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Ceramic Matrix Composites [and Discussion]

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Ceramic matrix composites

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SiC–SiC coposites exhibit a non-brittle behaviour when the fibre–matrix bonding is controlled by the use of an interphase with a layered structure or microstructure, such as pyrocarbon, hex-BN or $(\mathrm{SiC–PyC})_n$ multilayers. The best mechanical properties are achieved when there is a balance between the crack deflection and load transfer functions of the interphase. SiC–SiC composites are sensitive to oxidation but their stability in oxidizing atmospheres can be improved by tailoring their composition and microstructure.

1. Introduction

Ceramic matrix composites (CMCs), which consist of a ceramic matrix reinforced with ceramic fibres, are potential candidate materials for structural applications at high temperatures owing to their non-brittle mechanical behaviour and to the well-established thermal stability and high melting points of most ceramics. The CMCs which have been the most studied during the past two decades are the carbon–carbon (C–C), the SiC–matrix composites (i.e. the C–SiC or SiC–SiC, where the nature of the fibres is indicated first) and the oxide–matrix composites (such as the SiC–silica-based glass–matrix composites).

C–C composites have been designed initially to withstand short exposures at extremely high temperatures (e.g. in rocket engines or re-entry thermal protection), during which part of the material is usually consumed. More recently, their use has been extended to applications of longer duration but at much lower temperatures (e.g. in brake discs). Despite several outstanding advantages, the C–C composites suffer from a high sensitivity to oxidation even at very low temperatures (e.g. 500 °C). Their oxidation resistance has been improved by incorporating oxidation inhibitors to the matrix or/and adding external protective coating to the composite. However, these solutions might not be efficient enough for very severe use conditions (e.g. repeated load/temperature cycling under oxidizing atmospheres).

The best choice in terms of long-duration compatibility with chemically aggressive environments would be all-oxide composites. However, in the present state of knowledge and technology, some of their constituents, namely, the fibres and the interphases (used to bond in an appropriate manner the fibres to the matrix, as will be discussed later), have not been yet fully identified. Conversely, various oxide matrices with melting points close to or higher than 2000 °C (e.g. mullite, α-alumina, yttria, stabilized zirconia) have already been studied and processing techniques are available.

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SiC–matrix composites seem to be an acceptable compromise with a view to medium-temperature range applications (i.e. at 1000–1500 °C) in oxidizing atmospheres. The SiC–matrix can be formed, as can its carbon counterpart, by both gas or liquid phase routes. High-performance SiC fibres (in terms of strength and creep resistance at 1000–1500 °C) are already studied at the laboratory scale. The weak point of the SiC–SiC composites might be the interphase material (presently, an anisotropic carbon). However, recent research results suggest that the situation could be significantly improved.

The aim of the present contribution is to show the potential of SiC–SiC composites as high-temperature structural materials, and to discuss the improvement which has been achieved during the past few years as well as the weak points which still limit their applications.

2. The CMC concept

It is known from the early work of Aveston *et al.* (1971) that a CMC can exhibit non-brittle mechanical behaviour (although all its constituents are intrisically brittle), provided the fibre volume fraction is high enough and the fibres are not too strongly bonded to the matrix. Under such conditions, the brittle matrix (which fails first since its failure strain is much lower than that of the fibres, typically 0.1 and 1% respectively, for a SiC–SiC composite) undergoes microcracking up to a saturation state beyond which the load is carried by the fibres alone. In this process, each matrix microcrack is deflected parallel to the fibre surface by the weak interface which acts thus as a fuse (protecting the fibre from an early failure). Conversely, when the fibre–matrix (FM) bonding is too weak, the fibre is debonded over a very considerable length and the debonded interface no longer exhibits enough load transfer ability. Thus there should be a balance between the crack deflection and the load transfer functions. When this requirement is fulfilled, CMCs exhibit nonlinear stress–strain behaviour under tensile loading up to failure strains close to that of the fibres, i.e. typically 0.5–1%, which is an outstanding feature for a ceramic material.

The FM bonding mainly stems from thermal residual stresses (TRS) coupled to fibre surface roughness as well as from chemical bonds. The residual stresses are generated, during cooling from processing-temperature (typically, about 1000 °C) to ambient, as a result of coefficient of thermal expansion (CTE) mismatch. The TRS are compressive when $\alpha_\mathrm{m} > \alpha_\mathrm{m}^\mathrm{r}$ (α_m being the matrix CTE and $\alpha_\mathrm{m}^\mathrm{r}$ the radial CTE of the fibre). The latter result from interdiffusion phenomena occurring at the FM interface during processing.

To control the FM bonding, an interphase (often referred to as the third constituent of the CMCs) is generally used. The interphase consists of a submicrometre thin film of a compliant material with a low shear stress, which is usually deposited at the fibre surface before composite processing (it can also be formed *in situ* during processing). The interphase has several key functions. First, it should properly deflect the matrix microcracks while providing enough load transfer, as previously mentioned. Second, it may also at least partly absorb the TRS (present when $\alpha_\mathrm{m} \neq \alpha_\mathrm{m}^\mathrm{r}$), thus acting as a buffer and requiring a minimum thickness of interphase material. Third, the interphase may play the role of a diffusion barrier when the FM couple is very reactive. Finally, the interphase should be compatible with the fibres, the matrix and the environment.

