Microstructure and Failure Behavior of Double Anti-Oxidation Coating on SiC$_f$/SiC-CMC

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Abstract. In this paper, BN interfacial phase was prepared on SiC fiber surface and CVD SiC gradient coating was prepared on the surface of SiC$_f$/SiC-CMCs composite. CVD SiC coatings were fabricated by the pyrolysis of methyltrichlorosilane (MTS) in hydrogen at a low pressure of 5-10kPa. The ratio of MTS to hydrogen is 1 to 12. Oxidation behaviour is examined by placing the material with coats in air. The oxidizing temperatures were varied from 100°C to 1200°C. Optical microscope and SEM were used to observe the surface morphology and microstructure of coatings. XRD was used to characterize the phase composition. The results indicated that the Oxidation of SiC/SiC-CMC is the most serious at 800°C. Tensile strength test shows that the fracture strength of the material is the lowest and with the increase of temperature to 1200°C, the tensile strength of the material increases. Tensile strength test shows that the fracture strength of the material is the lowest and with the increase of temperature to 1200°C, the tensile strength of the material increases.

1. Introduction

SiC/SiC composites have the characteristics of low density, high strength, high modulus and oxidation resistance, and still maintain high fracture strength at high temperature. It was considered as the most potential material which can replace super alloy for high temperature structure and can be used in the temperature resistant part of high push weight ratio engine. It has a wide range of application prospects in the hot end of aero-engine, such as combustion chamber, turbine guide vane, liner and so on[1,2]. In order to ensure the service reliability of the engine, a high performance coating with high tightness and zero defects must be prepared to block the oxygen channel. It is very important to study the oxidation and failure behaviour of coatings at high temperature.

2. Experimental procedure

In this paper, the gradient SiC coating was fabricated on the surface of SiC/SiC-CMC by the pyrolysis of methyltrichlorosilane (MTS) in excess hydrogen at a low pressure of 5Kpa. The ratio of MTS to H$_2$ was controlled to vary in the range of 5~12. Then the oxidation tests of coated samples and uncoated samples were carried out in air atmosphere at high temperature 1200 °C. And the thermal shock tests were carried out between the change of room temperature ~ 1200 °C 5 times circulation. Then the SEM were used to observe the microstructure of the coating. The failure behaviour of the coating was investigated, and the failure mechanism of the coating is discussed preliminarily. Please follow these instructions as carefully as possible so all articles within a conference have the same style to the title page. This paragraph follows a section title so it should not be indented.
3. Results and discussion

3.1. Analysis of characteristic of SiC/SiC-CMC prepared by PIP process
The SiC fiber used to toughen and reinforce in SiC/SiC-CMC system is very important. Once SiC fibre is oxidized, the phenomenon of "pore linear oxidation" occurs, that is, oxidation begins at the end of SiC fiber and takes place along the fiber length[3]. It will cause the properties of the composite to degrade or even break. Pure SiC material theoretically has good oxidation resistance at medium and high temperature (900 ~1100 °C). The SiC fiber used at present is mostly prepared by polycarbosilane cracking (pip) process, due to the limitation of technological conditions, SiC fiber is not completely high purity the purity and contains free C. As a result, SiC fiber faces the hidden danger of oxidation at medium and low temperature (600 ~1000 °C). Moreover, there are a lot of free C and pores in SiC/SiC-CMC prepared by PIP process. Pores are usually classified into two groups: micropores located inside the fiber tows and macropores located among fiber tows as shown in figure1. Under the combined action of them, there are a large number of oxygen channels in sic ceramic matrix composites reinforced by sic fiber, which greatly reduces the oxidation resistance of sicf/sic composites. The appearance of cracks is commonly considered to be induced by stress concentration around sharp edges of pores inside the material.

![Figure 1. Morphology of fracture surface of SiC/SiC -CMC.](image)

3.2. Effect of interface on anti-oxidant performance.
The bonding mode between fiber and matrix leads to the high brittleness of SiCf/SiC-CMC[4]. Boron Nitride (BN) or C interface phase is usually prepared on the surface of sic fiber as de-bonding interfaces to transfer load. In addition, these layers before fabricating the matrix can protect the fibers from chemical attack, can improve the toughness and a prolonging the lifetime of the SiCf/SiC-CMC.. These layers reduce the bonding strength between fibers and matrix such that the interphase can absorb and deflect the micro-cracks formed in the brittle matrix [5-7]. The carbon interface is easier to oxidize, while the BN coating oxidizes more slowly at a higher temperature, making it more durable than the carbon coating in a larger temperature range. As shown in figure 2, BN attached to the fiber surface is beneficial to the load and crack deflection. Usually, there are some micro cracks in a single SiC coating. When the temperature is more than 1100 °C, BN reacts with the oxygen that enters the matrix through the microcracks to form a glass B2O3, which is attached to the surface of the fiber. In general, the following reactions occur when BN encounters oxygen.

