Journal of the European Ceramic Society **14** (1994) 177–188

Oxidation Effects on the Mechanical Properties of 2D Woven C/SiC Composites

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(Received 8 October 1993; revised version received 10 February 1994; accepted 8 March 1994)

Abstract

The effects of oxidizing treatments on the room-temperature tensile properties of 2D woven C/SiC composites partly protected with a SiC seal-coating have been investigated between 700°C and 1400°C, for durations corresponding to a maximum of 6% relative mass loss. Results have shown three main mechanisms of composite property degradation corresponding to three well differentiated morphological changes. Oxidation at low temperatures (<800°C) induced a drastic decrease of the composite tensile properties in relation to a notch-like partial degradation of the carbon fibers located near the matrix microcrack tips. The intermediate temperature ageing treatments (800 < T < 1100°C) resulted in a less important decrease of the tensile properties in connection with rupture arising from the sudden overloading of the inner carbon plies. At high temperatures (>1100°C), ageing treatments led to a limited decrease of the tensile properties owing to a combined notch/overloading effect taking place only at high stress levels from the superficial degradation of the composite reinforcement. Both decreasing the oxygen content of the environment (i.e. from pure oxygen to dry air) or using unstabilized materials (i.e. unaged at 1600°C under argon prior to the oxidizing treatments) resulted in a better oxidation resistance.

Der Effekt der Oxydationsbehandlung auf die Zugeigenschaften bei Raumtemperatur von 2D-geflochtenen C/SiC-Verbunden, teilweise geschützt durch eine SiC-Versiegelung, wurde für den Temperaturbereich zwischen 700°C und 1400°C und Zeiten, die einem Maximum von 6% an relativem Masseverlust entsprechen, untersucht. Die Ergebnisse weisen auf drei Hauptmechanismen hin, die die Verbundeigenschaften verschlechtern und drei klar unterscheidbaren Veränderungen in der Morphologie entsprechen. Oxydation bei niedrigen Temperaturen (<800°C) führt zu einer drastischen Abnahme der Zugeigenschaften des Verbunds, verbunden mit einer kerbähnlichen, teilweisen Degradierung der Kohlenstoff-Fasern, die sich in der Nähe eines Mirkorisses in der Matrix befinden. Die Alterungsbehandlung bei mittleren Temperaturen (800 < T < 1100°C) ergab eine bedeutend geringere Verschlechterung der Zugeigenschaften beim Bruch, der aus der plötzlichen Überbelastung der inneren Kohlenstoffstränge erfolgte. Bei hohen Temperaturen (> 1100°C) führte die Alterungsbehandlung zu einer begrenzten Verschlechterung der Zugeigenschaften infolge einer Kombination aus Kerb-/Überbelastungseffekt. Dieser Effekt tritt nur bei hohen Spannungen auf, die durch die Degradierung der Verbundverstärkungen an der Oberfläche hervorgerufen werden. Sowohl die Verringerung des Sauerstoffgehalts der Umgebung (d.h. von reinem Sauerstoff zu Luft) als auch die Verwendung von nichtstabilisiertem Material (d.h. ungealtert bei 1600°C unter Argon vor der Oxydationsbehandlung) ergab eine bessere Oxydationsbeständigkeit.

L'influence de traitements oxydants sur les propriétés en traction à température ambiante de composites 2D tissés C/SiC partiellement protégés par un revêtement externe de SiC a été étudiée entre 700°C et 1400°C, pour des durées maximales correspondant à une perte relative de masse de 6%. Les résultats ont mis en évidence trois mécanismes principaux de dégradation des propriétés mécaniques en relation avec trois modes différents d'évolutions morphologiques. L'oxydation à basse température (<800°C) a provoqué une chute importante des propriétés en traction, en relation avec une dégradation partielle en forme d'entaille des fibres de carbone situées au voisinage des fonds de fissures matricielles. Les vieillissements effectués à des températures intermédiaires (800 < T < 1100°C) ont

Journal of the European Ceramic Society 0955-2219/94/$7.00

résulté en une chute moins importante des propriétés mécaniques, liée à un mode de rupture provenant de la surcharge soudaine des strates de carbone internes. A haute température (>1100°C), les traitements de vieillissement ont conduit à une décroissance limitée des propriétés en traction du fait de la combinaison d'un effet d'entaille et de surcharge ayant lieu uniquement à des niveaux de contrainte élevés, à partir de la dégradation superficielle du renfort fibreux. Un abaissement du taux d'oxygène de l'environnement gazeux (i.e. de l'oxygène pur à l'air sec) et/ou l'utilisation de matériaux non stabilisés (i.e. n'ayant pas été traités à 1600°C sous argon avant oxydation) conduisent à une meilleure résistance à l'oxydation.

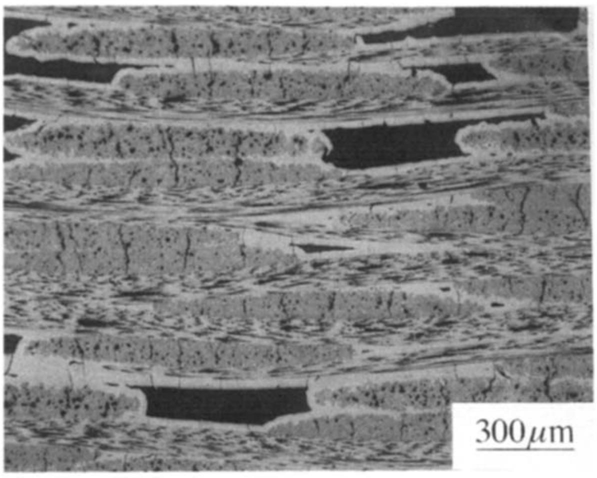

Fig. 1. Optical micrograph of a polished section of a 2D C/SiC composite stabilized at 1600°C under inert gas.

1 Introduction

The increasing interest in carbon-based materials is related to major attractive properties such as lightness, elevated mechanical strength and thermal stability. Carbon fibers are thus extensively used in the aerospace industry which requires structural materials intended for high temperatures and aggressive environments. Composite materials consisting of carbon fibers embedded in a silicon carbide matrix are excellent potential candidates for such applications, for they combine both the elevated specific properties of carbon fibers with the high oxidation resistance of the SiC matrix. However, the various thermomechanical cycles encountered by these materials when processed and/or in service result in the onset of matrix microcracking.[1,2] If this matrix multiple-microcracking phenomena is an important advantage from a mechanical point of view, since it primarily contributes (in conjunction with fiber/matrix debonding) to the non-linear/non-catastrophic tensile behavior and high impact resistance of this class of material, such is not the case when the oxidation resistance is considered. As a matter of fact, microcracks represent an easy path for the diffusion of oxygen towards the carbon reinforcement and therefore significantly reduce the protective role played by the SiC matrix. Consequently, for high-temperature applications, additional external protection, in most cases based on oxide coatings, has to be used.[3-5] However, none of the existing protective systems have proved to be entirely reliable for long time exposures up to 1600°C (and $P \leq 100$ kPa). It is therefore of great importance to get a good knowledge of the changes which may be induced by oxidation on the mechanical properties of the material when the external protection is no longer efficient.

The aim of the present investigation was to study experimentally the oxidation effects on the tensile behavior of 2D woven C/SiC composites having no other complementary protections than a simple SiC seal-coating.

