



Phase separation induced macroporous SiOC ceramics derived from polysiloxane

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Received 24 June 2014; received in revised form 9 September 2014; accepted 18 September 2014
Available online 7 October 2014

Abstract

Macroporous SiOC ceramics have been fabricated through crosslinking and pyrolysis of a two-component polysiloxane (PSO) precursor consisting polyhydrosiloxane (PHMS) and tetravinylcyclotetrasiloxane (D_4Vi) utilizing phase separation of linear polydimethylsiloxane (PDMS) in PSO. The crosslinking of PSO is initiated by Pt-catalyzed hydrosilylation between PHMS and D_4Vi concurrently; and at the meantime phase separation also occurs, forming PSO-rich and PDMS-rich phases. The morphology of PDMS phase in the obtained PSO/PDMS gel can be easily tailored from isolated phase to continuous phase by tuning the initial PDMS concentration. Subsequent pyrolysis treatment yields macroporous SiOC ceramics in which pores arise from thermal depolymerization and evaporation of the PDMS phase. The obtained SiOC ceramics possess controllable morphologies with closed-pores structure, worm-like continuous structure or stacking-particulates structure, which perfectly resembles the morphology of respective PSO/PDMS gel.

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Keywords: Porous ceramic; Phase separation; Silicon oxycarbide; Polymer-derived ceramics; Polydimethylsiloxane

1. Introduction

Porous ceramics have been widely applied in various extremely harsh circumstances,^{1–3} such as molten metal filtration, corrosive gas separation or high-temperature thermal insulation, due to their outstanding thermal/chemical stability and good mechanical properties. Their microstructures such as porosity, morphology and grain orientation can strongly affect their properties and performances. For instance, ceramics with close pores can be used as thermal insulation material for aerospace plane or as transpiration material for missile warhead due to their ultralow heat transfer efficiency;⁴ while ceramics with bicontinuous structures can be employed for advanced transportation as a result of their unique permeability.^{5,6}

Silicon oxycarbide (SiOC) ceramics, as an important kind of oxygen-containing polymer-derived ceramics (PDCs), show excellent mechanical properties and physical/chemical

stabilities in high-temperature, oxidative and corrosive environments.^{7,8} Porosities with different characters (pore size between 0.5 and 800 μm and pore volume between 20 and 90%) have been introduced into SiOC ceramics through different routes,^{9–14} such as replica, sacrificial template, direct forming or 3-D printing, etc. Among these techniques, generating pores in PDCs by phase separation, in which liquid and/or solid soluble polymers are used as pore former instead of solid templates, is especially elegant and facile. In this process, the precursor and pore-former can generate two isolated phases by phase separation, and then the pore-former phase can be decomposed or etched to form pores and/or channels in the precursor-derived ceramic phase. Block-copolymers templates have also been utilized as structuring agents for the fabrication of ordered micro-, meso- and macro-porous PDCs.^{15,16} Recently, liquid–liquid phase separation combined with crosslinking and emulsion processing has been used to prepare macroporous PDCs as well as SiOC particles.^{17–19}

Polydimethylsiloxane (PDMS), which is non-toxic and low-cost, has been used as pore former for fabricating porous SiOC accompanied by phase separation. It decomposes to cyclic and

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linear dimethylsiloxane oligomers and completely escapes from the matrix at intermediate temperature during pyrolysis (above 400 °C) which avoids introducing other elements or impurities into the SiOC ceramics. PDMS, intrinsic or modified, has been added into sol–gel precursors,²⁰ PSO oils and/or resins^{21–24} at high proportions (>40 wt.%) to fabricate meso- and macro-porous SiOC with high surface area. However, little attention has been paid to design tailorable porous SiOC for different requirements and application utilizing the phase separation of PDMS.

In this work, the SiOC ceramics possessing controllable morphologies have been successfully fabricated by tuning the initial PDMS concentration, and a systematic investigation of the influence of the concentration of PDMS in the range ≤ 30 wt.% PDMS is presented and discussed. The phase morphology and microstructure of PSO/PDMS gels and corresponding SiOC ceramics as the changing of PDMS amount are studied, and the relationship of the phase separation process and phase morphology of the obtained SiOC is mainly discussed.

2. Experimental

To synthesize porous SiOC ceramics, linear methyl-terminated polydimethylsiloxane (PDMS, $\text{Me}_3\text{SiO}[\text{SiMe}_2\text{O}]_n\text{SiMe}_3$, $\text{Me}=\text{CH}_3$, molecular weight: $\sim 17,000$, viscosity: 500 mPa s, Kewei, Tianjin, China) was used as pore directing agent. Polyhydromethylsiloxane (PHMS, $\text{Me}_3\text{SiO}[\text{SiHMeO}]_n\text{SiMe}_3$, n is 56 estimated by ^{29}Si NMR, molecular weight: ~ 3500 , viscosity: 100 mPa s, Kaihuasantai, QuZhou, China) and tetramethyltetravinylcyclotetrasiloxane (D_4Vi , $[-(\text{CH}_2=\text{CH})\text{SiMeO}^-]_4$, Zhejiang Sanmen Qianhong, TaiZhou, China) were selected as two-component PSO precursors. Platinum divinyltetramethyldisiloxane complex ($\text{Pt}[\text{ViMe}_2\text{SiOSiMe}_2\text{Vi}][\text{ViMe}_2\text{SiOSiMe}_2\text{OH}]$, Shenzhen Anpin Silicone Materials Co. Ltd., ShenZhen, China) was employed as catalyst for the crosslinking of PHMS and D_4Vi by hydrosilylation of Si–H and $\text{CH}=\text{CH}_2$ groups. All the chemicals were used directly without further treatment of purification.

