Structural changes induced by heavy ion irradiation in titanium silicon carbide

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ABSTRACT

Carbide-type ceramics, which have remarkable thermomechanical properties, are sensed to manufacture the fuel cladding of Generation IV reactors that should work at high temperature. The MAX phases, and more particularly titanium silicon carbide, are distinguished from other materials by their ability to have some plasticity, even at room temperature. For this study, polycrystalline Ti_3SiC_2 was irradiated with ions of different energies, which allow to discriminate the effect of both electronic and nuclear interactions. After characterization by low-incidence X-ray diffraction and cross-sectional transmission electron microscopy, it appears that Ti_3SiC_2 is not sensitive to electronic excitations while nuclear shocks damage its structure. The results show the creation of many defects and disorder in the structure, an expansion of the hexagonal close-packed lattice along the c axis, and an increase in the microstrain yield.

Keywords: Ti_3SiC_2, ion irradiation, nuclear and electronic interactions, low-incidence X-ray diffraction, cross-sectional transmission electron microscopy

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1. Introduction

The Gas Fast Reactor (GFR), one of the six systems considered by the Generation IV International Forum (GIF), is designed for nominal working at both high temperature and high helium pressure [1]. These working conditions led to the selection of non-oxide ceramics as cladding material for the fuel. Therefore, researches aiming at understanding the behavior under irradiation of carbides were carried out in recent years [2-7].

Among the studied materials, titanium silicon carbide can be distinguished by its propensity to combine the properties of ceramics with those generally attributed to metals [8-14]. Indeed, like most of the MAX phases, Ti_3SiC_2 is stiff (Young's modulus of 352 GPa [15,16]), tough (toughness of 9 MPa $m^{1/2}$ [16,17]) and soft (hardness of 6 GPa), both thermal and electrical conductor (37 W m^{-1} K^{-1} [18] and $4.5x10^6$ Ω^{-1} m^{-1} [19,20], respectively), and resistant to thermal shocks [15,21,22]. In particular, the plasticity of Ti_3SiC_2 at room temperature may be explained by its nanolamellar structure, which confers to Ti_3SiC_2 material a propensity to delaminate under the effect of mechanical stress [22-24]. However, if the behavior of this material has already been studied under various conditions more or less extreme [20,21,25-28], except few articles related to Ti_3SiC_2 that were recently published [29-32], and others related to $Ti_3(Si,Al)C_2$ [33-36], no study has been conducted on the irradiation behavior of Ti_3SiC_2.

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Therefore, in this study, the damage of Ti_3SiC_2 under irradiation is analyzed from the structural point of view, using both low-incidence X-ray diffraction and cross-sectional transmission electron microscopy.

2. Experimental

2.1. Material

The studied material is a polycrystalline Ti_3SiC_2 provided by 3-ONE-2 (Vorhees, NJ, USA). Like most Ti_3SiC_2 bulk samples, our specimens contain impurities: about 19% of $TiC_{0.92}$ and 7% of $TiSi_2$ (estimation by X-ray diffraction). The samples provided in the form of plates are cut into parallelepipeds of about 10x5x5 mm^3, and one face is polished with diamond paste with a particle size down to 1 micron. Finally, they are irradiated on the polished face.

2.2. Irradiations

The neutron irradiations that occur in the reactor have been simulated with ions to allow characterization of the irradiated samples without special precautions. Table 1 summarizes the irradiations performed in this study: knowing that the GFR should work at high temperature, in addition to the effect of both the energy and the fluence, the effect of irradiation temperature was investigated.

Table 1: Irradiations performed for this study.

Beamline	Ion	Temperature (K)	Fluences (m^{-2})
ARAMIS	4 MeV Au	298	10^{16}, 10^{17}, 10^{18}, 10^{19}
		773	10^{16}, 10^{17}, 10^{18}, 10^{19}
		1623	10^{19}
IRRSUD	74 MeV Kr	298	10^{16}, 10^{17}, 10^{18}, 10^{19}
		773	10^{16}, 10^{17}, 10^{18}, 10^{19}
	92 MeV Xe	298	10^{16}, 10^{17}, $2x10^{17}$, $4x10^{17}$, $8x10^{17}$, 10^{18}, $2x10^{18}$, $4x10^{18}$, $8x10^{18}$, 10^{19}, $1.3x10^{19}$
		573	10^{16}, 10^{17}, 10^{18}, 10^{19}
SME	930 MeV Xe	298	10^{15}, 10^{16}, 10^{17}, $4.5x10^{17}$
		773	10^{15}, 10^{16}, 10^{17}, $4.5x10^{17}$

The kinetic energy of a neutron is predominantly transferred to the primary knock-on atom (PKA) of the target in an elastic collision. Following this shock, the PKA becomes a projectile and causes nuclear interactions with atoms of the target. Thus, the low-energy ions, which induce mainly nuclear shocks, are used to simulate neutron irradiations. This is the reason to carry out irradiation with 4 MeV ions provided by the ARAMIS accelerator of CSNSM (Orsay, France).

