

CNT-PyC-SiC/SiC double-layer oxidation-protection coating on C/C composite

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Ceramic coatings such as SiC are applied on carbon fiber/carbon composite materials (C/C) to protect them from oxidation in air at elevated temperatures [1-2]. However, the mismatch of CTEs between coating and C/C generally give rise to cracks in the coating so that the coating fails to prevent the diffusion of oxygen. To overcome this problem, multi-layer coatings or functional graded coating were applied either to seal the cracks of coating or alleviate the stress that cause cracking in the coating [3-7]. Even though, problem still exists because weak bonding between coating and C/C may cause the collapse of the coating system under severe thermal cycling.

In our previous report, we proposed an alternative method by incorporating carbon nanotubes (CNTs) in the coating system, to enhance the bonding strength between C/C and SiC coating, and suppress the cracking in coating [8]. However, a complete prevention of cracking has not been achieved though CNTs improved the bonding strength between C/C and coating, and decreased the number of cracks in the coating. In this letter, we reported CNT-PyC-SiC coatings prepared by depositing pyrolytic carbon (PyC) on CNTs previous to SiC deposition and effects of PyC deposition on the cracking of the coating and the oxidation-protecting behavior.

The growth of CNTs on C/C samples ( $4.5 \times 4.5 \times 4.5 \text{ mm}^3$ ) was performed as described in the previous report [8]. The deposition of PyC was carried out in a tubular reactor at  $1150^\circ\text{C}$  under a pressure of 4 kPa with the flow rate of  $\text{CH}_4$  20 ml/min for 5, 10, and 15 min, respectively. After PyC deposition, SiC was deposited in the same reactor by changing the gas flow. The deposition conditions of SiC were as follows: the deposition temperature was  $1150^\circ\text{C}$ ; the pressure of reactor was 4 kPa, and the flow rates of  $\text{H}_2$  and Ar were 30 ml/min and 50 ml/min, respectively; the vaporization rate of methyltrichlorosilane (MTS) was  $6.7 \times 10^{-4}$  mol/min; the deposition time was 60 min. In addition, we also prepared SiC coated C/C that is denoted as C1, and CNT-SiC coated C/C denoted as C2. The CNT-PyC-SiC samples with PyC deposited for 5, 10 and 15 min were denoted as C3, C4 and C5, respectively. The morphology and structure of

carbon nanotubes, PyC, SiC and the coatings were observed using SEM and TEM. The cracks in the coating were counted using an optical microscope and SEM. The oxidation behavior of C/C samples with coatings was evaluated in TGA at 1200°C for 2 hours in air of 30 ml/min.

Fig. 1(A) shows the as-grown CNTs on C/C surface, which were *in situ* grown using Fe-Co catalyst at 700°C. These CNTs had average diameter of about 50 nm and covered the whole surfaces of C/C. After pyrolytic carbon deposition at 1150°C for 5 to 15 min, the diameter of CNTs, which had twisted morphology, increased to 140-200 nm, depending upon the deposition time, as shown in Fig. 1(B)-(D). In addition to the thick CNTs, there are also some long, thin nanotubes. These nanotubes had been grown from the catalyst remained on C/C or CNTs during the deposition of pyrolytic carbon. TEM observation showed these nanotubes had a more ordered structure than those as-grown CNTs. Generally, the higher temperature resulted in more ordered CNT structure.

The subsequent deposition of SiC resulted in CNT-PyC-SiC coating, whose morphology is shown in Fig. 2. The CNT-PyC-SiC coating shows similar surface morphology to that of CNT-SiC or SiC coating. Cracks still exist in the coating, but the number of cracks in the coating was much fewer. Observation of cross section of the CNT-PyC-SiC coatings reveals that they consist of two layers with different morphology; one is CNT-PyC-SiC layer and the other SiC layer (Fig.3). SiC first deposited into the CNT-PyC framework, and after densification, SiC further deposited on the top of the CNT-PyC-SiC layer. It is noteworthy that the boundary between C/C and CNT-PyC-SiC layer is not distinct, since CNTs grew from the pores in C/C surface and the following pyrolytic carbon deposition made them fixated in the substrate. This suggests that the bonding of CNT-PyC-SiC coating to C/C should be stronger than a direct SiC coating on C/C. In addition, the boundary between CNT-PyC-SiC layer and SiC layer is neither a straight one as seen from Fig. 3. This suggests that CNT-PyC-SiC layer also has a strong bonding to SiC layer.

Fig. 4 shows the mass change of the coated C/C samples after oxidation at 1200°C for 2 hours. SiC coated C/C lost ca. 50% of mass after 2 h oxidation, while CNT-SiC coated C/C shows 13% mass loss. With the PyC deposition, the CNT-PyC-SiC coated C/C shows less mass loss than CNT-SiC coating, or has a better oxidation-protection. With increasing PyC in the coating, the CNT-PyC-SiC coating exhibits better oxidation-protection behavior, although a complete oxidation-protection has not been achieved.

