Journal of the European Ceramic Society 21 (2001) 2407–2412
www.elsevier.com/locate/jeurceramsoc

# Improvement in oxidation resistance of carbon by formation of a protective $SiO_2$ layer on the surface

Young-Hag Koh [a], Oh-Sang Kwon [a], Seong-Hyeon Hong [a], Hyoun-Ee Kim [a,*], Seok-Keun Lee [b]

[a] *School of Materials Science and Engineering, Seoul National University, Seoul, 151-742, South Korea*
[b] *Research Institute of Industrial Science and Technology, Pohang, 790-330, South Korea*

Received 8 December 2000; received in revised form 3 February 2001; accepted 17 February 2001

## Abstract

Solid carbon was coated with silicon dioxide ($SiO_2$) to improve the oxidation resistance at elevated temperatures. $SiO_2$ was deposited on the surface of carbon via gas phase transport. Coating was carried out by exposing the carbon next to a bed of SiC powder in a flowing $H_2$–$H_2O$ gas at 1400°C for 1 h. The formation of $SiO_2$ layer was strongly dependent on the water vapor pressure ($P_{H_2O}$) in the gas stream. When the $P_{H_2O}$ was around $1.3\times10^{-2}$ atm, a dense and uniform $SiO_2$ layer was formed on the carbon surface. The layer was crystalline (cristobalite) and slightly cracked apparently due to the thermal expansion mismatch. The oxidation resistance of the carbon was improved markedly by the coating layer. When oxidized in air under the same conditions, the weight loss of the coated specimen was reduced by more than a factor of 5 compared to the uncoated specimen. This improvement in oxidation resistance was attributed to the retardation of oxygen transport through the coating layer.

*Keywords:* Carbon; Coating; Oxidation resistance

## 1. Introduction

Carbon is a well-known engineering material for high-temperature applications, such as heaters, rocket nozzles, and electrical contacts, because of its unique physical, mechanical and electrical properties.[1] Carbon-based materials are also widely used as refractory materials in the iron and steel making industry because of its high thermal conductivity, non-wetting behavior and high resistance to slag.[2]

However, the application of carbon-based materials has been severely restricted because of its poor oxidation resistance at elevated temperatures in oxidizing environments. In order to improve the oxidation resistance of the carbon-based refractory materials, anti-oxidant additives such as Al, Si, Mg, and SiC are often employed.[3–5] For instance, when Al is added to a MgO–C refractory, the Al reacts with CO (g) to form $Al_2O_3$ (s) and C (s) resulting in filling open pores and consequently improving the oxidation resistance. However, the most common approach to improve the oxidation resistance of carbon is to coat the material with refractory materials such as SiC, $Al_2O_3$, $TiO_2$ and various oxide glasses.[6–10] In this case, thermal expansion coefficient, adhesion, and capability as an oxygen barrier are important parameters to consider. It was reported that a SiC coating using a CVD process was effective in protecting the carbon from oxidation at high temperatures up to 1700°C.[6] However, a more economical and effective coating method needs to be developed for wider engineering applications.

Previously we developed a coating procedure utilizing SiO gas generated by a reaction between SiC and $H_2O$ gas in a $H_2$ gas stream.[11] When the partial pressure of SiO gas is high enough, $SiO_2$ smoke is formed in the gas stream. If a material is placed in the $SiO_2$ smoke region, part of $SiO_2$ is deposited and subsequently becomes a dense and uniform layer. The $SiO_2$ layer was very effective in retarding the oxygen transport to the sample surface. Remarkable improvements in oxidation resistance

---

* Corresponding author. Fax: +82-2-884-1413.
*E-mail address:* kimhe@snu.ac.kr (H.-E. Kim).

