

# Enhancement of the oxidation resistance of the interfacial area in C/C composites.

## Part III: the effect of oxidation in dry or wet air on mechanical properties of C/C composites with internal protections

S. Labruquère, J.S. Gueguen, R. Pailler\*, R. Naslain

*Laboratory for Thermostructural Composites (UMR 5801 CNRS-Snecma-CEA-UB1) University of Bordeaux-1, 3 Allée La Boétie, 33600 Pessac, France*

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### Abstract

Tensile tests were carried out on C/deposit/C composites (100 nm B–C, Si–B–C and Si–C deposits) both before and after oxidation tests at 600 °C under dry or wet air flow for a time of 500 min. The composite failure stresses do not show a decrease when compared to the failure stress of C/C composites. Mechanical properties of composites are affected by damages induced during the oxidation tests. The more important the mass loss, the lower the failure stress. Only a slight influence of oxidation damage at interfacial zones was observed because the yarns within the loading axes are not affected at the sample gage level by the oxidation that progresses mainly from the ends of the samples. © 2002 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

Carbon–carbon composites maintain their strength in inert atmospheres up to about 2000 °C (C/C)<sup>1</sup>. However, in most applications they are subject to oxidizing environments and their oxidation gives rise to a decrease in their mechanical properties.<sup>2–4</sup>

The aim of this work was to study:

- (i) the mechanical properties of C/C, C/B–C/C, C/Si–B–C/C, C/Si–C/C<sup>1</sup> composites both before and after oxidation tests under dry or wet air flows. The fabrication and the oxidation of these composites under dry air flow were reported in part II of this work.<sup>5</sup>
- (ii) the oxidation resistance and the mechanical properties of these composites after a thermal treatment at 2200 °C.
- (iii) the oxidation resistance of thermally treated C/C composites infiltrated by isothermal/isobaric chemical vapour infiltration (CVI) with Si–B–C products.

### 2. Experimental

#### 2.1. Materials

3D-needled preforms supplied by the SEP division of Snecma Moteurs (Le Haillan, France) were used. They were produced from oxidized PAN fibres (M) and were further heat treated at 1600 °C under vacuum (M preform).

M preforms were densified by way of pyrocarbon introduced by CVI in order to obtain C/C composites. A 100 nm layer (B–C, Si–B–C or Si–C) was deposited on the fibre surface of the M preforms before the carbon infiltration. C/B–C/C, C/Si–B–C/C and C/Si–C/C composites were thus obtained. Experimental procedures used to fabricate these composites are described in part II of this work.<sup>5</sup>

A high temperature treatment (HTT) was carried out during several hours under vacuum at 2200 °C on the C/C, C/B–C/C, C/Si–B–C/C and C/Si–C/C composites in order to improve the crystallinity of the carbon.

Finally, a thermally treated C/C composite was infiltrated with “Si–B–C” by chemical vapor deposition (infiltrated C/C composites). Treatments were carried out during 2 or 4 h. Si–B–C infiltration conditions are described in part I of this work.<sup>6</sup>

\* Corresponding author. Tel.: +33-5-56-84-47-18; fax: +33-5-56-84-12-25.

E-mail address: pailler@lcts.u-bordeaux.fr (R. Pailler).

<sup>1</sup> Materials labeled as follows: fibre/interphase/matrix.

## 2.2. Characterization and experimental procedures

Tensile test samples with 25 mm gauge length were machined from the composites, in the Y direction (i.e. one of the main fibre directions) for the mechanical tests (Fig. 1). The test samples were loaded under tension at a rate of 0.05 mm/min to the deformation at failure using an electromechanical machine (4505 Instron). The deformations were measured using a contact extensometer.

The oxidation of the specimens was performed with a thermogravimetric analyser (TAG24 from Setaram) under dry and wet conditions (500 l/h, 3 vol.% H<sub>2</sub>O air flow; 50 °C/min heating rate up to the test temperature). Isothermal treatments at 600 °C were carried out for a time of 500 min.

Specimens were examined after the mechanical tests with a high resolution Scanning Electron Microscope (SEM) (S4 500 from Hitachi).

## 3. Results

### 3.1. Oxidation of C/C composites

The oxidation resistance of the C/C, C/Si–B–C/C, C/B–C/C and C/Si–C/C composites was studied under dry air flow at 600 °C and at atmospheric pressure in part II of this work (Fig. 2) and can be summarized as follow:

- Oxidation of C/C composites occurs preferentially at the fibre–matrix (FM) interfacial zones and progresses all along the carbon fibres into the body of the material.
- Boron-rich Si–B–C deposits reduce the oxidation rate of the composite. The Si–B–C deposit oxidizes faster than the carbon and leads to a volume increase. Hence, a glassy phase is formed at the beginning of the oxidation test at the FM interfacial zones and this glassy phase limits further oxygen access.

