Synthesis and Characterization of SiC Ceramics for High Temperature Resistant Coatings and Matrix*

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SiC ceramics are expected as oxidation resistant coating material for Carbon/Carbon (C/C) composites. In the present study, SiC ceramics were synthesized through Sol-Gel method with low environmental impact. The gels were synthesized from ethylalcohol, methyltriethoxysilane (MTES), hydrochloric acid (HCl) and purified water (H₂O), and it was pyrolyzed at 1 000, 1 500 and 1 700°C. The structures of gels after heat treatment were analyzed by X-ray diffraction (XRD). XRD results indicated that β -SiC were obtained in the present method and crystallization was increased with increasing heat treatment temperature. There was little weight change in synthesized SiC obtained at 1 000°C in air, which results in lower weight changes in SiC coated C/C composites comparing with bare C/C composites. However, SiC coated C/C composites were also oxidized because of the generation of cracks during heat treatment at 1 000°C. Residual tensile strength of SiC coated C/C composites were also higher than that of bare C/C composites after 5 minutes oxidation.

Key Words: Carbon/Carbon Composites, SiC, Oxidation, Sol-Gel Method

1. Introduction

Carbon fiber reinforced carbon matrix composites (C/C composites) retain specific strength, specific toughness and any other mechanical properties at high temperature in an inert atmosphere or in vacuum. From this view point, they are expected as only materials for the structures of aerospace applications and micro gas turbine used at higher than 1 500°C. However, C/C composites have serious disadvantage such as oxidation in high temperature in air. They are degraded at temperatures as low as about 500°C and oxidation protection systems have been developed⁽¹⁾.

To improve the oxidation resistance of C/C composites, many ceramics coatings have been studied and some coatings have been used for space shuttle. Necessary requirements for coatings are high oxidation resistance, low volatility and chemical and mechanical compatibility with C/C composites at high temperatures in atmosphere⁽²⁾.

As SiC ceramics have the potential to satisfy these

properties, they have been expected and studied^{(3),(4)}. Typically, they are deposited by the CVD method⁽⁵⁾. The advantages of CVD process are that it is able to fabricate uniform and compact coatings. On the other hand, this process has the disadvantages such as high environmental impact, difficulty in application to the structures with the complicated geometry.

In the present paper, we fabricated SiC coatings on the C/C composites with Sol-Gel method which is low environmental impact, low cost and simple procedures and confirmed its oxidation resistance.

2. Experimental Procedure

2.1 Specimens

The C/C composite materials, AC200, (Across Co.) with PAN-based carbon fibers, T300 (TORAY Co.) were used in this study. The laminate configuration was 2D cross-ply, [0/90/0/90/0]. They were cut into coupon specimen. The specimen size was 155 mm × 8 mm × 2.1 mm.

2.2 Synthesize procedures of SiC coatings

Methyltriethoxysilane (MTES) was used as precursor silicon alkoxide (Shin-Etsu Chemical Co., Ltd.). The transition metal alkoxide used as inorganic sources was Ti(O-i-Pr)₄. To improve stability against hydrolysis, Ti(O-i-Pr)₄ and acetylacetone were mixed at 1 : 2 molar ratio and stirred for 1 h.

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Ethylalcohol, methyltriethoxysilane (MTES), hydrochloric acid (HCl), purified water (H₂O) and transition metal alkoxide complex were mixed with a molar ratio of ethanol : MTES : HCl : H₂O : mixture = 3 : 1 : 0.01 : 2 : 0.2. First, MTES was mixed with HCl. After 5 minutes stirring at 40°C, transition metal alkoxide complex and H₂O were added to the mixture. The solution was stirred at 40°C until transparent sol was obtained. The sol was kept at 40°C for two hours and the C/C composites were dipped in the mixture. Then they were kept at 40, 60 and 120°C each for 1 day. The gel was pyrolyzed at 1 000, 1 500 and 1 700°C for two hours in argon gas (Ar) with a heating rate of 3°C/min and cooling rate of 6°C/min.

2.3 X-ray diffraction measurement

XRD analysis was used to characterize the structure of 3 kinds of heat treated gels. X-ray diffraction was obtained with CuK α radiation at 40 kV and 300 mA. The samples were scanned from 10°(2 θ) to 80°(2 θ) at a scan rate of 1° per minute.