Previous work devoted to other ceramic matrix composites (CMCs) has established some correlations between the loss of strength and the microstructural changes induced by oxidation.[6-8] For carbon fiber-reinforced glass matrix composites, the loss of strength was essentially related to the degradation of the reinforcement. Conversely, for SiC/SiC or SiC/glass composites,[7,8] changes in the mechanical behavior proved to be related to modifications of the fiber/matrix load-transfer conditions induced by a degradation of the carbon interphase (whose function is to optimize these load-transfer conditions).[9]

The present work follows a previous study aimed at establishing the kinetics and mechanisms of oxidation of similar 2D C/SiC composite materials.[10] Oxidation was found to be mainly governed by the diffusion of oxygen through the seal-coating/matrix thermal microcracks generated upon cooling from the processing temperature (by a fiber/matrix CTE mismatch, see Fig. 1). The observed changes in the rate of oxidation with temperature and/or duration of ageing treatments, as well as the depth of penetration of the oxidizing attacks were thus both related to (i) the opening of the thermal microcracks, which decreases with an increase in temperature, and (ii) the reactivity towards oxygen of both SiC and the carbon constituents which, conversely, increases with an increase in temperature. Three main temperature domains corresponding to different oxidation kinetics regimes/degradation modes were found as follows:

—At low temperatures, oxidation kinetics were controlled by chemical reactions between carbon and oxygen. Since the reactivity of the carbon phases (i.e. fiber and interphase) is low as compared to the rate of diffusion of the gaseous species, the carbon reinforcement was uniformly degraded all over the samples.

—At intermediate temperatures, diffusion of the gaseous species through the SiC seal-coating microcracks became the oxidation rate-controlling step. The degradation of the carbon phases was non-uniform, decreasing gradually from the surface to the bulk of the samples.

—At high temperatures, the important reactivity of the carbon phases coupled to the limited oxygen flux diffusing through narrow SiC seal-coating microcracks (rapidly sealed by silica) led to a degradation strictly localized at the surface of the material (i.e. at the seal-coating microcrack tips).

The relationships which were found between oxidation kinetics, ageing temperature and degradation modes are schematically represented in Fig. 2, for two different states of the 2D C/SiC material. The 'reference' material received a supplementary post-processing heat treatment at 1600°C under an argon inert atmosphere. This treatment (referred to as a stabilizing heat treatment) was aimed at avoiding possible interacting effects resulting from changes in the microstructure and/or the composition of the constituents when aged at temperatures exceeding the processing temperature (i.e. 1000°C). It resulted in (i) changes in the physicochemical characteristics of the composite constituents (especially the ex-PAN fiber[11] and (ii) an increase in the matrix/seal-coating thermal microcracks density and average opening. Consequently, in the absence of this stabilizing treatment, a lower average crack-closing temperature coupled to a higher reactivity towards oxygen of the carbon phases led to systematically narrower temperature domains. In addition, the onset of a new thermomechanical damage induced by the CTE mismatch resulted in an important increase of the oxidation kinetics over 1200°C.

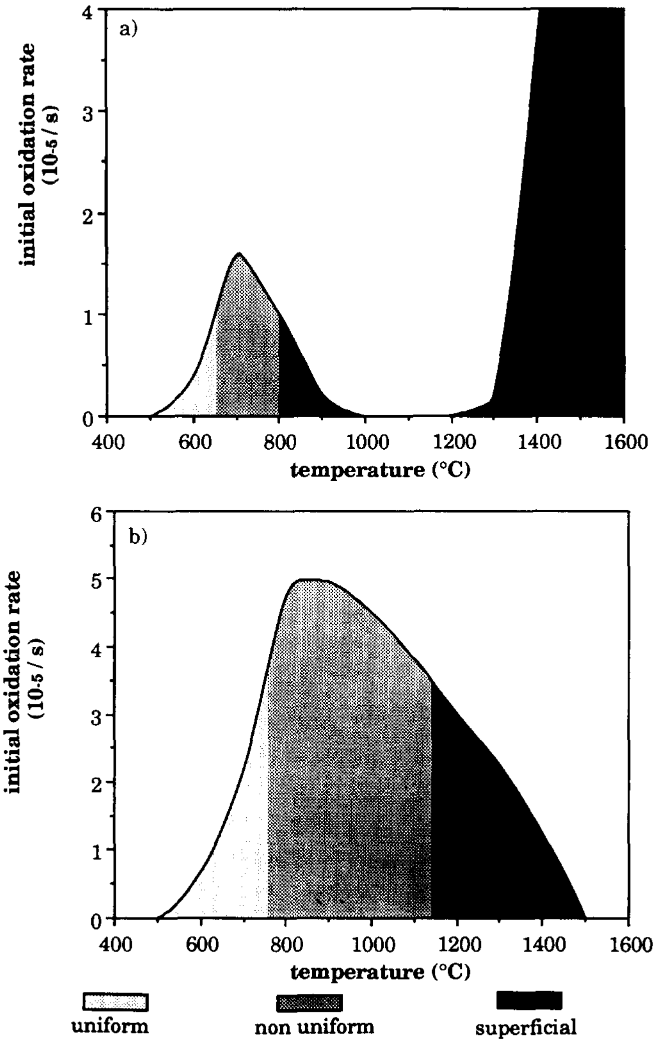

Fig. 2. Dependence of the initial oxidation rate, in association with the different oxidation modes, on the ageing temperature (under flowing oxygen) for 2D C/SiC composites (a) as-processed and (b) stabilized at 1600°C under inert gas.

2 Experimental Procedure

The composite material used in the present investigation has been elaborated by SEP (Société Européenne de Propulsion) according to the so-called isothermal–isobaric CVI process from a fibrous preform consisting of a 0° stack of ex-PAN carbon fiber (high strength carbon fiber HR T300 from Toray) two-dimensional (plain-weave) fabrics. In a first step, the fibers were coated *in situ* with a pyrocarbon (PyC) interphase of mean thickness in the range 0·5–1 μm, formed from cracking of CH_4. In a second step, the carbon-coated preform was infiltrated by the SiC matrix formed *in situ* from a CH_3SiCl_3/H_2 mixture, at about 1000°C, according to the ICVI process which has been described elsewhere.[12,13] These processing steps resulted in a material having a density close to 2 g cm^{-3}, a fiber content of approximately 40 vol.% and a residual porosity in the range 10–15%. Once cut to their final dimensions and prior to testing, tensile samples were coated with a CVD-processed SiC layer of the order of 100 μm in mean thickness. Finally, most of the samples were thermally stabilized by a heat treatment performed at 1600°C under an inert atmosphere. This material thus processed and heat treated (stabilized) constituted the reference material used in the major part of the study. Nevertheless, for purpose of comparison, some samples were also tested in the as-processed (unstabilized) state. The average room-temperature physical and mechanical properties of the 2D C/SiC composites are listed in Table 1.

Table 1. Room-temperature physical and mechanical property data for 2D woven C/SiC composites

	As-processed	*Stabilized*
Fiber fraction (%)	40	40
Density (g cm^{-3})	2	2
Seal-coating microcracks: average width (μm)	1·2	2·5
Elastic modulus (GPa)	90 ± 5	70 ± 5
Ultimate tensile strength (MPa)	390 ± 20	390 ± 20
Strain to rupture (%)	0·85 ± 0·05	0·90 ± 0·05
Stress at matrix microcracking saturation (MPa)	250 ± 20	180 ± 20

Tensile tests were performed at room temperature, at a constant strain rate of 0·1% min^{-1} (monitored by a clip-on extensometer), using flat dog-bone shape specimens of 200 mm total length and 40 × 8 × 3 mm^3 gage section. Specimens were tested in the as-processed states (stabilized and unstabilized) and/or after various oxidizing treatments performed between 700°C and 1400°C. Two different oxidizing atmospheres, namely dry oxygen and a nitrogen/oxygen 80/20 mixture (equivalent to dry air) were successively used, at a constant total pressure of 100 kPa. Two specimens were tested for each ageing condition. In order to concentrate the oxidizing attacks in the gage section and thus to preserve good clamping conditions, sample ends were coated all over with a phosphorous oxide based film. However, because of variations of composition during the ageing treatments, the presence of such a coating rendered impossible any direct mass variation measurement. Therefore, durations of the ageing treatments were selected from previous TGA data performed on film-free samples,[10] and corresponded to 2 and 6% of equivalent relative mass loss, respectively. By extension the ageing treatments performed on the materials will be thus further referred to as 2 and 6% mass loss treatments (the corresponding durations being listed in Table 2).

