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C(B) materials as interphases in SiC/SiC model microcomposites

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A specific test procedure has been developed to compare the high temperature lifetimes of SiC/SiC microcomposites with various interphases in air and under mechanical loading. The interphases, namely pure pyrocarbon (PyC) or C(B) materials with uniform or variable boron contents in the thickness, were prepared by chemical vapour deposition (CVD). Uniform addition of boron in PyC interphases improved their oxidation resistance and consequently the lifetimes of the microcomposites. However, room temperature tensile tests have shown that this improvement occurs to the detriment of the mechanical properties even when a non-brittle behaviour is maintained. In the case of variable boron contents, compositional gradient interphases (CGI) in which boron content increases from the fibre interface to the matrix interface allow the mechanical fuse properties of PyC to be combined with the oxidation resistance of a C(B) material.

1. Introduction

The SiC–SiC ceramic matrix composites (CMCs) can be used at high temperature for thermal engine and spatial devices. Their mechanical tensile failure strength is mainly controlled by the crack propagation mode at the interface between the fibre and the matrix, i.e. by the strength of fibre–matrix bonding. The fibre/matrix coupling can be tailored by depositing on the fibre (before the deposition of the matrix) a submicrometre thin film referred to as the "interphase", consisting of a material with a low stiffness and a low shear strength. This material plays the role of "mechanical fuse", i.e. favours the deflection of matrix cracks along the interphase and protects the fibre against mechanical damaging. SiC–SiC composites, including a pyrolytic carbon interphase, are known to exhibit a non-brittle behaviour, related to the anisotropic microtexture of PyC [1, 2].

Nevertheless, an important drawback of this interphase material is its ability to form gaseous carbon oxides under oxidizing atmospheres above 750 K . To improve the oxidation resistance of PyC, it was interesting to introduce boron in this material [3]. Owing to the liquid state of B_2O_3 and to its low volatility in the 800–1400 K temperature range, the oxidation of the interphase could be at least partially inhibited without reducing the mechanical fuse properties of pyrocarbon responsible for the toughness of SiC/PyC/SiC composites.

The aim of the present contribution was to study the ability of the C(B) materials prepared by CVD as described in reference [3] to play the role of interphase in SiC/SiC composite materials. The experimental study was carried out by using microcomposites. A microcomposite is a model composite consisting of one single fibre coated with the interphase and embedded in the matrix. It represents one of the possible elementary cells of the composite and can be easily prepared by CVD. The various microcomposites were characterized in terms of (i) tensile strength at ambient temperature and (ii) high temperature lifetime in air under mechanical loading, for which a specific test procedure has been developed.

2. Experimental procedure

2.1. Preparation of microcomposites

The fibres used for the fabrication of the microcomposites are Nicalon (a Si–C–O fibre (ceramic grade, NL 200)) fibres and have received a pre-treatment in order to improve the fibre–interphase bonding (SEP treatment [4]). The C(B) interphases were deposited by low pressure chemical vapour deposition (LPCVD) on the fibres by using the conditions defined in reference [3] (i.e. precursor gas compositions in the system C_3H_8–BCl_3–H_2, temperature in the range 1000–1300 K, pressure of a few kPa). The coating-times were adjusted in order to obtain interphases with a total thickness of 0.4 or 0.5 μm. LPCVD interphase deposition was followed by growth of the SiC matrix (about 2.5 μm thick) from the classical precursor CH_3SiCl_3–H_2 at a temperature of about 1223 K (Fig. 1). With these thicknesses, the microcomposites properly simulate the actual composites ($V_f = 50\%$).

Five batches of microcomposites containing uniform interphases with different compositions corresponding to the C(B) materials described in reference [3], were prepared by using various BCl_3 contents in the precursor gaseous mixtures (Table I).

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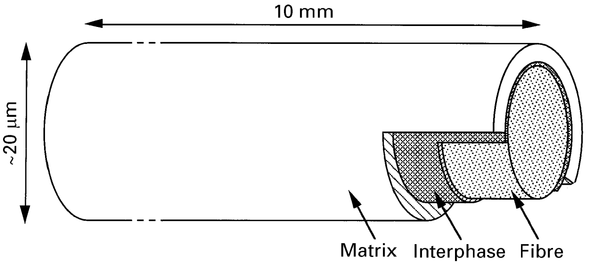

Figure 1 A schematic diagram of a typical microcomposite specimen prepared by CVD.