In a typical synthesis, equal amount of PHMS (6 g) and D_4Vi (6 g) were mixed, as the PSO, by magnetic stirring for 30 min together with Pt-catalyst (0.1 g). Subsequently, different amount of PDMS (5 to 30 wt.%) was added into the mixture and kept stirring for 60 min. Then, the mixture was filled into glass molds ($\Phi = 17 \pm 0.5$ mm) and crosslinked to form cylindrical PSO/PDMS gels (denoted as PSO/PDMS-X, where X is the PDMS concentration) at 50 °C for 6 h and 80 °C for 2 h. Afterward, the shaped PSO/PDMS gels were pyrolyzed at 1000 °C in flowing argon for 1 h at a ramp of 5 °C/min to form porous SiOC ceramics (denoted as SiOC-X, where X is the initial PDMS concentration).

The morphology of the cross-section of PSO/PDMS gels and porous SiOC ceramics were observed by scanning electronic microscopy (SEM, S4800, Hitachi, Japan). The chemistry of the PSO/PDMS gels and the SiOC ceramics were characterized by Fourier transform infrared spectroscopy (FTIR, Ruili WQF-510, Beijing, China) and ^{29}Si solid-state NMR spectroscopy (Infinty

plus 300 WB, Varian, CA, USA). The pyrolysis behavior of the materials was analyzed by thermogravimetry analysis (TGA, Netzsch STA 449F3, Waldkraiburg, Germany) in flowing argon with a ramp rate of 10 °C/min, using thin piece of gel ($m = 10 \pm 2$ mg) rather than powders in order to mimic the real pyrolysis behavior of bulk PSO/PDMS gels in the furnace during the heating. The yield and linear shrinkage during pyrolysis were calculated based on the mass and dimension of the final SiOC ceramics and initial PSO/PDMS gels. The bulk densities and porosities of the ceramics were measured by Archimedes method using water as medium. Densities, porosities and pore sizes of SiOC-10, SiOC-20 and SiOC-30 were also measured by mercury intrusion porosimetry (AutoPore IV 9500 V1.07, Micromeritics, US) after breaking the ceramics into small pieces. The crystallinity and crystal phase content of SiOC ceramics were characterized by X-ray diffraction (XRD, Rigaku D/MAX 2500V/PC, Tokyo, Japan) using CuK_α X-ray.

3. Results and discussions

PDMS, PHMS and D_4Vi are miscible to form homogeneous transparent solution and crosslinked into polymeric gels by Pt-catalysis under heating. Due to the absence of active functional groups on PDMS, crosslinking reaction only occurs between different PSO components (PHMS and D_4Vi). During the crosslinking, phase separation is observed as the liquid turns from transparent to opaque just when the liquid seems solidification. The elasticity of the forming PSO networks should make a significant contribution to this phase separation, and the excessive PDMS are extruded from the network and form a separate phase. This elastic-force induced phase separation is commonly observed during the polymerization of monomers or polymers mixed with linear molecules.^{25,26} Therefore, the true PSO/PDMS gel should consist of two phases with colloidal dimensions, i.e. solid and liquid phases with length scales below 100 nm (or at least below 1 μm).

The obtained PSO/PDMS gels are white rubber-like resins (Fig. 1), rather than the pure PSO gel which is transparent and rigid.²⁷ The reason is the gel possesses a hybrid network structure in which PSO function as a ‘hard’ crosslinked network and inert PDMS as a ‘soft’ isolated dispersed phase. Furthermore, the gel becomes more opaque as the initial PDMS concentration increases (Fig. 1b), due to the larger sizes of PDMS phase and PSO phase confirmed by the following SEM observation. The chemistry of these gels is then analyzed by FTIR spectra (Fig. 2). All gels exhibit a strong broad band at 1110 cm^{-1} resulted from Si–O–Si stretching vibration. This band becomes broader and gradually splits into two or more overlapping bands as increasing PDMS concentration in the gels, suggesting that PSO chains become branched or more complex since the insertion of PDMS into PSO affects the crosslinking of PHMS and D_4Vi to some extent. The sharp peaks at 1259 and 788 cm^{-1} can be assigned to the bending and stretching vibrations of Si–Me^{27,28} in PHMS, D_4Vi and PDMS, and the stretching and bending vibrations of C–H of Si–Me appear at 2970 and 1407 cm^{-1} ,²⁸ respectively. Apart from these peaks, a new peak at 1140 cm^{-1} has been observed on the left shoulder of

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