Table 2. Influence of thermal oxidizing treatments on the tensile properties of 2D C/SiC composites

Material and environment	*Ageing treatment*			*Tensile properties*	
	Temperature (°C)	*Time (s)*	*$\Delta m/m_0$ (%)*	*σ_R (MPa)*	*ε_R (%)*
Stabilized, flowing oxygen		None		390 ± 20	0·85 ± 0·05
	700	1 500	2	280 ± 10	0·6 ± 0·05
	700	2 700	6	190 ± 5	0·38 ± 0·01
	900	200	2	270 ± 10	0·55 ± 0·03
	900	600	6	200 ± 3	0·45 ± 0·05
	1 200	300	2	285 ± 10	0·68 ± 0·05
	1 200	800	6	260 ± 5	0·58 ± 0·04
	1 400	800	<2	335 ± 10	0·79 ± 0·05
	1 400	1 850	2	285 ± 10	0·65 ± 0·05
Stabilised, flowing air		None		390 ± 20	0·85 ± 0·05
	700	3 200	2	310 ± 10	0·65 ± 0·05
	700	7 200	6	280 ± 10	0·6 ± 0·05
	900	1 050	2	310 ± 15	0·67 ± 0·08
	900	3 200	6	290 ± 5	0·63 ± 0·02
	1 200	1 300	2	330 ± 10	0·75 ± 0·05
	1 200	4 300	6	300 ± 5	0·65 ± 0·02
	1 400	1 850	<2	360 ± 5	0·78 ± 0·01
As-processed, flowing oxygen		None		390 ± 20	0·90 ± 0·05
	700	1 500	<2	320 ± 20	0·75 ± 0·05
	700	2 700	2	290 ± 20	0·68 ± 0·05
	700	5 900	6	215 ± 5	0·5 ± 0·03
	900	8 600	2	280 ± 20	0·65 ± 0·05
	900	32 000	6	260 ± 5	0·58 ± 0·05
	1 400	800	2	335 ± 10	0·8 ± 0·03
	1 400	1 850	6	310 ± 10	0·77 ± 0·05

Loading/unloading cycles and acoustic emission monitoring were used in order to follow the occurrence and the propagation of damage into the materials during the tests.

Fractured specimens were examined using optical microscopy and scanning electron microscopy (SEM) to determine morphological changes and composite failure behavior.

3 Results

3.1 Tensile behavior prior to oxidizing treatments

The room-temperature tensile properties of both the as-processed and stabilized materials are summarized in Table 1, in terms of Young's modulus, stress and strain to rupture, and stress at matrix microcracking saturation (as determined by acoustic emission recording).

The tensile stress–strain curves obtained for both materials are plotted in Fig. 3. The general phenomena associated with these tensile behaviors may be more easily assessed from the typical stress–strain curve shown as an example in Fig. 3(b). The two composites behave as typical damage-bearing materials, i.e. exhibiting an extended non-linear stress–strain domain up to rupture. In addition, as a consequence of the onset of damage upon processing, no linear/elastic part may be clearly seen at the beginning of the curves.[1,14] Three distinct domains corresponding to three different steps in the onset and the extension of the damage phenomena may be further noted from the curves. The first domain (I) exhibits a knee along with a nearly constant increase in the cumulative *AE* events versus strain curve and corresponds to the multiplication of matrix microcracking and fiber/matrix partial debonding until saturation is reached. The second domain (II) represents a transition involving crack opening and fiber sliding, marked by a change of curvature in the stress–strain curve and a noticeable decrease in the rate of accumulation of *AE* events. The last part of the curve is linear and corresponds to the elongation of the fibers which entirely carry the load until rupture occurs. In this third domain (III), the rate of accumulation of *AE* events remains seemingly constant. Loading/

unloading cycles point out the damage consequences, i.e. a progressive decrease in the material longitudinal stiffness along with an extension of residual strains.

Comparison of the tensile behavior of the as-processed and stabilized composites shows that the apparent Young's modulus (fitted from the beginning of the curves) and the stress at matrix microcracking saturation (beginning of domain II) were decreased by the stabilizing treatment. Conversely, the ultimate tensile stress and tensile strain remained highly comparable (see Table 1). Moreover, consecutively to this stabilizing treatment, the transition domain (i.e. domain II) appeared to be less extended while exhibiting more markedly the appearance of a plateau.

The fracture surface of the two materials, as shown in Fig. 4, displays extensive pull-out of both individual tows and, inside each tow, of the carbon fibers. This phenomena is significantly more pronounced for the stabilized material.

Thus, the increase in matrix microcracking and more especially fiber/matrix debonding induced by the stabilizing treatment has mainly resulted in a decrease of the fiber/matrix bond strength.

3.2 Environmental effects on the tensile properties

Results from all the tensile tests performed on the 2D C/SiC composites under various ageing conditions are summarized in Table 2. As a result of the weak level of mass losses encountered by the materials during the ageing treatments, no signifi-

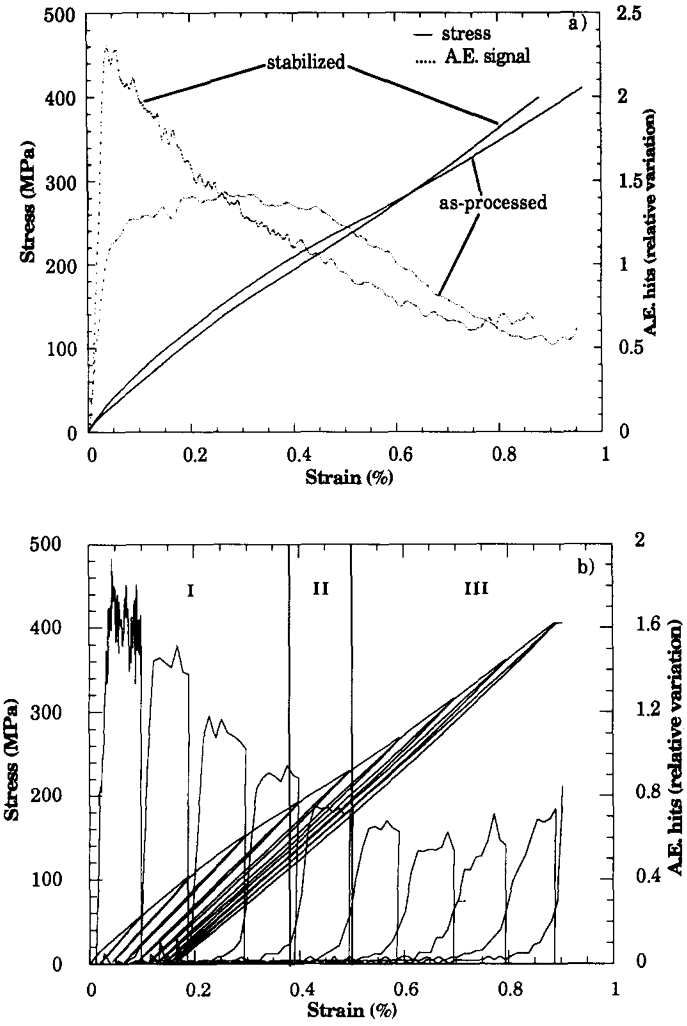

Fig. 3. Room-temperature tensile stress–strain curves and relative variations of cumulative AE events for 2D C/SiC composites: (a) comparison between the as-processed and the stabilized materials; (b) stress-strain curve with cycling for the stabilized material.

