Effect of co-deposited SiC nanowires and carbon nanotubes on oxidation resistance for SiC-coated C/C composites

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Abstract

To protect carbon/carbon composites (C/Cs) against oxidation, SiC coating toughened by SiC nanowires (SiCNWs) and carbon nanotubes (CNTs) hybrid nano-reinforcements was prepared on C/Cs by a two-step technique involving electrophoretic co-deposition and reactive melt infiltration. Co-deposited SiCNWs and CNTs with different shapes including straight-line, fusiform, curved and bamboo dispersed uniformly on the surface of C/Cs forming three-dimensional networks, which efficiently refined the SiC grains and meanwhile suppressed the cracking deflection of the coating during the fabrication process. The presence of SiCNWs and CNTs contributed to the formation of continuous glass layer during oxidation, while toughened the coating by introducing toughening methods such as bridging effect, crack deflection and nanowire pull out. Results showed that after oxidation for 45 h at 1773 K, the weight loss percentage of SiC coated specimen was 1.35%, while the weight gain percentage of the SiCNWs/CNTs reinforced SiC coating was 0.03052% due to

the formation of continuous glass layer. After being exposed for 100 h, the weight loss percentage of the SiCNWs/CNTs reinforced SiC coating was 1.08%, which is relatively low.

Keywords: Co-deposition; Carbon nanotubes; SiC nanowires; Carbon/carbon composites; SiC coating; Oxidation resistance

1. Introduction

Owing to excellent properties at high temperatures, such as high strength-to-weight ratio and good thermal shock resistance, carbon/carbon composites (C/Cs) are considered as a leading candidate for high temperature application in aeronautical and aerospace field [1–3]. However, C/Cs showed significant oxidation degradation under oxidizing environment above 773K, which limited their application in oxygen-containing environment [4–6]. Numerous studies showed that the anti-oxidation property of C/Cs could be improved by preparing an oxidation-resistant coating [7–8]. So far, various coating systems, especially the silicide coatings have been fabricated on the surface of C/Cs to enhance its isothermal oxidation resistance [9–11]. Among these coatings, SiC ceramic is regarded as one of the most promising materials for protect C/Cs at high temperature due to its excellent anti-oxidation property and good compatibility with C/Cs [8] [12][13].

In spite of the outstanding properties of SiC coating, while its application in oxidizing atmosphere is limited because of the mismatch of coefficient of thermal expansion (CTE) between SiC coating ($\alpha=5 \times 10^{-6} / \text{K}$) and C/Cs ($\alpha=1 \times 10^{-6} / \text{K}$), which will induce the cracks in the coating under service during rapid cooling-down

process, and lead to the failure of the coating eventually [7]. Many methods have been employed to solve this issue [14], such as introducing carbon nanotubes (CNTs) [15], SiC nanoparticles [16], SiC whiskers [17–18] and SiC nanowires (SiCNWs) [19–24] into the SiC coating. The introduction of these reinforcement phases aimed to improve the toughness of the coating and reduce the size of cracks. CNTs are more suitable for reinforcing the coating than whiskers and nanoparticles due to the CNTs exhibit high mechanical strength, high electronic and thermal conductivity [25–26]. Nevertheless, SiC coating toughened by SiCNWs and CNTs hybrid reinforcement has not yet been thoroughly investigated. To date, there are limited papers comparing the microstructures and characteristics of the SiC coatings prepared by reactive melt infiltration with and without SiCNWs and CNTs hybrid reinforcement, which might be ponderable for practical applications.

In this work, SiCNWs and CNTs hybrid reinforcement toughened SiC coating were prepared on C/Cs by a two-step technique involving electrophoretic deposition (EPD) and reactive melt infiltration (RMI) (as shown in Fig. 1). Firstly, SiCNWs and CNTs were deposited on C/Cs using EPD to increase the oxidation resistance for SiC-coated C/Cs. Secondly, the treated specimens were coated with SiC via the reactive melt infiltration technique. The effect of the co-deposition of SiCNWs and CNTs on the microstructure and oxidation behavior of the SiC coating was analyzed.

