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Microstructure and properties of C_f/SiC composites with thin SiCN layer as fiber-protecting coating

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Abstract

C_f/SiC composites were prepared first by chemical vapor infiltration for formation of SiCN coating on the fiber surface, then by polymer infiltration and pyrolysis for SiC densification process. The effect of SiCN content on microstructure and mechanical properties of the composites was investigated. As the content of deposited SiCN increased, the density of the composites gradually increased. Simultaneously, the bending strength and proportional limit stress were also improved. When the preform density after SiCN deposition reached about 1.01 g/cm^3, the ultimate bending strength and proportional limit stress of the final densified composites were enhanced to 386 MPa and 302 MPa, respectively. The fracture behavior of the fabricated composites was totally changed after SiCN deposition. Long fiber pullout dominated the fracture surfaces for composites with deposited SiCN, while for the one without fiber coating no fiber pullout was observed.

Keywords: B. Carbon composites; C. Flexural strength; Coating; Polymer infiltration and pyrolysis

1. Introduction

Continuous carbon fiber reinforced silicon carbide matrix composites (C_f/SiC) are promising candidates for aerospace and aircraft components for their low density, enhanced degree of damage tolerance and high reliability [1,2]. Several low-temperature fabrication techniques, including chemical vapor infiltration (CVI), polymer infiltration and pyrolysis (PIP) and reaction sintering (RS), have been extensively investigated for the fabrication of such composites [3–7].

PIP has been considered as an efficient processing technique for in-situ fabrication of large-dimensional and complex-shaped components based on organometallic preceramic precursors [8]. In the pyrolysis process, the carbon fiber is usually sensitive to active organic fragments released during polymer pyrolysis and fiber property declines rapidly. On the other hand, the fiber/matrix interfacial domain is a critical region for the mechanical properties of C_f/SiC composites [9], because load transfer from the matrix to the fiber through such a region consisted of a thin coating layer of one or several deposited materials [10,11]. Thus, a layer of proper interphase is extremely necessary to be designed on the fiber surface to prevent the chemical reaction between the reinforcing fiber and the active species and efficiently transfer matrix load to the fiber. The interphases play these important roles in the composites and effects of different interphases (e.g. PyC, SiC, and BN) on the mechanical properties of the composites were extensively reported [12,13]. Usually, a thin layer of SiC is deposited from methyltrichlorosilane (MTS) around the carbon fiber as a protecting interphase to achieve fine composite property [14]. However, during the SiC deposition process, a large amount of hydrogen chloride evolves, which easily corrodes the metal components of the equipments and is also quite harmful to the environment. It is necessary to develop another environment-friendly precursor to deposit the fiber coating for carbon fiber protection in the fabrication process.

In the present study, a carbon-rich precursor, hexamethyldisilazane (HMDS) was used to deposit SiCN coating

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to protect the carbon fiber from chemical erosion. We employed 3D braided preforms as the reinforcement in developing C_f/SiC composites by PIP with SiC powder as inert filler in the first infiltration process. Effect of content of deposited SiCN on the mechanical properties and microstructural evolution of the fabricated composites was evaluated.

2. Experimental procedure

2.1. Preform preparation

HTA-3K carbon fiber (Toho Tenax Co., Japan) was used for composite preparation. Typical parameters of the carbon fiber are listed in Table 1. 3D preforms were braided by four-step processing by Nanjing Glassfiber Research and Design Institute (Nanjing, China). The fiber volume fraction in the preform was controlled at about 40%.

2.2. Interphase deposition

Before SiCN deposition, a thin layer of pyrocarbon (PyC) was deposited using methane (CH_4) as precursor on the fiber surface. The thickness of PyC coating was controlled at about 0.3 μm. HMDS was selected for deposition of SiCN with H_2 as both diluting and carrying gas. Different contents of SiCN were deposited around the carbon fibers to protect them from chemical erosion of pyrolysis-released species in densification process.

2.3. Preform densification

The preceramic polymer for matrix derivation in the present experiment was polycarbosilane (PCS; from National University of Defense and Technology, China). The ceramic yield is 60.5 wt% by TG test. As the inert filler material for the matrix, SiC powder with an average grain size of 0.5 μm was utilized. The SiCN deposited preforms were first infiltrated by a kind of slurry containing 40 wt% SiC particles. After drying, the samples underwent a high-temperature pyrolysis in nitrogen atmosphere to convert the polymer into ceramic matrix. Subsequently, the samples underwent another five PIP cycles using PCS as precursor (with no filler). The pyrolysis step was conducted at 1200 °C in flowing nitrogen atmosphere. Each kind of uncoated preform underwent only six PIP cycles for comparison.

