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Macroporous polymer-derived SiO_2/SiOC monoliths freeze-cast from polysiloxane and amorphous silica derived from rice husk

Niloofar Soltani[a,b,c,*,1], Ulla Simon[b,1], Amin Bahrami[a,b,c,1], Xifan Wang[b], Sören Selve[d], Jan Dirk Epping[e], Martin I. Pech-Canul[c], Maged F. Bekheet[b], Aleksander Gurlo[b]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 D.F., Mexico
[b] Fachgebiet Keramische Werkstoffe/Chair of Advanced Ceramic Materials, Institut für Werkstoffwissenschaften und – technologien, Technische Universität Berlin, Hardenbergstraße 40, 10623 Berlin, Germany
[c] Centro de Investigación y de Estudios Avanzados del IPN Unidad Saltillo, Ave. Industria Metalúrgica No. 1062, Parque Industrial Saltillo-Ramos Arizpe, Ramos Arizpe, Coahuila, 25900, Mexico
[d] Center for Electron Microscopy, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
[e] Institute of Chemistry: Metalorganics and Inorganic Materials, Technische Universität Berlin, Straße des 17. Juni 135/C2, D-10623 Berlin, Germany

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ABSTRACT

A freeze-casting route towards macroporous SiOC/SiO_2 ceramic nanocomposites from preceramic polymers was developed. Amorphous SiOC/SiO_2 monolith with pore channels aligned along the freezing direction were obtained from commercially available methyl-phenyl-vinyl-hydrogen polysiloxane (Silres® H62C) and amorphous silica derived from rice husk ash freeze-cast with water or tert-butyl alcohol, crosslinked and pyrolyzed at 1100 °C in nitrogen. The influence of processing parameters such as solvent (tert-butyl alcohol or water), polymer to silica ratio (2:1, 1:1, 1:2), cooling rate (2, 4, 6 °C/min) and pre-crosslinking of polysiloxane on the porosity and structure of the obtained ceramic nanocomposites were assessed by X-ray tomography, XRD, solid state NMR, scanning electron microscopy and mercury porosimetry. The microstructure of SiOC ceramics derived from the Silres H62C polysiloxane was studied as well.

1. Introduction

Considerable attention has been paid in recent years to the fabrication of macroporous ceramics with controllable pore size and geometry suitable for a variety of emerging applications such as thermal insulation, gas separation, catalysis and bone replacement [1–4]. Defined macroporosity in ceramics is usually created during processing by using replica materials, sacrificial fillers, direct foaming or additive manufacturing techniques [3,5]. Freeze-casting, also known as ice templating, has gained increasing interest in recent years. During freezing, the liquid phase (e.g. water) solidifies and crystallizes and thus acts as a porogen, leaving pores behind after its sublimation [6]. The pore structure of the freeze-cast materials is to a large extent influenced by the processing parameters such as cooling rate and direction, solid content in the formulation, and the final heat treatment [1,6–11]. Solvent in combination with freezing conditions is crucial for defining pore geometry [6,9], i.e. water typically leads to lamellar, camphene and cyclohexane – dendritic, and tert-butyl alcohol – prismatic materials [6,9]. Water-based freeze casting has been most extensively reported in literature, especially for the processing of macroporous oxides such as Al_2O_3, ZrO_2 and zeolites [7,12,13].

Polymer derived ceramics (PDCs), synthesized by the pyrolysis of preceramic polymers such as polysiloxanes, polycarbosiloxanes and polycarbosilanes, is an emerging group of ceramic materials [14]. Tailoring the molecular structure of preceramic polymers offers a wide range of microstructural features that in turn determine the physicochemical properties of resulting PDCs. Adjusting pyrolysis conditions (gas atmosphere, temperature, heating rate) allows for the control over the phase composition, porosity and microstructure of the resulting ceramics [15,16]. One of the main challenges in the processing of PDCs, however, is the high volume shrinkage during the polymer-ceramic transformation. This can be circumvented by the addition of fillers or by modifying the polymer structure [14].

