

Preparation of oxidation-protective SiC coatings for C/SiC composites by pulsed chemical vapor deposition

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Single-layer SiC coatings and multilayer (C/SiC)_n coatings for oxidation protection of C/SiC composites were prepared by a pulsed chemical vapor deposition (pulsed CVD) method, a modification of pulsed chemical vapor infiltration (pulsed CVI). Pulsed CVD enabled the original pores in the substrates to be filled by the coatings, which contributed to improved adhesion between the coatings and the substrates. No deposition defects were observed in the dense SiC coatings. Multilayer (C/SiC)_n coatings could dissipate thermal stresses in the coatings, which reduced the number and width of micro-cracks in the coatings and accordingly improved the oxidation-protection capability of the coatings. Oxidation tests in dry air showed that the oxidation resistance of the coated composites was significantly improved compared with that of the uncoated ones.

Key words: C/SiC composites, SiC coatings, Pulsed CVD, Oxidation.

Introduction

Continuous carbon fiber reinforced silicon carbide (C/SiC) composites are very promising structural materials for high temperature applications, including for components of gas turbine engines, spacecraft re-entry thermal protection systems, attachments for hot section components, etc. [1-3]. The composites used in these applications are subjected to high temperature oxidizing environments for extended periods of time. However, C/SiC composites lack sufficient oxidation resistance because there are always channels for oxygen diffusion in the composites, including micro-cracks arising from mismatch in coefficients of thermal expansion between the matrices and the fiber reinforcements, and unavoidable residual pores during the preparation of the composites. Therefore, oxidation protective coatings are indispensable.

SiC is fundamental coating material for oxidation protection of C/SiC composites. Firstly, it is inherently matched with the substrate. Secondly, the oxidation of SiC is passive up to 1700 °C and the SiO₂ formed has a low oxygen diffusion coefficient and a certain ability to seal the coating cracks [4]. CVD SiC coatings have been intensively studied by some researchers. However, deposition defects and large amounts of micro-cracks existed in these coatings [5-10], which became channels for oxygen diffusion and lowered the protection effectiveness of the coatings. Besides, all those SiC coatings were prepared by isothermal isobaric low pressure CVD (LPCVD).

Pulsed CVI has been widely used for infiltration of C or SiC matrices within C or SiC fiber preforms to fabricate continuous fiber reinforced ceramic matrix composites [11-14]. In this technique, total pressure cycling is applied to periodically regenerate the entire gas phase. Each pulsed includes three steps: source gas loading; holding at the desired pressure; gas evacuation. This method allows deep infiltration of precursor gases followed by deposition of ceramic materials in the pores of the porous body.

In this study, pulsed CVI was modified to pulsed CVD to deposit single-layer SiC coatings and multilayer (C/SiC)_n coatings on C/SiC composites with a certain porosity. The microstructure of the coatings was studied and the coated composites were subjected to oxidation tests in dry air.

Experimental

Fabrication of specimens

A two dimensional C/SiC (2D C/SiC) composite was fabricated by a polymer precursor infiltration and pyrolysis (PIP) method using polycarbosilane (PCS) as precursor [15]. The total porosity of the as-prepared composite was 17%, with an open porosity of 5%. The as-received composite was machined and substrates with a size of 3 mm × 5 mm × 40 mm were obtained. Closed pores became open on the surface of the composite after machining.

Single-layer SiC coatings and multilayer (C/SiC)_n coatings were deposited on the supported substrates by pulsed CVD in a quartz tube in a horizontal furnace. The deposition temperature was maintained at 1050 °C. Methyltrichlorosilane (MTS) was used as the source of SiC and H₂ as the carrier gas. The carrier gas was bubbled through the MTS precursor which was maintained at 20-25 °C, and the molar ratio of H₂ to MTS was 4. Methane was used as source gas

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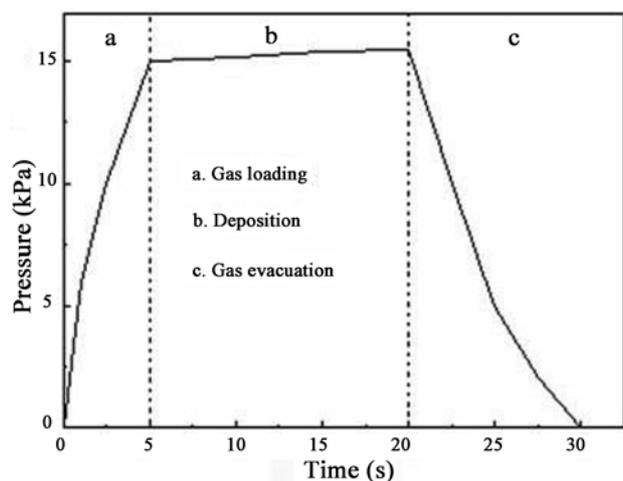


Fig. 1. A pressure sequence in the pulsed CVD process.

