A carbon nanotube-enhanced SiC coating for the oxidation protection of C/C composite materials

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Abstract

A carbon nanotube-enhanced SiC (CNT-SiC) coating was deposited on C/C composites to improve the oxidation resistance of C/C. The CNT-SiC coating was prepared by direct growth of CNTs on C/C surface at 700ºC followed by deposition of SiC using chemical vapor deposition at 1150ºC for 1 hour. SiC was deposited on the CNTs as well as the interface between CNTs and C/C, making CNTs strongly rooted on C/C surface. The final CNT-SiC coating consisted of two layers: the CNT-SiC layer and SiC layer. In comparison to the SiC coating, the CNT-SiC coating showed fewer cracks and a better oxidation resistance because the CNTs reduce the stress in the coating caused by the mismatch of the coefficient of thermal expansion between C/C and SiC.

Keywords: Carbon nanotubes; Carbon/carbon composites; Chemical vapor deposition; coating.

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1. Introduction

Carbon fiber reinforced carbon composite materials (C/Cs) combines the high refractory properties, lightweight of graphite material with high fracture toughness of fiber reinforcement; therefore, they have been applied in some extremely severe service conditions such as nose cone and leading edge of space shuttle, brake disk of airplanes and racing cars [1]. However, lack of stability in air at elevated temperature restricted their application fields. The anti-oxidation coatings for C/Cs, typically SiC, had thus been employed to protect C/C from burn-off [2].

The mismatch between the coefficients of thermal expansion (CTEs) of SiC and C/C, however, leads to cracking in the coating, leaving paths for diffusion of oxygen. Multilayer coating systems with stress alleviation layer and glass forming layer had been developed to decrease the cracking and seal the cracks during oxidation [3-8]. In this paper, an alternative carbon nanotube/SiC (CNT/SiC) coating was employed for the oxidation protection of C/C composites.

Carbon nanotubes (CNTs) with extremely high mechanical strength and high ductility have been used in composite materials to improve strength of plastic [9] or fracture toughness of ceramics [10]. In our previous short report [11], it was known that the incorporation of CNTs in SiC coating improved the oxidation resistance and thermal shock resistance of the coating. In this paper, we reported in a detail the deposition process and microstructure of CNT-SiC coating and the mechanism of its oxidation resistance.

2. Experimental

2.1 Growth of CNTs on C/Cs

C/C plates (provided by Osaka Gas Co. Japan) were cut to a size of $4.5 \times 4.5 \times 4.5$ mm^3. Catalytic CVD method was used to grow directly CNTs on the surface of C/C samples. First, C/C samples were impregnated in an ethanol solution of cobalt nitrate and iron nitrate with Co/Fe ratio of 7:3. After dried at 110ºC for 1 hour, the C/C samples were subsequently set in a CVD reactor for growth of CNTs. When the temperature of the reactor reached 700ºC with a heating rate of 10ºC/min in N_2, H_2 with a rate of 100

ml/min was flowed to reduce the catalyst into metallic state for 30 min. Subsequently, C_2H_2 was flowed with the rate of 20 ml/min for 20 min to synthesize CNTs.

2.2 Deposition of SiC coating and pyrolytic carbon

The deposition of SiC on C/C and CNT-covered C/C samples were conducted using low-pressure CVD technique in an alumina reactor with an inner diameter of 30 mm. The deposition conditions were as follows; the deposition temperature was 1150ºC; the pressure of deposition was 4 kPa, and the flow rates of H_2 and Ar were 30 ml/min and 50 ml/min, respectively; the vaporization rate of methyltrichlorosilane (MTS) was 6.7×10^{-4} mol/min; the deposition time was 60 min. For some samples, pyrolytic carbon (PyC) was deposited using CH_4 as carbon source before SiC deposition and the obtained coating is called CNT/PyC/SiC coating.

2.3 Characterization

The oxidation behaviors of C/C samples with coatings were evaluated in thermogrammatic analysis with a heating rate of 10ºC/min up to 1200ºC in N_2, and then held at 1200ºC in air of 30 ml/min. The morphology and structure of carbon nanotubes and SiC coatings were examined using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM).

3. Results and Discussion

3.1 Morphology and microstructure of CNTs

A typical morphology of the C/C samples used in the experiment is shown in Fig. 1A. In pristine C/C, some large pores with a size of about several hundred micrometers and small pores with a size of about several micrometers were observed. After C/C samples were impregnated with catalyst precursor solution and subsequently calcined at $700^{\circ}C$, catalyst nanoparticles were formed on the surfaces of C/C samples as shown in Fig. 1B. Due to the rough surface of C/C at nano-scale, nanoparticles were uniformly distributed on the surface without apparent coarsening.