In general, cracks arise in SiC coating on C/C on cooling from the deposition temperature to room temperature due to the mismatch of their CTEs [5]. These cracks turn out to be paths for the oxygen diffusion. Therefore, the oxidation rate of the samples is dependent upon the cracks in the coating. Since the cracks in the coating were almost in same direction normal to the fiber axis, we were able to count the cracks of the coatings easily under an optical microscope, and correlated the average numbers of cracks with oxidation rate and plotted in Fig. 5. On average, there are 35 cracks in a surface of SiC coated C/C sample, and the number of cracks decreased significantly to 13 for CNT-SiC coating. For CNT-PyC-SiC coating, with increasing PyC amount, the number of cracks in coating decreased further. From Fig. 5, we can see that the oxidation rate of the samples decreased as the number of cracks in a coating decreased. However, the relation of the oxidation rate with the number of cracks is not linear. There may be other parameters affecting the diffusion of oxygen, for example, the width and depth of cracks. Especially in CNT-PyC-SiC, some cracks may not extend into the CNT-PyC-SiC layer.

One role of PyC is to weaken the bonding between CNT and SiC. In micro-scale composite like carbon fiber/SiC composite materials, PyC layers are often deposited on the surface of carbon fibers to weaken the interface bonding and to deflect the cracks in order to improve the toughness [9]. The rough fracture surface of CNT-PyC-SiC layer in comparison to the smoothness of SiC layer as shown in Fig. 3, indicated that the crack

was deflected by the CNTs. The crack deflection is beneficial for the toughness of the coating. In addition, the PyC deposition increased the carbon amount of CNT-PyC-SiC layer, which has a CTE between those of carbon and SiC. The CNT-PyC-SiC with an intermediate CTE alleviate the stress in SiC layer caused by the mismatch of CTE between C/C and SiC, somewhat like a functionally graded coating. The lower level of stress in SiC coating thus gave rise to fewer cracks in the coating.

In our study, the thickness of the coating was about 20  $\mu\text{m}$  in comparison to more than 100  $\mu\text{m}$  coatings reported by other researchers [5-7]. Here we mainly try to demonstrate the effect of CNT-PyC and possibility to improve the coating system. We think it still needs to combine with other refractory materials in order to achieve a complete oxidation-resistance coating system in a practical application.

In summary, in situ growth of CNTs on C/C followed by pyrolytic carbon deposition made the CNT firmly fixated on C/C. The resulting CNT-PyC-SiC/SiC double-layer coating had no clear boundary with the C/C surface, thus had a strong bonding. With increasing PyC amount in the coating, CNT-PyC-SiC coating showed fewer cracks and a higher oxidation resistance. The effect of PyC is believed to alleviate stress in coating by an interlayer with an intermediate CTE and deflect the cracks. Although the complete oxidation resistance had not been achieved, CNT-PyC undoubtedly played an important role in the improvement of bonding strength and stress alleviation. In a real coating, it still needs other layers to achieve complete resistance. The in situ CNT-PyC deposition provides a new means to improve the reliability of the oxidation resistance coating system.

#### **ACKNOWLEDGEMENTS**

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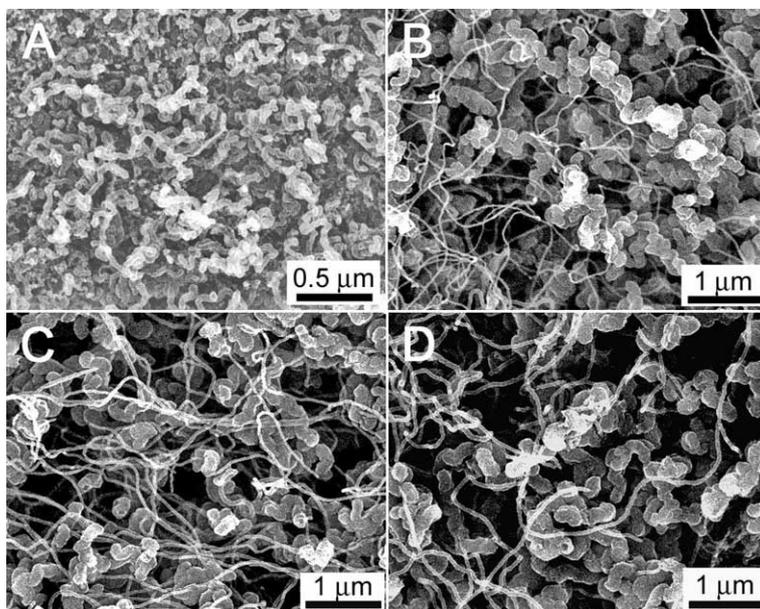


Fig. 1. Morphology of carbon nanotube as-grown (A) and after PyC deposition for 5 min (B), 10 min (C), and 15 min (D).

