PII: S0955-2219(96)00204-X

Effect of Ageing Treatments at High Temperatures on the Microstructure and Mechanical Behaviour of 2D Nicalon/C/SiC Composites. 2: Ageing under CO and Influence of a SiC Seal-Coating

C. Labrugère, L. Guillaumat, A. Guette & R. Naslain

Laboratoire des Composites Thermostructuraux (UMR 47, CNRS-SEP-UB1), 3 allée de la Boétie, Domaine Universitaire, 33600-Pessac, France

Abstract

2D-Nicalon/C/SiC composites fabricated by CVI, either uncoated or protected with a SiC CVD seal-coating, have been aged at 1100–1300°C under vacuum or carbon monoxide. They experienced a weight loss due to the decomposition of the $SiO_{2x}C_{1-x}$ phase present in the fibers and to secondary reactions between carbon (from the fibers and the interphase) and the fiber decomposition products (CO and SiO). The change occurring in the chemical composition and microstructure of the composites has been studied by EPMA, AES and TEM/PEELS and in their mechanical behavior by tensile and push-out tests at ambient. The degradation process is slowed down by the CO pressure either applied externally to or generated within the composites as the result of the confinement of SiO/CO by the SiC coating. When aged between 1100 and 1200°C, the composites fail at relatively high strain and stress with a plateau-like feature for the tensile curve whereas those aged at 1300°C are brittle when treated under vacuum even with a SiC coating, or non-brittle with a low failure stress when treated under CO. © 1997. Published by Elsevier Science Limited. All rights reserved.

Resumé

Des composites 2D-Nicalon/C/SiC élaborés par CVI, revêtus ou non par un seal-coat de SiC CVD, ont été vieillis entre 1100 et 1300°C sous vide ou sous monoxyde de carbone. Ils présentent une perte de masse due à la décomposition de la phase $SiO_{2x}C_{1-x}$ au sein des fibres et à des réactions secondaires entre le carbone (des fibres et de l'interphase) et des produits de décomposition de la fibre (CO et SiO). L'évolution de la composition chimique

et de la microstructure de ces composites a été étudiée par EPMA, AES et TEM/PEELS tandis que leur comportement mécanique a été identifié par des essais de traction et de push-out à l'ambiante. Le processus de dégradation est ralenti par une pression de CO, qu'elle soit appliquée de l'extérieur, ou générée dans le composite à la suite du confinement de SiO/CO par le seal-coat de SiC. Les composites vieillis entre 1100 et 1200°C cassent à un niveau de contrainte et d'allongement relativement élevé avec une courbe de traction à 'plateau' tandis que les matériaux vieillis à 1300°C sont soit fragiles lorsqu'ils sont traités sous vide même revêtus d'un seal-coat de SiC, soit non fragiles avec une faible contrainte à rupture lorsqu'ils sont traités sous CO.

1 Introduction

2D-SiC/C/SiC composites fabricated from Nicalon (NLM 202, Nippon Carbon, Japan) fabric preforms according to the chemical vapor infiltration (CVI) process have been reported to undergo chemical degradation when they are aged under vacuum or argon at high enough temperature (i.e. beyond about 1100°C).[1–8] This degradation is primarily related to the decomposition of the metastable $SiO_{2x}C_{1-x}$ ternary phase of the Nicalon fibers which occurs with an evolution of gaseous species (mainly CO and to a less extent SiO).[1,9] Furthermore, secondary reactions are thought to occur between the fiber decomposition gaseous products (particularly SiO) and free carbon from the fiber itself and from the interphase (as pyrocarbon) which is used in most ceramic matrix composites (CMC) to achieve a proper bonding between the fiber and the matrix. As this degradation mechanism proceeds, free carbon is progressively consumed with the formation of large

SiC crystals at the fiber surface and an overall SiC grain growth in the bulk of the fibers. This degradation mechanism has important consequences. It yields a weight loss $\Delta m/m_0$ and a change in the mechanical behavior of the composites. This change is related to the weakening of the fiber–matrix (FM) bonding as the pyrocarbon interphase is progressively consumed and to that of the fibers themselves (as the result of the decomposition and SiC grain growth phenomena).[1]

The kinetics of the degradation process depend on the ageing conditions (i.e. temperature, pressure and nature of the atmosphere: the weight loss rate increases as temperature is raised and as pressure is lowered). The degradation process is slowed down when the treatment is performed under a pressure of argon (e.g. 70 kPa) with respect to ageing under vacuum, at least as long as the temperature is low enough (i.e. for $T <$ 1300°C).[1,6] Thus, it has been thought interesting to study the effect on the degradation process of the composites, of an external pressure of CO (which is the main gaseous species involved in the degradation mechanism) applied to the materials during the ageing treatments. Furthermore, it was assumed that a SiC seal-coating, deposited by CVD on the composite surface prior to the ageing treatment, might have a somewhat similar effect, in as much as it could make the evolution of the gaseous decomposition products more difficult and thus generate internal pressures of CO and SiO.

The aim of the present contribution, which is a continuation of the first part[1] devoted to the ageing under vacuum or argon of uncoated composites, was to study the influence of an external pressure of CO and that of a SiC seal-coating on the ageing of 2D-SiC/C/SiC composites, in terms of chemical composition, microstructure, FM bonding and mechanical behavior under tensile loading at room temperature.

2 Experimental

2.1 Materials
The materials used in the present study are 2D-SiC/C/SiC composites with a bidimensional Nicalon fiber architecture and fabricated according to the CVI-process.[10] Prior to the infiltration of the SiC matrix, the fibers have been coated with a film (mean thickness: $\approx$ 0·1 μm) of a pyrocarbon interphase through the cracking of a hydrocarbon precursor (mainly CH_4). All the infiltration steps have been performed at moderate temperatures (900–1100°C) and reduced pressures (a few kPa or 10 kPa), as is the rule in isothermal/isobaric CVI.[10]

The Nicalon fibers have a mean diameter of 14 μm and their chemical composition (in at%) was found to be close to: Si(35)-C(48)-O(17) by electron probe micro-analysis (EPMA), in the as-processed composites. The fibers were observed to be surrounded by a thin (5–10 nm) amorphous layer of a mixture of carbon and silica, assumed to be formed during the fabrication of the fibers and/or that of the composites.[11,12]

The pyrocarbon interphase consists of a quasi-isotropic nanoporous carbon over the majority of its thickness. However, very near the fiber surface (i.e. within about 20 nm), the carbon atomic layers tend to be aligned locally parallel to the fiber surface (Fig. 3 in Ref. 1) as previously mentioned by other authors.[1,11,12]

In the as-received state, the 2D-SiC/C/SiC composites exhibit a non-linear stress-strain behavior (Fig. 18 in Ref. 1) with a Young's modulus of about 230 GPa, the failure occurring at relatively low stress and strain ($\sigma_r \approx$ 150 MPa; $\varepsilon_r \approx$ 0·17%), with limited fiber pull-out.

The ageing treatments and then the tensile tests have been performed on samples machined as 100 $\times$ 10 $\times$ 3 mm^3 bars, as shown in Fig. 1(a) (the bars being orientated with their length parallel to one of the fiber directions, namely directions 1 or 2). The samples have been aged either in the as-machined state (i.e. uncoated) or coated with a 15 μm thick SiC seal-coating (the coating being deposited by CVD, after machining, on all sample faces) (Fig. 1(b)).

2.2 Ageing treatments
The ageing treatments have been performed directly on the tensile specimens. The specimen was hung to a microbalance (D101, Cahn, USA) in order to record the weight loss continuously, $\Delta m/m_0$ and heated with a graphite susceptor, as shown in Fig. 2, in Ref. 1. The ageing treatments were conducted either at constant volume under a pressure of carbon monoxide (or argon) up to one atmosphere, or under vacuum (the residual pressure being in the range 10^{-1} to 10^{-3} Pa). As shown in Tables 1 and 2, the uncoated samples were aged under CO atmospheres only (at pressures ranging from 45 to 100 kPa) since the treatments under vacuum or argon have been already studied in Ref. 1. Conversely, the SiC-coated samples were aged under all conditions (i.e. under vacuum, argon and carbon monoxide).

2.3 Characterization
The compositional and microstructural evolution of both the fibers and FM interfacial zones during ageing have been studied on polished cross-sections, thin foils or fracture surfaces, by electron
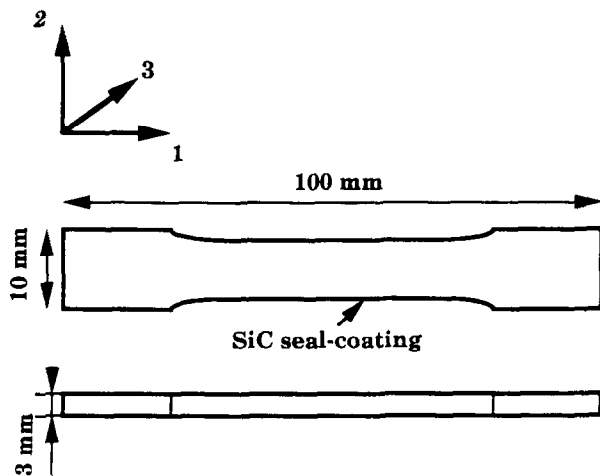
(a)
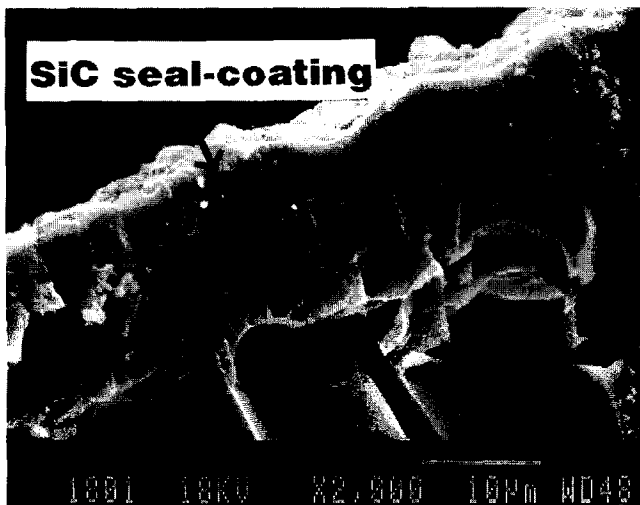
(b)

Fig. 1. Tensile test specimen of 2D-SiC/C/SiC composites coated with a 15 μm SiC seal-coating: (a) shape, fiber orientation and dimensions, (b) SEM image of the SiC seal-coating.

Table 1. Ageing conditions applied to the uncoated 2D-SiC/C/SiC tensile specimens treated under CO atmospheres and resulting weight losses

Material reference	Pressure of CO (kPa)	Ageing temperature (°C)	Ageing time (h)	$\Delta m/m_0$ (%)
0 As-received	none	none	none	none
13 aged	70	1100	139	-0·43
14 aged	45	1200	58	-0·71
15 aged	70	1200	64	-0·83
16 aged	45	1300	21	-4·7
17 aged	80	1300	20	-2·1
18 aged	100	1300	63	-2·9

Table 2. Ageing conditions applied to SiC seal-coated 2D-SiC/C/SiC composites and resulting weight losses

Material reference	Ageing atmosphere (Pa)	Ageing temperature (°C)	Ageing time (h)	$\Delta m/m_0$ (%)
19 aged	Vacuum (4×10^{-4})	1100	24	-0·02
20 aged	Vacuum (5×10^{-3})	1200	12	-0·13
21 aged	Vacuum (6×10^{-2})	1200	78	-0·15
22 aged	Vacuum (5×10^{-4})	1200	108	-0·13
23 aged	Argon (7×10^{4})	1200	75	-0·17
24 aged	Vacuum (6×10^{-2})	1300	17	-2·6
25 aged	Vacuum (1×10^{-2})	1300	28	-5·2
26 aged	Argon (9×10^{4})	1300	24	-1·2
27 aged	CO (7×10^{4})	1300	128	-0·26

probe micro-analysis (EPMA; Camebax, Cameca, France), transmission electron microscopy (TEM; 2000 FX, Jeol, Japan), electron energy loss spectroscopy (EELS; 300 kV TEM, Philips with PEELS analyzer, Gatan); and Auger electron spectroscopy (AES; PHI-590, Perkin-Elmer), according to classical procedures which have been presented in part 1.[1] One should emphasize that all the analyses have been performed at or near the failure surface of each specimen in order to derive a correlation between the chemical/microstructural degradation of the sample and the change observed in its mechanical behavior.