2. Experiment

C/C specimens (10 mm × 10 mm × 10 mm) were used as substrates for coating, which were cut from bulk 2D C/Cs with a density of 1.71 g/cm³. The preparation of

the 2D C/Cs was as follows: Carbon felts (0.4g/cm^3 , Yixing Tianniao High Technology Co., Ltd., Jiangsu, China) were fabricated by alternatively stacked carbon fiber webs and non-woven layers by a needle-punching technique, which were chosen as the porous preform materials. The fabrics were deposited by pyrolytic carbon (PyC) through thermal gradient chemical vapor infiltration (TCVI) process. During TCVI process, methane gas (CH_4) was used as carbon source and nitrogen (N_2) was used as carrier gas. The deposition temperature was 1000°C - 1300°C . After 100-200 h, the density of the porous preforms was about 1.70 - 1.75 g/cm^3 . After being hand-abraded using 300 grit SiC paper and ultrasonically cleaned with ethanol, they were dried at 80°C for 24 h. C/C specimens were divided into two groups, one of which was co-deposited SiCNWs and CNTs film through EPD. The other group was pure C/Cs without any treatment for comparison. SiCNWs (92% purity) were provided by Zhuo Xi High-tech (Xi'an, China). An aqueous suspension of commercially available multi-walled CNTs (97% purity) were provided by Timesnano (Chengdu, China).

EPD is a mild method with low energy consumption and outstanding ability to homogeneously coat complex shapes with easily controlled film thickness and density [27–29]. A schematic of the EPD process is illustrated in Fig. 2. The detailed process for EPD was conducted as follows: firstly, the CNT aqueous suspensions were diluted with isopropanol by volume ratio of 1:10, and SiCNWs were added into the mixed solution by weight ratio of 1:1500. They were dispersed with isopropanol and then homogenized in ultrasonic bath for 4 h. Secondly, a stainless steel cylinder with the diameter of 50 mm was vertically placed on an EPD cell containing SiCNWs and

CNTs suspension, which was used as anode. The cathode, a C/C specimen connected with a copper wire, was fixed in a plastic frame. And then, C/C specimen was immersed in the center of the stainless steel cylinder. The experiment was conducted using an electrophoresis apparatus (PowerPac Basic, Bio-Rad Laboratories, Inc., USA), which was performed at a constant voltage of 60 V. The time of EPD was 120 s. The thickness of the co-deposited SiCNWs and CNTs film can be adjusted by controlling the voltage and EPD time [14].

Finally, pure C/Cs and EPD treated C/Cs were both coated with SiC ceramic coating using the same reactive melt infiltration technique. Powder compositions for the reactive melt infiltration process were as follows: 60–80 wt.% Si (Jiuling Smelting Co., Ltd., Shanghai, China), 10–25 wt.% graphite (Carbon Plant, Xi' an, China) and 5–15 wt.% Al_2O_3 (Guoyao Chemical Reagent Co., Ltd., Shanghai, China). All the above powders were analytical grade with the granularity of 300 mesh. Then the powder mixtures were blending for 3 h using a blender. The specimens and the powder mixtures were placed in a graphite crucible with a graphite lid, and then heated in an argon atmosphere to 1873–2273 K and held at that temperature for 2 h by an electric furnace with the pressure of 3 kPa. After the coating deposition, the furnace cooled down to room temperature naturally. The specimens were removed from the graphite crucible and ultrasonically cleaned to remove impurity.

Isothermal oxidation test of the SiC coated samples were carried out at 1773 K in static air in a furnace to evaluate the anti-oxidation ability of the coating. The specimens were taken out from the furnace and cooled down naturally. The mass of

the coated C/C specimens was measured by an electronic precision balance with a sensitivity of ± 0.1 mg. Subsequently, they were put into the furnace again for the next cycle. Weight change percentages of the specimens were calculated by the following equation [30-31]:

$$W\% = \frac{m_0 - m_1}{m_0} \times 100\% \quad (1)$$

Where m_0 and m_1 represent the initial and final mass of the specimens for each cycle during isothermal oxidation process.

