

## Feature Article

# Research on the Oxidation-Protective Coatings for Carbon/Carbon Composites

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## Abstract

Anti-oxidation coatings are the key technique for carbon/carbon (C/C) composites used as the thermal structural materials. The microstructure and oxidation behavior of several kinds of high-performance ceramic coatings for C/C composites prepared in Northwestern Polytechnical University were introduced in this paper. It showed that the ceramic coatings such as SiC, Si-MoSi<sub>2</sub>, SiC-MoSi<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-mullite-SiC and SiC/yttrium silicate/glass coatings possessed excellent oxidation resistance at high temperatures, and some of these coatings were characterized with excellent thermal shock resistance. The SiC-MoSi<sub>2</sub> coating system has the best oxidation protective property, which can effectively protect C/C composites from oxidation up to 1973 K. In addition, the protection and failure reasons of some coatings at high temperature were also provided.

**Keywords:** Carbon/carbon composites, Oxidation, Coating

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## 1. Introduction

Carbon/carbon (C/C) composites exhibit outstanding mechanical properties, particularly at high temperatures. However, the applications of C/C composites as engineering materials in re-entry shields of space vehicles, disk brakes, and heating elements at high temperatures are often limited by their oxidation in oxygen containing atmospheres [1]. It is, therefore, important to improve the resistance of these materials towards air oxidation at high temperatures [2, 3].

Since oxidation is a surface related degradation phenomenon, oxidation resistant coatings are the logical choice for protecting C/C composites at high temperatures. In recent papers, many oxidation resistant coatings such as SiC/barium boron aluminosilicate glass+MoSi<sub>2</sub>/barium boron aluminosilicate glass+Y<sub>2</sub>O<sub>3</sub> [4], SiC/B<sub>4</sub>C [5], (Si<sub>3</sub>N<sub>4</sub>+SiC)/C [6] and so on had been developed. But it is always difficult to find some high performance coatings that can effectively protect C/C composites for a long time, especially at high temperatures (above 1773 K).

The research work on the oxidation protective coating for C/C composites has been undergone for more than ten years in our laboratory and some attractive achievements have been obtained. In this paper, several high-performance coatings prepared by us were described, and the microstructure and oxidation behavior were partly discussed as well.

## 2. Some High Performance Coatings

### 2.1. Glass coating

#### 2.1.1. Phosphate glass coating

Phosphate coating is an efficient technique to protect carbon/carbon (C/C) composites for airplane brake from oxidation. The starting composition of the phosphate glass chosen as coating materials was phosphoric acid, silicon oxide, phosphates, etc. [7]. These materials were mixed adequately to form the phosphate slurry. The 'as-prepared' phosphate slurry was brushed directly on C/C composites to obtain the coated samples, which were then heated at 1173-1373 K for 1 h in a nitrogen atmosphere. The oxidation test result showed that the weight loss percent of the coated sample was less than 1.12% at 973 K for 66 h (Fig. 1). After the thermal cycle between 1173 K and 298 K for 100 times, the weight loss percent was only 1.6% (Fig. 2), which indicated a good adhesion between the phosphate glass coating and C/C substrate. The 'as-achieved' coating was characterized by a dense structure with the SEM analysis and could provided C/C with the abilities of anti-oxidation below 1273 K, which can be used as the protection coating of C/C composites for airplane brake.

#### 2.1.2. SiC doped borosilicate glass coating

The coating powders used for preparing the SiC doped borosilicate glass coating were a mixture of SiC, borosilicate

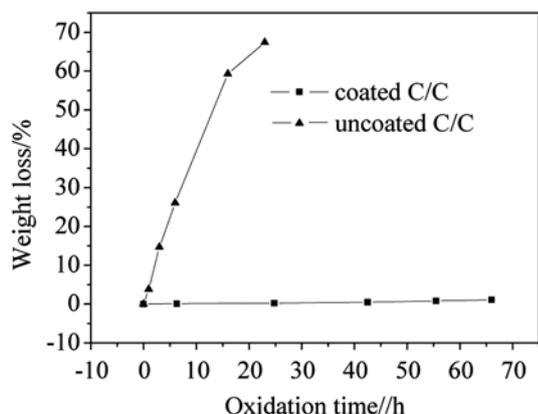


Fig. 1. Isothermal oxidation curves of the C/C samples with and without the phosphate coating.

