foams were used) were fixed separately on the sample holder of the µ-CT. The voltage was 60 kV, the tube current was set to 160 µA, and the distance of the sample holder to the X-ray tube and detector was adjusted to obtain a voxel size of 10 µm³ for scanning of the complete samples (resp. 7 µm³ for foam pieces). The reconstruction of the datasets was performed with the software package Phoenix Datos |X 2.0 (GE Sensing & Inspection Technologies, Wunstorf, Germany). With the software CT Analyzer 1.18 (Skyscan/Brüker microCT, Kontich, Belgium) different structural parameters of the foams were calculated in a 3D mode. The thickness of ceramic lamellae and the width of lamellar pore channels were determined with the software CT Analyzer 1.18, too. For more details of the calculation procedure (e.g. thresholding and binarization) please refer to Betke et al.[23]

The compressive strength of the pyrolyzed foam samples was determined with the mechanical test machine TIRATEST 2820 (TIRA GmbH, Schalkau, Germany). Six samples of each series were measured. To ensure a uniform pressure distribution to the planar faces, a cardboard was placed underneath and over the foams and the compression stamp. The traverse-speed was set to 2 mm min⁻¹. The compressive strength was calculated by scaling the maximum force to the loaded area of the sample.
4 Results and discussion

4.1 Rheological behavior of the coating slurries

The shear stress of the three slurries prepared with wet-milled SILRES®MK powder are presented as a function of the shear rate, see Figure 2. Since the flow curves of the slurries prepared with the dry-milled powder show comparable results, they are not shown here. The viscosity increases with increasing solid content, whereby for 20 vol. % and 30 vol. % of solid load the viscosity values are almost identical. Figure 2. This behavior is related to the increasing amount of particles, which results in an increase of the shear resistance and gets significant for a solid load above 30 vol. % of the coating slurry.[23–25]

![Figure 2. Flow curves of preceramic slurries (wet-milled powder) with three different solid contents.](image)

A shear thinning behavior of the slurries is advantageous for the replica method [25–27], as an almost ideal impregnation (penetration of the slurry into the template foam cells and windows) is possible at higher shear rates due to a lower viscosity by movement the template within the coating slurry. Right after finishing the coating process a draining off of the slurry is prevented due to a viscosity increase by reducing the shear stress to zero. In this coating system the viscosity is very low for a given shear rate in comparison to standard suspensions suitable for the replica technique (shear rate of 1 s⁻¹ shear stress is in the range of 100 Pa, referring to Voigt et al. [27].)[25, 28]

No yield strength was found when the slurries were characterized. Both, a low viscosity and the lack in yield strength, is critical for template coating. However, draining off of the coating was prevented by a fast transfer of the samples into the freezer.

The parameters $K$ and $n$ describing the flow behavior as determined by the Power-Law model are listed in Table 2. The Power-Law model was chosen because of the slurry shows a shear-thinning behavior without yield strength. Further information can be found in the literature.[29–33]

| Sample/Parameter | $K$/Pas$^a$ | $n$  |
|------------------|-------------|------|
| 20 vol. %        | 37.15       | 0.72 |
| 30 vol. %        | 28.64       | 0.67 |
| 40 vol. %        | 161.34      | 0.59 |

- $K$: consistency factor
- $n$: flow index
The Power-Law model serves as a mathematical description of the shear thinning or shear thickening process of suspensions having non-Newtonian flow behavior.\cite{21, 22} The flow index $n$ decreases for an increasing solid content of the slurry and indicates that the fluid has a shear thinning flow behavior. The consistency factor $K$ describes in which extent the suspension “works” against the shear stress and represents the shear stress at a shear rate of 1.0 s$^{-1}$. The more the suspension consists of particles, the harder it is to move it with the plate, what is one reason for the highest $K$-value for the 40 vol. %-slurry. The experimental data fit well to the Power-Law model for a particular range of the shear rate, as shown in Figure 2.

4.2 Microstructure of the foams

Heat treatment

Since ceramic processing based on preceramic polymers is connected to cross-linking and pyrolysis, the SEM micrographs in Figure 3 show the microstructures of dried, cross-linked and pyrolyzed samples with respect to the lamellar pore channels. All four samples were prepared from the wet-milled powder and a slurry with a solid content of 30 vol. %.

