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Microstructure characteristics of silicon carbide coatings fabricated on C/C composites by plasma spraying technology

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Abstract

A functional gradient SiC coating on C/C composites has been developed using a novel process which is the combination of plasma spraying technology with reaction-formed heat-treatment. Microstructure observation and phase identification of the SiC coatings were analyzed by scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. Experimental results showed that a uniform silicon coating was deposited on C/C composite by plasma spraying technology. The reaction between the silicon coating and C/C substrate occurred during the heat-treatment at temperature of 1450 °C and 1600 °C in argon environment, respectively. A continuous SiC coating was formed on the surface of the C/C substrate. And a layer of SiC/C convention layer was formed on the near-surface area of the substrate, which was resulted from the molten silicon penetrating into the open pores and consequently reacting with the C/C composites. The thickness of the formed SiC coatings was closely related to the original silicon coatings.

Keywords: SiC coating; Plasma spraying technology; Microstructure; Heat-treatment

1. Introduction

Carbon fiber reinforced carbon (C/C) composites are outstanding high-temperature structure candidate materials for their many unique properties, such as low density, high strength, high thermal shock resistance and excellent retention of mechanical properties at high temperature. However, the applications of C/C composites are commonly limited to inert atmospheres and vacuum environment owing to their oxidation character. C/C composites can be oxidized above 450 °C in an environment containing oxygen and the oxidation rate increases fast with increase in temperature. Therefore, studies concentrated on the oxidation mechanisms of C/C composites and ways to protect the composites to highest possible temperature have been developed simultaneously with the development of C/C composites. It has been realized that surface coating is the most effective process for improving the resistance to oxidation of C/C composites, especially at high temperature (>1000 °C) [1,2].

Silicon carbide was selected as a wonderful protective coating to carbon materials from the standpoint of its capability to resist oxidation, high melting point and its physical compatibility with C/C composites. SiC coatings were not only applied as single protective coatings but also used as an internal buffer layer in multilayer coating systems for C/C composites [3,4]. Two types of processes are generally applied to fabricate SiC coating on C/C substrates: chemical vapor deposition (CVD) and carbothermal reduction [5]. CVD is popular for its convenience and continuous reaction process. While the SiC coating prepared by CVD technology is dense, its poor compatibility with C/C usually results in crack formation. Therefore a secondary treatment is often required after the fabrication of CVD-SiC [6–8]. Carbothermal reduction is a reactive formation process, whereby C/C substrates are surrounded by and heated together with silicon

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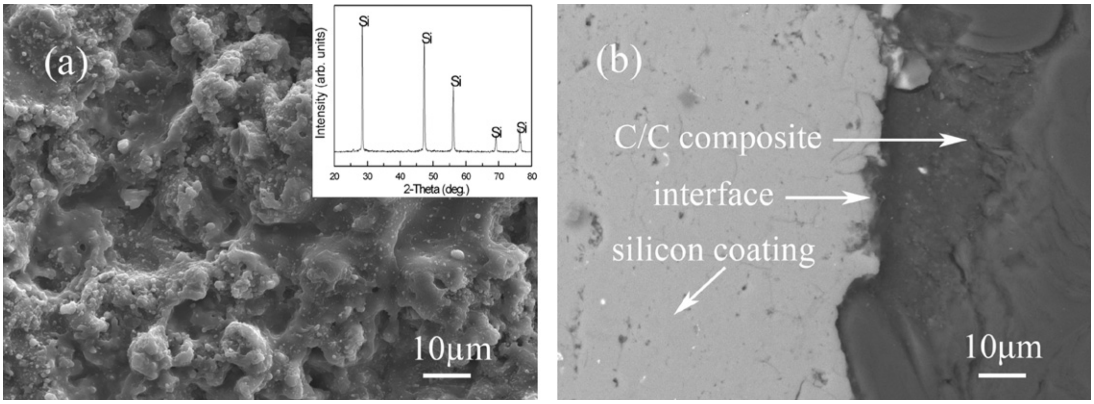

Fig. 1. The surface and cross-section morphologies of plasma sprayed silicon coatings.

