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# HEAVY IONS INDUCED DAMAGES IN Ti<sub>3</sub>SiC<sub>2</sub>: EFFECT OF IRRADIATION TEMPERATURE

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## ABSTRACT

Thanks to their refractoriness, carbides are sensed as fuel coating for the IV<sup>th</sup> generation of reactors. Among those studied, the Ti<sub>3</sub>SiC<sub>2</sub> ternary compound can be distinguished for its noteworthy mechanical properties: the nanolamellar structure imparts to this material some softness as well as better toughness than other classical carbides such as SiC or TiC. However, under irradiation, its behaviour is still unknown. In order to understand this behaviour, specimens were irradiated with heavy ions of different energies, then characterised. The choice of energies used allowed separation of the effects of nuclear interactions from those of electronic ones. Thus, AFM, SEM and XRD techniques allowed to note an important spoiling due to nuclear collision whereas electronic interactions would induce the formation of hills and the expansion of the unit cell. Irradiations at higher temperatures allowed to study the effect of temperature on these results.

Key words: Ti<sub>3</sub>SiC<sub>2</sub>, irradiation, heavy ions, AFM, SEM, XRD

## INTRODUCTION

As part of Generation IV International Forum (GIF), new systems are studied, from the point of view of the reactor as well as the fuel cycle. These systems are characterised by an increased security level, better economic competitiveness, and an ability to recycle all the fuel in order to upgrade to a fissionable material and minimize long-lived waste production by transmutation. Among the six systems considered by the GIF, the Gas Fast Reactor (GFR) is studied in France; it is designed to work under helium-pressure and high-temperature (1100-1300 K).

These working conditions led to the selection of non-oxide refractory ceramics as fuel coating. Thus, carbides turn out to be great candidates thanks to their remarkable mechanical and thermal properties. However, their behaviour under irradiation has to be studied in more details.

Among the studied carbides, the ternary Ti<sub>3</sub>SiC<sub>2</sub> presents some interesting prospects. Indeed, in 1972 Nickl *et al.*<sup>1</sup> remarked that this material, which was synthesized for the first time by a Viennese group in 1967<sup>2</sup>, is abnormally soft for a carbide. Actually, Pampuch *et al.*<sup>3,4</sup> and Lis *et al.*<sup>5-7</sup> demonstrated that this material is both stiff (Young's modulus of 325 GPa) and soft (Vickers hardness of 6 GPa). Moreover, like Goto *et al.*<sup>8</sup> some years before, they noted that the hardness of this carbide decreases as the applied load increases; this property led them to qualify Ti<sub>3</sub>SiC<sub>2</sub> as a “ductile ceramic”.

These interesting mechanical properties led to think about Ti<sub>3</sub>SiC<sub>2</sub> as fuel coating material; actually, its ability to be damage tolerant against mechanical solicitations was expected to be true against irradiations. Nevertheless, besides one paper to be published<sup>9</sup>, no information is available about its behaviour under irradiation.

Therefore, the aim of this study is a better knowledge of the behaviour under irradiation of  $\text{Ti}_3\text{SiC}_2$ , and more particularly the effect of the irradiation temperature.

## EXPERIMENTAL

The studied material is a polycrystalline commercial compound provided by 3-ONE-2 (Voorhees, NJ, USA). Pure bulk of  $\text{Ti}_3\text{SiC}_2$  is quite difficult to synthesize: the as-received material consists of about 80 %  $\text{Ti}_3\text{SiC}_2$ , 15 %  $\text{TiC}$ , and 5 %  $\text{TiSi}_2$  (estimation by X-Ray Diffraction). Figure 1 shows the surface state of the as-polished specimens through Atomic Force Microscopy (AFM); the lower hardness of  $\text{Ti}_3\text{SiC}_2$  compared with the  $\text{TiC}$  and  $\text{TiSi}_2$  phases can be noted.

