



Fabrication and ablation property of carbon/carbon composites with novel SiC–ZrB₂ coating

Dong HUANG, Ming-yu ZHANG, Qi-zhong HUANG, Li-ping WANG, Xian TANG, Xin YANG, Kai TONG

State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

Received 9 December 2014; accepted 24 March 2015

Abstract: A novel SiC–ZrB₂ coating was prepared using a two-step technique by slurry-sintering and chemical vapor reaction on carbon/carbon (C/C) composites. The SiC–ZrB₂ coating was composed of the scattered ZrB₂ phase and the continuous SiC phase. It was observed that a good adhesion was built between the coating and the C/C composites. The SiC–ZrB₂ coating samples exhibited a better ablation resistance in comparison with the uncoated C/C composites. The SiO₂–ZrO₂ barrier layer, the heat dissipation of the gaseous products and the pinning effect of ZrO₂ all contributed to the good ablation resistance of the SiC–ZrB₂ coated composites.

Key words: ablation; coating; microstructure; carbon/carbon composites

1 Introduction

C/C composites have attracted much attention due to their low coefficient of thermal expansion (CTE), good strength at high temperature, high thermal conductivity, and good ablation resistance and thermal shock resistance [1–3]. These excellent properties make C/C composites the promising structural materials used in high temperature environment such as nose tips, leading edges, nozzles of solid rocket motor and other thermal protection systems (TPS) for space vehicles [4,5]. However, poor oxidation resistance (above 773 K) and severe ablation environments (high-pressure gas and high velocity grains) have greatly restricted their high temperature application [6,7]. Therefore, improving ablation resistance at ultrahigh temperature (>2273 K) is crucial to extend applications of C/C composites.

Surface coating technology is one of the effective ways to protect C/C composites from oxidation and ablation at high temperature [8–11]. SiC coatings have attracted extensive attention because of their ability to generate dense SiO₂ layer and lower coefficient of thermal expansion (CTE) mismatch than other ceramic materials [12–14]. However, the molten SiO₂ glass (melting point 1943 K) due to the oxidation of the SiC is

easy to be peeled off by the high velocity gas during ablation because of its low viscosity at an ultra-high temperature (>2273 K), which possibly resulted in the poor ablation resistance of the SiC coating. It has been reported that introducing both SiC and Zr-based ceramics at the same time can further improve the ablation resistance and oxidation resistance of the composites under ultra-high temperature environments (>2273 K) because of the formation of less volatile silica-containing scales [15–21]. So, the introduction of ZrB₂ into SiC coating is considered as a promising method to provide ablation protection for C/C composites at ultra-high temperature.

In the present work, a novel SiC–ZrB₂ coating for C/C composite was reported, using a two-step technique which combines slurry-sintering with chemical vapor reaction (CVR). The introduction of ZrB₂ particles was easy and low cost, and the obtained SiC–ZrB₂ coating samples showed a good ablation resistance. The microstructural characteristics and ablation property of the ZrB₂–SiC coatings were investigated and the ablation mechanisms were discussed.

2 Experimental

Before coating, the C/C composites (homemade

Foundation item: Projects (51404041, 51304249) supported by the National Natural Science Foundation of China; Project (2015JJ3016) supported by the Natural Science Foundation of Hunan Province, China; Project (2011CB605801) supported by the National Basic Research Program of China; Project supported by the State Key Laboratory for Powder Metallurgy Foundation, Central South University, Changsha, China.

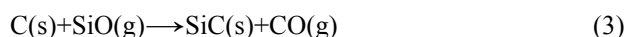
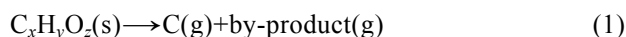
Corresponding author: Ming-yu ZHANG; Tel: +86-731-88877671; Fax: +86-731-88836078; E-mail: csuzmy@csu.edu.cn

DOI: 10.1016/S1003-6326(15)64012-2

from the 2D needled carbon fiber preform, Center South University, China, density 1.73 g/cm^3) were cut into bulks with dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$. After being ground with 800 grit SiC papers, the samples were ultrasonically cleaned and dried at 373 K for 1 h.

