Oxidation behavior of SiC nanoparticle-SiC oxidation protective coating for carbon/carbon composites at 1773 K

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Oxidation protective coatings, typically ceramics, are considered to be an effective method for preventing carbon/carbon (C/C) composites from oxidation at high temperature. SiC ceramic is especially investigated as an attractive coating material because of its good mechanical properties, good physical–chemical compatibility with C/C matrix and excellent oxidation resistance [1,2]. The difficulty in developing SiC coating comes from the mismatch of the coefficient of thermal expansion (CTE) between SiC and C/C matrix, which leads to cracking and even debonding in the coatings under severe temperature change in service [3]. To solve this problem, functionally gradient coatings [4] or multilayer coatings [5] were developed by several researchers and acquired success at some extent.

On the other hand, SiC nanoparticles (SiC NPs) are regarded as excellent reinforcement and toughening for metal or ceramics materials [6,7]. Therefore, we introduced SiC NPs into SiC coating in order to increase the toughness of SiC ceramic coating, which will reduce cracking in the coating by alleviate the stress and improve the oxidation protective ability of SiC ceramic coating. However, up to now, there are no reports of utilizing the SiC NPs-SiC coating for protecting the C/C composites from oxidation.

A SiC NPs-SiC coating including a C/SiC gradient inner layer was prepared by slurry and pack cementation. The oxidation behavior of the coating at 1773 K in air was investigated.

Small cube specimens (10 mm × 10 mm × 10 mm) as substrates were cut from bulk 2D-C/C composites (prepared by TCVI) with a density of 1.70 g/cm^3. Before coating, the specimens were hand-polished with 400 and 800 grit SiC papers orderly, then cleaned ultrasonically with distilled water and dried at 373 K. The C/SiC gradient inner layer was prepared by two-step slurry and pack cementation technique reported earlier [8]. Commercially available phenol formaldehyde resin and fine graphite powders (300 mesh) were used to form the pre-coated carbon layer by slurry and carbonization treatment in a nitrogen atmosphere at 1073–1273 K. The second step was to prepare the C/SiC coating on the surface of pre-coated carbon layer by a pack cementation process with Si, C and Al_2O_3 powders in argon atmosphere at 1873 K for 2 h. The SiC NPs-SiC outer coating was prepared on the surface of C/SiC coated C/C composites by pack cementation. The Si, graphite powders and SiC NPs (about 20 nm in size) were used to prepare the SiC outer layer with SiC nanoparticle dispersion. In order to obtain the homogenous distribution of SiC NPs, the polypropylene acid natrium (NaPAA) was used as dispersant and distilled water as solvent, the SiC NPs were dispersed and then mixed with other pack powders ultrasonically in a breaker. After this processing, the mixed powders was placed in grinding jar to blend, and then they were dried overnight in a drying furnace at approximately 373 K. Finally, the above mixed powders were used as the pack materials to prepare the SiC NPs-SiC outer layer. The pack cementation temperature was 2073–2273 K.

The isothermal oxidation tests of the coated samples were carried out at 1773 K and the thermal shock experiments were also performed between 1773 K and room temperature. The cumulative weight changes of the samples were reported as the function of oxidation time and thermal cycling times. The crystalline structure, phase composition and morphology of the coatings were analyzed by X-ray diffraction (XRD, X' Pert PRO) using Cu Kα radiation, scanning electron microscopy (SEM, JSM-6460, 6700) with energy dispersive spectroscopy (EDS).

Fig. 1a illustrates the surface SEM micrograph of SiC NPs-SiC coating. It could be found that a compact and crack-free coating was formed. X-ray diffraction analysis shows that the as-prepared coating was composed of Si, β-SiC and α-SiC (Fig. 2). Otherwise, β-SiC peaks in the 60° of 2θ broadened, which indicated the SiC crystal grains with very small size were found in the coating. The cross-section SEM image of the coating is shown in Fig. 1b. It reveals that the multiphase coating is not uniform in thickness, from 150 to 250 μm, and there are no penetration cracks or big holes in the coating. In addition, as shown in this image, a lot of pack powders infiltrated into the inside of C/C composites through the pinholes or interfaces between carbon matrix and carbon fiber, and interleaving

