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SiC coating toughened by SiC nanowires to protect C/C composites against oxidation

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Abstract

A dense SiC coating toughened by SiC nanowires was prepared on carbon/carbon (C/C) composites using a two-step technique of chemical vapor deposition (CVD) to protect them against oxidation. The morphologies and crystalline structures of the coatings were characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction. SiC nanowires played a role in decreasing the size of the cracks and improving the thermal shock resistance of the coating. The result of thermal shock between 1773 K and room temperature for 21 times indicates that, compared with the SiC coating without SiC nanowires, the average size of the cracks in the SiC coating toughened with SiC nanowires reduced from 5 ± 0.5 to 3 ± 0.5 μm. The weight loss of the SiC coated C/C composites decreased from 9.32 to 4.45% by the introduction of SiC nanowires.

Keywords: D. Carbon; D. SiC; Oxidation; Reinforcement

1. Introduction

Carbon/carbon (C/C) composites exhibit many excellent high temperature properties, such as high strength-to-weight ratio, resistance to thermal shock, low coefficient of thermal expansion (CTE) and retention of strength at high temperature. Therefore, they are considered as the ideal thermal structural materials for applications in the aircraft and aerospace fields [1,2]. However, C/C composites show significant oxidative degradation during exposure to an oxidizing atmosphere above 723 K, which limits their applications in thermal structure fields [3,4]. In this case, application of coatings is considered as a key method to address the oxidation problem [5,6]. SiC coating has been attracted extensive attention not only because of its good compatibility with C/C composites, but also its ability to form self-healed silica glass with low oxygen permeability [7–9]. However, the mismatch of CTE between SiC coating and C/C composites easily results in the crazing and debonding of the coating, which induces the failure of the coating [10,11].

To resolve the above problem, an efficient strategy is to introduce a second phase as the reinforcement materials to improve the toughness of the coating, such as nanotubes and whiskers [12–15]. Carbon nanotubes (CNTs) have been used as reinforcing materials in the coating system to enhance the coating/matrix bonding strength and suppress cracking in the coating. However, a complete prevention of cracking has not been achieved though CNTs improved the coating/matrix bonding strength and decreased the number of cracks in the coating. In our previous research, SiC whiskers were used as the reinforcing materials in the SiC coating for C/C composites, which can play a positive role. But large-size SiC whiskers on the surface of C/C composites will baffle the infiltration of SiC coating through the whisker layer into C/C composites to a certain extent, which is disadvantageous to the coating/matrix interface bonding.

SiC nanowires have been attracting considerable attention due to their excellent properties, such as high thermal stability, high strength and high toughness [16]. SiC nanowires have yield strengths over 50 GPa, which is much larger than the corresponding values of microscale SiC whiskers (16 GPa) [17]. Furthermore, the size of the SiC nanowires is much smaller than that of SiC whiskers, which is advantageous to the infiltration of SiC. Compared with the CNTs, SiC nanowires

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have a better oxidation resistance and compatibility with SiC coating. Provided that SiC nanowires could grow in the pores in the surface of C/C composites, the pinning effect would be formed at the coating/matrix interface, enhancing their bonding strength. Therefore, SiC nanowires are considered as potential reinforcements in SiC coating on C/C composites with their excellent properties.

In the present work, a simple and low-cost method was put forward to improve the toughness of SiC coating by introducing SiC nanowires by a two-step technique. Firstly, SiC nanowires were prepared on the surface of C/C composites by chemical vapor deposition (CVD) without any catalyst. Then, SiC was deposited by the second step CVD in the porous SiC nanowire layer to form a dense coating. The microstructure and thermal shock resistance of the coatings were investigated.

2. Experimental

Small C/C composite specimens (10 mm × 10 mm × 10 mm) used as substrates were cut from bulk two dimensional C/C composites with a density of 1.75 g cm^{-3}. They were hand-abraded using 300 grit SiC paper, cleaned ultrasonically with ethanol and dried at 373 K for 2 h.

