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Internal protection of C/C composites by boron-based compounds

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Abstract

Boron-based protections were used on carbon fibre preforms in order to protect interfacial zones in C/C composites from oxidation. Wet treatments (H_3BO_3 in aqueous solution) and B–P CVD-coatings are not stable under low pressures at 1000 °C (the matrix deposition conditions in conventional CVI). Hence, they could not be used as C/C composite internal protections. Boron-ion implantation in carbon fibres improves their tensile strength by healing superficial carbon fibre defects but is not efficient as an internal protection in C/C composites, the boron-ions being implanted too far from the carbon fibre surface. B–C CVD-deposits are also not very efficient as internal protections. They oxidize faster than the carbon and lead to an important volume decrease. Holes are then formed at the interfacial zones at the beginning of the oxidation of the C/B–C/C composite passing from the surface to the core of the material. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Boron-based coatings; C/C composites; Composites; Interfaces; Oxidation protection

1. Introduction

Applications of carbon–carbon (C/C) composites at high temperatures are often limited by oxidation of the carbonaceous phases in oxygen containing atmospheres. Boron is known to protect carbonaceous materials. It is usually accepted that substitutional boron acts as an inhibitor to carbon oxidation. The following explanations have been proposed: (1) substitutional boron redistributes the π electrons, lowers the Fermi level of graphite and thereby inhibits the desorption of CO and CO_2; (2) substitutional boron enhances the graphitisation of carbon; (3) as the carbon is consumed, boron oxide forms on the surface and acts as a diffusional barrier and an active site blocker.[1]

Jacques[2] shows that the oxidation resistance of C (B) materials obtained by chemical vapour deposition (CVD) is better than that of pure pyrocarbon. This feature is due either to the improvement of the structural organisation (low boron content materials) or to the coating of the whole material with a stable boron oxide layer (materials with a higher boron content).

Kowbel[3] has studied the effect of boron ion implantation on the oxidation behaviour of a three-dimensional C/C composite. Boron ion implantation increased the oxidation onset temperature by 150 °C and decreased the oxidation rate by two orders of magnitude at 500 °C, compared with the untreated composite. The mechanism of the oxidation protection by boron implantation appears to be a combination of boron oxide formation upon oxidation, inhibition via steric blockage of active sites and electron-transfer-inhibited CO desorption.

The oxidation of a C/C composite first takes place at the fibre/matrix interface[4]. Further, we have shown that boron rich Si–B–C deposits are very efficient as internal protection in C/C composites.[5] From this study we have derived the characteristics of the deposit, which are necessary to protect efficiently C/C composites from internal oxidation. The deposit needs: (1) to be stable at 1100 °C under low pressures [chemical vapour infiltration (CVI) conditions], (2) to resist reaction with carbon fibres in order to keep good mechanical properties, (3) to oxidize faster than the carbon and (4) to oxidize with a volume gain to prevent oxygen access to the interfacial zones.

The aim of this work was to protect C/C composite interfacial zones by using boron-based protections on carbon fibre preforms. In this study three boron based

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protections have been tested: first, a B_2O_3 film obtained from an orthoboric acid solution, secondly B–C and B–P coatings obtained by chemical vapour deposition (CVD) and thirdly boron ion implantation on carbon fibres.

Oxidation resistance of coated carbon fibre preforms was studied, and the efficiency of these deposits as interphases in a C/C composite was considered. Boron ion implantation was carried out on a C/C composite in order to understand better the oxidation of the implanted carbonaceous materials.

2. Experimental procedure

2.1. Materials

Three kinds of ex-PAN carbon fibre 3-D needled preforms supplied by Snecma Moteurs (Le Haillan, France) were used. The first was fabricated from M carbon fibre and heat-treated at 1600 °C under vacuum (M preform). The second was produced from oxidized PAN fibres (N) and was further heat-treated at 1600 °C under vacuum (N preform). The third were yarns made of low modulus carbon fibres. These yarns have been only used to study B–P deposit oxidation resistance.

N-preforms were densified by pyrocarbon following chemical vapour infiltration (CVI) in order to obtain C/C composites.[6] Rectangular specimens ($10\times10\times1$ mm^3) were machined from these materials. Their surfaces were carefully polished with diamond pastes of decreasing size (successively 30/15/6/3 μm). Then, the as-prepared specimens were washed with distilled water in an ultrasonic bath and finally heat treated at 950 °C under high vacuum in order to remove impurities introduced during polishing.

2.1.1. Pretreatment of carbon fibre preforms by H_3BO_3

Carbon fibre preforms were impregnated with a 10 vol.% alcohol solution of orthoboric acid at 80 °C. Then the samples were dried under dry air flow at 150 °C for 2 h (H_3BO_3- pretreatment).

2.1.2. Boron-ion implantation on carbon fibres and C/C composites

Ion implantation was performed with 100 keV B ions to doses of 10^{17} ions/cm^2 on carbon fibres (M fibres) and on polished C/C composite specimens (B^+ implantation was carried out at INASMET, Camino de Portuetxe, 12, B8 de Igara, San Sebastian, Spain).

For this treatment, 20 cm length carbon fibres were fixed on a frame. This frame turned during the implantation treatment allowing exposure of the whole surface of the carbon fibres.

The C/C composite specimens were implanted on one side, then on the other leaving the edges without direct exposure to the B^+ ion beam.

2.1.3. C (B) and B (P) coatings on carbon fibre preforms

The B–C and B–P coatings were prepared by CVD [5] from BCl_3–C_3H_8 and BBr_3–PBr_3 gas mixtures.

The composition of the gaseous precursors is defined by the following ratios:

$\alpha = 100\times Q\ (BCl_3)/(Q\ (BCl_3) + Q(C_3H_8))$ for B–C experiments and $\beta = 100\times Q\ (BBr_3)/(Q(BBr_3) + Q(PBr_3))$ for B–P experiments where Q_i stands for the gas flow rate of species *i*.

The hydrogen flow rate was 200 cm^3 min^{-1} for the different experiments.

B–C coating experiments have been carried out on carbon fibres of N preforms and B–P coatings on carbon fibre yarns. Three different B–C coatings (termed BC1, BC2 and BC3) were deposited on the carbon fibre preforms. The atomic percentage of boron in these deposits was respectively 18, 28 and 33 (Table 1). Two different B–P coatings referred to as BP1 (close to stoichiometry) and BP2 (boron rich coating) and corresponding to different B/P atomic ratios, were deposited on the carbon fibres (Table 1).

2.2. Techniques

Oxidation tests were performed in a TAG24 thermogravimetric analyser from SETARAM. Tests were carried out under dry flowing air (50 ml/min) under atmospheric pressure. A 50 °C/min heating rate was used up to 650 °C. The temperature was kept at this value during the oxidation test.

Surfaces were examined using a high-resolution scanning electron microscope (SEM, S4500 from Hitachi).

The composition of the C (B) and B (P) materials deposited on the carbon fibre preforms was determined by an electron probe micro-analyser (EPMA, CAMEBAX from CAMECA) in which the concentration was derived from X-ray line intensities by using the wave length dispersive X-ray spectroscopy mode (WDS).

