

ANTIOXIDATION OF C/C COMPOSITE BY A COUPLING OF SiC GRADIENT WITH ZIRCON OVERCOATING

O. YAMAMOTO¹, T. SASAMOTO¹ and M. INAGAKI²

¹ Kanagawa Institute of Technology, Atsugi-shi, 243-02 JAPAN

² Hokkaido University, Kita-ku, Sapporo, 060 JAPAN

INTRODUCTION

The improvement of an oxidation resistance of carbon/carbon composites is one of the important problems to be solved. Two effective methods have been proposed; dispersion of fine particles of carbides and borides in the carbon-carbon composites and coating of thin film of carbides and oxides on the composites.

In the present work were studied the formation of SiC-concentration gradient in a carbon/carbon(C/C) composite by silicon impregnation process and overcoating with zircon thin film by sol-gel process. The oxidation resistance of the resulting composites was also examined.

EXPERIMENTAL

The substrates used were 2-dimension C/C composites(CX31, Toyo Tanso Corp., Japan) with the size of 15 X 20 X 10 mm. They were made by laying up the sheets of PAN-based carbon fibers using a pitch matrix and densified by the repetition of carbonization and pitch impregnation.

The C/C composite substrates were embedded into a silicon powder with 10 μm size in a graphite crucible and then heated for various hours at 1450 $^{\circ}\text{C}$ under an argon gas flow. Thus, a concentration gradient of SiC was endowed with the surfaces of the composites. The details of the preparation procedure have been reported in our previous paper[1].

For zircon overcoating, zirconium tetra-butoxide $[\text{Zr}(\text{OC}_4\text{H}_9)_4]$ (ZrBu) and silicon tetra-ethoxide $[\text{Si}(\text{OC}_2\text{H}_5)_4]$ (TEOS) were selected as starting materials. Two alcoholic solutions of ZrBu and TEOS were mixed to be a ratio (ZrBu/TEOS) of 1.0. This precursor solution was coated by dipping the composites with SiC-concentration gradient. The sol film on the substrates was kept at room temperature for

48 h, to carry out the hydrolysis-condensation reaction to gelation. The gel films on the substrates were heated at either 250 or 350 $^{\circ}\text{C}$ for 4 h in air and then at 1000 $^{\circ}\text{C}$ for 1 h in argon to form zircon thin films on the surfaces of the C/C composites.

The oxidation resistance test for the composites thus treated was carried out by an electric thermobalance with a sensitivity of 0.1 mg at the temperature of 1000 and 1400 $^{\circ}\text{C}$ under the flow of air with a rate of 200 cm^3/min . The weight loss per unit area of the initial surface of the composite was measured as a function of time. The surface of the samples before and after the oxidation was observed by scanning electron microscope(SEM) and also examined by XRD measurement.

RESULTS AND DISCUSSION

The SiC-concentration gradient seemed to be different between two directions parallel and perpendicular to the sheet of carbon fibers. The concentration gradients of SiC with the depth from the surface along the directions parallel and perpendicular to the carbon fiber sheet were determined.

In the composite reacted for 1 h, only small amount of SiC was formed and no concentration gradient of SiC was detected in the depth up to 1.5 mm. After the reaction for 3 h, however, the concentration gradient of SiC in the composite was observed, decreasing slowly until 0.4 mm and then steeply in a range of 0.4-0.6 mm. Although a concentration gradient of SiC was formed by heating for 6 h, the gradient was detected in a shallow range.

In Fig. 1, the thickness of zircon film formed after the heating at 1000 $^{\circ}\text{C}$ for 1 h in argon is plotted against the pulling-out velocity of the C/C composite from the precursor solution.

The thickness of the zircon film increases with increasing the pulling-out velocity. This fact seems to be due to a faster hydrolysis-condensation reaction of ZrBu and TEOS than the falling-down velocity of the precursor solution. The film prepared by the velocity below 0.2 cm/s appeared to be homogeneous and no crack was observed after the crystallization at 1000 °C. At the velocity above 0.2 cm/s, the crystallized zircon film showed a cracking and peeling-off from the substrate surface. The formation of crystalline zircon in the thin film was confirmed by XRD.