The aged samples were tested at room temperature under tensile loading (Instron 8501) at a constant strain rate of 0·05% per min. The evolution of the FM-bonding (resulting from the chemical/microstructural degradation of the material) was assessed qualitatively through indentation push-out tests (Onera, France) conducted on specimens

less than 300 μm in thickness prepared according to a technique similar to that used for the TEM thin foils. The load was applied on the fiber with a flattened Vickers indentor at a rate of the order of 0·12 μm s^{-1} and measured with a 2N load cell. The displacement was measured with a capacitive sensor. In the absence of satisfactory models for this kind of composite, no attempt has been made yet to derive interface parameter values from the push-out test data.

3 Results

3.1 Weight loss during the ageing treatment

The weight loss $\Delta m/m_0$ experienced by the composites during the ageing treatments as a function of time, is shown in Figs 2 and 3 for the uncoated and SiC-coated tensile test specimens ($m_0 \approx 8$ g), respectively. For a given temperature, e.g. 1300°C, the weight loss is less when the composite is aged under an atmosphere of CO (with respect to ageing under vacuum or argon) and when it has been coated with a SiC seal-coating prior to the ageing treatment.

For the uncoated specimens aged under an atmosphere of CO, the weight loss exhibits the following features: (i) it increases as temperature is raised from 1100 to 1300°C, at constant CO
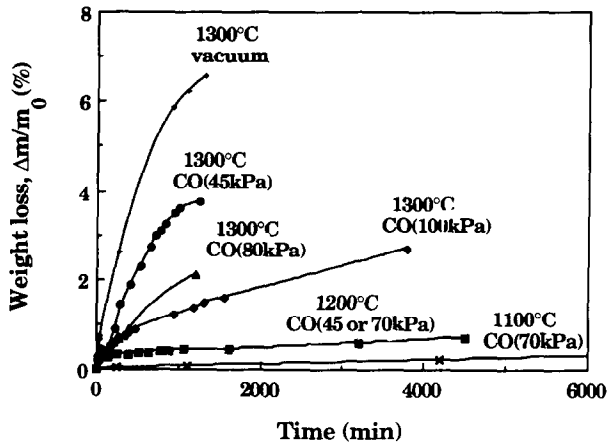
Fig. 2. Variations of the weight loss experienced by uncoated 2D-SiC/C/SiC composite specimens as a function of time, during ageing treatments performed in CO atmospheres under various conditions. The curve corresponding to an ageing treatment under vacuum is shown for purpose of comparison.
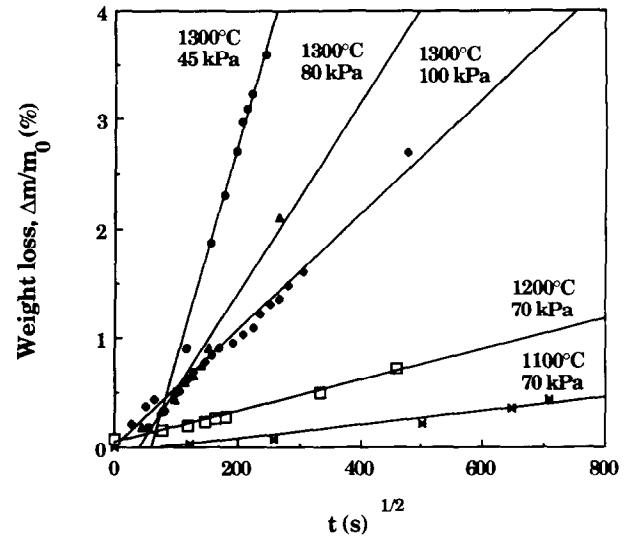

Fig. 3. Variations of the weight loss experienced by 2D-SiC/C/SiC composite specimens coated with a SiC seal-coating, as a function of time, for various ageing conditions. The curve corresponding to the uncoated specimen is shown for purpose of comparison.

Fig. 4. Variations of the weight loss experienced by uncoated 2D-SiC/C/SiC specimens as a function of the square root of time, during ageing treatments performed in CO atmospheres under various conditions.
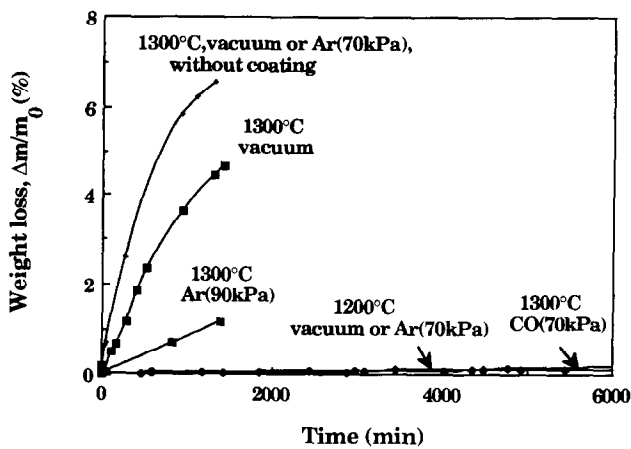

Fig. 5. Arrhenius plots for the thermal variations of the kinetic constants k (defined as the slopes of the straight lines shown in Fig. 4) characterizing the weight loss of 2D-SiC/C/SiC uncoated composites aged under vacuum (residual pressure: 10^{-1} to 10^{-3} Pa) or an atmosphere of argon or carbon monoxide.

pressure (e.g. 70–80 kPa) and (ii) at a given temperature (e.g. 1300°C), it decreases as the pressure of CO is raised. The effect of the CO pressure appears to be much more significant at high temperatures. As an example, increasing the CO pressure from 45 to 80 kPa has an obvious effect on the value of $\Delta m/m_0$ at 1300°C whereas the same CO pressure increase has a negligible effect on the weight loss at 1200°C. Furthermore and as already reported in part 1 for the ageing treatments under vacuum or argon, the variations of $\Delta m/m_0$ as a function of the square root of time are linear at least in a first approximation (Fig. 4).[1] The slopes k of the related straight lines have been used to characterize the kinetics of the weight loss process. Their thermal variations (Arrhenius plot) are shown in Fig. 5. Although the data points were limited in number (since ageing was conducted directly on tensile test specimens), each Arrhenius plot can be analysed as a straight line
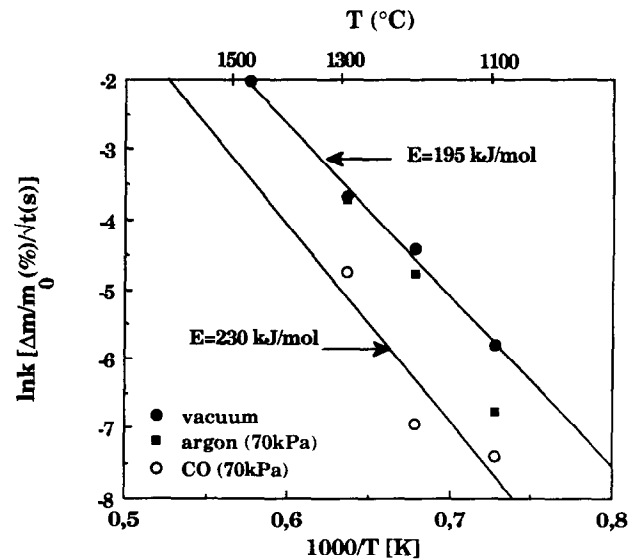
and used to derive an apparent activation energy, which has been observed to be of about 230 kJ mol^{-1} (i.e. slightly higher than that corresponding to ageing under vacuum or argon). Thus, the use of a CO ageing atmosphere slows down the degradation process of the composites.

The data in Fig. 3 clearly show that the use of a 15-μm thick SiC seal-coating is another efficient way to slow down the degradation process. As an example, the specimen aged at 1200°C during 100 h either under vacuum or argon, has experienced a weight loss of only 0·15%. Under similar conditions (1200°C, 94 h, vacuum), that reported for the uncoated composite in Ref. 1, Table 4, was 6·3%.[1] Although the beneficial effect due to the

SiC seal-coating is much less significant at higher temperatures, e.g. 1300°C, it still exists. This last feature suggests that beyond about 1200°C, a 15-μm-thick SiC seal-coating deposited by CVD is no longer perfectly gas-tight, with respect to the evolution of the fiber decomposition gaseous products (CO and SiO). This assumption is further supported by the fact that the weight loss becomes negligible at 1300°C when combining the slowing down effect of the SiC seal-coating with that of a CO atmosphere.
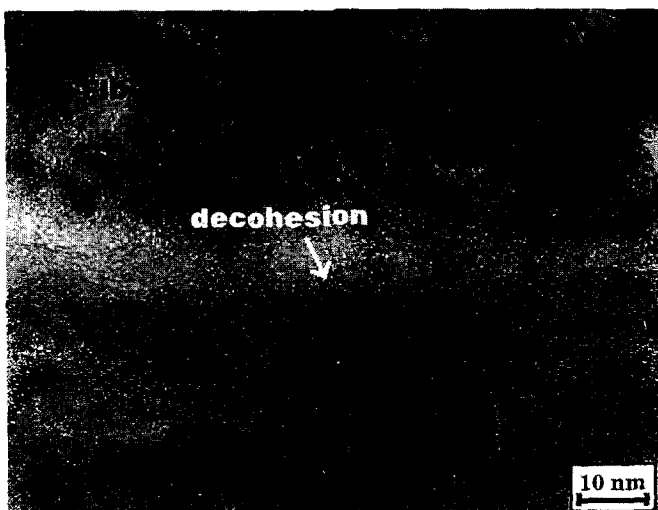
3.2 Chemical and microstructural analysis of the fiber and FM interfacial zone in aged composites

3.2.1 Composites aged under CO

The pyrocarbon interphase remains basically unchanged in the bulk when the composites are aged up to 1300°C (with $45 < P_{CO} < 100$ kPa),
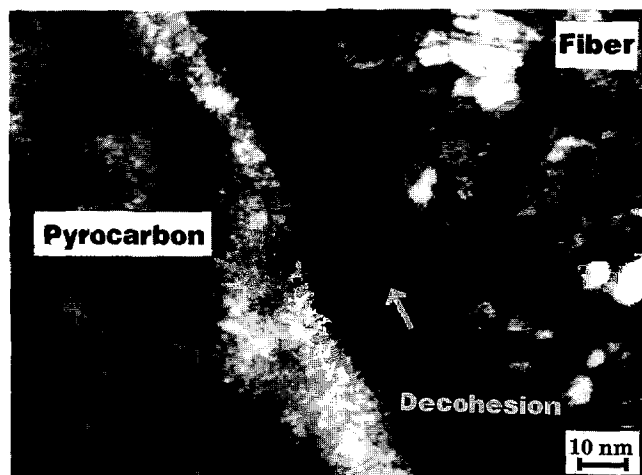

(a)

(b)

Fig. 6. TEM images showing decohesion near the pyrocarbon/fiber interface in fractured tensile test specimens of uncoated 2D-SiC/C/SiC composites aged at 1300°C under CO: (a) dark field image (C_{002}) (ageing time: 63 h; $P_{CO} = 100$ kPa), (b) lattice fringe image (ageing time: 21 h; $P_{CO} = 45$ kPa).

with or without a SiC seal-coating, as shown by TEM-analysis (Figs 6 and 7). However, the anisotropic part of the interphase (i.e. the first 20 nm in contact with the fiber in the as-received composite) is observed to have undergone decohesion near the fiber surface, in the fractured tensile test specimens which have been aged at 1200 or 1300°C (Fig. 6).