0955-2219/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(01)00213-8

were observed in non-oxide ceramic materials such as AlN and $TiB_2$ utilizing this coating procedure.[12,13] In the present research, we formed a protective $SiO_2$ layer on the surface of solid carbons by exposing them to a high $P_{SiO}$ atmosphere, achieved by exposing SiC powder to a flowing wet $H_2$ atmosphere at 1400°C. The microstructural and the compositional evolution of the coating layer were observed to determine the optimum coating conditions. The effect of the coating layer on the oxidation resistance of the carbon specimen was estimated by monitoring the weight loss of specimens during the oxidation processes.

## 2. Experimental procedure

The specimens were prepared by machining the commercially available graphite blocks (Grade IG-15, Takuma, Tokyo, Japan) into a bar shape with dimensions of 3×4×25 mm. The samples were ground with a 200-grit diamond abrasive wheel and subsequently polished with diamond pastes down to 1 μm. Then the specimens were ultrasonically cleaned in acetone and isopropyl alcohol.

The polished bars were placed next to a bed of SiC powder (HCST GmbH & Co., Goslar, Germany) in a resistance-heated alumina tube furnace with a $H_2$–$H_2O$ gas flowing system. Hydrogen gas was purified by passing columns of $CaSO_4$ and activated alumina. The water vapor pressure ($P_{H_2O}$) was controlled by bubbling $H_2$ through distilled water at various flow rates and measured with a hygrometer (MMS-35, Panametrics, Inc., Waltham, MA, USA). Total gas pressure was slightly greater than 1 atm. Dry $H_2$ gas ($P_{H_2O} < 5\times10^{-4}$ atm) was used during heating and cooling stages to minimize the oxidation, and the actual coating was performed at 1400°C for 1 h with the wet $H_2$ gas at a flow rate of 1.2 cm/s. Additional processing details are described elsewhere.[11–13]

Specimens with and without the coating layer were oxidized in air at temperatures between 600 and 800°C for up to 20 h. The heating rate was 10°C/min and, after the coating process, the specimens were cooled slowly in the furnace. The oxidation resistance was estimated by measuring the weight loss during the exposure. X-ray diffraction (XRD) patterns and energy dispersive spectroscopy (EDS) were employed to determine the phase and composition of the coating layer. A scanning electron microscope (SEM) was used to observe the morphology of the layer.

## 3. Results and discussion

### *3.1. Formation of $SiO_2$ coating layer*

When the solid carbon was exposed to a flowing $H_2$–$H_2O$ gas in the presence of SiC powder, a $SiO_2$ layer was formed on the surface of the specimen. The property of the layer was strongly influenced by the water vapor pressure ($P_{H_2O}$) in the gas. The surface morphologies of specimens before and after the coating are shown in Fig. 1(A)–(D). Before the coating, even though the specimen was polished down to 1 μm, there were several voids on the surface of the specimen, as shown in Fig. 1(A). After coating in an atmosphere with low $P_{H_2O}$ level ($\leqslant 7\times10^{-3}$ atm), no significant change in the surface morphology was observed [Fig. 1(B)]. When the $P_{H_2O}$ was increased to $1.3\times10^{-2}$ atm, the surface was completely covered with a continuous layer as shown in Fig. 1(C). SEM observation with higher magnification revealed that the layer was slightly cracked, apparently due to the thermal expansion mismatch between the newly formed layer and the carbon substrate (coefficients of thermal expansion of graphite and $SiO_2$ are $6\times10^{-6}$ and $10\times10^{-6}$/°C, respectively).[14] However, when the $P_{H_2O}$ increased further to $2\times10^{-2}$ atm, the surface was not completely covered with the coating material, Fig. 1(D).

The coating layer was characterized by XRD patterns presented in Fig. 2. Before the coating, there are only carbon peaks as shown in Fig. 2(A). The XRD pattern was not changed when the specimen was coated with $P_{H_2O} < 7\times10^{-3}$ atm, which is consistent with the SEM observations. When the $P_{H_2O}$ was increased to $1.3\times10^{-2}$ atm, strong $SiO_2$ (cristobalite) peaks along with a weak SiC peak were detected, as illustrated in Fig. 2(B). These results indicate that $SiO_2$ was deposited on the surface of specimen and subsequently crystallized into cristobalite. It is believed that the SiC was formed by a reaction between the $SiO_2$ and the carbon substrate. When the $P_{H_2O}$ was higher than $2\times10^{-2}$ atm, less $SiO_2$ was formed on the surface as expected from the SEM micrograph shown in Fig. 1(D).