- Silicon-rich Si–B–C and Si–C deposits oxidize slower than the carbon and oxidation progresses at the fiber-deposit and the deposit matrix interfaces.
- B–C deposits oxidize rapidly but lead to a volume decrease. Hence, a hole is formed around the carbon fibres at the beginning of the oxidation test.

The oxidation resistance of C/C and C/boron-rich Si–B–C/C composites was studied under wet air flow (Fig. 3). Oxidation under wet air flow leads to an increase of the oxidation rate ( $\times 3$ ) compared to oxidation in a dry air flow for a given material. As for dry air flow experiments, the Si–B–C deposit reduces the oxidation rate of the composite by a factor of 6.

Fig. 4 shows SEM micrographs of C/C and C/Si–B–C/C composites thermally treated at 2200 °C. Decohe- sion occurs at the interfacial zones (fibre–deposit, deposit–matrix) and an increase of the oxidation rate of the composites is observed (Fig. 5). Thermally treated C/Si–B–C/C, C/Si–C/C and C/B–C/C composites present a better oxidation resistance than the thermally treated C/C composite.

Thermally treated C/C composites were infiltrated with a boron-rich Si–B–C deposit during 2 or 4 h. The oxidation resistance of these composites was studied and compared to that of C/C, C/B-rich Si–B–C/C composites and thermally treated C/C composite (Fig. 6). The Si–B–C infiltration improves the oxidation resistance of the composite. The oxidation rate of an infiltrated composite (4 h) is equal to that of a C/B-rich Si–B–C/C composite.

### 3.2. Mechanical tests

Mechanical properties of coated carbon fibres have been studied in part I of this work.<sup>6</sup> The presence of a 100 nm coating on the carbon fibres decreases their failure stress.

#### 3.2.1. Mechanical tests on as-processed composites

Fig. 7a shows the stress–strain curves of the C/C composites with different interphases. The Young's

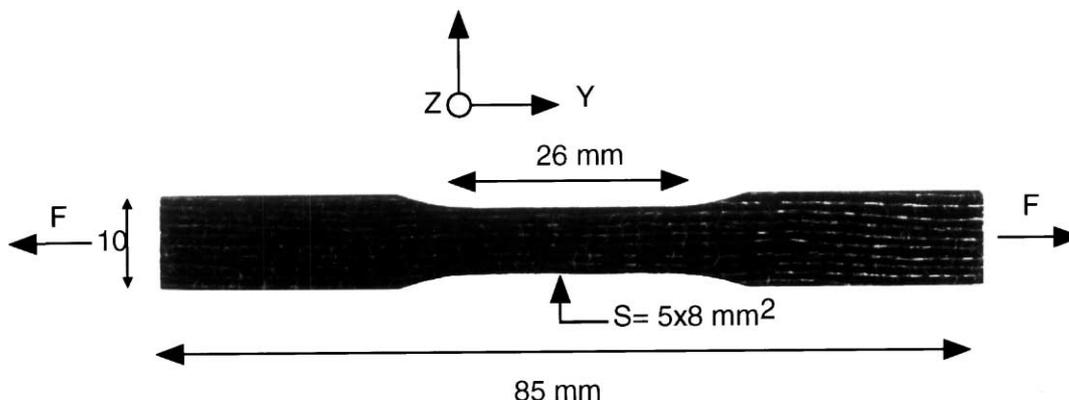


Fig. 1. Description of a tensile mechanical test sample.