In the uncoated composites aged at 1200°C (with $\Delta m/m_0 = 0.83\%$) oxygen has accumulated near the fiber surface (i.e. over a depth of about 40 nm), as shown by both AES depth profile analysis (Fig. 8) and EELS data (Table 3). This narrow zone, which can be locally very rich in oxygen, is thought to be a mixture of silica and carbon. Within the fiber, the chemical composition is close to that of the fiber in the as-supplied
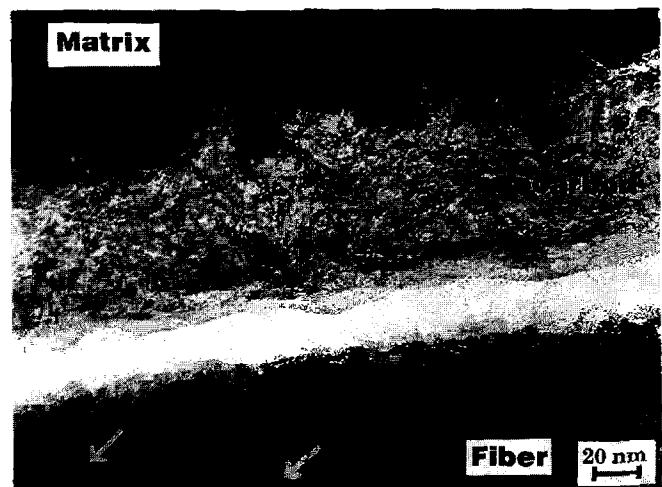
(a)
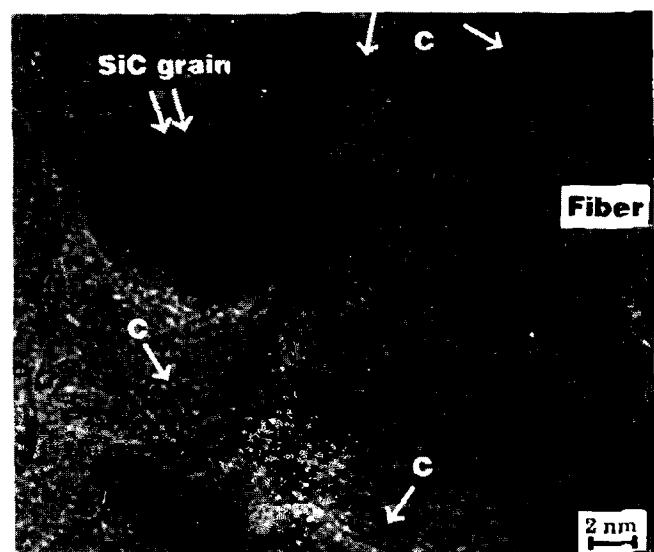
(b)

Fig. 7. TEM images of SiC-coated 2D-SiC/C/SiC composites aged at 1300°C (128 h) under CO (70 kPa): (a) bright field image of the FM interfacial zone (the arrows show the SiC crystals in the fiber), (b) lattice fringe image of a zone near the fiber surface (depth 0.5-1 μm) (the simple arrows show the carbon BSU, and the double arrows the SiC crystals).

composite (Table 4) with a slightly lower value of the C/Si atomic ratio (1·12 and 1·37, respectively). Finally, for these rather mild ageing conditions ($\Delta m/m_0 = 0.83\%$), the SiC grain growth associated with the degradation of the fibers remains limited (mean SiC grain size: 4–5 nm).
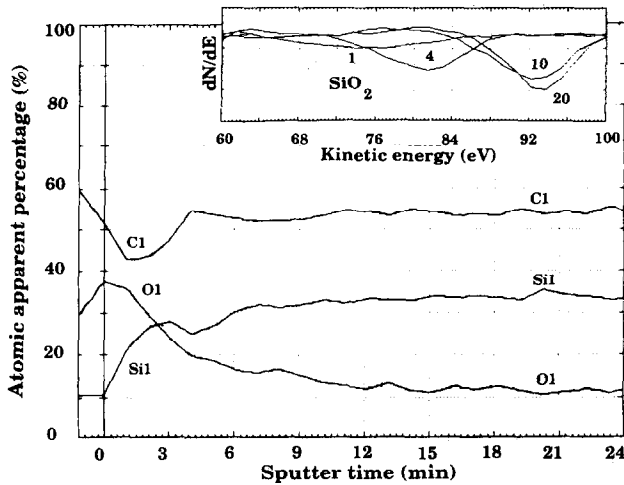

Fig. 8. AES radial depth profiles recorded from the surface of a pulled-out fiber present at the failure surface of an uncoated 2D-SiC/C/SiC composite aged at 1200°C for 58 h under an atmosphere of CO (45 kPa) and tensile tested. The sputtering rate was 8 nm/min (reference: Ta_2O_5). The shift of the Si_{LVV} transition as a function of etching time (respectively: 1, 4, 10 and 20 min) is shown in the inset.

Table 3. O/Si and C/Si atomic ratios as assessed by PEELS analysis as a function of the distance from the surface of Nicalon fibers in thin foils of 2D-SiC/C/SiC composites aged under various conditions

Material reference	Ageing treatment conditions	Distance from fiber surface (nm)	O/Si atomic ratio	C/Si atomic ratio
15	1200°C-64 h	≈ 5	0·59	1
	CO(70 kPa)	30	0·47	1·2
	Uncoated	200	0·42	1·4
	specimen	6000	0·36	≈ 1
21	1200°C-78 h	≈	1·18	2·5
	Vacuum	≈	0·4	≈ 1
	SiC-coated	220	0·34	≈ 1
	specimen	410	0·26	≈ 1

In the uncoated composites aged under more severe conditions in terms of weight loss ($T = 1300°C$, $\Delta m/m_0 > 2\%$) there is a clear correlation between the weight loss experienced by the composite, on the one hand, and both the decrease in oxygen concentration and SiC grain growth in the fibers, on the other hand (Fig. 9 and Table 4), as previously reported in part 1 for the ageing treatments under vacuum or argon. However, for a given weight loss, the growth of the SiC crystals within the fibers is more limited for the composites aged under CO than for those treated under vacuum (part 1).[1] As an example, for $\Delta m/m_0 = 4\%$, the SiC crystal mean size is of the order of 9 nm for the material aged under CO (specimen 16) whereas it is of about 20 nm for that aged under vacuum (Fig. 9). Furthermore, a similar SiC grain mean size (i.e. 7–9 nm) has been observed for a composite (specimen 18) aged under different conditions in terms of time and P_{CO}, but which has indeed experienced a rather similar weight loss ($\Delta m/m_0 = 4.7$ and 2·9 for specimens 16 and 18, respectively) and whose fibers exhibit close residual compositions (with same oxygen concentration) (Table 4).
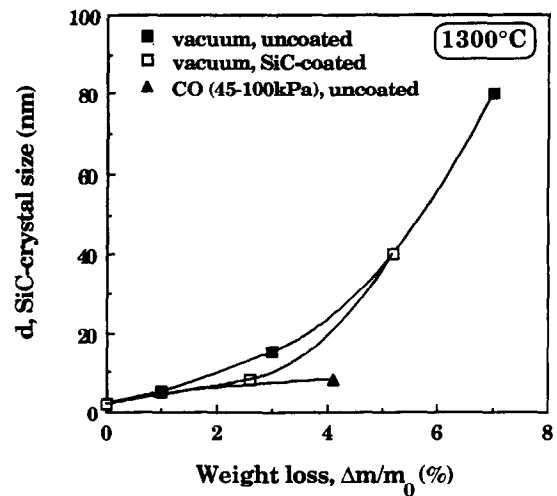
Fig. 9. Correlation between the SiC grain growth in the Nicalon fibers and the composite weight loss, in 2D-SiC/C/SiC composites aged at 1300°C under various conditions.

Table 4. Chemical composition of Nicalon fibers (as assessed by EPMA) in 2D-SiC/C/SiC composites aged under various conditions

Materials reference	Ageing conditions	$\Delta m/m_0$ (%)	Atomic %			C/Si at. ratio
			Si	C	O	
0	as-received	0	35	48	17	1·37
15	1200°C-64 h-CO(70 kPa)	−0·83	38·5	43	18·5	1·12
16	1300°C-21 h-CO(45 kPa)	−4·1	38	60	7	1·82
18	1300°C-63 h-CO(100 kPa)	−2·9	35	58	7	1·66
21	1200°C-78 h-vacuum	−0·15	37	45	18	1·22
24	1300°C-17 h-vacuum	−2·6	39	53	8	1·36
27	1300°C-128 h-CO(70 kPa)	−0·26	40	44	16	1·10

Materials 15, 16, 18: uncoated; materials 21, 24, 27: coated with a 15-μm-thick SiC seal-coating. The uncertainty on the at% is estimated to be of the order of 1%.

Fig. 10. AES radial depth profiles recorded from the surface of a pulled-out fiber present at the failure surface of a SiC-coated 2D-SiC/C/SiC composite aged at 1300°C for 128 h under an atmosphere of CO (70 kPa) and tensile tested (sputtering rate: 8 nm/min; reference Ta_2O_5).

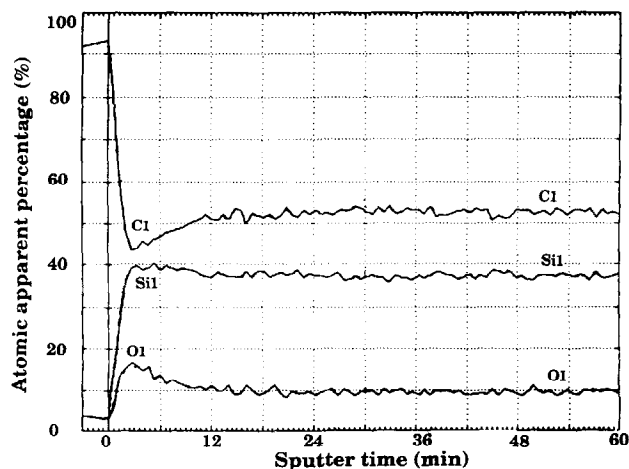In the SiC-coated composite (specimen 27) which has been aged for a long time at 1300°C under CO, the SiC grain mean size in the fibers is again of the order of 8 nm although the weight loss is now extremely low (i.e. 0·26%) with respect to those observed for the uncoated specimens (2·9 and 4·1%, for specimens 16 and 18). With respect to the as-supplied composite (specimen 0), there has been a slight change of composition in the bulk of the fibers with a decrease in the C concentration, an increase in the Si concentration and correlatively a decrease in the C/Si atomic ratio (Table 4). Conversely, the oxygen concentration has remained almost unchanged, a feature which is consistent with the extremely low weight loss. The carbon BSUs appear to be rather well interconnected, at least near the fiber surface (i.e. over a depth of about 1 μm which was observable by TEM in the thin foil) (Fig. 7(b)). Finally and as shown in Fig. 10, oxygen seems to have accumulated near the fiber surface (i.e. over a thickness of about 50 nm).

