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Oxidizing ageing effects on SiC–SiC composites

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The effects of oxidizing ageing at 800 and 1400°C were investigated on two unprotected SiC–SiC composites differing in the thickness of the carbon interlayer between the fibres and the matrix. Three-point bending tests showed that ageing generally induces an embrittlement and a weakening of the material. Fractographic observations and microstructural analyses allowed this damage to be correlated with a strengthening of the bonding at the interfaces related to their oxidation. At 1400°C, this phenomenon is however limited by passive oxidation and by a change in the crystallographic structure of the silica created at the interfaces.

1. Introduction

Ceramic–ceramic composites have been recently developed for high-temperature applications requiring a high level of reliability. The aeronautical and space industries are especially interested in such types of material to produce engine components or thermal protection of structures.

Due to the fact that most of these materials are sensitive to oxidation, a surface protection is generally necessary to prevent the oxidation of the bulk material for these applications [1]. However, a fail-safe concept requires that local damage in the protecting layer does not lead to rapid destruction of the component through oxidation. From this point of view, the study of the oxidation of ceramic–ceramic composites remains an important field of research for checking the reliability of existing materials even when protected, as well as for improving the oxidation resistance of future ones.

This paper is interested in this subject, concerning the oxidation of two unprotected SiC–SiC composites. The oxidation mechanisms were investigated by analytical and microstructural techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron probe microanalysis (EPMA), as well as their consequences for the mechanical properties of the material.

2. Materials

Two different materials produced by Société Européenne de Propulsion (S.E.P.) were tested. Both were unprotected two-dimensional SiC–SiC composites processed from Nicalon fibres (Nippon Carbon), the matrix being deposited using a cracking vapour impregnation (CVI) process requiring temperatures of about 1000 °C.

The fibres, whose average diameter was about 14 μm, were gathered together in yarns containing around 500 fibres. The yarns were woven according to a satin-type pattern with a 1.6 mm period. The final materials were characterized by a porosity varying from 15 to 20% and a fibre content of about 40%.

The first material (material 1) contained NLP 101 fibres while the second (material 2) was based on NLM 202 ones. The chemical compositions of these fibres and their principal mechanical properties are summarized in Table I [2]. The lower oxygen content of NLM 202 fibres makes them slightly more stable versus temperature.

The main difference between the two materials was related to the deposition of carbon on the fibres before the impregnation by the matrix. This technique is currently used for improving the mechanical properties at room temperature to optimize the fibre–matrix bond. Material 1 was characterized by thin carbon interlayers (thickness varying from 35 to 70 nm) whereas material 2 contained thicker ones (from 140 to 200 nm).

3. Results

3.1. Mechanical testing

Three-point bending tests were performed at room temperature on both materials in the as-received state and after thermal ageing. Ageing durations of 1, 10, 100 and 1000 h were investigated in air at 800 and 1400 °C, the specimens being slowly heated and cooled to avoid any damage due to thermal shock. Six specimens were tested in each condition.

Samples were cut respectively from plates of 5 and 6 mm thicknesses for materials 1 and 2, which corresponds to a minimum of 10 layers of fabric. 2 mm thick specimens were tested parallel to the layer-plane with a span of 18 mm.

During the loading, monitoring of the acoustic emission allowed the initiation of damage to be detected: in these types of material it is related to multiple cracking of the matrix [3]. The damage to the virgin material at room temperature also corresponds to a change in the behaviour of the material: the

TABLE I Principal characteristics of the fibres

Property	Fibre	
	NLP 101	NLM 202
Composition (wt %)		
SiC	69	66
C	7	17
SiO_2	24	17
Fracture strength (GPa)		
24 °C	1.29	1.5
800 °C	1.07	1.35
1000 °C	0.93	1.22
1200 °C	0.69	0.96
1300 °C	0.53	0.79
Young's modulus (GPa)		
24 °C	147	200
800 °C	127	194
1000 °C	109	186
1200 °C	83	171
1300 °C	64	154

