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The improvement in oxidation resistance of carbon by a graded SiC/SiO_2 coating

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Abstract

A dense functionally gradient SiC/SiO_2 coating has been developed to improve the oxidation resistance of carbon at elevated temperatures. SiC was coated on the surface of a graphite substrate by a reaction between thermally evaporated silicon and carbon at 1400 °C. The SiO_2 layer was deposited by exposing the SiC coated specimens next to a bed of Si powder in a flowing H_2–H_2O gas ($P_{H_2O} = 2.6\times10^{-2}$ atm) at 1400 °C. The formed SiC/SiO_2 layers were dense and had gradient compositions with good adhesion to the carbon substrate. However, as the coating thickness increased, the coating layer became cracked and delaminated from the substrate due to thermal stress. The specimens with the continuous SiC/SiO_2 layer showed a remarkably improved oxidation resistance up to 1200 °C.

Keywords: Carbon; Coatings; FGM; Oxidation resistance; SiC/SiO_2 coatings

1. Introduction

Many studies have been performed to improve the oxidation resistance of carbon-based materials over the past 60 years.[1] Two different approaches for the oxidation protection have been proposed: introduction of anti-oxidant additives such as Al, Si, and SiC in carbon-containing refractory materials,[2–5] and deposition or coating with refractory ceramics such as SiC, Si_3N_4, and oxide glasses, particularly, in carbon/carbon composites.[6–15] Among them, a SiC coating is considered to be most effective in protecting the carbon from oxidation at high temperatures up to 1700 °C. However, the SiC coating obtained by either chemical vapor deposition (CVD) or direct reaction with molten silicon contains many defects (pores, pinholes, or cracks) due to the large thermal expansion mismatch between the coating and the substrate.[11,12,15] These defects provide a path for oxygen to migrate to the underlying substrate. As a result, several efforts have been made to seal the cracks in the ceramic coating using a glass sealant,[6,12] a functionally gradient coating,[8,9] or a multilayer coating.[7,14] However, there are still unsolved issues such as the high cost and complex process which must be overcome for wider engineering applications.

In earlier work,[16] a SiO_2 layer was deposited onto the surface of carbon by exposing the carbon to a bed of SiC powder in a flowing H_2–H_2O gas at 1400 °C for 1 h. The SiO_2 coating layer improved the oxidation resistance of the carbon by more than a factor of 5. This improvement was attributed to the retardation of oxygen transport through the coating layer because the diffusion coefficient of oxygen through the SiO_2 layer is very low.[17] However, the SiO_2 coating layer was slightly cracked even though the layer initially appeared to be continuous, and the SiO_2 layer offered little protection from oxidation at temperatures above 800 °C. In some cases, the morphology of the deposited SiO_2 consisted of droplets instead of forming a continuous layer. A similar non-wetting behavior between glass and carbon/carbon composites has been observed previously.[6] For instance, the contact angle of glass on a C/C composite surface increased with increasing SiO_2 content in a binary SiO_2–B_2O_3 glass, that is, reflecting a decreased wettability.[6] In addition, a careful investigation showed

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that a continuous SiO_2 layer was formed when a thin SiC layer was formed between SiO_2 coating and carbon substrate.[16] It has been reported that SiO_2 has a better wettability to SiC than to carbon.[6,12] Therefore, in this study, two coating layers (SiC and SiO_2) were formed successively on the carbon block by chemical vapor reaction (CVR) and chemical vapor deposition (CVD), and the oxidation resistance of the coated specimens was examined.

2. Experimental procedure

The substrate material used in this experiment was a commercially available carbon block (Grade IG-15, Takuma, Tokyo, Japan), which was machined into a bar shape with dimensions of 3×4×25 mm. The specimens were ground with a 200-grit diamond abrasive wheel and subsequently polished with diamond pastes down to 1 μm. The polished samples were ultrasonically cleaned in acetone and ethyl alcohol followed by oven drying.

