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TEM observations of SiC-SiC materials with a carbon interphase after tests at high temperature

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Résumé. — Une étude microstructurale a été réalisée en MET sur des matériaux SiC-SiC recuits à l'air jusqu'à 1300° C et après essais de fluage sous vide entre 1000-1400° C. Les évolutions microstructurales de ces composites sont discutées en fonction de leur comportement mécanique.

Abstract. — A microstructural investigation has been performed by TEM on SiC-SiC materials annealed in air up to 1300° C and after creep experiments under vacuum in the temperature range 1000-1400° C. Microstructural modifications of these composites are discussed with respect to the macroscopic mechanical behaviour of SiC-SiC materials.

1. Introduction.

A considerable interest has been developed recently in ceramic materials especially on fibre-reinforced-ceramic-matrix-composites (CMC). SiC-SiC composites belong to this class of materials. On the basis of their thermomechanical properties they are good candidates for potential use in energy production systems (gas/turbines), aerospace applications (thermal protection parts of the HERMES shuttle)...

High temperature properties of these fibrous ceramic composites depend on their microstructure and particularly on the fibre-matrix interface. An effort has been made to investigate the different parts of these materials. Thus a detailed characterization of interface structures has been performed by using techniques such as TEM, HREM and EELS [1-5]. The degradation of the material after high temperature treatments in agressive atmosphere has been also studied, for example the fibre modification after heat treatments in air or in neutral atmosphere [6-7].

This paper reports a microstructural investigation of SiC-SiC materials after high temperature annealing in air and after creep experiments under vacuum. These results are analyzed with respect to the macroscopic behaviour of the composite and compared with previous work.

2. Materials and experimental procedure.

In the SiC-SiC composites([1]) investigated in this work, the reinforcement is a two directional isotropic tissue made of ceramic SiC fibres([2]). These so-called SiC fibres contain SiC (65 wt%), free carbon and a significant amount of oxygen combined to silicon, deeply present in the fibre. These fibres are amorphous or nanocrystalline. The oxygen in the fibre is introduced at the beginning of the process during the reticulation of the polycarbosilane in air near 200° C. The preforms made of a 2D cloth of SiC fibres are chemically infiltrated from a gaseous flow. The matrix is deposited by using the chemical vapor infiltration method (CVI) and consists mainly of columnar β-SiC crystals with a large size (0.3 μm). These crystals are highly faulted.

In order to obtain optimal mechanical properties, a carbon film is deposited on the fibres before the SiC - infiltration process. The thickness of this carbon layer in our materials is equal to 0.1 μm. Such materials are presented on the two optical micrographs (Fig. 1a and 1b).

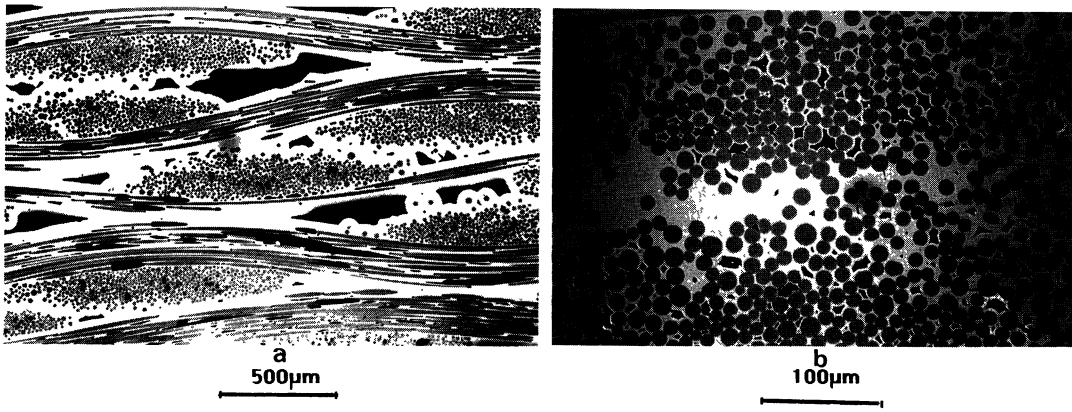

Fig. 1. — a) and b) Optical micrographs of SiC-SiC materials.

