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Crack-healing capability and high temperature oxidation resistance of multilayer coatings for carbon-carbon composites

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Carbon fiber reinforced carbon matrix composites (carbon-carbon composites) are degraded very rapidly by oxidation above 400 degree C in air, and need to be protected by an oxidation resistant coating. Diverse properties are required for the coating, and the requirements can be satisfied by using a multilayer coating. We designed and fabricated a multilayer coating which had high temperature resistant refractory ceramic layers and a functional SiOC glass layer. The SiC refractory ceramic layers were prepared by CVD using silane gas as a source. The functional layer was prepared by a solution method using siloxane polymers. Oxidation tests for carbon-carbon composites coated with multilayer coating showed no weight change for the duration of 23 hours at 1500 degree C and after nine times thermal shock at a heating or cooling rate of 300-1500 K per minute. Microstructural analysis showed that the cracks were formed in the SiC layer but healed by SiOC glass. The excellent high temperature oxidation resistance was due to the self-healing action of the functional glass layer.

Key words: Coatings, Chemical vapour deposition, Oxidation resistance, Ceramics, Multilayer structure, Carbon-carbon composites.

Introduction

Carbon fiber reinforced carbon matrix composites (hereafter carbon-carbon composites) have excellent thermal and mechanical properties and can be used for structural parts at elevated temperature or refractory materials at high temperatures. However, a carbon-carbon composite is rapidly degraded by oxidation at temperatures above 400 degree C in an air or other atmosphere containing oxygen, and fails in a relatively short time [1-3]. To solve the oxidation problem of carbon-carbon composites, two types of methods have been used: oxidation inhibitors, and oxidation resistant coatings. Active sites for oxidation can be adsorbed and thus eliminated by using inhibitors such as halogens, phosporus, or boron compounds. The oxidation rate has been dramatically reduced by using oxidation inhibitors. While they were effective at relatively lower temperatures, the external coating method has been used to block the oxygen from carbon-carbon composites for the high temperature applications [4, 5].

For a coating to be used at high temperatures one requires good hardness, strength, refractoriness, wear resistance, toughness, mechanical and chemical compatibility with the substrate, and low oxygen/carbon permeability. Ceramic materials such as refractory oxides, carbides, borides, or nitrides are generally good candidates since they have good refractoriness, mechanical strength, and hardness. But they have low toughness, and thus are prone to cracking under mechanical or thermal stresses at high temperatures. One typical example is silcon carbide (SiC) which has excellent thermal properties but poor toughness. The difference in the thermal expansion coefficients of SiC and carbon-carbon composite is very large, about 50%, and the SiC coating may fail due to a thermal stress during heating or cooling.

An SiC coating with multiple layers of changing SiC/C ratio has been suggested to lower the thermal stress. But the result was not so favorable, because the coating became cracked and lost oxidation resistance [6]. A coating of silica glass on top of the silicon carbide or other refractory ceramic layers has also been attempted. It was an effective idea because silica has a very low oxygen penetration rate. However, at high temperatures above 1200 degree C, the silica glass was crystallized and degraded. On the other hand, silicon oxycarbide glass was stable up to 1500 degree C and can be used for an additional layer of the coating [7]. When a thermal stress in the coating is not avoidable, a possible solution is using a silicon oxycarbide glass layer to heal cracks formed in the coating [8].

We suggest here to use multilayer coatings consisting of three layers: an SiC outer layer, an SiOC glass layer in the middle, and an SiC inner buffer layer. We expected that the glass layer would act as a barrier for inhibition of the diffusion of oxygen, and also as a healer for the cracks formed in the brittle refractory SiC layers. We report the processing and oxidation test results for the multilayer coating in this paper.

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Experimental Procedures

The multilayer coating was fabricated on a substrate of a carbon-carbon composite. The SiC outer layer and inner layers were deposited by a chemical vapor deposition (CVD) method under a vacuum condition at 1100 degree C. The deposition conditions were determined by a thermodynamic calculation made by Choi and Yun [9]. The carrier and dilution gas was hydrogen (99.99%) and the precursor was methyltrichloro-silane (MTS, CH_3SiCl_3, 99%). The ratio of hydrogen to MTS gas was 1 and 10 for the inner and outer layers, respectively. The functional layer in the middle was prepared by dip coating and heat treatment of siloxane inorganic polymer at 1150 degree C in argon. X-ray diffractometry (XRD) was performed for the phase analysis of the coating materials. To avoid the overlap problem of x-ray photons from the coating layer and the substrate both having the same carbon contents, an SiC or SiOC layer deposited on Al_2O_3 was used for XRD analysis. The oxidation resistance tests of carbon-carbon composites with multilayer coatings were performed at 1500 degree C in air with a flow rate of 1000 sccm. The samples were inserted in and pulled out of the furnace repeatedly nine times at intervals of 1-8 hours. The total period of time the sample spent in the furnace was 23 hours. During each insert and pull-out action, the sample experienced thermal shocks corresponding to 300-1500 K/min. The weight of the samples was measured each time of pull-out. The microstructure and composition were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and an electron probe microanalyzer(EPMA).

