JOURNAL OF MATERIALS SCIENCE 30 (1995) 2115–2120

TEM studies of damage induced in SiC_f–SiC composites irradiated with swift Xe ions

I. SEBIRE-LHERMITTE, J. VICENS, J. L. CHERMANT, M. LEVALOIS,
E. PAUMIER
LERMAT, URA CNRS No 1317, ISMRA, 6 Bd Maréchal Juin, 14050 CAEN Cedex, France

This paper concerns the behaviour of a structural ceramic matrix composite, SiC_f–SiC, irradiated with swift xenon ions, with a fluence of up to 10^{15} Xe cm^{-2}. Damaged materials were investigated by transmission electron microscopy along the beam penetration. Damages are mainly located at the fibre–matrix interfaces, where amorphous zones are evinced in the turbostratic carbon interphase, as well as in the fibres themselves. Latent tracks have also been observed in the fibre close to the fibre–matrix interface.

1. Introduction

Ceramic matrix composites (CMC), i.e. ceramic fibre reinforced ceramics, are under development for use in space as aeronautical structures for high temperatures, for vanes, heat exchangers or gas turbines, or for structures working in very severe environments. It is therefore necessary to test their chemical and thermomechanical behaviour under such environmental conditions. Long silicon carbide fibres in a silicon carbide matrix, SiC_f–SiC, belong to this class of materials. Thus, an important amount of work has already been performed on SiC_f–SiC in order to understand either their process route, their mechanical properties or their structural evolution under various atmosphere (see for example [1–8]).

2. Problems concerning the use of structural materials in space

CMC have been developed for space applications, and are used in parts of launching satellite motors, e.g. throat nozzles, flame holders, exit cones, jet vanes, liquid propellant engine chambers, ramjet chambers, leading edges or thermal protection panels. These parts are subjected to the space environment, where many components exist: atomic oxygen, solar ultraviolet (u.v.) irradiation, flow of particles (electrons and protons), micrometeorites [8–11]. Moreover, beyond atmospheric protection, these parts may meet various types of primary radiation, e.g. particles trapped in Van Allen's belt, cosmic radiation and solar emissions especially during eruptions [12]. The interaction of primary radiation with matter produces secondary radiation. So, it is important to predict the degradation of those materials subjected to such a space environment: this is essential both for the conception and design of mechanical and thermal systems for space devices [10].

However, no attempt has yet been undertaken to investigate possible structural modifications in the conditions of use except with the long duration exposure facility (LDEF) satellite [11] and the French cooperative passive paylod (FRECOPA) experiment, where "soft" materials were partially studied: i.e. glass fabric with teflon, Mylar, Delrin, joints, Velcro and some metallic materials [13]. With the Grand Accélérateur National d'Ions Lourds (GANIL), which is a national large accelerator for swift heavy ions, it may be possible to simulate the effect of a cosmic beam, which is not too far from real behaviour. Moreover, under irradiation, a mixing effect which will lead to a structural modification of the material by atomic mobility and anisotropic modification under such high energy, by transformation of matter along the tracks, could occur also.

So, GANIL's facilities have been used to subject some ceramics and ceramic matrix composites to a very high energy xenon beam.

This paper deals with preliminary studies of transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) of SiC_f–SiC composites irradiated by swift Xe ions.

3. Experimental procedure

3.1. Materials

SiC_f–SiC composites used in this investigation consisted of a woven bidirectional continuous SiC fabric layer, infiltrated by SiC chemical vapour (CVI) [14]. The fibres used were ceramic grade Nicalon NLM 202, consisting of four phases: the fibres, the matrix, the pores (small into the yarns and very large between the yarns) and, at higher magnification, the carbon interphase (Fig. 1a, b). To improve the mechanical properties of these materials a carbon interphase was deposited around the fibres before chemical vapour infiltration of the SiC matrix (Fig. 1b).