Firstly, the ZrB_2 -resin carbon was prepared from powder of ZrB_2 ($15 \text{ }\mu\text{m}$, purity $>99.1\%$, Aladdin Co., Ltd., Shanghai, China) and phenolic resin solution. The phenolic resin powders were dissolved in ethyl alcohol with a ratio of 20 g per 100 mL and used as phenolic resin solution. The ZrB_2 powders were added into the dissolved phenolic resin solution to make the slurry. The mass ratio of ZrB_2 to resin was 1:2. The slurry was brushed directly on the surface of the C/C composites. The samples were dried at 423 K and then carbonized at 1173 K for 2 h in N_2 atmosphere. The thickness of the ZrB_2 -resin carbon layer was 30–40 μm by 2–3 times of brushing according to Eq. (1). The mass fractions of SiC and ZrB_2 in the coating were 71.52% and 18.48%, respectively.

Secondly, the outer SiC coating was prepared by CVR. The SiO generator was produced using SiO_2/Si mixture at 1773–2123 K (Eq. (2)). The CVR SiC was produced during the reaction of SiO with the substrate at 2373–2573 K (Eq. (3)) [8,21].



The ablation resistance of the SiC- ZrB_2 coating for C/C composites was tested using a plasma generator (Multiplaz, 3500) with cylindrical samples ($d30 \text{ mm} \times 10 \text{ mm}$, Fig. 1(a)) [15]. The erosion direction of the flame and the axial orientation of the samples were parallel to the Z direction of the carbon felts (needled direction, Fig. 1(b)). The working current and voltage of the plasma generator were 6 A and $(160 \pm 1) \text{ V}$,

respectively. The inner diameter of the plasma gun tip was 2 mm, and the distance between the gun tip and the sample was about 10 mm. The samples were exposed to the flame, and the maximum temperature of the ablation center reached as high as 2573 K, as confirmed by an optical pyrometer. Both linear and mass ablation rates were calculated based on the thickness and mass changes before and after the ablation. More than five tests were made for each sample, and the presented results were the averages of these ablation rates.

The microstructural characterization was carried out using scanning electron microscopy (SEM, FEI Nova Nano SEM230), backscattered electron images (BSE, FEI Nova Nano SEM230), energy dispersive spectrometer (EDS, FEI Nova Nano SEM230) and X-ray diffraction (XRD, Rigaku Dmax/2550VB+18 kW).

3 Results and discussion

3.1 Microstructure of SiC- ZrB_2 coating

Figure 2 shows the images of the C/C samples with SiC- ZrB_2 coating after brushing and carbonization. The ZrB_2 -resin carbon covers the surface of the samples completely, and no holes are observed (Fig. 2(a)). Figure 2(b) indicates that ZrB_2 particles (white phase) are dispersed uniformly in the resin carbon (gray black phase). The average grain size of ZrB_2 is in the region of 10–20 μm micrometers (Fig. 2(c)). It is observed that the ZrB_2 particles are combined strongly with resin carbon after the carbonization. Figure 2(d) shows the BSE image of the cross section of the ZrB_2 -resin carbon. There is no lamination in the ZrB_2 -resin carbon layer after brushing several times. The thickness of the ZrB_2 -resin carbon layer is 20–30 μm .

Figure 3(a) shows the SEM image of the surface of the SiC- ZrB_2 coatings after CVR. It can be seen that ceramic grains are coarse, and appear to be rubble-like

