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Preparation of Carbon Material with SiC-Concentration Gradient by Silicon Impregnation and its Oxidation Behaviour

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Abstract

A carbon material with a SiC-concentration gradient was prepared by a silicon impregnation process. In order to prepare the carbon material with a SiC-concentration gradient without any adhesion of metallic silicon, the weight of silicon powder per physical surface area of the carbon substrate was in the range of $3{\cdot}9$–$4{\cdot}1\ \mathrm{g\,cm^{-2}}$ *and then heating the carbon substrate in silicon powder at 1450°C for 3 h, but the amount of silicon powder beyond this range resulted in the adhesion of metallic silicon. The concentration of SiC along the thickness in the sample obtained decreased rapidly up to 0·5 mm and gradually in a range of 0·5–1·0 mm. A remarkable improvement in the oxidation resistance was observed on the sample with a SiC-concentration gradient at 1400°C, which was due to the formation of a protective film of* SiO_2 *glass on the surface. In the results of the thermal shock test in the sample, no destructions and no cracking of the samples were observed.*

Ein kohlenstoffhaltiges Material mit einem SiC-Konzentrationsgradienten wurde mittels Siliziumimprägnierung hergestellt. Um das kohlenstoffhaltige Material mit einem SiC-Konzentrationsgradienten ohne Adhäsion von metallischem Silizium herzustellen, wurde eine Siliziumpulverbelegung der Substratoberfläche von $3{\cdot}9$–$4{\cdot}1\ \mathrm{g\,cm^{-2}}$ *gewählt, und das Kohlenstoffsubstrat in Siliziumpulver bei 1450°C für 3 h wärmebehandelt. Eine Siliziumpulverbelegung unterhalb dieser Werte resultierte in Adhäsion von metallischem Silizium. Die SiC-Konzentration, gemessen von der Oberfläche aus ins Innere der Probe, nahm bis zu einer Tiefe von 0·5 mm stark ab, während sie sich zwischen 0·5–1·0 mm nur allmählich verringerte. Proben mit einem SiC Konzentrationsgradienten zeigten bei 1400°C eine bemerkenswerte Verbesserung der Oxidationbeständigkeit. Der Grund hierfür liegt in der Bildung eines* SiO_2*-Glasfilms auf der Oberfläche. Thermoschocktests ergaben keine Schädigung der Proben und keine Rißbildung.*

Du carbone avec un gradient de concentration en SiC a été préparé par imprégnation avec du silicium. Pour éviter qu'il y ait adhésion de silicium métallique sur ce carbone avec gradient de concentration en SiC, on a utilisé un poids de poudre de silicium par surface de substrat carbone de l'ordre de $3{\cdot}9$–$4{\cdot}1\ \mathrm{g\,cm^{-2}}$ *et le substrat de silicium pendant 3 h; l'emploi d'une plus grande quantité de poudre de silicium a provoqué l'adhésion de silicium métallique. La concentration de SiC dans le profil de l'échantillon obtenu diminue rapidement jusqu'à 0·5 mm de la surface, puis progressivement entre 0·5–1·0 mm. On a observé une amélioration notable de la résistance à l'oxydation de l'échantillon avec gradient de concentration en SiC à 1400°C, en raison de la formation d'un film protecteur de verre* SiO_2 *à la surface. Aucun endommagement ou fissuration des échantillons n'a été observé lors des essais de résistance au chocs thermiques.*

1 Introduction

Carbon materials are important for high-temperature applications because of their high strength, high modulus, excellent thermal shock resistance and light weight.[1] Therefore, they have been widely used as engineering materials, such as electrical contacts, high-temperature heat exchangers, rocket nozzles, rocket noses and leading edges of aircraft wings, etc.[2] However, their uses have been greatly restricted due to poor oxidation resistance at high temperatures in an oxidizing atmosphere. To have a good oxidation resistance is one of the most important properties for the carbon materials. In order to solve this problem, the carbon–ceramic composites of C–SiC and the coating of SiC thin films were studied by different authors.[1–11] In these composite and carbide coating, the improvement of oxidation resistance is supposed to be caused by the formation of SiO_2 protective film above 1000°C, in some cases B_2O_3 being contained. The following disadvantages, however, were pointed out: the carbon–ceramic composites at high temperatures suffer the excellent mechanical properties of carbon materials and the SiC coating causes some cracks because of a large difference in thermal expansion coefficient between carbon substrate and SiC thin film.

