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Journal of the European Ceramic Society 30 (2010) 3267–3270

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Technical note

$MoSi_2$-based oxidation protective coatings for SiC-coated carbon/carbon composites prepared by supersonic plasma spraying

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Received 10 March 2010; received in revised form 3 June 2010; accepted 15 June 2010
Available online 11 July 2010

Abstract

To protect carbon/carbon (C/C) composites against oxidation, $MoSi_2$-based oxidation protective coatings for SiC-coated carbon/carbon composites were prepared on them by supersonic plasma spraying. The $MoSi_2$-based coatings primarily consist of $MoSi_2$, Mo_5Si_3 and glassy SiO_2. Only a few pinholes and some microcracks are observed on the surface and no through-thickness cracks penetrate the cross-section. Weight loss of the $MoSi_2$-based coated specimens is only 1.14% after 400 h oxidation in air at 1773 K and the coated C/C composites remain intact after 11 thermal cycles between 1773 K and room temperature. The outstanding anti-oxidation ability is mainly attributable to the formation of SiO_2-based layer on the surface of $MoSi_2$-based coatings.

Keywords: Carbon/carbon composites; SiC; $MoSi_2$-based coatings

1. Introduction

Due to their excellent mechanical properties and thermal shock resistance, carbon/carbon (C/C) composites have been considered as one of the most important materials for the nozzle and throat parts of aircraft engine that require thermal stability.[1] However, the easy oxidation of C/C composites at temperatures above 723 K greatly limits their applications in oxygen-containing atmosphere.[2]

Multi-layer coatings are efficient method to protect C/C composites from oxidation at high temperatures.[3] Because of its good physical and chemical compatibility, SiC is widely used as the bonding layer between C/C composites and outer layers.[4,5] $MoSi_2$ has a high melting point and excellent high-temperature oxidation resistance and corrosion resistance, which makes it an attractive material as an outer layer in an oxidative atmosphere at high temperatures. Up to now, a number of coating techniques, such as slurry,[6] chemical vapor deposition[7] and pack cementation,[8] have been used to obtain $MoSi_2$-based coatings. However, these techniques have some limitations. For example, the $MoSi_2$-based coatings prepared by slurry and chemical vapor deposition have a weak bonding strength, in this case, the coatings might be easily blown off by erosion air at high temperature. Free Si is inevitably existent in the $MoSi_2$ coatings prepared by pack cementation, leading to holes and cracks in the coatings. Supersonic plasma spraying with plasma temperature in the region of 10,000 K and in jet velocities of up to 600 m/s is a novel method to prepare coating. The powders are carried and delivered into the plasma jet by gas. After being melted and accelerated, the powders impinge on the substrate to form a compact coating.[9,10] Up to now, few literatures have been published on the preparation of $MoSi_2$-based coatings for C/C composites by supersonic plasma spraying technique.

In the present work, in order to improve the oxidation resistance of C/C composites, $MoSi_2$-based coatings were prepared on the surface of the SiC-coated C/C composites by supersonic plasma spraying. The microstructures and oxidation protective ability of the coatings were investigated.

2. Experimental details

Specimens (Ø5 mm × 15 mm) used as the substrates were cut from bulk 2D C/C composites with density of 1.70 g/cm^3.

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doi:10.1016/j.jeurceramsoc.2010.06.007

Table 1
Details of the spraying parameters for the $MoSi_2$-based coatings.

Spraying voltage	370–400 V
Spraying current	115–140 A
Primary gas (Ar) flow rate	3.6–4.4 m^3/h
Secondary gas (H_2) flow rate	1.0–1.5 m^3/h
Carrier gas (Ar) flow rate	0.016–0.024 m^3/h
Powder feed rate	About 20 g/min
Spraying distance	100 mm
Nozzle diameter	5.5 mm

After abraded with 100, 300 and 500 grits SiC paper, the specimens were ultrasonically cleaned in acetone, and then were dried at 373–423 K for 1–2 h. The SiC bonding layer was prepared by pack cementation with Si, C, and Al_2O_3/B_2O_3 powder in an argon atmosphere at 1973–2173 K for 2 h. The preparation details were reported elsewhere.[11] The outer $MoSi_2$-based coatings were prepared by supersonic plasma spraying. The $MoSi_2$ powders provided by Zhengzhou Songshan Heating Elements Co., Ltd., China were used as spraying powders. Their purity is higher than 99.9 wt.%, and the particle diameter is about 10 μm. The spraying system consists of plasma torch, powder feeder, gas supply, water cooling circulator, control unit with PC interface and power supply unit. Details of the spraying parameters were listed in Table 1.