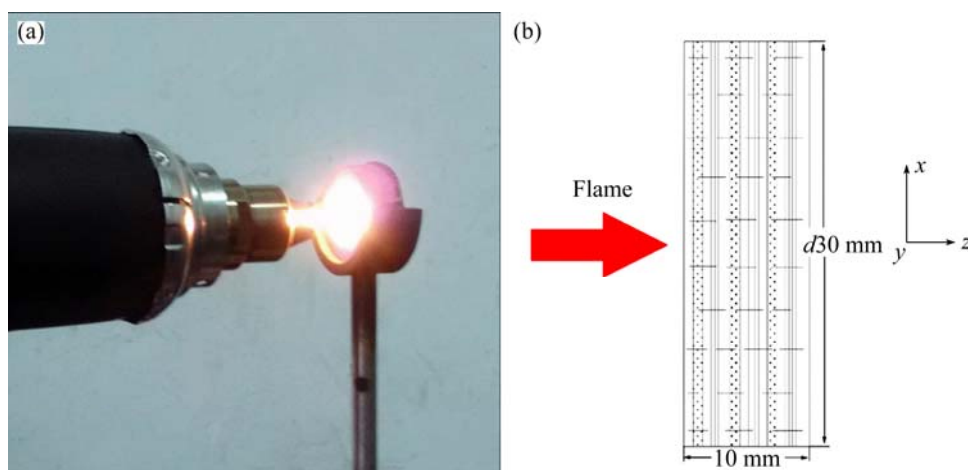


Fig. 1 Images of ablation test: (a) Plasma torch; (b) Ablated direction

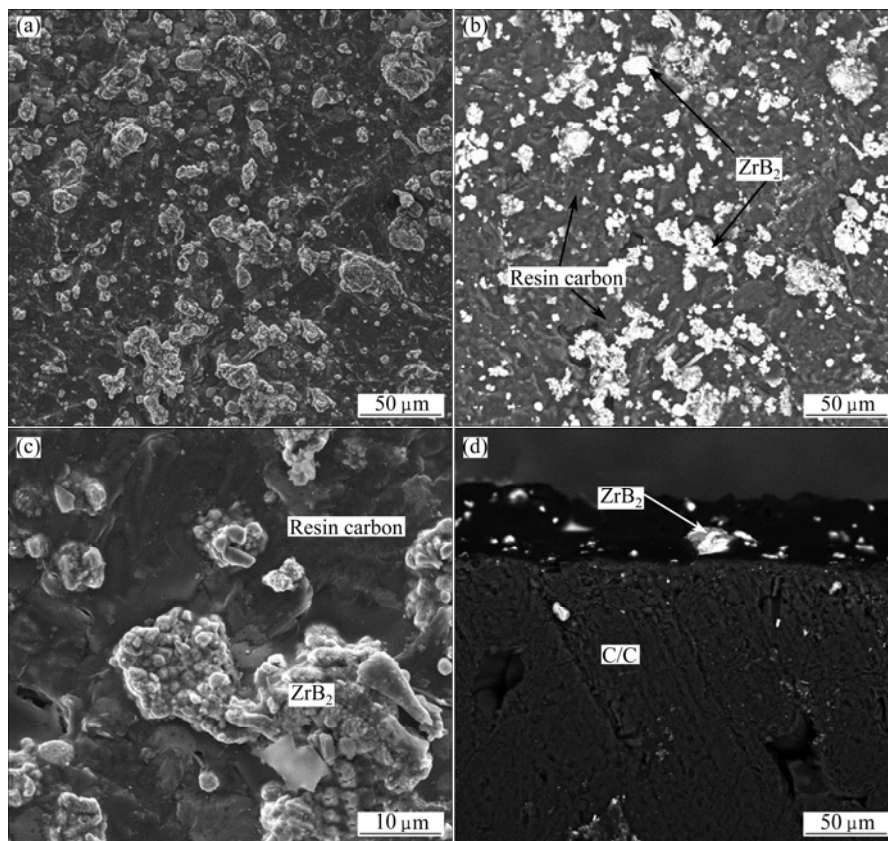


Fig. 2 SEM images and BSE images of samples after brushing and carbonization: (a) Low magnification SEM image of surface; (b) Low magnification BSE image of surface; (c) High magnification SEM image of surface; (d) BSE image of cross section