In the present work, the carbon material with a SiC-concentration gradient at its surface was prepared by a silicon impregnation process. The dependence of SiC gradient on impregnation conditions and the oxidation resistance of the resultant material were studied.

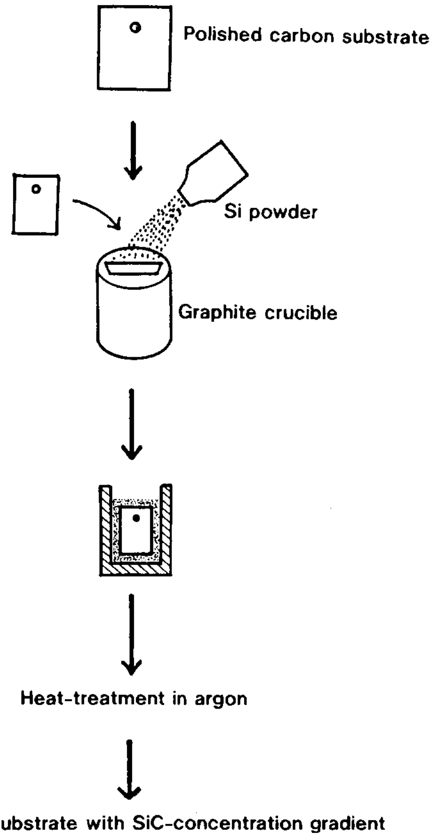


Fig. 1. Preparation procedure of the carbon substrate with a SiC-concentration gradient by silicon impregnation process.

2 Experimental Procedure

The preparation procedure of a carbon material with a SiC-concentration gradient is shown in Fig. 1. The carbon substrates used were an isotropic high-density graphite with the size of 20 × 20 × 5 mm and a glassy carbon with 20 × 10 × 2 mm size, of which the bulk densities were 1·77 and 1·50 g cm^{-3}, respectively. The surface of the substrates were polished with 3·0 μm diamond powder, and then washed in acetone to remove the impurities from their surfaces. These substrates were inserted into a silicon powder in 10 μm size in a graphite crucible, all of their surfaces being covered by silicon powder, and then heated up to a temperature between 1200 and 1450°C under an argon flow with a rate of 100 cm^3 min^{-1}.

In order to know the concentration gradient of SiC along the thickness of the substrates, the surface of the sample was polished by a diamond paste and X-ray diffraction (XRD) pattern on the surface was measured. By several repetitions of polishing and subsequent XRD measurement, the following intensity ratio, I_{SiC}, was plotted against the polished thickness:

$$I_{SiC} = \frac{(102 \text{ peak area of SiC})}{(102 \text{ peak area of SiC}) + (002 \text{ peak area of graphite})}$$

The intensity ratio, I_{SiC}, is only a measure of SiC content averaged over a volume, which is defined by the irradiated area and the transmitted depth of X-ray, the latter depending on the content of silicon. However, we preferred to obtain the information on the gradient of SiC along the depth of the substrate averaged over a certain area, rather than to measure the distribution of silicon by using a cross-section of the substrate and scanning the probe in an electron probe X-ray microanalyser.

The oxidation-resistance tests were carried out by an electric thermobalance at 600, 1000 and 1400°C under the air flow with a rate of 50 cm^3 min^{-1}. The weight change per unit physical surface area of the substrate was determined from the weights before and after oxidation. The surface and the cross-section of the oxidized samples were also observed by scanning electron microscope (SEM).

3 Results and Discussion

3.1 Gradient of SiC in carbon substrates

The carbon substrates with a SiC-concentration gradient were obtained at 1450°C without any adhesion of metallic silicon, only when the weight of silicon powder per physical surface area of the substrate was in a range from 3·9 to 4·1 g cm^{-2}. If the