The chemical homogeneity of deposits was characterised by auger electron spectroscopy (AES) with simultaneous Ar^+ etching. This technique was used to record the composition/ depth profile in the boron ion implanted fibres.

Table 1
Experimental conditions used to synthezise B–C and B–P coatings and boron, carbon and phosphorous content of the different deposits

Sample	BC1	BC2	BC3	BP1	BP2
Temperature (°C)	950	950	950	90	900
Total pressure (kPA)	1	1	1	5	6
α (%)	55	70	85		
β (%)				17	88
% B	18	28	33	49	84
% C	82	72	67		
% P				51	16

The tensile strength of monofilaments (treated or not) was tested at room temperature with an apparatus and a procedure which have been described elsewhere.[7] For each condition, about 20 single fibre specimens were tested at a gauge length $L = 10$ mm. The failure stress was calculated from the load at failure and from the diameter previously measured on each specimen by laser interferometry. Finally, the Young's modulus of the fibre was calculated from the slope of the stress–strain curve at the origin, taking into account the machine compliance and assuming a linear relationship up to failure.

3. Results: treatment of carbon fibre preforms by H_3BO_3

3.1. Thermal pretreatment

TGA was carried out on H_3BO_3-pretreated preforms using a 20 °C/min heating rate from 25 to 700 °C under pure argon flow. An important mass loss is observed between 150 and 400 °C (Fig. 1).

A mass gain of the preform of 37.5 mg was measured at the end of the H_3BO_3-pretreatment. This mass gain was 20.5 mg after the thermal treatment. Hence, it can be supposed that the mass loss observed at low temperature corresponds to the formation of boron oxide according to the following equation:

$$2H_3BO_3 \rightarrow BO_3 + 3\ H_2O \quad (1)$$

Indeed, the transformation of 37.5 mg of H_3BO_3 will lead theoretically to the formation of 21 mg of B_2O_3.

3.2. Fibre surface morphology

Scanning electron microscopy was performed on H_3BO_3-pretreated N fibre preforms. Aggregates are observed on the carbon fibre surface (Fig. 2a). Fig. 2b shows the same carbon fibre preform after the thermal treatment and the oxidation test (15 wt. % loss). The thermal treatment leads to the formation of a continuous and homogeneous oxide film. It is noteworthy that no pitting is observed on the fibre surface after oxidation (pitting characteristic of a catalytic oxidation was observed on oxidized N fibres [4]).

3.3. Oxidation rate

TGA experiments were carried out in air on untreated or treated preforms. As shown in Fig. 3, the H_3BO_3 treatment improves the oxidation resistance of the preform. The oxidation rate of the H_3BO_3 treated preform is 3 times lower than that of its untreated counterpart. It is interesting to note that a slight increase of the oxidation resistance is observed for preforms treated with H_3BO_3 and then washed with distilled water. As for

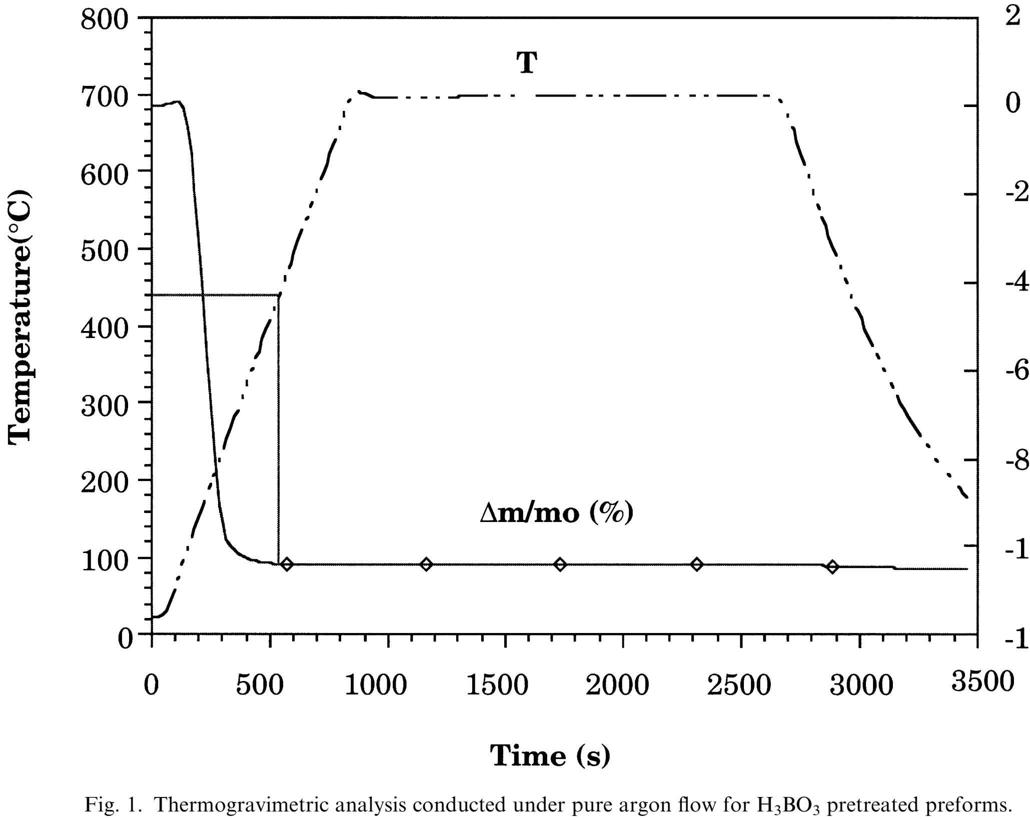

Fig. 1. Thermogravimetric analysis conducted under pure argon flow for H_3BO_3 pretreated preforms.

