

Oxidation behavior and property degradation of nuclear-grade C/C composites oxidized in air

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Oxidation behavior and property change after oxidation of several nuclear-grade C/C composites were evaluated. A chemical reaction appeared to control the oxidation rate of C/C composites below 650–700 °C through thermo-gravimetric oxidation analyses. The activation energy of the oxidation reaction in the chemical-reaction controlled oxidation regime was 196.6 kJ/mol and 165.4 kJ/mol for 1501YR and CX-270G composites, respectively, which were within a similar range as nuclear graphites. The properties of C/C composites such as flexural strength, inter-laminar shear strength and thermal diffusivity were largely degraded even at the oxidative weight loss of 1–3%. A preferential oxidation at the inter-bundle and fiber/matrix interfaces more sensitively affected the inter-laminar shear strength and the transverse thermal diffusivity than the flexural strength and the in-plane thermal diffusivity.

Key words: C/C composite, oxidation, property change, nuclear application.

Introduction

Carbon-carbon (C/C) composites have been widely used for high-temperature structural applications because they possess excellent mechanical properties such as high specific strength and thermal shock resistance [1]. In the nuclear industry, the composites have been considered for plasma facing materials in fusion reactors [2] and high-temperature structural parts in gas cooled reactors [3]. In a high-temperature gas cooled reactor, the composites are being considered for the application of various high-temperature structural parts such as control rod components, core restraint belts, tie rods, upper plenum shroud, hot duct insulation cover sheets, and floor blocks [4–6]. However, carbon-based materials are susceptible to oxidation at temperatures above 400 °C. Therefore, the oxidation behavior and property degradation at high temperature in air considering accidental air ingress should be evaluated and the data base is needed to be established before the deployment of composites.

In this study, the oxidation behavior and the property change after oxidation of several nuclear-grade C/C composites were evaluated. The oxidation experiments were performed at various temperatures in an air atmosphere. The activation energy of the oxidation reaction in a chemically controlled oxidation regime was calculated from the oxidation rate. The thermal

and mechanical properties such as thermal diffusivity, flexural strength, and inter-laminar shear strength (ILSS) were measured before and after oxidation.

Experimental procedure

Four different grades of C/C composites were used in this study and typical characteristics of the composites are described in Table 1. Oxidation behavior was evaluated for 1501YR and CX-270G composites using TGA (TGA-N1500, Scinco Ltd. Co., Korea), which has a temperature accuracy of ± 0.1 °C and weight sensitivity of 0.1 μ g. The oxidation temperatures were between 550 ° and 1200 °C in an atmosphere of synthetic dry air consisting of 79 vol.% N₂ and 21 vol.% O₂. The heating rate to the oxidation temperature was controlled at 10 °C/min. The specimen dimension for the oxidation experiment was 10 × 5 × 2 mm and the samples were hung on Pt wire through a hole made at the upper region of the sample. The gas flow rate was maintained at 50 cm³/min and the gas flow was switched from Ar to air at the target oxidation temperature.

Flexural strength, ILSS and thermal diffusivity were measured for CX-270G, ICU-10 and CC28NHPS composites. For the property measurement before and after oxidation, the specimens were oxidized using a tube furnace at 550 °C in air with a flow rate of 500 cm³/min. The oxidation temperature was fixed to 550 °C to insure a uniform oxidation throughout the specimen volume. The nominal oxidation weight losses were controlled to 1% and 3% to study the property changes at different weight losses.

The flexural strengths of three grades of C/C

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Table 1. Typical characteristics of the C/C composites used in this study.

Grade	1501YR	CX-270G	ICU-10	CC28NHPS
Manufacturer	SGL	Toyo Tanso	Ibiden	Tokai Carbon
Type of fiber	PAN, 3K satin weave	PAN, 6K plain weave	Pitch, Chopped felt	PAN, Plain weave
Fiber fraction (vol%)	unknown	50	36	60
Matrix formation method, Raw material	Resin infiltration and baking, Phenolic resin	Resin infiltration and baking, Phenolic resin	Resin infiltration and baking, Resin	Non-disclosed
Density (g/cm ³)	1.58	1.63	1.62	1.76
Impurities	40-60 ppm	< 5 ppm	< 5 ppm	< 39 ppm
Maximum heat treatment temperature	2200 °C	2800-3000 °C	2000 °C	2800 °C

composites before and after oxidation were measured by a three-point method using the specimens with dimensions of $60 \times 10 \times 2$ mm. The span length and cross-head speed were 50 mm and 0.5 mm/min, respectively. The ILSSs of the C/C composites were measured by loading in compression of a double-notched specimen. The nominal dimensions of the specimen length, distance between notches, specimen width, notch width and specimen thickness were 30.0, 6.0, 15.0, 0.50 and 4.0 mm, respectively. The crosshead speed was 0.5 mm/min. The ILSS was calculated using the equation, $ILSS = P_{max}/Wh$, where P_{max} is the applied maximum load, W is the specimen width and h is the distance between the notches. The thermal diffusivity was measured using a laser flash method (Netzsch LFA-457) with specimens with dimensions of 12.5 mm in diameter and 3 mm in thickness.