However, as the damage induced by this irradiation is localized in a small volume (Figure 1), characterization of the irradiated area can turn out to be tricky. Therefore, irradiations with higher energy ions have been carried out on the IRRSUD beamline at GANIL (Caen, France) with 74 MeV Kr and 92 MeV Xe ions. These irradiations generate nuclear shocks that increase with the depth (Figure 1), allowing the characterization of the damage as a function of dpa (number of "displacements per atom" of the target).

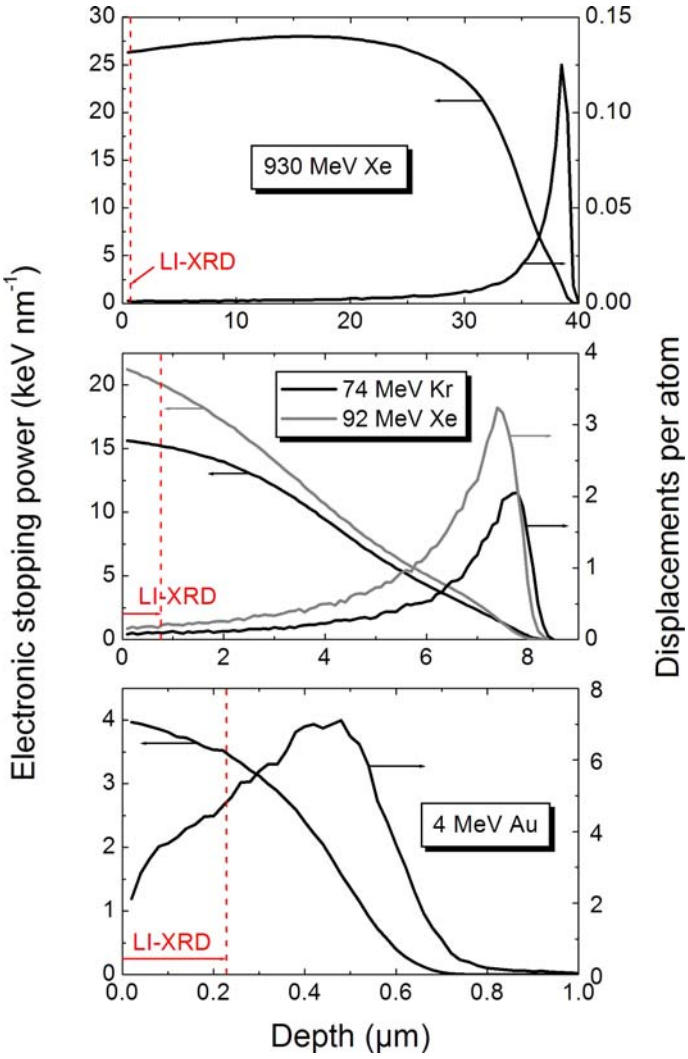

Figure 1: Electronic stopping power and number of displacements per atom induced by each irradiation as a function of the depth in Ti_3SiC_2; dpa are for the maximal fluence (10^{19} m^{-2} for 4 MeV Au, 74 MeV Kr and 92 MeV Xe, $4.5x10^{17}$ m^{-2} for 930 MeV Xe). Data were determined with the TRIM-2008 code [37].

Nevertheless, at the beginning of the range, electronic interactions induced by the irradiations performed on IRRSUD are important. To discriminate the effect of both electronic and nuclear interactions, irradiations with a higher energy have been carried out on the SME beamline at GANIL with 930 MeV Xe ions; for these irradiations, nuclear shocks can be considered as negligible along the first 30 microns (Figure 1). The fluences reached for this irradiation are lower than those of other irradiations (Table 1): this is due to the fact that the flux used for this irradiation was reduced to avoid the heating of the specimens. Anyway, in several materials sensitive to electronic interactions, it was shown that such fluences can cause significant damage [38-40].

2.3. Characterization techniques

The as-irradiated samples were characterized by low-incidence X-ray diffraction (LI-XRD). The diffractometer used was a Siemens D5000 equipped with copper anticathode (0.154 nm). The diffractograms were recorded between 5° and 90° in 2θ scale, under an incidence of 1° for samples irradiated with 4 MeV Au ions, and 3° for other irradiations. Under these incidences, the X-ray intensity in Ti_3SiC_2 decreases by a factor of 2.72 at a depth of 230 nm and 760 nm respectively [41-43]. An aluminum-made mask was placed on the virgin part of some specimens partly irradiated.