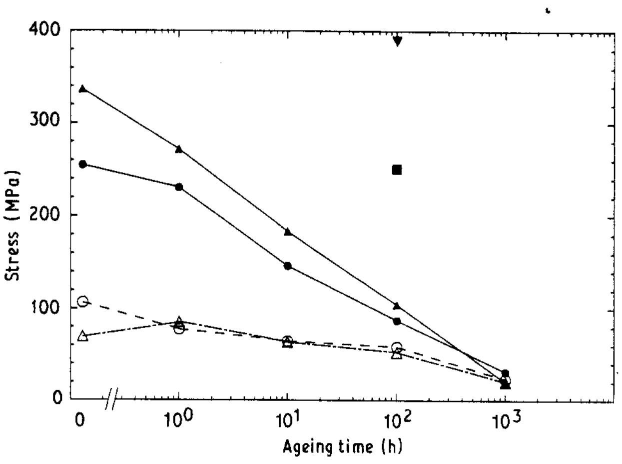

Figure 1 Change in strength σ_r and first damage stress σ_d versus ageing time at 800 °C under air and under vacuum. Material 1: (●) σ_r, (○) σ_d under air, (■) σ_r under vacuum. Material 2: (▲) σ_r, (△) σ_d under air, (▼) σ_r under vacuum.

modulus of elasticity decreases, the dissipative behaviour leading finally to the fracture of the residual intact fibres.

The first damage stress (σ_d) and the strength (σ_r) are plotted versus time in Figs 1 and 2, respectively after 800 and 1400 °C ageing under air. Except for material 1 aged at 1400 °C, ageing induced a strong decrease in strength, which tended to become equal to the first damage stress. On the other hand, the latter remained approximately constant. As the initiation of damage in the material is mainly dependent on the resistance of the matrix, this observation indicates that the matrix is little affected by ageing. These results are well correlated with the changes in the behaviour of the materials, ageing inducing generally an embrittlement of the material [2].

Bending tests were also performed on a few specimens aged for 100 h at 800 °C under vacuum. The results, plotted in Fig. 1, did not reveal any significant weakening. Hence the observed degradation of the mechanical properties of the composites was attributed to oxidation.

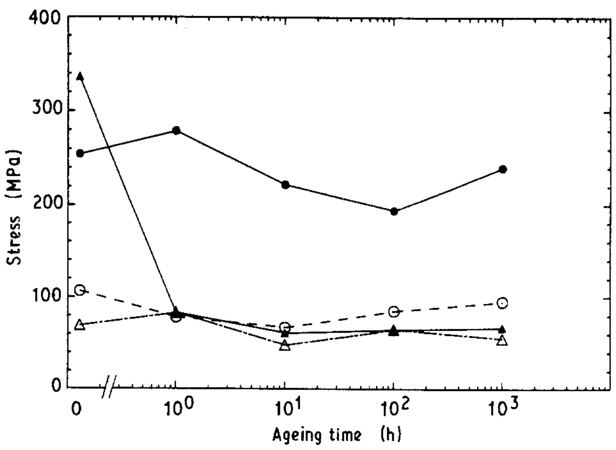

Figure 2 Change in strength and first damage stress versus ageing time at 1400 °C under air. Material 1: (●) σ_r, (○) σ_d. Material 2: (▲) σ_r, (△) σ_d.

Moreover, assuming a negligible effect of ageing on the strength of the matrix, the changes in the mechanical properties of the composites can be due to the degradation of either the fibres or the interfaces. A rapid survey of the literature showed that the weakening of the fibres during oxidizing ageing at 800 °C was not sufficient to cause the effect observed on the composite [4]. Hence oxidation of the carbon interfaces was the main origin of the degradation of the mechanical properties of the materials.

3.2. Fractographic examination

SEM observations were carried out on fracture surfaces of as-received and aged materials (1000 h at 800 and 1400 °C under air). For both composites, they showed the following:

(i) As-received specimens were characterized by numerous pulled-out fibres, typical of a composite having a satisfactory bond between the fibres and the matrix. The same type of fracture surface was also observed on specimens aged at 800 °C under vacuum.

(ii) The brittle behaviour observed at 800 °C (Fig. 3) was always associated with a flat fracture surface (very short pull-out).

(iii) Both previous types of fracture surface were present simultaneously in materials aged at 1400 °C: the edges (free surfaces) exhibited a flat surface (Fig. 4) whereas many pulled-out fibres were observed in the bulk material (Fig. 5). The thickness of material affected by oxidation (flat surface) was about 30 and 50 μm for materials 1 and 2, respectively.