The composition of the coating layer was confirmed by EDS analyses. Before coating, only carbon peaks were detected as shown in Fig. 3(A). After coating with $P_{H_2O} = 7 \times 10^{-3}$ atm, small Si and O peaks were observed along with a strong C peak [Fig. 3(B)]. These results indicated that the surface of the specimen was covered with a thin and presumably amorphous $SiO_2$ layer. With increasing the $P_{H_2O}$ to $1.3\times10^{-2}$ atm, strong Si and O peaks were detected while the C peaks were completely disappeared, Fig. 3(C), which supports that the surface was completely covered with a relatively thick $SiO_2$ layer.

When the fracture surface of the specimen coated at 1400°C for 1 h with $P_{H_2O} = 1.3 \times 10^{-2}$ atm was observed with SEM, the thickness of the coating layer was about 0.7 μm, as shown in Fig. 4. These results indicate that there is an optimum range of $P_{H_2O}$ at which the dense and continuous $SiO_2$ layer is formed on the surface of carbon at 1400°C.

When a SiC powder is exposed to $H_2$–$H_2O$ atmosphere at elevated temperatures, different reactions

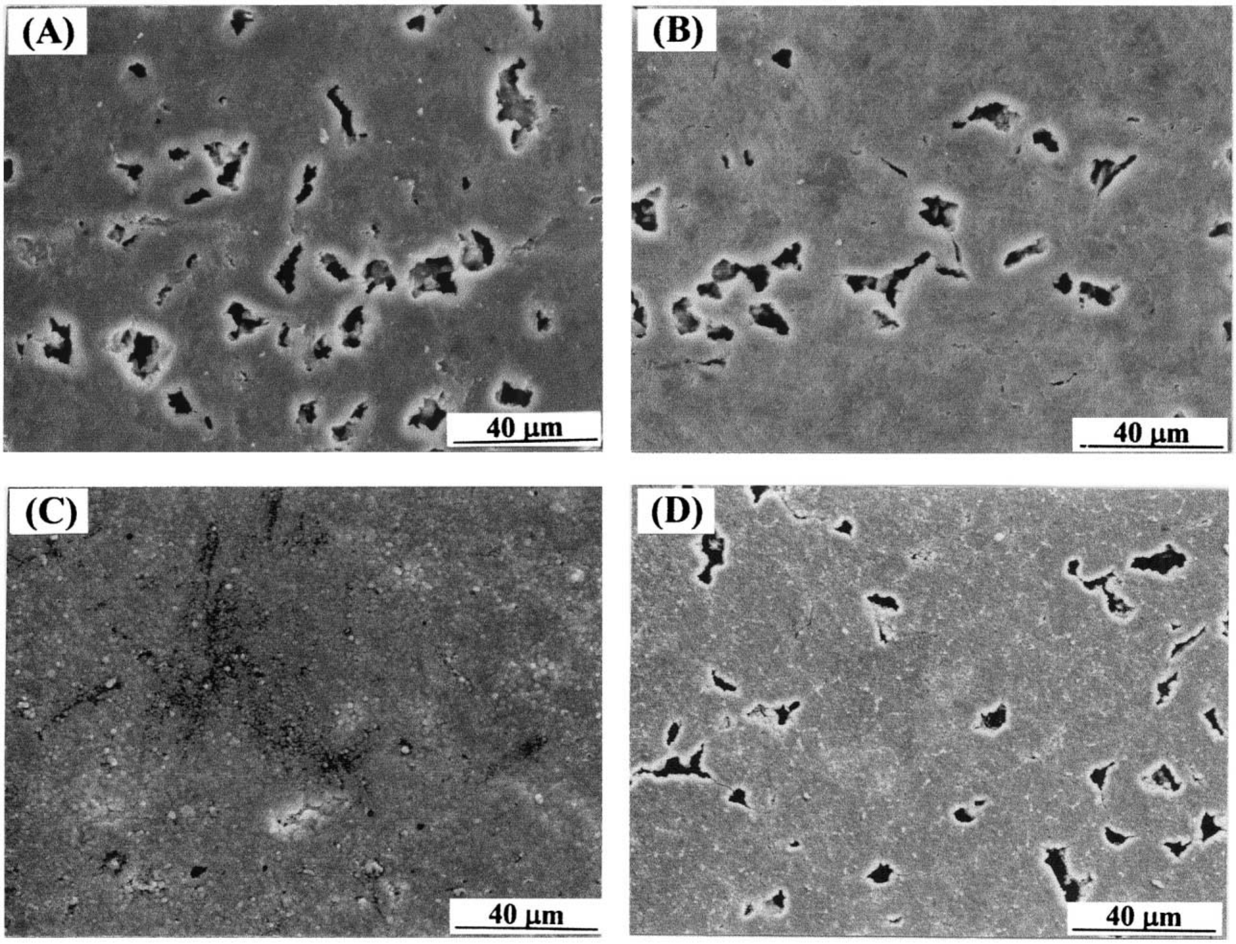

Fig. 1. Surface morphologies of the specimens (A) before coating; and after coating at 1400°C for 1 h in $H_2$–$H_2O$ atmosphere with (B) $P_{H_2O} = 7\times10^{-3}$ atm, (C) $P_{H_2O} = 1.3\times10^{-2}$ atm, and (D) $P_{H_2O} = 2\times10^{-2}$ atm.

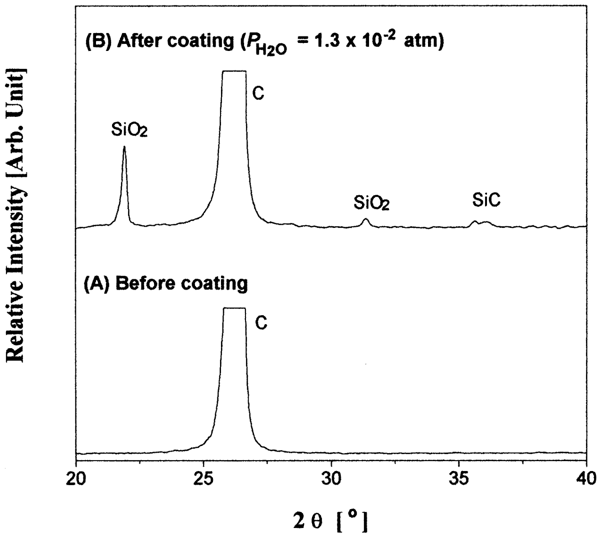

Fig. 2. X-ray diffraction patterns of the specimens (A) before coating and (B) after coating in flowing $H_2$–$H_2O$ atmosphere with $P_{H_2O} = 1.3\times10^{-2}$ atm.

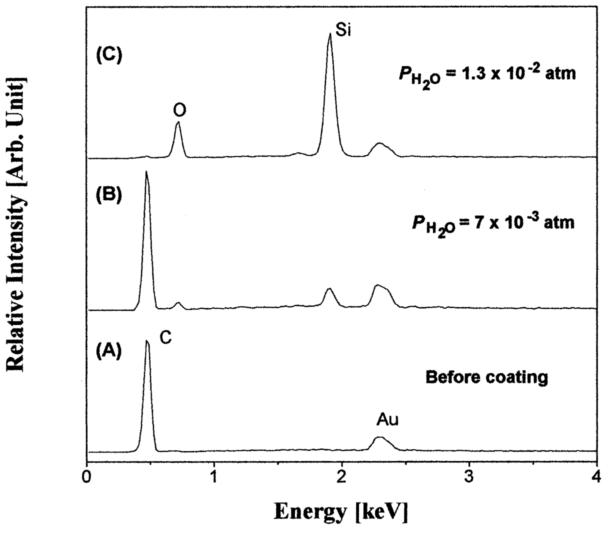

Fig. 3. EDS analyses of the sample surface (A) before coating; and after coating in flowing $H_2$–$H_2O$ atmosphere with (B) $P_{H_2O} = 7\times10^{-3}$ atm and (C) $P_{H_2O} = 1.3\times10^{-2}$ atm.