From the present status of knowledge and technology, the best interphases are those with a layered crystal structure or microtexture (e.g. pyrocarbon, hexagonal-BN or mica-type oxides) (Naslain 1993), the layers being oriented parallel to the fibre surface and weakly bonded to one another. Other interface/interphase concepts have been suggested but have not yielded high-performance CMCs, up to now (Kerans 1993).

3. Fabrication of SiC–SiC composites

The SiC–SiC composites considered here are fabricated from continuous SiC-based fibres, according to a low-temperature/low-pressure gas phase route, the chemical vapour infiltration (CVI) process, which has been described in detail elsewhere (Naslain 1992). In a first step, the interphase material, i.e. pyrocarbon (PyC) or hex-BN, is deposited within the fibre preform, from gaseous precursors (respectively, a hydrocarbon or a BF_3–NH_3 mixture) at about 1000 °C and under a pressure of a few kPa or 10 kPa. Interphase thickness ranges from 0.1 to 1 μm. In a second step, the SiC–matrix is infiltrated according to a similar method, from a mixture of methyltrichlorosilane CH_3SiCl_3 (MTS) and hydrogen (Naslain & Langlais 1986). SiC–SiC composites processed by CVI exhibit some residual open porosity (typically, 10–15%). This feature has both some advantages and drawbacks. On the one hand, the residual pores which are regularly distributed in the material, act as crack initiators and contribute to yield homogeneous microcracking of the intertow SiC–matrix. On the other hand, the residual pores, being interconnected, favour the in-depth diffusion of oxygen when the composite is exposed to oxidizing atmospheres. For this reason, an external coating (consisting of a glass-forming material such as SiC) is usually deposited, in a last step, on the composite surface by chemical vapour deposition (CVD) in order to seal the residual pores. Finally it is worth noting that the SiC–matrix deposited by CVD/CVI is textured (with the $\langle 111 \rangle$ direction of the cubic SiC-crystals perpendicular to the substrate) and contains residual stresses due to crystal growth defects (Bobet *et al.* 1993).

4. Mechanical behaviour and effect of the interphase texture

The mechanical behaviour of two-dimensional SiC–SiC composites, e.g. under tensile loading along one of the two fibre directions, has been significantly improved over time as the processing conditions, the texture of the PyC-interphase and the FM bonding, came to be better controlled (figure 1).

The first two-dimensional SiC–SiC composites, fabricated from Si–C–O fibres (e.g. Nicalon, from Nippon Carbon) with no pyrocarbon coating, were essentially brittle, owing to the too strong FM bonding (Naslain 1993) (composite of type D, inset in figure 1). Later, the use of a pyrocarbon coating yielded composites exhibiting some nonlinear stress–strain behaviour (composites of type C). However, the poor control of the FM interfacial zone in terms of the texture of the PyC interphase and bonding between the PyC interphase and the fibre, resulted in limited matrix microcracking and early failure of the fibres and composite (with typically, $\sigma^{R} \approx 180$ MPa and $\epsilon^{R} \approx 0.2\%$).

The role played by the PyC-interphase has been clearly established in more recent materials, namely composites of type A and B, corresponding respectively

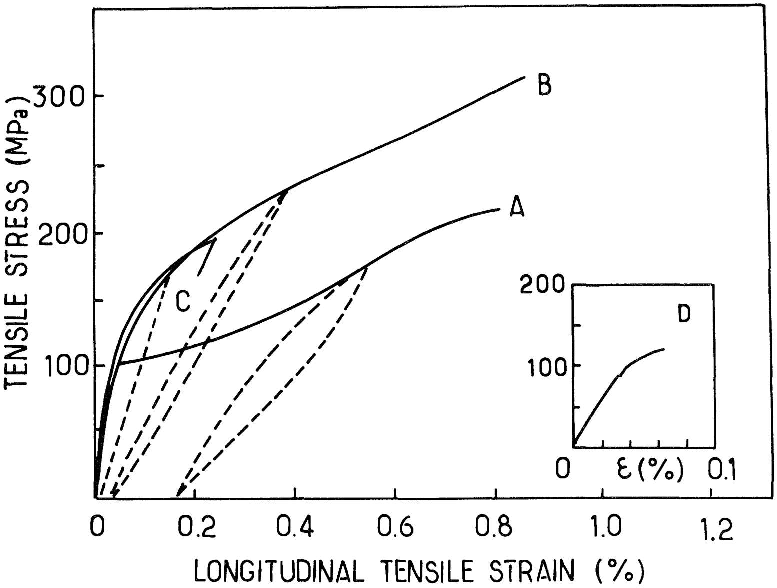

Figure 1. Tensile curves at ambient for various as-processed two-dimensional SiC–PyC–SiC composites fabricated by CVI from Nicalon fibres. After Cojean (1991) and Naslain (1993).

