The Oxidation of SiC Fiber and SiC Fiber Reinforced Boron Phenolic Resin Composite

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Abstract. The SiC fiber was thermally treated in air atmosphere and the SiC fiber reinforced boron phenolic resin composite was prepared by hot molding process by introducing inorganic ceramic particles. The thermal stabilities, the surface microstructures, the diameter and oxygen mental content variations, and the crystal structures of SiC fiber heated and kept for 0.5 h and 1h at different high temperatures were investigated through TG, SEM, XRD analysis. The cross-section morphology of the composite also observed. The results showed that the SiC fiber had good thermal resistance at high temperature in N₂, however it was easy to be oxidized at high temperature in air. When heated from 25 °C to 1600 °C and kept for 1 h, the fiber was oxidized to SiO² and the fiber surface was coarse and cracked. With the temperature increasing, the diameter of the fiber decreased and the oxygen content increased. Highly different form the cross-section morphology of SiC fiber itself heated in air, the cross-section morphology of SiC fiber in composite was weakly oxidized and the cross section was smooth and there was no distinct oxidation layer existing.

Keywords. SiC fiber, oxidation, SiC fiber reinforce phenolic resin composite.

1. Introduction
Due to the unique physical and chemical properties of wear resistance, corrosion resistance, oxidation resistance, high elastic modulus, high hardness and high strength, the SiC materials has received extensive attention in many fields [1-4]. Especially, the SiC and its composite exists good high temperature resistance, thus the SiC and its composite have a wide range of applications in national defence, aerospace, and civil fields [2]. Now, three generations of silicon carbide fibers have been developed. Compared with the first and second generations SiC fibers, the third generation SiC fibers have obvious improvement in heat-resistance, oxidation-resistance and creep-resistance, which promotes the development of SiC/SiC composite materials [5].

Some elements modification to SiC fiber affected the structure and properties of SiC fiber. Zhang [2] prepared SiC-ZrC composite ceramic fibers and SiC-ZrB₂ composite ceramic fibers, and SiC-ZrC composite ceramic fibers exhibited excellent heat resistance and oxidation resistance. After being kept at 1600 °C or 1800°C for 1h in air atmosphere the fiber structure remains dense. When heated from room temperature to 1100 °C~1400 °C in air, the oxidizing layer without crack and hole can be observed, and the thickness of the oxidizing layer increased with the heating temperature rising. When heated at 1400 °C in air the thickness of the oxidizing layer reached to 400 nm, and the inner structure remained the same to that of unheated fiber.
The researches of SiC fiber and its composite were focused on the ceramic matrixed composite, the metal matrixed composite and some glass matrixed composite for the high temperature resistance [6-8]. There was no research of SiC fiber and its polymer matrixed composite, may be caused by the distinct high temperature property differences of polymer matrix with that of SiC fiber. Only some functional polymer matrixed composite modified by SiC fiber were reported [9].

In this research, the oxidation of SiC fiber and its polymer matrix composite in air were investigated in order to promote the application of SiC fiber in polymer matrix ablative materials.

2. Experimental

2.1. Materials
Boron phenolic resin (BPF, THC-400) was purchased from Shaanxi Taihang Fire Resistant Polymer Co., Ltd. Anhydrous ethanol (Sinopharm Chemical Reagent Co. Ltd) was used as a solvent. SiC fiber Cansas-3303 was supplied by Fujian Liya Materials Com. MoSi₂ was purchased from Shanghai Bowei Applied Materials Technology Co., Ltd. Glass frit B (the softening temperature range of 550-830°C and the main compositions of 70.8% SiO₂, 14.05% Na₂O, 8.72% CaO, 3.86% MgO, 0.92% Al₂O₃, and 0.4% K₂O) were purchased from GuiZhou Wylton Jinglin Electronic Material Co., Ltd.

2.2. Preparation of SiC Fiber Reinforced Boron Phenolic Resin Composite by Introducing MoSi₂ and Glass Frit Powder
The SiC fiber was as the originals supplied, then heated from 25 ℃ to high temperature at 10 ℃/min and kept at target temperature for 0.5 and 1 h.

