

OXIDATION BEHAVIORS OF C/B₄C/SiC TERNARY COMPOSITE AND ITS SELF-HEALING PROPERTY

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Introduction

Although carbon materials are expected to be a high temperature structural material, they oxidize when they are exposed to an oxidizing atmosphere over 500°C. Therefore, we carried out the researches to get carbon base composite materials with an excellent oxidation resistance by adding B₄C and SiC particle to the carbon material. We clarified that the C/B₄C/SiC ternary composite had an excellent oxidation resistance caused by formation of a borosilicate glass protective film on the surface [1]. The boron-rich borosilicate glass was formed during oxidation at relatively low temperatures of around 800°C and silicon-rich one was formed at relatively high temperatures of around 1200°C. Thus, behaviors of preventing oxidation for the composite were quite different depending on oxidation temperature [2]. This property of preventing oxidation may suggest that the composite can detect oxidizing environment and prevent itself from the following progressive oxidation by forming the protective oxide. Further experiments were carried out for examining whether the composite has another property, such as "self-healing property", which means the composite reconstructs a new protective film on its surface when the protective film is damaged or removed.

In this paper, constituent of the protective films and in-depth distribution of the constituent in the composites are examined, and the effects of a degree of damage on the self-healing ability of the composite are also clarified.

Experimental

The sample used was C/B₄C/SiC composite material fabricated in our laboratory. A compact of the composite precursor was made of mixed powders of raw coke, B₄C and SiC with a ratio of 51.2:10.0: 38.8 in mass%, and then the compact was sintered at 2150°C under atmospheric pressure of argon. The protective glass film was constructed in an electric furnace heated at 800°C and 1200°C for 10 h in dry air atmosphere (self-protected sample). Based on the concept of self-healing, the

protective film formed should be damaged on-situ during oxidation at elevated temperatures by removing it partly from the composite. However, there are some technical problems in this method. Therefore in this study, we made groove through sliding of 44N-loaded Vickers indenter or shaving out of one side surface (4x44mm) of the self-protected sample by 50µm, 500µm or 1000µm in depth respectively with abrasive paper at room temperature (damaged sample). The damaged sample was oxidized again in the electric furnace under the same conditions for the formation of the primary protective film and allowed the composite to heal the damage by means of a new protective film (self-healed sample).

The surface of the self-protected sample, the damaged sample and the self-healed sample was observed by SEM and morphological changes were examined. Mass change before and after oxidation was measured, constituent was measured by X-ray photoelectron spectroscopy (XPS), and amount of glass phase on the composite was calculated from the mass change before and after hydrofluoric acid treatment. Flexural strength of the notched sample was also examined by four-point bending test before and after healing. Notch was formed by a diamond-fixed steel saw, and was 300µm in width and 500µm in depth.

Results and Discussion

The original sample showed an excellent oxidation resistance with quite less mass loss than that of the carbon material at the temperatures ranging from 600°C to 1400°C in dry air. Mass change of the sample during oxidation was balanced between a mass loss of carbon into CO and a mass gain of B₄C and SiC into B₂O₃ and SiO₂. The mass change appeared to level off within 10h, due to the passive oxidation forming of the protective surface glass. In addition, morphological change by oxidation was observed in the region less than 50µm in depth of the sample and sample volume change before and after oxidation was less than 1vol.%. From SEM observation of the self-protected sample during oxidation at 800°C and 1200°C for 10h, the sample was covered with flat and

smooth borosilicate glass, which was identified by XPS. At 800°C oxidation, the glass phase was formed not only on the sample surface but also inside of the sample, and some pores were observed on the surface. At 1200°C oxidation, flat, smooth and dense glass film with thickness of about 20-40µm was formed on the sample surface, and the film formed at 1200°C had no pores.