TABLE I Compositions of the uniform C(B) interphases obtained at $T = 1223$ K, $P = 1.0$ kPa and various initial gas phase ratios $\alpha = 100 \times Q(\mathrm{BCl_3})/(Q(\mathrm{C_3H_8}) + Q(\mathrm{BCl_3}))$ where Q(i) represents the gas flow rate of species i under standard conditions

C(B) interphase	α (%)	Boron content (at %)
I (pure PyC)	0	0
II	30	8
III	50	15
IV	70	20
V	85	33

Four batches of microcomposites containing compositional gradient interphases (CGI) were also prepared:

(i) interphase A in which the boron content increases discontinuously from the fibre interface to the matrix interface;

(ii) interphase A′ is similar to interphase A but the boron content reaches a higher value near the matrix;

(iii) interphase A^{-1} is similar to interphase A but the compositional gradient is reversed;

(iv) interphase B in which the boron content changes alternately from 0 to 20%.

These four interphases are schematically described in Fig. 2. They are constituted by a succession of layers obtained by changing the precursor gas composition along the experiment.

2.2. Characterization

The physicochemical characterization of each uniform C(B) coating has been reported in reference [3]. The CGI-interphases (e.g. A and B) were characterized by Auger electron spectroscopy (AES) depth profiling.

For the mechanical characterization, about twenty microcomposites per batch with a $L = 10$ mm gauge length were tensile tested at room temperature according to a single fibre tensile test procedure which has been described elsewhere [5, 6].

The various batches of microcomposites with a 10 mm gauge length were submitted to thermal ageing in air under a constant load, within a specifically designed heating system (Fig. 3). Each specimen was vertically maintained in the heating area between two SiC CVD filaments (dia. = 100 µm) with an alumina-based adhesive. Given load (from 15 to 40 g depending on the microcomposite diameters and the desired stress) was carefully hooked to the bottom end of each SiC CVD filament in the cold area. The stress was chosen, for each set of microcomposites, very

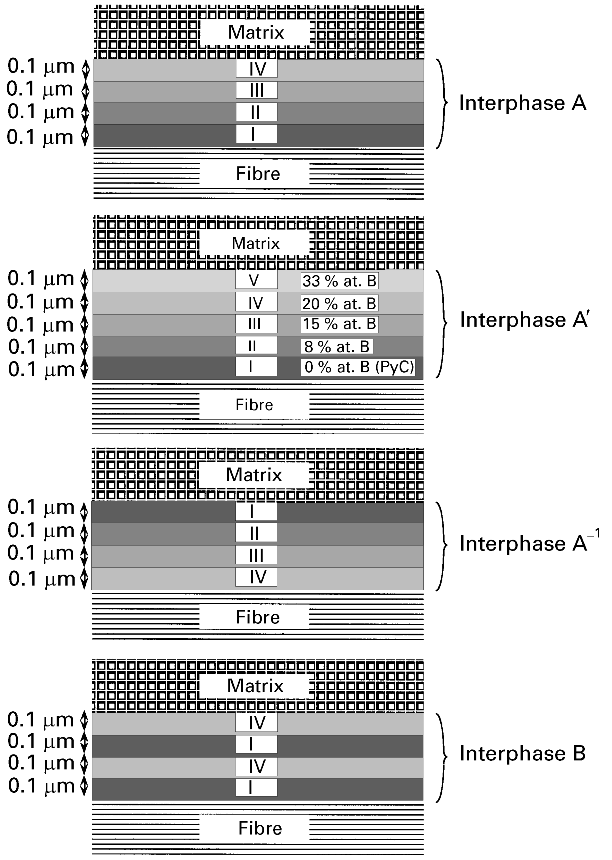

Figure 2 Schematic diagrams of interphases with varying composition across the thickness.

