STUDIES ON THE PROCESSING OF SiBOC FOAMS FROM METHYLVINYL BOROSILOXANE

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by

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ABSTRACT

Ceramic foams are a new engineering material used for various purposes, such as high-temperature insulation, filters, soundproofing, catalyst supports, bone implants, and preforms for polymer-ceramic and metal-ceramic composites. They have a unique combination of desirable properties, including chemical inertness, excellent thermal shock resistance, very low thermal conductivity, very low coefficient of thermal expansion, high-temperature stability, and low dielectric constant. Ceramic foams are typically made from silicon carbide, silicon nitride, partially stabilized zirconia, mullite, and alumina, requiring expensive high-temperature sintering. Preceramic polymers have largely solved this problem, as they can be processed at much lower temperatures (above 1000 °C) and ambient pressure. Among the polymer-derived ceramics, SiOC and SiBOC glass-ceramics exhibit reasonably high Young's moduli, hardness values, glass transition, and crystallization temperatures. In addition, SiOC and SiBOC ceramic foams are realized from easily synthesizable and low-cost polymer precursors such as polysiloxane and polyborosiloxane and thus offer a cost-effective approach to realizing ceramic foams. This thesis describes the research on processing SiBOC ceramic foams from an in-house developed ceramic precursor polymer, viz., methylvinylborosiloxane (MVBS). In this study, SiBOC foams are prepared for the first time by using MVBS, without any fillers, with different foaming methodologies – by using melamine foam as a replica, using urea crystals as a sacrificial template, using natural cotton as a preform for processing carbon-fiber embedded SiBOC foam, and by using aluminosilicate fibers as template and

reinforcement for SiBOC foams. The focus was developing ceramic foams with different methodologies to suit various applications. The SiBOC foams produced are evaluated for their density, compressive strength, thermal conductivity, oxidation resistance, and morphology. The SiBOC foams exhibit low density, moderate compressive strength, and excellent oxidation resistance up to 1300 °C and are candidate materials for thermal protection in an oxidizing atmosphere at high temperatures.

A novel methodology is developed to prepare cellular SiBOC foams by precipitating methylvinylborosiloxane oligomers within a melamine formaldehyde foam scaffold. The preparation of cellular SiBOC foams from MVBS using a reticulated PMF foam template of smaller cell size (~ 200 PPI) has been demonstrated. The conventional procedure involving impregnation followed by squeezing, drying, and ceramization results in a SiBOC foam body with a hollow core by the migration of MVBS molecules to the surface during drying by capillary action due to the smaller cell size of the PMF foam template and high solubility of MVBS in ethanol. The migration to the surface is prevented by precipitating the MVBS by dipping the impregnated PMF foam in distilled water before drying, wherein the web of the PMF foam acts as a scaffold for the growth of the MVBS precipitate. The cellular SiBOC ceramic foams of uniform pore structure from the core to the surface are realized by drying the precipitated MVBS followed by heat treatment at 1500 °C in an inert atmosphere. The density, thermal conductivity, and compressive strength of the SiBOC foams are modulated in the ranges of 0.18-0.39 g.cm^{-3}, 0.08-0.13 W.m^{-1}K^{-1} and 0.3 to 0.87 MPa, respectively, by using MVBS solution concentrations in the range of 37 to 73 wt.%. The SEM microstructures show a combination of open and closed cell structures, and the population of closed cells increases with an increase in MVBS solution concentration. The average pore size decreases from 145 to 93 μm when the MVBS solution concentration increases from 37 to 73 wt.%. Extensive crystallization and phase separation of the amorphous SiBOC foam occurs at temperatures beyond 1600 °C.

The processing of SiBOC foam is developed by another novel and simple sacrificial template method using urea crystals as a pore template. Ethylenediamine (EDA) is used as a novel crosslinking agent for the gelation of MVBS solution. The gelation occurs at room temperature due to the formation of an adduct between electron-deficient boron in the MVBS oligomer backbone and the amino groups of EDA containing a lone pair of electrons. The gelation time of MVBS is modulated from 240 to 3.25 h using EDA concentration in the range of 0.33 to 10 wt.%. The pastes prepared by mixing MVBS solution, EDA, and urea powder show high viscosity and highly shear thinning behavior, amenable for shaping by molding. The urea crystals from the gelled body were quickly removed by leaching with water without collapsing the solidified body. The SEM micrograph shows the presence of rectangular rod-like pores resulting from the urea particle template, which increases with an increase in urea concentration. The SiBOC foam sintered at 1500 °C is amorphous, as evidenced by XRD analysis. TEM micrograph indicates the presence of a few nanocrystals of β-SiC and turbostratic carbon layers in the amorphous SiBOC matrix. The foam density could be modulated in the range of 0.739 to 0.215 gcm^{-3} using urea concentrations of 50 to 88 vol.% of MVBS solution. The SiBOC foams show compressive strength and thermal conductivity in the ranges of 2.75 to 0.2 MPa and 0.262 to 0.073 $Wm^{-1}K^{-1}$, respectively. The SiBOC foam produced exhibited excellent oxidation resistance up to 1300 °C.

Carbon fiber-embedded SiBOC composite foam was realized in another novel approach using natural cotton and MVBS. The carbon fiber-embedded SiBOC foam was realized with a density of 0.61 to 0.27 g.cm^{-3}, with thermal conductivity in the range of 0.277 to 0.128 Wm^{-1}k^{-1}. Removal of carbon fibers by oxidation at 900 °C results in SiBOC foam of reduced density of 0.46 to 0.28 g.cm^{-3}and reduced thermal conductivity 0.098 to 0.065 Wm^{-1}k^{-1}. However, the foams with an initial density of less than 0.4 g.cm^{-3}were found to be too fragile after carbon removal by oxidation at 900 °C. SEM micrographs studied the morphology of the foams concerning the transition of MVBS to SiBOC on heat treatment to 900 and 1500 °C. It is observed that the MVBS deposits have a rough texture, which indicates that MVBS oligomers dry and deposit as discrete particles, i.e., there is no plastic flow of MVBS before solidifying when heated up to 175 °C. However, on heating to 900 °C, the microstructure changes to a consolidated smooth texture. This indicates that between 175 °C and 900 °C, the MVBS might have undergone plastic flow. The foam exhibits hierarchical porosity, i.e., ~ 8 µm pore sizes due to removing carbon fibers embedded in the SiBOC matrix and ~ 117 µm pore sizes from the pores in the parent fiber-embedded SiBOC foam. The foam exhibits oxidation resistance up to 1300 °C, indicating the developed foam's potential as thermal protection for re-entry vehicles.

Aluminosilicate fiber-SiBOC composite foams were made by a simple method using commercially available aluminosilicate wool. MVBS solutions impregnated on a compressible aluminosilicate fiber preform were dried and heat-treated for crosslinking and ceramization to produce ceramic fiber-SiBOC composite foams (CF). The MVBS solution concentrations in the range of 29 to 54 wt.% modulated the density, compressive strength, and thermal conductivity of CF

in the ranges of 0.71 to 0.46 g.cm^{-3}, 0.79 to 0.39 MPa, 0.21 to 0.13 Wm^{-1}K^{-1}, respectively. Incorporating aluminosilicate fiber decreased the thermal conductivity by 18% compared to monolithic SiBOC foams, but it did not contribute to the compressive strength. However, exposure of the CFs to air atmosphere at 1300 °C for 90 minutes increased their compressive strength by up to 46 %. The low thermal conductivity and ability to resist oxidation prove the high potential of the realized CFs for use as a thermal protection material up to 1300 °C in oxidizing atmospheres.