He⁺ Irradiation Induced Cracking and Exfoliating on the Surface of Ti₃AlC₂

H. H. Shen^{1,2}, L. Ao³, F. Z. Li¹, S. M. Peng¹, H. B. Zhang^{1*}, K. Sun², X. T. Zu^{3*}

¹Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900,
China

² Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109,
USA

³ School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu
610054, China

* Author to whom correspondence should be address;
E-mail address: xtzu@uestc.edu.cn (X.T. Zu), hbzhang@caep.cn (H. B. Zhang).
Tel.: +86 28 83202130 (X.T. Zu), +86 816 2497408 (H. B. Zhang).

Abstract

We report a systematic study of the effects of a 400 keV helium ion beam irradiation on the surface morphology and crystal structure of Ti_3AlC_2 by combined scanning electron microscopy, grazing incidence X-ray diffraction and transmission electron microscopy. Helium irradiation experiments were performed at both room temperature and 500 °C, respectively, with fluence up to $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$. After irradiation, intragranular orientated cracks grew along the $(10\bar{1}0)_{\text{Ti}_3\text{AlC}_2}$ plane and the surface has started to exfoliate. The formation of the cracks is mainly attributed to the reduction of the lattice parameter along the a direction induced by ion irradiation, and the crack growth is affected by the grain size and the content of impurity phase TiAl_3 . The surface exfoliation is due to the blistering of He bubbles at the projected depth.

Keywords: MAX; Ti_3AlC_2 ; Helium irradiation; Orientated cracks; Surface exfoliating.

1 Introduction

$M_{n+1}AX_n$ (MAX) phases [1, 2], with M is an early transition metal, A is an A-group element (mostly IIIA and IVA), and X is either C and/or N, have been attracting much attention since Nowotny [3] synthesized a large number of carbides and nitrides. Fabrication and characterization of new types of MAX phases were developed by Barsoum *et al.* in 1990s [1, 2]. A MAX phase usually has a hexagonal structure with the $P6_3/mmc$ symmetry. Its structure is comprised of two-dimensional closed packed A layers linked by Ti_6C octahedra [2]. The MAX phases show a combined properties of both metal and ceramic, such as good electrical and thermal conductivity, excellent thermal shock resistance, high elastic stiffness as well as easy machinability [1-6]. Over 70 MAX phases [4] have been synthesized or theoretically predicted. Some of such phases have also been reported to have good irradiation damage tolerance [7-16], which leads them to be candidate materials for future fission and fusion reactors with much higher burn-up, requiring the materials to survive up to 200 dpa [17, 18].

Ti_3AlC_2 [10, 12, 13, 19, 20] and Ti_3SiC_2 [7, 14, 21, 22] are two major MAX phases. Their irradiation resistances subjected to ion irradiation, such as He [11-13, 21, 23] and heavy ions [14, 16, 22, 24-27], have been investigated. Heavy Au and Xe ion irradiations have been performed on Ti_3SiC_2 to differentiate the effects due to nuclear and electronic interaction [16, 22]. Phase transition from α -phase to β -phase was observed in Ti_3AlC_2 after 7 MeV Xe^{26+} irradiation [28, 29]. Electron irradiation on Ti_3AlC_2 has been explored by Huang *et al.* [30] to analyze the formation mechanism of Frenkel pairs. Very recently, Tallman *et al.* [7, 8] studied the effect of neutron irradiation on several MAX phases and found that irradiation had resulted in lattice distortion of Ti_3SiC_2 and formation of dislocation loops. Irradiation tolerances of different MAX phases have also been theoretically studied [9, 19]. In addition, Flem *et al.* [31] performed in-situ TEM studies to

elucidate the irradiation damage and deformation mechanism on a very small scale.

It should be mentioned that full amorphization of the MAX phases has not been observed even under irradiation with dose up to 52 dpa with the experiments performed either [10, 13, 24] at room temperature (RT) [13] or high temperatures [24]. This was attributed to the A layer atoms offering spaces to accommodate structure defects [7, 9] and the formation of nanograins providing higher density of boundaries. Nevertheless, irradiation induced substantial crystal structure defects [12, 14, 27, 31], volume expansion [24, 27] and the dissociation of Ti_3SiC_2 to TiC [8, 11], have been reported to cause the volumetric swelling [32]. Surface microcracks were also observed by Ang *et al.* [32] in neutron irradiated Ti_3AlC_2 samples which were attributed to irradiation induced anisotropic swelling and microstrain [7, 29, 32]. Significant grain boundary cracking has been observed in Ti_3AlC_2 and Ti_2AlC under Ni^{4+} irradiation at 400 °C, but not in Ti_3SiC_2 [25].

Although the effects of He irradiation on Ti_3AlC_2 at RT and 500 °C have been reported by Wang *et al.* [13], Yang *et al.* [10] and Patel *et al.* [12], respectively. A systematic investigation of irradiation damage with respect to He fluence and temperature is still limited in the literature. The mechanisms of the He bubble evolution and the formation of microcrack have not been well understood. In the present study, we report our systematical study on the surface microstructure evolution of Ti_3AlC_2 bulk samples irradiated with a 400 keV He^+ at both RT and 500 °C.