Mechanical tests (three point bending tests) were performed at high temperatures in air with samples in flatwise orientation [1, 3] for which the notch plane is normal to the plane of the laminates. These samples were not protected and tested up to 1300° C. The detailed experimental procedure is given elsewhere [8].

Creep experiments have been performed in three point bending under vacuum (10^{-4} Pa) in a temperature range 1000 - 1400° C, with long time exposures (20 – 200 h).

Thin slices of these specimens (400 μm) were cut with a diamond saw and polished down to 80 - 100 μm. Discs (2.3 and 3mm in diameter) were ion-milled (Ar^+, 6kV([3])) for TEM observations([4]).

Electron microscopic observations were performed on samples after creep experiments and after annealing in air up to 1300° C with a short time exposure (20 mn). Samples annealed in air at 1200° C with long time exposures (40-200h) have also been studied.

([1]) Société Européenne de Propulsion, Bordeaux, France.
([2]) Nicalon fibres (ceramic grade) from Nippon Carbon, Japan.
([3]) Ion. Tech. Thinner, Teddington (U.K).
([4]) Jeol 100 CX and 200 CX microscopes.

3. Mechanical behaviour of SiC-SiC materials in air as a function of the test temperature.

Flexural tensile stress σ_r calculated at fracture and elastic modulus values have been measured with respect to the test temperature. They have revealed the change in the mechanical behaviour as a function of the temperature [9]. The results are plotted in figures 2a and 2b.

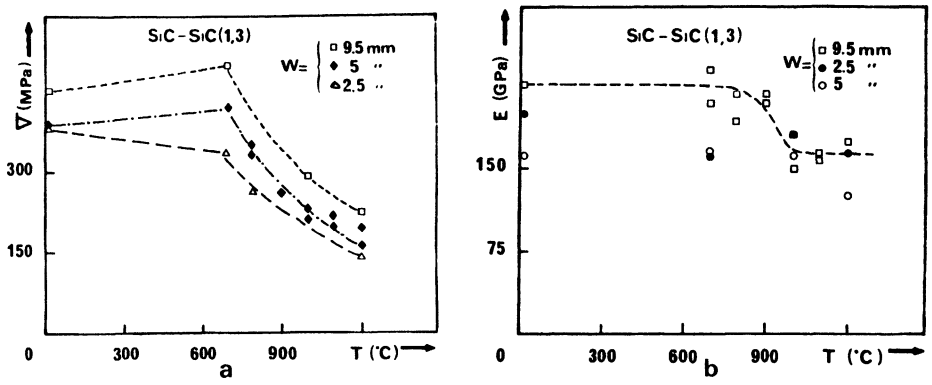

Fig. 2. — a) Flexural strength of SiC-SiC materials as a function of test temperature in air for three specimen thickness W. b) Elastic modulus E of SiC-SiC [1,3] materials as a function of test temperature in air for three specimen thickness W.

Figure 2a shows the change in the flexural tensile stress with test temperature for three groups of specimens of different thickness W (W = 2.5, 5 and 9.5 mm). A continuous decrease of σ_r appears for $T > 700°C$. The elastic modulus E measured from the linear part of the load-deflection curve is also a slightly decreasing function of the test temperature (Fig. 2b). It is noteworthy that the initial value of 210 GPa at room temperature for the composite is almost identical to the fibre modulus.

Figures 3a and 3b show the load *versus* deflection curve for the 700°C (Fig. 3a) and 1000°C (Fig. 3b) tests. For the low temperature test ($T < 700°C$), there is a change in the slope of the composite loading curves at approximately one-half of the maximum load. It is due to the onset of fibre/matrix interface microcracking. This behaviour disappears for the high temperature test (Fig. 3b) a feature which might be assigned to a structural modification of the fibre-matrix interface as it will be shown in a following section.