The specimens were heated at 1773 K in air with an electrical furnace to investigate the isothermal oxidation behavior. After due time oxidation, the samples were directly removed from the furnace and quickly cooled to room temperature. The specimens were weighed at room temperature by an electronic balance with a sensitivity of ±0.1 mg before and after the oxidation. Cumulative weight changes (weight loss percentage, %) of the samples were calculated and reported as a function of oxidation time. The morphology and crystalline structure of the $MoSi_2$-based coatings were analyzed by scanning electron microscopy (SEM, JSM 6460), X-ray diffraction (XRD Rigaku D/max-3C) with a Cu Kα radiation of wavelength 0.154 nm, energy dispersive spectroscopy (EDS, INCA) and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra) with a monochromatic Al Kα source.

3. Results and discussion

Fig. 1 shows the surface XRD of the $MoSi_2$-based coatings. It can be seen that the coatings consists of $MoSi_2$ and Mo_5Si_3. Besides an amorphous SiO_2 phase should be formed in the coatings because of rapid solidification after plasma spraying. During the process of spraying, the plasma arc temperature could reach around 10,000 K, where $MoSi_2$ powders could be quickly molten and react with oxygen in air according to Eqs. (1) and (2). Because of the volatilization of MoO_3 at high temperature, there are only $MoSi_2$, Mo_5Si_3, and SiO_2 in the coatings. Table 2 displays the surface EDS analyses of the $MoSi_2$-based coatings. The O, Si and Mo element content in the coatings is 14, 45, and 41 at.%, respectively. Moreover, the mole of percentage content of $MoSi_2$, Mo_5Si_3 and SiO_2 calculated by law of conservation of mass, is about 40, 28 and 32%, respectively. At high temperatures, SiO_2 in the coatings with low viscosity and good fluidity could effectively seal the pores or cracks on the coatings surface. Moreover, in high-temperature application, high creep resistance of materials is required. Mo_5Si_3 has significantly higher creep resistance compared to $MoSi_2$, which improves the creep resistance of the $MoSi_2$-based coatings. Therefore the partial oxidation of $MoSi_2$ powders has no negative effect on the oxidation resistance of the coatings.

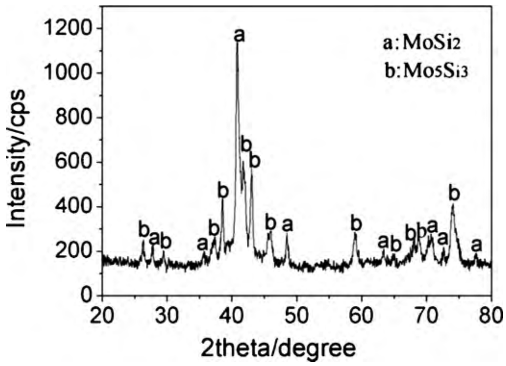

Fig. 1. XRD pattern of the $MoSi_2$-based coatings.

$$2MoSi_2 + 7O_2 = 4SiO_2 + 2MoO_3 \tag{1}$$

$$5MoSi_2 + 7O_2 = Mo_5Si_3 + 7SiO_2 \tag{2}$$

Fig. 2(a) shows the surface morphology of the $MoSi_2$-based coatings. The coatings surface is dense, only some microcracks and a few pinholes can be observed. The cross-section image (Fig. 2(b)) shows that the $MoSi_2$-based coatings are about 50 μm in thickness without penetrating crack or hole. Moreover, no obvious crack and hole at the interface between the inner SiC coating and the outer $MoSi_2$-based coatings are observed, which indicates a good bonding.