2 Experimental methods

2.1 Sample preparation

The Ti_3AlC_2 samples used in this study were synthesized by a hot pressing method. Commercially available Ti (99%, 200 mesh), Al (99%, 300 mesh) and graphite (99%, 200 mesh) powders with a molar ratio of 3:1.1:1.88 were weighed and used as the starting

materials for fabricating Ti_3AlC_2 . The three powders were firstly dry mixed in a resin jar, followed by ball milling for 12 hours and then sieved. The mixed powders were put into a graphite die and were compressed uniaxially at 5 MPa. Then they were heated up to 1500 °C under an Ar atmosphere for 1 hour. Finally, the as-obtained bulk samples were cooled down to RT and were held for 5 minutes before releasing the pressure. The final samples were collected for further testing after their surface contaminations had been removed.

All samples for He irradiations were cut into pieces with size of approximate 5 mm (L) $\times$ 5 mm (W) $\times$ 3 mm (T) from the bulk samples by a diamond saw. Prior to irradiation, these samples were firstly mechanically grinded with wet SiC paper (grit 320-2400) and were subsequently polished using colloidal alumina with 1 μm and then 0.05 μm grades to obtain fresh and smooth surfaces.

2.2 Helium irradiation

The irradiation parameters were designed based on simulation using SRIM program that is commonly used to predict the local dose of implanted ion species in solid materials [33, 34]. SRIM code was also used to calculate the irradiation induced damage and He concentration in the matrix after He irradiation. The displacement energies used for Ti, Al and C are 25 eV, 25 eV and 28 eV [11], respectively. It should be mentioned that Ti_3AlC_2 is a highly anisotropic crystalline material, the experimental ion penetration depth and irradiation damage may deviate from the calculated value as SRIM assumes an amorphous/isotropic material.

He irradiation experiments were conducted at Michigan Ion beam Laboratory (MIBL) in University of Michigan [35]. The irradiation parameters are listed in Table 1. All the implantations were performed at an energy of 400 keV resulting in a calculated project range of 1330 nm with the ion beam being incident normal to the surfaces of the samples.

The irradiations were performed at RT and 500 °C, respectively, with He fluence up to $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$ at a helium flux of $0.78 \times 10^{14} \text{ He}^+/(\text{cm}^2 \cdot \text{s})$. Figure 1 shows SRIM calculated irradiation induced damage (dpa) as a function of depth. It shows that the damages of 2.1 dpa, 4.2 dpa and 8.4 dpa at the depth of 1330 nm are in correspondence with the fluencies of $0.5 \times 10^{17} \text{ He}^+/\text{cm}^2$, $1.0 \times 10^{17} \text{ He}^+/\text{cm}^2$ and $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$, respectively. The He concentration at the projected depth increases from 3.2 at.% for the $0.5 \times 10^{17} \text{ He}^+/\text{cm}^2$ fluence to 11.6 at.% for the $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$. To be convenience in the following statements, the samples were designated and tabulated in Table 1 as LT2.1, LT4.2, LT8.4 for RT irradiations and HT2.1, HT4.2, HT8.4 for high temperature (500 °C) irradiations based on the irradiation temperature and fluence.

2.3 TEM specimen preparation

Cross-sectional transmission electron microscopy (TEM) specimens with thickness of ~100 nm were prepared by a focused ion beam (FIB) in-situ lift-out technique using a Helios 650 Nanolab workstation [36, 37]. Firstly, a platinum protection layer was deposited over the area of interest ($15 \text{ } \mu\text{m} \times 2 \text{ } \mu\text{m}$) prior to ion beam cutting to protect the surface from ion damage. Then, two large stair-step trenches were made by the ion beam on both sides of the Pt deposited area leaving a thin lamella which was subsequently pre-thinned to a thickness of about 1 μm before cutting its bottom and the two vertical sides at a low angle. The lamella was then transferred and glued onto a TEM half-grid. Finally, the specimen was thinned down to ~100 nm at 5 keV with a beam current of 12pA.

2.4 Microstructure characterizations

The crystal structures of the samples were examined by a grazing incidence X-ray diffraction (GIXRD) using an X'pert PRO MPD (Panalytical, Holland) with a Cu $K\alpha$

radiation working at 40 kV and 40 mA. The GIXRD patterns were collected using a step size of 0.02° in the 30° - 45° 2θ range, with a step time of 3s. The grazing angle was set at 2.3° corresponding to an X-ray penetration depth of 1350 nm. This was calculated by the Mass-Absorption-Calculator in X'Pert Highscore software using a density of Ti_3AlC_2 4.5 g/cm^3 [1, 2]. The surface microstructures of the original and irradiated samples were studied using a scanning electron microscope (SEM) (Helios 650 Nanolab workstation, FEI Company, USA) with an EDAX energy dispersive spectroscopy (EDS) system attached for mapping the element distributions of Ti, Al and C. The SEM was operated at 20 kV with a current of 0.8 nA. Additionally, the samples were also examined by bright-field image (BF), annular dark-field image (ADF) and selected area electron diffraction (SAED) in a JEOL 2010F TEM operated at 200 kV in both TEM and STEM modes.

