Structural Distortion and Defects in Ti_3AlC_2 irradiated by Fe and He Ions *

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Ti_3AlC_2 samples are irradiated in advance by 3.5 MeV Fe-ion to the fluence of 1.0×10^{16} ion/cm^2, and then are implanted by 500 keV He-ion with the fluence of 1.0×10^{17} ion/cm^2 at room temperature. The irradiated samples are investigated by grazing incidence x-ray diffraction (GIXRD) and transmission electron microscopy (TEM). GIXRD results show serious structural distortion, but without amorphization in the irradiated samples. Fe-ion irradiation and He-ion implantation create much more serious structural distortion than single Fe-ion irradiation. TEM results reveal that there are a large number of defect clusters in the damage region, and dense spherical He bubbles appear in the He depositional region. It seems that the pre-damage does not influence the growth of He bubbles, but He-ion implantation influences the pre-created defect configurations.

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As a new type of material, MAX phases (where M is an early transition metal, A is an A-group element (mostly ⅢA and ⅣA), and X is either C and/or N) possess a combination of metallic and ceramic properties, such as easy machinability, high thermal and electrical conductivities, good thermal shock resistance, excellent high-temperature resistance to oxidation and corrosion.[1,2]

The 312-type MAX phases (especially Ti_3SiC_2/Ti_3AlC_2) are representative materials of MAX phase family and have been attracting an intensive investigation in recent years due to their excellent performances, particularly on the irradiation resistance.[3] In previous studies,[4–9] various heavy ions and He-ion were used to irradiate Ti_3SiC_2 or Ti_3AlC_2. It was found that the disorder in lattice increases with the irradiation dose (from several to dozens of displacements per atom (dpa)), and they still retain crystalline and nano-lamellar structure without any amorphization, illustrating excellent resistance to irradiation damage. The materials exhibit a dramatic damage recovery under the high temperature irradiation.[4,5,10] There are also some reports in response to neutron irradiation, in which the formation of defects,[11] anisotropic swelling and micro-cracking[12] in Ti_3SiC_2 and Ti_3AlC_2 were investigated.

Effects of He in nuclear materials have already attracted enormous attention.[13–15] In reactor, He from nuclear reaction (n, α) plays an important part in deterioration of nuclear materials, including formation of He bubbles, swelling, embrittlement and so on. Some effects of He in Ti_3AlC_2 have also been studied,[16–19] such as cracking, formation and growth of spherical He bubbles, and their characters vary with temperature.

However, so far the effects of He in MAX materials were studied almost by single He-ion implantation. As its damage cross section is very low, the single He-ion implantation creates an environment with slight damage but rich in He atoms in materials, i.e., high appmHe/dpa. Actually, He effects in materials with relatively low appmHe/dpa are closer to the real conditions in a nuclear reactor, which are very significant in nuclear materials. However, they are rarely investigated in MAX materials.

In this work, we have used the Fe-ion irradiation and He-ion implantation successively (Fe+He) to produce an environment with lower appmHe/dpa than the single He-ion implantation. The microstructural variation in Ti_3AlC_2 at different radiation parameters is investigated using the grazing incidence x-ray diffraction (GIXRD) analysis and the transmission electron microscopy (TEM) observation.

The Ti_3AlC_2 samples were prepared by the Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences (CAS). Ion irradiation experiments were carried out at room temperature (RT) in 320 kV multi-discipline research platform for highly charged ions equipped with an electron cyclotron resonance (ECR) ion source in the Institute of Modern Physics, CAS. Samples were irradiated by

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3.5 MeV Fe-ion at the fluences of 1.0×10^{16} ion/cm^2, to produce an amount of defects in advance. Then, the irradiated samples were implanted with 500 keV He-ion at the fluence of 1.0×10^{17} ion/cm^2.

We have used the SRIM 2008 code[20] with the Kinchin–Pease quick calculation mode to simulate damage caused by Fe-ion irradiation and He-ion depositional concentration, as shown in Fig. 1. The damage near the peak is about 10 dpa, and the depth of He-ion depositional peak is approximately corresponding to the damage peak created by Fe-ion irradiation to ensure that He-ion could deposit in the high damage region.

The crystal structure of the samples was examined by GIXRD using a Philips X'pert diffractometer with Cu $K\alpha$ radiation. The x-ray diffraction data was collected between 30° and 80° in 2θ scale with an incidence of 5° with the corresponding maximum depth of about 1.7 μm. Cross-sectional TEM specimens were prepared by a focused ion beam (FIB) lift-out method. The TEM observation was performed with an FEI TECNAI G2 F20 and all micrographs were taken at 200 kV.