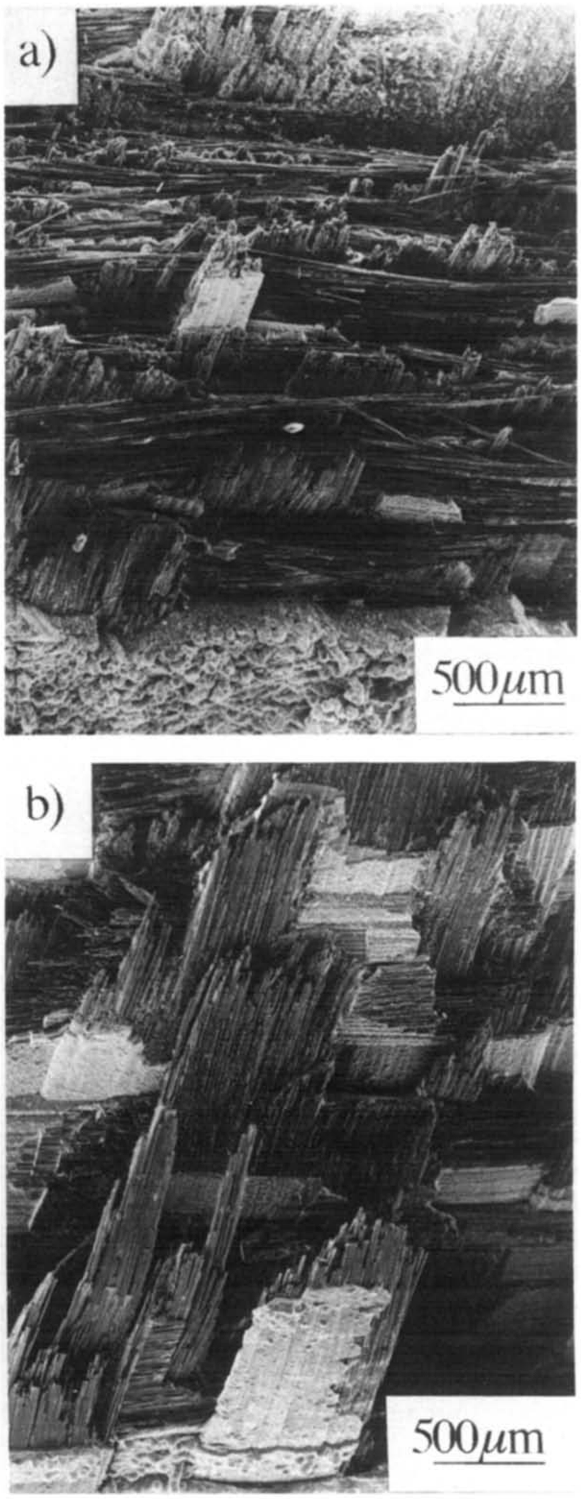

Fig. 4. SEM micrographs showing the fracture surfaces of 2D C/SiC tensile specimens (a) as-processed and (b) stabilized at 1600°C under inert gas.

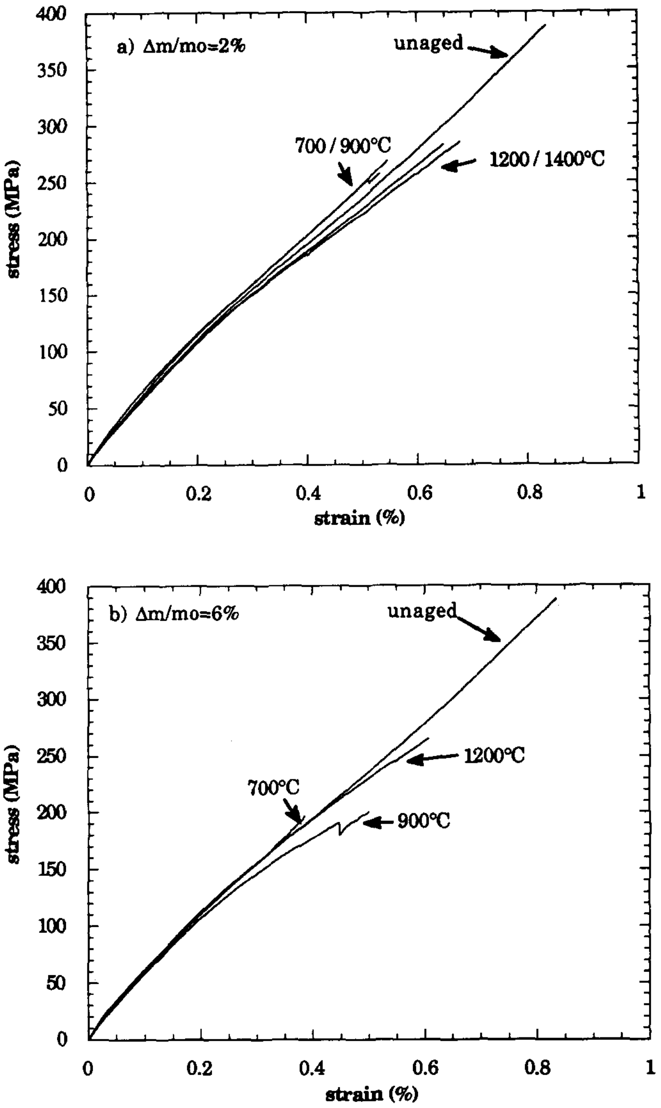

Fig. 5. Room-temperature tensile stress–strain curves for stabilized (heat-treated) 2D C/SiC composites variously aged under flowing oxygen (P = 100kPa) for durations corresponding to (a) 2% and (b) 6% of relative mass loss.

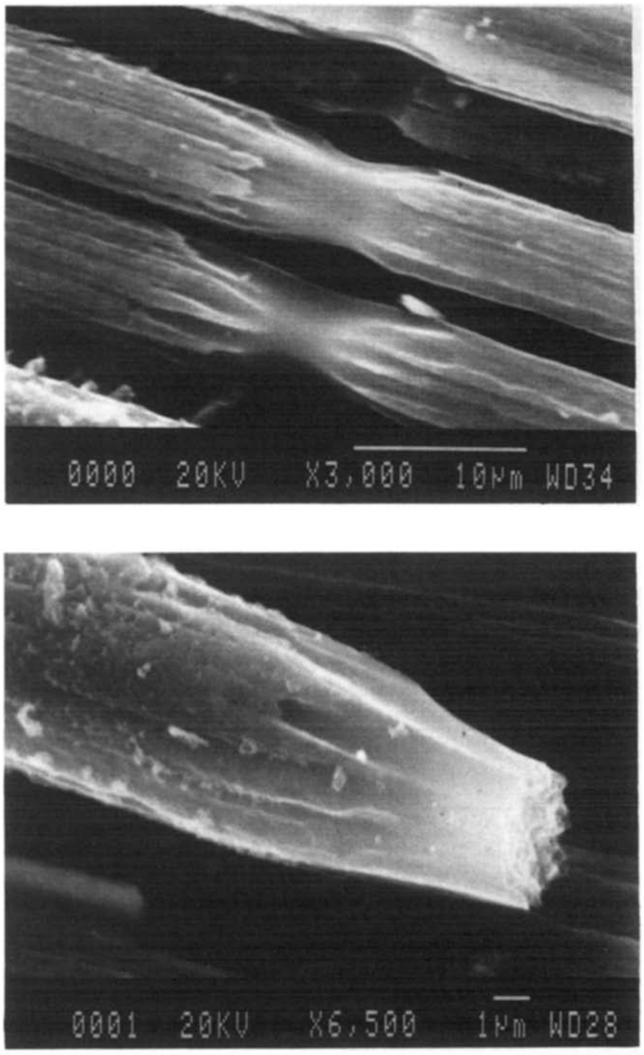

Fig. 6. SEM micrographs revealing (a) the periphery and (b) the fracture surface of the carbon fibers of a composite aged at 700°C under flowing oxygen (P = 100kPa) for a duration corresponding to a relative mass loss of 6%.

cant changes in apparent Young's modulus were noticed under any ageing conditions for both as-processed and stabilized materials.