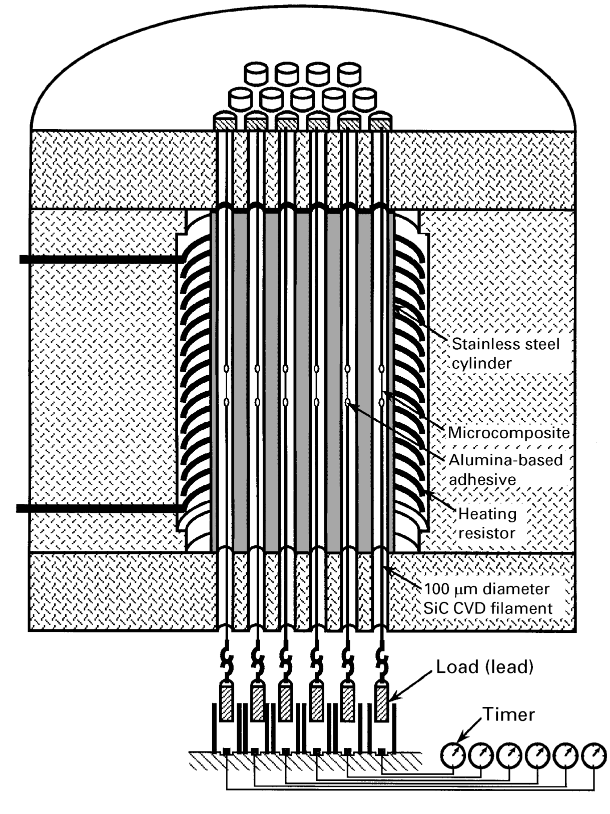

Figure 3 A schematic diagram of the apparatus used for measuring the SiC/SiC microcomposites' lifetime at high temperature in air and under mechanical loading.

close to the proportional limit identified from the stress–strain curves previously established at room temperature. When the temperature reached the set-point of 873 K or 973 K (for which pure pyrocarbon is rapidly gasified), the lifetime (i.e. the time before failure) of each microcomposite was automatically measured by means of a device connected with timers which detect the load fall.

3. Results

3.1. Interphases with uniform compositions

3.1.1. Mechanical behaviour

Average tensile mechanical characteristics at ambient temperature for the five batches of microcomposites containing interphases with uniform composition are presented in Table II. Fig. 4 displays a typical stress–strain curve for each kind of interphase. The introduction of boron in the PyC-interphase lowers the mechanical characteristics of the microcomposites at room temperature: the average failure strength decreases by about one third of its initial value when the boron content reaches 15 at %, then this decrease seems to stabilize for boron content increasing up to 33 at % (interphases III, IV and V) since a brittle behaviour is never really observed. These results are in agreement with those previously reported by Lowden *et al.* [7] and Kmetz *et al.* [8]. Microcomposites without interphase (matrix directly deposited on the fibre) have been prepared and exhibited as expected a brittle character. Furthermore, from tensile tests on fibres only coated with C(B) interphase (V), it has been shown that the mechanical characteristics do not exhibit a significant decrease in comparison to those of fibres only coated with pure PyC-interphase. So, the decrease in the failure strength of the microcomposites when the boron content increases cannot be due to a degradation of the fibres during the boron containing interphase processing.

3.1.2. Behaviour under oxidizing conditions

Owing to the statistical dispersion of the results, the behaviour of the microcomposites during an ageing treatment in air under load are represented for each batch by the percentage of unbroken microcomposites versus time to failure (as shown in Fig. 5). The best interphase (i.e. which has the best oxidation resistance when the SiC matrix in the microcomposite is cracked) corresponds to the lowest decrease of unbroken microcomposites percentage versus time. This test procedure does not give an absolute lifetime assessment of each kind of microcomposite, but permits a simple comparison between the various batches.

At 973 K and under 600 MPa (Fig. 5), increasing the boron content within the interphase clearly improves the oxidation resistance. All the microcomposites with a pure PyC-interphase are broken during the first day of exposure, conversely, only 20% of the microcomposites with an interphase containing 33% of boron are broken after 3 days of exposure.

TABLE II Average tensile mechanical characteristics of the SiC/SiC microcomposites. I: pyrocarbon interphase; II to V: C(B) interphase with increasing boron content. ε_{PL} and σ_{PL} are the yield strain and stress, ε_F and σ_F are the strain and stress at failure. Standard deviations are indicated between parentheses

Materials	ε_{PL} (%)	σ_{PL} (MPa)	ε_F (%)	σ_F (MPa)
Batch I (PyC)	0.31 (0.06)	851 (159)	1.24 (0.61)	1594 (372)
Batch II	0.25 (0.07)	750 (113)	0.97 (0.58)	1351 (378)
Batch III	0.22 (0.03)	639 (104)	0.54 (0.18)	922 (88)
Batch IV	0.19 (0.04)	550 (120)	0.51 (0.12)	985 (96)
Batch V	0.22 (0.06)	635 (156)	0.45 (0.11)	968 (144)

