Multiscale investigation of the creep behaviour of a 2.5D C$_f$-SiC composition

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This paper deals with some results on the creep behaviour of a 2.5D C$_f$-SiC composite. This material fabricated by CVI was tested in tension under an argon partial pressure for temperatures ranging from 1273 to 1673 K and stresses between 110 and 220 MPa. Results regarding creep curves (strain-time) and strain rate-time curves tend to confirm the existence of a secondary stage. Damage-stress and damage-time curves are also presented. The limits of the Dorn's formalism are evidenced as well as the occurrence of a damage process leading to a so-called damage-creep mechanism. In order to explain this macroscopic creep behaviour of the composite, investigations at the mesoscopic, microscopic and nanoscopic scales were necessary. Five modes of matrix microcracking are observed together with different pull-out features regarding the extracted fibre surface. The damage accumulation via matrix microcracking appears to be a time dependent mechanism. Two modes of interfacial sliding are evidenced: at 1473 K and 220 MPa, the pyrocarbon (PyC) interphase is fractured leading to debonding between carbon layers, while at 1673 K, there is a loss of anisotropy of the PyC layer close to the matrix and, thus, an interfacial sliding appearing as a viscous flow. To elucidate the role of the carbon fibres, a nanoscale study via HREM has been conducted. An increase of the mean diameters of the basic structural units (BSUs) and of the areas of local molecular orientation (LMOs) within the fibres has been observed when increasing temperature under 220 MPa. In fact, these changes do not contribute to the macroscopic strain. Therefore, this restructuration effect has been called "nanocreep" of the carbon fibre as it appears to have a negligible contribution to the macroscopic creep behaviour of the 2.5D C$_f$-SiC composite.
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1. Introduction

A new generation of 2.5D C$_f$-SiC composites has been developed for potential long term applications under severe conditions of stress and temperature. In order to predict their lifetime under such conditions, creep, fatigue and rupture tests are necessary to perform [1, 2]. In this study, we will only focus on the creep behaviour of these materials.

The classical creep mechanisms are governed by motions of vacancies or dislocations or by diffusion [3]. In such a classical approach, Dorn's general formalism applied to the macroscopic creep responses (i.e. strain as a function of time) gives access to an activation energy, Q, and a stress exponent, n, which refer to a defined mechanism for an homogeneous and isotropic material. For numerous ceramic materials and ceramic matrix composites (CMCs), it appears that the mechanisms responsible for strain under various types of stresses (bending, tension, compression) involve damage accumulation. For creep testing of CMCs, a so-called damage-creep mechanism has been proposed aside from the classical creep mechanisms [4, 5]. Thus, understanding the whole creep mechanism for a par-

ticular CMC under stress is a complex issue involving numerous elemental mechanisms at different scales which requires various mechanical tests coupled with microstructural investigations.

In this paper, the macroscopic creep responses of the 2.5D C$_f$-SiC composite are presented first, with a classical analysis through Dorn's formalism. Afterwards, a seek for other mechanical parameters is developed in order to highlight the damage part involved in the creep behaviour of such anisotropic materials. An insight into the tested materials is proposed, from the mesoscopic scale down to the nanometric one, to identify the origin of the damage accumulation and some potential classical creep mechanisms within the constituents. Thus, the whole creep mechanism for this 2.5D C$_f$-SiC composite, in our field of investigation, is expected to be understood.

2. Material and experimental devices
2.1. Material
The composite under investigation is based on high strength ex-PAN carbon fibres for which Guigon's

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microstructural model has been adopted as a reference [6]. This model distinguishes the longitudinal sections from the transverse ones. In the longitudinal sections, two types of elemental domains can be found oriented parallel to the fibre axis: short ones, called basic structural units (BSUs), which associate into larger ones, called areas of local molecular orientation (LMOs). In transverse sections, only BSUs are observed, randomly oriented. Thus, the nanostructure of the carbon fibres is made of transversally disoriented carbon sheets longitudinally oriented parallel to the fibre axis.

The so-called "2.5D" architecture corresponds to a stack of five plain woven carbon clothes with a certain interlocking between them. The densification of the preform is achieved according to the chemical vapour infiltration process (CVI), [7]. A pyrocarbon interphase is deposited on the fibres prior to the β-SiC matrix infiltration. In addition, one can notice the presence of transverse pre-existing microcracks in the as-received material, which results from processing related residual stresses due to the thermal expansion coefficient mismatch between the fibres and the matrix [2, 8].

2.2. Experimental devices
2.2.1. Mechanical testing
For creep tests on such composites, a new specific high temperature tensile device has been developed and optimised with a special care concerning especially the load frame alignment, the thermal gradient and its sta-

bility, the temperature and strain measurements and the pressure variations [1, 9, 10].

Creep tests have been performed in tension under argon partial pressure (50 mbar), for temperatures ranging from 1273 to 1673 K and for stresses between 110 and 220 MPa.

2.2.2. Microstructural investigation
The microstructural study was first conducted at the mesoscopic scale in order to evidence the array of matrix microcracks and its evolution, using a scanning electron microscope (JSM 6400, Jeol, Japan). Both the edge and the surface of the samples were observed.

The pyrocarbon interphase at the fibre/matrix interface as well as the carbon fibres were characterised by transmission and high resolution electron microscopies (TEM & HREM). Thin foils of 3 mm in diameter were prepared from transverse and longitudinal samples cut in the 2.5D C_f-SiC specimens. After polishing and dimpling, the final thinning is achieved by ion-milling. Two microscopes operating at 200 kV were used: a Jeol 2010 (Jeol, Japan) and a Topcon EM 002B (Topcon, Japan).

