

The oxidation behaviour of two- and three-dimensional C/SiC thermostructural materials protected by chemical-vapour-deposition polylayers coatings

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The oxidation behaviour of two- and three-dimensional C/SiC protected by a chemical-vapour-deposition (CVD) ceramic coating was studied. The elements used to achieve the surface protection were silicon, boron and carbon, preferably forming SiC, B or B₄C. The best results were obtained with the trilayer coatings, that is with, SiC as the internal layer, boron or boron carbide, as the intermediate layer and an external SiC layer. To get a good protection in a large temperature range, from 450 to 1500 °C, the total thickness of the trilayers must be higher than 160 µm and the intermediate layer thickness must be higher than 5 µm. Morphological characterization of oxidized samples has shown that, for intermediate oxidation temperatures, a glass was produced in the cracks. When the oxidation temperature was equal to or higher than 1300 °C, sealing of the cracks was rarely observed, but the oxidation resistance remained satisfactory.

1. Introduction

To widen the application range of carbon-carbon materials restricted by oxidation at high temperatures, ceramic-matrix materials with carbon-fibre reinforcement have been developed [1]. The high strength and exceptional fracture toughness of these composites, combined with their refractory properties and their resistance to erosion, corrosion and wear, make them ideal candidates for numerous advanced high-temperature structural applications. But this type of material is characterized by a non-negligible porosity (especially between the sheets of two-dimensional (2D) materials) and by internal and external multicracking due to the differences between the thermal coefficients of expansion of the fibres and the SiC matrix and because of the manufacturing thermal stress. So it is necessary to deposit a sealing coat to perfect the protection of the carbon fibres. In fact, high refractory and oxidation-resistant ceramic coatings are able to provide a helpful contribution to the solution of this problem, as has been pointed out [2]. But the refractory coatings are not efficient at both low and high temperatures, so protection by one coating in a wide temperature range is difficult to achieve. The solution, which consists of associating different layers with complementary oxidation properties, was developed in a previous study [3]. The elements Si-B-C and

especially elemental boron or the compounds SiC or B₄C were chosen in order to provide this protection. From the different solutions (based on a polylayer concept) which were tested, a trilayer coating gave excellent results in the protection of two-dimensional or three-dimensional (3D) C/C composites. This trilayer is made of an internal SiC layer, an intermediate boron or boron-carbide layer and an external SiC layer [3].

The same type of protection, deposited by a chemical-vapour-deposition (CVD) technique is tested here on two-dimensional and three-dimensional C/SiC from 450 to 1500 °C in air. The influence of the total thickness and of the intermediate-layer thickness was also studied. The airtightness and the ability of repairing cracks caused by a mechanical stress were estimated at ambient temperatures after high-temperature cycles. The protection mechanism is partially explained using a morphological study of oxidized samples.

2. Preliminary aspects

2.1. The choice for the multilayer coating

A previous study [3] justified the choice of the three elements silicon, boron and carbon and the way of associating them in a multilayer coating to achieve a

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good protection of two-dimensional and three-dimensional C/C against oxidation. The main advantage in the development of a multilayer coating is the possibility of associating complementary specific properties and of gaining the advantages of each layer while limiting their drawbacks. Moreover, the problem of the protection of the two-dimensional or three-dimensional C/SiC materials is not fundamentally different from the problem encountered in the protection of two-dimensional or three-dimensional C/C composites.

The main difference is due to the SiC matrix, which, while being intrinsically oxidation resistant is micro-fissured so that oxygen can still access the carbon fibres especially at low and intermediate temperatures (450–1000 °C). So the trilayer coatings (which have given excellent results for the protection of two-dimensional or three-dimensional C/C) were tested on two-dimensional and three-dimensional C/SiC. The efficiency of this protection will be compared with the protection achieved using one SiC monolayer.

2.2. Experimental techniques.

2.2.1. CVD devices

The experimental set-up has been described in detail elsewhere [3]. The experiments were made inside a hot-wall reactor. A graphite susceptor (where the samples are hung) was heated with a high-frequency generator. The mixing gas was introduced from a nozzle from the bottom, to induce the natural and the forced convection. In all the experiments, a constant mass-flow rate was employed. The hydrogen and methane used had a volume purity of 99.995%; and the boron trichloride and the methyltrichlorosilane (MTS) used had a volume purity of 99.9%.

2.2.2. Substrates

The substrates were fine-textured prepolished graphite with an average density of 1.75, they were cleaned in alcohol in an ultrasonic device and dried, to measure the deposition rate and two-dimensional C/SiC or, less commonly, three-dimensional C/SiC composites provided by Société Européenne de Propulsion (SEP) for the oxidation tests. The size of the samples was $20 \times 10 \times 2 \text{ mm}^3$ for two-dimensional C/SiC, $20 \times 10 \times 3 \text{ mm}^3$ for the three-dimensional C/SiC and cylindrical sheets – of diameter 25 mm and thickness 2 and 5 mm respectively for the two-dimensional C/SiC and three-dimensional C/SiC – were used for the airtightness tests.

2.2.3. The oxidation device

The cyclic oxidation tests were made in Laboratoire de Combustion et Systèmes Réactifs (LCSR) and the SEP laboratories. The oxidation device and the test procedure were described in a previous paper [3]. The mass variation $\Delta m/m$ (in wt %) was measured as a function of oxidation time.

2.2.4. Characterization of the deposits

A precision balance gave the mass increase of each sample after deposition. The thickness measurements were obtained on polished cross-sections with the help of a metallographic microscope.

The chemical composition of the SiC deposits was obtained from an electronic microprobe analysis by measuring the Si content, and it was obtained for B₄C with a nuclear method described in [4]. A metallographic microscope and scanning electron microscopy (SEM) were used to study the morphologies of the oxidized samples.

2.3. CVD of B, B₄C and SiC

The choice of the experimental conditions for each type of layer of the coating was justified in a previous study [3]. So the same experimental parameters were chosen for the deposition of SiC, B and B₄C.

$$\text{SiC: } \alpha = [\text{H}_2]_0/[\text{MTS}]_0 = 10, T = 1127^\circ\text{C},$$

$$F = 0.320 \text{ g min}^{-1} \text{ and } P = 0.395 \text{ atm.}$$

$$\text{B: } [\text{H}_2]_0/[\text{BCl}_3]_0 = 22, T = 1027^\circ\text{C},$$

$$F = 0.400 \text{ g min}^{-1} \text{ and } P = 0.395 \text{ atm.}$$

$$\text{B}_4\text{C: } [\text{H}_2]_0/[\text{BCl}_3]_0 = 3.7, [\text{BCl}_3]_0/[\text{CH}_4]_0 = 3.5,$$

$$T = 1050^\circ\text{C}, F = 0.320 \text{ g min}^{-1} \text{ and}$$

$$P = 0.395 \text{ atm.}$$

where $[X]_0$ represents the initial number of moles of X, α the inlet molar ratio, T the temperature, F the total mass flow rate and P the total pressure.