The SiC/SiO_2 coating on the carbon block was conducted in two steps. First, a SiC layer was coated on the surface of the substrate by CVR. Second, a SiO_2 layer was deposited on the SiC coated specimen by CVD. For SiC coating, the polished bars were loosely contacted with a Si powder (325 mesh, 99%, Aldrich Chemical Company Inc.) in an alumina tray, which was located in a resistance-heated alumina tube furnace with an Ar gas flowing system. The SiC coating was carried out at 1400 °C (below the melting point of Si, 1412 °C) for 2 h in an Ar atmosphere. During the coating process, solid Si was thermally evaporated and reacted with the carbon resulting in the formation of SiC on the surface of the substrate. For SiO_2 deposition, the SiC coated bars were placed next to a bed of Si powder in the same tube furnace with a H_2–H_2O gas flowing system. The water vapor pressure (P_{H_2O}) was controlled by bubbling H_2 in distilled water at various flow rates, which was measured with a hygrometer (MMS-35, Panametrics, Inc., Waltham, MA, USA). The SiO_2 coating was conducted at 1400 °C up to 4 h at a P_{H_2O} of 2.6×10^{-2} atm with a flow rate of 1.2 cm/s. Additional processing details are described elsewhere.[16]

Specimens with and without the coating layer were oxidized in air at temperatures between 600 and 1200 °C for 1 h. The heating rate was 10 °C/min and the specimens were furnace-cooled after the oxidation. The oxidation resistance was estimated by measuring the weight loss during the exposure. X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) were employed to determine the phase and composition of the coating layer, respectively. Scanning electron microscope (SEM) was used to observe the morphology of the coating layer.

3. Results and discussion

3.1. Formation of SiC/SiO_2 coating layers

The surface morphologies of the specimens before and after the chemical vapor reaction are shown in Fig. 1. The polished bars contained several voids on the surface [Fig. 1(A)]. After the reaction for 2 h, most of surface voids had either partially or completely disappeared and the surface appeared to be smooth [Fig. 1(B)]. During the reaction, there was a weight gain of 0.75 wt.% and it is believed that the voids were filled with the reaction products. The XRD patterns of the specimens before and after the reaction are shown in Fig. 2. Before the coating, there were only carbon peaks [Fig. 2(A)]. After the coating, the peaks for SiC were detected along with carbon peaks [Fig. 2(B)]. There was no SiO_2 peak observed, which indicates that oxidation was completely prohibited during the reaction. Therefore, the thermally evaporated Si reacted with carbon and formed SiC on the surface of the carbon block. A preliminary oxidation test (800 °C for 1 h) of the SiC coated carbon bar showed that the oxidation resistance was only slightly improved compared to the untreated

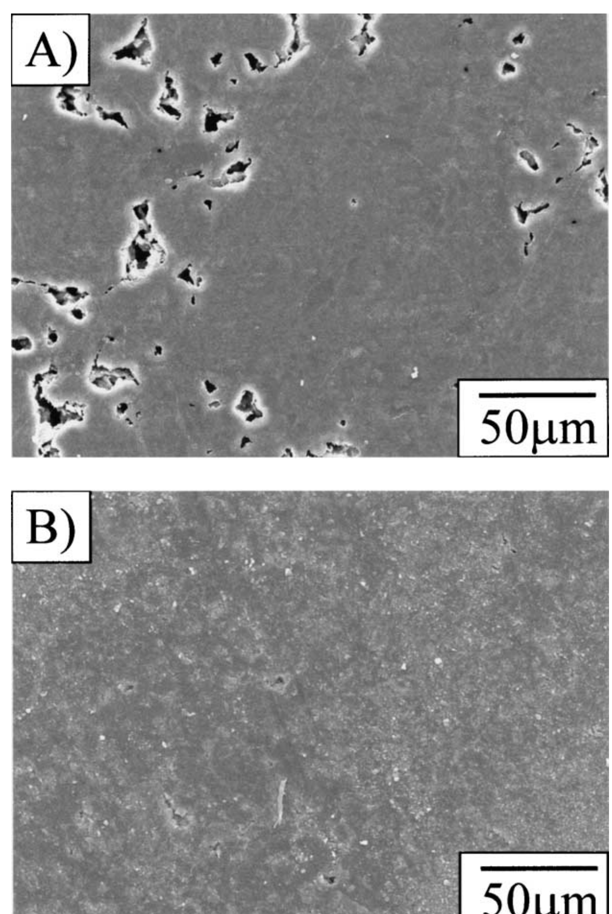

Fig. 1. Surface morphologies of the specimens (A) before and (B) after the SiC coating by CVR at 1400 °C for 2 h.

