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Oxidation analysis of 2D C/ZrC–SiC composites with different coating structures in CH_4 combustion gas environment

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Abstract

2D C/ZrC–SiC composites were fabricated by chemical vapor infiltration combined with polymer slurry infiltration and pyrolysis. Liquid highly branched polycarbosilane was used as the pre-ceramic precursor. In order to improve the oxidation resistance, three kinds of coating structures were prepared on C/ZrC–SiC composites: pure zirconium carbide coating, SiC–ZrC coating, and ZrB_2–SiC coating. Structural evolutions of the as-produced composites after oxidation in CH_4 combustion gas atmosphere at about 1800 °C were investigated and compared. Based on a model of the oxidation process, the mixture ZrB_2–CVD SiC showed the best oxidation resistance.

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Keywords: A. Precursors: organic; B. Composites; B. Surfaces; Oxidation mechanism

1. Introduction

Carbon fiber reinforced silicon carbide composites (C/SiC) are one of the most promising structural materials for high temperature applications [1,2]. C/SiC composites have a high thermal stability and are usually considered useful up to 1650 °C. However, they have a low durability except in inert atmospheres. At higher temperatures (>1700 °C), the oxidation of the fiber, interphase and matrix cooperatively influence the oxidation behavior of C/SiC composites in oxygen atmosphere [3,4]. Thus, reducing oxidation at high temperature in oxygen environment is the challenge to extend application of C/SiC composites. As a rule this problem is usually resolved by applying oxidation-resistant coatings.

Because the oxidation of SiC is passive up to 1650 °C and the formed SiO_2 film has a low oxygen diffusion coefficient, SiC is the fundamental coating material for high temperature oxidation protection of structural composites [5]. SiC coating prepared by chemical vapor deposition (CVD) shows different oxidation behavior in various environments, such as air and combustion atmosphere [6–8]. But at $T > 1800$ °C, the oxide film is a poor barrier to oxygen diffusion because of the high evaporation rates of silicon oxide and the deterioration of the oxide film.

Researchers have been looking for new solutions to provide oxidation/ablation protection for C/SiC composites at ultra-high temperatures [9]. Zirconium and its composites have exceptional properties. Especially, zirconium carbide (ZrC) and zirconium boride (ZrB_2) have attracted much attention. They have melting points over 3000 °C, relatively low densities, and the abilities to form refractory oxide zirconia scales (melting point 2770 °C) [10]. However, these oxide coating are porous and do not provide oxidation protection. Thus, the poor oxidation resistance of ZrB_2 and ZrC makes them seldom to be used alone. The addition of SiC has been shown to effectively improve the oxidation resistance of ZrB_2 [11,12].

In the present paper, 2D C/ZrC–SiC composites were prepared by chemical vapor infiltration and polymer slurry infiltration with a high-branched polycarbosilane (HBPCS) as the pre-ceramic precursor. Three kinds of coating structures have been applied on the composites surface, i.e. (i) mixture of SiC with CVD ZrC, (ii) mixture of ZrB_2 with CVD SiC, and (iii) pure ZrC coating for comparison. Microstructure changes after oxidation in CH_4 combustion gas environment at about 1800 °C were investigated and compared. The erosion mechanism of different coating structures was discussed based on the oxidation results.

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2. Experimental procedure

2.1. Fabrication of 2D C/ZrC–SiC composites

The whole process for sample preparation is shown in Fig. 1. T-300^{TM} carbon fiber (Toray, Japan) was employed to fabricate fiber preforms. The preform with fiber content of 40 vol% was shaped by lamination of 2D-carbon cloth. A thin pyrolytic carbon layer was deposited on surface of the carbon fiber as the interfacial layer by chemical vapor infiltration (CVI) with C_3H_6 at 960 °C. The sample was then pretreated for graphitization at 1800 °C for 2 h. The C/SiC composite was prepared by chemical vapor infiltration of SiC at 1000 °C of the prepared preform. Methyltrichlorosilane (MTS, CH_3SiCl_3) was used for the SiC precursor. After CVI, the composites were machined and polished to obtain 40 mm × 20 mm × 3.5 mm substrates.