These conditions allowed high deposition rates to be obtained typically $10\text{--}30 \mu\text{m h}^{-1}$, so that many samples can be produced for the oxidation tests in the shortest time. Each layer was deposited in at least two treatments. At every operation, the tungsten wire which was used to hang the samples up was displaced, and the samples were turned upside down. So it was possible to obtain protection on all the surfaces of the samples and the problem of the thickness non-uniformity which results from these high deposition rates was solved.

3. Two-dimensional C/SiC protection against oxidation, from 450 to 1500 °C

Before setting out the results of the oxidation tests and the microstructural study, it is necessary to specify the sources of weight gain or loss produced by the oxidation. The weight gain can arise from the oxidation of boron or the boron carbide into boron oxide ($\Delta m/m = +218 \text{ wt } \%$ and $\Delta m/m = +155 \text{ wt } \%$, respectively) or from the oxidation of silicon carbide into silicon dioxide ($\Delta m/m = +50 \text{ wt } \%$). On the other hand, weight loss occurs when the carbon of the fibres is oxidized, and possibly when the B₂O₃ oxide or a borosilicate oxide is vaporized above 850 °C.

The $\Delta m/m$ values given in the Figures 1, 3, 4, 8–11, are the results of these combined effects, and accurate conclusions can only be derived from additional information given by examination of the microstructures.

3.1. Oxidation tests results and morphological analysis

At $T = 450^\circ\text{C}$, the cracks which remain in the refractory deposits were widely open because the oxidation temperature was very different from the deposition temperature. In contrast, at 450°C , the reactivity of the carbon with oxygen was relatively low as is shown by the weight loss of an uncoated two-dimensional C/SiC fibre after a time $t = 60$ h (run number NC1, $\Delta m/m = -2.3$ wt %) in Fig. 1. A $60\ \mu\text{m}$ SiC monolayer deposited on all the surface of a two-dimensional C/SiC fibre contributes to the reduction in the weight loss (run number C1 $\Delta m/m = -0.2$ wt % at $t = 60$ h). The weight loss was again reduced when the protection was assumed to be a trilayer deposit which, however, had a higher total thickness (run numbers 298 and 302 with $\Delta m/m = -0.04$ wt % and $\Delta m/m = -0.06$ wt %, respectively).

In this case, it seems that the total thickness plays a more important role than the formation of an oxide, which remains very limited at 450°C . When the route for the oxygen to reach the carbon fibres through the cracks of the coating is longer, the oxidation is more limited. In fact, the diffusion in the gas phase of the oxygen and of the products of the carbon oxidation is reduced; this is also a result of the intermediate boron or boron carbide layer allowing a little reduction of the width of the cracks due to the growth of a solid oxide.

Examination (Fig. 2) of a polished cross-section of sample number 298 showed that the fibres are oxidized very little or not at all; this confirmed the efficiency of the protection. It should be noticed that this good protection was obtained in spite of some crack propagation which was observed between the boron-carbide intermediate layer and the two SiC layers in Fig. 2.

carbon was much higher than at 450°C . A sample without any external protection on its machined faces (run number NC2) exhibited a weight loss of $\Delta m/m = -33$ wt % after only 1 h. At this temperature, the

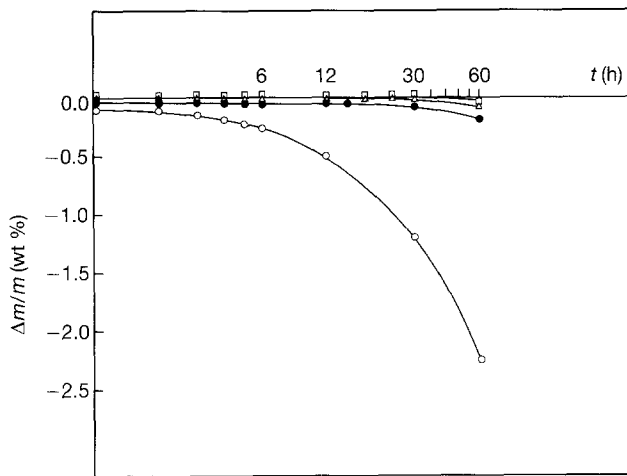


Figure 1 The two-dimensional C/SiC cyclic oxidation tests at 450°C in air, ($\Delta m/m = f(t)$ in wt %): (□) 298, SiC ($90\ \mu\text{m}$) + B_4C ($50\ \mu\text{m}$) + SiC ($60\ \mu\text{m}$); (Δ) 302, SiC ($90\ \mu\text{m}$) + B_4C ($15\ \mu\text{m}$) + SiC ($60\ \mu\text{m}$); (○) NC1, uncoated, and (●) C1, SiC ($60\ \mu\text{m}$).

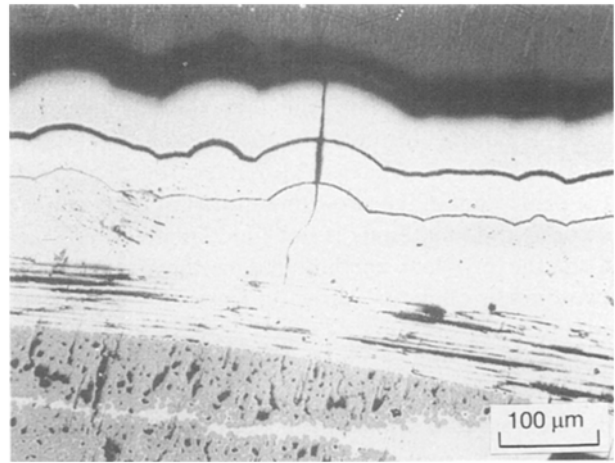


Figure 2 A polished cross-section of run number 298 after the cyclic oxidation tests at $T = 450^\circ\text{C}$.