These observations led to the conclusion that the weakening and embrittlement induced by ageing of the composite were due to a bonding of the fibre–matrix interfaces. For this reason, further attention was paid to analysis of the interfaces using different techniques.

3.3. Microprobe analysis

Microprobe analyses were carried out on both materials in the as-received state and after ageing (100 h

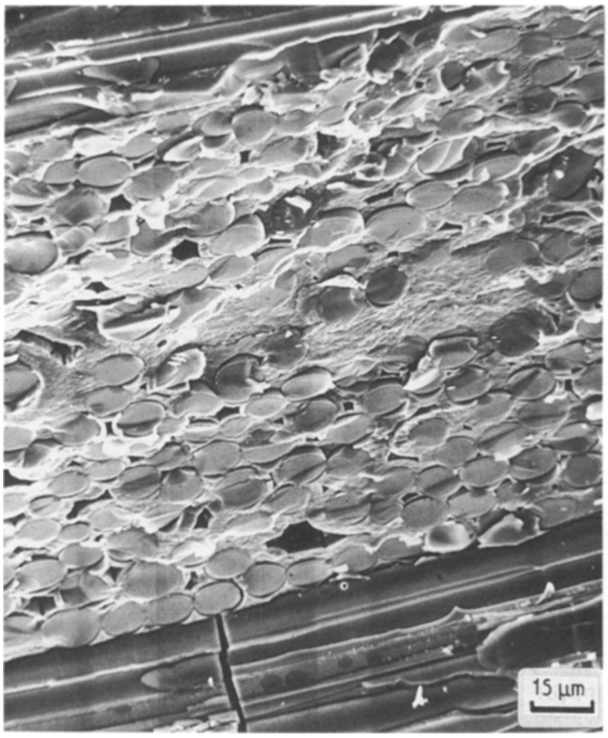

Figure 3 Fractography of SiC–SiC material 2 after 1000 h at 800 °C under air.

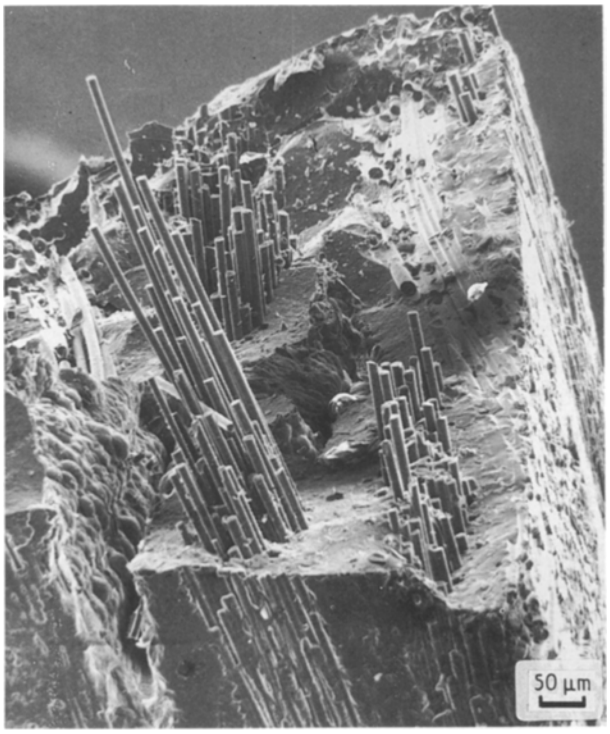

Figure 4 Fractography of SiC–SiC material 2 after 1000 h at 1400 °C under air.

Figure 5 Fractography of the bulk of material 2 after 1000 h at 1400 °C under air.