Results and Discussion

Fig. 1(a) shows a XRD pattern for SiC layer deposited on an Al_2O_3 substrate as a test under the same conditions as that of the CVD process on carbon-carbon composites. Single phase of SiC was found to be successfully deposited. The coating was in the preferred orientation of the 111 crystallographic plane of β-SiC. Fig. 1(b) shows the XRD pattern for the functional layer on alumina substrate prepared by dip coating and heat treatment at 1150 degree C. XRD patterns for the layer prepared at 1250 and 1500 degree C are also posted for comparison. The pattern has a large diffuse peak at about 2θ = 22 degrees diffraction angle, and slight undulations at 36 and 65 degrees. The large peak is clearly from the short range ordering of silicon and oxygen atoms in the silica glass network. TEM analysis showed only an amorphous structure without the presence of silicon carbide phase. These result verified that the functional layer was of the glass structure of silicon oxycarbide. This result was consistent with a study in which $SiO_{4-n}C_n$ tetrahedra were found to be the structural basis of glass made from polysiloxane [10, 11].

Fig. 2(d) shows the back-scattered electron image of the multilayer coatings on a substrate. Dark regions at the

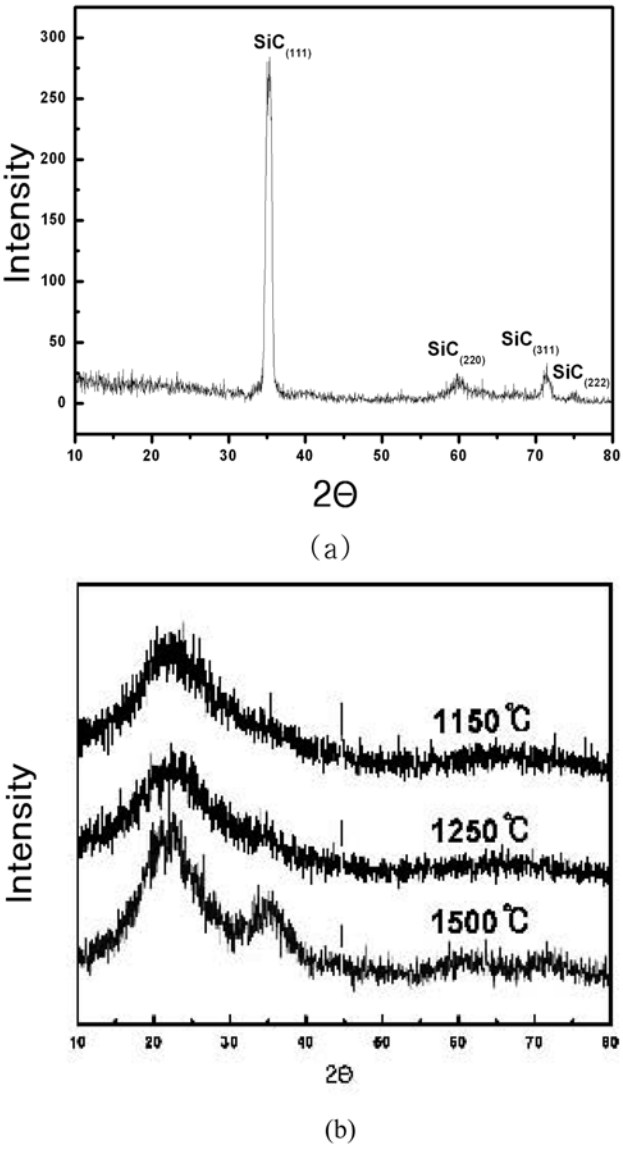


Fig. 1. Results of x-ray diffraction analysis for (a) the refractory layer and (b) the functional layer.

bottom and top are carbon-carbon composite and mounting plastics, respectively. The bright region is the refractory coating layer. The narrow region in grey is the functional layer. The result of the EPMA analysis showed that the outer and inner layers were silicon carbide. The functional layer was a silicon oxycarbide with a composition of $SiO_{1.43}C_{0.66.}$ Oxygen atoms in the silica network may have been replaced by carbon atoms, forming a Si-O-C network [10, 11].