Table 1
Preparation conditions of plasma sprayed silicon coatings.

Parameters	Values
Chamber pressure (mbar)	100
Spray distance (mm)	300
Power (kW)	42.0
Primary gas/Ar (slpm)	50
Secondary gas/H_2 (slpm)	10
Powder feed rate (g min^{-1})	10.0

powder or silicon compounds in a reactor. The coatings prepared by carbothermal reduction possess a gradient distribution of SiC in the C/C substrate, which results in reduced stress produced by different coefficients of thermal expansion, therefore they have a good compatibility with C/C substrate. However, the surface of the sample prepared by carbothermal reduction method is not easy to be cleaned after fabrication and the thickness of the formed SiC coating is non-uniform [9,10].

Plasma spray technology is widely applied in traditional fields for its high deposition rate, capability of handling complex extended surfaces and relatively low cost. During the spraying process, powder is sent to the center of the plasma flame, where the temperature is high to several thousands centigrade, and melted, speeded up to impact on the substrate or the pre-deposited layer, forming the coatings. Plasma sprayed coatings normally have dense and uniform microstructure. Due to the characteristic of plasma spraying technology, it is especially suitable for the fabrication of coating materials of high melting point, such as B_4C, ZrB_2, W and so on [11–13]. However, SiC decomposes at 2300 °C and vaporizes directly at 2700 °C when it is heated to high temperature, therefore SiC coating could not be fabricated directly by plasma spraying technology [14].

In the present work, a new process of preparing SiC coating for C/C composites was developed upon the combination of the plasma spraying technology with the conventional reaction-formed process. Silicon coatings were fabricated on the surface of C/C composites using plasma spraying technology and then they were heat-treated in protective environment. The influences of temperature on the formation process of SiC coatings were analyzed and the microstructure of the formed SiC coatings was characterized.

2. Experimental procedures

2.1. Materials

The composite used was a bulk-needled-felt reinforced carbon composites with density of 1.72×10^3 kg/m^3 which was fabricated at Shanghai University, China. Specimens with the size of 10 mm × 15 mm × 5 mm were cut from the composite plates. The C/C substrate samples were grit-blasted with alumina abrasive and cleaned in alcohol using supersonic machine. Then they were dried at 120 °C for 1 h for the plasma spraying deposition. Commercially available silicon powders having purity of 99.0% (Nan'an Sanjing Silicon Refining CO., Ltd., China) were used as the feedstock for the fabrication of silicon coatings. The grain size of the silicon particles ranged from 10 μm to 80 μm.

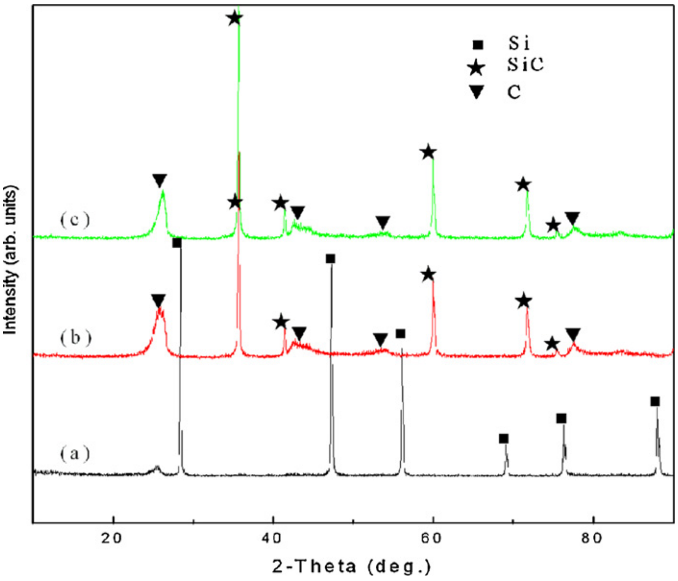

Fig. 2. XRD patterns of silicon coatings after heat-treatment at different temperatures for 1 h: (a) 1200 °C, (b) 1450 °C, (c) 1600 °C.