3 Results

3.1 Microstructure of Ti_3AlC_2 original sample

Figure 2(a) is a SEM image showing the surface morphology of the Ti_3AlC_2 original sample which shows that the Ti_3AlC_2 has a lath-shaped microstructure with grain size (in length) ranging from $\sim 20 \text{ }\mu\text{m}$ to $\sim 60 \text{ }\mu\text{m}$. Fig. 2(b) and 2(c) show Ti and Al element maps collected from the area shown in Fig. 2(a). Fig. 2(d) shows the GIXRD pattern collected from the original sample. It can be concluded from the GIXRD pattern that the original sample consists of majority of Ti_3AlC_2 phase and a few of TiAl_3 impurity phase (PDF 065-7847). The Ti_3AlC_2 has a hexagonal structure with $P6_3/mmc$ symmetry and the lattice parameters (LP) are $a = 0.3072 \text{ nm}$ and $c = 1.8496 \text{ nm}$. The TiAl_3 has a tetragonal structure with $I4/mmm$ symmetry.

The crystal structure of the Ti_3AlC_2 sample was further identified by SAED in a TEM.

Fig. 3(a) and 3(b) show the STEM-ADF image and Al element map of the original sample. The SAED patterns taken from the Al-enrich area and the dark area were shown in Fig. 3(c) and 3(d), which were indexed as Ti_3AlC_2 and TiAl_3 phases with the zone axis of $[10\bar{1}0]$ and $[110]$, respectively. To confirm the crystal structure of the impurity phase, four SAED patterns (not shown) were taken along a different zone axis by tilting the TEM double-tilt holder to reconstruct the crystal.

3.2 He irradiation induced surface damages

Figure 4 shows a series of SEM images for the samples irradiated at RT (first row) and 500 °C (second row), respectively. On the surface of the LT2.1 sample, a great many of intragranular cracks were seen to form after irradiation. The cracks grew parallel to the c direction of the Ti_3AlC_2 crystal. With the increase of He fluence, surface exfoliating began for the LT4.2 sample, as shown in Fig. 4(b), in which the inset presents a magnified image of the surface exfoliating area. The exposed fresh surface is not flat. The layered structure of the Ti_3AlC_2 phase is confirmed and the cracks grow along the c direction. As shown in Fig. 4(c), the features of orientated cracks and surface exfoliating can also be found in the LT8.4 sample. It was evident that the number of orientated cracks and area density of surface exfoliating were remarkably increased with irradiation dose increasing up to 8.4 dpa.

Compared to the LT2.1 sample, there was no obvious change in the surface of the HT2.1 sample irradiated at 500 °C, which is in agreement with the experimental observation by Huang *et al.* [29], as shown in Fig. 4(d). Once the irradiation fluence has reached 4.2 dpa, the microcracks indicated by arrows started to become visible, implying that the formation of orientated cracks was related to the irradiation dose. With the dose being further increased to 8.2 dpa, there have formed much more orientated cracks

accompanied by the presence of surface exfoliations. Helium irradiation induced the anisotropic swelling in the structure of Ti_3AlC_2 , which causes the formation of the cracks [32]. The aggregation of He bubbles at the projected depth results in surface blistering [13] and then evolves to the observable surface exfoliating with the increasing He fluence, as shown in Fig. 4(f). In this case, the exposed surface in the exfoliating area is smooth, which is comparative to that induced by anisotropic swelling. The surface exfoliation was not observed in the Ti_3AlC_2 sample with He implanted even up to $1.0 \times 10^{18} \text{ He}^+/\text{cm}^2$ using an accelerating energy of as low as 50 keV [13]. Above all, the irradiation parameters, including irradiation fluence, temperature and ion energy, play very important roles in the formation of surface damages by ion irradiation.

3.3 He irradiation induced crystal structure defects

Figure 5 and Figure 6 show BF images and SAED patterns for Ti_3AlC_2 samples irradiated at RT and 500 °C, respectively. It can be seen that He irradiations result in damaged surface layers with thickness being in accordance with the SRIM simulation. To analyze the irradiation induced defects in the Ti_3AlC_2 crystal, two SAED patterns were taken from the irradiated and non-irradiated areas in a same Ti_3AlC_2 grain.

Three TEM specimens were prepared by FIB from the RT irradiated samples across the cracks. It is clear that the cracks pass through the whole irradiated layer and extend to the non-irradiated bulk. Fig. 5(b) and 5(c) show the SAED patterns from the irradiated and non-irradiated areas marked in Fig. 5(a). Both of patterns can be indexed as Ti_3AlC_2 with zone axis of [0001] and have no remarkable differences. Combining Fig. 5(a) with Fig. 5(b), it is determined that the crack grows along the $(10\bar{1}0)$ crystal plane of the Ti_3AlC_2 phase. This is an interesting phenomenon since the crack is favorably formed along the Al atom layer that was expected by theoretical calculation [9]. The cracks were also observed

for samples irradiated to 4.2 dpa and 8.4 dpa. The preferential direction of those cracks were confirmed to be $(10\bar{1}0)$ crystal plane by SAED patterns with zone axis of $[08\bar{8}1]$ for Fig. 5(e) and $[04\bar{4}1]$ for Fig. 5(h). No significant change can be found from the SAED patterns after irradiation. As the irradiation induced defects in Ti_3AlC_2 prefer to accumulate in the Al layer, it may not clear to see the defects from the viewing direction close to c -axis.

