A PROCESSING ROUTINE FOR LAYERED Si_3N_4/SiCN STRUCTURES WITH GRADED MULTISCALAR POROSITY

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INTRODUCTION

Porous non oxide ceramics are interesting materials for uses in energy and environmental related fields such as catalysis and separation. The excellent mechanical and thermal properties and also the chemical stability make ceramics very effective. Especially the use of preceramic polymers opens up new processing methods and leads to flexibility in shaping, enabling the manufacturing of layered structures and coatings.

Layered ceramic structures with multiscalar porosity can be used as membranes for gas separation at high temperatures. They generally consist of a microporous selective layer responsible for the separation, and a macro-porous support providing the mechanical stability. Usually, there has to be an intermediate layer bridging the difference in pore size and possible chemical variations between selective layer and support.[1] The aim of this work is to find a processing routine for layered structures with multiscalar porosity solely consisting of Si_3N_4 and comparable polymer-derived materials.

EXPERIMENTS & EXAMINATIONS

Two types of support structures were prepared, serving as substrates for the following layers. A composite intermediate layer was deposited via dip coating, onto which a selective layer was applied.

Support structures: Type A supports were prepared using a poly(vinyl)silazane as polymer precursor and UHMW-PE as sacrificial filler, resulting in amorphous silicon carbonitride with a porosity of about 42 % after pyrolysis.[2] [3] Type B supports were prepared via slip casting and partial sintering of silicon nitride yielding a porosity of about 50 %.

Intermediate layer: The intermediate layer was prepared using a combination of preceramic polymer and silicon nitride particulates (the same materials as for the supports). The poly(vinyl)silazane serves as a binder for the particulates, yielding a composite layer after pyrolysis. The layer was deposited using dip coating of slurry containing both the polymer and the particulates (in a ratio of 1:1.4). To achieve sufficient slurry stability, the particulates were modified by a silanization treatment using 3-aminopropyltrimethoxysilane. Through variation of solvent content in toluene, a slurry composition yielding a satisfactory intermediate layer was found. The use of two different slurries were necessary due to filtration effects caused by the different pore structures of the two support types.

Selective layer: The selective layer was deposited via dip coating using a solution of the poly(vinyl)silazane used for the previous layers in toluene/hexane. Preliminary optimization tests were carried out on glass plates and the results compared to a model from Landau and Levich.[4] To avoid infiltration of the substrate, an additional masking with polystyrene was conducted. After crosslinking, the selective layer was stable and the polystyrene was burnt out during pyrolysis.

RESULTS AND DISCUSSION

A layered structure with multiscalar porosity was achieved on both of the support types. The scanning electron microscopy pictures of each processing step can be seen in figure 1.

The type A supports have a porosity of approximately 42 % with ink bottle type pores, type B supports 50 % with uniform pores. For the preparation of the intermediate layer, a higher solvent concentration of the slurry was necessary for the slip cast supports than for the polymer derived (PDC) supports due to the previously mentioned filtration effects. Using 91 wt.% toluene for the slip cast and 80 wt% toluene for the PDC supports, a crack-free, continuous composite intermediate layer with approximately 30 µm in thickness could be prepared. Under use of the masking step (polystyrene), it was possible to prepare a thin (approximately 1 µm) selective layer on top of the intermediate layer, whilst preserving the porosity of the underlying layers.

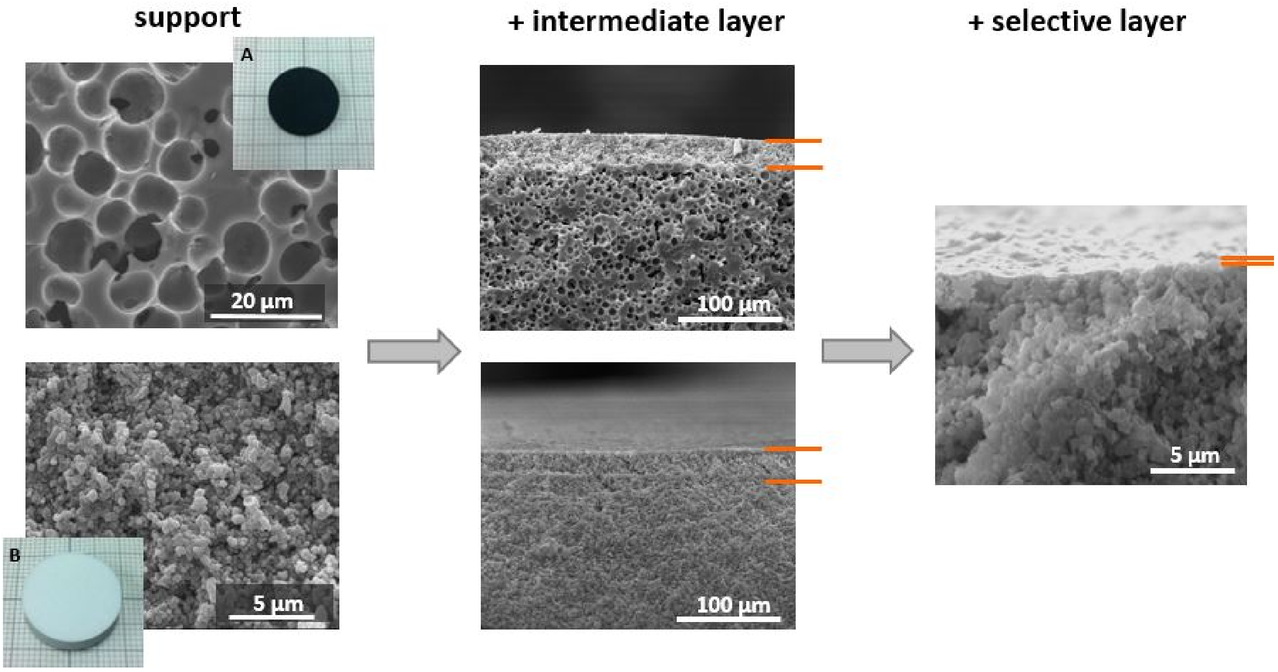

Figure 1: SEM micrographs of the layered silicon (carbo)nitride structures in every processing step

CONCLUSION

Using preceramic polymers, it is possible to prepare layered structures with multiscalar porosity using dip coating processes. A practicable routine was developed, but further optimization is necessary. Since these structures are proposed for high temperature gas separation membranes, the generation of microporosity in the selective layer and their stability have to be characterized and optimized.

REFERENCES

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