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Silicon carbide crack healing by chemical vapor deposition

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The combined reactor core and reflector of the very high temperature reactor (VHTR) is supported by a graphite support column composed of several types of graphitic material. Graphite in the VHTR reacts readily with O_2, thereby forming CO_2. Increasing the resistance of graphite to oxidation is therefore essential to its use as a high-temperature structural material. Conventional silicon carbide (SiC) is widely used as a carbon coating material that is resistant to oxidation. SiC was deposited by E-beam evaporation coating as a functionally gradient material. However, SiC was susceptible to the formation of cracks during thermal shock. These cracks acted as a pathway for the transport of O_2 to the graphite substrate. Therefore, this study aimed to heal the cracks via chemical vapor deposition (CVD) and thereby prevent oxidation resulting from the abovementioned cracks. Crack healing was investigated at thermodynamically calculated methane ratios of 0.35-0.55. Micrographs obtained at a methane ratio of 0.55 revealed homogeneously faceted surface structures. A dense SiC coating layer appeared necessary for effective crack healing. Therefore, crack healing was performed at a methane ratio of 0.55 by CVD. In that case, cracks were completely healed by the ~0.1-mm-thick chemical-vapor-deposited coating. In contrast, cracks persisted on the surface after crack healing by chemical vapor reaction (CVR). The SiC coating produced via CVD constitutes a promising method for crack healing stemming from thermal shock; this coating is well-suited for use in the VHTR and various semiconductor industries.

Key words: SiC, Crack healing, Chemical vapor deposition, Chemical vapor reaction.

Introduction

The very high temperature reactor (VHTR) is defined as a helium-cooled, graphite moderated reactor with a core outlet temperature in excess of 900 °C and a long-term goal of achieving an outlet temperature of 1000 °C [1]. The high temperatures enable applications such as process heat or hydrogen production via the thermochemical sulfur-iodine cycle. Reactor core and reflector is supported by a graphite support column with several different kinds of graphite material in designs of VHTR [2]. Oxidation of graphite components is inevitable owing to oxidants impurities from a graphite outgassing and a leakage in a heat exchanger [3]. When air ingress occurs, oxygen can attack the internal pores of graphite components and enlarge the pores, eventually resulting in loss of mechanical strength. The mechanical properties of graphite are severely degraded by oxidation, the oxidation of graphite has been widely studied to analyze the safety of the reactors and assess the operational life of core structures [4-7].

Graphite, with its advantages of high thermal conductivity, low-thermal expansion coefficient, and low elasticity, has been widely used as a high-temperature structural material. On the other hand, graphite can easily react with oxygen even at temperatures as low as 400 °C, resulting in CO_2 formation. To apply graphite as a high-temperature structural material, therefore, it is necessary to improve its resistance to oxidation [8].

Conventional silicon carbide (SiC) has good high temperature strength and resistant to oxidation. Chemical vapor deposited (CVD) SiC has also been widely used as carbon coating material for protection oxidation due to properties such as high hardness, similar thermal expansion coefficient as graphite and good resistance to oxidation. Therefore, SiC has recently been considered a good candidate protective coating to operate in high-temperature, corrosive, and high-wear environments [8].

However, the most important problem is oxidation in crack of thermally shocked SiC. These cracks are pathways for oxygen to reach the graphite substrate [9]. Then oxygen attack the graphite so that crack healing is required to protect graphite. It is well known that SiC exhibits a very interesting crack healing ability. However, very few studies have been made on the crack healing behavior systematically, as a function of crack-healing temperature and time, crack healing environment and chemical composition of SiC [10]. SiC has been considered the best coating material owing to its desirable mechanical properties, a coefficient of thermal expansion close to that of carbon, and a high resistance to oxidation [11]. It is therefore necessary to develop oxidation protective CVD coating technology on graphite for VHTR core support structure.