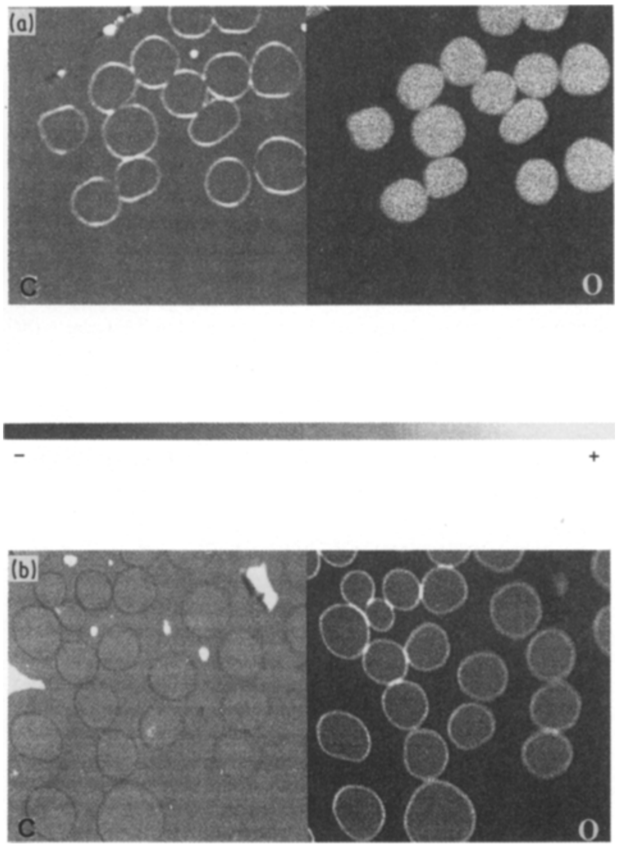

Figure 6 X-ray maps of carbon and oxygen for material 2 (a) as received and (b) aged 100 h at 800°C under air.

under air at 800 and 1400 °C). X-ray maps were obtained for carbon and oxygen and are presented in Fig. 6 [5].

The as-received material 2 exhibited a carbon-rich ring around the fibres, which corresponds to the interphase deposited on the fibres before impregnation by the matrix. In contrast, this ring was not observable on material 1 because its thickness was too small compared to the microprobe resolution.

After 800 °C ageing, the fibres of both materials were surrounded by an oxygen-rich ring having a low carbon content. ☐ 1400 °C ageing induced different effects on both materials. In material 1, oxygen was present around the fibres only close to the free surfaces of the specimens (a thickness of less than 100 μm was concerned): this observation can be correlated with the edge effect previously noted during the fractographic examinations. For material 2, oxygen-rich interfaces were also observed in the bulk material, in which they coexist with unoxidized ones.

Finally, it is worth noting that the excess in oxygen always corresponds to a lack of carbon.

3.4. Transmission electron microscopy

In order to identify more precisely the nature of the interlayers, TEM examinations of the interfaces were carried out on as-received and aged (100 h under air at 800 and 1400 °C) materials.

All the observations and microanalyses were performed with a TEM/STEM Philips EM 430, equipped with X-ray and electron energy-loss spectrometers. Different techniques were used to identify the structure of the interface: high resolution electron microscopy (HREM), electron energy-loss spectrometry (EELS) with a probe size of 10 nm in the imaging mode, and microdiffraction. After mechanical polishing to a thickness of 100 μm, the foils were dimpled to 20 μm and ion-thinned at liquid nitrogen temperature.

On as-received materials, EELS analyses revealed the presence of carbon between the fibres and the matrix (Fig. 7). Lattice imaging associated with diffraction patterns allowed turbostratic carbon to be identified, characterized by an interplane distance of 0.37 nm. Near the fibres, the carbon planes were arranged preferentially parallel to the fibre surface, while getting entangled together far from the fibre (Fig. 8). The measured thickness of the carbon interphase was varying from 35 to 70 nm for material 1 and from 140 to 200 nm for material 2.

After 800 °C ageing, an amorphous compound was detected at the interfaces by means of the diffraction patterns. Moreover, on EELS spectra, the presence of the silicon *L*2,3 and oxygen *K* edges allowed us to identify it as silica, whose thickness was about 250 nm for both materials. These observations, summarized in Fig. 9, are in good agreement with results published in the literature concerning the formation of amorphous silica at intermediate temperatures, remaining stable during cooling down to room temperature [6].

