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SiC coating on various nuclear-grade graphite substrates by chemical vapor reaction

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The dependence of high-temperature oxidation and the thermal shock resistance behavior of α-SiC coated nuclear-grade graphite substrates were investigated at elevated temperatures. The surfaces of three kinds of nuclear-grade graphite substrates were coated with α-SiC by chemical vapor reaction (CVR) at a temperature of 1600 °C and a pressure of 1.3 Pa in a pure polysilicon gas atmosphere. Thermal shock and oxidation resistance tests were performed at 1000 °C and 1300 °C respectively, in which the samples were taken out of a box furnace and directly exposed to air at room temperature. It was found that the initial microstructure of the graphite substrates plays an important role in determining the final thermal properties of the α-SiC coatings when using the CVR method.

Key words: SiC, Coating, CVR, Oxidation, Thermal shock, Microstructure.

Introduction

Carbon and graphite materials are chemically stable and have low densities and high strength at elevated temperatures. However, the use of graphite materials has been restricted owing to tSheir poor oxidation resistance at elevated temperatures in an oxidizing atmosphere. Oxidation protection for carbon materials has been studied for the past 60 years, and silicon carbide (SiC) is currently considered the best coating material because of its good mechanical properties and resistance to oxidation and because of the fact that its coefficient of thermal expansion is close to that of carbon [1-3]. Graphite is used for fuel elements in high-temperature gas-cooled reactors (HTRs). To improve the safety of HTRs, oxidation resistance is very important. Some methods have been developed to apply SiC coatings on graphite balls for the fabrication of fuel element matrices of HTRs [4, 5], but these methods are difficult to apply within the framework of a mass production process.

It is therefore necessary to develop a convenient method for the mass production of SiC coatings on graphite [6]. Chemical vapor reaction (CVR) coating, in which molten silicon reacts at the surface of the graphite substrate to form SiC, is an effective way to produce SiC coatings on graphite [7]. However, the chemical vapor reaction process often results in a high defect density; because oxygen can corrode the substrate through these defects, the oxidation resistance of such coatings is not sufficient at elevated temperatures. Another problem is that the coating formation behavior can be quite different when a different carbon material is used [8]. The present study was conducted to investigate the relationship between thermal properties such as the oxidation and thermal shock resistance and the microstructure of SiC coatings produced by CVR on top of various nuclear-grade graphite substrates.

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Experimental Procedure

Three different nuclear-grade graphite substrates (provided by Toyo Tanso and SGL Carbon, Japan) were used in this experiment. The properties of the graphite substrates are summarized in Table 1.

The graphite substrates were machined into bar-shaped specimens with dimensions of $10 \times 30 \times 5$ mm^3. The SiC coatings were developed on the graphite substrates by CVR at a temperature of 1600 °C for 80 min and 160 min at a pressure of 1.3 Pa The 80 min duration is required for forming a 5 μm SiC coating layer by CVR, and the duration was doubled to 160 min to investigate the relationship between deposition time and coating layer thickness. During the coating process, solid polysilicon was thermally evaporated

Table 1. Properties of the three nuclear-grade graphite substrates used in the present study.

	A	B	C
Manufacturer	Toyo Tanso	SGL Carbon	
Fabrication	Iso-molded	Vibro-molded	Iso-molded
r_{Bulk} (g/cm^3)	1.77	1.85	1.81
$r_{Compressive}$ (MPa)	78	75-69	97
$r_{Tensile}$ (MPa)	25	22.8-20.3	28
Ash content	< 20	60	11

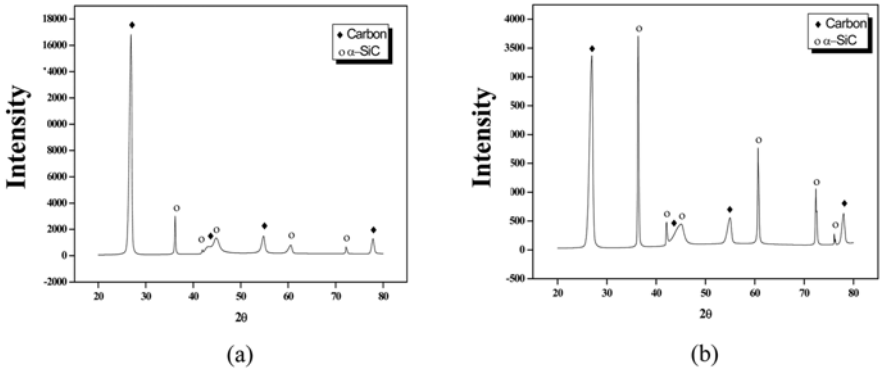

Fig. 1. XRD patterns of the SiC-coated specimens prepared by CVR with reaction times of (a) 80 and (b) 160 min at 1600 °C.

and reacted with the graphite, thus forming SiC at the surface of the substrates.