The sequence of material failures has also been studied by optical and scanning electron microscope observations (SEM).

For low temperature tests ($T < 700°C$), SEM observations show a large extent of fibre pull-out ($\sim 100\ \mu m$) from the bundles normal to the crack plane (Fig. 4a, specimen tested at 700°C). Surfaces of rupture in such a specimen are covered by debris of SiC matrix.

At higher temperatures, a straight propagation of the crack indicates that the fibre/matrix interface is stronger as observed in optical microscope. The linearity of the loading curve confirms also modifications of the fibre-matrix interface which is no favorable to a fibre sliding mechanism. Thus no crack mouth bridging is observed in optical microscope. Moreover SEM images show a brittle rupture surface (Fig. 4b).

Main conclusions of the macroscopic studies are the following:

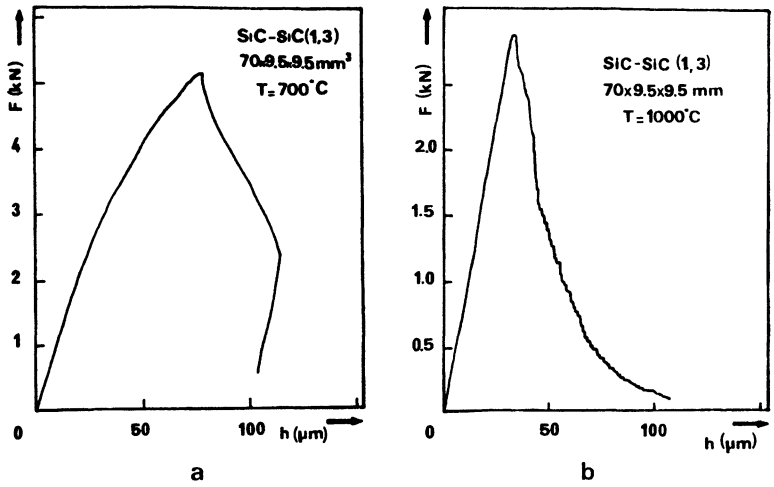

Fig. 3. — a) Experimental flexural curves of un-notched SiC-SiC specimen of dimensions $70 \times 9,5 \times 5$ mm,^{3} tested at 700° C. b) Same specimen tested at 1000° C.

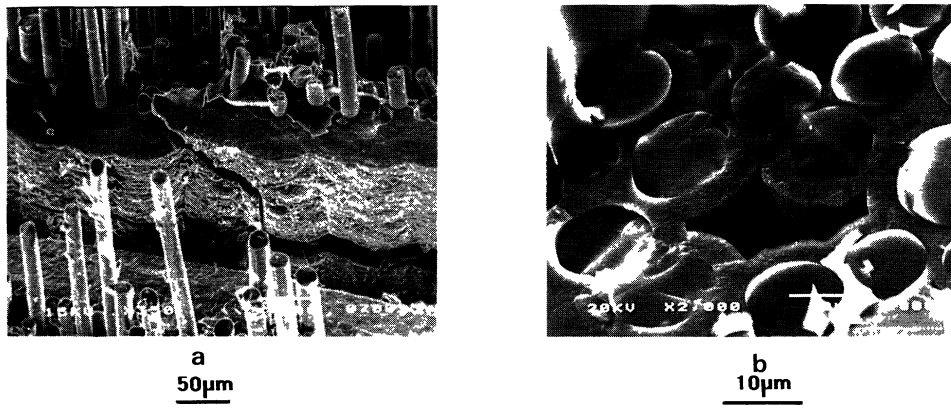

Fig. 4. — a) Scanning electron micrograph of the fractured surfaces of SiC-SiC composites tested at 700° C. b) Scanning electron micrograph of the fractured surfaces. Specimen tested at 1000° C.

– at relatively low temperatures ($T < 700$°C), the specimen deforms first elastically. This is followed by a non-linear part of the loading curve due to the matrix cracking and the fibre sliding in the matrix.

– at higher temperature in air, an interface modification occurs which prevents the fibres from sliding.