Variations of lattice parameters were determined using the TuneCell tool of Diffractplus EVA software provided by Bruker. The measure of the microstrain yield was conducted by evaluating the broadening of the (104) peak of Ti_3SiC_2 (the most intense isolated peak), and by considering that the crystallite size is large enough not to induce broadening; this consideration is motivated by observations made by Electron Back-Scatter Diffraction (EBSD), which allowed us to highlight a crystallite size greater than 1 µm [29].

Some samples were also observed by cross-sectional transmission electron microscopy (X-TEM) with a view to both understand the damage noted by LI-XRD and observe the defects induced by irradiation. The microscope used was a 200 kV Jeol 2010F, equipped with a field emission gun.

These techniques were also applied on an as-polished and no irradiated sample, so-called virgin sample, to highlight the differences induced by irradiation.

3. Results

3.1. Disorder and defects

Figure 2 shows diffractograms recorded on several irradiated samples, which complete a previous study [30].

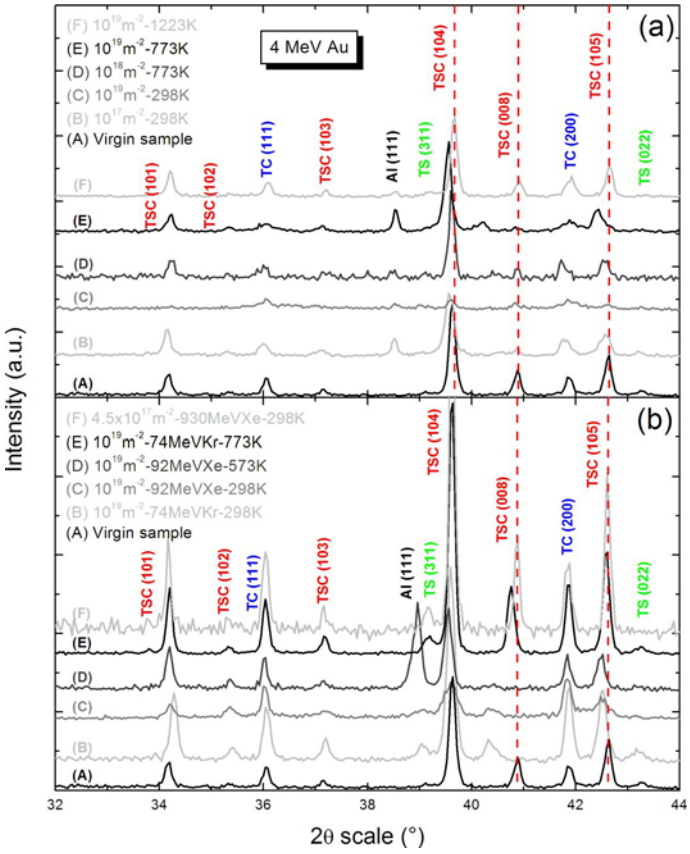

Figure 2: Diffraction pattern of samples irradiated with (a) 4 MeV Au ions (analysis angle: 1°), and (b) high-energy ions (analysis angle: 3°); Al (111) peaks are due to an aluminum-made mask placed on the virgin part of partly irradiated samples.

Concerning the 4 MeV Au ion irradiation, we have shown a significant change of the material structure at 298 K, which was attributed to some loss of crystallinity; this phenomenon can be observed through both a decrease of the peak intensity and a rise in the baseline. By comparing these diffractograms with those obtained for specimens irradiated at 773 K (Figure 2a), the damage seems less important at this latter temperature, indicating a positive effect of the temperature on the material damage. This positive effect is even more noticeable for the sample irradiated at 1223 K, the diffractogram being identical to that of the virgin sample.

Concerning the 92 MeV Xe ion irradiation, we have also shown a significant change in the material structure at 298 K, but less significant than for 4 MeV Au ion irradiation. This result may also be noticed on the diffractogram obtained from the specimen irradiated at 298 K with 74 MeV Kr ions to 10^{19} m^{-2} (Figure 2b). It is noteworthy that, like for 4 MeV Au ion irradiation, the higher the irradiation temperature, the lower the damage induced by irradiations with 74 MeV Kr or 92 MeV Xe ions.

Another interesting result is that, for 930 MeV Xe ion irradiation, no change in the diffractograms is noticeable (Figure 2b). For materials sensitive to electronic interactions, the fluences reached in this study may lead to a whole amorphization of the material [38-40]; thus, it seems that electronic excitations are not harmful to Ti_3SiC_2.

