JMEPEG (2008) 17:111–114
DOI: 10.1007/s11665-007-9146-8
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1059-9495/$19.00

Effect of Pyrolysis Temperature on the Properties of Three-Dimensional Silica Fiber Reinforced Nitride Matrix Composites

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(Submitted January 12, 2007; in revised form February 28, 2007)

Three-dimensional silica fiber reinforced nitride matrix composites (3D SiO_{2f}/nitride composites) were prepared through four cycles of vacuum infiltration of a hybrid precursor and pyrolysis under ammonia atmosphere. The effects of pyrolysis temperature on densification behavior, mechanical properties, and microstructures of the composites were investigated. With the increase of pyrolysis temperature from 800 to 1300 °C, the density of SiO_{2f}/nitride composites increased from 1.83 to 1.88 g/cm^3, while the flexural strength decreased from 148 to 53 MPa, and the elastic modulus decreased from 41.5 to 25.1 GPa. The higher temperatures cause serious damage to silica fibers. The properties of silica fibers and the reinforcing mechanism determine the mechanical properties of the composites.

Keywords composites, fracture, mechanical properties, microstructure, nitrides

1. Introduction

With the development of aerospace technologies, more and more advanced materials are required to be originated and fabricated. Take, for example, high-temperature wave-transparent materials, they have become the requisite of hypersonic aircraft (Ref 1).

Silica fibers, with excellent dielectric properties, ablation resistance, thermal shock damage resistance, chemical stability and flexibility, are suitable for fabricating high-temperature antenna window materials to meet the requirements of communication, control, and thermal protection of spacecrafts (Ref 2). During the last years, continuous silica fiber reinforced ceramic matrix composites have been developed, such as SiO_{2f}/SiO_2 and SiO_{2f}/Si_3N_4 composites (Ref 3-6).

However, as the temperature increases, the mechanical properties of silica fibers degrade significantly. When the residual strength is too low, the fibers will have no efficient reinforcement. Therefore, the preparation temperature is considerable.

In this paper, a wave-transparent silica fiber reinforced composite with a hybrid matrix containing BN and Si_3N_4 was prepared by the process of precursor infiltration and pyrolysis, which can be carried out at low temperatures. The effects of the pyrolysis temperature on densification behavior, mechanical properties, and microstructures of the composites were characterized.

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2. Experimental

Silica fibers used in the present work were produced by Jingzhou Feilihua Quartz Glass Corporation (Hubei, China) with properties listed in Table 1. Three-dimensional fabrics, with fiber volume fraction about 45%, were woven by Beijing FRP Research and Design Institute (Beijing, China).

The starting preceramic precursor, a low-viscosity transparent liquid was synthesized by mixing perhydropolysilazane (PHPS) and borazine (Ref 7), the ratio between them was no more than 1/10 (vol.). Borazine was synthesized by thermolysis of $H_3N{\cdot}BH_3$ in a pressure vessel (Ref 8), and PHPS was synthesized by the ammonolysis of di-chlorosilane-pyridine (Ref 9).

The composites were prepared by precursor infiltration and pyrolysis according to the following steps. First, the fabric was infiltrated with hybrid precursor in vacuum. Then, the preform filled with precursor was cured at about 100 °C in nitrogen with a pressure of about 8 MPa. Finally, the cured preform was pyrolyzed in ammonia at different temperatures.

The infrared spectrum of hybrid precursor was examined by Avatar 360 Fourier transform infrared spectrometer. The crystalline phase and its preferred orientation were characterized by x-ray diffractometry at a wavelength of 1.5418 Å (Cu $K\alpha$ radiation). The bulk density of the composites was calculated from the weight-to-volume ratio. The mechanical properties were determined in a three-point test machine (CSS-1101) 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.

3. Results and Discussion

3.1 Structures of Hybrid Precursor and Its Pyrolytic Product

The infrared spectrum of hybrid precursor is shown in Fig. 1. Compared with references (Ref 10, 11), absorption peaks located at 3440, 2490, 2100, 1490 cm^{-1} and 850 to 980 cm^{-1} are assigned to N-H, B-H, Si-H, B-N, and Si-N-Si groups. Figure 2 shows the XRD pattern for the pyrolytic product at 1300 °C. Most of the characteristic diffraction peaks of h-BN located at 26.7°(002), 41.6°(100), 76.1°(110) are obvious and the characteristic diffraction peaks of α-Si_3N_4, located at 23.3°(110), 27.0°(200), 33.6°(101), 36.0°(120), 41.3°(201), 52.1°(301), 69.0°(321), 84.5°(421), and so on, are observed. When it is pyrolyzed at high temperatures, the precursor will be converted to ceramics mixed by BN and Si_3N_4.