Table 1
Properties of HTA carbon fiber.

Type	Diameter (μm)	Density (g/cm^3)	Filaments/ yarn	Tensile strength (MPa)	Elastic modulus (GPa)
HTA	7	1.76	3000	3920	235

2.4. Physical and mechanical properties

The as-infiltrated composites were cut and ground into 2.5 mm × 4 mm × 36 mm rectangles for bulk density, open porosity and three-point-bend testing. The density and open porosity of each sample were measured by the Archimedes method. The flexural strength by three-point-bend testing was conducted on an Instron 5566 (Canton, MA) universal testing machine, with a cross-head speed of 0.5 mm/min and a span of 24 mm. Young's modulus was calculated from the data recorded during three-point-bend testing. Fracture toughness was measured by single edge notched beam (SENB), with a notch depth of 2.45 mm, dimension of 2.5 mm × 5 mm × 36 mm, a cross-head speed of 0.05 mm/min and a span of 20 mm. The composite microstructure was investigated by an electron probe microanalyzer (EPMA, JXA-8100, JEOL, Tokyo, Japan) on both polished cross sections and fracture surfaces. The element distribution of the deposited coating was measured by Auger electron spectrum (AES) and distribution of the pore diameter in the composite was determined by mercury porosimetry.

3. Results and discussion

3.1. Characterization of the as-deposited SiCN layer

Fig. 1 shows the morphologies of the surface and cross section of the deposited SiCN on carbon fiber surface. Ball-shaped deposited particles with a diameter of about 100 nm packed on the fiber surface is shown in Fig. 1(a). Fig. 1(b) shows cross section of the deposited SiCN coating, illustrating that the coating is smooth and uniform. The boundary between the fiber and the SiCN coating is clear and abrupt, which means that no thermal diffusion occurred during the deposition process.

Distribution of elements Si, C, N, and O in the SiCN coating from the surface detected by AES is plotted as a function of sputtering depth in Fig. 2. It is observed that O/Si ratio is about 2 for the first 6 nm thickness, which means the extreme surface of several nm is mainly composed of SiO_2. The O content decreases sharply to a stable value of below 2% in the first 15 nm thickness. The surface of the deposited SiCN was slightly oxidized in air. Below the first 15 nm thickness, the coating has a constant element distribution.

3.2. Physical and mechanical properties of C_f/SiC composites

Some physical and mechanical properties of the composites with different contents of deposited SiCN are listed in Table 2. It can be easily seen that the bulk density increased with the increase of SiCN content, while the variation of open porosity had an opposite tendency. This phenomenon might be attributed to increased volume fraction of deposited SiCN for the density of deposited

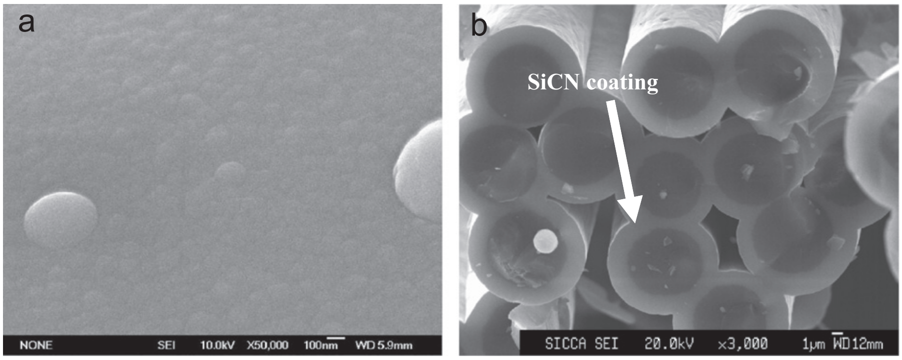

Fig. 1. Surface (a) and cross section (b) morphology of the as-deposited SiCN coating.

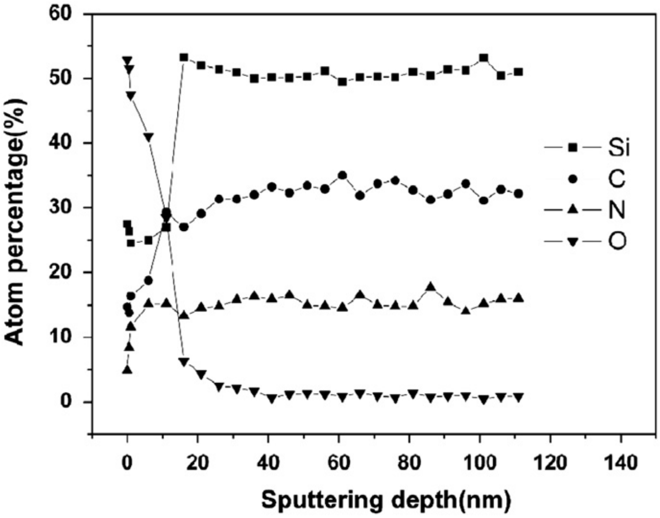

Fig. 2. Element distribution in the as-deposited SiCN coating.

