JOURNAL OF MATERIALS SCIENCE 31 (1996) 6163–6169

Oxidation behaviours of carbon/carbon composite with multi-coatings of LaB_6–Si/polycarbosilane/SiO_2

R. WANG, H. SANO, Y. UCHIYAMA, K. KOBAYASHI
Department of Materials Science & Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki, 852 Japan

The influence of multi-coatings of LaB_6-Si/polycarbosilane/SiO_2 on the oxidation behaviour of carbon/carbon composite materials was investigated in the temperature range from 500 to 1400 °C. The additives of LaB_6–Si offered lower oxidation rates and accelerated increases in oxidation rates at temperatures below 900 °C. The coating of polycarbosilane (PCS) improved the compatibility of the coating on the carbon/carbon composite and lowered the oxidation rates of the LaB_6–Si coated composite below the transition temperature. With the SiO_2 coating, the cracks of the LaB_6–Si/PCS coating was sealed and a good oxidation resistance of the LaB_6–Si/PCS/SiO_2 coated composite was found at temperatures up to 1300 °C.

1. Introduction

Carbon fibre-reinforced carbon composites (C/C composites) are potentially useful materials in applications requiring strength and toughness, at high temperatures combined with low weight [1]. Potential uses range from those in aircraft, hypersonic aerospace vehicles and the automotive industry to biomedical and refractory applications. These composites retain their strength, modules and mechanical properties to temperatures higher than those tolerated by other materials [2, 3].

Strong covalent bonding gives a low carbon atom diffusion which, combined with the highly anisotropic graphite crystal structure, suggests exceptional creep resistance for graphitized carbons [4]. However, the rapid reaction of carbon with oxygen at temperatures as low as 500 °C causes rapid degradation of the composite [5] and thus effective protection against oxidation for C/C composites at temperatures of 1000 °C and above must be developed. Both inhibitors, such as phosphorus and the halogens incorporated into the graphite matrix [6, 7] and oxygen diffusion barriers [4, 5, 8, 9] have been investigated. Any inhibitors, diffusion barriers or coatings used to protect the composite from oxidation must prevent the diffusion of oxygen or oxide products and have a low volatility, to prevent corrosion occurring in fast flowing gas streams. Meanwhile, all interfaces must exhibit both chemical and mechanical compatibility. The latter is overriding issue in the choice of suitable coatings.

For the improvement of the oxidation resistance of carbon materials at higher temperatures, it is difficult for a single coating to meet all the needs of protection in an oxidation environment. If good thermomechanical and chemical stability are to be achieved, the multi-coatings of a number of refractory materials will be required. The multi-coatings of LaB_6–Si/polycarbosilane/SiO_2 has been investigated in the present work. This paper reports the oxidation behaviours of the composite with an polycarbosilane (PCS) impregnated LaB_6–Si layer both with and without SiO_2 coating by sol–gel technique. The additives of LaB_6–Si play a role of diffusion barriers to lower the oxidation rates of the composite at temperatures below 900 °C. The impregnation of PCS improved the compatibility of the coating layer on the composite and the oxidation resistance below the transition temperature. The SiO_2 coatings by sol–gel technique sealed cracks in the applied protective layer. The oxidation resistance of the multi-coated C/C composites has been improved up to 1300 °C.

2. Experimental procedure

The C/C composite materials (CCM-290C, Nippon Carbon Co.) were used in the present work. Fibres were acrylic staple and in two-dimensional mat lay-up (Fig. 1). The temperature of final treatment was 2200 °C. The specimens had been made into sheets with the size about 4 × 5 × 0.7 mm. These sheets were dipped in lanthanum borate (LaB_6) slurry that was made from LaB_6 powder (< 10 μm in size) and polyethanol (as a binder) with the mixing ratio of 1 g:20 ml. After drying at 800 °C for 2 h, 2000 °C treatment had been carried out for 1 h in argon. Then they were dipped in silicon slurry made from silicon powder (< 50 μm in size) and polyethanol and dried at 800 °C for 2 h.

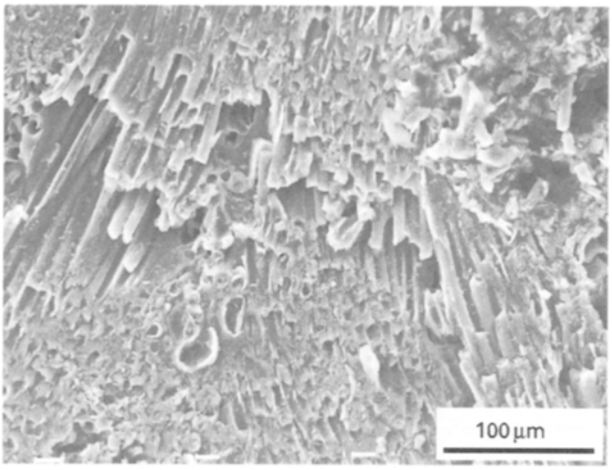

Figure 1 The micrograph of the surface of uncoated C/C composite used in present work.