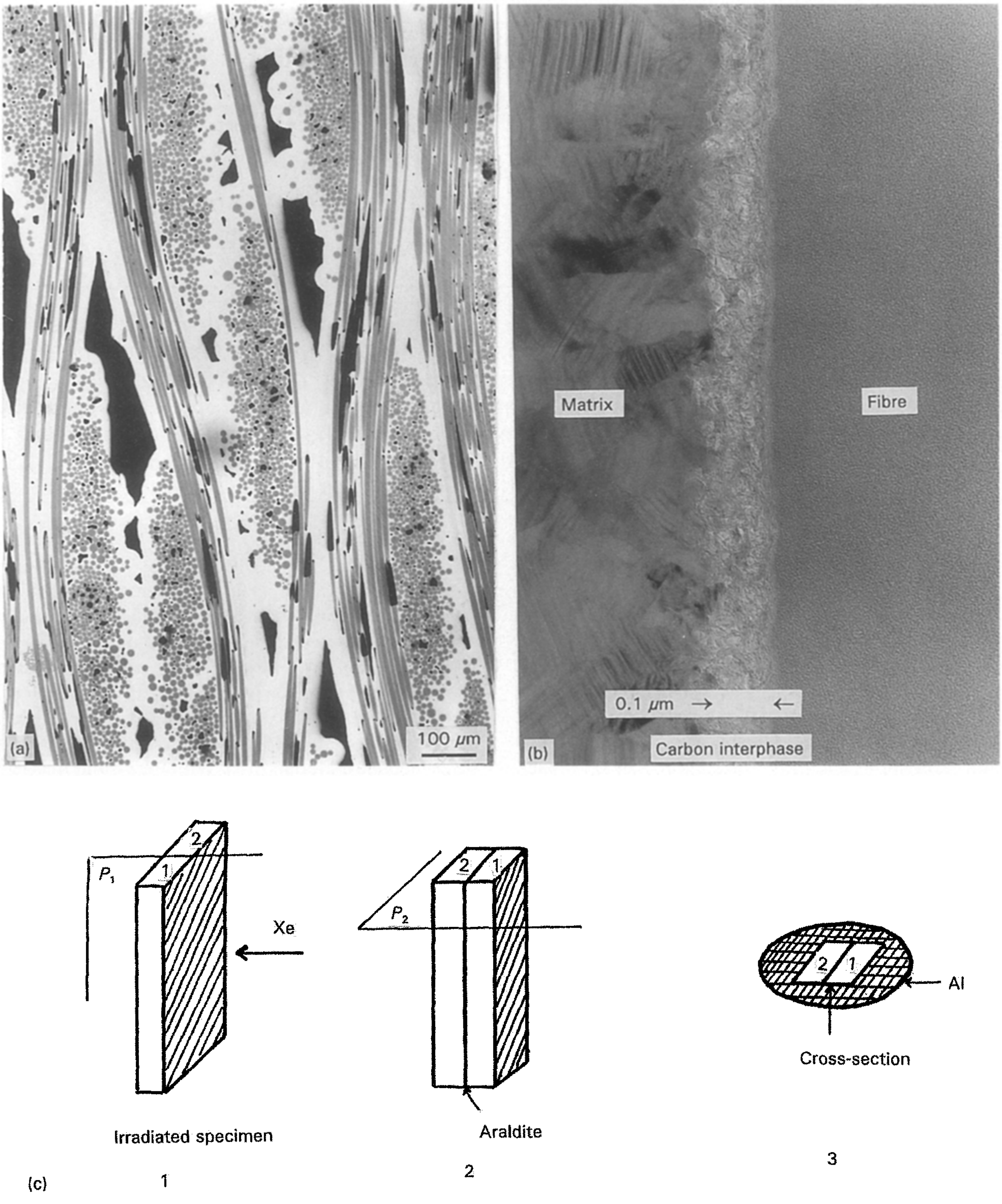

Figure 1 (a) Optical micrograph of SiC_f–SiC composite. Transverse and longitudinal sections of the fibres are observed. Matrix appears white coloured on the figure and the dark regions are pores. (b) TEM micrograph of as-received SiC_f–SiC composite showing the carbon interphase between fibre and matrix. (c) 1, Irradiated SiC_f–SiC specimen is cut along the plane, P_1, containing the ion beam direction. 2, Parts 1 and 2 stuck with araldite, then inserted in an aluminium cylinder (3 mm in diameter). 3, Cross-sectioned sample along the P_2 plane before ion thinning, allowing TEM observations of the whole irradiated region.