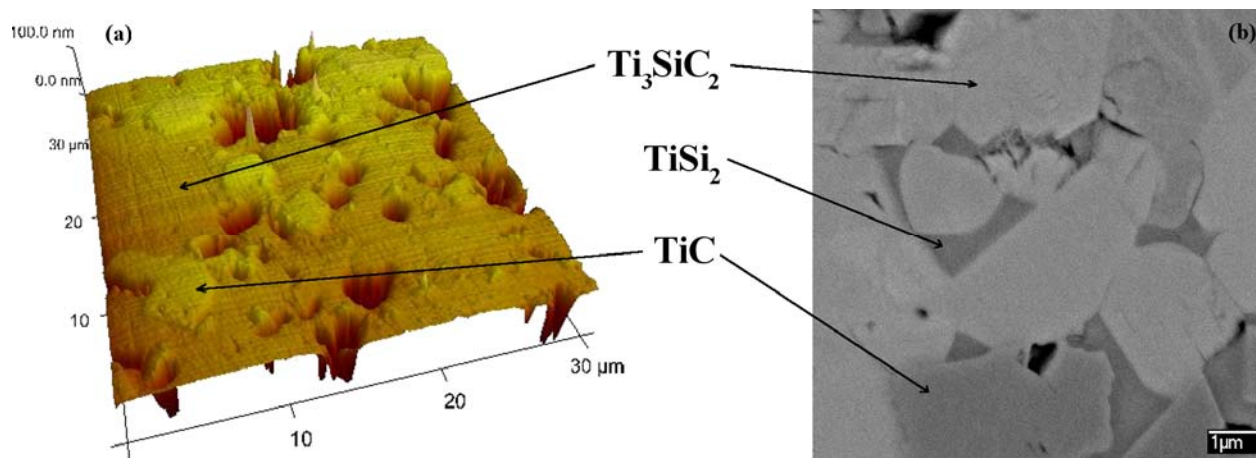


Figure 1. Surface of as-polished  $\text{Ti}_3\text{SiC}_2$  by (a) AFM and (b) back-scattered electrons FEG-SEM.

The as-received specimens were polished with diamond suspensions down to 1  $\mu\text{m}$ . They were subsequently irradiated with heavy ions. This kind of irradiation aims to simulate the interactions present in reactors (impacts of fission products, recoil atoms of alpha-decays, and neutrons) without the drawback of activating the specimens.

When heavy ions penetrate through a solid, they get decelerated *via* two different processes, namely, elastic collisions with target nuclei (with nuclear stopping power  $S_n$ ) and inelastic collisions with target electrons (with electronic stopping power  $S_e$ ). In order to understand the effects of both nuclear and electronic interactions on  $\text{Ti}_3\text{SiC}_2$ , two kinds of irradiation were performed.

The first one, named “high energy irradiation”, was made with ions delivered by the IRRSUD accelerator at the GANIL (Caen, France). The energy of these ions reaches several dozen of MeV; for this range of energy, ion path consists in a long zone of electronic interactions (some microns) at the end of which nuclear collisions occur. Thus, studying only the first microns, effects of electronic interactions can be understood. In order to study the effect of electronic stopping power, two different ions were used at the GANIL: 74 MeV Kr and 92 MeV Xe ions, which respectively lead to a maximum electronic stopping power of 15.6 and 21.3  $\text{keV nm}^{-1}$ . Irradiations with Kr were carried out at room temperature (RT) and 773 K whereas the ones with Xe were at RT and 573 K.

The second one, called “low energy irradiation”, was achieved with the 4 MeV Au ions of the ARAMIS accelerator at the CSNSM (Orsay, France). This kind of irradiation essentially leads to nuclear collisions. This irradiation was carried out at RT, 773 K and 1223 K.

Each kind of irradiation was carried out for 4 ion fluences:  $10^{12}$ ,  $10^{13}$ ,  $10^{14}$ , and  $10^{15} \text{ cm}^{-2}$ ; the fluence is the number of ion by surface unit. The Table I gives some irradiation parameters determined by the TRIM code<sup>10</sup>.

Table I. Irradiation parameters

Ion	Au	Kr	Xe
Mass (amu)	197	86	129
Energy (MeV)	4	74	92
Projected range ( $\mu\text{m}$ )	0.52	7.81	7.60
Nuclear stopping power (keV/nm)	3.29	0.07	0.16
Electronic stopping power (keV/nm)	4.0	15.6	21.3

To characterise surface modifications to the samples, two microscopic methods were used: Field Emission Gun Scanning Electron Microscopy (FEG-SEM) and AFM. The structure of the irradiated zone was analysed by Low Incidence X-Ray Diffraction (LI-XRD) technique.

## RESULTS

### Low Energy Irradiations

The irradiations performed with 4 MeV Au ions essentially lead to nuclear shocks, which generally cause an important disorder in the materials. As noted elsewhere<sup>9</sup>, this disorder is visible on diffractogrammes from a fluence of  $10^{14} \text{ cm}^{-2}$  for irradiations performed at RT, whatever the phase.

