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Influence of SiC additive on the ablation behavior of C/C composites modified by ZrB_2–ZrC particles under oxyacetylene torch

Lei Liu, Hejun Li*, Xiaohong Shi, Qiangang Fu, Wei Feng, Xiyuan Yao, Chang Ni

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, PR China

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Abstract

To determine the effect of SiC additive on the ablation behavior of carbon/carbon composites modified by ZrB_2–ZrC particles (C/C–Z), C/C–Z and C/C–Z with SiC additive (C/C–Z–SiC) were ablated by oxyacetylene torch for different times up to 240 s. Results showed the improved ablation property of C/C–Z–SiC in comparison with C/C–Z during the initial 120 s but depletion of the improvement with the ablation further proceeding. Meanwhile, the recorded surface temperature of C/C–Z–SiC was lower than that of C/C–Z under the same ablation condition during the initial 160 s after which they tended to be the same. The ablated surface center morphology of C/C–Z–SiC implied that a SiO_2 rich layer was formed beneath the chalked ZrO_2 outer layer within 120 s ablation while the SiO_2 rich layer was almost depleted beyond 240 s. The formation and depletion of SiO_2 rich layer from oxidation of SiC additive dominated the distinct ablation behaviors of C/C–Z–SiC and C/C–Z.

Keywords: D. SiC; Carbon/carbon composites; Ablation; ZrB_2

1. Introduction

Ultra high temperature ceramics (UHTCs) modified carbon/carbon (C/C) composites for improving the ablation resistance have been largely reported in the last two decades. Among these works, ZrB_2–ZrC (Z) modified C/C composites (C/C–Z) have attracted increasing attention and many methods have been attempted to fabricate the composites. All methods, including slurry infiltration [1,2], precursor infiltration and pyrolysis (PIP) [3,4], reactive melt infiltration (RMI) [5–7], chemical vapor decomposition [8], thermal spray technology [9] and combination of them [10,11], have been successfully used to prepare C/C–Z composites. Meanwhile, the ablation properties of pitch-derived ZrC/C composites [12], C/C–ZrC composites [13] and C/C–ZrB_2 [14] composites were evaluated by oxyacetylene torch, showing a better ablation resistance than that of pristine C/C composites as more ingredients of UHTCs were added. C/C–ZrC [5,6] ablated by laser also displayed a better ablation property than C/C and C/SiC composites. Besides, C/ZrC composites showed a four-layer microstructure after ablation by oxyacetylene torch [15]. Recently, many investigations have concentrated on the ablation behavior of C/C–Z with SiC additive (C/C–Z–SiC) [16–18]. Some studies suggested that SiC additive could improve the ablation property of Z or Z modified C/C composites [19,20] since the melted SiO_2 could fill in the porous ZrO_2 and block the infiltration of oxidizing species. Nevertheless, some other researches showed that the SiC additive led to more serious ablation of C/C–Z [1,2]. Because there have been few works making a direct comparison between C/C–Z–SiC and C/C–Z composites, it is hard to assess whether the SiC additive is beneficial to the improvement of ablation property of C/C–Z or not. In other words, the effect of SiC on the ablation of C/C–Z is still unclear. Therefore, we believe it is necessary and meaningful to clarify the ablation mechanism in order to optimize the composition of UHTCs modified C/C composites.

*Corresponding author. Tel.: +86 29 88495004; fax: +86 29 88492642.
E-mail address: lihejun@nwpu.edu.cn (H. Li).

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In the present work, Z and Z–SiC particles were deposited into carbon fiber fabric using the traditional PIP process and then the doped fabrics were densified by pyrocarbon and finally graphitized. To understand how SiC works during the ablation of Z modified C/C composites, C/C, C/C–Z and C/C–Z–SiC (with the same Z concentration as C/C–Z) were ablated by oxyacetylene torch with a relative low heat flux of $2.38 \pm 10\%$ MW/m^2 for different times until termination at 240 s. The comparison of ablation rates, recorded surface temperatures and ablated morphologies of the prepared composites provided a good guidance to understand the ablation mechanism of C/C–Z–SiC.

