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Improvement of oxidation resistance of unidirectional C_f/SiO_2 composites by the addition of SiC_p

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Abstract

Unidirectional carbon fiber reinforced fused silica composites (uni-C_f/SiO_2) with addition of different contents of SiC particle (SiC_p) were prepared by slurry infiltrating and hot-pressing. The model of oxygen infiltrating into the composite was supposed according to the characterization of fiber/matrix interface observed by transmission electronic microscope (TEM). The oxidation process of the composite was analyzed by thermogravimetry and differential scanning calorimeter (TG-DSC) method and the oxidation resistance was evaluated by the residual flexural strength and the fracture surface of the composite after heat treatment at elevated temperatures method. The results showed that the oxidation of carbon fiber started at 480 °C and ended at 800 °C and the oxidation of SiC_p started at above 1000 °C in the composite. The addition of 20 wt.% SiC_p had a better oxidation resistance. According to the characterization of fiber/matrix interface observed by TEM, gaps existed at the fiber/matrix interface which resulted from the CTE mismatch of carbon fiber and SiO_2 matrix. While the CTE mismatch between SiC_p and SiO_2 matrix could also result in the pre-existing gaps in the matrix. The oxygen penetrated along the gaps and simultaneously reacted with carbon fiber ends and SiC_p, which filled the gaps at the fiber/matrix interface and the pre-existing gaps in the matrix and subsequently prevented oxygen from infiltrating inward.

Keywords: B. Composites; B. Interface; C. Thermal expansion; D. SiC; D. C_f/SiO_2

1. Introduction

As a family of carbon fiber reinforced glass matrix composites, carbon fiber reinforced fused silica composite (C_f/SiO_2) have demonstrated a wide range of attributes, including high strength, high stiffness, excellent toughness, low density, unique wear resistance, and environmental stability for space structural applications [1–3]. One of the major disadvantages of this type of composite is oxidation of carbon fiber at elevated temperatures in air [4,5]. The oxidation process can be expressed as follows:

$$2C_{(s)} + O_{2(g)} = 2CO_{(g)} \quad (1)$$

$$2CO_{(s)} + O_{2(g)} = 2CO_{2(g)} \quad (2)$$

Gao et al. [6] reported that carbon fiber was oxidized from 400 °C and burnt out at 700 °C in the carbon fiber reinforced phenylethynyl-terminated poly(etherimide) composite through analyzing the TG-DTG data. Prewo and Batt [7] had studied the oxidation resistance of carbon fiber reinforced glass composites in both unstressed and stressed conditions. His results showed that the strength of the composite was significantly degraded after exposure at 540 °C in air and the glass matrix was not found to prevent the degradation but simply to limit it to a gradual process progressing from the composite surfaces inward. In fact, silicon carbide possesses excellent high-temperature mechanical properties, good oxidation, corrosion and wear resistance [8–10]. At high temperatures SiC was oxidized wherein a protective scale of SiO_2 was formed on the surface by the reaction:

$$SiC_{(s)} + (3/2)O_{2(g)} = SiO_{2(s)} + CO_{(g)} \quad (3)$$

It could prevent oxygen from infiltrating and the oxidation of carbon fiber was retarded [11,12]. Many researchers had

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employed the SiC as oxidation inhibitors to provide oxidation protection for carbon based composites [13–15]. However, little report was found to investigate the effect of SiC particle on oxidation resistance of carbon fiber reinforced fused silica composite.

In this work, the unidirectional carbon fiber reinforced fused silica composites (uni-C_f/SiO_2) with the addition of different contents of SiC_p were prepared by slurry infiltrating and hot-pressed sintering method. The oxidation process of the composite was analyzed by TG-DSC method. After heat-treated at elevated temperatures, the residual flexural strength, microstructure and phase compositions were examined and the mechanism of oxidation resistance was discussed.