Raman (Raman, RENISHAW invia Raman Microscope) characterization was used to study the graphitic structure evolution of the co-deposition of SiCNWs and CNTs film and C/C specimens. The crystalline structures of the SiCNWs/CNTs-reinforced SiC coating was analyzed by X-ray diffraction (XRD, PANalytical X' Pert Pro, Netherlands) with Cu K α ($\lambda = 0.1542$ nm), 0.03° step size and $0.28^\circ/\text{s}$ scan speed radiation. Field emission scanning electron microscope (SEM, ZEISS Supra 55) and transmission electron microscopy (TEM, FEI Tecnai F30 G2) were used to identify the morphology and structures of the specimens.

3. Results and discussion

3.1. Morphology of SiCNWs and CNTs film

For the co-deposition of SiCNWs and CNTs film, the value of I_D/I_G suggests a significantly change. In Fig. 3, there are four main bands in Raman spectra of the co-deposited SiCNWs and CNTs film (curve (a)). The two bands located at $\sim 789 \text{ cm}^{-1}$ and $\sim 966 \text{ cm}^{-1}$ are the characteristic peak of SiC [32]. The disorder-induced D band ($\sim 1348 \text{ cm}^{-1}$) and the tangential G band ($\sim 1575 \text{ cm}^{-1}$) were the characteristic peak of

CNTs [30]. From curve (a) in Fig. 3, SiCNWs and CNTs film has been successfully co-deposited on C/Cs. The substrate covered with CNTs and SiCNWs film has an I_D/I_G of 0.504, which indicates a significantly decrease in the graphization degree of C/Cs (curve (b), ~ 0.789). This decreased value of the I_D/I_G suggests a significantly change on the C/Cs surface after the co-deposition.

The deposited SiCNWs and CNTs film (shown in Fig. 4(a)) shows a dense structure with the thickness around $20 \pm 2 \mu\text{m}$ and they are randomly oriented and bridged with each other (seen in Fig. 4(b)). An enlarged image shown in Fig. 4(c) reveals the formation of SiCNWs were with various shapes including straight-line shape, fusiform shape and bamboo shape. Among that the bamboo shaped SiCNW consists of some nodes and a thinner stem. In addition, various shapes of CNTs with straight and curly can be detected. Plenty of pores generated within the SiCNWs and CNTs structure, which is beneficial to the flowing of Si during reactive melt infiltration technique.

As shown in the Fig. 5(a)–(c), the as deposited SiCNWs have a diameter in the range of 100–500 nm, CNTs have a diameter in the range of 10–100 nm, and both of them were over ten micrometers in their lengths, measured from more than eighty SiCNWs and CNTs using Digital Micrograph software. It also can be observed that the surface morphology of SiCNWs is rugged, and CNTs distributed in the structure provided by the SiCNWs.

3.2. Phase composition and microstructure evolution of as-deposited SiC coating

The surface of the two kinds of specimens show a significantly difference after being coated with SiC grains. Fig. 6 shows the micro-structure of the SiC coating

without (Fig. 6(a)) and with (Fig. 6(b)) SiCNWs and CNTs film. The shape and dimension of SiC crystals are significantly changed, the SiC crystals grown without SiCNWs and CNTs is in a hexagonal shape with the size about 60–100 μm . In contrast, the SiC crystals of the SiCNWs and CNTs modified SiC coating are spherical with a dimension about 6–10 μm , which is significantly smaller. Moreover, these spherical particles interconnect with each other forming a dense structure. The difference is mainly attributed to the introduction of the SiCNWs and CNTs film. The grown process of the SiCNWs and CNTs modified SiC coating is heterogeneous nucleation. Plenty of nucleation points provided by the as-deposited SiCNWs and CNTs are beneficial to the growth of SiC grains to form coating on the surface of SiCNWs and CNTs. The grown process needs lower ΔT (degree of under cooling) and ΔG (Gibbs free energy) than that of SiC coating without the SiCNWs and CNTs film. So the less nucleation points can be supplied for the growth of the SiC grains without SiCNWs and CNTs, which is unfavorable for SiC crystal nucleation. And the nucleation of SiC crystal is suppressed due to release a great deal of heat energy during the growth of SiC grains.