The liquid highly branched polycarbosilane with allyl groups was synthesized in the Advanced Materials Laboratory at Xiamen University [13,14]. 20 wt% ZrC powder with an average grain size of 1 μm (Beijing Mountain Technical Development Center, China) was mixed into HBPCS by magnetic stirring. The slurry was vacuum infiltrated into the substrates and pyrolysized at 900 °C for two cycles to realize further densification.

2.2. Coating systems preparation

ZrB_2/ZrC/SiC coatings were used in order to increase the oxidation resistance. The first kind of coating structure (#1) was prepared as follows: two more cycles of polymer slurry infiltration and pyrolysis (PIP) process were conducted on the composite. Subsequently, a heat-treatment in flowing argon at 1400 °C for 2 h was carried out in order to stabilize the composite matrix. Finally, a ZrC layer was deposited on the surface of this specimen by chemical vapor deposition. As for the CVD ZrC process, $ZrCl_4$, CH_4, and H_2 were used as precursors. The deposition temperature was controlled in the 1300–1400 °C range [15].

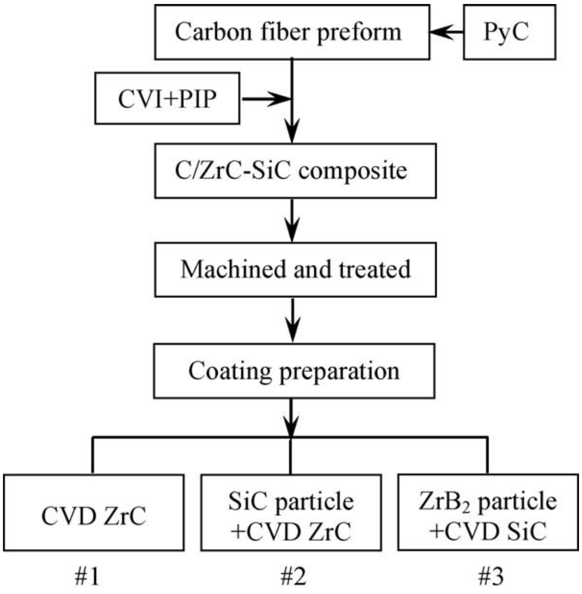

Fig. 1. Experimental procedure for preparation of C/ZrC–SiC composites with different coating structures.

For the preparation of the other two kinds of coating structures, the same heat-treatment on the composites at 1400 °C for 2 h was firstly conducted. A SiC powder (1 μm, Beijing Mountain Technical Development Center, China) layer was then pasted on the composite, followed by depositing a ZrC coating (#2). In this process, CVD ZrC will penetrate in the gaps between SiC powders and form a mixture of SiC–ZrC coating with a layer of dense ZrC on the top. Likewise, ZrB_2 powder (1 μm, Beijing Mountain Technical Development Center, China) was pasted on the composite followed by depositing a SiC layer on its top (#3).

2.3. Oxidation tests

The oxidation tests were carried out in a CH_4 combustion wind tunnel (Fig. 2). The wind tunnel possesses a controlled environment chamber [16] providing various kinds and concentrations of oxidizing gas. For each kind of coating structure, the oxidation test was repeated at least three times. During the test, the specimen was vertically exposed to the flame for 30 min. A mixture of O_2 and CH_4 was charged into the combustion chamber and spark ignited. The gas-flow velocity was about 20 m/s. The flame temperature at the center was 1800 ± 30 °C, which was stabilized by controlling the flux of each component gas (mass flow controller was 5850i series of BROOKS, Japan). The calculated combustion gas composition is listed in Table 1.

2.4. Measurement and characterization

Microstructures of the specimens were observed by scanning electron microscope (SEM, JSM-6700F) and the elemental analysis was conducted by energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) investigations were carried out by using a Rigaku D/max-2400 diffractometer (Tokyo, Japan) with copper Kα radiation. Data were digitally recorded in a continuous scan in the range of angle (2θ) from 15° to 75° with a scanning rate of 0.08°/s.