100 phr BPF was ground into micro-size powders, and then dissolved in 100 phr ethanol. Fillers of 60 phr MoSi₂ and 15 phr glass frit were added to BPF ethanol solution by mechanical stirring at 80 ℃ until a homogeneous blend. Then the SiC fiber was impregnated with the blends to achieve composite prepreg. Put the prepreg layer by layer into the mold, and then molded and cured through a hot compression molding technique with the cure procedure of 80 ℃ for 1 h, 100 ℃ for 1 h, 120 ℃ for 2 h, 160 ℃ for 3 h and 180 ℃ for 2 h under 10 MPa pressure.

2.3. Characterization
Thermogravimetric analysis was performed on a thermogravimetric analyzer (STA449c, NETZSCH, Germany) at a heating rate of 10 ℃/min (in air and in N₂ atmosphere). Samples were analyzed from room temperature to 1600 ℃. The morphology of the fiber and the composite sample after thermal heating was identified by a Scanning Electron Microscopy (SEM, JSM-5610LV, JEOL, Japan). Samples were sputter-coated with gold before observation. The crystal phases of the residues after thermal heating were characterized with a D8 Advance Rotation Anode High Power X-ray Diffractometer (Bruker Germany). XRD data were obtained from 10° to 80° (2θ) at a step of 5°/min.

3. Results and Discussion

3.1. The Oxidation Analysis of SiC Fiber by TG
Figure 1 showed the mass variation of SiC fiber with the temperature by TG analysis. As shown in figure 1(a), there was a bit of weight loss before 600 ℃ in air, and it may be caused by the pyrolysis and release of the organic coating agent and adsorbed water on the SiC fiber surface [10]. When the temperature was up to 600 ℃ and higher, the SiC fiber was oxidized, and then resulted in the weight gain. With the temperature increasing, the weight gain was greatly fast. When the temperature was 1550 ℃, the oxidation weight gain was near 8%.
When heated in N\textsubscript{2} atmosphere, the mass variation of SiC fiber with the temperature was significantly different. With the temperature rising, the weight of SiC fiber changed a little, the weight loss was about 2\% when the fiber was heated from room temperature to 1550 °C, which may be resulted by the pyrolysis of the organic protective coating and the absorbed water, so it was thermally stabilized in N\textsubscript{2}.

### 3.2. Surface Microstructures of SiC Fiber Heated at High Temperature

Figure 2 showed the SEM graphs of SiC fiber heated and held for 0.5h at (a) 1000 °C, (b) 1200 °C, (c) 1400 °C and (d) 1600 °C in muffle furnace. There was no obvious change on the surface when the target heating temperature was under 1400 °C. However, when the heating temperature was up to 1600°C and kept for 0.5h the fiber surface was severely destroyed. The fiber were cracked and fractured, and evenly stripped off in big pieces, which indicated the heavy oxidation of the SiC fiber at 1600 °C in air.

Figure 3 shows the SEM graphs of SiC fiber heated for 1h at (a) 25 °C, (b) 1000 °C, (c) 1200 °C, (d) 1400 °C and (e) 1600 °C. When the temperature was lower than 1400°C, the fiber surface was nearly the same as the original and the same as those heated for 0.5 h. However, the SiC fiber surface was
coarse, grooved and cracked when the temperature was up to 1600 °C, so it was similar to that of the oxidized surface kept for 0.5 h, and even more severely destroyed. When the fiber was cooled down, it was very brittle. So the SiC fiber may not suitable to apply in high temperature of 1600°C and oxidizing atmosphere for longer time than 0.5 h.

![Figure 3](image)

**Figure 3.** SEM graphs of SiC fiber heated and held for 1h at (a) 25°C, (b) 1000°C, (c) 1200°C, (d) 1400°C and (e) 1600°C.

### 3.3. The Oxygen Content and Diameter Variation of SiC Fiber Heated at High Temperature

The oxygen content on the surface of the SiC fiber was tested by SEM-EDS. As shown in table 1, the oxygen content on the surface was increased with the heating temperature rising and the heating time extending. The oxygen mental content was similar when the heating temperature was lower than 1400 °C heated for 0.5 h and 1 h. Especially heated at 1600 °C, the oxygen mental content was greatly increased from 47.16% to 54.45% when the heating time extended from 0.5 h to 1 h, which indicated that the SiC fiber was oxidized greatly at 1600 °C.
### Table 1. The oxygen content on the surface of SiC fiber after heated (%).

| Holding time | 25 °C | 1000 °C | 1200 °C | 1400 °C | 1600 °C |
|--------------|-------|---------|---------|---------|---------|
| 0.5h         | 0     | 5       | 14.76   | 33.09   | 47.16   |
| 1h           | 0     | 5.09    | 16.39   | 34.28   | 54.45   |

Table 2 showed the fiber diameter variations with different holding time and temperature. With the heating temperature increasing, the diameter of SiC fiber decreased gradually resulted from the oxidation of the fiber. At 1000 °C and 1200 °C, the diameter of the fiber held for 1h was shorter than that of the fiber held for 0.5 h. Heated at 1400 °C and 1600 °C, the holding time had effects on the diameter. The diameter of the SiC fiber heated and held for 1h was 13.8 μm and 13.6 μm, and it was a little bigger than that of the SiC fiber heated and held for 0.5 h, may be caused by the oxidation layer expansion.