2.4 Oxidation test

Measurements of the oxidation behavior of all specimens were carried out with a TGA-50 (Shimadzu Corp.). Specimens were heated to the test temperatures (1 000°C) with a heating rate of 50°C/min in flowing Ar (200 mL/min) and kept for 5 minutes at test temperatures. And then they were exposed in flowing air (80%N₂, 20%O₂, flow rate 100 mL/min). Sensitivity of the balance was ± 0.1 mg and specimen dimension was 3 mm $\times$ 3 mm $\times$ 2.1 mm.

2.5 After oxidation tensile test

Test conditions and schematic diagrams are shown in Figs. 1 and 2, respectively. Specimens were heated to 1 000°C with a heating rate of 20°C/s in flowing N₂ and kept 5 minutes. And then they were exposed in flowing air (80%N₂, 20%O₂, flow rate 100 mL/min) for 5 minutes. Then specimens were heated by an infrared lamp

with $\phi 8$ mm spot area. Subsequently N₂ were introduced and the specimen was cooled in a furnace. The specimens after oxidation were tensile tested at room temperature in atmosphere. The cross head speed was 0.1 mm/min.

3. Experimental Results

Figure 3 shows the results of X-ray diffraction pattern of the ceramics obtained at 1 000, 1 500 and 1 700°C heat treatments. For 1 000°C heat treatment, the obtained pattern was significantly broad, which revealed amorphous. This pattern is due to amorphous silica and disordered carbon, which are both detected at $2\theta = 23^\circ$. From this pattern, the structure of the gel heated at 1 000°C is considered to be composed from silicon oxycarbide. As higher heat treatment temperatures, all peaks showed intense and narrower ones. Their peaks are consistent with peaks of β -SiC and crystallization is increased with increasing heat treatment temperature. In addition, cracks increased with increasing heat treatment temperatures, as shown in Fig. 4.

Figure 5 shows the weight change of bulk SiC heat treated at 1 000 and 1 500°C. There are little weight change in bulk SiC heat treated at 1 000 and 1 500°C. However, the number of cracks which existed in the ob-

Fig. 2 Schematic diagrams of experimental arrangement

Fig. 1 Conditions of oxidation tensile test

Fig. 3 XRD patterns at various temperatures

(a) 1000°C heat treatment (b) 1500°C heat treatment (c) 1700°C heat treatment

Fig. 4 Appearance of ceramics heat treated at (a) 1000°C, (b) 1500°C and (c) 1700°C

Fig. 5 Oxidation behavior of bulk gel at 1000 and 1500°C HT

(a) 120°C heat treatment (b) 1000°C heat treatment

Fig. 6 Specimens surface of (a) heat treated to 120°C (b) heat treated to 1000°C

tained ceramics increases with increasing heat treatment temperature, as shown in Fig. 4. These results suggest that low heat treatment temperature is useful for the coating of C/C composites, in spite of the low crystallinity. In the present study, oxidation resistant coatings were fabricated on C/C composites with 1000°C heat treatment.

Figure 6 (a) and (b) show the optical micrographs for surface of gel coated C/C composite after 120 and 1000°C heat treatment, respectively. After 120°C heat treatment, there are some cracks with small opening displacement. However, after 1000°C heat treatment, there are many cracks with large opening displacement because of the shrinkage of the gels. The average crack displacement is about 10 μm. From the cross-sectional observation, the coating is dense and debonding between coating and C/C composites is not observed. The average thickness of the coating is 35.4 μm.

Figure 7 shows the weight change of bare C/C com-

Fig. 7 Oxidation behavior of bare and SiC coated C/C

Fig. 8 Tensile strength of oxidized bare C/C and SiC coated C/C

(a) Bare C/C

(b) SiC coated C/C

Fig. 9 Apparent geometry of (a) bare C/C and (b) SiC coated C/C after oxidation tensile test

posites with and without SiC coatings. It is found that weight change of SiC coated C/C composite is lower than the that of bare C/C composite. However, SiC coated C/C composite was also oxidized to some extent. Coating cracks shown in Fig. 6 cause such oxidation. During oxidation tests, oxygen goes through the opening part of cracks and oxidizes C/C composites. In this reason, SiC coated C/C composites became hollow structure, that is, only SiC coating was left.