TEM observations have been performed to investigate the fibre-matrix interface in samples annealed in air at different temperatures.

4. Microstructure evolution of SiC-SiC materials annealed in air at high temperature. TEM observations.

4.1 SAMPLES ANNEALED IN AIR WITH SHORT TIME EXPOSURES. — For a short time exposure, i.e. 20 mn in a temperature range 700-1300°C, a microstructural change in the material has been observed for the highest temperatures.

Figures 5a and 5b show, as an example, a view of the fibre-carbon interphase-matrix in a sample annealed at 700°C. Fibres are amorphous or nanocrystalline and the matrix consists of columnar crystals. An enlarged part of the carbon interphase area is presented in figure 5b. The aspect of the turbostratic carbon can be seen as well as a good contact between the carbon interphase and fibres. After an annealing at 900°C there is no clear modification of this interface. However, a slight change in mechanical properties is observed at this temperature (Fig. 2a).

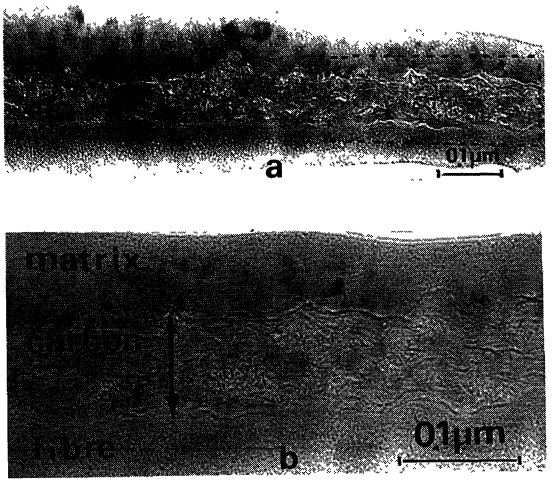

Fig. 5. — a) TEM micrograph of the interface between CVI SiC matrix-carbon interphase- SiC fibre in sample annealed at 700°C in air. b) Enlarged part of a).

Figure 6 is a micrograph of a sample annealed at 1300°C. It clearly shows decohesions inside the turbostratic carbon layer located at the boundary between the fibre and the carbon interphase. But, in this case, there is no modification of the microstructural aspect of the turbostratic carbon.

Figures 7a and 7b confirm the precedent observation in a different area consisting of the contact zone between two fibres separated only by the carbon layer. Decohesion lengths are about 0.25 μm. In contrast to figure 6 where the lamellar structure of the pyrocarbon appears, figures 7a and 7b illustrate the modification of the interphase microstructure where discontinuities like clusters or cavities ($\simeq$ 25 to 50 nm) can be seen (Fig. 7b).

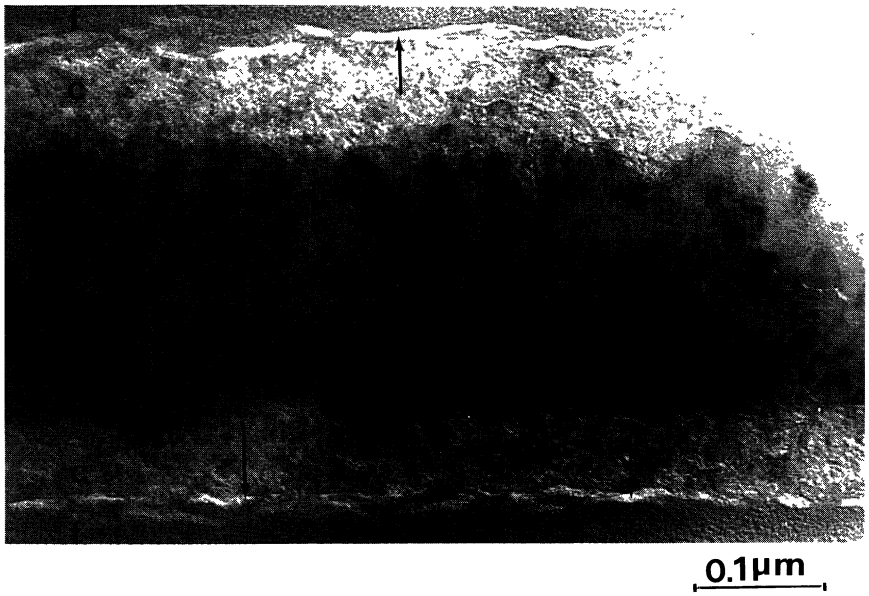

Fig. 6. — Specimen annealed at 1300° C in air. TEM observation of debonding cracks at the fibre-carbon interphase.

