



Microstructure and ablation resistance of carbon/carbon composites with a zirconium carbide rich surface layer



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ABSTRACT

Zirconium carbide (ZrC) rich surface layer with a thickness of 80–100 μm was prepared on carbon/carbon (C/C) composites. The ZrC-rich layer consisted of submicron ZrC particles, homogeneously dispersed in the carbon matrix. The mass ablation rate of the composite with the ZrC-rich layer was 69% lower than that of the bare C/C composites. The ZrC-rich layer could seal the surface pores and cracks to restrain the preferential ablation in the defect area and form a continuously melting ZrO_2 layer to prevent the carbon from oxidizing during ablation. The strengthened ZrC-rich layer could reduce the mechanical denudation of the composites.

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1. Introduction

Carbon/carbon (C/C) composites are lightweight and exhibit good thermal shock resistance that makes them attractive for aerospace applications [1,2]. However, the rapid oxidation at ultrahigh temperature and pressure severely limits their application in advanced aerospace systems. Adding refractory carbides into the carbon matrix is an effective way to improve the ablation resistance of the C/C composites [3,4]. Until now, various refractory carbides, such as zirconium carbide (ZrC), hafnium carbide (HfC), silicon carbide (SiC)–ZrC, and zirconium diboride (ZrB_2)–ZrC, have been added into C/C composites to improve the ablation resistance [5–9]. Various defects in the surface of the composites, such as micropores and cracks, decrease the ablation resistance [10,11]. On one hand, the open pores and cracks allow oxygen to enter inside C/C composites, thus accelerating the oxidation of C/C composites. On the other hand, the carbon in pores and cracks, as the oxidation active sites, easily reacts with oxygen, resulting in a large consumption of carbon [12]. Yin et al. [13] reported that the ablation of C/C composites starts at the open pores. Fan et al. reported [14] that a low level of porosity in C/SiC– Ti_3SiC_2 composites resulted in better ablation resistance. Thus, the minimization of surface defects is an effective way to further improve the ablation resistance of C/C composites. It is possible to fill the micropores and cracks using refractory metal oxides/carbides.

Recently, microwave hydrothermal process is considered as the most efficient method for the synthesis of nanopowders because of

rapid volumetric heating, increased reaction rates, good homogeneity, and high reproducibility [15,16]. Moreover, the nanopowders can infiltrate into the open pores and defects of the composites due to rapid mass transfer and good penetration ability of the hydrothermal system. Thus, microwave hydrothermal process is an efficient method to synthesize refractory metal oxides in the micropores and cracks. Cao et al. [17] introduced aluminum phosphate particles into the interbundle pores of C/C composites to improve the oxidation resistance of C/C composites at low temperatures. The mass loss of the C/C composites at 200 °C was only 18.5 mg/cm^2 after the oxidation for 10 h. The oxidation rate was almost constant after the oxidation at 600 °C for 6 h.

In this study, C/C composites containing ZrC was treated by a microwave hydrothermal process to fill the surface micropores and cracks by ZrO_2 particles. Then, the C/C composites were further treated by a graphitization process to form a ZrC-rich surface layer. The microstructure and ablation resistance of the composites were investigated. The ablation mechanism of the composites was elucidated.

2. Experimental

2.1. Fabrication of composites

The composites were prepared from bulk needled carbon fiber felts with a density of 0.40 g/cm^3 . The felts were infiltrated to the density of 0.80 g/cm^3 by an isothermal chemical vapor infiltration (ICVI) process as reported previously [18]. Zirconium tetrachloride (ZrCl_4 , analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as the ZrO_2 precursor.

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Fig. 1 shows the flowchart for the preparation of C/C composites with a ZrC-rich layer. 1 M $ZrCl_4$ solutions and 2 M NaOH solution were prepared by dissolving required quantities in distilled water. The original pH of the $ZrCl_4$ solutions before adding NaOH is ~ 0.9 . Then, the pH value of the solution was set to 5 using a 2 M NaOH solution. The prepared solution and carbon fiber felts were transferred into a Teflon autoclave. The hydrothermal reaction was carried out in a microwave accelerated reaction system for 40 min at 200 °C, and then the resulting felts were dried at 80 °C. The microwave hydrothermal reactions were conducted in a microwave accelerated reaction system (MARS-10, Sineo Microwave). The system operates at a 2.45 GHz frequency with 0–100% of full power (1200 ± 50 W) and can be controlled by a temperature (260 °C max). The reaction vessel was connected to an optical probe to monitor and control the temperature during synthesis.

After the pretreatment, thermal gradient chemical vapor infiltration (TCVI) was used to densify the carbon fiber perform. Methane was used as the carbon source. Finally, the C/C composites were graphitized at 2500 °C for 2 h in an argon atmosphere [19]. The prepared C/C composites containing ZrC were named as C/C–ZrC. The ZrC content was 5.56 wt% in the C/C–ZrC samples. The C/C–ZrC samples were treated again by a microwave hydrothermal process under the same conditions mentioned above. The treated C/C–ZrC composites were named as C/C–ZrC–ZrO₂. Then, the C/C–ZrC–ZrO₂ samples were further treated by a graphitization process. The graphitized C/C–ZrC–ZrO₂ samples were named as C/C–ZrC–ZrC.