3. Results and discussion

3.1. Microstructure of the 2D C/ZrC–SiC composite

Fig. 3 shows the cross-sections of as-produced C/ZrC–SiC composite. Between fibers and the ZrC–SiC matrix, SiC matrix

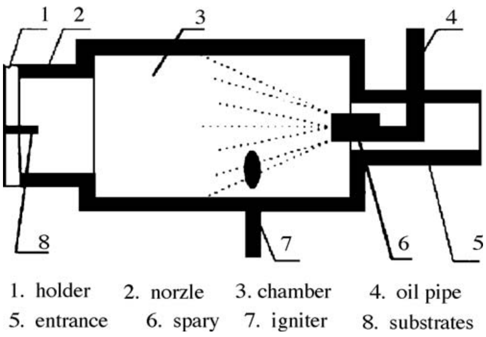

Fig. 2. Schematic of the combustion wind tunnel.

Table 1
Combustion gas composition.

	Components			
	O_2	H_2O	CO_2	Other
mol.%	16.1	55.3	27.6	1.0

which was formed by CVD process is obviously observed (Fig. 3b). Furthermore, it can be seen that there are still few pores in the composite (Fig. 3a). During the PIP process, the liquid PCS will fill surrounding both the CVD SiC matrix and the ZrC particles. After pyrolysis, the derived SiC integrates ZrC particles in the composites (Fig. 3b). ZrC slurry prefers to fill large pores between the fiber bundles. Hence, the channels from the surface to the inner of composite can be easily blocked by ZrC and pyrolysized SiC. Further infiltration of the slurry thus becomes much difficult after several PIP cycles. The density measured by the Archimedes method for the final composite is about 2.34 g/cm^3 with an open porosity of about 12%.

3.2. Microstructure of coatings

The cross-sections of different coating structures are shown in Fig. 4. ZrC coating with a thickness of about 8 μm is

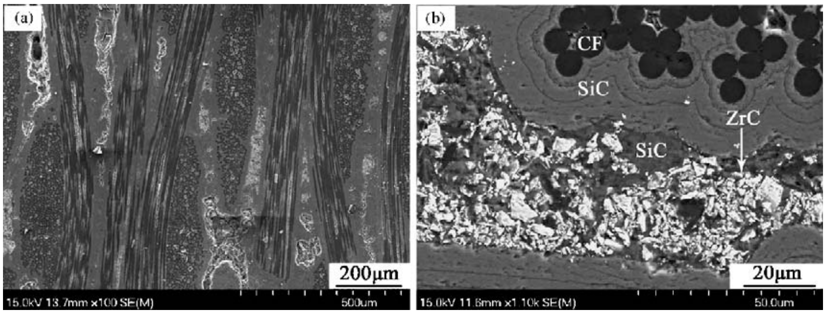

Fig. 3. Cross-sections of as-received C/ZrC–SiC composites. CF: carbon fiber, (a) a low magnification and (b) a high magnification.