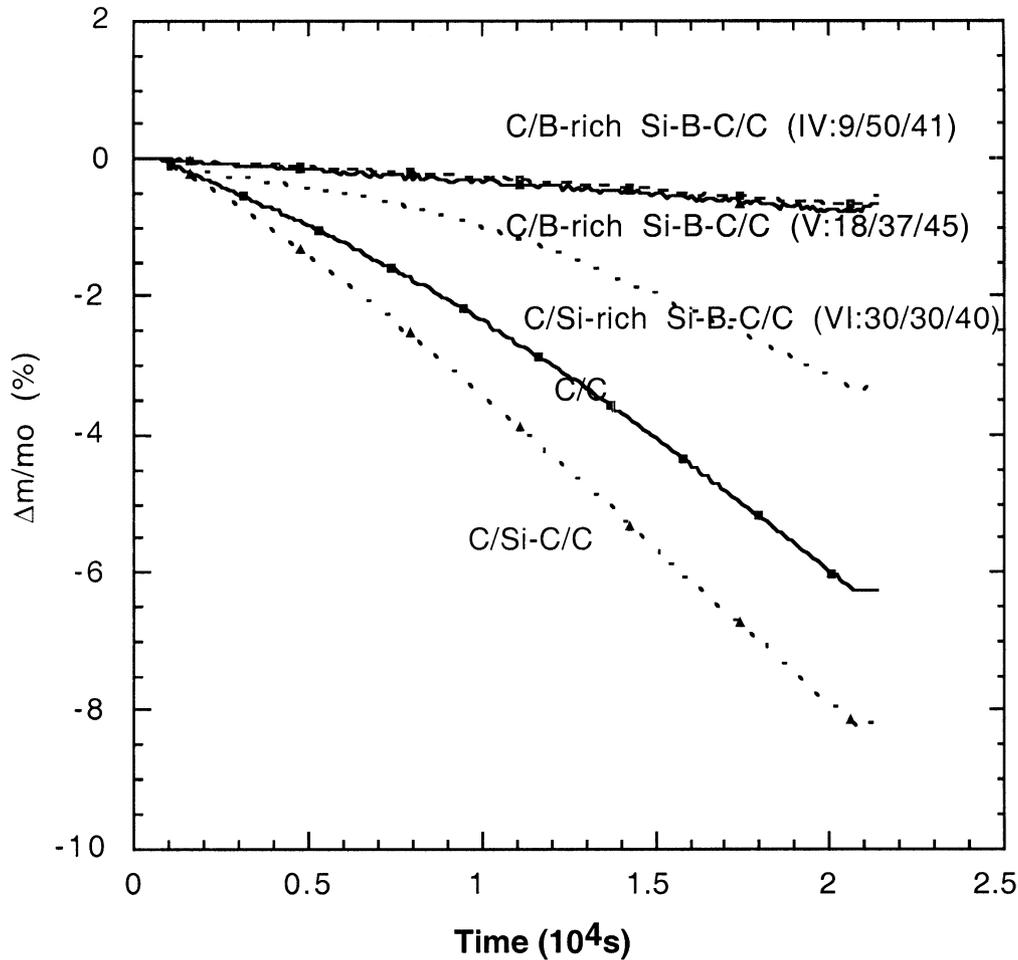


Fig. 2. Thermogravimetric analyses conducted at 600 °C under dry air flow for different composites<sup>5</sup>.

moduli of C/Si-B-C/C composites are higher than those of the other composites (28 GPa compared to 21 GPa for the C/C). Failure stresses and strains are about the same for the different composites.

Whatever the nature of the interphase, the rupture surfaces show limited pull-out (Fig. 8a). In contrast, when the Si-B-C deposit surface has been oxidized (few minutes at 600 °C) before the carbon matrix infiltration, the deposit shows a glassy surface and the pull-out is significant (Fig. 8b) and associated with low modulus and failure stress and high failure strain.

### 3.2.2. Mechanical tests on composites oxidized under dry air

Composites were oxidized for 500 min at 600 °C under dry air flow. Fig. 7b shows the stress-strain curves of the composites after the oxidation test. For C/C, C/B-C/C, C/Si-rich Si-B-C/C composites a decrease of about 20% of the failure stress and of  $\approx 15\%$  of the Young's modulus was observed. C/B-rich Si-B-C/C and C/Si-C/C composites display a decrease of the failure stress of 6% and 30%, respectively.

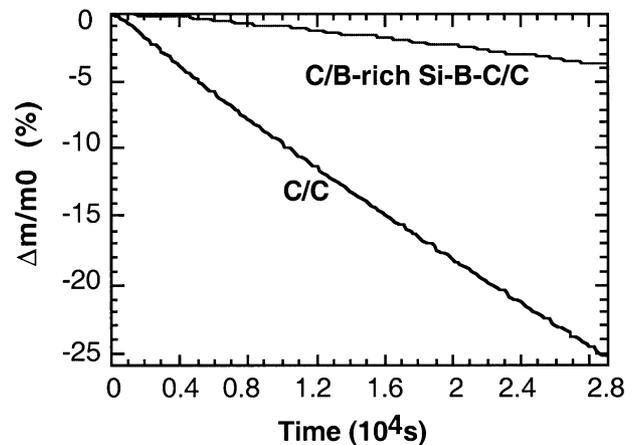


Fig. 3. Thermogravimetric analyses conducted at 600 °C under wet air flow for C/C and C/Si-B-C/C composites.

### 3.2.3. Mechanical tests on composites oxidized under wet air

C/C and C/Si-B-C/C (100 nm boron-rich deposit) composites were oxidized for 500 min at 600 °C under wet air flow and then characterized by mechanical tests (Fig. 9).