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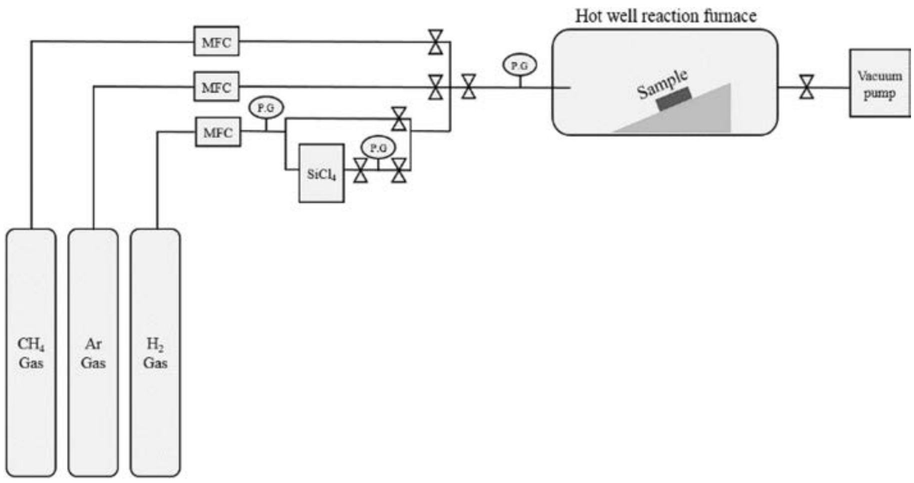

Fig. 1. Schematic of the CVD system used for crack healing.

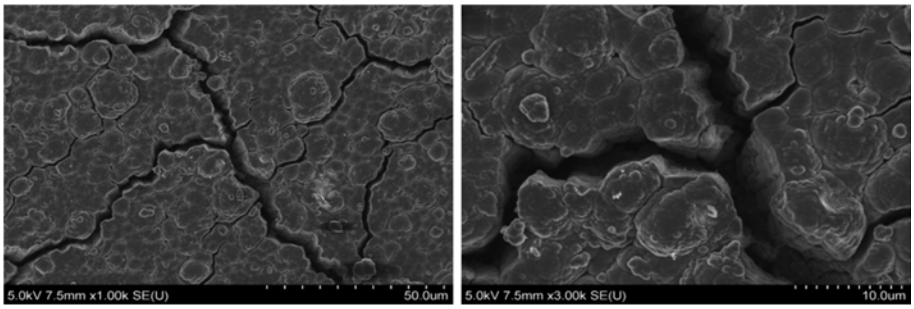

Fig. 2. Micrographs obtained at magnifications of (a) × 1000 and (b) × 3000 of the cracks formed during thermal cycling of the SiC coating layers.

In this study, the aim is crack healing by using CVD to prevent the oxidation from crack. Crack healing condition was considered in thermodynamically calculated methane ratio 0.35-0.55. Then, healed SiC by CVD at optimized healing condition was compared to that by CVR.

Experimental Procedures

The aim of this study is to heal cracks by using a SiC coating produced via CVD to prevent oxidation through cracks formed on the surface after thermal cycling tests.

CVD reactor

An alumina hot-wall-type tube reactor (Φ 70 × 1000 mm) was used for crack healing by the CVD. The source gas was supplied and controlled by a mass flow controller (MFC). In addition, H_2, Ar, CH_4, and liquid $SiCl_4$ were used as the ambient gas, purging gas, C source and the Si source, respectively. The flow mass of gaseous $SiCl_4$ (which was carried via bubbling by H_2 gas) was calculated from the flow rate of the carrier gas, vapor pressure of $SiCl_4$, and the bubbler temperature. In addition, the equilibrium gas composition was determined from equation (1) as follows [12]:

$$F_r = \frac{F_C P_r}{P_0 - P_r} \tag{1}$$

Where, P_0, F_r, F_c, and P_r are the respective output pressure, flow mass of the reactant, flow mass of the carrier, and vapor pressure of the reactant.