3. Results
3.1. Macroscopic scale
Some strain-time creep curves obtained are presented in Fig. 1. Regarding their general aspect it can be said, on the one hand, that the higher the stress and the
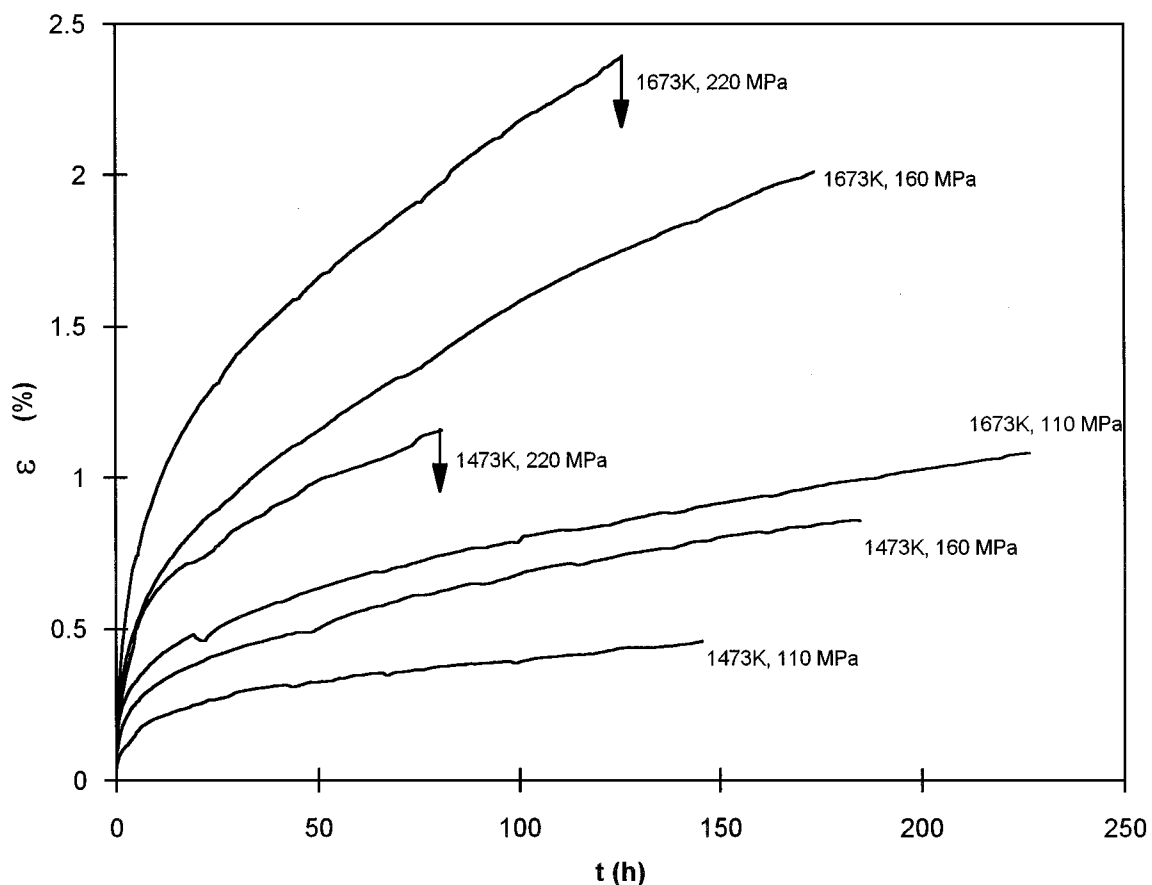

Figure 1 Strain-time, ε-t, curves for a 2.5D C_f-SiC composite creep tested in tension under partial pressure of Ar, at 1473 and 1673 K, under different stresses.
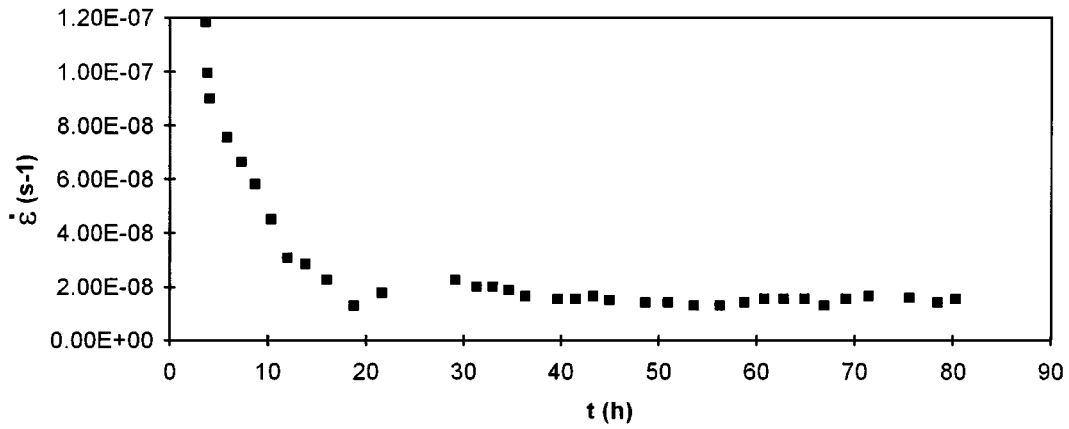
1473K, 220 MPa