Results and Discussion

Analysis of oxidation behavior

Isothermal oxidation weight losses of 1501YR and CX-270G composites were measured at temperatures between 550 ° and 1200 °C. Fig. 1 shows the oxidation rates of the composites calculated from the isothermal oxidation results. The 1501YR composite exhibits a little higher oxidation rate than the CX-270G composite and there are some scatters in the oxidation rate at high temperatures. For both composites, the oxidation is accelerated above 650 °C.

The oxidation mechanism of carbon-based materials has been known to be divided into three regimes [7]. The oxidation rate is controlled by a chemical reaction between the oxidant and carbon at low temperatures. In the chemically controlled oxidation regime, concentrations in the reactants and products are uniform in the specimen and gas environment and a homogeneous oxidation occurs in the specimen. A significant degradation of the properties occurs in this regime. As the temperature increases, the rate of the chemical reaction increases more rapidly than the diffusion rate

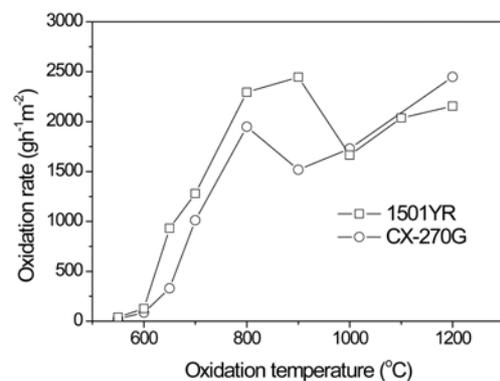


Fig. 1. Oxidation rates of 1501YR and CX-270G composites as a function of oxidation temperature.

of oxidant through the pores and thus the pore diffusion of oxidant limits the oxidation rate. In the in-pore diffusion controlled regime, less property degradation occurs than in the kinetically controlled regime. At higher temperatures, the oxidation reaction takes place mostly at the outer surface of the specimen and the oxidant gas flow to the specimen surface limits the oxidation reaction. In this mass transport controlled regime, the oxidation has little effect on the properties. To identify the oxidation mechanism as a function of temperature, Arrhenius plots of the oxidation rate were obtained for 1501YR and CX-270G composites as shown in Fig. 2. There is a transition from the chemical reaction to the in-pore diffusion controlled regime at around 650 ° and 700 °C for 1501YR and CX-270G composites, respectively. However, it is difficult to discriminate clearly a transition between the in-pore diffusion and the mass transport controlled regimes. The activation energies of the oxidation reaction in the chemically controlled regime were calculated as 196.6 and 165.4 kJ/mol with correlation coefficients of 0.9325 and 0.9975 for 1501YR and CX-270G composites, respectively.

Fig. 3 shows typical microstructures of the 1501YR composite after oxidation tests at 550 °, 700 ° and 900 °C. At the oxidation temperature of 550 °C, the

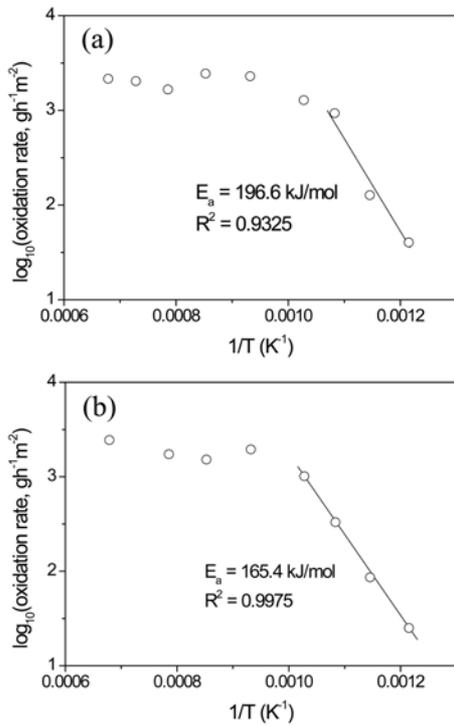


Fig. 2. Arrhenius plots of oxidation rates of (a) 1501YR and (b) CX-270G composites oxidized in air.

