

Microstructure and Ablation Behavior of C/C Composites Doped with ZrB₂

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Abstract: ZrB₂ was first introduced into carbon preforms through ultrasonic and vacuum immersion-carbonthermal reduction method. After densification using thermal gradient chemical vapor infiltration and graphitization, ZrB₂ doped C/C composites were prepared. The oxyacetylene ablation results show that the linear and mass ablation rates of the composites after doping with 6.87wt% ZrB₂ decreased by 64.9% and 67.5%, respectively. The ablation of C/C composites is mainly controlled by thermochemical and thermophysical reactions and mechanical denudation does not play a dominant role. The evaporation of ZrO₂/B₂O₃ during ablation would take away large amounts of heat, reducing the thermal impact of flame to the ablation surface.

Key words: ablation; ZrB₂; C/C composites; ZrO₂

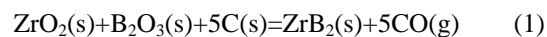
C/C composite is an alternative for ultra high-temperature structural applications due to its excellent properties^[1]. However, the ablation resistance of C/C composites is not good enough to meet the high demands in severe environments. In order to achieve better ablation properties at ultra high-temperature and high-pressure environment, various refractory metal compounds^[2] have been introduced into C/C composites, such as ZrC^[3], TaC^[4], HfC^[5], SiC^[6]. Recently, ZrB₂ has received much attention because of its outstanding properties such as high melting point ($\geq 3000^{\circ}\text{C}$) and good resistance to thermal shock^[7]. Meanwhile, the high melting point (2700°C) and low vapor pressure of its oxide (ZrO₂) may allow ZrO₂ to form a film on the matrix which can effectively slower the diffusion rate of oxygen^[8]. So the impregnation of ZrB₂ into C/C composites may be a good way to promote the ablation properties of C/C composites. In the present work, a novel ultrasonic and vacuum immersion-carbonthermal reduction method was developed to prepare ZrB₂ doped C/C composites. The effects of ZrB₂ on the ablation properties of C/C composites and the ablation mechanism were investigated.

1 Experimental

1.1 Preparation of ZrB₂ doped C/C composites

The needled carbon fiber felts (0.45 g/cm^3) with

$\phi 80\text{ mm} \times 10\text{ mm}$ were impregnated in prepared solution. The preparation process of the solution used for infiltration was as follows, according to carbonthermal reduction reaction (Eq. 1), a certain amount of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), boric acid (H_3BO_3) and phenolic resin as sources of zirconia, boron oxide, and carbon respectively, were dissolved in the requested amount of ethanol under constant stirring. Then the felts were put into the solution and vibrated in an ultrasonicator under the power of 40% for 0.5 h, followed by vacuum impregnation for nearly 0.5 h. Then the felts remained in the solution under normal atmospheric pressure for several hours. The impregnated felts were dried in air and then heated up to 1500°C in an electronic furnace, and held at this temperature for 2 h in an argon atmosphere to form ZrB₂ by Eq. 1. The samples were weighed before infiltration and after heat treatment to determine the mass of ZrB₂ in the felts.



The doped/undoped carbon felts were densified through thermal gradient chemical vapor infiltration (TCVI) process using methane gas as the carbon precursor^[9], followed by graphitization at 2500°C for 2 h. The content of ZrB₂ was calculated by the mass ratio of ZrB₂ and C/C composites. The prepared samples were labeled ZW- x in which x indicates the content of ZrB₂(wt%) in C/C composites.

1.2 Ablation testing and microstructure analysis

The ablation testing was carried out in an oxyacetylene

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flame with plate specimens ($\phi 30\text{mm} \times 10\text{mm}$), the plane of which was perpendicular to the flame. The flame was measured to be around 3000°C by an optical pyrometer and specimens were exposed to the flame for 30 s. To estimate the ablation properties of samples, the linear/mass ablation rates were calculated by thickness/mass change before and after ablation test. Phase and morphology of the composites were investigated by X-ray diffraction (XRD, χ' Pert Pro MPD), scanning electron microscope (SEM, SUPRA-55) combined with an energy dispersive spectroscopy (EDS).