to a weak and a stronger FM bonding (figure 1). In composite A, as soon as matrix microcracking starts, the fibres are debonded over long distances owing to the weak FM bonding (figure 2*a*) with several important consequences: (i) a strong decrease in the load transfer capability of the FM interfacial zone (since the fibres are rapidly debonded from the PyC-interphase) at the beginning of the nonlinear σ–ϵ domain and (ii) a rapidly achieved matrix microcracking saturation state, the microcracks being very few, limited to the intertow SiC and widely spaced. These features are responsible for the 'plateau-like' aspect of the σ–ϵ tensile curve (figure 1). Beyond microcrack saturation, the applied load is essentially carried by the fibres (almost totally debonded from matrix), the matrix microcracks becoming more and more widely opened. Finally, failure occurs at a high strain (0.8–1%) and with extensive fibre pull-out. In such composites, microcrack deflection (the fuse function) occurs near the interface between the Si–C–O fibre and the PyC interphase. It is related to a thin bilayer (thickness of a few 10 nm) consisting of a sublayer of a silica-based glass on the fibre side and a sublayer of strongly anisotropic pyrocarbon (with the atomic planes parallel to the fibre surface) on the PyC interphase side (Cojean 1991; Droillard 1993). It is generally accepted that the silica sublayer results from a surface decomposition/oxidation of the metastable Si–C–O fibres.

The mechanical behaviour of composite B is very different, owing to the occurrence of a different deflection mode of the matrix microcracks itself related to an improved structure of the FM interfacial zone and to better processing conditions (figure 2*b*). In composite B, the PyC interphase is now strongly bonded to the fibre (i.e. the fibre–PyC interface is no longer the weakest link) and still consists of an anisotropic pyrocarbon whose atomic layers are parallel to the fibre surface without being continuous (as they are in graphite). A key difference between composites A and B is that the matrix microcracks are deflected within

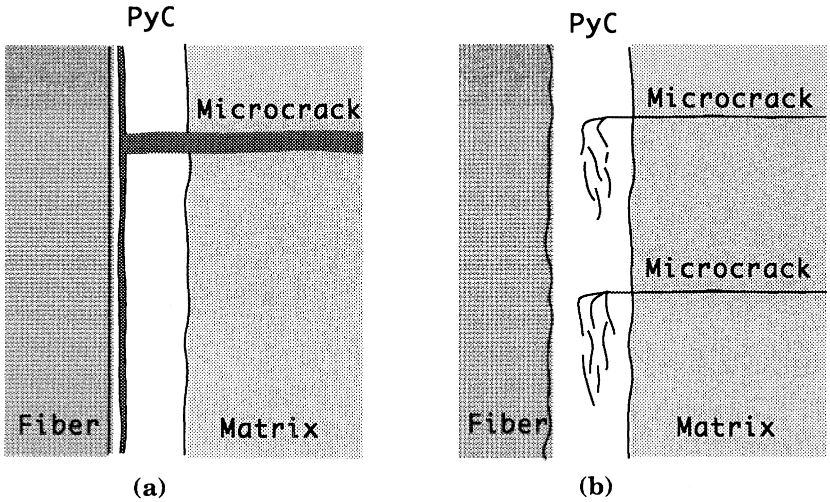

Figure 2. Microcrack propagation paths (schematic) near the fibre–matrix interfacial zone in two-dimensional SiC–PyC–SiC composites fabricated by CVI from Nicalon fibres: (*a*) composites of type A and (*b*) composites of type B. After Droillard (1993).

the PyC-interphase (and not at the fibre surface) in B. Each microcrack is deflected in an infinity of nanocracks formed between the carbon atomic planes, i.e. it is here the whole interphase which is acting as a fuse (whereas in A it is a weak interface at the fibre surface) (Droillard 1993). This new crack deflection mechanism has very important consequences: (i) the FM bonding is not totally destroyed, i.e. as the matrix microcracks are deflected within the interphase, the FM interphase zone keeps enough load transfer ability, thus (ii) matrix microcracking can proceed further (i.e. it occurs both within the SiC intertow matrix (as in A) but also within the SiC–matrix in the 0° tow), the saturation state being only achieved near composite failure, the cracks being numerous and weakly opened (Aubard 1992). Finally, failure occurs at a high failure stress (close to 400 MPa) and high failure strain but with very limited fibre pull-out (since the FM bonding is stronger, as is confirmed by the narrow unloading/reloading loops and by fibre push-out data).

These results clearly show that the best material in terms of mechanical properties is that, composite B, corresponding to the stronger FM bonding (and not, as often reported in the literature, that with the weaker FM bonding exhibiting extensive fibre pull-out) in which an appropriate balance between the crack deflection and load transfer functions of the FM interfacial zone has been achieved during processing.