Morphological changes of the damaged sample by self-healing is shown in Fig.1. The groove with about 200µm in depth and about 500µm in width was observed on the sample surface. The original texture of the sample would be meant to appear in the groove, however, the glass, which seems to be spread out by the indenter, was observed in the groove. After healing, damaged part of samples oxidized at 800°C or 1200°C was covered with glass phase, and depth of groove decreased due to the formation of new glass phase at the damage part and/or the inflow glass liquid from undamaged part into the groove. From this result, it can be concluded that the C/B₄C/SiC ternary composite has the self-healing function, however, the mechanisms of this phenomena and quantitative information could not be obtain from this experimental result.

In-depth distribution of constituent for green sample and the self-protected sample with and without shaving of the sample surface was shown in Table 1. The self-protected sample without shaving has no carbon, B₄C and SiC constituent on the sample. The amount of B₄C was almost the same values around 11 mass% excluding the self-protected sample without shaving. The amount of carbon was less and the amount of SiC was much than that of the green sample, and the values were showing a tendency to close to the original one, when the measured point was far from surface. However, the values did not accorded to the original one at 1000µm in depth. These results indicated that the oxidation during self-protecting the composite influenced constituent of the sample more than 1000µm in depth.

Table 2 shows mass change, glass phase content and B/Si ratio of the protective films of the self-healed sample. The absolute value of mass change for the 50µm-damaged sample was remarkably high and their content of glass phase formed was remarkably low among the samples. The values were showing a tendency to close to that of the undamaged sample as a function of an increment in depth. As the change of constituent shown in Table 1, it is thought that the decrease of carbon would be due to the oxidation of the carbon without a forming protective oxide in the sample. The increase of SiC was considered to be due to the reason that the SiC showed a less oxidative

ability than the carbon and B₄C, and then the mass ratio of SiC increased with relative large decrement of carbon and small decrement of B₄C in the composite. The concentration of B₄C might be balanced between carbon and SiC. The change of mass and glass phase content observed in Table 2 have some relation to the constituent of the sample surface before self-healing as shown in Table 1. These results indicated that the self-healing behavior of the sample was differed from degrees of the damage for the sample, in which showed different constituent.

A kinetic analysis of the self-healing property was also examined, as shown in Fig.2. The 50µm-damaged sample with self-healing at 800°C needs less time to be a stable condition than that of the sample with self-healed at 1200°C, and the 800°C-sample shows large mass gain. It might be caused by the reason that the 50µm-damaged sample before self-healing at 800°C had less carbon and much B₄C and SiC as an inhibitor for oxidation than that of the 1200°C-sample.

Figure 3 shows flexural strength of the damaged sample with notch before and after healing at 800°C and 1200°C. Comparing the green sample to the sample before self-healing, which can be described the “self-protected sample”, the flexural strength was degraded by oxidation with self-protecting at 800°C and 1200°C. Unfortunately, the flexural strength was also degraded by oxidation with self-healing at 800°C and 1200°C, respectively.

Conclusion

The C/B₄C/SiC ternary composite had the self-healing function to heal the damaged part.

The self-healing behavior of the composite was differed from the samples with different degrees of the damage and temperatures for the sample, in which showed different constituent.

The flexural strength of the composite was degraded during self-protecting and self-healing, respectively

References

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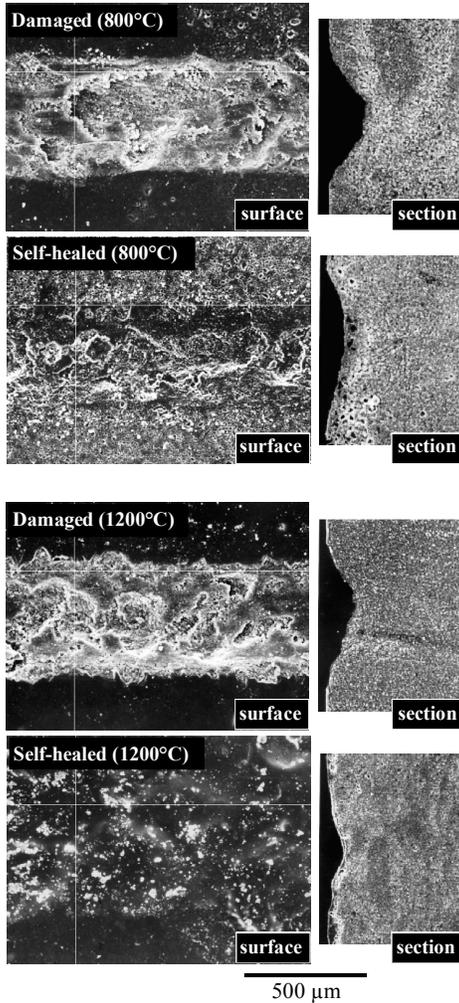