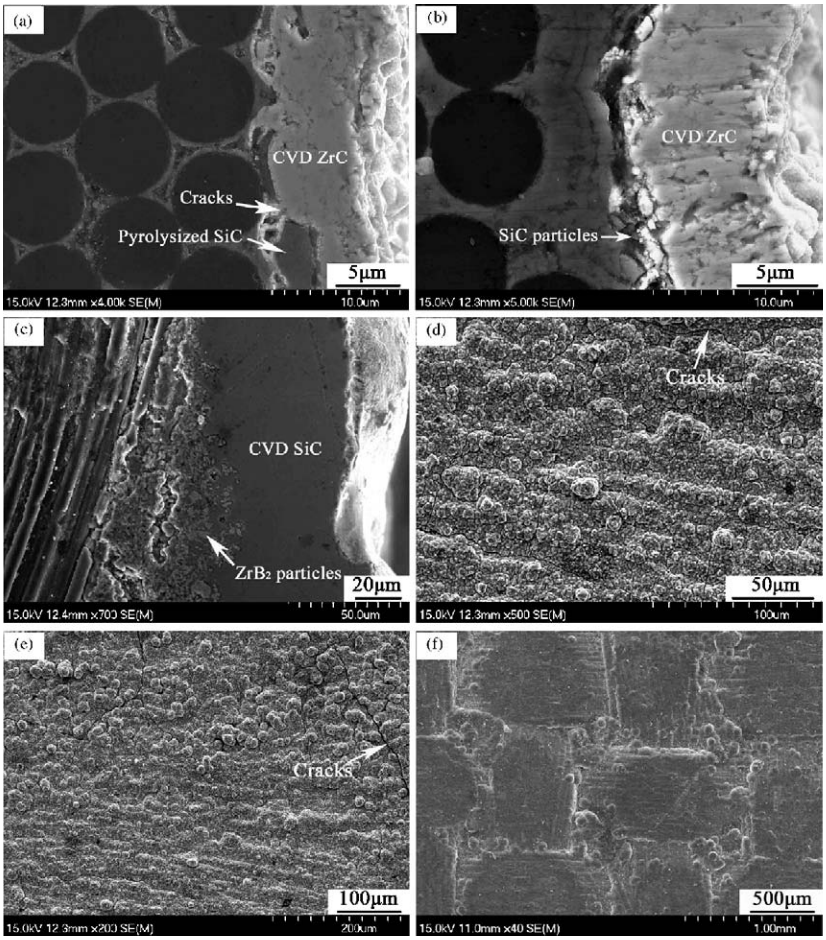

Fig. 4. Cross-sections of different coating structures (a) #1 CVD ZrC coating, (b) #2 SiC–ZrC mixture coating, (c) #3 ZrB_2–SiC mixture coating and surface morphologies for (d) #1 (e) #2, and (f) #3 specimens.

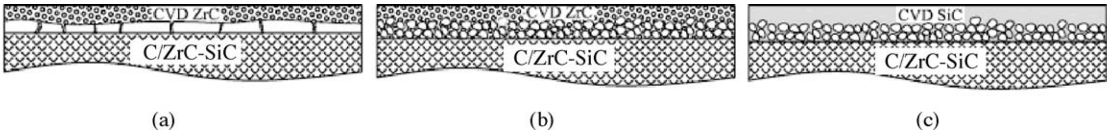

Fig. 5. The schematics of coating structures for (a) #1 CVD ZrC coating, (b) #2 SiC–ZrC mixture coating and (c) #3 ZrB_2–SiC mixture coating.

observed on the top of #1 (Fig. 4a) and #2 (Fig. 4b) specimens. As we know, before the deposition of ZrC, cracks will be formed on composites surface due to the intrinsic shrinkage during the polymer–ceramic conversion process (Fig. 4a). During the CVD process, ZrC will firstly fill such cracks. Another ZrC layer will be subsequently deposited on the top of the composite (Fig. 4a).

As shown in Fig. 4c, the ZrB_2 particles are embedded in the CVD SiC to form a mixture layer of ZrB_2 and SiC. Another SiC layer is on its top, which is formed during the deposition process of SiC filling the gaps between ZrB_2 particles. Similarly, a mixture layer of SiC and ZrC is formed on the surface of the #2 specimen with a CVD ZrC layer on its top (Fig. 4b). Meanwhile, a small amount of micro-cracks are found on the surface of #1 and #2 specimens (Fig. 4d and e). This may be due to the mismatch of thermal expansion coefficient between CVD ZrC and SiC. The schematic pictures of the three different coatings are shown in Fig. 5.