5. Effect of the environment

SiC is known to have an excellent resistance to oxidation up to about 1500 °C as long as the oxidation regime remains passive (i.e. with the formation of a protective scale of glassy silica). However, even under such conditions, SiC–PyC–SiC composites have at present two weak points: (i) the fibres which do not consist entirely of SiC (Nicalon-type fibre also contains some free carbon and a metastable ternary phase $SiO_{2x}C_{1-x}$) (Bodet *et al.* 1995) and (ii) the pyrocarbon interphase.

(a) Effect of an inert environment

As shown in figure 3, two-dimensional SiC–PyC–SiC composites (type C), fabricated from Si–C–O fibres (Nicalon-type) and aged under vacuum or argon, exhibit a decrease in their mechanical behaviour at ambient temperature. This decrease is observed for ageing treatments performed beyond about 1100 °C and is related to the decomposition of the fibres. At $T > 1100\,^{\circ}\mathrm{C}$, the $SiO_{2x}C_{1-x}$ phase decomposes with an evolution of CO and SiO, the latter reacting with the free carbon of the fibres and the interphase, with two important consequences: (i) grain growth of the SiC-nanocrystals of the fibres (since they are no longer separated from each other by the silicon oxycarbide amorphous phase), resulting in a weakening of the fibres and, more importantly, (ii) a weakening of the load transfer capability of the FM interfacial zone (since the PyC-interphase is progressively consumed and replaced by a void), as supported by TEM analysis and push-out data (Labrugère *et al.* 1993).

The thermal stabiblity of two-dimensional SiC–PyC–SiC composites in vacuum or inert atmospheres could be improved in two ways. First and as mentioned in § 3, a SiC seal-coating can be applied to the composite. Under such conditions, the decomposition of $SiO_{2x}C_{1-x}$ is slowed down by an internal pressure of CO and SiO. However, this solution might become ineffective under load cycling (with microcracking of the seal-coating). A better alternative would be to use fibres which no longer contain the $SiO_{2x}C_{1-x}$ phase, such as the Si–C fibres obtained by an electron beam curing/pyrolysis process, from polycarbosilane precursors. Such fibres (in which the oxygen content is only 0.5 wt%) are stable up to about 1500 °C (Takeda *et al.* 1992).

(b) Effect of an oxidizing environment

In an oxidizing atmosphere (e.g. the air), the weak point of SiC–PyC–SiC composites is the pyrocarbon interphase (assuming that the problem related to the stability of the fibres has been solved, as discussed in § 5 *a*). However, under specific conditions, SiC–PyC–SiC composites behave as self-healing materials.

When, say, a rectangular sample of one-dimensional SiC–PyC–SiC composite (with a SiC seal-coating on the four faces parallel to the fibre direction) is submitted to an oxidation treatment, chemical reactions occur according to the following overall equations:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}, \tag{1}$$

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}, \tag{1'}$$

$$SiC_{(s)} + 2O_{2(g)} \rightarrow SiO_{2(s)} + CO_{2(g)}, \tag{2}$$

$$SiC_{(s)} + \tfrac{3}{2}O_{2(g)} \rightarrow SiO_{2(s)} + CO_{(g)}. \tag{2'}$$

Since, in this example, the oxidation process is a one-dimensional phenomenon, an annular pore is formed around each fibre as the PyC-interphase is progressively consumed (equations (1) or/and (1′)) (figure 4*a*). Thus oxygen (and in the opposite direction CO or/and CO_2) has to diffuse along the pore to react with the PyC-interphase. During this diffusion, oxygen reacts with the pore wall (i.e. the fibre and the matrix) to give a silica scale (equation (2) and (2′)). All these phenomena can be modelled, in this simple case, the results depending mainly on the temperature and the PyC interphase thickness. An example of a simulation is

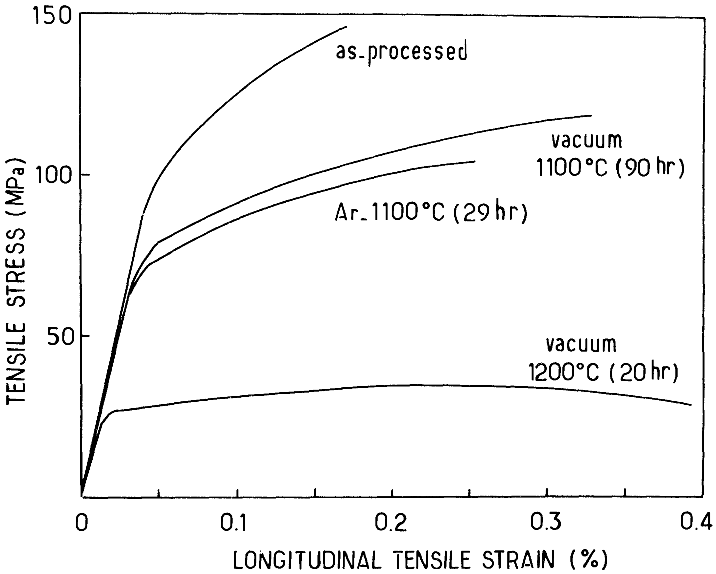

Figure 3. Effect of ageing treatments on the tensile curve at ambient of two-dimensional SiC–PyC–SiC composites (type C) fabricated by CVI from Nicalon fibres. After Labrugère *et al.* (1993).