2 Results and discussion

2.1 Ablation properties and microstructure characterization

The ablation properties of the samples are shown in Table 1. The linear and mass ablation rates of pure C/C composites were $12.33 \mu\text{m/s}$ and 5.35 mg/s , respectively. It can be found that both ablation rates decrease with the increase of ZrB_2 contents. After adding 6.87wt% ZrB_2 , the linear and mass ablation rates of C/C composites are $4.33 \mu\text{m/s}$ and 1.74 mg/s , respectively. The linear and mass ablation rates of ZW-6.87 are decreased by 64.9% and 67.5%, respectively.

Figure 1 shows XRD patterns of ZrB_2 doped C/C composites before and after ablation. The samples were mainly composed of ZrB_2 and carbon before ablation. ZrB_2 particles (the white phase) distributed uniformly in the matrix, and no reunion can be observed over the entire section of

the sample (Fig. 2). Combined with EDS analysis (Fig. 3(d)), the composites consist of C, ZrB_2 and ZrO_2 after and no reunion can be observed over the entire section of the sample (Fig. 2). Combined with EDS analysis (Fig. 3(d)), the composites consist of C, ZrB_2 and ZrO_2 after ablation. ZrO_2 comes from the oxidation of ZrB_2 . The XRD pattern after ablation does not show the peak of other oxidation product, because B_2O_3 would volatilize completely in the high temperature due to its low boiling point (1500°C).

2.2 Ablation morphology and behavior analysis

Figure 3 shows the SEM images of ablative surface of C/C composites ablated for 30 s, in which fibers are perpendicular to the flame direction. The white particles scattered on the ablative surface of doped composites are ZrO_2 according to XRD (Fig. 1) and EDS (Fig. 3(d)) analysis. Meanwhile, the amount of white particles increases with the growth of ZrB_2 contents in samples. Carbon fibers and matrix of all the specimens are eroded after ablation, which separate the carbon fibers and matrix and lead to the gap between fiber bundles. The fibers become thinner and were ablated into sharp needle shapes due to the oxidation^[10]. Because of the susceptibility of the fiber-matrix interface to ablation, the ablation would extend along it, and fibers and matrix become thinner. Then the gap between carbon fibers and matrix is formed. Some fractured fibers can also be observed among needle-shaped fibers on the ablative surface, which is caused by the mechanical shearing force of the ablation flame. The fibers of the samples with ZrB_2 contents below 3.42wt% have a smooth surface (Fig. 3(a)–(c)), whereas the surface of fibers of sample ZW-6.87 (Fig. 3(d)) is relatively coarse. Pits clearly appear on the surface according to the high magnification SEM image (Fig. 3(f)) and white ZrO_2 particles can be observed on the top of the pits. Moreover, there are some fiber fragments on the ablative surface of sample ZW-6.87 (Fig. 3(d)), which suggests that fibers of sample ZW-6.87 are easier to fracture.

Table 1 The ablation rates of doped C/C and pure C/C composites

Samples	Linear ablation rate/ $(\mu\text{m}\cdot\text{s}^{-1})$	Mass ablation rate/ $(\text{mg}\cdot\text{s}^{-1})$
ZW-0	12.33	5.35
ZW-1.41	10.67	4.68
ZW-3.42	7.12	3.04
ZW-6.87	4.33	1.74

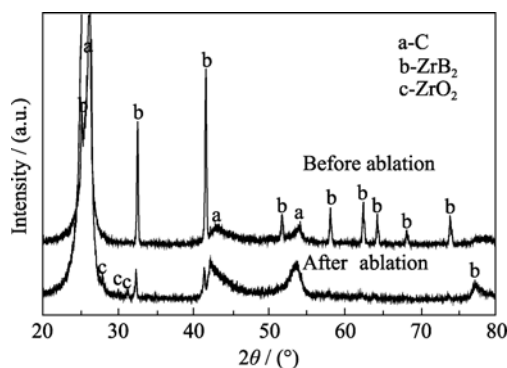


Fig. 1 XRD patterns of ZrB_2 doped C/C composites before and after ablation

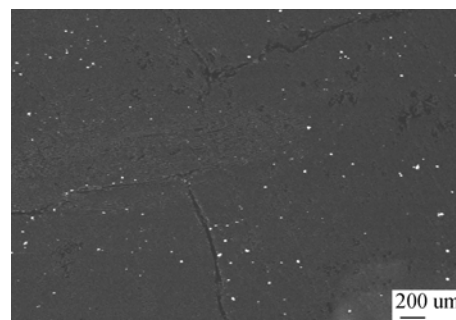


Fig. 2 Backscattered electron image of the cross section of ZrB_2 doped C/C composites before ablation