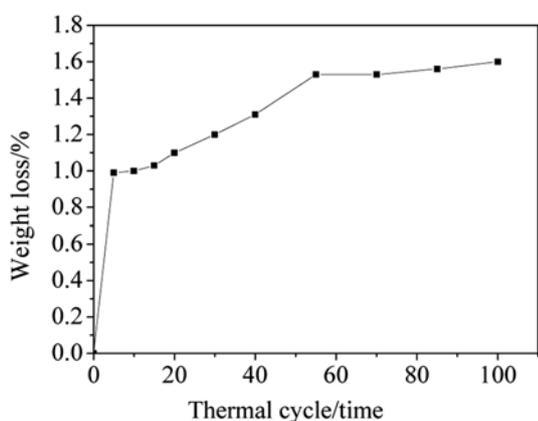


Fig. 2. Thermal cycle curve of the C/C sample with phosphate coating.

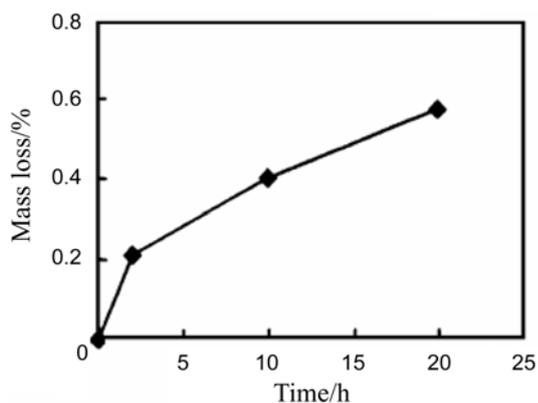


Fig. 3. The mass loss of SiC doped borosilicate glass coated C/C composites at 1673 K in air.

glass and clay [8]. Samples coated with the powder slurry were dried at 573 K for 2 h, and then were heated at 1873 K for 1 h in a nitrogen atmosphere. The thickness of the coating was controlled artificially by brushing times, which was in the range of 200-400  $\mu\text{m}$ . The isothermal oxidation

test at 1673 K in air showed that the coating could protect C/C composites from oxidation for 20 hours, and the weight loss of the coated C/C was only 0.6% (Fig. 3).

### 2.1.3. SiC/glass double-layer coating

In order to protect C/C composites operating at 1573 K from oxidation, a magnesium boron aluminosilicate (SABM) glass coating was prepared on the surface of the SiC coated C/C [9].

The inner-layer SiC coating was prepared by pack cementation. The powder composition of pack cementation was as follows: 65-80 wt.% Si, 10-25 wt.% graphite and 5-15 wt.%  $\text{Al}_2\text{O}_3$ . The C/C specimens and pack mixtures were put in a graphite crucible, and then were heat-treated at 1873 K for 2 h in an argon protective atmosphere. The outer-layer glass coating was obtained by slurry. The starting composition of SABM glass was 60-75 wt.%  $\text{SiO}_2$ , 15-25 wt.%  $\text{B}_2\text{O}_3$ , 5-15 wt.% MgO and 2-10 wt.%  $\text{Al}_2\text{O}_3$ . The slurry made by mixing SABM glass,  $\text{MoSi}_2$  particles,  $\text{AlPO}_4$  (the borosilicate glass/ $\text{MoSi}_2$ / $\text{AlPO}_4$  weight ratio was 14:5:1) and ethanol was brushed directly to the surface of SiC coated C/C. The samples were then heated at 1573 K for 1 h in an argon atmosphere.

From the cross-section micrograph of the double-layer coated C/C composites (Fig. 4), the average thickness of the double-layer coating is about 350  $\mu\text{m}$ , and cracks or large holes cannot be found at the interface between the SiC and the glass coatings. In the outer-layer glass coating, there are two kinds of particles (characterized as grey and white). By EDS analysis, the grey and white phases could be distinguished as SABM glass and  $\text{MoSi}_2$ , respectively.

Fig. 5 shows the oxidation curves of the coated C/C composites in air at 1573 K. It can be seen that the weight loss of the monolayer SiC coated sample quickly increases with time and is up to 2.98% after oxidation for 12 h. By adding a double-phase glass coating of SABM- $\text{MoSi}_2$  produced by the slurry on the SiC coated C/C composites,

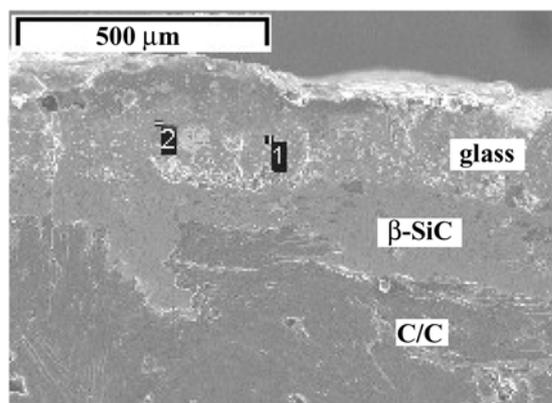


Fig. 4. A SEM micrograph of the cross-section of the double-layer coating on C/C composites.

