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# Preparation and characterization of a silicon oxycarbide coating with crack-healing capability for silicon carbide ceramics

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**Silicon carbide ceramics have good mechanical and thermal properties, but they have a failure problem by brittle fracture due to fast crack growth. Attempts were made to self-heal cracks in ceramics. The SiC ceramics were coated with silicon oxycarbide glass films which were prepared by dip-coating and pyrolysis of polymer precursors. The crack-healing capability was evaluated by mechanical testing and microstructural analysis. Cracks were artificially generated in the sample by either micro indentation or notch making. Healing treatments at 1100, 1300, 1400, or 1500 ºC were made. Bending strengths were measured before and after crack growth and a healing treatment. It was found that the strength dropped low by the generation of cracks but was fully recovered after the healing treatment. The cracks were found filled and healed by the coating material.**

**key words: Four point bending strength test, Coating, Crack-healing.**

## Introduction

Carbide ceramics are used for structural or coating materials since they have high strength, refractoriness, and wear resistance [1]. But they have a failure problem by brittle fracture due to the fast growth of cracks in their bodies. In particular when the ceramics are used for the oxidation resistant coating of carbonaceous materials, generation of a tiny crack may lead to the introduction of oxygen through the crack opening, and the total burning of the body. For the solution of the brittle failure problem, one may find two methods: removal of defects or suppression of the crack growth. Basically complete removal of defects is impossible [2]. Toughened ceramics with various types of hybrid microstructure having particles, fibers, films, or layers were designed and successfully prepared. They were effective for enhancing the fracture toughness and suppressing the crack growth [3]. However, the toughness achieved was not high enough to meet the requirement for structural or mechanical parts. Moreover, the toughened ceramics with a complicated microstructure needed a higher cost of production, causing limitation of industrial applications.

Crack healing rather than suppressing the growth have been attempted. Nam et al. tried to form silicon oxide on the internal surface of cracks by the oxidation on various ceramics such as SiC, $Si_3N_4$, SiAlON, and $Al_2O_3$/SiC composites [4-7]. Ando *et al*. could heal cracks in mullite/SiC composites [8]. Yun *et al*. [9] reported that the healing of cracks was possible in a silicon carbide coating film for the oxidation resistance of carbon-carbon composites. They found that the cracks in the coating film were successfully healed by the glass and the life time of carbon composites was lengthened 50 times in air at 1500 ºC. If glass could heal cracks in a coating film, it may also heal cracks in the bulk ceramics.

In this study, self-healing cracks in silicon carbide bulk ceramics by a preparing silicon oxycarbide coating film on the surface was attempted. The healing function was evaluated by strength measurements and microstructural analysis after the healing treatment.

## Experimental Procedures

### Preparation of the coating films

The silicon oxycarbide coating was prepared by dip-coating and pyrolysis of a polymer precursor on the silicon carbide ceramic bulk samples with a 99% purity and a 99.9% density (SSangyong Materials Co., Korea). The SiC samples had bar shapes with $3 \times 4 \times 36$ mm$^3$ dimensions. The polymer solution was prepared by dissolving 33, 40, 45, or 50 weight % of polymethylsilsesquioxane (GE Toshiba) in ethyl alcohol. The viscosity of the polymer solution was measured to examine the time of stabilization. The polymer coating film was made by a dip-coating method at a constant speed of 1-4 cm minute$^{-1}$. After drying, the ceramic samples with polymer films were heat-treated at 1150 ºC in an argon atmosphere for two hours to make a silicon oxycarbide coating [10-12]. The heating schedule was very slow for the gentle removal of organic materials from the films. It took eight steps and 55 hours to finish the heating schedule. The micros-

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tructure and composition of the coating films were examined by scanning electron microscopy (SEM) and an electron probe microanalyzer (EPMA).

### Crack generation and growth

The cracks were artificially formed in the samples on purpose to test the crack healing capability. Two methods were used to generate cracks: a notch method or indentation method. For the notch method, each bar-shaped sample was notched at the center of the surface along the lateral direction with a width of 0.3 mm. For the indentation method, samples were indented at the center surface under a one kilogram load with a Vickers diamond indenter. The indenter was positioned such that the diagonal axis of the indent was parallel to the lateral axis of the bar-shaped sample. Cracks of average 15 μm lengths were found generated at the four corners of the indents.