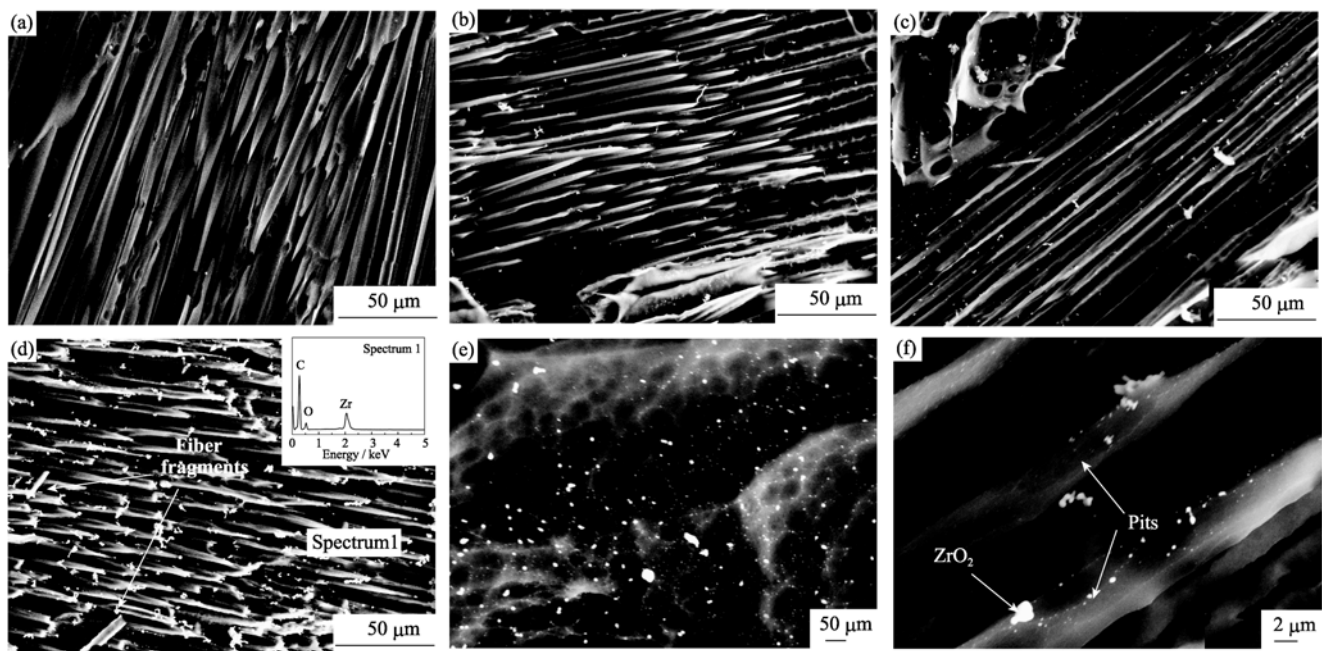
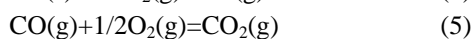
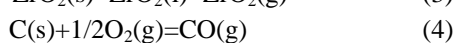
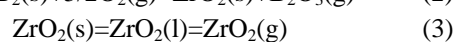
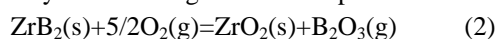


Fig. 3 SEM images of the ablative surface of the samples ablated for 30 s and EDS pattern of ZrB₂ doped C/C composites after ablation (a) Pure C/C composite; (b) ZW-1.41; (c) ZW-3.42; (d) ZW-6.87 and EDS pattern corresponding to spot 1; (e) High resolution SEM image of the carbon matrix of ZW-6.87; (f) High resolution SEM image of fibers of ZW-6.87

There is a big difference between the ablation morphologies of carbon matrix of pure and doped C/C composites. The matrix of pure C/C composite is composed of pure pyrocarbon and the ablated surface is smooth. On the other hand, the matrix of doped composite consists of pyrocarbon and ZrB₂, and the ablated surface becomes rough. Figure 3(e) shows the high resolution SEM image of the carbon matrix of ZW-6.87. It is clear that the ablated surface shows honeycombed structure and there are a lot of ZrO₂ particles on the top of it, indicating that ZrO₂ has better resistance to ablation than pyrocarbon in the oxyacetylene flame. It may also be inferred that the ablation properties of pyrocarbon and ZrB₂ are different. And the difference leads to various degrees of erosion and the formation of such a honeycombed structure.