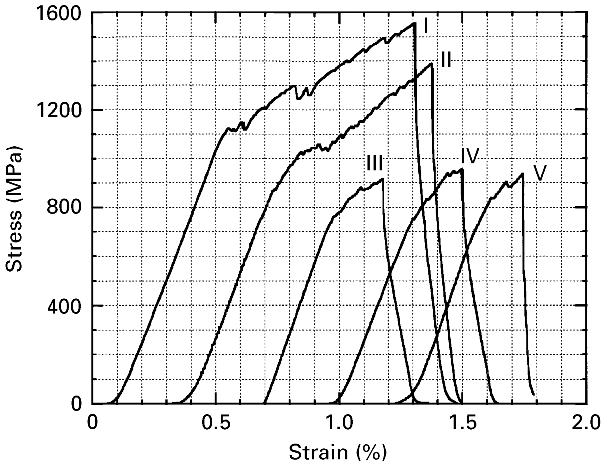

Figure 4 Typical tensile stress–strain curves at room temperature for SiC/SiC microcomposites with different kinds of uniform C(B) interphases (curves are offset horizontally for clarity).

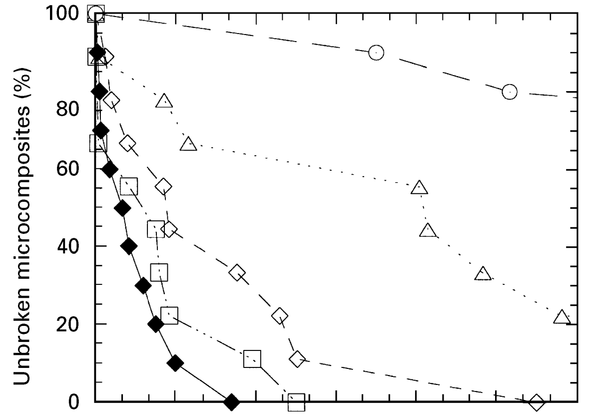

Figure 5 Plots of the percentage of unbroken microcomposites versus time. The microcomposites with different C(B) interphases were subjected to 600 MPa load at 973 K in air. ◆, I; □, II; ◇, III; △, IV; ⊙, V.

3.2. Interphases with variable composition

3.2.1. AES depth profiling

As expected, AES depth profiles displayed in Fig. 6 confirm the occurrence of the four successive layers in both interphases A and B.

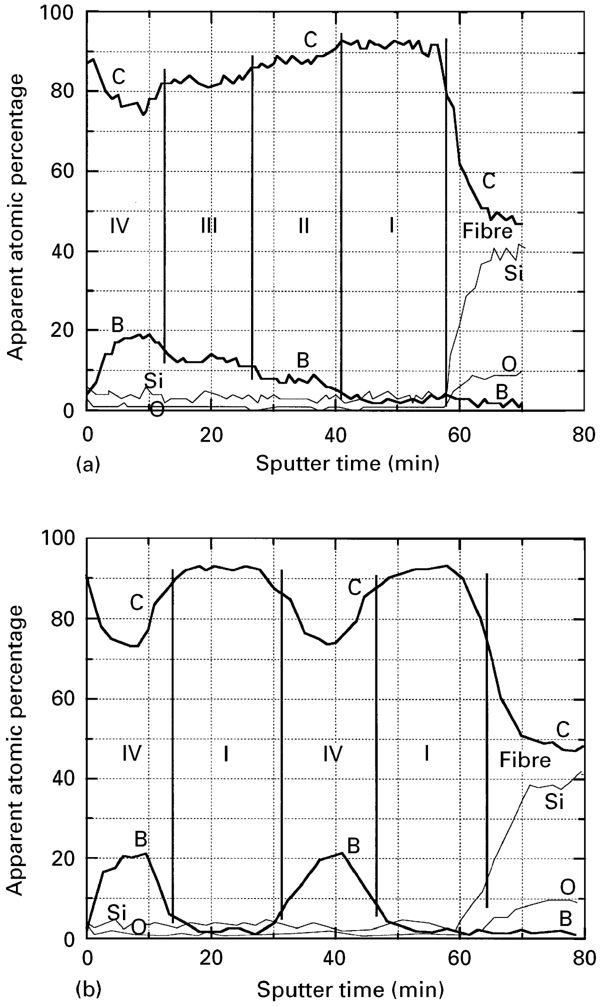

Figure 6 AES atomic concentration profiles for interphases A (a) and B (b) deposited on Nicalon fibre. (Sputter rate: 10 nm min^{-1}; ref. Ta_2O_5).