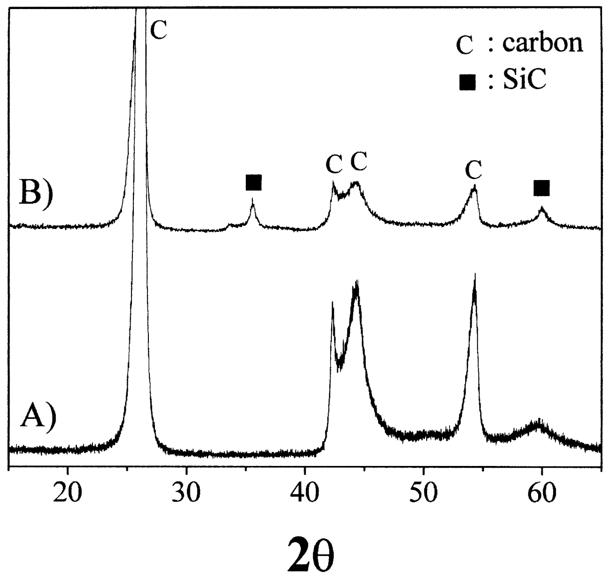

Fig. 2. XRD patterns of the specimens (A) before and (B) after the SiC coating by CVR at 1400 °C for 2 h.

carbon bar. It is believed that the coated SiC does not form a dense and continuous layer to prevent the oxygen diffusion.

When a Si powder is exposed to H_2–H_2O atmosphere at evaluated temperature, an active or passive oxidation occurs depending on the water vapor pressure (P_{H_2O}).[18] If the P_{H_2O} is low, an active oxidation occurs by generating SiO gas according to the reaction:

$$Si(s) + H_2O(g) = SiO(g) + H_2 \quad (1)$$

If the P_{H_2O} is too high, a passive oxidation occurs by forming a protective SiO_2 film, as shown in the reaction:

$$Si(s) + 2H_2O(g) = SiO_2(s) + 2H_2 \quad (2)$$

A SiO_2 smoke is formed in the active–passive transition when the partial pressure of SiO gas is sufficiently high. The SiO_2 deposition was conducted in this regime and the optimum P_{H_2O} for SiO_2 deposition was experimentally determined to be 2.6×10^{-2} atm in this study.

The surface and fracture surface morphologies of the specimen (SiC pre-coated) deposited with SiO_2 at 1400 °C for 1 h in H_2–H_2O atmosphere with P_{H_2O} of 2.6×10^{-2} atm are shown in Fig. 3. The surface was completely covered with a continuous layer [Fig. 3(A)] and the deposited layer firmly adhered to the substrate [Fig. 3(B)] although there were still some fine cracks present. The thickness of the coating layer was estimated to be ~3 μm. The XRD pattern showed that the coating layer consisted of SiO_2 (cristobalite) and SiC (Fig. 4) suggesting that SiO_2 was deposited on the surface and subsequently crystallized into cristobalite during the CVD process. The composition profiles for a cross-section of a SiC/SiO_2 coated specimen measured by the line scanning mode in EDS are shown in Fig. 5.