![Figure 3. SEM-micrographs of (a) freeze-dried, (b) freeze-dried and cross-linked and (c) freeze-dried, cross-linked and pyrolyzed samples manufactured with a 30 vol. % solid-loaded slurry with the wet-milled preceramic polymer powder, (d) sample dried under ambient conditions.](image)

SEM images of the pyrolyzed foams show lamellar pore channels inside of the foam struts that are a result of freezing and freeze-drying. The freeze-formed pores are parallel aligned, and it was found that this type of alignment is independent on the solid load.

Replica foams without freeze-drying process and the same slurry do not have any lamellar pore channels, Figure 3 (d). Therefore we state, that the development of lamellar structures is a consequence of freeze processing consisting of freezing and freeze drying. While freezing leads to the formation of water-ice crystals at ambient pressure, drying leads to the removal of these ice crystals by sublimation. These two process steps are not part of processing in the foam shown in Figure 3 (d). The struts show smaller non lamellar pores which are a result of the pyrolysis process, whereby the cross-linked preceramic material undergoes a mass loss of more than 20 vol. % after pyrolysis at 800 °C. These pores could be closed if pyrolysis temperature is increased or fillers are used. More information dealing with the thermal rearrangement and gas release in polymer pyrolysis can be found elsewhere.\cite{34–43}

Milling process

Milling of the preceramic polymer powder, with addition of water led to smaller particles \cite{44} with a more uniform shape and rounded edges, compared to the sharp edges of dry-milled powders. Figure 4 shows (a) the particle size distribution of the wet-milled and the dry-milled powder, (b-d) the microstructure of the untreated, dry-milled and wet-milled powder.
Porosity measurements and determination of pore size distributions were performed by microcomputer tomography. The lower the solid content inside of the coating slurry was, the higher was the porosity and the width of the lamellar pore channels. Prior to the calculation of porosity, the bulk density of the pyrolyzed samples was measured with helium pycnometry. The value of the bulk density is 2.259 g cm\(^{-3}\). Samples prepared of dry- and wet-milled powders show the same bulk density, both sample series prepared with SILRES®MK powder. The foam porosity was calculated with the following equation (3):

\[
P_{\text{total}} = 1 - \frac{\rho_{\text{geometric}}}{\rho_{\text{bulk}}} \times 100\%.
\]  

(3)

whereby the geometric density is calculated by dividing the weight of the sample to its volume:

\[
\rho_{\text{geometric}} = \frac{m_{\text{sample}}}{V_{\text{sample}}}.
\]  

(4)

Based on the values listed in Table 3 the open strut porosity of the samples was determined with equation (5):

\[
P_{\text{Strut}} = 1 - \frac{m_{\text{piece in CT}}}{V_{\text{piece in CT}}} \div \rho_{\text{bulk}}
\]  

(5)
Table 3. Geometric values of samples, volume of pyrolyzed sample piece determined with µCT, calculated strut porosity and width of ceramic lamellae and lamellar pore channels.

| Parameter/ Sample | \( \rho_{\text{geometric}} \) | \( P_{\text{total}} \) | \( m_{\text{piece in CT}} \) | \( V_{\text{piece in CT}} \) | \( P_{\text{Strut}} \) | Width of ceramic lamellae | Width of lamellar pore channels |
|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Unit              | (g/cm\(^3\))     | (%)              | (g)              | (cm\(^3\))      | (%)              | (µm)             | (µm)             |
| 30 vol. % dry     | 0.15             | 93.30            | 0.0386           | 0.138            | 87.65            | 57.62            | 55.31            |
| 30 vol. % wet     | 0.14             | 93.44            | 0.0574           | 0.197            | 87.12            | 53.92            | 51.17            |
| 40 vol. % wet     | 0.20             | 90.96            | 0.0193           | 0.045            | 81.11            | 33.72            | 42.34            |

The strut porosity decreases with an increase of solid content, for wet- and dry-milled powder the strut porosity is almost identical and in general the porosity of samples being in the range from 91 % to more than 93 % is very high.

