FABRICATION AND MICROSTRUCTURE OF C/C-ZRC-SIC AND C/C-HFC-ZRC-SIC COMPOSITES

Lin Xu[1,2*], Wei Li[1], Xinchao Li[1], Jia Cheng[1], Zhen Fan[1], Yongzhong Song[1], Zhihai Feng[1]
1, Science and Technology of Advanced Functional Composite Laboratory, Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, China
2, Science and Technology on High Strength Structure Materials Laboratory, Central South University, Changsha 410083, China
* Corresponding author：xulinhit@126.com（Lin Xu）

ABSTRACT: To increase the oxidation of carbon/carbon (C/C) composites at high or ultrahigh temperature, C/C-ZrC-SiC and C/C-HfC-ZrC-SiC composites were fabricated by precursor infiltration and pyrolysis (PIP). The microstructure, mechanical properties and ablation resistance were investigated and discussed. Results show that the appropriate PyC interface can act as carbon resource to form carbides during high temperature pyrolysis. It can also protect carbon fibers from reaction with oxygen and other impurities during high temperature treatment. These two kinds of material can keep excellent mechanical properties at high temperature until to 2000 ^{o}C in inert atmosphere. They also possess good ablation resistance at high temperature (2800K) under oxidation environment, which being attributed to the formation of Zr-Si-O glass or Hf-Zr-Si-O glass.
Keywords: Ultrahigh temperature ceramic matrix composite, C/C composite, Mechanical properties, Ablation resistance

1. Introduction

Carbon fiber reinforced carbon (C/C) composites are considered as one of the most promising candidates for high-temperature structural applications in aerospace due to their excellent properties, such as low density, high strength, low coefficient of thermal expansion, good thermal shock resistance, good friction wear properties and high retention of strength in inert environment to temperature above 2500^{o}C [1]. However, C/C composites are prone to oxidize above 450^{o}C in oxygen-containing environment [1-3]. Therefore, improving oxidation resistance at high or ultra-high temperature is crucial to extending the application of C/C composites.

Introducing ultra-high temperature ceramics (UHTCs) into C/C composites can improve the oxidation and ablation resistance of C/C composites because they have high melting point, good chemical inertness and low evaporation properties. In the last few years, many efforts have been made to develop C/C-UHTCs composites [4-14], such as C/C-ZrB_2-SiC, C/C-ZrC-SiC, C/C-TaC-SiC, C/C-ZrB_2-ZrC-SiC, C/C-ZrB_2-TaC-SiC. However, there are few reports on the high temperature mechanical properties of C/C-UHTCs composites in the open literature.

In this paper, two kinds of C/C-UHTCs composites namely C/C-ZrC-SiC and C/C-HfC-ZrC-SiC composites were prepared by PIP process using liquid ZrC/SiC and HfC/ZrC/SiC precursor. The microstructure, mechanical properties at different temperature was investigated and discussed. Ablation property under ultra-high temperature was also characterized, in an attempt to illustrate the effect of the UHTCs phase on the anti-oxidation and anti-ablation behavior of C/C composites.

2. Experimental

2.1 Preparation of C/C-UHTCs composites

Two dimensional (2D) needle carbon fiber felts with density of ~0.45g/cm^3 used as the reinforcement for C/C-UHTCs composites were densified through chemical vapor infiltration (CVI) process to porous C/C composites with a density of 1.1~1.2 g/cm^3. The thickness of pyrolytic carbon (PyC) on the surface of carbon fibers was 8~10μm after CVI process. The liquid ZrC/SiC and HfC/ZrC/SiC precursor (Institute of Chemistry, Chinese Academy of Science, Beijing, China) with weight ratio of Zr to Si and Hf & Zr (Hf: Zr=1:1) to Si being 4:1 were used as ceramic precursors. Details of the novel liquid precursor are provided in Ref [15]. The C/C-UHTCs composites were fabricated by 12 cycles of vacuum infiltration with the above mentioned liquid precursor into the porous C/C composites, drying in a drying oven, and heat treatment at 1500^{o}C for 2h in an argon protective atmosphere furnace. The density of the C/C-ZrC-SiC composites was 1.9~2.2g/cm^3.

