Effect of C/C preform density on oxidation properties of C/C-SiC composites

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Abstract. In order to study the effect of C/C preform on the oxidation properties of C/C-SiC composites, four kinds CVD-SiC coated C/C-SiC composites with different initial densities of C/C preform were prepared. The thermogravimetric oxidation behavior from 25 to 1450℃ of prepared C/C-SiC composites and the isothermal oxidation of CVD-SiC coated C/C-SiC composites under static air at 1500℃ were studied. And the bending properties of SiC coated C/C-SiC composites before and after oxidation were investigated. The results show that the initial oxidation temperature of C/C-SiC composites increases first and then decreases with the increase of initial C/C density, which is determined by the porosity and SiC content of the composites. When the C/C density is 1.0 g/cm³, the initial oxidation temperature is 633℃. The CVD coated C/C-SiC composites with initial C/C density of 1.0 g/cm³ exhibited the best static oxidation resistance at 1500℃. The weight loss is 4.23% after oxidation for 10 h at 1500℃, and the bending strength retention rate is 71.2%.

1. Introduction

C/C-SiC composites combine the advantages of carbon fiber, SiC matrix and fiber reinforced ceramic matrix composites. The most prominent feature is that some carbon matrix in C/C composites is replaced by SiC matrix with better oxidation resistance and high hardness [1]. It is a new functional integrated composite material which combines thermal protection, structural load-bearing and oxidation resistance. Since its emergence as a high temperature thermal structural material, it has been widely used in aerospace, mechanical engineering and braking systems [2-4].

The preparation of C/C-SiC is mainly divided into two steps. Firstly, porous C/C composites are prepared by chemical vapor infiltration (CVI) or polymer infiltration and pyrolysis (PIP), and then SiC matrix is prepared by CVI, PIP or reactive melt infiltration (RMI) [5-10]. As the key intermediate in the preparation of C/C-SiC composites, the basic structural parameters (such as density, porosity and structure, etc.) of C/C porous materials have a significant effect on the structure and mechanical properties of C/C-SiC composites.

CVI and PIP method has attracted much attention due to its advantages of low preparation temperature, designable matrix structure and easy preparation of complex shape components. Du [6] studied the effects of infiltration solution concentration and preform density on the density and mechanical properties of C/C-SiC composite. Yang [7] et al. prepared C/C-SiC composites with density of 1.34, 1.52 and 1.62 g/cm³ by liquid phase densification using PCS as precursor. The flexural strength and oxidation resistance at 1500℃ of C/C-SiC composites were compared. At present, the research work of C/C-SiC composites mainly focuses on the study of rapid densification and mechanical properties...
by CVI+RMI process. There are few reports on the effects of different C/C initial densities on the oxidation resistance C/C-SiC by PIP. In this paper, the thermogravimetric oxidation behavior of C/C-SiC composites prepared with different C/C preform densities was studied. And then the isothermal oxidation resistance and bending properties of C/C-SiC composites coated with CVD-SiC coating were investigated under static air at 1500°C for long time.

2. Experimental

2.1. Preparation and properties of CVD coated C/C-SiC composites

The C/C-SiC composites were fabricated by CVI and PIP process. Porous 2D needle C/C preform with densities of 0.8, 1.0, 1.2 and 1.4 g/cm³ by CVI were infiltrated using PCS (Yellow-brown solid with softening point of 210°C) as precursor, and then pyrolyzed at 1100°C. C/C-SiC composites were prepared by repeating PIP process for eight times. The density and porosity of C/C-SiC composites are 1.78, 1.84, 1.96, 1.70g/cm³ and 13.30, 9.52, 5.51, 7.17% respectively. SiC coatings were prepared by low-pressure chemical vapor deposition (LPCVD) using MTS as precursor, hydrogen as reaction gas and argon as dilution gas. The deposition temperature was 1150-1250°C, and the pressure was 4-8 kPa.

2.2. Measurement

Thermogravimetric test was carried out in STA 409 PC/PG synchronous thermal analyzer of NETZSCH Company with the size of 4×4×4 mm. The starting temperature was 25°C, the ending temperature was 1450°C, and the heating rate was 10°C/min. The composite material was cut into 55×10×4 mm dimensions for oxidation and bending mechanical properties testing. The isothermal oxidation tests of the coated specimens were carried out in air at 1500°C in an electrical furnace. The specimens were weighted by an electronic balance with a sensitivity of ± 0.1 mg. Flexural strengths of the coated specimens before and after oxidation were measured by three-point bending test on the CMT-5304 universal machine with the span of 40 mm and the strain rate of 0.5 mm/min. The crystalline structure and microstructure of C/C-SiC composites were structurally analyzed by X-ray diffraction (XRD, X’ Pert PRO) and scanning electron microscopy (SEM, JSM-6460).