The samples irradiated at high temperatures (773 K and 1223 K) have not yet been characterized by LI-XRD. Nevertheless, we hope to observe a decrease of disorder due to a greater mobility of atoms making up the samples and to an annealing of the defects by the temperature. This decrease would be a good result if we consider the nominal operating temperatures of the GFR.

In terms of surface conditions, no changes were found before a fluence of  $10^{15} \text{ cm}^{-2}$ . At room temperature, we noticed a microstructure that we attributed to a sputtering depending on the orientation of crystallites<sup>9</sup>. It is interesting to note that this microstructure is less pronounced during irradiation carried out at 773 K, regaining a microstructure similar to the as-polished specimen for irradiation at 1223 K (cf. Figure 2).

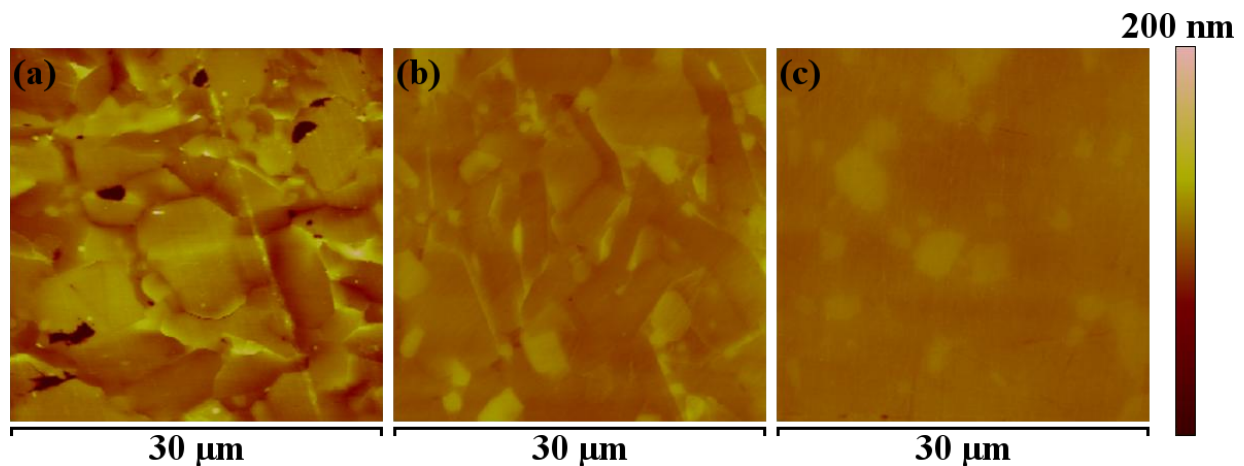


Figure 2. Surface of  $\text{Ti}_3\text{SiC}_2$  after a  $10^{15} \text{ cm}^{-2}$  4 MeV Au irradiation at (a) RT, (b) 773 K, and (c) 1223 K.

### High Energy Irradiations

Concerning the high-energy irradiations, we noted by LI-XRD some disorder from  $10^{14} \text{ cm}^{-2}$  for 92 MeV Xe irradiation at RT, but only for phase  $\text{Ti}_3\text{SiC}_2$ ; this disorder is noticeable through a rise of the baseline. Moreover, we noticed an expansion of the hexagonal unit cell of  $\text{Ti}_3\text{SiC}_2$  along c axis without change in the unit volume<sup>9</sup>. This result is also true for 74 MeV Kr irradiation at RT.

The temperature has two effects on XRD results. First, a drop-off of the rise of baseline shows a decrease of the disorder as a function of temperature. Second, the unit cell is less expanded for irradiation with 92 MeV Xe at 573 K to be almost unchanged compared with virgin sample for the irradiation with 74 MeV Kr at 773 K. Note that whatever the irradiation, the change of the unit cell parameters occurs at constant unit volume (cf. Figure 3).