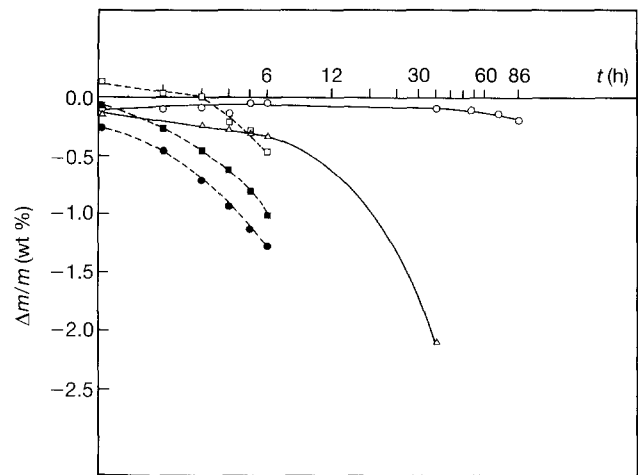


Figure 3 The two-dimensional C/SiC cyclic oxidation tests at 850°C in air, ($\Delta m/m = f(t)$ in wt %): (□) 149, SiC ($30\ \mu\text{m}$) + B_4C ($3\ \mu\text{m}$); (■) 146, B_4C ($3\ \mu\text{m}$) + SiC ($30\ \mu\text{m}$); (●) 145, B ($2\ \mu\text{m}$) + SiC ($30\ \mu\text{m}$); (○) 157, SiC ($180\ \mu\text{m}$); (Δ) 157, SiC ($120\ \mu\text{m}$); NC2, uncoated ($\Delta m/m = -33$ wt %).

boron or the boron-carbide oxidation was also faster than at 450°C and this can lead to a fusible oxide. So the production of this boron oxide may be capable of sealing the cracks of the deposits. This sealing may be made easier by the fact that the cracks partially close as the oxidation temperature approached the deposition temperature.

Fig. 3 shows the behaviour of samples covered either by SiC monolayers or by thin bilayers made of boron or boron carbide and SiC. The oxidation of two-dimensional C/SiC is not prevented by $30\ \mu\text{m}$ thick bilayers. The time corresponding to a weight loss of $\Delta m/m < -2$ wt % does not seem to exceed about 10 h (run numbers 149, 146 and 145). Run number 149 had an initial weight gain corresponding to the oxidation of the boron carbide on all the surface of the sample. Then a continuous weight loss appeared as soon as the oxide film began to flow by gravity or to vaporize, removing the protection. For run numbers

146 and 145, the boron or the boron carbide stays under the SiC layer. So small quantities of boron oxide were confined inside the cracks, and the direct initial weight loss gave a better idea of the oxidation of the substrate through a thin fusible oxide in direct contact with carbon.

Fig. 4 shows the oxidation resistance of the trilayer coatings. When the total thickness was equal to about 40 μm , the trilayers ensured better protection than the bilayers in terms of the weight loss (run numbers 151, 152 and 148). Moreover, the increase in the total thickness seemed to have a positive effect on the oxidation resistance of the coated substrates.

When the thickness was higher than 160 μm and when a boron-based intermediate coating existed (see Fig. 4, run numbers 158, 297 and 301), there was either no weight loss for a long oxidation duration (run numbers 301 and 158) or there was a low weight gain when the boron-based coating was thick (run number 297). In this last case, the boron-based oxide production was favoured.

At 850 $^{\circ}\text{C}$, the best protection was obtained by trilayers with a total thickness higher than 160 μm and an intermediate layer with a thickness between 5 and 50 μm

Nevertheless, 5 μm seems to be a very low limit, and it would be better to include a safety margin by using a larger thickness.

Otherwise, examination with a metallographic microscope of the cracks in the coating has shown that they were usually 4 μm thick or less. But, sometimes, more important defects may exist. Figs 5–7, which are SEM micrographs (run numbers 297 and 301) confirmed the protection mechanism: a vitreous phase appears clearly in the cracks. When the temperature was stabilized at 850 $^{\circ}\text{C}$, the cracks were probably filled in, but because of the thermal shock caused by the rapid decrease in temperature from 850 $^{\circ}\text{C}$ to

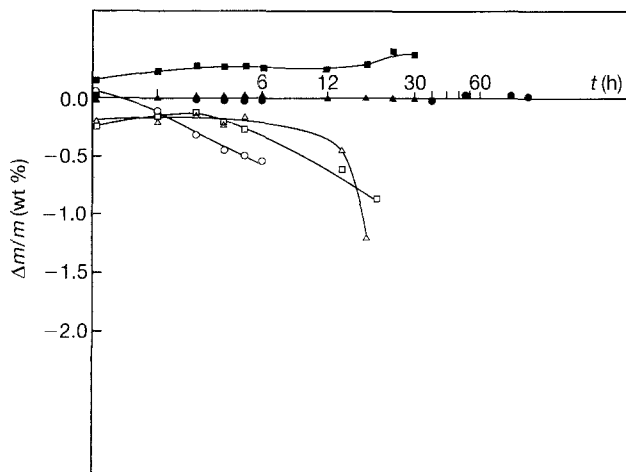


Figure 4 The two-dimensional C/SiC cyclic oxidation tests at 850 $^{\circ}\text{C}$ in air, ($\Delta m/m = f(t)$) in wt %: (Δ) 151, SiC (20 μm) + B (2 μm) + SiC (15 μm); (\square) 152, SiC (20 μm) + B₄C (3 μm) + SiC (15 μm); (\circ) 148, B₄C (3 μm) + SiC (30 μm) + B₄C (3 μm); (\blacksquare) 297, SiC (90 μm) + B₄C (50 μm) + SiC (60 μm); (\bullet) 158, SiC (150 μm) + B (4 μm) + SiC (20 μm); (\blacktriangle) 301, SiC (90 μm) + B₄C (15 μm) + SiC (60 μm).