Ablation is an erosive phenomenon accompanied with a removal of parts of the materials by combined thermomechanical, thermochemical, and thermophysical factors due to high temperature, pressure and velocity of the hot gases of combustion flame^[11-13]. According to XRD patterns (Fig. 2) and the ablation morphology analysis, the following reactions may occur during the ablation process:



ZrB₂ consumes part of the oxygen in ablative environment according to Eq. 2 to weaken the oxidation of carbon

fiber and matrix during ablation. The melting point of ZrO₂ is lower than the flame temperature. So the evaporation of oxidation products ZrO₂/B₂O₃ (Eq. 2 and Eq. 3) would absorb lots of heat from oxyacetylene flame and reduce the thermal erosion to ablation surface, which is conducive to reducing the ablation rate and improving the resistance to ablation. It can be concluded that higher contents of ZrB₂ will enhance the positive effects during ablation. It is convincible that the contents of ZrB₂ play a dominant role in determining the ablation properties of C/C composites.

A larger number of ZrO₂ grains are found on the top of the pits on the surface of matrix and fibers (Fig. 3(e) and 3(f)), which suggests that the addition of ZrO₂ improves the ablation resistance of C/C composites. It can be inferred that ZrO₂ has better resistance to ablation than pyrocarbon in oxyacetylene flame. The formation of ZrO₂ from the oxidation of ZrB₂ increases the ablation resistance of the carbon matrix, and therefore improves the ablation performances of the composites. However, the formation of pits would damage the fibers. Therefore the fibers are less resistant to the mechanical denudation of ablation flame, which would reduce the anti-ablation properties of the composites. But the samples with higher ZrB₂ contents have lower ablation rates according to Table 1. This suggests that ablation is dominated by thermochemical and thermophysical reactions instead of mechanical denudation.

3 Conclusions

ZrB₂ doped C/C composites were prepared via subsequent procedures: ultrasonic and vacuum immersion of carbon performs in prepared solution, heat treatment, densification through thermal gradient chemical vapor infiltration (TCVI) and graphitization. The linear and mass ablation rates of C/C composites are decreased by 64.9% and 67.5%, respectively after adding 6.87wt% ZrB₂. The ablated surface of carbon matrix of pure C/C composites was very smooth, while that became extremely rough after ZrB₂ was doped. Carbon fibers are ablated into needled shapes and pits are formed on the fibers after adding ZrB₂, which leads to the increase in mechanical denudation rate of the composites. However, the ablation of the C/C composite is dominated by thermochemical and thermophysical reactions instead of mechanical denudation. Moreover, the evaporation of oxidization products ZrO₂/B₂O₃ absorbs lots of heat from oxyacetylene flame to reduce the thermal impact and slower the ablation rate of the composites.

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ZrB₂ 改性 C/C 复合材料微观结构及烧蚀性能的研究

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摘要: 采用超声波真空浸渍-碳热还原法将 ZrB₂ 引入碳纤维预置体, 结合热梯度化学气相渗透、高温石墨化工艺制备了 ZrB₂ 改性 C/C 复合材料. 氧-乙炔烧蚀测试结果表明, 添加了 6.87 wt% ZrB₂ 后, C/C 复合材料的线烧蚀率和质量烧蚀率分别下降了 64.9% 和 67.5%. 分析表明, C/C 复合材料的烧蚀主要是由热化学和热物理反应控制, 机械剥蚀在烧蚀过程中仅起到次要作用. 烧蚀产物 ZrO₂/B₂O₃ 在烧蚀过程中的挥发会带走大量的热, 从而减少了烧蚀火焰对烧蚀表面的热冲击.

关键词: 烧蚀; ZrB₂; C/C 复合材料; ZrO₂

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