

Improved Oxidation Resistance of C/C Composites by a Compositionally Graded TiC/SiC/C Interlayer

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For improvement of the oxidation resistance of C/C composites, interlayers consisting of functionally graded materials (FGM) were fabricated by melt infiltration pretreatments before applying the CVD SiC coating. Instead of the simple SiC/C layer, we prepared a TiC/SiC/C graded layer using Si-TiC mixed slurry. The TiC content in the TiC/SiC/C graded layer could be controlled by changing the composition of the Si-TiC slurry. At the slurry composition of Si:TiC = 2:1, the coated C/C composite showed the lowest weight loss less than 2.5% after the oxidation test at 1000°C for 5 h. The crack width and oxidative weight loss increased at higher TiC contents.

Key words: C/C composite, FGM, melt infiltration, oxidation resistance

1. INTRODUCTION

Carbon fiber-reinforced carbon (C/C) composites exhibit excellent mechanical properties such as high strength and thermal shock resistance, and can perform well structurally at extremely high temperatures [1,2]. These enable the composites to apply to plasma facing materials for fusion reactors and various high temperature structural materials [3,4]. Their widespread application is, however, hindered by a high reactivity to active species like oxygen and hydrogen at high temperatures [5,6].

Chemically vapor deposited (CVD) silicon carbide (SiC) extensively used for the oxidation resistance of the C/C composites suffers from microcracking due to the coefficient of thermal expansion (CTE) mismatch of SiC with the C/C materials. Recently, a number of studies have been undertaken to form SiC/C graded layers between the SiC and C/C using various techniques to minimize the CTE mismatch, but with only a limited success [7-9]. Among the techniques to fabricate SiC/C graded layers, the reactive infiltration of Si melt is a simple and inexpensive process. In this technique the Si melt infiltrates into pores of the C/C composite and reacts with the composite to form the SiC/C graded layer [9,11].

In this study, we prepared a compositionally graded TiC/SiC/C layer instead of the simple SiC/C layer by applying Si-TiC slurry coating on the C/C composite and performing infiltration reaction above the melting temperature of Si. After the infiltration reaction the CVD SiC layer was coated on the TiC/SiC/C layer and the cracking behavior of the top SiC layer was investigated. The oxidation resistance of the SiC-coated C/C composite with the TiC/SiC/C interlayer was compared to that of the composite with the SiC/C interlayer.

2. EXPERIMENTAL PROCEDURE

The composite material used in this work was a

two-dimensionally woven C/C composite (CX-31, Toyo Tanso, Japan) with a specific density of 1.61 g/cm³. Samples with a size of 15 × 15 × 3 mm were cut from the composite panel and polished down to #2000 SiC paper. The powders used to make slurries were Si and TiC powders with average particle sizes of 2 and 3.5 μm, respectively. The Si and TiC powders were mixed in a polyethylene bottle containing SiC balls using a planetary ball mill. Methyl ethyl ketone (MEK) and polyvinyl-butylal (PVB) were used as solvent and binder, respectively [12] and the solid content in the slurry was controlled to ~33 vol.%. The molar ratio of TiC to Si, Si:TiC, was varied to 3:1, 2:1, 1:1 and 2:1 in order to investigate the effect of TiC content in the TiC/SiC interlayer on the oxidation resistance. Pure Si slurry without TiC was also prepared by the same procedure.

The polished C/C specimens were dipped into the slurries and then the slurry-coated specimens were dried in an oven. The melt infiltration experiments were performed in a graphite-resistance furnace in a vacuum environment. The slurry-coated specimens were placed in a graphite box and heat treated at 1450°C for 30 min. After the melt infiltration treatment the specimens were coated again with the pure SiC using the CVD method. The CVD coating was carried out in an alumina tube in a horizontal furnace. Methyltrichlorosilane (MTS, 99%, Aldrich Chemical Co. Ltd., USA) was used as the source of SiC. Hydrogen (H₂) gas was used as a carrier and diluent gas. The carrier gas was bubbled through the MTS precursor which was maintained in a 0°C bath. The flow rate of MTS was controlled by controlling that of the carrier gas. The deposition was carried out at 1300°C, 25~50 torr and the thickness of the CVD SiC layer was controlled to be about 100 μm. For the oxidation experiments, the CVD coating was performed twice on both sides of the specimens.

Oxidation tests for the CVD SiC-coated specimens were performed in an alumina tube furnace at 1000°C

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for 5 h with flowing 50 sccm synthetic air. Surfaces and cross-sections of the coated composites were examined using a scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS). Cracks developed in the CVD SiC coating layer were observed using SEM. From the SEM micrographs the width of the cracks was measured by an image analyzer. The phases present in the coating layers were analyzed using a X-ray diffractometry (XRD, D/MAX-3C, Rigaku Co., Japan). The experimental procedure is summarized in Fig. 1.

