Preparation and Properties of C\textsubscript{f}/SiC-ZrC Ultrahigh Temperature Ceramic Matrix Composites

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Abstract. Ultra-high temperature materials have many excellent properties, such as high melting point, high specific strength, high thermal conductivity, high conductivity, corrosion resistance and good chemical stability, which make them become high temperature structural materials for aircraft in extreme environments. C\textsubscript{f}/SiC-ZrC ultra-high temperature ceramic matrix composites were fabricated by the combined process of chemical vapor deposition and precursor infiltration pyrolysis (CVI-PIP) in this study. The phase composition and microstructure features of the composites were characterized using X-ray diffraction, scanning electron microscopy. A PyC layer was observed as the interfacial layer between carbon fiber and the ultrahigh temperature ceramic matrix. It can protect the carbon fiber from damage during the cyclic PIP process. Nano crystalline ZrC particles were observed in the composites. The ablation mechanisms of the composites were tested in arc-jet wind tunnel and it exhibited good ablation-resistant properties. The ablation mechanism of composite materials in wind tunnel environment is discussed.

1. Introduction

The Ultra-high temperature materials refer to those materials that can work at temperatures above 2000\textdegree C. Now, high temperature resistant materials which can adapt to extreme environments such as hypersonic flight, atmospheric reentry and rocket propulsion systems mainly include refractory metals, graphite, C/C, ultra-high temperature ceramics and their composites. Ultra-high temperature ceramics mainly include carbides, borides, nitrides and oxides of refractory metals such as ZrB\textsubscript{2}, ZrC, TaN, HfB\textsubscript{2}, etc. They were needed for the nose caps, sharp leading edges and rocket engines of hypersonic aerospace vehicles because of excellent mechanical and ablation properties. \cite{1-3} However the inherent brittleness and poor thermal shock resistance of ceramic materials limits their application. C/C composites are easily oxidized under aerobic conditions above 450\textdegree C. They were severely ablated at ultra-high temperature and extreme environment, resulting in a sharp decline in mechanical properties. The continuous carbon fiber reinforced ultra-high temperature ceramic matrix composites not only overcome the brittleness of ceramic materials, but also have good oxidation resistance \cite{4-5}. Recent years, many scholars have done a lot of research on it.

Matrix modification is the effective way to improve the oxidation resistance and ablation resistance of C/C composites. The C/C-ZrC composites were prepared by high temperature pyrolysis of
precursors.[6] The Cf/SiC-ZrC composites were prepared by polymer impregnation pyrolysis (PIP) under the condition that the mass ratio of poly-organic zirconium and PCS was 1:1, the heat treatment temperature and time were 1500°C and 120s respectively[7]. The C/C-SiC-ZrC composites were prepared by reactive infiltration (RMI) process [8]. The effects of mass ratio of SiC/ZrC on the mechanical properties and ablation resistance of C/C-SiC-ZrC composites were studied [9].

In this study Cf/SiC-ZrC ultra-high temperature ceramic matrix composites were fabricated by the combined process of chemical vapor deposition and precursor infiltration pyrolysis (CVI-PIP).

2. Experimental

2.1. Materials
In this study, carbon fibre performs were alternately laminated with T700 6K carbon fibre and T700 12K mesh tire by needling process, as shown in Figure 1. PCS and polyzirconium carbonate were used as the precursor of SiC and ZrC ceramics matrix. Analysis of pure xylene used as the precursor solvent.

![Figure 1. Structure of carbon fibre preforms.](image)

2.2. Preparation
Cf/SiC-ZrC composites were prepared according to the following four steps. Firstly, carbon fibre preforms were formed which density was 0.4-0.5g/cm³. Secondly, the pyrolytic carbon was fabricated with liquefied petroleum gas as carbon source, Ar as dilution gas and protective gas by CVI. Thirdly, SiC and ZrC ceramics matrix were introduced through PIP. PCS was dissolved in xylene with a mass ratio of 1:1. Then it mixed with polyzirconium carbide at a mass ratio of 1:12. The C/C composites were impregnated in the precursor mixed solution at pressure of 6-8 MPa and cured after holding pressure for 2 hours. In vacuum drying chamber, curing temperature in N₂ atmosphere is 90°C for 3h and 140°C for 4h. After curing, the composites were pyrolysis at 1000°C to 1550°C respectively. At last, a layer of SiC coating was deposited on the surface of the composites by CVD.

2.3. Characterizations
The bulk density (ρ) of the sample was calculated by measuring the volume (V) and mass (M) of the monolithic sample by the formula of ρ=M/V. The phase composition of the composites was characterized using X-ray diffraction. The surface, cross section and fracture morphology of the
composites were observed by SEM. EDS was used to analyze the changes of interfacial element composition of fiber matrix in composites. The micro-zone composition of composites was characterized using EDS. The ablation mechanisms of the composites were tested in wind tunnel.

3. Results and discussion

3.1. Carbon interface layer
Fiber/matrix interface is an important component of ceramic matrix composites. The interface controls the energy absorption mechanisms of interface debonding, crack deflection and branching, fiber breakage and pull-out. When the interface bonding is too strong, the cracks in the matrix are easy to diffuse directly into the fibers and brittle fracture occurs easily. When the interfacial bonding is too weak, the load cannot be effectively transferred from the matrix to the fibers, and the strengthening and toughening effect of the fibers cannot be exerted.