Fig.1 SEM micrographs of the damaged sample and self-healed one during oxidation at 800 or 1200°C for 10h.

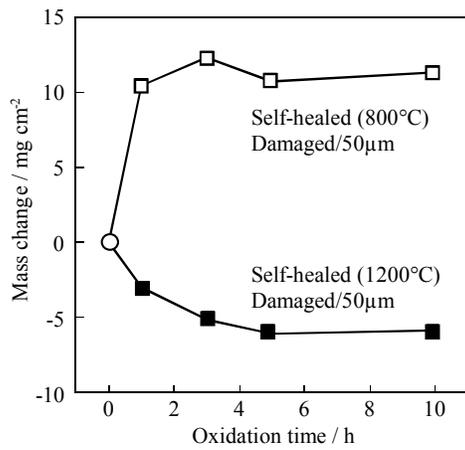


Fig.3 Mass change of the damaged sample during oxidation at 800 or 1200°C for 10h.

Table 1 In-depth distribution of constituent of the sample before and after oxidation at 800 and 1200°C for 10h detected by XPS.

Sample	C	B ₂ C	SiC
	/ mass%		
green	49.1	10.4	40.5
Self-protected (800°C)			
Damaged/0μm	undetected	undetected	undetected
Damaged/50μm	37.8	11.0	51.2
Damaged/500μm	40.8	11.4	47.8
Damaged/1000μm	42.2	11.5	46.3
Self-protected (1200°C)			
Damaged/0μm	undetected	undetected	undetected
Damaged/50μm	40.2	11.1	48.7
Damaged/500μm	45.1	10.3	44.6
Damaged/1000μm	46.4	10.3	43.3

Table 2 Mass change, glass phase content and B/Si ratio of the sample after oxidation at 800 and 1200°C for 10h.

Sample	mass change / mg cm ⁻²	glass cont. / mg cm ⁻²	B/Si ratio / -
Self-healed (800°C)			
Damaged/0μm	-0.01	2.84	0.104
Damaged/50μm	1.10	0.94	0.096
Damaged/500μm	0.51	1.34	0.093
Damaged/1000μm	0.53	1.55	0.090
Self-healed (1200°C)			
Damaged/0μm	-0.02	4.11	0.189
Damaged/50μm	-0.63	0.71	0.184
Damaged/500μm	-0.35	1.58	0.218
Damaged/1000μm	-0.27	2.85	0.204

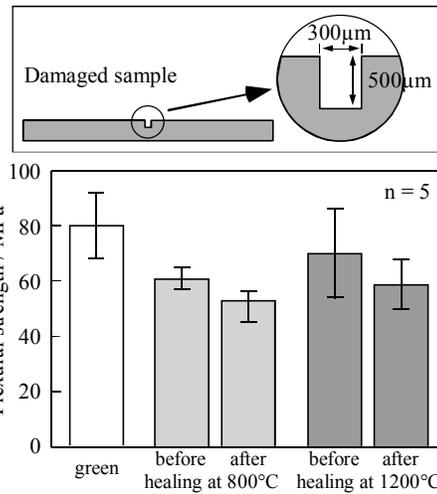


Fig.4 Flexural strength of the damaged sample with notch before and after healing at 800 or 1200°C for 10h.