3.2.1 Influence of the ageing temperature

Stress–strain curves obtained with stabilized 2D C/SiC composites aged in flowing oxygen between 700°C and 1400°C are reported in Fig. 5. All the oxidizing treatments corresponding to an equivalent relative mass loss of 2% result in a reduction in strength of approximately 30%, while the general aspect of the stress–strain curve is always preserved. Rupture occurs at the beginning of the third domain of the curves. For treatments corresponding to a relative mass loss of 6%, the effect of the ageing temperature on the tensile behavior becomes noticeable:

—At 700°C, the aspect of the stress–strain curve remains nearly unchanged, whereas the ultimate tensile strength is reduced by about 50%. SEM observations of the fracture surface, as shown in Fig. 6(a), show a local degradation of the carbon fibers and interphases in the vicinity of the crack tips. Rupture of the carbon fibers appears to be systematically located at these notch-like degradations (Fig. 6(b)).

—At 900°C, the ageing treatment also results in a loss of strength and strain to rupture of approximately 50%. However, the appearance of the stress–strain curve is no longer preserved, i.e. the third domain is barely observable and the stress obtained at a given strain is systematically reduced. Observation of the fracture surface reveals an increase in the degree of pull-out of the tows located near the surface of the sample (Fig. 7(a)). In addition, inside these outer tows, the carbon fibers appear to be more intensively degraded and debonded from the SiC matrix (Fig.7(b)).

—At 1200°C, the general aspect of the stress–

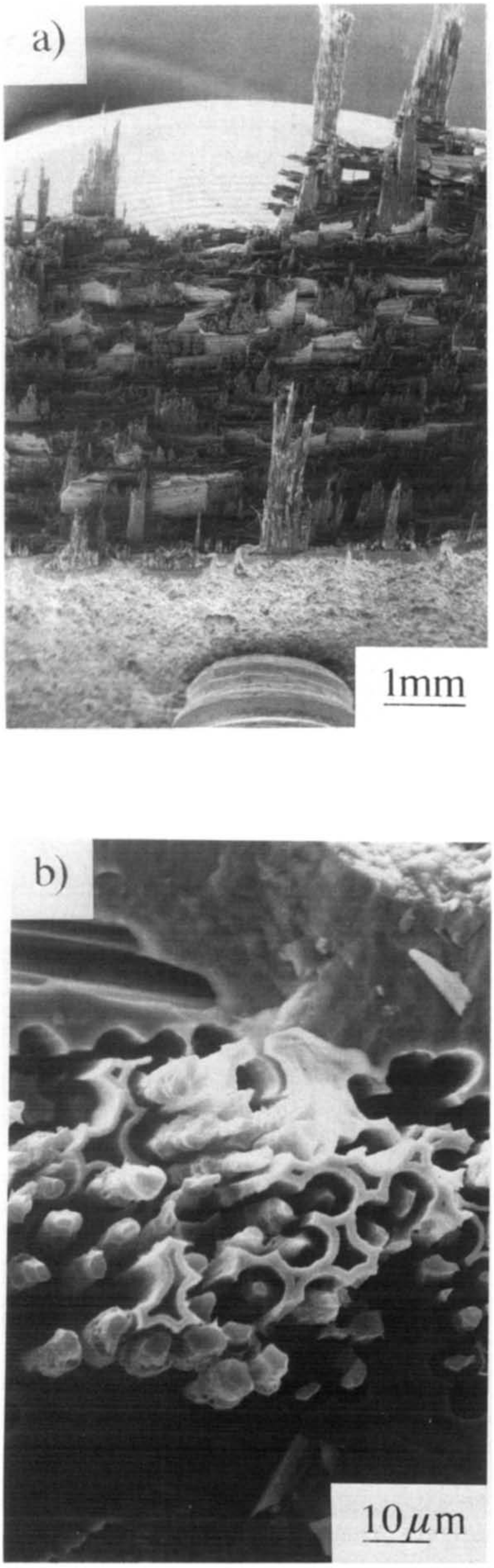

Fig. 7. SEM micrographs showing (a) the fracture surface of a stabilized 2D C/SiC composite aged at 900°C under flowing oxygen, P = 100kPa) for a duration corresponding to a relative mass loss of 6%, and (b) an outer carbon tow at a higher magnification.

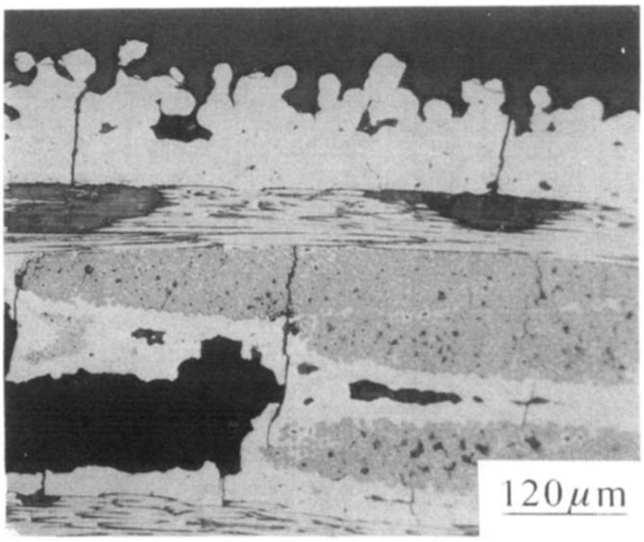

Fig. 8. Optical micrograph of a polished section of a stabilized 2D C/SiC composite aged under flowing oxygen (P = 100kPa) at 1400°C for a relative mass loss of 2%.