2.2. *Coating preparation and characterization*

The coating specimens were deposited with a Metco A-2000 vacuum plasma spraying equipment (Sulzer Metco F4-VB type gun, Switzerland). Argon and hydrogen were used as the plasma forming gases. The Twin-System (Plasma-Technick, Switzerland) was applied for a powder feeding. The used plasma spraying parameters are summarized in Table 1. After the preparation of silicon coating, the samples were heat-treated in an argon atmosphere at 1200 °C, 1450 °C and 1600 °C for 1 h, respectively.

The morphologies of the surface and cross-section of the coatings before and after heat-treatment were observed using a field emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Japan). The chemical composition of the coatings was analyzed by energy dispersive spectrometer (EDS, PN-5502, INCA ENERGY, UK). The phase composition of the coating was examined by an X-ray diffraction (XRD, RAX-10 X-ray diffractometer, Rigaku, Japan) operating with Cu Kα (λ = 1.54056 Å) radiation.

3. Results and discussion

3.1. *Characterization of plasma sprayed silicon coatings*

The surface and cross-section morphologies of the prepared silicon coating are illustrated in Fig. 1. Well-flattened splats and insufficiently flattened protuberances constituted the rough surface, which is the typical character of plasma sprayed coatings. The XRD pattern in the insert indicates that the coating consisted of cubic silicon having high crystallinity. From the cross-section morphology, it can be seen that the thickness of the as-received silicon coating was about 100 μm. The silicon coating was dense and small pores with sizes less