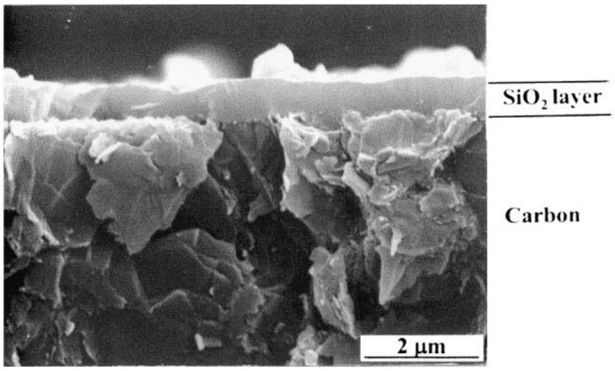

Fig. 4. SEM micrograph of fracture surface of the coated specimen in flowing $H_2$–$H_2O$ atmosphere with $P_{H_2O} = 1.3\times10^{-2}$ atm.

occur depending on the $P_{H_2O}$ level in the gas.[15,16] If the $P_{H_2O}$ is low, the following reaction is known to occur at temperatures above 1300°C.

$$SiC(s) + 2H_2O(g) = SiO(g) + CO(g) + 2H_2(g) \tag{1}$$

In this case, the partial pressure of SiO or CO ($P_{SiO}$ or $P_{CO}$) is proportional to the $P_{H_2O}$. However, when the $P_{SiO}$ is too high, $SiO_2$ ($s$) becomes stable and consequently the following reaction occurs.

$$SiC(s) + 3H_2O(g) = SiO_2(s) + 3H_2(g) \tag{2}$$

Once $SiO_2$ is formed on the surface of SiC by reaction (2), the $P_{SiO}$ decreases very rapidly. This variation in $P_{SiO}$ explains the different coating behavior depending on the $P_{H_2O}$ level. In other words, when the $P_{H_2O}$ is low, the $P_{SiO}$ is not high enough for the deposition of $SiO_2$ (s) on the carbon surface. The highest $P_{SiO}$ in this experiment is believed to have been achieved when the $P_{H_2O}$ was $1.3\times10^{-2}$ atm. When the $P_{H_2O}$ was higher than $2\times10^{-2}$ atm, reaction (2) occurs, so that the $P_{SiO}$ became too low again.

### *3.2. Effect of coating layer on the oxidation resistance of carbon*

The effect of the coating layer on the oxidation resistance of carbon was analyzed by monitoring the weight loss of the specimens exposed to air. When the carbon specimen without the coating layer was exposed to air at 600°C, weight loss occurred significantly, as presented in Fig. 5(A), as a result of oxidation reactions to form CO and $CO_2$ gases. After exposure to air at 600°C for 20 h, the weight loss reached up to 70%. Interestingly, the weight loss was not linear but increased with oxidation time. Increased surface area with proceeding oxidation was attributed to this weight loss behavior. When the carbon was coated with the $SiO_2$ layer by exposing to a $H_2$–$H_2O$ atmosphere at 1400°C for 1 h, the oxidation resistance was enhanced markedly as shown in Fig. 5(B). The weight loss was reduced by more than a factor of 5. In addition, the weight loss was linearly proportional to the time, implying the surface was not so severely destroyed by the oxidation reactions. This improvement in oxidation resistance was apparently due to the retardation of oxygen transport through the coating layer. The diffusion coefficient of oxygen through the $SiO_2$ layer is known to be very low.[17] As a matter of fact, the excellent oxidation resistance of Si-based ceramics (SiC and $Si_3N_4$) at elevated temperatures is due to the slow diffusion of oxygen through the $SiO_2$ layer.[18]

