Functionally gradient ceramic coating for carbon–carbon antioxidation protection

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Abstract

Functionally gradient ceramic coating provides an effective antioxidant protection to carbon/carbon composites at intermediate temperatures (below 1000°C) by the formation of a B_2O_3 glass from the oxidation of boron phases. The glass flows and seals the cracks to prevent further oxygen penetration. A protection layer based on SiC, B_4C and $Al_8B_4C_7$ phases was obtained by carbon conversion of the composite using a pack cementation process with a powder mixture of the ZrB_2–SiC–Al_2O_3 system. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

SiC ceramic coatings provide excellent antioxidation protection to carbon-carbon composites at high temperatures. Such coatings are refractors and oxidation resistant due to silica thin film formation. The very low oxygen permeability provides good oxidation protection.[1,2]

Ceramic coatings applied to carbon/carbon composites then have microcracks due to the CTE (coefficient of thermal expansion) mismatch of the coating material ($\alpha_{SiC} = 5 \times 10^{-6}$ K^{-1}) and the carbon substrate ($\alpha_{C/C} = 1 \times 10^{-6}$ K^{-1}) in the fiber direction.[3]

Microcracks create a free path for oxygen penetration, causing protection failure. This failure occurs between the temperature of carbon oxidation and that of the recovery of coating protection. In this temperature range, the viscosity of the SiO_2 is too high to flow, and crack sealing will not occur.[4]

Vitreous sealant can be applied to the external surface of the protection layer to overcome this problem. Borate glasses, phosphates, zircon, mullite and modified SiO_2 with TiO_2, LiO_2 and Al_2O_3 addition are used for this purpose. Several cycles of impregnation and thermal treatment are needed to obtain a glass coherent layer.[5–7]

Multilayer coating is another technique used as ceramic coating, based on deposition of glass former materials by CVD process, both internal or external to the SiC layer. Long periods of time are necessary to form a satisfactory layer and cracks at interfaces have been reported.[8–11] The high cost of advanced coating systems also limits the commercial applications of C–C composites.

This work suggests a gradient functional coating based on SiC and a B_4C concentration gradient layer, formed by the use of a pack process, with a mixture from the ZrB_2/SiC/Al_2O_3 system. The superficial carbon is converted to SiC, without cracks or defects at the substrate/coating interface.

2. Experimental procedure

A commercial 2D carbon-carbon composite (CFRC), Kkarb Type A, provided by Kayser Aerotech Inc was used in this work. It is basically a laminated composite, with rayon-based carbon fibers in a five-harness satin weave in a carbon matrix, derived from a resin/pitch blend, specific gravity 1.36 g/cm^3 and 45% fiber volume.

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The CFRC rectangular sample, with $7 \times 5 \times 3.5$ mm^3 dimensions, was covered by a powder mixture of 40 $ZrB_2 + 50$ SiC + 10 Al_2O_3 wt.% and packed in a graphite crucible with dimensions $50 \times 50 \times 50$ mm^3. ZrB_2 and α-SiC were provided by Elektroschmeltzwerk Kempten GmbH (15 and 1 μm particle size respectively) and the α Al_2O_3 was SG A-16 Alcoa (sub-micron particles). The graphite crucible with the sample and powder mixture was dried for 16 h at 200°C and heat treated for 6 h at 1600°C, with a heating rate of 10°C/min in an argon flow of 100 ml/min in a tubular graphite furnace. After cooling, the composite was removed from the graphite crucible, and its surface ultrasonically washed in acetone for 5 min. Scanning electron microscope (SEM) was used to perform a cross-section examination of the as-formed and oxidized coating. EDS was
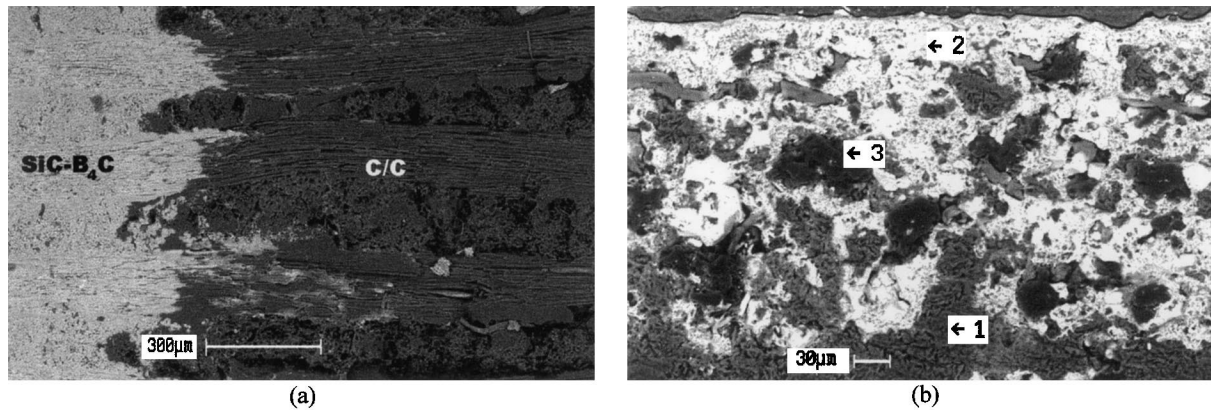