The results obtained by LI-XRD are in agreement with the observations made by X-TEM (Figure 3). Before irradiation, Ti_3SiC_2 does not contain any defects (see the virgin area of Figure 3a), and its nanolamellar structure is noticeable on both the micrographs and the diffraction patterns (3 spots of low intensity between 2 more intense ones) (Figure 3b).

After irradiation, no defect has been observed on samples irradiated with 930 MeV Xe ions, confirming the insensitivity of Ti_3SiC_2 to electronic excitations. On the contrary, many defects appearing as black dots (see irradiated area of Figure 3a) are present in other samples. These black dots are too small to be identified by TEM; as evocated by Le Flem *et al.* they could be clusters of Frenkel pairs or dislocation loops [33]. The concentration of these black dots increases with depth for samples irradiated on the IRRSUD beamline, confirming that they are induced by the nuclear shocks.

Moreover, when the number of dpa increases, the nanolamellar structure of Ti_3SiC_2 disappears (Figure 3c and d); this may be observed on the micrographs as well as on the diffraction patterns. However, the close-packed stacking of the hexagonal structure is still notable; hence it seems that the material does not become amorphous. We could not determine the cause of the disappearance of the nanolamellar structure. But considering the crystal structure of Ti_3SiC_2 [19,44,45], it seems that the most likely hypothesis to explain this damage of nanolamellar structure would be the substitution of silicon atoms by titanium ones (and/or vice versa) due to nuclear shocks, inducing the creation of defects like Ti_{Si} (and/or Si_{Ti}); this hypothesis was also propounded by Le Flem *et al.*, who noted similar results in their material [33].

The increase of the temperature reduces the concentration of black dots as well as the damage of the nanolamellar structure (Figure 3e).

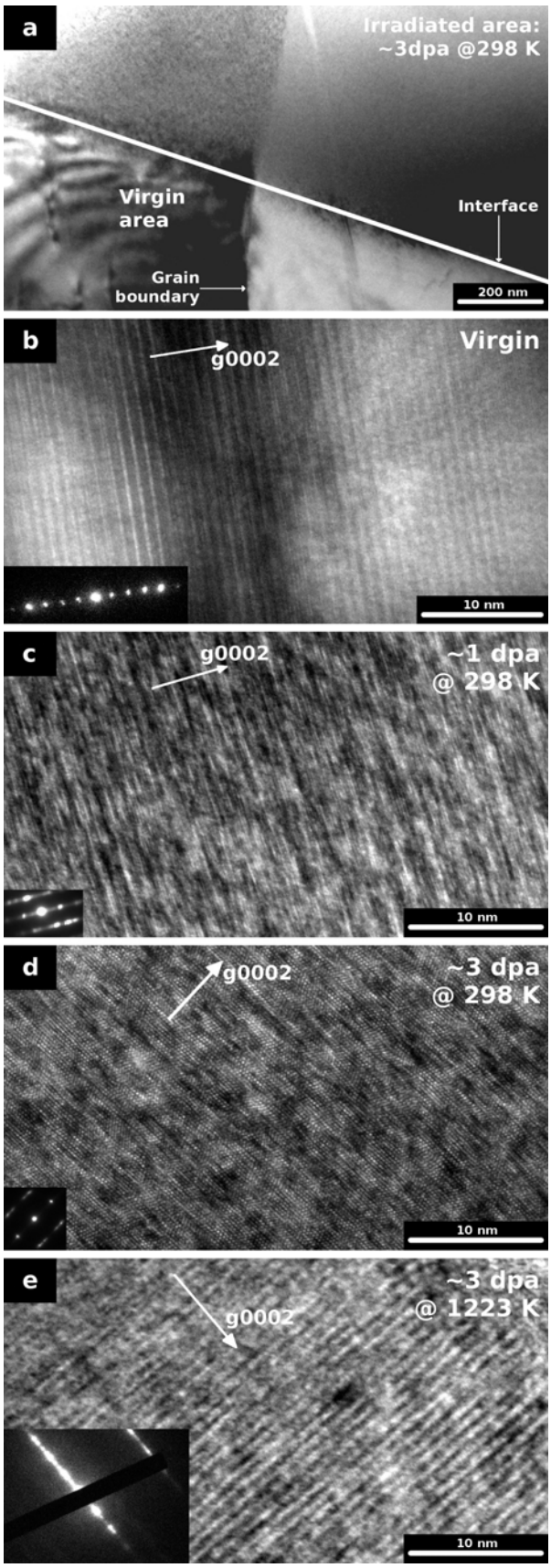

Figure 3: (a) X-TEM picture of an overview of the interface between the irradiated and the virgin areas of the sample irradiated at 298 K with 4 MeV Au ions to 10^{19} m^{-2}. (b-e) High resolution X-TEM pictures: (b) virgin sample, (c) and (d) sample irradiated at 298 K with 92 MeV Xe ions to 10^{19} m^{-2}, obtained at the beginning and at the end of the ion range respectively, and (e) sample irradiated at 1223 K with 4 MeV Au ions to 10^{19} m^{-2}. Vector noted g0002 is perpendicular to <0002> planes.