Oxidation tests for carbon-carbon composites with multilayer coating were performed at 1500 degree C for 23 hours. For comparison carbon-carbon composites without the coating were tested at 1450 degree. As shown in Fig. 3, the composite without the coating was burnt out completely in air after just an hour of heating. However, the composite with a multilayer coating showed barely no weight change (< 1%) and endured the high temperature

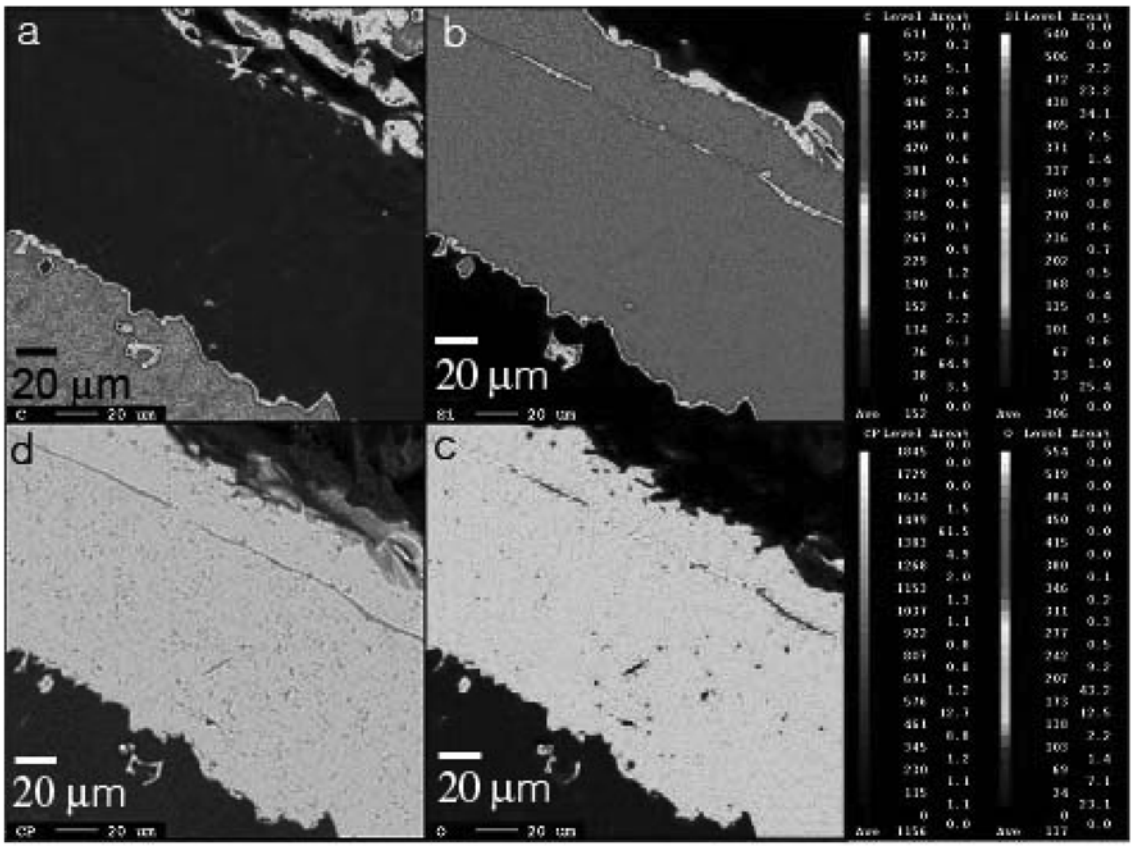


Fig. 2. Results of electron probe microanalysis (EPMA) showing x-ray maps of (a) carbon, (b) silicon, and (c) oxygen elements, and (d) backscattered image of carbon-carbon composite with multilayer coating. In the image (d), the dark region at the bottom is the carbon-carbon composite, and the bright region is the multilayer coating. The thin grey line corresponds to the functional layer.

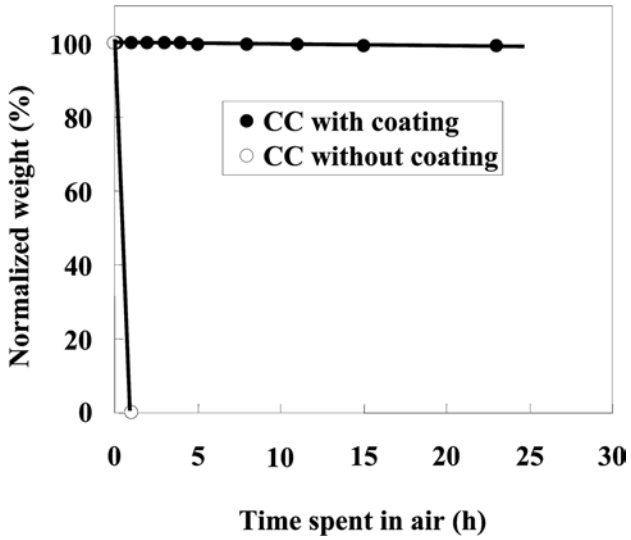
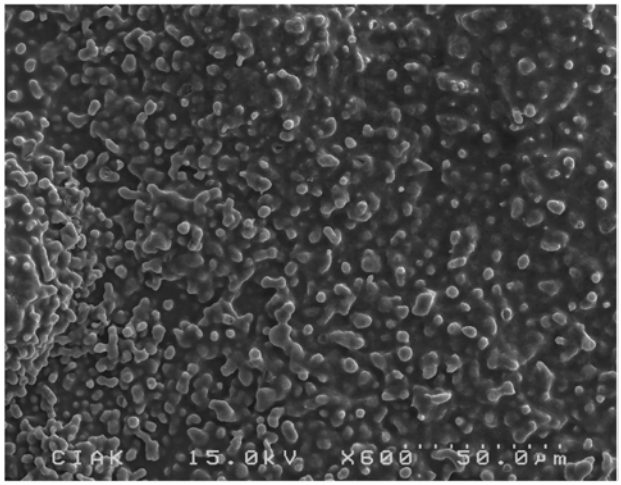