Fig. 1. SEM micrography of C–C/SiC–B$_4$C composite: (a) cross-section of the converted layer and (b) details of the coating microstructure.
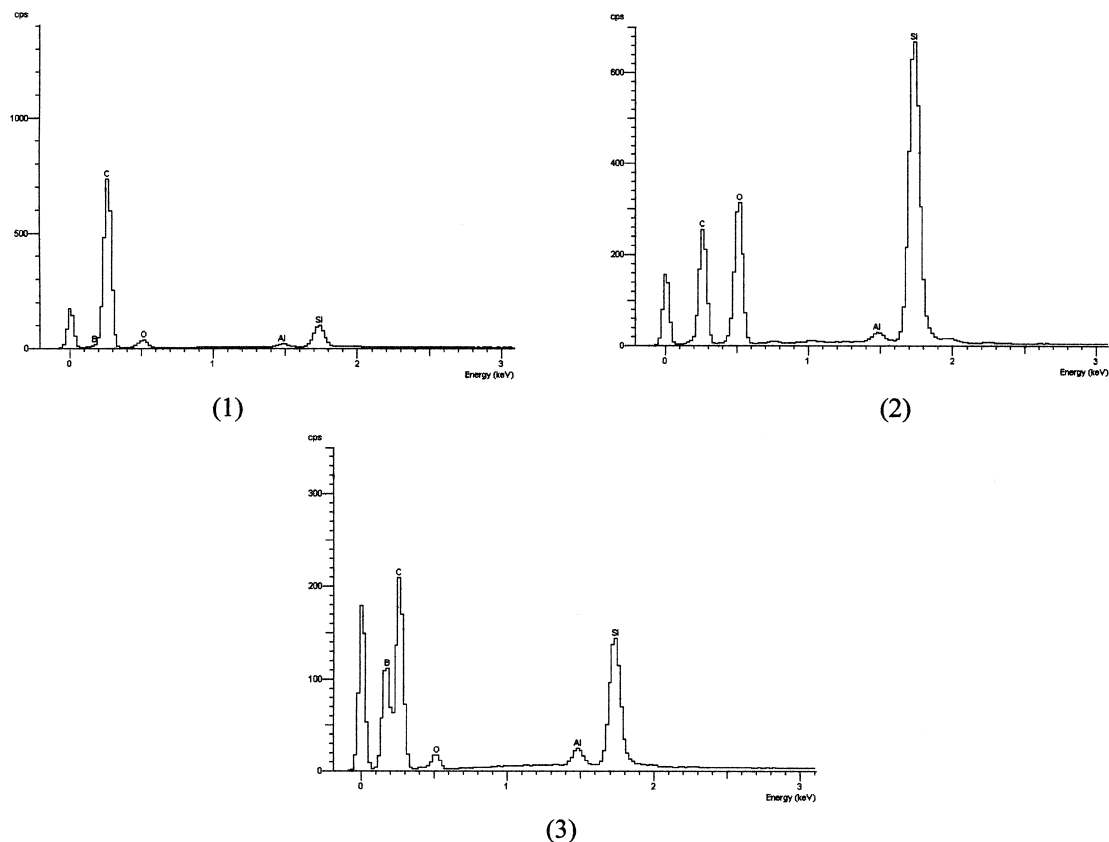

Fig. 2. EDS spectrogram of the points designated by the numbers in Fig. 1(b).

employed to provide chemical elementary analysis. The phase identification through the thickness of the coating layer was performed by X-ray diffraction. A layer of 50 μm was removed by conventional ceramografic procedure before each analysis.

The oxidation resistance of two coated composites was evaluated using thermogravimetric analysis (TGA) on a Dupont 2100 Analyzer. Rectangular test specimens with $7\times5\times3,5$ mm^3, previously dried were loaded onto a platinum basket sample holder. They were subsequently heated with a rate of $10°C/min$, from room temperature to $800°C$ under a dry air (< 5000 ppm moisture) flow of 100 ml/min, remaining for 3 h at this temperature.