3.2.2 SiC-coated composites aged under vacuum

As already established in Section 3.1, the composites protected with a 15-μm-thick CVD seal-coating, experience a very low weight loss when aged under vacuum at 1200°C. For an ageing time of $\approx$ 100 h, it is only 0·13% (specimen 22, Table 2) whereas it has been reported to be of the order of 6% for the uncoated composite (specimen 4, Table 1 in Ref. 1). This feature correlates with the results of the analyses performed in situ on the fibers. First, the chemical composition of the fibers in the bulk (particularly the oxygen concentration) is almost unchanged (Table 4). Second, the grain growth in the fibers is limited, the SiC crystal mean size being of the order of 5 nm (Fig. 11(a)),

Fig. 11(a). TEM analysis of a SiC-coated 2D-SiC/C/SiC composite after ageing under vacuum (residual pressure: 6 × 10⁻² Pa) at 1200°C for 78 h: dark field image (C_{002} and β SiC_{111}) of the fiber/pyrocarbon interfacial zone.

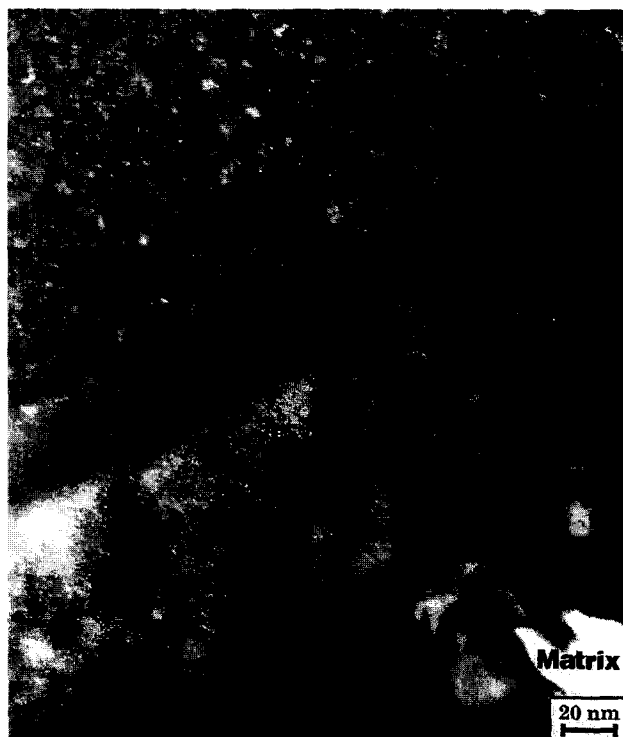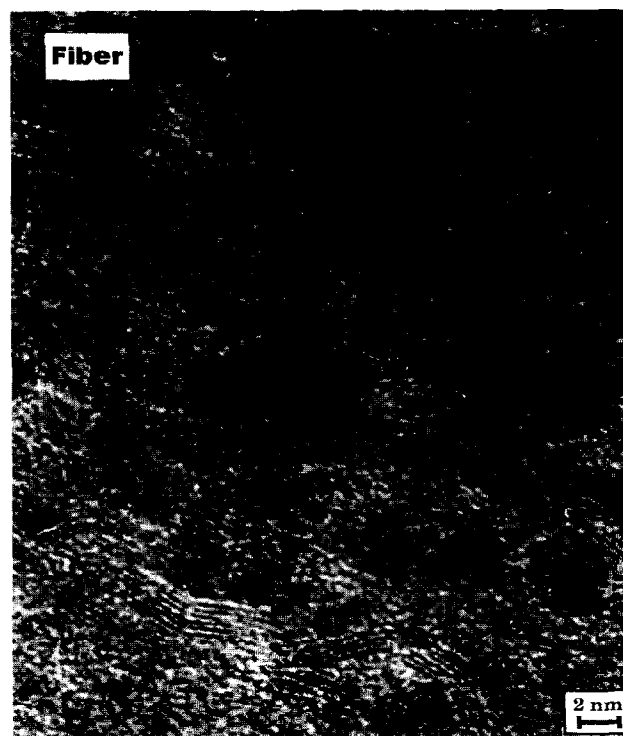Fig. 11(b). TEM analysis of a SiC-coated 2D-SiC/C/SiC composite after ageing under vacuum (residual pressure: 6 × 10⁻² Pa) at 1200°C for 78 h: lattice fringe image of the fiber at a depth of 0·5–1 μm from the fiber surface.

although the free carbon appears to be better organized (the BSUs being interconnected and forming a network around the SiC crystals) (Fig. 11(b)). The most noticeable change in the

SiC-coated specimens aged at 1200°C under vacuum, deals with the FM interfacial zone. The pyrocarbon interphase remains basically unchanged in thickness and microstructure even after an ageing time as long as ≈ 100 h (Fig. 12). However, the pyrocarbon/fiber interface is significantly altered: (i) an additional thin layer (Fig. 11(a)), assigned to a mixture of silica and carbon on the basis of AES analysis (Fig. 13) and EELS data (specimen 21, Table 3), has grown at the fiber surface, its thickness increasing as the ageing duration is raised (Fig. 14) and (ii) this carbon/silica layer seems to exhibit defects (e.g. nanopores and/or decohesion) after tensile testing, at least for the longer ageing times (Fig. 12). All these features suggest a weakening of the FM-bonding.
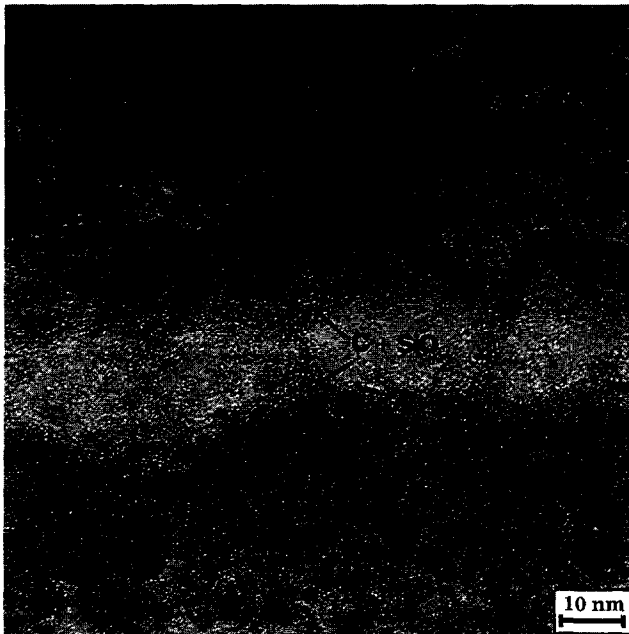
The confinement of the fiber decomposition products (CO and SiO) within the composites due to the SiC seal-coating, is no longer effective when the temperature of the vacuum ageing treatment is set at or beyond 1300°C. As a result, the weight loss experienced by the SiC-coated composites (e.g. 5·2% for $t = 28$ h; specimen 25 in Table 3) becomes close to that reported in part 1 for the uncoated composites aged under similar conditions (6·9% for $t = 24$ h; specimen 7 in Ref. 1, Table 1).[1] Thus, it is not surprising that both the fibers and the FM interfacial zones are observed to undergo a compositional and microstructural change similar to that reported in part 1 for the uncoated composites. There is first a decrease of the oxygen concentration in the fibers, which is, however, slower for the SiC-coated composites. As an example, the residual O concentration in specimen 24 (Table 4) is still 8 at% for the SiC-coated composite for $t = 17$ h, whereas it was only 1 at% for the uncoated composite (specimen 12; $t = 24$ h, Ref. 1, Tables 1 and 2).[1] Correspondingly, there is an increase of the carbon concentration of same magnitude for both composite types. Second and as shown in Fig. 9, the SiC grain growth in the fibers is similar for the SiC-coated and the uncoated composites, for a given weight loss value. Third, the FM interfacial zone undergoes the same evolution with: (i) a progressive gasification of the pyrocarbon interphase associated with the growth of large size SiC crystals at the fiber surface over a depth of 50–80 nm (Fig. 15(a)) and (ii) the growth of an amorphous silica-rich layer at the fiber surface, for longer ageing durations (Fig. 15(b)). These features suggest that the FM-bonding may have been dramatically lowered (not to say destroyed) and the fibers significantly weakened (due to both grain growth in the bulk and large surface flaws formation).

Fig. 12. TEM lattice fringe image of the FM interfacial zone in a SiC-coated 2D-SiC/C/SiC composite aged under vacuum at 1200°C for 108 h and tensile tested.
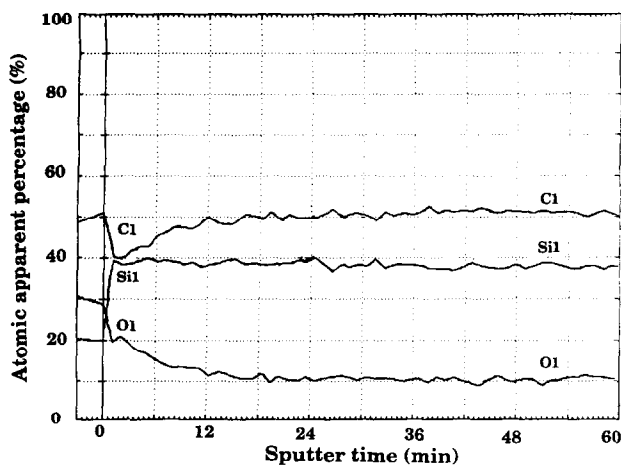

Fig. 13. AES radial depth profiles recorded from the surface of a pulled-out fiber present at the failure surface of a SiC-coated 2D-SiC/C/SiC composite aged under vacuum at 1200°C for 108 h and tensile tested (sputtering rate: 8 nm/min; reference Ta_2O_5).
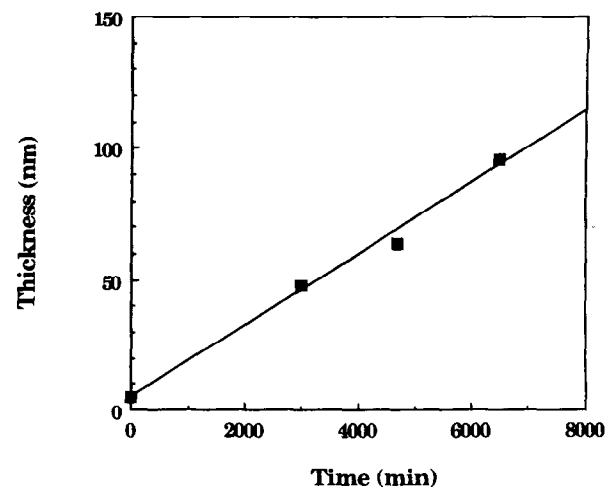

Fig. 14. Variations of the thickness of the C + SiO_2 layer grown at the fiber surface, as a function of the ageing time, in SiC-coated 2D-SiC/C/SiC composites treated under vacuum (residual pressure: 10^{-1} to 10^{-3} Pa) at 1200°C.