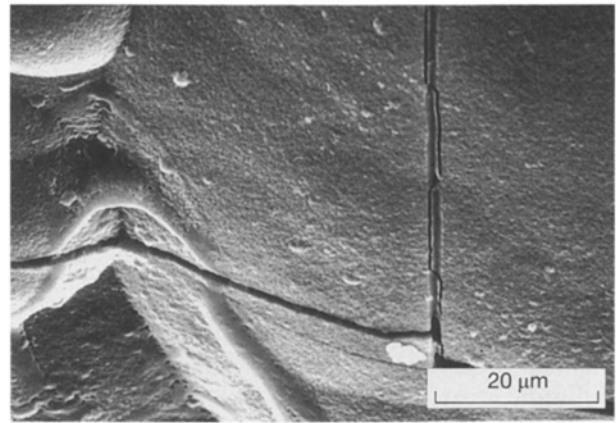


Figure 5 The surface morphology of run number 301 after the cyclic oxidation test at $T = 850^{\circ}\text{C}$.

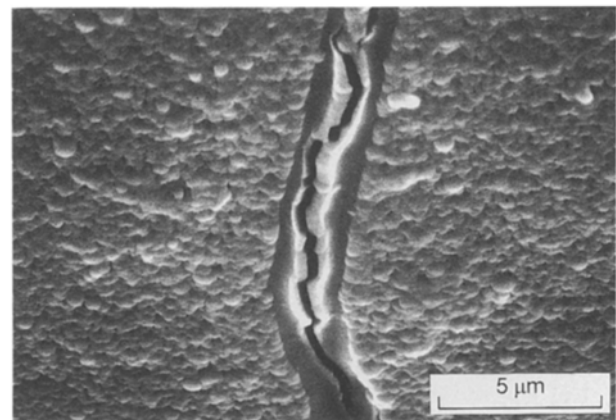


Figure 6 The surface morphology of run number 301 after the cyclic oxidation test at $T = 850^{\circ}\text{C}$ (At larger magnification than Fig. 5).

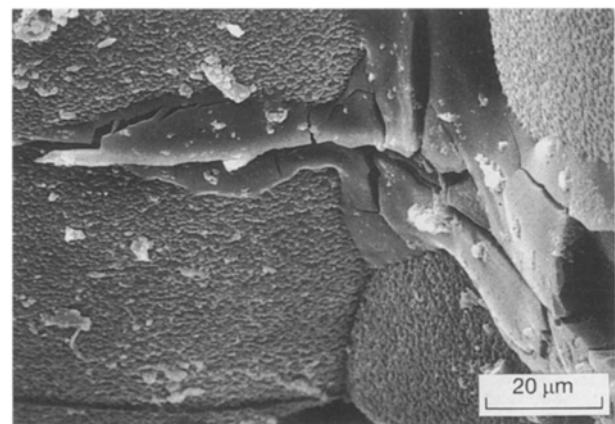


Figure 7 The surface morphology of run number 297 after the cyclic oxidation test at $T = 850^{\circ}\text{C}$.

room temperature the glass was broken, either in the middle or on one or the other borders of the cracks.

The boron oxide formation was important because the boron carbide intermediate layer is thick. The glass can even flow out of the cracks when the defect size is sufficiently large, for example, on sample number 297 (Fig. 7).

In conclusion, for this oxidation study at 850 °C, it should be pointed out that an examination of the curves of $\Delta m/m$ (in wt %) as a function of time and of the micrographs of run numbers 297 and 301 prove the validity of the protection provided by these types of trilayer coatings.

At $T = 1300$ °C, when the temperature is stabilized, the cracks in the coating should theoretically be closed, because the deposition temperature is lower. Taking into account the differences between the expansion coefficients of the fibres, the matrix and the coating, the coating should be in compression and the diffusion of oxygen and carbon oxides through the cracks should be very slow. But when the temperature increases from room temperature to 1300 °C (or decreases to room temperature) the cracks of the material briefly open.

Fig. 8 presents the oxidation results of two-dimensional C/SiC recovered with SiC monolayers. The thickness varies from 60 to 180 μm . As a reference, uncoated two-dimensional C/SiC is almost totally oxidized after $t = 1$ h (run number NC3, $\Delta m/m = -46.5$ wt %).

The increase in the thickness of the SiC monolayers favourably improves the oxidation resistance of two-dimensional C/SiC. A 60 μm SiC monolayer (run number C2) contributes to the slowing down of the oxidation, but a 120 μm SiC monolayer (run number C3), or better still a 180 μm SiC monolayer (run numbers 213 and 192), permits a quite low weight loss to be obtained after $t = 30$ h.

For run number C3, the weight loss increases after every thermal cycle as if the carbon surface accessible to the oxygen increases in importance. In contrast, for run numbers 213 and 192, the weight loss is almost the same after every thermal shock. These two examples seem to confirm that oxidation of the two-dimensional C/SiC is possible, mainly when the temperature increased, from room temperature to 1300 °C (or when it decreases from 1300 °C to room temperature).

It should also be noted that the weight loss is larger for run number 213 than for run number 192, al-

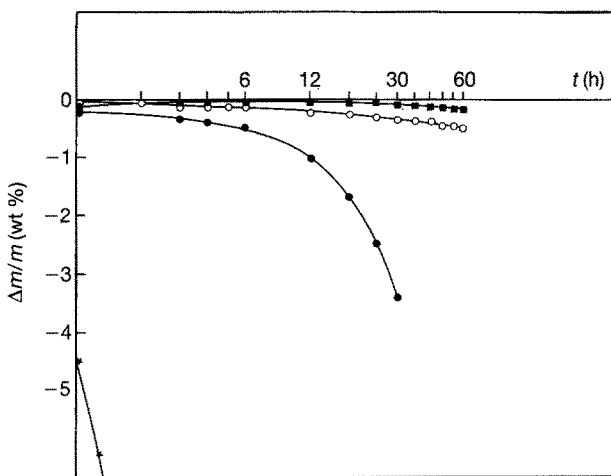


Figure 8 The two-dimensional C/SiC cyclic oxidation tests at $T = 1300$ °C in air ($\Delta m/m = f(t)$ in wt %): (★) C2, SiC (60 μm); (●) C3, SiC (120 μm); (○) 213, SiC (180 μm); (■) 192, SiC (180 μm); NC3, uncoated ($\Delta m/m = -46.5$ wt % at $t = 1$ h).

