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Review paper

Oxidation behavior of oxidation protective coatings for PIP–C/SiC composites at 1500 °C

Xiang Yang*, Li Wei, Wang Song, Chen Zhao-hui

Key Laboratory of Advanced Ceramic Fibers & Composites, National University of Defense Technology, Changsha 410073, People's Republic of China

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Abstract

Three-dimensional carbon fiber reinforced silicon carbide (C/SiC) composites were fabricated by precursor infiltration and pyrolysis (PIP) with polycarbosilane as the matrix precursor, SiC coating prepared by chemical vapor deposition (CVD) and ZrB_2–SiC/SiC coating prepared by CVD with slurry painting were applied on C/SiC composites, respectively. The oxidation of three samples at 1500 °C was compared and their microstructures and mechanical properties were investigated. The results show that the C/SiC without coating is distorted quickly. The mass loss of SiC coating coated sample is 4.6% after 2 h oxidation and the sample with ZrB_2–SiC/SiC multilayer coating only has 0.4% mass loss even after oxidation. ZrB_2–SiC/SiC multilayer coating can provide longtime protection for C/SiC composites. The mode of the fracture behavior of C/SiC composites was also changed. When with coating, the fracture mode of C/SiC composites became brittle. When after oxidation, the fracture mode of C/SiC composites without and with coating also became brittle.

Keywords: C/SiC composites; Oxidation protective coating; Slurry; Chemical vapor deposition

Contents

1. Introduction

Polymer impregnation and pyrolysis (PIP) is a major manufacturing process of C/SiC composites. Compared with chemical vapor infiltration (CVI), PIP has many advantages such as lower component fabrication time to reduce costs significantly and the low fabricating temperature [1–5]. However, they have a low durability except in inert atmospheres. At higher temperatures (>1200 °C), the oxidation of the fiber, interphase and matrix cooperatively influence the oxidation behavior of C/SiC composites in oxygen atmosphere [6,7]. Consequently, PIP C/SiC composites need oxidation protection when exposed to oxidizing environment at high temperatures.

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* Corresponding author. Tel.: +86 731 84576165; fax: +86 731 84573165.
E-mail address: shmily_0427@163.com (Y. Xiang).

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Currently, three primary methods are used to apply oxidation protection coating on the surface of carbon materials: pack cementation, chemical vapor deposition (CVD) [8] and slurry method [9]. Among these methods, pack cementation has to be carried out above 1800 °C [10]. In this regard, pack cementation is not suitable for PIP C/SiC composites.

In this work, ZrB_2–SiC coating prepared by slurry painting, and ZrB_2–SiC/SiC multilayer coating prepared by CVD with slurry painting, were applied on PIP C/SiC composites, respectively. The oxidation of substrate and two coated samples at 1500 °C was investigated.

2. Experimental

2.1. Specimen preparation

Three-dimensional braided carbon fibers (T-300, ex-PAN carbon fiber, Toray) were used as the reinforcement [4]. PCS with molecular weight ~1742 and soften point ~175 °C was synthesized in our laboratory. Firstly, the polydimethylsilane was decomposed in an autoclave under N_2, when the temperature was during 360–490 °C. Secondly, the products were dissolved in xylene, and then the impurities were filtrated. Finally, the PCS was fabricated from the solution by the reduced pressure distillation [11]. Xylene was used as solvent for PCS.

The C/SiC composites denoted as raw sample were prepared using 9–12 cycles of infiltration of PCS–xylene solution and subsequently pyrolysis at 1200 °C under an inert atmosphere [1].

A ZrB_2–SiC coatings were used in order to increase the oxidation resistance. A ZrB_2 powder (2.5 μm, Dandong Chemical Engineering Institute Co. Ltd., China) with PCS was then pasted on the composite. In this process, CVD SiC will penetrate in the gaps between ZrB_2 powders and form a mixture of ZrB_2–SiC coating with a layer of dense SiC on the top.