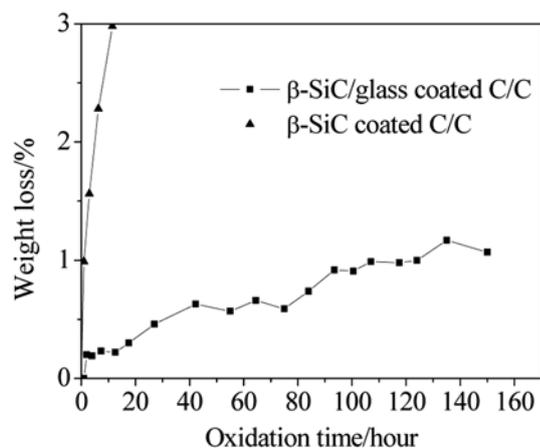


Fig. 5. Thermal oxidation curves at 1573 K of the coated C/C composites.

the oxidation resistance of the sample is improved largely, and the weight loss is only 1.07% after oxidation for 150 h. In addition, the sample has endured thermal cycling between 1573 K and room temperature for 20 times, and no increasing trend of the weight loss rate is found, from which it can be inferred that the coating has excellent thermal stress resistance. During the oxidation test, the alternate occurrence of the debonding and regeneration of glass resulted in the step shape of the weight-loss curve.

## 2.2. Silicide ceramic coating

### 2.2.1. SiC coating

SiC coating was produced by a two-step pack cementation [10]. Powder compositions for the two-step pack cementation process were as follows: 65-80% Si, 10-25% graphite and 5-15%  $\text{Al}_2\text{O}_3$  for the first step, and 70-80% Si, 5-15% SiC, 7-20% graphite and 2-15%  $\text{Al}_2\text{O}_3$  for the second step. The C/C specimens were packed by the first pack mixtures and were heated at 1873 K for 2 h under slightly flowing argon gas. The second pack cementation process was performed at 2173 K for 2 h to obtain the dense SiC coating, in which the free silicon was distributed.

The XRD analysis showed that the inner coating obtained from the first step pack cementation was a  $\beta$ -SiC layer and the outer coating formed by the second step was composed of  $\alpha$ -SiC, Si and  $\beta$ -SiC. The surface SEM image of the coating prepared by the two-step pack cementation revealed the formation of a dense and crack-free surface (Fig. 6).

The isothermal oxidation curves of the coated C/C composites at 1773 K in air are shown in Fig. 7. It can be seen that the weight loss of the SiC coated sample is only 0.63% after oxidation for 310 h and the corresponding weight loss rate is  $0.9 \times 10^{-5} \text{ g/cm}^2 \cdot \text{h}$ . In addition, the sample was exposed to thermal cycling between 1773 K and room temperature for 21 times during oxidation test, and no

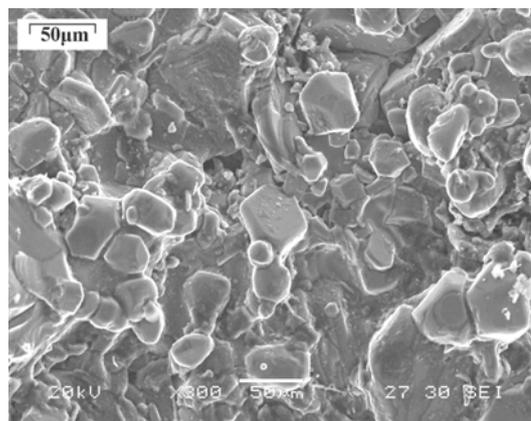


Fig. 6. Surface SEM micrograph of the coating obtained by the two-step pack cementation.