of C. The pulsed CVD process involved the following sequence, as represented in Fig. 1: (a) injection of the gaseous precursor in 5 s; (b) deposition of C or SiC by maintaining the pressure at 15 kPa for 15 s; (c) evacuation of the pulsed CVD reaction chamber down to vacuum, the reaction products and unreacted source species being pumped out of the chamber. Two single-layer SiC coatings with different thicknesses, 20 μm and 40 μm , were prepared by adopting different numbers of pressure pulses. Multilayer $(\text{C}/\text{SiC})_n$ coatings was prepared by multi-deposition. Firstly a C layer was deposited on the C/SiC composites, and then a SiC layer was deposited on the C layer. The deposition of C and SiC layers was repeated for 20 times and the number of pressure pulseds for each layer was controlled to obtain a proper layer thickness. Finally, a thick outermost SiC layer was deposited.

Oxidation tests

Oxidation tests in dry air were conducted at 1500 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$ on uncoated C/SiC composites, on C/SiC composites coated with the single-layer SiC coating 40 μm in thickness, and on C/SiC composites coated with multilayer $(\text{C}/\text{SiC})_n$ coatings. In the tests, the samples placed upon a corundum support were put inside or taken out of the furnace directly to air within about 15 s. The specimens were separately weighted after oxidation for 0 h, 5 h, 10 h, 15 h, 20 h and 25 h, and the relative weight changes of the specimens were calculated.

Characterization of specimens

X-ray diffraction analysis (XRD, D/Max 2550 v, Rigaku, Tokyo, Japan) was conducted on the prepared single-layer SiC coatings. The polished surface morphology of uncoated 2D C/SiC composites and surface and cross section morphologies of the SiC coatings were observed with a scanning electron microscope (SEM, JSM 6700F, JEOL, Tokyo, Japan), which was also used to observe the fracture surfaces of the oxidized uncoated and coated 2D C/SiC composites.

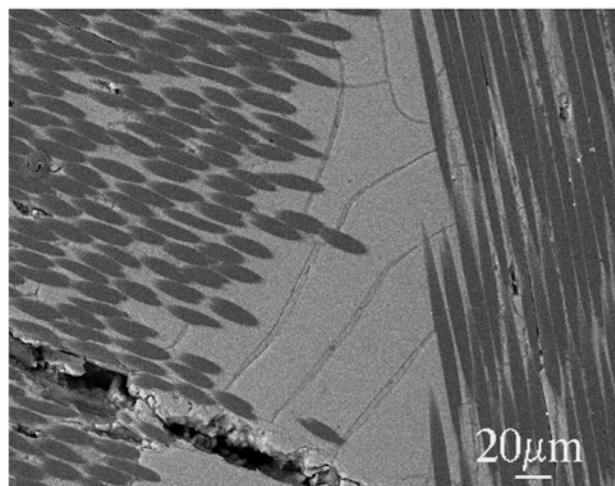


Fig. 2. Polished surface micrograph of a 2D C/SiC composite.

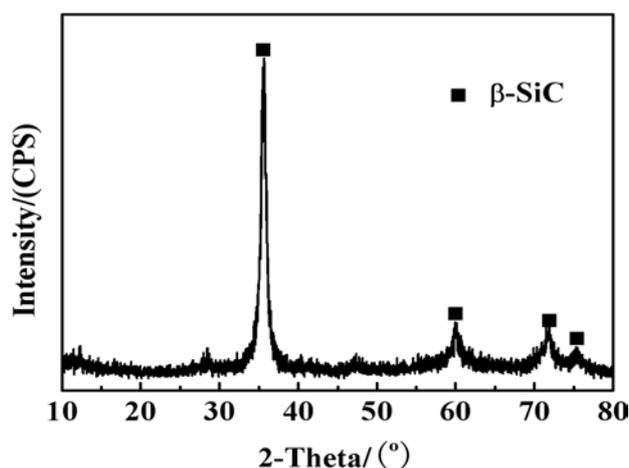


Fig. 3. XRD pattern of SiC coating.

Results and Discussion

Microstructure of the single-layer SiC coatings

Fig. 2 shows the polished surface morphology of an uncoated 2D C/SiC composite. It can be seen that pores existed in the composite. PIP involves the pyrolysis of a polymer precursor during which pores are formed due to gas evolution and volumetric shrinkage of the pre-ceramic polymer [16, 17]. These pores must be filled during the pulsed CVD process, otherwise they would become channels for oxygen diffusion in oxidizing environments.

An XRD pattern of the single-layer SiC coatings is shown in Fig. 3. All of the diffraction peaks belong to β -SiC, which reveals that pure phase SiC coatings were obtained by pulsed CVD.