3.2. Change in lattice parameters

Previously, we showed that irradiation with 92 MeV Xe ions induces both an expansion of the hexagonal lattice of Ti_3SiC_2 along the c axis, and a contraction along the a axis [30]. These variations seemed to occur without change in the unit cell volume. In this study, additional measurements were performed (Figure 4); measurements on specimens irradiated with 930 MeV Xe ions are not shown because no change in lattice parameters could be highlighted.

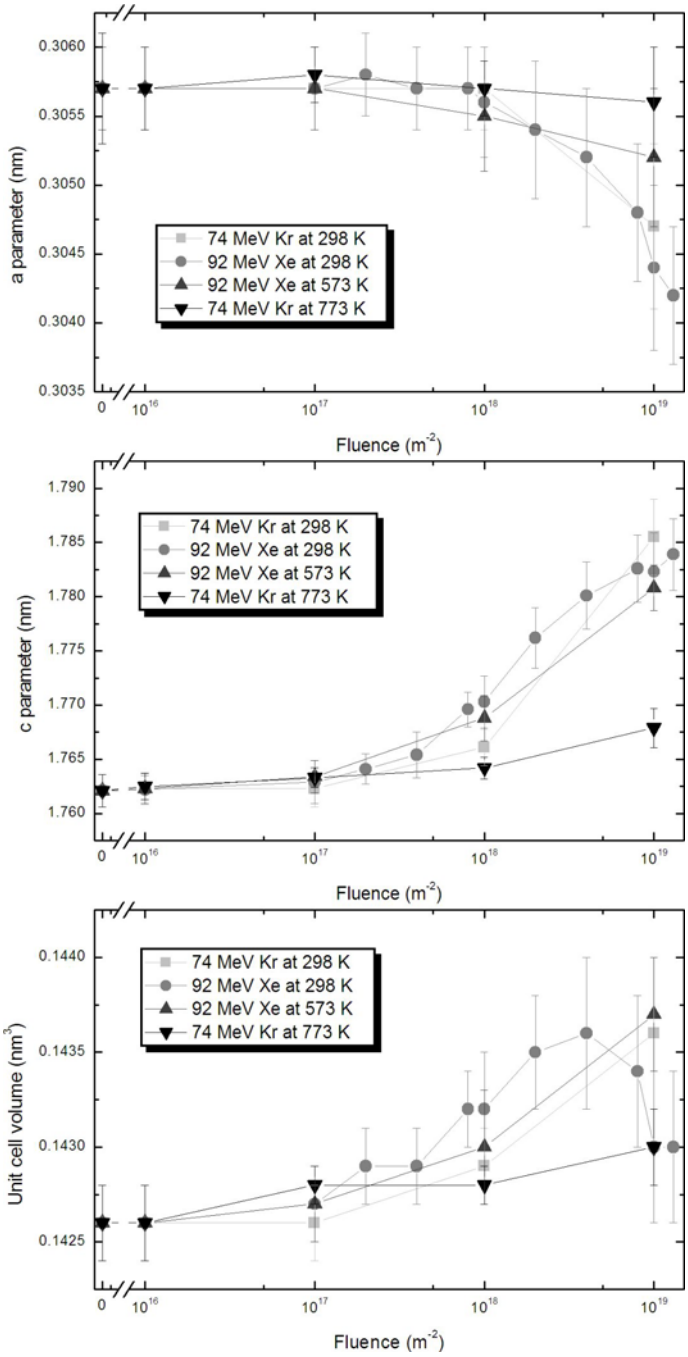

Figure 4: Change in lattice parameters as a function of ion fluence for irradiations performed on IRRSUD.

For the 92 MeV Xe irradiations at 298 K, the contraction along the a axis would begin from about 10^{18} m^{-2}, while the expansion along c would start from about 2 to $4x10^{17}$ m^{-2}; the variations seem to be the same for irradiations with 74 MeV Kr ions. Contrary to what had previously been concluded with data on samples irradiated with 92 MeV Xe ions to 10^{18} and 10^{19} m^{-2} [30], these changes induce an increase of the unit cell volume that reaches a maximum for irradiation with 92 MeV Xe ions, and not for irradiation with 74 MeV Kr ions. This difference will be discussed later on.