3.2. Experimental procedure

SiC_f–SiC samples ($10 \times 5 \times 0.7\ mm^3$) were irradiated at the GANIL accelerator by swift Xe ions ($E = 5.5$ GeV) with fluences up to 10^{15} Xe cm^{-2}. During the experiments, the specimens were irradiated at steps of 90 s separated by an interval of 10 s. Nevertheless, the temperature of the targets was raised by up to 900 K, depending on the beam current density (average value: 50 nA e cm^{-2}). SiC single crystals were irradiated under the same conditions. The results have been published previously [15].

The implantation zone was located at 535 µm from the surface of the samples as calculated by the TRIM programme [16]. However, this value does not take into account large porosities which may be present in the bulk of the material. This zone is not visible by optical microscopy, in contrast to irradiated SiC single crystals [15].

In order to observe the whole irradiated area, cross-sections were prepared as shown in Fig. 1c. Two parts of the irradiated sample were stuck with araldite, according to the scheme shown in Fig. 1c (2) and then inserted into an aluminium cylinder. Finally, thin slices (100 µm thick) were cut in such a way as to observe most of the irradiated area (Fig. 1c (3)). The slices were mechanically ground (down to 20 µm thick) and then ion milled with an argon flux.

TEM observations were performed using a Jeol 200 CX microscope and HREM studies were carried out with a Topcon 002B, operating at 200 kV.

4. Results and discussion

Previous studies have shown that fibres are described by a continuum of SiC_xO_y (with $x + y = 4$) tetrahedra, surrounding small β SiC crystals [17–19]. Recently, the composition of the fibre has been proposed to be $SiC_{1.03}O_{0.32}$, which corresponds to 11 wt % oxygen, 27 wt % carbon and 62 wt % silicon. By studying the fine structure of the X-ray emission bands it was suggested that these elements were combined of 46 vol % SiC, 34 vol % SiC_xO_y and 20 vol % free carbon, with oxycarbide in the outermost regions of the fibre, which are richer in oxygen [20]. Moreover, a very thin silica layer is sometimes observed at the fibre surface. Interphases between fibres and matrix are made of turbostratic carbon, which very often appears parallel to the main direction of the interface. The matrix consists of highly faulted columnar SiC crystals.

The different parts of the SiC_f–SiC materials described above have been carefully studied in TEM and HREM after irradiation experiments and no structural modifications could be detected in the specimens irradiated with fluences up to 10^{14} Xe cm^{-2}. The cross-section of a sample irradiated with 10^{15} Xe cm^{-2}, then prepared as indicated in Fig. 1c and ion thinned, is shown at low magnification in Fig. 2a. The ion beam direction is indicated on the micrograph in the two parts, 1 and 2. These two parts are stuck together along the interface in such a way that the area close to the implantation zone is visible in part 1 and the area close to the irradiated surface is visible in part 2. TEM observations reveal that structural damage of the sample varies with depth. Fig. 2b is a schematic representation of the ion thinned cross-section. Part 1 of the cross-section, located close to the implantation zone (535 µm deep), reveals damages in areas denoted b and c. Area c is more heavily damaged than area b, as illustrated in the following. The area denoted a is located behind the implantation zone and remains intact after irradiation. In part 2, close to the surface of the specimen, damage is detected from 185 µm deep (area denoted b). In this area b, which extends approximately 185–470 µm deep, the main structural modification appears in the carbon interphase. Turbostratic carbon can be observed either locally amorphous as illustrated in Fig. 3a (arrowed zones) or highly amorphous (Fig. 3b). As a result of this amorphism, many decohesions appear between the fibres and matrix as shown in Fig. 3c. It must be noted that a previous study of irradiation (10 keV H_2^+) damage in graphite also revealed an amorphous process [21].