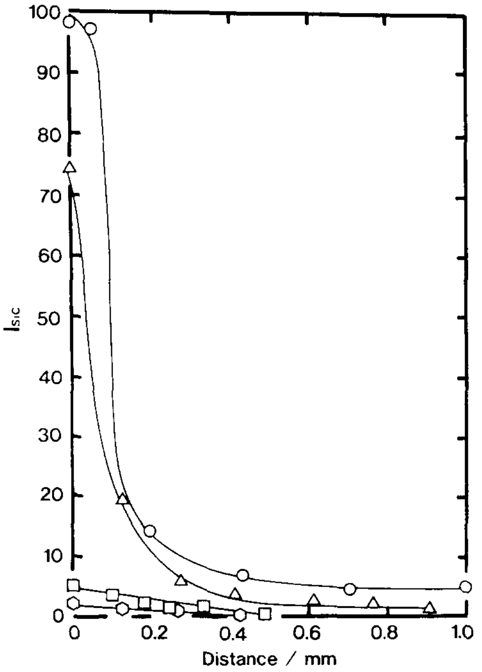
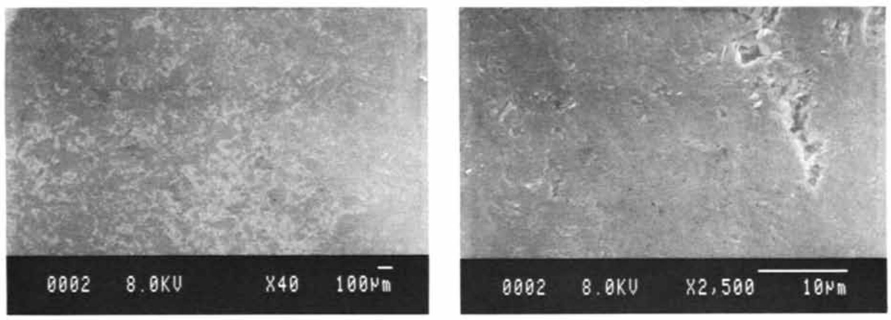


Fig. 2. Gradient of SiC-concentration along the thickness of the isotropic graphite substrates after heating at ○, 1200°C; □, 1300°C; △, 1400°C; and ○, 1450°C for 3 h.

amount of silicon powder was beyond this range, the metallic silicon always adhered on the surface of the substrate. Also, the heat treatment above 1500°C resulted in the adhesion of metallic silicon. From the XRD measurements, the crystal structure of SiC formed on the surface was confirmed to be of a hexagonal type.

Figure 2 shows the concentration gradient of SiC along the thickness of the isotropic graphite substrate obtained by heating at various temperatures for 3 h. Below 1300°C, only a small amount of SiC was formed and no SiC was detected after polishing to 0·5 mm thick. At 1450°C, however, the as-prepared surface only gave the diffraction peaks of SiC, no graphite, and a concentration gradient of SiC in the substrate was observed; the concentration of SiC along the thickness decreased rapidly up to 0·5 mm and then gradually in a range 0·5–1·0 mm. Although a concentration gradient of SiC was formed by heating at 1400°C, a certain amount of graphite was still detected in the as-prepared surface by the powder pattern. These results suggested that it is essential to heat the isotropic graphite substrate in silicon powder above the melting point of silicon (1410°C), in order to form SiC at the surface and a concentration gradient of SiC in the graphite substrate.

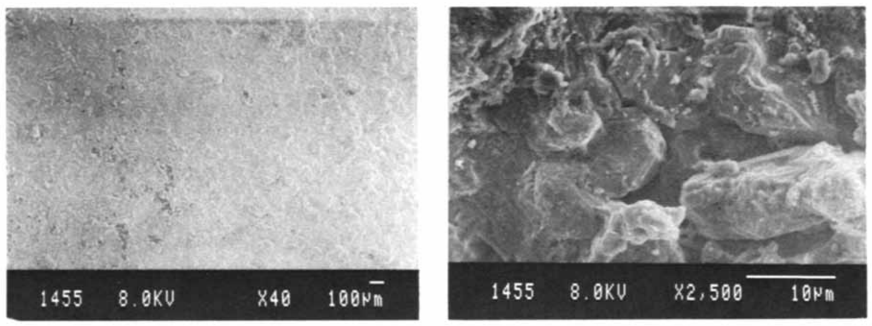
On the other hand, no SiC was formed on the surface of the glassy carbon substrates by heating below 1400°C. By heating at 1450°C, the SiC gradient was observed in a shallow range of depth up to 0·4 mm, but SiC coexisted with carbon at the surface. The reason for this large difference between



(a) (b)

Isotropic high-density graphite

(A)



(a) (b)

Carbon material with SiC-concentration gradient

(B)

Fig. 3. SEM micrographs of (A) the surface of the isotropic graphite substrate polished, and of (B) the surface of the carbon substrate with a SiC-concentration gradient obtained: (a) low magnification, (b) high magnification.

