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The conversion mechanism of SiC conversion layers on graphite substrates by CVR (Chemical Vapor Reaction)

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The effects of graphite substrate properties such as the density and the pore size distribution on the conversion behavior of graphite surface were investigated. Graphite substrates and silica powder in graphite crucible were treated by a chemical vapor reaction method. In this process, SiO vapor was created, infiltrated into the graphite substrate, and the β -SiC conversion layer was formed. The XRD patterns of conversion layers produced from vapor-solid (SiO-C) reaction were identified as β -SiC (3C type, zinc blende structure). In the cross-sectional microstructure, the B specimen showed simply an interface, whereas the A specimen showed an interlayer with an average SiC : C ratio of 1 : 3 in chemical composition. It seemed that the formation of the interlayer in the A specimen was caused by a high nucleation rate due to the low density or the pore size distribution during the CVR process. Ultimately, the microstructural features of conversion layers reveal that the pore size distribution and the density of substrates were important factors in the formation of conversion layer.

Key words : SiC conversion layer, Graphite substrate, Chemical conversion.

Introduction

Generally, Chemical Vapor Deposition (CVD) method has been used for the fabrication of SiC coatings and SiC layers for complex and large scale components can be easily formed by a CVR method in comparison with a CVD method. Also, the SiC conversion layer formed by the CVR method has good adherence with the graphite matrix. The CVR method [1] is based on the carbothermal reduction process [2-5] in which a SiC intermediate phase is formed during the reduction process of silica and carbon. The chemical reaction between the silica and carbon has been applied to the formation of a SiC conversion layer on carbon material [6], and the synthesis of SiC powder and silicon [7]. Of particular importance to the steel and the ceramic industries is the generation of silicon monoxide gas (SiO) via the interaction between silica and carbon, and the SiO/CO ratio of reaction conditions has been considered for a long time [8].

The carbothermal reduction process can be classified into two steps as follows. The first step is the reduction of silica by carbon, this step is composed of the formation of SiO, CO, and the formation of SiC (intermediate phase) between SiO and carbon [3, 9-10]. The second step is the reduction of silica by SiC, this step is composed of the formation of SiO and CO from SiC and silica, and the formation of SiC from SiO and CO. First step

$SiO_2(s) + C(s) \rightarrow SiO(v) + CO(v)$	(1)
CO(1) + OO(1) + OO(1)	$\langle \mathbf{O} \rangle$

$SiO(v) + 2C(s) \rightarrow SiC(s) + CO(v)$ (2))
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$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(v)$	(3)
Second step	

$$2\operatorname{SiO}_2(s) + \operatorname{SiC}(s) \to 3\operatorname{SiO}(v) + \operatorname{CO}(v) \qquad (4)$$

$$SiO(v) + 3CO(v) \rightarrow SiC(s) + 2CO_2(v)$$
 (5)

 $SiO_2(s) + CO(v) \rightarrow SiO(v) + CO_2(v)$ (6)

In this study, the SiC conversion layer was produced *via* a CVR method, which is based on the carbothermal reduction process. Also, the conversion mechanism of SiC conversion layers was investigated, the observation of cross-sectional morphology and the phase analysis were carried out by scanning electron microscopy (SEM), X-ray diffraction (XRD) and wave dispersive spectroscopy (WDS).

Experimental

In this study, silica powder (average particle size: 17 μ m, Junsei, Chemical Co. Japan) and A (density: 1.66 gcm⁻³, UCAR Co.), B (density: 1.85 gcm⁻³, Seung-lim Carbon, Co.) graphite substrates were used for the formation of SiC conversion layers. The particle size distribution of silica powder was measured (Stocks' law, MICRO-MERITICS INSTRUMENT Co.). The specific surface area of graphite substrates measured by N₂ BET method (QUANTACHROME Co.) was A: 9.132 m²g⁻¹, B: 8.427 m²g⁻¹.

Figure 1 shows the surface morphology of A and B

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Fig. 1. Surface morphology of A and B graphite substrate.

graphite substrate. Figure 2 shows the pore size distribution of A and B graphites, which were examined by a mercury porosimeter. The A graphite shows rather a continuous distribution pattern in the range of 0.001 μ m to 10.0 μ m, but the B graphite shows a relatively discontinuous pattern in the range from 0.001 μ m to 1.0 μ m.

