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Effects of precoating and calcination on microstructure of 3D silica fiber reinforced silicon nitride based composites

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Abstract: Three-dimensional silica fiber reinforced silicon nitride based composites were fabricated by preceramic polymer infiltration and pyrolysis method using perhydropolysilazane as a precursor. The effects of precoating and high temperature calcination on the microstructures of the composites were investigated by scanning electron microscopy. For the composite without a precoating, the fracture surface is plain, and the fiber/matrix interfaces become very unclear after calcination at 1 600 ℃ due to intense interfacial reactions. The composite with a precoating shows tough fracture surface with distinct fiber pull-outs, and the fiber/matrix interfaces are still clear after calcination at 1 600 ℃. It is the appropriate precoating process that contributes to the good interfacial microstructures for the composite.

Key words: silica fiber; precoating; preceramic polymer; silicon nitride based composites; microstructure

1 Introduction

Continuous fiber reinforced ceramic matrix composites, such as C/SiC, C/Si-C-N, C/Si-O-C and SiC/SiC systems[1−5], have received considerable attention because of their excellent thermal stability, light mass and high toughness, etc. Among various reinforcing fibers, silica fiber is suitable for fabricating thermal protection and high temperature antenna window materials due to its excellent ablation resistance, dielectric properties, chemical stability and flexibility. During the last decades, silica fiber fabric reinforced silica or phosphate based composites have been developed using sol-gel, electrophoretic infiltration or slip casting processes[6−11], but all these composites show relatively low density and strength due to the sensitive surface of silica fibers and the strong fiber/matrix interfacial bonding. What's more, little work has been done to date on continuous silica fiber reinforced non-oxide ceramic matrix composites because it is so arduous to pack ceramic matrix densely into silica fiber preforms.

In earlier work[12,13], three-dimensional silica fiber reinforced silicon nitride based composites (3D SiO_2/Si_3N_4), were prepared innovatively by preceramic polymer infiltration and pyrolysis method using perhydropolysilazane as a precursor, showing that strong fiber/matrix bonding of the composites led to brittle failure and low strength. In this paper, to find appropriate fiber pretreatment processes to suppress the possible fiber/matrix interfacial reactions at high temperatures, 3D SiO_2/Si_3N_4 composites were prepared by different pretreatment processes, and the microstructures of the composites calcined at high temperatures were investigated by scanning electron microscopy(SEM).

2 Experimental

The silica fibers used in this study were produced by Feilihua Quartz Glass Corporation (Jingzhou, China) with a purity of not less than 99.95%, a density of 2.2 g/cm^3 and a tensile strength of 1 700 MPa. Three-dimensional four-directional silica fiber preforms, with the fiber volume fraction of about 44%, were woven by Nanjing Fiberglass Research and Design Institute, China. Perhydropolysilazane, the preceramic polymer, was synthesized by the ammonolysis of dichlorosilane-pyridine adduct[14, 15]. The as-synthesized precursor was a transparent liquid with a low viscosity of 30−50 mPa·s (25 ℃).

The composites were prepared according to the

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following stages. The fiber preforms were pretreated and infiltrated by the precursor in vacuum, then the preforms filled with the precursor were cured at 100−200 ℃ for 1−3 h in an inert atmosphere, and finally fired at 800 ℃ in anhydrous ammonia. The infiltration-pyrolysis cycles were repeated for 4−5 times to densify the composites. Moreover, an additional precoating on the surface of the fibers was used before the first infiltration cycle to prepare another group of composites for comparison. The above samples were calcined to 1 600 ℃ for 2 h in an inert atmosphere to study the effect of temperature on the microstructures of the composites. The composites without and with precoating were denoted as "SS800" and "SS800P", and the corresponding samples calcined at 1 600 ℃ were denoted as "SS800-1600" and "SS800P-1600" respectively.

The fracture surfaces of the composites were examined by JSM-5600LV scanning electron microscope or Sirion 200 field emission scanning electron microscope.

3 Results and discussion

The SEM micrographs of the fracture surface of sample SS800 are illustrated in Fig.1. The fracture surface of SS800 is plane without any fiber pull-outs (see Fig.1(a)), implying poor reinforcement of the fibers and a typical brittle fracture behavior. With low viscosity and good wettability, the precursor is efficiently infiltrated into the inter- and intra-yarns of the silica fiber preform, leading to a low porosity. The fiber/matrix interfaces are unclear due to strong interfacial adhesion, and only the fiber near pores partly maintains its shape, leaving one side identifiable and the other side adhered tightly to the matrix (see Fig.1(b)). There are distinct microcracks in the matrix and on the surface of the fibers due to the thermal mismatching of silica fibers and polymer-derive silicon nitride matrix. Since the precursor has highly reactive Si-H chemical bonds, there can be strong chemical reactions between the silica fibers and the precursor during high temperature pyrolysis.