With the growth of CNTs at $700^{\circ}C$, the C/C samples were covered with a layer of CNTs, as shown in Fig. 2A and Fig. 2B. The thickness of the CNT layer varied from 5–

10 μm due to the varying length and curving of CNTs. The growth of CNTs in the pores of C/C was also observed. Although the as-grown CNTs showed good binding to C/C due to the rough surface of C/C, the overloading of the catalyst was not favorable since the overgrowth of CNTs resulted in easily peeling of CNT layer. According to TEM observation of CNTs as shown in Fig. 2C and Fig. 2D, the CNTs had diameter ranging from 10 nm to 50 nm and exhibited curved shape and less ordered structure, suggesting that the as-grown CNTs might not have high mechanical strength.
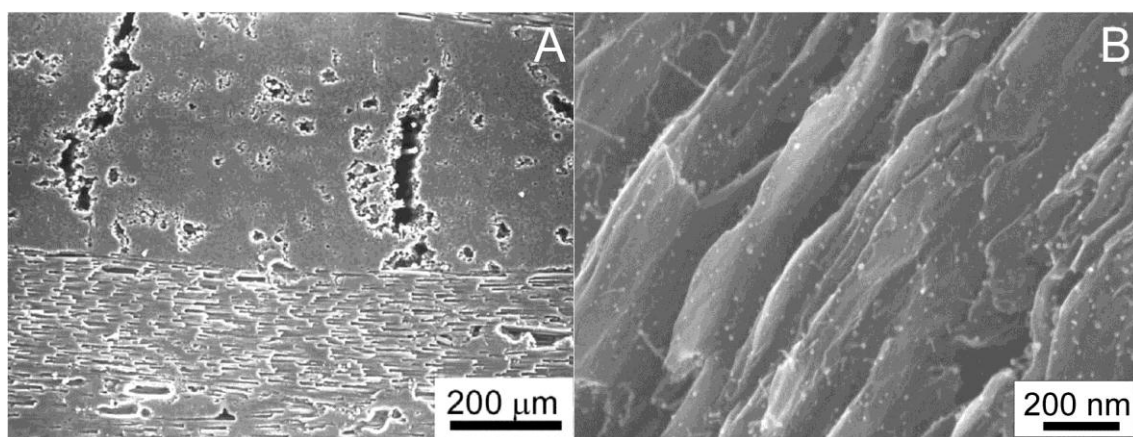

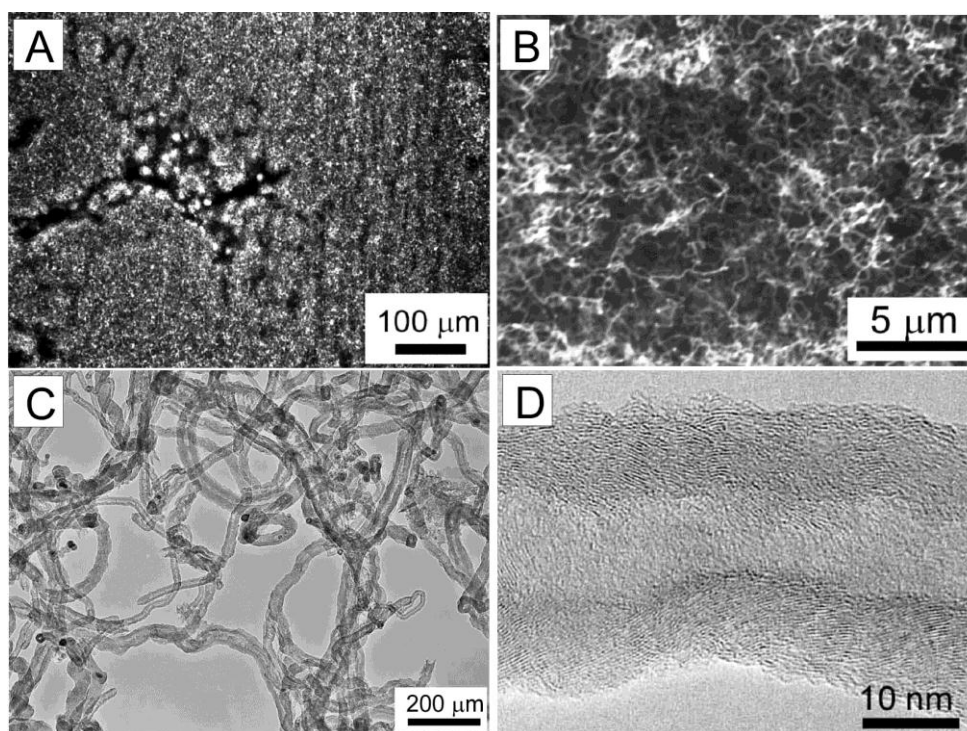Fig. 1 SEM micrograph of C/C and catalyst nanoparticles loaded on C/C.