Two single-layer SiC coatings with thicknesses of 20 μm and 40 μm respectively were prepared. Their surface and polished cross sectional morphologies are shown in Fig. 4 and Fig. 5, respectively. In Fig. 4(a) and Fig. 5(a), it is noticed that no original pores in the substrates are observed. They were completely filled by SiC particles in the

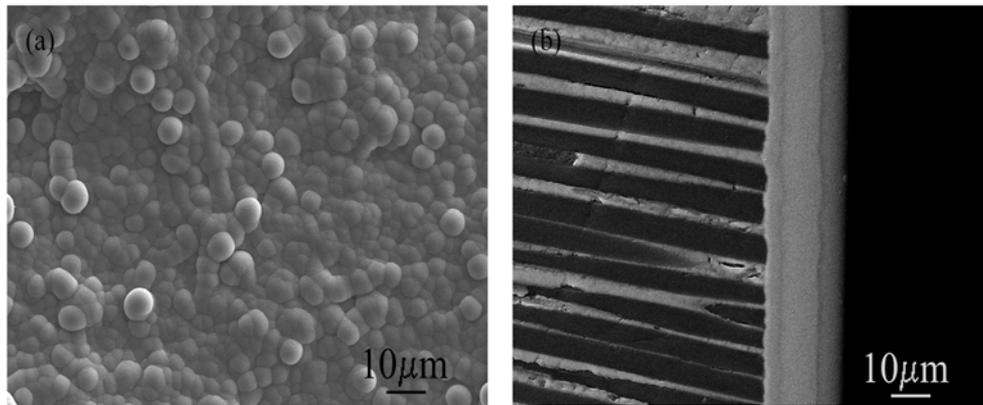


Fig. 4. Micrographs of the single-layer SiC coating with a thickness of 20 μm (a) surface, (b) polished cross section.

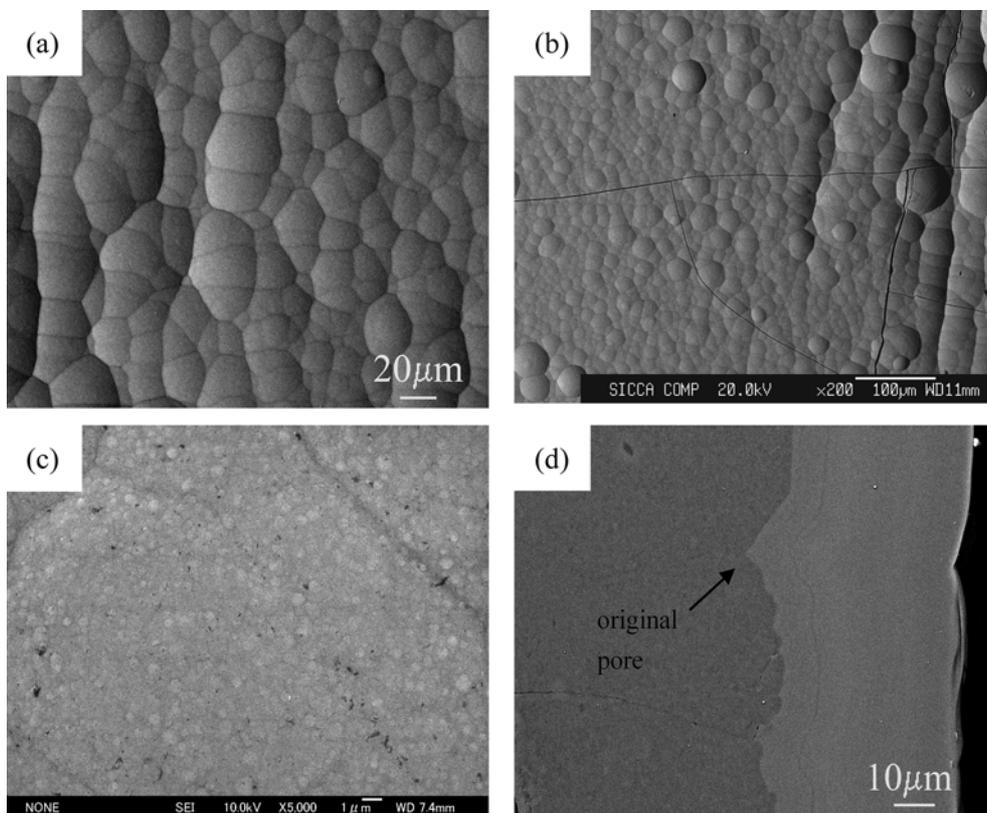


Fig. 5. Micrographs of the single-layer SiC coating with a thickness of 40 μm (a), (b) surface at low magnifications, (c) surface at a higher magnification, (d) polished cross section.

coatings after the pulsed CVD process. Pulsed CVD is a modification of pulsed CVI process, which has usually been used for infiltration of ceramic matrices within porous fiber preforms and has exhibited a capability to fill deep pores. At the end of each cycle in pulsed CVD process, the reaction chamber and the substrates were evacuated down to vacuum, which was obviously favorable to the infiltration of source gas in the pores in the substrates at the beginning of the next cycle. By contrast, in the conventional CVD process, the gaseous reaction products hinder the incoming of source gas into the pores. Therefore, pulsed CVD is more suitable for the deposition of coatings

on substrates with a certain porosity, such as oxidation-protective SiC coatings on C/SiC composites. Fig. 5(d) also shows that the original pores in the 2D C/SiC composites were filled. The filling of the pores in the substrate by particles in the coating led to better adhesion of the coating with the substrate.