Figure 2 Creep rate-time, $\dot{\varepsilon}$-t, curves for a 2.5D C_f-SiC composite creep tested in tension under partial pressure of Ar, at 1473 K, under 220 MPa.

temperature, the higher the strain. On the other hand, the creep curves present a short transient stage followed by a long steady state, as confirmed by strain rate-strain or time curves (Fig. 2). In that experimental field of investigation, the mean strain rates in the stationary stage are in the 10^{-8}–10^{-9} s^{-1} range, but even for tests conducted until rupture, no tertiary stage has been observed. If the classical Dorn's formalism is now used to describe the steady state as:

$$\dot{\varepsilon}_{ss} = A\sigma^n \exp\left(\frac{-Q}{RT}\right)$$

(with: $\dot{\varepsilon}_{ss}$, the creep rate in the steady state; A, a constant without dimension, related to the structure of the deformed material; σ, the applied stress; n, the stress exponent; Q, the activation energy of the activated mechanism; R, the gas constant; T, the temperature), it appears that with a stress exponent $n = 1.8$–2 and an activation energy $Q = 60$–80 kJ $\cdot$ mol^{-1}, this equation fits the stationary stage.

However, these values of n and Q are not suitable with the creep of either the fibre nor the matrix. For ex-PAN high modulus carbon fibres, the stress exponent is close to 7–8.5 and the activation energy close to 1000–1200 kJ $\cdot$ mol^{-1} [11, 12], whereas for the chemi-

cal vapour deposited (CVD) silicon carbide creep tested in compression, $n = 2.3$–3.7 and $Q = 175$ kJ $\cdot$ mol^{-1} [13].

Thus, it appears that the creep behaviour of the composite in our experimental field of investigation is not controlled by the classical creep of the fibre or the matrix. Therefore, the Dorn's formalism is not well-suited to analyse the macroscopic mechanical responses of the composite.

So unloading-reloading cycles were then performed during creep tests in order to reach some parameters from the damage mechanics, as proposed by Kachanov [14], such as the different elastic moduli, the elastic and inelastic strain, the damage parameter, the strain at the end of the reloading. The damage parameter, D, is defined as:

$$D = 1 - E_i/E_0$$

where E_i is the elastic modulus of the damaged material at a time i, and E_0 the elastic modulus of the undamaged composite. At first, damage upon step-loading tests in tension was evaluated at 1473 and 1673 K (Fig. 3). The study of the evolution of the different parameters mentioned above tends to show that the composite is more damageable at 1473 K and more viscoplastic at
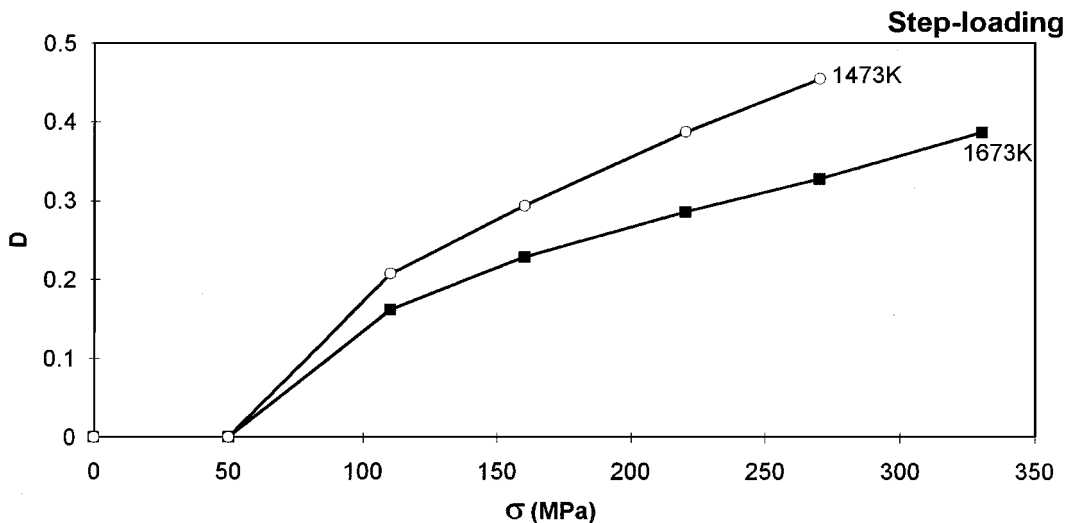