No cracks were seen in the sample irradiated at 500 °C, which is in accordance with the results obtained from SEM images. Fig. 6(b) and 6(c) show the SAED patterns of the HT2.1 sample taken from the non-irradiated and irradiated areas marked in Fig. 6(a), respectively along the $[21\bar{3}0]$ zone axis of Ti_3AlC_2 . With the increase of irradiation to 2.1 dpa, all the diffraction spots become more or less diffused, indicating the production of point defects. Some of diffraction spots in Fig. 6(c) (labeled by arrows) change to be much brighter, while others become weaker. It should be mentioned that the labeled spots can also be indexed as TiC with fcc structure along $[101]$ direction, implying the dissociation of Ti_3AlC_2 to TiC. The formation of TiC has been reported by Tallman *et al.* and Song *et al.* [8, 11] in the samples by neutron and He ion irradiation. With fluence increasing up to 4.2 dpa, all of the spots viewed from $[10\bar{1}0]$ direction change to be significantly diffused, which is likely due to the production of much more structural defects. Once the dose had reached to 8.4 dpa, most of the diffraction spots became weaker and even disappeared in the SAED patterns with the rest no longer circular, forming a polycrystalline ring pattern. These transformations were attributed to the structure distortion or the disappearance of Ti_3AlC_2 nanolamellar structure [29]. The diffraction spots labeled in Fig. 6(h) for Ti_3AlC_2 phase can also be indexed as twin crystal of TiC phase with an angle of 110° along $[110]$ viewing direction. The labeled spots of TiC overlap with those polycrystalline rings, which indicates that He irradiation causes the Ti_3AlC_2 grain broken and leads to the formation of

TiC nanograins [14]. Diffraction patterns with complete amorphous ring-like features were not obtained even from the sample irradiated at the highest irradiation dose, indicating the excellent irradiation resistance of Ti_3AlC_2 .

Figure 7 shows the GIXRD patterns collected from the original samples irradiated to different fluences at RT (lower part) and 500 °C (upper part), respectively. All of the patterns were indexed as Ti_3AlC_2 phase with the three major peaks labeled as $(10\bar{1}3)$, $(10\bar{1}4)$ and $(10\bar{1}5)$. It should be pointed out that subtle changes were found on $(10\bar{1}3)$ and $(10\bar{1}4)$ peaks. The $(10\bar{1}3)$ peak shifts towards the higher 2θ angle while the $(10\bar{1}5)$ peak shifts towards the lower angle, suggesting that a crystal distortion occurred after irradiation. At RT, the position of $(10\bar{1}5)$ peak continuously drops with the increasing He fluence. However, the crystal structure of Ti_3AlC_2 is not further modified with the He fluence for 500 °C irradiations. The Ti_3AlC_2 structure parameters of Ti_3AlC_2 , a -LP, c -LP and cell volume, were derived from the GIXRD patterns and tabulated in Table 2.

At RT, reduction of a -LP and expansion of c -LP, leading to the volume expansion, were observed in the sample irradiated to 2.1 dpa, as shown in Fig. 8(a). However, with the fluence increasing from 2.1 dpa to 8.4 dpa, the reduction of a -LP changes from 0.65% to 0.16% and the expansion of c -LP drops from 3.61% to 1.09%. The two major peaks (111) and (002) of TiC overlap with the $(10\bar{1}3)$ and $(10\bar{1}5)$ peaks of Ti_3AlC_2 . The intensity of the $(10\bar{1}4)$ peak is highest in the Ti_3AlC_2 phase. As shown in Table 2, both of the relative intensity of $(10\bar{1}3)/(10\bar{1}4)$ and $(10\bar{1}5)/(10\bar{1}4)$ are remarkably increased with the He fluence, suggesting that the dissociation of Ti_3AlC_2 to TiC occurred during irradiation [8, 11]. The bonding between Ti and Al is weaker relative to Ti-C bonds, which can induce the removal of Al layer leaving the TiC unchanged [13]. At 500 °C, the continuous reduction of a -LP and expansion of c -LP were found with the increasing He fluence, which is contrary to the result from the RT irradiation. The He bubbles aggregating at Al layer

induce the c -LP expansion and volume expansion, as shown in Fig. 8(b) [12, 13]. From the intensity ratios of $(10\bar{1}3)/(10\bar{1}4)$ and $(10\bar{1}5)/(10\bar{1}4)$, the formation of TiC phase was confirmed, which is in good agreement with the SAED result.

4 Discussions

Microcracks have been observed by Huang *et al.* [29] and Ang *et al.* [32] in Xe²⁶⁺ and neutron irradiation Ti₃AlC₂. However, there was not any report on the formation of orientated cracks in He ion irradiated Ti₃AlC₂. The cracks reside in the $(10\bar{1}0)$ plane of Ti₃AlC₂. Clark *et al.* [25] found that significant surface cracking occurred in Ni⁴⁺ irradiated Ti₃AlC₂ and Ti₂AlC at 400 °C to 30 dpa, but no significant cracking was observed for those samples irradiated at 700 °C to the same dose. Those microcracks found before were disordered and were expected to be associated with the anisotropic swelling and significant stresses in the irradiated area [29]. It is well known that the Al layer, having larger lattice space, represents nano-scale interfaces that function as natural sinks for point defects [7, 32]. Therefore, it is easily understood that the microcracks grow along the c -plane, which is in comparison to our findings. The interaction between Ti and C atoms is quite strong [1, 9, 19, 21, 38], it is hard for the cleavage between TiC grains.