The first step technique of CVD for preparing SiC nanowires on the surface of C/C composite samples is described as follows: the mixture of high-purity SiO_2, Si and C powder was put into a graphite crucible. C/C composite specimens were placed above the mixture powder in a graphite crucible with a graphite lid and placed in an electrical furnace, which was then heated to 1773 K in an Ar atmosphere for 2 h to form SiC nanowires. After depositing SiC nanowires, the C/C composite specimens were put in CVD furnace and SiC was deposited in the porous SiC nanowire layer to form the dense SiC nanowire-toughened SiC coating. Methyltrichlorosilance (MTS) was used as the source, which was brought into the reaction room by H_2 bubbling. H_2 was used as the carrier gas and Ar was used as the diluent gas. The deposition conditions of SiC were as follows: the deposition temperature was 1100 °C; the pressure of reactor was 0.1 MPa, and the flow rates of H_2, MTS and Ar were 350 mL min^{-1}, 100 mL min^{-1} and 450 mL min^{-1}, respectively; the deposition time was 2 h.

Thermal shock experiments were carried out in air flowing by natural convection in a corundum tube furnace to investigate the thermal shock resistance of the coating. After the furnace was heated up to 1773 K, the samples were put into the furnace and maintained at that temperature for 3 min, then were taken out of the furnace and kept at room temperature for 3 min. And then the samples were put directly into the furnace again for the next thermal shock. During thermal shock tests, the weight of the samples was measured at room temperature by electronic balance with a sensitivity of ±0.1 mg. Weight change percentages ($\Delta W\%$) of the samples were calculated by the following equation.

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

where m_0 and m_1 are the weight of the samples before thermal shock and after thermal shock, respectively. Three samples for each kind of sample were tested and the final weight change percentages were obtained by computing the average values of three samples.

The morphologies and crystalline structures the coatings were analyzed by JSM-6460 scanning electron microscopy (SEM), Tecnai G^2F30 transmission electron microscopy (TEM) and X'Pert PRO X-ray diffraction (XRD).

3. Results and discussion

XRD pattern of the SiC nanowires is shown in Fig. 1. It shows a typical β-SiC crystal, which was obtained from the as-grown SiC nanowires on C/C substrate. Three characteristic peaks can be found at 35.70°, 60.08° and 71.83°, respectively. The indexing of these peaks shows that they are the diffractions of the (1 1 1), (2 2 0) and (3 1 1) crystalline planes of a cubic lattice, which is in good agreement with the known results for β-SiC. In addition, diffraction peaks of C also can be detected corresponding to the C substrate.

Fig. 2(a) shows SEM image of the as-grown SiC nanowires on the surface of C/C substrate. It clearly reveals that the diameter of SiC nanowires is 50–400 nm. SiC nanowires are generally several tens of microns in length and randomly oriented with straight or branched lengths. From Fig. 2(b), it can be observed that the surface morphology of SiC nanowires oriented with straight or branched lengths is rugged, as shown in the TEM image (Fig. 2(d)). Since the rugged surface of SiC nanowires has more interfaces than that of smooth surface with the same length, the rugged surface of SiC nanowires could provide quantities of interfaces, which could provide many nucleus for SiC nucleation, and improve the SiC grains deposition uniformity. Furthermore, the rugged surface of SiC nanowires will require more energy when being pulled from the coating substrate, and enhance the bonding strength between SiC nanowires and the coating. Cross-section SEM image of C/C composites shows some SiC nanowires grew in the pores in the surface of C/C composites (Fig. 2(c)), which could form the pinning effect at the coating/matrix interface, and enhance their bonding strength.

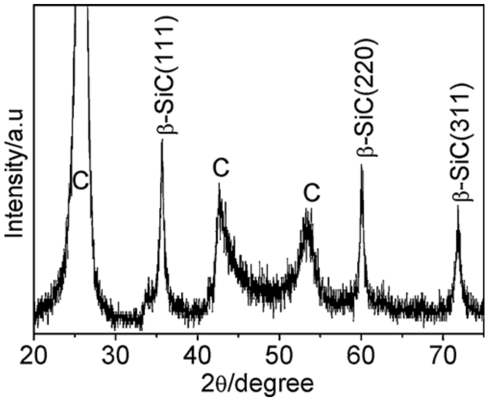

Fig. 1. XRD pattern of the as-grown SiC nanowires on the surface of C/C composites.