Fig. 3 presents the isothermal oxidation curves of the coated C/C composites at 1773 K in air. The weight loss of the monolayer SiC-coated C/C composites increases quickly along with oxidation and reaches to 7.4% after oxidation for only 9 h. After applying supersonic plasma spraying to $MoSi_2$-based coatings, the oxidation resistance of the samples increases significantly, and the weight loss is only 1.14% after oxidation for 400 h. The oxidation protective ability is superior to those of the SiC/Si-Mo coatings prepared by slurry[6] or pack cementation.[8] The oxidation behavior of $MoSi_2$-based coatings for SiC-coated C/C composites can be divided into three processes from the oxidation curves (Fig. 3). In the first stage of oxidation (0–330 h), SiO_2 in the coatings with low viscosity and good fluidity could effec-

Table 2
Surface EDS analyses of the $MoSi_2$-based coatings.

Element	Atomic%
O K	14
Si K	45
Mo L	41
Total	100

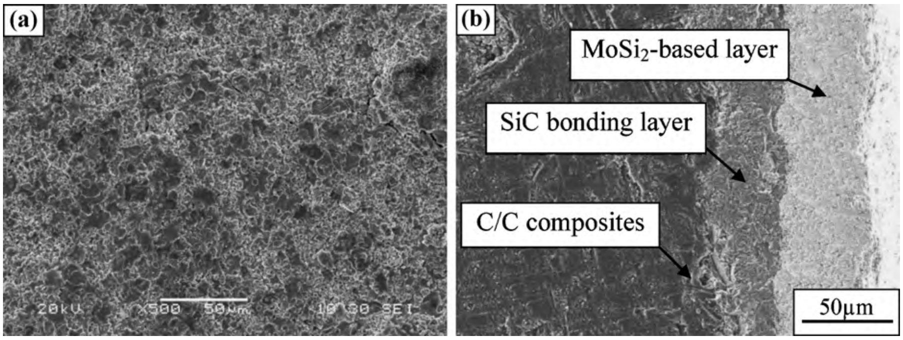

Fig. 2. SEM micrographs of the $MoSi_2$-based coatings (a) surface morphology, (b) cross-section.

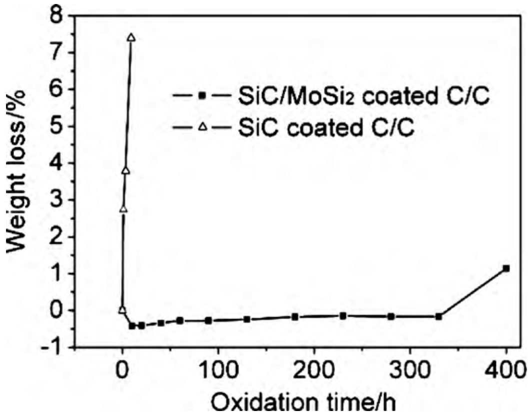

Fig. 3. Isothermal oxidation curves of the coated C/C samples in air at 1773 K.

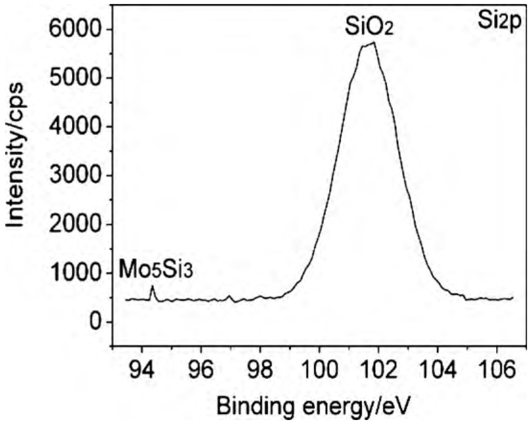

Fig. 4. XPS Si_{2p}-spectra of the surface of the coatings after oxidation for 400 h.