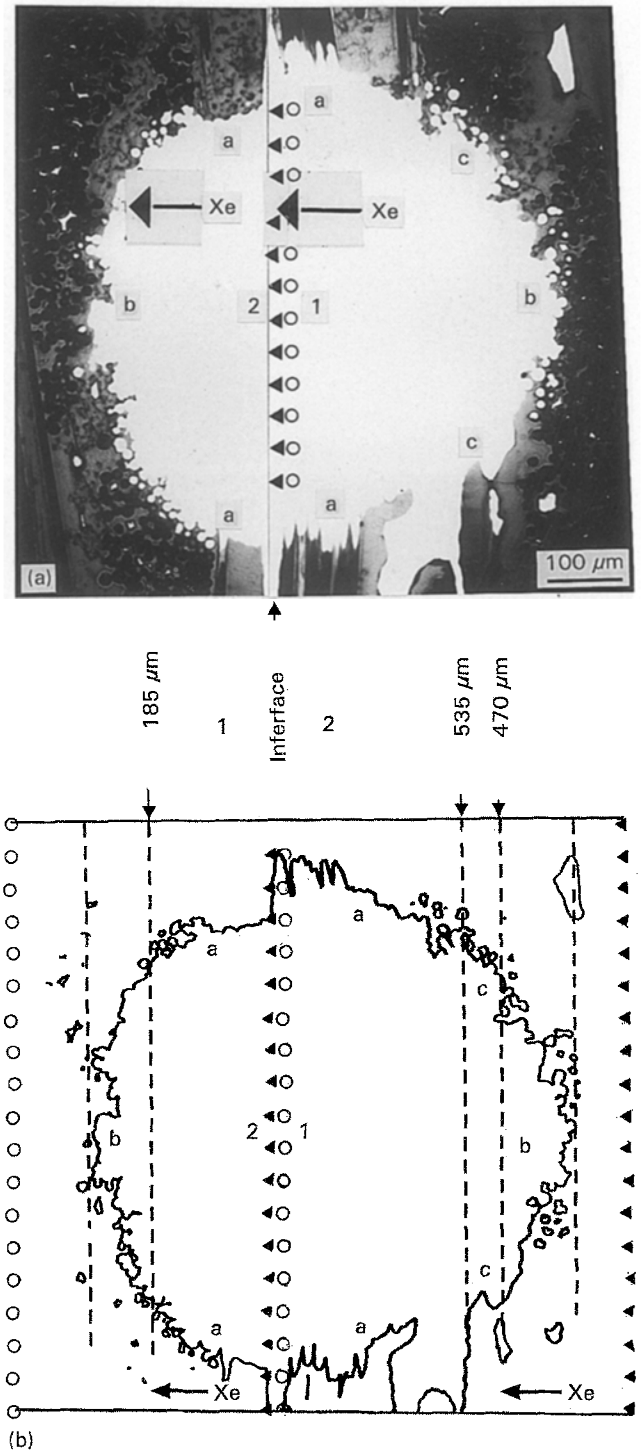

Figure 2 (a) Sample irradiated with 10^{15} Xe cm^{-2}. Optical micrograph of a cross-section of parts 1 and 2 after ion thinning. The different areas a, b and c in parts 1 and 2 were determined by TEM observations. (b) Schematic diagram of the cross-section. The different regions a, b and c of irradiation damage are localized with respect to depth. The beam direction has been indicated.

HREM observations of fibres situated in areas a and b reveal the usual nanocrystalline SiC structure of the fibre (Fig. 4a): SiC crystals of a few nanometers in size in an amorphous matrix, as shown previously [22]. The characteristic diffraction ring