Figure 3 Damage, D, curves obtained during step-loading tensile tests on a 2.5D C_f-SiC composite as a function of the applied stress, σ.
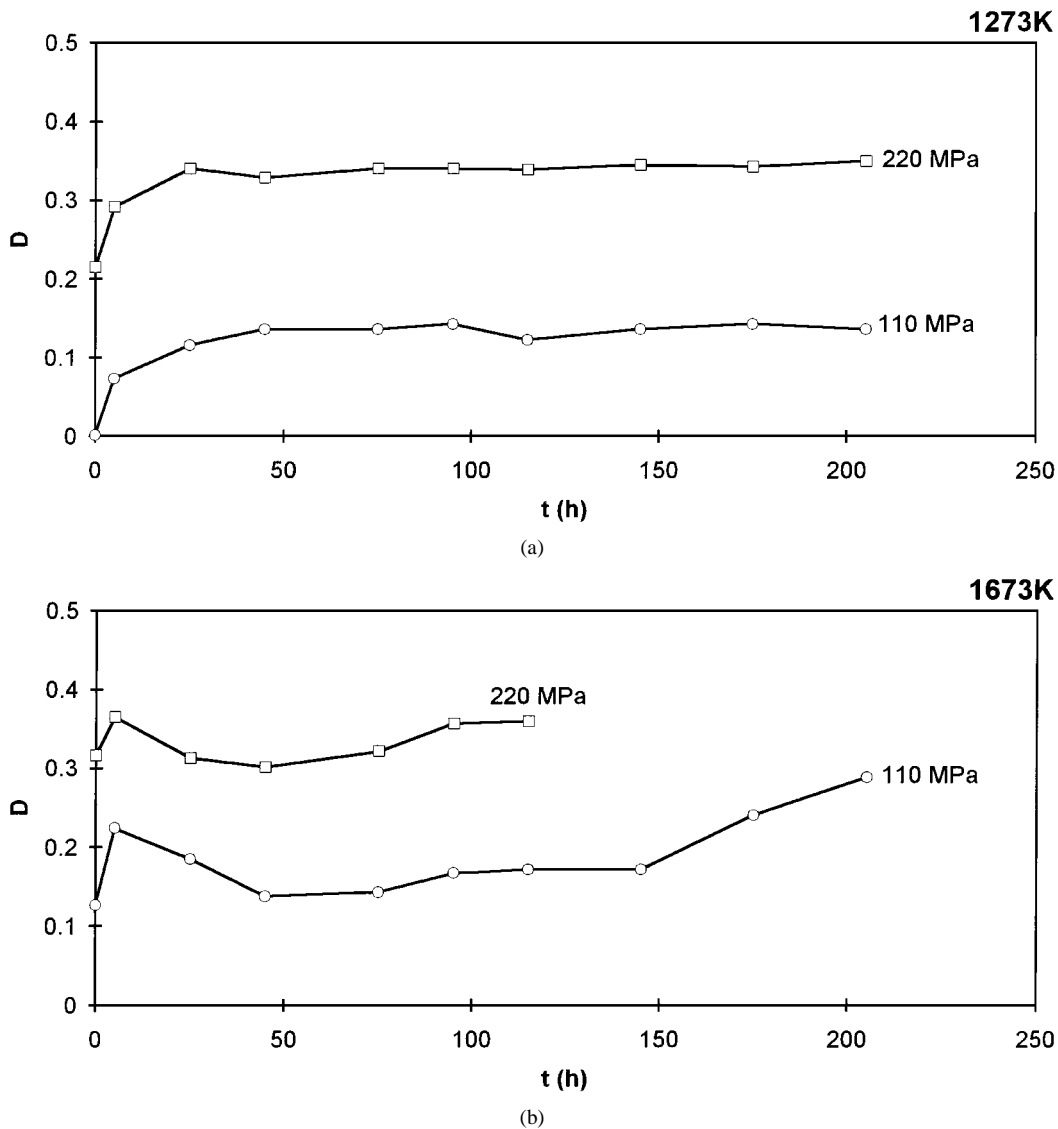
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Figure 4 Damage evolution as a function of time for a 2.5D C$_f$-SiC composite creep tested in tension under partial pressure of Ar, at 1273 K (a) and 1673 K (b).

1673 K. During creep tests, we have then measured the damage evolution rather as a function of time than as a function of stress [1]. In fact, the curves obtained, $D = f(t)$, testify of a damage evolution, even though it appears quite complex (Fig. 4).

At 1273 K, damage is mainly accumulated in the transient creep stage, then no more evolution of the damage parameter is observed. At 1673 K, there is a first damage accumulation upon loading and during the first hours of the creep experiment, followed by an apparent reduction of the damage parameter. At low stress, this parameter tends to stabilise over a long period of time, whereas at high stress the stabilisation appears shorter, followed by a second damage accumulation.

At that macroscopic scale, it seems difficult to identify the origin of such damage accumulation and evolution. Therefore microstructural investigations have to be conducted at different scales to highlight creep and damage processes.

3.2. Mesoscopic and microscopic scales
Using a scanning electron microscope (SEM), five modes of matrix microcracks have been identified: lon-

gitudinal and transverse microcracks in the longitudinal (i.e. parallel to the loading direction) and transverse (i.e. perpendicular to the loading axis) bundles, and interply microcracks. Some are presented in Fig. 5.

At 110 MPa, whatever the temperature is, only transverse microcracks are observed. At higher stresses, interply cracks initiate and propagate, then longitudinal microcracks appear. It has also been noticed that the higher the stress and the temperature, the higher the opening of the cracks.

Original step-creeping tests were performed at 1673 K and 220 MPa, to elucidate the sequence of the different microcracking mechanisms. At first, opening of the transverse pre-existing cracks occurs, then the interply cracks initiate at the macropores and connect to each other, and finally the longitudinal cracks in the transverse bundles appear. The opening of transverse and interply microcracks leads to the failure of the composite.