The deposition conditions have a significant effect on the surface structure and crystallinity of the SiC coating used for crack healing. As such, the crack healing behavior was systematically investigated as a function of the methane ratio (0.35-0.55), at a fixed temperature and pressure in the hot wall reactor of 1300 °C and 1 Torr, respectively; maximum healing was expected at this temperature [13]. Fig. 1 shows the CVD deposition system used for the healing.

Crack specimens

Layers of SiC were first coated onto cylindrical graphite via physical vapor deposition (PVD) using the e-beam evaporative coating method. Functionally gradient layers of SiC/C coating with compositions varying from SiC to graphite were formed through electron beam mixing. The specimens were then thermally cycled at temperatures of 500-1000 °C. Although the coated layers remained intact, i.e., delamination did not occur, cracks formed (Fig. 2) in the film after testing. These cracks are apparently the main oxidation path for graphite.

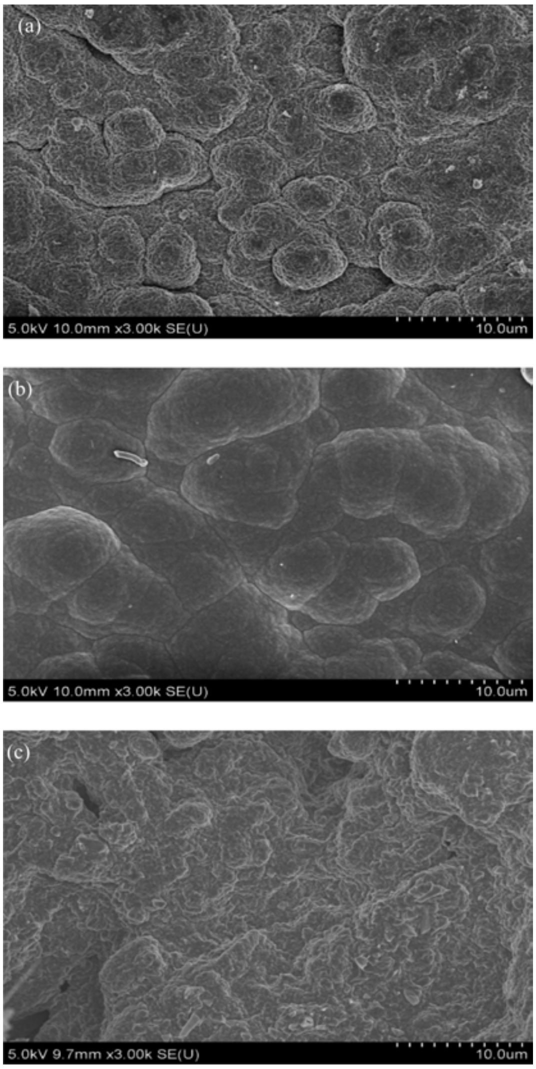

Fig. 3. SEM micrographs of SiC coatings deposited at methane ratios of (a) 0.35, (b) 0.45, and (c) 0.55.