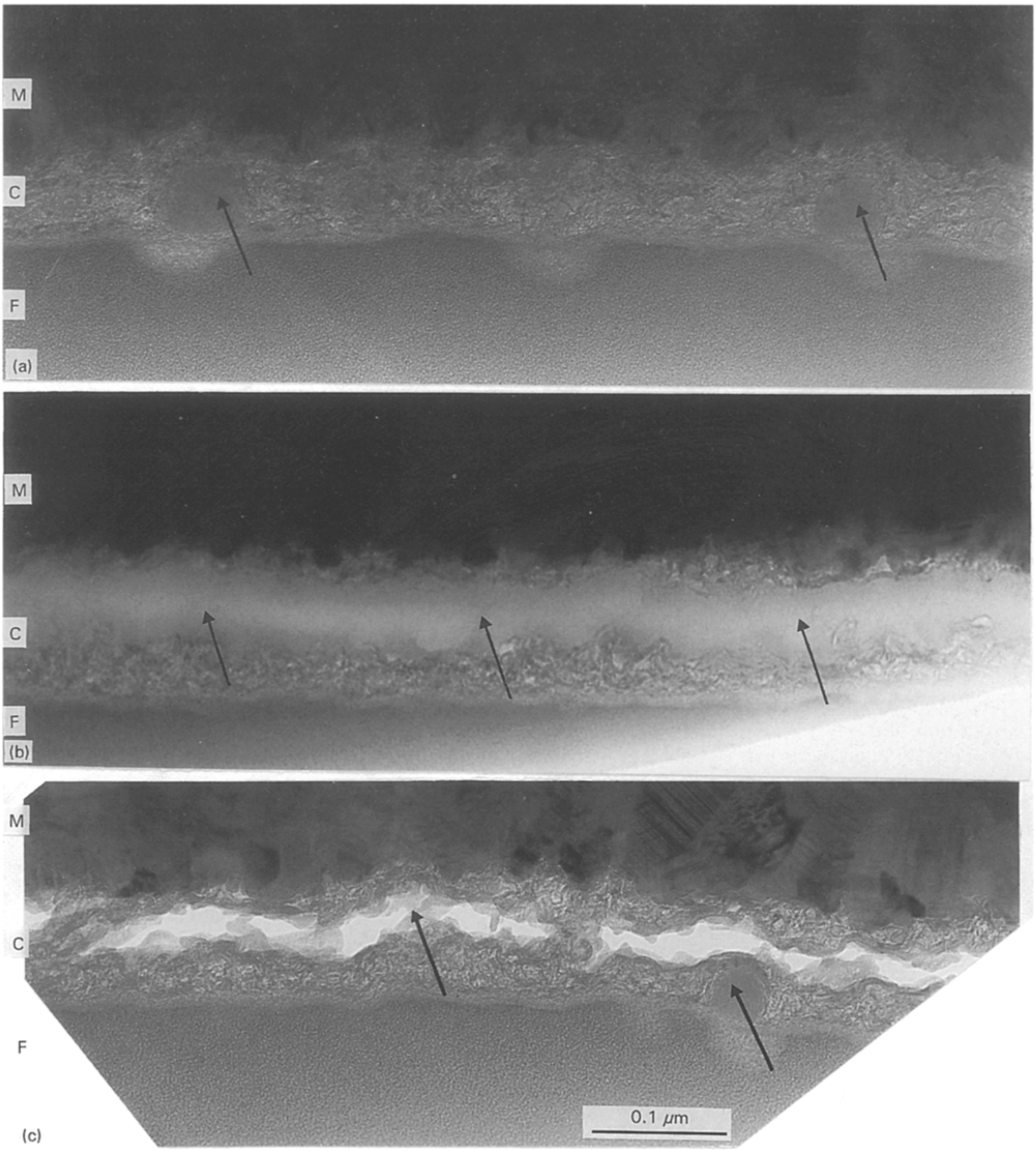

Figure 3 TEM observations of an irradiated SiC_f–SiC composite: (a) local amorphism (arrowed) in the carbon interphase; (b) the turbostratic carbon is greatly amorphous (arrowed zone); and (c) decohesion in the amorphous carbon (arrowed) of the interphase.

($d_{111} = 0.25$ nm) of SiC crystals is also presented on the insert in Fig. 4. On the contrary, fibres located in area c, close to the implantation zone, appear totally amorphous (Fig. 4b). In this case the 111 diffraction ring disappears and a diffuse pattern is observed (inserted part of Fig. 4b).