Fig. 4(a) and Fig. 5(a) show that the SiC coatings were very dense, consisting of a large number of cloud-cluster shape spherical particles with a size of several micrometres. From the high magnification micrograph, Fig. 5(c), it can be determined that each particle was actually an aggregate composed of large amounts of nanometre SiC crystallites.

Polished cross sections of the two single-layer SiC coatings with thicknesses of 20 μm and 40 μm are shown in Fig. 4(b) and Fig. 5(d), respectively. The coatings adhered very well to the substrates, with no deposition defects. In order to control deposition defects in the SiC coatings prepared by low pressure CVD, the deposition rate must be very low (about 0.7 $\mu\text{m}/\text{h}$) [10], which led to an increase in preparation time. By contrast, the deposition rate in pulsed CVD was more than 2 $\mu\text{m}/\text{h}$.

The thickness of the coating was controlled by the number of pulses in the pulsed CVD process. The number of pulses for the SiC coating with a thickness of 40 μm was twice that for the one with a thickness of 20 μm . Accordingly, the duration of the whole pulsed CVD process for the 40 μm thick coating was twice that for the 20 μm thick one. From Fig. 4 (a) and Fig. 5 (a), it can be observed that the size of SiC particles in the 40 μm thick coating was much larger than that in the 20 μm thick one. It can be concluded that the longer the pulsed CVD process lasted, the larger the particles in the SiC coating were. Particles underwent growth as the deposition time was increased. However, it should be noted that each particle was an aggregate of large amounts of nanometre SiC crystallites. As the deposition time was extended, the size of SiC particles was increased, while that of SiC crystallites remained unchanged.

It can be seen from Fig. 5(b) that many micro-cracks existed in the SiC coating. The micro-cracks arose from mismatch in coefficients of thermal expansion (CTE) between the SiC coating and the C/SiC composite. In this study, the fibers in the C/SiC composite were T300 C fibers, whose CTEs along the fiber axis and in the fiber radial direction are $1.1 \times 10^{-6}\text{C}^{-1}$ and $6.8 \times 10^{-6}\text{C}^{-1}$, respectively [18]. Also, the CTE of SiC is $4.7 \times 10^{-6}\text{C}^{-1}$ [19]. Therefore, along the fiber axis, the CTE of the C/SiC composite is smaller than that of the SiC coating; while the CTE of the C/SiC composite is larger than that of SiC coating in the fiber radial direction. Consequently, when the temperature was lower than the preparation temperature of the SiC coating (1050 $^{\circ}\text{C}$), along the fiber axis, a tensile stress was produced in the SiC coating,

which induced micro-cracks perpendicular to fiber axis in the SiC coating. By contrast, in the fiber radial direction, a compressive stress was produced in the SiC coating, which had no negative effect on the SiC coating due to the high compression strength of SiC.

Mechanisms and microstructure of the multilayer (C/SiC)_n coating

In C/SiC composites, a (C/SiC)_n multilayer interphase between C fibers and SiC matrices are often designed and fabricated to adjust the bonding between fibers and matrices. When micro-cracks in the SiC matrices propagate to the (C/SiC)_n multilayer interphase, deflexion of the micro-cracks occurs in the interphase, which improves the fracture toughness of the C/SiC composites [20]. Also, the (C/SiC)_n multilayer interphase can dissipate thermal stresses arising from the mismatch in CTE between the C fibers and the SiC matrices [21]. It is well-known that multilayered structures can dissipate stresses. Enlightened by the functions of the (C/SiC)_n multilayer interphase in C/SiC composites, multilayer (C/SiC)_n coatings were fabricated to dissipate the thermal stresses caused by the mismatch in CTE between the SiC coating and the C/SiC composite, which accordingly reduced the micro-cracks in the SiC coating. In the (C/SiC)_n multilayer interphase in C/SiC composites, the thickness of each C or SiC layer is usually between 100 and 300 nm [22]. In light of this, the thickness of each C layer in the multilayer (C/SiC)_n coatings fabricated in this study was around 200-300 nm. To avoid the negative influence of C layers on the oxidation resistance of the coating, the thickness of each SiC layer was set around 1 μm and a thick SiC outermost layer with a thickness of tens of micrometres was adopted.