2.2 Properties and characterization

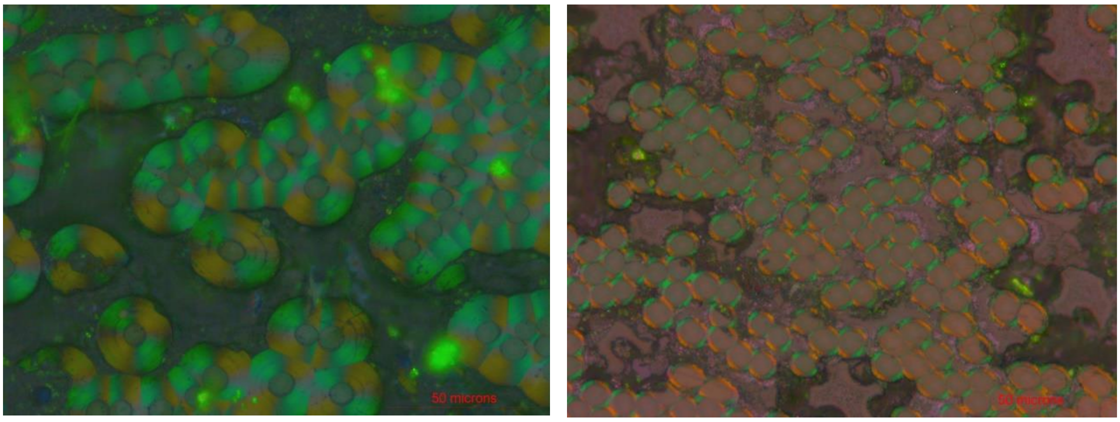
The densities of samples were measured by the Archimedes' method. Tensile strength was measured using unilateral stretching methods applying DqES415-2005 [16]. Flexural strength was measured applying QJ2099-91[17] with three-point flexure methods. Compressive strength was measured using one-dimensional compression methods applying DqES293-94 [18]. All mechanical properties were measured from room temperature up to 2000^{o}C in an inert gas atmosphere. A minimum number of five specimens were tested for each experimental condition. The phase compositions of the composites were characterized by X-ray diffraction (XRD) with Cu Kα radiation. The microstructure features and fractured surfaces of the composite were observed using scanning electron microscopy (SEM) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS).

The high temperature anti-ablation test was conducted under supersonic conditions using an arc-heated wind tunnel. The plate specimens with 100mm × 100mm × 10mm were used. The stagnation pressure and simulated flight Mach number of the supersonic flow at the exit nozzle were 0.5MPa and 6.0, respectively. The total temperature of the flow was Tt = 2800K. The total test duration was 600s. After oxidation, the microstructure features of the composite were observed using SEM and EDS.

3. Results and discussion

3.1 Microstructure of C/C-UHTCs composites

Fig.1 shows the OM image comparison of PyC interfacial layer before and after PIP process. It is shown that the thickness of PyC interface reduced from 8~10μm to 1~2 μm after repeated precursor infiltration and high temperature pyrolysis. This PyC layer is beneficial to improve the mechanical properties due to the increasing preform stiffness and preventing damage to the carbon fibers in the subsequent processing [9]. Results show that the appropriate PyC interface can act as carbon resource to form carbides during high temperature pyrolysis. It can also protect carbon fibers from reaction with oxygen and other impurities during high temperature treatment.



(a) before (b) after

Fig.1 Comparison of PyC layer on carbon fibers after PIP process

Fig.2 and Fig.3 show typical cross-section morphology of C/C-ZrC-SiC and C/C-HfC-ZrC-SiC composites. It is shown that the C/C-UHTCs composite are relatively dense and UHTC phase are dispersed homogenously in the composites, including white ZrC, HfC phase and gray SiC phase.