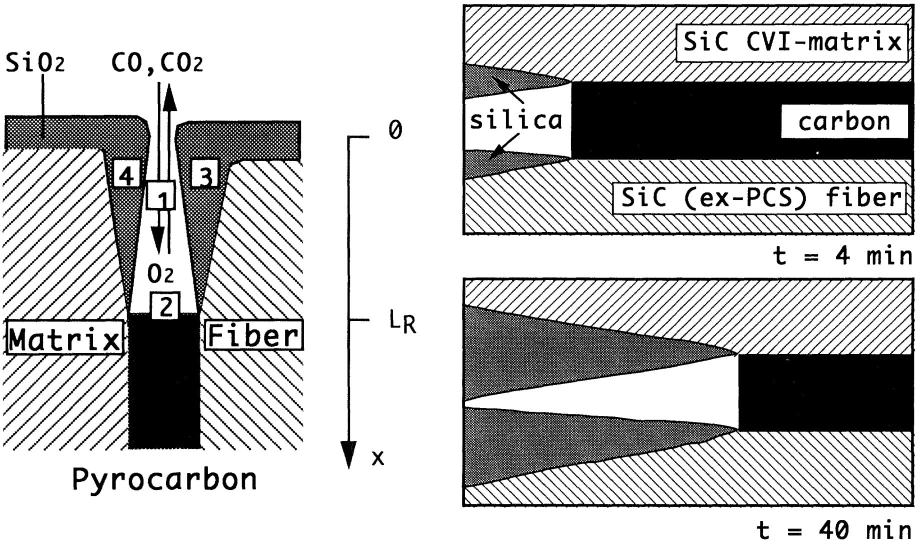

Figure 4. Effect of an oxidizing atmosphere on one-dimensional SiC–PyC–SiC model composites: (*a*) elementary phenomena involved (1: diffusion of O_2, CO–CO_2; 2: oxidation of the carbon interphase; 3, 4: oxidation of the fibre surface and matrix), (*b*) simulation of the oxidation phenomena for an oxidation performed in pure oxygen ($P = 100$ kPa) at 1200 °C. After Filipuzzi & Naslain (1994).

shown in figure 4*b* (Filipuzzi *et al.* 1994). When the temperature is high enough and the PyC interphase thin, the silica scales seal the pore and the oxidation stops.

The effect of both the temperature and the interphase thickness on the length of carbon l_r which is consumed as a function of time is shown in figure 5. For

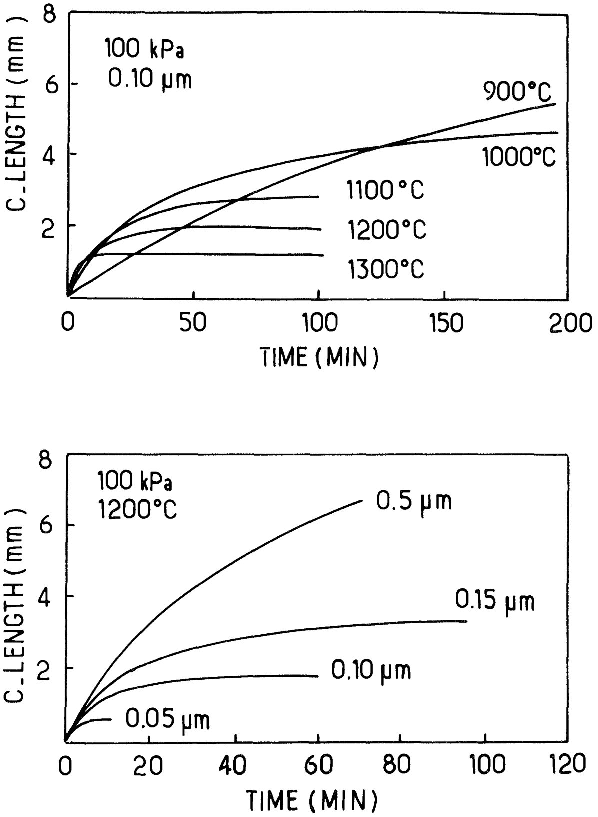

Figure 5. Effect of temperature (*a*) and interphase thickness (*b*) on the kinetics of oxidation of the PyC interphase in model one-dimensional SiC–PyC–SiC composites, as derived from simulation. After Filipuzzi & Naslain (1994).

a given interphase thickness, oxidation proceeds in-depth at low temperatures (since the formation rate of silica is too low) and, conversely, it is limited to near the external surface at high temperatures (figure 5*a*). A similar effect is observed at constant temperature when the PyC-interphase is varied (figure 5*b*).

Thus the effect of an oxidizing atmosphere on SiC–PyC–SiC composites is more dramatic at low temperatures ($500 < T < 1000\,^{\circ}\mathrm{C}$) than at higher temperatures where the material is self-healing.