Considering the wetting ability on the carbon materials, PCS was chosen for impregnating on the composite coated with LaB_6–Si. Any coatings used to protect composites from oxidation should prevent the diffusion of oxygen and have good adherence to the substrate. Generally, polar solutions have a bad wetting ability to be coated on carbon materials. PCS has an excellent solubility in various non-polar organic solvents, like *n*-hexane, toluene and xylene, at ambient temperatures. The PCS had been dissolved by toluene in the ratio of 1 : 10. The impregnation of PCS was carried out for the LaB_6–Si-coated composite by dipping in the PCS solution and sintering at 1000 °C in nitrogen. Then SiO_2 coating was prepared on the PCS-coated composites with sol–gel technique.

For the SiO_2 coating, the precursor solution was prepared by mixing silicon tetraethoxide ($Si(OEt)_4$), ethanol (EtOH) in a molar ratio of 1 : 20. Then H_2O as a catalyst, containing 6.3 wt % HNO_3, was added to the solution in a molar ratio of $H_2O/Si(OEt)_4$ of 1 : 5. The solution was stirred at 60 °C for 45 min for partial hydrolysis. After the solution was cooled to room temperature, the composites with LaB_6–Si/PCS coating were dipped in the precursor solution and then treated at 800 °C for 0.5 h in nitrogen.

Measurements of the oxidation kinetics of the composite with and without coatings were carried out in a vertically mounted furnace in flowing air (flow rate 30 $cm^3 min^{-1}$) between room temperature and 1400 °C. The specimen was held in a platinum wire cage suspended on steel wire links from the mass balance. The control of the furnace temperature and collection of kinetic data were carried out with a computer. Specimens were allowed to cool in air and characterized using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Oxidation behaviour of LaB_6–Si-coated C/C composite

Fig. 2 shows Arrhenius plots for both uncoated C/C composite and a LaB_6–Si-coated composite at temperatures up to 1100 °C. For both specimens, two steps of oxidation rates were shown with transition temperature about 900 °C. A significant increase in oxidation rate was shown below 900 °C. Above 900 °C this increase was notably reduced, with the curves relatively flattened out. From the data of the Arrhenius plots, the values of apparent activation energy were about 110 KJ mol^{-1} at lower temperature and 15 KJ mol^{-1} at higher temperature for the uncoated C/C composite. Mckee [10] and Yasuda and colleagues [11] have discussed the mechanism of uninhibited C/C composite. For the oxidation of uncoated C/C composite in air, the low-temperature rate-limiting step was likely to be the chemical reaction on the composite surface, to give oxidation products and leave defects in the carbon network. At the higher temperatures the rate was then controlled by oxygen diffusion into pores and adsorption at active sites. This results in a lowering of the activation energy as the temperature increases.

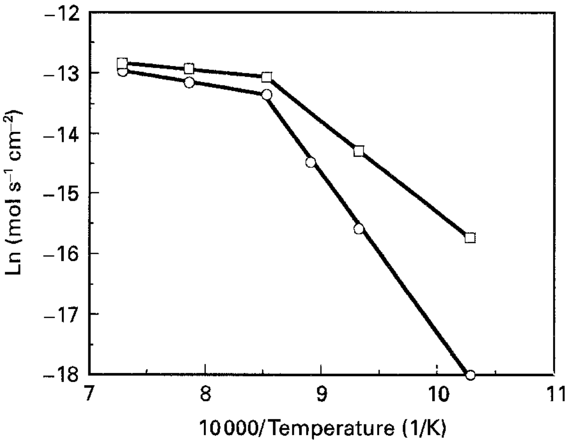

Figure 2 The Arrhenius plots for the uncoated composite (□) and LaB_6–Si-coated composite (○).