3.2.2. Mechanical behaviour

Average tensile mechanical characteristics at ambient temperature for the batches A, A′, A^{-1} and B are presented in Table III. Fig. 7 displays a typical stress–strain curve for each kind of interphase. Here, the compositional gradient interphase (CGI) A confers the best mechanical characteristics. The behaviour is very close to that obtained with a pure PyC-interphase. The microcomposites with CGI A′ exhibit good mechanical characteristics but are slightly weaker than those with the interphase A. The data for the microcomposite with interphase A^{-1} show that the reverse of the compositional gradient results in a catastrophic effect. For the microcomposite with interphase B, the mechanical characteristics are rather moderate in spite of a high proportional limit stress.

TABLE III Average tensile mechanical characteristics of the SiC/SiC microcomposites with C(B) interphase, varying in composition across the thickness. ε_{PL} and σ_{PL} are the yield strain and stress, ε_F and σ_F are the strain and stress at failure. Standard deviations are indicated between parentheses

Materials	ε_{PL} (%)	σ_{PL} (MPa)	ε_F (%)	σ_F (MPa)
Batch A	0.24 (0.05)	751 (127)	1.20 (0.47)	1486 (295)
Batch A′	0.27 (0.06)	769 (87)	0.89 (0.26)	1340 (147)
Batch A^{-1}	0.23 (0.07)	686 (83)	0.56 (0.12)	1027 (116)
Batch B	0.34 (0.10)	1001 (154)	0.61 (0.31)	1234 (190)

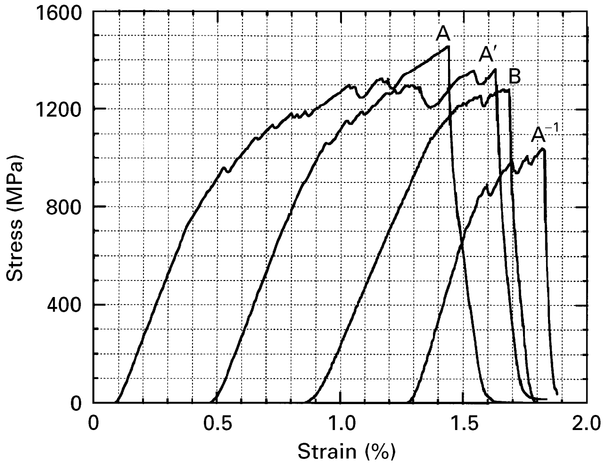

Figure 7 Typical tensile stress–strain curves at room temperature for SiC/SiC microcomposites with C(B) interphases, varying in composition across the thickness (curves are offset horizontally for clarity).

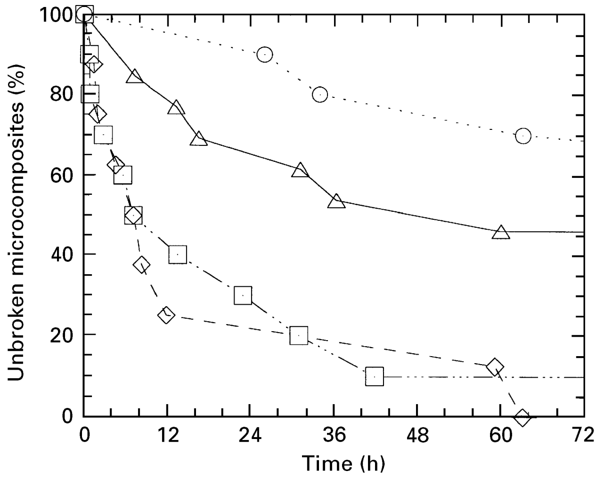

Figure 8 Plots of the percentage of unbroken microcomposites versus time. The microcomposites with interphases varying in composition were subjected to 600 MPa load at 973 K in air. ⊙, A′; △, A; ⊡, B; ◇, A^{-1}.