A focus on the fracture surfaces of the samples tested under 220 MPa, at 1473 and 1673 K reveals some differences from one specimen to another. At 1473 K, the fibre pull-out length is quite short (Fig. 6a) and the pyrocarbon at the surface of the extracted fibres appears
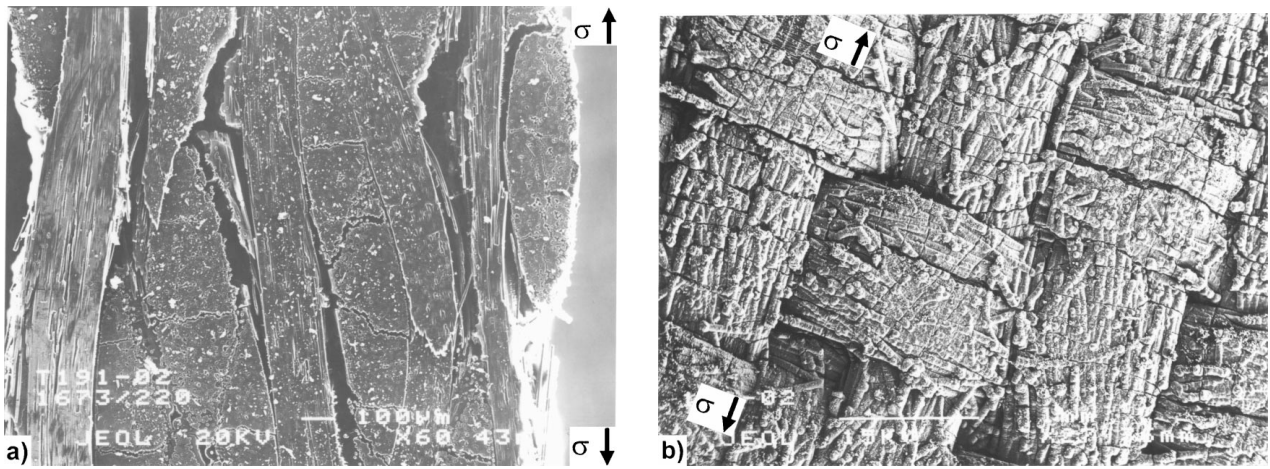
Figure 5 SEM micrographs of the edge (a) and the surface (b) of a 2.5D C_f-SiC composite creep tested in tension under partial pressure of Ar, at 1673 K, under 220 MPa.
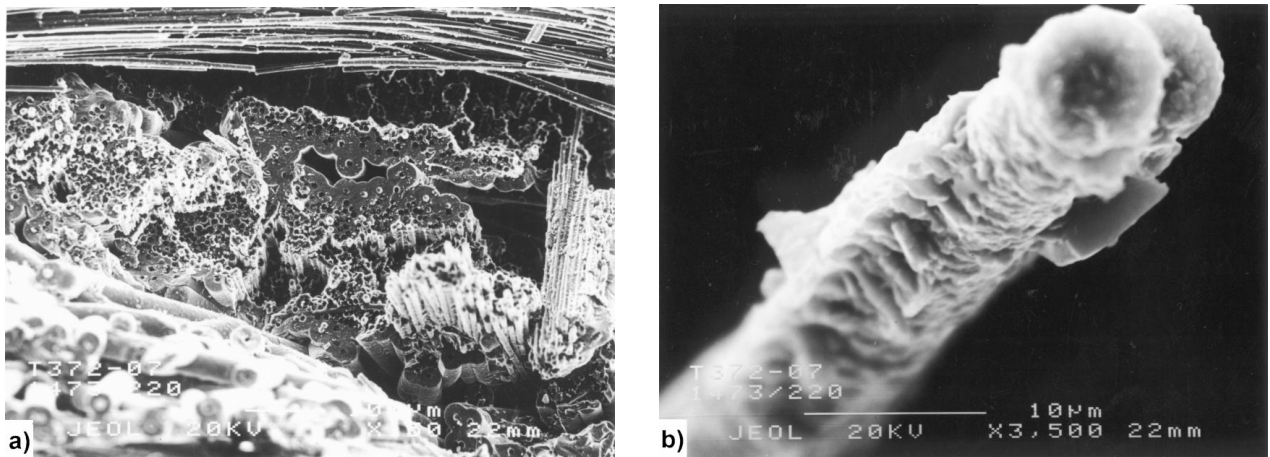

Figure 6 SEM microfractographies of a 2.5D C_f-SiC composite creep tested at 1473 K, under 220 MPa: (a) global view (b) surface of an extracted fibre.
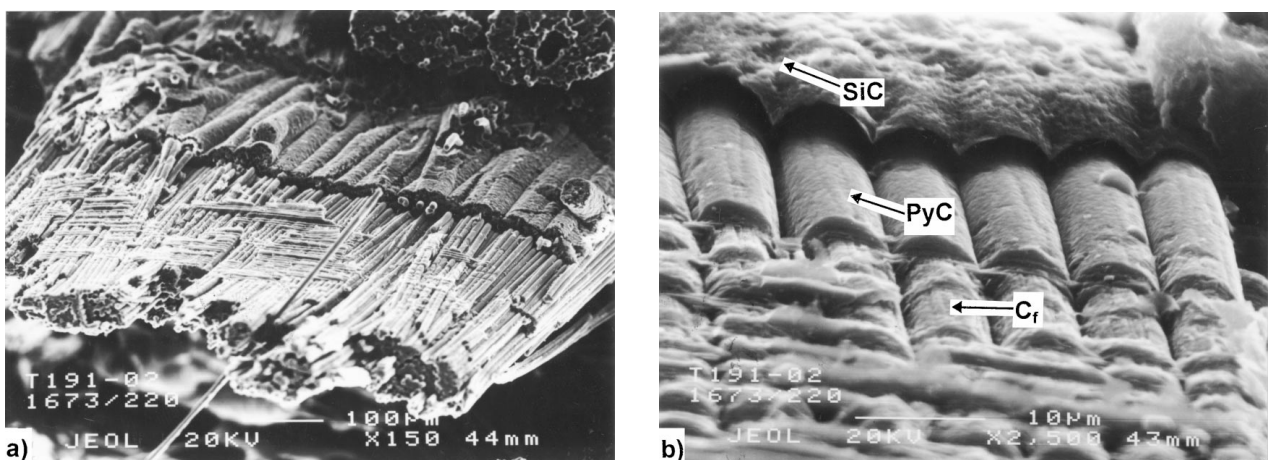

Figure 7 SEM microfractographies of a 2.5D C_f-SiC composite creep tested at 1673 K, under 220 MPa: (a) global view (b) surface of some extracted fibres.

degraded and rough (Fig. 6b). On the contrary, the fibre pull-out length is longer at 1673 K (Fig. 7a) and the pyrocarbon surface is smooth (Fig. 7b).