To test the oxidation resistance, specimens both with and without SiC layers were oxidized in air at 1300 °C for 1 hr and subsequently slowly cooled in a furnace to room temperature. To determine the thermal shock resistance, the SiC-coated specimens were preheated to 1000 °C and kept at that temperature for 1 hr. The specimens were then subjected to thermal shock by removing them from the furnace and exposing them immediately to air at room temperature. Investigations of the SiC coatings prepared by CVR were carried out by means of X-ray diffraction (XRD), optical microscopy using a camscope, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA).

Results and Discussion

Fig. 1 shows the XRD patterns of samples prepared by CVR with reaction times of 80 min and 160 min at 1600 °C. The XRD analysis confirmed that the coating layer mainly consisted of -SiC and graphite. This result agrees well with the general tendency of CVR-prepared SiC coatings, in that the coating properties mainly depend on synthesis temperature and reaction time [9]. With an increase in the synthesis temperature, the thickness of the SiC layer formed increased and most of the graphite was converted to -SiC at temperatures above 1500 °C. Extended reaction times also result in -SiC-enriched coating layers. Because of the slow diffusion rate of Si in graphite, it is necessary to allow for a sufficient reaction time to form a solid -SiC coating layer [10].

The results of EPMA analysis of the cross sections of the SiC-coated specimens prepared by CVR with reaction times of 80 and 160 min at 1600 °C are shown in Fig. 2. The SiC coating layers became thicker and denser with increasing CVR reaction time. The thickness of the SiC coating on top of the graphite substrate was somewhat more than two times larger for a reaction time of 160 min than for a reaction time of 80 min.

The oxidation resistance of the SiC layers was evaluated by monitoring the surfaces of the specimens

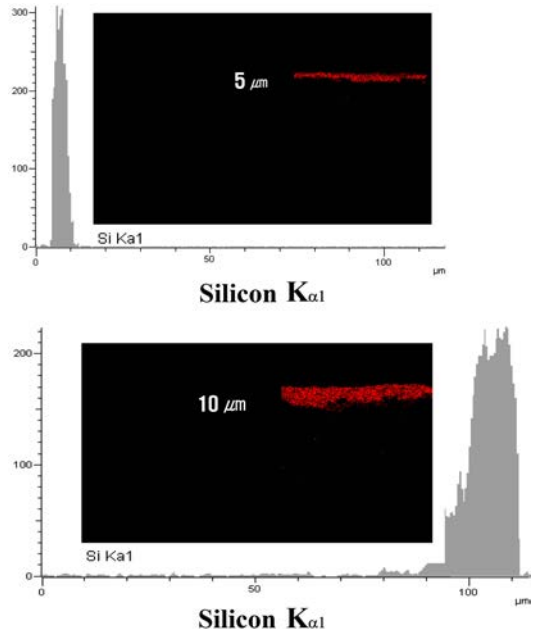

Fig. 2. EPMA analysis of the cross sections of the SiC-coated specimens prepared by CVR with reaction times of (a) 80 and (b) 160 min at 1600 °C.

after heating them to 1300 °C for 1 hr and then immediately exposing them to air. It is known that the oxidation resistance of SiC coatings synthesized by CVR is usually insufficient because of the presence of a large number of pinholes, pores, or even cracks [11].

The upper row of Fig. 3 shows the cross-sectional morphologies of the three different graphite substrates before CVR coating. The surfaces of the specimens after coating and performing the oxidation resistance test at 1300 °C for 1 hr in an electric furnace are shown in the lower row of Fig. 3. As evident from Fig. 3, the surface morphology of specimen B before coating showed several voids, whereas samples A and C looked relatively clean and dense.

Many white spots appeared on the surface of specimen B after the oxidation test, as seen in the middle lower frame of Fig. 3. These white spots are caused by surface cracks in the coating layer, which provide access to the graphite substrate for oxygen