Ageing at 800 °C induced for both materials (differing by the thickness of their original carbon interface) the creation of an amorphous silica interlayer. The latter was the origin of a strong chemical or mechanical bond between the fibres and the matrix, leading

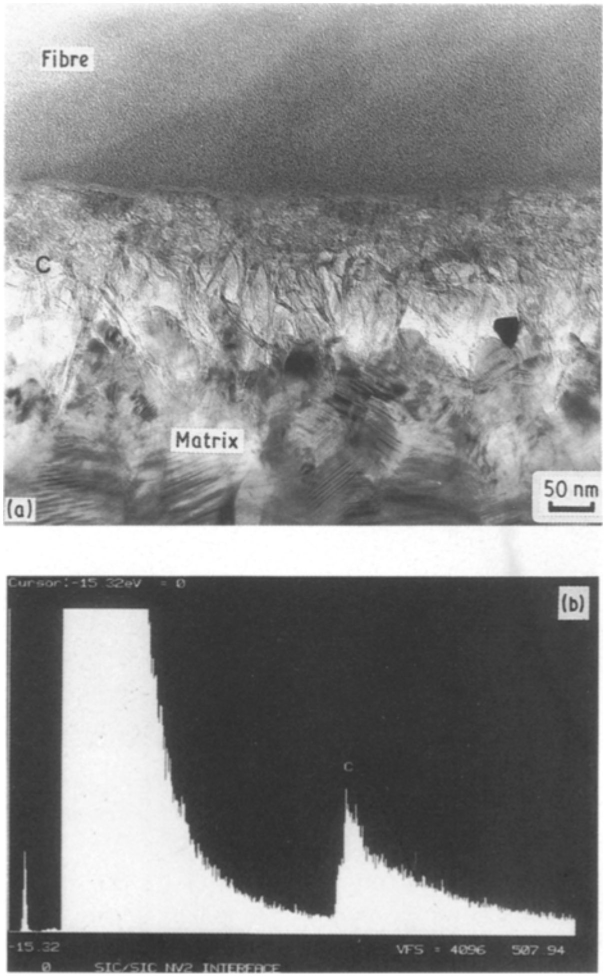

Figure 7 (a) TEM interface observation of as-received SiC–SiC material 2 and (b) X-ray spectrum of the carbon interphase.

Figure 8 HREM of carbon interphase, material 2.

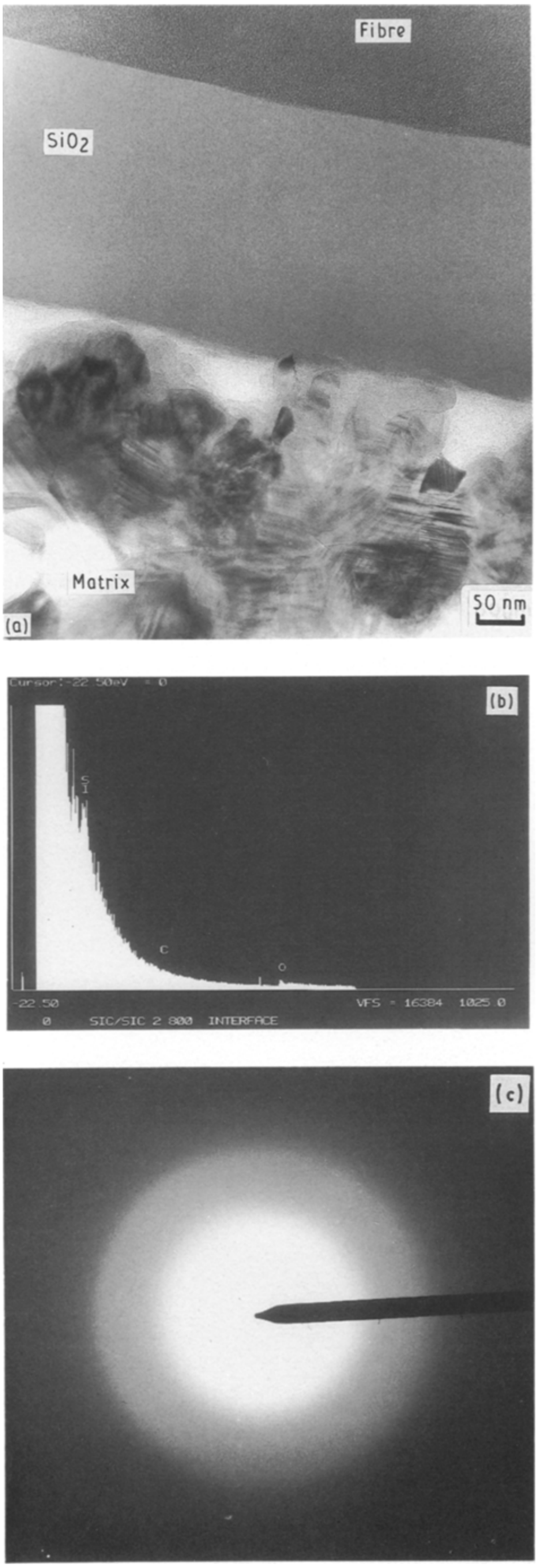

Figure 9 (a) TEM interface observation of material 2 aged 100 h at 800 °C under air, (b) X-ray spectrum and (c) diffraction pattern.

finally to an important embrittlement of the composite.