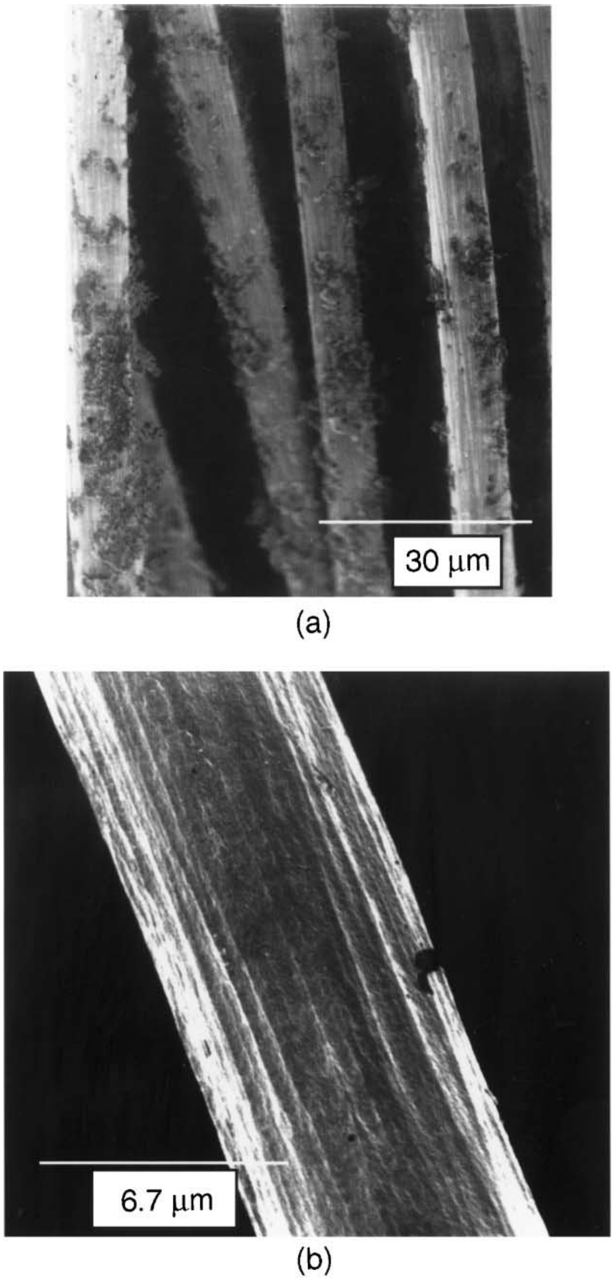

Fig. 2. Morphology of the fibre surface in N preforms after a H_3BO_3 pretreatment : (a) as-pretreated fibres, (b) after the oxidation test.

oxidized H_3BO_3-treated preforms, no pitting was observed on those washed samples at the end of the oxidation test (Fig. 4).

4. Results: boron ion implantation on carbon fibres and C/C composites

The boron concentration profiles for the two specimens are shown in Fig. 5. The B^+ implantation with an incident dose of 10^{17} ions/cm^2 yields a maximum concentration of boron at 600 nm depth, where it was determined to be 20 at.%. The C/C composite specimen with the same incident dose shows a maximum in boron concentration at a depth of 660 nm; in this case the boron concentration is 27 at.%.

No modification of the sample surfaces has been observed after an implantation with a dose of 10^{17} boron ions/cm^2. An implanted carbon fibre displayed a glassy film at the fibre surface after 8 h and 20 min of isothermal oxidation under dry air flow at 650 °C.

Fig. 6 shows a boron-ion implanted C/C composite after 5 h and 30 min of isothermal oxidation under dry air flow at 600 °C. A continuous film is formed on the matrix of the composite. A film of oxide is also observed on the carbon fibre section but it is not continuous.

For boron ion implanted carbon fibres, no improvement of the oxidation resistance is observed from 0 to 22 mass % loss compared to untreated fibres (Fig. 7a). After 22 mass % loss a slight improvement of the oxidation resistance is observed. In a first approximation (neglecting carbon fibre oxidation from the ends),

$$\frac{\Delta m}{m_0} = \frac{r^2}{R^2} - 1$$

with r the oxidized fibre radius and R the initial fibre radius. After a total mass loss of 22%, the fibre radius decrease is 0.36 µm. For the implanted C/C composite, a slight increase of the oxidation resistance is observed after a total mass loss of 3% (Fig. 7b).

Mechanical tests were performed on untreated and boron ion implanted M fibres (Table 2). An important increase of the failure stress is observed after boron ion implantation without any noticeable change in the Young's modulus. This behaviour may be due to an "amorphisation" of the carbon fibre surface during boron ion implantation and hence, a decrease of the number/size of the defects located at the fibre surface.

5. Results: B(C) and B(P) coated carbon fibre preforms

Oxidation tests were carried out (i) on B–C coated carbon fibre N preforms (0.5×0.5×1 cm^3) (ii) on B–P coated carbon fibre yarns (1×0.1×0.1 cm^3 yarns were treated by CVD).

5.1. Morphology

Examples of B–C and B–P coated carbon fibres are shown in Fig. 8. The external fibre surface seems to be rather smooth and homogeneous for deposits.

After an oxidation test, B–C deposits lead to the formation of a glassy film at the carbon fibre surface (Fig. 9).

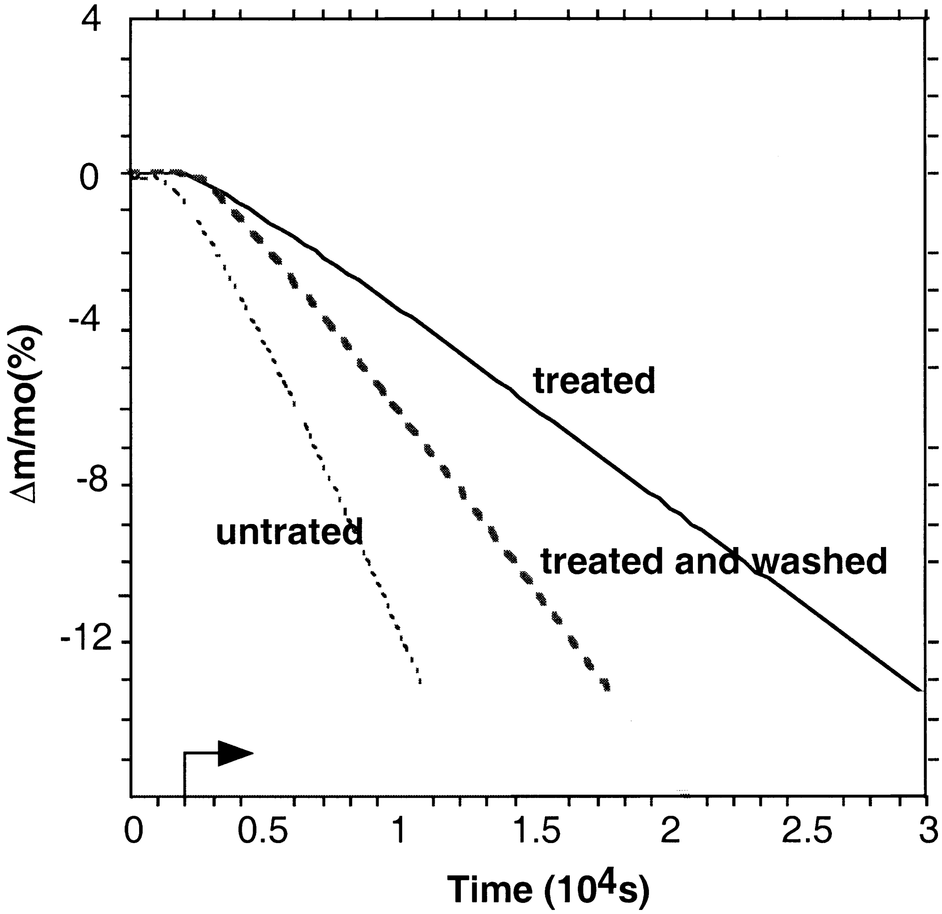

Fig. 3. Thermogravimetric analyses conducted under dry flow air for untreated, H_3BO_3 treated and treated/washed N preforms. (A temperature of 650 °C is first obtained and the temperature is then maintained at this value.)

Boron rich B–P coatings (BP2) form a glassy film at carbon fibre surfaces (Fig. 10b). Conversely, the BP coating (BP1) is not totally oxidized at the end of the oxidation test (Fig. 10a). It is less sensitive to oxidation than boron rich B–P coatings and than the carbon fibres themselves. Oxidation occurs from the carbon fibre ends.