Fig. 2 SEM and TEM images of CNTs directly grown on the surface of C/C.

3.2 Morphology of SiC coating and CNT-SiC coating

SiC coatings were deposited on C/C surface at 1150ºC for 1 hour. XRD profiles showed that the coating was β-SiC. Fig. 3 shows the morphology of the SiC coating on C/C and its polished cross-section. The SiC coating was uniformly deposited on the surface of C/C sample with a thickness of about 12 μm. The SiC coating showed granular morphology with small crystallines growing in random direction. Cracks were observed in the coating, which were formed on cooling from 1150ºC to room temperature due to the mismatch of CTE between SiC and C/C.
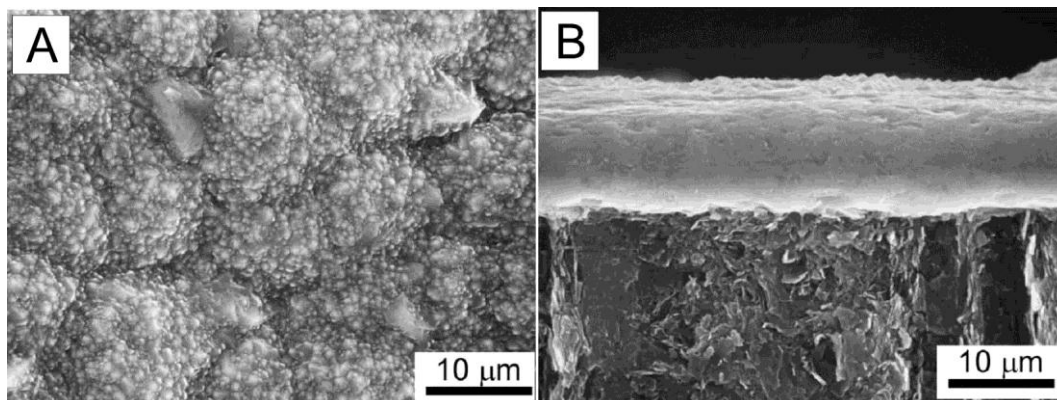

Fig. 3 The morphology of surface (A) and cross-section (B) of SiC coating deposited at 1150ºC for 1 hour on the C/C surface.

For the deposition of SiC on CNTs-coated C/C, low pressure is required for the precursor gases to diffuse rapidly into the porous CNT layer. With SiC deposition for 5 min, SiC spherical particles with diameter of 300 nm were formed on CNTs (Fig. 4A). After deposition of 10 min, SiC covered the CNTs completely and formed continuous coating on CNTs (Fig. 4B). In a general, it is difficult for SiC to nucleate on CNTs due to the inert graphene surface and small diameter of CNTs. Once nucleation of SiC occurred on CNTs, the growth on the nuclei would be faster than formation of new nuclei on CNTs, thus resulting in pearl-like SiC particles on CNTs. As the spherical particles became large enough to contact each other, a continuous SiC coating on CNTs was formed. Furthermore, the observation of cross-section of the coating verified SiC also deposited on the interface between CNTs and C/C as shown in Fig. 4C and Fig. 4D.