Fig. 3. Oxidation test results showing weight change of carbon composites with multilayer coatings after repeated heating at 1500 degree C in air, and without a coating at 1450 degree C in air.

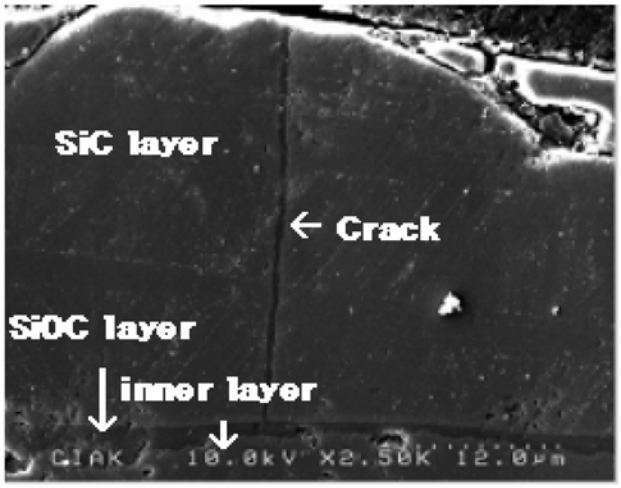
oxidizing environment and thermal shocks for nine times (total 23 hours) of heating.

Fig. 4 gives surface and cross-sectional micrographs of the SiC layer after oxidation test. A granular phase was formed on the surface after the oxidation test (Fig. 4(a)). EDS analysis showed these were of silicon oxide, which was a protective layer against oxidation. Considerable numbers of cracks were found in the cross-section of the coating after the oxidation test. Fig 4(b) shows one of the cracks formed in the outer layer. The driving force must be from the thermal expansion mismatch between the composite substrate and the silicon carbide coating. The difference in thermal expansion coefficients was about 50%, which may have caused a high thermal stress after the heating and cooling cycle. Since the thermal stress is exerted in the direction parallel to the coating layer, cracks are formed perpendicular to the coating layers.

It was surprising that the sample showed excellent oxidation resistance even with cracks in the coating because oxygen could have penetrated through the cracks and degraded the carbon materials. Interestingly, all cracks were found to be filled with solid materials, as can be seen in Fig 4(b). EDS results showed that the composition of the material filling the cracks was the same as that of the functional layer. The SiOC glass of functional layer must have moved by viscous flow under the action of a capillary force. The crack with a submicrometer width may have exerted a capillary force for the flow. If cracks in the silicon carbide layer are healed by the capillary action of amorphous material in the functional



(a)



(b)

Fig. 4. SEM micrographs of (a) the surface and (b) the cross section of a carbon-carbon composite with multilayer coating after the oxidation test. In (b), a crack formed perpendicular to the coating, but was healed.

layer, carbon-carbon composites can be safely protected from the oxidizing air. The excellent thermal shock and oxidation resistance which these composites showed was due to the self-healing function of the multilayer coating.

Conclusions

A multilayer coating for the oxidation resistance of carbon-carbon composites was designed and prepared. A multilayer coating consisted of three layers, an outer, middle, and inner layer. The outer and inner layers were of SiC and were prepared by CVD. The middle layer was of SiOC glass and was prepared by a solution method. Oxidation resistance tests for the carbon-carbon composite with multilayer coatings were performed at 1500 degree C in flowing air. They showed no weight change after 23 hours of exposure in air at 1500 degree C and nine times thermal shock at 300-1500 K/min. The excellent oxidation resistance was due to the crack healing action of the SiOC glass in the functional layer. All cracks formed by the thermal expansion mismatch between the coating and the substrate were healed by the capillary action of glass.

The result of the present study showed the possibility that the lifetime of the hard but brittle ceramic coating can be increased dramatically using a SiOC glass layer with a self-healing function. It also showed that carbon-carbon composites or graphite can be used at high temperature for much longer time by use of a multilayer coating of our design.

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