Figure 9 shows the atomic arrangement of Ti₃AlC₂ crystal structure viewing from $[11\bar{2}0]$ direction. As known by Nowotny [3], the structure of Ti₃AlC₂ is constructed by a 2-dimension close-packed Al intercalating into the TiC lattice [21]. TiC twin crystals with angle of 110° are separated by the Al layer [1]. As can be seen from Fig. 9, the (111) and (002) planes of TiC phase are parallel to the $(10\bar{1}3)$ and $(10\bar{1}5)$ of Ti₃AlC₂ phase. For fcc-TiC, the {111} planes are the habit planes with low defect formation energy. So, the implanted He atoms are favorably incorporated into the {111} planes [39] inducing the TiC lattice expansion. This expansion and the accumulation of He bubbles in the Al layer were

thought to contribute to the c -LP expansion of Ti_3AlC_2 . The irradiation could also produce a lot of point defects, which leads to the shrinkage of the TiC cell volume, and then causes the decrease of the a -LP of Ti_3AlC_2 phase. It was proposed that the formation of orientated cracks is strongly related to the a -LP reduction. The formation of the crack in a crystal structure is equal to the introduction of new grain boundary that can trap He atom. The post-implanted He atoms would migrate to the crack to form bubbles rather than preferred to the Al layer. The crystal structure starts to relax and lose internal stress due to the formation of cracks, which leads to the recovery of structure with the increasing He fluence. However, the number of crack increases remarkably with the fluence due to the He bubble aggregation along $(10\bar{1}0)$ plane. The c -LP expansion between grains causes the phenomenon of surface exfoliation.

In contrast to RT irradiations, there is no crack observed in the surface of HT2.1. The main reason of this difference is due to the less residual structure defects in TiC produced by the He irradiation at 500 °C than that at RT, as the thermal energy aids recombination faster which reduces the defect concentration. The density of defects increases with the He fluence, which causes the continuous reduction of a -LP. The cracks start to appear once the a -LP reduction reaches a critical value of 0.49%, which further proves the direct relationship between the a -LP reduction and the formation of cracks. The reason need to be further investigated by theoretical approach to understand if the change of elastic modulus in a direction is greater than that of c direction. The continuous He irradiation would causes much higher He bubble density at the projected depth, and then gives rise to the surface exfoliation in the HT8.4 sample.

As shown in Fig. 4(a), the grain size is relatively smaller and the content of TiAl_3 impurity phase is lower in the area 1 denoted by rectangle frame. The Ti_3AlC_2 grain is free of crack in that area 1. Thus, it is assumed that the existence of TiAl_3 phase is beneficial for

the relaxation of microstrain induced by irradiation.

5 Conclusions

Helium irradiation damage on Ti_3AlC_2 with respect to He fluence and irradiation temperature were systematically investigated by GIXRD, SEM, EDS and SAED techniques. Results show that the orientated cracks, which grow preferentially along $(10\bar{1}0)$ crystal plane, are present in the surface of Ti_3AlC_2 after irradiation to 2.1 dpa at RT. The density of cracks increases with increasing dose up to 8.4 dpa. The reduction of α -LP, enhanced by the irradiation defects, was thought to be a crucial factor leading to the formation of cracks. It is supposed that He atoms tend to aggregate at pre-formed cracks rather than the Al layer with lower defect formation energy.

For the samples irradiated at 500 °C, the surface exfoliating starts to appear on the surface after irradiated to $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$. The formation of surface exfoliating is attributed to the He bubble blister at the projected depth. Once the α -LP reduction reaches a critical point, the orientated cracks start to appear when Ti_3AlC_2 is irradiated to $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$.

The grain size of Ti_3AlC_2 and the content of TiAl_3 are taken into account as factors affecting the formation of orientated cracks, since the grain size is relatively smaller and the number of cracks is very few in those areas with higher content of TiAl_3 . This conclusion can offer valuable reference for the preparation of Ti_3AlC_2 ceramic with much higher irradiation resistant properties.

Acknowledgement

This research was funded by the National Natural Science Foundation of China (Grant No. 91326102, 21601168 and 51532009), the Science and Technology Development

Foundation of China Academy of Engineering Physics (Grant No. 2013A0301012), and the NSAF Joint Foundation of China (U1630126). H. B. Zhang is grateful to the foundation by the Recruitment Program of Global Youth Experts and the Youth Hundred Talents Project of Sichuan Province. The JEOL-2010F TEM used for this investigation were funded by National Science Foundation Grants (Grant No. DMR-9871177) and the Helios FIB under the support of the College of Engineering at University of Michigan. The authors would like to acknowledge F. N. Naab at the University of Michigan for performing the He ion irradiations.

References

- [1] M.W. Barsoum, The $M_{N+1}AX_N$ phases: A new class of solids: Thermodynamically stable nanolaminates, *Prog. Solid St. Chem.* 28 (2000) 201-281.
- [2] M.W. Barsoum, T. El-Raghy, Synthesis and Characterization of a Remarkable Ceramic: Ti_3SiC_2 , *J. Am. Ceram. Soc.* 79 (1996) 1953-1956.
- [3] V.H. Nowotny, Strukturchemie einiger Verbindungen der Übergangsmetalle mit den elementen C, Si, Ge, Sn, *Prog. Solid St. Chem.* 5 (1971) 27-70.
- [4] W.Y. Ching, Y. Mo, S. Aryal, P. Rulis, Intrinsic Mechanical Properties of 20 MAX-Phase Compounds, *J. Am. Ceram. Soc.* 96 (2013) 2292-2297.
- [5] N.V. Tzenov, M.W. Barsoum, Synthesis and Characterization of Ti_3AlC_2 , *J. Am. Ceram. Soc.* 83 (2000) 825-832.
- [6] Y.W. Bao, X.H. Wang, H.B. Zhang, Y.C. Zhou, Thermal shock behavior of Ti_3AlC_2 from between 200 °C and 1300 °C, *J. Eur. Ceram. Soc.* 25 (2005) 3367-3374.
- [7] D.J. Tallman, L. He, B.L. Garcia-Diaz, E.N. Hoffman, G. Kohse, R.L. Sindelar, M.W.