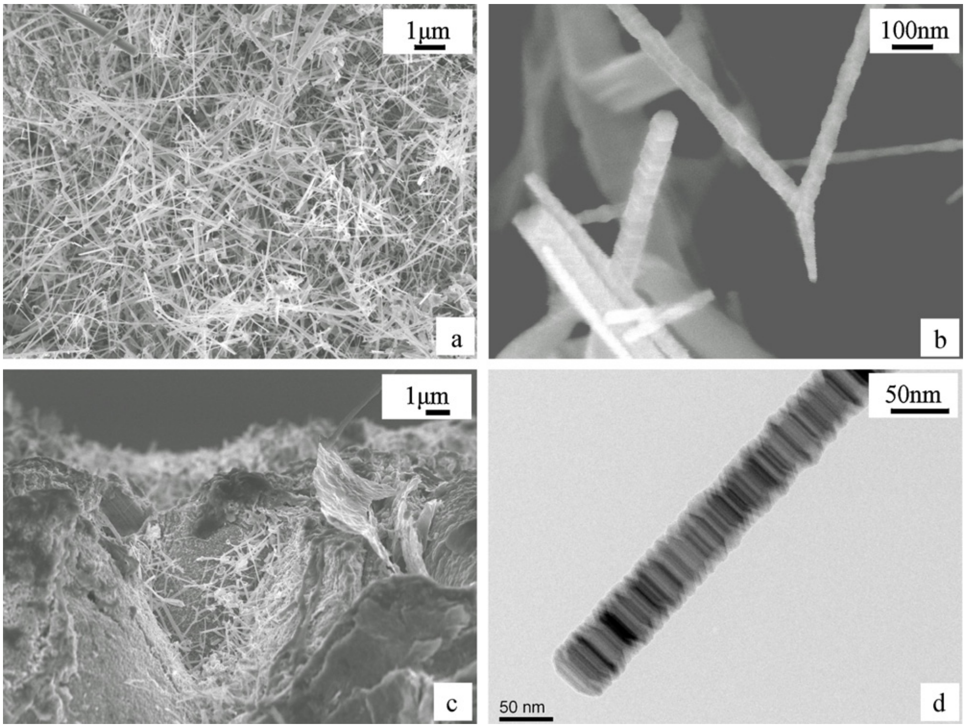

Fig. 2. Micrographs of the as-grown SiC nanowires on the surface of C/C composites. (a) SEM image of the surface of C/C composites; (b) SEM image of the SiC nanowires; (c) SEM image of the cross-section of C/C substrate; (d) TEM image of the SiC nanowires.

XRD patterns of the coatings obtained by the second step CVD are shown in Fig. 3. It indicates the formation of β-SiC in both of the coatings. In addition, the diffraction peaks of C are very high. The reason of that might be the thickness of the coatings is less than 30 μm, so the X-ray could easily detect C/C substrate beneath them. Compared with curve a in Fig. 3, curve b has a much lower diffraction peak of C and a higher diffraction peak of β-SiC, inferring that the thickness of the coating with SiC nanowires is larger than that of the SiC coating without SiC nanowires. Cross-section SEM micrographs of the SiC coatings show that, compared with the coated C/C composites without SiC nanowires, the thickness of the coating with SiC nanowires increased from 8 to 30 μm, which is caused by that SiC nanowires accelerate the SiC deposition rate.

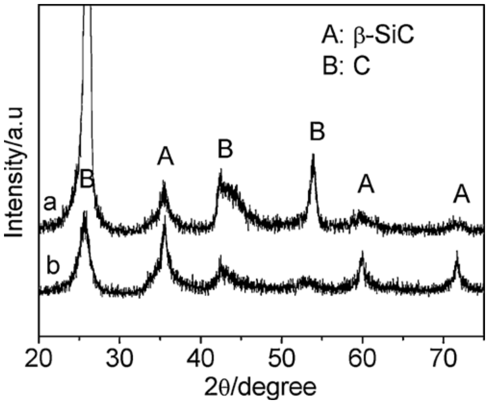

Fig. 3. XRD patterns of the coatings (a) without and (b) with SiC nanowires.

Fig. 4(a) shows surface SEM micrograph of the SiC coating without SiC nanowires. It clearly reveals that the coating exhibits a porous and nubbly structure. In addition, a microcrack can be found on the surface of the coating, which was formed during the cooling process from the preparation temperature to room temperature due to the mismatch of CTE between the coating and substrates. Surface SEM image of the coating with SiC nanowires shows the formation of a dense and crack-free surface (Fig. 4(b)). After depositing SiC nanowires, the deposition uniformity of SiC grains was improved by providing many nucleus for SiC nucleation. At the same time, the SiC nanowires, as reinforcing phases, could play an important role in avoiding the cracking of the coating caused by the mismatch of CTE between the coating and substrates.