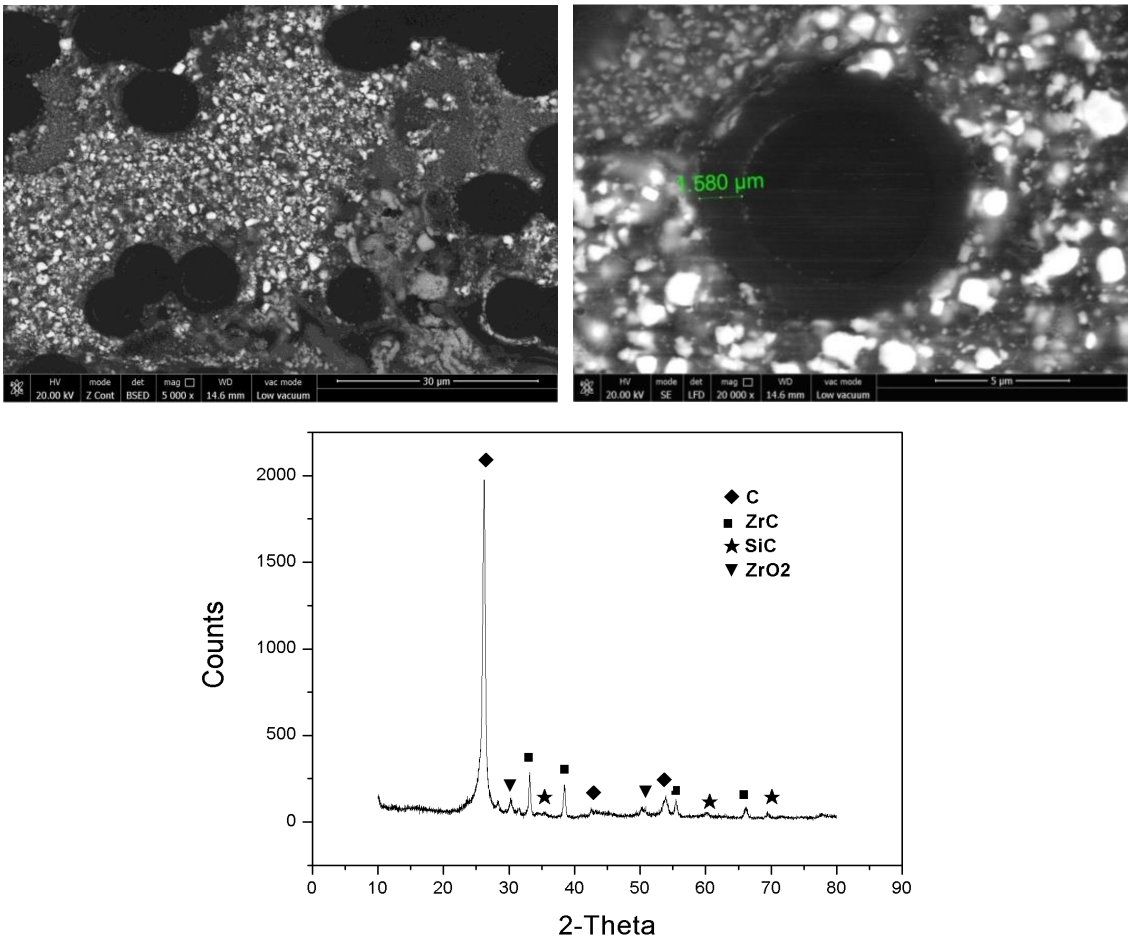


Fig.2 SEM images and XRD pattern of C/C-ZrC-SiC composites.