As for the CVD SiC process, methyltrichlorosilane (MTS, CH_3SiCl_3) with a molar ratio of 10 between H_2 and MTS, which was carried by bubbling hydrogen in gas phase and argon as the dilute gas to slow down the chemical reaction rate during deposition. The deposition temperature was controlled in the 1100 °C for 5 h at reduced pressure of 3 kPa.

2.2. Oxidation tests

The substrate and two coated samples were heated at 1500 °C in air for 2 h. The samples were weighed after oxidation tests by an electronic balance with a sensitivity of ±0.001 mg. Three-point bending tests were used to evaluate the flexural strength of C/SiC composites with the span/height ratio of 15 and a crosshead speed of 0.5 mm/min before and after oxidation.

The morphologies and crystalline structures of the samples were analyzed by scanning electron microscopy (SEM, JSM-5600LV).

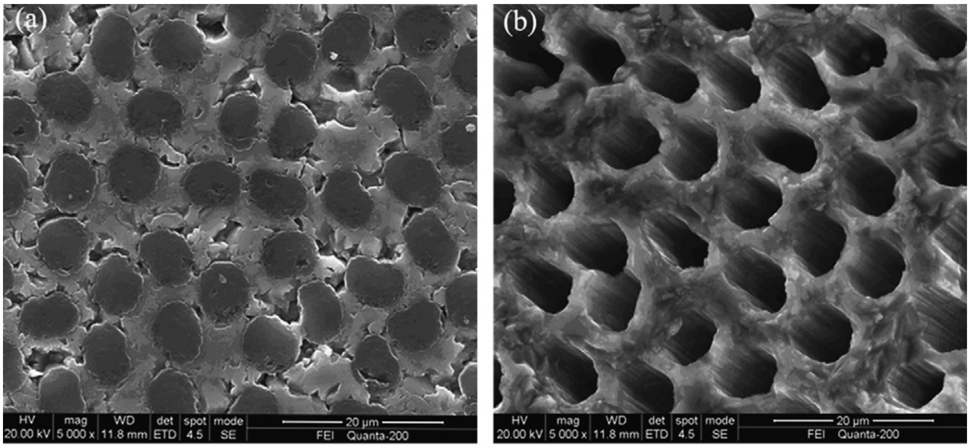
3. Results and discussion

3.1. Oxidation of C/SiC composites without coating

Morphologies of C/SiC composites before and after oxidation are shown in Fig. 1. The open porosity is less than 11% [11], while after oxidation at 1500 °C for 2 h, many holes appear on the surface (Fig. 1(b)). SEM image (Fig. 1(b)) shows that the composites becomes very loose and many microcracks emerge. It is concluded that C/SiC composites has been severely damaged after oxidation in air at 1500 °C. Oxidation reactions take place in the whole composite simultaneously and quickly, these is almost no C fiber in the composites (Fig. 1(b)), while after 2 h oxidation at 1500 °C, the mass loss reaches 13.19%, the C/SiC composites retain only 45.7% of original flexural strength, which means that the C/SiC is almost invalidation.

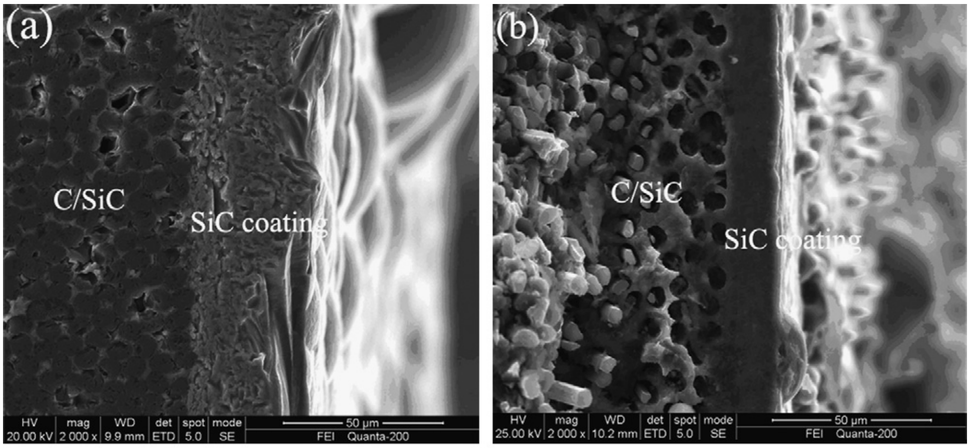
3.2. Oxidation of C/SiC composites with CVD SiC coating