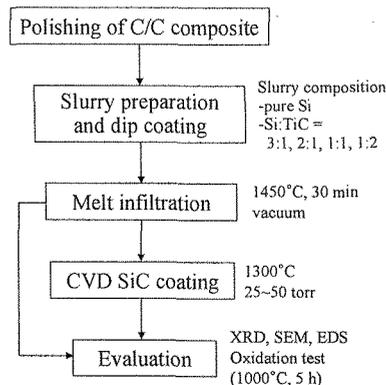


Fig. 1. Schematics of experimental procedure.

3. RESULTS AND DISCUSSION

The aim of adding TiC particles to Si slurry is to fabricate the TiC/SiC/C composite interlayer between the CVD SiC coating and C/C composite. The TiC/SiC/C interlayer is expected to reduce the tensile stress of the CVD SiC layer or preferentially, to introduce a compressive stress into the SiC layer during cooling after the CVD process because the CTE of TiC is larger than that of SiC. The formation of the TiC/SiC graded layer using a CVD method has been reported by Kawai *et al.* [13]. In this study, we have tried to form the TiC/SiC layer using the more cost-effective melt infiltration process.

Fig. 2 shows the typical XRD patterns of the infiltrated composites, which had been coated with

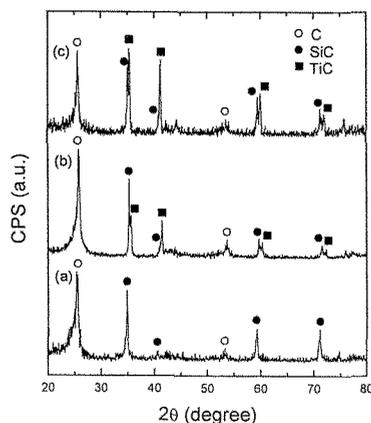


Fig. 2. XRD patterns of the samples coated with slurries of (a) pure Si, (b) Si:TiC = 3:1, and (c) Si:TiC = 1:1 after infiltration reaction at 1450°C for 30 min.

slurries of various TiC contents. The pure Si-coated composite (Fig. 2(a)) shows SiC and C phases. The C peaks are considered to be originated from the C/C substrate. The free Si was not detected within the resolution of the XRD method, showing that the infiltrated Si melt reacted with the C/C composite to form SiC. Just after the infiltration process for the Si-TiC slurries, the reaction layer consisted of two distinct layers, a porous layer and below that, a dense layer on the surface of the C/C composite. The porous and loose layer with a thickness about 100 μm , which consisted of TiC, SiC and Ti_3SiC_2 phases, was removed before the analyses and CVD coatings. The phases present in the dense layer are TiC and SiC, as can be seen in Figs. 2(b) and 2(c). The content of TiC in the reaction layer increases as the content of TiC in the Si-TiC slurry increases. Because too large amount of TiC in the interlayer will introduce an excessive compressive stress in the CVD SiC layer and the SiC layer can be peeled off, the TiC content should be controlled to be an optimum level. The TiC content in the interlayer has a great effect on the cracking behavior of the SiC layer and consequently the oxidation resistance as will be described later.

Fig. 3 shows the cross-sectional microstructure of the composite infiltrated with pure Si melt. At the surface region of the C/C composite a dense SiC-rich layer with a thickness about 15 μm can be seen. Below this layer, the SiC phase was formed at the periphery of the C fiber. The amount of the SiC phase decreased from the surface of the C/C composite, forming the SiC/C compositionally graded layer.

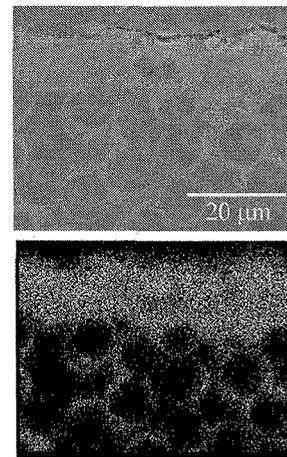


Fig. 3. SEM micrograph for the cross-section of the specimen infiltrated with pure Si and the EDS mapping image for Si.

Fig. 4 represents a typical cross-section of the Si-TiC slurry coated-composite after the infiltration reaction at 1450°C. Instead of the pure SiC, TiC/SiC composite interlayer with a thickness of 5~10 μm was formed. It can be seen in the TiC/SiC layer that there is a concentration gradient of TiC within the limited thickness. Below the TiC/SiC layer, the SiC/C graded layer was formed by the infiltration of the Si melt as in the case of the pure Si-coated composite. Within the SiC/C graded layer, a little amount of TiC could be also

