

# OXIDATION-PROTECTING BEHAVIOR OF CNT-PYC-SiC NANOCOATING ON C/C

*Guo-Bin Zheng, Hironori Mizuki, Hideaki Sano, Yasuo Uchiyama*  
*Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, Japan*

## Abstract

In a previous study, carbon nanotube-SiC (CNT-SiC) nanocoating on C/C composite materials was found to have a better oxidation-protecting effect than SiC coating because the former had fewer cracks. In this study, pyrolytic carbon (PyC) was deposited on CNTs and followed by deposition of SiC, so CNT-PyC-SiC nanocoatings were obtained. It was found that PyC was not deposited homogeneously on the surface of carbon nanotubes. Instead, the PyC was deposited on carbon nanotubes in the form of granules. The oxidation tests showed that the oxidation-protecting effect of CNT-PyC-SiC nanocoating increased with the deposition time of PyC interlayer. It is thought that CNT-PyC-SiC had an intermediate CTE between SiC and C/C, thus had a role to alleviate the stress in the coating, which caused fewer cracks in the coating.

## Introduction

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. 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 address this issue, 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 [1-4]. 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 in the coating system, to enhance the bonding strength between C/C and SiC coating, and curb the cracking in coating [5]. 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 report, we prepared CNT-PyC-SiC coatings by depositing pyrolytic carbon (PyC) on CNTs previous to SiC coating. The effects of PyC deposition on the cracking of the coating and the oxidation-protecting behavior were examined.

## Experimental process

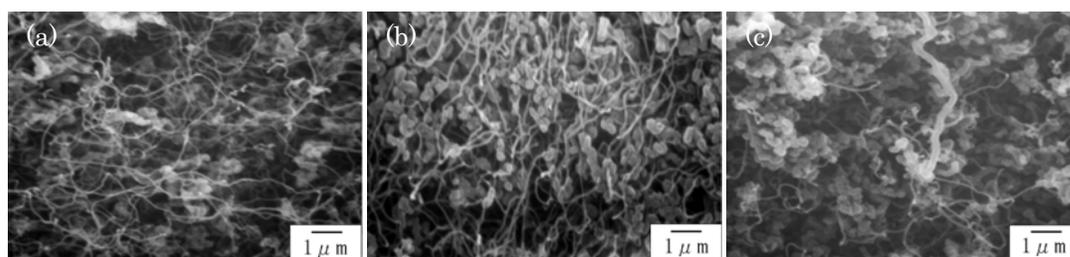
The growth of CNTs on C/C samples ( $4.5 \times 4.5 \times 4.5 \text{ mm}^3$ ) was performed as described in the previous report [5]. The deposition of PyC was carried out in a tubular reactor at  $1150^\circ\text{C}$  under a pressure of 4 kPa with the flow rate of  $\text{CH}_4$  20 ml/min for 5, 10, 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 oxidation behavior of C/C samples with coatings was evaluated in TGA at  $1200^\circ\text{C}$  for 2 hours in air of 30 ml/min.

## Results and discussion

We observed the PyC coating deposited directly on C/C surface, and found that coating was quite uniform. However, the PyC deposited on carbon nanotubes shows very different morphology as shown in Figure 1. Rather than a coating, a great number of granules can be seen in the samples after PyC deposition for 5, 10 or 15 min. Besides the granules, TEM observation also showed that some irregular graphene layers deposited on CNTs as shown in Figure 2, which were the initial stage of the PyC. Further deposition resulted in the growth of the irregular graphenes into granules. It suggests that nucleation of PyC on carbon nanotubes was not uniform. It is considered that the difficulty to form a uniform coating is due to the small curvature of CNT surface.

The SiC coating on CNT-PyC shows similar morphology to that of CNT-SiC or SiC coating. Cracks still exist in the coating as shown in Figure 3. The cross section of the coating shows that it consists of two layers, one is CNT-PyC-SiC layer and the other SiC layer. SiC first deposited into the CNT framework, and after densification, SiC further deposited on the top of the CNT-PyC-SiC layer. However, the boundary between C/C and CNT-PyC-SiC layer is not distinct, since CNTs grew from the pores in C/C surface just as roots of plants