In addition, some micro-cracks can be seen in Fig. 6(a), which will lead to the thermal stress concentration during oxidation. Once coming to a certain degree, the thermal stress (concentrated at the tip of the micro-cracks) will force the micro-cracks to expand, and finally form penetrative cracks within the coating. On the contrary, no obvious cracks appeared in the SiCNWs and CNTs film modified SiC coating showing in Fig. 6(b). The insert graph in Fig. 6(b) is the partial magnification of the

SiCNWs and CNTs film modified SiC coating. Since the rough surface of SiCNWs and CNTs can provide more interfaces than that of the smooth surface with the same length, it could generate lots of interfaces and nuclei for SiC nucleation. Therefore, the uniformly distributed of nucleation is conducive to increase the compactness of SiC coating. Meanwhile, the rugged surface of SiCNWs and the structure formed by CNTs and SiCNWs will improve the mechanical property[13, 19] by enhancing bonding strength of the coating and C/Cs, therefore, it needs more energy when pulling SiCNWs out of the SiC coating.

SiCNWs and CNTs were used as reinforcing phases, which could play an important role in avoiding the cracking generation and deflection of the coating caused by the mismatch of CTE between the substrates and the coating.

The XRD pattern of SiC coating reinforced by SiCNWs and CNTs is shown in Fig. 6(c). It can be observed that the coating was composed of α -SiC, β -SiC and Si phases. Moreover, the intensity of the SiC diffraction peaks is very strong, which suggests a good crystallization of the SiC grains. The generation of SiC phase is derived from the chemical reaction between C and Si. In addition, Si diffraction peaks can also be found, which is caused by the excess Si powders in original pack materials. The XRD pattern shows that SiC ceramic was successfully formed by reactive melt infiltration technique and has a good crystallization of the SiC grains.

Fig. 6(d) and Fig. 6(e) are the high magnification SEM images of SiCNWs and CNTs existed within SiC coating, separately. The continuous glass layer generated on the SiC surface owe to the reinforcement by SiCNWs and CNTs, which indicates that

SiCNWs and CNTs can modify the coating and reduce the quantity and size of the micro-cracks in certain level. The CNTs (Fig. 6(e)) were surrounded by SiC coating, which exhibit a strong and coherent interface bonding with SiC coating. The curly shape of CNTs can provide a better capability to release thermal stress during isothermal oxidation process, which is helpful to reduce the size of the micro-cracks and form a continuous coating.

Simultaneously, the fracture morphology of the SiC coating on C/Cs toughed by SiCNWs and CNTs were observed in Fig. 6. Numerous SiCNWs and CNTs connect with the grain can be clearly detected, as shown in Fig. 6f, which contribute to improve the toughness of the coating and restrain the crack to extend. When the SiCNWs and CNTs are pinned into the adjoining coating (Fig. 6(e) and (f)), the stress will be effectively transferred to the SiCNWs and CNTs. The load will be borne by the SiCNWs and CNTs due to their excellent mechanical properties and result in an increase in elastic modulus and the hardness of the coating [14].

3.3. Oxidation mechanism

The oxidation protective ability of the coating with and without SiCNWs and CNTs film were investigated at a temperature of 1773 K in air. The weight loss percentage curves of the two kinds of specimens during oxidation were shown in Fig. 7.

From Fig. 7, the weight loss percentage of the SiC coated C/C specimen without SiCNWs and CNTs film was 1.35% after isothermal oxidation at 1773 K for 45 h. While toughened by the co-deposition of SiCNWs and CNTs film, coated specimen

gains its weight in the beginning 45 h and then comes to lose weight. As the oxidation time reaches up to 45 h, the weight gain percentage was 0.03052%. After being exposed for 100 h, the weight loss percentage of the specimen was only 1.08%. This result indicated that the SiC coated C/C specimen without SiCNWs and CNTs film exhibited a poor oxidation protective ability. After incorporating the SiCNWs and CNTs into the coating, the weight loss percentage of C/C composites has been significantly decreased.