Fig. 6 shows the polished cross section morphology of a prepared multilayer (C/SiC)_n coating. The multilayered structure can be clearly observed, the dark layers being C and the grey layers being SiC. Each layer was closely adhered to each other and the coating was very well bonded to the substrate. The thicknesses of all SiC layers were below 1.5 μm and the thicknesses of most of the C layers were approximately 200 nm. There were 20 C

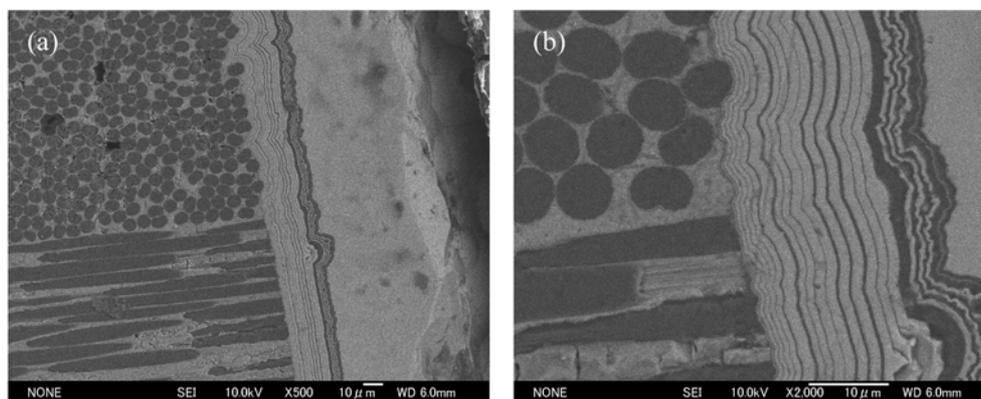


Fig. 6. Polished cross section micrographs of a multilayer (C/SiC)_n coating (a) lower magnification, (b) higher magnification.

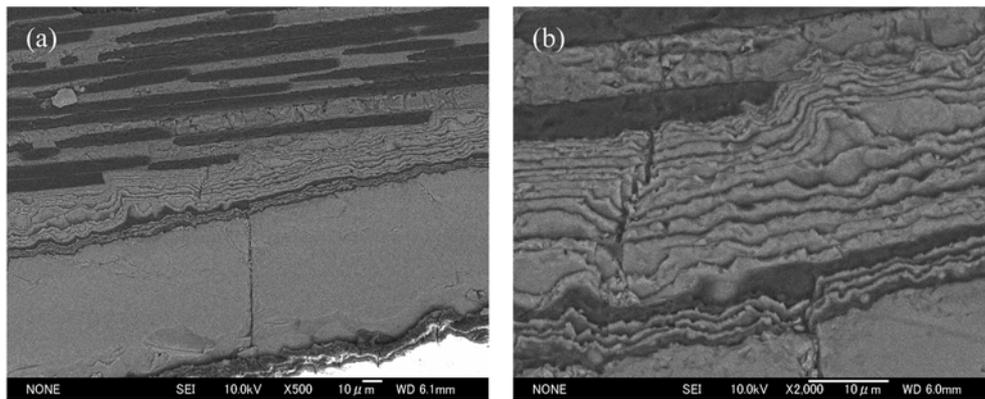


Fig. 7. Crack deflection in a multilayer $(C/SiC)_n$ coating (a) lower magnification, (b) higher magnification.

layers and 20 SiC layers. The outermost SiC layer was about 60 μm thick.

Through-thickness micro-cracks still existed in the outermost SiC layer. However, deflexion of the micro-cracks occurred when the micro-cracks propagated to the $(C/SiC)_{20}$ multilayered structure, which is shown in Fig. 7. This is very similar to the deflexion of micro-cracks in the $(C/SiC)_n$ multilayer interphase in C/SiC composites [22], which indicated that the mechanisms and functions of a $(C/SiC)_{20}$ multilayered coatings resembled those of the $(C/SiC)_n$ multilayer interphase. The deflexion of micro-cracks from the thick outermost SiC layer in the $(C/SiC)_{20}$

multilayered coatings was obvious favorable. On the one hand, it facilitated an improvement of the fracture toughness of the coating. On the other hand, it elongated the diffusion path of oxidizing gas through the micro-cracks in the coating, which weakened the negative impact of the micro-cracks on the oxidation resistance of the coating.

Because the multilayered structure could dissipate thermal stresses, the thermal stress in the multilayer $(C/SiC)_n$ coating was significantly reduced compared with that in the single-layer SiC coating. Fig. 8(a) is a surface micrograph of the multilayer $(C/SiC)_n$ coating at low magnification. It can be observed that there were still some micro-cracks in the