Table 1 The properties of silica fibers

Purity, %	Density, g/cm^3	Tensile strength, MPa	Elastic modulus, GPa	Diameter, μm
≥99.95	2.2	1700	78	6 to 8

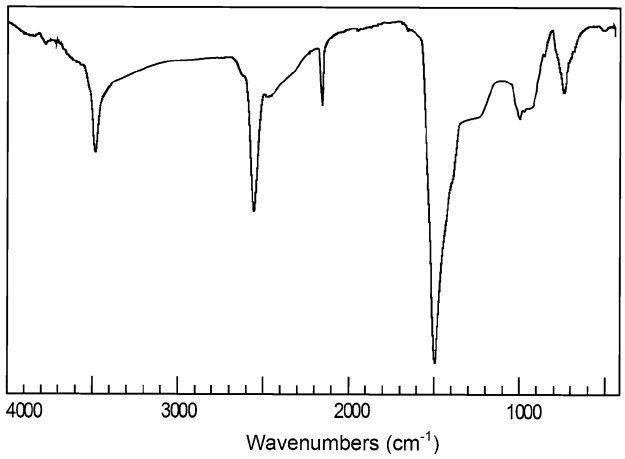

Fig. 1 Infrared spectrum of hybrid precursor

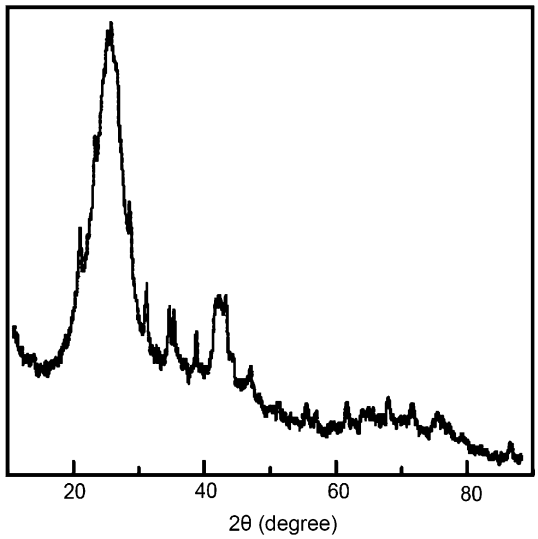

Fig. 2 XRD pattern of the pyrolytic product at 1300 °C

3.2 Densification of the Composites

The density of the composites prepared at different temperatures as a function of pyrolysis cycles is plotted in Fig. 3. Repeated infiltration and pyrolysis cycles are required to densify the composites due to the shrinkage of precursor when it is pyrolyzed. It could be observed that the density curves exhibited fast mass gains in the beginning two pyrolysis cycles due to the high infiltration efficiency and ceramic yield of precursor, and the mass gain became slower after the third pyrolysis cycle. With the increase of prolysis temperature, further pyrolysis of the precursor takes place and higher density composites are obtained. The curves of the composites prepared at 1000 °C and 1300 °C nearly overlap, which indicates a comparatively complete pyrolysis of the precursor at about 1000 °C

3.3 Mechanical Properties and Microstructures of the Composites

The main properties of 3D SiO_{2f}/nitride composites are listed in Table 2. The load-displacement curves are illustrated in Fig. 4, and the micrographs of the fracture surfaces of the composites are shown in Fig. 5. As is seen, the composites pyrolyzed at 800 °C have outstanding mechanical properties

Table 2 The properties of 3D SiO_{2f}/nitride composites prepared at different temperatures

Pyrolysis temperature, °C	Density, g/cm^3	Flexural strength, MPa	Elastic modulus, GPa
800	1.83	148.2	41.5
1000	1.87	83.4	33.1
1300	1.88	53.3	25.1

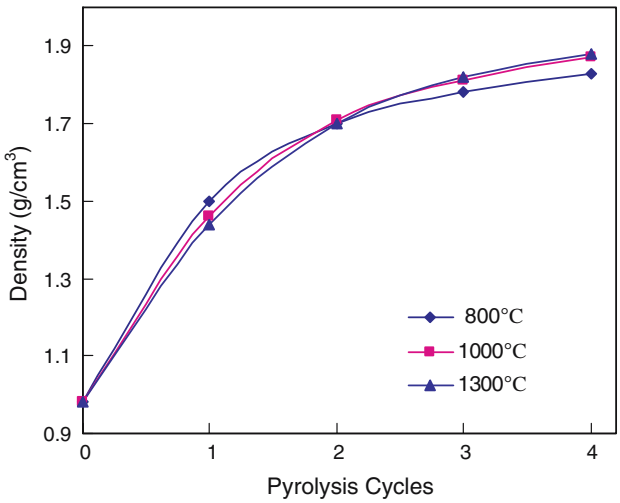

Fig. 3 Densification curves of 3D SiO_{2f}/nitride composites prepared at different temperatures