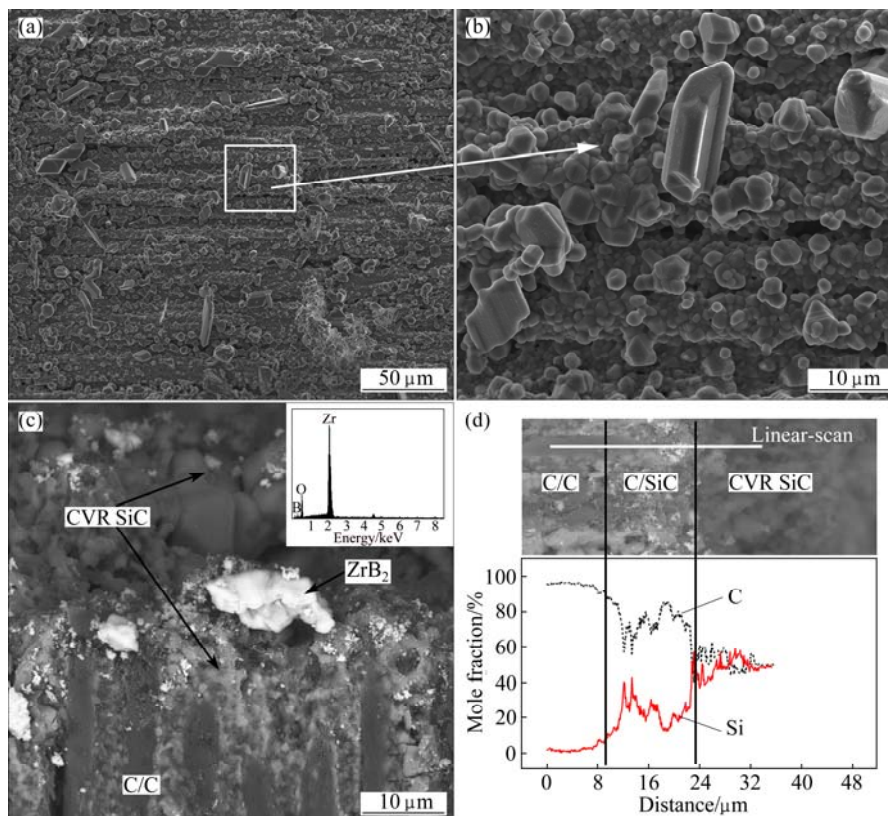


Fig. 3 Microstructures of SiC–ZrB₂ coatings after CVR: (a) Low magnification SEM image; (b) High magnification SEM image of area framed by white line in Fig. 3(a); (c) BSE image and EDS pattern of cross section; (d) Linear scan analysis of cross section

on the surface of the coating. The XRD pattern (Fig. 4) shows that three obvious characteristic peaks at 35.7° , 60.1° and 71.8° , are corresponding to the diffraction of (111), (220) and (311) crystalline planes of a FCC lattice, respectively, which are in good agreement with the known results for β -SiC. No peaks of ZrB_2 or C phase are observed, indicating that the sample surface is completely covered with the CVR SiC coating. Higher magnification image of the surface (Fig. 3(b)) shows that both large and small sizes of the SiC grains have been formed after CVR process. The small ones absorb the C/C composite directly, whereas the large ones are present on the surface of the small SiC grains. Figure 3(c) shows the BSE images of the cross section of the ZrB_2 -SiC coating. It can be seen that the SiC- ZrB_2 coating is mainly composed of the scattered ZrB_2 phase and the continuous SiC phase. The ZrB_2 phase (white part) is wrapped in the CVR layer (gray part) and confirmed by EDS analysis. It is known that the resin carbon around the ZrB_2 powder reacts with SiO to form SiC by the carbothermic reaction (Eq. (3)). It is believed that ZrB_2 powders and CVR SiC phase are bonded through mechanical bond and the intermolecular forces between them. Linear scan analysis (Fig. 3(d)) has shown that a C/SiC gradient layer can be formed between the carbon substrate and CVR SiC due to the permeation and reaction of SiO vapor in the carbothermic reaction [8,21]. As a result, a continuous change of the elastic modulus and the CTE of the coating occurs at the transitional interface, which makes the thermal stress release effectively and improves the bonding strength between the coatings and the substrates. It therefore can be concluded that a good adhesion can be built between the CVR SiC- ZrB_2 composite coating and C/C composites.

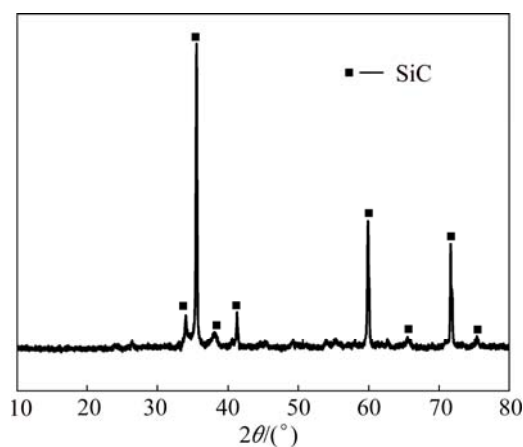


Fig. 4 XRD pattern of SiC- ZrB_2 coating

3.2 Ablation resistance of ZrB_2 -SiC coating

Figure 5 shows the macro-photographs of the C/C composites before and after coating. A compact and

gray-green ceramic coating is formed after CVR process. Some shiny grains on the surface of the coatings are proved to be the larger SiC grains according to Fig. 5(b).