For the CVR process, the surface of graphite substrates in the pellet form of 3 mm \times 5 mm \times 7 mm was ground by SiC abrasive paper # 800, 1000, 1500, 2000, then, the bare graphite specimens were inserted into the graphite crucible which was filled with SiO₂ powder. To control the discharging behavior of SiO and CO gas, the same amount of silica powder was loaded into a graphite crucible. Figure 3 represents the schematic diagram for the CVR process. The inner wall of the graphite crucible was coated with BN-spray (Advanced Ceramics co.) and covered with graphite foil to prevent the reaction of the silica melt during the process. The chemical conversion process of graphite was performed at 1750°C and 1850°C, in nitrogen gas.

The SiC conversion layer was analyzed using an Xray diffractometer (Ni-filter, CuK α -radiation). The specimens were sliced with a diamond saw and polished, and then, the back-scattered image of cross-sections was observed by SEM without a conductive coating.



Fig. 2. Pore size distribution of A and B graphite substrate.



Fig. 3. Schematic diagram for the preparation of SiC conversion layer.

The chemical composition of the interface and boundary were analyzed by WDS.

The amount of vapor and solid phases created from the Si-O-C-N₂ system at the reaction temperature and equilibrium state was investigated with the SOLGASMIX program. Input values for the calculation were based on the stoichiometric composition of silica and graphite with a total pressure of 1.01×10^5 Pa. Thermodynamic data of the JANAF Table was used. From these results, the main vapor species and partial vapor pressure were determined.

Result and Discussion

Figure 4 shows the XRD patterns of the conversion



Fig. 4. XRD patterns of the surface of SiC coating layer produced on A and B substrate at 1750°C for 2 hrs and 1850°C for 2 hrs.

layers. The protective layers on graphite substrates showed the beta-SiC structure of the cubic zinc blende type. The XRD patterns of the converted A-graphites at 1750°C and 1850°C showed SiC peak alone and the patterns of converted B graphites exhibited both SiC and graphite peak. Therefore, it was suggested that the density and the particle size of the graphite substrate had a substantial effect upon the diffusion of gaseous silicon monoxide into the substrate and the conversion. Consequently, these results indicate that the SiO diffusion and the conversion for A-graphite as compared to B substrate proceeded more easily. In the conversion process, the CO gas exhaustion in the surface region of the B specimen is sluggish, thus, the conversion temperature will be increased rapidly with this increment of CO gas pressure, after all, the residual carbon remains in the conversion layer of the B sample.

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The transformation of graphite materials into β -SiC (zinc blende structure) might be thought of as following. At elevated temperature, the graphite materials show an appreciable C-axis expansion behavior so that the prismatic planes have a large reactivity. Therefore, it was thought that the conversion of the graphite substrate was achieved by the interaction of SiO gas and carbon crystalline planes (or atomic sites) which have larger reactivity than others. Probably, such a process will include the decomposition of SiO molecules and the insertion of Si into the layer structure. As a result, the crystalline units of graphite are converted into the tetrahedral units as shown in Fig. 5 and such units in lattice constitute the zinc blende structure.

Figure 6 shows the cross-sectional micrographs of conversion layers fabricated at 1850°C, 2 hrs. Figure 6(a) and (b) show the SiC conversion layer and the boundary between the outer conversion layer and the substrate. While the A-specimen of Fig. 6(a) represented the interlayer below the SiC conversion layer, the B specimen of Fig. 6(b) showed a definite boundary. The formation of an interlayer in the A specimen seemed to be due to a rapid nucleation rate in a boundary area during CVR process. Finally, the boundary area in the A specimen will have a mixed composition of SiC and carbon. Also, this suggestion was verified by mapping the cross section of specimen using WDS, the average ratio of SiC:C for the interlayer was 1:3. SiC conversion layers in Fig. 6(c), (d) represent the morphology of connected and grown grains. As shown in Fig. 6(c), (d), the conversion layer of the B specimen reveals rather coarse SiC grains in comparison to the A-specimen. It was thought that the



Fig. 5. Schematic illustration on transformation of graphite into β -SiC.