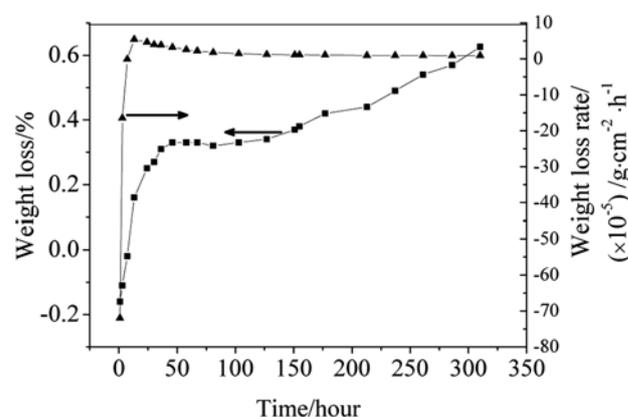
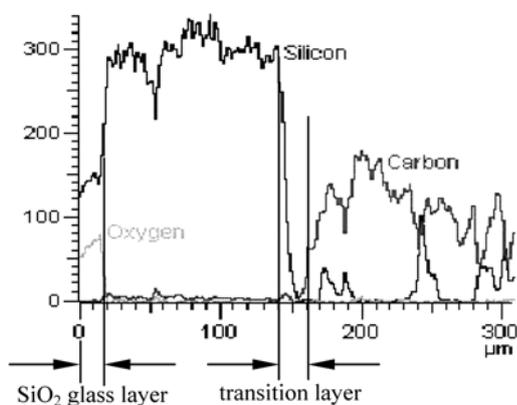
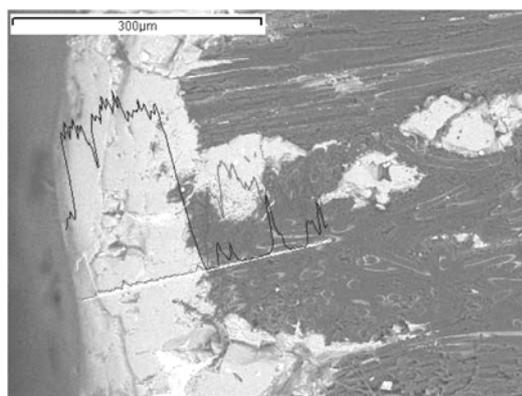


Fig. 7. Isothermal oxidation curves of the SiC coated C/C composites in air at 1773 K. The negative weight loss means weight gain.

increasing trend of the weight loss rate was found. Therefore, the SiC coating prepared by the two-step pack cementation has excellent oxidation and thermal shock resistance.

From the cross-section image of the SiC coated C/C composites after oxidation at 1773 K for 310 h (Fig. 8), the coating is still dense, in which no obvious cracks are found. By element line scanning analyses, oxygen is only existent in the range between the coating surface and about 20  $\mu\text{m}$  distance from the surface, which indicates the formation of  $\text{SiO}_2$  glass layer on the SiC coating surface. The  $\text{SiO}_2$  glass layer could efficiently prevent oxygen from diffusing to the C/C surface. In addition, from the C/C-coating interface to the C/C matrix, the concentration of the Si element decreased gradually in the range of almost 18  $\mu\text{m}$ , implying that a gradient SiC transition layer was obtained, which was advantageous to improve the thermal stress resistance of the coating.

The weight decreasing of the coated sample is thought to



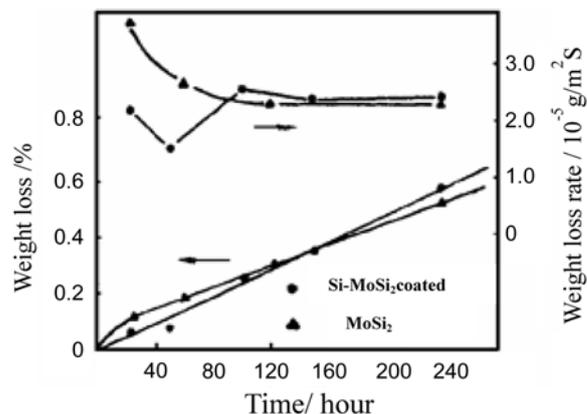
**Fig. 8.** The SEM cross-section and the element line scanning results of the as-prepared coating on C/C composites after oxidation at 1773 K for 310 h.

occur owing to the formation of holes on the SiO<sub>2</sub> glass coating surface and to the chipping of some glass off the coating surface.

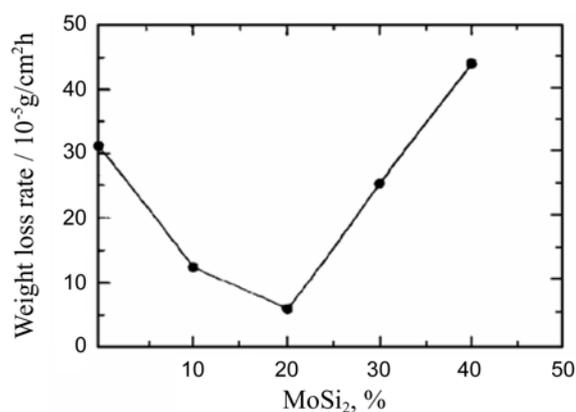
### 2.2.2. Si-MoSi<sub>2</sub> coating

Si-MoSi<sub>2</sub> coating was prepared by a pack cementation process with the pack powders of Si and MoSi<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> [11]. The process was conducted at 2073 K for 2 h in an argon atmosphere. Fig. 9 displays the oxidation test results of the Si-MoSi<sub>2</sub> coated C/C and the MoSi<sub>2</sub> material. The oxidation curves of these two different materials are almost the same, which indicates that the weight loss of the coated sample was due primarily to the volatilization of MoSi<sub>2</sub>. From Fig. 9, we also can find that after 240 h oxidation at 1773 K in air, the mass loss of the Si-MoSi<sub>2</sub> coated C/C is less than 0.6%. Therefore, the Si-MoSi<sub>2</sub> coating prepared by pack cementation processes exhibits excellent oxidation resistance. Fig. 10 gives the influence of MoSi<sub>2</sub> content in the multi-coating on the oxidation resistance of the coating. It reveals that the best oxidation resistant property could be achieved when the MoSi<sub>2</sub> content is kept at 20 wt.% [12].