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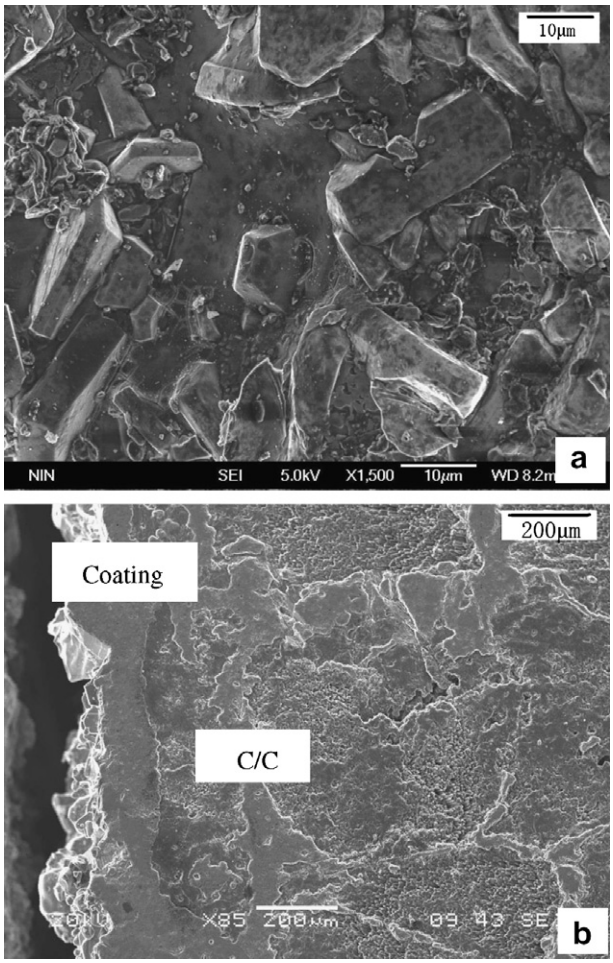

Fig. 1. Surface and cross-section SEM images of the SiC NPs-SiC coating: (a) surface and (b) cross-section.

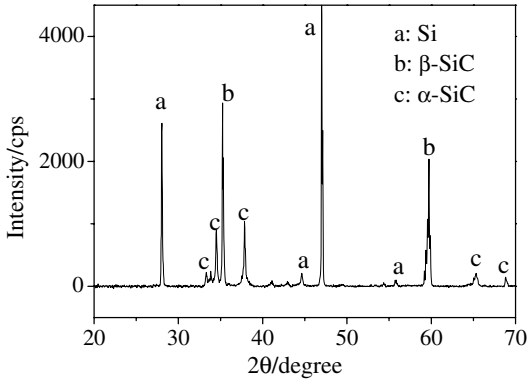

Fig. 2. XRD pattern of the SiC NPs-SiC coating surface.

structure was formed, which could increase bonding strength between the coating and the C/C matrix. Therefore, the dense SiC NPs-SiC coating can be prepared by the pack cementation technique, which is expected to have good oxidation protective property at 1773 K.

The isothermal oxidation and fitting curves of the C/C composites with the SiC NPs-SiC coating in air at 1773 K are shown in Fig. 3. It is clear that the weight loss of the coated specimens is only 0.27% after oxidation for 215 h, which exhibits better oxidation protective ability than SiC coating without SiC NPs (0.27% after oxidation at 1773 K for 30 h) [2]. Introducing the SiC NPs into the SiC coating could improve the oxidation protective ability of the SiC coating. Based on the oxidation temperature of the coated specimens, a passive oxidizing reaction might be dominant on the surface of the SiC NPs-SiC coated specimens in the furnace. Glass phase SiO_2 with very low oxygen permeability was formed on the coating surface (Fig. 4a), which can efficiently protect C/C matrix from oxidation. The XRD pattern (Fig. 5) of the coating after oxidation for 215 h shows that a new SiO_2 glass phase appeared, which verifies the above-mentioned oxidation reaction between the coating and oxygen. The passive oxidation of SiC is a weight gain processing. As shown in Fig. 3a weight gain occurred in the specimens at the initial oxidation stage (under 9 h). However, the weight gain of coated specimens exhibited decreasing trend due to the integrality SiO_2 layer could not be formed, the C/C matrix could not be protected absolutely and it would be oxidized. In this stage (Fig. 3I), the oxidation kinetics is typically described in terms of parabolic law. With the oxidation time extending (18–143 h), the surface of the coating changed entirety into SiO_2 glass. Therefore, the transformation of SiC in silica entails a weight gain and the oxidation of C/C matrix in CO or CO_2 entails a mass loss exhibits almost equivalent, the coated sample exhibits slight weight loss with very slow speed and the weight loss vs oxidation time follows the exponential growth law. After 143 h oxidation in air at 1773 K, excessive gas pressure was generated beneath the SiO_2 film by the gases from the oxidation of SiC NPs-SiC coating or C/C matrix and these gases got out through the SiO_2 film when the gas pressure reached a high value, which resulted in the formation of some holes on the glass layer (Fig. 4a). As shown in Fig. 4b and c, the holes in the coating included two kinds of types, that is, closed holes and open holes. These closed holes are not considered as the main reason of the weight loss of the coated specimens, because they did not provide channel for the quick diffusion of oxygen to C/C matrix. However, these open holes became the channel of the oxidation of the C/C matrix. As a result, weight loss vs oxidation time follows a quasi-linear manner. The weight loss of the coated specimens increased quickly with the oxidation time. The cross-section SEM image of the coating after oxidation for 215 h at 1773 K indicates a slight oxidation under the open hole and the carbon matrix has been oxidized prior to the carbon fiber. Therefore, the weak weight loss of the coated sample was primarily due to the formation of the open holes in the coating during the oxidation test. Moreover, the SiC NPs-SiC coating exhibited excellent thermal shock resistance. The sample could undergo the thermal cycling between 1773 K and room temperature for 40 cycles, no spallation or peeling is found, and the weight loss of the coated specimens is only 1.52% (Fig. 3b).

