Formation Mechanism of SiC Gradient in Carbon Materials

Osamu Yamamoto*, Yasutoshi Dote*, Tadashi Sasamoto* and Michio Inagaki**

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High-density isotropic graphite substrates with and without a notch produced at the surface were contacted with metallic silicon and heated at 1350 and 1450°C. The contribution of open pores in the substrates for the formation of SiC-gradient was discussed. At 1350°C, no SiC-gradient was observed at the surface of the substrate without the notch, but the gradient in the substrate was formed at 1450°C. On the substrates with notch, fibers were formed on the notch wall of the substrate heated at 1350°C. By heating at 1450°C, however, SiC was detected at the portion beyond the nose of notch. In present study, it was expected that small amount of O2 are enclosed in the open pores and in the notch. Based on the expected reactions among silicon, carbon and oxygen, the formation of SiC-gradient in the substrate at 1450°C was found to be possibly formed due to the reaction between carbon on the wall of pores and SiO gas through the open pores from the surface of the substrate.

KEYWORDS : SiC, Gradient material, Reaction, Carbon, Silicon

1. Introduction

Carbon materials are attractive materials for many applications, because of their light weight and excellent high strength at high temperatures exceeding 2000°C. In order to use them as high temperature structural materials, however, their uses have to be restricted in an inert atmosphere. Therefore, the improvement of the oxidation resistance of carbon materials is one of the important problems to be solved and many researches have been reported.

We proposed to make a couple of SiC-gradient in the carbon material and oxide thin film coating on it, in order to improve the oxidation resistance of carbon materials and got successful results. The carbon materials with this couple were found to have a marked oxidation resistance and an effective thermal-shock resistance at the temperatures ranging from liquid nitrogen to 1400°C. The carbon materials with SiC concentration gradient from their surface were prepared by a simple procedure; original carbon materials were embedded in a powder of metallic silicon and heated up to 1450°C in Ar atmosphere. However, it was not clarified how SiC concentration gradient in carbon materials was formed by the reaction between molten silicon and solid carbon materials. In order to understand the formation of SiC-gradient, the vapor of metallic silicon itself is difficult to be considered because the vapor pressure of silicon at 1033 K is as low as 3.0 x 10^5 Pa. And also no possibility of SiC evaporation because the vapor pressure is much lower than that of silicon

In the present work, high-density isotropic graphite blocks with and without a notch produced at their surface were used as samples and reacted with pressed metallic silicon. The importance of pores in carbon substrate for the formation of SiC-gradient was demonstrated by studying the wall of the notch, which was regarded as simulated pores and the mechanism for the formation of SiC-gradient was discussed.

2. Experimental

Fig.1 (a) shows the size and shape of the carbon materials used in this study. The carbon substrates used were the blocks of isotropic graphite with the size of 10 mm x 15 mm, of which the bulk density was 1.77 g/cm^3 (Toyo Tanso Co., Ltd, IG11). The surface of the substrates was polished with 3.0 μm diamond powder and then washed in acetone with supersonic agitation for 5 min to remove the impurities from their surface. The notch with the maximum width of 30 μm and the depth of 400 μm was produced on the surface of graphite block by using a diamond cutter.

Silicon powder with an average particle size of 3.0 μm was pressed with 1.0 GPa pressure and the disk of 10 mm x 2 mm size was prepared. A set of graphite substrate and pressed silicon powder was placed in a graphite crucible, as illustrated in Fig.1 (b). An Al2O3 block of 200 g was put on the substrate in order to obtain a good contact between carbon and silicon. The crucible containing this set was heated at 1350 and 1450°C for 3 h in high purity Ar gas.

In order to know the concentration gradient of SiC along the thickness of the substrates, the surface of samples after heating was polished by a diamond paste and X-ray diffraction (XRD) pattern on the surface was measured. An energy-dispersive X-ray analysis (EDX) was carried out to examine the concentration of silicon at the notch portion. And also, the surface of samples after heating was observed by scanning electron microscope (SEM).
3. Results

Fig. 2 (a) and (b) show the changes of XRD patterns along the thickness of the substrates without notch heated at 1350 and 1450°C, respectively. No adhesion between graphite substrate and metallic silicon was observed. The surface of the sample heated at 1350°C gave a weak 102 diffraction peak of α-SiC, in addition to 002 diffraction peak of graphite (see Fig. 2 (a)). However, no SiC was observed even at the depth of 0.05mm. After heated at 1450°C, on the other hand, the surface of the substrate gave only the peak of α-SiC, no graphite. With several repetitions of polishing along the thickness, the intensity of the peak of α-SiC decreased, accompanying the increase of the intensity of 002 line of graphite (see Fig. 2 (b)). From these results, the sample heated at 1450°C was found that SiC was formed gradually along the depth from the surface of carbon substrate. At 1350°C, it seems that no concentration gradient of SiC was obtained.