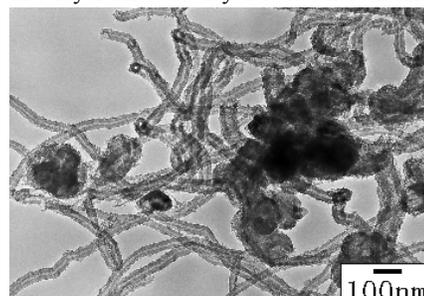


**Figure 1.** Pyrolytic carbon deposited on CNTs for 5 min (a), 10 min (b) and 15 min (c).

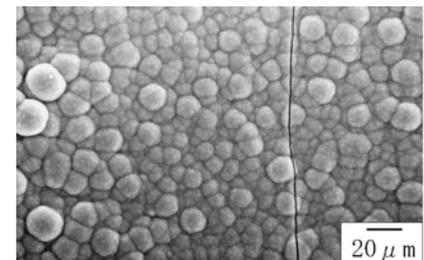
grow deep into the earth. This suggests that the bonding of CNT-PyC-SiC coating to C/C should be stronger than a simple SiC coating. In addition, the boundary between CNT-PyC-SiC layer and SiC layer is neither distinct, because CNTs are not in same length. This suggests that CNT-PyC-SiC layer also has a strong bonding to SiC layer. But it also allowed the crack of SiC layer extending into the CNT-PyC-SiC layer.

Figure 4 shows the mass change of the coated C/C samples after oxidation at 1200°C for 2 hours. One can see that 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 because there are still cracks in CNT-PyC-SiC coating as shown in Figure 4 and oxygen could diffuse through these cracks. This indicates that the oxidation rate of the samples is dependent upon the cracks. 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 Figure 5. In average,

there are 35 cracks in a surface of SiC coated C/C sample, and the number of cracks decreased significantly to 13



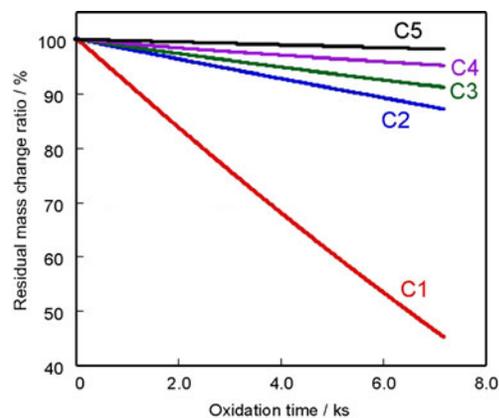
**Figure 2.** TEM image of CNTs after PyC deposited for 5 min.



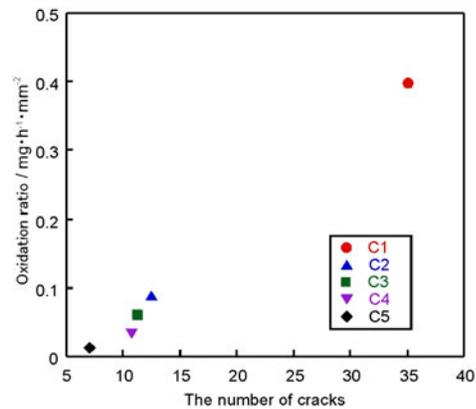
**Figure 3.** SEM image of CNT-PyC-SiC coating.

for CNT-SiC coating. For CNT-PyC-SiC coating, with increasing PyC amount, the number of cracks in coating decreased further. From Figure 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 extended into the CNT-PyC-SiC layer.

The initial aim 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. However, there seems to be no evidence that the bonding between CNT and SiC was weakened, since the PyC mainly deposited on CNTs in the form of granule instead of a thin layer. 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 functional graded coating. The lower level of stress in SiC coating thus gave rise to fewer cracks in the coating.



**Figure 4.** Mass change of C/C with various coating at 1200°C in air.



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

## Conclusions

Pyrolytic carbon deposited on CNTs in the form of granules rather than uniform coating. 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.

## ACKNOWLEDGEMENTS

This work is supported by the Ministry of Education, Science, Sports and Culture of Japan through the Grant-in-Aid for Scientific Research, Grant No. 16760645.

## References

- [1] Westwood ME, Webster JD, Day RJ, et al, J. Mater. Sci. 1996; 31: 1389-1397.
- [2] Wang RD, Sano H, Uchiyama, et al, J. Mater. Sci. 1996; 31: 6163-6169.
- [3] Buchanan FJ, Little JA. Surface and Coatings Technology, 1992; 53:137-46
- [4] Aoki T, Hatta H, Hitomi T, Fukuda H, Shiota I, Carbon, 2001;39:1477-1483
- [5] Zheng GB, Mizuki H, Sano H, Uchiyama Y, Carbon2006, Scotland, UK, July, 2006.