Furthermore, latent tracks have been clearly imaged in fibres located in area b, and an example is presented on Fig. 5. Such tracks have not often been evinced by TEM investigations on ceramics, except in yttrium garnet magnetic insulators, superconducting cuprates or in silica [23, 24]. Tracks in SiC fibres which are perfectly aligned along the ion beam direction have a stronger contrast close to the interface between the fibre and the carbon interphase. A faint contrast of these tracks is still visible inside the fibre. The size of the tracks is estimated to be 1 nm. Recently, electron probe microanalysis of Nicalon fibres showed that the oxycarbide phase is richer in oxygen in the outermost regions ($\simeq 200$ nm) of the fibre [20]. Due to the structural and chemical heterogeneity of the Nicalon fibre, it is not yet possible to be precise about the nature of these tracks. However, TEM observations seem to indicate that they are formed in the region of the fibre which is richer in oxygen.

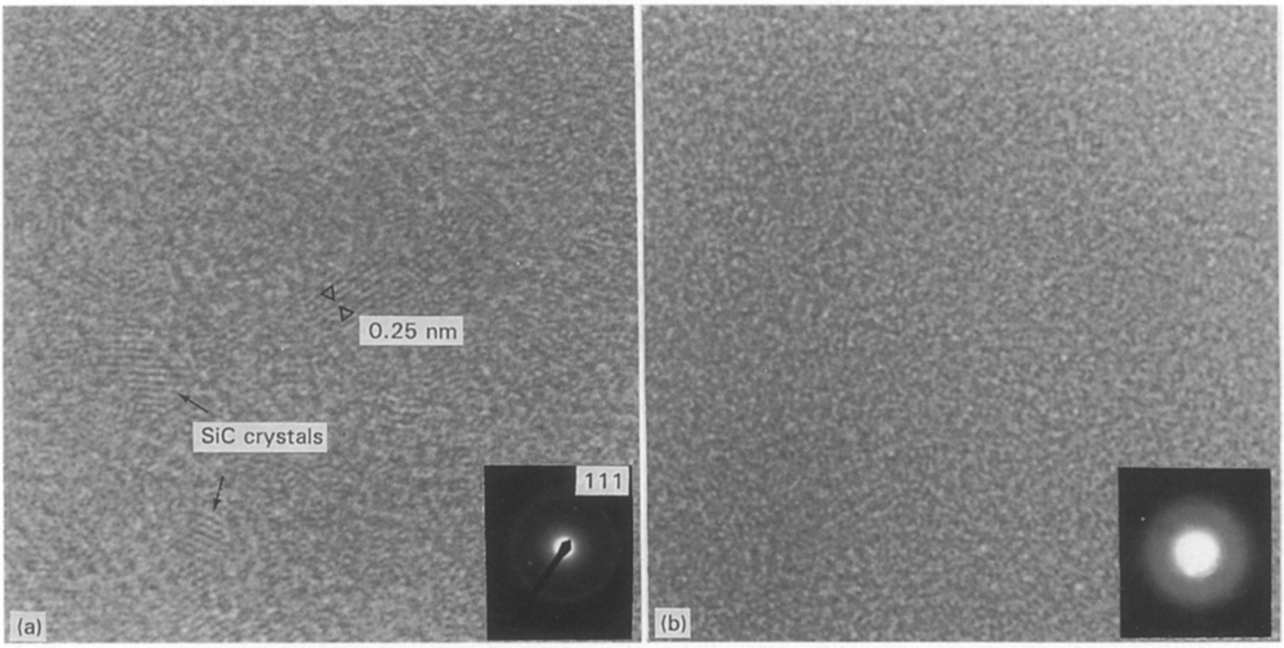

Figure 4 Irradiated SiC$_f$–SiC composite HREM observations of the fibres: (a) fibre located close to the surface of the sample (area a), and (b) fibre located close to the implantation zone (area c).

