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Short communication

High strength three-dimensional silica fiber reinforced silicon nitride-based composites via polyhydridomethylsilazane pyrolysis

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Abstract

Three-dimensional silica fiber reinforced silicon nitride-based composites were fabricated through polyhydridomethylsilazane pyrolysis at 500–600 °C in flowing anhydrous ammonia atmosphere. The characteristics of the precursor-derived product, the mechanical properties and microstructures of the composites were investigated by FT-IR, elemental analysis, XRD, flexural strength and SEM. The polymer-derived product was a low-carbon near ceramic material with an empirical formula of $Si_{1.0}N_{1.38}C_{0.01}O_{0.04}H_{0.78}$. Due to the low viscosity and high ceramic yield of the precursor, the as-received composites exhibited a relatively high density of 1.73 g/cm^3 after four infiltration–pyrolysis cycles. The composites were amorphous, showing a high flexural strength of 114.5 MPa and a non-brittle failure behavior. It was the controlled fiber/matrix interface that ensured the reinforcement ability of the silica fibers and the high strength of the composites.

Keywords: A. Precursors; D. Silicon nitride; Silica fiber; Ceramic matrix composites

1. Introduction

Continuous fiber reinforced ceramic matrix composites (CFCMC) have received considerable attention for structural applications because of their excellent thermal stability, light weight and damage tolerance imparted by the reinforcing fibers. Although various CFCMC have been developed during the last decades, such as C/SiC and SiC/SiAlON systems [1,2], there are few composites appropriate for electromagnetic window materials of spacecraft. Three-dimensional silica fiber reinforced silica composites (3D SiO_2/SiO_2) have been fabricated as an electromagnetic window material through sol–gel and slurry infiltration or electrophoretic infiltration processes, but resulting in relatively low flexural strength of no more than about 75 MPa [3–5]. Generally, the high temperature processing of conventional inorganic ceramic systems will lead to serious degradation of silica fibers, therefore, it is arduous to pack ceramics as matrix densely into silica fiber preforms to acquire high strength composite materials. However, preceramic polymer infiltration and pyrolysis (PIP) process could be a promising method to fabricate non-oxide ceramic matrix composites due to its effectiveness in relatively low temperatures.

As is known, silicon nitride (Si_3N_4) is appropriate for high performance electromagnetic window materials [6], but to date there have been few reports on continuous silica fiber reinforced silicon nitride matrix composites. Semff prepared a continuous silica fiber reinforced silicon nitride-based composites via polysilazane infiltration method [7], but the composites were limited to two-dimensional silica fiber cloth reinforced systems, lacking extensive studies on the properties and microstructures. In our previous work [8,9], perhydropolysilazane (PHPS) was used as precursor to prepare three-dimensional silica fiber reinforced silicon nitride composites by PIP method. In this study, another precursor, polyhydridomethylsilazane (PHMS), was used to fabricate high strength silicon nitride-based composites reinforced by three-dimensional silica fiber.

2. Experimental

Silica fibers used in present work were produced by Feilihua Quartz Glass Company (Jingzhou, China), and woven into three-dimensional four-directional fabric with a fiber volume

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Table 1
The properties of silica fibers

Purity (%)	≥99.95
Density (g/cm^3)	2.2
Tensile strength (MPa)	1700
Elastic modulus (GPa)	78
Diameter (μm)	6–10
Dielectric constant	3.78
Loss angle tangent	0.0001

fraction of ~44% by Nanjing Fiberglass Research and Design Institute (Jiangsu, China). The properties of the silica fibers are shown in Table 1. The starting preceramic oligomer, methylhydridosilazane (MHS), was synthesized by the ammonolysis of CH_3SiHCl_2, and the oligomer was a mixture of mainly cyclic species $[CH_3Si(H)NH]_n$ [10,11]. Three-dimensional silica fiber reinforced silicon nitride-based composites (denoted as "3D-SSC") were prepared according to the following three stages. Firstly, the silica fiber preform was pretreated and infiltrated with low-viscosity liquid MHS in vacuum. Secondly, the preform filled with MHS was cured at 150–250 °C for 3–5 h in nitrogen atmosphere, during which MHS was highly cross-linked into gum-like polyhydridomethylsilazane (PHMS). Finally, the cured preform was pyrolyzed at 500–600 °C in flowing anhydrous ammonia atmosphere (99.999% purity, Guangming Special Gas Corp., Dalian, China). The infiltration-cure-pyrolysis cycles were repeated for four times to densify the composites.