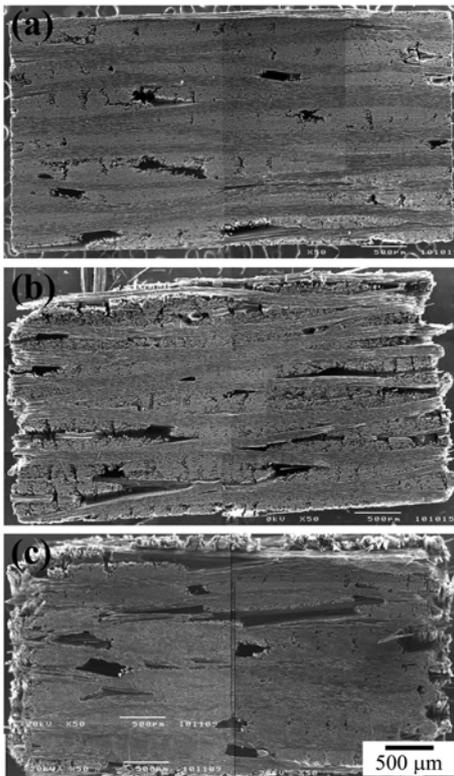


Fig. 3. SEM cross-sectional microstructures of 1501YR composites oxidized at (a) 550 °C, (b) 700 °C and (c) 900 °C.

inter-bundle and intra-bundle porosities are increased while the specimen surface maintains the original shape. This infers a uniform oxidation throughout the

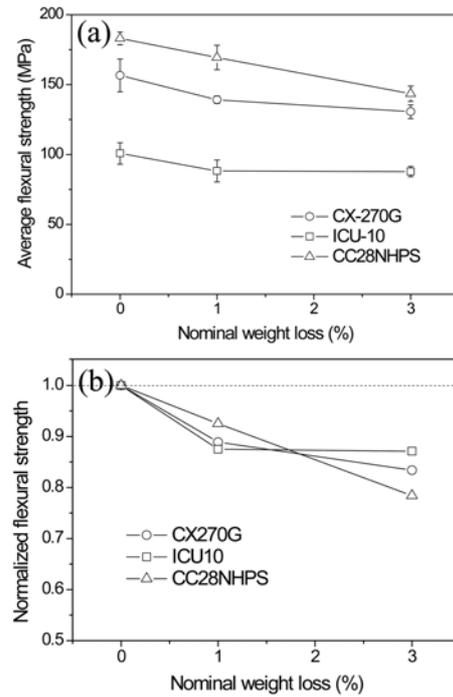


Fig. 4. Average (a) and normalized (b) flexural strengths of C/C composites as a function of nominal weight loss. Error bars represent \pm (one standard deviation).

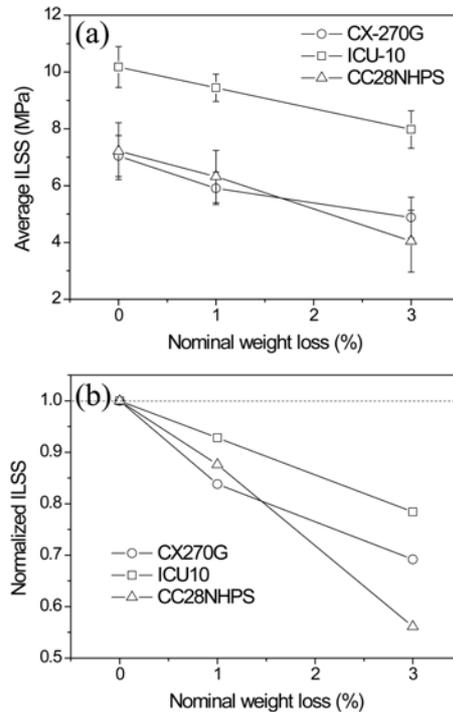


Fig. 5. Average (a) and normalized (b) interlaminar shear strengths of C/C composites as a function of nominal weight loss. Error bars represent \pm (one standard deviation).

specimen volume, i.e., the chemically controlled oxidation reaction. A preferential oxidation at the specimen surface and damage inside the specimen can be observed for the specimen oxidized at 700 °C. On the other hand, the specimen oxidized at 900 °C shows an exclusive