\[
4\text{BN(s)} + 3\text{O}_2 (g) = 2\text{B}_2\text{O}_3 (c) + 2\text{N}_2 (g) \quad (1)
\]

\[
4\text{BN(s)} + 7\text{O}_2 (g) = 2\text{B}_2\text{O}_3 (c) + 4\text{NO}_2 (g) \quad (2)
\]

\[
4\text{BN(s)} + 3\text{O}_2 (g) = 2\text{B}_2\text{O}_3 (\text{amor}) + 2\text{N}_2 (g) \quad (3)
\]
4BN(s) + 7O₂(g) = 2B₂O₃(amor) + 4NO₂(g)  \hspace{1cm} (4)

As the last barrier of material failure and improve the strength bending effect. Therefore, the bending strength of the SiCf/SiC-CMC containing interface layer does not decrease much at 1200 °C.

3.3. Structure and morphology of SiC/SiC ceramic matrix composite coating

As shown in figure 3, it is clear that the pores on the surface of SiC/SiC composites were filled by CVD SiC coating. It has been with a good effect of isolating oxygen. The main failure phenomenon of gradient coating at high temperature is the cracks of the coating, and the cracks are mainly caused by the internal stress of the coating. Thermal shock tests were carried with SiC/SiC composite with different thickness coatings of 120µm, 65µm and 45µm. The results show that the thick coating is more likely to crack, although it was shown to be tightly bonded to the matrix before testing. This is mainly due to the greater stress produced during the thermal shock. When the crack becomes the diffusion channel of oxygen, the oxidation rate of the matrix will rise sharply.

3.4. Analysis of oxidation properties of SiC/SiC-CMC

At present, there is no fixed understanding of the oxidation mechanism of pure SiC. Volatile SiO and CO will be formed on the surface when the surface temperature or oxygen partial pressure is low. The
reaction formula is the consumption of oxygen barrier layer on the surface of SiC/SiC-CMC. It is the Process of weight loss of materials.

\[
\text{SiC (S)+ O}_2 (g) = \text{SiO (S) + CO (g)} \quad (5)
\]

when the surface temperature or oxygen partial pressure is high, it is process of weight gain of materials[8].

\[
\text{SiC(s) + 2O}_2(g)=\text{SiO}_2(s) + \text{CO}_2(g) \quad (6)
\]

\[
\text{SiC(s) + 3/2O}_2(g) = \text{SiO}_2(s) + \text{CO}(g) \quad (7)
\]

It causes oxygen to enter the material, which greatly accelerates the oxidation rate. The appearance of pores in the SiC/SiC-CMC, as shown in figure 5, makes the mechanical properties of SiC/SiC-CMC decline even destroy.

![Figure 5. The microstructure of oxidized SiC/SiC composites.](image)

The excellent oxidation resistance of SiC coating is due to the protective effect of low oxygen diffusion coefficient and thermal expansion coefficient of the SiO\(_2\) film on SiC. But, there is a great difference between the thermal expansion coefficient of SiC and SiO\(_2\), and the phase transition volume effect occurs with temperature changing, which will cause the SiO\(_2\) coating to crack during thermal shock cycle.

![Figure 6. Curve of bending strength with temperature.](image)
Figure 6 shows the bending strength of the coating with and without coating at different temperatures, it is found that the bending strength of the material can be improved by CVD SiC coating, but the bending strength of the material near 1100 °C is increased. This is due to the reaction of Si with O2 on the surface of the coating to form SiO2.

4. Conclusions
The gradient CVD SiC with dense and uniform antioxidant coating was prepared by CVD process. The bending strength of composites with gradient CVD SiC coating is obviously better than that of composite without coat above 900 °C.

The thermal shock resistance of composite with gradient CVD SiC coating is obviously better than that of without coating. Cracks will occur when the coating reaches a certain size by only ones thermal shock test from room temperature to 1200°C. No cracks was found on the gradient CVD SiC coating with suitable thickness and no defects after thermal shock cycles of 5 times at the same temperature.

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