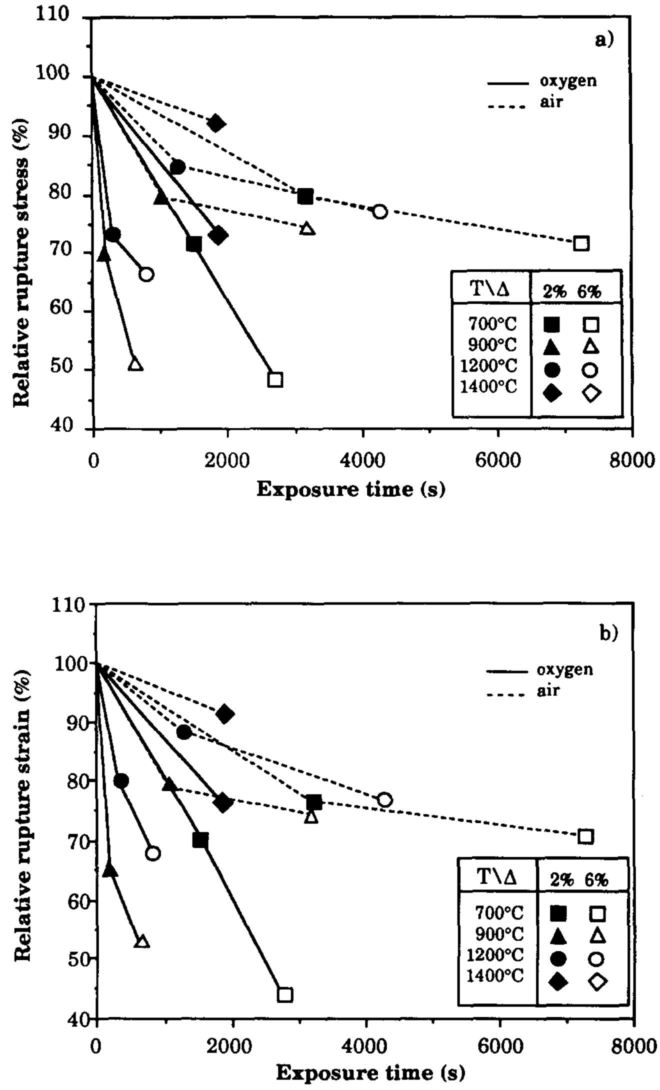

Fig. 9. Comparison of the room-temperature ultimate tensile properties of stabilized 2D C/SiC composites aged under flowing air and oxygen (a) rupture stress and (b) rupture strain.

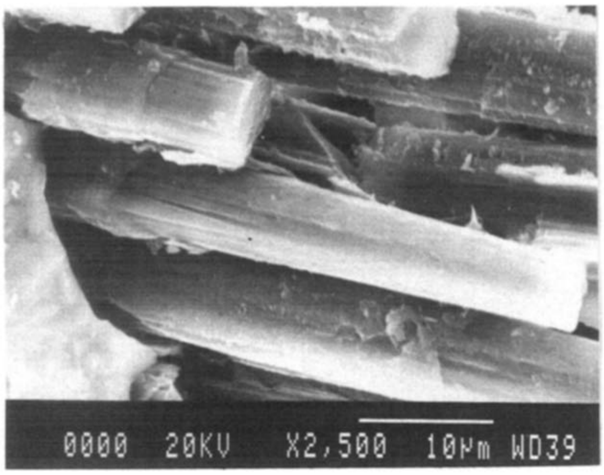

Fig. 10. SEM micrograph revealing the periphery of carbon fibers from the fracture surface of a stabilized 2D C/SiC composite aged at 700°C under dry air (P = 100kPa), at a relative mass loss of 6%.

strain curves is preserved, while rupture, on average, takes place at the end of the second domain, with a corresponding decrease in ultimate strength of about 35%.

—Because of the rapid sealing of the SiC seal-coating microcracks by silica, a relative mass loss of 6% could not be obtained at 1400°C.[10] For a relative mass loss of 2%, oxidation remained superficial and located near the seal-coating microcrack tips. Notch-like superficial clusters of oxidised carbon constituents pores were thus generated (Fig. 8).

3.2.2 Influence of the atmosphere composition

Similar ageing treatments performed on stabilized 2D C/SiC composites in dry air (P = 100kPa) in place of oxygen led to noticeable differences in the residual tensile behavior. Nearly no substantial change in the appearance of the stress–strain curves may be observed, while rupture values appear to be almost similar whatever the ageing treatment performed. Comparisons between variations of rupture values as a function of temperature for samples aged under both atmospheres are plotted in Fig. 9. SEM observation of the fracture surface of the composite aged in air at 700°C also shows a local attack of the carbon fibers. However, the appearance of this degradation is not as sharp as that developed in pure oxygen (compare Figs 10 and 6(a)). Ageing at 1400°C still results in a superficial attack of the carbon phases but, contrary to ageing treatments performed in pure oxygen, no notch-like clusters of oxidized carbon constituents appear at the microcrack tips (Fig. 11).

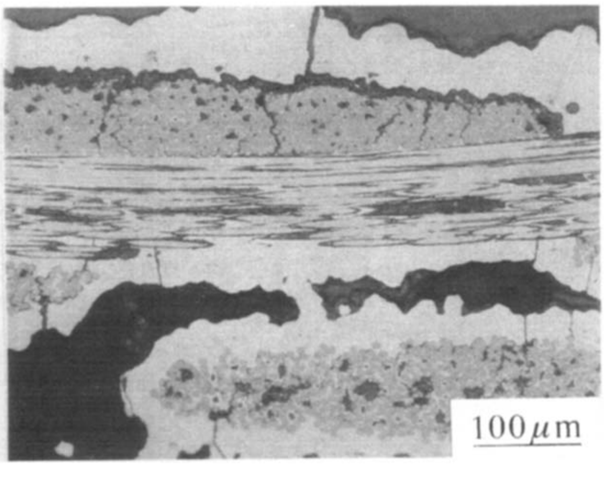

Fig. 11. Optical micrograph of a polished section of a stabilized 2D C/SiC composite aged under dry air (P = 100kPa) at 1400°C for a relative mass loss of 2%.

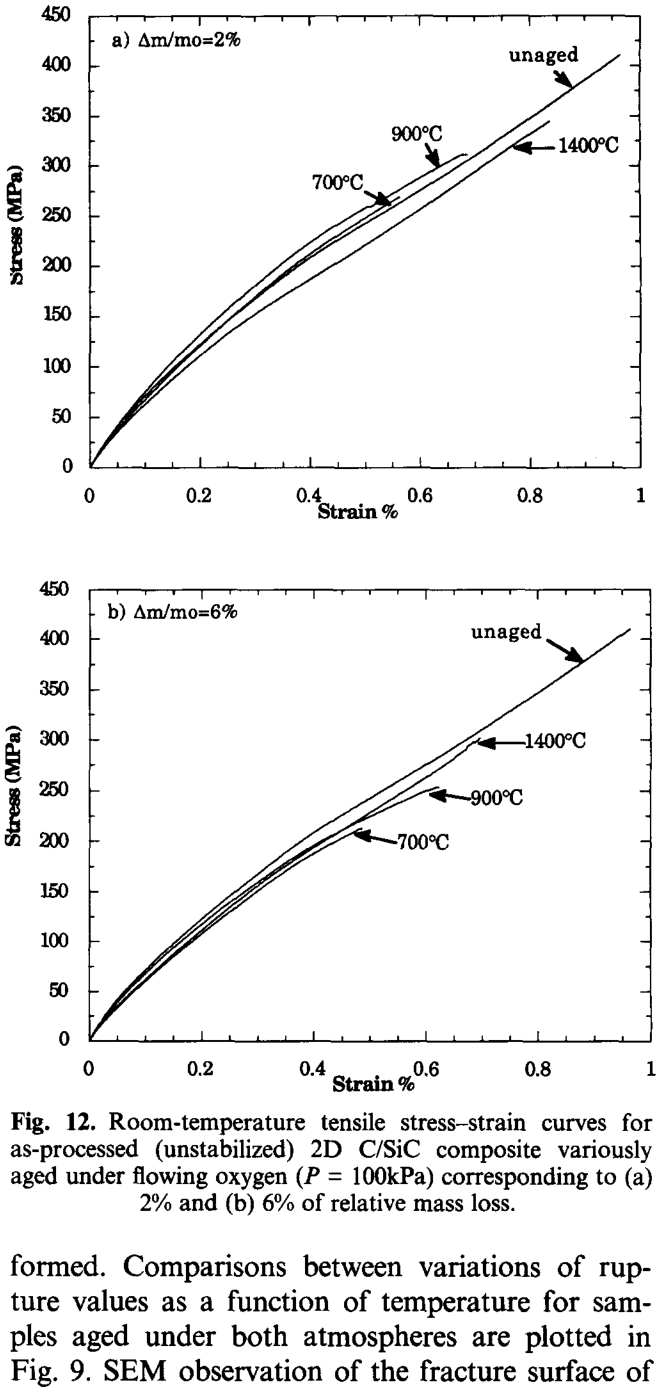

Fig. 12. Room-temperature tensile stress–strain curves for as-processed (unstabilized) 2D C/SiC composite variously aged under flowing oxygen (P = 100kPa) corresponding to (a) 2% and (b) 6% of relative mass loss.