Fig. 5(a) shows fracture surface SEM micrograph of the SiC coating with SiC nanowires. It clearly exhibits that the coating has a loose and porous structure, which could alleviate thermal stress caused by the mismatch of CTE between the coating and substrates, and avoid the cracking and spalling of the coating. Fracture surface of the coating is rugged (Fig. 5(a)), on which some notches, nanowire-toppings and a little pullout of SiC nanowires can be found, as shown in Fig. 5(b). SiC nanowires in the coating play an important role in deflecting or bridging cracks by absorbing energy, which would limit the enlarging of the microcracks. When microcracks propagate near the SiC nanowires, the propagation of microcracks will be retarded or even stopped. With further increase of the external force, microcracks will show markedly abrupt deflection or bridging along or around SiC nanowires. The propagation path of microcracks will increase, which needs much more energy, thus

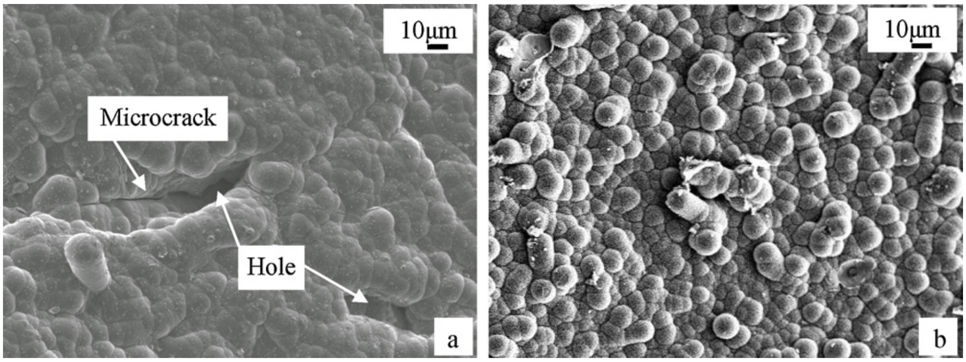

Fig. 4. Surface SEM micrographs of the SiC coatings (a) without and (b) with SiC nanowires.

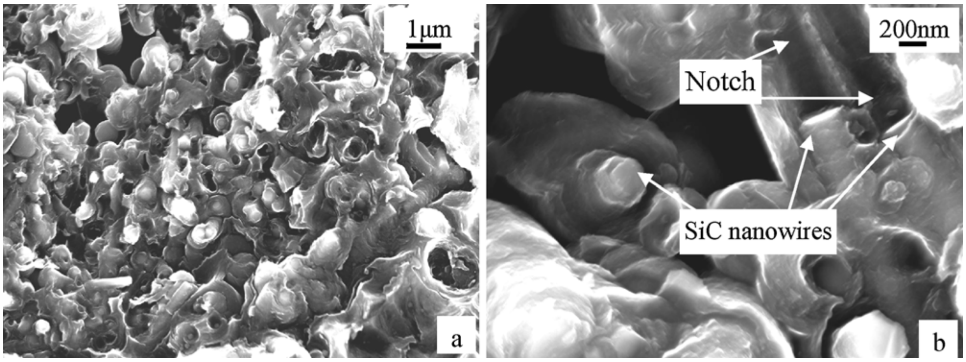

Fig. 5. Fracture surface SEM micrographs of the SiC coating with SiC nanowires at different magnifications. At (a) low and (b) high magnification.

the enlarging of the microcracks will be limited. In addition, SiC nanowires are random-orientedly in the coating (Fig. 5(b)), which is beneficial to the reinforcement efficiency of SiC nanowires. The broken SiC nanowires can be observed, but the debonding of SiC nanowires cannot be detected. Generally, the debonding of SiC nanowires occurs easily at the coating-nanowire interface. This suggested that SiC grains by the second step CVD formed an excellent interfacial bonding with SiC nanowires.