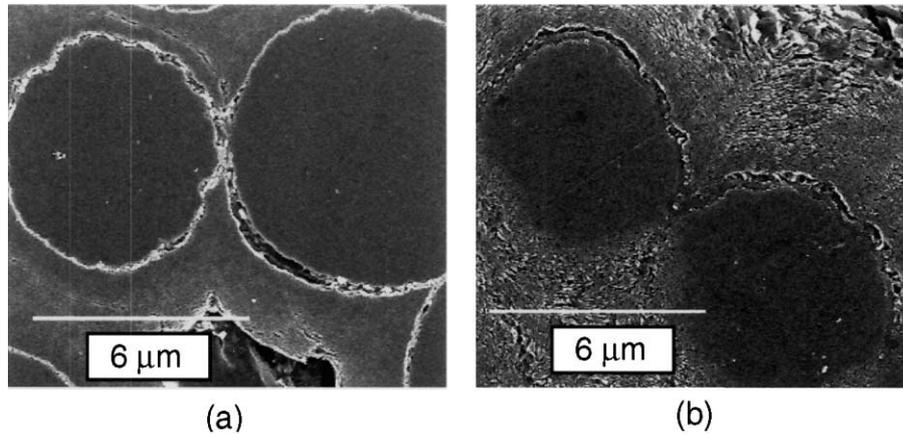


Fig. 4. Surfaces of (a) a C/C composite and (b) a C/Si-B-C/C composite after a thermal treatment at 2200 °C.

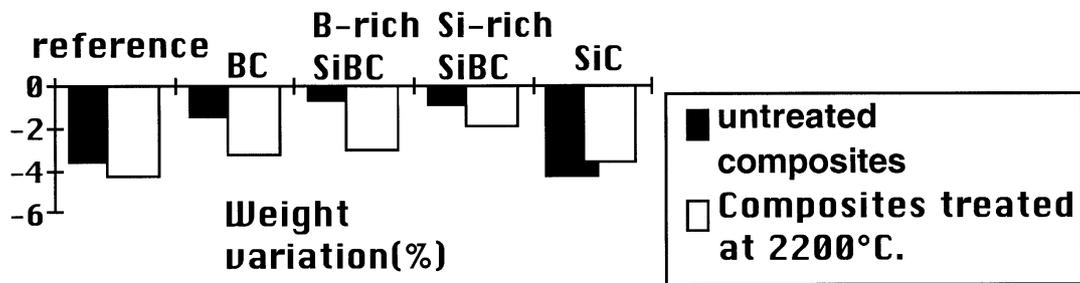


Fig. 5. Weight variation of untreated and thermally treated at 2200 °C C/C, C/Si-B-C/C, C/B-C/C and C/Si-C/C composites after an oxidation test of 500 min at 600 °C under dry air flow.

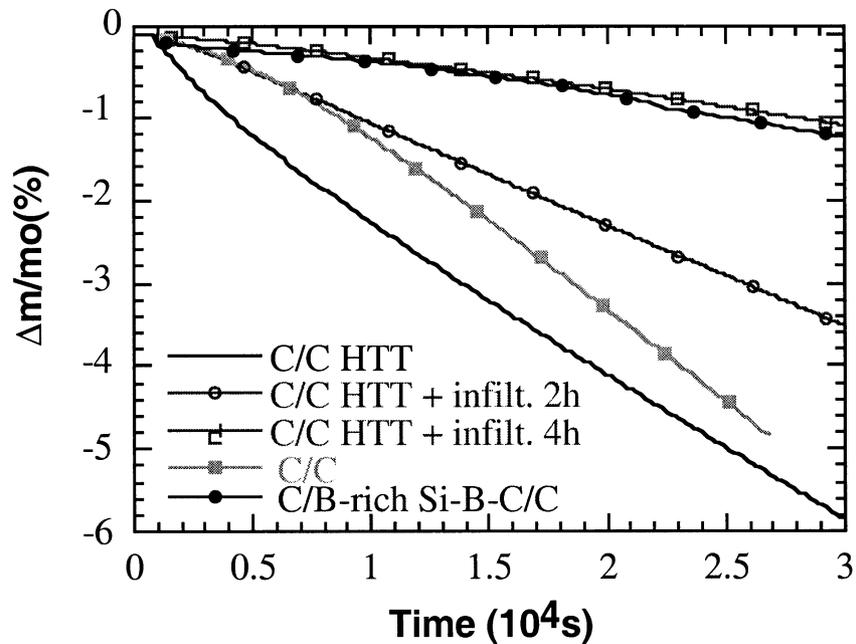


Fig. 6. Thermogravimetric analyses conducted at 600 °C under dry air flow for untreated and thermally treated C/C composites (C/C HTT), C/B-rich Si-B-C/C composite, and thermally treated C/C composites reinfiltred 2 or 4 h with a Si-B-C deposit.