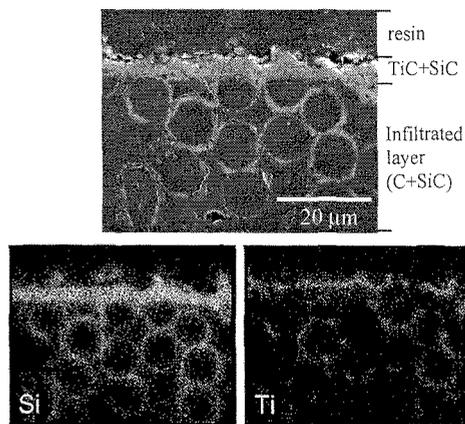


Fig. 4. SEM micrograph for the cross-section of the composite coated with Si:TiC = 3:1 slurry and the EDS mapping images for Si and Ti.

found. It can be seen from this microstructure that the TiC/SiC/C graded layer could be fabricated by the infiltration reaction of the Si-TiC slurry into the C/C composite. A backscattered electron micrograph for the surface of the TiC/SiC layer is shown in Fig. 5. The TiC and SiC phases show an interpenetrating microstructure and there had been some grain growth and sintering of TiC particles.

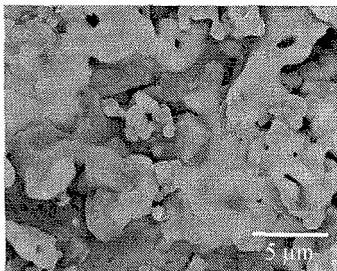


Fig. 5. Backscattered electron micrograph for the surface of the composite coated with Si:TiC = 3:1 slurry after infiltration reaction.

The CVD SiC coating was applied on the TiC/SiC/C layer and the cracking behavior of the SiC layer was investigated. Fig. 6 shows the average crack width in the CVD SiC layer with varying the slurry composition. The crack width decreases by the addition of TiC into the slurry, in other words, by the formation of the TiC/SiC/C interlayer instead of the simple SiC/C interlayer. It means that the tensile stress exerted on the CVD SiC layer could be reduced by the introduction of the TiC/SiC/C interlayer. At high TiC contents, however, the crack width increases again, suggesting an excess amount of TiC phase above an optimum content can be detrimental to the mechanical integrity of the SiC layer.

The oxidation resistance of the C/C composites after CVD SiC coating was also evaluated with varying the slurry composition. The weight loss after oxidation test is shown in Fig. 7. The result of oxidation test has a similar trend to that of the average crack width shown in Fig. 6. In the previous reports [14-16], the crack width correlates reasonably well with the oxidation resistance of the coated C/C composites. The weight loss after the

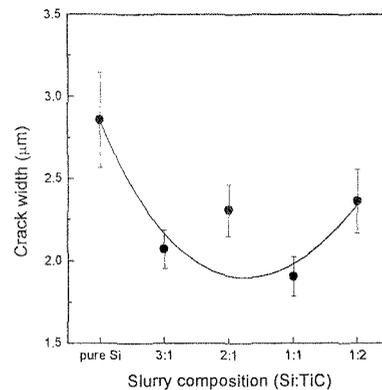


Fig. 6. Average widths of cracks developed in the CVD SiC layer as a function of slurry composition.

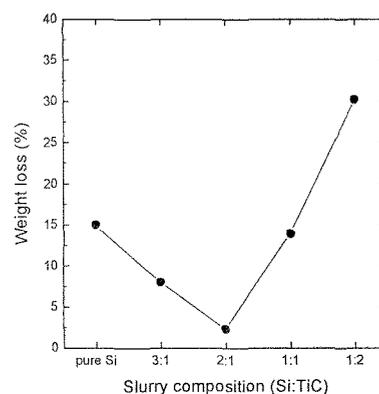


Fig. 7. Result of oxidation test at 1000°C for 5 h as a function of slurry composition.

oxidation test decreases with the increase of TiC content in the Si-TiC slurry and shows a minimum value at the composition of Si:TiC = 2:1. A higher amount of TiC is not beneficial to the oxidation resistance and the composite coated with the 1:2 slurry shows the worst oxidation behavior. This may be due to a delamination of the SiC coating layer caused by an excessive stress at the interface between the SiC layer and TiC/SiC interlayer. In order to improve the oxidation resistance further, a thicker TiC/SiC reaction layer might be needed for an effective compositional gradient in the TiC/SiC interlayer. In addition, it is required a compositional profile with a low TiC content at the interface between the SiC coating and TiC/SiC interlayer to avoid the excessive stress at the interface.

4. CONCLUSIONS

Compositionally graded TiC/SiC/C layers could be successfully fabricated by applying the Si-TiC slurry coating on the C/C composite and performing the infiltration reaction above the melting temperature of Si. The cracking behavior and oxidation resistance of the SiC-coated C/C composite with the TiC/SiC/C interlayer were improved compared to those of the composite with the SiC/C interlayer. Excess TiC contents in the TiC/SiC layer, however, were deleterious to the oxidation resistance may be due to the excessive stress developed at the interface between the SiC coating and TiC/SiC interlayer.

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