Concerning the effect of temperature, it seems that the highest temperature, the lowest changes in both a and c parameters, confirming the beneficial effect of temperature to reduce irradiation damage.

Finally, on the diffractograms of samples irradiated with 4 MeV Au ions (Figure 2), a peak is noticeable between the (104) and (008) peaks of Ti_3SiC_2. Moreover, by paying attention to both (104) and (105) peaks of Ti_3SiC_2, they appear to be deformed compared with that of the virgin sample, and shifted to lower 2θ. After comparing both of these phenomena with the diffractograms of specimens irradiated on the IRRSUD beamline, especially with the one irradiated at 298 K with 74 MeV Kr ions to 10^{19} m^{-2} (Figure 2), it appears that despite the low incidence angle (1°) the diffractograms of samples irradiated with 4 MeV Au ions present a contribution of both the irradiated area and the virgin one located at about 1 micron (Figure 1). Therefore, these irradiations also induce a variation of lattice parameters, and then it seems that the change in lattice parameters is due to nuclear shocks. Unfortunately, due to the degradation of the crystallinity of the samples with the 4 MeV Au ion fluence, only three diffraction patterns (of samples irradiated at 298 K to 10^{17} m^{-2}, and at 773 K to both 10^{18} and 10^{19} m^{-2}, see Figure 2) allow one to notice a peak shift: it is hence not possible to present the evolution of lattice parameters as a function of the fluence or irradiation temperature. Nevertheless, this result will enrich the discussion.

3.3. Change in microstrain yield

Through X-TEM observations of irradiated samples, the crystallite size does not seem to decrease. That is why, in a first approximation, we consider that the broadening of the Ti_3SiC_2 diffraction peaks is only due to an increase of the microstrain yield (see section 2.3.); from a Williamson and Hall analysis, Liu *et al.* have also noticed that the peak broadening induced by identical irradiations, but on $Ti_3Si_{0.90}Al_{0.10}C_2$, is only due to an increase of the microstrain yield [34]. Moreover, since the diffraction patterns of specimens irradiated with 4 MeV Au ions partly consist of the virgin material located at the end of the irradiated thickness, measurements of the broadening of the (104) peak does not allow to obtain information arising from the irradiated area alone. Therefore, no measurement has been performed for these irradiations.

The materials irradiated on the IRRSUD beamline at 298 K show an increase of the microstrain yield as a function of the fluence (Figure 5). As for the lattice parameter changes, irradiation with 92 MeV Xe ions causes larger variations compared with the virgin sample than irradiation with 74 MeV Kr ions.

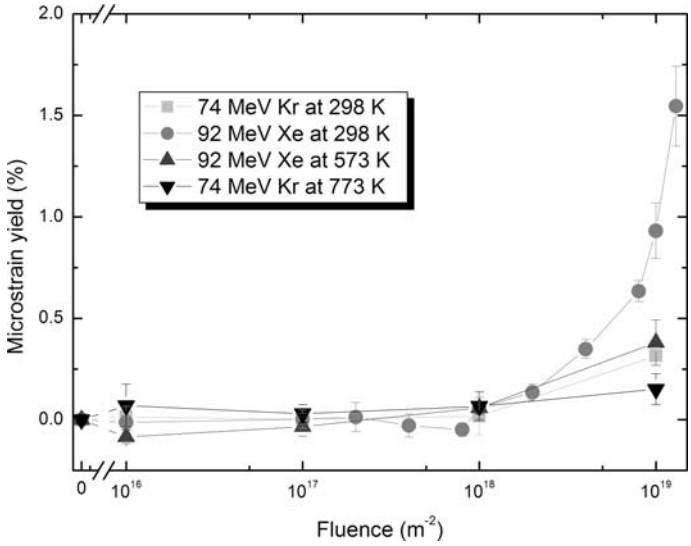

Figure 5: Variation of the microstrain yield as a function of ion fluence for irradiations carried out on IRRSUD.

The effect of temperature is still beneficial concerning the irradiation damage because the higher the temperature, the lower the microstrains in the Ti_3SiC_2 crystal (Figure 5).

These results can be completed by two other observations. First, given that the observations by X-TEM did not reveal deformation fields in the crystal, and that no variation of lattice parameters was measured by LI-XRD, it seems

reasonable that no broadening has been observed for specimens irradiated with 930 MeV Xe ions. Second, some broadening measurements carried out on the (008) peak have led to both trends and values similar to those presented for the (104) peak: thus, variations of the microstrain yield induced by irradiation appear as isotropic.