2. Experimental procedures

Fused silica powder ($SiO_2 > 99$ wt.% pure, and average particle size around 2.8 μm), PAN-based carbon fiber (2800 MPa average tensile strength, and 6–7 μm in diameter), silicon carbide powder (α-SiC > 98 wt.% pure, and average particle size around 0.5 μm) were used as starting materials. According to the four compositions: C_f/SiO_2 (CS0), C_f/SiO_2 + 10 wt.%SiC (CS1), C_f/SiO_2 + 20 wt.%SiC (CS2), C_f/SiO_2 + 30 wt.%SiC (CS3), the prepregs were prepared by infiltrating the continuous carbon fiber into the slurry containing SiO_2 and SiC_p and then dried, stacked in a graphite die. Finally, the samples were hot-pressed into 35 mm × 30 mm × 10 mm at 1350 °C for 0.5 h under a pressure of 20 MPa in N_2 atmosphere. All composites were unidirectional reinforced and contained approximately 30 vol.% of carbon fibers. Density measurements were performed based on Archimedes principle. And the relative densities (RD) of CS0, CS1, CS2 and CS3 samples were 97.6%, 97.4%, 95.0% and 89.0%, respectively.

TG-DSC was carried out to investigate the oxidation behavior from room temperature (RT) to 1300 °C at a speed of 10 °C/min in NETZSCH STA 449C in a flowing air (20 ml/min).

The specimens were machined into bars of 36 mm × 4 mm × 3 mm, and heated to 500 °C, 700 °C, 900 °C, 1100 °C and 1300 °C at a speed of 10 °C/min and soaked for 3 h in air, respectively. Five specimens were tested for each sample. The weights of the samples were measured before and after the soaking. The soaked samples were examined by X-ray diffractometer (D/max 2550V). Flexural strength of the samples was tested by three-point bending method with a span of 30 mm and a cross-head speed of 0.5 mm/min at RT in air (Instron-1195). And the fracture surfaces of the samples were observed by electron probe X-ray microanalyser (EPMA) (JXA-8100). The microstructural features of fiber/matrix interface were examined using transmission electronic microscope (TEM, Model 200CX, JEOL, Japan).

3. Results and discussion

Fig. 1a and b shows the TG-DSC curves of the CS0 and CS2 samples, respectively. From the TG curve (Fig. 1a), it can be seen that oxidation of the carbon fiber started at 480 °C and it was burnt out at 800 °C, accompanying with maximum weight loss of 17.3%. With the temperature increasing to 1300 °C, no further weight loss happened. From the DSC curve (Fig. 1a), the exothermic peak appears at 717.9 °C, which is in accordance with the reactions (1) or (2). For the sample with the addition of SiC_p (CS2), the carbon fiber was oxidized from 490 °C and it ended at 770 °C. The maximum weight loss of 16.4% was kept till 1020 °C (Fig. 1b). After that, the weight loss decreased with the increase of temperature. In the light of reaction (3), it can be attributed to that SiC_p was oxidized to SiO_2 and the molecular weight of SiO_2 is higher than that of SiC. It also indicated that SiC_p reacted mildly with the oxygen in air after 1020 °C. From the DSC curve (Fig. 1b), the exothermic peak appeared at 716.8 °C, which was almost the same as that of CS0 sample.

Fig. 2 shows the mass loss of all samples after heat-treated at elevated temperatures. It can be seen that the total mass loss of all samples was less than 2.5% after soaked at 500 °C for 3 h, because carbon fiber started to oxidize at 480 °C or 490 °C (Fig. 1a and b). Such results are in agreement with those of Gao et al. [6] and Prewo and Batt [7]. Up to 700 °C, the mass loss of all samples increased linearly. Between 700 °C and 900 °C, the maximum mass loss of all samples appeared and there was approximately 20% mass reduction. For the CS0 sample, the curve of mass loss became flat between 900 °C and 1100 °C. A slight increase of mass loss appeared when the soaking temperature was 1300 °C. The mass loss of the CS1, CS2 and