### Table 2. The diameter of SiC fiber heated at high temperature (μm).

| Holding time | 25°C | 1000°C | 1200°C | 1400°C | 1600°C |
|--------------|------|--------|--------|--------|--------|
| 0.5h         | 15.6 | 14.2   | 14.3   | 13.6   | 13.5   |
| 1h           | 15.6 | 14.1   | 13.9   | 13.8   | 13.6   |

### 3.4. XRD Analysis of SiC Fiber Heated at High Temperature in Air

Figure 4 showed the XRD spectra of SiC fiber heated at high temperature and held for 1 h. As shown in figure 4, the SiC fiber was thermally stabilized at high temperature under 1400 °C. When heated and held at 1600 °C, the SiC fiber was oxidized distinctly and transformed to SiO$_2$, but the transforming temperature was higher than that of 1400 °C reported by Zhang [2]. It was consistent with the results of TG data and SEM graphs. In addition, in the oxidation process of SiC, the jar product is SiO$_2$. The molecular weight of SiC is 40 g/mol, the the molecular weight of SiO$_2$ is 60 g/mol. When the SiC was oxidized fully, the weight change rate is 50%, and the weight change rate was about 8% shown by TG analysis, so the theoretical oxidation was near 16% when heated from room temperature to 1550 °C.

![XRD spectra of SiC fiber heated at high temperature and held for 1h in air.](image)

### Figure 4. XRD spectra of SiC fiber heated at high temperature and held for 1h in air.

### 3.5. Cross-Section Morphology of SiC Fiber in Air and in Composite

The SiC fiber was heated from room temperature to high temperature and held for 1h at target temperature, and the cross-section morphology of the fiber was shown in figure 5.
Figure 5. The cross-section morphology of SiC fiber heated at high temperature and held for 1h in air: (a) 25°C; (b) 1000°C; (c) 1200°C; (d) 1400°C; (e) 1600°C.

Shown by figure 5, the fiber surface was smooth at 25°C and 1000°C, and the fiber surfaces were coarse and had a thin oxidation layer. With the heating temperature increasing, the oxidation layer was even thick and coarse. When the heating temperature was 1600°C the oxidation layer was about 1.8μm and there was stripping of the oxidized layer.

Figure 6. The cross-section morphology of SiC fiber reinforced boron phenolic resin composite, heated at 1200°C and held for 2h.
Figure 6 showed the cross-section morphology of SiC fiber reinforced boron phenolic resin composite, heated at 1200℃ and held for 2h. Highly different form the cross-section morphology of SiC fiber itself heated in air, the cross-section morphology of SiC fiber in composite was weakly oxidized and the cross section was smooth and there was no distinct oxidation layer existing.

In the composite, accompanied by the pyrolysis boron phenolic resin at high temperature, the glass frit melted created strong adhesion between the particles and the fibers [11], furthermore the glass frit melted can isolate the oxygen invading to the fiber, so the component in the composite protected the oxidation of the SiC fiber at high temperature.

4. Conclusions

The SiC fiber was heated from 25℃ to different target temperature and kept for 0.5 h and 1 h in muffle furnace. The SiC fiber reinforced boron phenolic resin composite was prepared by hot molding process by introducing inorganic ceramic particles. TG analysis showed that the SiC fiber had good thermal resistance at high temperature in N₂. When heated from 25℃ to 1600℃ and kept for 1h, the SiC fiber was oxidized to SiO₂ and the fiber surface was coarse and cracked. With the temperature increasing, the diameter of the fiber decreased and the oxygen content increased. The cross-section morphology indicated distinct oxidation layer of SiC fiber itself heated in air. However, the cross-section morphology of SiC fiber in composite was weakly oxidized, and the cross section was smooth and there was no distinct oxidation layer existing.

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