Morphologies of C/SiC composites with CVD-SiC coating before and after oxidation are shown in Fig. 2, the oxidation products include SiO_2, shown in Fig. 3, The cross-section SEM image, shown in Fig. 2(b), reveals that continuous SiO_2 glass has been formed accompanied with C/SiC composites. The



(a) Before oxidation (b) After oxidation

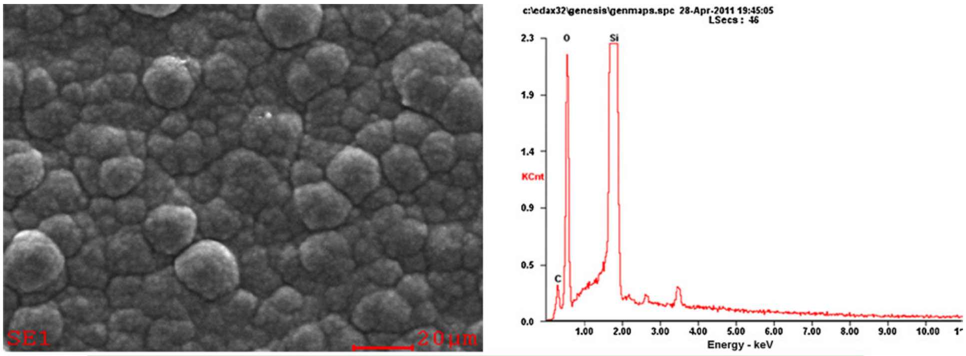
Fig. 1. PIP–C/SiC composites (a) before and (b) after oxidation.



(a) Before oxidation

(b) After oxidation

Fig. 2. PIP–C/SiC composites with CVD SiC coating (a) before and (b) after oxidation.



Element	Wt%	At%
C	10.96	19.83
O	19.31	26.22
Si	69.73	53.94

Fig. 3. EDS of PIP–C/SiC composites with CVD SiC coating after oxidation.

reactions occurring during the oxidation process at about 1500 °C are as follows [12]:

$$2SiC(s) + 3O_2(g) = 2SiO_2(s) + 2CO(g) \qquad (1)$$

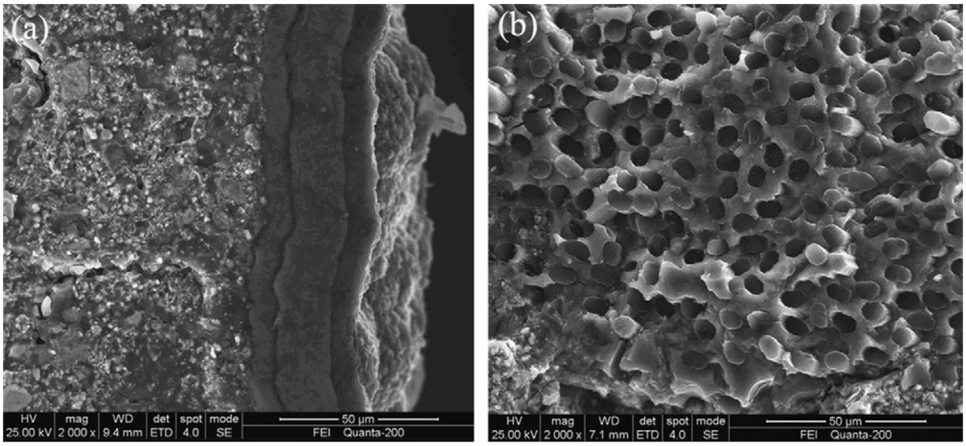
After oxidation, because of the open porosity of the composites, cracks and pores existing may be the channels for the oxidized gas and stream to diffuse into the interior of the composites. While after 2 h oxidation at 1500 °C, there is little fiber in the composites (Fig. 2(b)), the mass loss reaches 4.6%, C/SiC composites with CVD–SiC coating retain 71.9% of original flexural strength. At 1500 °C, SiC, and C are rapidly oxidized into SiO_2 glass and CO. Simultaneously, CO in the coating and composites are formed in the SiO_2 glass when the pressure exceeds the critical value. Then the coating is out of service. Therefore, single CVD–SiC coating cannot provide oxidation protection for C/SiC composites at 1500 °C for long time.