At higher magnification via transmission and high resolution electron microscopies (TEM and HREM), the pyrocarbon interphase in the composite tested at 1473 K and 220 MPa appears broken within its thickness, with rough cracks lips. On the matrix side, one

can notice the highly anisotropic texture of the pyrocarbon layer with lenticular pores from place to place. So the rupture of the interphase occurs by decohesion between carbonaceous layers (Fig. 8).

At 1673 K, the pyrocarbon interphase is not broken but degraded over a mean distance of a hundred nanometers. The remarkable point here is the disappearance of the formerly anisotropic layer close to the
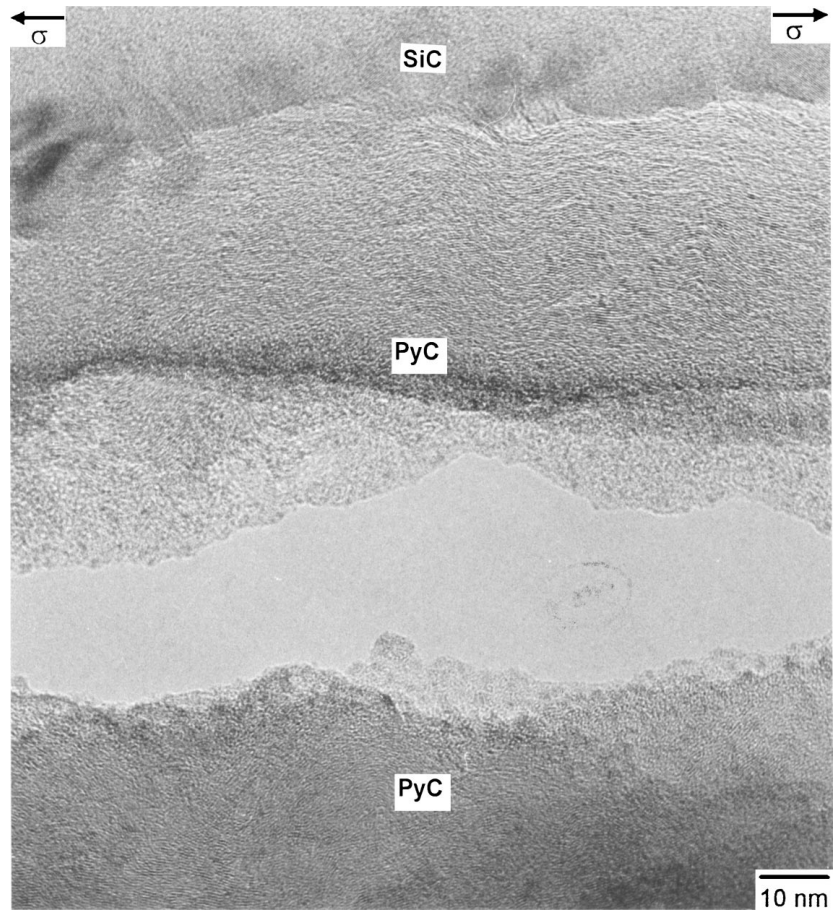
Figure 8 HREM micrograph of the pyrocarbon interphase in a 2.5D C_f-SiC composite creep tested at 1473 K, under 220 MPa.
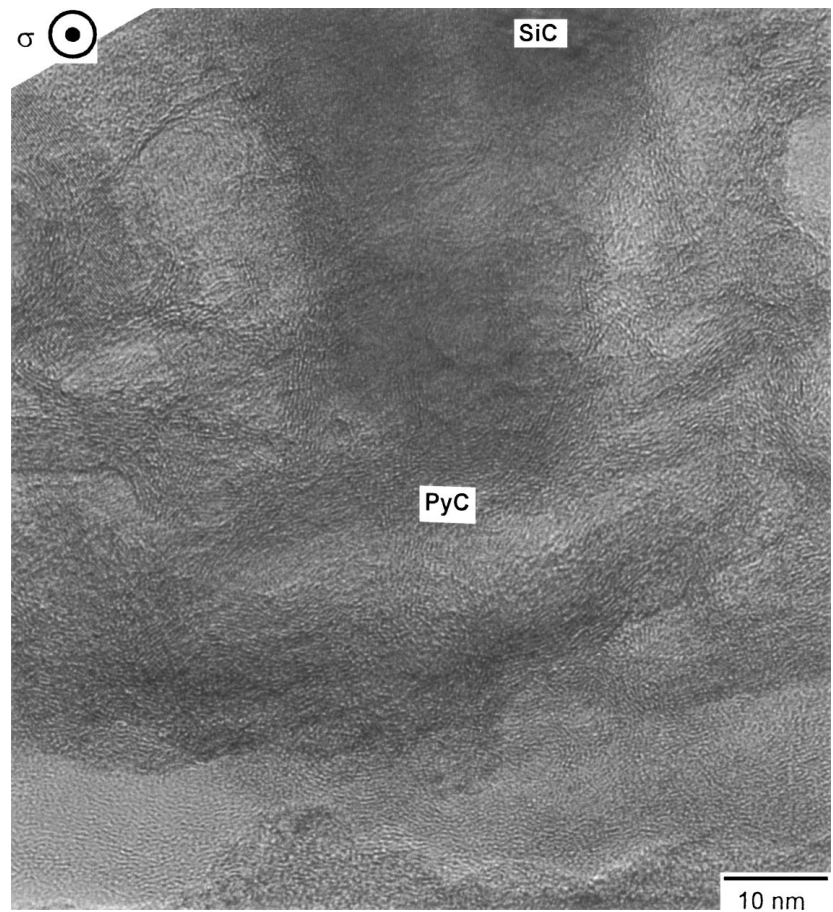