The compatibility of SiC–PyC–SiC composites with oxidizing atmospheres could be improved at least in two directions. One way is to replace the PyC interphase by, for instance, a multilayered $(\mathrm{SiC{-}PyC})_n$ interphase where the thickness of each PyC sublayer is reduced to a few nm or 10 nm (see figure 5*b* and 6) (Droillard 1993). Another way is to replace pyrocarbon by hex-BN which has a similar layered crystal structure (and thus can act as a fuse) but exhibits a much higher oxidation resistance (figure 7) (Economy & Lin 1977). The oxidation of hex-BN starts at *ca.* 850 °C (instead of *ca.* 450 °C for PyC) and yields an oxide, B_2O_3, which is liquid in a wide temperature range ($500 < T < 1100\,^{\circ}\mathrm{C}$), wets SiC and is known for its healing properties. SiC–BN–SiC composites have been prepared and characterized. However, in the present status of the research, their mechanical properties are not yet as good as those of their SiC–PyC–SiC counterparts.

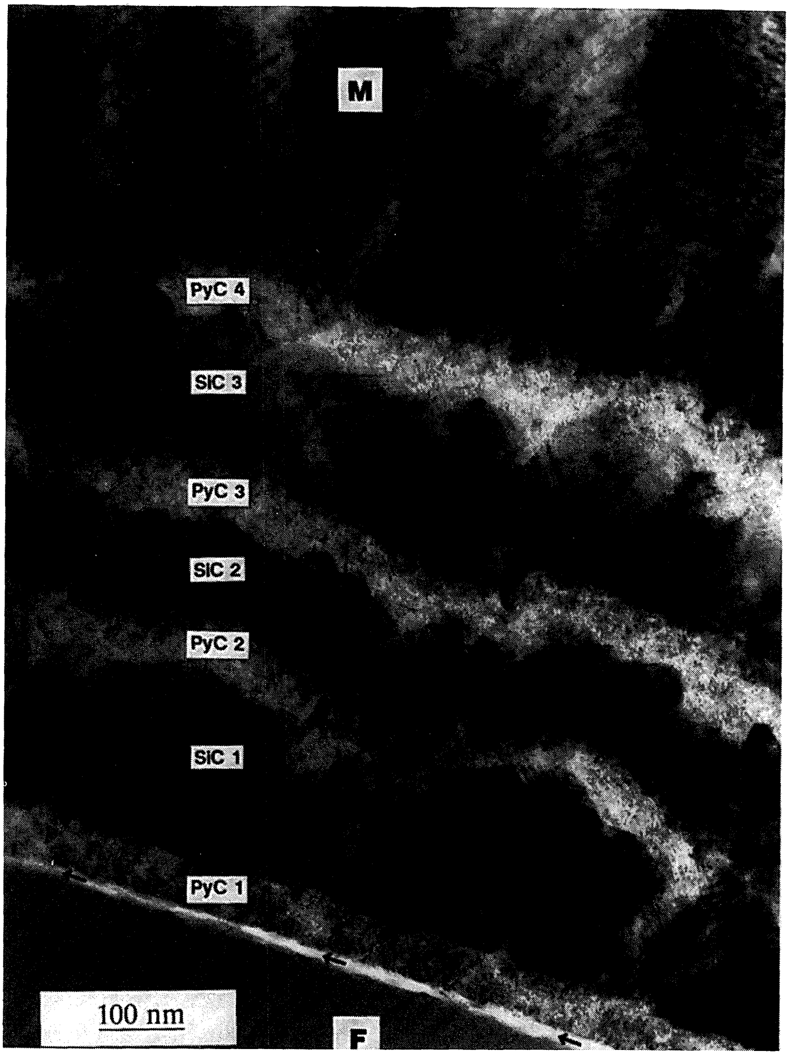

Figure 6. TEM image of the fibre–matrix interfacial zone in a two-dimensional SiC–SiC composite with a multilayered (PyC–SiC)$_n$ interphase. After Droillard (1993).

Additionally, very little is known about their mechanical behaviour in oxidizing atmospheres (Naslain *et al.* 1991; Prouhet *et al.* 1994).

6. Conclusion

SiC–SiC composites exhibit a non-brittle mechanical behaviour when the fibre–matrix bonding has been properly controlled during processing via the use of an interphase. Efficient interphase materials are those with a layered crystal structure or/and microtexture, such as pyrocarbon, hex-BN or (SiC–PyC)$_n$ multilayers.