Freeze-casting has rarely been investigated for the processing of macroporous PDCs or their composites [17–21].Since the preceramic polymers are not soluble in or miscible with water,

* Corresponding author at: Circuito Exterior S/N, Circuito de la Investigación Científica, Ciudad Universitaria, 04510, Mexico City, Mexico.
E-mail addresses: niloofar.soltani@iim.unam.mx, nilufar.soltani@gmail.com (N. Soltani).
[1] Contributed equally.

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other solvents such as camphene, cyclohexane and tert-butyl alcohol have been applied for freeze-casting yielding in materials with dendritic and cellular pore geometries. Except the study [19], all aforementioned works utilized either the pre-cross-linked polymers or polymer-derived ceramic powders as, for example, in a recent report about hierarchically ordered micro-meso-macroporous ceramic monoliths freeze-cast from silica sol mixed with a SiOC powder derived from a commercial polysiloxane [22]. To the best of our knowledge, preceramic polymers have not yet been processed with a water-based freeze-casting technique without being pre-cross-linked.

The main goal of the present study is to develop a freeze-casting methodology that allows fabrication of macroporous ceramic monoliths from liquid preceramic polymers. The main emphasis is laid on the processing of amorphous ceramics in environmentally friendly solvents (water) with carbon neutral green additives (silica from rice husk) [23].

2. Materials and methods

2.1. Materials

A commercial methyl-phenyl-vynil-hydrogen polysiloxane (Silres®H62C, denoted as LH62C afterwards, Wacker Chemie GmbH, Germany) was used as received, without further purification. Crosslinking of the polymer – chosen according to the thermal analysis data from [24] – was performed in argon at 250 °C for 2 h with a heating rate of 1 °C/min. The resulting material (labeled as CH62C afterwards) was ground with planetary ball mill PM4 (Retsch, Germany) for 1 h to produce fine powder (≤60 μm sieve grating). Amorphous silica powder derived from rice husk ash was used as a filler. The extraction method of silica from rice husk ash is reported elsewhere [25–27]. Amorphous silica consists of primary loose nanosized particles assembled in a secondary particle agglomerate of approximately 5–10 μm surrounded by a shell, a specific surface area of 150 m^2/g and a density of 1.6 g/cm^3 [28]. Distilled water (W) and tert-butyl alcohol (TBA, $(CH_3)_3OH$, Merck, Germany) were applied as solvents in the freeze-casting process. Dextrin from potato starch (Sigma-Aldrich) and polyvinylbutyral (PVB, $(C_8H_{14}O_2)_n$ Kuraray America Inc., USA) were used as the binders for the water and alcohol containing phase, respectively. Sodium dodecylbenzenesulfonate (DBSS, $CH_3(CH_2)_{11}C_6H_4SO_3Na$, Sigma-Aldrich) was used as an emulsifier in the water-based routes. Polyethylenimine (PEI, $(C_2H_5N)_n$, MW 10.000, 99% purity, Polysciences PEI Inc., USA) and citric acid (CA, $HOC(COOH)(CH_2COOH)_2$, Roth, Germany) were used as dispersants for water-based and TBA-based slurries, respectively.