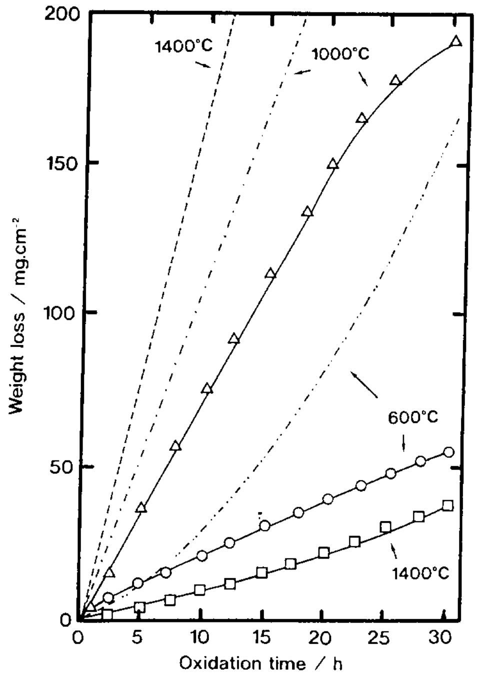


Fig. 4. Changes of weight loss with oxidation time on the sample with a SiC-concentration gradient at ○, 600°C; △, 1000°C; and □, 1400°C; and on the isotropic graphite substrate at —··—, 600°C; —·—, 1000°C; and —— 1400°C.

the formation of SiC in the isotropic graphite and that in the glassy carbon substrates seems to be due to the existence of open pores at the surface of isotropic graphite, but not at glassy carbon.

In Fig. 3, the surface appearance of the sample obtained from the isotropic graphite substrate at 1450°C was compared with the original surface. From this observation, it was found that the SiC layer formed on the surface consists of the particles with average diameter of 10 μm and also contains many pores of about 12 μm diameter.

3.2 Oxidation resistance

In Fig. 4, the weight loss per unit physical surface area by oxidation at different temperatures is plotted as a function of oxidation time on the sample with a SiC-concentration gradient prepared from the isotropic graphite at 1450°C. In the same figure, the oxidation loss for the original isotropic graphite is shown for the comparison. A remarkable improvement in oxidation resistance is observed on the sample with SiC-concentration gradient at a temperature of 1400°C, the rate of oxidation loss being about one-eleventh of the original. At 600°C, the weight loss by oxidation is also improved slightly giving a SiC-concentration gradient to the graphite. At 1000°C, however, no effect of SiC formation on oxidation resistance of graphite is observed.

Figure 5 shows the surfaces of the sample with a SiC-concentration gradient prepared from the isotropic graphite and oxidized for 30 h at each temperature. The surfaces of the samples oxidized at 600 and 1000°C were rough, as those of the sample before oxidation (see Fig. 3). However, the surface oxidized at 1400°C looks smooth, which is reasonably supposed to be due to the formation of a glass on the surface.

