POROUS POLYMER DERIVED SiCN-CERAMIC WITH DIRECTIONAL PORE STRUCTURE OBTAINED BY FREEZE CASTING

Richard Obmann and Thomas Konegger

E164-CT - Institute of Chemical Technologies and Analytics

INTRODUCTION

Porous ceramics are interesting materials as substrate of membranes or catalysts because of their high inner surface area, their excellent mechanical as well as thermal properties, and their chemical stability. Polymer derived ceramics (PDC) offer wide possibilities in new processing methods, easy shaping and are especially interesting for new pore templating approaches[1].

Freeze casting is a technique to obtain aligned pores in ceramic materials in general and in PDCs in particular. So far, only SiOC and SiC ceramics have been processed in this manner, using solid preceramic precursors such as polysiloxane or polycarbosilane[2]. To obtain SiCN, poly(vinyl)silazane (PSZ) is generally used, which is a liquid precursor. The aim of this work is to develop a processing routine for freeze casting PSZ with a focus on crosslinking the precursor at low temperatures.

MOTIVATION AND EXPERIMENTAL

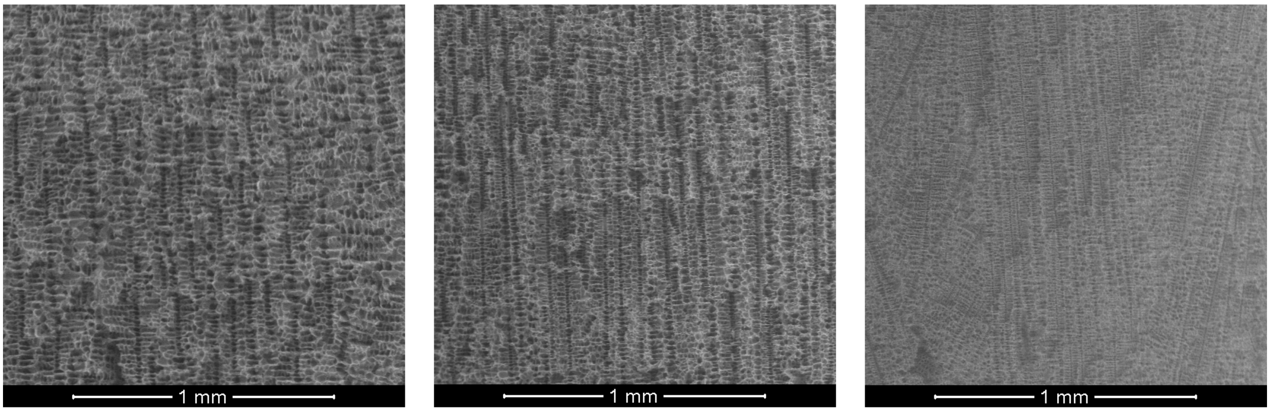
Liquid poly(vinyl)silzane is generally crosslinked at elevated temperature to obtain a solid green body. As freeze casting is performed at temperatures below the freezing point of the solvent, thermal crosslinking of the precursor is not possible without destroying the structure of the solidified solvent, which acts as pore directing agent.

By employing a photopolymerization technique,[3] it was possible to crosslink PSZ at low temperatures. The pore structure directed by the dendritically grown solvent was not affected or destroyed. Subsequently, the solvent was removed via sublimation, leaving crosslinked PSZ as the negative image of the crystallized solvent. To enhance green body strength, the prepared samples were thermally crosslinked before they were converted into ceramic materials at 1000 °C in nitrogen atmosphere.

The amount of precursor in the mixture precursor/solvent and the cooling rate while freeze casting were varied to evaluate the respective influence of these parameters on the resulting pore structure as well as porosity.

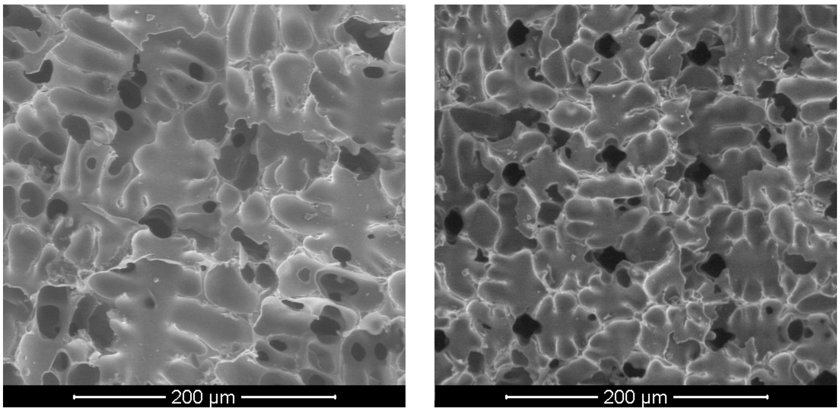
RESULTS AND DISCUSSION

PSZ was successfully crosslinked at low temperatures using a photopolymerization technique, conserving the structure of the solvent acting as pore template. An increase in PSZ content in the starting mixture leads to narrower pores and higher number of pores, shown in figure 1. Furthermore, it was shown that the total porosity follows a linear trend in dependence of initial PSZ content. The effect of the cooling rate is shown in figure 2. Cooling at high rates results in more ordered pore structures than cooling at low rates.



15 wt% precursor content   20 wt% precursor content   30 wt% precursor content

Figure 1: Pore structure of pyrolyzed specimens as a function of initial PSZ content (SEM micrographs of sections parallel to freezing direction).



Cooling rate 2K/min   Cooling rate 8K/min

20 wt% precursor content

Figure 2: Pore alignment depending on cooling rate during freezing (SEM micrographs of sections perpendicular to freezing direction.

CONCLUSIONS

Using a photopolymerization technique, it was possible to generate porous SiCN ceramic with directional pore structure derived from a liquid poly(vinyl)silazane precursor by shaping via freeze casting. The initial polymer content in the solution as well as the cooling rate during freezing significantly influence both pore structure and total porosity. Even though a practicable routine for producing samples has been developed, further development involving the polymerization step is required in order to minimize crack formation. Furthermore, samples will be further characterized using Hg-porosimetry, testing of mechanical properties, and testing of gas permeability.

REFERENCES

[1] Konegger T., Williams L. F. and Bordia R. K., “Planar, Polysilazane-Derived Porous Ceramic Supports for Membrane and Catalysis Applications“, J. Am. Ceram. Soc 98 (2015), 3047-3053.

[2] Vakifahmetoglu, C, Zeydanli D. and Colombo P., “Porous polymer derived ceramics”, Mater. Sci. Eng., R 106 (2016), 1-30.

[3] Reddy S. K., Cramer N. B., Cross T., Raj R. and Bowman C. N., “Polymer-Derived Ceramic Materials from Thiol-ene Photopolymerizations”, Chem. Mater (2003), 4257-4261.