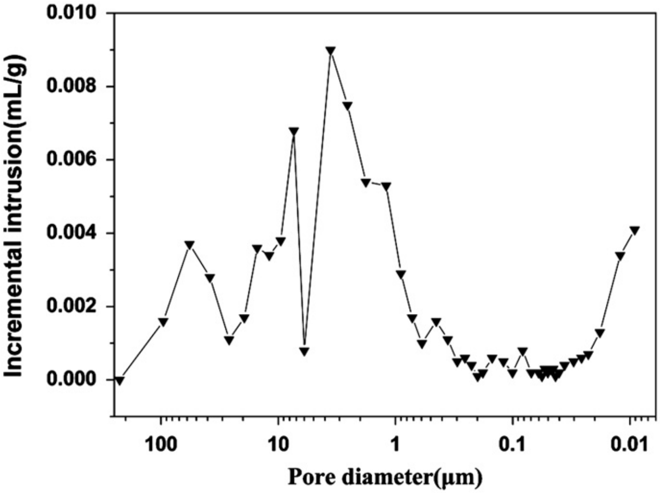

Fig. 3. Distribution of interior pore diameter in C_f/SiC composite with high SiCN content (SiCN coated preform density of 1.01 g/cm^3).

SiCN is higher than that of PIP-derived matrix. Meanwhile, the values for the ultimate bending strength (UBS) and proportional limit stress (PLS) also gradually increased. The highest values were obtained at SiCN deposited preform density of 1.01 g/cm^3. The room-temperature UBS and PLS of the composite reached 386 MPa and 302 MPa, respectively. However, for the composite with un-deposited SiCN preform (un-deposited preform density 0.70 g/cm^3), the flexural strength was at a low level of only 46 MPa. Other mechanical properties were not measured as quite poor values can be expected for such a composite. As reported by Suo et al. [15], Si element in the polymer-derived matrix diffused into the C fiber during pyrolysis at high temperature, which led to strong fiber/matrix bonding and decline in fiber property. When SiCN coating was deposited, the SiCN layer acting as a diffusion barrier avoided the diffusion of Si from the matrix to the fiber. As a result, significantly high strength of the fiber after pyrolysis process was retained and the flexural strength for the composite was considerably improved. The reason causing rapid strength decline of bare carbon fiber in the precursor-pyrolysis process should be further investigated.

Distribution of residual open pores in the as-pyrolyzed C_f/SiC composite with high SiCN content is plotted in Fig. 3. It is observed that open pores with main diameters of 3 μm, 10 μm and 60 μm locate in the composites. Residual pores with diameter of 3 μm are assumed to be the intra-bundle pores. The other two kinds of residual pores may be the large inter-bundle ones.

3.3. Microstructural evolution

Fig. 4 shows the typical SEM micrographs of the polished cross sections of the coated composite with high SiCN content. In Fig. 4(a), some isolated large inter-bundle pores could be observed even after several PIP cycles, which is a commonly observed phenomenon in PIP-derived composites with low PIP efficiency in filling such large inter-bundle pores. As shown in Fig. 4(b), well-consolidated matrix formed in the intra-bundle regions and some small residual pores were easily observed. In Fig. 4(c), the deposited SiCN was observed at the fiber boundary and the thickness of SiCN layer was about 1 μm. PyC interphase was not distinguished very clearly from the carbon fiber for the same element composition (Fig. 5).

Table 2
Properties of as-pyrolyzed C_f/SiC composites.