3.2.3. Behaviour under oxidizing conditions

Fig. 8 shows that at 973 K and under 600 MPa the behaviour of materials with interphases A and A′ is similar to those of materials with interphases IV and V, respectively (Fig. 5). Therefore, in these conditions, the oxidation resistance of these CGIs is as high as if they were only made of their highest boron content part. For the microcomposites with the interphase A^{-1}, one can again observe the disastrous effect of reversing the compositional gradient. For the batch B, the sequence selected for the interphase seems to be inefficient since the behaviour is hardly improved in comparison to pure pyrocarbon.

Thermal ageing at a lower temperature (873 K) shows on the one hand that microcomposite lifetimes are globally maintained despite a higher applied stress

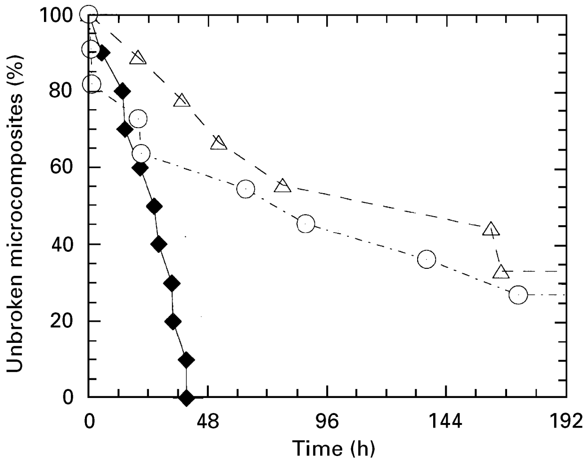

Figure 9 Plots of the percentage of unbroken microcomposites versus time. The microcomposites with interphases I (◆), A (△) and A′ (⊙) were subjected to 800 MPa load at 873 K in air.

(800 MPa) and on the other hand, that the CGIs A and A′ keep their improved behaviour with respect to pure pyrocarbon (Fig. 9). However, the behaviour of the microcomposites with the interphase A′ is here slightly lowered when compared to those with the interphase A probably owing to weaker mechanical characteristics that make the microcomposite more sensitive to the applied stress.

4. Discussion

4.1. Mechanical behaviour

By considering only C(B) interphases (II to V), the mechanical test data could be explained by the large decrease of the C(B) material anisotropy (measured in reference [3] when boron content increases), which unfavours the deflection of matrix cracks along the interphase. However, interphase I (pure pyrocarbon) involves the best mechanical characteristics despite a rather weak anisotropy [3]. From a comparison between the microcomposites with pure pyrocarbon and C(B) interphases, it appears that the most anisotropic interphase does not lead to the best results in terms of mechanical fuse function. This feature could be explained by the segregation of a second phase when boron content exceeds the solubility limit of boron in graphite (2–3% according to Lowell [9]): boron excess is no more inserted in the pyrocarbon network by substitution. This second phase could contribute to lower locally the material compliance and limits the ability of this interphase to deflect the cracks and decrease the mechanical fuse efficiency. Therefore, C(B) materials with such boron contents exhibit a worse capacity for limiting the propagation of matrix cracks towards the fibre than pure pyrocarbon. This result shows that the mechanical characteristics such as stress and strain at failure are not only controlled by the anisotropy of the interphase but also by its homogeneity at the submicrometric scale.

For C(B) interphases with varying composition across the thickness, only a compositional gradient in which the boron content increases from the fibre interface to the matrix interface leads to a good mechanical fuse function. Such a material can gradually deflect matrix cracks before they reach the fibre; it represents an optimum with respect to a reverse gradient such as in A^{-1} or a sequence such as in B. Microcomposites with gradient A′ interphase being slightly less performant than those with type A interphase, it seems that the boron content near the matrix cannot be increased beyond 20–30% without lowering the mechanical characteristics. Owing to their anisotropy and composition, the various layers exhibit probably different thermal expansion coefficients. This feature results in different interfacial shear strength which modify locally the ability of the interphase to deflect the matrix cracks. The presence of an anisotropic layer within the interphase is necessary but its location and its surrounding seem to be also very important.