3.2.3 Thermally unstabilized material

Noticeable differences may be observed between the stabilized and the unstabilized 2D C/SiC composites when tested under tension after similar ageing treatments performed in flowing oxygen (Fig. 12). After 2% of relative mass loss, the general aspect of the stress–strain curves remains

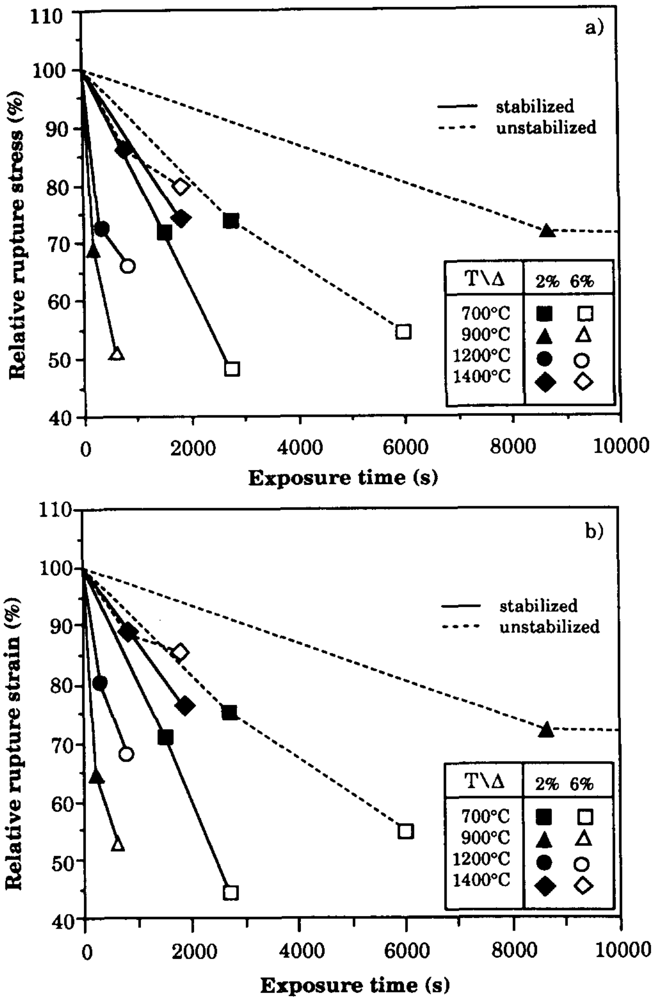

Fig. 13. Comparison of the room-temperature ultimate tensile properties of as-processed and stabilized 2D C/SiC composites variously aged under flowing oxygen (P = 100kPa); (a) rupture stress and (b) rupture strain.

globally preserved as long as ageing temperatures are inferior to 1000°C, whereas a decrease of the apparent damage strengthening rate becomes noticeable at higher temperatures. After 6% of relative mass loss, ageing treatments performed at 700°C and 900°C also result in a decrease of the apparent damage strengthening rate. Simultaneously, reductions in rupture values become noticeably temperature dependent. Figure 13 displays a comparison between the variations of stress and strain to rupture as a function of temperature for both materials. Results obtained at 1200°C do not appear on this plot, as the unstabilized composite was nearly unoxidized because of a thermally induced microcrack closure.[9] Differences between the ultimate tensile values of the two composites appear to be proportionally more important at high temperatures (i.e. 1400°C) than at lower temperatures (i.e. 700°C and 900°C).

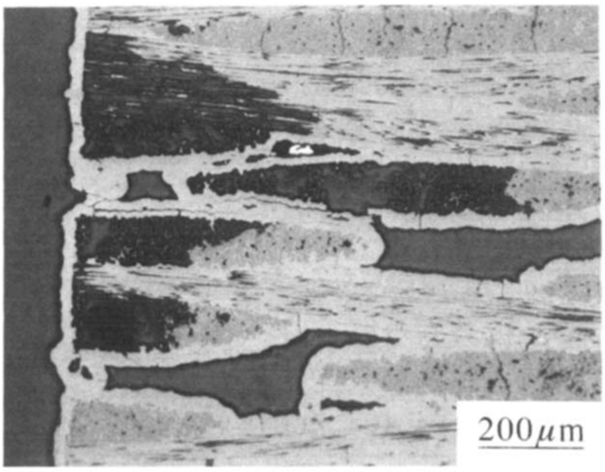

Fig. 14. Optical micrograph of a polished section of an as-processed (unstabilized) 2D C/SiC composite aged at 1400°C under flowing oxygen (P = 100kPa), for a relative mass loss of 6%.

Morphological analyses performed after oxidation on the unstabilized 2D C/SiC composites revealed similar forms of degradation as for the stabilized material, but occurring at different temperatures.[10] Non-uniform degradation already took place at 700°C and the fracture surface consequently reveals an intense pull-out of the outer tows. At 900°C and 1400°C, the oxidation of the as-processed composites remains superficial. However, at 1400°C oxidation takes place preferentially near the lateral sides of the specimens (Fig. 14), while at 900°C notch-like clusters of oxidized carbon constituents are present in the vicinity of all the seal-coating microcrack tips.

4 Discussion

4.1 Mechanisms of composite property degradation

Three temperature domains corresponding to different mechanisms controlling the oxidation behavior of the 2D C/SiC composites were previously found.[10] Each of these mechanisms also proved to be associated with a particular mode of morphological changes induced by oxidation concerning the degradation of the carbon reinforcement: uniform (at low temperatures), non-uniform (at intermediate temperatures) and superficial (at high temperatures). These different modes of degradation of the carbon phases may in turn be associated with different oxidation-induced changes in the mechanical behavior of the composite materials, as discussed extensively thereafter. It is, however, of some importance to note that in all cases, and most likely because of the low values of relative mass losses induced by the ageing treatments investigated (i.e. less than 6%), no substantial decrease of the initial equivalent Young's modulus was found to occur. Such a result suggests that the load was still entirely carried by the initial surface of the samples at the beginning of the tensile tests. Thus, mechanisms other than a simple reduction of the load-bearing surface induced by the disparition of the carbon fibers (as is the case with long-term ageings[6]) are taking place.

4.1.1 Uniform degradation

Oxidizing treatments performed at $T < 700°C$ result in the simultaneous degradation of the carbon fibers and interphase all over the composite material. The carbon interphase is preferentially consumed near the microcrack tips where free surfaces are present. Locally uncoated fibers are then mainly oxidized near their surfaces, where the reactivity is particularly high,[11] leading to the notch-like degradation observed in Fig. 6(a). The fraction of interphase consumed during the moderately extended oxidizing attacks (i.e. corresponding to relative mass losses of less than 6%) is too weak to induce noticeable changes in the fiber/matrix load-transfer conditions. The appearance of the stress–strain curves remains thus largely unchanged. However, when entering the second domain of the curves governed by fiber/matrix sliding and microcrack opening, the part of the tensile load sustained by these degraded fibers is sufficient to cause their premature rupture and consequently the composite sudden rupture. The tensile rupture strength therefore also logically decreases with an increase in the depth of the fiber notch, that is to say with an increase in the duration of the ageing treatment.