The weight loss per unit area of the initial surface by oxidation at 1400 °C is plotted in Fig. 2 as a function of oxidation time on three composites, the as-received C/C composite, after the formation of SiC-concentration gradient and after overcoating with zircon. At 1400 °C, an improvement in oxidation resistance is found to be effective by the combination of a SiC-concentration gradient with overcoating of zircon film with thickness of 1.5 μm, the oxidation loss being about one-hundredth of the as-received C/C composite at 1400 °C and even no loss being detected after 30 h at 1000 °C. On overcoating of zircon with the thickness of 0.5 μm, the weight loss with oxidation time is also improved slightly, which is about one-eighth at 1000 °C and one-fourth at 1400

°C during 30 h. No pronounced improvement of oxidation resistance is found on the composite with SiC-gradient without zircon overcoating, its weight loss being comparable with the as-received composite at 1000 and 1400 °C.

From the XRD measurement, the surface oxidized at 1000 °C for 30 h gave only diffraction peaks of zircon. By the oxidation at 1400 °C, however, the diffraction peaks of ZrSiO₄, tetragonal-ZrO₂ and α-SiO₂ was detected, suggesting the phase separation of ZrSiO₄ at the contact with the composite substrate.

REFERENCES

1. O.Yamamoto, K.Imai, T.Sasamoto & M.Inagaki, J. Eur.Ceram.Soc., 12, 435(1993).

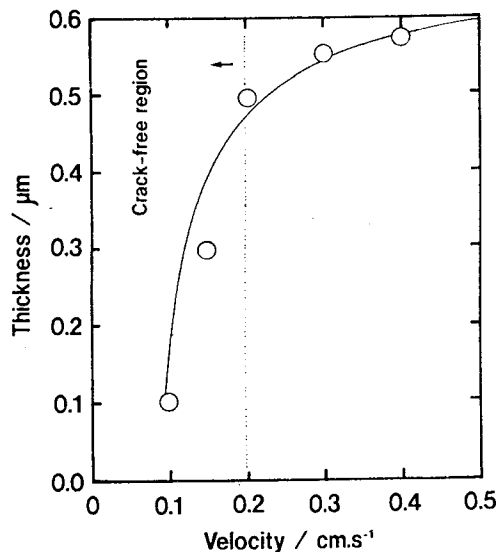


Figure 1 Dependence of the thickness of the zircon coating film on the pulling-out velocity from the precursor solution.

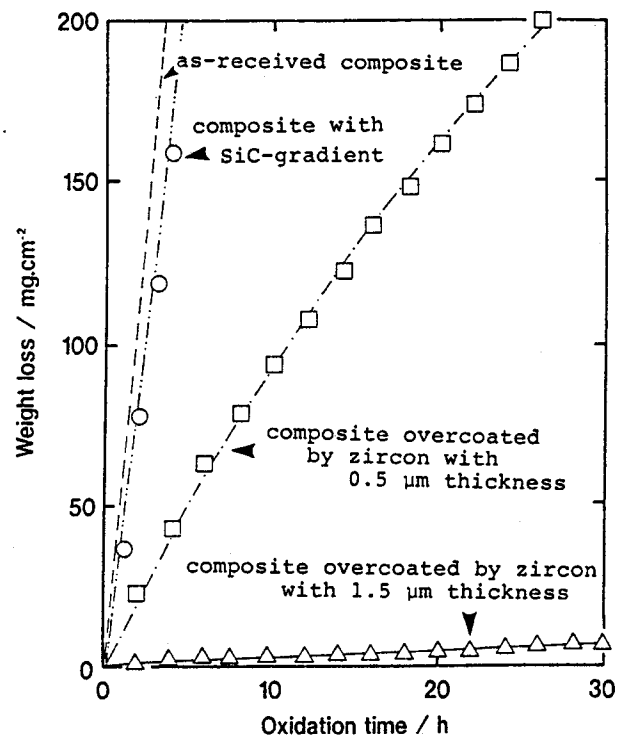


Figure 2 Changes of weight loss with the time of oxidation at 1400 °C in air.