3.3 Mechanical behavior at ambient

3.3.1 Under tensile loading

The tensile stress-strain curves recorded for 2D-SiC/C/SiC composites aged under various conditions, are shown in Figs 16(a) and 16(b) for the uncoated and SiC-coated specimens, respectively. They fall into three different categories: (i) the curves which are close to that of the as-received composites (with however a lower proportional limit and a higher failure strain), (ii) the curves exhibiting a plateau-like shape beyond the proportional limit and (iii) the linear curves typical of a brittle behavior.
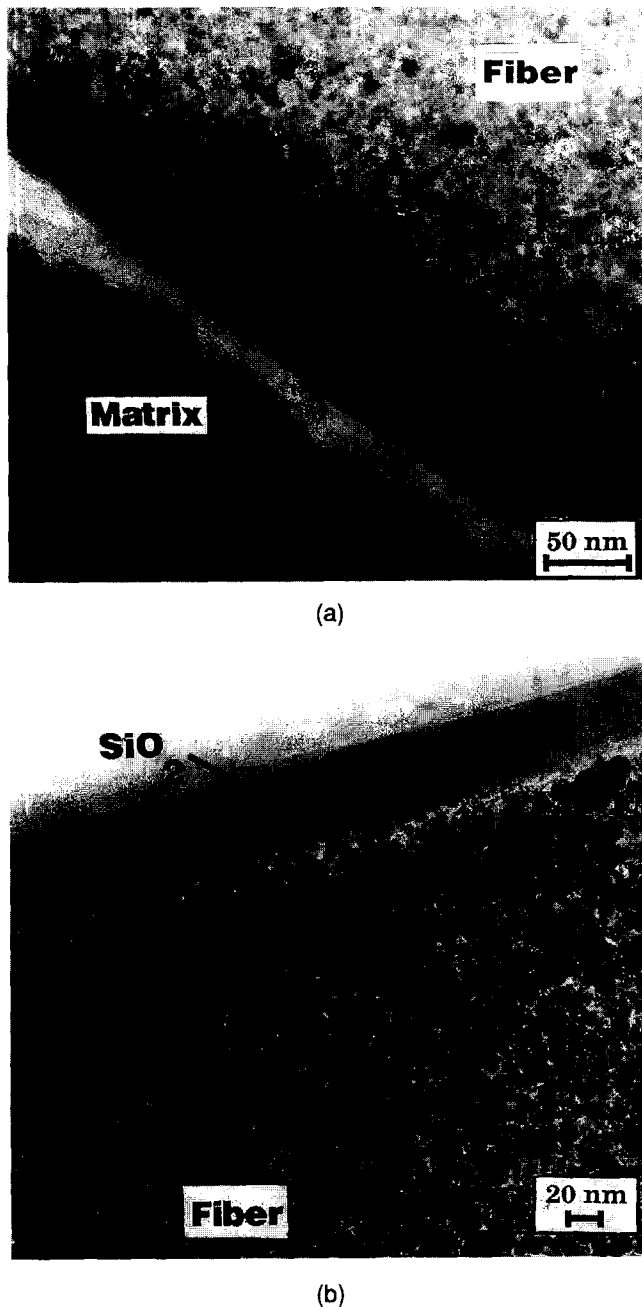
The as-received composite (sample 0) exhibits a tensile stress-strain curve with a limited non-linear domain corresponding to damage localized near the macropores left in the material by the CVI process, as well as within the transverse tows, as previously reported by Aubard.[13] The corresponding microcracks in the failed specimens can only be observed after surface chemical etching (e.g. with the Murakami reagent) in as much as they become perfectly closed when the specimen is unloaded.

The SiC-coated composite which has been aged under mild conditions (viz. 24 h at 1100°C under vacuum, with $\Delta m/m_0 = 0.02\%$; specimen 19 in Table 2), exhibits a mechanical behavior close to that of the as-received material (Fig. 16(b)). However, microcracks are observable without any surface chemical etching, in polished longitudinal sections of the failed specimen. This feature suggests that the FM interfacial zone has already undergone some degradation during the ageing treatment thus allowing more decohesion to occur between the fibers and the matrix. As a result, the fibers can be loaded to a higher strain. Under such conditions, the composite itself fails at a higher strain (i.e. 0.3% for the specimen 19 versus 0.17% for the specimen 0), the matrix microcracks exhibiting some residual opening after failure.

(a)

Fig. 15. TEM images (bright field) of SiC-coated 2D-SiC/C/SiC composites aged under vacuum (residual pressure: 3 × 10⁻² Pa) at 1300°C: (a) FM interfacial zone after an ageing treatment of 17 h and (b) pyrocarbon/fiber interface after an ageing treatment of 28 h.
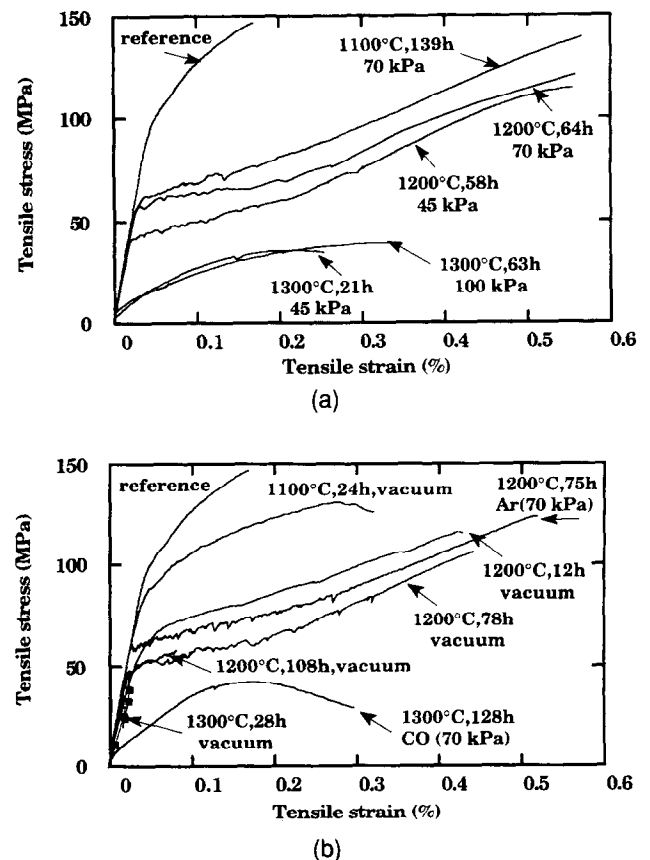
(a)

(b)

Fig. 16. Tensile stress-strain curves recorded at ambient for 2D-SiC/C/SiC composites after ageing under various conditions: (a) uncoated specimens aged under CO atmospheres, (b) SiC-coated specimens after ageing under vacuum (residual pressure: 10⁻¹ to 10⁻³ Pa), argon or CO.

The tensile stress-strain curves with a plateau-like shape are observed for the composites which have experienced a slightly higher weight loss during ageing, namely $0.4\% < \Delta m/m_0 < 0.8\%$ for the uncoated specimens aged under CO at 1100–1200°C and $0.13\% < \Delta m/m_0 < 0.17\%$, for the SiC-coated specimens treated under vacuum or argon at 1200°C (Tables 1, 2 and Fig. 16(a),(b)). Their main features, i.e. a low proportional limit, a plateau-like shape and a pseudo-linear domain before failure, are those of the composites of type A, previously described by Naslain,[11] Cojean *et al.*,[12] Jouin *et al.*[14] or Guillaumat.[15] These features suggest that a rather significant weakening of the FM-bonding has occurred during the ageing treatments, which correlates with the degradation of the fiber–pyrocarbon interface already mentioned in Sections 3.2.1 and 3.2.2. Firstly, there is a dramatic decrease of the proportional limit whose value depends on the weight loss experienced by the composite during the ageing treatment (viz. it falls from ≈ 85 MPa to as low as ≈ 40 MPa when $\Delta m/m_0$ increases from 0 to 0.71%, in Fig. 16(a)). Furthermore, the lowest values of the proportional limit are observed for those composites in which a well-developed silica–carbon amorphous layer, known to correspond to a weak FM bonding,[11,15] has been formed at the fiber surface during ageing, namely specimens 14 and 22 (Figs 8, 13, 16(a),(b)). Secondly, the microcracks which are formed in the rather narrow stress range corresponding to the plateau-like domain, are not numerous and run across the whole specimen thickness (in planes roughly perpendicular to the load axis), as shown in Fig. 17(a). Their mean spacing, i.e. 1.27 mm, is large and corresponds roughly to the mean distance between the residual macropores. Furthermore, the residual opening of the microcracks is large, as shown in Fig. 17(a) for an unetched failed specimen, a feature which is largely responsible for the rapid decrease of the secant modulus as the applied load is increased beyond the proportional limit. Thirdly, in the last domain of the tensile curve (viz. beyond a strain of $\approx 0.25\%$), the applied load is mainly carried by the fibers alone up to the failure of the composite which still occurs at a relatively high stress, i.e. 75 to 95% that of the as-received composite (Table 5). This result clearly shows that the fibers have not been too severely damaged during the ageing treatments and correlates with the limited SiC grain growth in the fibers (the size of the SiC crystallites being less than 5 nm for $\Delta m/m_0 < 1\%$, as shown in Fig. 9) as well as with the limited degradation of the fiber surface. All the composites aged under these moderate conditions (with $0.1\% < \Delta m/m_0 < 0.8\%$)
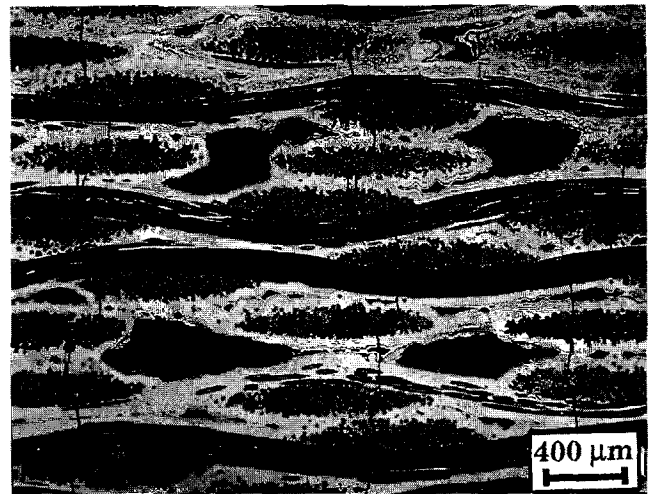
(a)
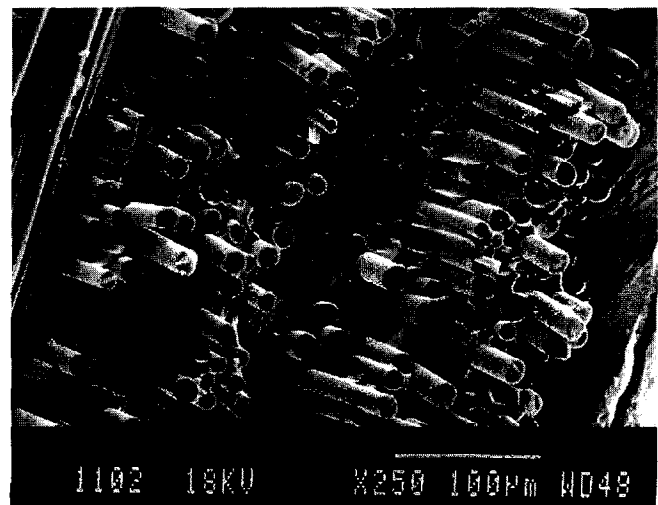
(b)

Fig. 17. Micrographs of a SiC-coated 2D-SiC/C/SiC composite (specimen 21) aged under vacuum (78 h at 1200°C; residual pressure: 6×10^{-2} Pa) and tensile tested at ambient showing: (a) the state of damage related to the matrix microcracks (optical micrograph; unetched specimen) and (b) the fiber pull-out at the failure surface (SEM micrograph).

exhibit a failure strain which is much higher than that of the pristine composite and seems to depend slightly on the nature of the ageing treatment atmosphere. It is of $\approx 0.55\%$ for the specimens aged at 1200°C under CO or Ar and only $\approx 0.43\%$ for those treated under vacuum at the same temperature (whereas $\varepsilon_r \approx 0.17\%$ for the as-supplied composite (Table 5)). Finally and as shown in Fig. 17(b), the failure surface of the composites exhibits a moderate fiber pull-out in contrast with the extensive pull-out usually associated with weak FM-bonding and tensile curves of the plateau-like type.