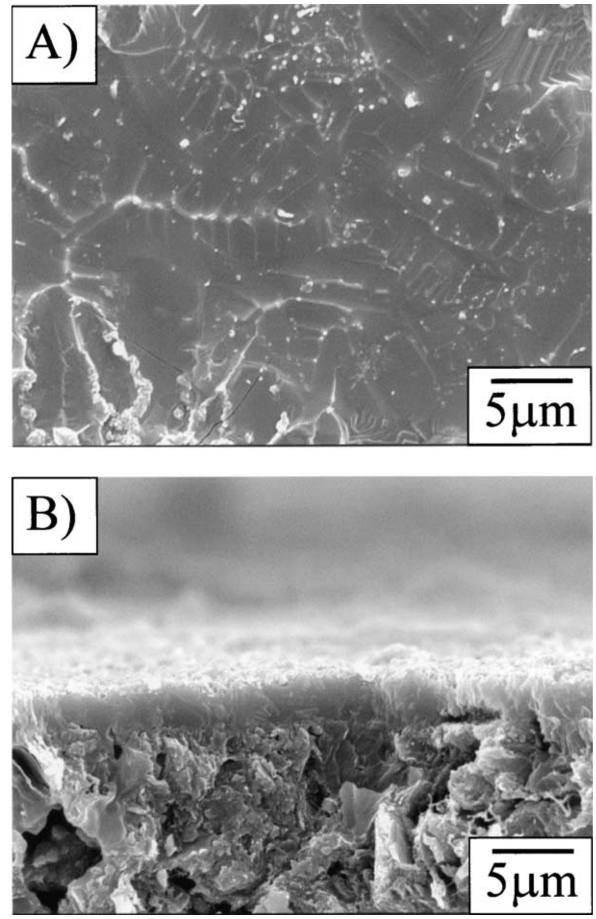

Fig. 3. (A) Surface and (B) fracture surface morphologies of the SiO_2 deposited specimen (SiC pre-coated) at 1400 °C for 1 h.

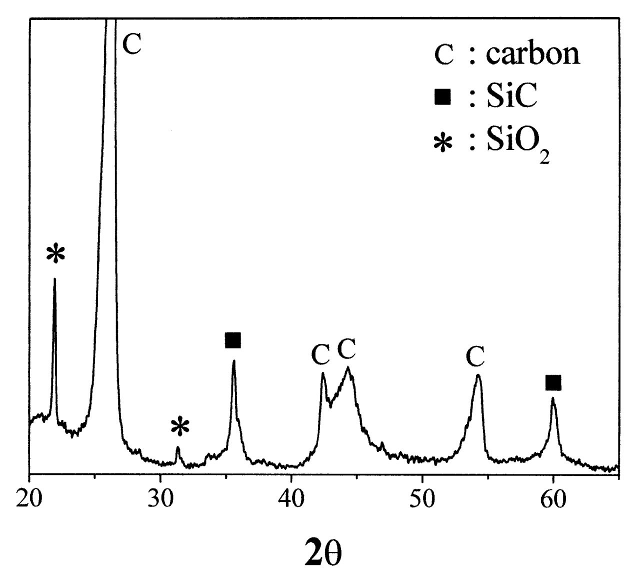

Fig. 4. XRD pattern of the SiO_2 deposited specimen (SiC pre-coated) at 1400 °C for 1 h.

The concentration of silicon (Si) was almost constant from the surface to 1.5 μm and decreased gradually up to 4 μm. The oxygen (O) concentration decreased gradually

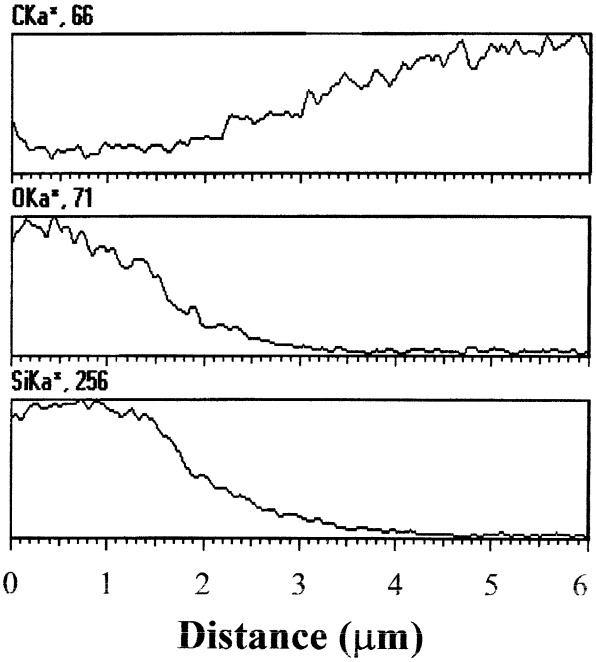

Fig. 5. The elemental distribution profiles for a cross-section of the SiO_2 deposited specimen (SiC pre-coated) at 1400 °C for 1 h by a line scanning mode in EDS.

up to 3.5 μm while the carbon concentration (C) increased between 2 and 4 μm. There was no distinct composition boundary to distinguish the SiO_2, SiC, and carbon layer and further work such as TEM is necessary to estimate the thickness of each layer. This fact indicates that the two step processes (CVR and CVD) produced compositionally graded SiC and SiO_2 layers on the surface of carbon. It appears that the graded SiC/SiO_2 layers resulted in good adhesion to the substrate by reducing the thermal and wettability mismatch.