5.2. Oxidation resistance

For B–C coated carbon fibre preforms, a rapid mass loss is observed at the beginning of the oxidation test (Fig. 11a). It corresponds to a rapid and total oxidation of the B–C deposit [5]. The B–C deposits improve the oxidation resistance of carbon fibres. For example, mass loss rate of the BC3 (Table 1) sample is divided by four compared to the untreated preform.

For the BP1 sample a slight improvement of the oxidation resistance is observed compared to the reference (Fig. 11b). The mass loss rate is divided by 3 compared to the untreated yarn. For the BP2 sample (boron-rich deposit), an important improvement of the oxidation resistance is observed (Fig. 11b). The mass loss rate is divided by 25 compared to the untreated yarn. At the beginning of the oxidation test, no mass gain is observed. From 0 to 58 min an oxidation rate of 0.5%/s

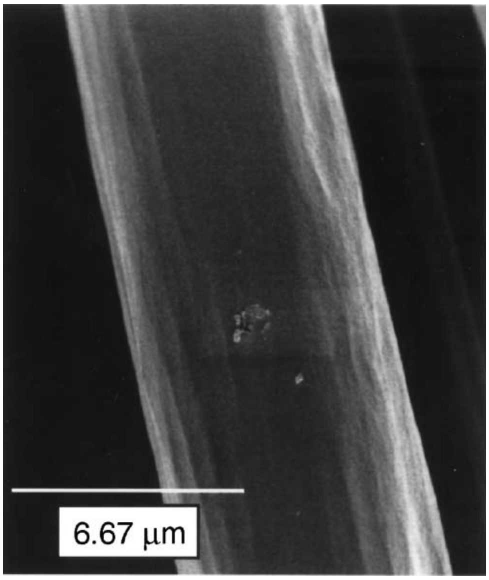

Fig. 4. Fibre surface of a carbon fibre in a N preform which has been successively treated with H_3BO_3, washed with distilled water and finally oxidized.

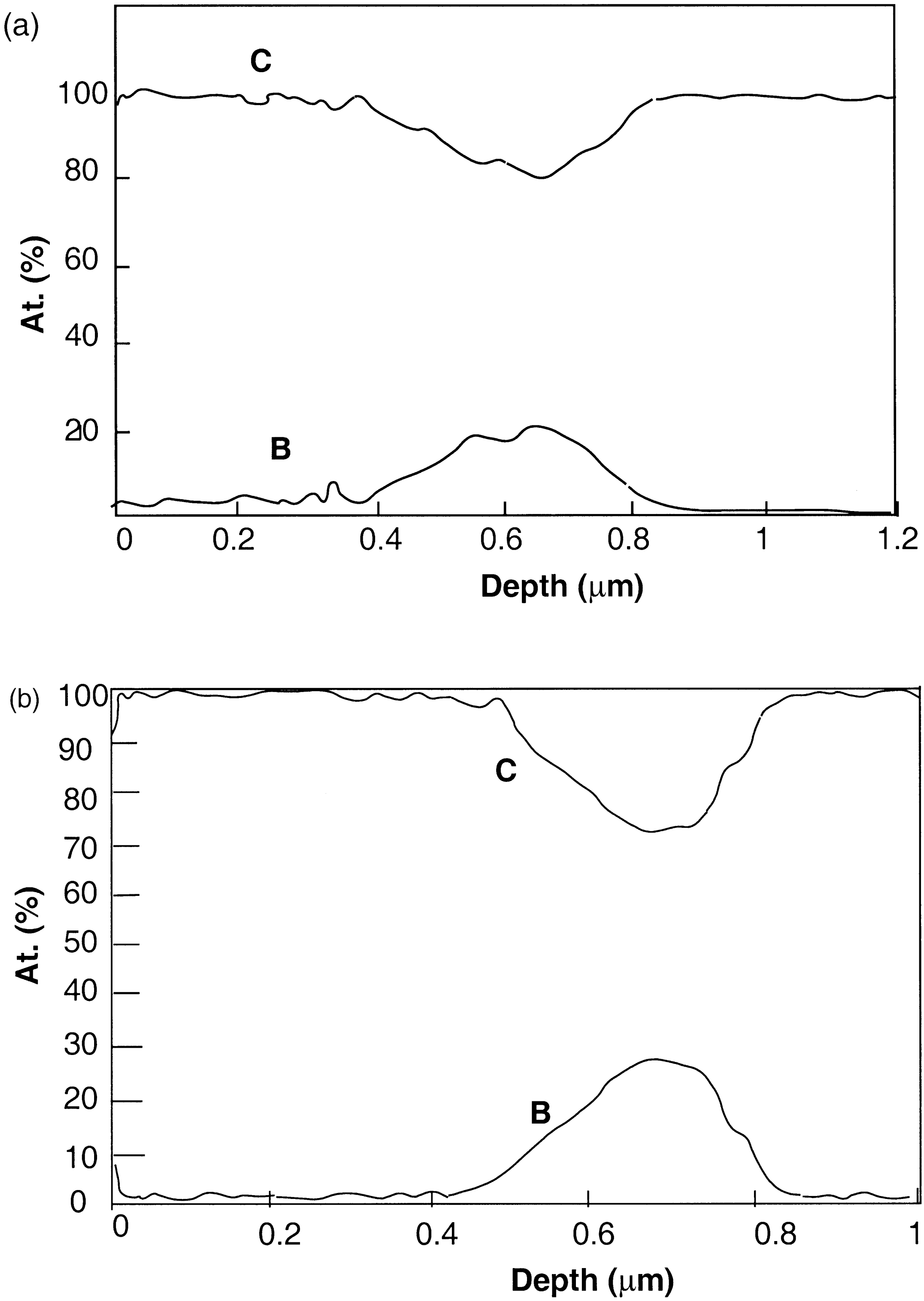

Fig. 5. Auger electron spectrum of: (a) a boron ion implanted carbon fibre and (b) a boron ion implanted C/C composite.

is obtained. Thereafter the oxidation rate is equal to 1.15%/s.

A boron-rich B–P coating (BP2) was deposited on carbon fibre N preforms. An important mass gain was observed at the beginning of the oxidation test (Fig. 12).

5.3. Thermal stability

A thermal treatment was carried out on BP2 sample in the TGA apparatus using a 20 °C/min heating rate from 25 to 1000 °C under an argon flow (Fig. 13). No

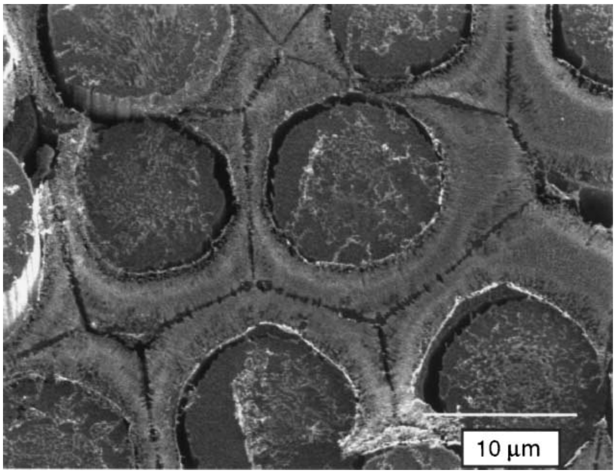

Fig. 6. Boron-ion implanted C/C composite surface after the oxidation test.