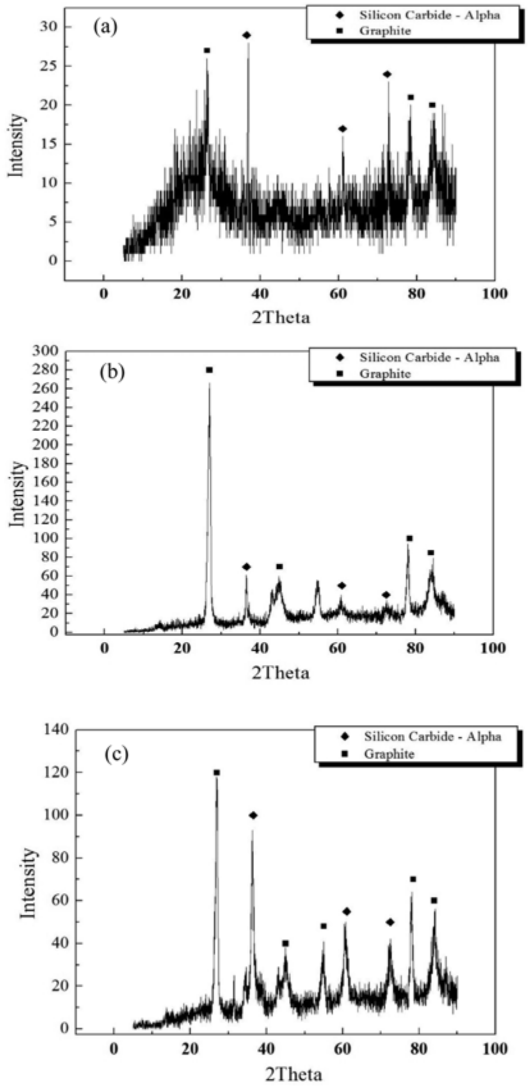

Fig. 4. XRD patterns of coatings deposited at methane ratios of (a) 0.35, (b) 0.45, and (c) 0.55.

Crack healing condition

Ar gas (50 sccm) was used to purge the remaining gas. Furthermore, when the temperature reached 1300 °C, H_2 gas was supplied for 10 min in order to remove hydrocarbon impurities. Reaction gases were then supplied to the reactor once the gas flow stabilized. The flow rate of the reaction gas was varied from 0.35-0.55 (i.e., ($CH_4/CH_4 + SiCl_4$)) and a H_2 ratio ($H_2/CH_4 + SiCl_4$ of 25 was used in order to obtain homogeneous crack-healing [13]; the flow rates of the reaction gas were determined from thermodynamic calculations. The CVD was performed for a total of 180 min. In addition, SiC coating via chemical vapor reaction (CVR) was performed for 160 min at a temperature and pressure of 1600 °C and 1.3 Pa, respectively, in a vacuum furnace. The crystalline state of the crack-healed specimens was determined from X-ray diffraction (XRD) measurements. Furthermore, the microstructure of the layers was examined and the corresponding thickness was determined by using a field emission scanning electron microscope (FE-SEM) [14].

Results and Discussions

Owing to its high hardness, strength, and resistance to oxidation, SiC is a promising candidate coating material for the heat exchangers used in the VHTR; SiC is a typical ceramic material with a wide range of uses. SiC crack healing via CVD coating is essential to preventing oxidation of the graphite. In this work, SiC crack healing was performed at thermodynamically calculated methane ratios ($CH_4/CH_4 + SiCl_4$) of 0.35-0.55 and a fixed hydrogen ratio in order to obtain homogenous coatings. A supply of CH_4 gas and liquid $SiCl_4$ were used as the C source and carried through H_2 gas (via bubbling) as a Si source, respectively.

Preliminary SiC coating on the graphite substrate

Fig. 3 shows micrographs of the SiC coatings deposited at various methane ratios on the graphite