Density of SiCN coated perform (g/cm^3)	Density of final composite (g/cm^3)	Open porosity (%)	Bending strength (MPa)	Proportional limit stress (MPa)	Fracture toughness (MPa m$^{1/2}$)	Elastic modulus (GPa)
0.70 (non-coated)	1.59 ± 0.03	21.1 ± 0.5	46 ± 4	–	–	–
0.92	1.66 ± 0.01	16.0 ± 0.6	230 ± 35	193 ± 16	11.4 ± 2.1	76 ± 11
1.01	1.72 ± 0.02	14.7 ± 0.2	386 ± 22	302 ± 20	6.6 ± 0.4	76 ± 12

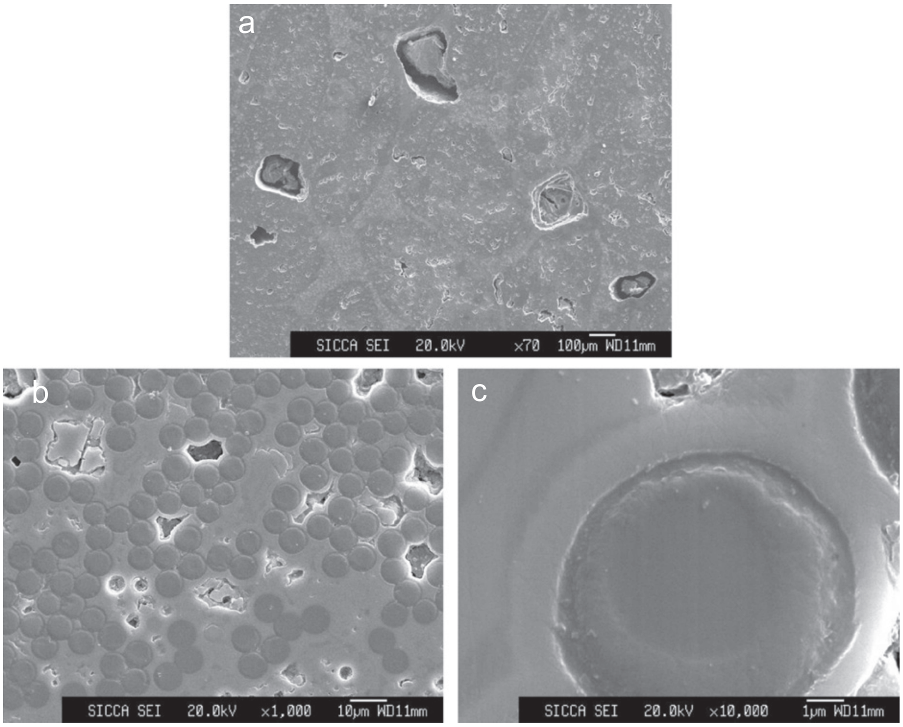

Fig. 4. SEM micrographs for the composites with high SiCN content (SiCN coated preform density of 1.01 g/cm^3).

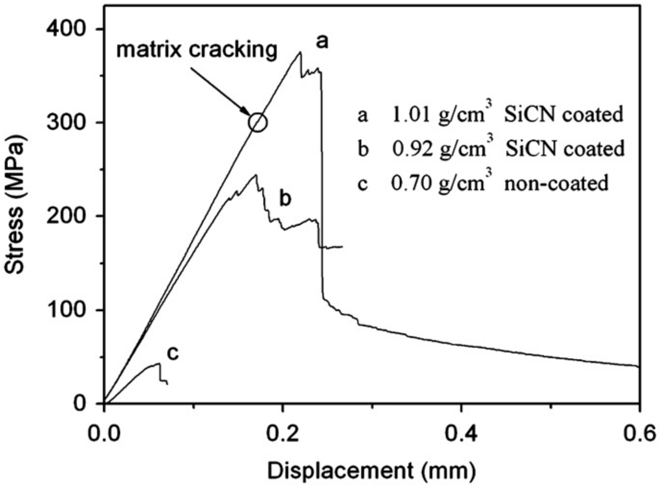

Fig. 5. Flexural stress–displacement curves of the composites with different SiCN coated preform densities.

Stress–displacement curves from the three-point bending test are plotted in Fig. 5. With the incorporation of SiCN coating between the reinforcing fiber and matrix, the fracture behavior was completely changed. The three curves have quite different appearance, with obvious difference in characteristics such as UBS, PLS, and stress-decline process indicating consistency with the data listed in Table 2. The curve for uncoated composite demonstrates a catastrophic and early failure mode whereas for the SiCN coated composites, the curves indicate a typical non-brittle fracture behavior for fiber-toughened composites. Linear deformation, matrix cracking, fiber debonding from the matrix and bundle failure are the main characteristics during the failure process. Composite with high SiCN content exhibited a linear deformation stage, and then an onset of nonlinearity was observed at the stress of about 300 MPa, indicating occurrence of microcracks in the matrix. Such a high PLS may be attributed to the following two factors. First, mechanical resistance of the matrix was enhanced for the increased fraction of deposited SiCN. Second, the deposited thick SiCN coating means quite dense and strong domain near fiber/matrix interface, which is beneficial for load transfer. After reaching maximum load, the curve drops rapidly, indicating bundle failure and formation of strong