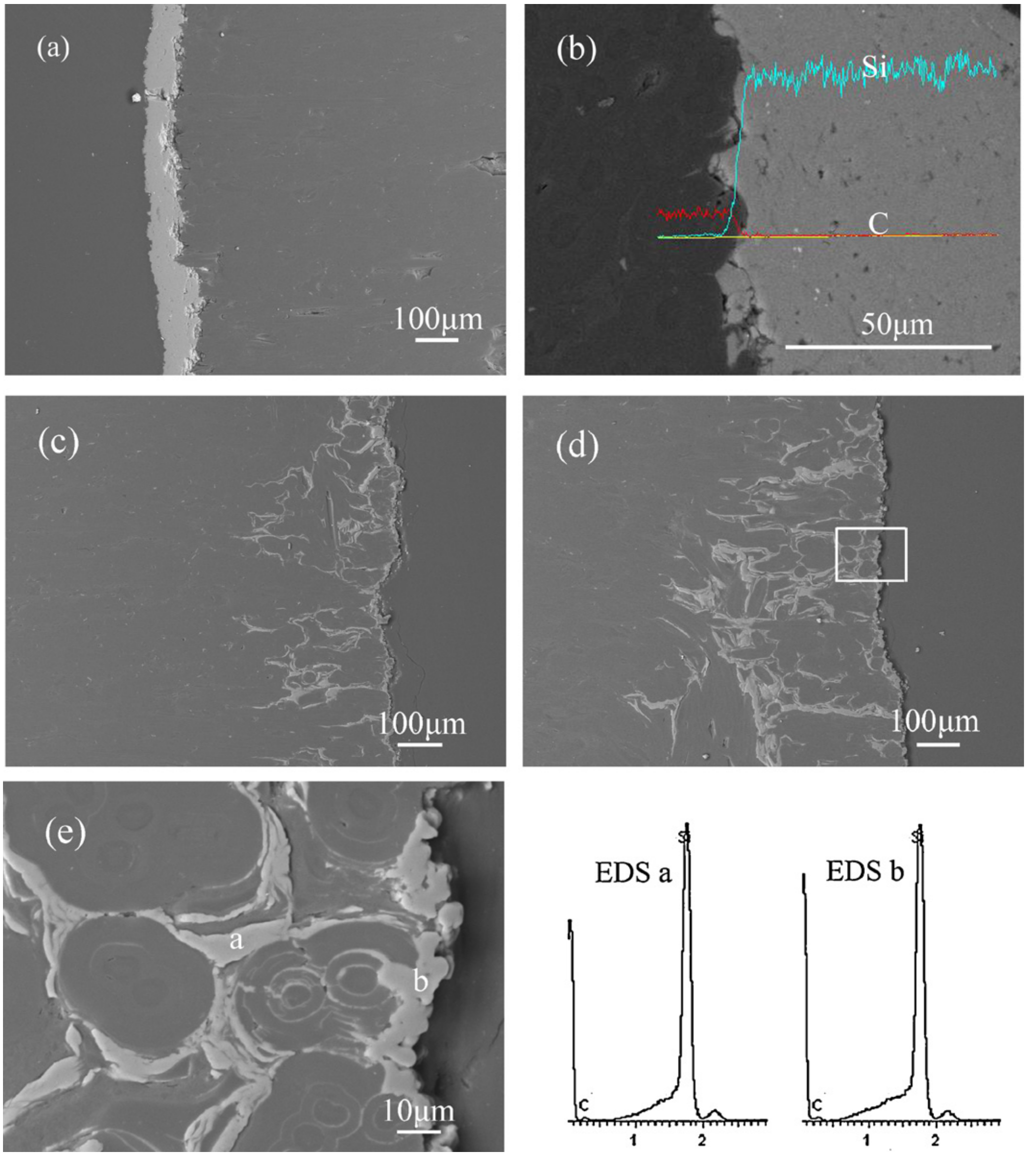

Fig. 3. The cross-section morphologies and EDS results of silicon coatings after heat-treatment at different temperatures for 1 h: (a) and (b) 1200 °C, (c) 1450 °C, (d) 1600 °C, (e) high magnification of (d).

than 5 μm randomly distributed in the coating. The interface of the as-sprayed coating and the C/C substrate was tight.

3.2. Characterization of silicon carbide coating

Fig. 2 illustrates the XRD patterns of the coatings after heat-treatment at different temperature for 1 h. For the sample treated at 1200 °C, only peaks corresponding to cubic silicon were presented, which was same to that of the original silicon coating. Strong peaks corresponding to β-SiC were detected for the samples treated at 1450 °C and 1600 °C, indicating that plasma sprayed silicon coating reacted with carbon and the reaction converted the surface of the C/C substrate into a layer containing crystalline SiC. The peak corresponding to carbon was also observed, which was supposed to originate from free carbon existing in the conversion zone or from the substrate beneath.

Fig. 3 shows the cross-sectional micrographs of the samples treated at 1200 °C, 1450 °C and 1600 °C, respectively. It can be seen that the microstructure of the coating treated at 1200 °C had little change compared with that of the original silicon coating (Fig. 3a). The interface of the coating and the C/C substrate was paid attention to and the distribution of element of Si and C was measured using EDS, as illustrated in Fig. 3b. The EDS results showed that no obvious SiC was detected. The melting point of silicon is about 1410 °C. According to the Si–C phase diagram, the reaction between Si and C could effectively take place over 1410 °C [14].

For the samples treated at 1450 °C and 1600 °C, a continuous thin SiC layer was observed on the top of the substrate, which was in accordance with the XRD results, as showed in Fig. 3c and d. The reaction mechanism between solid carbon and molten silicon has been studied and was proved that SiC was formed through a solution-reprecipitation mechanism