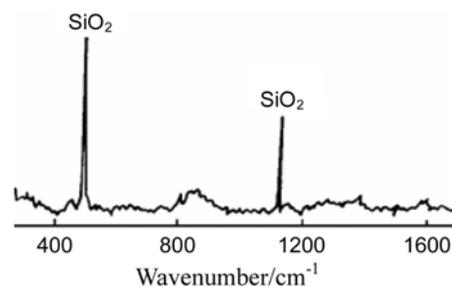
In order to make the oxidation protective mechanism of the Si-MoSi<sub>2</sub> coating clear, the Raman spectrum analysis of



**Fig. 9.** Oxidation test result at 1773 K of the Si-MoSi<sub>2</sub> coated C/C composites.

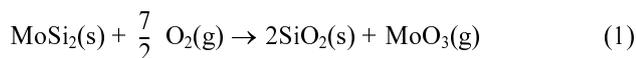


**Fig. 10.** The influence of MoSi<sub>2</sub> content in the multi-coating on the oxidation resistance.



**Fig. 11.** A Raman spectrum of the coating after oxidation for 242 h.

the coating after oxidation for 242 h in air was performed (Fig. 11). It shows a formation of SiO<sub>2</sub> scale, which may be generated during the reactions as shown in equations (1) and (2). This implies that the SiO<sub>2</sub> scale produced slowly by the oxidation of Si and MoSi<sub>2</sub> at high temperature acts as the protective and self-sealing material in the oxidation environment, which provides Si-MoSi<sub>2</sub> with excellent oxidation resistance [13].



### 2.2.3. SiC-MoSi<sub>2</sub> coating

SiC-MoSi<sub>2</sub> coating was produced by pack cementation and infiltration process [14]. The SiC bonding and buffering layer was prepared using the mixture of Si, SiC, and Al<sub>2</sub>O<sub>3</sub> as pack powder. The C/C samples were embedded in the pack powder and heated at 1873 K in an argon protective atmosphere to form a SiC inner-layer coating. The outer coating was produced at a higher temperature using MoSi<sub>2</sub> as the infiltration material.

The XRD patterns of the ‘as-prepared’ coatings displayed the formation of SiC, Si and MoSi<sub>2</sub> crystallites in the coating.

Fig. 12 displays the isothermal oxidation test results of the SiC-MoSi<sub>2</sub> coated C/C composites. It shows that the multi-coating could effectively prevent C/C from oxidation at 1773 K for 420 h. The corresponding weight loss rate is kept at  $0.5 \times 10^{-5} \text{ g/cm}^2\text{-h}$ , inferring an excellent oxidation resistance of the multi-coating.

Figs. 13 and 14 reveal the isothermal oxidation test results

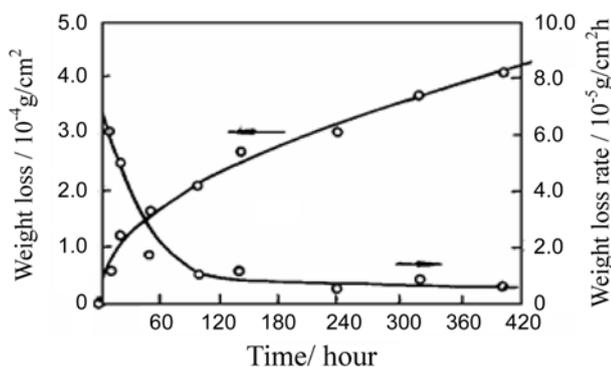


Fig. 12. Oxidation test result at 1773 K of the SiC-MoSi<sub>2</sub> coated C/C.

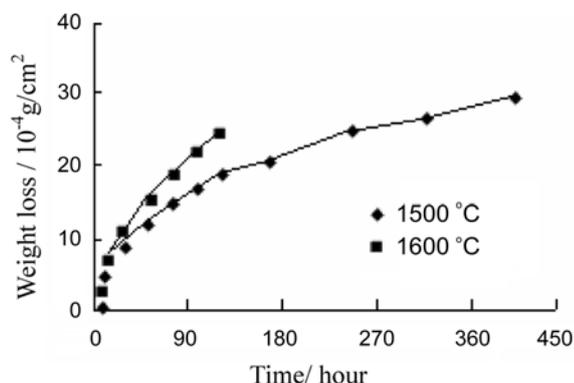


Fig. 13. Oxidation test result at 1773 K and 1873 K of the SiC-MoSi<sub>2</sub> coated C/C.