To investigate the pore size distribution, the thickness of the lamellar pore channels and the ceramic lamellae within the struts, defined pieces of foam sample were investigated with µ-CT and the data was evaluated with the CTAnalyzer software. The results are shown in Figure 5 and Table 3.

![Figure 5](image1.png)  
*Figure 5. Width of ceramic lamellae (■ / ● / △) and lamellar pore channels (□ / ◦ / △) determined by µ-CT data with structure separation and structure thickness function (3D analysis).*

The width of ceramic lamellae increases with an increased solid content in the preceramic slurry, and the width of lamellar pore channels was found to behave inversely. The width change of the lamellar pore channels and the ceramic lamellae is illustrated in Figure 6, exemplified with samples from the wet-milled powder with a (a) 20, (b) 30 and (c) 40 vol. % solid content of the coating slurry.
In summary it can be stated that the freezing and freeze-drying process leads to the formation of lamellar pore channels separated by dense ceramic lamellae. The width of lamellar pore channels decrease and the width of ceramic lamellae increases with an increasing solid content in the coating slurry. Both effects are in accordance to the literature, found for bulk materials processes via freezing and freeze−drying [13, 14, 17, 45] Furthermore, an increased number and thickness of dendritic-like features (Figure 7) connecting the lamellar pore channels was found with an increasing solid content of the coating slurries, in this work from 20 vol. % to 40 vol. %.

**Compressive strength**

The compressive strength correlates with the solid content of the preceramic coating suspension. The higher the solid content, the more stable are the foams. This is due to the increase of the ceramic lamellae thickness, the decreasing width of lamellar pore channels and the increased number and thickness of dendritic-like features between lamellar pore channels, Figure 6, Figure 7. Hence, the solid content determines the porosity of the pyrolyzed samples.[46] The extent of porosity acts contrary to the aim of highly mechanical stable foams, but our goal was to maximize the porosity, but anyway, the samples have to have a stability high enough to handle them. Therefore, mechanical strength suffered from high share of porosity among produced foams. Additionally the separate measurements induce variant compressive strength values, which is basically due to the inherently fracturable foam microstructure. During compression, only a small number of struts has to retain the total weight force operated to the foam sample. As the load of individual struts is not implicitly homogeneous within a sample series, collapse may appear at diversify values.[47]
Precise numerical figures are not given here as numerous affecting conditions concerning the measuring system are existent and therefrom the numerical figures are not significant.\cite{48} Despite this, there is a visible trend: as the solid content increases, the compressive strength of the samples increases. \textbf{Figure 8} shows the compressive strength of the produced foams to the foam porosity.\cite{5, 14}

\textbf{Figure 9}. SEM-micrographs of freeze-dried; cross-linked and pyrolyzed samples with a slurry-solid content of 20 vol. % from (a) dry-milled powder and (b) wet-milled powder; both inserts show microstructure with a smaller magnification to illustrate the parallel alignment of ceramic lamellae and lamellar pore channels.

Furthermore, the powder milling process influenced the mechanical stability of the samples. Foams produced with wet-milled powder consisted of smaller particles without sharp edges and a more uniform shape, which leads to more consistent ceramic lamellae, \textbf{Figure 4}, \textbf{Figure 7}, \textbf{Figure 9}. 
5 Conclusion

Freeze-dried replica foams from water based preceramic polymer slurries were successfully prepared. The solid load in the coating slurries was varying from 20 vol.% and 40 vol.%, a solid load of 30 vol.% and more lead to mechanically stable polymer derived ceramic foams. The freeze-dried PDC foams possess a low compressive strength, which was assigned due to the parallel alignment of lamellar shaped pores within the pore struts, Figure 9.

Acknowledgements

This work was carried out in the frame of a scholarship from the International Graduate School MEMoRiAL, which is funded by the European Structural Investment Funds under the code and number MEMoRiAL 64 1003 2013, which grateful acknowledged. The authors wish thank to Diethard Kürschner for his help with the freeze-dryer, Michael Schwidder for viscosity measurements and Andreas Schlinkert for particle size distribution measurements; all persons are from the Faculty for Process Engineering of the Otto-von-Guericke-University, Magdeburg. We also thank Ulf Betke for his kind replay to our questions.

Conflict of interest

The authors state no conflict of interest.

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