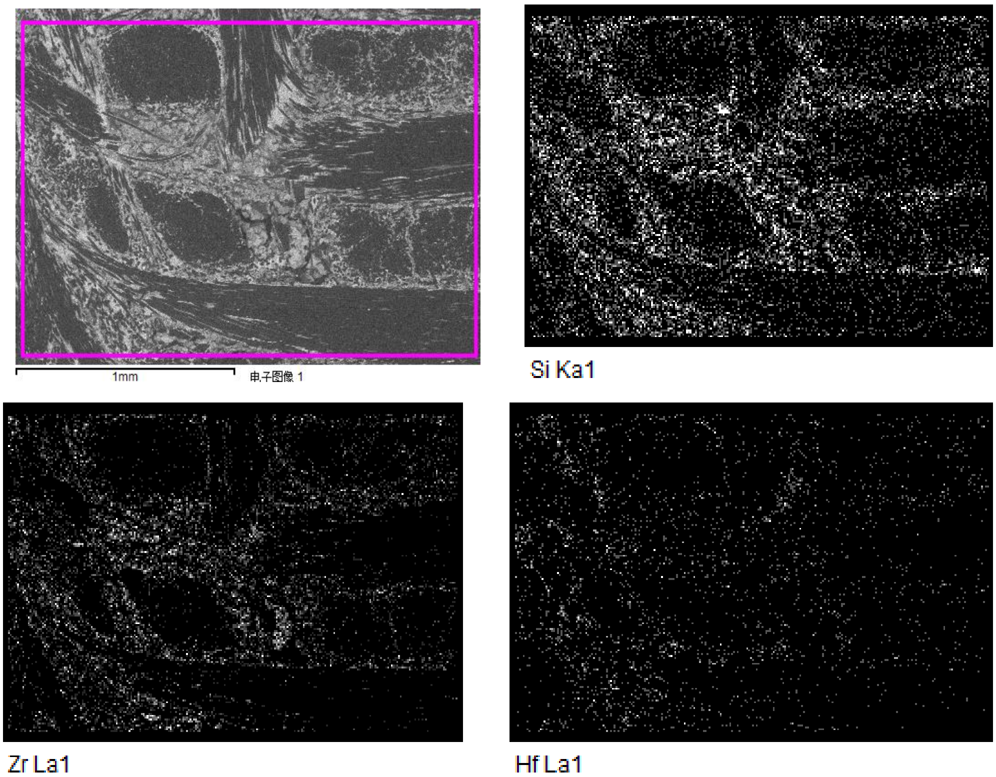


Fig.3 SEM image and EDS maps of C/C-HfC-ZrC-SiC composites.

3.2 Mechanical properties

The mechanical properties of the obtained C/C-ZrC-SiC composites are summarized in Table 1. As shown, the tensile strength of obtained two kind materials is ~100MPa. The flexural strength and compressive strength of the composites are 130 MPa and 134 MPa, respectively, which are at the same level of reported C/C-UHTCs composites produced through different method with the same kind of carbon fiber felts [7,9,10-13].

Table 1 Mechanical properties of C/C-ZrC-SiC and C/C-HfC-ZrC-SiC composites.

Materials	Density (g/cm^3)	Tensile strength (MPa)	Flexural strength (MPa)	Compressive strength (MPa)
C/C-ZrC-SiC	2.05	96	130	134
C/C-HfC-ZrC-SiC	2.11	106	165	195

The fracture surface photographs of the C/C-ZrC-SiC and C/C-HfC-ZrC-SiC composites are given in Fig.4 and Fig.5. A rough fracture surface with lots of pulled out carbon fibers and interface debonding can be clearly seen, showing typical non-brittle fracture behaviors. Owning to the carbon fibers being pulled out and crack propagation along PyC interfaces, a great amount of energy will be absorbed in the fracture process, which is beneficial to improving mechanical properties such as toughness. Moreover, the surface of the pulled out fibers is rather smooth, indicating that the fibers are well protected in the PIP and high temperature pyrolysis process. This result is very important to the mechanical property of the C/C-UHTCs composites.