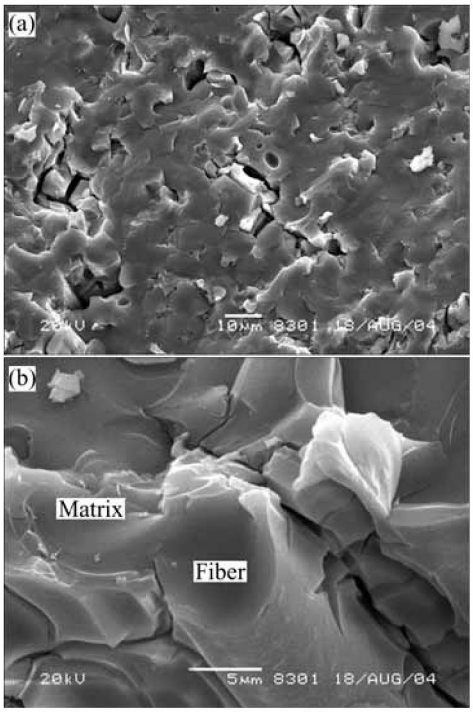

Fig.1 SEM micrographs of fracture surface of sample SS800

Fig.2 shows SEM micrographs of the fracture surface of sample SS800P. There are distinct fiber pull-outs (see Fig.2(a)), and the silica fibers are identifiable clearly from the matrix (see Fig.2(b)). In contrast to Fig.1, the moderate interfacial adhesion in Fig.2 ensures the good capability of fiber reinforcement, suggesting a better mechanical property.

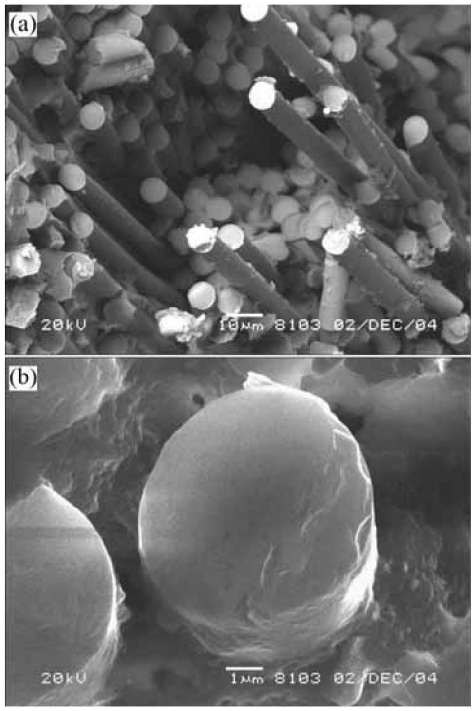

Fig.2 SEM micrographs of fracture surface of sample SS800P

The load-displacement curves of the sample SS800 and SS800P are illustrated in Fig.3. The load of SS800 is almost linear with the displacement until a catastrophic failure. While SS800P demonstrates a non-brittle failure behavior with higher fracture load and displacement, showing a better deformation resistant ability. The flexural strength of SS800P is 144.9 MPa, while SS800 has a flexural strength of just 33.5 MPa. The results of the mechanical property of the samples are in accordance with the microstructures shown in Fig.1 and Fig.2. It is

noteworthy that the flexural strength of 144.9 MPa is much higher than that of the silica fiber reinforced silica or phosphate composites[6−11].

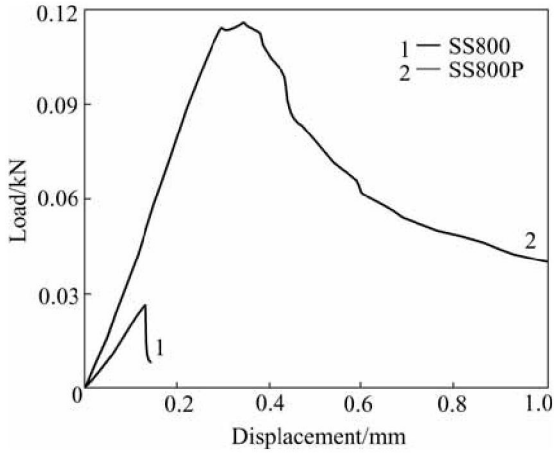

Fig.3 Load-displacement curves of 3D SiO_2/Si_3N_4 composites

Fig.4 presents SEM micrographs of the fracture surface of sample SS800-1600. Strongly deformation is found for the composite by a macroscopic observation, and the micrograph of the fracture surface is disordered with unclear fiber/matrix interfaces (see Fig.4(a)). A typical magnified image shows a deformed silica fiber with a microcrack in the irregular cross-section (see Fig.4(b)). This is probably due to further interfacial reactions and atomic diffusion of silica fibers and polymer-derived silicon nitride matrix at high temperatures. In the previous study[13], crystallized silica fibers and silicon nitride matrix were observed by X-ray diffraction patterns for the composites calcined at 1 600 ℃, and these crystalline phases can also be responsible for the microstructure characteristics shown in Fig.4.