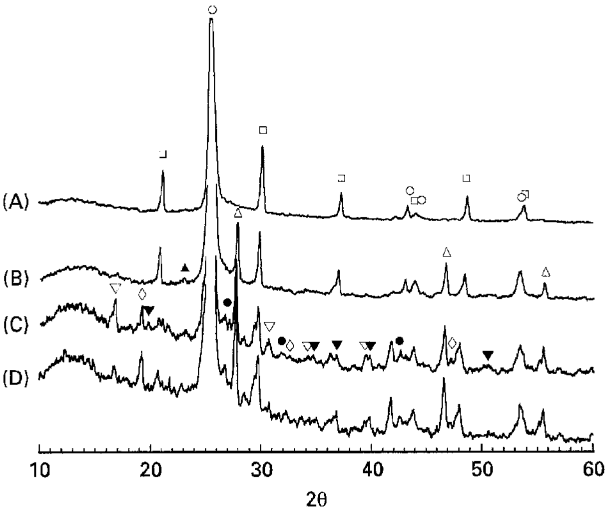

Figure 3 The X-ray profiles of the C/C composites with different coatings: (a) with LaB_6; (b) with LaB_6–Si; (c) with LaB_6–Si/PCS; (d) with LaB_6–Si/PCS/SiO_2. CuK_α, Ni filter, CPS 400, 1° – 0.15 mm – 1°, scanning speed 2° min^{-1}. (○) C; (△) Si; (●) LaC_2; (▽) La_2O_3; (□) LaB_6; (◇) SiO_2; (▲) B_2SiO_5; (▼) B_2O_3.

In the present work, LaB_6 and Si were coated on C/C composite and then treated at 2000 °C in argon and 800 °C in nitrogen, respectively. Boron carbide and lanthanum carbide were not found after adding LaB_6 and 2000 °C treatment. After coating with Si and 800 °C treatment, due to a small amount of oxygen in the binder (polyethanol) or furnace tube that would react with LaB_6–Si powders, the low-melting point phase of B_2O_3–SiO_2 was detected by X-ray diffraction as shown in Fig. 3. This result agreed with the SiO_2–B_2O_3 phase diagram [12]. After adding LaB_6 and 2000 °C treatment, the values of d(0 0 2) and Lc(0 0 2) of graphite were calculated. Both values were larger than the values of the uncoated composite. This is not enough evidence to show the improvement of the graphitization, as shown in other work [13]. Fig. 4 shows the surfaces of the composites after adding LaB_6. LaB_6 powder dispersed on the surface of the composite, but the whole area of the composite surface could not be covered. After coating with Si and 800 °C treatment, the loose powder layer was located on the surface of composites, as shown in Fig. 5a. The larger pores with the width of about 60 μm were found in the powder layer. The existence of the larger pores was likely due to the particle size used in the present work. Fig. 5b shows that the additives of LaB_6–Si were filled into the open pore of the C/C composite. At the lower temperatures, the oxidation rate was still controlled by the surface reaction. The additives of LaB_6–Si powders decreased the oxidation rates of the composite due to the decreasing of the exposed surface areas, as shown in Fig. 2. However, the effects of these additives were dependent on the compatibility of additives and the composite. The increase of reaction rates, caused by processes such as pitting, surface etching, and channel formation, would degrade the combination between the additives and the composite and decrease the protective effects of the additives. The Arrhenius plot of the LaB_6–Si-coated composite in Fig. 2 indicates that these additives gave lower oxidation rates of the composite at lower temperatures, while below 900 °C, the increase in oxidation rates for the coated composite was accelerated by four orders of magnitude at 700 °C. At higher temperatures, where the oxidation rate was controlled by gaseous diffusion, the effect of the additives was insignificant. In spite of the presence of B–Si–O system oxide, it did not form a complete layer to protect the composite from the diffusion of oxygen, because of the pores around the LaB_6–Si particles. Like other diffusion barriers [14], the LaB_6–Si coating on the composite gave an effective oxidation resistance in lower temperature range.

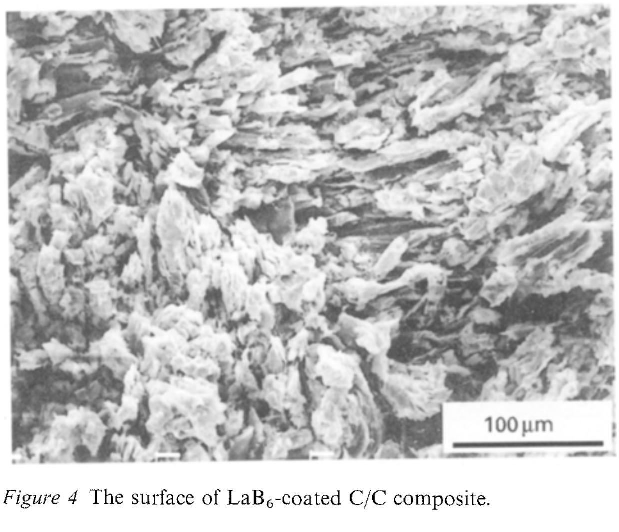

Figure 4 The surface of LaB_6-coated C/C composite.