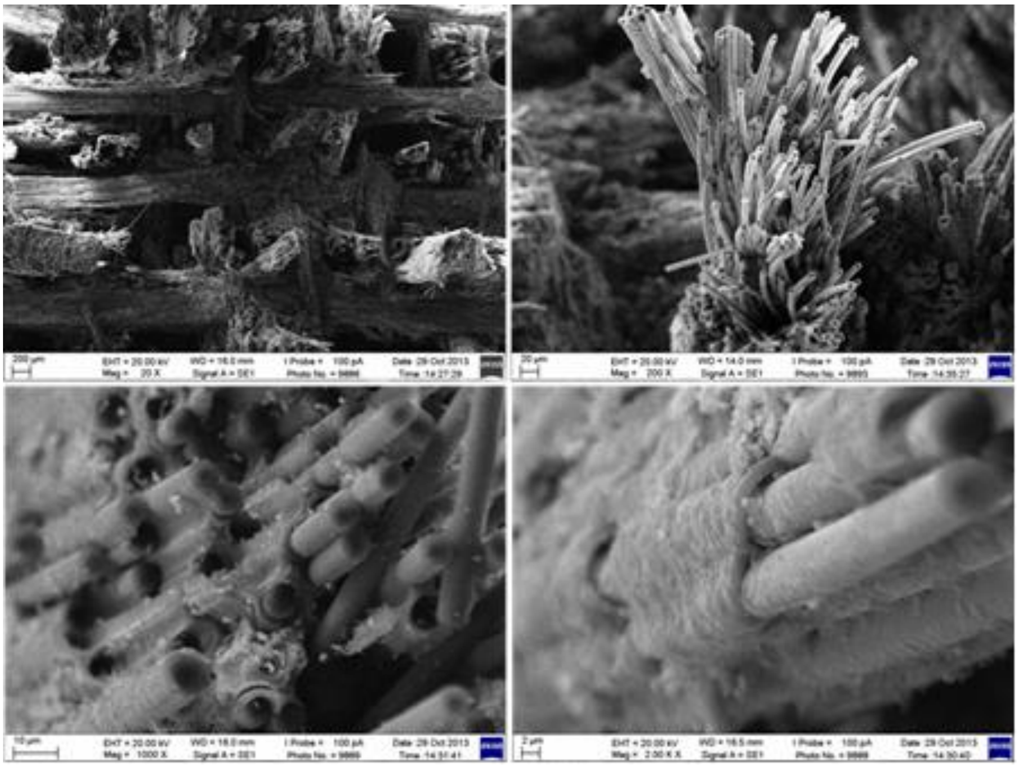


Fig.4 The fracture surfaces of C/C-ZrC-SiC composites

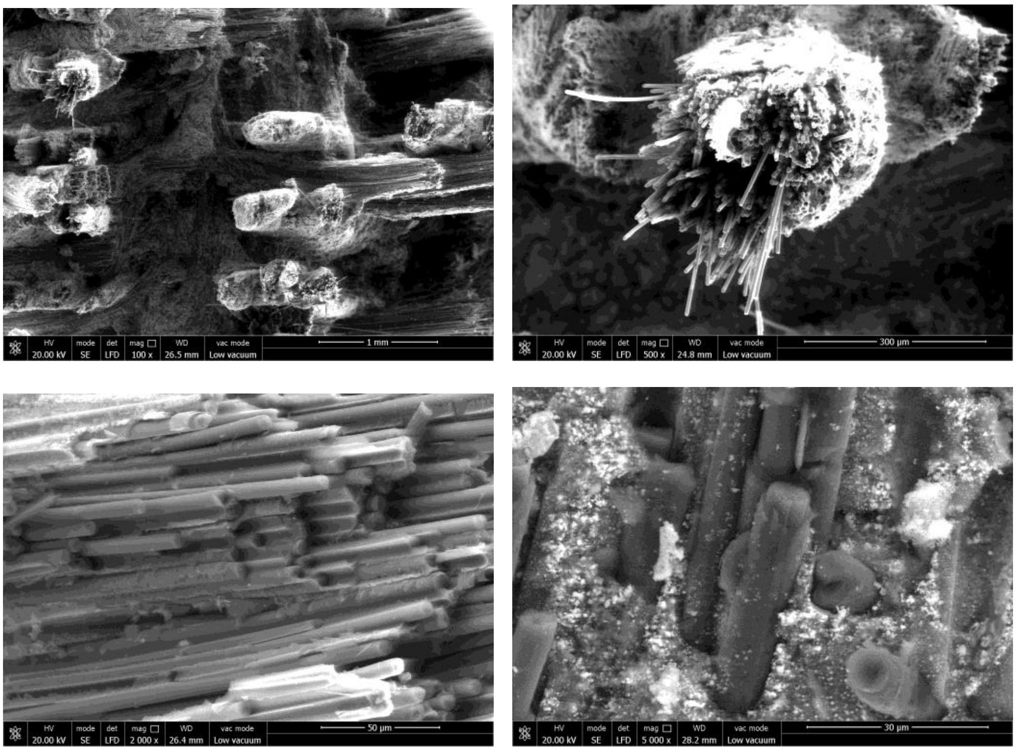


Fig.5 The fracture surfaces of C/C-HfC-ZrC-SiC composites

At elevated temperatures up to 2000 ^{o}C, in an inert gas atmosphere, the mechanical properties of C/C-ZrC-SiC are slightly higher than at room temperature. This unique characteristic is properly due to the continuous carbon fiber felts, similar to the behavior of C/C composites.