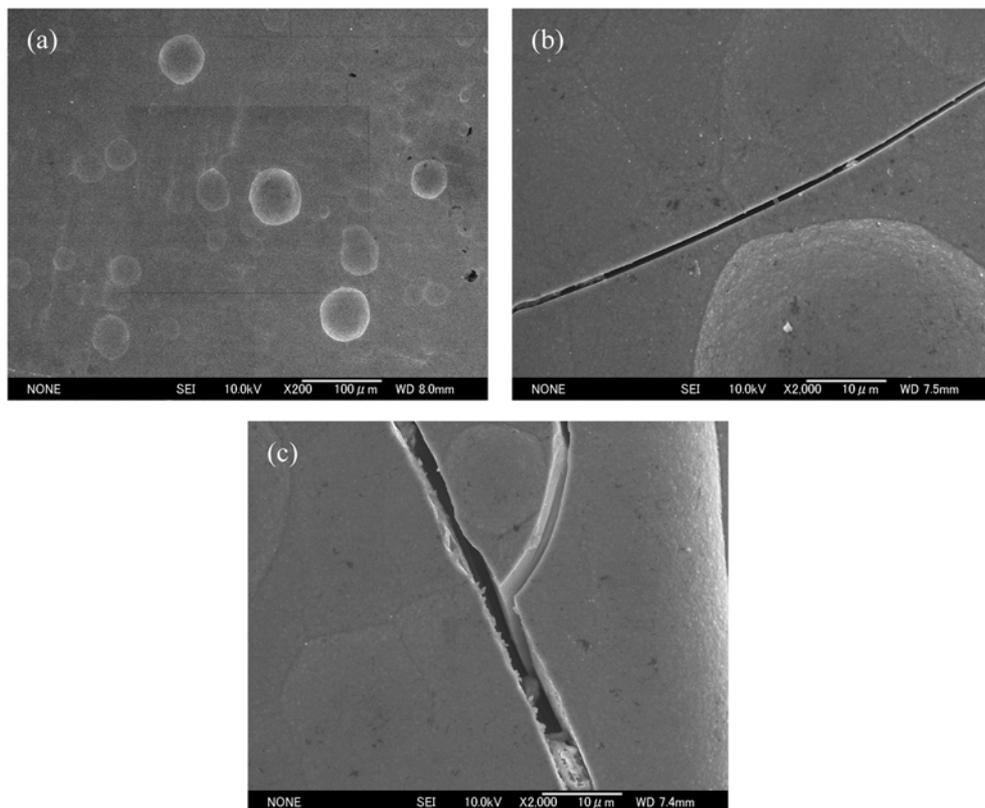


Fig. 8. Micro-cracks in different SiC coatings (a) the multilayer $(C/SiC)_n$ coating (lower magnification), (b) the multilayer $(C/SiC)_n$ coating (higher magnification), (c) the single-layer SiC coating with a thickness of 40 μm .

multilayer coating, but the number of micro-cracks was greatly reduced compared with that in the single-layer SiC coating (see Fig. 5(b)). Fig. 8(b) and (c) show high magnification micrographs of the micro-cracks in the multilayer $(C/SiC)_n$ coating and the single-layer SiC coating with a thickness of 40 μm , respectively. Obviously, the width of the former was significantly smaller than that of the latter. Besides, it should be noted that the multilayer $(C/SiC)_n$ coating was much thicker than the single-layer SiC coating. A larger thermal stress tends to be generated in a thicker coating. However, the number and width of micro-cracks in the multilayer $(C/SiC)_n$ coating were drastically reduced compared with those in the single-layer SiC coating. This obviously indicated that the thermal stress in the multilayer $(C/SiC)_n$ coating was greatly dissipated by the $(C/SiC)_n$ multilayered structure.

Oxidation tests of the uncoated and coated composites

In dry air, the oxidation of C/SiC composites and composites coated with the single-layer SiC coating or the multilayer $(C/SiC)_n$ coating involves the following reactions:

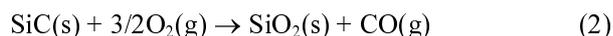
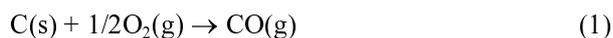


Fig. 9 shows the relationship between the relative weight changes and oxidation time at 1500 °C in dry air of the uncoated 2D C/SiC composites and composites coated with the single-layer SiC coating with a thickness of 40 μm and the multilayer $(C/SiC)_n$ coating. The uncoated composites showed a large decrease in weight. At the beginning, the oxidation of SiC hardly happened. Without the protection of SiO_2 resulting from oxidation of SiC, C fibers were rapidly oxidized and consumed due to easy access of oxygen into the composites, which explained the sharp weight loss in the first five hours. As the time increased, SiC was gradually oxidized, which resulted in the formation of protective SiO_2 in the composites. SiO_2 slowed down the diffusion of oxygen into the composites, hindering the oxidation of C fibers. Besides, the transformation from SiC to SiO_2 led to an increase in weight. That is the reason why there was a little decrease in weight loss as the oxidation time increased.

The composites coated with the two types of SiC coatings exhibited much smaller weight losses than uncoated composites. Due to the protection of the SiC coatings and the SiO_2 film formed during oxidation, it was difficult for oxygen to diffuse into the composites. However, the coated composites still showed a gradual increase in weight loss as the oxidation time increased. This was because the oxidation-protection effectiveness of SiC coatings relied on the SiO_2 film formed, but the integrity of the SiO_2 film was damaged as the oxidation time increased because of the generation of growth stresses and thermal stresses in the film [7]. The composites with the multilayer $(C/SiC)_n$ coatings showed similar oxidation behavior to the composites coated with the single-layer