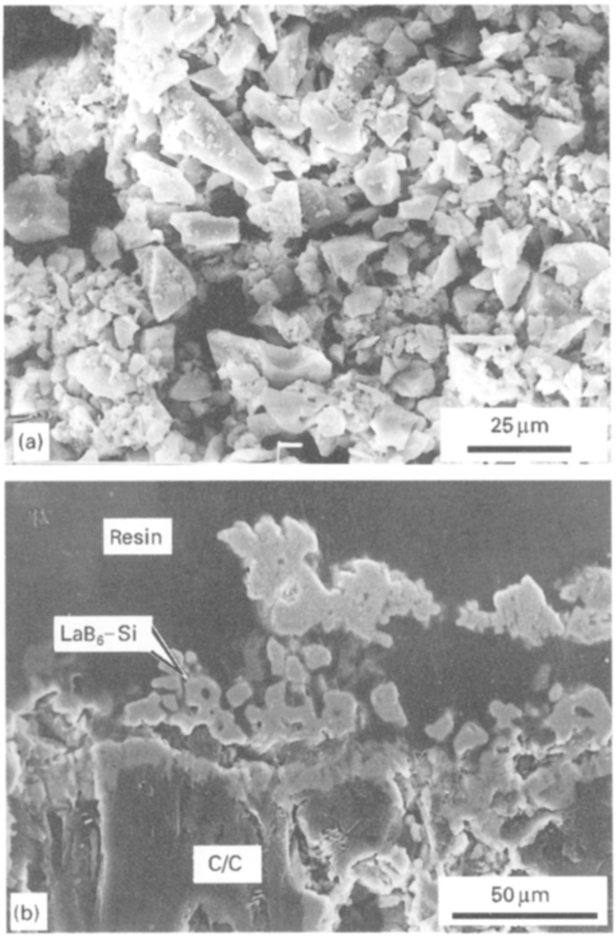

Figure 5 The surface (a) and section (b) of LaB_6-Si-coated C/C composite.

3.2. Oxidation behaviour of PCS-coated C/C composite with LaB_6–Si

The solution of PCS–toluene was impregnated into the pores around LaB_6–Si particles, as shown in Fig. 6a, and PCS was coated on the composite after 1000 °C treatment in the present study. Because of the remarkable shrinkage of PCS solution when toluene was vapourized, the cracks formed in the PCS coating on the composite, as shown in Fig. 6b. When fired in an inert atmosphere, PCS starts to decompose at about 500 °C. At about 800 °C, it transforms into a black amorphous inorganic polymer with loss of organic groups. The release of organic groups results in the oxidation of a part of LaB_6–Si powder. The oxides of lanthanum, boron and silicon were found by X-ray diffraction, as shown in Fig. 3c. Fig. 3c also shows the appearance of LaC_2 in the composite. The formation of lanthanum carbide on the surface of the composite gives an improvement of compatibility

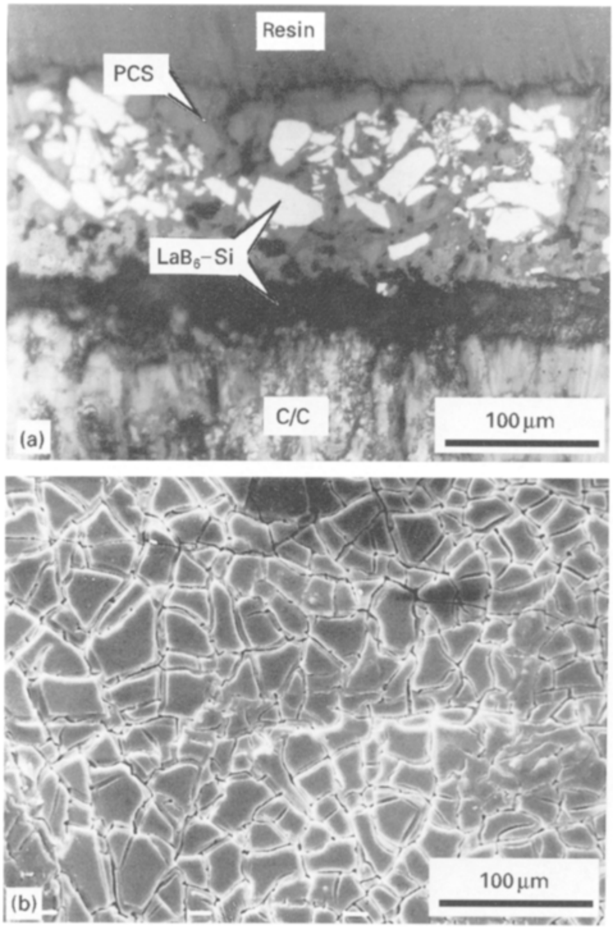

Figure 6 The section (a) and surface (b) of LaB_6–Si/PCS-coated C/C composite.