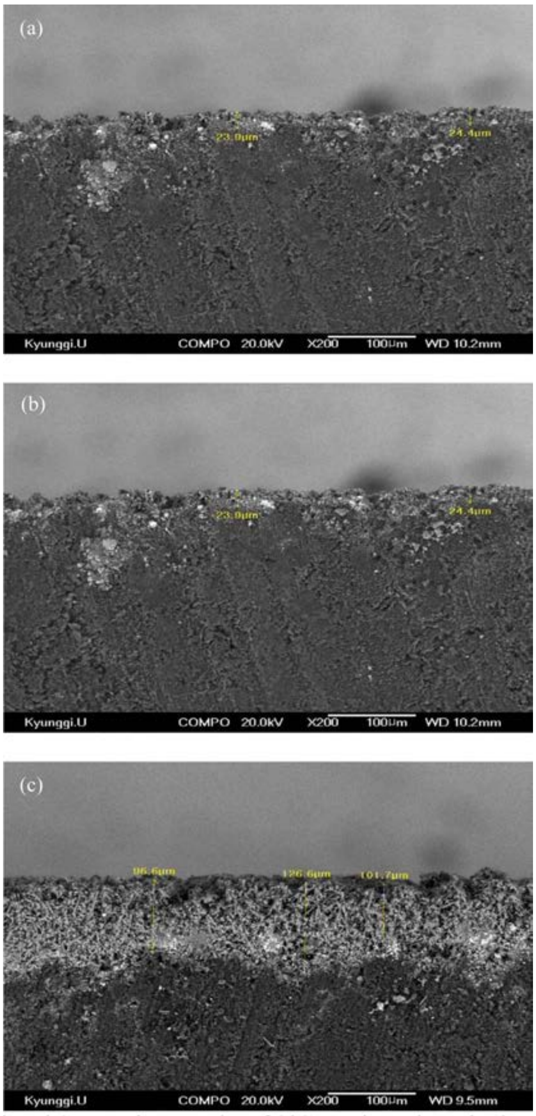

Fig. 5. Cross-sectional SEM micrographs of SiC coatings deposited at various specimen positions. (a) D1, (b) D2, and (c) D3.

substrate. These depositions were performed as trials before the actual deposition for crack healing by CVD was conducted. As the figure shows, the faceted surface features become rounded with increasing methane ratio. The morphology of the SiC deposited at a methane ratio of 0.35 (Fig. 3(a)) indicates that insufficient source gas was supplied for the formation of a dense SiC coating layer. However, homogeneous faceted layers (Fig. 3(c)), which are typical of chemical-vapor-deposited SiC coatings, were formed at a ratio of 0.55. Dense SiC coating layers are required to prevent oxidation through the cracks, and hence crack healing is performed at a methane ratio of 0.55.

Fig. 4 shows XRD patterns of the coatings deposited at various methane ratios. Peaks corresponding to SiC are observed in all cases but their relative intensities vary with the methane ratio. As the figure shows, the relative intensity of the SiC peak to that of graphite

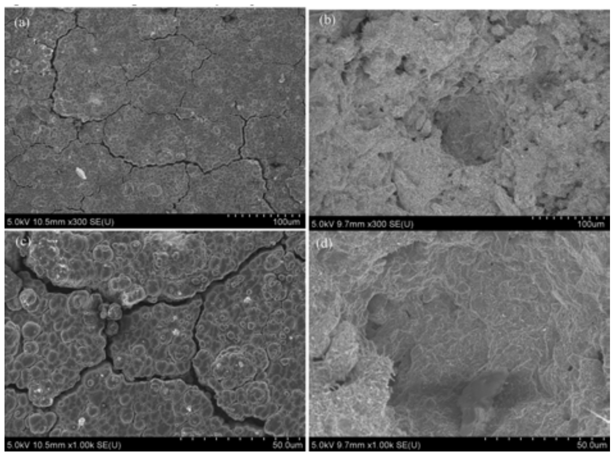

Fig. 6. SEM micrographs of the SiC surface; these micrographs were obtained at magnifications of (a)-(b) × 300 and (c)-(d) × 1000 before and after crack healing by CVD, respectively.

increases with increasing methane ratio. Moreover, the peaks corresponding to SiC constituted the main peaks (Fig. 4(a)) in the pattern, although SiC exhibited poor crystallinity, as indicated by the corresponding peak to background ratio. This indicates the low level of crystallinity of the coatings deposited on the surface of the graphite substrate. However, the relative intensity of these peaks was lower than those of their counterparts occurring at higher methane ratios. As Fig. 4(b) and 4(c) show, the {111} diffraction peak increased significantly owing to increased crystallinity, and hence denseness, of the SiC layers with increasing methane ratio.