An oxycarbide coating was applied on the notched or indented samples by dip-coating and heat treatment under the same conditions indicated above. Crack growth treatments were made on the samples by applying a compressive force to generate and grow cracks. The compressive force was applied by a universal testing machine (Instron Inc.) with a loading speed of 0.01 mm minute$^{-1}$. When a sound signal was detected at the time of crack extension, the loading was stopped.

Whether the coating would be made before or after the crack growth needed to be decided. When the coating was made after the crack growth, the cracks were filled with polymer coating materials. Decomposition of the polymer materials during heat treatment would expand and extend cracks. The remaining hydrocarbon materials inside cracks would make the analysis complicated. Thus, the coating was made before the crack growth to leave the crack opening empty.

### Healing treatment and characterization

Healing treatment was made on the samples having cracks by a heat treatment in an argon atmosphere for six hours at 1100, 1300, 1400, or 1500 ºC. The heating rate was five degrees per minute. Four point bending strengths were measured for the samples before and after the healing treatment and also for the reference samples [13]. The notched or indented surfaces of the sample were placed downwards so that a tensile stress would be applied to the surface during a four-point bending strength test. Before and after the healing treatment, the cracks were observed by an optical microscope and a scanning electron microscope. The chemical composition was examined using an electron probe microanalyzer (EPMA).

## Results and Discussion

The viscosity of the polymer solutions was measured after mixing as a function of aging time. As shown in Fig. 1(a), it increased initially but was stabilized after 80 minutes except for the case of the 50% solution. The

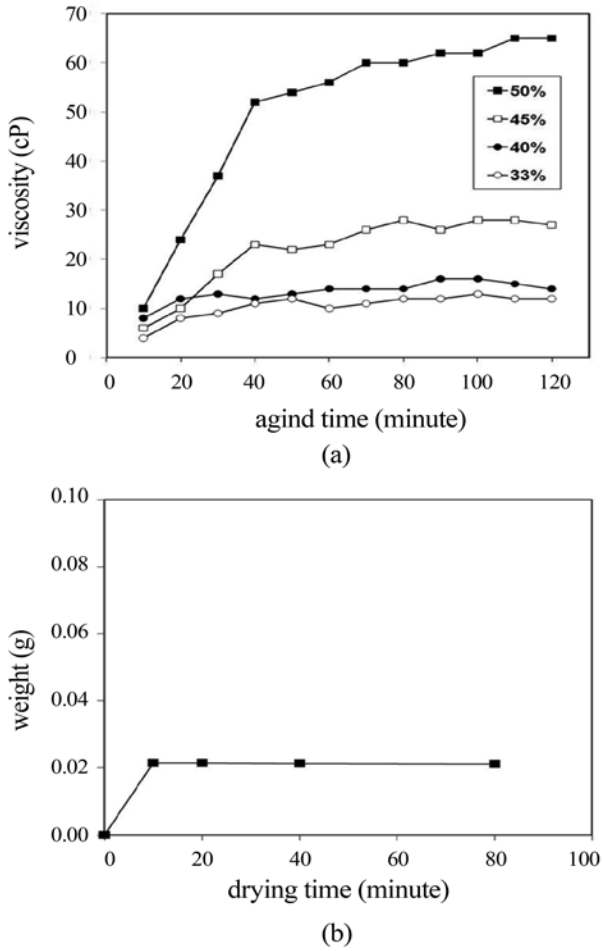



**Fig. 1.** Change in (a) the viscosity of the polymer solution with aging time, and (b) the weight of the film with drying time.