1400 °C aged specimens were characterized by the coexistence of turbostratic carbon and silica inter-

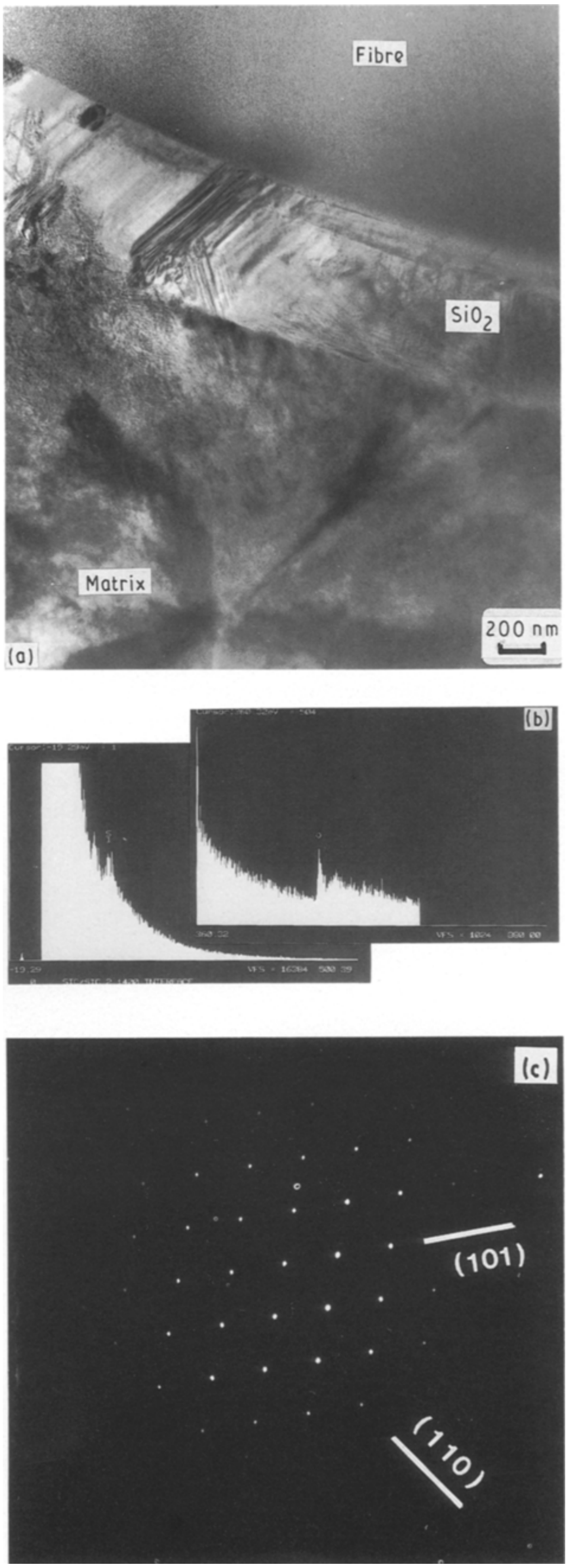

Figure 10 (a) TEM interface observation of material 2 aged 100 h at 1400 °C under air, (b) X-ray spectrum and (c) diffraction pattern.

layers, depending on the access of oxygen to the interface. However, contrary to 800 °C ageing, silica was crystallized in the α-cristobalite form identified by the electronic diffraction pattern. Its thickness varied from 200 to 600 nm. Fig. 10 illustrates this result. According to the literature [7], silica was probably created at 1400 °C in the β-cristobalite variety which transformed during cooling to α-cristobalite at about 250 °C. This transformation occurred with an important shrinkage (3 to 7%) which probably weakened the bonding at the interface, so the extracted fibres in the bulk of material 2 could correspond either to carbon or cristobalite interfaces.