The nonlinear mechanical behaviour and the high toughness of SiC–SiC composites are related to the occurrence of damaging phenomena including matrix microcracking. The best mechanical properties (in terms of failure stress, failure

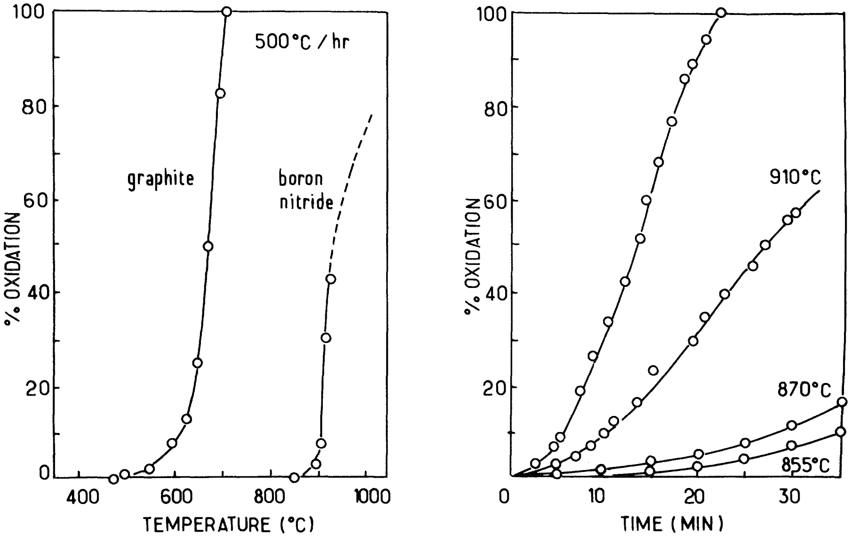

Figure 7. Oxidation of BN-fibres: (*a*) as compared to that of carbon fibre, (*b*) kinetics of oxidation for various temperatures. After Economy & Lin (1977).

strain, energy release rate and fatigue resistance) are achieved for rather strong fibre–matrix bonding (i.e. when there is a balance between the crack deflection and load transfer functions of the fibre–matrix interfacial zone). Under such conditions, failure occurs with limited fibre pull-out.

SiC–SiC composites are still sensitive to the effect of the environment by the fibres (which are often not stable enough at high temperatures) and the interphase (particularly, pyrocarbon). The use of more stable fibres (e.g. fibres without oxygen and whose composition is close to C/Si = 1), seal-coating and hex-BN interphase would undoubtedly significantly increase the compatibility of SiC–SiC composites with oxidizing atmospheres in the 1000–1500 °C temperature range.

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Discussion

T. KHAN (*Onera, Chatillon, France*). There is another potentially interesting class of CMCs, i.e. the glass matrix composites. Some of these materials seem to have a temperature capability of up to 1200 °C. Can these materials be compared with the SiC–SiC in terms of limitations, advantages and cost?

R. R. NASLAIN. The glass (or glass-ceramic) matrix composites have been designed for long-duration applications at medium temperatures (typically 600–1000 °C) in oxidizing atmospheres. Several factors seem to limit the high-temperature capability of these materials, including (i) the creep of the matrix (which still contains some amorphous and viscous phase even ceramization) and (ii) the nature of the *in situ* formed interphase (whose main constituent, carbon, is sensitive to oxidation at very low temperatures). In contrast, the SiC–matrix in SiC–SiC composites is more resistant to creep (it is fully crystalline and SiC melts with decomposition only at about 2500 °C). Additionally, the interphase in SiC–SiC composites is not formed *in situ* as the result of a fibre–matrix chemical reaction. It is deposited on the fibre before the infiltration of the matrix. Thus it is not necessarily carbon (hex-BN has already been successfully used and other interfacial materials and/or concepts are presently studied). The advantages of glass–matrix composites may be in (i) the rapidity of their processing, (ii) the variety of composition of the matrix, and (iii) the absence of significant residual porosity (they are gas and liquid tight). Very large structural parts (such as those used for the thermal protection of spacecraft) can be fabricated with SiC–

SiC composites (in the 2 m size) and their high-temperature capability seems to be much higher. Finally, the main part of the cost of both composites is related to the fibres. The processing time of SiC–SiC composites is higher but a very large number of parts can be treated simultaneously and as a result the processing time per part is probably of the same order not to say lower. It is noteworthy that C–C is competitive with steel in brake disks.

M. Steen (*Institute of Advanced Materials, Joint Research Centre, European Commission, Petten, The Netherlands*). How may thermal cycling affect the oxidation resistance of SiC–SiC composites? Is it possible to integrate the isothermal oxidation kinetics over the temperature range of interest to obtain the cyclic oxidation rate, or is there an acceleration effect to be considered?