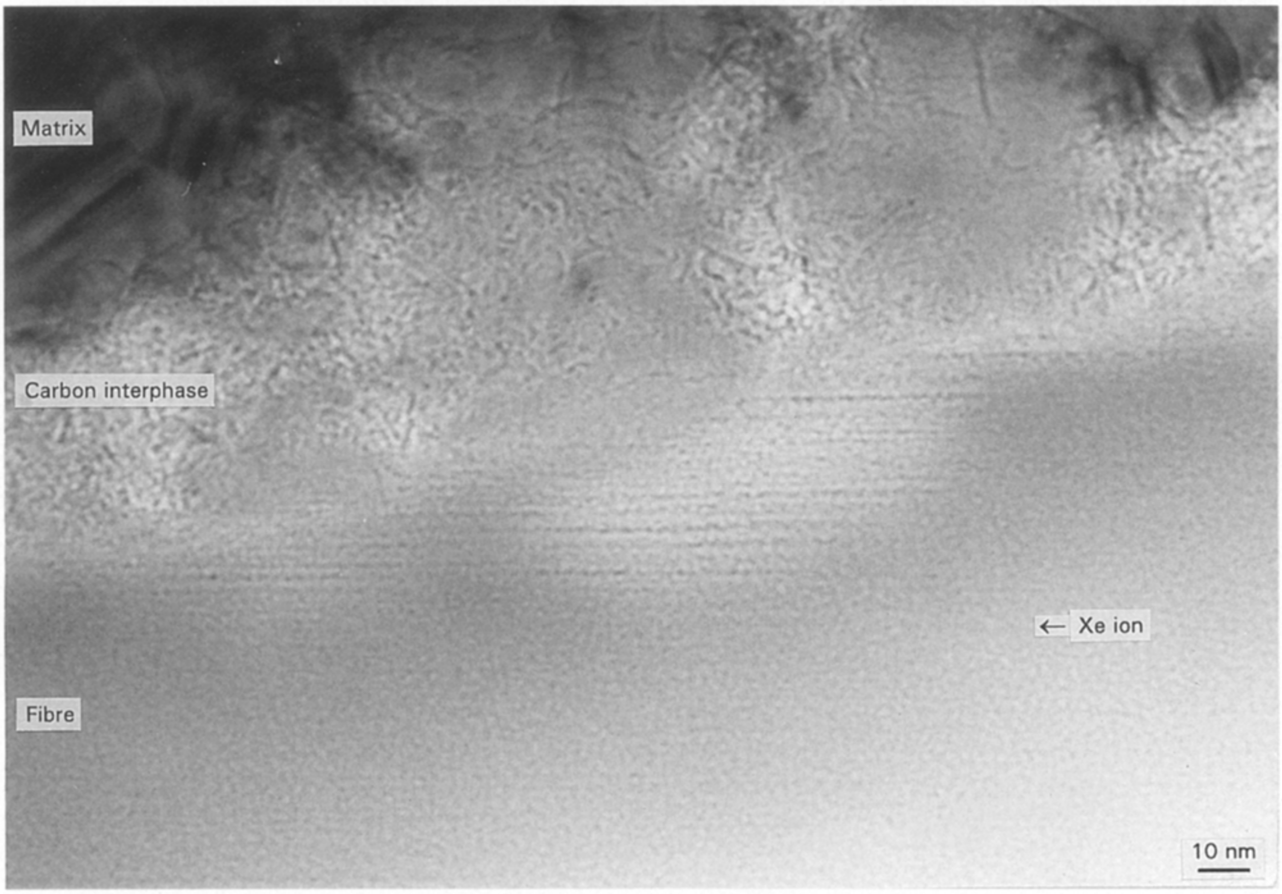

Figure 5 Sample irradiated with a fluence of 10^{15} Xe cm^{-2}. Latent tracks imaged in the outermost region of the fibre. The ion beam direction has been indicated.

5. Conclusions

In summary, ion irradiation damage in SiC$_f$–SiC composites arises only for very high values of 10^{15} Xe cm^{-2}. They take place mainly in the interphase between the fibre and the matrix. Turbostratic carbon is locally amorphous and decohesions appear in the interphase. Moreover, close to the implantation zone, the small β SiC crystals disappear in the fibres. To our knowledge, this is the first time that latent tracks (resulting from ion induced electronic excitation) have been detected in such materials, but further investigation is necessary precisely identify this phenomenon. In particular, track damage has already been observed in SiO_2 [23], and this it seems important to understand the role of oxygen in the formation of tracks in the fibre. Finally, one can consider from these first analyses of irradiated SiC_f–SiC which are damaged only for a very high fluence value, that a minimum effect on the structural properties of these materials has to be expected in conditions of use in a hostile space environment.