- Barsoum, Effect of neutron irradiation on defect evolution in Ti_3SiC_2 and Ti_2AlC , J. Nucl. Mater. 468 (2016) 194-206.
- [8] D.J. Tallman, E.N. Hoffman, E.a.N. Caspi, B.L. Garcia-Diaz, G. Kohse, R.L. Sindelar, M.W. Barsoum, Effect of neutron irradiation on select MAX phases, Acta Mater. 85 (2015) 132-143.
- [9] S. Zhao, J. Xue, Y. Wang, Q. Huang, Ab initio study of irradiation tolerance for different $\text{M}_{n+1}\text{AX}_n$ phases: Ti_3SiC_2 and Ti_3AlC_2 , J. Appl. Phys. 115 (2014) 023503.
- [10] T. Yang, C. Wang, C.A. Taylor, X. Huang, Q. Huang, F. Li, L. Shen, X. Zhou, J. Xue, S. Yan, Y. Wang, The structural transitions of Ti_3AlC_2 induced by ion irradiation, Acta Mater. 65 (2014) 351-359.
- [11] P. Song, J. Sun, Z. Wang, M. Cui, T. Shen, Y. Li, L. Pang, Y. Zhu, Q. Huang, J. Lü, Irradiation resistance properties studies on helium ions irradiated MAX phase Ti_3AlC_2 , Nucl. Instrum. Methods Phys. Res. Sect. B 326 (2014) 332-336.
- [12] M.K. Patel, D.J. Tallman, J.A. Valdez, J. Aguiar, O. Anderoglu, M. Tang, J. Griggs, E. Fu, Y. Wang, M.W. Barsoum, Effect of helium irradiation on Ti_3AlC_2 at 500°C, Scripta Mater. 77 (2014) 1-4.
- [13] C. Wang, T. Yang, S. Kong, J. Xiao, J. Xue, Q. Wang, C. Hu, Q. Huang, Y. Wang, Effects of He irradiation on Ti_3AlC_2 : Damage evolution and behavior of He bubbles, J. Nucl. Mater. 440 (2013) 606-611.
- [14] L. Zhang, Q. Qi, L.Q. Shi, D.J. O'Connor, B.V. King, E.H. Kisi, D.K. Venkatachalam, Damage tolerance of Ti_3SiC_2 to high energy iodine irradiation, Appl. Surf. Sci. 258 (2012) 6281-6287.

- [15] K.R. Whittle, M.G. Blackford, R.D. Aughterson, S. Moricca, G.R. Lumpkin, D.P. Riley, N.J. Zaluzec, Radiation tolerance of $M_{n+1}AX_n$ phases, Ti_3AlC_2 and Ti_3SiC_2 , *Acta Mater.* 58 (2010) 4362-4368.
- [16] J.C. Nappé, P. 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.* 385 (2009) 304-307.
- [17] S.J. Zinkle, G.S. Was, Materials challenges in nuclear energy, *Acta Mater.* 61 (2013) 735-758.
- [18] S.J. Zinkle, L.L. Snead, Designing Radiation Resistance in Materials for Fusion Energy, *Annu. Rev. Mater. Res.* 44 (2014) 241-267.
- [19] J. Xiao, C. Wang, T. Yang, S. Kong, J. Xue, Y. Wang, Theoretical investigation on helium incorporation in Ti_3AlC_2 , *Nucl. Instrum. Methods Phys. Res. Sect. B* 304 (2013) 27-31.
- [20] M. Bugnet, V. Mauchamp, P. Eklund, M. Jaouen, T. Cabioc'h, Contribution of core-loss fine structures to the characterization of ion irradiation damages in the nanolaminated ceramic Ti_3AlC_2 , *Acta Mater.* 61 (2013) 7348-7363.
- [21] H.F. Zhang, B.D. Yao, L.Q. Shi, D.J. O'Connor, J. Huang, J.Y. Zhang, W. Ding, Y.X. Wang, Roles of silicon-layer in Ti_3SiC_2 materials response to helium irradiation: New insights from first-principles calculation, *Acta Mater.* 97 (2015) 50-57.
- [22] J.C. Nappé, I. Monnet, F. Audubert, P. Grosseau, M. Beauvy, M. Benabdesselam, Formation of nanosized hills on Ti_3SiC_2 oxide layer irradiated with swift heavy ions,