Fig. 5 shows cross-sectional images of the SiC coatings deposited on specimens at various positions in the reactor. D1, D2, and D3 denote the 3-cm-spaced positions of specimens on a boat located at the center of the reactor. SiC layers in the D2 and D3 positions were thicker than those formed at D1 indicating that the thickness and structure of the coating can be controlled by varying the specimen position. As such, crack healing was performed at position D3 at which thick and dense coatings could be obtained.

Crack healing by CVD

Fig. 6 shows micrographs of the SiC surface after crack healing via CVD. Specimens were deposited for 180 min at 1300 °C and a methane ratio of 0.55. The cracks were completely healed, and hence absent from the surface, after the CVD. Furthermore, as predicted from Fig. 5, the coatings must be 0.1 mm thick in order for the cracks to be healed. The optimum and minimum thickness of the SiC coating required for crack healing has not been determined yet. However, the coatings produced in the current study are believed to be thicker than this optimum value. Moreover, the results indicated that cracks formed during the thermal cycling test were completely healed by the CVD; these

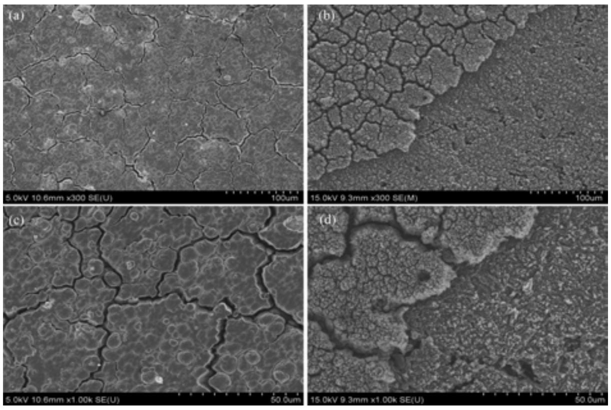

Fig. 7. SEM micrographs of SiC surface. These images were obtained at magnifications of (a)-(b) × 300 and (c)-(d) × 1000 before and after crack healing by the CVR, respectively.

healed cracks are expected to act as a protective layer against oxidation.

Comparison of CVR and CVD

Fig. 7 shows micrographs of the SiC surfaces after crack healing by the CVR. The micrographs reveal that cracks persist on the surfaces; i.e., the CVR method was ineffective in healing the cracks. This method may have led to the formation of Si seeds on the surface owing to C emanating only from the region between the cracks, which expose a C source. Therefore, the CVR method results in incomplete crack healing owing to the reaction, between Si gas and the C source, which gives rise to SiC. In other words, the CVR has negligible effect on crack healing.

Conclusions

The XRD and SEM results indicated that the rounded structure obtained at a methane ratio of 0.55 gave rise to the optimum surface morphology of the SiC coating for crack healing. The relative intensity of the peaks corresponding to SiC increased with increasing methane ratio. Furthermore, the thickness and quality of the coating varied with the position of the specimen; position D3 was determined to be the optimum position for crack healing. Therefore, SiC crack healing for resistance against oxidation was achieved after thermal cycling by performing CVD at position D3 and at a methane ratio of 0.55.

Cracks were completely healed (Fig. 6) and a non-optimum thickness of 0.1 mm of the crack healing layers was predicted. In addition, SEM observations and the results of XRD analysis indicated that the chemical-vapor-deposited crack-healed surfaces might act as a protective layer that provide increased resistance against oxidation; the oxidation resistance will be investigated in detail in the near future. In contrast, the CVR had negligible effect on crack healing owing to insufficient C emanating from the cracks.

In conclusion, cracks in the SiC surface were successfully healed via CVD of thermally cycled surfaces; however, CVR had negligible effect on crack healing. Therefore, CVD constitutes a promising method for healing cracks created by thermal shock and protecting the surface against C oxidation in the VHTR.

Acknowledgments

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