Therefore, the densification of CNT/SiC coating consisted of two processes; the deposition on the interface between C/C and CNTs layer, and the deposition on the surface of CNTs. The growth of CNTs and deposition of SiC inside the pores of C/C were also observed, which contributed to the strong bonding between C/C and the CNT-SiC coating.
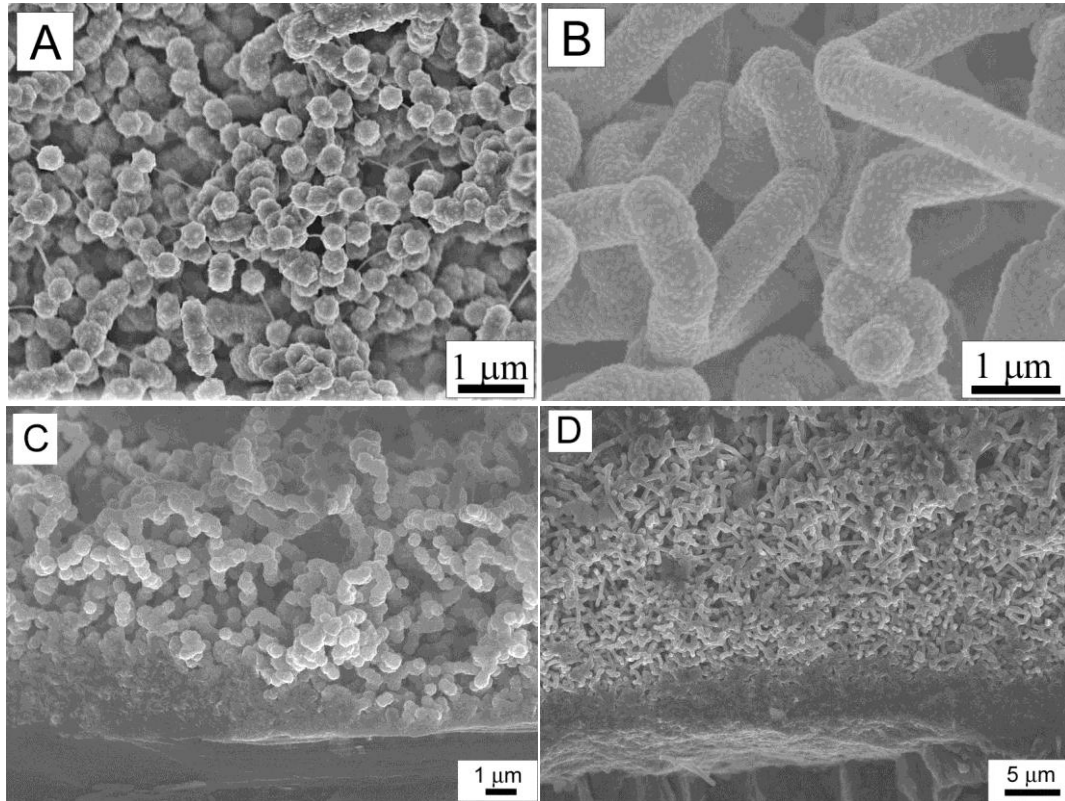

Fig. 4 The morphology of SiC deposited on CNTs for 5 min (A) and 10 min (B) at 1150ºC.

With further depositon of SiC, the CNT layer was densified and an outerlayer SiC formed as shown in Fig. 5A. The final coating actually consisted of two layers, the inner CNT/SiC layer and outer SiC layer. The fracture surface showed that the SiC layer had a smooth fracture surface, while the CNT/SiC layer showed rough fracture surface due to the existence of CNTs. The CNT/SiC layer bonded well with C/C because CNT grew from the rough surface of C/C and deposition of SiC made the layer firmly rooted in C/C.

If pyrolytic carbon was deposited on CNTs prior to SiC coating, then we get coating

consisted of CNT-PyC-SiC layer and SiC layer [11], as shown in Fig. 5B. They showed similar morphology as CNT-SiC coating. A difference can be observed at high magnification with CNT-PyC-SiC showing a thick fiber due to the deposition of PyC on CNTs. Despite the rough fracture surface, no long pullout of CNTs was observed, suggesting a strong interface between CNTs and SiC.
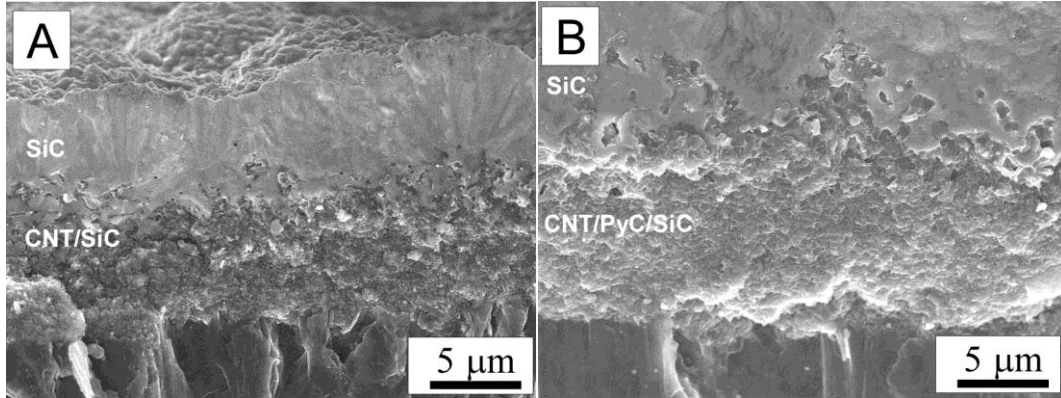

Fig. 5 The cross-section (A) of CNT-SiC coating and CNT-PyC-SiC coating (B) that were prepared at 1150ºC. The coatings consisted of two layers: the outer SiC layer and inner CNT-SiC or CNT-PyC-SiC layer.