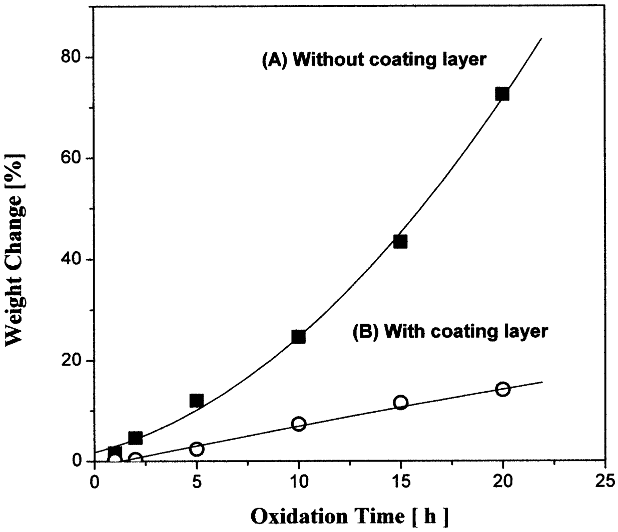

Fig. 5. Weight changes of the specimen (A) without and (B) with the coating layer exposed to air at 600°C for up to 20 h.

The effect of the coating layer on the oxidation resistance is well illustrated by SEM micrographs after the oxidation. The surface of the specimen without the coating layer was severely destroyed by oxidation in air at 600°C for 20 h as shown in Fig. 6(A). The increase in weight loss rate with oxidation time is well explained by this micrograph. The micrograph of the coated specimen after oxidation under the same conditions is shown in Fig. 6(B). The surface was well preserved compared to the specimen without the coating layer.

The improvement in oxidation resistance was observed also at different temperatures. Fig. 7 shows the weight loss of specimens oxidized in air at temperatures between 600 and 800°C for 1 h. This figure indicates that the weight loss was reduced by a factor of 5 by coating the solid carbon with the $SiO_2$ layer.

The effect of the coating layer on the oxidation resistance is most clearly illustrated in Fig. 8. When the uncoated specimen with a bar shape [Fig. 8(A)] was oxidized in air at 800°C for 1 h, the specimen was severely destroyed as shown in Fig. 8(B). In contrast, the coated specimen maintained its original dimensions after oxidation under the same conditions, Fig. 8(C).

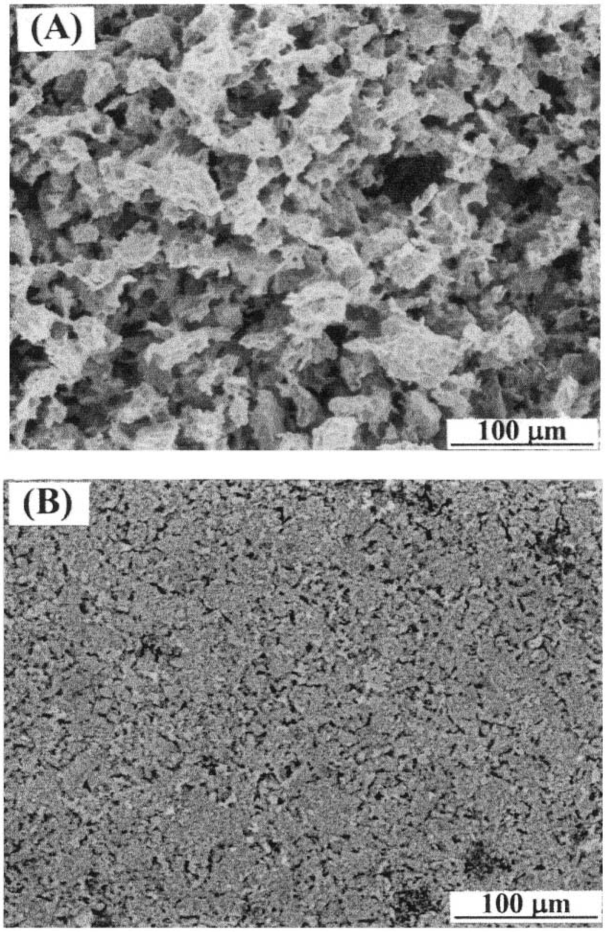

Fig. 6. Surface morphologies of the specimen (A) without and (B) with the coating layer after oxidation at 600°C for 20 h.

