Fabrication and ablation resistance research of C/ZrC-SiC composites

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Abstract. C/ZrC-SiC composites were prepared by precursor impregnation pyrolysis (PIP) process. The ablation resistance of the composites was studied. The residual mechanical property of the composites after ablation was compared and analyzed. The results show that the prepared C/ZrC-SiC composites have good ablation resistance under high temperature oxidation environment. The ablation amount in large area is less than 0.1 mm. The ablation products on the surface of the composites are mainly composed of SiO\textsubscript{2} and ZrO\textsubscript{2}, forming a denser oxide film, which has a good protective effect on the structure of the composites. The data of residual mechanical properties indicate that the synergistic effect of high temperature and thermal stress under ablation environment may lead to the decrease of mechanical strength of composites.

1. Introduction
With the increase of flight speed, high reliability and reusability of aircraft, more and more requirements are put forward for materials. Therefore, it is urgent to carry out research on ultra-high temperature and ablation resistant materials. Ultra-high temperature ceramic matrix composites are a new kind of ultra-high temperature materials, which have important applications in the leading edge, wing rudder, engine combustion chamber, engine tail nozzle and other components of the new generation hypersonic vehicle [1-3].

C/ZrC-SiC composite is a widely used ultra-high temperature ceramic matrix composite [4-8], which has the advantages of low density, ablation resistance, oxidation resistance and good mechanical properties. The thermal structure parts of aircraft are exposed to high temperature and high speed gas, and they work under oxidative atmosphere. The phenomenon of oxidative ablation is very serious. In addition, the mechanical properties of materials are also very important during high speed flight. Therefore, it is very urgent to study the ablation mechanism of high temperature ceramic matrix composites and its residual mechanical properties after service for improving the performance of materials.

In this paper, C/ZrC-SiC composites were prepared using zirconium-silicon integrated ceramic precursor. The ablation resistance of C/ZrC-SiC composites was tested. The ablation mechanism and mechanical properties of C/ZrC-SiC composites under high temperature oxidation environment were studied, which laid a foundation for further improving the ablation resistance of C/ZrC-SiC composites in the future.
2. Experiment

2.1. Preparation of C/ZrC-SiC Composites

Carbon fiber preform was prepared by Jiangsu Tianniao Science and Technology Co., Ltd. The braiding method is puncture. The initial volume density of the preform is 0.5 g/cm$^3$. Polycarbosilane (PCS) is produced by Suzhou Sailifei Company. Its softening point is 170-220 °C, and the yield of ceramics is 58%. Zirconium-silicon integrated ceramic precursor (ZS) is synthesized by Institute of Chemistry Chinese Academy of Sciences.

Carbon fiber preforms deposit pyrolytic carbon interfacial layer in the depositing furnace. When the density of the preforms reaches 1.30 g/cm$^3$ or higher, and then, they are impregnated repeatedly with ZS precursor and Polycarbosilane solution until the density exceeds 2.10 g/cm$^3$ When the weight increment is less than 1.0%. C/ZrC-SiC composites are prepared.

2.2. Ablation Performance Test of C/ZrC-SiC Composites

The surface of the sample was ablated by oxyacetylene flame. Considering the long-term oxidation resistance of C/ZrC-SiC composites, the ablation conditions were as follows: the diameter of the nozzle was 2 mm, the ablation angle was 90 degrees, and the distance from the muzzle of oxyacetylene to the center of the sample surface was 20 mm. Oxygen pressure is 0.4 MPa, acetylene pressure is 0.095 MPa, the ratio of oxygen flow rate to acetylene flow rate is 2:1, ablation time is 600 s, sample size is 30 mm *10 mm.

2.3. Analysis And Characterization

According to Archimedes principle, the volume density of C/ZrC-SiC composites was measured by drainage method. The bending strength of the composites was measured by three-point bending method using INSTRON 4505 electronic universal testing machine. The specimen was straight strip with a size of 55 mm *10 mm *4 mm and a loading rate of 0.5 mm min$^{-1}$.

Microscopic morphology of the samples was observed by Hitachi S4800 scanning electron microscopy in Japan. Elemental composition (EDS) of the material surface and ablated surface was analyzed by SYSTEM SIX energy spectrometer. The shear strength of the specimens was measured by short beam shearing method. The size of the specimens was 18 mm x 6 mm x 43 mm. The oxyacetylene test was carried out at Dalian University of Technology in 2300K oxidation environment for 600 seconds.