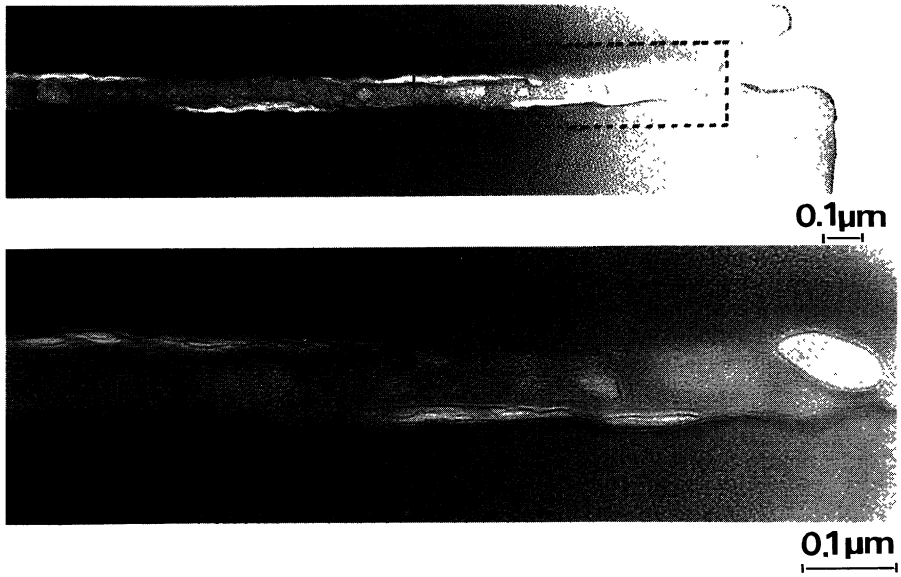

Fig. 7. — a) Specimen annealed at 1300° C in air. Modification of the carbon interphase area located between two fibres. b) Enlarged part of a).

4.2 SAMPLES ANNEALED IN AIR WITH LONG TIME EXPOSURES. — The microstructural change in the carbon interphase has also been observed after a long time exposure in air (40h) at 1200° C. A high number of interface observations has been realized on different samples. The disappearance