2. Experimental procedure

2.1. Composite preparation

Ceramic particles were deposited into T300 PAN-based carbon fiber fabricated needle punched disk felts (0.45 g/cm^3) by the traditional PIP process using a certain amount of organic Z precursor (purchased from Chinese Academy of Sciences, ceramic production ratio was about 33 wt%) and polycarbosilane (PCS, ceramic production ration was about 64 wt%) in dimethylbenzene solution. After immersion under vacuum for 20 min, impregnated felts were taken out and dried in a drying oven at 90 °C for 24 h. Afterward, the dried carbon felts were heat treated in a flowing Ar atmosphere at 1400–1800 °C for 2 h. In the heat treatment process, Z and SiC particles were formed in the carbon fiber felts. The mass of ceramic particles in each felt was calculated according to

$$m_{ceramic} = m_1 - m_0 \quad (1)$$

where m_0 and m_1 are the masses of carbon felt before impregnation and after heat treatment, respectively. For comparison, the felts of C/C–Z and C/C were heat treated together with those of C/C–Z–SiC.

When the expected ceramic content was achieved, all the carbon felts were densified through a thermal gradient chemical vapor infiltration (TCVI) process at 950–1150 °C for 110 h using methane as a carbon source. After the final step of graphitizing at 2200–2500 °C for 2 h in a flowing Ar atmosphere, ceramic-modified C/C composites and pure C/C composites were fabricated. The total mass percentage of Z–SiC particles in C/C–Z–SiC (1.87 g/cm^3) was about 10.0% (ratio of $m_{ceramic}$ and the final mass of relative composites) while the mass ratio (Z:SiC) was 3:2. Moreover, the mass percentage of Z in C/C–Z (1.89 g/cm^3) was about 6.1% which is the same as that of Z in C/C–Z–SiC.

Disk samples (∅30 mm × 10 mm) were cut from the prepared composites and lightly abraded with 80 and 400 grit SiC paper before ablation test.

2.2. Ablation test and characterization

The ablation test was carried out under oxyacetylene torch with a heat flux of $2.38 \pm 10\%$ MW/m^2 according to Tang et al. [1] for different times. The inner diameter of the oxyacetylene gun tip was 2 mm and the distance from the gun tip to the sample was 10 mm. The ablation angle was 90°. Other parameters about the O_2 and C_2H_2 were displayed in Table 1.

Table 1
Parameters of O_2 and C_2H_2 for the ablation test.

	Pressure (MPa)	Flux (L/s)
O_2	0.4	0.24
C_2H_2	0.095	0.18

The linear and mass ablation rates were calculated according to Eqs. (2) and (3). The ultimate data was the average of three samples.

$$R_l = \frac{\Delta d}{t} \quad (2)$$

$$R_m = \frac{\Delta m}{t} \quad (3)$$

R_l is the linear ablation rate; Δd is the change of the sample's thickness at central region before and after ablation; R_m is the mass ablation rate; Δm is the sample's mass change before and after ablation; and t is the ablation time.

The surface temperature was measured by an infrared thermometer (Raytek MR1SCSF) in 2-color mode with an error of $\pm 0.75\%$.

The phase analysis of prepared composites before and after ablation was conducted by X-ray diffraction (XRD, X'Pert Pro MPD). Morphologies and chemical compositions of the prepared and ablated composites were investigated by scanning electron microscopy (SEM, JSM6460) combined with energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure and ablation property

Fig. 1 shows the cross-section morphology of the prepared samples and the corresponding EDS analysis. It is shown that the doped ceramic particles are embedded in the carbon matrix in the high magnified SEM (left inferior corner of Fig. 1(b)) where the white phase is Z, the gray phase is SiC and the black phase is carbon (C). These results were also confirmed by EDS analysis. In the lower magnification SEM images, we can find that the fine ceramic particles are distributed uniformly in the cross-section of both composites. The uniform micro-structure would contribute to the persistent anti-ablation property which is helpful to predict the lifespan of component in practical application. The EDS mapping analysis elucidates the element constitution of the two composites: C/C–Z consists of C and Zr while C/C–Z–SiC is comprised of C, Si and Zr. No other impurities were detected. The absence of B in the mapping analysis is attributed to the inherent characteristic of light element.

Fig. 2 shows the ablation rates of different composites versus ablation time. It is easy to find that the modified C/C