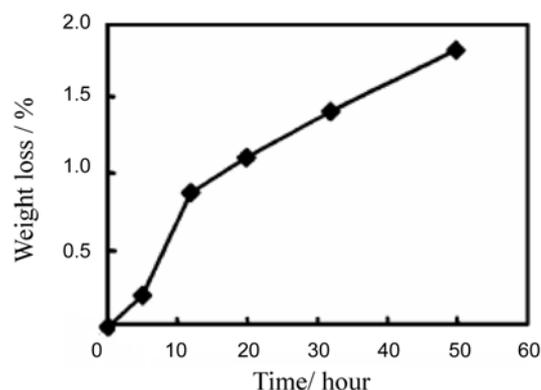


Fig. 14. Oxidation test result at 1973 K of the SiC-MoSi<sub>2</sub> coated C/C.

in air at 1873 K [15] and 1973 K [8], respectively. From the weight loss curve at 1873 K, we can forecast that the SiC-MoSi<sub>2</sub> multi-coating could protect C/C composites from oxidation at 1873 K for 400 h. At 1973 K, the SiC-MoSi<sub>2</sub> multi-coating could provide an oxidation resistance of almost 50 h. Up to now, the anti-oxidation property of the SiC-MoSi<sub>2</sub> multi-coating is in a leading position.