An increase in the deposition time to 2 h resulted in an increase in the coating thickness to 4 μm. However, the surface and fracture surface morphologies showed that the coating layer was slightly cracked and began to delaminate, as shown in Fig. 6. Further increase of the deposition time (4 h) resulted in severe cracks on the surface and part of the coating layer had peeled off from the substrate. The cracking and delamination is due to the thermal expansion mismatch between the coating layer (SiO_2) and the substrate. When the SiO_2 coating layer is relatively thin, a good bond strength between the coating layer and the substrate is maintained. As the thickness of the coating layer increases, stress from the thermal expansion mismatch increases, which eventually results in surface cracking and delamination of the coating layer. Therefore, the optimum deposition time for a continuous, well-bonded SiO_2 layer on the SiC coated carbon substrate under a P_{H_2O} of 2.6×10^{-2} atm is 1 h.

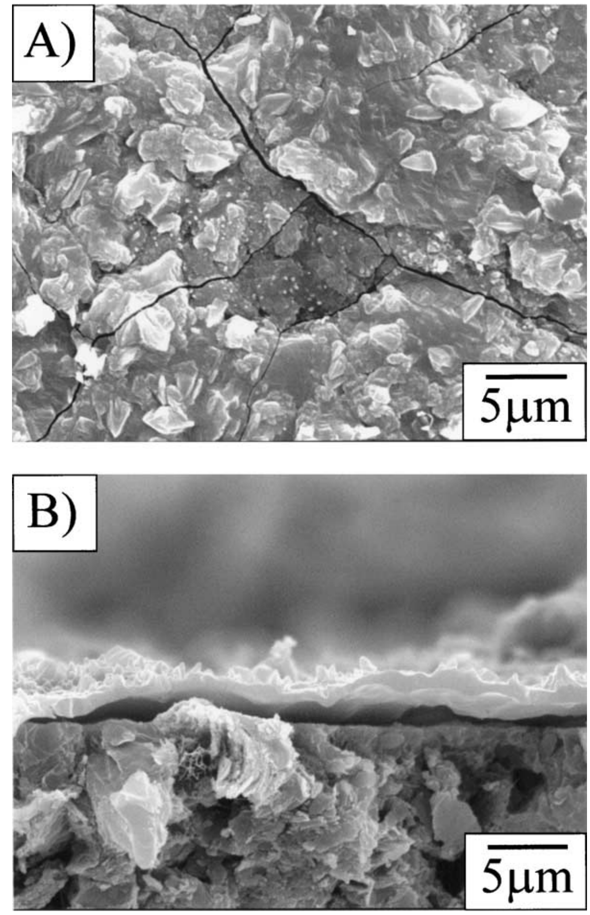

Fig. 6. (A) Surface and (B) fracture surface morphologies of the SiO_2 deposited specimen (SiC pre-coated) at 1400 °C for 2 h.

3.2. Evaluation of oxidation resistance

The effect of the SiC/SiO_2 coating layers on the oxidation resistance was evaluated by monitoring the weight loss of the specimens exposed to air at elevated temperatures for 1 h. Fig. 7 shows the weight changes during isothermal oxidation for the samples with and without the coating layers. A significant weight loss occurred in the specimen without the coating layer, which reached up to 98% when exposed at 800 °C. In contrast, the weight loss was significantly reduced in samples with the SiC/SiO_2 coating layers and thus, the oxidation resistance was remarkably enhanced. A negligible weight loss was observed for the samples with the coating layers when exposed at 600 °C for 1 h. With increasing temperature, the weight loss increased gradually and reached up to 20–30% at 1200 °C depending on the SiO_2 deposition time. The specimen with the SiO_2 coating deposited for 4 h had a higher weight loss than the others although it had a thicker SiO_2 coating layer. This is due to the severe surface cracks on the coating layer, which provide an oxygen path to the carbon. However, it should be noted that the increase of the weight loss slowed down after 800 °C for the specimen