Figures 8 and 9 show the result of tensile tests after oxidation for bare C/C composites and SiC coated C/C composites. Tensile strength of SiC coated C/C composites are higher than that of bare C/C composites. From the optical micrograph shown in Fig. 8, it is clarified that bare C/C composite was oxidized seriously. These results are consistent with the results of oxidation tests. However, SiC coated C/C composites are also oxidized by the oxygen from coating cracks. Further study is necessary for the process of sol polymerization and gel pyrolysis.

4. Discussion

When the temperature $T < 973$ K, the oxidation rate is controlled by the oxygen diffusion rate through the boundary layer of air flow (BDR). The oxidation rate of the bare C/C composite, dW/dt , in the BDR region is well approximated by the following simple expression⁽⁶⁾,

$$\frac{dW}{dt} = \frac{D_b C_g}{\delta} \quad (1)$$

where C_g , D_b and δ are the oxygen concentration in the far field, the diffusion constant and the thickness of the boundary layer, respectively. D_b and δ can be calculated from^{(7), (8)}

$$D_b = 5.9529 \times 10^{-24} \frac{\sqrt{T^3 \left(\frac{1}{M_{air}} + \frac{1}{M_{CO}} \right)}}{P \sigma_{air}^2 \Omega_{air}} \quad (2)$$

$$\delta = \psi \left(\frac{\mu L}{\rho V} \right)^{0.5} \quad (3)$$

where, T , P , M , σ , Ω , ψ , μ , L , ρ and V in Eqs. (2) and (3) are oxidation temperature, total pressure, molar mass of the gaseous species, collision diameter, collision integral⁽⁸⁾, viscosity, representative length, density and gas flow velocity, respectively.

The oxidation rate of the SiC coated C/C composites is controlled by oxygen diffusion rate through the coating cracks. In this case, the oxidation rate of the SiC coated C/C composites is approximated by the diffusion model⁽⁹⁾. According to Ref. (9), the oxidation rate of the SiC-coated C/C composites, dW/dt is given by

$$\frac{dW}{dt} = \frac{24}{32} \frac{J_{total}}{\chi} \quad (4)$$

where J_{total} is the total oxygen diffusion rate by all coating cracks. The factor χ , which is related to prevention the inward diffusion by the outward diffusion of carbon oxides, is given by

$$\chi = \frac{-\chi_{top}}{\ln \left(\frac{1}{1 + \chi_{top}} \right)} \quad (5)$$

where χ_{top} is the molar fraction of oxygen on the surface of the coating.

The oxidation damage depth in bare C/C composite can be calculated from Eq. (1) and the density of the C/C

composites, ρ . In SiC coated C/C composites, the oxidation damage depth are also calculates based on the diffusion model⁽¹⁰⁾. By assuming that semi-circular oxidation damage will appear in the C/C substrate, the radius of the oxidation damage, r , is given by

$$r = \sqrt{\frac{2 \times \frac{24}{32} N_{O_2} t}{\pi \rho}} \quad (6)$$

where t is oxidation time and N_{O_2} is the total amount of oxygen diffusing through the coating crack. Residual strength after oxidation can be calculated from the cross-sectional reduction.

The weight change calculated from Eqs. (1) and (4) is compared with that obtained in the oxidation tests in Fig. 7. It follows from this figure that the calculated results agree reasonably well with the experimental values. This results show that there is no oxygen diffusion through SiC coating area. Oxygen diffuses only through the coating cracks. That is, the SiC coating obtained via sol-gel route is effective against oxidation.

The residual strength of bare and SiC coated C/C composites calculated by cross-sectional reduction are 21.9 MPa and 39.7 MPa, respectively. These results are lower than the experimental results, as shown in Fig. 8. In the C/C composite, many transverse cracks were generated due to large thermal residual stress. The transverse cracks act as paths of oxygen diffusion, and slight oxidation precedes in ward. The sealing of transverse cracks is important to improve the mechanical properties of C/C composites.

5. Conclusions

- (1) SiC ceramics with high oxidation resistance at 1000°C were fabricated from methyltriethoxysilane.
- (2) Oxidation resistance and tensile strength after oxidation of 1000°C heat treated SiC coated C/C composites were superior to those of bare C/C composites.

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