2.2. Tests and characterization

The open porosity and bulk density of the prepared specimens were measured by the Archimedes method according to the ASTM C-20 standard. The content of filler in the C/C–ZrC–ZrO₂ and C/C–ZrC–ZrC samples was calculated using the following equation.

$$C_{filler} = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m_1 are the mass of the C/C–ZrC samples before and after the treatment, respectively. The details of the composites prepared are listed in Table 1.

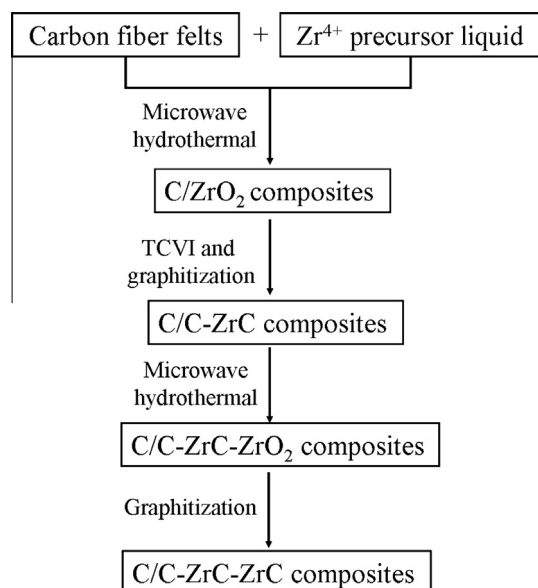


Fig. 1. Schematic for the preparation of a ZrC-rich surface layer on the C/C composites.

Table 1

Density and open porosity of the C/C–ZrC, C/C–ZrC–ZrO₂, and C/C–ZrC–ZrC samples.

Samples	Density (g/cm ³)	Open porosity (%)	Filler content (wt%)
C/C–ZrC	1.76	6.5 ± 0.1	–
C/C–ZrC–ZrO ₂	1.79	2.3 ± 0.2	0.45
C/C–ZrC–ZrC	1.78	2.4 ± 0.3	0.38

The ablation of the composites was carried out using an oxyacetylene torch for the plate specimens ($\varnothing 30 \times 10$ mm²). The ablation parameters were set as previously reported [12]. The inner diameter of the oxyacetylene gun tip was 2 mm and the distance between the gun tip and the specimen was 10 mm. During the test, the flame temperature was estimated to be approximately 3000 °C. The specimens were exposed to the flame for 60 s. The linear ablation was performed at the sample center. The mass ablation rate was the average of the entire sample. Six-point average thickness and weight changes, obtained from the measurements taken before and after the ablation process, were used to calculate the linear and mass erosion rates.

The phase composition of the composites was investigated by X-ray diffraction (XRD, X'Pert Pro MPD). The microstructure of the composites was investigated by scanning electron microscopy (SEM, JSM6460) combined with energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Density of the samples

Table 1 lists the density and open porosity of the C/C–ZrC, C/C–ZrC–ZrO₂, and C/C–ZrC–ZrC samples. The density of the composites increased after the hydrothermal treatment, indicating that ZrO₂ or ZrC was introduced into the C/C–ZrC samples. Moreover, the open porosity of the C/C–ZrC composites dramatically decreased, indicating that the open pores and cracks were filled by the ZrO₂ or ZrC.

3.2. XRD and SEM analysis

Fig. 2 shows the XRD patterns of the composites. The C/C–ZrC samples are composed of C and ZrC. A ZrO₂ peak is present in the C/C–ZrC–ZrO₂ samples, indicating that ZrO₂ was introduced into

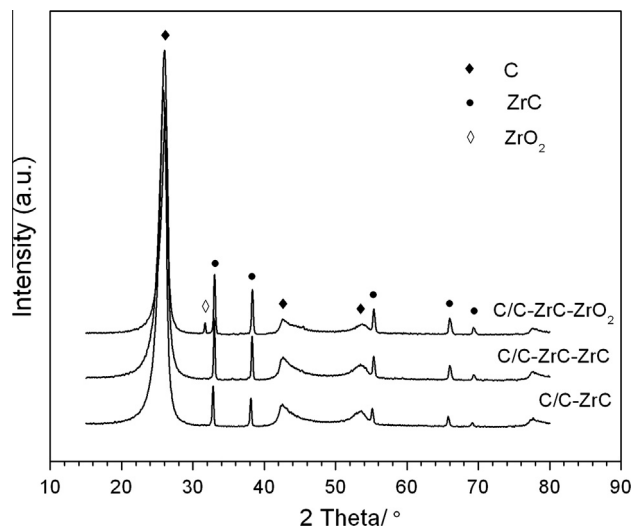


Fig. 2. XRD patterns of the C/C–ZrC, C/C–ZrC–ZrO₂, and C/C–ZrC–ZrC samples.

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