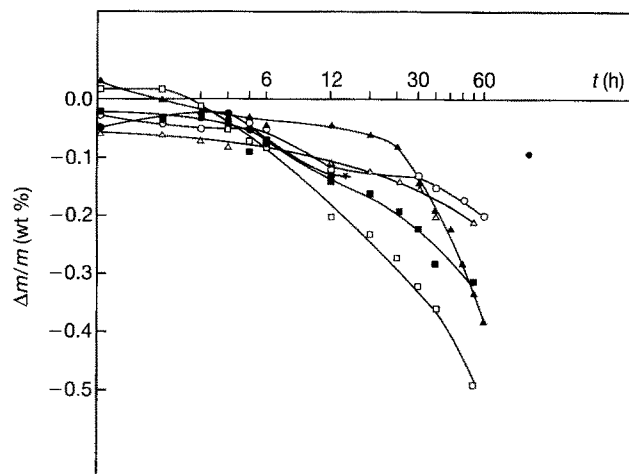


Figure 9 The two-dimensional C/SiC cyclic oxidation tests at $T = 1300$ °C in air ($\Delta m/m = f(t)$ in wt %): (□) 215, SiC (60 μm) + B_4C (5 μm) + SiC (60 μm); (○) 165, SiC (155 μm) + B (4 μm) + SiC (15 μm); (■) 211, SiC (120 μm) + B_4C (5 μm) + SiC (40 μm); (△) 209, SiC (120 μm) + B_4C (10 μm) + SiC (60 μm); (▲) 193, SiC (180 μm) + B (8 μm) + SiC (60 μm); (●) 194, SiC (180 μm) + B_4C (10 μm) + SiC (60 μm); (★) delaminated.

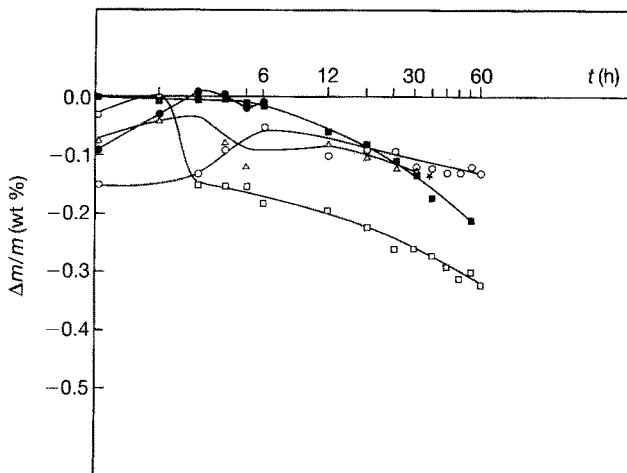


Figure 10 The two-dimensional C/SiC cyclic oxidation tests at $T = 1300$ °C in air ($\Delta m/m = f(t)$ in wt %): (△) 191, SiC (240 μm) + B (4 μm) + SiC (30 μm); (●) 197, SiC (240 μm) + B_4C (5 μm) + SiC (30 μm); (■) 212, SiC (200 μm) + B_4C (15 μm) + SiC (85 μm); (○) 189, SiC (240 μm) + B (8 μm) + SiC (60 μm); (□) 195, SiC (240 μm) + B_4C (10 μm) + SiC (60 μm); (★) delaminated.

though these two samples are both recovered with a coating of the same thickness.

The reproducibility problem which had been pointed out with the results at $T = 850$ °C was also found at $T = 1300$ °C, and it has the same explanation. On the other hand, the protection offered by a SiC monolayer appears not to be perfect.

Figs 9 and 10 present the cyclic oxidation behaviour of two-dimensional C/SiC coated by trilayers (SiC, B or B_4C , and SiC). The total thickness of the deposits varies from about 125 μm to about 310 μm . First, it should be noted that the weight loss, after $t = 60$ h at 1300 °C and several thermal shocks, remains lower or equal to -0.5 wt % for all the samples; this is already

an important progress since an empirical criterion indicates that a material which has lost $\Delta m/m = -2$ wt % has only lost 30% of its mechanical properties.

If the oxidation behaviour of run number C3 in Fig. 8 and the run number 215 in Fig. 9 are compared, it is possible to evaluate the benefit which is provided by a 5 μm boron-carbide intermediate layer. The values of $\Delta m/m$ for the same total thicknesses are -3.5 wt % for run number C3 and -0.35 wt % for run number 215 after $t = 30$ h. For a total thickness between 165 and 300 μm , it is not possible to give a general rule about the influence of the total thickness on the weight losses after $t = 60$ h. The weight losses are between -0.13% and -0.38% , but they are not systematically at their lowest when the total thickness is high or vice versa. This remark also applies to the influence of the thickness of the intermediate boron-based coating when it increases from 5 to 15 μm .

But, at a given total thickness and a given intermediate layer thickness, it seems that the lowest weight losses are obtained when the intermediate layer is of boron rather than boron carbide (run numbers 165 and 211, Fig. 9, or run number 189 and run number 195, Fig. 10).

Apart from this, the weight losses are quite regular with time, but some changes in the gradient of the curves $\Delta m/m = f(t)$ are observed (run number 195 between $t = 2$ h and $t = 3$ h, run number 193 between $t = 24$ h and $t = 30$ h). These changes may arise from the appearance or the blow up of some defects in the coatings which leads to a temporarily greater weight loss before the protection becomes efficient again (run number 195), or to an acceleration of the weight loss when the defect is not repaired (run number 193). On the other hand, it seems that too large an increase in the total thickness favours the appearance of an interstratum delamination (run numbers 197 and 194) which can be related to an increase in the shear stress inside the substrate instead of the coating when it is very thick. The morphological characterization will be reported in the following paragraphs which discuss the oxidation results at $T = 1500^\circ\text{C}$ because most of the samples tested at $T = 1300^\circ\text{C}$ were also subsequently tested at $T = 1500^\circ\text{C}$.

In conclusion it should be noted that a perfect stabilization of the weight loss has not been observed at 1300°C which is in contrast to the results obtained at 850°C for two-dimensional C/SiC, or between 850 and 1500°C for three-dimensional C/C. The protection is thus not fully obtained, but the oxidation is highly reduced. To avoid the risk of delamination, a total thickness in the range 160–200 μm with an intermediate boron-based coating layer of about 10 μm would be the best solution.

At $T = 1500^\circ\text{C}$, the cracks of the coatings are theoretically closed because the deposits have been made at lower temperature and the coatings are working in compression. But when the temperature increases from room temperature to 1500°C (or decreases from 1500°C to room temperature) the cracks are partially opened for a short time. Oxidation is most likely at this moment.

At $T = 1500^\circ\text{C}$, only run number 303 was tested directly; the other run numbers were tested at 1300°C . The weight loss which is reported at a time of 1 h is the weight loss obtained after 60 h and several thermal shocks at $T = 1300^\circ\text{C}$.