During the oxidation process of the coated specimens at 1773 K, the phenomenon of the weight change can be explained by the following equations [34–36]:

According to the equations (2)–(4), the weight-increasing phenomenon of the coated specimen reinforced with SiCNWs and CNTs could be expounded clearly. While the oxidation of C/C composites with weight-decreasing processes might be interpreted by the equations (5) and (6). Thus the weight gain process of the coated specimens during oxidation is mainly induced by the oxidation of the SiC coating, while the weight loss process of the coated specimens is mainly caused by the oxidation of the C/C substrate and the volatility of oxidation production. Whether the

specimen gain or lose weight concerns two factors: the oxidation dynamics of the coating and the compactness of the coating.

A phenomenon of particular interest is the slope of the weight loss curve changes with the increase of oxidation time after introducing SiCNWs and CNTs. Firstly, the curve decreases from 0 h to 15 h, and turns almost flat from 15 h to 25 h, after 25 h the curve shows an increase, then turns flat again after 70 h. The slope changes of the curve indicate different oxidation mechanisms control the oxidation behavior of the coated C/C specimens. The weight gain process indicates that the dense structure of the SiC coating, which was formed by the introduction of the co-deposition of SiCNWs and CNTs by EPD. This dense structure can protect the specimen from oxidation. With the increase of oxidation time, the weight loss process of the coated specimens is mainly caused by the oxidation of the C/C substrate and the volatilization of oxidation production. The schematic illustration of the isothermal oxidation process of the coating is presented in Fig. 8.

As the SiC-coated specimens were oxidized at high temperature (Fig. 8 (a)), SiC coating was enclosed by oxygen. The continuous melting SiO_2 glass layer was formed at the top of coating (Fig. 8 (b)), which contributes to the crack-healing and reduce the formation of the gap at the beginning of oxidation. As the extensive of the oxidation time, the depletion of SiC coating can induce the formation of the gap. This depletion is occurred by the oxidation and sublimation. The former results in the formation of CO_2 (g) and CO (g) (equation (2) and (3)), while the latter leads to the formation of the protective SiO_2 (equation (2), (3) and (4)) glass layer. Once the oxidation products

including liquid glass phase are difficult to seal cracks (Fig. 8(c)), oxygen can penetrate into the coating, and lead to the degradation of C/C composites (Fig. 8(d)).

As for the SiCNWs/CNTs-toughened SiC coating, oxygen can contact with coating to react directly (Fig. 8e). The oxidation of SiC and Si occurs when being exposed to the air at the beginning of oxidation (equation (2) and (3)), the oxidation rate of which is faster than the self-healing stage. This process is controlled by the oxidation of SiC and Si, and the oxidation products result in the weight gain. With the oxidation time increased, the existence of SiCNWs and CNTs, which is composed by various shapes, sizes and properties, contributes to the formation of a protective and continuous SiO₂ glass layer on the surface of the coating (Fig. 8(f)). The generated glass layer own well fluidity and low oxygen diffusion at elevated temperatures, which conduces to restrict the cracks growth within the coating and prevents oxygen from diffusing to C/C composites. The oxidation process is controlled by the oxidation diffusion. Nevertheless, few micro-cracks still form in the coating during cooling period (Fig. 8(g)), which provide the channel for oxygen diffusion to the interface between coating and the C/C substrate. Therefore, carbon would react with oxygen, and release CO and CO₂ gasses (Fig. 8(h) and (i)). This moment the coated specimen exhibits rapid weightlessness. After the oxidation for 25 h, the curve showed a rising trend. The generation of CO₂ and CO results from the formation of the holes and bubbles in the generated glass layer [37]. As the oxidation time goes on, these micro-cracks sealed quickly at 1773 K with the expansion of Si and SiC phases in the coating [36] and the bridge of the SiCNWs and CNTs. A large number of the

gases (CO , CO_2) would be accumulated at the interface between the glass layer and the coating, which would then exert certain pressure for the glass layer, leading to the generation of the bubbles in the glass layer (Fig. 8(i)). Once the pressure of these gases exceed the surface tension of the bubbles, these gases would get out through the glass layer due to the low viscosity of glass layer at 1773 K, left the holes within the glass layer (Fig. 8(j)). It can be concluded that the isothermal oxidation protective ability of the coating can be significantly increased by introducing SiCNWs and CNTs.