Infrared spectra were recorded on liquid-coated KBr plates (for MHS) and KBr pellets containing ground powder samples (for solid PHMS and the pyrolytic product thereof) by Avatar 360 FT-IR spectrometer (Nicolet Instrument Corp., Wisconsin, USA). Elemental analysis for Si, N, C, O and H were obtained for PHMS-derived product by Analysis and Test Center of 230 Institute of Nuclear Industry (Changsha, China). X-ray diffractometer (D8 Advance, Bruker/Axs Corp., Germany) was used to examine the as-received composites. The density of the composites was monitored by Archimedes method. The flexural strength of the composites was determined on a computer controlled universal testing machine (WDW-100, Changchun Research Institute of Testing Machines, Jilin, China) with a span of 30 mm and crosshead speed of 0.5 mm/min carried out at a test piece 4 mm wide and 3 mm thick. Microstructures of the composites were examined on JSM-5600LV scanning electron microscope (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan).

3. Results and discussion

Fig. 1a illustrates the infrared spectrum of MHS, with absorption peaks located at 3380/1180 cm^{-1} (N–H), 2960/2900 cm^{-1} (C–H_3), 2100 cm^{-1} (Si–H), 1260 cm^{-1} (Si–CH_3) and 930 cm^{-1} (Si–N–Si) indicating a molecular formula of $[CH_3Si(H)NH]_n$ [11]. In comparison with Fig. 1a, the intensity of N-H vibration peaks for PHMS (see Fig. 1b) became weaker, suggesting a crosslinking mechanism of deprotonation of N–H groups with the elimination of hydrogen [11]. Under the pyrolysis condition for preparing 3D-SSC, PHMS-derived product (i.e., the matrix for the composites) showed a near ceramic transformation with disappeared or extremely weak absorption peaks of N–H, C–H_3, Si–H, Si–CH_3, and strong absorption peaks in the vicinity of 930 cm^{-1} assigned to asymmetric Si–N–Si stretching vibration (see Fig. 1c).

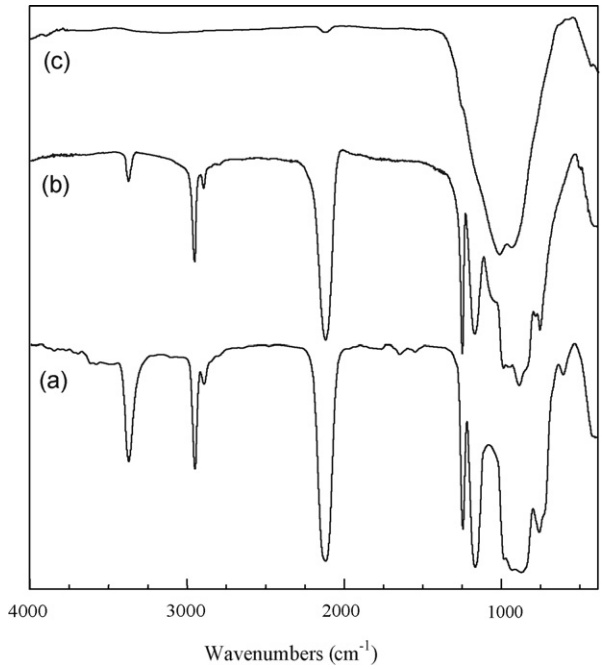

Fig. 1. Infrared spectra of: (a) methylhydridosilazane; (b) polyhydridomethylsilazane; and (c) polyhydridomethylsilazane-derived product after pyrolysis at 500–600 °C in ammonia atmosphere.

Carbon containing polysilazanes, in principle, could gave low-carbon silicon nitride-based ceramics when pyrolyzed in reactive ammonia atmosphere, and the carbon removal was extremely effective at 400–600 °C [12]. In the present study, PHMS-derived product at 500–600 °C in flowing ammonia was whitish in color with a ceramic yield of 70–75 wt.%, and the elemental analysis gave an empirical composition of $Si_{1.0}N_{1.38}C_{0.01}O_{0.04}H_{0.78}$ (Si, 57.1 wt.%; N, 39.4 wt.%; C, 0.3 wt.%; O, 1.4 wt.%; H, 1.6 wt.%).