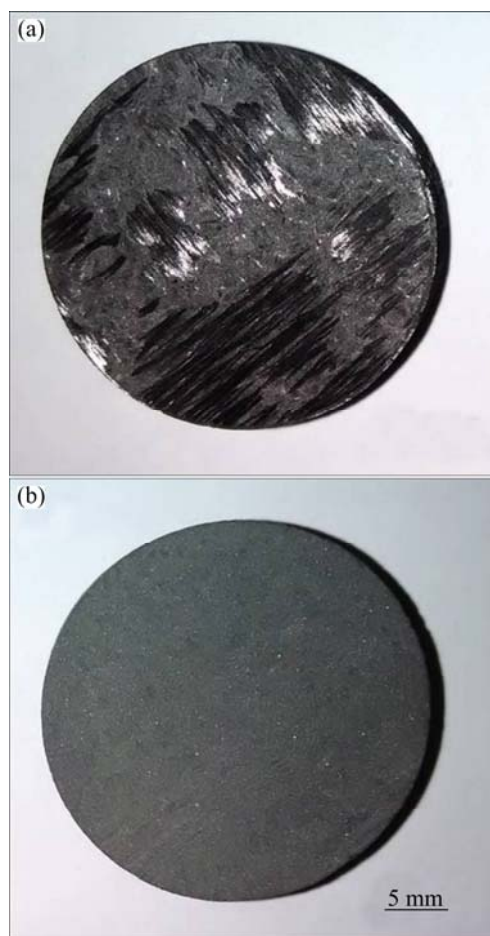


Fig. 5 Macro-photographs of C/C composites before (a) and after (b) coating

The photographs of the samples after ablation for 120 s and 240 s are shown in Fig. 6. The coating in the ablation center has been stripped off and the carbon fibers are ablated after ablation for 120 s. However, some ceramic oxides residues are observed on the surface, and the linear ablation is slight. The SiC- ZrB_2 coating samples show a better ablation resistance than uncoated C/C composite after 120 s ablation test (Table 1). The mass and linear ablation rates of the coated samples are 0.83 mg/s and $2.37 \mu\text{m/s}$, respectively. And those of uncoated samples are 2.23 mg/s and $15.25 \mu\text{m/s}$, respectively. In addition, the coating has been destroyed completely after 240 s ablation, and a large ablated hole is present on the surface (Fig. 6(b)). The mass and linear ablation rates of the coating samples are close to those of the uncoated ones (Table 1).

Figure 7 shows the SEM images and EDS analysis of ablation center of coating samples after 120 s. Figure 7(a) indicates that the SiC- ZrB_2 coating has been stripped off in the ablation center. The SiC- ZrB_2 coating

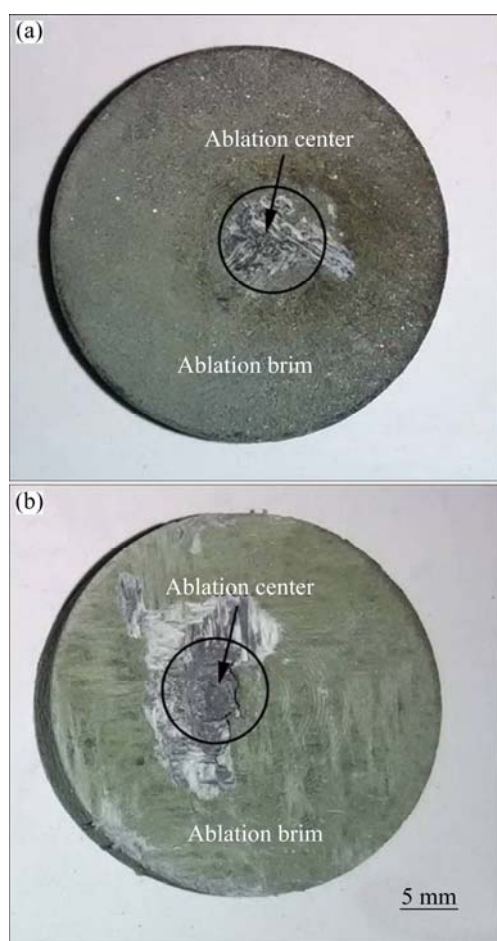


Fig. 6 Macro-photographs of SiC–ZrB₂ coating after ablation for 120 s (a) and 240 s (b)