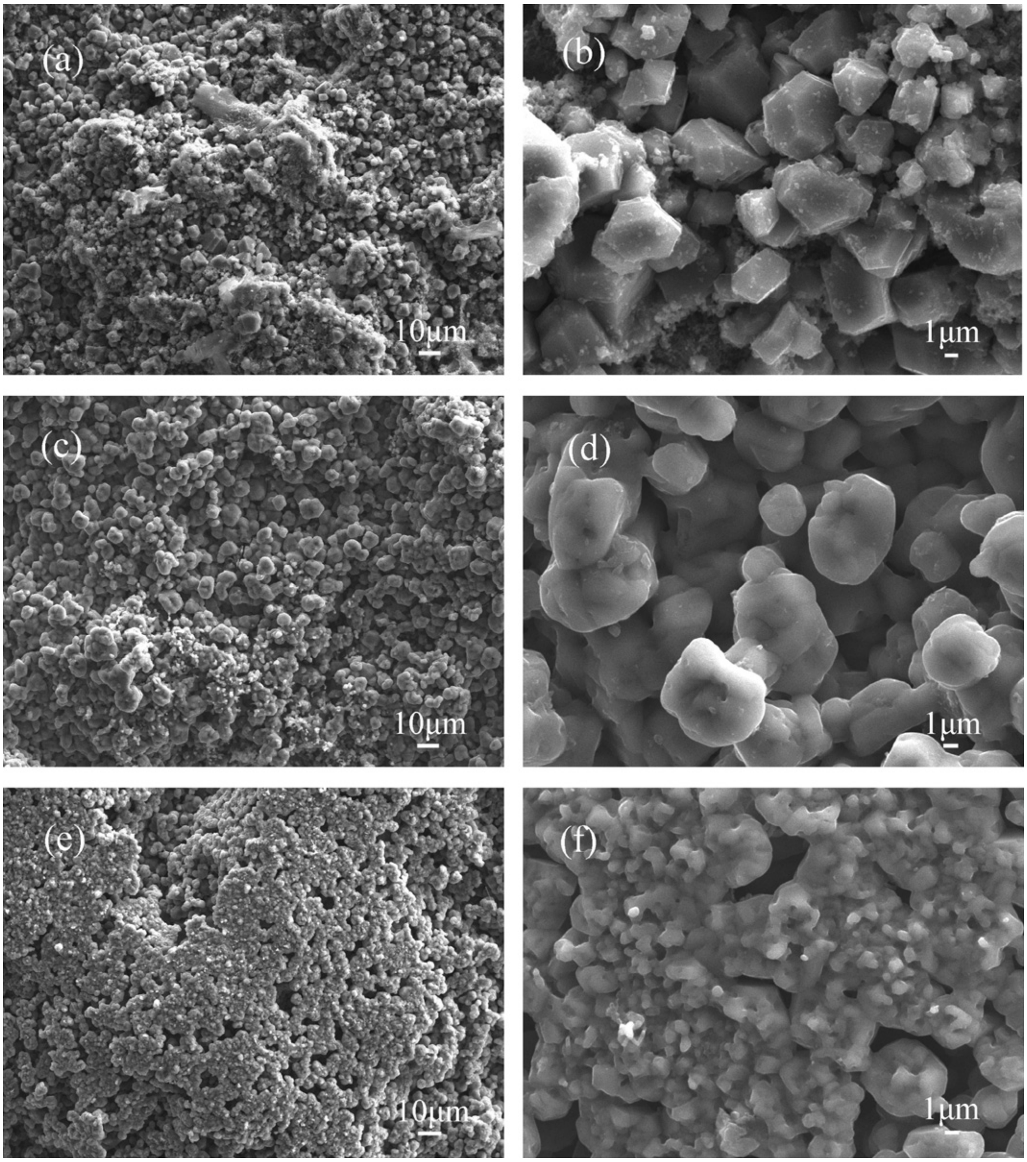

Fig. 4. The surface morphologies of silicon coatings after heat-treatment at different temperatures for 1 h: (a) and (b) 1200 °C, (c) and (d) 1450 °C, (e) and (f) 1600 °C.

on a micro-scale [15,16]. At the same time, silicon penetrated into deeper region through micropores or gaps between carbon fibers and cabon matrix. The EDS results proved that SiC was formed in the inside of the C/C composite, indicating that silicon infiltrated into the substrate and the reaction with carbon proceeded. As a result, open pores or gaps near the surface of C/C were filled by the formed SiC and a functionally gradient SiC/C conversion layer was produced as a top zone on the C/C composites [17]. This SiC/C convention layer was good for minimizing the thermal expansion mismatch between the C/C substrate and the SiC coatings on the surface of the substrate. Therefore it enhanced the adhesion force of the coatings on C/C substrates. It also can be seen that the thickness of the SiC/C convention layer increased with increase in temperature. For the same treatment time, the maximum thickness of convention layer was about 300 μm for the sample treated at 1450 °C, while it was about 500 μm for the ones treated at 1600 °C. The viscosity of silicon melt decreased with increase in temperature [18]. Therefore it was supposed that the viscosity change of silicon melt contributed to this phenomenon.