3.3. Oxidation of C/SiC composites with ZrB_2–SiC/SiC multilayer coating

Based on the above analysis, it can be inferred that the evaporation of SiO_2 and CO lead to the failure of the C/SiC composites with and without CVD–SiC coating. Our purpose is thus to develop the coating system with dense barriers. The designed ZrB_2–SiC/SiC multilayer coating, from inside to outside, was ZrB_2–SiC → SiC. When being oxidized at 1500 °C, the coated sample kept little mass change during 2 h, which suggests that the coating can protect the C/SiC composites from oxidation at that temperature. ZrB_2–SiC/SiC coating is the key point for little change before and after oxidation. Little fiber is damaged in the composites (Fig. 4), an oxidation reaction concerning ZrB_2 powder takes place as follows:

$$2ZrB_2(s) + 5O_2(g) = 2ZrO_2(s) + 2B_2O_3(g) \qquad (2)$$

The aforementioned studies show that defects are unavoidable in CVD–SiC coating, thus, oxidation for ZrB_2 powder will be inevitable. For ZrB_2 oxidized at elevated temperatures, ZrO_2 and gaseity B_2O_3 are formed [13]. Appreciable volatilization of B_2O_3 starts at above 1200 °C leaving ZrO_2 on the coating system [14]. The oxidation channels could be sealed by the oxides. The PIP–SiC matrix together with fiber is less oxidized. Almost no change of the morphology was thus observed. Based on the self-sealing and anti-diffusion capability, the coating has good oxygen resistance. The weight loss for this sample is of



(a) Before oxidation (b) After oxidation

Fig. 4. PIP–C/SiC composites with ZrB_2–SiC/SiC coating (a) before and (b) after oxidation.

course the smallest among the three specimens. After soak at 1500 °C for 2 h under static air, the C/SiC composites with ZrB_2–SiC/SiC coating retain 94.2% of original flexural strength and the mass loss only has 0.4%. The results prove that the ZrB_2–SiC/SiC coating protect C/SiC composites effectively.

3.4. The influence of different coating on the microstructures and mechanical properties of composites

The mechanical properties of C/SiC composites with different coatings are listed in Table 1. It was clear that the density of C/SiC composites increased with different coatings. At the same time, the flexural strength of C/SiC composites greatly increased with the coatings, because porosity between the fibers and matrix was filled. And after oxidation, C/SiC composites without coating were oxidation badly, the fibers were vanished, the flexural strength changed to 243.7 MPa. With the SiC coating, the flexural strength of C/SiC composites changed from 655.3 MPa to 471.0 Mpa, with the ZrB_2–SiC/SiC coating, the flexural strength reserved 618.8 MPa. The reason for the increase of the flexural strength was thought as the resistance of the coatings to the oxidation condition. So the effects of coating on the mechanical properties were remarkable.