4. Discussion

The first important result arising from this study is that titanium silicon carbide is not very sensitive to electronic excitation. In other word, if an electronic stopping power threshold for the formation of latent tracks in this material exists, it would be greater than 28 keV nm^{-1}. This result is not proper to Ti_3SiC_2 since most of metals [46,47], but also some ceramics such as SiC [48-50] or TiC and $TiSi_2$ (secondary phases present in the samples, which do not seem to be affected by electronic interactions either) require huge electronic energy loss to be damaged by such interactions.

On the contrary, nuclear shocks create many defects and cause the loss of the nanolamellar structure of Ti_3SiC_2, albeit without leading to amorphization like in the case of SiC for doses reaching some tenths of dpa [51-57]. It was shown that defect creation reduces dislocation mobility, and increases hardness [58]. Similarly, the nanolamellar structure confers some plasticity to Ti_3SiC_2 [17,24,59,60], and consequently the nuclear shocks could embrittle this material. Liu *et al.* studied the variation of hardness by nano-indentation of aluminum-doped Ti_3SiC_2 samples after irradiation with both 74 MeV Kr and 92 MeV Xe ions [35,36]; the substitution of silicon atoms by aluminum would be an effective way to eliminate TiC while increasing the resistance to oxidation of Ti_3SiC_2, and without changing its mechanical properties [61-63]. In these studies, they have actually shown an increase in hardness with ion fluence, as well as a decrease of the irradiation effect when the temperature increases. Moreover, for the highest fluences reached at room temperature (10^{19} and $2x10^{19}$ m^{-2} for 74 MeV Kr and 92 MeV Xe respectively), they have not noted any cracking at the indentation corners, indicating that Ti_3SiC_2 still retains some plasticity. However, the dpa generated by this irradiation at the surface (< 1 dpa, see Figure 1) are low compared with the dose required to cause the loss of the nanolamellar structure (Figure 3).

Contrary to what had been assumed previously [30], the evolution of lattice parameters appears to be due to nuclear shocks: first there is no change for irradiations with 930 MeV Xe ions, and second there is some strong variation for those with 4 MeV Au ions. To verify this hypothesis, we plotted the evolution of lattice parameters as a function of dpa for irradiations performed at room temperature (Figure 6). We have also added the values obtained for samples irradiated with 930 MeV Xe ions, and those for the sample irradiated at 298 K with 4 MeV Au ions to 10^{17} m^{-2} (0,038 dpa); for the latter one, the estimation of the a parameter is tarnished by a significant error due to the superposition of diffractograms of both virgin and irradiated areas.

After fitting the experimental data with arbitrary functions (linear for the a parameter and power of exponent between 0 and 1 for the c parameter, see Figure 6), it appears that changes in lattice parameters are directly attributable to nuclear shocks. The evolution of the unit cell volume (obtained from the functions determined for a and c) shows a maximum, as noted on the plot of the unit cell volume for irradiation with 92 MeV Xe ions at 298 K (Figure 4). Hence, it seems that there is a critical dose beyond which the volume of the unit cell decreases. This critical dose is estimated to be ~0.1 dpa: it corresponds to a fluence of $6.3x10^{18}$ m^{-2} for 92 MeV Xe ions, a result in accordance with Figure 4. Concerning the irradiations with 74 MeV Kr ions, the critical dose corresponds to a fluence of $1.2x10^{19}$ m^{-2}, so that the maximum was not reached for this irradiation (fluence up to 10^{19} m^{-2}). Eventually, according to the results obtained as a function of temperature (see variations of the unit cell volume in Figure 4), it seems that the critical dose increases with increasing temperature.

Results also show that nuclear shocks, certainly through the changes in lattice parameters, increase microstrains in Ti_3SiC_2. To obtain this conclusion, we assumed that the peak broadening is only due to microstrains, so that the crystallite size is large enough not to induce peak broadening. Liu *et al.* have also conducted such measurements on their materials ($Ti_3Si_{0,90}Al_{0,10}C_2$) after Rietveld refinement [34]. Thus, they have shown an increase of the microstrain yield, of the same order of magnitude for the same irradiations at the same temperatures; this result supports our hypothesis concerning the origin of the peak broadening.