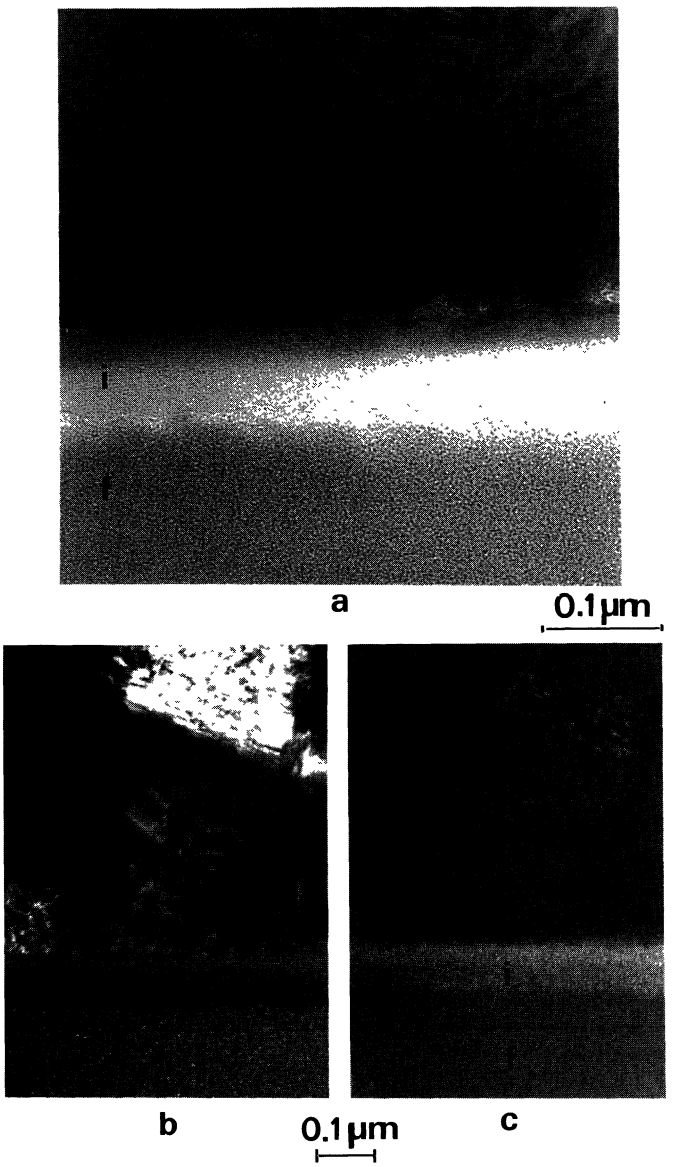

Fig. 8. — a) Specimen annealed at 1200°C in air for 40h. The turbostratic carbon has disappeared and has been partly replaced by an amorphous silica layer. This layer is heterogeneous. Bright field micrograph, showing the interphase (i) between a fibre (f) and the SiC matrix (m). b) $SiC_{111} - C_{10}$ dark field image of another interface in the same sample shown in a). c) Corresponding $SiO_2 - C_{002}$ dark field image.

of the turbostratic carbon structure has been confirmed in many cases. The turbostratic carbon is partly replaced by an amorphous silica layer. This modified interphase is heterogeneous. Figure 8 is an example where, in contrast to the precedent case (Fig. 6), the fibre-matrix interphase is highly modified by the oxidation process. On this micrograph, the heterogeneous aspect is revealed by the formation of two different layers, one of them is situated close to the matrix zone. It appears

darker on the bright field image (Fig. 8a). Two dark field images of another interphase of the same sample are presented in figures 8b and 8c. Figure 8b has been imaged by selecting a part of the $SiC_{111} - C_{10}$ rings. The amorphous silica layer is not in contrast on this micrograph. The figure 8c is a $SiO_2 - C_{002}$ dark field image and the whole interphase is in contrast. These two dark field micrographs confirm the heterogeneity of the interphase after oxidation in air. They indicate that the SiO_2 layer is formed preferentially at the contact zone between fibres and the carbon interphase. However other analyses have to be performed to identify more accurately the heterogeneous nature of the interphase after annealing in air.

5. Creep experiments of SiC-SiC materials under vacuum.

Creep experiments of SiC-SiC composites have been performed at high temperatures (1000-1400°C) in a stress range 50-250 MPa and for long time exposures (20-200 h). The experimental procedure used to derive the creep parameters and detailed results have already been published [10,11].

Main results are summarized in figure 9 on a creep rate-stress plot ($\dot{\epsilon} - \sigma$) in logarithmic scale for all the temperature range investigated. It appears that the general behaviour of these materials cannot be described by one single mechanism. For example at 1200 and 1300°C two deformation mechanisms will occur with a different activation energy value. Moreover a decrease of the maximum stress value is observed whereas the creep rate has approximately the same value $\left(10^{-8} - 10^{-9}s^{-1}\right)$. TEM observations have been performed on these samples after creep experiments in order to assess the microstructural evolution of SiC-SiC materials: fibre-matrix interface and fibre modifications.