Table 1 Ablation resistance of C/C composite before and after coating

Material	Mass ablation/ (mg·s ⁻¹)		Linear ablation/ (μm·s ⁻¹)	
	120 s	240 s	120 s	240 s
Uncoated C/C	2.23	2.35	15.25	15.31
SiC–ZrB ₂ coated C/C	0.83	1.79	2.37	11.37

is not destroyed in the ablation brim because the temperature and the combustion gas velocity in the ablation brim are much lower. Figure 7(b) shows the SEM images of the ablation center. Some carbon fibers have been seriously eroded, and appear to be needle-like. Others are damaged slightly under the protection of the ceramic residues. High magnification image (Fig. 7(c)) indicates that some glass layers are left on the surface of un-ablated carbon fibers. EDS analysis indicates that the residues are composed of ZrO₂ and SiO₂. It can be concluded that the ceramic residues play a positive role in the ablation resistance.

In order to further understand the ablation mechanism, the microstructures of coating after ablation

for 60 s and before being stripped off, have been investigated, the results are shown in Fig. 8. There are some cracks and holes on the surface, which could provide channels for the diffusion of O₂ into the composite (Fig. 8(a)). A shallow pit is present on the surface of the ablation center (Fig. 8(b)), because the high-speed combustion gas has blew away the molten ceramic oxides at the ultra-high temperature. High magnification image (Fig. 8(c)) shows that some molten ceramic oxides have been formed in the shallow pit, and EDS analysis indicates that the oxides are SiO₂ and ZrO₂ (Fig. 8(d)). XRD pattern (Fig. 9) indicates that the surface is covered with ZrO₂ and SiO₂ glassy layer from the oxidation of ZrB₂ and SiC, which also illustrates the statement mentioned above. No B₂O₃ (boiling point 1773 K) has been detected on the ablated surface, which indicates that B₂O₃ has been evaporated during ablation at ultra-high temperature (above 2573 K). The molten SiO₂ glass (melting point 1973 K) suffered from shearing forces resulted from the flame with high temperature, high velocity and pressure. However, the refractory ZrO₂ could prevent SiO₂ from peeling off and act as a pinning effect for the molten SiO₂ due to its high melting point (2953 K). The SiO₂–ZrO₂ layer acts as an effective barrier which can prevent oxygen from diffusing into the composite due to its low oxygen diffusivity.

3.3 Ablation mechanism

Based on the above analysis, we propose several processes which show the ablation mechanism of the SiC–ZrB₂ coatings (Fig. 10).

1) The SiC–ZrB₂ coating is rapidly oxidized to produce SiO₂, ZrO₂ and B₂O₃ according to Eq. (4) and Eq. (5). The SiC–ZrB₂ coating (in situ barrier) and its ceramic oxides layer (low oxygen diffusivity) act as an effective barrier which can prevent oxygen from diffusing into the composite due to its low oxygen diffusivity.

2) The fusion and evaporation of SiO₂ (melting point 1943 K) and B₂O₃ (melting point 723 K) will dissipate the heat, resulting in the temperature on the surface of composite decreasing.

3) The refractory ZrO₂ could have a pinning effect for the molten SiO₂ due to its high melting point (2953 K), which can prohibit the peeling or exfoliation of the molten SiO₂ during ablation. The refractory oxide scales formed may give the composites a capability to withstand the ultra-high temperature ablation.

As the ZrO₂–SiO₂ layer has been largely destroyed after ablation for 240 s, the ZrO₂ residues cannot act as an intact protective layer. As a result, the carbon fibers are ablated due to the oxidation (Eq. (7)) and scouring, and the ablation rate is increased compared with that for