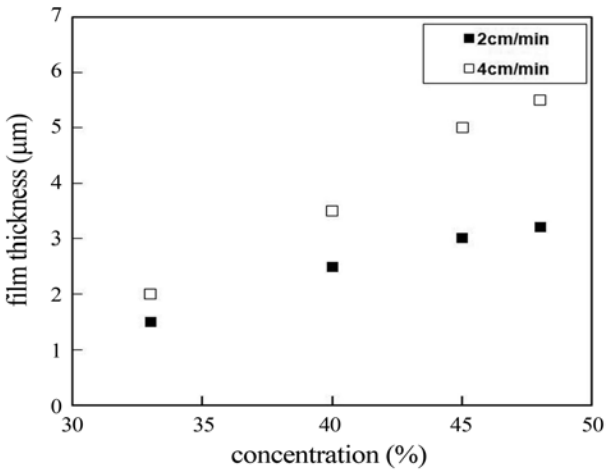



**Fig. 2.** Change in the thickness of the polymer film with concentration at two or four cm minute$^{-1}$ dip-coating speed.

weight of the coating film was measured as a function of the drying time. As shown in Fig. 1(b), the weight did not change from 10 minutes after dip-coating, indicating that the drying was completed in 10 minutes. After the dip-coating, the thickness of the polymer film was found increased with the dipping speed as expected (Fig. 2). It also increased

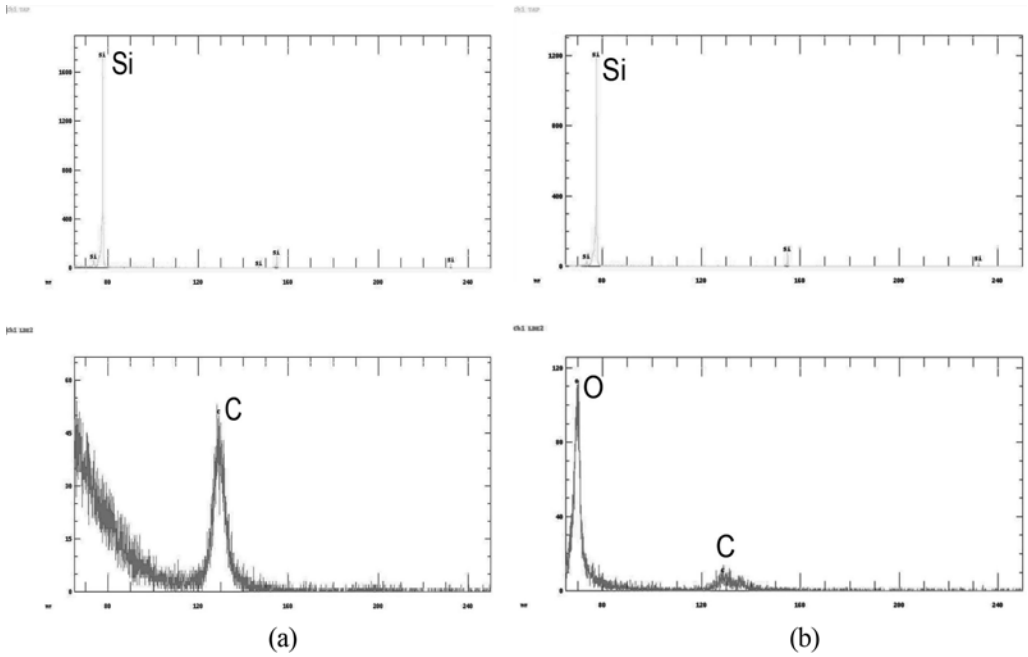



**Fig. 3.** Electron probe microanalyzer spectra (a) from the ceramic substrate and (b) from the coating film.

with the concentration of the solution. A coating film with a thickness of 5 μm could be prepared under the condition of a speed of 4 cm minute$^{-1}$ and a 45% solution concentration. Compositional analysis showed that the ceramic substrate had silicon and carbon elements, while the coating film had silicon, carbon and oxygen, indicating that a silicon oxycarbide was successfully formed in the coating film (Fig. 3).