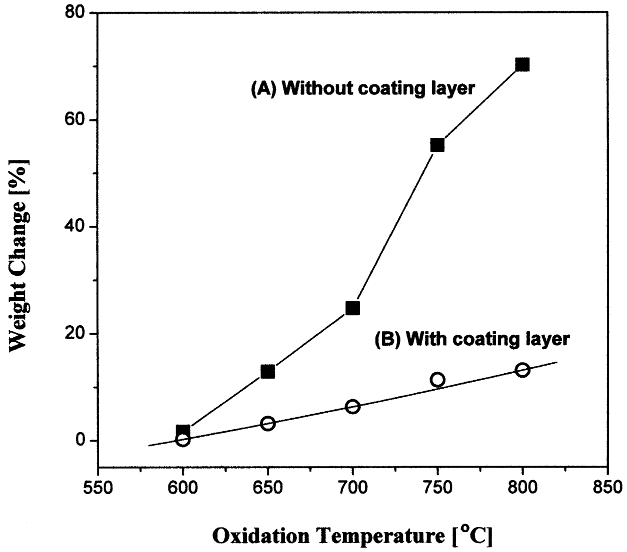

Fig. 7. Weight changes of the specimens (A) without and (B) with the coating layer exposed to air at various temperatures for 1 h.

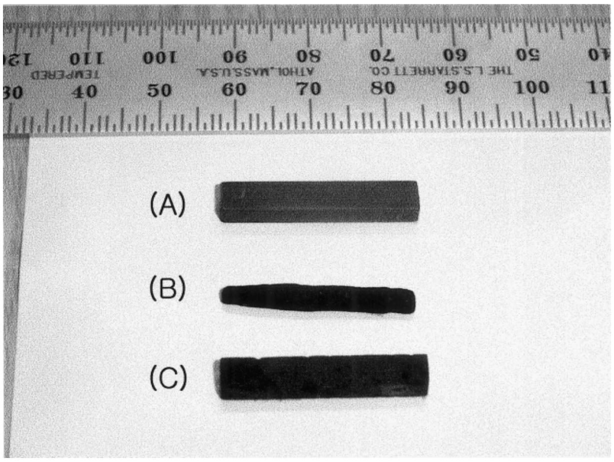

Fig. 8. Shape of specimens (A) before oxidation; (B) uncoated and (C) coated with $SiO_2$, after oxidation in air at 800°C for 1 h.

## 4. Summary and conclusions

When solid bar shaped carbon was exposed to a flowing $H_2$–$H_2O$ atmosphere with the presence of SiC powder at 1400°C, a dense and continuous silica ($SiO_2$) layer was formed on the surface. The SiO gas, generated by the reaction between the SiC and $H_2O$, was deposited on the sample surface to form the $SiO_2$ layer. The coating process was strongly influenced by the $P_{H_2O}$ level in the gas stream. When the $P_{H_2O}$ was $< 7\times10^{-3}$ atm, the $P_{SiO}$ was too low for $SiO_2$ deposition on the specimen. When the $P_{H_2O}$ in the $H_2$ was too high, the $P_{SiO}$ became low again because of the $SiO_2$ formation on the surface of SiC powder. The dense $SiO_2$ layer was formed when the $P_{H_2O}$ was around $1.3\times10^{-2}$ atm. The oxidation resistance of carbon was improved by more than a factor of 5 by the coating layer. The improvement was clearly due to the retardation of oxygen transport through the coating layer.