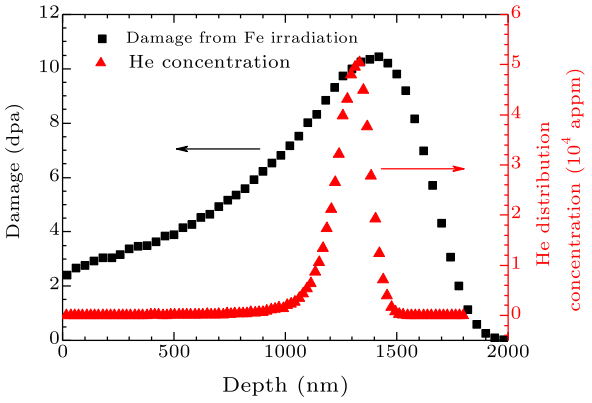


Fig. 1. Damage level (dpa) created by Fe-ion irradiation and He-ion depositional concentration produced by He-ion implantation vary with depth in Ti_3AlC_2, respectively. Data were calculated by the SRIM2008 code.

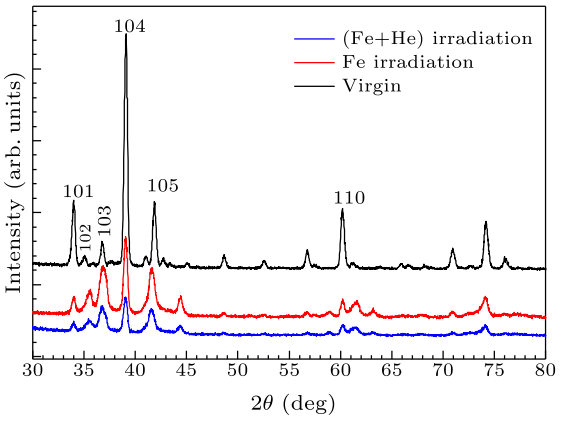


Fig. 2. GIXRD patterns of virgin and irradiated samples at various parameters.

The GIXRD patterns of the virgin sample and the irradiated samples at different fluences are shown in Fig. 2. It is shown that the intensities of diffraction peaks decrease significantly and some peak widths broaden with original (103), (105) after irradiation, similar to the structural changes reported in Ti_3AC_2 (A=Al/Si),[5,6,16,21] which indicates the lattice distortion due to various defects and the lattice micro-strain induced by irradiation.

For the single Fe-ion irradiation with 1.0×10^{16} ion/cm^2, a shift of (102) peak towards higher diffraction angle implies the changes of lattice parameters. Moreover, two new peaks at 44.3° and 61.4° (2θ) appear after irradiation. These phenomena have also been found in Xe-ion irradiated Ti_3AlC_2,[6] revealing the phase transition from α phase to β phase. For the sample with (Fe+He) irradiation, the intensities of peaks decrease further, meaning that the lattice structure suffers from more serious distortion. However, there are no other new peaks appearing and no evidence of TiC_x formation. Irradiated Ti_3AlC_2 samples retain a high level of crystallinity and present a good tolerance of amorphization.

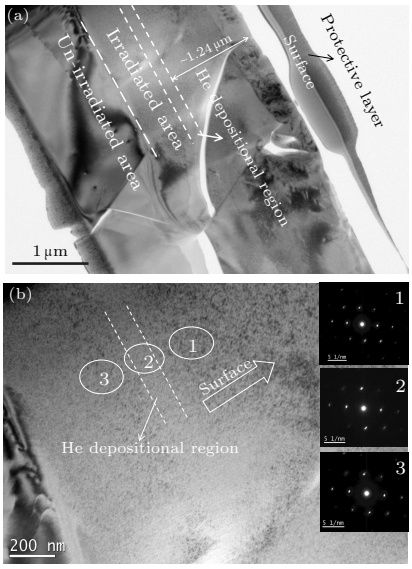


Fig. 3. Cross-sectional bright-field TEM image of the full Ti_3AlC_2 sample irradiated by Fe and He ions, respectively (a), and amplified TEM image at the end of ion range (b). The banded region between two white dashed lines in two images is regarded as the He depositional region. The insets of the TEM image show the selected area electron diffraction patterns (SAED) taken from three circular regions in (b).

Figure 3(a) gives a low-magnification TEM micrograph of the full Ti_3AlC_2 sample with (Fe+He) irradiation. A band between two white dashed lines is identified as the He depositional region at the depth of ~1.24 μm. This is consistent with SRIM ion penetration depth calculations provided above. Note that there is a loose protective layer upon the surface that was made during the sample preparation process be-

fore FIB performance. Figure 3(b) shows an amplified TEM image at the end of ion range with high damage. It can be seen clearly that this irradiated region is riddled with a significant number of defect clusters and dislocation loops created by ion irradiation. SAED patterns of three circular regions (marked as 1, 2 and 3, respectively, including He depositional region) along ion incidence direction with different depths, as shown in Fig. 3(b) (left insets), are representative of crystalline grains, without any evidence of amorphization. This is in agreement with the results obtained by GIXRD. It is found that SAED patterns 1 and 3 are almost similar. Defect clusters and dislocations just diffuse slightly diffraction spots in both the SAED patterns. For comparison, however, some diffraction spots become quite weak in SAED pattern 2, indicating that three regions still have identical structure, but He depositional region has more serious lattice distortion than the other two vicinities. The further decrease of intensities of diffraction peaks in GIXRD pattern with (Fe+He) irradiation should originate from He depositional region.