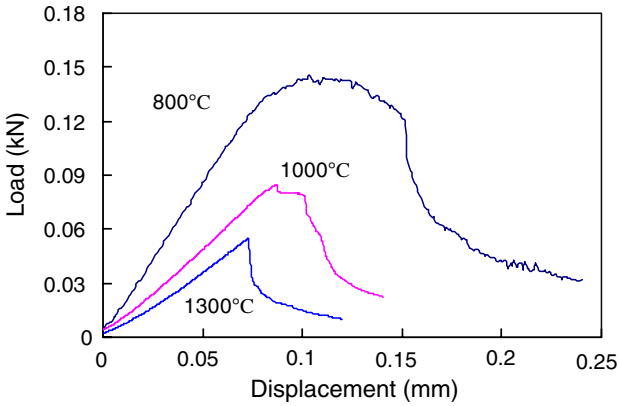

Fig. 4 Load-displacement curves for 3D SiO_{2f}/nitride composites prepared at different temperatures

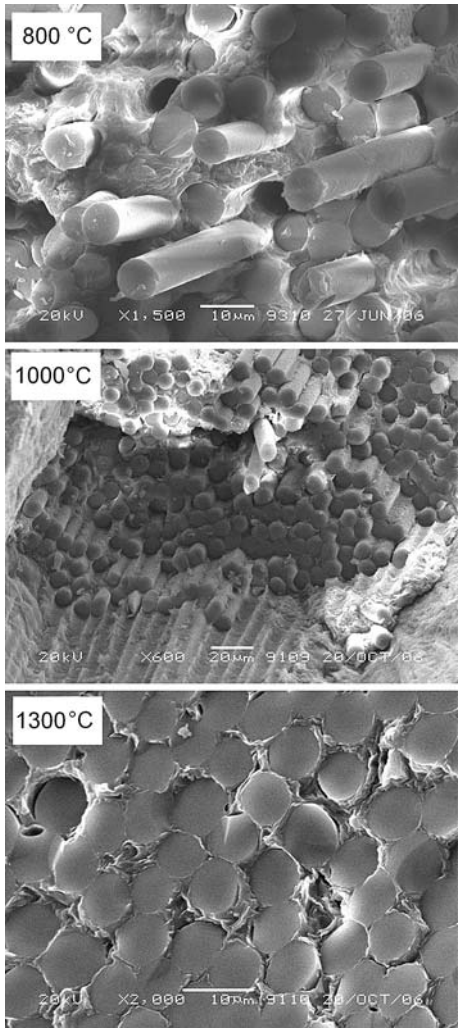

Fig. 5 SEM micrographs of the fracture surfaces of 3D SiO_{2f}/nitride composites prepared at different temperatures

due to little damage to silica fibers. The flexural strength and elastic modulus reach 148 MPa and 41.5 GPa, respectively. Excellent toughness can be recognized from the load-displacement curve. At the same time, obvious fiber pull-out can be observed from scanning electron microscopy, which can absorb lots of energy before the composites is destroyed, exhibiting the effectiveness of fiber reinforcement.

When the composites are prepared at 1000 °C, the strength of silica fibers degrades seriously. Therefore, the mechanical properties of SiO_{2f}/nitride composites degrade, too. The load-displacement curve shows that the composites have a considerable toughness. Some fiber pull-out can be found from the micrograph, but large-scale debonding between fibers and matrices are observed, which is the main reinforcement mechanism of the silica fibers.

The composites prepared at 1300 °C have poor mechanical properties. The sudden decline in the load-displacement curve and the flat fracture surfaces without any fiber pull-out show an apparent brittleness of the composites. When silica fibers are treated to 1300 °C, they are damaged badly and become fragile, with little strength. Fibers cannot supply efficient reinforcement to the matrices any more, consequently, the composites prepared at 1300 °C are weak and brittle.

4. Conclusions

3D SiO_{2f}/nitride composites were prepared from a hybrid precursor by precursor infiltration and pyrolysis at different pyrolysis temperatures. Their densification behavior, mechanical properties, and microstructures were evaluated. The following conclusions can be drawn from the present investigation.

(1) The process of precursor infiltration and pyrolysis is a fast and convenient rout to prepare dense SiO_{2f}/nitride composites. The composites pyrolyzed at elevated temperature exhibit higher mass gain. The densities of the composites pyrolyzed at 800, 1000, and 1300 °C are 1.83, 1.87, and 1.88 g/cm^3, respectively.

(2) The pyrolysis temperature affects the mechanical properties of SiO_{2f}/nitride composites. With the increase of pyrolysis temperature, the flexural strength and elastic modulus decrease. The composites prepared at 800 °C exhibit excellent mechanical properties, while the composites prepared at 1300 °C are weak and brittle. The different mechanical properties are determined by different performances of fibers and different reinforcing mechanisms.

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