Table 2
Mechanical properties of M fibres and boron ion implanted carbon fibres

	Failure stress (MPa)	Failure strain (%)	Young's modulus (GPa)
M fibres	3629±702	1.07±0,21	342±31
Boron ion implanted M fibres	6117±742	1.8±0,33	345±33

mass loss was observed which shows that the deposit is stable at 1000 °C under atmospheric pressure. The problem is that this deposit is not stable at 1000 °C under low pressures (CVI conditions).

5.4. Mechanical behaviour

Mechanical properties of carbon fibres coated with boron-based deposits have been reported elsewhere.[4] There is a decrease of the tensile failure strength due to the brittle behaviour of coated fibres. The coating thickness is the parameter dictating the value of the failure stress (Fig. 14). Hence, only thin deposits permit retention of good mechanical properties.

6. Discussion

The H_3BO_3 treatment leads to the formation of a continuous and homogeneous B_2O_3 film on carbon fibres. Carbon fibre oxidation occurs by oxygen diffusion through the B_2O_3 film. Hence, an improvement of the preform oxidation resistance is observed. Moreover, no pitting at the fibre surface is observed at the end of the oxidation test. The B_2O_3 film hinders catalytic impurities from wetting the carbon fibre surface and no catalytic oxidation was observed.

The thermal stability of boron oxide deposit has been studied previously. McKee [8] has reported that at temperatures higher than 1000 °C and in presence of water vapour, borate species were appreciably volatile. Hence, it would be impossible to deposit carbon by CVI on these B_2O_3 coated carbon fibre preforms, since carbon deposition occurs at around 1000 °C under low pressures (in these conditions the B_2O_3 film is not stable).

A B_2O_3 film cannot be used directly as interphase in a C/C composite. However, it is interesting to treat carbon fibre preforms with an H_3BO_3 solution, and then to remove the deposit by washing the treated preforms in distilled water. This treatment removes catalytic impurities from carbon fibre surface and improves preform oxidation resistance (Fig. 3). SEM micrograph of Fig. 4 shows that a homogeneous oxidation occurs after this treatment.

For boron-ion implanted carbon fibres, a slight increase of the oxidation resistance is observed after a decrease of 0.36 µm of the fibre radius. A B_2O_3 film starts to form and to protect carbon fibres from oxidation when oxygen has access to the implanted boron species [it was determined that boron was implanted from 0.38 to 0.87 µm from the surface (Fig. 5)]. Hence, boron ions were implanted too far from the surface to lead to a good oxidation protection of carbon fibres.

Boron ion implantation on carbon fibres cannot be used to protect C/C composite interfacial zones in the studied conditions. Indeed, a hole will be formed at interfacial zones before the formation of the B_2O_3 film. It will be interesting to implant boron at the very surface of carbon fibres to achieve a higher oxidation resistance.

Finally, boron ion implantation in carbon fibres significantly improves their tensile failure strength.

Oxidation tests carried out on boron-ion implanted C/C composites show that the boron oxide distribution was not uniform. Because the matrix is composed of well aligned graphitic carbon crystallites ($AE = 22°$[4]) compared to the fibre, this preferred orientation may facilitate boron accumulation in the matrix, the percentage of carbon sheet edges being higher than at the surface of fibres. As for untreated C/C composites, a preferential interfacial oxidation is observed.

Boron-rich B–P and B–C deposits lead to the formation of a glassy phase under dry air flow at 650 °C, at the carbon fibre surface.

For B–C coatings, the deposit oxidation is very rapid and carbon oxidation occurs by oxygen diffusion through the glassy film. The problem is that the B–C deposit oxidation leads to an important mass loss and volume decrease ($\Delta < 1$, Δ being the coefficient of Pilling and Bedworth[5]). In a C/B–C/C composite the B–C deposit oxidation leads to the formation of a hole around the carbon fibres (Fig. 15).

For boron-rich B–P coated carbon fibre yarns, the mass gain due to the glassy film formation is balanced

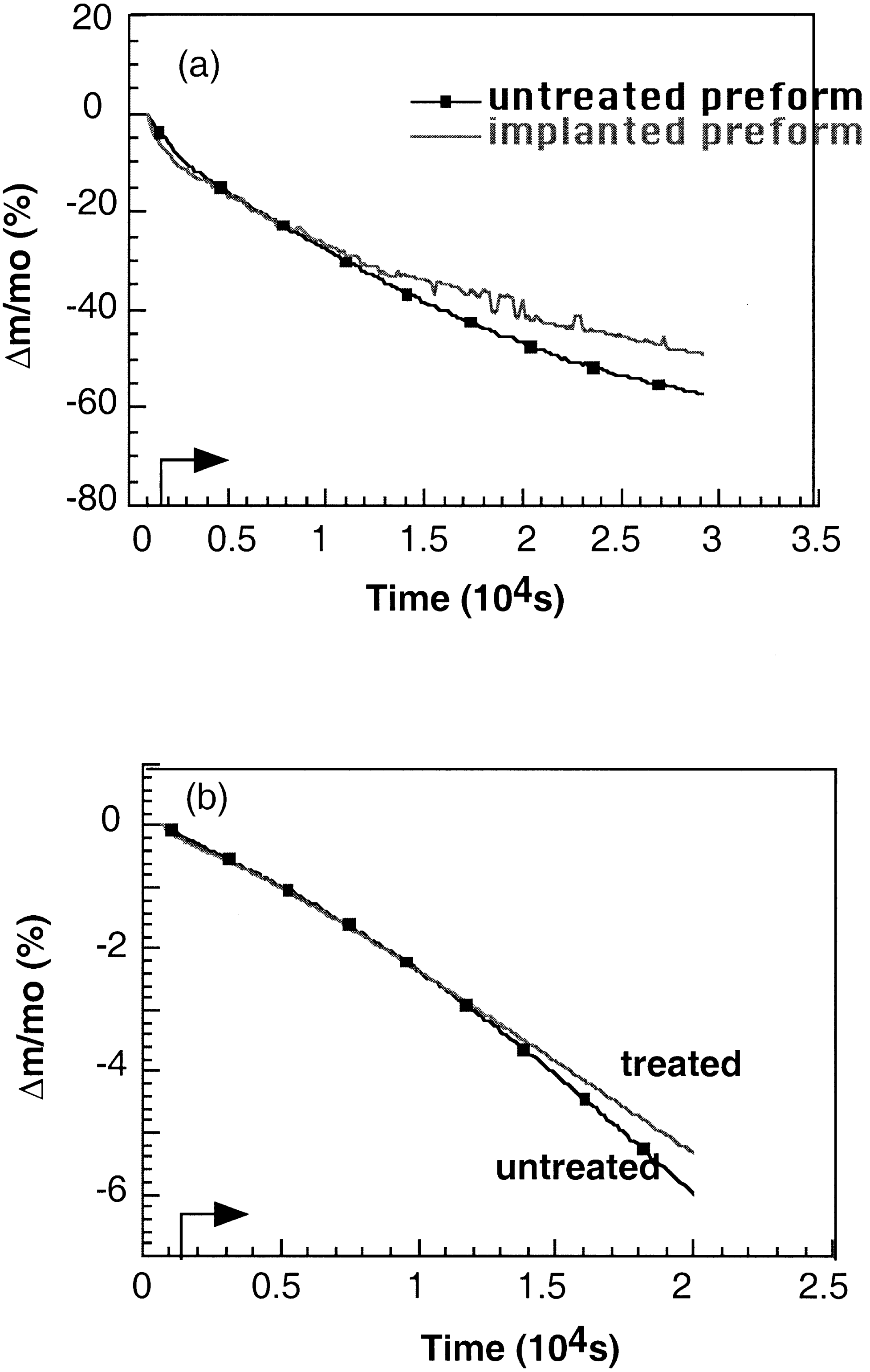

Fig. 7. Thermogravimetric analyses conducted at 650 °C under dry flow air on (a) untreated and boron-ion implanted M fibres and (b) boron-ion implanted C/C composites. (A temperature of 650 °C is first obtained and the temperature is then maintained at this value.)

