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Fabrication of macroporous SiC from templated preceramic polymers

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Macroporous SiC with a highly ordered pore array was prepared for the first time using low molecular weight SiC preceramic polymers such as polymethylsilane or polycarbosilane by utilizing sacrificial colloidal silica crystalline arrays, as a template which were subsequently etched off after pyrolysis in an argon atmosphere.

Preceramic polymers as non-oxide ceramic precursors have been considered mainly for conventional applications such as fibers, composites and coatings.[1] Some success has been achieved in commercial Nicalon fibers and aerospace composites. In particular, silicon carbide (SiC) is a promising material for high temperature membrane applications. This is because it is capable of withstanding high temperatures and mechanical stresses, and corrosive environments. In spite of these advantages, preparing good-quality porous SiC substrates, for use in the preparation of meso- and microporous membranes, still presents a challenging technical problem.[2] Since the discovery of the M41S mesoporous family,[3] intense research in mesoporous oxide ceramics in order to develop various nanotechological routes for nanoarchitectural materials has been reported. Recently, a class of mesoporous or macroporous carbon[4] and polymers[5] were reported using mesoporous or colloidal silica materials as a removable template. However, only a few reports devoted to the synthesis of porous non-oxide ceramic frameworks are available. Schnick *et al.* reported the preparation of polymeric mesoporous silicon imides and nitrides from silicon amine precursors in the presence of NH_3 and solvents with surfactants, but no discussion was made at the pyrolyzed ceramic level.[6] Alternatively, a MCM-41 like structure was obtained by ammonolysis of a silicon halide with different hydrocarbons. This yielded ammonium halide nanocrystals, which were subsequently removed by calcination in ammonia.[7] However, there has been no report of non-oxide ceramics with a regular pore array prepared from liquid preceramic polymers. In this study, uniform porous SiC ceramics were prepared for the first time by infiltrating the polymeric precursors into an array of monodisperse 500 nm silica spheres.

The silica spheres were synthesized using a previously reported procedure.[8] The filtered colloidal silica particles were washed with distilled water several times to remove any surfactants and then dried in a oven at 70 °C for 7–8 h. In order to fabricate the close-packed silica template, a suspension of the silica spheres in absolute ethanol was allowed to stand and slowly separate into two phases, a silica layer and an ethanol layer through sedimentation. After decanting the solution above the silica deposit, the silica layer was dried at room temperature and in a vacuum oven at 100 °C overnight. Polymethylsilane (PMS), as a SiC precursor, was synthesized using the method described in the literature[9] and polycarbosilane (PCS; $[–Si(H)(CH_3)CH_2—]_n$) purchased from the Nippon Carbon Co. A 30 wt% solution of PMS and PCS, each dissolved in anhydrous tetrahydrofuran (99.9%, Aldrich), was added to the dried silica templates to fill the void space between the silica particles under a nitrogen atmosphere at room temperature for 24 h. The polymer–silica composite was gently dried using a vacuum pump (ULVAC GLD-201) at 50 °C for 2 h to remove the solvent. The resulting mixture was then cured at 160 °C for 6 h in mechanical vacuum condition. The composite was heated at 1200 °C for 1 h in an argon atmosphere at a heating rate of 10 °C min^{-1} (5 °C min^{-1} in the temperature range 200–600 °C due to the characteristic weight loss). The pyrolyzed composite was dissolved in 48% aqueous HF (J. T. Baker 9560-01) to remove the silica template. The resulting porous SiC was washed with distilled water and dried at 100 °C for 6 h. Using the PMS ceramic precursor, the pyrolyzed ceramic–silica composite retained 63 wt% of the dried impregnated polymer–silica composite. After removing the silica templates, the porous SiC was obtained as a 38 wt% residue, which is higher than the 30% of the reported ceramic yield.[10] This suggests that voids in the silica templates can be readily wetted and efficiently filled with polymer by only a single infiltration, presumably due to capillary pressure. However, the PCS displayed less impregnation into the templates. This was shown by only 11 wt% of the porous SiC remaining after the etching process. This suggests that the difference in the extent of infiltration into the silica templates is mostly related to molecular weight of the polymers. As determined using gel permeation chromatography, liquid PMS showed number average molecular weight of 700 (M_n) and a weight average molecular weight of 1400 (M_w), while solid PCS had M_n = 1136 and M_w = 3944. This indicates that PMS easily diffuses with a higher mobility into the templates than PCS. Therefore, one can expect to gain a denser solid network structure with repeated infiltration.[11]

Fig. 1 shows scanning electron microscope (SEM) images of fractured surfaces of the macroporous SiC obtained from PMS and PCS. As expected, the PMS-derived porous SiC produced a significantly longer range of ordered pore arrays than the PCS-derived SiC. Macroporous SiC with a homogeneous regularity was achieved only by a single infiltration with the polymeric precursor. In particular, the gentle release of decomposed gases during pyrolysis at a low heating rate below 600 °C was necessary because faster gaseous evaporation under fast ceramization would be harmful to the homogeneous pore order. Interestingly, small windows were observed in each macropore, which corresponded to the contact points between the initial neighboring silica spheres. Therefore, the pores were interconnected in three dimensions through the windows. The X-ray diffraction (Rigaku D/Max-2B, X-ray Source: Cu-Kα = 0.154 nm) pattern of the PMS-derived porous SiC showed peaks corresponding to the characteristic (111), (220) and (311) planes of β-SiC.[12] In particular, weak peaks around 28 and 47° (2θ) indicated excess Si in the SiC from the PMS,[13] while no such peaks were observed in the PCS-derived SiC product.[10] It