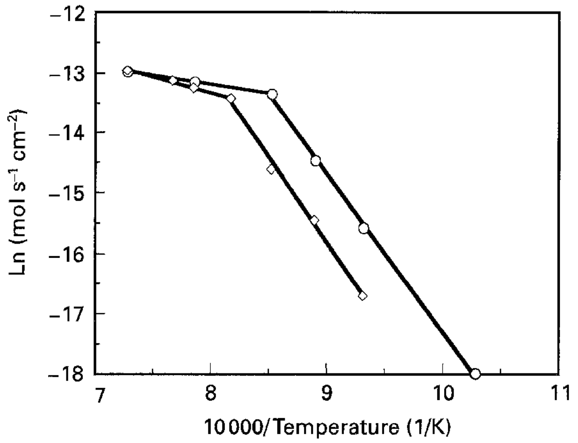

Figure 7 The Arrhenius plots for the composites with different coatings: (○) with LaB_6–Si; (◇) with LaB_6–Si/PCS.

between the composite and the coating layer and decreases the active sites in the carbon network.

Fig. 7 shows the Arrhenius plots for the composites with and without PCS coating. Below 950 °C, due to the additives of LaB_6–Si, the increase in oxidation rates for the PCS-coated composite was shown to be almost the same as the increase for the composite without PCS coating. Below 950 °C, relative to the oxidation rate of the composite without PCS, the oxidation rate of the composite with PCS was decreased by one order of magnitude. The shift of transition temperature from the surface reaction to the gaseous diffusion indicated the change of effective surface area for the oxidation reaction. The smaller the effective surface area is, the higher the transition temperature. In the present work, the decrease of the effective surface area was likely to be the impregnation of PCS and the formation of LaC_2. However, the shrinkage of the PCS during the vaporization of the toluene solvent produced serious cracks in the PCS coating. These cracks made the coating unsuccessful in protecting the composite from the diffusion of oxygen at higher temperatures. The high-temperature oxidation rate was still controlled by gaseous diffusion.

3.3. Oxidation behaviour of the SiO_2-coated C/C composite with LaB_6–Si/PCS

For the problem of microcracking occurring in any protective layer, boron, boron compounds and silicon compounds are often included in the composite to form borate or B–Si–O system glasses, which can flow to give crack sealing [10, 15]. In the present work, B–Si–O oxide was formed after adding LaB_6–Si, but it was not successful in sealing the serious cracks in the PCS coating. Sol–gel technique was employed to make a SiO_2 coating on the composite. The solution of $Si(OEt)_4$ was used as the precursor solution. When firing over 50 °C, the precursor was changed into SiO_2 gel and released EtOH gas and H_2O vapour. From Fig. 2, the formation of new phases was not

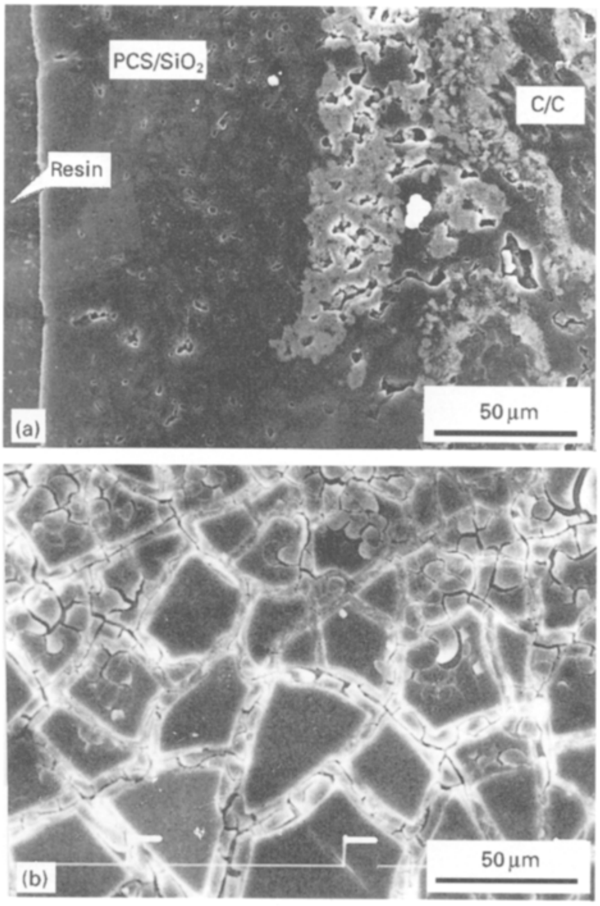

Figure 8 The section (a) and surface (b) of LaB_6–Si/PCS/SiO_2-coated C/C composite.

found in the coated C/C composite after SiO_2 coating. Fig. 8 shows the SiO_2 coating sealed into the cracks of the PCS coating. No open cracks that crossed the coating layer were observed in the PCS–SiO_2 coating layer, as shown in Fig. 8a, although microcracks were found on the surface of the SiO_2 coating, as shown in Fig. 8b. Fig. 9 shows the results of isothermal oxidation at 1100 °C for the coated composites. The oxidation for the SiO_2 coated composite was not shown at