Figure 9 HREM micrograph of the pyrocarbon interphase in a 2.5D C_f-SiC composite creep tested at 1673 K, under 220 MPa.
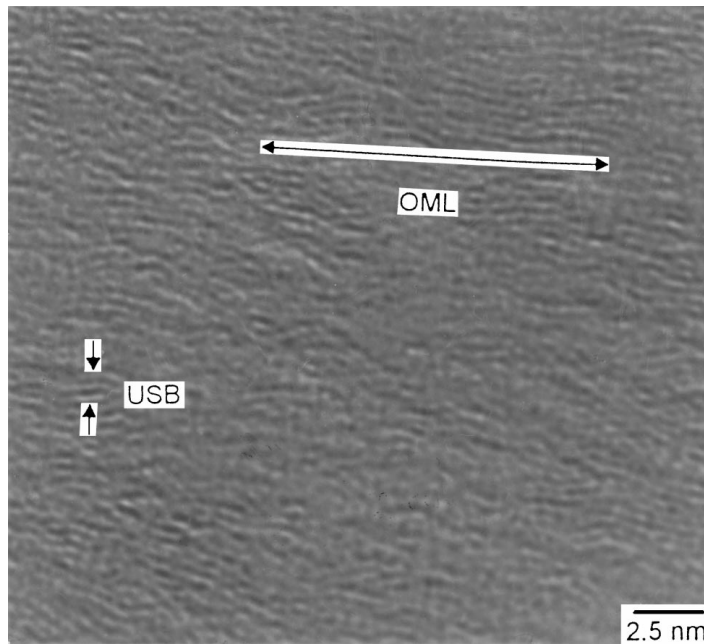
Figure 10 HREM micrograph of the longitudinal section of the carbon fibre in an as-received 2.5D C$_f$-SiC composite.

matrix observed in the as-received material (Fig. 9), and still present at 1473 K.

At these two scales, the damage part of a damage-creep mechanism is illustrated. Nevertheless, an investigation down to the nanometric scale has to be conducted in both the fibre and the matrix to highlight a potential classical creep mechanism.

3.3. Nanoscopic scale

Using HREM, no significant structural changes have been observed in the β-SiC matrix. It can be considered then that there is no creep of the matrix.

The nanostructural study of the fibre in the as-received composite was presented previously [15]. The mean diameter of BSUs and LMOs are 0.8–1 and

12.5 nm respectively. The nanostructure of the fibre in the as-received state is fully consistent with Guigon's model in both longitudinal and transverse sections. Fig. 10 presents a high resolution micrograph of the carbon fibres in the as-received composite.

After creep test at 1473 K, under 220 MPa, for 82 hours, the structure of the fibre has only evolved slightly. The size of the BSUs remains unchanged while the LMOs diameter increases up to 14 nm.

In materials tested at 1673 K, under 220 MPa, for 120 hours, the structural evolution is more significant. The BSUs evolve slightly up to a diameter of 1–1.5 nm, whereas the LMOs reach a diameter of 18 nm (Fig. 11). This evolution is confirmed in transverse sections where the radius of curvature of the carbon sheets appears larger than in the as-received material.
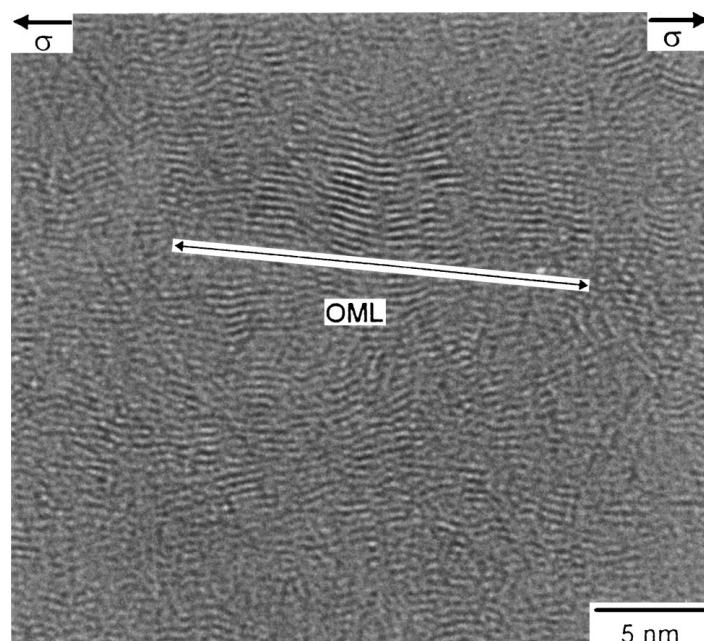

Figure 11 HREM micrograph of the longitudinal section of the carbon fibre in a 2.5D C$_f$-SiC composite creep tested at 1673 K under 220 MPa.