3.3. Oxidation behavior of 2D C/ZrC–SiC composites with different coating structures

The three specimens were exposed simultaneously in a CH_4 combustion wind tunnel for 30 min at about 1800 °C. The morphologies of these oxidized specimens are shown in Fig. 6. Compared with the un-oxidized samples (Fig. 4d and e), severe damage of #1 and #2 specimens is observed (Fig. 6a and b), while the surface of #3 specimen shows almost no change (Figs. 4f and 6c). The weight loss of #1 and #2 specimens are 7.08% and 6.50%, i.e. much higher than that of 1.06% for #3 specimen. XRD patterns (Fig. 7) and element analysis of #1 and #2 specimens (Fig. 6a and b) after oxidation reveal that the oxidation products include SiO_2 and ZrO_2 (white phase) or their compounds. The reactions occurring during the oxidation process at about 1800 °C are as follows [17]:

$$SiC + (3/2)O_2 \rightarrow SiO_2 + CO \tag{1}$$

$$ZrC + (3/2)O_2 \rightarrow ZrO_2 + CO \tag{2}$$

Sample #1 has been severely damaged after exposure in CH_4 combustion gas environment although a ZrC coating had been deposited on its surface. When oxidized, ZrC forms porous ZrO_2 and CO. These materials show rapid oxidation with linear (non-protective) reaction kinetics, which allows entire specimens to be oxidized in relatively short periods of time. Moreover, the water vapor formed by the reactions in the combustion atmosphere will also accelerate the oxidation of the composites [18]. The coating schematic picture of #2 is shown

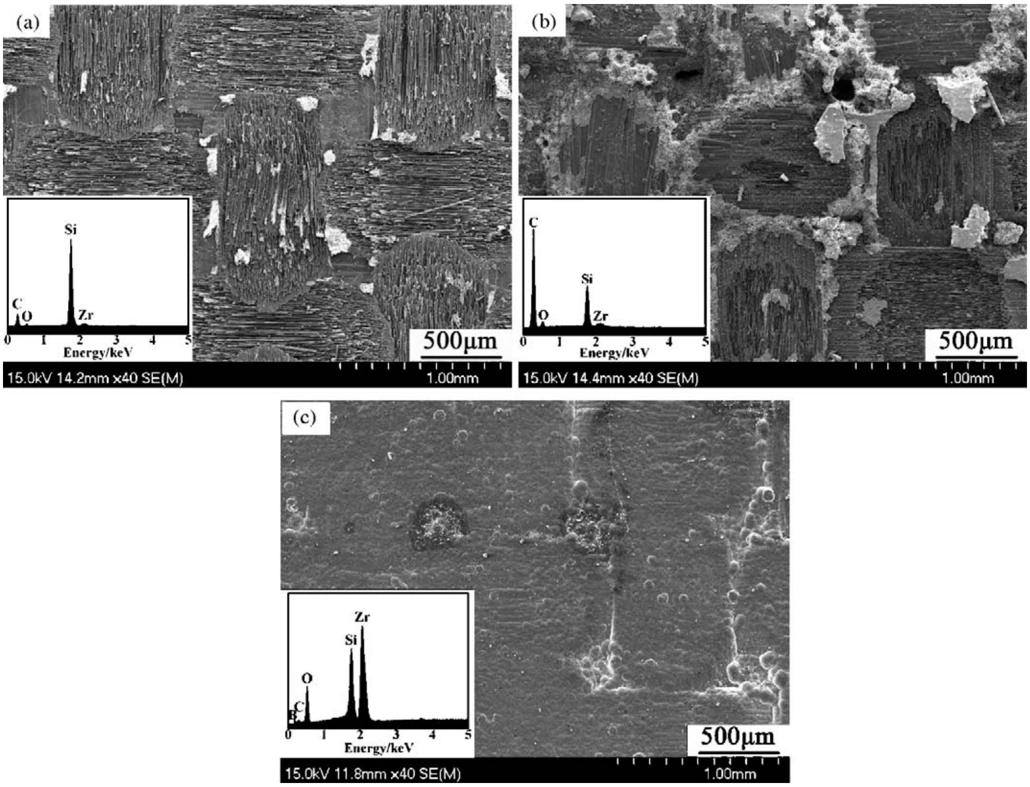

Fig. 6. Surface morphologies of the specimens after oxidation: (a) #1 CVD ZrC coating, (b) #2 SiC–ZrC mixture coating and (c) #3 ZrB_2–SiC mixture coating.