Acknowledgements

The authors wish to thank Dr S. Bouffard (CIRIL) for helpful discussions, the technical staff of CIRIL for its help during irradiation experiments, Dr. F. Abbé from SEP for fruitful discussion, the Director of GANIL for granting beam time, and SEP (Etablissement de Bordeaux, France) for providing SiC_f–SiC samples. One author (ISL) would like to thank the CNRS (France) and SEP (France) for their financial support.

References

1. R. NASLAIN, *J. Alloys Comp.* **188** (1992) 42.
2. T. M. BESMANN, B. W. SHELDON, R. A. LOWDEN and D. P. STINTON, *Science* **253** (1991) 1104.
3. T. CUTARD, D. FARGEOT, C. GAULT and M. HUGER, *Rev. Comp. Mat. Avancés* **3** (1993) 113.
4. N. FRETTY and M. BOUSSUGE, *Comp. Sci. Technol.* **37** (1990) 177.
5. M. H. ROUILLON, M. DRISSI-HABTI, T. DESPIERRES and M. GOMINA, *Rev. Comp. Mat. Avancés* **3** (1993) 145.
6. P. REYNAUD, P. BRENET, D. ROUBY and G. FANTOZZI, in "Comptes-Rendus des Huitièmes Journées Nationales sur les Composites", JNC 8, edited by O. Allix, J. P. Favre and P. Ladeveze (Amac 1992) p. 531.
7. J. VICENS, M. H. ROUILLON, P. FOURVEL, F. ABBE, M. GOMINA and J. L. CHERMANT, *Microsc. Microanal. Microstruct.* **2** (1991) 75.
8. X. YANG and R. J. YOUNG, *J. Mater. Sci.* **28** (1993) 2536.
9. C. MIGLIONICO, C. STEIN and L. E. MURR, *ibid.* **26** (1991) 5134.
10. A. PAILLOUS, *Ann. Chim. Fr.* **17** (1992) 333.
11. A. F. WHITAKER, *Adv. Mater. Proc.* **4** (1991) 29.
12. J. BOURRIEAU, *Ann. Chim. Fr.* **17** (1992) 7.
13. N. BEAUCLAIR, *Air & Cosmos* **1346** (1991) 38.
14. F. CHRISTIN, R. NASLAIN and C. BERNARD, in "Proceedings of the Seventh International Conference on CVD", edited by T. O. Sedwick and H. Lydtin, (The Electrochemical Society, Princeton, NJ, 1979) p. 499.
15. I. LHERMITTE-SEBIRE, J. VICENS, J. L. CHERMANT, M. LEVALOIS and E. PAUMIER, *Phil. Mag. A* **69** (1994) 237.
16. J. P. BIERSACK and L. G. HAGG, *Nucl. Instr. Meth.* **174** (1980) 257.
17. M. MONTHIOUX, D. COJEAN, O. DELVERDIER, P. LECOUSTUMER and V. MADIGOU, *Microsc. Microanal. Microstruct.* **2** (1991) 47.
18. C. LAFFON, A. M. FLANK, P. LAGARDE, M. LARIDJANI, R. HAGEGE, P. OLRY, J. COTTERET, J. DIXMIER, J. L. MIQUEL, H. HOMMEL and A. P. LEGRAND, *J. Mater. Sci.* **14** (1989) 1503.
19. H. HOMMEL, J. L. MIQUEL and A. P. LEGRAND, *Ind. Ceram.* **849** (1990) 344.
20. BLEAY, A. R. CHAPMAN, G. LOVE and V. D. SCOTT, *J. Mater. Sci.* **27** (1992) 5389.
21. KOUHEI N. KUSHITA and KIICHI HOJOU, *Ultramicrosc.* **35** (1991) 289.
22. I. LHERMITTE-SEBIRE, M. GOMINA and J. VICENS, *J. Microsc.* **169** (1993) 197.
23. T. A. TOMBRELLO, *Nucl. Instr. Meth.* **B2** (1984) 555.
24. F. STUDER, C. HOUPERT, D. GROULT and M. TOULEMONDE, *Rad. Eff. Def. Solids* **110** (1989) 55.

Received 11 August 1993
and accepted 8 September 1994