The healing function was evaluated by observation of the crack morphology and maintenance of bending strength after the healing treatment. The length and width of the cracks generated by the notch method were larger than that by the indentation method. After the crack growth treatment, the length and width were about 2 mm and 5-10 μm respectively in the notch method, while in the indentation method they were less than 1 mm and 0.75 μm. The bending strengths were measured for the samples before and after the healing treatment. Fig. 4 and Fig. 5 show the bending strength data of samples at each step

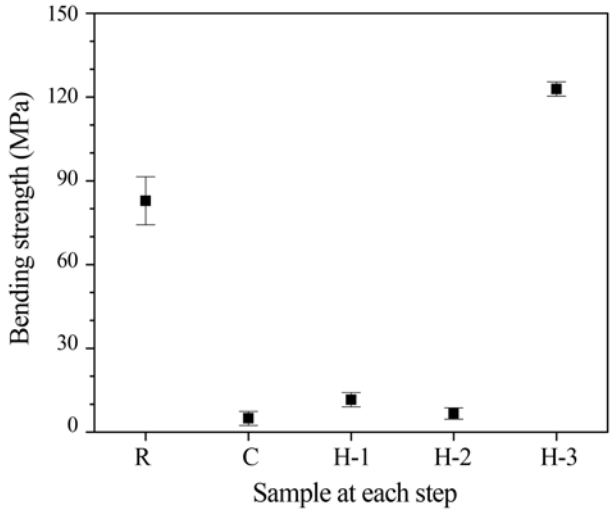



**Fig. 4.** Bending strengths of the samples at each step for the case of the notch method. R : reference samples after making a notch and before the crack growth treatment, C : reference samples after making a notch and crack growth treatment, H-1 : samples healing treated at 1100 °C, H-2 : samples healing treated at 1300 °C, H-3 : samples healing treated at 1400 °C.

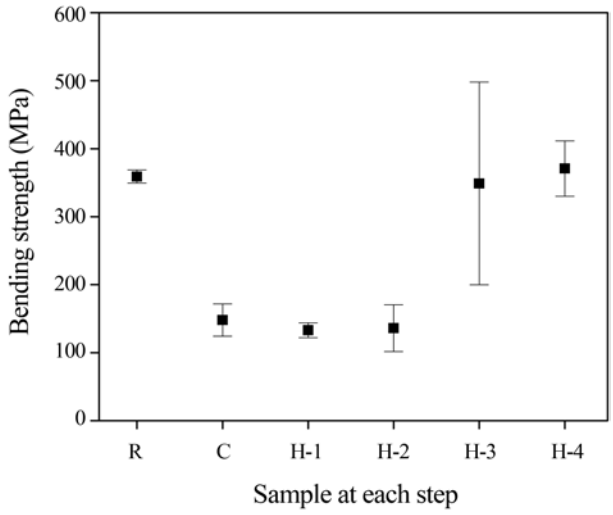



**Fig. 5.** Bending strengths of the samples at each step for the case of the indentation method. R : reference samples after indentation and before the crack growth treatment, C : reference samples after the indentation and the crack growth treatment, H-1 : samples after healing treatment at 1100 °C, H-2 : samples after healing treatment at 1300 °C, H-3 : samples after healing treatment at 1400 °C, H-4 : samples after healing treatment at 1500 °C.

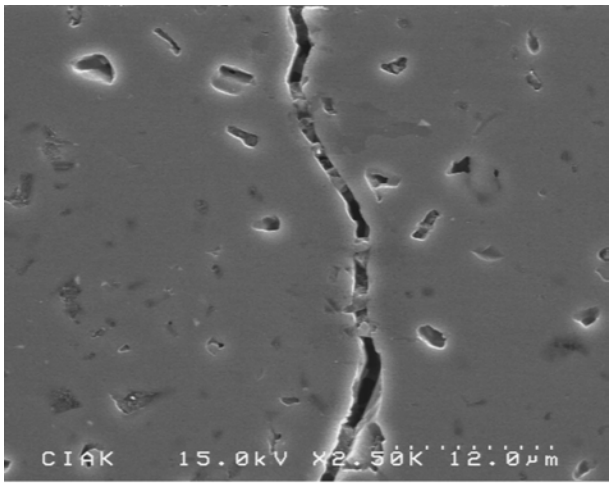
of the crack growth and healing treatment for the case of the notch method and indentation method, respectively. It was expected that the bending strength decreases with crack generation, but increases with crack healing. When the cracks were generated, the samples became weaker as expected. The strength of samples with cracks generated by the notch method was much lower than the one by the indentation method. This may be because cracks generated by the notch method were wider and longer. A higher stress is concentrated at the tip of cracks when they are larger in width or in length [14]. The samples with wider and longer cracks may reach the critical stress earlier and fail under lower loads.