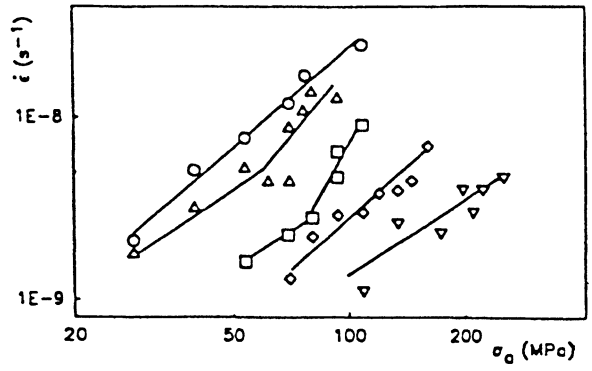

Fig. 9. — Creep rate-stress ($\dot{\epsilon} - \sigma$) plot in logarithmic scale at different temperatures: (▽) 1100°C, (◇)1150°C, (□) 1200°C, (△) 1300°C, (○) 1400°C.

In contrast with the observation of materials annealed in air, we have not detected any decohesion at the fibre-matrix interface or a clear microstructural modification of the carbon interphase.

The main microstructural modification of the material has been observed in the fibre. It consists of a recrystallization for $T > 1200$°C. Different diffraction patterns from areas located inside the fibres as well as the corresponding dark field images are shown in figures 10a to 10f.

Figures 10a and 10b present diffraction patterns of a fibre after creep at 1000°C (Fig. 10a) and 1200°C (Fig. 10b). The dark field micrograph (Fig. 10c) has been imaged by selecting a part of

SiC_{111} ring of the diffraction pattern (Fig. 10b). Figure 10d is a high resolution image of the fibre. β-SiC crystals, highly faulted, can be seen in a fibre partly amorphous after a creep experiment at 1200° C. After creep at 1400° C, the crystal size of the fibre is about 50 nm (Fig. 10e). Figure 10f is the corresponding diffraction pattern of the fibre crept at 1400° C. The stress effect on this recrystallization process will have to be further investigated.