3. Discussion

3.1. Oxidation behavior of C/C-SiC composites

The oxidation behavior of different C/C-SiC composites in air was compared by thermogravimetric analysis, as shown in Figure 1. The oxidation process can be divided into the following four stages: no weightlessness stage, rapid weightlessness stage, weightlessness reduction stage and weightlessness balance stage. The rapid weight loss is mainly due to the rapid oxidation of carbon fiber and matrix carbon. In weight loss reduction stage, the weight loss rate of the composite decreases with the increase of temperature because of the oxidation of SiC matrix. On the one hand, the oxidation of SiC shows oxidation weight gain, and its oxidation rate increases with the increase of temperature. On the other hand, its oxidation product SiO₂ can effectively reduce the permeability of oxygen and slow down the oxidation of composites. Therefore, the oxidation rate of composites decreases with the increase of temperature at this stage. The weight loss rate of C/C-SiC composites increases sharply with the increase of oxidation temperature, reaching the maximum value at 900-1000°C, and then decreases with the increase of temperature, and then tends to zero. The final residual mass decreases with the increase of C/C density. Combined with the corresponding TG-DTG data (as shown in table 1), the oxidation behavior of the composite was further analyzed. The initial oxidation temperature of samples increases first and then decreases with the increase of C/C density. The composites prepared with a density of 0.8 and 1.4 g/cm³ had a low oxidation starting temperature, and the composites began to lose weight at
544°C. When the C/C density is 1.0 g/cm³, the initial oxidation temperature is 633°C, which infers that the C/C-SiC composite material prepared by C/C with a density of 1.0 g/cm³ has the best oxidation resistance. SiC can improve the initial oxidation temperature of the material by occupying the surface active point [11]. However, when the initial density of C/C is 0.8 g/cm³, the prepared C/C-SiC composite material has a high porosity, and the pores provide channels for oxygen infiltration, so the initial oxidation temperature of the composite material is low. So the initial oxidation temperature of C/C-SiC composite is determined by the porosity and SiC content.

Table 1. The TG-DTG analysis results of C/C-SiC composites by C/C with different density

| C/C density (g/cm³) | T_i (°C) | T_max (°C) | R (wt.%) |
|---------------------|---------|------------|---------|
| 0.8                 | 544     | 900        | 49.8    |
| 1.0                 | 633     | 929        | 46.4    |
| 1.2                 | 573     | 929        | 40.2    |
| 1.4                 | 544     | 974        | 35.4    |

The temperature of maximum oxidation rate increases with the increase of C/C density. The temperature point of the maximum oxidation rate is mainly affected by the SiC content. Because SiC began to slowly oxidize at 800°C, and its oxidation performance was oxidation weight gain. At the same time, the slow oxidation of SiO₂ can partially slow down the diffusion of oxygen into the material, thus reducing the oxidation rate. The higher the SiC content is, the more obvious the above phenomenon is. The oxidation weight loss rate of the material starts to decrease at a lower temperature. Therefore, the temperature of maximum oxidation rate of C/C-SiC composites prepared by low density C/C preform is lower. However, the porosity of the C/C-SiC composite prepared with low density C/C is relatively large, which leads to poor oxidation resistance of the composite at the initial oxidation stage. In conclusion, the oxidation properties of C/C-SiC composites prepared in this study are mainly due to the interaction of SiC content and sample defects, and the composites with a density of 1.0 g/cm³ have good oxidation property.
3.2. High temperature oxidation resistance of SiC coated C/C-SiC composites

In order to further investigate the oxidation resistance of C/C-SiC composite at high temperature for a long time, the SiC coating was prepared by CVD on the surface of C/C-SiC composite. Figure 2 shows the XRD spectrum of SiC coating prepared by CVD process. The diffraction peaks of SiC (111), (220) and (311) planes were corresponded to 35.7°, 60.3° and 72.1° respectively, which shows that the SiC coating prepared by CVD is mainly composed of β-SiC.

Figure 2. XRD pattern of the surface of the coating prepared by CVD

Figure 3 shows surface and cross section SEM photos of SiC coating prepared by CVD method. The coating is cauliflower like, mainly composed of SiC pellets, which are fully fused between balls. The section morphology of CVD-SiC coating shown that the coating thickness was relatively uniform, about 50 µm. The coating appears in two distinct layers, mainly due to two cycle of SiC deposition. At the same time, obvious deposition defects, i.e. penetrating cracks, can be found in the coating.