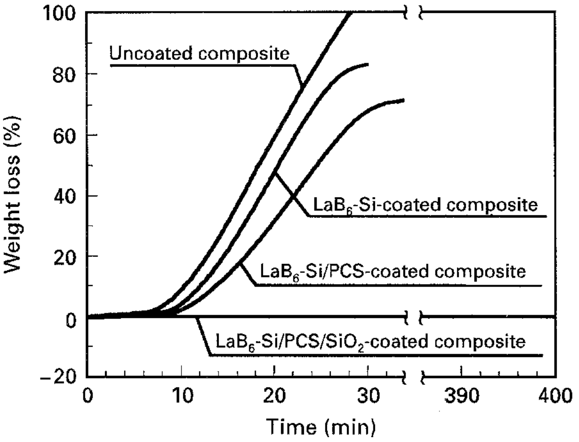

Figure 9 The weight loss of the composites with different coatings in flowing air (30 $cm^3 min^{-1}$) at 1100 °C.

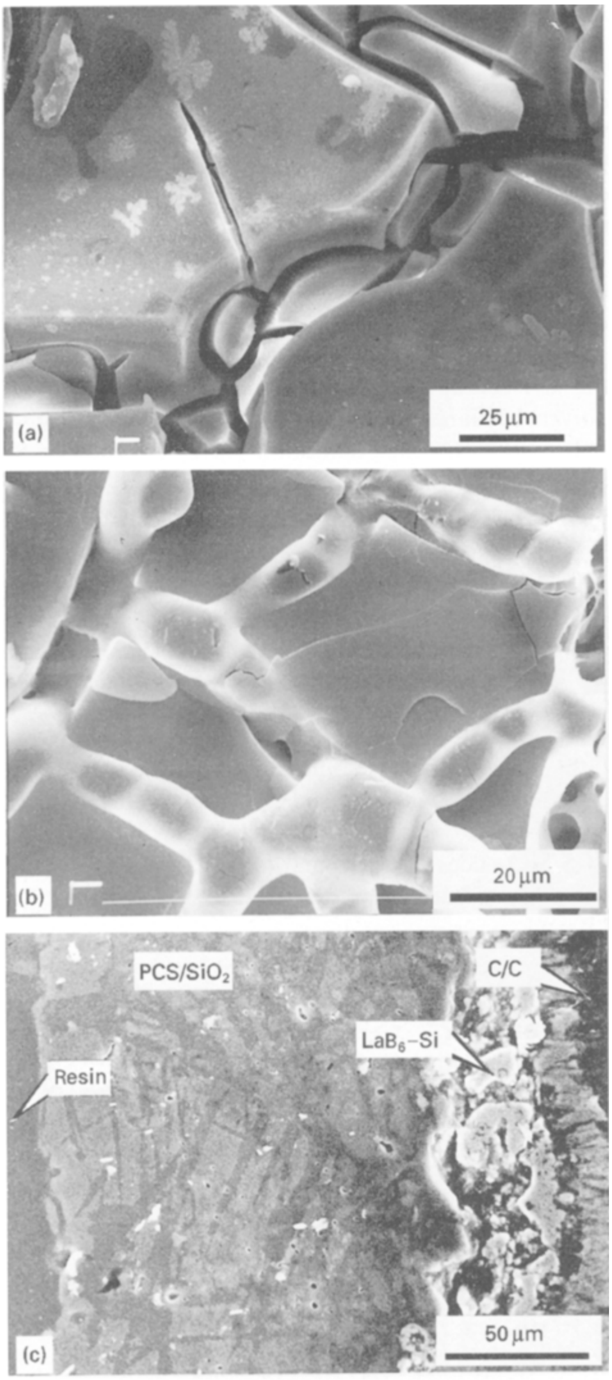

Figure 10 SEM micrographs of the coated composites after 1100 °C oxidation: (a) surface of LaB_6–Si/PCS; (b) surface of LaB_6–Si/PCS/SiO_2; (c) section of LaB_6–Si/PCS/SiO_2.

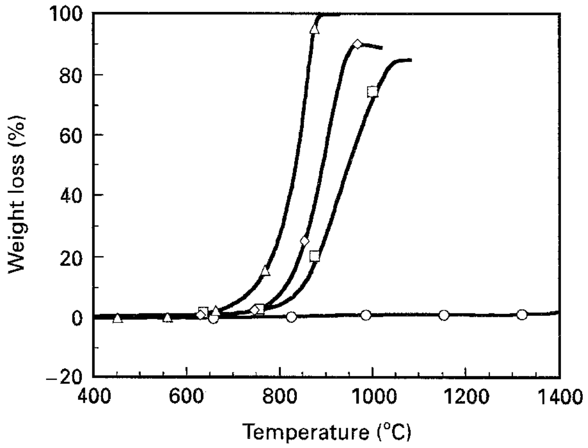

Figure 11 The weight loss of the composites with different coatings in flowing air (30 $cm^3 min^{-1}$), the temperature was raised in a fixed rate of 2.5 °C min^{-1}. (△) uncoated composite; (◇) LaB_6–Si-coated composite; (□) LaB_6–Si/PCS-coated composite; (○) LaB_6–Si/PCS/SiO_2-coated composite.