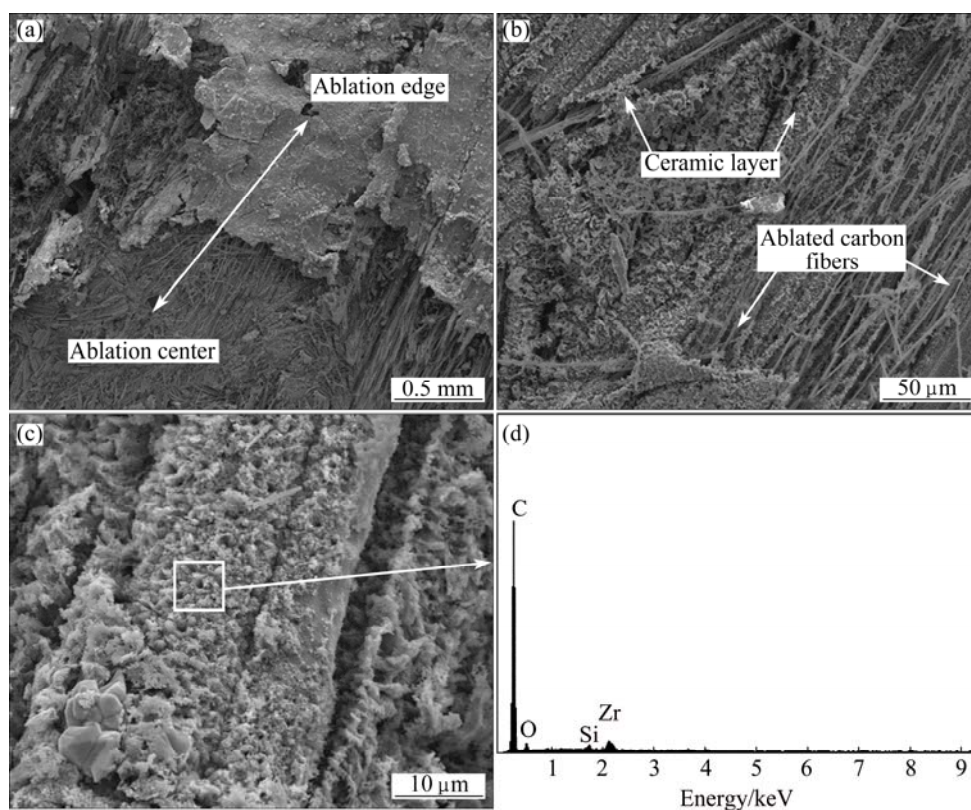


Fig. 7 Microstructures of SiC-ZrB₂ coating after ablation for 120 s: (a) Ablated surface between center and brim; (b) Low magnification SEM image of ablation center; (c) High magnification image of ablation center; (d) EDS pattern of ablation center

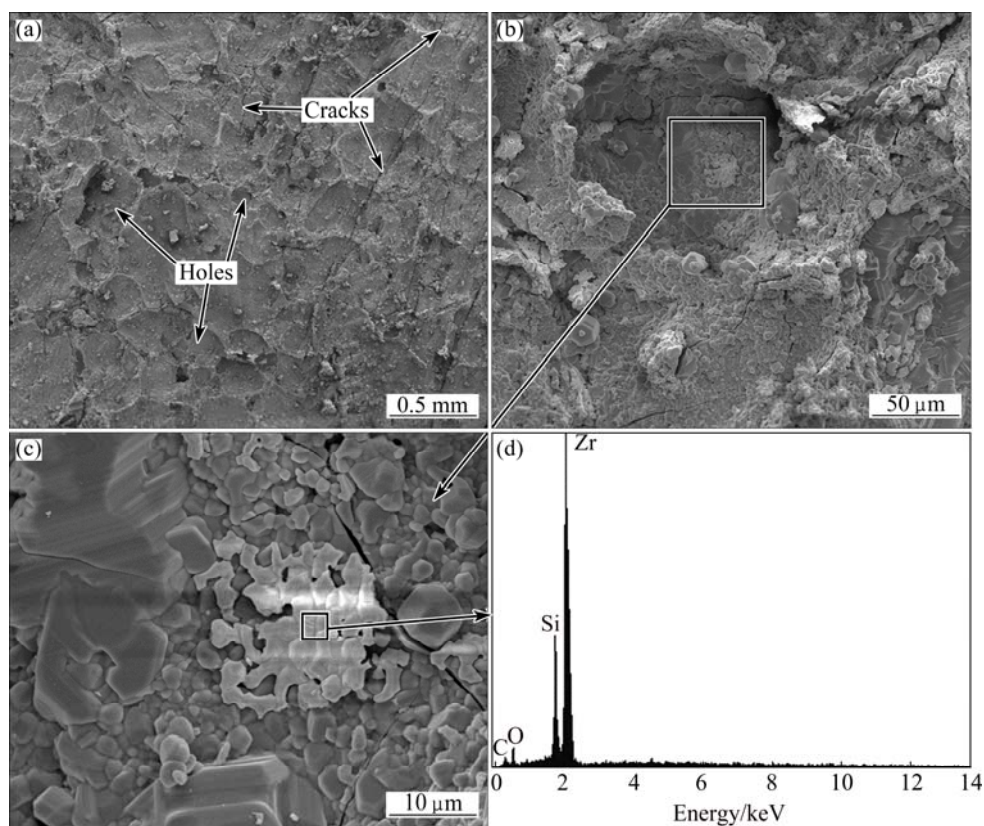


Fig. 8 Microstructures of SiC-ZrB₂ coating after ablation for 60 s: (a) Low magnification SEM image of surface; (b) Ablated hole; (c) High magnification image; (d) EDS pattern