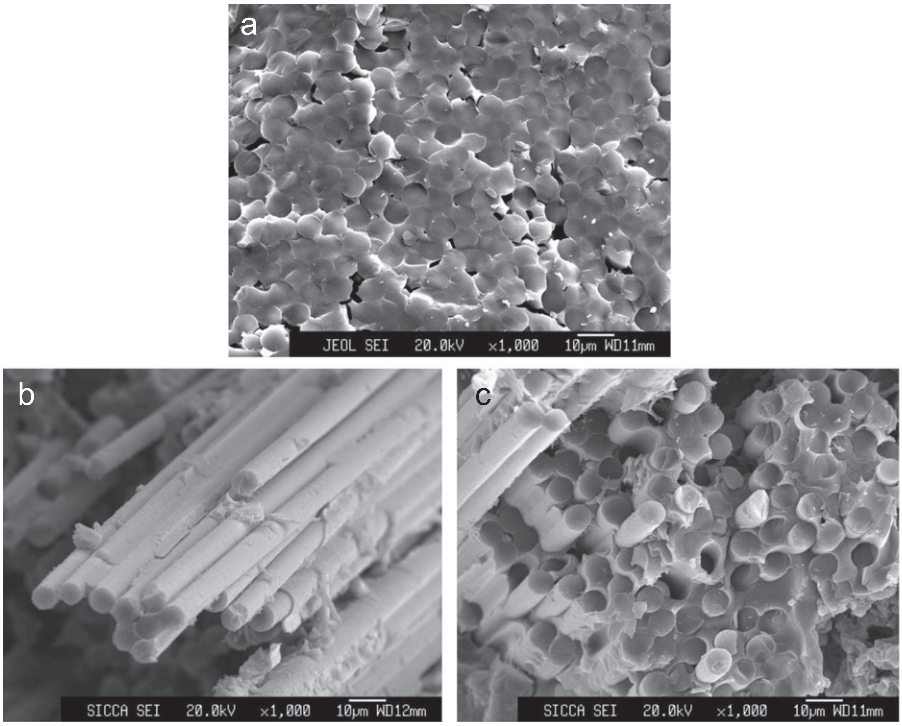

Fig. 6. Fracture micrographs of the three kinds of composites. (a) Uncoated composite, (b) coated composite with low SiCN content, and (c) coated composite with high SiCN content.

fiber/matrix bonding whereas, for the composite with low SiCN content (SiCN deposited preform density of 0.92 g/cm^3), the stress drops gradually, indicating fiber debonding and sliding from the matrix for the formation of weak interfacial bonds.

3.4. Fracture behavior

Typical fracture surfaces of the fabricated composites after bending test are shown in Fig. 6. As shown in Fig. 6(a), the fracture surface is very planar and no pullout fibers are observed for the composite with no SiCN deposition, which indicates that the fibers were seriously damaged in the pyrolysis process and the strength declined seriously. With the increase of the load in the testing process, cracks evolved in the matrix first and propagated directly perpendicular to the fiber, but could not be deflected. Thus, the fibers were sheared off by the cracks and therefore smooth fracture surface was generated while for composite with deposited SiCN, the evolved cracks could be deflected parallel to fiber axis along the loosely formed PyC interphase, resulting in long fiber pullout. As shown in Fig. 6(b), a number of long pull-out fibers dominated the fracture surface. However, a significantly decreased number of pullout fibers and a few long pores left by the pull-out fibers are observed in Fig. 6(c), indicating that strong interfacial bonding limited the fiber pullout from the matrix with increased content of deposited SiCN. This phenomenon is consistent with the corresponding stress–displacement curves and is beneficial for enhancement of the bending strength.

4. Conclusions

3D C_f/SiC composites were fabricated by PIP using bare and SiCN pre-coated fibers. The mechanical properties and fracture behavior were significantly modified by depositing SiCN coating on the fiber surface. The maximum levels achieved are a maximum stress of 386 MPa and a proportional limit stress of 302 MPa with a low density of 1.72 g/cm^3 when the density of SiCN coated preform reached 1.01 g/cm^3. The present results clearly demonstrated the possibility of increasing stress by deposition of SiCN coating on the surface of carbon fiber. Further investigation will be performed on enhancement of bulk density by incorporation of nano-scale SiC filler and optimization of preform structure, fiber type and matrix modification to optimize the mechanical properties.

Acknowledgments

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