The CNTs have high density (number in unit area) near the surface because they grew from the surface or pores. With increase of the distance from the surface, the number of CNTs decreases since the curved CNTs were not in same length. In this way, there exists a gradient distribution of CNTs through the thickness of CNT-SiC layer and CNT-PyC-SiC layer.

Fig. 6 The mass changes of C/C (A), C/C with SiC coating (B), C/C with CNT-SiC coating (C) and C/C with CNT-PyC-SiC (D) coating in the oxidation at 1200ºC in air.

3.3 Oxidation tests

Fig. 6 shows the mass loss of the samples in the oxidation tests at 1200ºC in air for 2 hours. C/C disappeared completely after oxidation for 70 min. The SiC-coated C/C samples lost 55% of its mass in 2 h, while the
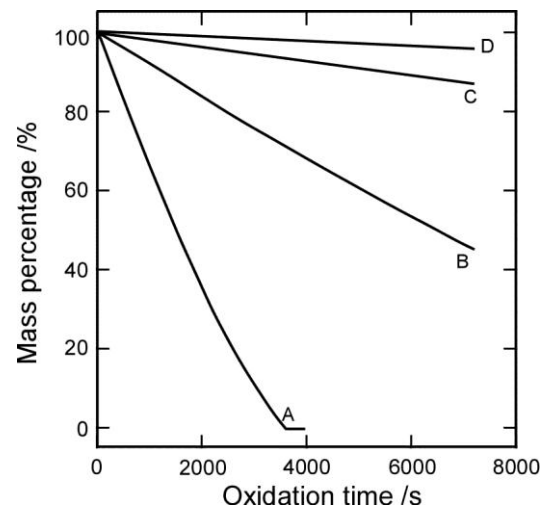
CNT-SiC-coated samples lost 15% of its mass in 2 hours. This indicated that the CNT-SiC samples have an oxidation rate about 1/3 of the SiC-coated samples. C/C with CNT-PyC-SiC coating showed roughly 5% mass loss.

The oxidation of C/C is caused by the diffusion of oxygen through the cracks in the coating that were formed during the cooling from high temperature. The oxidation of carbon materials has two main steps: the diffusion of gases (O_2 and CO_2) and the surface reaction between O_2 and C. Previous researches showed that the oxidation of carbon materials in air at 1200ºC was diffusion-rated process [12], because the surface reaction was very rapid. In the present C/C with CNT-SiC coating, the Fe-Co particles remained in C/C would catalyze the oxidation process, making the surface oxidation reaction even faster. Therefore, the oxidation rate of the C/C with coating is controlled by the oxygen diffusion through the cracks for the coating significantly reduced the oxygen diffusion rate. By assuming the diffusion of oxygen through the cracks follows the Fick's Law (the width of cracks is larger than mean free path of O_2) and the gradient of O_2 is homogeneous, the diffusion rate of oxygen through the cracks is expressed as

$$R = AD_O \frac{\partial P_{O2}}{\partial x} = nA_c D_O p_{O2} / d \tag{1}$$

where D_o is diffusion coefficient, p_{O2} the pressure of O_2 in air and d the thickness of coating, A the cross section surface area of the cracks, n the number of cracks and A_c the average opening area of crack. Therefore, the oxidation rate of coated-C/Cs is proportional to the number of cracks and inversely proportional to the thickness of coating.

SEM observations indicated that the cracks were almost in one direction, normal to the carbon fiber direction in C/C, since C/C in this direction have a very small thermal expansion. When the samples with SiC coating were cooled from high temperature, the coating layer would be in tensile stress, causing cracks in coating if the tensile stress exceeded the strength of coating [13]. The number of the cracks in one surface of the coating was counted under optical microscopy. It was found that the number of cracks in the SiC coating was about 21-30, while that in the CNT-SiC coating and CNT-PyC-SiC was about 11-14 and 5-7 respectively in one surface of 4.5mm×4.5mm.