Figure 2 shows the SEM of the carbon interface layer between carbon fiber and matrix. The pyrolytic carbon as the interface layer in carbon fiber preform can improve the mechanical properties of the material and change the fracture behavior of materials from brittle to Non-brittle. On the other hand, pyrolytic carbon has excellent high temperature strength. It can effectively improve the high temperature mechanical properties of materials.

![Figure 2. SEM of the carbon interface layer.](image)

![Figure 3. Phase analysis of composites at different temperatures.](image)
3.2. Phase analysis of composites at different temperatures
The phase analysis of Cf/SiC-ZrC composites after pyrolysis at different temperatures is shown in Figure 3. It can be seen from the figure that ZrO2 exists in the matrix after pyrolysis at 1300°C. When the pyrolysis temperature is 1550°C, the matrix compositions are SiC and ZrC. Figure 4 shows the microtopography and elemental analysis of the composites prepared under 1550°C. The holes and carbon interface layer left when the fibers are pulled out can be obviously seen from the figure. The elemental analysis shows oxygen element exists in the composites. The precursor of zirconium carbide is very sensitive to moisture in air and easy to hydrolyze to ZrO2. This may be the reason for the existence of oxygen.

3.3. Oxidation resistance
The density of C/SiC-ZrC composites reached 1.95g/cm³ after 14 cycles of impregnation-pyrolysis process. The macroscopic and microscopic morphology of composites after ablation assessment in arc-jet wind tunnel is shown in Figure 5. After ablation, the structure of the composite plate is intact, the shape of the composite plate hardly changes, and there is no obvious denudation on the surface. The composites exhibit good oxidation resistance.
The SEM photographs of the composites after ablation is shown in Figure 6. The oxidation of carbide ceramics at ultra-high temperature can produce a high viscosity and compact oxide layer. The oxide layer contains a small amount of glass phase, which seals and fills the cracks and defects in the oxide layer, and greatly reduces the channel and diffusion rate of oxygen into the material. So it has good antioxidant activity.

As for C/α-SiC-ZrC composites the ablation process in arc-jet wind tunnel can be divided into three stages. In the first stage, SiC is first oxidized to SiO₂. With the increase of surface temperature, because of the low melting point of SiO₂, a continuous molten SiO₂ protective layer was formed on the ablated surface. It prevents oxygen from entering. In the second stage, when the ablation temperature continues to rise and reaches the boiling point of SiO₂, SiO₂ start evaporating. ZrC is oxidized to ZrO₂ particle and it pinned in the molten silica layer, which reduces the volatilization of silica. In the third stage, when the ablation surface temperature reaches above the melting point of ZrO₂, both SiO₂ and ZrO₂ melt. Because the viscosity of SiO₂ is very low at high temperature, the viscosity of the mixture is also low. It is easy to blow off the ablated surface in the air stream. So ablation marks can be seen on the surface of composites plate. But the ablation is not obvious because of the short time. In a word, the C/α-SiC-ZrC composites have good oxidation resistance at high temperature.

4. Conclusion

The C/α-SiC-ZrC composites were fabricated by the combined process of chemical vapor deposition and precursor infiltration pyrolysis (CVI-PIP). The density of the composites reached 1.95g/cm³ after 14 cycles of impregnation-pyrolysis process. The optimum pyrolysis temperature of composites is 1550°C and it exhibits excellent oxidation resistance in arc-jet wind tunnel test.

References

[1] Fahrenholtz W G, Hilmas G E, Talmy I G 2007 Refractory diborides of zirconium and hafnium Am Ceram Soc. 90 1347-64
[2] Chamberlain A L, Fahrenholtz W G, Hilmas G E 2004 High strength ZrB₂-based ceramics Am Ceram Soc. 31 1170-72
[3] Opekà M M, Talmy I G, Wuchina E J 1999 Mechanical, Thermal, and Oxidation Properties of Hafnium and Zirconium Compounds Europ Ceram Soc. 19 2405-14
[4] Silvestroni L, Sciti D, Melandri C 2010 Toughened ZrB₂-based ceramics through SiC whisker or SiC chopped fiber additions Europ Ceram Soc. 30 2155-64
[5] Paul A, Jayaseelan D D, Venugopal S 2012 UHTC Composites for hypersonic applications Am Ceram Soc Bull. 91 22-29
[6] Liu C X, Chen J C, Su Z A 2014 Pyrolysis mechanism of ZrC precursor and fabrication of C/C-ZrC composites by precursor infiltration and pyrolysis Transaction of Nonferrous Metals Society of China. 24 1779-84
[7] Li Q G, Zhou H J, Dong S M 2012 Fabrication and comparisonof 3D Cf/ZrC-SiC composites using ZrC particles/ polycarbosilane and ZrC precursor/polycarbosilane Ceramics International 38 5271-75
[8] Wang Y G, Zhu X J, Zhang L T 2012 C/C-SiC-ZrC composites fabricated by reactive melt infiltration with Si 0.87 Zr 0.13 alloy Ceramics International. 38 4337-43
[9] Feng B, Li H J, Zhang Y L 2014 Effect of SiC/ZrC ratio on the mechanical and ablation properties of C/C-SiC-ZrC composites Corrosion Science 82 27-35