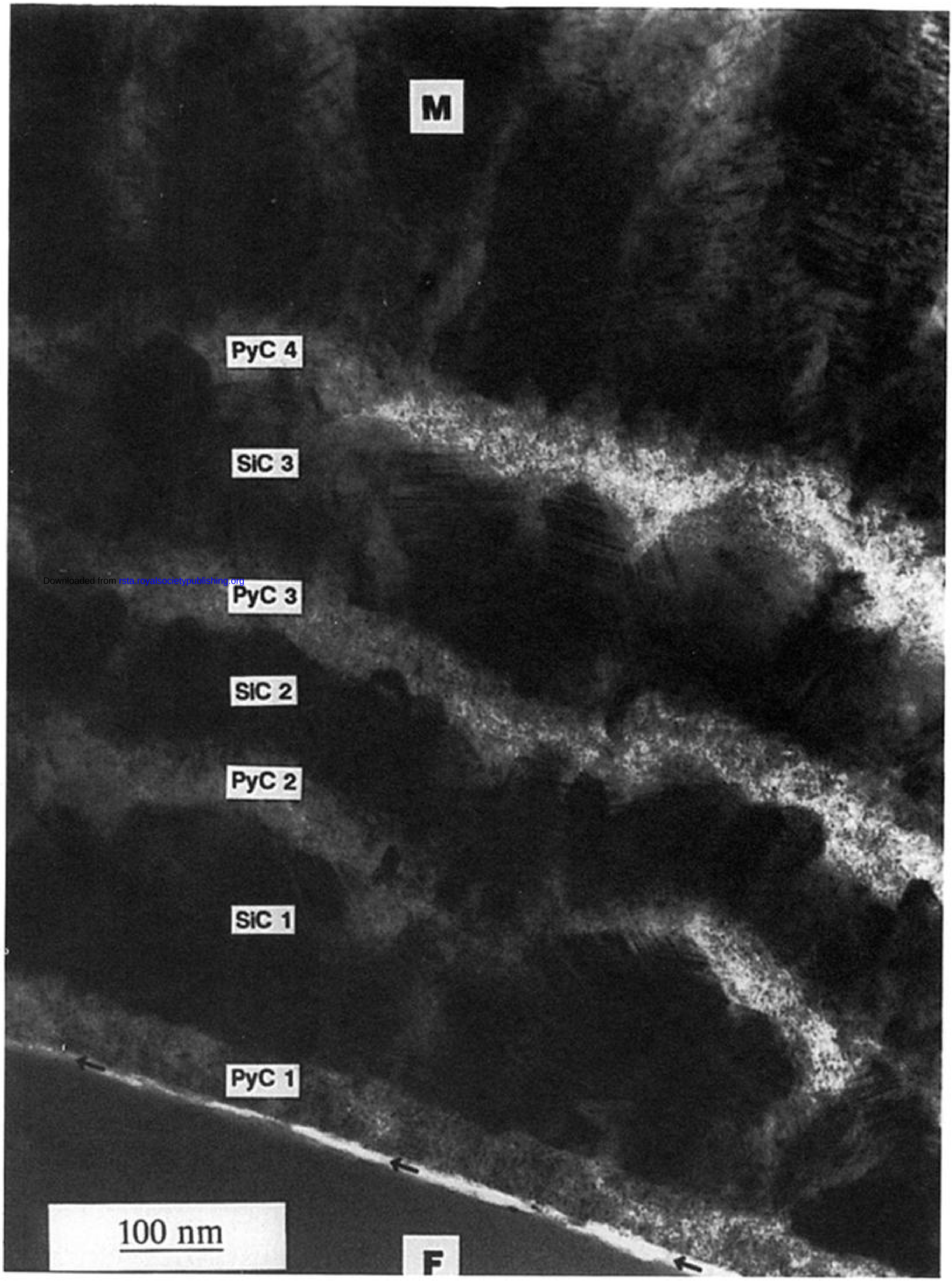
R. R. Naslain. Two factors control the overall oxidation kinetics of SiC–SiC composites: (i) the intrinsic oxidation kinetics of the components (the fibres, the interphase and the matrix), and (ii) the rate of the in-depth diffusion of oxygen (and in the opposite direction, that of the carbon oxides). During a thermal cycling test, there is no obvious reason that could justify a change in the intrinsic oxidation kinetics of the constituents. Conversely, thermal cycling may enhance the microstructural damage stage of the composite: (i) new microcracks could be formed, and (ii) the pre-existing microcracks could be periodically re-opened. As a result, the overall oxidation rate can be accelerated (remembering that the oxidation of SiC–SiC composites with pyrocarbon interphase is much more severe at low temperatures, i.e. 400–700 °C, if the external coating undergoes microcracking, since, under such conditions, the rate of formation of the silica protective layer is extremely slow). The effect of thermal cycling on the lifetime of SiC–SiC composites in air is indeed an issue, on which a large effort of research is currently being expended.

Peter Holmes (*ABB Management AG, Baden–Dättwil, Switzerland*). Can the model of oxidation loss of the carbon interface and formation of a silica plug be used to predict the length of fibre interface lost before the plugging occurs at various temperatures of exposure?

R. R. Naslain. Yes, the model of oxidation loss of the carbon interphase and formation of silica plug can be used (and has already been used) to predict the length of interphase consumed before plugging occurs, in SiC–PyC–SiC unidirectional composites, at various temperatures, for PyC interphases of different thicknesses and in atmospheres with different oxygen partial pressures. For more details see Filipuzzi & Naslain (1994) or Filipuzzi (1991).

Additional references

Flipuzzi, L. 1991 Ph.D. thesis, no. 593, University of Bordeaux.



igure 6. TEM image of the fibre–matrix interfacial zone in a two-dimensional SiC–SiC composite with a multilayered $(\mathrm{PyC{-}SiC})_n$ interphase. After Droillard (1993).