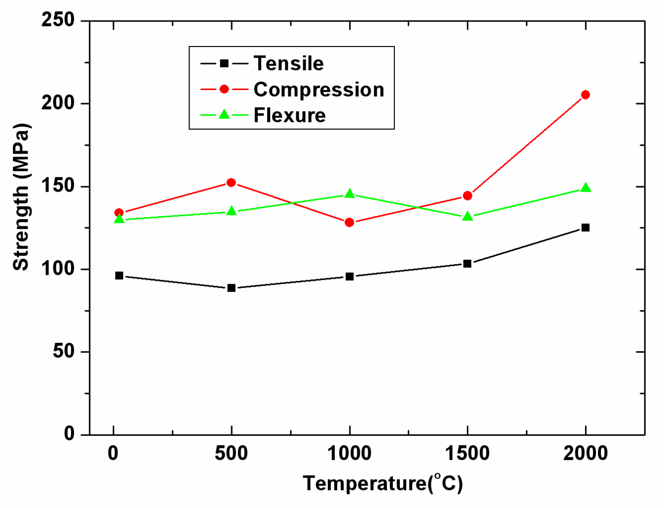


Fig.6 High temperature mechanical properties of C/C-ZrC-SiC composites

3.4 Ablation properties

The high temperature property of the C/C-UHTCs is important. Thus, the ablation resistance of the C/C-ZrC-SiC composite was tested under supersonic conditions using an arc-heated wind tunnel. The total temperature of the flow was Tt = 2800K. Fig.7 shows the surface appearance photograph of C/C-ZrC-SiC composites after ablation for 600s. As shown in Fig.7a, amount of light color phase with gray matrix are clearly observed among fiber bundles. EDS analysis indicated that this area consists of O, Si, Zr elements, which is believed to a mixture of ZrO_2 and SiO_2. ZrO_2 appears to form a porous skeleton and can provide mechanical integrity to the silicate liquid glass. Silica glass was retained and distributed in the zirconia grain boundary and the surface, which provide increased inhibition of the inward access of oxygen. Meanwhile, the mass and linear ablation rate after ablation for 600s are 3.6×10^{-1} mg/cm^{2}s and 5.4×10^{-2} mm/s, respectively. Therefore, the obtained C/C-UHTCs composites have excellent high-temperature properties.

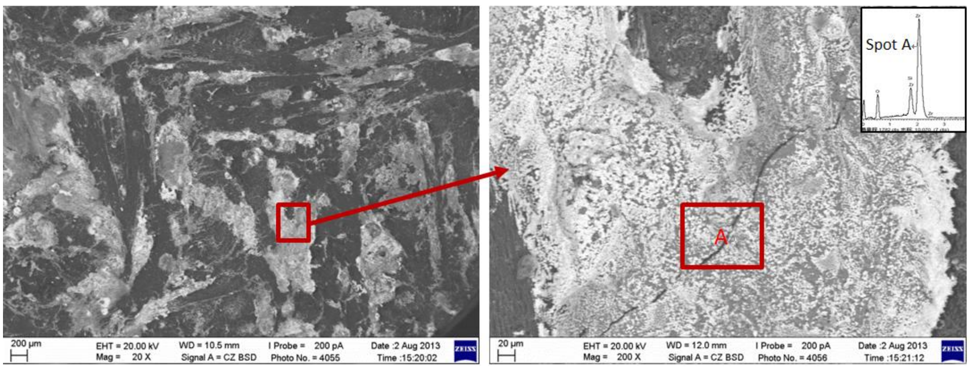


Fig.7 SEM images of C/C-ZrC-SiC composites after ablation

4. Conclusion

In this paper, two kinds of C/C-UHTCs composites namely C/C-ZrC-SiC and C/C-HfC-ZrC-SiC composites were prepared by PIP process using liquid ZrC/SiC and HfC/ZrC/SiC precursor. The microstructure, mechanical properties at different temperature was investigated and discussed. Ablation property under ultra-high temperature was also characterized under supersonic conditions using an arc-heated wind tunnel. Results show that the composites have good mechanical and excellent ablative properties.

Acknowledgements

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