As shown in Fig. 4 for the case of the notch method, the strength of the sample with a notch was 83 MPa as determined by a four point bending test. The bending strength decreased to 5 MPa by the crack growth treatment as expected. However, it was recovered to 118 MPa after the healing treatment at 1400 °C. Heat treatment at 1100 or 1300 °C did not give a considerable recovery of the bending strength. The strength of 118 MPa after the healing treatment was even higher than the one of 83 MPa before healing. The reason may be that not only the internal defects such as cracks but also the surface defects such as machining flaws were healed by the heat treatment.

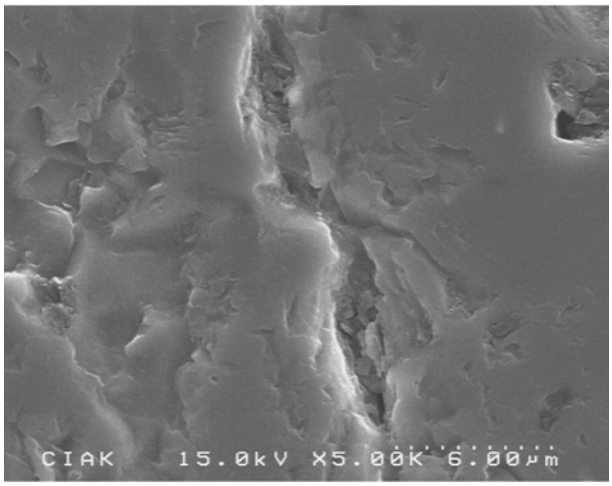
For the case of the indentation method, the results showed similar trends to the case of the notch method even though the strengths were higher. As shown in Fig. 5, the strength which was 360 MPa after the indentation, decreased to 150 MPa by the crack growth treatment. Since longer cracks make a higher stress concentration, the strength of the sample after the crack growth treatment could be lower than the one before the treatment. The strength was found recovered to 350-370 MPa by the healing treatment at 1400 or 1500 °C. But the healing treatment at 1100 or 1300 °C did not give any recovery in the strength level.

The recovery of strength by the heat treatment may be due to the crack healing. Scanning electron microscopy before and after the healing treatment showed that the cracks were empty after a healing treatment at 1100 or 1300 °C, but fully filled after a healing treatment at 1400 or 1500°C as shown in Fig. 6. In general, the failure of the ceramic sample starts from the crack tip where the stress is concentrated. When the crack opening is filled with a solid material, the stress concentration is greatly relieved. The samples having filled cracks have a higher strength.

A crack could be filled either by viscous flow of a glass material or by oxidation and formation of a silica film on the internal surface of the crack. If the samples had been heat-treated in air, the latter case would have been possible. But in the present case, the samples were heat treated in an argon atmosphere, and so there is no possibility of oxidation. A crack and its vicinity were analyzed by electron probe microanalysis (EPMA). Fig. 7 shows a crack




(a)




(b)

**Fig. 6.** SEM micrographs of samples showing (a) cracks unfilled after heat-treatment at 1100 °C, and (b) cracks filled after heat treatment at 1400 °C.

in a secondary electron image, and X-ray maps of oxygen, silicon, and carbon respectively from the upper right in the counterclockwise direction. The results showed that the cracks were filled with a material having silicon, oxygen, and carbon elements. This implies that the glass materials moved from the surface coating to the cracks. At 1100 or 1300 °C, the temperature may not have been high enough to make glass fluid enough to flow and heal the cracks. In a future study, the viscosity and the flow rate of the silicon oxycarbide glass will be examined.