Reschke and co-authors studied the in-situ carbon content adjustment in polysilazane derived bulk ceramics (or functionally graded ceramic materials) with the carbon contents in the range of 0–14 wt.% (or 0.3–16.2 wt.%), and an accelerating movement of the carbon-free region towards the center of the specimen was observed with prolonged dwelling time at certain temperatures [13,14]. In our study, the interconnected network in the silica fiber fabric improved the effective reaction area for the inward diffusion of ammonia into the body, as well as outward diffusion of gaseous reaction products (CH_4 and other hydrocarbons), thus leading to a low carbon content and homogeneous composites. With proper pyrolysis temperature (500–600 °C), long soaking time in ammonia (more than 3 h for each pyrolysis cycle) and appropriate specimen size (just about 5–10 mm thick), it was successful to prepare 3D-SSC with low-carbon near ceramic state matrix homogeneously distributed from the surface to the interior of the composites.

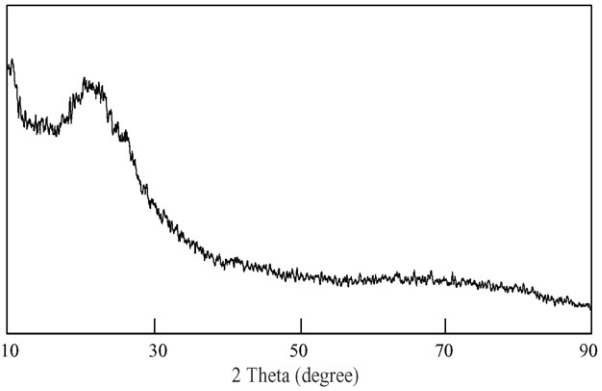

Fig. 2. X-ray diffraction pattern of the as-received 3D-SSC composites.

The X-ray diffraction pattern of 3D-SSC composites is shown in Fig. 2. No crystalline phases were observed in the as-received composites, suggesting an amorphous state of the silica fibers and PHMS-derived matrix. As a result, the amorphous state of silica fibers gave less degradation, thus contributing to a good reinforcement ability for the composites. Fig. 3 illustrates the load–displacement curve of the composites during three-point flexural strength test. The composites showed an elastic response in the beginning with displacement increasing linearly depending on the load, then a non-linear behavior near the peak load followed by a gradual decreasing. The flexural strength of the as-received composites was 114.5 MPa, much higher than that of the 3D SiO_2/SiO_2 composites fabricated by sol–gel or electrophoretic infiltration processes [3–5]. The density of 3D-SSC composites was 1.73 g/cm^3, and the relative density was about 87.6%.

Generally, during the flexural strength test, the failure behavior of fiber reinforced composites is strongly dependent on the nature of the fiber/matrix interface. In this study, 3D-SSC composites exhibited a good composites behavior and mechanical property, suggesting an ideal microstructure. Fig. 4 shows the SEM micrographs of the fracture surfaces of 3D-SSC composites after flexural test and shearing destroy by transient impact load. Distinct fiber pull-outs, which will improve the toughness, damage tolerance and reliability, were

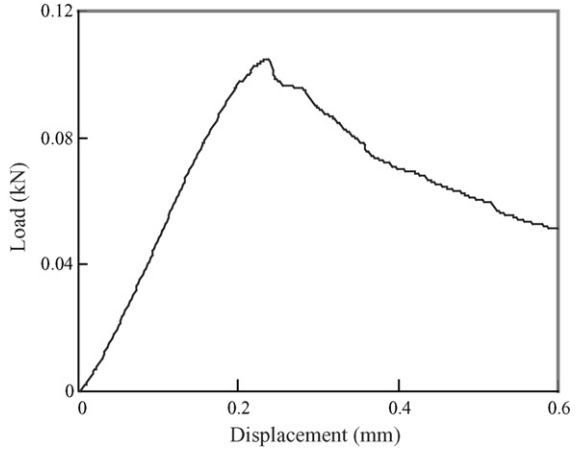

Fig. 3. Load–displacement curve of the as-received 3D-SSC composites.