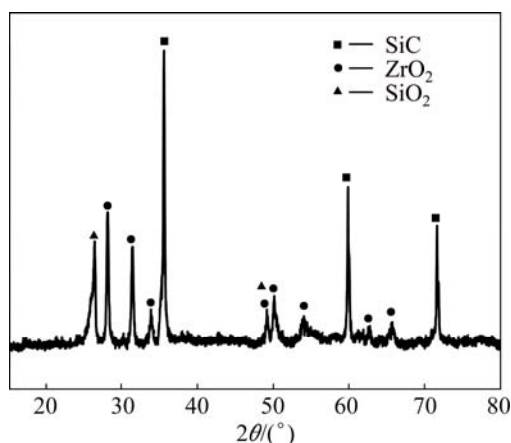


Fig. 9 XRD pattern of SiC-ZrB₂ coating after ablation for 60 s

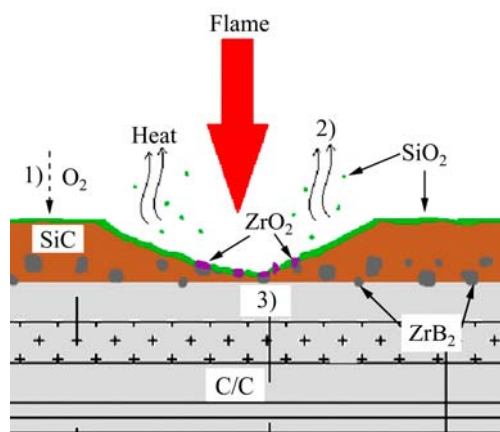
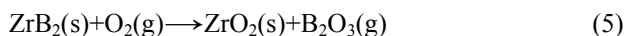


Fig. 10 Ablation mechanism of SiC-ZrB₂ coating

120 s (Table 1). And then SiC-ZrB₂ coating failed in protecting composites from corrosion (Fig. 6(b) and Table 1).



4 Conclusions

1) A novel SiC-ZrB₂ coating was fabricated on the C/C composites using slurry-sintering and chemical vapor reaction. The ZrB₂ phases were dispersed uniformly in the SiC-ZrB₂ coatings, and a good adhesion can be built between the coating and the C/C composite.

2) The plasma ablation test indicated that the coating samples possessed a good ablation resistance. The linear and mass ablation rates of the SiC-ZrB₂ coating samples are 0.83 mg/s and 2.37 μm/s after ablation for 120 s, respectively.

3) The good ablation resistance is attributed to the low oxygen diffusivity ZrO₂-SiO₂ barrier layer and a pinning effect of refractory ZrO₂ phase in the present work. As the ZrO₂-SiO₂ layer has been largely destroyed after ablation for 240 s, the SiC-ZrB₂ coating failed in protecting composites from corrosion.

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一种新型的 SiC–ZrB₂ 涂层包覆 C/C 复合材料的制备及烧蚀性能

黄 东, 张明瑜, 黄启忠, 王丽平, 汤 贤, 杨 鑫, 童 凯

中南大学 粉末冶金国家重点实验室, 长沙 410083

摘 要: 利用两步工艺结合泥浆烧结法和化学气相反应法在 C/C 复合材料表面制备了一种新型的 SiC–ZrB₂ 涂层。SiC–ZrB₂ 涂层由分散的 ZrB₂ 相和连续的 SiC 相组成, 涂层与 C/C 复合材料基体结合较好。与 C/C 复合材料相比, SiC–ZrB₂ 涂层包覆 C/C 复合材料试样具有更好的抗烧蚀性能。SiO₂–ZrO₂ 陶瓷层的阻氧作用、气态氧化产物的散热以及 ZrO₂ 的钉扎作用是涂层试样具有良好抗烧蚀性能的主要原因。

关键词: 烧蚀; 涂层; 显微结构; C/C 复合材料

(Edited by Yun-bin HE)