Detailed explanations are given based on SEM investigations for the as-deposited coatings after oxidation. Fig. 9(a) exhibits the surface SEM **image** of the SiC coated C/Cs without SiCNWs and CNTs after oxidation at 1773 K for 45 h. Fig. 9(b) is the SEM image of the SiC coating toughed by SiCNWs and CNTs after oxidation for 100 h. For the specimen without SiCNWs and CNTs, there are abundant pits and cracks on the surface of the SiC coatings (Fig. 9(a)). It is resulted from the evaporation of gaseous and mismatch of CTE between coating and C/C substrate, respectively. Whereas for the specimen containing SiCNWs and CNTs, these defects are significantly decreased (Fig. 9(b)). As shown in Fig. 9(b), the micro-crack first extended toward coating, and then it does not go straight through the holes, bubbles or the continuous glass layer, but deflects and finally comes to an end. Compared with the specimens without SiCNWs and CNTs, the cracks within the reinforced coating were discontinuously, which can not extend straightly from the beginning to the end, but deflect to a certain degree. Besides, the “crack termination” can be observed from

part A in Fig. 9(b). It also can be seen that a continuous SiO₂ glass layer formed on the coating due to its oxidation. As a result, the existence of SiCNWs and CNTs contribute to the deflection or the termination of micro-cracks. There is no big-scale micro-cracks in the coating, and these micro-cracks are small in width and length. These appearances indicate that the generated micro-cracks are due to the volume change of SiO₂ glass during the cooling process [38].

The co-deposited SiCNWs and CNTs could decrease the oxygen diffusion and control the flow of melted SiO₂ to form a continuous glass layer. The co-deposited SiCNWs and CNTs was used as the reinforcement composites to elevate the toughness of the coating and decrease the size of cracks, which could contribute to protect the C/Cs with their own properties. The continuous glass layer indicates that self-heal rate is faster than SiC coating containing without SiCNWs and CNTs.

Moreover, obvious differences are also observed from the SiC coating with and without SiCNWs and CNTs after oxidation **at 1773 K** (as shown in Table 1). The amount of the holes and pits in the neat SiC coating is 25-33/mm² and only 5-10/mm² for the SiC coating with SiCNWs and CNTs. The diameters of the holes among them are 16-52 μm and 25-33 μm, respectively. The size of the microcracks of the SiC coating without SiCNWs and CNTs is 5-10 μm and 0.8-1.5 μm for latter one. The differences among the micro-cracks, holes and pits may come from the introduction of the co-deposition of SiCNWs and CNTs. Oxygen can penetrate into the C/C matrix through these micro-cracks, and then bring about the oxidation of C/Cs. The micro-crack within SiC coating without SiCNWs and CNTs is much larger, the

coating need longer time to self-sealing than the oxygen penetrate into C/C substrate through the through-thickness, C/Cs would be oxidized during this process. With the toughening effect of SiCNWs and CNTs, the formation of SiO₂ is quicker than that of the oxygen penetrates into C/C substrate through the through-thickness, the micro-cracks of small size will be decreased or eliminated quickly. The difference of the quantity and the diameter of the holes and pits were attributed to the existence of SiCNWs and CNTs. Fig. 9(c) is a representative pullout feature of numerous SiCNWs within the micro-crack that prevents the micro-crack from widening. It can be clearly observed that the size of micro-crack decreases from $1.5\pm0.5\ \mu\text{m}$ to $0.8\pm0.5\ \mu\text{m}$. Owing to the existence of the SiCNWs and CNTs, the micro-crack becomes narrow. In addition, at the top of the SiC nanowire the diameter was smaller than the joint of framework, and which occurred large deformation. It implied that the nanowires contribute to reduce the size of micro-cracks. Therefore, it is reasonable to believe that the SiCNWs and CNTs contribute to the alleviation of the thermal stress and the decreasing of the occurrence of the pits and defects of the coating. The XRD pattern (Fig. 9(d)) demonstrates that the oxidized coating consists of SiC, SiO₂ and Si phases.