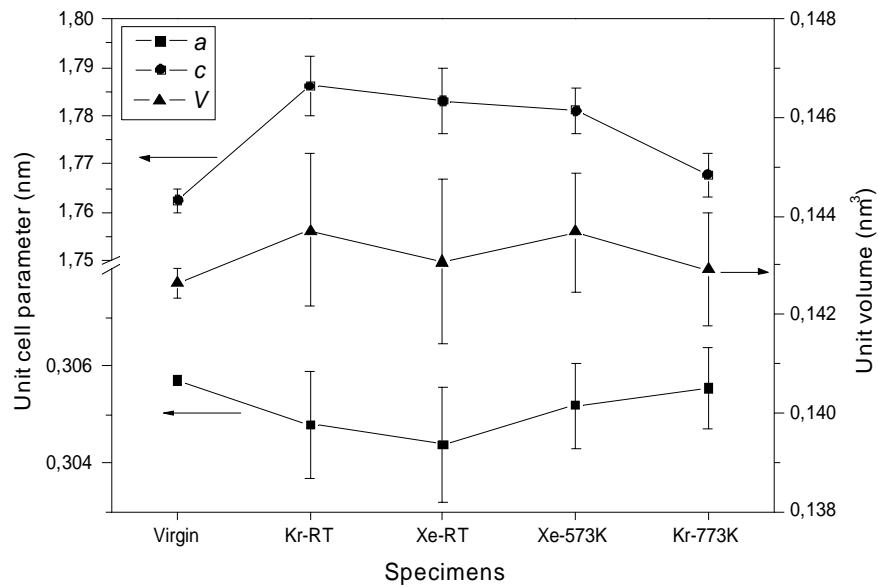


Figure 3. Evolution of  $\text{Ti}_3\text{SiC}_2$  unit cell parameters as a function of irradiation parameters for high energy irradiation; lines are only to guide the eye.

With regard to the change in the surface, the first notable point that, unlike irradiation with 92 MeV Xe at RT, the 74 MeV Kr irradiation does not cause changes whatever the fluence or temperature. Concerning the 92 MeV Xe irradiation, we underlined the formation of hills on  $\text{Ti}_3\text{SiC}_2$  phase and a revelation of the microstructure due to a different behaviour under irradiation of the secondary phases against  $\text{Ti}_3\text{SiC}_2$ <sup>9</sup>. The difference that is noted for these two high-energy irradiation suggests the existence of an electronic stopping power threshold beyond which there is modification of the surface of the samples.

At 573 K, the surface state of our samples after 92 MeV Xe irradiation is quite similar to irradiations at RT. However, if the revelation of microstructure is always obvious, we can notice that the shape of the hills slightly varies; actually, as shown in Figure 4, they seem larger than for irradiation at RT. This coalescence phenomenon could be compared with the one noted during sintering, suggesting a transfer of matter by temperature.

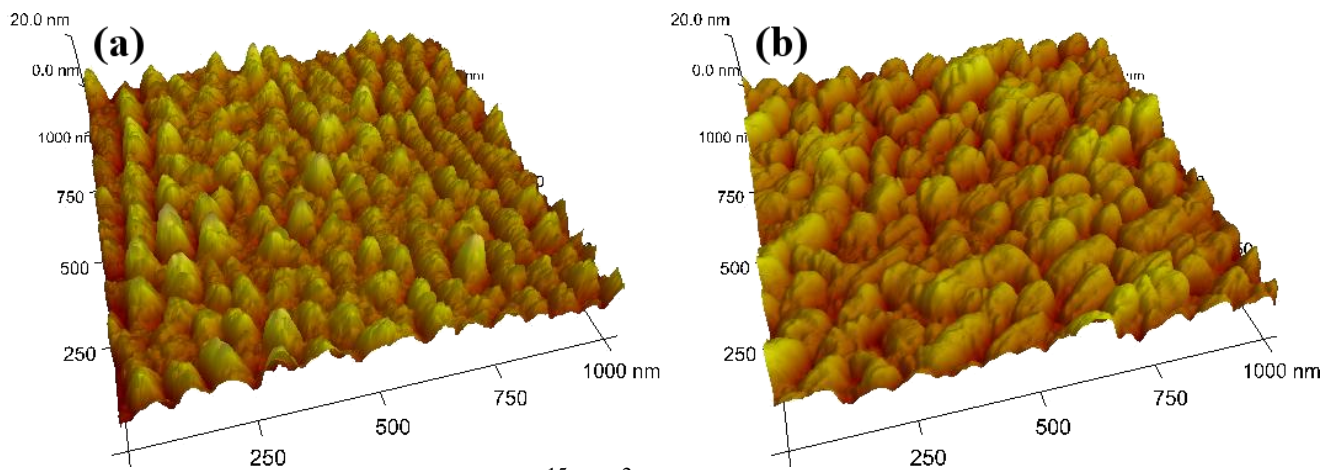


Figure 4. Surface of  $\text{Ti}_3\text{SiC}_2$  after  $10^{15} \text{ cm}^{-2}$  92 MeV Xe irradiation at (a) RT and (b) 573 K.