Cross-section SEM micrograph of the SiC coating without SiC nanowires is shown in Fig. 6(a). The coating is about 8 μm in thickness, and the coating/matrix boundary is obvious. In addition, a through-coating microcrack can be found in the coating, indicating the coating has a poor oxidation protective ability. As shown in the higher magnification image (Fig. 6(c)), some microcracks can be observed at the coating/matrix interface, which is disadvantageous to their interfacial bonding. The CTE of C/C composites is about $1.0 \times 10^{-6}\,K^{-1}$, while that of SiC is $4.5 \times 10^{-6}\,K^{-1}$, so the thermal stress will be caused due to the mismatch of their CTE. The existence of the microcracks will lead to the thermal stress concentration during thermal shock. As the thermal stress at the tip of the microcracks exceeds a certain value, microcracks will enlarge and form some through-coating cracks in the coating. Furthermore, some microcracks can also be detected near the coating in C/C substrate, which also would form through-coating microcracks in the coating during the preparation of the coating process. After introducing SiC nanowires, the low magnification cross-section SEM image of the coating shows the formation of a dense and crack-free coating that increases to 30 μm in thickness (Fig. 6(b)). The coating/matrix boundary is difficult to be distinguished, since SiC nanowires grow in the pores in the surface of C/C composites, which could form the pinning effect at the coating/matrix interface, and enhance their bonding strength. High magnification image of the coating with SiC nanowires is shown in Fig. 6(d), indicating a dense and flaw-free coating. SiC nanowires with random orientation can be found in the coating, which could effectively improve the thermal shock resistance of the coating.

The weight loss curves of the coated C/C composites during thermal shock between 1773 K and room temperature are shown in Fig. 7. The weight loss curves of the coated C/C composites can be characterized by straight lines, since the oxidation process of C/C composites is mainly controlled by the rate of O^{2-} reaction with C/C substrate during thermal shock. The slopes of these straight lines are different, indicating different thermal shock resistance. Before adding SiC nanowires, the slope of the straight line is $0.45\ g\ time^{-1}$. After introducing SiC nanowires, the slope of the straight line decreases to $0.21\ g\ time^{-1}$, indicating this modified coating possesses better thermal shock resistance. After thermal cycles between 1773 K and room temperature for 21 times, the weight loss of C/C composites with SiC coating toughened by SiC nanowires is only 4.45%, while that of the SiC coating without SiC nanowires is up to 9.32%. Moreover, the weight loss of C/C composites with SiC coating toughened by SiC nanowires is

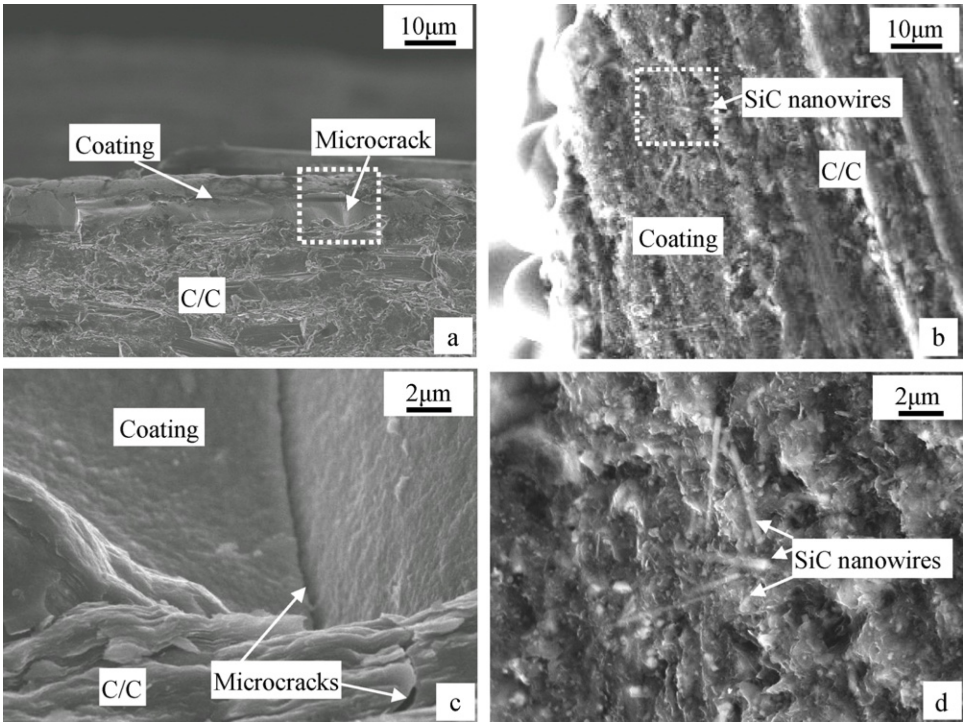

Fig. 6. Cross-section SEM micrographs of SiC coatings at different magnifications. (a) Without SiC nanowires at low magnification; (b) with SiC nanowires at low magnification; (c) without SiC nanowires at high magnification; (d) with SiC nanowires at high magnification.