Figure 3. SEM micrographs of the SiC coating prepared by CVD (a) surface; (b) cross-section

In order to investigate the effect of oxidation weight loss on the mechanical properties of coating composites, the oxidation test was stopped when the oxidation weight loss was 4.0-5.0 %. The coating composites all exhibit oxidation weight loss, and the oxidation weight loss increases with the increase of oxidation time (as shown in figure 4). When the C/C density is 0.8g/cm³, the weight loss is 4.58% after oxidation for 5 h. While the C/C density is 1.0g/cm³, the weight loss reaches 4.23% after 10 h oxidation. However, as the density of C/C preform continue to increase, the oxidation performance of the composites decreases again. Especially when the C/C density is 1.4g/cm³, there will be obvious oxidation holes in C/C-SiC composite due to the failure of oxidation protection of local SiC coating. In conclusion, C/C-SiC composites with initial C/C density of 1.0 g/cm³ exhibit good high temperature oxidation resistance.

Figure 5 shows the SEM photos of surface and section of coated C/C-SiC samples after static air oxidation for 10 h at 1500°C. It can be seen that a layer of oxide film is formed on the surface. Due to the mismatch of thermal expansion coefficient between coating and C/C-SiC composite during rapid cooling from 1500°C to room temperature, the tensile stress of the coating results in cracking or
peeling of the coating. The appearance of coating defects provides diffusion channels for oxygen, which leads to oxidation of carbon matrix and carbon fibers. Figure 5(b) shows that the carbon matrix is obviously oxidized and the carbon fibers are acicular due to oxidation.

![Figure 4. Oxidation curves of CVD-SiC coated C/C-SiC composites in air at 1500 °C](image)

**Figure 4.** Oxidation curves of CVD-SiC coated C/C-SiC composites in air at 1500 °C

![Figure 5. SEM micrographs C/C-SiC after oxidation at 1500 °C for 10 h (a) surface; (b) cross-section](image)

**Figure 5.** SEM micrographs C/C-SiC after oxidation at 1500 °C for 10 h (a) surface; (b) cross-section

The residual bending strength of coating C/C-SiC composite after oxidation is shown in table 2. When the C/C density is 1.0 g/cm³, the bending strength retention rate of the composite is 71.2% after oxidized for 10 h at 1500 °C. And the C/C density is 1.4 g/cm³, large oxidation holes appear locally due to oxidation of the composites, and the bending strength cannot be tested. C/C-SiC composites with initial C/C density of 0.8 g/cm³ have low final density (1.78 g/cm³) and high content of defects such as voids in the composites, which provide a channel for oxygen permeation into the composites, so their oxidation resistance is not ideal. However, the content of SiC phase infiltrated into C/C-SiC composites with initial C/C density of 1.4 g/cm³ is relatively low, so it also shows poor oxidation resistance. According to the weight loss and the residual bending strength after oxidation at 1500 °C, the composites with initial C/C density of 1.0 g/cm³ have the best oxidation resistance.

**Table 2.** Flexural strength of coated C/C-SiC composites after oxidation

| C/C density (g/cm³) | Flexural strength of C/C-SiC (MPa) | Flexural strength after oxidation (MPa) | Retention rate (%) |
|---------------------|------------------------------------|----------------------------------------|-------------------|
| 0.8                 | 207.9                              | 159.4                                  | 76.7%             |
| 1.0                 | 170.7                              | 121.6                                  | 71.2%             |
| 1.2                 | 161.9                              | 110.6                                  | 68.3%             |
| 1.4                 | 147.5                              | /                                      | /                 |


4. Conclusion
The initial oxidation temperature of C/C-SiC composites prepared by PIP process increases first and then decreases with the increase of initial C/C density. When the preform density is 1.0 g/cm³, the initial oxidation temperature of C/C-SiC composites reaches 633°C. And the composite exhibits good oxidation resistance at 1500°C in static air after the preparation of CVD-SiC coating on C/C-SiC composites. After oxidation for 10 h, the weight loss was 4.23% and the bending strength retention rate was 71.2%. The oxidation resistance of C/C-SiC composites is mainly affected by SiC content and material defects. The C/C-SiC composites with C/C preform density of 1.0 g/cm³ have relatively excellent oxidation resistance. This study can provide theoretical support for the performance optimization of C/C-SiC composites.

5. References
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