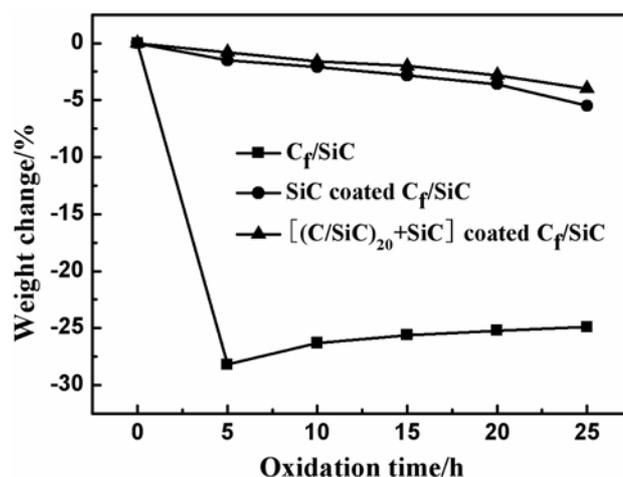


Fig. 9. Oxidation curves at 1500 °C in air of uncoated 2D C_f/SiC composites and composites coated with the two different types of pulsed CVD SiC coatings.

SiC coating, but the weight loss of the former was slightly less than that of the latter. The reason was that micro-cracks in the two coatings were all sealed at 1500 °C (the sealing temperature of micro-cracks was roughly 1050 °C) and micro-cracks were no longer diffusion channels for oxygen. The damage to the SiO_2 film, which was the same for the two SiC coatings, decided the oxidation behavior. However, the multilayer $(C/SiC)_n$ coating was thicker than the single-layer SiC coating. Therefore, the diffusion path of oxygen in the former was longer than that in the latter, which explained the better oxidation protection provided by the former.

The fracture surfaces after oxidation at 1500 °C for 25 h of the uncoated 2D C/SiC composites and composites coated with the two types of SiC coatings are shown in Fig. 10. Because the C fiber reinforcements were two dimensional, fibers in two directions could be seen in the fracture surfaces. Obviously, C fibers were almost completely consumed after oxidation, leaving holes in the fracture surface of the uncoated composites (Fig. 10(a), (b)). By contrast, few C fibers of the composites coated with the single-layer SiC coating were oxidized, but the fiber pull-outs in the fracture surfaces were short (Fig. 10(c), (d)). C fibers of the composites coated with the multilayer $(C/SiC)_n$ coating were barely oxidized, and the fiber pull-outs in the fracture surfaces were long (Fig. 10(e), (f)). Both the microstructural analysis and the oxidation weight loss testing demonstrated that the oxidation resistance of the 2D C/SiC composites with SiC coatings was significantly improved compared with that of the uncoated composites.

Fig. 11 shows the relationship between the relative weight changes and oxidation time at 900 °C in dry air of the uncoated 2D C/SiC composites and composites coated with the two types of SiC coatings. It can be observed that the oxidation curve of the uncoated composites at 900 °C was similar to that at 1500 °C, but the weight loss at 900 °C was larger than that at 1500 °C. The