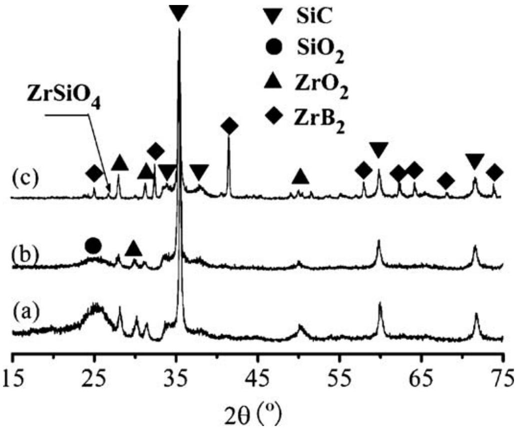

Fig. 7. XRD patterns of specimens after oxidation: (a) #1 CVD ZrC coating, (b) #2 SiC–ZrC mixture coating and (c) #3 ZrB_2–SiC mixture coating.

in Fig. 5b. During the oxidation process, the top ZrC will be oxidized very fast, similar to #1. As the flame reaches the mixture layer, the ZrC between SiC powders would be oxidized at the same rate as before. Without ZrC bond, the SiC or its oxide SiO_2 will be easily blown off owing to mechanical erosion of the high gas-flow in combustion atmosphere.

After losing the coating systems, cracks and pores existing in C/ZrC–SiC composites may be the channels for the oxidized gas and stream to diffuse into the interior of the composites. Oxidation reactions take place in the whole composite simultaneously and quickly. The ZrC–SiC matrix cannot withstand oxidation environment with high heat flux and high pressure gas flow any more because the protecting silica layer becomes active and can be easily blown off. The subsequent oxidation of fiber and interphase results in complete degradation of the composites. Thus, the weight loss for these two samples is much higher. The XRD patterns (Fig. 7) and EDS analysis (Fig. 6) of #1 and #2 specimens are almost the same, suggesting the identical oxidation behavior of these two composites. Meanwhile, sample #2 shows a close oxidation morphology and weight loss to #1 with a pure ZrC coating. It is suggested that, without the protection of the outer coating, the role of SiC powders in sample #2 and the pyrolysized SiC in sample #1 is the same.

The ZrB_2–SiC mixture coating for #3 specimen is the key point for little change before and after oxidation. ZrO_2 and zirconium silicate ($ZrSiO_4$) are found in #3 specimen after oxidation (Figs. 6c and 7c), which reveals that in the combustion environment, besides the aforementioned reactions for SiC, an oxidation reaction concerning ZrB_2 powder takes place as follows:

$$ZrB_2 + (5/2)O_2 \rightarrow ZrO_2 + B_2O_3 \tag{3}$$

Previous studies show that defects are unavoidable in CVD SiC coating [19], which will result in oxygen diffusion inward and oxidation of the composites. Thus, oxidation for ZrB_2 powder will be inevitable. For ZrB_2 oxidized at elevated temperatures, ZrO_2 and liquid B_2O_3 are formed [20]. The B_2O_3 provides significant oxidation protection at lower temperatures, before it evaporates. However, appreciable volatilization of B_2O_3 starts at above 1200 °C leaving ZrO_2 on the coating system [21]. XRD pattern (Fig. 7c) and element analysis (Fig. 6c) for #3 specimen indicate that ZrB_2 particles still exist in the composite after oxidation. It means that SiC coating protects the interior area of the composite including ZrB_2 powder from further oxidation at higher temperature (>1200 °C). During the oxidation process, the combustion gas with a high flow rate and a larger amount of H_2O will accelerate the silica and zirconium oxide formation on the coating and matrix. Different to #1 and #2 specimens, the oxidation channels for #3 specimen could be sealed by the oxides. The PyC interlayer together with fiber is less oxidized. Almost no change of the morphology for #3 specimen was thus observed. The weight loss for this sample is of course the smallest among the three specimens.

4. Conclusions

2D C/ZrC–SiC composites were fabricated by the CVI process combined with the PIP method. The results indicate that pure ZrC coatings can be easily oxidized and result in a complete degradation of the composites, whereas ZrB_2–CVD SiC coating could fully fulfill the advantages of refractory compounds to improve oxidation resistance.

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