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TABLE I Comparison of creep results for different CMCs

Material	Architecture	Atmosphere	Effort	Temperature (K)	Stress (MPa)	Creep rate (s^{-1})	Reference
SiC$_f$-SiC	2D	Vacuum	3-pts bending	1373–1673	50–300	10^{-9}–10^{-8}	[16]
SiC$_f$-Si$_3$N$_4$	1D	Air	Tension	1590	60–200	10^{-10}–10^{-8}	[17]
Al$_2$O$_{3f}$-SiC	2D	Air	Tension	1223–1373	150–300	10^{-10}–10^{-8}	[18]
C$_f$-SiC	2.5D	Argon	Tension	1273–1673	110–220	10^{-9}–10^{-8}	This study

4. Discussion

The study of the macroscopic creep of the 2.5D C$_f$-SiC composite has revealed a good creep resistance, compared to other ceramic matrix composites (Table I) [16–18], with strain rates in the 10^{-8}–10^{-9} s^{-1} range.

The analysis of the strain-time curves has evidenced the limits of the Dorn's formalism when applied to composite structures. The equation fits the experimental curves but gives no information about the mechanism responsible for creep. This could have been expected, as C$_f$-SiC composites do not agree with the hypotheses of homogeneity and isotropy of the Dorn's formalism.

The damage mechanics brings new elements in the understanding of the creep behaviour of such composites which seems to be governed by a so-called damage-creep mechanism [4, 5]. This mechanism must be considered as a specific mechanism for CMCs (and also for monolithic ceramics), if the test temperature and the applied stress are not high enough. The effective damage can be evidenced using scanning and transmission electron microscopies.

Considering the different types of cracks, observed via SEM, the straightening of the longitudinal bundles parallel to the loading direction is admitted to be one of the driving forces for damage [19]. In fact, such a straightening induces interply cracks and then flexural efforts in the transverse bundles, which lead to the formation of longitudinal cracks.

The evolution of the microcrack array, evidenced by step-creeping tests, tends to show that damage accumulation via matrix microcracking is a time-dependent mechanism.

Concerning the pyrocarbon interphase evolution in creep tested composites, the SEM characterisation of the fracture surfaces is consistent with the TEM and HREM observations.

As a result, it can be said that, at 1473 K, the rupture of the fibre/matrix interphase arises by debonding between the carbon layers. Then the interfacial sliding corresponds to a dry friction between two rough solids.

At 1673 K, the loss of anisotropy of the pyrocarbon layer close to the matrix makes us consider the interfacial sliding as a viscous flow. These two types of interfacial sliding appear to be time-dependent too. So the macroscopic strain upon creep tests of the 2.5D C$_f$-SiC composite is due to the combination of these five modes of matrix microcracking with two modes of fibre/matrix interfacial sliding, according to a time-dependent mechanism comparable to a slow crack growth (SCG), [20, 21].

For high modulus carbon fibres creep tested in tension above 2373 K and 700 MPa, a stress exponent of 7.5–8 and an activation energy of 1000–1200 kJ · mol^{-1} have been determined [11, 12] which is far from the values obtained for the 2.5D C$_f$-SiC composite. The creep mechanism for high modulus carbon fibres operates by sliding of crystallites, controlled by bulk diffusion of individual carbon atoms, and leads to much larger carbon sheets within the fibres.

In the case of the 2.5D C$_f$-SiC composite, considering the values of the stress exponent (1.8–2) and the activation energy (60–80 kJ · mol^{-1}), the macroscopic creep of the fibre is not likely to occur and its contribution to the macroscopic creep strain can be considered as negligible.

However, a restructuration effect characterised by an increase of the LMOs diameter has been evidenced. Guigon has demonstrated that a structural evolution of a high strength PAN-based carbon fibre remains possible at temperature between 1373 and 1973 K, as far as the fibre still contains nitrogen [22]. The LMOs diameter can then increase due to lateral welding of BSUs according to Watt's denitrogenation mechanism [23, 24].

Thus, the restructuration effect of the carbon fibres in creep tested 2.5D C$_f$-SiC composites is attributed to a lateral junction of LMOs with the adjacent BSUs, by denitrogenation according to the Watt's mechanism, activated in the combined fields of stress and temperature. This is what we have defined as "nanocreep" of the carbon fibre, which can be considered as the first stage of the whole creep mechanism for carbon fibres [25].

5. Conclusion

The macroscopic mechanical responses upon creep tests have shown the good creep resistance of the 2.5D C$_f$-SiC composite, but require to investigate the mechanisms occurring at different scales down to the nanometric one.

The time dependence of the creep strain is encountered at the mesoscopic and microscopic scales in five modes of matrix microcracking and two modes of interfacial sliding which combine into a mechanism comparable to slow crack growth (SCG). Thus, the damage part of the damage-creep mechanism for this 2.5D C$_f$-SiC composite, in our field of investigation, has been clearly identify.

The creep part of such a damage-creep mechanism has been evidenced by a nanoscopic study. It appears that the contribution of classical creep mechanisms to the macroscopic strain is negligible. In fact, no structural changes have been evidenced in the matrix whereas a slight evolution has been characterised at the nanometric scale within the fibres. Therefore we

proposed to call this restructuration effect "nanocreep" of the carbon fibre, as it corresponds, at the nanometric scale, to the first stage of the macroscopic creep of carbon fibres.

The damage-creep mechanism is then fully illustrated in the particular case of C_f-SiC composites.

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