The protection provided by the 180 μm SiC monolayers allowed the weight loss to be limited even after 60 h (run number 213 $\Delta m/m = -0.5$ wt %; and run number 192 $\Delta m/m = -0.3$ wt %; Fig. 11). This $\Delta m/m$ which is given in the text is the difference between the weight loss after $t = 60$ h at 1300°C and the weight loss after $t = 60$ h at $T = 1500^\circ\text{C}$. An uncoated two-dimensional C/SiC would have lost all its carbon in less than 1 h. The protection is ensured by the slow growth of a SiO_2 film which can cover the external surface, and the airtightness of the sample is improved. Nevertheless, the fact that the weight gain provided by the formation of SiO_2 is not sufficient to stabilize the weight loss, proves that an oxidation of the carbon fibres still occurs.

A 5 μm boron-based intermediate layer improves the degree of protection (run number, 215 $\Delta m/m = -0.2$ wt % and run number 160, $\Delta m/m = -0.15$ wt %), while a 180 μm SiC monolayer has a large weight loss (run number 213, $\Delta m/m = -0.5$ wt %; run number 192, $\Delta m/m = -0.3$ wt %; after $t = 60$ h). When the total thickness and the intermediate-layer thickness increase, there is no weight loss; but this result was obtained in a static oxidation test (run number 193 and run number 189).

The improvement in the behaviour may be explained by at least three factors. The external SiC layer is the most important factor when the temperature is stabilized at 1500°C . The intermediate boron-based layer leads to an improved protection by the boron oxide production within the opened cracks when the temperature increases from room temperature to 1500°C or when it decreases from 1500°C to room temperature). Finally, an increase in the total thickness increases the distance which separates the oxygen

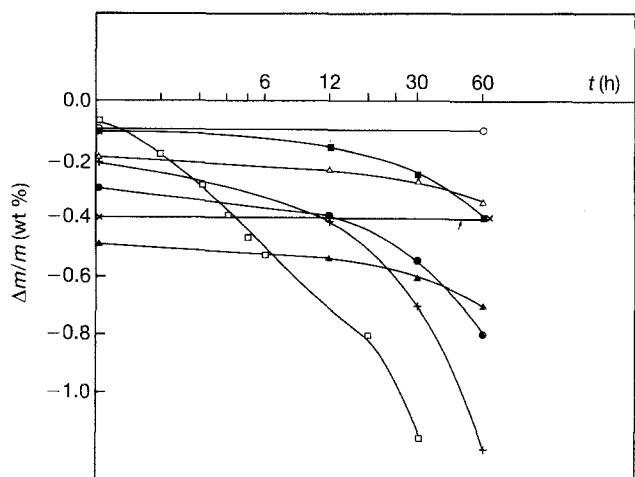


Figure 11 The two-dimensional C/SiC cyclic oxidation tests at $T = 1500^\circ\text{C}$ in air, ($\Delta m/m = f(t)$ in wt %): (●) 213, SiC (180 μm); (■) 192, SiC (180 μm); (▲) 215, SiC (60 μm) + B_4C (5 μm) + SiC (60 μm); (□) 303, SiC (60 μm) + B_4C (15 μm) + SiC (60 μm); (△) 160, SiC (155 μm) + B (4 μm) + SiC (15 μm); (×) 193, SiC (180 μm) + B (8 μm) + SiC (60 μm); (+) 212, SiC (180 μm) + B_4C (10 μm) + SiC (60 μm); (○) 189, SiC (240 μm) + B (8 μm) + SiC (60 μm).

from the carbon and it contributes to slowing the carbon oxidation.

Nevertheless, at 1500°C some reproducibility problems also remain, as they do at lower temperatures. Run number 303 had a higher weight loss after $t = 30$ h than run number 215, with which it can be compared. This is also true for run numbers 212 and 189. The examination of some micrographs provides some answers to these problems.

First, Fig. 12 shows a 180 μm SiC monolayer on a two-dimensional C/SiC (run number 213) which is cracked perpendicularly to the surface of the substrate. At the surface, it is possible to see a SiO₂ vitreous film. The width of the cracks increases to 5 μm and the fibres are attacked near the far end of the cracks. So the protection against the oxidation is not complete. Two-dimensional comparison between the micrographs of run numbers 212 and 189 in Figs 13 and 14, respectively, identifies one of the reasons which leads to the lack of reproducibility. The multilayer of run number 212 is cracked both perpendicularly and parallel to the surface of the substrate at the interfaces between the different multilayers. This multicracking favours the development of a network

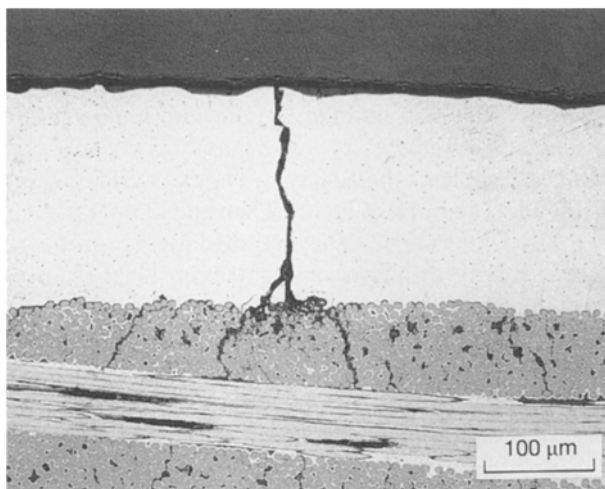


Figure 12 A polished cross-section of run number 213 after the cyclic oxidation tests at $T = 1300^\circ\text{C}$ and $T = 1500^\circ\text{C}$.

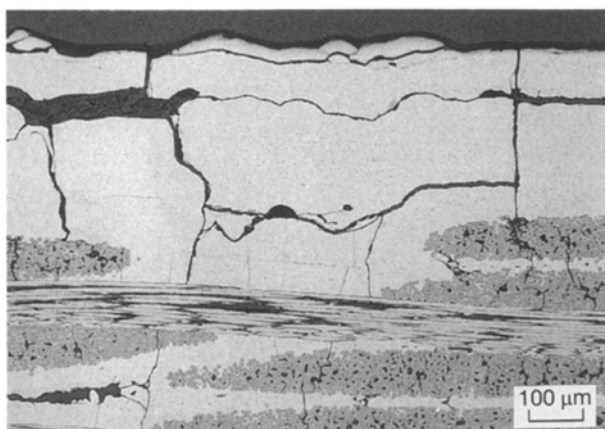


Figure 13 A polished cross-section of run number 212 after the cyclic oxidation tests at $T = 1300^\circ\text{C}$ and $T = 1500^\circ\text{C}$.