The surface morphologies of the samples after heat-treatment at different temperatures are presented in Fig. 4. It is found that the coating surface is greatly modified after the heat-treatment and is different from the original silicon coating. For the sample treated at 1200 °C, it can be seen that there are many silicon grains with irregular shape in different sizes of micrometers formed (Fig. 4a and b). The formation mechanism of small silicon grains was still unclear and needed further exploration. For the sample treated at 1450 °C, the shape of the formed particles changed to be nearly round and some particles connected with each other (Fig. 4c and d). Combined with the XRD result, it indicated that the isolated particles were SiC particles. From Fig. 4e and f, it can be seen that the sintering phenomenon of SiC particles happened for the sample treated at 1600 °C. Many SiC particles connected with each other. It can be seen that the surface morphologies of the samples were greatly different from each other and the formation temperature have influence on the surface morphologies of the coatings. Zhu et al. [19] prepared SiC coating at 1600 °C, 1800 °C, 1950 °C on graphite substrate, respectively. They also found that the microstructure of the formed SiC coatings was greatly affected by the temperature of formation.

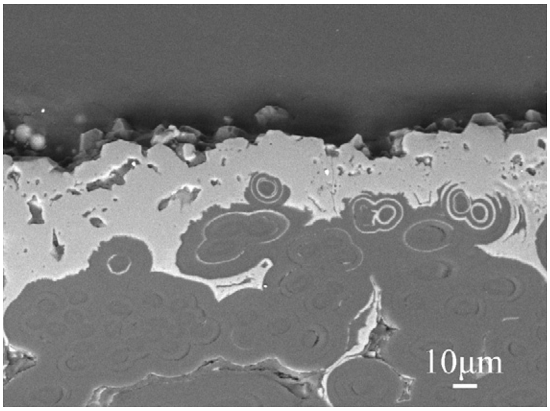

Fig. 5. Characterization of thick silicon coating after heat-treatment at 1600 °C for 1 h.

For analyzing the effect of the original silicon coating thickness on the formation of SiC coating, a thick silicon coating about 400 μm was also deposited on C/C substrate and the heat-treatment at 1600 °C for 1 h was preceded. It was found that silicon was totally converted to SiC and a SiC coating with thickness about 20–30 μm was formed on the surface of C/C composite, as presented in Fig. 5. The coating was compact, though some small pores existed in the interior of the coating. No microcracks was found in the coating. At the same time, the phenomenon of silicon infiltration and reaction with carbon took place and a SiC/C layer formed on the top area of the C/C substrate. The results indicated that thick SiC coating could be prepared by the presented method and the thickness of the previous silicon coatings have great influence on the thickness of the formed SiC coatings.

4. Conclusions

Silicon coatings were deposited on C/C composites using plasma spraying technology and then heat-treated at different temperature. It was found that no SiC was formed and the composition of the coating was not changed after the treatment at 1200 °C. SiC coating was formed on the surface of C/C composite by the reaction of silicon coating and the C/C substrate after treatment at the temperature above the melting point of silicon. And a gradient SiC/C layer formed at the top area of the substrate at the same time. The surface of the SiC coatings was composed of SiC particles. The thickness of the formed SiC coating was greatly influenced by the thickness of the original silicon coating. Thin (less than 10 μm) and thick (20–30 μm) uniform SiC coatings were formed using the presented method. The present work indicates that plasma spraying technology combining with heat-treatment could be a suitable method for fabricating protective SiC coatings on C/C composites.

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