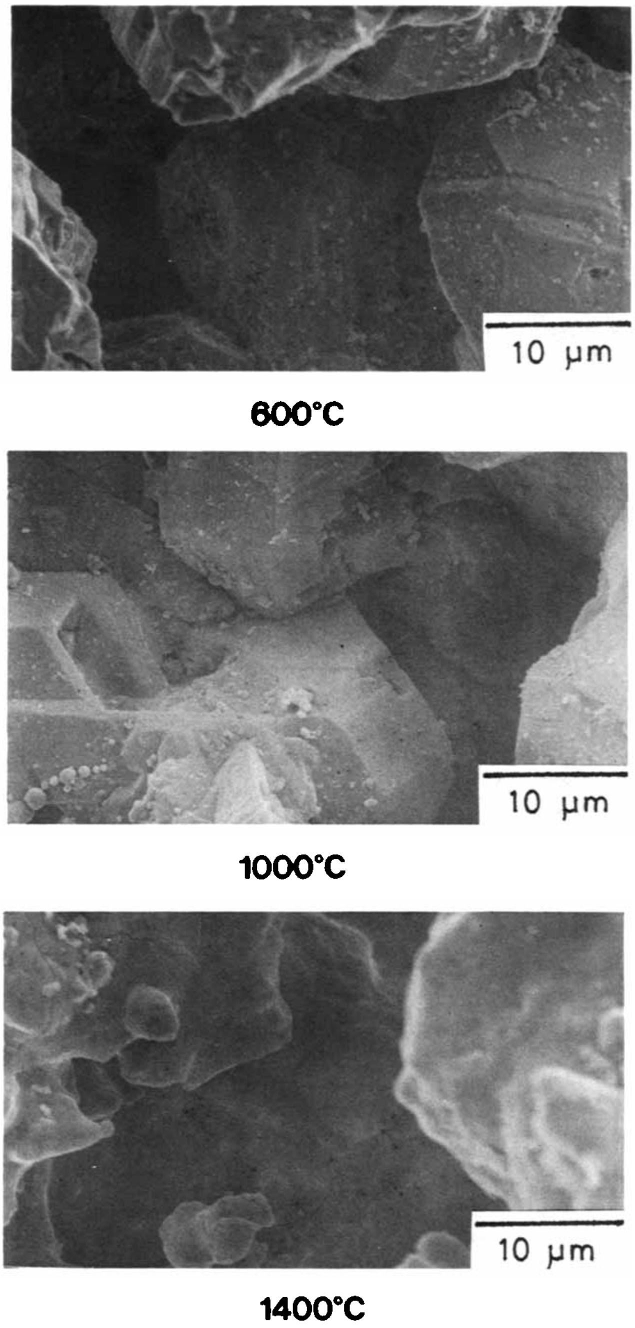


Fig. 5. SEM micrographs of the surface of the sample with a SiC-concentration gradient after oxidizing for 30 h at each temperature.

The XRD patterns of the surfaces of the samples oxidized for 30 h at each temperature are shown in Fig. 6. The surface oxidized at 600°C gives only 102 diffraction peak of α-SiC. By the oxidation at a temperature above 1000°C, however, the 101 diffraction peak of α-cristobalite appears, which seems to be formed by the crystallisation of the glass phase formed on the surface during cooling to room temperature. The intensity of 101 line of α-cristobalite increases with the increase of oxidation temperature, but that of 102 line of α-SiC is still

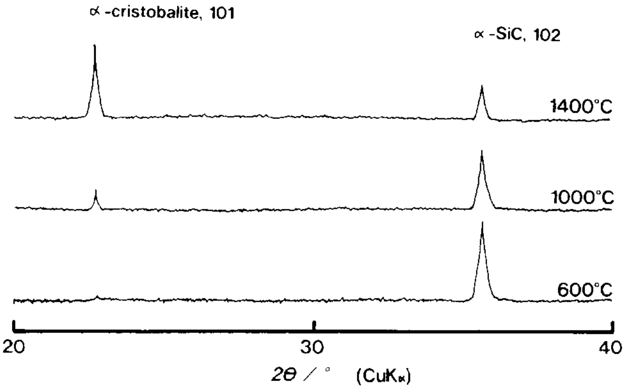


Fig. 6. XRD patterns of the surface of the sample with a SiC-concentration gradient after oxidizing for 30 h at each temperature.

observed even after oxidation at 1400°C. This result suggests that the glass film formed on the surface of the sample during oxidation is strongly limited in its thickness and SiC remains near the surface even after oxidation at 1400°C for 30 h.

In Fig. 7, the cross-sections of the samples with a SiC gradient after the oxidation for 30 h at each temperature are shown. On the sample oxidized at 600°C, the formation of large pores even at the centre of the substrate is observed. These large pores seem to be formed due to the diffused oxygen through the open pore on the surface. At 1400°C, on the other hand, the formation of pore is not appreciable.

These results show that the oxidation resistance of the sample with a SiC-concentration gradient is mainly due to the formation of a protective film of SiO_2 glass on the surface. This SiO_2 glass is reasonably supposed to be formed from SiC during its oxidation. For covering all the surface of the sample by this glass film, it seems to be necessary to be heated around 1400°C to have enough fluidity.

3.3 Thermal-shock resistance

A thermal-shock test was carried out on the sample with a SiC-concentration gradient by quenching the sample plate from 1400°C to liquid nitrogen temperature. No destructions and no cracking of the samples were observed. Kumakawa *et al.*[12] reported that the SiC/C functionally gradient material has both effective thermal-shock resistance and thermal barrier characteristics. This high thermal-shock resistance of the present sample seems to be due to the concentration gradient of SiC layer which allows the continuous relaxation of the difference in thermal expansion between SiC layer and carbon substrate.