Two different kinds of tensile curve shape are observed for the composites aged at 1300°C, depending on the degradation experienced by

Table 5. Mechanical characteristics measured at room temperature under tensile loading, of 2D-SiC/C/SiC in the as-received state and after ageing under various conditions

Ref.	Ageing treatment	$\Delta m/m_0$ (%)	σ_r (MPa)	ε_r (%)	E (GPa)
0	none (as-received)	0	146	0·17	230
13	1100°C-139 h-CO(70)[a,b]	−0·43	139	0·57	218
14	1200°C-58 h-CO(45)	−0·71	110	0·56	190
15	1200°C-64 h-CO(70)	−0·83	120	0·56	190
16	1300°C-21 h-CO(45)	−4·7	35	0·21	80
17	1300°C-20 h-CO(80)	−2·1	35	0·25	83
18	1300°C-63 h-CO(100)	−2·9	38	0·33	100
19	1100°C-24 h-vac.[c]	−0·02	130	0·32	235
20	1200°C-12 h-vac.	−0·13	115	0·43	190
21	1200°C-78 h-vac.	−0·15	105	0·44	220
22	1200°C-108 h-vac.	−0·13	57	0·08	201
23	1200°C-75 h-Ar	−0·17	123	0·52	235
24	1300°C-17 h-vac.	−2·6	49	0·18	160
25	1300°C-28 h-vac.	−5·2	40	0·02	146
26	1300°C-24 h-Ar	−1·2	49	0·39	177
27	1300°C-128 h-CO(70)	−0·26	41	0·17	210

[a]Pressure in kPa is given in parentheses.
[b]Uncoated materials, 13–18.
[c]Protected with SiC seal-coating; 19–27.

the fibers and FM interfacial zones, as shown in Fig. 16(a),(b). When the composite (even protected with a SiC seal-coating) has been aged under vacuum and has experienced a high weight loss (e.g. 5·2% for specimen 25), the mechanical behavior of the material is brittle (Fig. 16(b)). This feature is obviously related to the fact that the fibers, under such severe ageing conditions, have been strongly damaged due to both chemical reactions and SiC grain growth (mean SiC crystallite size: 40 nm), as further supported by the decrease in the Young's modulus of the composite (i.e. ≈ 150 MPa instead of ≈ 230 MPa for the pristine material). Conversely, all the composites aged under CO at 1300°C exhibit a non-linear stress-strain curve, whatever the weight loss experienced by the materials. Under such conditions, the damage occurs almost instantaneously with few microcracks localized near the residual macropores. Then the applied load is progressively transferred to the fibers up to the composite failure which occurs at a strain which is still relatively high (with respect to that of the as-supplied composite), namely 0·2–0·3%, but at a very low stress. These features are related to the strong degradation of the FM interfacial zone and the weakening of the fibers, as already mentioned in Sections 3.2.1 and 3.2.2.

3.3.2 As assessed through push-out tests

Push-out tests have been performed on thin slices cut in: (i) the as-received composite, (ii) one sample of SiC-coated composite aged under vacuum at 1200°C and exhibiting a tensile curve with a plateau-like domain (specimen 21) and (iii) one

sample of SiC-coated composite aged under CO at 1300°C (specimen 27).

The results are shown in Fig. 18 and Table 6. There is obviously a progressive evolution of the load-displacement curve as the ageing conditions become more severe. The values of F_d and F_c (defined as the loads corresponding to the beginning and total FM interface debonding, respectively,[16–18] which are clearly different for the pristine material, tend to be identical for the aged composites. Furthermore, they regularly decrease as the ageing conditions are more severe and their values correlate with those of the proportional limit derived from the tensile curves. No attempt was made to derive interface parameters from the push-out data, as already mentioned in part 1, lacking an appropriate model.[1]
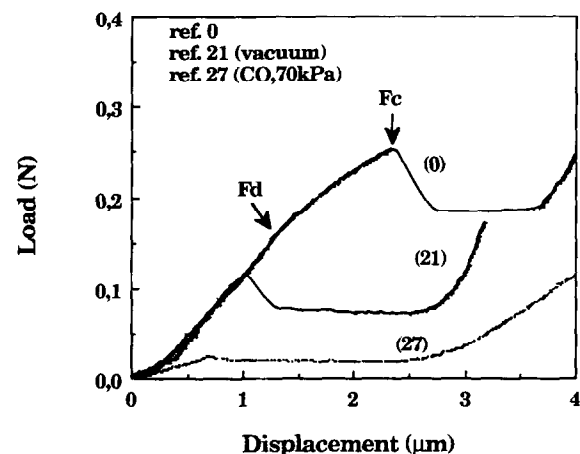

Fig. 18. Typical push-out test curves recorded numerically for SiC-coated 2D-SiC/C/SiC composites, as-received or aged under vacuum (residual pressure: 6 × 10⁻² Pa) or CO atmosphere. The measurements were performed on 250-μm thick slice specimens.

Table 6. Push-out test data for as-received and aged SiC-coated 2D-SiC/C/SiC composites, measured on fibers 15 μm in diameter

Ref.	Ageing treatment	$\Delta m/m_0$ (%)	F_d (MPa)	F_c (MPa)	σ_{elast} (MPa)
0	None (as-received)	0	0.17 ± 0.02	0.29 ± 0.04	85
21	1200°C-78 h-vacuum	-0.15	0.08 ± 0.03	0.10 ± 0.03	45
27	1300°C-128 h-CO(70 kPa)	-0.26	0.04 ± 0.02	0.04 ± 0.02	25

Each F_d and F_c value is the mean of 15–20 measurements. σ_{elast} is the proportional limit derived from tensile tests performed on the same specimens.
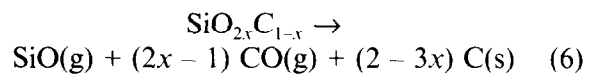
4 Discussion

It has been shown in part 1[1] that the degradation of the mechanical behavior of 2D-SiC/C/SiC composites resulting from ageing treatments performed under argon or vacuum has mainly two origins: (i) the intrinsic decomposition of the metastable Si–C–O Nicalon fibers which occurs beyond about 1100–1200°C with an evolution of gaseous species (CO and SiO) and a grain growth of the SiC nanocrystals and (ii) chemical reactions between these gaseous species (mainly SiO) and the carbon of the interphase resulting in the growth of a layer of large size SiC crystals at the fiber surface (acting as new surface flaws) and consuming the interphase thus destroying the FM-bonding. The data which have been presented in the present work (Section 3) have clearly shown that the detrimental effects of the ageing treatment can be minimized and even suppressed when the 2D-SiC/C/SiC composites are aged under a CO atmosphere and/or when they have been coated with a SiC-CVD coating. In both cases the thermal stability improvement which has been observed, more effective at 1200°C than at 1300°C, is primarily related to the fact previously reported by several authors[2,19] that a high enough pressure of CO can slow down or even suppress the decomposition of the Si–C–O Nicalon fibers. This CO pressure is here either applied externally (ageing in a CO atmosphere) and/or generated internally by the use of a dense SiC-CVD seal-coating (confining the gaseous decomposition products of the fibers within the composites). Several aspects of the experimental study will be further discussed in the following.

4.1 Chemical degradation mechanisms

The chemical degradation mechanisms responsible for the weight loss experienced by the composites and for the chemical/microstructural change experienced by the fibers and FM interfacial zones during ageing, still remain a matter of speculation and have been already discussed in part 1.[1] Only the effect of the pressure of CO will be qualitatively discussed here.
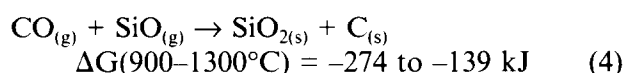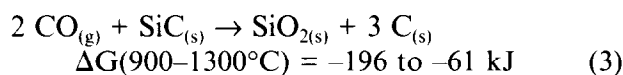
4.1.1 Ageing under mild conditions (T ≤ 1200°C)

As shown in Tables 1 and 2 and Figs 2 and 3, both the uncoated composites aged under CO (with $45 < P_{CO} < 70$ kPa) and the SiC-coated composites aged under vacuum (with $4 \times 10^{-4} < P < 6 \times 10^{-2}$ Pa) or argon (P = 70 kPa), have experienced very low weight loss (viz. 0.4–0.8% for the former and only 0.13–0.17% for the latter). These results clearly show that the evolution of gaseous species (CO and SiO, with CO/SiO > 4) mainly due to the decomposition of the fibers reported in part 1 for the uncoated composites aged under vacuum or argon (and responsible for weight losses as high as 6% for 100 h at 1200°C) almost no longer occurs. In other words, the two chemical reactions presented in part 1 as mainly responsible for the weight loss and corresponding to the following equations (numbered as in part 1):

$$SiO_{2x}C_{1-x} \rightarrow$$
$$SiO(g) + (2x - 1)\ CO(g) + (2 - 3x)\ C(s) \quad (6)$$

$$SiO(g) + 2\ C(s) \rightarrow SiC(s) + CO(g) \quad (1)$$

where $SiO_{2x}C_{1-x}$ is the silicon oxycarbide of the Nicalon fibers,[1,2,20–22] are now shifted to the left hand side. It thus appears that the CO pressure effectively stabilizes the metastable fibers (presumably the $SiO_{2x}C_{1-x}$ ternary phase), as already discussed by several authors on the basis of thermodynamic and/or experimental considerations.[2,19] This mechanism is also consistent with: (i) the very limited growth of the SiC crystallites in the fiber bulk (their size being of the order of 4–5 nm for $\Delta m/m_0 < 1\%$, as shown in Fig. 9, versus 1–2 nm for the pristine fibers) and (ii) the fact that the pyrocarbon interphase is not consumed and SiC crystals are not formed at the fiber surface (eqn (1)), in contrast to what has been reported in part 1.