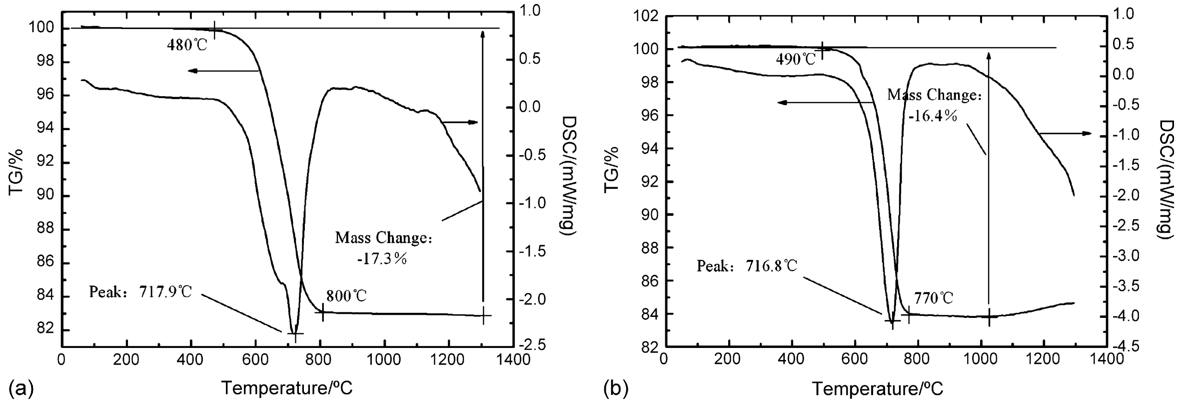

Fig. 1. The TG-DSC curves of samples: (a) CS0; (b) CS2.

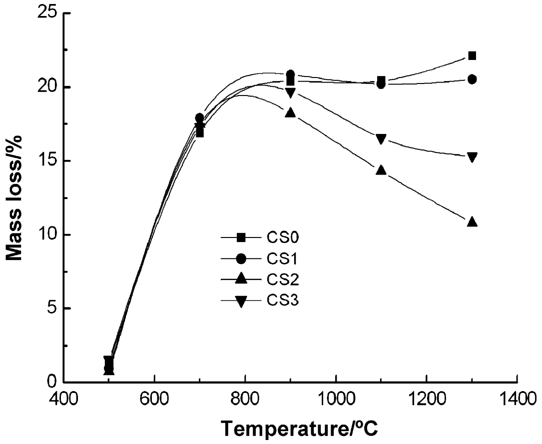

Fig. 2. The mass loss of the samples with different contents of SiC_p after heat-treated at elevated temperatures for 3 h.

CS3 samples decreased from 900 °C to 1300 °C because of the oxidation of SiC_p mentioned above. Especially, the total mass loss of CS2 sample was only 10.8%, the lowest one among these samples.

X-ray diffraction patterns of CS2 sample before and after heat-treated at different temperatures are shown in Fig. 3. After heat-treated at 900 °C and 1100 °C for 3 h, respectively, the peak intensity of SiC weakened which indicated the depletion of the SiC_p. While SiO_2 matrix remained amorphous. Up to 1300 °C, cristobalite phase began to appear, which was attributed to the crystallization of silica matrix and partially to the crystallization of amorphous silica from the oxidation of SiC_p.

Table 1 listed the flexural strength and standard deviation tested at different temperatures for 3 h. Before soaking, flexural strength of the samples decreased after the addition of SiC_p. The RD of the CS0, CS1, CS2 and CS3 were 97.6%, 97.4%, 95.0% and 89.0%, respectively. After adding SiC_p, the viscosity of fused silica increased, which retarded the process of densification at the same sintering temperature. The RD accounted for the decrease of flexural strength for these samples. Generally, flexural strength of the samples decreased with the increase of soaking temperature. This is because carbon fiber was oxidized during soaking and the strengthening effect of carbon fiber degraded. But after soaked at 500 °C for 3 h, flexural strength of CS1 and CS2 samples were higher than those of as-prepared ones, increasing from 423.5 MPa and 431.8 MPa to 480.5 MPa and 612.3 MPa, respectively. It may be attributed to the change of interface state between carbon fiber and SiO_2 matrix, such as the relaxation of stress, incurred by the CTE mismatch among carbon fiber, the SiC_p and the SiO_2 matrix [16]. Up to 700 °C, with the oxidation of carbon fiber and the mass loss of samples (see Fig. 2), the flexural strength of all samples decreased sharply. With the increase of soaking temperature, flexural strength went down further. Furthermore, for CS3 sample, cracks can be seen by eyes on the surface after soaked at 1300 °C for 3 h, which was attributed to the thermal expansion resulted from the excessive SiC_p in the composite. It also can explain why the flexural strength of CS3 sample degraded soaked at 1300 °C for 3 h.