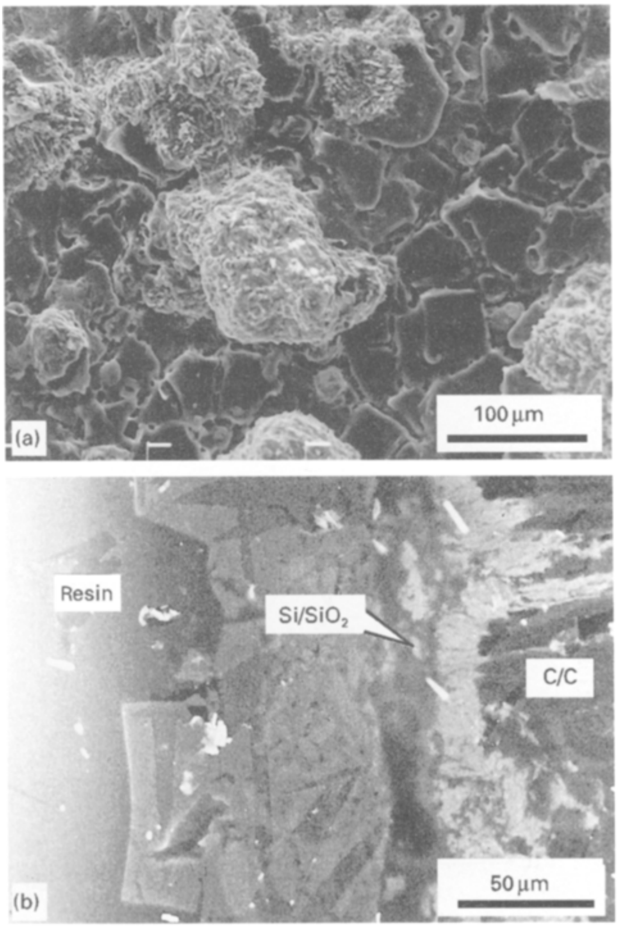

Figure 12 The surface (a) and section (b) of LaB_6–Si/PCS/SiO_2-coated composite after 1400 °C oxidation.

1100 °C over 5 h. After the isothermal oxidation, the composites with and without SiO_2 coating were characterized using scanning electron microscopy, as shown in Fig. 10. The oxidation of the PCS without SiO_2 coating appeared at specific active sites, as shown in Fig. 10a, but did not appear in the PCS with SiO_2 coating, as shown in Fig. 10b. Compared to the composite without SiO_2 coating, the cracks of the PCS coating were sealed completely by SiO_2. This sealing did not fill into the interfaces between the coating layer and the C/C composite, as shown in Fig. 10c. It was suggested that the wetting of SiO_2 on the PCS coating was improved in oxidized circumstances, and that a continuous coating layer can be formed at the exterior of the coating. The continuous coating of PCS–SiO_2 protects the C/C composite from the corrosion of oxygen over 1100 °C.

Fig. 11 shows the weight loss of the C/C composites with different coatings as a function of temperature. A little weight loss (less than 2 wt %) was found for the SiO_2 coated composite at temperatures up to 1400 °C. It is known that boron oxide is appreciably volatile at high temperature. Greene and Margrave [16] calculated the values for the vapour pressures of various boron oxide species from thermodynamic data. The results of their work suggested that the vapour pressure of HBO_2 was over 1 mmHg (at $P_{H_2O} = 1$ atom) at 900 °C; the vapour pressure of B_2O_3 was about 10^{-2} mmHg at 1000 °C and 1 mmHg at 1400 °C. In the present work, it is expected that H_2O and EtOH released from the precursor solution resided and formed the boron hydroxide in the composites. The vapourization of hydroxide resulted in the weight loss at the temperatures of 800–1000 °C, as shown in Fig.11. When the temperature was over 1300 °C, the vapourization of B_2O_3 became notable with increase in temperature. On the other hand, the oxidation of PCS at specific active sites and the vapourization of SiO_2 were found on the surface of PCS coating, as shown in Fig. 12a. Carbon oxides and SiO_2 would be produced by the oxidation of PCS coating. Fig. 12b shows a section of the composite after the oxidation at 1400 °C. A glass layer enclosing Si powders was formed on the surface of the C/C composite. Fig. 13 shows the results of the isothermal oxidation for the coated composites at different temperatures. The coating gave a better protection at temperatures up to 1300 °C, while the weight loss of the composite was increased gradually at 1400 °C. It is suggested that the coatings were degraded by the vapourization of B_2O_3 and SiO_2 and could not protect the composite from the diffusion of oxygen at 1400 °C.