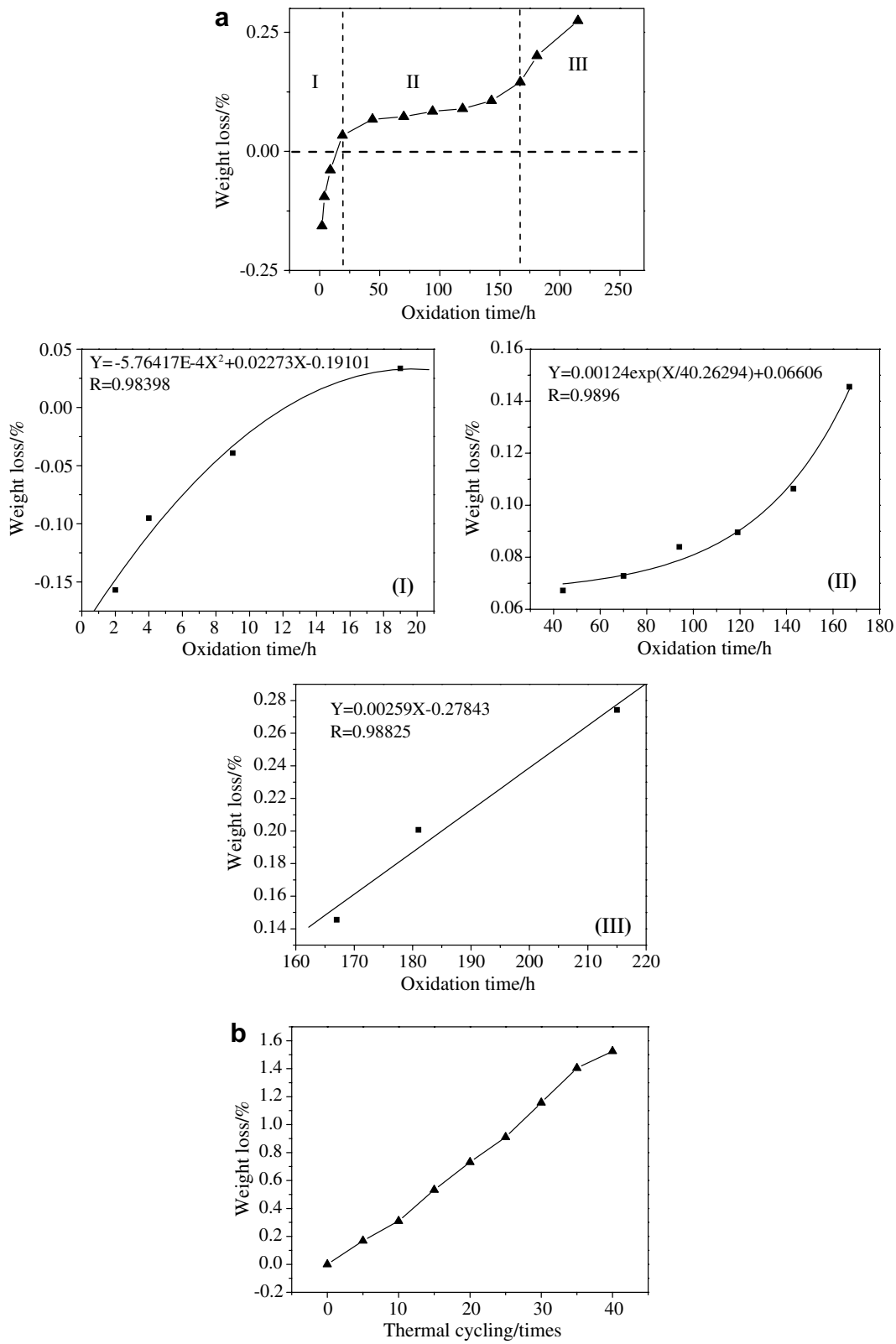

Fig. 3. The oxidation curves of the coated specimens: (a) the isothermal oxidation at 1773 K and fitting curves and (b) the thermal cycling oxidation between 1773 K and room temperature.