3. Results and discussion

The SEM microstructure related to the cross section of the converted layer is shown in Fig. 1. The coating thickness is around 200 μm, and appears to be uniform where the fiber bundles are parallel to the surface. Higher coating penetration occurs where fiber bundles are perpendicular to the surface, and this feature is related to the easier penetration of reaction gas through the cracks at matrix/fibers interface. No discontinuities (cracks or adhesion) are observed between the coating and substrate. Fig. 1(b) shows a microstructure, with higher magnification. The EDS spectrograms obtained from the points designated by numbers 1–3 are summarized in Fig 2. It shows the carbon substrate (1) and two distinct regions of the coating: a bright region rich in Si (2) and dark particles rich in boron and Si (3).

Fig. 3 shows the X-ray diffraction pattern of the coating obtained at its surface and at each 50 μm of its thickness. The identified phases at the sample surfaces were β-SiC and $Al_8B_4C_7$, from the conversion reaction, and ZrB_2 from the powder mixture. At 50 μm depth, $βSiC$ and $Al_8B_4C_7$ phases were identified. At 100 μm the phases $βSiC$, $Al_8B_4C_7$ and B_4C were present. The obtained coating described in this work has a β-SiC matrix, with a dispersed $Al_8B_4C_7$ phase, and a inner region rich in B_4C. Such coating shows a compositional gradient from the surface to the inner layers.

Weight change occurs by oxidation of the carbon–carbon coated with the compositional gradient layer, at $800°C$ in dry air. The results were compared with those obtained with samples subjected to a pack mixture 60 $SiC + 30$ $Si + 10$ Al_2O_3 wt.%, reported by Rogers,[6] heat
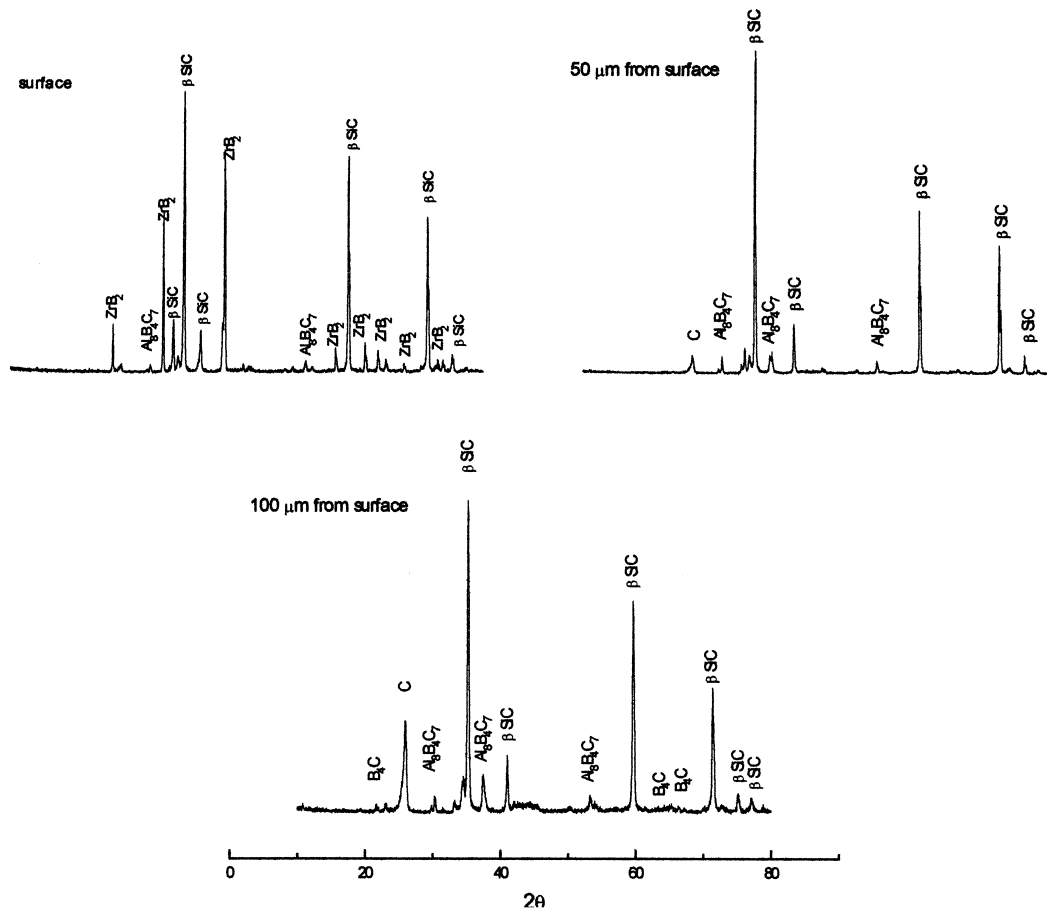