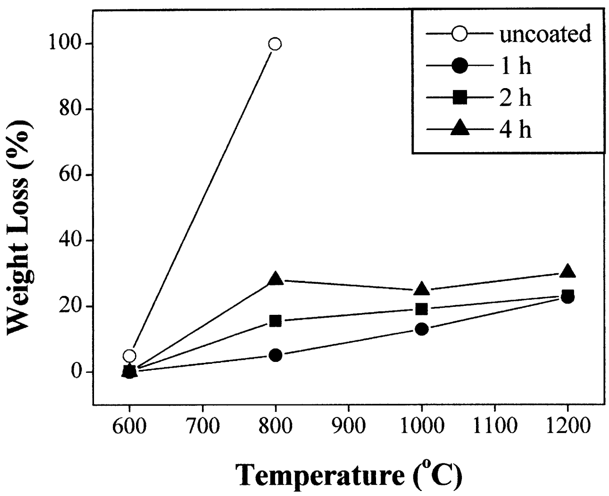

Fig. 7. Weight changes of the specimens exposed to air at various temperatures for 1 h; (A) uncoated and SiO_2 deposited specimens (SiC pre-coated) for (B) 1 h, (C) 2 h, and (D) 4 h.

deposited for 4 h. In a previous study,[14] different oxidation mechanisms were proposed depending on the different temperature ranges for carbon–carbon composites with a three layer coating; oxidation through the cracks at low temperature, sealing of the coating cracks, and oxidation through the coating at high temperature. Based on the suggested mechanisms, the leveling off of the weight loss in the samples deposited for 4 h could be attributed to the occurrence of crack healing. When the surface cracks are sealed, the oxidation is controlled by the diffusion of oxygen through the oxide film and oxidation is then retarded because the diffusion coefficient of oxygen through the SiO_2 layer is very low.[17]

Fig. 8 shows the surface morphologies of the SiC/SiO_2 coated specimens after the oxidation test. After being exposed to air at 800 °C, there were micro-cracks on the surface but the continuous SiC/SiO_2 layer was still preserved [Fig. 8(A)]. However, the specimen exposed at 1200 °C showed severe surface cracks and pinholes, and the integrity of the coating layer was considerably damaged.

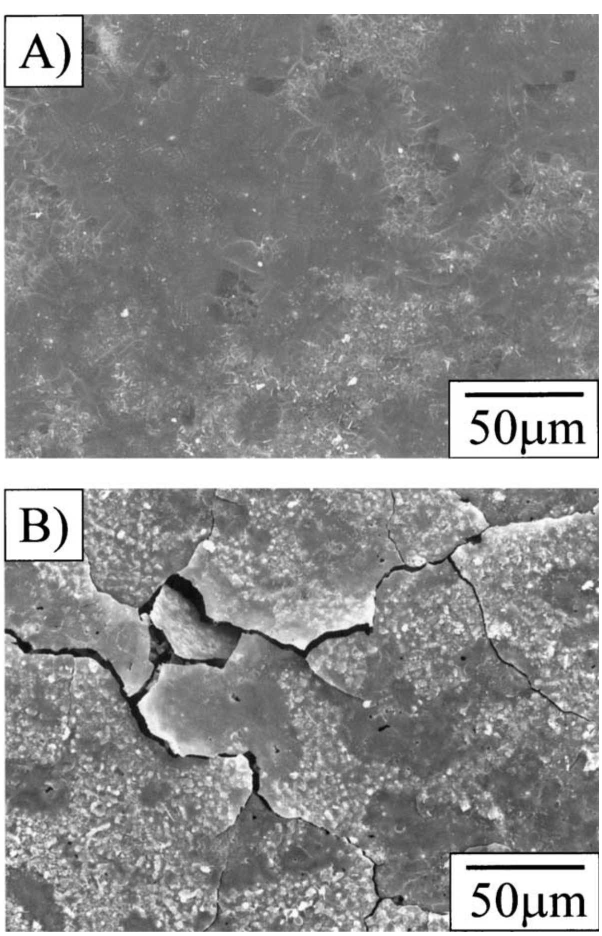

Fig. 8. Surface morphologies of the specimens after isothermal oxidation at (A) 800 °C and (B) 1200 °C for 1 h.

4. Summary and conclusion

A two step process, CVR and CVD, successfully produced dense, compositionally gradient SiC/SiO_2 layers on the surface of the carbon substrate. The intervening SiC layer greatly reduced the thermal expansion mismatch and the wettability between the SiO_2 layer and the substrate resulting in relatively crack-free and well bonded coating layers. The continuous SiC/SiO_2 layer effectively enhanced the oxidation resistance of carbon up to 1200 °C.

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