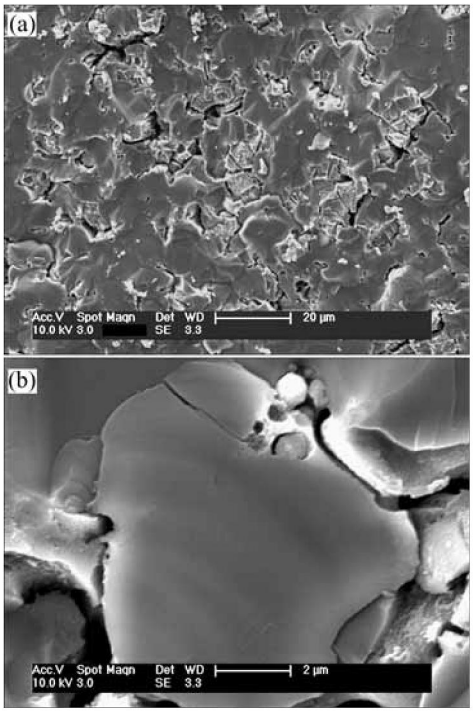

Fig.4 SEM micrographs of fracture surface of sample SS800-1600

Fig.5 illustrates SEM micrographs of the fracture surface of SS800P-1600. Different from Fig.4, the fiber/matrix interfaces of SS800P-1600 are still clear (see Fig.5(a)). The fracture surface is relatively planar with the matrix composed of uniform micro-crystallites and the silica fibers maintaining their round shapes very well (see Fig.5(b)).

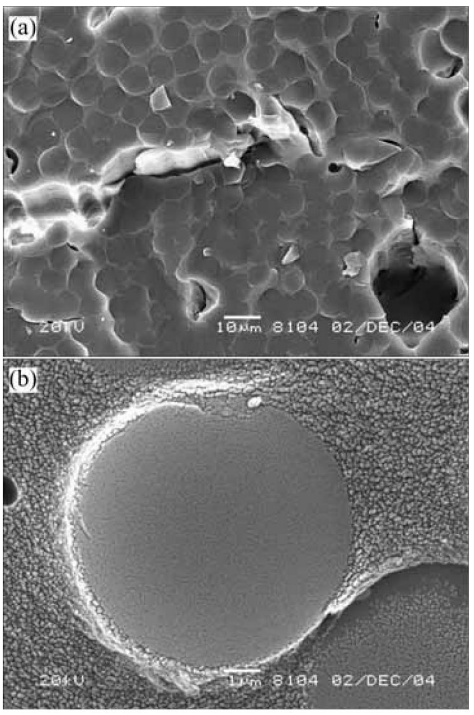

Fig.5 SEM micrographs of fracture surface of sample SS800P-1600

The fatal defect of silica fiber is its degradation behavior at high temperatures, and almost all the silica fiber reinforced ceramic matrix composites have the same problem of poor mechanical properties[6−11]. In this study, the fiber/matrix interfacial bonding is tight for the composites without precoating, and the interfaces become more unclear after calcination at high temperatures. However, an additional precoating process before polymer infiltration has successfully alleviated the possible interfacial reactions, showing relatively weak fiber/matrix bonding, good state of the silica fibers and clear fiber/matrix interfaces even after calcination at 1 600 ℃. The silica fibers, without distinct deformation at high temperatures, will keep the good shape of the entire composites to meet the requirements for aerodynamic shapes or electromagnetic wave transmission.

Such composites may be appropriate for short term and high temperature applications as thermal protection system or electromagnetic windows for high velocity spacecraft.

4 Conclusions

1) Fiber pretreatment process has a great influence on the microstructures of 3D SiO_2/Si_3N_4 composites. Appropriate precoating can alleviate the fiber/matrix interfacial adhesion and improve the mechanical property.

2) After calcination at high temperatures, 3D SiO_2/Si_3N_4 composites show stronger fiber/matrix interfacial reactions and a tendency to brittle fracture. However, the composite with fiber precoating still exhibit clear fiber/matrix interfaces.

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