However even under such mild ageing conditions under CO, some change in the materials has occurred during ageing, namely: (i) the growth of a carbon/silica layer at the fiber surface and (ii) a decrease of the carbon concentration in the fiber bulk. It is not yet fully understood whether these two phenomena are interrelated or not. Firstly, the experimental data shown in Table 3 and Figs 8

and 12–14, establish that oxygen and carbon accumulate at the fiber surface in both uncoated specimens aged under CO and SiC-coated specimens treated under vacuum. The AES analysis suggesting that oxygen is bonded to silicon as in silica (inset in Fig. 8), one could reasonably assume that a silica/carbon layer is formed at the fiber surface, its thickness increasing linearly as a function of time, as shown in Fig. 14 for the SiC-coated specimens. Several equations could be written to take into account the formation of a silica/carbon mixture at the fiber surface, under a pressure of CO, as for example:

$$2 \text{ CO}_{(g)} + \text{SiC}_{(s)} \rightarrow \text{SiO}_{2(s)} + 3 \text{ C}_{(s)}$$
$$\Delta G(900\text{–}1300°C) = -196 \text{ to } -61 \text{ kJ} \qquad (3)$$

$$\text{CO}_{(g)} + \text{SiO}_{(g)} \rightarrow \text{SiO}_{2(s)} + \text{C}_{(s)}$$
$$\Delta G(900\text{–}1300°C) = -274 \text{ to } -139 \text{ kJ} \qquad (4)$$

In such tentative mechanisms, the silica/carbon layer would be the result of a chemical reaction between the CO atmosphere and either the SiC nanocrystals from the fiber surface (eqn (3)) or SiO(g) formed by some decomposition of the silicon oxycarbide at the fiber surface (eqn (4)). Equation (4) might be preferred in as much as the SiC-matrix has not been observed to undergo any chemical evolution (eqn (3)) during the long ageing of SiC-coated composites (specimen 27). Secondly, the EPMA analyses performed on the fibers (Table 4) in aged composites, can only be explained by assuming that some carbon migration has occurred from the bulk of the fiber to the fiber surface (according to a mechanism which is still unknown), providing thus another explanation for the carbon accumulation near the fiber surface, i.e. over at least 500 nm (Table 3, Figs 8 and 13). As shown in Tables 7 and 8, the evolution of the fiber bulk composition (as assessed by EPMA) in composites aged at 1200°C, with respect to the as-received material, can only be explained by assuming that nine atoms of carbon (uncoated specimen aged under CO) and five atoms of carbon (SiC-coated specimen aged under vacuum), per 100 atoms of Si + C + O, have left the fiber core with no decrease in the oxygen concentration.

4.1.2 Ageing under more severe conditions (T = 1300°C)

When the composites are aged at 1300°C (i.e. 200°C beyond the decomposition threshold usually reported for Nicalon fibers), the application of an external moderate pressure of CO, e.g. 40 kPa (ageing on uncoated specimens) or that of a SiC seal-coating (ageing under vacuum) are no longer effective for reducing significantly the degradation of the materials, at least when taken independently. As an example, the weight loss is 4·7% and 5·2%, for specimens 16 and 25, respectively (Tables 1 and 2 and Figs 2 and 3). These results show that such a CO pressure is too low to impede the decomposition of the silicon oxycarbide and such a CVD seal-coating is not gas-tight enough to confine the gaseous decomposition products of the fibers within the composite.

Table 7. Evolution of the chemical composition of the fiber (in the bulk) in uncoated 2D-SiC/C/SiC composites aged under a CO atmosphere

	Species removed	Atomic percentages in fiber bulk		
		Si	C	O
(a) 1200°C-20 h-CO (70 kPa)				
As-received material		35	48	17
Assumed ageing model	9 C(s)	35	39	17
Calculated composition		38·5	42·9	18·7
Experimental composition		38·5	43	18·5
(b) 1300°C-63 h-CO (100 kPa)				
As-received material		35	48	17
Assumed ageing model	8 SiO (g)	27	44	5
	4 CO (g)			
Calculated composition		35·5	57·9	6·6
Experimental composition		35	58	7
(c) 1300°C-21 h-CO (45 kPa)				
As-received material		35	48	17
Assumed ageing model	10 SiO (g)	25	46	5
	2 CO (g)			
Calculated composition		32·9	60·5	6·6
Experimental composition		33	60	7

The nature and mole numbers of species removed from the initial composition have been semi-empirically determined in order to achieve the best fit with the experimental composition in the aged composites (as assessed by EPMA).

These conclusions are further supported by the fact that the weight loss falls to 2·1% when the CO pressure is raised to 80 kPa (uncoated specimen 17) and to 1·2% when the high vacuum is replaced by an atmosphere of argon (90 kPa) for the ageing of SiC-coated composites (specimen 26). Finally, the composite experiences almost no weight loss when both the effect of a high external CO pressure (100 kPa) and that of a SiC seal-coating are combined (viz. $\Delta m/m_0 = 0.26\%$ for a five-day ageing treatment at 1300°C; specimen 27 in Table 2).

The chemical/microstructural change occurring in the SiC-coated specimens aged under high vacuum is basically similar to that reported in part 1 for the uncoated materials, suggesting that the chemical mechanisms involved are the same, with however minor differences. Firstly, CO and SiO resulting from the decomposition of the fibers are formed in a molar ratio, i.e. ≈ 2 (Table 8(b)), which is significantly lower than for the uncoated composites aged under similar conditions (where CO/SiO > 4) (part 1).[1] Secondly, the same phenomena, namely a gasification of the pyrocarbon interphase coupled to the growth of large SiC crystals at the fiber surface (Fig. 15(a)) on the one hand, and the formation of a silica/carbon layer near the fiber surface (Fig. 15(b)) on the other hand, still occur. However, the thickness of that layer is about twice that observed for the uncoated composites aged under similar conditions (viz. 70–80 nm versus 30–40 nm). This difference might be explained by a more noticeable shift of eqn (4)

to the right hand side, for the SiC-coated specimens, caused by the confinement of CO and SiO within the material.

When uncoated 2D-SiC/C/SiC composites are aged at 1300°C under an atmosphere of CO (with $45 < P_{CO} < 100$ kPa), there is still some chemical degradation of the materials in terms of weight loss (Fig. 2). However, the fibers undergo a different chemical evolution and the pyrocarbon interphase is not consumed. The data shown in Tables 7(b) and (c) suggest that the decomposition of the fibers (eqn (6)) yields a SiO–CO gas mixture which is now SiO-rich (with SiO/CO molar ratios equal to 4–5), owing to the effect of the external CO pressure. This feature might be related to the fact that the silicon oxycarbide is not a stoichiometric compound. Depending upon the nature of the atmosphere (i.e. an external atmosphere of CO or SiO), the composition of the $SiO_{2x}C_{1-x}$ tetrahedra might change in a different manner, the decomposition gas mixture being accordingly SiO- or CO-rich. Furthermore, there is a significant increase in the carbon concentration of the fibers (58–60 at% in the aged composites versus 48 at% in the as-received material) and additionally, the pyrocarbon interphase is not consumed. These results suggest that the secondary reaction according to eqn (1) is significantly shifted to the left hand side, due to the external pressure of CO. As a result, the SiC grain growth in the fibers remains limited, with respect to that for the composites aged under vacuum (Fig. 9). As an example, for $\Delta m/m_0 = 4\%$, the SiC crystallite size is ≈ 8 nm for

Table 8. Evolution of the chemical composition of the fiber (in the bulk) in SiC-coated 2D-SiC/C/SiC composites aged under vacuum (residual pressure: 10^{-1} to 10^{-3} Pa) or CO atmosphere

	Species removed	Atomic percentages in fiber bulk		
		Si	C	O
(a) 1200°C-78 h-vacuum				
As-received material		35	48	17
Assumed ageing model	5 C(s)	35	43	17
Calculated composition		36·8	45·3	17·9
Experimental composition		37	45	18
(b) 1300°C-17 h-vacuum				
As-received material		35	48	17
Assumed ageing model	7 CO(g)	31	41	6
	4 SiO (g)			
Calculated composition		39·7	52·6	7·7
Experimental composition		39	53	8
(c) 1300°C-21 h-CO (45 kPa)				
As-received material		35	48	17
Assumed ageing model	6 C(s)	35	39	14
	3 CO (g)			
Calculated composition		39·8	44·3	15·9
Experimental composition		40	44	16

The nature and mole numbers of species removed from the initial composition have been semi-empirically determined in order to achieve the best fit with the experimental composition in the aged composites (as assessed by EPMA).

the specimens aged under CO and ≈ 20 nm for those aged under vacuum. Thus, the degradation mechanisms of the composites are somewhat different depending on the nature of the atmosphere, which might explain the fact that the apparent activation energies are slightly different (E_a ≈ 195 kJ mol^{-1} under vacuum and E_a ≈ 230 kJ mol^{-1} under CO).

Finally and as already mentioned, the SiC-coated composites aged at 1300°C under an atmosphere of CO, experience a very low weight loss (only 0·26% after 128 h). The EPMA data shown in Table 8(c) suggest that there is both an evolution of CO and a carbon migration from the fiber bulk. Conversely, there is no evolution of SiO. These results might be explained by assuming that SiO, formed according to eqn (6), is either consumed in the fiber bulk, according to eqn (1) (since there is a decrease in carbon concentration, viz. from 48 to 44 at%) and/or at the fiber surface, according to eqn (4) (in as much as the thickness of the silica/carbon layer increases from 5–10 nm to 60 nm, for specimen 27).

4.2 Degradation kinetics and SiC crystallite growth

Although limited in number (the ageing treatments were performed directly on tensile test specimens, as already mentioned), the data presented in Section 3.1 suggest that the weight loss kinetics are diffusion-rate-controlled (Figs 4 and 5). Furthermore, the weight loss experienced by the composites during the ageing treatments (mainly due to fiber decomposition) and the growth of the SiC crystallites within the fibers, seem to be interrelated phenomena, as already pointed out by many authors in studies of the intrinsic decomposition of Nicalon fibers.

Thus, the features of the degradation kinetics of the composites can be used to obtain indirectly some insight into the kinetics of growth of the SiC crystallites within the fibers. Shimoo *et al.* have used the Avrami–Erofeev equation to model the decomposition of Si–C–O and Si–C–Ti–O fibers.[23] In their model, the degree of decomposition of the fibers after ageing at a given temperature during a time t, is defined as $X = \Delta W_{(t)}/\Delta W_{(f)}$, where $\Delta W_{(t)}$ and $\Delta W_{(f)}$ are the weight loss at time t and the weight loss corresponding to complete decomposition, respectively. They have observed that the variation of X as a function of time, obeyed the Avrami–Erofeev equation,[24] namely:

$$-Ln(1 - X) = k.t^m \qquad (7)$$

or $\quad$ Ln [−Ln(1 − X)] =Ln k + m.Ln t $\qquad$ (7')

where k is a kinetic parameter and m an exponent whose value depends on the growth mechanism
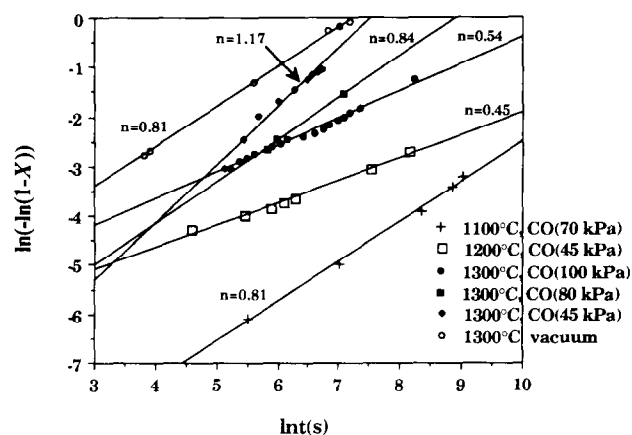

Fig. 19. Treatment of the weight loss data recorded for uncoated 2D-SiC/C/SiC composites aged under CO or vacuum (residual pressure: 10^2 Pa), according to the Avrami–Erofeev model (equation (7')).

and growth morphology (with 0·5 < m < 4). Their data when treated according to eqn (7'), yield for m, a value of 1·5 for T > 1300°C and a value of 1 for T < 1200°C, for the decomposition of the Si–C–O Nicalon fibers (ceramic grade). From these results, Shimoo *et al.* concluded that the growth of the SiC crystallites is diffusion-controlled and occurs according to a three-dimensional growth mechanism (1·5 < m < 2·5), although the reported m values could also be compatible with a two- (1·0 < m < 2·0) and even a one- (0·5 < m < 1·5) dimensional growth.[23]

A similar approach has been tentatively used here, defining the degree of a degradation of the composite, X, as the ratio between the weight loss measured at a given time t, $\Delta W_{(t)}$, and that, $\Delta W_{(f)}$, corresponding to completion of the degradation process, with $\Delta W_{(f)}$ = 11%.[23] The weight loss data corresponding to the ageing treatments performed on uncoated specimens aged under CO (Fig. 2) have been treated according to eqn (7'). As shown in Fig. 19, the variations of Ln [−Ln (1 − X)] as a function of Ln t are linear in a first approximation with a value of m ranging from ≈ 0·5 to ≈ 1·2. These low m values are compatible with the diffusion-rate-controlled character of the composite degradation already mentioned. However, it is not known yet whether they necessarily mean a low dimension growth morphology (the SiC crystallites growing in a fibrous medium, i.e. a one-dimensional medium, but the weight loss being only partly due to the fiber decomposition in the composites).