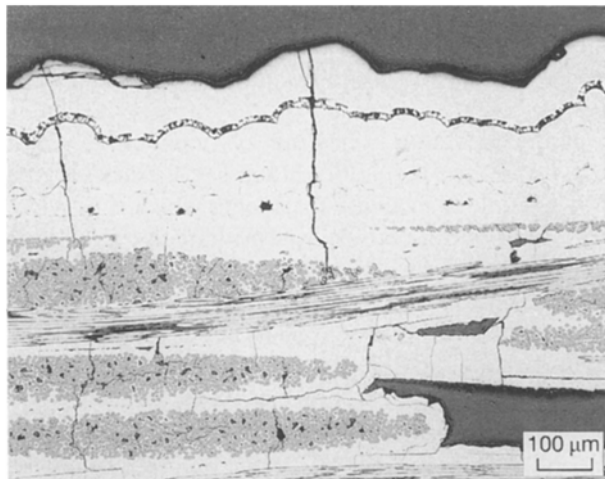


Figure 14 A polished cross-section of run number 189 after the cyclic oxidation tests at $T = 1300^\circ\text{C}$ and $T = 1500^\circ\text{C}$.

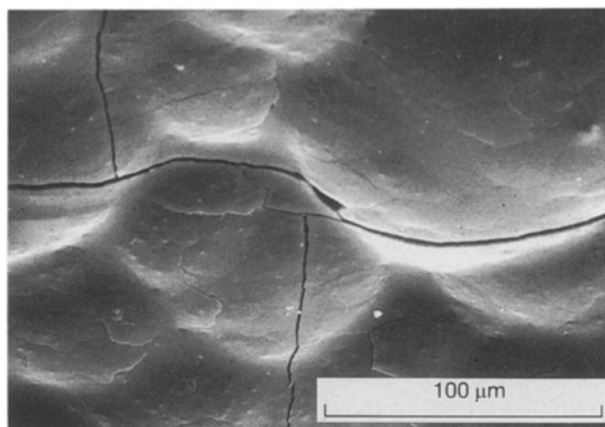


Figure 15 The surface morphology of run number 303, SiC (60 μm) + B₄C (15 μm) + SiC (60 μm), after the cyclic oxidation test at $T = 1500^\circ\text{C}$.

which creates a lot of access for oxygen to the carbon fibres. In run number 189, however, the cracks are almost always perpendicular to the surface. The width is close to 4–5 μm and the diffusion of the gas is reduced.

In Figs 13 and 14, the intermediate layer is modified by boron oxide formation. In the first case (run number 212), the fibres have clearly been attacked at the far end of some of the cracks. In the second case (run number 189), some fibres have been very slightly oxidized and the good protection level obtained after 60 h at $T = 1300^\circ\text{C}$ and 60 h at $T = 1500^\circ\text{C}$ is confirmed. The decohesion observed for run number 212 seems to come from a preferential brittleness at the interfaces between different coating layers.

Fig. 15 (run number 303) shows the morphology of an oxidized SiC surface at $T = 1500^\circ\text{C}$ with the SiO₂ cracking at room temperature. Fig. 16 (run number 303) shows that some areas have been well protected. In fact, in run number 303, the oxidation arises from larger defects (see Fig. 17). The vitreous phase, which is found on the border of the crack, seems to have been pushed away as if some gas has escaped from the material, creating or widening the crack.

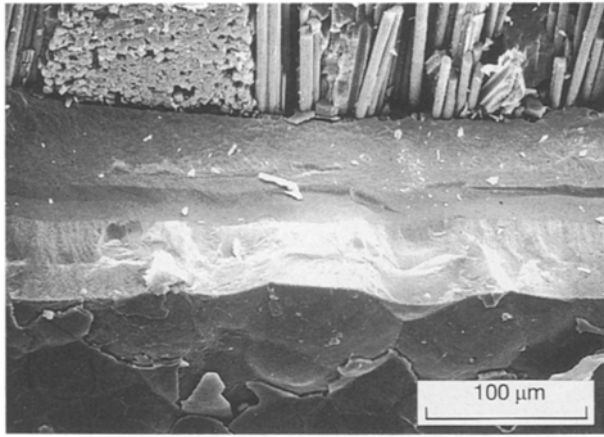


Figure 16 The morphology of a fracture on run number 303, SiC (60 μm) + B₄C (15 μm) + SiC (60 μm), after the cyclic oxidation test at $T = 1500^\circ\text{C}$.

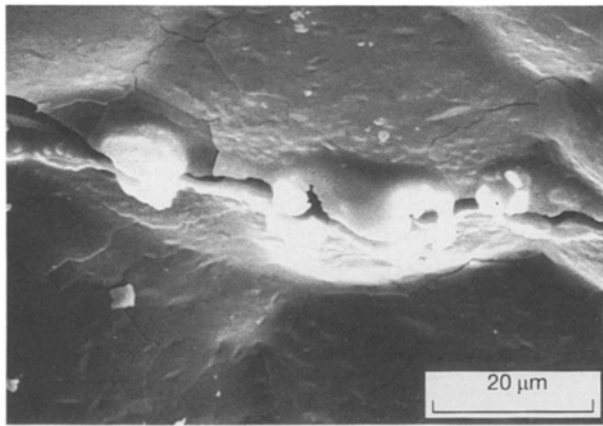


Figure 17 The surface morphology of run number 303, SiC (60 μm) + B₄C (15 μm) + SiC (60 μm), after the cyclic oxidation test at $T = 1500^\circ\text{C}$.

All these problems were not encountered when the protection of two-dimensional C/C or three-dimensional C/C was studied.

3.2. Two-dimensional C/SiC airtightness

A system of measurement has been perfected in the SEP laboratories to evaluate the airtightness of composite materials. The samples were discs 25 mm in

diameter. One side was maintained under an air pressure of 30 bars and the other side was maintained under a primary vacuum. The leakage flow was measured and it is given in $\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$ in Table I.