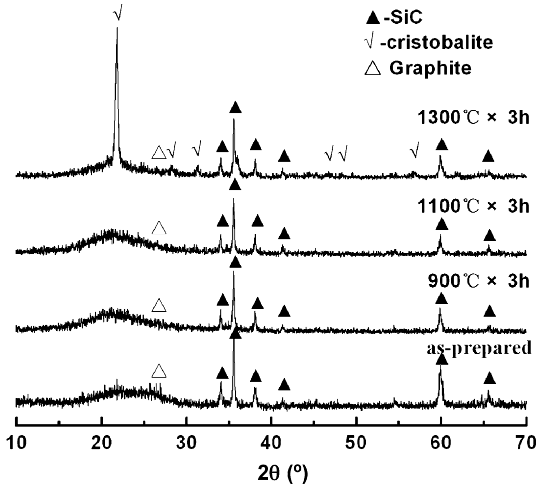

Fig. 3. X-ray diffraction patterns of CS2 sample after heat-treated at elevated temperatures for 3 h.

Table 1
The residual flexural strength and standard deviation of the samples after heat-treated at elevated temperatures for 3 h

	Flexural strength and standard deviation (MPa)			
	CS0	CS1	CS2	CS3
RT	667.3 ± 33.8	423.5 ± 27.9	431.8 ± 28.3	461.0 ± 55.2
500 °C	427.5 ± 41.5	480.5 ± 52.5	612.3 ± 24.7	443.3 ± 44.3
700 °C	173.5 ± 19.5	179.3 ± 23.5	202.4 ± 28.5	180.6 ± 25.0
900 °C	48.5 ± 4.8	67.3 ± 5.3	106.9 ± 16.1	87.4 ± 7.1
1100 °C	63.5 ± 8.7	58.5 ± 6.4	68.2 ± 3.4	71.6 ± 5.8
1300 °C	15.7 ± 3.4	16.8 ± 3.4	64.9 ± 9.6	21.6 ± 4.2

Fig. 4 shows the typical fractographs of samples after heat-treated at 1300 °C for 3 h. Many holes appear on the fracture surface of the CS0 (Fig. 4a) and CS1 (Fig. 4b) samples, which is attributed to the oxidation of carbon fiber. It is clear that 10 wt.% SiC_p addition has no apparently positive effect to protect the carbon fiber from oxidizing. From the CS2 (Fig. 4c) and CS3 (Fig. 4d) samples, the carbon fibers were oxidized from the edge to the center of the samples and then holes left. The completely oxidized width of CS2 sample was about 0.3 mm, far less than that of 1.0 mm of CS3 sample. The pullout of carbon fiber can be seen on the fracture surface of CS2 and CS3 samples.

Consider an ideal unidirectional composite. The feature of fiber/matrix interface plays an important role in the properties of composite. Fig. 5a and b shows the TEM micrographs of CS0 and CS2 samples. From the Fig. 5a, it can be seen that gaps exist at the interface between the carbon fiber and SiO_2 matrix. It was attributed to the mismatch of the coefficient of thermal expansion (CTE) between the carbon fiber and SiO_2 matrix. As for carbon fiber, the CTE is anisotropic due to the orientation of graphite grain. The CTE perpendicular to the carbon fiber varies from 9×10^{-6} °C^{-1} to 20×10^{-6} °C^{-1} with the elastic modulus and the orientation of graphite [17]. While the fused silica (SiO_2) is just 0.54×10^{-6} °C^{-1}, gaps will appear at the