2.2. Processing

The experimental procedure used in this study is summarized in the flowchart presented in Fig. 1. Table 1 summarizes the experimental parameters varied in this study along with the abbreviations of the specimens. The nomenclature of monoliths was defined based on the type of preceramic polymer (L for LH62C, C for CH62C), ratio of preceramic polymer to silica filler (21 for 2:1, 11 for 1:1, and 12 for 1:2, respectively), and solvent (W for water, TBA for tertbutyl alcohol). Formulations with a total of 30 wt.% loading of preceramic polymer and the amorphous silica filler were stirred in a solvent (W or TBA) with the additives for 4 h. The freeze-casting was performed in a home-made freeze-casting setup that allows for an unidirectional solidification with controlled cooling rates of 2, 4 and 6 °C/min [29]. After the freezing process, all water-based samples were dried in a freeze-dryer (Christ Gamma 2–20, Martin Christ Gefriertrocknungsanlagen GmbH, Germany) at −30 °C under vacuum (0.03 mbar) for ≥3 days. Because the vacuum pump in a freeze-dryer was not equipped with membrane filter for TBA solvent, the Schleck technique was used for sublimation of TBA. After sublimation, the cold samples are carefully removed from the acrylic glass mold. Green bodies fabricated with LH62C polymer were thermally cross-linked by placing them for 2 min in the furnace pre-heated to 300 °C. Finally, all samples were pyrolyzed at 1100 °C under nitrogen atmosphere for 4 h with a heating rate of 3 °C/min. For improving the mechanical strength of the monoliths and to study phase separation processes within the polymer-derived matrix, an additional pyrolysis step at 1400 °C with 3 °C/min for 4 h under argon atmosphere was performed.

2.3. Characterization

Total pore volume and pore size distribution of the whole unbroken monoliths were measured by mercury porosimetry in Porosimeter 2000 WS (Carlo Erba, Italy). To obtain information about the size and orientation of the pores in the scaffolds, X-ray tomography measurements were conducted on unbroken whole monoliths in a home-made setup [30]. The setup consists of a C7942CA-02 flat panel detector (Hamamatsu, Japan) and a L8121-03 microfocus X-ray tube (Hamamatsu, Japan), which was operated at 100 kV. Tomographic reconstructions were computed using VGStudioMAx. The volumetric shrinkage was calculated from the lateral dimensions of the monoliths before and after pyrolysis.

The pore morphology of the monoliths was characterized by Scanning Electron Microscopy (SEM) in a SU8030 microscope (Hitachi, Japan) on the samples cut-off perpendicular to the freezing-direction. The prepared samples for SEM characterization were cut from the same height of all monoliths. Transmission Electron Microscopy (TEM) characterization was performed on a TECNAI $G^2$20 S-TWIN (FEI, Oregon, USA) with LaB_6 electron gun, operated at 200 kV. A Gatan MS794 P CCD camera and DigitalMicrograph software package were used for image recording and evaluation. For elemental analysis, an EDX (EDAX) r-TEM SUTW detector is coupled to the TEM. The samples for TEM characterization were crushed and dispersed in ethanol, then a 3 μl drop was applied on a holey carbon film, supported on a 300 mesh Cu-TEM-grid. The samples were dried in air at 40 °C.

X-ray diffraction (XRD) patterns were recorded on powdered samples in Philips PW 1830 diffractometer operated at 30 mA and 40 kV with CuKα1 = 0.15406 nm radiation with a step time of 10 s and step size of 0.02°. Rietveld refinement was performed using the FULLPROF program [31]. The profile function 7 (Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry function) [32] was used in all refinements. The resolution function of the instrument was obtained from the structure refinement of LaB_6 standard. Solid state $^{29}Si\{1H\}$ single pulse and MAS cross polarization (CP) measurements were carried out on powdered samples in a Bruker Avance II spectrometer at an external magnetic field of 9.4 T (i.e. a 1H resonance frequency of 400 MHz) using a standard Bruker 4 mm double-resonance H-X MAS probe under MAS rotation of 10 kHz ^{29}Si NMR spectra were fitted with a combination of Gaussian and Lorentzian functions using the procedure of F. Massiot et al. [33].

3. Results and discussion

3.1. SiOC ceramics derived from the Silres H62C polysiloxane

Although Silres®H62C was applied as a preceramic polymer in a number of studies [24,34–45] the structure of the ceramics derived therefrom was not addressed in sufficient detail. This issue hinders a direct comparison of the influence of the silica filler on the struc-

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