## Conclusions

Silicon oxycarbide glass coating films with a crack healing function were prepared on the surface of silicon carbide ceramic materials by dip-coating and heat-treatment. The crack healing function was tested by measuring the bending strength of the samples after the generation of cracks and after a healing treatment. The strengths dropped after the

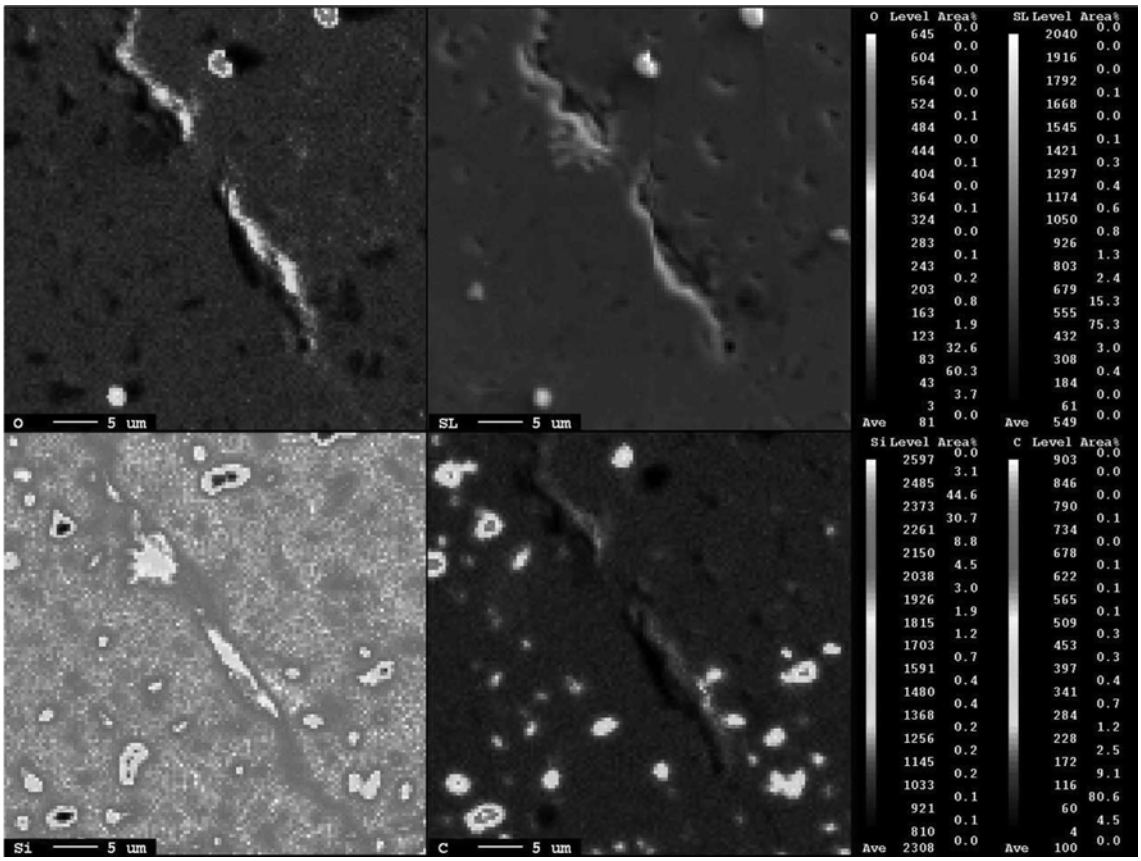



**Fig. 7.** SEM micrograph (top right) of cracks healed after healing treatment at 1400 ºC, and X-ray maps of carbon k-line (bottom right), oxygen k-line(top left), silicon k-line(bottom left).

generation of cracks but fully recovered after the healing treatment. The temperature was a critical factor: cracks were healed at 1400 or 1500 ºC but not healed at 1100 or 1300 ºC. Cracks were found filled with silicon oxycarbide glass after the healing treatment. The viscous flow of the glass at high temperature was the reason for the crack filling and healing.

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