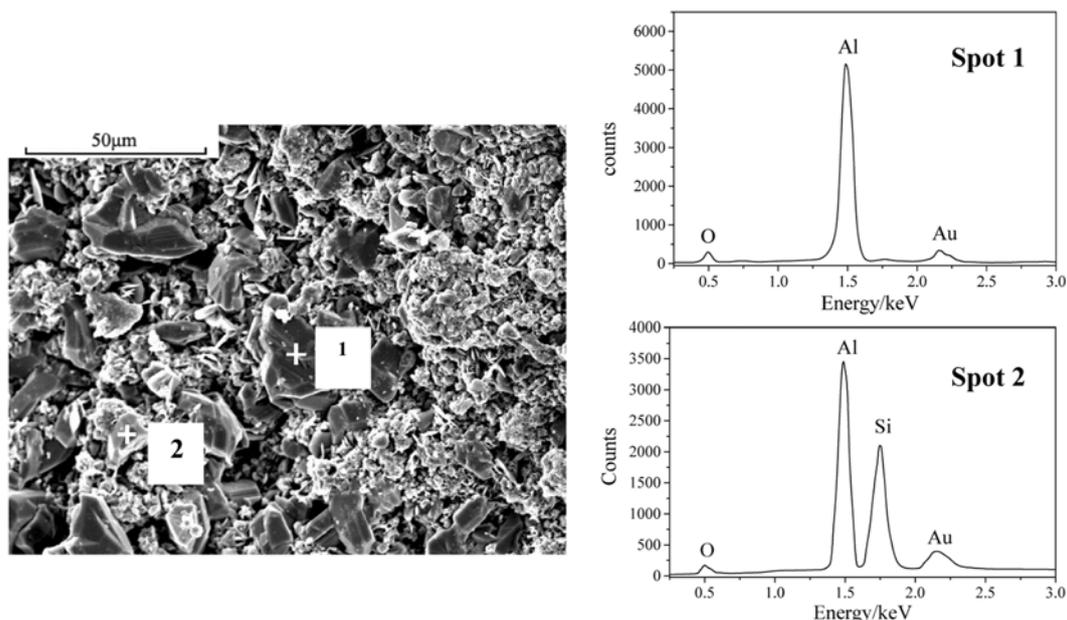
## 2.3. Silicate ceramic coating

### 2.3.1. Al<sub>2</sub>O<sub>3</sub>-Mullite-SiC multi-coating

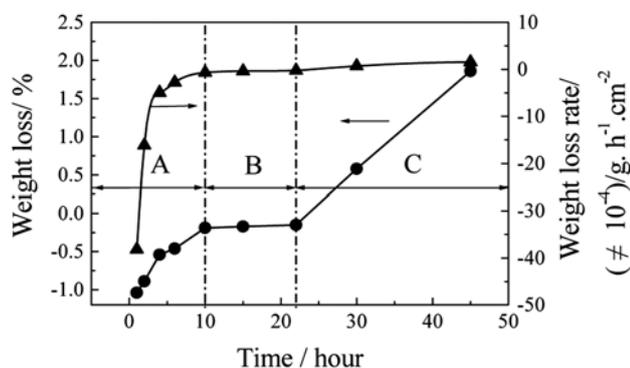
Mullite-Al<sub>2</sub>O<sub>3</sub>-SiC oxidation protective coating was prepared by a two-step pack cementation process [16, 17]. Pack chemistries for the pack cementation process were as follows: 40-45 wt.% Si, 38-42 wt.% SiC, 3-6 wt.% C and 5-9 wt.% Al<sub>2</sub>O<sub>3</sub> for the first process, and 22-29 wt.% SiO<sub>2</sub>, 50-60 wt.% Al<sub>2</sub>O<sub>3</sub>, 3-9 wt.% Si and 4-8 wt.% C for the second process. The first pack cementation was conducted at 1873 K for 2 h, and the second one was performed at 2073 K for the same time [18].

From the microstructure of the multi-coating surface on C/C composites (Fig. 15), there are two kinds of crystalline particles (characterized as grey and white) in the coating. By EDS analysis, the grey and white phases could be discriminated as corundum (1) and mullite (2), respectively. The corundum particles are bigger than the mullite ones and most of the holes among the corundum particles are filled with small mullite crystallites.

The results of the isothermal oxidation test in air at 1873 K are shown in Fig. 16. After oxidation in air for 45 h, the weight loss of the coated C/C composites is only 1.86%, and the corresponding weight loss rate is  $1.51 \times 10^{-4} \text{ g/cm}^2\text{-h}$ . According to the oxidation curve showed in Fig. 16, the oxidation behavior of the coated C/C composites could be divided into three processes, marked as A, B and C, respectively. With the oxidation less than 10 h (process A), the sample gains weight due to the formation of SiO<sub>2</sub> glass. From 10 to 22 h (process B), the weight loss rate of the



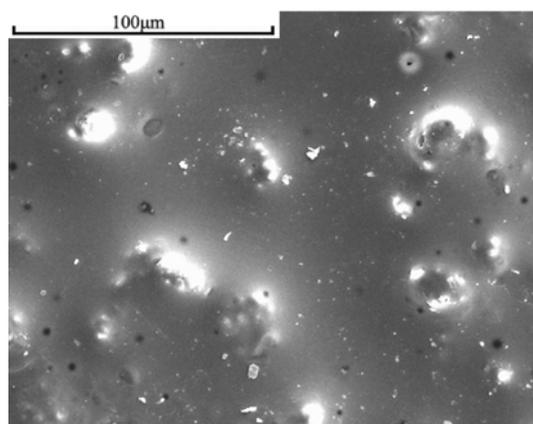
**Fig. 15.** A SEM micrograph and spot EDS analyses of the surface of the 'as-prepared' multi-coating on C/C composites. 1: aluminum oxide 2: mullite.



**Fig. 16.** Isothermal oxidation curves of the C/C composites with a multi-coating in air at 1873 K. The negative weight loss means weight gain.

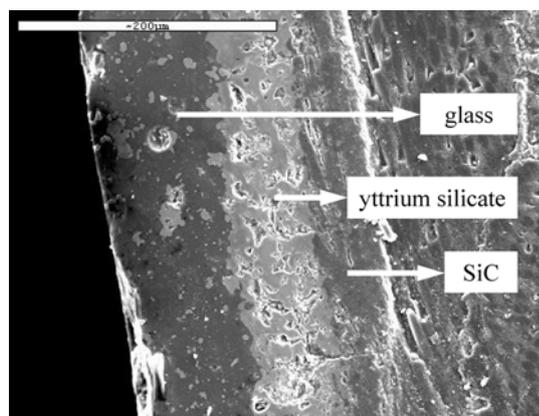
sample is almost constant. Above 22 h (process C), the weight loss rate increases linearly with the prolonging of oxidation time. Additionally, the sample has endured thermal cycling between 1873 K and room temperature for nine times, and no cracks and destruction were found, from which it can be inferred that the coating has excellent thermal shock resistance. After 45 h oxidation at 1873 K in air, the coating surface was observed with the scanning electron microscope, and it was found that a smooth glass layer was formed on the coating surface (Fig. 17). It also displays that some small holes and big gas bubbles were formed on the coating surface, which resulted in the failure of the coating.