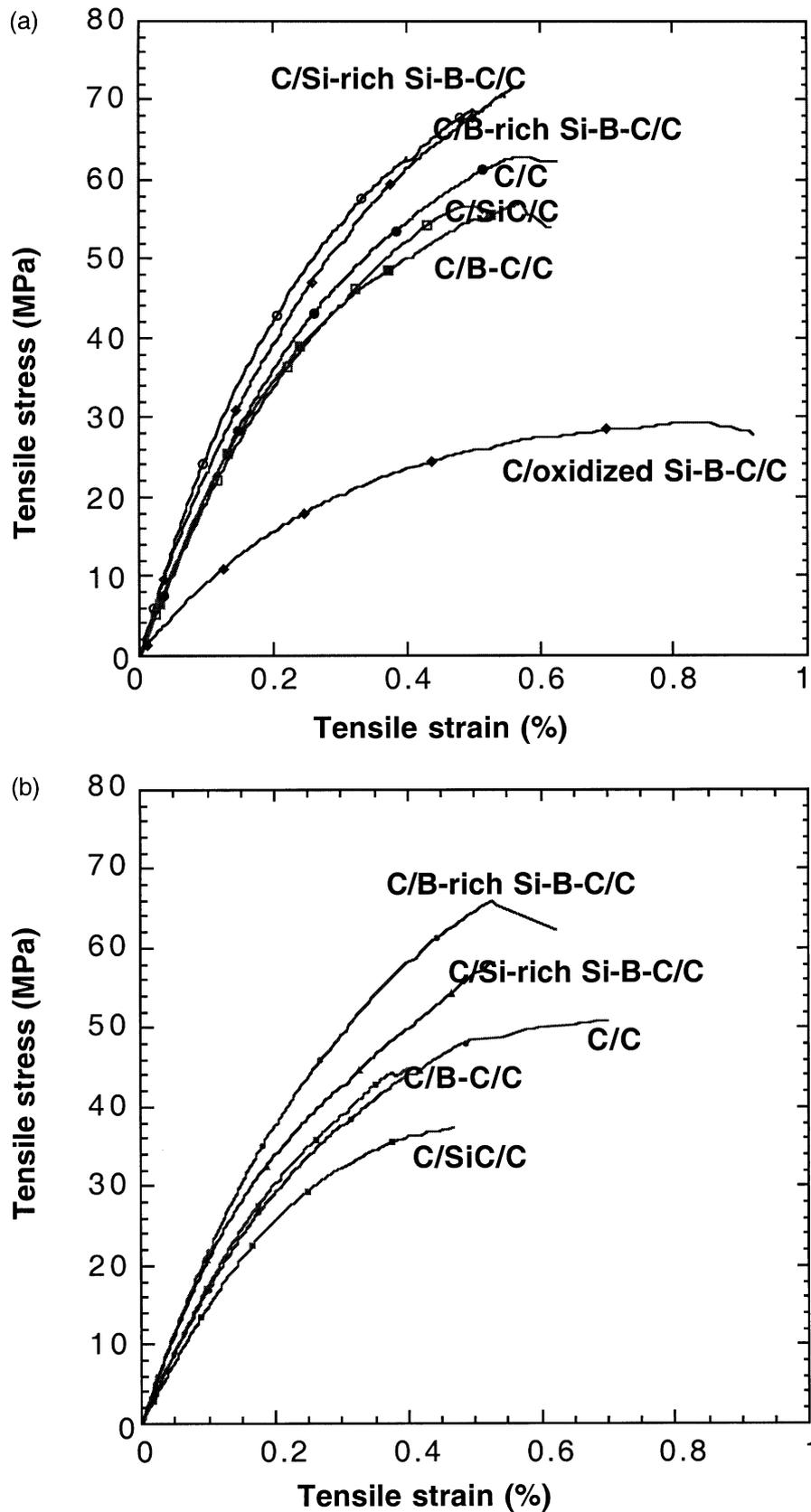


Fig. 7. Tensile curves recorded at room temperature for various composites (a) before (a) and (b) after oxidation tests.