4 Conclusion

The carbon material with a SiC-concentration gradient was obtained from the high-density isotropic graphite by a silicon impregnation process, and its oxidation behaviour was investigated.

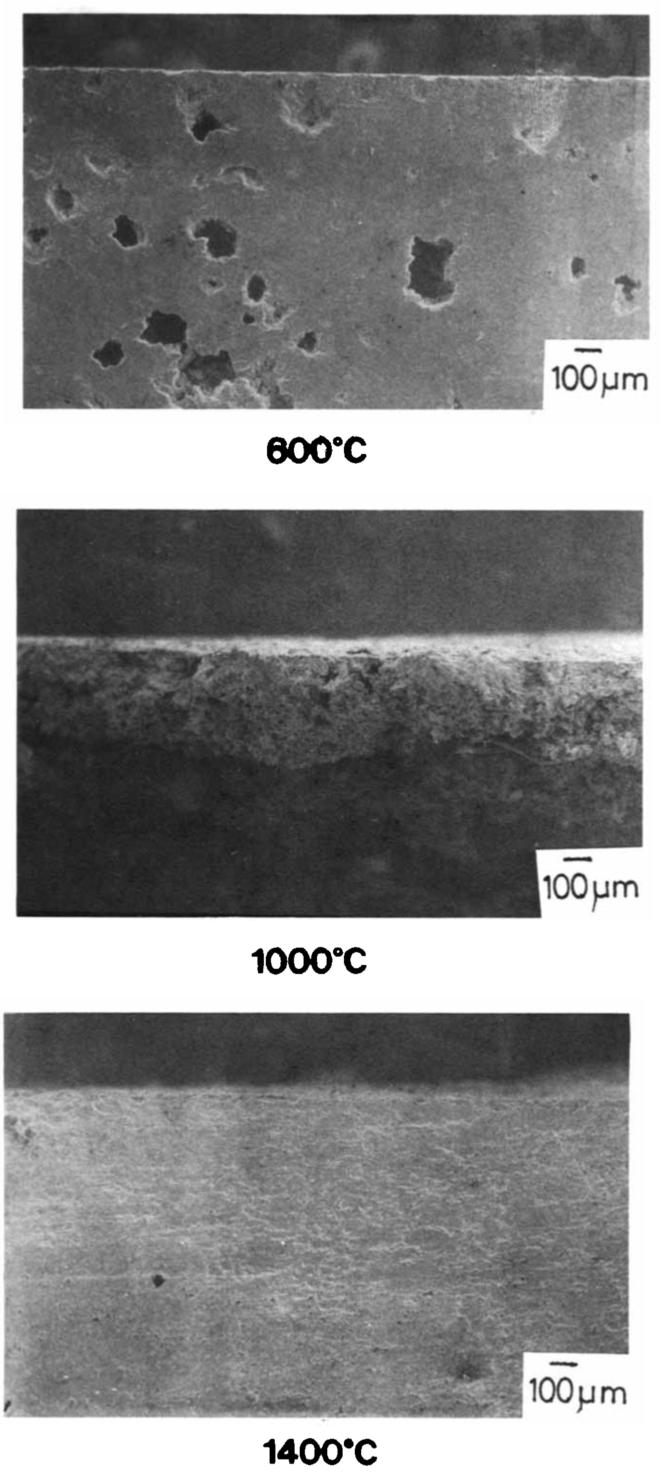


Fig. 7. SEM micrographs of the cross-section of the sample with a SiC-concentration gradient after oxidising for 30 h at each temperature.

(1) The carbon material with a SiC concentration gradient was prepared by heating the isotropic graphite substrate with certain amount of silicon powder at 1450°C for 3 h. In order to avoid an adhesion of metallic silicon, the amount of silicon powder relative to the physical surface area of the substrate has to be in the range 3·9–4·1 g cm^{-2}.

(2) The carbon material with a SiC-concentration gradient showed a good oxidation resistance at 1400°C and the rate of the weight loss was one-eleventh of the original isotropic graphite. This oxidation resistance was mainly due to the formation of SiO_2 film on the surface.

Acknowledgments

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