The substrates with notch were reacted with silicon for 3h in Ar gas at 1350 and 1450°C. No adhesion of metallic silicon
Fig. 3 Line analysis for Si of the notch portion in carbon substrates heated for 3h in Ar gas at 1350 and 1450°C.

Fig. 4 SEM-micrographs of the notch portion in carbon substrates heated for 3h in Ar gas at (a) 1350 and (b) 1450°C.

Fig. 5 XRD patterns of notch portion in carbon substrates heated for 3h in Ar gas at (a) 1350 and (b) 1450°C.

was observed even at the portion of notch. At the part apart from the notch, the changes in XRD pattern along the depth of substrate were exactly the same as shown in Fig. 2, no SiC gradient at 1350°C and a marked gradient at 1450°C. However, certain amount of silicon was detected at inside wall of the notch by EDX line analysis for SiKα, as shown in Fig. 3. At 1350°C, silicon is observed up to the nose point of the notch, of which concentration shows some scattering, supposedly due to the presence of large carbon grains and pores. By heating at 1450°C, however, silicon is detected at the portion beyond the nose of notch.

Fig. 4 shows SEM-micrographs on the same notch walls. At 1350°C, many fibrous materials were observed (see Fig. 4 (a)), whereas at 1450°C no fibers but the particles with about 10 μm size were found (see Fig. 4 (b)). From XRD on the same notch wall heated at 1350°C, only graphite is found, but, no silicon compounds are detected, neither α-SiC, α-SiO2 nor metallic silicon, as shown in Fig. 5 (a). On the notch wall heated at 1450°C, SiC is clearly observed (Fig. 5 (b)).

From these results of EDX and XRD measurements and SEM observation described above, the particles observed at 1450°C seems to be SiC and fibers detected at 1350°C were supposed to be amorphous SiO2.

4. Discussion

By heating the high-density graphite substrate at 1450°C, the surface contacted with silicon gave only SiC, no graphite, and
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A concentration gradient of SiC in the substrate was observed in our previous work\(^1\) and also in the present work on the substrate without notch. In the case of glassy carbon without open pores, however, only a small amount of SiC was observed at the surface but no graphite in its inside even at 1450°C\(^7\). On carbon materials with high porosity, such as C/C composites, a concentration gradient of SiC was easily obtained by reacting with silicon at 1450°C\(^11\), \(^7\). These results suggest that it is highly possible for the open pores on the surface of carbon substrates to participate in the formation of SiC-gradient. Ikeda et. al carried out the preparation of SiC within the pores in carbon materials and reported that SiC was formed to be reacted with SiO gas generated by the reduction of SiO\(_2\) within pores\(^18\).

Many open pores existed on the surface of carbon substrates used in this study and a small amount of O\(_2\) was enclosed in the open pores and in the notch. In these pores including notch, the following reactions among silicon, carbon and oxygen were reasonably expected\(^19\), \(^20\):

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 \quad \text{(1)} \\
C + O_2 & \rightarrow 2CO \quad \text{(2)} \\
SiO_2 + CO & \rightarrow SiO + CO_2 \quad \text{(3)} \\
2C + SiO & \rightarrow SiC + CO \quad \text{(4)}
\end{align*}
\]

Based on these reactions, the following mechanism for the formation of SiC-gradient in carbon substrate, that is, the formation of SiC far from the surface contacted with metallic silicon, can be assumed; CO and SiO gas is initially generated by the oxidation of silicon and carbon. And SiO gas thus generated is diffused into the carbon substrate through open pores. At 1450°C, the SiO gas reacts with carbon on the wall of pores and resulted in SiC on the surface of pores. Temperature of 1350°C is not enough to promote the reaction between carbon and SiO gas \(\text{Eq. (4)}\) and result in the formation of fibrous SiO\(_2\) during cooling of the sample.

In conclusion, SiC-gradient in carbon substrate was possibly formed due to the diffusion of SiO gas through the open pores from the surface of the substrate and it resulted in a concentration gradient of SiC.

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References