## CONCLUSION

In this study, we demonstrated a different behaviour of  $\text{Ti}_3\text{SiC}_2$  under low energy and high energy irradiation. Thus, if the nuclear shocks tend to create an important disorder as well as a sputtering of the surface, the electronic interactions essentially cause an expansion of the unit cell along c axis and the formation of hills beyond an electronic stopping power threshold between 15.6 and 21.3  $\text{keV nm}^{-1}$ .

Temperature seems to have two different effects. The first one, as it can be noticed in other carbides like  $\text{SiC}^{11-14}$ , is an annealing effect of the irradiation defects: decrease of disorder whatever the irradiation, of unit cell expansion due to high energy irradiations, and of the surface changes for the 4 MeV Au irradiation. The second one is the enlarging of the hills. We understand this effect as a transfer of matter due to both the temperature and the electronic interactions.

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## REFERENCES

- <sup>1</sup>J.J. Nickl, K.K. Schweitzer, P. Luxenberg, Gasphasenabscheidung im Systeme Ti-C-Si, *J. Less-Common Metals*, **26**, 335-353 (1972).
- <sup>2</sup>W. Jeitschko, H. Nowotny, Die Kristallstruktur von  $\text{Ti}_3\text{SiC}_2$  - ein neuer Komplexcarbidge-Typ, *Monatsh. Chem.*, **98**, 329-337 (1967).
- <sup>3</sup>R. Pampuch, J. Lis, L. Stobierski, M. Tymkiewicz, Solid Combustion Synthesis of  $\text{Ti}_3\text{SiC}_2$ , *J. Eur. Ceram. Soc.*, **5**, 283 (1989).
- <sup>4</sup>R. Pampuch, J. Lis, J. Piekarczyk, L. Stobierski,  $\text{Ti}_3\text{SiC}_2$ -based materials produced by self-propagating high temperature synthesis and ceramic processing, *J. Mater. Synth. Process.*, **1**, 93 (1993).
- <sup>5</sup>J. Lis, R. Pampuch, L. Stobierski, Reactions during SHS in a Ti-Si-C system, *Int. J. Self-Propag. High-Temp. Synth.*, **1**, 401 (1992).
- <sup>6</sup>J. Lis, R. Pampuch, J. Piekarczyk, L. Stobierski, New ceramics based on  $\text{Ti}_3\text{SiC}_2$ , *Ceram. Int.*, **19**, 219 (1993).
- <sup>7</sup>J. Lis, Y. Miyamoto, R. Pampuch, K. Tanihata,  $\text{Ti}_3\text{SiC}_2$ -based materials prepared by HIP-SHS techniques, *Mater. Lett.*, **22**, 163-168 (1995).
- <sup>8</sup>T. Goto, T. Hirai, Chemically vapor-deposited  $\text{Ti}_3\text{SiC}_2$ , *Mater. Res. Bull.*, **22**, 1195-1201 (1987).

<sup>9</sup>J.C. Nappé, Ph. Grosseau, F. Audubert, B. Guilhot, M. Beauvy, M. Benabdesselam, I. Monnet, Damages induced by heavy ions in titanium silicon carbide: effects of nuclear and electronic interactions at room temperature, *J. Nucl. Mater.*, in press.

<sup>10</sup>J.F. Ziegler, <http://www.srim.org/>.

<sup>11</sup>S. Zinkle, L. Snead, Influence of irradiation spectrum and implanted ions on the amorphization of ceramics, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms*, **116**,92-101 (1996).

<sup>12</sup>W. Weber, N. Yu, L.M. Wang, N.J. Hess, Temperature and dose dependence of ion-beam-induced amorphization in  $\alpha$ -SiC, *J. Nucl. Mater.*, **244**,. 258-265 (1997).

<sup>13</sup>W. Weber, W. Jiang, S. Thevuthasan, Accumulation, dynamic annealing and thermal recovery of ion-beam-induced disorder in silicon carbide, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms*, **175-177**, 26-30 (2001).

<sup>14</sup>W. Weber, L.M. Wang, N. Yu, N.J. Hess, Structure and properties of ion-beam-modified (6H) silicon carbide, *Mater. Sci. Eng., A*, **253**, 62-70 (1998).