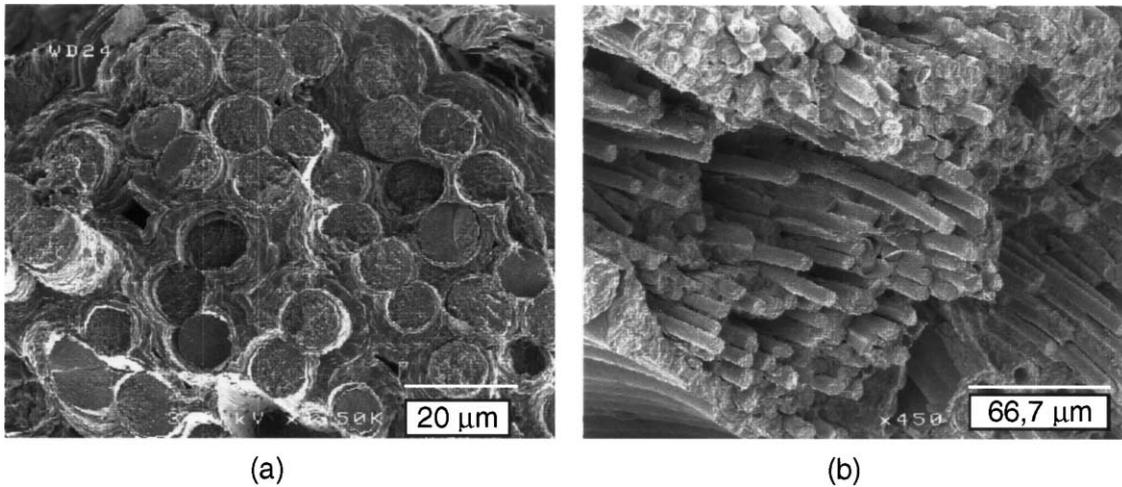


Fig. 8. C/Si-B-C/C composite surface with a (a) 100 nm or (b) an oxidized B-rich Si-B-C deposit after the traction test.

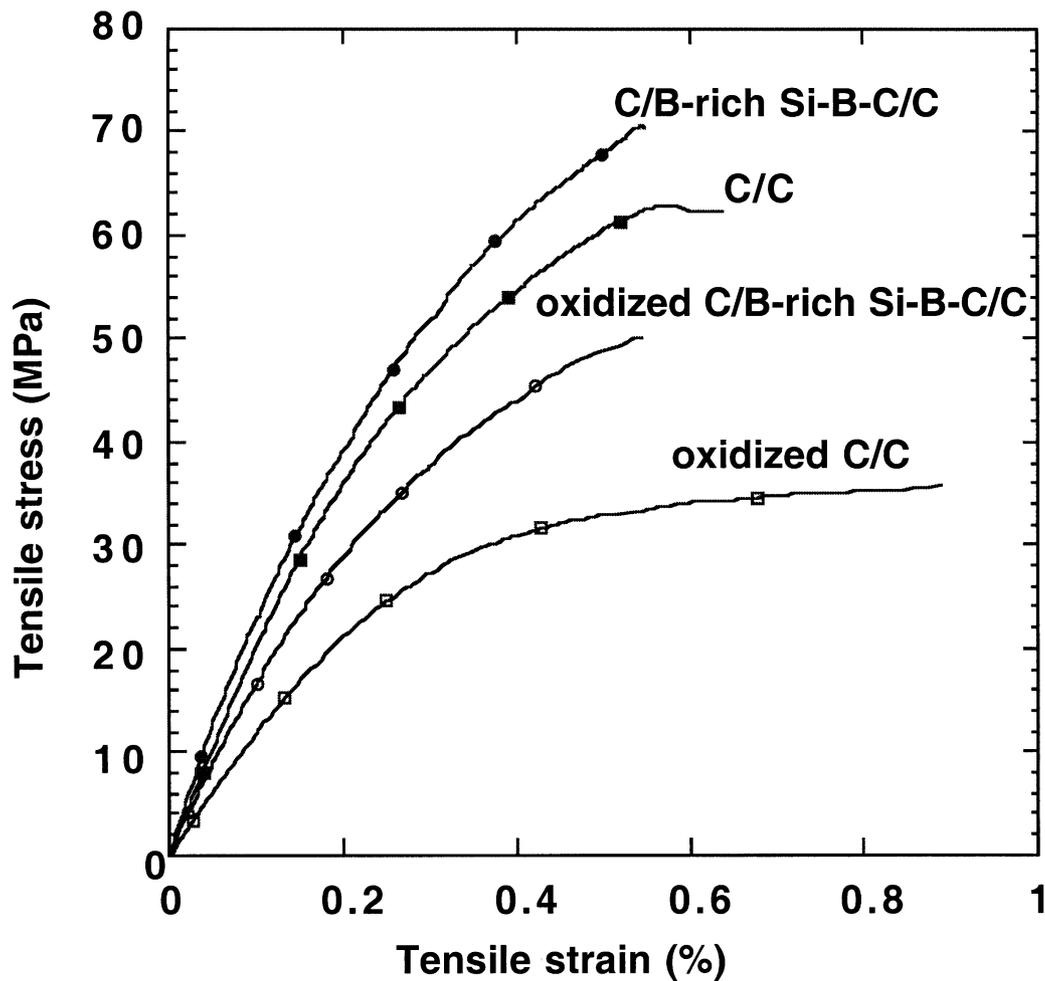


Fig. 9. Mechanical characteristics of (a) C/C and (b) C/B-rich Si-B-C/C composites before and after oxidation tests in wet air flow.