4.2. Oxidation resistance

Several authors have shown that (i) low boron additions in graphite inhibit the oxidation of carbon and (ii) the formation of a molten B_2O_3 glass acts as a physical barrier against oxygen diffusion for higher boron contents [10–14]. In a previous study of the physicochemical properties of various C(B) materials [3], it has been reported that only a small amount of boron is needed (less than 8 at %) to protect pyrocarbon against oxidation in dry air at 973–1073 K. Moreover, Lowden *et al.* [7] reported that low uniform boron contents in C(B) interphases (about 3 to 5 at %) were enough to yield SiC/SiC composites exhibiting no change in failure strength after annealing at 1273 K in air for 24 h. However, it is necessary according to the present data to reach 33 at % B to obtain microcomposites without failures during such an exposure time at the lower temperature of 973 K. This discrepancy is probably because of the difference between the test procedures used. On the one hand, the oxidation of Lowden *et al.*'s specimens was not carried out under load, therefore open matrix cracks were not present and oxygen did not have an easy access to the interphase. On the other hand, at 1273 K (ageing temperature used by Lowden *et al.*) in air, the matrix SiC can form SiO_2 which can combine locally with B_2O_3 and thus reinforce the action of the protecting glass [15]. Fig. 10a and b show a microcomposite with a C(B) interphase after tensile test performed at room temperature and thermal ageing in air at 973 K under constant load, respectively. In the first case, a classical matrix crack is observed. In the second case, a condensed material, probably a B_2O_3-based glass has been formed together with carbon oxide evolution and has sealed the matrix crack, thus preventing air access to the interphase. At 873 K, the improved oxidation resistance of the C(B) materials can be preserved owing to the low melting point of the B_2O_3-based glass, which limit the diffusion of the oxygen through the interphase towards the fibre close to the initial matrix cracks. Consequently, the major part of the interphase is kept intact and the fibre–matrix bonding is maintained.

For compositional gradient interphases, if the highest boron content part is located near the matrix, the

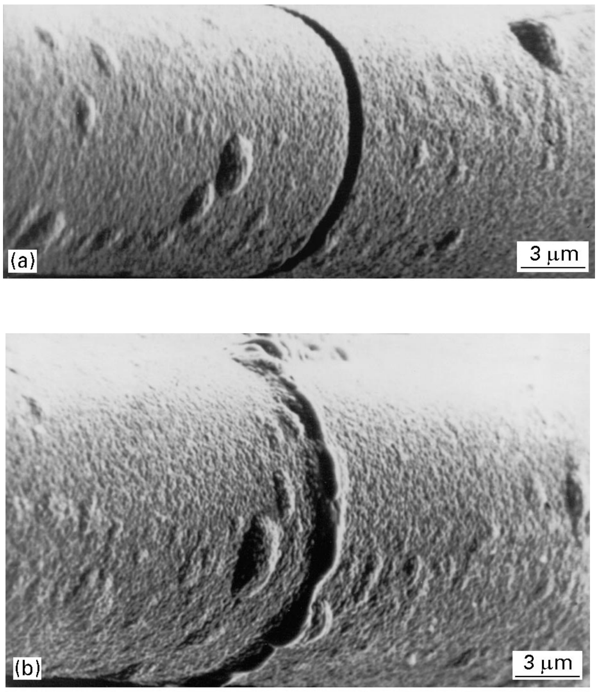

Figure 10 SEM micrographs of microcomposites with a C(B) interphase (a) after tensile test at room temperature and (b) after thermal ageing at 973 K in air under 600 MPa load.

whole interphase is protected. But when the pyrocarbon is near the matrix as in the reverse gradient A^{-1} interphase, it is more rapidly submitted to matrix cracks and consequently to air attack. The somewhat disappointing results for interphase B could be explained by the greater pure pyrocarbon volume (2 layers/4 = 50 vol %) compared to interphase A and also by the fact that the second pyrocarbon layer lies near the matrix.

5. Conclusions

The introduction of various amounts of boron (from 8 to 33 at %) within the pyrocarbon interphase of SiC/SiC microcomposites improves their high temperature lifetimes in air and under mechanical loading but reduces their room temperature stress and strain at failure. By varying discontinuously the boron content across the interphase from 0% close to the fibre to 20 or 33% near the matrix, it is possible to build a microcomposite whose room temperature mechanical characteristics are very similar to those with pure pyrocarbon interphase, and high temperature lifetimes in air and under mechanical loading are highly improved. Such a compositional gradient interphase can gradually deflect the matrix cracks and protect the material against oxidation; the boron-rich layers giving rise to a B_2O_3-based glass which can seal matrix cracks.

Acknowledgements

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