4.3 Mechanical behavior

As shown in Fig. 16(a),(b) the degradation of the mechanical behavior is already apparent for the composites aged at 1100°C. However, it remains relatively limited as long as the weight loss is low

enough (e.g. 0·02% for SiC-coated specimen 19 aged at 1100°C under vacuum). The slight decrease in both the proportional limit and the slope of the non-linear domain, suggests that some weakening of the FM bonding has already occurred.

The degradation of the mechanical behavior is much more significant when the weight loss experienced by the composites is further increased within the narrow 0·1–1% range. Under such conditions, all the tensile stress-strain curves exhibit the same features, i.e. a low proportional limit, a plateau-like shape beyond the proportional limit, an almost linear domain before failure and a high failure strain (uncoated specimens 13, 14, 15 aged under CO and SiC-coated specimens 20, 21, 23 aged under vacuum or argon). All these features can be explained by an important weakening of the FM bonding whereas the fiber strength is not yet too severely lowered. The weakening of the FM bonding, which is clearly apparent from the push-out test results (specimen 21; Fig. 18), is related to the growth of a carbon/silica layer at the fiber/pyrocarbon interface (Figs 8, 13) observed to be often porous (Fig. 12) and already reported to be responsible for low FM bonding in such composites.[11,12,15] Under the ageing conditions considered here (i.e. for $0·1 < \Delta m/m_0 < 1\%$), the decomposition of the Si–C–O fibers remains limited, as supported by both the low values of the weight loss and the absence of significant SiC grain growth (crystallite size: 4–5 nm vs 1·5–2 in the pristine fibers), owing to the combined effects of the SiC-matrix, the SiC seal-coating and/or the external CO atmosphere. As a result, they still have a high load-bearing capability. Thus, when the matrix microcracking is achieved (end of the tensile curve plateau), the fibers, which are now largely debonded from the matrix, carry the applied load alone (quasi-linear domain before failure) and the failure of the composite occurs at a high strain and a still relatively high stress.

The mechanical behavior of the composites aged at 1300°C, is still more severely degraded whatever the nature of the composite and the ageing conditions. In the worst case (specimen 25; $\Delta m/m_0 = 5·2\%$), the mechanical behavior is that of a brittle material (Fig. 16(b)), owing to the severe decomposition of the fibers and the gasification of the carbon interphase. Conversely, the composites (coated or uncoated) still exhibit a non-linear mechanical behavior after ageing at 1300°C under CO (specimens 16, 18, 27), in as much as the carbon interphase is not consumed. However, the FM load transfer is low as supported by the push-out test data (Fig. 18). Finally, the composites fail at low stresses in as much as the fiber strength is

severely degraded (due to the formation of large SiC crystals at the fiber surface and SiC grain growth in the bulk).

5 Conclusions

From the results which have been presented and discussed in Sections 3 and 4, the following conclusions can be drawn:

(i) The degradation of 2D-SiC/C/SiC composites occurring during ageing at high temperatures is slowed down when the materials have been protected with a SiC CVD seal-coating and/or when the ageing treatment is performed under an atmosphere of CO. Both ways are effective up to about 1300°C. They rely on the stabilization of the $SiO_{2x}C_{1-x}$ phase present in Nicalon fibers by a CO pressure (applied externally or generated within the composite as a result of the confinement of the fiber decomposition products in the material due to the coating).

(ii) As long as the weight loss experienced by the composite remains low enough (i.e. for $\approx 0·1 < \Delta m/m_0 < 1\%$ and $1100 < T < 1200°C$), the main change in the material occurs at the fiber surface in the form of the growth of a carbon/silica layer. This phenomenon dramatically weakens the fiber–matrix bonding. As a result, the tensile stress-strain curves exhibit low proportional limits and a plateau-like shape. Under such ageing conditions, the fibers are not too severely degraded and the composites fail at a high strain (0·5 to 0·6%) and at a stress which is still relatively high ($\approx 70\%$ of that observed for the as-received material).

(iii) When the composites have been aged under still more severe conditions (i.e. with $\Delta m/m_0 > 1\%$ and $T = 1300°C$), the change in the material is more drastic. The SiC-coated composites aged under vacuum are brittle, the SiC coating being no longer gas-tight with the result that the CO internal pressure is not high enough to impede the fiber decomposition and the pyrocarbon interphase gasification. Conversely, all the composites aged under CO still exhibit a non-brittle behavior (the carbon interphase being no longer consumed, but very weakly bonded to the fiber). However, under such ageing conditions, failure occurs at a low stress in as much as the fibers are severely weakened by SiC grain growth.

Composites (GS-4C), supported by CNES, CNRS, DRET, MRES, Aerospatiale, SEP and SNECMA. The authors are indebted to B. Humez (LCTS) and F. Barrière (SEP) for their contribution to the mechanical tests, M. Lahaye and M. Chambon (CUMEMSE-UB1) for their assistance in the AES and TEM analyses, Y. Khin (CEMES-LOE, CNRS-Toulouse) and F. Doux (SEP) for their contribution to the PEELS analyses. They acknowledge the assistance that they received from SEP through the supply of the samples and valuable discussions with P. Olry, S. Loison and J. M. Jouin.

References

1. Labrugère, C., Guette, A. & Naslain, R., Effect of ageing treatments at high temperatures on the microstructure and mechanical behavior of 2D-Nicalon/C/SiC composites. 1: Ageing under vacuum or argon. *J. Europ. Ceram. Soc.*, accepted (1995).

2. Bodet, R. & Lamon, J., Microstructural stability and creep behavior of Si–C–O (Nicalon) fibers in carbon monoxide and argon environments. *J. Amer. Ceram. Soc.*, in press.

3. Bodet, R., Comportement en fluage et évolution microstructurale de fibres issues de précurseurs organosiliciés. Thèse no 986, Univ. Bordeaux I, 1993.

4. Clark, T. J. & Jaffe, M., Thermal stability characterization of SiC ceramic fibers: I, Mechanical property and chemical structure effects. *Ceram. Eng. and Sci. Proc.*, 1986, 7[7–8], 901–913.

5. Sawyer, L. C. & Chen, R. T., Thermal stability characterization of SiC ceramic fibers: II, Fractography and structure. *Ceram. Eng. Sci. Proc.*, 1986, 7[7–8], 914–930.

6. Jaskowiak, M. H. & DiCarlo, J. A., Pressure effects on the thermal stability of silicon carbide fiber. *J. Amer. Ceram. Soc.*, 1989, 72[2], 192–197.

7. Clark, T. J. & Arons, R. M., Thermal degradation of Nicalon SiC fiber. *Ceram. Eng. and Sci. Proc.*, 1985, 6[7–8], 576–588.

8. Ishikawa, T. & Ichikawa, H., Strength and structure of SiC fiber after exposure to high temperature. *Pro. Electrochem. Soc.*, 1988, 85[5], 205–217.

9. Johnson, S. M., Degradation mechanisms of silicon carbide fibers. *J. Amer. Ceram. Soc.*, 1988, 71[3], C132–C135.

10. Naslain, R. & Langlais, F., CVD-processing of ceramic–ceramic composite materials. In *Tailoring Multiphase and Composite Ceramics*, ed. R. E. Tressler, G. L. Messing, C. G. Pantano and R. E. Newnham.

Plenum Press, New York, *Mater. Sci. Res.*, 1986, 20, 145–164.

11. Naslain, R., Fiber–matrix interphases and interfaces in ceramic matrix composites processed by CVI. *J. Composite Interfaces*, 1993, 1[3], 253–286.

12. Cojean, D., Monthioux, M. & Oberlin, A., Phénomènes interfaciaux dans des composites SiC/SiC 2D de propriétés mécaniques variées. Lyon 6–8 Nov. 1990. *Actes JNC7* ed. G. Fantozzi & P. Fleischmann. AMAC Publ., Paris, 1990, pp. 381–390.

13. Aubard, X., Modélisation et identification du comportement mécanique des matériaux composites 2D-SiC-SiC. Thèse de doctorat de l'Université de Paris VI, 24 November 1992.

14. Jouin, J. M., Cotteret, J. & Christin, F., SiC/SiC interphase: case history. Proc. 2nd European colloquium. In *Designing Ceramic Interfaces*, CEE-JRC, Petten (NL), 11–13 Nov. 1991.

15. Guillaumat, L. & Lamon, J., Multifissuration de composites SiC/SiC. In *Revue des composites et des matériaux avancés*, ed. J. L. Chermant and G. Fantozzi. Ed. Hermès, vol. 3 (hors série), 1993, pp. 159–171.

16. Rausch, G., Meier, B. & Grathwohl, G., A push-out technique for the evaluation of interfacial properties of fiber-reinforced materials. *J. Europ. Ceram. Soc.*, 1992, 10, 229–235.

17. Bright, J.D., Danchaivijit, S. & Shetty, D. K., Interfacial sliding friction in silicon carbide glass composites: a comparison of pullout and pushout tests. *J. Am. Ceram. Soc.*, 1991, 74[1], 115–122.

18. Kerans, R. J., Theoretical analysis of the fiber pullout and pushout tests. *J. Am. Ceram. Soc.*, 1991, 74[7], 1585–1596.

19. Bibbo, G. S., Benson, P. M. & Pantano, C. G., Effect of carbon monoxide partial pressure on the high temperature decomposition of Nicalon fibre. *J. Mater. Sci.*, 1991, 26[18], 5075–5080.

20. Schreck, Ph., Guterl-vix, C., Ehrburger, P. & Lahaye, J., Reactivity and molecular structure of silicon carbide fibres derived from polycarbosilanes. Part 1: Thermal behaviour and reactivity. *J. Mater. Sci.*, 1992, 27, 4237–4242.

21. Schreck, Ph., Guterl-vix, C., Ehrburger, P. & Lahaye, J., Reactivity and molecular structure of silicon carbide fibres derived from polycarbosilanes. Part 2: XPS analysis. *J. Mater. Sci.*, 1992, 27, 4243–4246.

22. Porte, L. & Sartre, A., Evidence for a silicon oxycarbide phase in the Nicalon silicon carbide fibre. *J. Mater. Sci.*, 1989, 24, 271–227.

23. Shimoo, T., Chen, H. & Okamura, K., Pyrolysis of Si–C–O fibers (Nicalon) at temperature from 1473 K to 1673 K. *J. Ceram. Soc. Japan*, 1992, 100[1], 48–53.

24. Rollett, A. D., Srolovitz, D. J., Doherty, R. D. & Anderson, M. P., Computer simulation of recrystallization in non-uniformly deformed metals. *Acta Metall.*, 1989, 37[2], 627–639.