In conclusion, an effective SiC NPs-SiC oxidation protection coating for C/C composites was produced by slurry and pack cementation. The double-layer coating could effectively protect the C/C composites from oxidation for more than 215 h at 1773 K and undergo the thermal shock between 1773 K and room temperature for 40 cycles. The

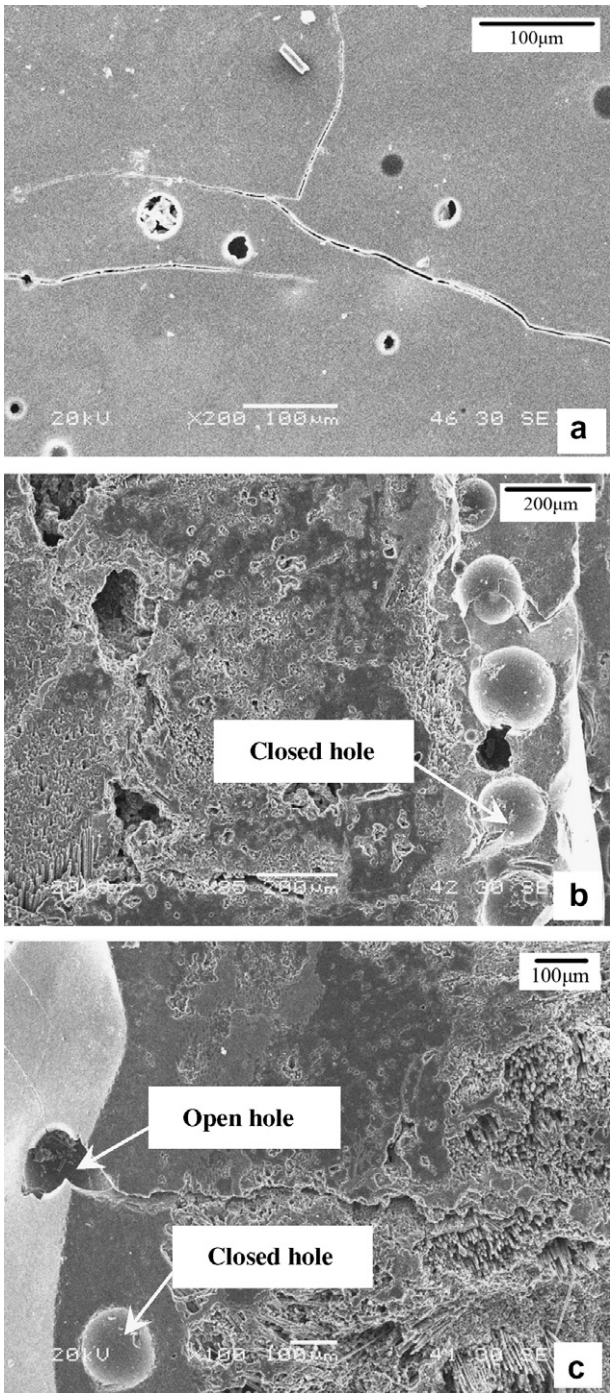

Fig. 4. Surface and cross-section SEM images of the coating after oxidation for 215 h at 1773 K: (a) surface and (b,c) cross-section.

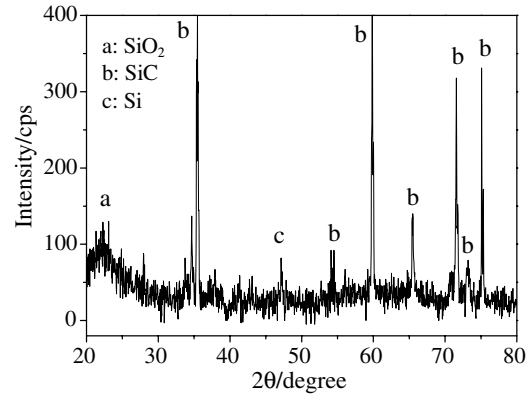

Fig. 5. XRD pattern of the SiC NPs-SiC coating after oxidation for 215 h at 1773 K.

open holes and closed holes were found after oxidation at 1773 K, and the open holes resulted in the weak weight loss of the coated samples.

Acknowledgement

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