After oxidation the C/Si-B-C/C and C/C composites show respectively a mass loss of 3 and 25% and a decrease of 20 and 40% of the failure stress, respectively.

#### 3.2.4. Mechanical tests on composites thermally treated at 2200 °C

Mechanical properties of composites were studied only for the C/C, C/B-rich Si-B-C/C and C/Si-C/C

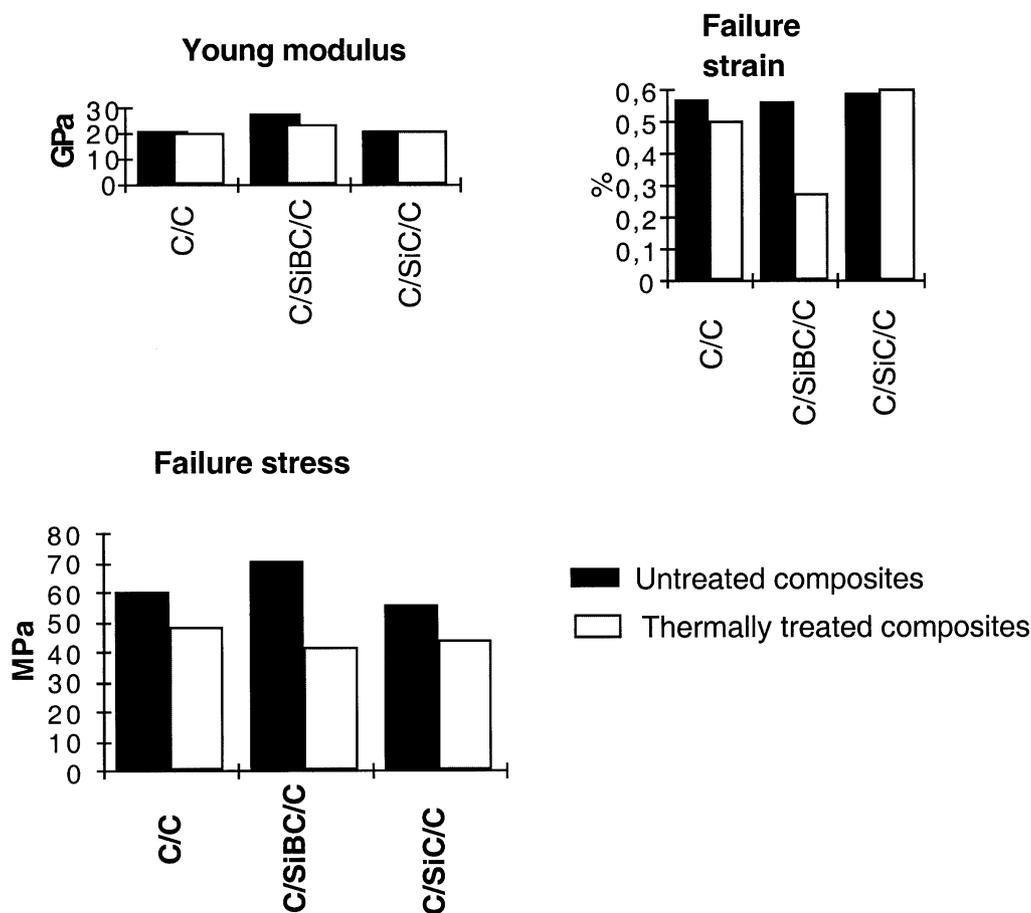


Fig. 10. Mechanical tensile characteristics of thermally treated composites.

composites (Fig. 10). After thermal treatment at 2200 °C, for the C/C and C/Si–C/C composites, the failure stress was reduced by about 20% but the Young's modulus and failure strain were not changed. For the thermally treated C/B-rich Si–B–C/C composite an important decrease of the failure stress and the Young's modulus was observed.