## References

1. Savage, G., *Carbon–Carbon Composite*. Chapmann & Hall, London, 1993.
2. Lee, W. E. and Moor, R. E., Evolution of in-situ Refractories in the 20th Century. *J. Am. Ceram. Soc.*, 1998, **81**, 1385–1410.
3. Yamaguchi, A., Behavior of SiC and Al added to carbon-contaning refractories. *Taikabutsu Overseas*, 1984, **4**, 14–18.
4. Taffin, C. and Poirier, J., The behavior of metal additions in MgO–C and $Al_2O_3$–C refractories. *Intercerm.*, 1994, **43**, 354–358.
5. Uchida, S., Ichikawa, K. and Niihara, K., High-temperature properties of unburned MgO-C bricks contaning Al and Si powder. *J. Am. Ceram. Soc.*, 1998, **81**, 2910–2916.
6. Moene, R., Boon, R. Th., Schoonman, J., Makkee, M. and Moulijn, J. A., Coating of activated carbon with silicon carbide by chemical vapor deposition. *Carbon*, 1996, **34**, 567–579.
7. Stuecker, J. N., Hirschfeld, D. A. and Martin, D. S., Oxidation protection of carbon-carbon composites by sol-gel ceramic coatings. *J. Mater. Sci.*, 1999, **34**, 5443–5447.
8. Kawabata, K., Yoshimatsu, H., Fujiwara, K., Mihashi, H., Hiragushi, K., Osaka, A. and Miura, Y., Oxidation resistance of

graphite powders coated with $Al_2O_3$-based oxides. *J. Ceram. Soc. Jpn.*, 1999, **107**, 832–837.

9. Yu, J., Ueno, S., Hiragushi, K. and Mizota, Y., Improvement in flowability, oxidation resistance and water wettability of graphite powder by $TiO_2$ coating. *Taikabutsu*, 1996, **48**, 533–534.
10. Isola, C., Appendino, P., Bosco, F., Ferraris, M. and Salvo, M., Protective glass coating for carbon-carbon composites. *Carbon*, 1998, **36**, 1213–1218.
11. Koh, Y.-H., Kong, Y.-M., Kim, S. and Kim, H.-E., Improved low-temperature environmental degradation of yttria-stabilized tetragonal zirconia polycrystals by surface encapsulation. *J. Am. Ceram. Soc.*, 1999, **82**, 1456–1458.
12. Koh, Y.-H., Choi, J.-J. and Kim, H.-E., Strengthening and prevention of oxidation behavior of AlN by formation of silica layer on the surface. *J. Am. Ceram. Soc.*, 2000, **83**, 306–310.
13. Koh, Y.-H., Kim, H.-W. and Kim, H.-E., Improvement in oxidation resistance of $TiB_2$ by formation of protective $SiO_2$ layer on surface. *J. Mater. Res.*, 2001, **16**, 132–137.
14. Ownby, P. D. and Stewart, R. W. Engineering properties of diamond and graphite, *Engineered Materials Handbook, Vol. 4, Ceramics and Glasses*, ASM International, USA, 1991, pp. 821–834.
15. Kim, H.-E. and Moorhead, A. J., Effect of hydrogen-water atmospheres on corrosion and flexural strength of sintered α-silicon carbide. *J. Am. Ceram. Soc.*, 1990, **73**, 694–699.
16. Kim, H.-E. and Moorhead, A. J., High temperature gaseous corrosion of $Si_3N_4$ in $H_2$–$H_2O$ and Ar–$O_2$ environments. *J. Am. Ceram. Soc.*, 1990, **73**, 3007–3014.
17. Zheng, Z., Tressler, R. E. and Spear, K. E., Oxidation of single crystal silicon carbide. *J. Electrochem. Soc.*, 1990, **137**, 854–858.
18. Jacobson, N. S., Corrosion of silicon-based ceramics in combustion environments. *J. Am. Ceram. Soc.*, 1993, **76**, 3–28.