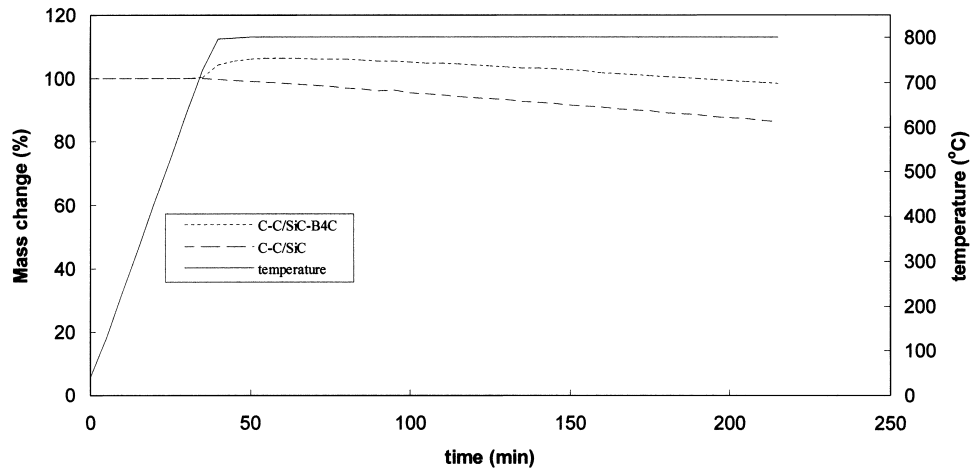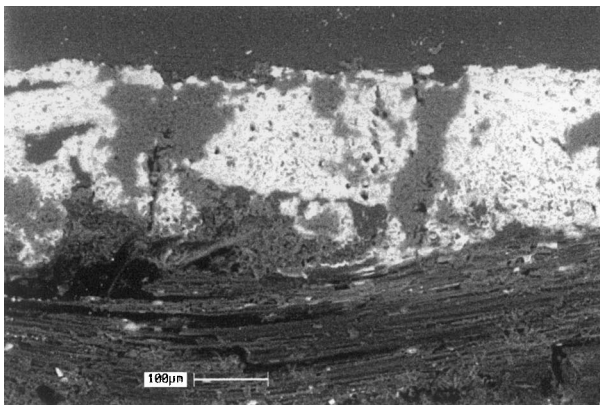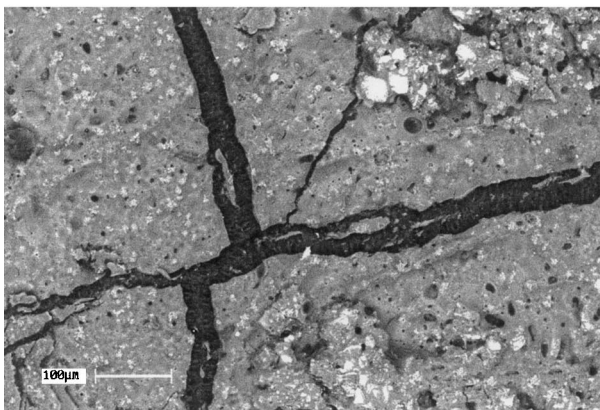Fig. 3. XRD pattern of the as-formed coating layer.

Fig. 4. Mass change during oxidation in air for C–C/SiC–B$_4$C and C–C/SiC–Si composites.

(a)

(b)

Fig. 5. SEM micrography of C–C/SiC-B4C after oxidation in air at 800°C: (a) cross-section of the coating and (b) cracks sealed on surface.

treated at 1700°C for 3 h in Argon atmosphere. The coating, in this case, consists of a βSiC and Si phases (SiC/Si coated C–C).