The average distant between cracks is 150 μm to 220 μm, while that in CNT-SiC coating and CNT-PyC-SiC is 320-410 μm and 1 mm.

There are several reasons for decreasing of cracks in coating with CNTs. The effect of CNTs depended upon the growth density or amount of CNTs on C/C, which was approximately 5-10 mass% of SiC. Therefore, the volume fraction of CNTs in the CNT-SiC layer reached 30%. Firstly, CNTs in SiC coating decrease the CTE of CNT-SiC layer. Since they have a gradient distribution of CNTs along the thickness as described above, the thermal expansion of the CNT-SiC layer gradually changed from the C/C-coating interface to the SiC layer, thus the stress in the coating was alleviated [14]. And this effect is further enhanced by the deposition of pyrolytic carbon. Secondly, CNT pullout and rough fracture surface may have contributed to the toughness of coating, thus making coating difficult to cracking. However, the CNTs grown directly on C/C, which did not have a typical multi-walled CNT (MWNTs) structure, probably had lower mechanical strength than that of typical MWNTs; therefore, CNTs-SiC were not able to prevent completely the cracking in the coating.

4. Conclusions

SiC coating prepared by CVD method at 1150ºC for 1 hour was homogeneous, but cracking occurred due to the mismatch of CTEs between the coating and C/C. CNT-SiC coating and CNT-PyC-SiC coating have two layers structure with inner CNT/SiC layer or CNT/PyC/SiC layer and outer SiC layer. The inner layers showed a strong bonding to C/C since CNTs rooted in the rough surface of C/C. The oxidation tests in 1200ºC showed the CNT/SiC coating had oxidation rate about one third of SiC coating, and CNT-PyC-SiC showed best oxidation resistance due to less cracking in the coating. These results demonstrated that CNTs in the coating were beneficial for the oxidation resistant coating. Although complete oxidation protection was not achieved with only CNTs, they can be used in multiple layer coating system.

References

[1] Fitzer E. The future of carbon-carbon composites. Carbon 1987; 25(2):163-90.

[2] Strife RJ, Sheehan JE. Ceramic coatings for carbon-carbon composites. Ceramic bulletin 1988; 67: 369-374.

[3] Westwood ME, Webster JD, Day RJ, Hayes FH, Taylor R. Oxidation protection for carbon fiber composites. J Mater Sci 1996; 31: 1389-1397.

[4] Aoki T, Hatta H, Hitomi T, Fukuda H, Shiota I, SiC/C multi-layered coating contributing to the antioxidation of C/C composites and the suppression of through-thickness cracks in the layer. Carbon 2001; 39: 1477-1483.

[5] Morimoto T, Ogura Y, Kondo M, and Ueda T, Multilayer coating for carbon-carbon composites, Carbon 1995; 33: 351-357.

[6] Kim JI, Kim WJ, Choi DJ, Park JY, Ryu WS. Design of a C/SiC functionally graded coating for the oxidation protection of C/C composites. Carbon 2005; 43: 1749-1757.

[7] Huang JF, Zeng XR, Li HJ, Li KZ, Xiong XB. Oxidation behavior of SiC–Al_2O_3-mullite multi-coating coated carbon/carbon composites at high temperature. Carbon 2005; 43: 1580-1583.

[8] Yamamoto O, Sasamoto T, Inagaki M. Antioxidation of carbon-carbon composites by SiC concentration gradient and zircon overcoating. Carbon, 1995; 33: 359-365.

[9] Tostenson ET, Ren ZF, Chou TW, Advances in the science and technology of carbon nanotubes and their composites: a review. Compos Sci Tech 2001; 61: 1899-1912.

[10] Yamamoto G, Omori M, Hashida T, Kimura H, A novel structure for carbon nanotube reinforced alumina composites with improved mechanical properties, Nanotechnology, 2008; 19: 315708.

[11] Zheng GB, Mizuki H, Sano H, Uchiyama Y, CNT–PyC–SiC/SiC double-layer oxidation-protection coating on C/C composite, Carbon, 2008; 46: 1808-1811.

[12] Bacos MP, Cochon JL, Dorvaux JM and Lavigne O, C/C composite oxidation model: II. Oxidation experimental investigations, Carbon, 2000; 38: 93-103.

[13] Teixeira V, Residual stress and cracking in thin PVD coatings, Vacuum, 2002; 64: 393-399.

[14] Liu W, Wei Y, Deng J, Carbon-fiber-reinforced C-SiC binary matrix composites. Carbon, 1995; 33: 441-447.