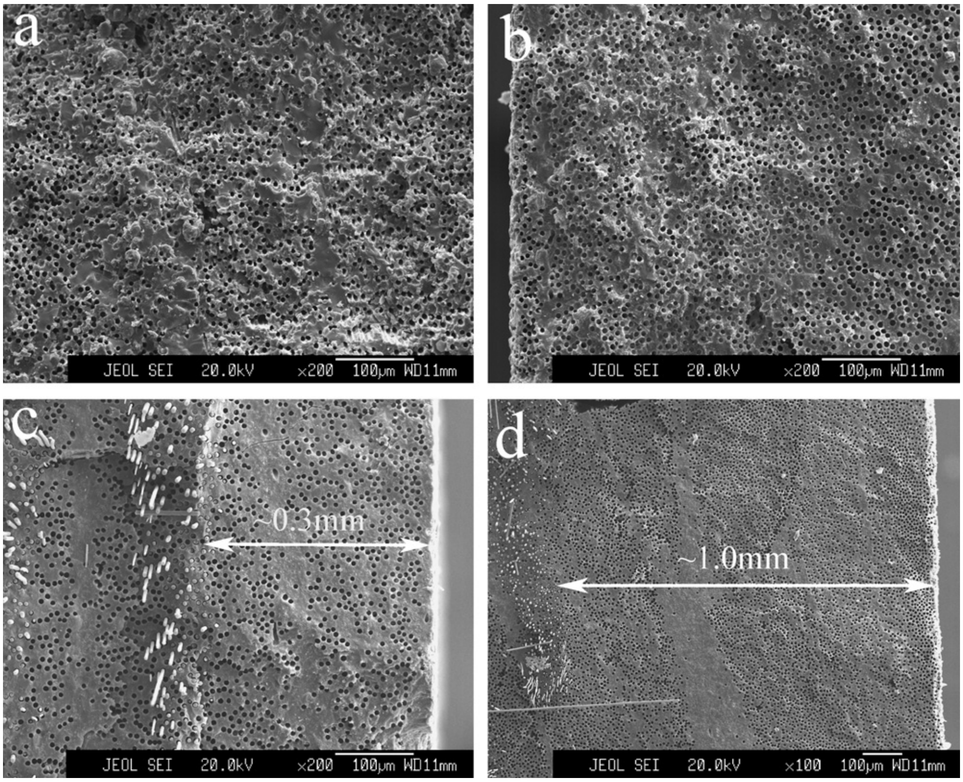

Fig. 4. Fracture surface of samples: (a) CS0; (b) CS1; (c) CS2; (d) CS3 after heat-treated at 1300 °C for 3 h.

fiber/matrix interface during the uni-C_f/SiO_2 composite cooled-down from the fabricated temperature. But parallel to the carbon fiber, the CTE is approximately $1 \times 10^{-6}\,^{\circ}C^{-1}$ and can well match with the SiO_2 matrix [1]. It indicated that the matrix did not contain transverse pre-existing cracks incurred by the thermal stress in the uni-C_f/SiO_2 composite. While after the addition of SiC_p, a part of SiC_p embedded at the interface between the carbon fibers and SiO_2 matrix as shown in Fig. 5b. Furthermore, the CTE of α-SiC is $5.12 \times 10^{-6}\,^{\circ}C^{-1}$, which will also result in the pre-existing gaps between the SiC_p and the SiO_2 matrix.

In the light of above analysis, the model could be supposed that describes the path of oxygen penetrating into the composites. Fig. 6a and b gives the schematic of the SiO_2 matrix, interface and carbon fiber and dispersed SiC_p. From the Fig. 6a without SiC_p, the oxygen would penetrate into the sample through the gaps at the fiber/matrix interface and then react with the carbon fiber ends. While with the addition of SiC_p (Fig. 6b), after the oxygen penetrated into the gaps parallel to the carbon fibers, it would simultaneously react with SiC_p and carbon fiber ends. The formed SiO_2 could fill the gaps at the fiber/matrix and consequently seal off the carbon fiber from the