To explore the toughening mechanism of the SiCNWs and CNTs, a series of experiments were carried out. For this purpose the specimens after oxidation were fractured by a hammer. The fracture of the SiC coated C/Cs with SiCNWs and CNTs after oxidation at 1773 K for 100 h were observed (Fig. 10). Fig. 10(a) displays the cross-section of SiC coating with the co-deposition of SiCNWs and CNTs after oxidation, from which plenty of drapes can be found near the fringe of the coating.

Fig. 10(b) is the magnification of Fig. 10(a), from which lots of SiCNWs can be observed. They are located at the drapes or on the cross-section. The presence of the drapes was due to the existence of SiCNWs, indicating that the coating toughened by the bridging or pulling out. In addition, the rugged shape of the drapes on the cross section implies that the existence of SiCNWs can increase the adhesion of the coating when being oxidized. Fig. 10(c) shows the fracture of the coating after oxidation at 1773 K. With the protection of the SiC coating, SiCNWs and CNTs were not oxidized completely. SiCNWs and CNTs were curled and deformed, which also confirmed that the existence of SiCNWs and CNTs, SiC coating can protect C/Cs from oxidation.

4. Conclusion

In this work, SiCNWs and CNTs film were co-deposited on C/Cs by EPD and then coated by SiC coating through reactive melt infiltration. The oxidation behavior at 1773 K in air has been investigated. The co-deposition of SiCNWs and CNTs film by EPD can modify the coating and reduce the micro-cracks to widening. The toughening mechanisms include the pullout, bridging and micro-crack deflection of SiCNWs and CNTs are studied. The different shapes of SiCNWs and CNTs are beneficial to the adhesion between C/Cs and SiC coating. The existence of SiCNWs and CNTs can contribute to form a continuous SiO₂ glass layer to provide a better anti-oxidation ability.

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Figure captions

Figure 1 Schematic diagram of the SiCNWs and CNTs hybrid reinforcement toughened SiC coating.

Figure 2 Schematic diagram of the co-deposition of SiCNWs and CNTs on C/C composites in EPD cell.

Figure 3 Raman spectra of the co-deposition of SiCNWs and CNTs (curve (a)) and C/C specimens (curve (b)).

Figure 4 SEM images of the specimen after the co-deposition of SiCNWs and CNTs by EPD for 120 s: (a) Cross section image; (b) Surface image; (c) Magnification of (b).

Figure 5 (a) Magnification of CNTs in (b); (b) TEM image of the co-deposition of SiCNWs and CNTs; (c) Magnification of SiCNWs in (b).

Figure 6 SiC coating without (a) and with (b) SiCNWs and CNTs; (c) XRD pattern of the SiCNWs/CNTs-reinforced coating; (d and e) High magnification of SiC coating containing SiCNWs and CNTs; (f) Bridging effect of the SiC coating toughened by SiCNWs and CNTs.

Figure 7 Variation in weight losses percentage of the SiC coated C/Cs during exposed to the atmosphere.

Figure 8 Schematic illustration of the isothermal oxidation process of the coating: (a)-(d) SiC coating; (e)-(h) SiCNWs/CNTs-toughened SiC coating.

Figure 9 SEM images of the SiC coated C/Cs after oxidation without (a) and with (b) the co-deposition of SiCNWs and CNTs; (c) Magnification of (b); (d) XRD pattern of

the coated specimens after oxidation tests.

Figure 10 (a) Cross section of SiC coating with the co-deposition of SiCNWs and CNTs after oxidation; (b) Magnification of (a); (c) Fracture of the coating after oxidation at 1773 K.

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Table 1 SiC coating contain without and with the co-deposition of SiCNWs and CNTsafter oxidation **at 1773K.**

specimens	Oxidation time (h)	Holes and pits (mm ⁻²)	Diameter of holes (μm)	Size of micro-cracks (μm)
Without SiCNWs and CNTs	45	23–28	16–52	5–10
With SiCNWs and CNTs	100	5–7	25–33	0.8–1.5