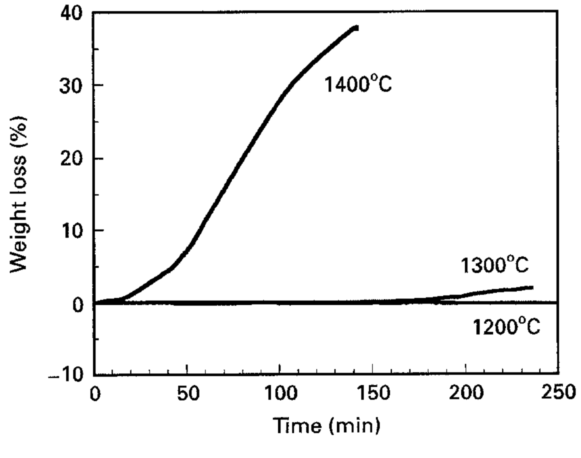

Figure 13 The results of isothermal oxidation for the composite with LaB_6–Si/PCS/SiO_2 coatings at different temperatures.

4. Conclusions

At temperatures up to 1100 °C, the oxidation rate of uncoated C/C composite materials was divided two steps. At lower temperatures, the oxidation rate was controlled by surface reaction rate; while at higher temperatures, the rate was limited by the oxygen diffusion rate.

For the LaB_6-Si-coated and LaB_6–Si/ PCS-coated composites, the oxidation rates were controlled by oxygen diffusion at temperatures over 900 °C and 950 °C under the experimental conditions. Below 900 °C, the additives of LaB_6–Si could lower the oxidation rates of the composite as diffusion barriers by over two orders of magnitude in the present experiments and gave a remarkably accelerated increase in oxidation rates. The coating of PCS sealed the larger pores around the LaB_6–Si particles and improved the compatibility between the coating layer and the C/C composite, due to the impregnation with polycarbosilane solution and the formation of LaC_2. Below 950 °C the oxidation rate of the PCS-coated composite was decreased by one order of magnitude, comparing to the rate of the composite without PCS.

A continuous protective layer that sealed smaller pores and cracks was formed after SiO_2 coating by sol–gel technique. The wetting of SiO_2 on PCS was improved in oxidation circumstances. The continuous coating layer was formed by SiO_2–PCS at the exterior of the coating and protected the C/C composite over 1100 °C. With increase of temperature, the glass layer enclosing Si powders formed on the surface of the C/C composite. For the C/C composite with LaB_6–Si/ PCS/SiO_2 coatings, a remarkable resistance for the onset of oxidation was shown at temperatures up to 1300 °C.

References

1. K. KOBAYASHI, *Now & Future* **4** (1992) 4.
2. G. M. SAVAGE, *Chemistry & Industry* **20 July** (1992) 525.
3. E. FITZER, *Carbon* **25** (1987) 163.
4. W. N. REYNOLDS, "Physical properties of graphite" (American Elsevier Publishing Company, New York, 1968).
5. D. W. MCKEE, *Carbon* **24** (1986) 737.
6. *Idem., ibid.* **22** (1984) 285.
7. G. M. MEHROTRA, Report 1991, Order No. AK-235 985.
8. I. OGAWA, *J. Mater. Sci. Lett.* **11** (1992) 296.
9. I. OGAWA, K. KOBAYASHI and S. NISHIKAWA, *J. Mater. Sci.* **23** (1988) 1363.
10. D. W. MCKEE, *Carbon* **25** (1987) 551.
11. E. YASUDA, S. KIMURA and Y. SHIBUSA, *Trans. JSCM* **6** (1980) 14.

12. T. J. ROCKETT and W. R. FOSTER, *J. Amer. Ceram. Soc.* **48** (1965) 78.
13. Y. UCHIYAMA, S. ARAKI, H. SANO and K. KOBAYASHI, in Proceedings of the 22nd Biennial Conference on Carbon, San Diego, July 1995, edited by American Carbon Society, p. 698.
14. KRISHAN L. LUTHRA, *Carbon* **26** (1988) 217.
15. K. KOBAYASHI, H. SANO, K. MAEDA and Y. UCHIYAMA, *J. Ceram. Soc. Japan* **100** (1992) 398.
16. F. T. GREENE and J. L. MARGRAVE, *J. Phys. chem.* **70** (1966) 2112.

Received 8 December 1995
and accepted 13 June 1996