- Nucl. Instrum. Methods Phys. Res. Sect. B 270 (2012) 36-43.
- [23] X.T. Zu, L. Yang, F. Gao, S.M. Peng, H.L. Heinisch, X.G. Long, R.J. Kurtz, Properties of helium defects in bcc and fcc metals investigated with density functional theory, Phys. Rev. B 80 (2009) 054104.
- [24] D.W. Clark, S.J. Zinkle, M.K. Patel, C.M. Parish, High temperature ion irradiation effects in MAX phase ceramics, Acta Mater. 105 (2016) 130-146.
- [25] J.C. Nappé, I. Monnet, P. Grosseau, F. Audubert, B. Guilhot, M. Beauvy, M. Benabdesselam, L. Thomé, Structural changes induced by heavy ion irradiation in titanium silicon carbide, J. Nucl. Mater. 409 (2011) 53-61.
- [26] J.C. Nappé, C. Maurice, P. Grosseau, F. Audubert, L. Thomé, B. Guilhot, M. Beauvy, M. Benabdesselam, Microstructural changes induced by low energy heavy ion irradiation in titanium silicon carbide, J. Eur. Ceram. Soc. 31 (2011) 1503-1511.
- [27] X. Liu, M. Le Flem, J.-L. Béchade, F. Onimus, T. Cozzika, I. Monnet, XRD investigation of ion irradiated $\text{Ti}_3\text{Si}_{0.90}\text{Al}_{0.10}\text{C}_2$, Nucl. Instrum. Methods Phys. Res. Sect. B 268 (2010) 506-512.
- [28] T. Yang, C. Wang, C.A. Taylor, X. Huang, Q. Huang, F. Li, L. Shen, X. Zhou, J. Xue, S. Yan, Y. Wang, The structural transitions of Ti_3AlC_2 induced by ion irradiation, Acta Mater. 65 (2014) 351-359.
- [29] Q. Huang, R. Liu, G. Lei, H. Huang, J. Li, S. He, D. Li, L. Yan, J. Zhou, Irradiation resistance of MAX phases Ti_3SiC_2 and Ti_3AlC_2 : Characterization and comparison, J. Nucl. Mater. 465 (2015) 640-647.
- [30] X. Huang, Y. Feng, Y. Dou, H. Tang, D. Ding, P. Tian, M. Xia, G. Qian, Y. Wang, X.

- Zhang, Effect of electron irradiation on Ti_3AlC_2 , *Scripta Mater.* 113 (2016) 114-117.
- [31]M. Le Flem, X. Liu, S. Doriot, T. Cozzika, I. Monnet, Irradiation Damage in $\text{Ti}_3(\text{Si,Al})\text{C}_2$: a TEM Investigation, *Int. J. Appl. Ceram. Technol.* 7 (2010) 766-775.
- [32]C. Ang, C. Silva, C. Shih, T. Koyanagi, Y. Katoh, S.J. Zinkle, Anisotropic swelling and microcracking of neutron irradiated Ti_3AlC_2 - $\text{Ti}_5\text{Al}_2\text{C}_3$ materials, *Scripta Mater.* 114 (2016) 74-78.
- [33]J.F. Ziegler, M.D. Ziegler, J.P. Biersack, SRIM - The stopping and range of ions in matter (2010), *Nucl. Instrum. Methods Phys. Res. Sect. B* 268 (2010) 1818-1823.
- [34]R.E. Stoller, M.B. Toloczko, G.S. Was, A.G. Certain, S. Dwaraknath, F.A. Garner, On the use of SRIM for computing radiation damage exposure, *Nucl. Instrum. Methods Phys. Res. Sect. B* 310 (2013) 75-80.
- [35]H.H. Shen, S.M. Peng, B. Chen, F.N. Naab, G.A. Sun, W. Zhou, X. Xiang, K. Sun, X.T. Zu, Helium bubble evolution in a Zr-Sn-Nb-Fe-Cr alloy during post-annealing: An in-situ investigation, *Mater. Charact.* 107 (2015) 309-316.
- [36]H.H. Shen, S.M. Peng, X. Xiang, F.N. Naab, K. Sun, X.T. Zu, Proton irradiation effects on the precipitate in a Zr-1.6Sn-0.6Nb-0.2Fe-0.1Cr alloy, *J. Nucl. Mater.* 452 (2014) 335-342.
- [37]H.H. Shen, X.T. Zu, B. Chen, C.Q. Huang, K. Sun, Direct observation of hydrogenation and dehydrogenation of a zirconium alloy, *Journal of Alloys and Compounds*, 659 (2016) 23-30.
- [38]S.C. Middleburgh, G.R. Lumpkin, D. Riley, Accommodation, Accumulation, and Migration of Defects in Ti_3SiC_2 and Ti_3AlC_2 MAX Phases, *J. Am. Ceram. Soc.* 96

(2013) 3196-3201.

- [39] Y. Zhou, Z. Sun, Crystallographic relations between Ti_3SiC_2 and TiC, Mater. Res. Innovations 3 (2000) 286-291.

Tables

Table 1. He⁺ irradiation conditions and the calculation damages at the projected depth of 1330 nm in the samples by SRIM.

Temperature / °C	Implantation Energy/ keV	Helium Fluence / (He ⁺ /cm ²)	Irradiation Damage / dpa	Helium Concentration at Projected Depth / at. %	Specimen Designation
RT	400	0.5 × 10 ¹⁷	2.1	3.2	LT2.1
		1.0 × 10 ¹⁷	4.2	6.2	LT4.2
		2.0 × 10 ¹⁷	8.4	11.6	LT8.4
500		0.5 × 10 ¹⁷	2.1	3.2	HT2.1
		1.0 × 10 ¹⁷	4.2	6.2	HT4.2
		2.0 × 10 ¹⁷	8.4	11.6	HT8.4

Table 2. The Ti_3AlC_2 crystal structure parameters, a -LP, c -LP and cell volume, calculated from the GIXRD patterns (Fig. 7) of specimens before and after He irradiation. The intensity ratio of $(10\bar{1}3)/(10\bar{1}4)$ and $(10\bar{1}5)/(10\bar{1}4)$ peaks are also tabulated in this table in the last two rows.