4.1.2 Non-uniform degradation

The increase of the carbon reactivity at intermediate temperatures (i.e. 900°C), results in a higher consumption of oxygen by the first carbon plies. Such a non-uniform degradation mode leads to the premature rupture of the more intensively degraded first plies upon loading. The sudden rupture of these first plies very likely induces an overloading effect on the inner plies which in turn also break. The fracture surface of the composite illustrates this difference in behavior between the surface and the bulk of the sample. As a matter of fact, the average pull-out length of the fiber tows is more important near the surface where a more important proportion of interphase has been consumed than in the center of the specimens.

4.1.3 Superficial degradation

At $T > 1200°C$, the carbon reactivity is important as compared to the rate of oxygen diffusion through the SiC seal-coating microcracks. Oxygen is thus immediately consumed at the microcrack tips, resulting in the development of pores under the SiC seal-coating. These pores are very likely to induce a notch effect in the composite leading to a sudden rupture when the load bearing capacity of the outer tows is exceeded. Before rupture, the aspect of the stress–strain curve is preserved owing to the important part of the composite which remains unoxidized. Since silica layers developed on the microcrack walls, the oxidation rate is thus progressively reduced until closure of the microcracks. Consequently, the rupture strength after oxidation is only related to the quantity of carbon consumed before sealing.

4.2 Effect of a decrease in the oxygen content

The 2D C/SiC composite has revealed a better tensile resistance in addition to the better oxidation resistance previously demonstrated[10] when the oxygen partial pressure of the surrounding environment is lowered. Decreasing the oxygen content modifies the distribution of the degraded zones mainly through a decrease in the reactivity of the carbon phases. These modifications in turn limit the mechanisms which are responsible for the mechanical degradation of the material.

At 700°C, since the decrease of oxygen content lowers the oxygen gradient and consequently the oxygen diffusional flux through the microcracks, the notch-like attack of the carbon fibers thus appear to be less extended in air than in pure oxygen (as schematically represented in Fig. 15).

The mechanisms responsible for loss of strength of the composite aged in air at 900°C have also to be related to a sudden overloading of the inner fiber tows, similarly to the test performed in oxygen. However, since the decrease of the carbon reactivity with the oxygen partial pressure attenuates the difference of degradation between the surface and the center of the composite reinforcement, this overloading effect is consequently less drastic.

The oxidizing attacks occurring at high temperatures in dry air also remain superficial (as in dry oxygen). However, these attacks, instead of remaining localized at the microcrack tips, rather propagate around the fibers tows. This feature may be also attributed to the reduction of the reactivity of the carbon phases towards oxygen which may therefore diffuse along the debonded tow/matrix zones.[10] The combined notch/overloading effects leading to the composite sudden rupture are thus substantially reduced.

4.3 Thermally unstabilized material

Observed results clearly show that the residual tensile strength of the composites is enhanced if the 1600°C stabilizing treatment is not performed prior to the oxidizing treatments. Such results have to be related to a translation of the three main temperature domains previously described.

As a matter of fact, prior to the stabilizing treatment, thermal microcracks present in the

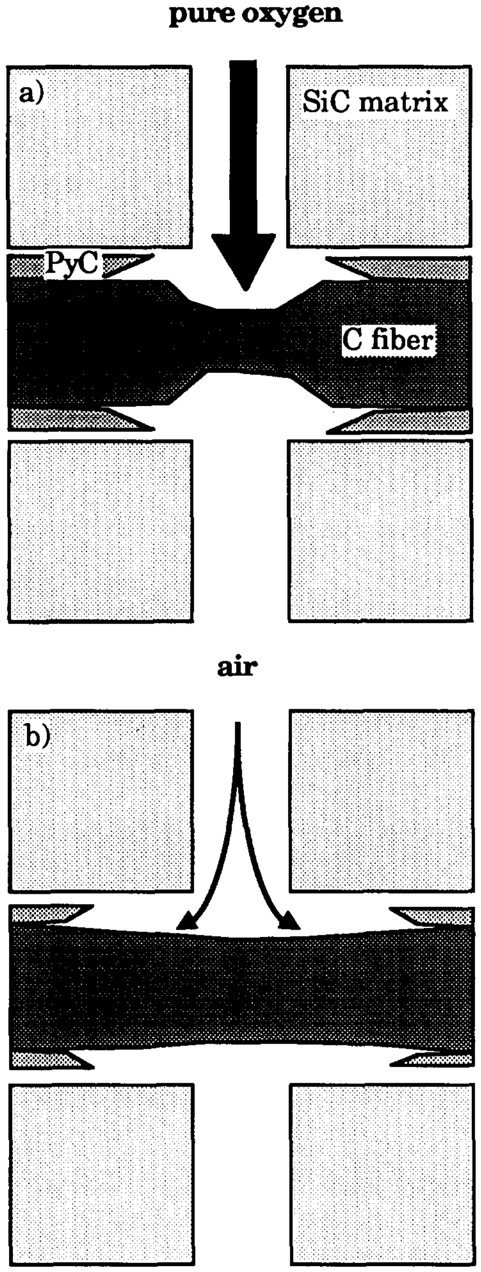

Fig. 15. Schematic representation of the differences in the degradation of the carbon phases induced by ageing treatments performed: (a) in pure oxygen and (b) in dry air.

material are thinner (see Table 1), while the carbon reactivity is higher.[10,11] The temperature domains corresponding to the mechanisms controlling the oxidation kinetics are therefore shifted to lower temperatures (see Fig. 2). Consequently, the stress and strain to rupture of the unstabilized composite aged at 700°C are comparable to those of the stabilized composite aged at 900°C for similar relative mass losses. A similar comparison can be made between the unstabilized composite aged at 900°C and the stabilized composite aged at 1200°C.

At 1400°C, however, the degradation mode of the reinforcement preferentially takes place in parallel to the plies of the composite. This phenomenon is related to the radial expansion of the carbon fibers. As a consequence, the pores formed during oxidation of the unstabilized composite at 1400°C do not induce any notch effect, which results in a strength to rupture decreasing more slowly than with the stabilized material.

5 Conclusions

Tensile tests performed at room temperature on 2D C/SiC composites variously aged in dry oxygen coupled to morphological observations of fractured specimens have shown the main mechanisms responsible for the oxidation induced loss of strength of the materials. These mechanisms have been correlated to three main degradation modes of the carbon reinforcement. Uniform degradation occurring during oxidation at low temperatures (<800°C) induces the premature composite rupture preferentially through a notch-like attack of the carbon fibers. Non-uniform degradation at intermediate temperatures ($800 < T < 1100$°C) causes the composite loss of rupture stress/strain by the sudden overloading of the carbon inner plies. Superficial degradation occurring at high temperatures (>1100°C) induces the composite premature rupture by a combined notch/overloading effect from the outer fiber tows. The tensile strength of the composites thus decreases less severely as the ageing temperature is increased.

Oxidation under pure oxygen enhances the mechanisms which are responsible for the decrease of the tensile properties. Thus, when the oxygen content is decreased, a better preservation of the composite tensile strength may be observed.

The stabilizing treatment performed at 1600°C in an inert atmosphere on 2D C/SiC composites after processing leads to a decrease in the oxidation resistance. This phenomenon may be explained by a translation of the three temperature domains.

Acknowledgements

This work has been supported by MRT and SEP through a grant given to F.L. The authors acknowledge the assistance that they received from SEP for the CVI processing of the materials and through valuable discussions. The authors are indebted to B. Humez for performing the tensile tests.

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