3. Results And Discussions

3.1. Morphology analysis

Sampling and analysis of ablated composites are carried out as shown in Fig. 1. According to the internal surface morphology of the ablated material, it can be found that the ablation depth of the composite material is small. From the figure, it can be seen that under the action of airflow scouring, the ablated oxide layer has a large number of granular bulges. The thickness of sample area is 10 mm before test, and the average thickness of sample area after ablation (including oxide layer) is 10.48 mm, which may be due to the increase of macro-thickness of material due to the protrusion of oxide layer. In order to measure the actual ablation amount of sample area, the oxide layer is removed by grinding the oxide layer. After the white oxide layer is completely removed, the average thickness of sample area is measured again at 9.92 mm. Based on this, it is estimated that the ablation amount in large area is less than 0.1 mm.
After analysis in many places on the surface of the sampling area, the bare morphology of the fibers was not found, which indicated that the oxide layer was continuous and the protective effect of the material was good.

**Figure 1** Microscopic Morphology Photographs at Different Positions in Sampling Area

Fig. 2 is a picture of element distribution of ablation products. It shows that the ablation products are mainly composed of SiO$_2$ and ZrO$_2$, and most of them are SiO$_2$. Figure 3 shows the micro-morphology of ablation products on the surface of the sample area. Table 1 shows the EDS analysis results of ablation products in Figure 3. The oxidation products are mainly composed of O, Si, Zr, Al, Mg and other elements. The atomic ratio of Si: Zr is about 9:1, (Si + Zr): O is 1:2, indicating that the oxidation products are mainly SiO$_2$ and ZrO$_2$; the oxide films on the surface are continuous, and no further oxidation reaction occurs inside the material.

**Figure 2** Elemental surface distribution of ablation products  **Figure 3** SEM photograph of ablation product surface morphology

| Element | Mass Ratio(%) | Atomic Ratio(%) |
|---------|--------------|----------------|
| O       | 42.58        | 60.44          |
| Si      | 33.46        | 27.06          |
| Zr      | 13.25        | 3.30           |
| Al      | 8.71         | 7.33           |
| Mg      | 2.00         | 1.87           |

**3.2. Mechanical Properties Analysis**
In order to compare the mechanical properties of composites before and after ablation, the ablated materials were sampled and processed to bending strength and shear strength test splines. Because the thickness of ablated parts of the material was different, the actual sampling thickness was based on the residual thickness of the material. By comparing and analyzing the mechanical properties of the samples with the corresponding thickness of the material body, the failure behavior of the materials under the examination conditions was explored. From the data in Fig. 4, it can be seen that the residual shear strength of the debris is about 80% of the body. From the data in Fig. 5, it can be seen that the residual bending strength data of debris are discrete. On the one hand, it may be due to the harsh assessment environment, which results in the different oxidation and ablation conditions at different parts and the uneven residual thickness, resulting in the large deviation of the calculated mechanical properties data. On the other hand, it is possible that the thermal stress in high temperature environment will damage the material to a certain extent, resulting in a decline in mechanical properties. The bending residual strength of the test spline (4mm thick) far away from the ablation surface can reach 92%, which indicates that the sampling position has a great influence on the mechanical properties of the residual strength.

**Figure 4.** Residual shear strength of composites

**Figure 5.** Residual flexural strength of composites

**Figure 6.** Residual mechanical properties data of composites

**Figure 7.** Morphology of fiber pulling out after ablation (left) and before ablation (right) (10μm)
In order to further eliminate the influence of residual ablation thickness on the test results of mechanical properties, the composites (ablation less than 0.1 mm) were sampled (all 4 mm thick), and the mechanical properties of the composites were compared with those of the bulk materials. The mechanical strength data of the body and the debris are shown in the figure 6. From the figure, it can be seen that the mechanical residual strength of the debris is maintained well.

To further explore the influence factors of mechanical properties of materials before and after ablation, the fracture morphology after fracture is analyzed by SEM. See Fig. 7. From the figure, it can be seen that the macro-morphology difference between the two is small, the fracture fiber pull-out morphology is slightly different, the fiber pull-out phenomenon at the fracture surface of the body is obvious, which shows that the matrix protects the fiber well and the fiber is not damaged. The brittle fracture of the fibers is the criterion, which indicates that the mechanical properties of the fibers may be affected by the destruction of the matrix at high temperature, resulting in the decrease of the residual mechanical strength of the materials.

4. Conclusions
(1) The C/ZrC-SiC composites prepared shows good ablation resistance and there were no pits and bare fibers on the surface of the composites.
(2) A denser oxide film mainly composed of SiO\textsubscript{2} and ZrO\textsubscript{2} is formed on the surface of the ablation products under high temperature oxidation environment has a good protective effect on the structure of the material.
(3) The data of residual mechanical properties of ablated materials indicate that the synergistic effect of high temperature and thermal stress under ablation environment may lead to the decrease of mechanical strength.

5. Reference
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