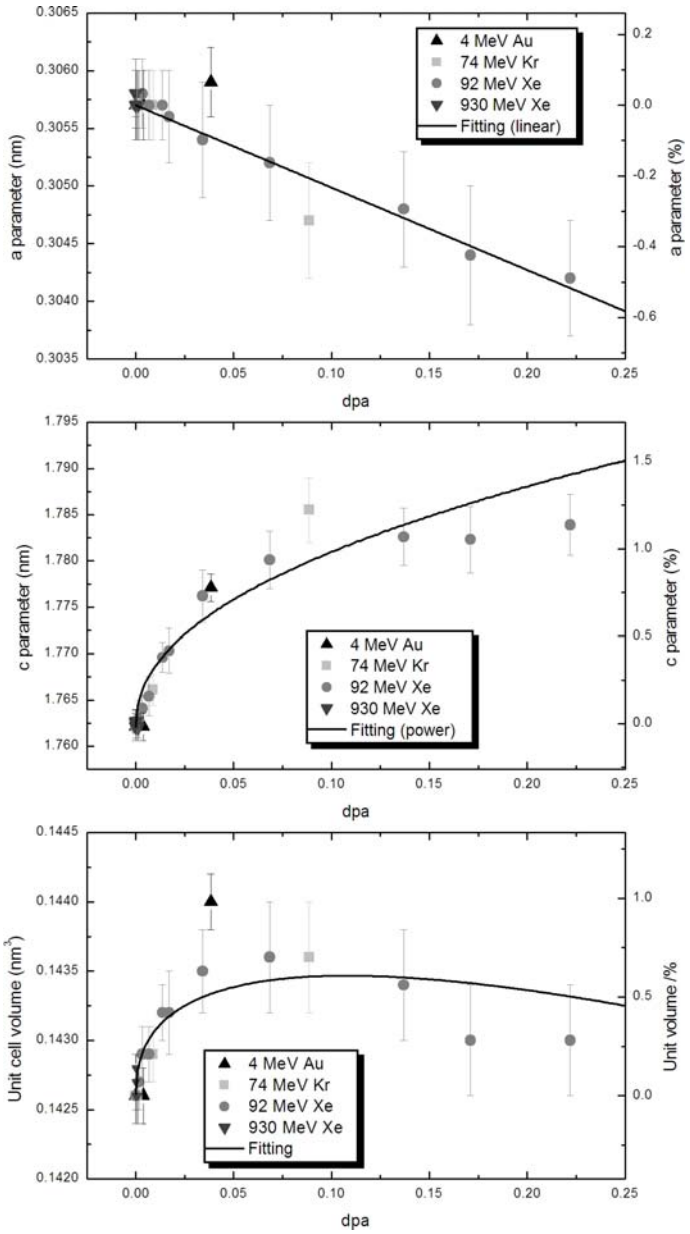

Figure 6: Change in lattice parameters as a function of the number of displacements per atom for irradiations performed at 298 K; the fitting curve of the unit cell volume data was obtained from those of a and c parameters.

The irradiations performed at high temperatures show a decrease in damage caused by nuclear shocks. Indeed, the creation of irradiation defects being an athermal phenomenon, an increase of the irradiation temperature increases the diffusion of species constituting a material. Therefore, the probability of recombination of Frenkel pairs (the main defect induced by nuclear shocks) increases with temperature, thereby reducing the effect of nuclear shocks. This result leads to the almost complete lack of damage in the sample irradiated at 1223 K, compared with the virgin sample, allowing Ti_3SiC_2 to be considered as a promising material for use as fuel cladding in the GFR.

Finally, by comparing this work with the one of Liu *et al.* [34], two results appear to be different. First, they noted for the high fluences, in both 74 MeV Kr and 92 MeV Xe, a difference in the relative intensities, and especially the intensity of the (102) peak that becomes larger than that of (101). This change, which is not noticeable in our diffraction patterns, would be due to the formation of β-Ti_3SiC_2 clusters in the irradiated area. Second, they did not report any change concerning the a parameter, regardless of the fluence. The origin of these discrepancies remains to be determined. However, possible explanations would be that either the materials studied are different (for instance concerning the effect of aluminum doping), or the techniques for both acquiring and processing diffraction data are not totally similar.

5. Conclusion

This work was devoted to the study of the structural behavior of Ti_3SiC_2 under irradiation. We first showed that this material is not sensitive to electronic interactions below 28 keV nm^{-1}. On the contrary, nuclear interactions greatly damage the structure of Ti_3SiC_2 without leading to amorphization. Ballistic collisions create defects that cause hardening of the material, and induce the loss of its nanolamellar structure that probably increase its brittleness. We also showed that nuclear interactions are the source of anisotropic changes in lattice parameters (expansion along c and contraction along a), which cause an increase of the unit cell volume up to a critical dose estimated at 0.1 dpa for irradiation performed at 298 K, and an increase of the microstrains in the crystal. An increase of the temperature of irradiation induce a significant decrease of the damage induced by nuclear interactions: Ti_3SiC_2 hence seems promising as an element of the GFR core component.

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