Fig. 5 is the load–displacement curves of C/SiC composites with various coatings. Fig. 6 is the load–displacement curves of C/SiC composites with various coatings after oxidation. Obviously, the pull-out mechanism was also changed with coatings. For the C/SiC composites without coating, there was mainly the fiber bundle pull-out when the load reached at the maximum. However, there was little fiber pull-out and short pull-out length with coatings, therefore it showed typical delayed fracture behavior of C/SiC composites without and with coating. The samples with coating showed brittle fracture behaviors.

After oxidation, SiC, ZrB_2 and C are rapidly oxidized into SiO_2 glass, ZrO_2 and B_2O_3, CO, the fibers in the samples were damaged, the oxidation channels could be sealed by the oxides. Therefore, it resulted in few fibers pull-out.

Table 1
The mechanical properties of C/SiC composites with different coatings.

	Density (g/cm^3)	Flexural strength before oxidation (MPa)	Flexural strength after oxidation (MPa)
C/SiC	1.93	533.1	243.7
C/SiC SiC coating	2.06	655.3	471.0
C/SiC ZrB_2–SiC/SiC coating	2.12	656.5	618.8

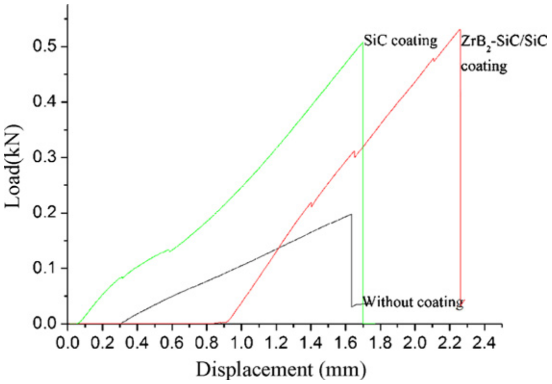


Fig. 5. Load–displacement curves of PIP–C/SiC with different coatings before oxidation.

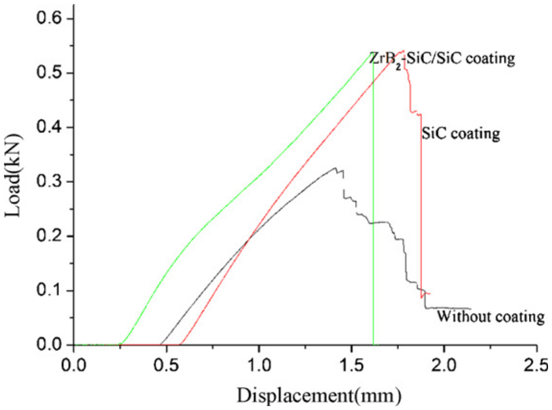


Fig. 6. Load–displacement curves of PIP–C/SiC with different coatings after oxidation.

4. Conclusions

C/SiC composites were prepared by the precursor infiltration and pyrolysis route, in order to improvement the oxidation behavior, and then were covered with two different coating. The oxidation of three samples at 1500 °C was compared, and their microstructures and mechanical properties were investigated. The following conclusions can be drawn from the present investigations:

(1) The mechanical properties of PIP–C/SiC composites with coating were excellent, especially the flexural strength 655.3 MPa with SiC coating and the flexural strength 656.5 MPa with ZrB_2–SiC/SiC coating.

(2) Effects on the oxidation behavior of C/SiC composites with coating were remarkable. Without coating, the mass loss of C/SiC composites reaches 13.19% and retain only 45.7% of original flexural strength; C/SiC composites with CVD–SiC coating retain 71.9% of original flexural strength and the mass loss reaches 4.6%; C/SiC composites with ZrB_2–SiC/SiC coating retain 94.2% of original flexural strength and the mass loss reaches 0.4%.

(3) The mode of the fracture behavior of C/SiC composites was also changed. When with coating, the fracture mode of C/SiC composites became brittle. When after oxidation, the fracture mode of C/SiC composites without and with coating also became brittle.

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