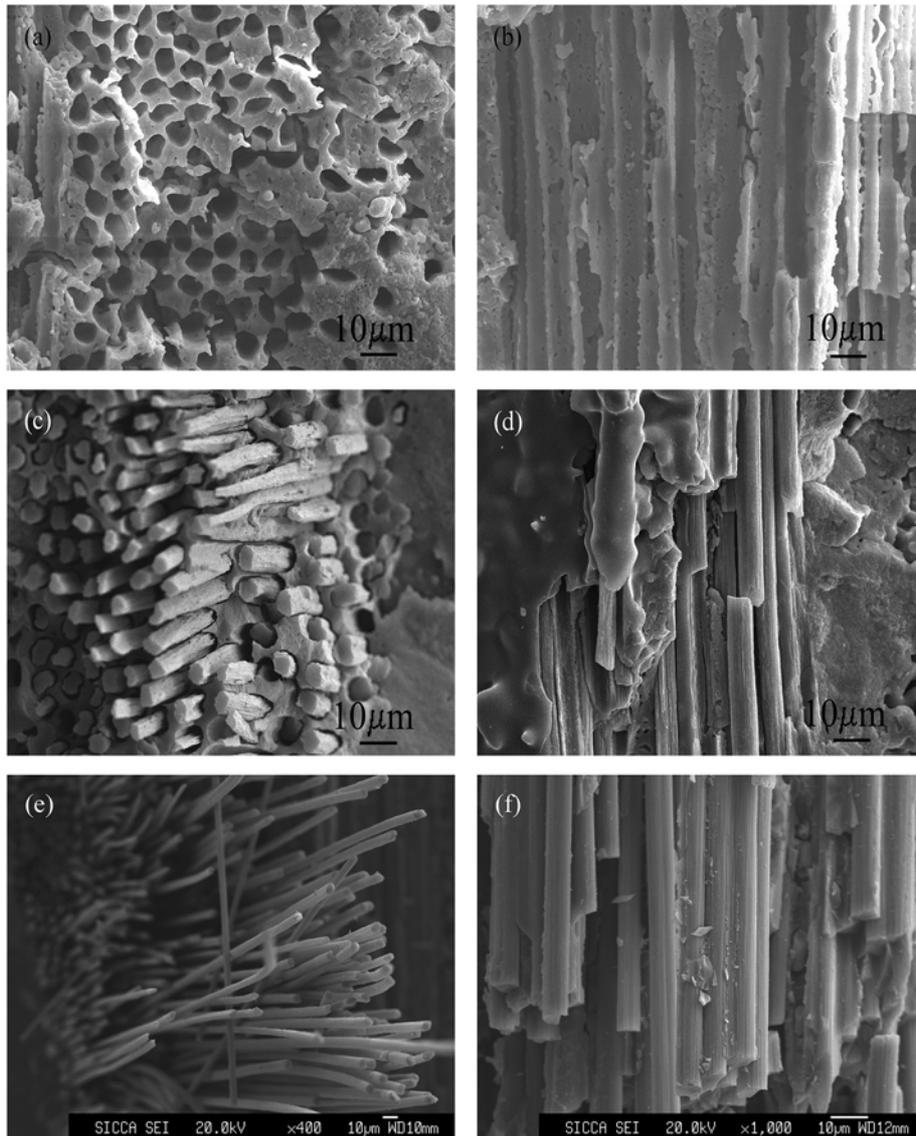


Fig. 10. Fracture surface micrographs after oxidation at 1500 °C in air of uncoated 2D C_f/SiC composites and composites coated with the two different types of pulsed CVD SiC coatings (a), (b) uncoated C_f/SiC , (c), (d) SiC coated C_f/SiC , (e), (f) $[(C/SiC)_{20} + SiC]$ coated C_f/SiC .

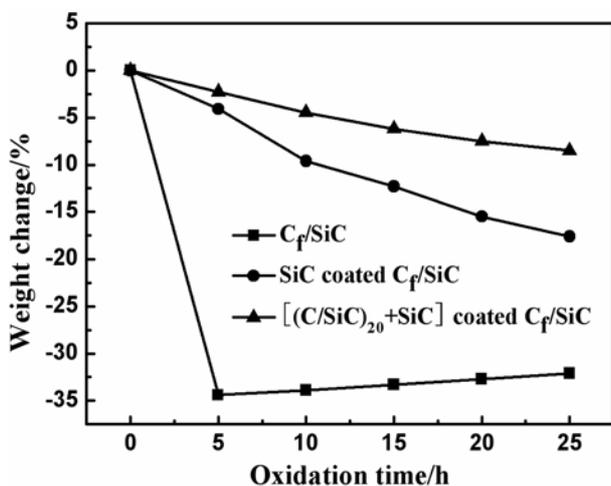


Fig. 11. Oxidation curves at 900 °C in air of uncoated 2D C_f/SiC composites and composites coated with the two different types of pulsed CVD SiC coatings.

reason was that at 900 °C the oxidation rate of SiC was much lower than that at 1500 °C [23], and the formation of SiO_2 film was very slow. The small SiO_2 film provided inadequate protection to the C fibers in the composites. At 900 °C, the weight losses of the composites coated with two types of SiC coatings were also larger than those at 1500 °C. That was because micro-cracks in the coatings were not sealed at 900 °C and micro-cracks were diffusion channels for oxygen. Another reason was that the oxidation rate of SiC to form SiO_2 was much lower at 900 °C. Because the multilayer $(C/SiC)_n$ coatings had many fewer and narrower micro-cracks than the single-layer SiC coatings, the weight loss at 900 °C of the composites coated with the former was much smaller than that of the composites coated with the latter. Obviously, the oxidation tests at 900 °C better demonstrated the advantage of the multilayer $(C/SiC)_n$ coating over the single-layer SiC coating.

Conclusions

(1) Pulsed CVD is a very promising method to prepare SiC coatings on C/SiC composites with a certain porosity. It allowed original pores in the substrates to be filled, contributing to the better adhesion of the coatings with the substrates. The as-prepared coatings were very dense, with no deposition defects. Particles in the coatings underwent growth as the deposition time increased.

(2) Multilayer (C/SiC)_n coatings could dissipate thermal stresses in the coating, which reduced the number and width of micro-cracks in the coatings. Additionally, through-thickness micro-cracks in the outermost SiC layer deflected in the (C/SiC)_n multilayered structure, which reduced the negative impact of micro-cracks on the oxidation resistance of the coating.

(3) The SiC coatings prepared by pulsed CVD significantly improved the oxidation resistance of C/SiC composites. At 1500 °C, the composites coated with the multilayer (C/SiC)_n coatings had similar oxidation behavior to the composites coated with the single-layer SiC coating; at 900 °C, the weight loss of the former was much smaller than that of the latter. The reason was that the multilayer (C/SiC)_n coatings had fewer and narrower micro-cracks than the single-layer SiC coatings, and micro-cracks were not sealed at 900 °C but were sealed at 1500 °C.

Acknowledgments

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