3.5. The oxidation process

All these observations allow an oxidation sequence to be proposed, according to the oxidation processes of non-oxide porous ceramics [8].

In the presence of oxygen, the carbon interphase firstly oxidizes, this phenomenon starting from the free surfaces of the specimens. Then, tubular channels are created between the fibres and the matrix, whose silicon carbide surfaces oxidize also, leading to the creation of silica. This oxidation mechanism (sometimes called "pipeline oxidation") has been already observed in SiC–glass composites [9].

For longer oxidation times and/or higher temperatures, the silica created on the surfaces exposed to oxygen tends to fill up the tubular channels, and then to stop the diffusion of oxygen and the oxidation of carbon. This phenomenon, called passive oxidation, drastically limits the further oxidation of the bulk material.

The final state of the material depends on the relative oxidation kinetics of the carbon, controlled by diffusion of the oxygen to the bulk of the material, and of the surface silicon carbide, leading to the passive oxidation. It represents the result of the competition between both oxidation reactions.

4. Discussion

The oxidation model previously described allows an interpretation of our results to be proposed. In our case, at 800 °C the rate of silica formation is very low and is rather independent of the distance to the free surface (the diffusion of oxygen along the tubular channels does not significantly limit the oxidation kinetics). Before the passive oxidation occurs, a bulk oxidation of the carbon interphases is possible, favoured by the small size chosen for the test specimens.

At 1400 °C, rapid oxidation of the silicon carbide leads to a passive oxidation of the material before the complete oxidation of the carbon interphases, so that the bulk material remains partially undamaged. Because of its thicker carbon interlayer which is the origin of its larger channels, material 2 is more difficult to protect against bulk oxidation than material 1. This fact explains the more intensive oxidation observed in the bulk material for composite 2, and as a consequence the more important loss in mechanical properties.

This oxidation process is in good agreement with SEM examinations performed on oxidized materials. An example is given in Fig. 11, which shows silica filling up the channels left by oxidation of the carbon interlayer.

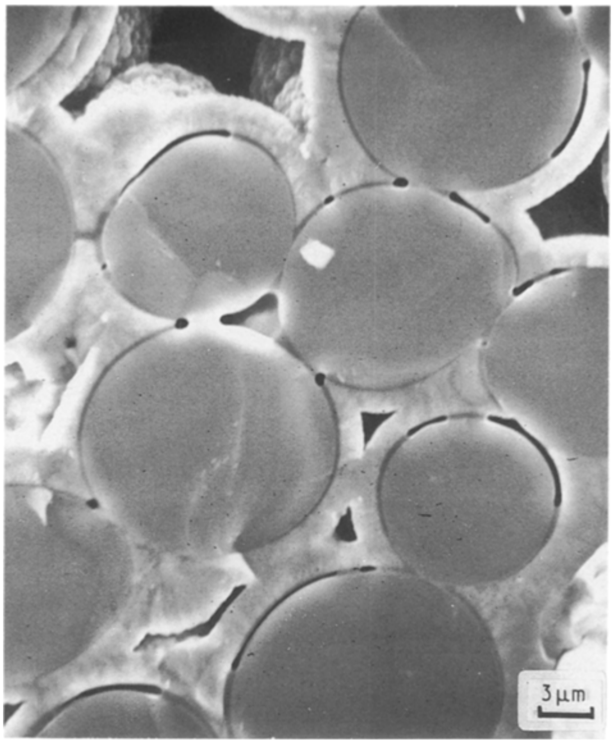

Figure 11 Oxidized interfaces of SiC–SiC material 2 observed after ageing for 1000 h at 1400 °C under air.

Moreover, the passive oxidation effect was confirmed by a specific test carried out on material 1. The strength of the material was not significantly affected by an ageing sequence of 100 h at 800 °C following 100 h at 1400 °C: the silica created during the first exposure avoided a further oxidation during the second one at 800 °C.

5. Conclusion

Optimizing the mechanical properties of a long-fibre ceramic–ceramic composite requires control of the bonding between fibres and matrix and, as a consequence, the introduction of interlayers. This study illustrates the problems related to the use of carbon as an interlayer material for applications involving high temperature and an oxidizing environment.

The use of surface protection drastically limits the damage induced in the bulk material by oxidation. In the longer term, however, the development of interlayers resistant to oxidation also appears necessary to improve the reliability of this type of material.

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