Fig. 6. Back scattered images of cross-sectional SiC conversion layers prepared on A and B substrate.

high infiltration and high conversion rate of the A graphite were due to the continuous pore distribution in the range of $0.01 \sim 10.0 \ \mu m$.

The cross-sectional morphologies of converted A and B specimen indicate that the B graphite compared to the A graphite is composed of small graphite grains and has a relatively dense microstructure as shown in the surface morphology of Fig. 1. Therefore, the slow infiltration of SiO gas into the B graphite would have caused a heterogeneity in connection and growth behavior. Also, the conversion layers are composed of small and large grains, which will be due to the specific microstructure of graphites fabricated from petroleum coke grains (filler) and pitch coke grains (binder).

The results of Fig. 4 and Fig. 5 could be supposed from the density of graphite substrates. Also, it was presumed that the different tendency of XRD patterns and back scattered images of SiC conversion layers were mainly due to the penetration amount of SiO vapor rahter than the difference of reaction rate between SiO vapor and graphite grains. Also the thickness of the SiC conversion layer was markedly dependent on the densities and pore size distribution of graphites. Besides, the conversion layer of the A graphite substrate which has lowest density showed the only SiC peaks without the graphite peak in the XRD patterns. Thus it was confirmed that the pore size distribution, the density of graphite as well as the appropriate



Fig. 7. Free energy variation of reduction process with temperature.

temperature were important factors in determining the conversion extent into the SiC layer.

In the thermodynamic relations of silica and carbon, the formation energy of SiC from the reaction of SiO gas and carbon shows negative values below 1500°C. But the formation energy of SiO gas is converted into a negative value about 1750°C, as shown in Fig. 7. Thus, it may be presumed that the formation of SiO gas is the rate-controlling step during the CVR process.

In the upper part of the SiC conversion layer, some SiC whiskers were observed. It could be thought that the formation of the SiC layer induces a decrease of the SiC/CO ratio during the conversion process. Although, most of the surface region of the graphite substrate is put into a stable state with SiC particles, and local regions of the graphite surface can be put into a stable state by the formation of SiC whiskers. Also it can be suggested that the two following reactions occurred competitively in the conversion process. The noticeable difference of the two reactions is the type of reactant phase, that is to say, [I] is the vapor-vapor reaction in contrast to the vapor-solid reaction of [II]. Generally, it is well known that the reactants, SiO and CO must be supplied for the production of SiC whiskers, thus, the formation of SiC whiskers could be expected.

 $SiO + 3CO \rightarrow SiC + 2CO$ [I] Formation of whiskers $SiO + 2C \rightarrow SiC + CO$ [II] Formation of polycrystals

The phase estimation with the SOLGASMIX-program indicated that the dominant vapor species of the SiO₂-C-N₂ system at the conversion temperature were SiO(v) and CO(v). The condition of the 1:3 ratio (stoichiometric ratio) included the SiC phase as a solid product, the 1:1 ratio (nonstoichiometric, carbon deficient ratio) did not show any solid phase. In these studies, the reaction conditions of the CVR process were controlled with the stoichiometric situation. The reduction with SiC requires a higher temperature than the CVR process temperature as well as the chemical reaction between SiO₂ and SiC.

Conclusions

The SiO gas created from the reaction of silica and graphite had reacted with the coke grains of the substrate, then, SiC conversion layer was produced on the graphite substrate. The conversion layer could be easily formed at 1850°C. Unlike the conversion layers of the B specimen, the conversion layers of the A specimen showed the β -SiC peaks without graphite

peaks in XRD patterns. From these XRD patterns, it seemed that the SiO diffusion into the graphite substrate and the conversion behavior were dependent on the density and pore size distribution of graphite. The cross-section of converted graphites showed a difference in that the A specimen had an interlayer between the outer SiC conversion layer and the unconverted graphite. On the other hand, the conversion layer of the B specimen in comparison with that of A specimen exhibited coarse grains and a heterogeneity in grain size. It seems that these results are based on the infiltration rate of SiO gas and the conversion behavior.

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