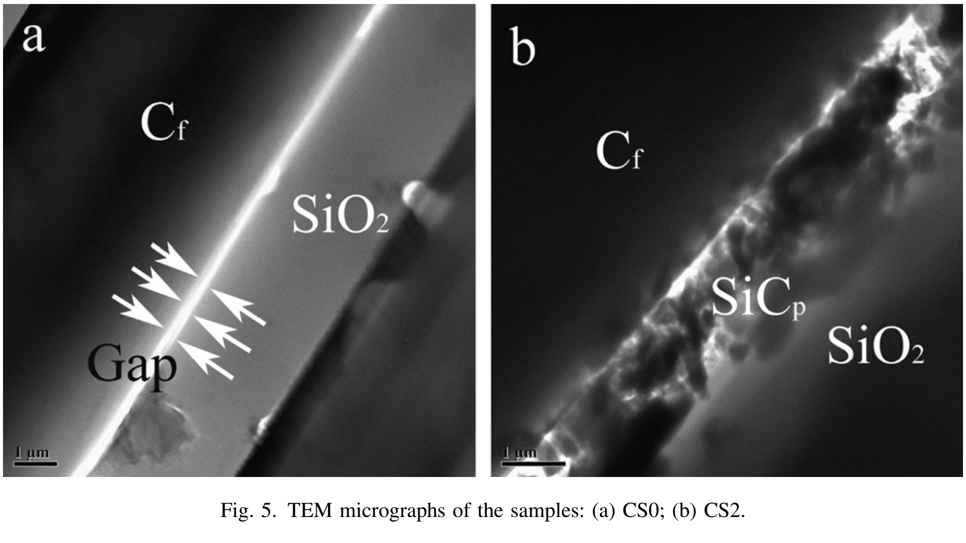

Fig. 5. TEM micrographs of the samples: (a) CS0; (b) CS2.

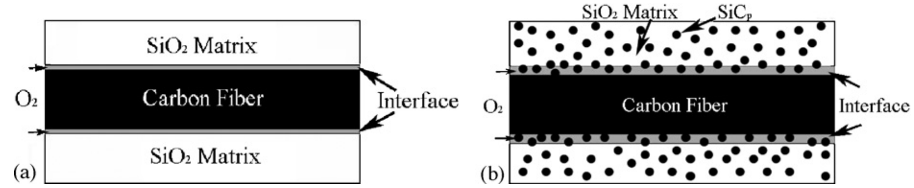

Fig. 6. Schematic of the interface of uni-C_f/SiO_2 composite without and with SiC_p: (a) without SiC_p; (b) with SiC_p.

outside oxygen, which retarded the oxygen further infiltrating into the gaps [18]. On the other hand, perpendicular to the carbon fibers the oxygen diffused slowly because of relatively compact SiO_2 matrix. When the oxygen passed through the matrix, it would react with the dispersed SiC_p and formed SiO_2, which filled the pre-existing gaps resulted from the CTE mismatch of SiO_2 matrix and SiC_p, thus depleted the oxygen and retarded the oxidization of the composite. Furthermore, the RD of CS3 sample was only 89.0%. The open porosity as well as the cracks incurred by the thermal expansion of excessive SiC_p resulted in the oxygen easily penetrating into the sample and reacting with carbon fibers during the soaking process. This is why the flexural strength of CS2 sample was higher than those of other samples even after soaked at 1300 °C for 3 h and had a better oxidation resistance.

4. Conclusions

1. The uni-C_f/SiO_2 composites with the addition of different SiC_p contents were prepared by slurry infiltrating and hot-pressing. TG-DSC showed the oxidation of the carbon fiber started at 480 °C and it was burnt out at 800 °C and the oxidation of SiC_p started at above 1000 °C in the composite. From the oxidation experiments, it indicated that the addition of 20 wt.% SiC_p had a better oxidation resistance.
2. According to the characterization of fiber/matrix interface observed by TEM, gaps existed at the fiber/matrix interface which resulted from the CTE mismatch of carbon fiber and SiO_2 matrix. While the CTE mismatch between SiC_p and SiO_2 matrix could also result in the pre-existing gaps in the matrix. The oxygen penetrated along the gaps and simultaneously reacted with carbon fiber ends and SiC_p, which filled the gaps at the fiber/matrix interface and the pre-existing gaps in the matrix and subsequently prevented oxygen from infiltrating inward.

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