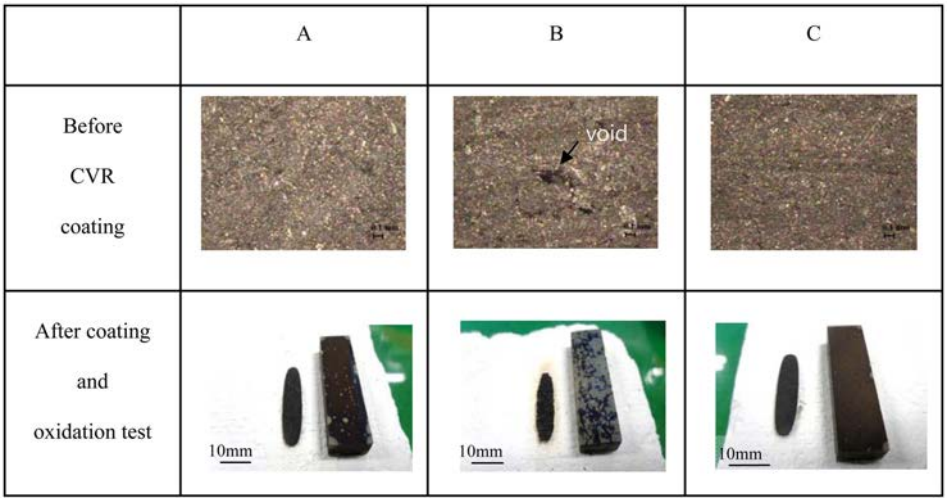

Fig. 3. Cross-sectional morphologies of three different graphite substrates before CVR coating (upper row) and upper surface of CVR-coated specimens after performing the oxidation resistance test at 1300 °C for 1 h (lower row). The notations A, B, and C refer to the different samples listed in Table 1.

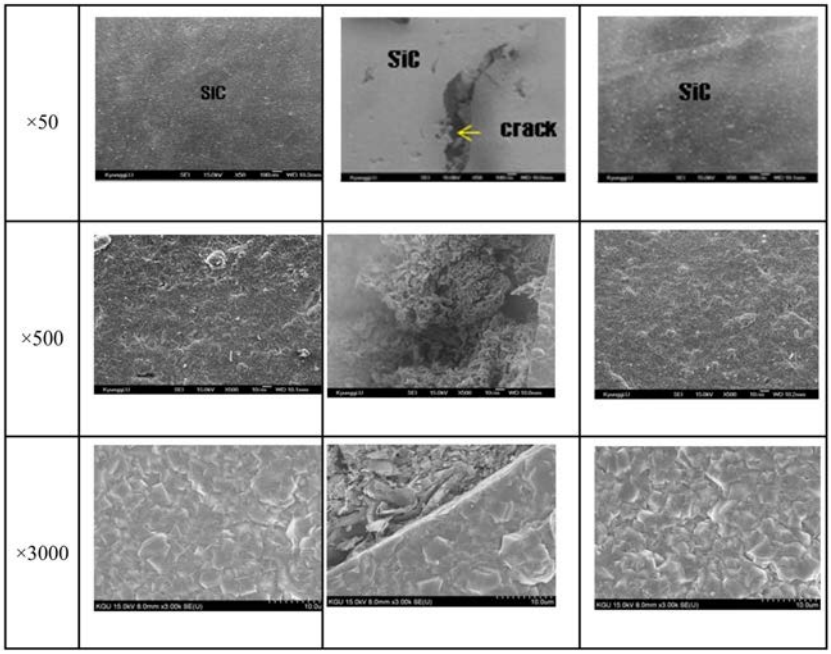

Fig. 4. Micrographs and surface morphologies of coated specimens using three different graphite substrates after the thermal shock test, which consisted of keeping the samples at 1000 °C for 1 hr and then subjecting them immediately to air at room temperature. The notations of A, B, and C in the figure refer to the different graphite substrates listed in Table 1.

molecules. These results indicate that the original surface conditions, particularly the presence of defects at the surface of the substrate, may affect the quality of the SiC coating. This means that the formation of carbon dioxide, carbon monoxide, and other residues on top of the graphite substrate after the oxidation test may be quite different, depending on the initial substrate conditions. It is concluded that control of the surface morphology of the substrate is very important for improving the oxidation resistance of SiC coatings formed by the CVR process.

The effect of the SiC coatings with respect to thermal shock resistance was evaluated by monitoring the surface of the specimens after exposing them to air at 1000 °C for 1 hr and then immediately exposing them to air at room temperature. As shown in Fig. 4, the thermal shock resistance behavior of the coated specimens is very similar to their oxidation resistance behavior. Many cracks were found at the surface of specimen B after the thermal shock test. By contrast, only a few cracks or other damage was found at the surfaces of samples A and C. Therefore, it is confirmed that the surface morphology of the substrates before coating is an important factor in determining the thermal properties of the coating layers, such as thermal oxidation and thermal shock resistance [12]. For a

successful SiC coating using the CVR method, careful substrate selection that takes into account the substrate surface conditions, as well as other factors, such as the manufacturer, is recommended.

Conclusion

When synthesizing silicon carbide (SiC) on graphite substrates by the CVR process, the SiC coating thickness and crystalline structure mainly depend on the synthesis temperature and reaction_times. After the oxidation test, one specimen showed many white spots at the surface. These white spots were caused by surface cracks in the coating layer, which provided access to the graphite substrate for oxygen molecules. The thermal shock resistance behavior of the coated specimens was very similar to their oxidation resistance, i.e., in two of the specimens, only a few cracks or other defects were found at the surface. Thus, the quality of the SiC coating mainly depends on the initial surface conditions of the substrate in terms of defects such as voids or microcracks. It is concluded that control of the surface morphology of the substrate is very important for improving the oxidation resistance and thermal shock resistance of SiC coatings formed by the CVR process.

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