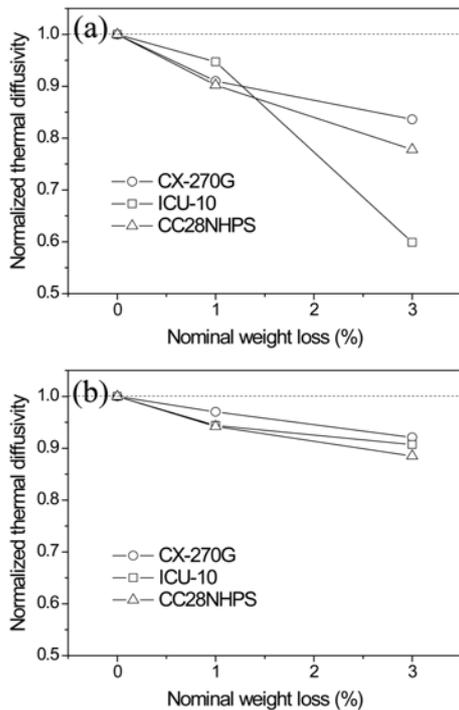


Fig. 6. Normalized transverse (a) and in-plane (b) thermal diffusivities of C/C composites at room temperature as a function of nominal weight loss.

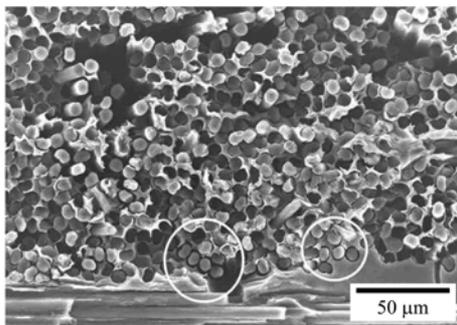


Fig. 7. SEM microstructure of C/C composite with about 3 wt% oxidative weight loss showing preferential damages at fiber/matrix interfaces (circled regions).

oxidation at the specimen surface, being a typical feature in the mass transport controlled oxidation regime.

Evaluation of properties

The flexural strength, ILSS and thermal diffusivity were measured for CX-270G, ICU-10 and CC28NHPS composites. Fig. 4 shows the change of flexural strengths of three composites as a function of the oxidative weight loss. The average flexural strength of the ICU-10 composite exhibits a rather lower value than those of the other two composites owing to a smaller volume fraction and a random distribution of fibers in the ICU-10 composite, which has a chopped felt structure. The ICU-10 composite, however, shows a less degradation of flexural strength at 3 wt% weight loss than the other composites as shown in Fig. 4(b).

Fig. 5 shows the change of ILSSs of three composites as a function of oxidative weight loss. The ILSS values are continuously decreased as the oxidative weight loss increases. The 2D plain-woven composites made by stacking fiber fabrics generally lead to an anisotropy of properties. In the ILSS test, the fracture occurs between fiber bundles owing to the 2-dimensional nature of the composite, which has a lack of fiber reinforcement through the thickness direction. Therefore, the 2D plain-woven composites, CX-270G and CC28NHPS, have lower ILSSs than the chopped felt composite, ICU-10, which has a random fiber reinforcement. The ILSS property was degraded to a larger extent by oxidation than the flexural strength as can be seen in Figs. 4(b) and 5(b). The inter-bundle and inter-ply porosities provide the diffusion path of the oxygen, and therefore a preferential oxidation occurs at the interface between fiber bundles [8]. This leads to a larger degradation of the ILSS property by oxidation than the flexural strength because the fracture occurs at the inter-bundle interface in the ILSS test.

Fig. 6 shows the effect of oxidation on the transverse and in-plane thermal diffusivities of three composites. The transverse thermal diffusivity is more largely degraded by oxidation than the in-plane thermal diffusivity. It is likely to be due to a preferential oxidation at the interface between fiber and matrix as shown in Fig. 7. The preferential oxidation at the fiber/matrix interface and also at the inter-bundle interface affects more seriously the thermal transport in the perpendicular direction to the fiber axis than in the parallel direction.

Conclusions

The activation energy of the oxidation reaction in the chemical-reaction controlled oxidation regime was calculated as 196.6 kJ/mol and 165.4 kJ/mol for 1501YR and CX-270G composites, respectively. The properties of the C/C composites such as flexural strength, inter-laminar shear strength and thermal diffusivity were degraded after oxidation even at the weight loss of 1–3%. In particular, the inter-laminar shear strength and transverse thermal diffusivity were more largely degraded by the oxidation. The property degradation was attributed to the preferential oxidation at the fiber/matrix and inter-bundle interfaces at the early stage of oxidation.

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