#### 4. Discussion

In contrast to the results with the tensile failure stresses of carbon fibers that drastically decrease when these fibers were coated with 100 nm deposit, C/deposit/C composite failure stresses do not show a decrease compared to the C/C failure stress. Moreover, the presence of a Si–B–C deposit leads to a slight increase of the Young's modulus. However, if the deposit–matrix bond is weak (due for example to a superficial oxidation of the deposit before the matrix deposition) an important decrease of the failure stresses and an important increase of the failure strain is observed associated with an important pull-out.

The mechanical properties of the composites are affected by damage induced during the oxidation tests. Table 1 shows the decrease of the failure stress after the

Table 1

Influence of the interphase and atmosphere on the failure stress decrease and the weight loss (after an oxidation test at 600 °C, 500 min)

Sample (oxidation conditions)	Weight loss (%)	Failure stress decrease after the oxidation test (%)
C/B-rich Si–B–C/C (under dry air)	1	6
C/B-rich Si–B–C/C (under wet air)	3	20
C/C (under dry air)	6.5	20
C/C (under wet air)	25	40

oxidation test (in%) together with the mass loss for different samples. The higher the mass loss, the more important the failure stress decreases. For example, a failure stress decrease of 20% is observed after oxidation of a C/C composite under dry air (6.5 mass% loss) and of 40% after oxidation under wet air (25 mass% loss). The oxidation location also has an influence on the data. The decrease of 20% of the failure stress after the C/C composite oxidation in dry air (6.5 mass% loss) is the same as that for a C/B-rich Si–B–C/C composite (3 mass% loss after oxidation in wet air). In the first case, a preferential oxidation of the FM interfacial

zones is observed in contrast to the second case where a glassy film is formed at the interfacial zones and limits oxygen access.<sup>5</sup> The relatively weak influence of the oxidation damage at interfacial zones on the mechanical properties could be explained by the fact that the yarns within the loading axes are not affected (at the sample gage level) by the oxidation that progresses mainly from the ends of the samples.

The thermal treatment at 2200 °C leads to some graphitisation of the matrix. Consequently, decohesion zones are formed at the interfacial zones. The enlargement of these decohesion zones permits a preferential access of oxygen and leads to an increase of the oxidation rate of the composites. An important increase of the mass loss is observed for the thermally treated C/B-rich Si–B–C/C composite compared to the untreated composite (Fig. 5). Boron-based deposits are not stable at 2200 °C and the deposit characteristics are not maintained after thermal treatment. The oxidation rate of the thermally treated C/C composites infiltrated subsequently with a boron-rich Si–B–C deposit during 4 h is equal to that of a C/B-rich Si–B–C/C composite. The B-rich Si–B–C deposit leads to a glassy phase at the decohesion zones at 600 °C under dry air flow and limits oxygen access in the composite.

A thermal treatment at 2200 °C of composites reduces their failure stress but the Young's modulus and failure strain were not changed except for the C/B-rich Si–B–C/C composite (a decrease of the Young's modulus is observed). The B-rich Si–B–C deposit could have been decomposed at high temperature and boron atoms could have diffused in the carbon resulting in a decrease of the mechanical properties of the fibre. Moreover the Si–B–C deposit could have recrystallised during the thermal treatment leading to a decrease of the mechanical properties of the composite.

## 5. Conclusion

C/deposit/C composite failure stresses are not decreased compared to C/C failure stress if the fibre–deposit and the deposit–matrix bonds are strong.

Oxidation tests lead to a mass loss and induce damage in the composite. At 600 °C, decohesion zones (i.e. FM interfaces) are preferentially oxidized. The presence of a Si–B–C interphase limits interfacial oxidation. A glassy phase is formed at the beginning of the oxidation test at FM interfacial zones and this limits oxygen access. The oxidation rate of composites under wet air flow is 3 times higher than that in dry air flow. The boron-rich Si–B–C deposits are as efficient under dry air flow as

under wet air flow decreasing by 6 the oxidation rate with respect to a C/C composite.

The mechanical properties of composites are affected by damages induced during the oxidation test. For a C/C composite, the more important the mass loss, the lower the failure stress. A relatively weak influence of the oxidation damage at interfacial zones on the mechanical properties was observed and this was explained by the fact that the yarns within the loading axes are not affected (at the sample gage level) by the oxidation that progresses mainly from the ends of the samples. It will be interesting to carry out flexural tests at 600 °C to test more closely the deposit efficiency.

A thermal treatment at 2200 °C of composites produces decohesion zones and particularly at the FM interfaces. Hence, a decrease of the oxidation resistance and of the mechanical properties is observed. An infiltration treatment (4 h) with Si–B–C fills decohesion zones and leads to the formation of a glassy phase during the oxidation test. Thus, oxygen access is limited and oxidation resistance is improved.

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