tively seal the pores or cracks on the coatings surface, which reduces the partial pressure of oxygen, $MoSi_2$ in the coatings is selectively oxidized to form Mo_5Si_3 and SiO_2 as Eq. (2), so the coated specimen exhibits mass gain. As the oxidation time prolonged, $MoSi_2$ is completely consumed, and Mo_5Si_3 begins to be oxidized to generate MoO_3 and SiO_2 according to Eq. (3), which is the main reason for the weight loss of the specimens after oxidation for 330 h.

$$2Mo_5Si_3 + 21O_2 = 10MoO_3 + 6SiO_2 \qquad (3)$$

Fig. 4 shows the XPS Si_{2p}-spectra of the surface of the coatings after oxidation for 400 h. The coating consists of SiO_2 and a small quantity of Mo_5Si_3. During oxidation test, SiO_2 is of low viscosity and good fluidity, and can efficiently fill microcracks and pinholes in the coatings to form a smooth glass layer with low diffusion coefficient of oxygen. So the outstanding oxidation protective ability of the coating mainly attributes to the formation of SiO_2-based film on the surface of $MoSi_2$-based coatings.

Fig. 5 exhibits microstructures of the surface and cross-section of the $MoSi_2$-based coatings after oxidation for 400 h. A smooth layer with some microcracks can be found on the surface of the coatings (Fig. 5(a)). These microcracks are resulted from the fast cooling from 1773 K to room temperature. They can self-heal at high temperature due to their small dimension. Moreover, no hole or penetrating crack are found from the cross-section image (Fig. 5(b)), indicating that the coatings have excellent oxidation protective ability. Compared with the cross-section image of the coating before oxidation, a SiO_2-based glass layer

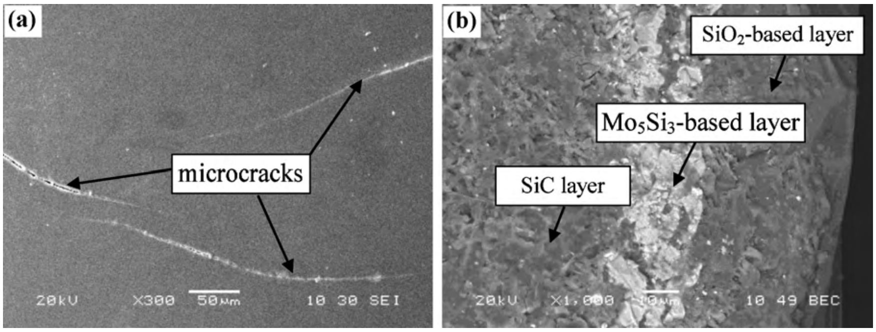

Fig. 5. SEM images of the $MoSi_2$-based coatings after oxidation for 400 h (a) surface morphology, (b) cross-section.

is formed on the surface of the $MoSi_2$-based coatings, and the $MoSi_2$-based layer change into Mo_5Si_3-based layer, owing to the oxidation of $MoSi_2$ according to Eq. (2).

In addition, the specimens endured 11 thermal cycles between 1773 K and room temperature during the oxidation test, and no visible hole or spallation were found on the surface of the $MoSi_2$-based coatings. Therefore, it is concluded that the coatings have excellent thermal shock resistance. It might be attributed to the good match of thermal expansion coefficient between the $MoSi_2$-based coatings and the inner SiC layer.

4. Conclusions

Dense $MoSi_2$-based coatings have been prepared on SiC-coated C/C composites by supersonic plasma spraying. It primarily consists of $MoSi_2$, Mo_5Si_3 and SiO_2, and possesses excellent oxidation protective ability. It can effectively protect SiC-coated C/C composites from oxidation for more than 400 h at 1773 K in air. The outstanding oxidation protective ability mainly attributes to the formation of SiO_2-based layer on the surface of $MoSi_2$-based coatings.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China under grant no. 90716024 and no. 50802075, and the “111” Project under grant no. 08040, and supported by NWPU Foundation for Fundamental Research and the Foundation of the State Key Laboratory of Solidification Processing in NWPU.

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