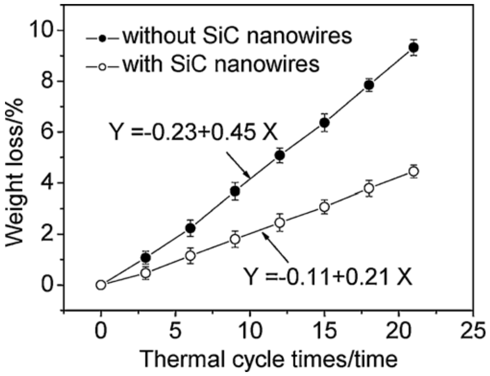

Fig. 7. Weight loss curves of coated C/C composites during thermal shock between 1773 K and room temperature.

only 3.07% after thermal cycles between 1773 K and room temperature for 15 times, but the weight loss of the SiC whiskers-SiC coated C/C composites has exceeded 3.07% after thermal cycles between 1073 K and room temperature for only 9 times [15], from which it can be inferred that the SiC coated C/C composites with SiC nanowires possesses better resistance to thermal shock than that of the SiC whiskers-toughened SiC coated C/C composites.

Fig. 8 shows surface SEM images of the SiC coatings after thermal shock between 1773 K and room temperature for 21 times. Some cracks can be found on the surface of the coating. These cracks might provide the ‘‘entrance channels’’ for oxygen to penetrate into the C/C matrix and lead to the oxidation of C/C composites. The cracks in the coating are considered to be formed due to the thermal stress caused by the mismatch of CTE between the coating and C/C composites.

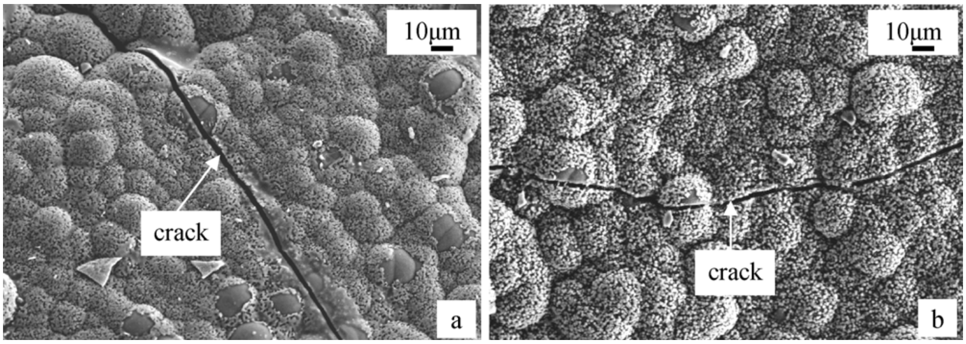

Fig. 8. Surface SEM micrographs of the SiC coatings (a) without and (b) with SiC nanowires after thermal shock between 1773 K and room temperature for 21 times.

Fig. 8(a) shows that the average size of the cracks in the coating is about 5 ± 0.5 μm. After introducing SiC nanowires, the average size of the cracks in the coating decreases to 3 ± 0.5 μm (Fig. 8(b)). Compared with the coating without SiC nanowires, these cracks extend zigzag in the coating toughened by SiC nanowires. The SiC nanowires play an important role in limiting the enlarging of the microcracks and inducing the deflection of the microcracks, which is advantageous in avoiding the formation of the through-coating cracks. So the thermal shock resistance of the coating with SiC nanowires is better than that of the coating without SiC nanowires.

4. Conclusions

A simple and low-cost method was carried out to improve the toughness of the SiC coating by introducing SiC nanowires. The result testifies that a dense SiC coating toughened by SiC nanowires can be obtained by a two-step technique of CVD. Observation of SEM and TEM confirms a relatively random-oriented distribution of SiC nanowires in the SiC coating. After introducing SiC nanowires, the size of the defects in the SiC coating could be decreased, and the thickness and thermal shock resistance of the SiC coating could be increased, respectively. This study provides an alternative means to improve the oxidation protective ability of the ceramic coating.

Acknowledgements

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