EFFECTS OF BORON DOPING AND BORON COATING ON OXIDATION BEHAVIOR OF C/C COMPOSITE

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INTRODUCTION

Boron atoms are known to form substitutional solid solution in graphite structure and the solid solubility limit is 2.35 atomic % at 2,620 K [1]. L. E. Jones et al [2] and K. Kobayashi [3] reported that the presence of boron inhibited carbon fiber oxidation. And McKee et al [4,5] and Ehrburger et al [6] found that boron oxide formed a diffusion barrier and decreased the oxidation rate of graphite and C/C composite.

This research was carried out to know the effects of boron doping and boron coating on the oxidation behavior of C/C composites .

EXPERIMENTAL

The 3 samples used for the experiment were as-received C/C composites which were made from PAN-based short carbon fiber with pitch and phenolform-aldehyde resin carbon matrix, (1) the boron-doped sample, (2) the boron coated sample and (3) the boron-doped sample with boron coating. The size of the samples was 5 x 5 x 1 mm.

The boron-coated samples were prepared by dipping the as-received samples or the boron-doped samples into polyethylene glycol solution mixed with metal boron powder and then by following heat-treatment at 300°C

Thickness of the boron film formed on the surface was estimated as about 80μm as shown in Fig.1. The boron-doped samples were prepared by heat-treatment of the boron-coated samples at 2000°C for 1 hr in N_2 gas.

Oxidation tests of those samples were carried out by TGA from room temperature to 1000°C in dry air, and mass loss was measured to clarify the effects of boron coating and boron doping on oxidation.

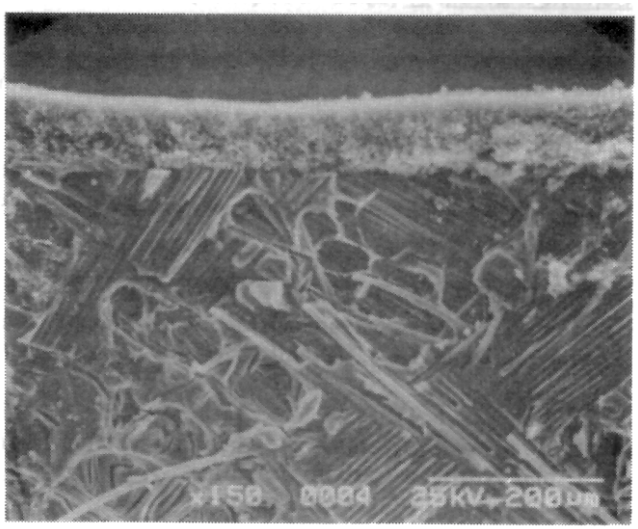

Fig.1. SEM observation of boron-deposited C/C composite with heat-treatment at 300°C.

For a simulation test when damage occurred to a protective coating of C/C composite, for some boron-coated samples. An uncoated hole of about 3.5 mm diameter was made on one coated surface where the inside of the C/C composite, with or without boron doping, was directly exposed to the outer oxidizing atmosphere through the hole, and morphological changes by oxidation with temperature were investigated.

RESULTS AND DISCUSSION

Almost no significant difference for d(002), d(004) and crystallite size, Lc(002), was observed between as-received C/C composite and the one heat-treated at 2000 °C. On the other hand, decrease of d(002) and d(004), and increase of Lc(002) were observed by

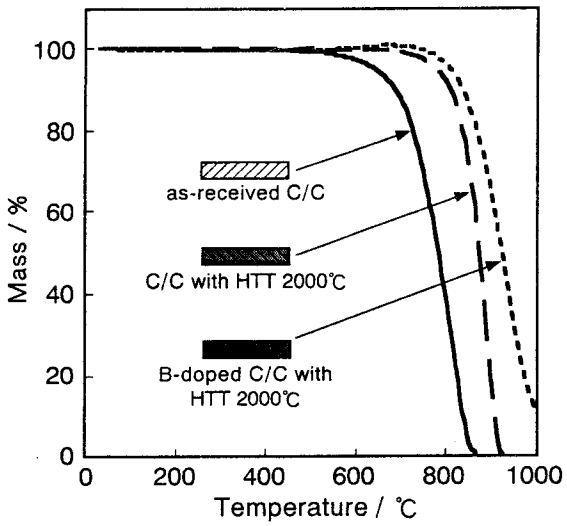

Fig.2. TGA curves of C/C composite.

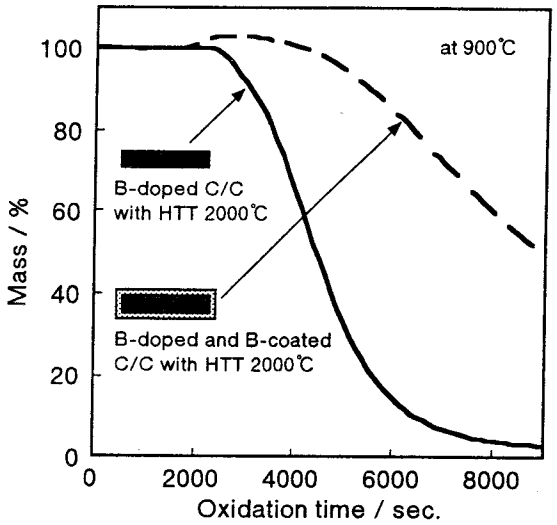

Fig.3. TGA curves of C/C composite.

boron doping at 2000°C treatment.

Mass change with oxidation temperature for the as-received sample, heat-treated sample at 2000°C and boron-doped sample at 2000°C showed that oxidation resistance improved by heat treatment and also by boron doping. That is, as-received sample started oxidation around 500°C, while oxidation started around 750°C for both the heat-treated and the boron-doped samples, and boron doping was shown as the best one against oxidation as shown in Fig. 2. Slight mass gain was observed for oxidation of the boron-doped sample around 700°C and the mass gain was thought to be due to formation of B_2O_3 from diffused boron in the sample. Boron coating over the sample gave also remarkable improvement against oxidation.

In the cases of boron coating, boron powder on the surface started oxidation around 600°C to form B_2O_3 glass and the glass layer protected against further oxidation. However vaporization of B_2O_3 glass occurred above 800°C and oxidation of the inside body proceeded with temperature. Boron doped sample with boron coating showed the best oxidation resistance among all the samples as shown in Fig.3.

Oxidation behavior of boron-coated samples which had an open hole on one side of the surface showed that oxidation started at the hole area and progressed vertically toward the bottom direction. It was thought that pit wall was covered and protected oxidation by B_2O_3 glass which flowed down from the hole edge. However in those cases, no significant difference was observed between the samples with and without boron doping.

In all cases oxidation proceeded generally by the order of firstly interface region, secondly matrix area and finally carbon fiber. This order was generally same for the boron-doped C/C composite.

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