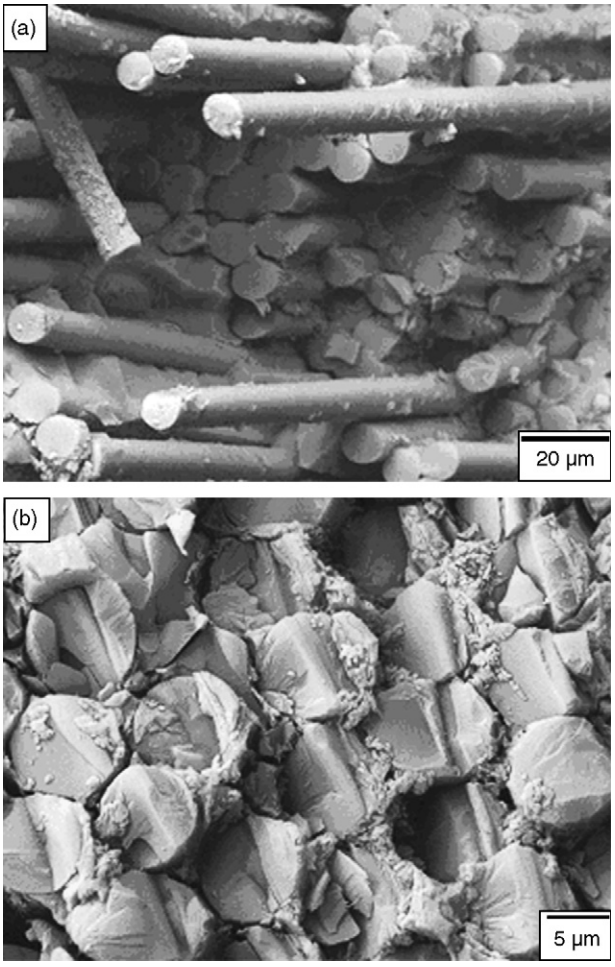

Fig. 4. SEM micrographs of the fracture surfaces of the as-received 3D-SSC composites: (a) after three-point flexural test and (b) after shearing destroy by transient impact.

observed in Fig. 4a. Relatively dense matrix, resulting from the good infiltration and high char yield of the precursor, was observed in Fig. 4b. The cross-section of silica fibers presented a good state, hence ensuring the effective reinforcement for the composites. Therefore, the above-mentioned preparation process for 3D-SSC was successful to acquire high strength composites, not only avoiding the strong adhesion of fiber/matrix interface, but improving the reinforcement ability of the silica fibers.

To prepare ceramic matrix composites applicable for electromagnetic windows of spacecraft, the reinforcing fabric must have a good structural integrity and transparence for microwave transmission, and ultra pure silica fibers are being preferred for that. However, exposure of silica fiber to 1000 °C for 1 h results in a reduction to 25% of the original tensile strength, and damage occurs at temperatures as low as 750 °C over a long time heat treatment [7]. Therefore, taking account into the embrittlement of silica fibers and also the carbon removal requirement for PHMS, the pyrolysis temperature for fabricating 3D-SSC composites in the present work was no more than 600 °C, thus resulting in an amorphous near ceramic state matrix. Such composites could be used as thermal protection or electromagnetic window materials to meet with

short term and high temperatures of high velocity spacecraft, and would result in further conversion to a ceramic material during the high temperature trajectory, but this high temperature condition would be experienced over a very short period of time (such as a few seconds), thereby without obvious fiber damage, especially in the interior of the material [7]. Higher pyrolysis temperatures (such as 800–1200 °C) will lead to a better ceramization of PHMS, but worse fiber degradation and stronger fiber/matrix adhesion, which are detrimental to the mechanical properties of the composites.

4. Conclusions

Three-dimensional silica fiber reinforced silicon nitride-based composites were prepared at 500–600 °C by the PIP method using polyhydridomethylsilazane as precursor. The as-received composites were amorphous with low-carbon silicon nitride-based ceramic matrix, showing a high flexural strength of 114.5 MPa. The PIP method is successful to fabricate high strength three-dimensional silica fiber reinforced silicon nitride-based composites with dense matrix and moderate fiber/matrix interfacial adhesion.

Acknowledgements

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