Structure Parameters	Virgin	LT2.1	LT4.2	LT8.4	HT2.1	HT4.2	HT8.4
a -LP / nm	0.3074	0.3054	0.3057	0.3069	0.3062	0.3061	0.3059
a -LP Reduction / %	/	-0.65	-0.55	-0.16	-0.39	-0.42	-0.49
c -LP / nm	1.8499	1.9167	1.8980	1.8700	1.8754	1.8805	1.8861
c -LP Expansion / %	/	3.61	2.60	1.09	1.38	1.65	1.96
Cell Volume / $\text{\AA}^3$	151.39	154.82	153.61	152.53	152.28	152.59	152.85
Cell Volume Expansion/ %	/	2.27	1.47	0.76	0.59	0.80	0.96
Intensity Ratio of $(10\bar{1}3)/(10\bar{1}4)$ Peaks / %	9.70%	57.41%	64.67%	67.28%	12.28%	22.66%	32.09%
Intensity Ratio of $(10\bar{1}5)/(10\bar{1}4)$ Peaks / %	29.23%	34.07%	49.21%	57.10%	26.03%	30.16%	37.80%

Figure Captions

Figure. 1. (Color online) SRIM results of 400 keV helium irradiation on Ti_3AlC_2 to fluence of $0.5 \times 10^{17} \text{ He}^+/\text{cm}^2$, $1.0 \times 10^{17} \text{ He}^+/\text{cm}^2$ and $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$, which induced a maximal damage of 2.1 dpa, 4.2 dpa and 8.4 dpa at a project depth of 1330 nm, respectively.

Figure. 2. (Color online) (a) SEM image of Ti_3AlC_2 before irradiation. EDS mapping of Ti (b) and Al (c) elements from the area shown in (a). (d) XRD pattern acquired from Ti_3AlC_2 before irradiation.

Figure. 3. (Color online) (a) STEM-ADF image of a Ti_3AlC_2 TEM specimen prepared by FIB method cutting across a grain boundary of Ti_3AlC_2 and TiAl_3 . (b) EDS mapping of Al element of the area shown in (a). (c) and (d) represent the SAED patterns taken from the Ti_3AlC_2 and TiAl_3 grains along the viewing direction of $[10\bar{1}0]$ and $[110]$, respectively.

Figure. 4. SEM images of Ti_3AlC_2 sample after He irradiation up to $2.0 \times 10^{17} \text{ He}^+/\text{cm}^2$ at RT ((a)-(c)) or 500 °C ((d)-(f)) showing: (a) orientated cracks marked by arrows in the surface of LT2.1 sample after irradiation; (b) He irradiation induced surface exfoliating in the LT4.2 sample with the area magnified and shown in the inset; (f) Surface exfoliating induced He bubble blister in the HT8.4 sample

Figure. 5. BF images ((a), (d), (g)) from sample LT2.1, LT4.2 and LT8.4 were shown in ((a)-(c)), ((d)-(f)) and ((g)-(i)), respectively. Helium irradiation induced an irradiated layer with a thickness around 1330 nm, which is followed by the non-irradiated bulk. SAED patterns taken from the non-irradiated area and irradiated area are shown in ((b), (e), (h)) and ((c), (f), (i)), respectively. The cracks are observed from the BF images for all three specimens. The SAED patterns in (b), (e) and (h) are indexed with the zone axis of $[0001]$, $[08\bar{8}1]$ and

$[04\bar{4}1]$, respectively. Based on the SAED patterns, it is evident that the cracks appeared in BF images have a preferred orientation laying on the $(10\bar{1}0)$ crystal plane of Ti_3AlC_2 .

Figure. 6. The BF images ((a), (d), (g)) of specimens HT2.1, HT4.2 and HT8.4 were shown in ((a)-(c)), ((d)-(f)) and ((g)-(i)), respectively. SAED patterns taken from the non-irradiated area and irradiated area are shown in ((b), (e), (h)) and ((c), (f), (i)), respectively. The SAED patterns in (b), (e) and (h) are indexed with the zone axis of $[21\bar{3}0]$, $[10\bar{1}0]$ and $[01\bar{1}0]$, respectively. With increasing irradiation dose, the diffraction spots in SAED pattern change to be dispersed at 4.2 dpa (f), and almost transform to polycrystalline rings at 8.4 dpa (i).

Figure. 7. (Color online) GIXRD patterns of Ti_3AlC_2 specimens after He irradiation at RT (lower part) and 500 °C (upper part) with fluence increasing from 0.5×10^{17} He^+/cm^2 to 2.0×10^{17} He^+/cm^2 were displayed from bottom to top.

Figure. 8. (Color online) The *a*-LP, *c*-LP (a) and cell volume (b) of Ti_3AlC_2 change as a function of irradiation temperature and fluence.

Figure. 9. (Color online) The atomic arrangement of Ti_3AlC_2 crystal structure viewing from $[11\bar{2}0]$ direction.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

(a)

(b)

Figure 9.