For run number 260-2 and run number 262-2, the leakage flow is higher when the samples have a protection coating. This result seems to indicate that the external coating, which mainly controls the permeability of the coating, is most probably cracked or at least that it has cracks which have got wider.

A morphological analysis confirmed this hypothesis and it also showed that the matrix itself was also more microcracked after the CVD treatment. Those samples were subjected to at least six thermal cycles of about 15 min when the temperature rapidly increased from room temperature to the deposition temperature or when it rapidly decreased from the deposition temperature to room temperature. These fast thermal cycles may have contributed to favouring the creation of new cracks or to the widening of old cracks.

Nevertheless, after a relatively long period of oxidation at $T = 1300^\circ\text{C}$ and at $T = 1500^\circ\text{C}$, the weight losses were rather smaller. The best result was obtained for the sample which had the largest total thickness. After the oxidation test, the permeability was lower as the production of glass during oxidation contributed to the decrease in the width of the cracks and to the improvement in the airtightness of the material.

3.3. Two-dimensional C/SiC oxidation behaviour after a mechanical strain

Four samples were maintained under static oxidation at 1300°C and/or at 1500°C after a flexural strength at room temperature (Table II).

For run numbers 192 and 215, a static oxidation test was carried out first at 1300°C for 60 h and then at 1500°C for another 60 h. The weight losses were, respectively, $-0.4 \text{ wt } \%$ and $-0.7 \text{ wt } \%$. Then a flexural strength of 150 MPa, corresponding to 30% of the strength necessary to fracture the sample, was applied to the two faces of the sample. The consequence of this mechanical strain was to damage the coating, creating a lot of new cracks or widening the old cracks. The static oxidation test was continued for 40 h at 1300°C and for 40 h at 1500°C and the weight losses were, respectively, $-1 \text{ wt } \%$ and $-2 \text{ wt } \%$.

TABLE I Two-dimensional C/SiC airtightness before and after the oxidation tests

| Run number | Trilayer | Leakage flow before coating ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$) | Leakage flow after coating ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$) | Oxidation test result | | Leakage flow after the oxidation tests ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$) |
|------------|---|--|---|--|---------------------|---|
| | | | | Test | $\Delta m/m$ (wt %) | |
| 260-2 | SiC (120 μm) + B ₄ C (10 μm) + SiC (60 μm) | 1-4 | 13 | 40 h at 1300°C + 65 h at 1500°C | -0.5 | 6 |
| 262-2 | SiC (180 μm) + B ₄ C (10 μm) + SiC (60 μm) | 1-4 | 14 | 65 h at 1300°C + 40 h at 1500°C | -0.2 | 6 |

TABLE II The isothermal oxidation test at $T = 1300^{\circ}\text{C}$ and/or 1500°C and the mechanical strain upon two-dimensional C/SiC

| Run number | Trilayer | Accumulated $\Delta m/m$ (wt %) | |
|------------|--|---|---|
| | | Oxidation test | Flexural strength of 150 MPa and oxidation test |
| 192- | SiC (180 μm) | 60 h at 1300°C + 60 h at 1500°C $\Delta m/m = -0.4\%$ | Flexural strength on two sides + 40 h at 1300°C + 40 h at 1500°C $\Delta m/m = -1\%$ |
| 215- | SiC (180 μm) + B_4C (5 μm) + SiC (60 μm) | 60 h at 1300°C + 60 h at 1500°C $\Delta m/m = -0.7\%$ | Flexural strength on two sides + 40 h at 1300°C + 40 h at 1500°C $\Delta m/m = -2\%$ |
| 193- | SiC (180 μm) B (8 μm) + SiC (60 μm) | 60 h at 1300°C + 60 h at 1500°C $\Delta m/m = -0.4\%$ | Flexural strength on one side + 8 h at 1500°C $\Delta m/m = -0.6\%$ |
| 211- | SiC (120 μm) + B_4C (5 μm) + SiC (40 μm) | 60 h at 1300°C $\Delta m/m = -0.3\%$ | Flexural strength on one side + 8 h at 1500°C $\Delta m/m = -0.9\%$ |

The same kind of procedure has been used to test run numbers 193 and 211, as described in Table II, except that a flexural strength of 150 MPa was applied on one side of each sample only and the static oxidation test was continued for only 8 h. The accumulated losses were, respectively, -0.6 wt % and -0.9 wt %. This study shows the ability of the multilayer to self-repair the cracks and to slow down the oxidation of the substrates for several hours at the high temperatures of 1300 – 1500°C .

4. Conclusion

This study has proved the relevance of a surface protection made from SiC on the two-dimensional C/SiC materials. The insertion of an intermediate layer of boron or boron carbide allows satisfying protection to be obtained in the temperature range 450 – 1500°C . The usefulness of this intermediate layer appears particularly important for the low and middle temperatures, whereas at higher temperatures (1300 or 1500°C), the difference in the protection with a thick SiC coating is less pronounced. In other respects, it was pointed out that the ternary coatings made with an intermediate coating of boron or boron carbide allows maintenance of nearly equal air tightness after oxidation. They also allow the influence of any damage to the material to be minimized or the oxidation behaviour under thermomechanical strength to be improved.

On the other hand, the variation of the thickness of the intermediate coating has been little studied, but the choice of a boron carbide coating of 10 – 15 μm seems to be a good compromise.

Next, it has been shown that an increase in the total thickness of the coating furthered a reduction in the weight loss of the materials during the static oxidations. This last statement must be qualified because the sensibility to delamination of the samples seems to increase when the thickness of the deposits and when

the temperature increase. From one protected sample to another, a lack of reproducibility appears in the oxidation behaviour.

This problem may be due to the elaboration process of the coatings as has been explained in Section 3.2. This problem would disappear in an industrial reactor. It may also be explained by the opening porosity between the sheets of the two-dimensional C/SiC substrates, which can vary from one sample to another.

The deposition rates which were used in this study, typically 20 or 30 $\mu\text{m h}^{-1}$, are too high to perfectly fill in those porosities. In an industrial reactor, the deposition rates (which must be lower) would be favourable to better filling in the porosity in depth.

It seems that the development of a multilayer in an industrial reactor with internal SiC (120 – 140 μm), intermediate B_4C (10 – 15 μm) and external SiC (40 – 60 μm) should be a good compromise to obtain satisfactory protection of two-dimensional C/SiC for 50 h or more.

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