by carbon fibre oxidation at the ends. At the beginning of the oxidation test two phenomena occur (Fig. 11b): (i) a mass gain due to the B–P deposit oxidation (B_2O_3 and P_2O_5 formation) (ii) a mass loss related to carbon fibre oxidation principally from the carbon fibre ends (the total oxidation rate of the yarn is about 0.5%/s). Then, after 58 min, the deposit is totally oxidized, the carbon fibre ends are covered by a glassy film and the

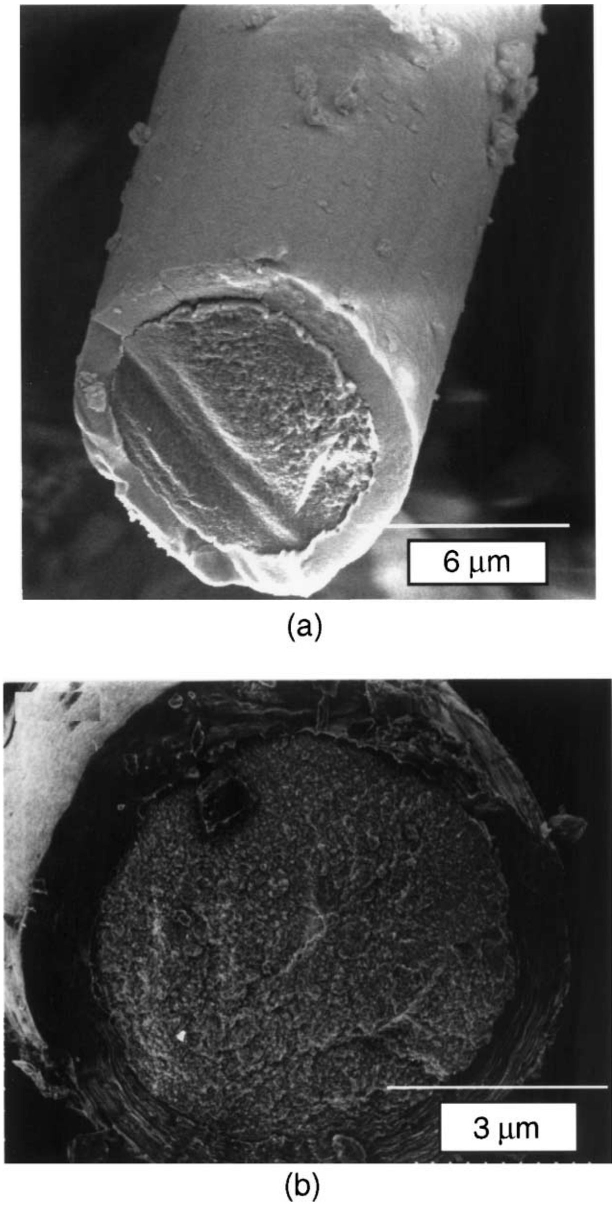

Fig. 8. Coated carbon fibre surface (a) BP coating (BP1), and B–C coating (BC3).

oxidation of carbon fibres occurs by oxygen diffusion through the film (the total oxidation rate of the yarn is about 1.15%/s). For boron-rich B–P coated N preforms (in this case the ends are covered by the deposit), a mass gain is observed at the beginning of the oxidation test (Fig. 12). Moreover, a volume increase occurs during the deposit oxidation (the calculated Δ coefficient is higher than 1 ($\Delta = 3.7$)). Boron-rich B–P deposits could be used as interphase in C/C composites. They will be very efficient to block oxygen access to interfacial zones (as boron-rich Si–B–C deposits[5]). The problem is that the matrix cannot be deposited by conventional CVI, the deposit being not stable at 1000 °C under low pressures.

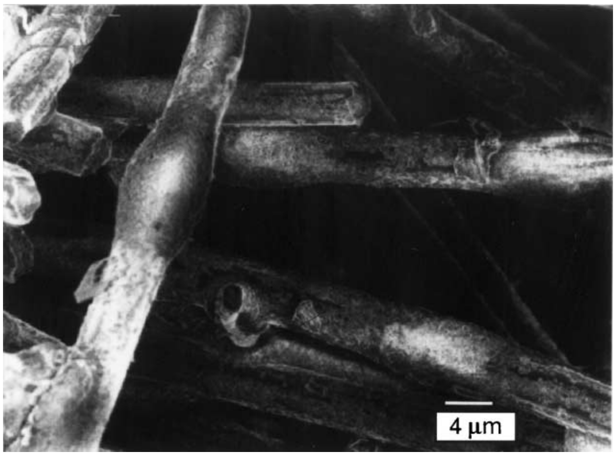

Fig. 9. Fibre surfaces after oxidation of B–C coated carbon fibres.

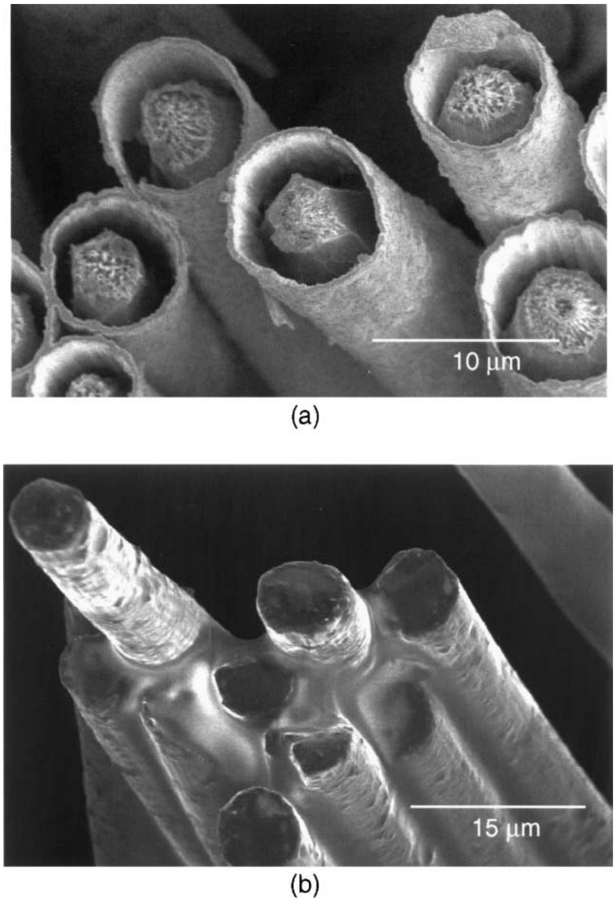

Fig. 10. Coated carbon fibres after an oxidation test: (a) BP1 coating and (b) BP2 coating.