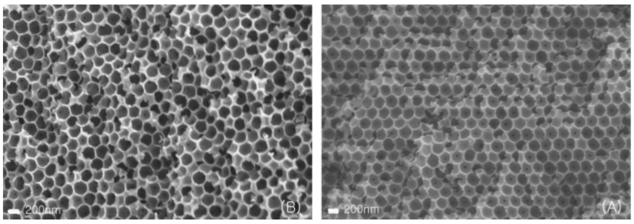

Fig. 1 SEM images of surface of macroporous SiC from PMS (A) and PCS (B). The images were obtained using a LEO 1455VP apparatus.

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is well known that PMS converts to SiC with excess Si while PCS converts to a carbon rich SiC. The results are consistent with the EDX (energy dispersive X-ray spectroscopy) measurements of the PMS- and PCS-derived porous SiC showing 51 wt% and 32 wt% for Si, and 48 wt% and 67 wt% for C with a negligible oxygen intensity, respectively. A broad peak of amorphous silica at the ceramic–silica composite completely disappeared after etching with HF. It is noteworthy that carefully drying the silica templates prior to infiltration was good for minimizing oxidation of the moisture-sensitive polymers from adsorbed water at the interface.

In Fig. 2, a transmission electron microscopic (TEM) image obtained from finely ground PMS-derived SiC definitely shows a three dimensional ordered pore structure. In particular, a pore size of 340 nm indicates about 30% shrinkage during the pyrolysis process by comparison with the 500 nm of the original silica spheres. It is reported that a similar extent of volume shrinkage is intrinsically caused by conversion to the dense ceramic from ~ 1.0 g cm^{-3} for the polymers with mass loss of the volatiles.[14] The wall thickness of the SiC framework was approximately 45 nm, which is similar to those of the macroporous oxides produced using other template methods.[15]

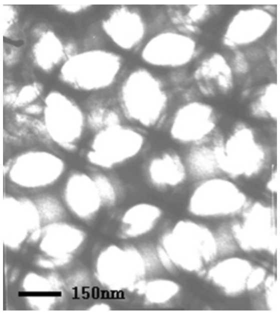

Fig. 2 TEM image of macroporous SiC from the PMS–silica composite at a ×88000 magnification. This image is obtained by using a CM20T apparatus.

Fig. 3 shows that the N_2 adsorption and desorption isotherms of the PMS-derived macroporous SiC exhibited a type IV behavior with hysteresis.[16] The BET surface area calculated from the N_2 adsorption isotherms were in the range 150–172 m^2 g^{-1} with a total pore volume of 0.24–0.26 cm^3 g^{-1}, which is highly porous even for the high temperature annealed samples.

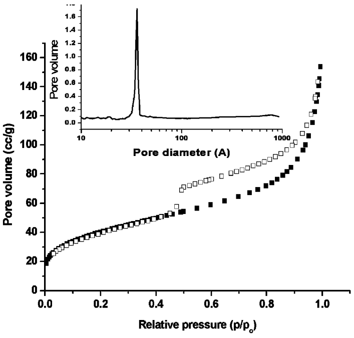

Fig. 3 N_2 adsorption (■) and desorption (□) isotherms of the porous SiC prepared from the preceramic polymer–silica composite. Insert: corresponding pore size distribution curve calculated from the N_2 adsorption isotherm by the BJH method. These graphs were obtained by using a Micromeritics, ASAP 2400 apparatus.

It was reported that polysiloxane-derived SiOC foams showed a BET surface area of approximately 400 m^2 g^{-1} when pyrolyzed at 600 °C but showed a much lower value of 100 m^2 g^{-1} at 1000 °C.[17] In addition, the average pore diameter calculated from the adsorption branch by the BJH method was approximately 5.1 nm with a narrow size distribution. This might be caused by pyrolysis of the polymer framework and the partially etched removal of the crystalline Si grains that are only accessed by HF, which are 6 nm in size based on calculations of XRD peak broadening by the Scherrer equation.[18] Furthermore, bimodal pore structures of macropores (340 nm) surrounded by microporous SiC walls were similarly observed as reported for porous silicates obtained by dual templating methods.[19]

In this work, it was clearly demonstrated that an ordered macroporous SiC was fabricated for the first time by infiltrating the polymeric precursors into a colloidal silica template. It is expected that the pore sizes can be easily controlled by monitoring the sizes of silica spheres by this method and others.[20] This provides a promising method for producing highly thermally and chemically stable non-oxide ceramics with tailored pore characteristics.

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