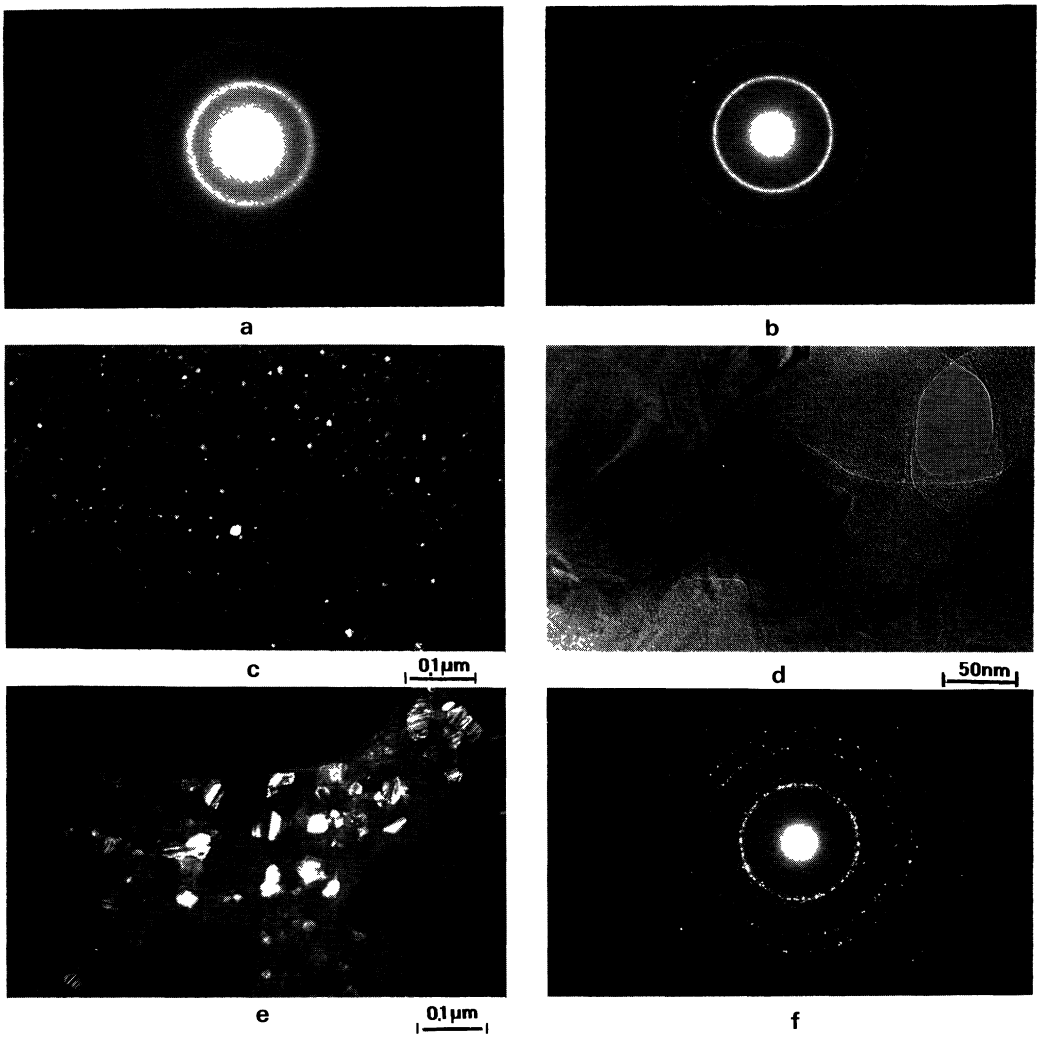

Fig. 10. — a) Diffraction pattern of a fibre after creep at 1000° C. b) Diffraction pattern of a fibre after creep at 1200° C. c) Corresponding dark field image of b) obtained by selecting a part of SiC_{111} ring. d) High resolution image of c). e) Dark field image obtained by selecting a part of SiC_{111} ring in a fibre crept at 1400° C. f) Corresponding diffraction pattern of e).

6. Discussion and conclusion.

The mechanical behaviour of SiC-SiC materials in air as a function of test temperature (room temperature - 1300°C) can be understood if a modification of the fibre-matrix interphase is assumed to occur [12]. We have effectively observed that the material behaves in a brittle manner at high temperatures $T > 700°C$ [8, 9, 12, 13].

TEM observations have shown that a clear modification of the fibre- matrix interphase in air takes place for the highest temperatures investigated (1200 – 1300°C). However the mechanical behaviour of the material indicates that this phenomenon might already occur beyond lower temperatures (i.e. $T > 700°C$). The interface modification is localized at the fibre-carbon interphase boundary. Moreover the observations performed after short time exposures in air suggest that the migration of oxygen along the fibres in probably responsible for the oxidation of the carbon interphase. This result is in agreement with the analyses performed by Fretty *et al.* [14, 15] on same materials annealed in air at high temperatures.

For long time exposures (40h at 1200°C), the modified interphase becomes more heterogeneous. In this case the turbostratic carbon has disappeared and has been replaced by different layers. Their precise chemical nature has still to be assessed. There is no modification of the fibre itself which always remains amorphous or nanocrystalline.

The fibre recrystallization observed in creep experiments under vacuum for $T > 1200°C$ is the main microstructural modification.

This result is in agreement with the previous observations already published and with the fibre degradation mechanism generally accepted [7].

The Nicalon fibre consists of β-SiC nanocrystals, "silica" and carbon [16]. The oxidized phase in this fibre is best described as a continuum of SiO_xC_y tetrahedra [17] surrounding the β-SiC crystals. Le Coustumer *et al.* [7] have show that "the grain boundaries" made of SiO_xC_y phases are destroyed beyond 1400° (in argon). This degradation process gives rise to the growth of β-SiC crystals by coalescence.

Under vacuum the same phenomenom has been detected in our samples at 1200°C. At this temperature a decrease of the maximum stress is observed. In the model developed by Abbé [10] in order to analyze the creep curve of SiC-SiC composites, this microstructural transformation (recrystallization) leads to stress relaxations and a modification of the interfacial shear strength value.

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