### 2.3.2. SiC/Yttrium silicate/glass multi-layer coating SiC/gradient composition yttrium silicate/glass multi-layer



**Fig. 17.** Morphology of the multi-coating on C/C after oxidation at 1873 K for 45 h.

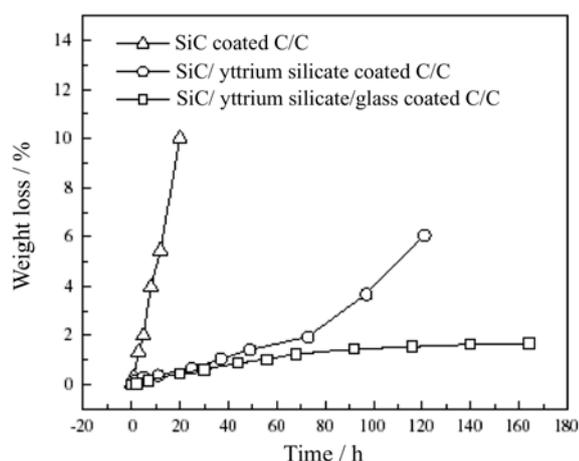
coatings were designed and prepared on C/C composites [19]. The SiC coating was prepared by pack cementation process with Si, C and  $\text{Al}_2\text{O}_3$  powders in an argon atmosphere at 2073 K for 2 h [20]. The  $\text{SiO}_2\text{-Y}_2\text{O}_3$  powder of different composites was synthesized and applied to SiC coated C/C composites by a plasma spray method. The sample surface was first coated with  $2\text{SiO}_2\text{-Y}_2\text{O}_3$ , then with  $1.5\text{SiO}_2\text{-Y}_2\text{O}_3$  and  $\text{SiO}_2\text{-Y}_2\text{O}_3$  in turn. The starting composition of the borosilicate glass was  $\text{SiO}_2$  68-72 wt.%,  $\text{Al}_2\text{O}_3$  1.5-3 wt.%,  $\text{B}_2\text{O}_3$  15-20 wt.%,  $\text{BaO}$  1.5-5 wt.% and  $\text{SrO}$  1.5-5 wt.%. The slurry made by mixing the borosilicate glass powder (75 wt%),  $\text{MoSi}_2$  (25 wt%) and ethanol was brushed to the surface of yttrium silicate coating. The samples were then heated at 1773 K in Ar for 2 h.



**Fig. 18.** A cross-section image of the SiC/yttrium silicate/glass coating.

The cross-section of the multi-layer coatings shows an obvious three-layer structure (Fig. 18). The thickness of the SiC bonding layer, yttrium silicate coating and glass outer-layer are around 70, 90 and 100  $\mu\text{m}$ , respectively. No gaps among the three layers and no obvious interfaces among the three different compositions of yttrium silicate are observed, which show good bonding between them. Though some pores can be found in the yttrium silicate coating, they are isolated each other and have almost no negative effect on the oxidation resistance of the coating.

Fig. 19 shows the isothermal oxidation curves of the samples at 1773 K. It can be seen that the SiC coated C/C composites reach almost 20% burn-off within 20 h. For the gradient composition yttrium silicate/SiC coated C/C, no obvious weight loss was measured within 10 h oxidation at 1773 K. After oxidation for 72 h, the weight loss of the coated sample was only 1.93%, while more than 73 h, the weight loss rate was increased rapidly with extending oxidation time.



**Fig. 19.** Isothermal oxidation curves of the coated samples at 1773 K in air.

The failure of the yttrium silicate coating was thought to be the reaction between yttrium silicate and  $\text{Al}_2\text{O}_3$  support [21]. Adding a glass outer layer, the oxidation resistance of the coated C/C was improved largely. After oxidation at 1773 K in air for 164 h, the weight loss was only 1.65%, which indicates that the SiC/gradient composition yttrium silicate/glass multi-layer coatings possess an excellent anti-oxidation property.

### 3. Summary

C/C composites possess unique mechanical properties at high temperatures. In non-oxidizing environments they can retain room temperature mechanical property above 2500 K. Oxidation protective coating is an efficient method for applying C/C composites in oxidizing environments.

In static air, phosphate, borosilicate, SiC, Si-MoSi<sub>2</sub>, SiC-MoSi<sub>2</sub>,  $\text{Al}_2\text{O}_3$ -mullite-SiC and SiC/yttrium silicate/glass coatings exhibit excellent oxidation resistance and thermal stress resistance. All the above coatings could offer a smooth glass scale during exposure to an oxidizing atmosphere, which could act as the self-sealing material and efficiently prevent oxygen from diffusing through the coatings to the C/C matrix.

Though the anti-oxidation methods for C/C composites in static air at temperatures below 1973 K have been studied, the more efficient coatings are still expected to develop further. The research direction of oxidation protective coating for C/C composites in future may be as follows:

(1) To develop higher-performance coatings for C/C composites and to achieve the requirements for a long-term application in air at temperatures above 1973 K.

(2) To prepare steady coating systems used in a gas-combustion and eroding environment at high temperatures for a long-term application.

(3) To apply the 'as-prepared' high-performance coatings on the surface of large-scale C/C components successfully.

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