The BP (BP1) deposit oxidizes slower than the carbon. In a C/BP/C composite oxidation will preferentially occur at decohesion zones i.e. at the fibre-deposit and deposit–matrix interfaces at observed with a SiC deposit.[5]

Possible directions for improving internal protection of C/C composites would be:

- to implant the boron on carbon fibres closer to the surface. It would be interesting to perform implantation tests at tensions lower than 100 keV.
- or to coat carbon fibres with a deposit that lead to a volume increase during the oxidation test and that is stable at 1000 °C under low pressures (matrix deposit conditions).[5]

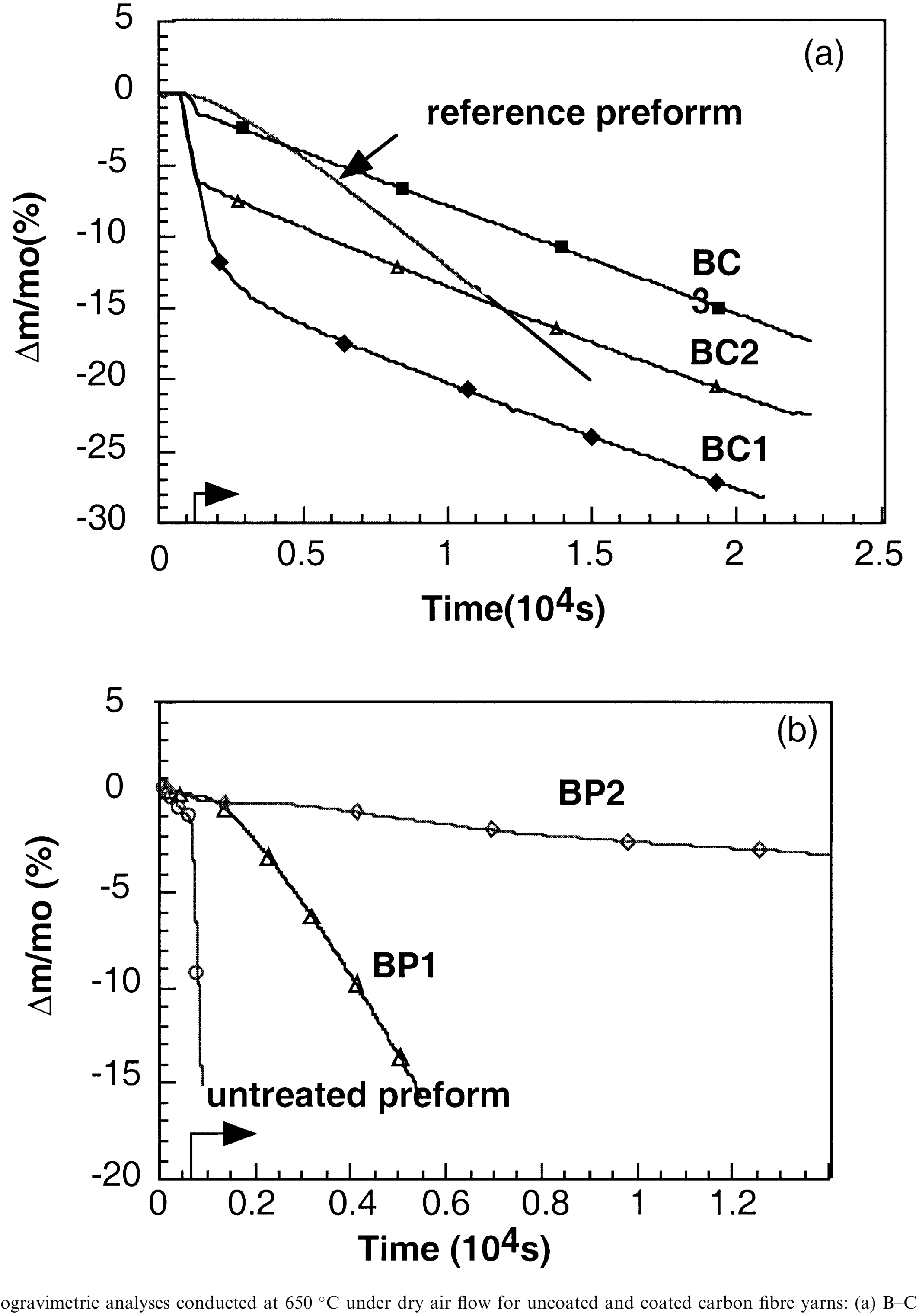

Fig. 11. Thermogravimetric analyses conducted at 650 °C under dry air flow for uncoated and coated carbon fibre yarns: (a) B–C coated carbon fibre preforms and (b) B–P coated carbon fibre yarns. (A temperature of 650 °C is first obtained and the temperature is then maintained at this value.)

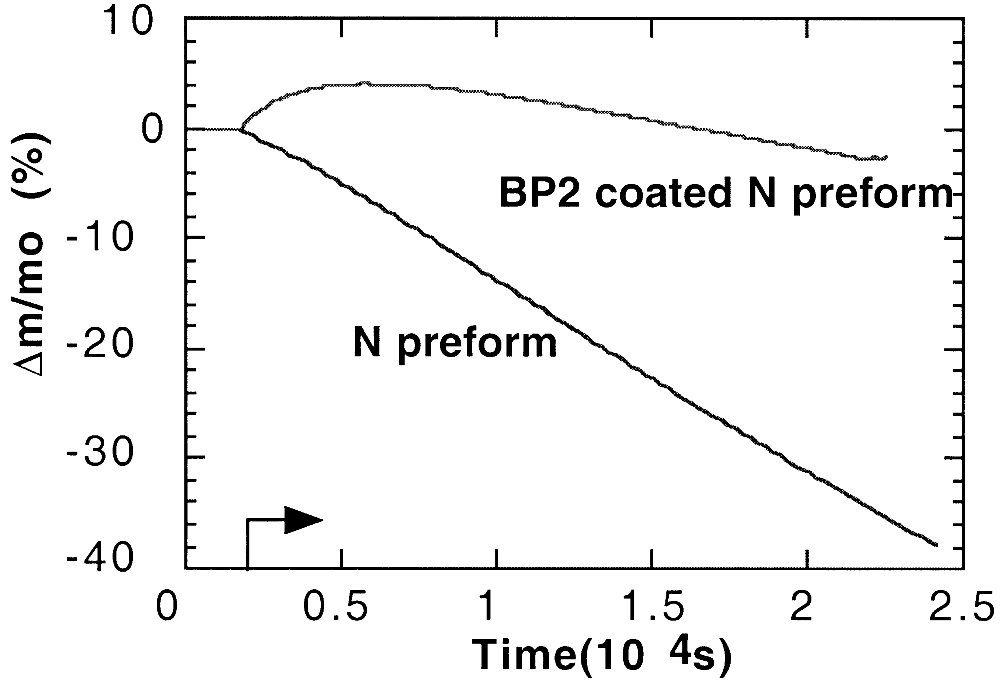

Fig. 12. Thermogravimetric analyses conducted at 650 °C under dry flow air for uncoated and B–P (BP2) coated carbon fibre N preforms. (A temperature of 650 °C is first obtained and the temperature is then maintained at this value.)