At 700°C the SiC/ZrB$_2$/Al$_2$O$_3$ coated composite initially gains weight; it then loses weight with time on exposure at 800°C, while the SiC/Si coated C–C loses
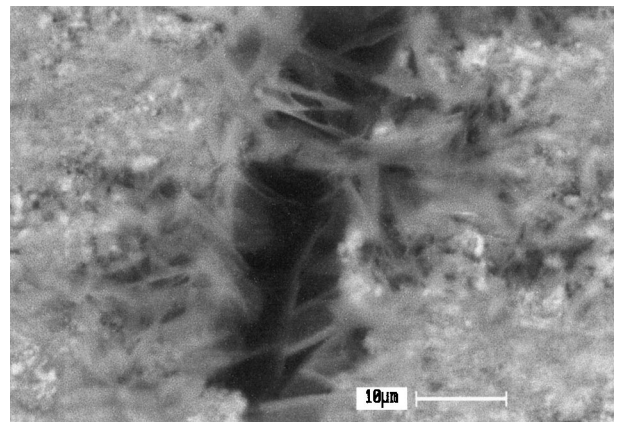

Fig. 6. SEM micrography of the crack sealed by glass.

weight continuously at 800°C (Fig. 4). A low level peak of B$_2$O$_3$ and some ZrO$_2$ peaks are identified in X-ray diffraction of the oxidized surface, indicating B$_2$O$_3$ glass formation from the oxidation of boron phases inside the cracks and at the surface by oxidation of ZrB$_2$ to form ZrO$_2$ and B$_2$O$_3$. The B$_2$O$_3$ glass formed from the B$_4$C at the inner layer of the coating flows along the walls of the SiC sealing the cracks. This feature can be observed in Fig. 5. The dark region is related to the presence of glass with lower atomic weight elements.

The efficiency of the self healing mechanism of the gradient functionally coating SiC/B$_4$C can be evaluated by the total mass changes after 3 h at 800°C, that is a gain around 2% with respect to this initial mass compared with a 15.57% loss of SiC/Si coating without sealants.

The EDS spectrograms of the glass inside the cracks (Fig. 6), shown in Fig. 7, indicates a rich boron glass at the base of the cracks and a rich silicon glass near the surface, probably a borosilicate glass. This results confirm that the B$_2$O$_3$ glass is initially formed at the inner layer, flows to the surface and reacts with silica from the SiC walls to form a borosilicate glass.
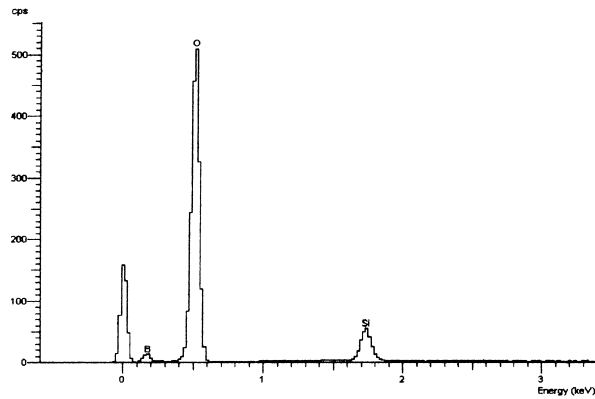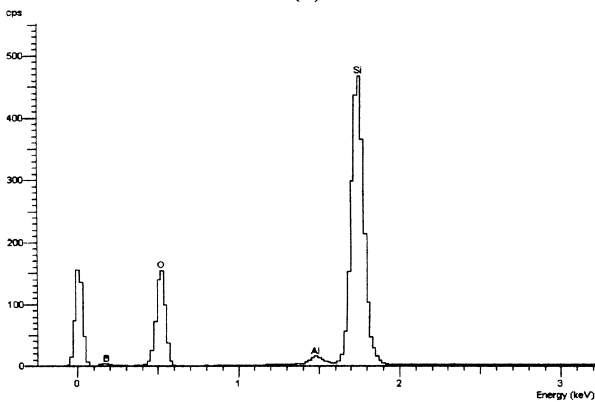
Fig. 7. EDS spectrogram of the glass inside the crack (a) near the substrate surface and (b) near the external surface.

At temperatures above 1000°C the antioxidant protection is based on SiO_2 thick films, generated from SiC oxidation. The protection is limited to 1300°C, for a short time exposure. Failure is caused by the disruption of the coating, originated by gas released from the reaction between the substrate and the coating phases.

4. Conclusions

A functionally gradient ceramic coating, incorporating a compositional gradient between SiC and B_4C in the coating layer, is formed by application of a pack cementation process using a mixture of 40 ZrB_2 + 50 SiC + 10 Al_2O_3 wt.%. This coating provides antioxidation protection for carbon–carbon composites at temperatures below 1000°C by the development of a self healing systems due to the oxidation of the boron phase, without the application of sealants over the coating surface.

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