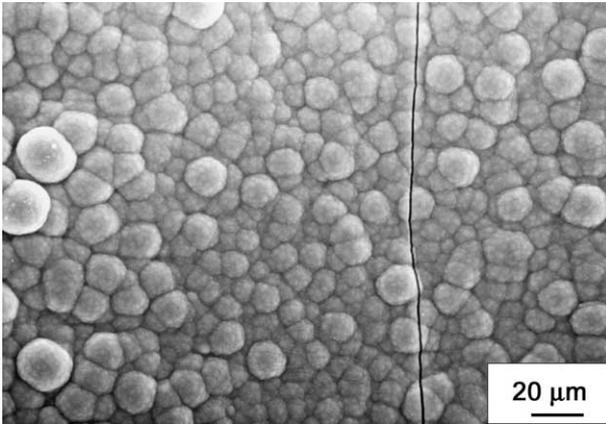


Fig. 2. Surface morphology of CNT-PyC-SiC coating with PyC deposition for 15 min and SiC deposition for 60 min.

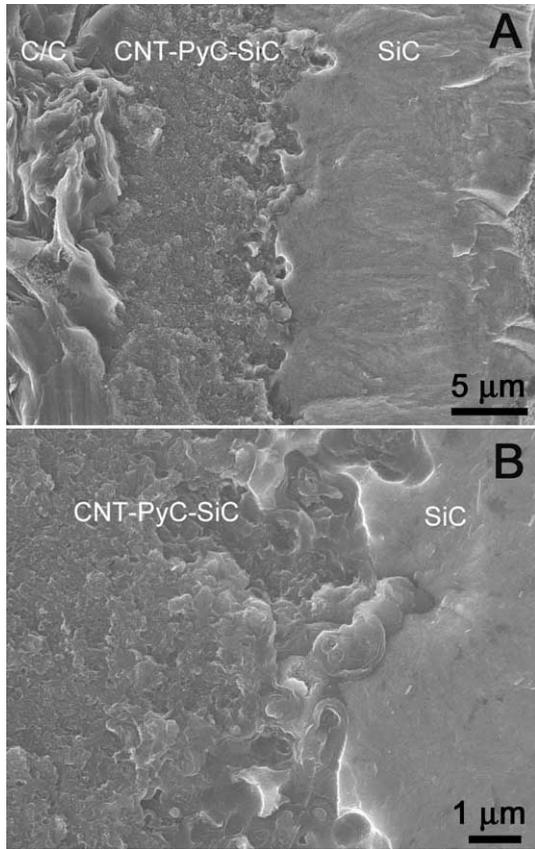


Fig. 3. Fracture surface of C/C with CNT-PyC-SiC coating (PyC deposition for 15 min and SiC deposition for 60 min).

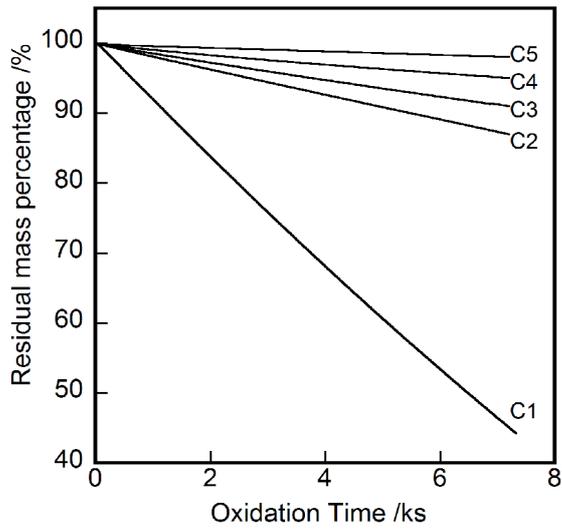


Fig. 4. Mass change of C/C with various coating at 1200°C in air (C1 for SiC coating, C2 for CNT-SiC coating, C3 for CNT-PyC5-SiC coating, C4 for CNT-PyC10-SiC coating, C5 for CNT-PyC15-SiC coating).

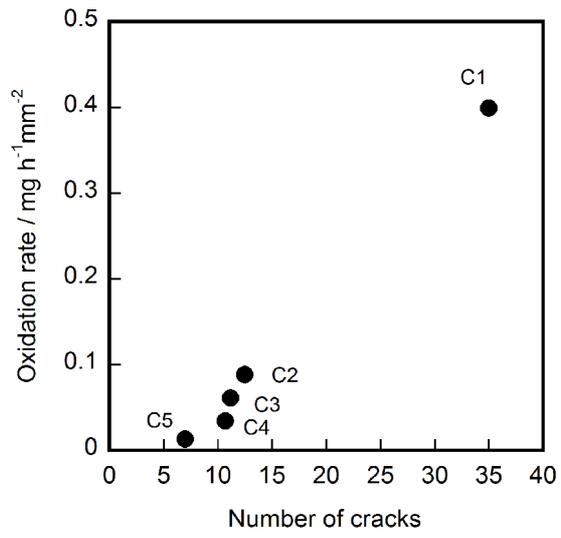


Fig. 5. Correlation of cracks in coating to oxidation rate of C/C with various coating at 1200°C in air.