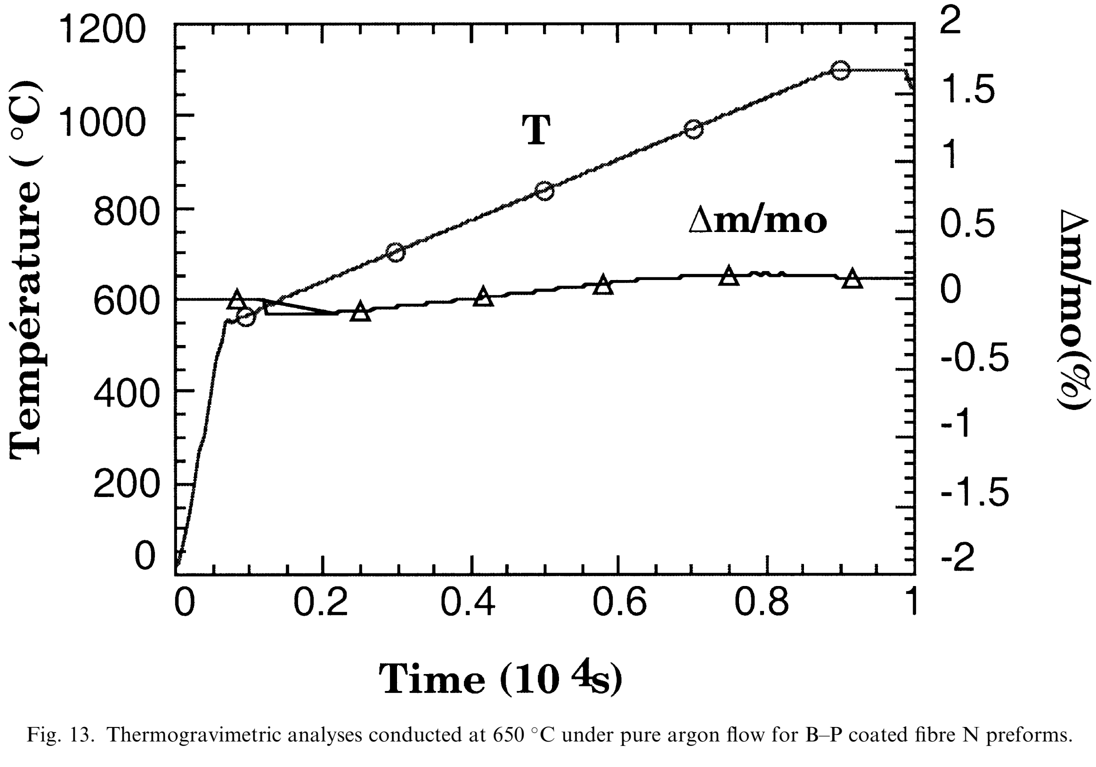

Fig. 13. Thermogravimetric analyses conducted at 650 °C under pure argon flow for B–P coated fibre N preforms.

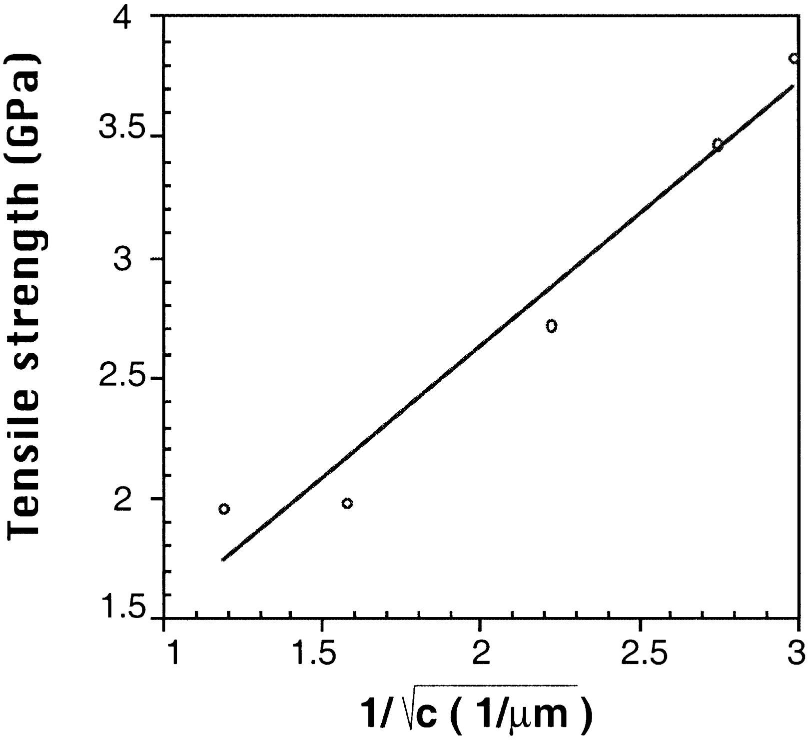

Fig. 14. Tensile strength versus the inverse of the square root of the deposit thickness.

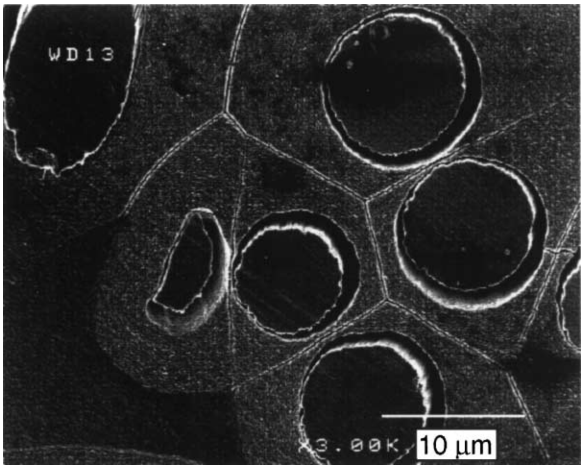

Fig. 15. C/B–C/C composite surface after oxidation.

7. Conclusion

Wet treatments (H_2BO_3 in aqueous solution) and B–P CVD-coatings are not stable under low pressures at 1000 °C. Hence, they could not be used as C/C composite internal protection if the matrix is deposited by conventional CVI. Carbon matrix deposited at a lower temperature (i.e. from a suitable precursor) might be a solution to test these internal protections.

For C/C composites fabricated from boron ion implanted carbon fibres, a hole will be formed before the formation of the B_2O_3 film that is to protect carbon fibres. Boron-ion implantation in carbon fibres cannot be used as internal protection in a C/C composite.

B–C deposits are not very efficient as internal protection. They oxidize faster than carbon and lead to an important volume decrease. So a hole is formed at interfacial zones at the beginning of C/BC/C composite oxidation. It is foreseen that B–C deposits with a higher boron content might be more efficient as internal protection.

Finally, boron ion implantation in carbon fibres improves their tensile strength, by healing superficial carbon fibre defects.

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