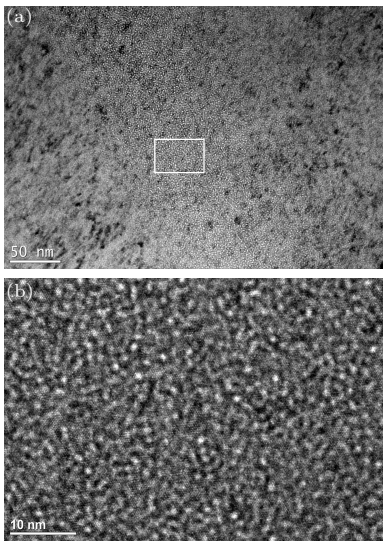


Fig. 4. (a) Cross-sectional bright-field TEM images of He depositional region of Ti_3AlC_2 sample irradiated by (Fe+He) ions. (b) High-resolution TEM image from white box in (a) showing He bubbles in detail.

Figure 4 presents the more magnified TEM images of He depositional region. It clearly shows that a great number of dense He bubbles uniformly distribute at the banded region (small white dots in this under focused image). To miniaturize the error, only isolated spherical He bubbles are statistically analyzed in Fig. 4(b), excluding the coalescent He bubbles. The largest He bubbles have diameters of about 1.6 nm, and the mean bubble radius is approximately 0.62 nm, which is derived from measurements of 106 spherical He bubbles in high-resolution TEM image. This is in agreement with previous reports of single He-ion implantation in Ti_3AlC_2,[16–18] in which the mean radius of spherical He bubbles is always hardly beyond one nanometer.

It is well known that the formation of He bubbles has very close relationship with concentrations of He and vacancy (or cavity). He atoms are easily captured by vacancies (or cavity) in their migration process, forming He-V clusters that always act as nucleations of He bubbles. They continually absorb new He atoms, vacancies or coalesce with other He-V clusters, and finally grow into He bubbles.[13] In this work, we have produced an environment with about 3.7×10^3 appmHe/dpa (from SRIM calculated result) in Ti_3AlC_2 by (Fe+He) irradiation. However, the single He-ion implantation can create an environment with about 1.7×10^4 appmHe/dpa. In comparison, the environment with low appmHe/dpa always indicates containing more vacancies (or cavities) corresponding to a certain amount of He atoms. Consequently, with a certain He content, environment with low appmHe/dpa should be helpful for nucleation of He bubbles in the preliminary stage and their further growth. In fact, however, our observations show that there is no obvious influence on the configurations of He bubbles whether appmHe/dpa is low or high in Ti_3AlC_2. This may have some relationship with high resistance to irradiation damage in this material.

In Ti_3AlC_2, the formation energy of anti-site defect between Ti and Al is low, only 3.13 eV.[22] Ion irradiation could be prone to produce a large number of anti-site defects (Ti_{Al} or Al_{Ti}),[6,8,9] causing the distribution of Ti and Al atoms in each layer, which is also responsible for the structural transformation. Some of the C atoms occupying the octahedral holes between the Ti layers in the virgin compound are displaced and moved to the new octahedral holes between the original Ti and Si (or Al) layers.[8,9] Thus formation of anti-site defects of cations and disorder of anions provide an alternative way to accommodate the defects from irradiation damage cascades, which is similar to the cases of complex oxides.[23] It is reasonable to assume that most of the vacancies created by initial Fe-ion irradiation are quickly annihilated or transform anti-site defects, thus only a minority of vacancies survive before the following He-ion implantation. Actually, up to now there are hardly reports on cavities in ion irradiated MAX materials even with high damage level. Therefore, the environment with low appmHe/dpa may not imply more vacancies (or cavities) than high appmHe/dpa in the ion irradiated Ti_3AlC_2. Note that He bubbles still present spherical shape, indicating that surface free energy dominates during their formation process.[24]

It is worth noting that Fig. 4(a) shows numerous large defect clusters scattering in the irradiated re-

gion, but few in the He depositional region. We believe that the large defect clusters should have existed in this region as well after Fe-ion irradiation. It can be inferred that the following He-ion implantation influences in part the pre-created defect configurations. He-V clusters are always captured by defect clusters, forming the nucleation of He bubbles. Considering the fact that our experiments were performed at RT, the growth of He bubbles should be dominated under non-thermal process.[25–27] They continuously grow with a mechanism of self-trapping by accumulation of deposited He atoms and vacancies from continuous radiation damage.[13,25] During the growth process, He bubbles will relieve the inner high pressure by the way of loop punching during which some small defects (like dislocation loops) bonding with He bubbles are dislodged. Therefore, some large defect clusters with He-V complexes may become smaller because of division of some small defects. This process probably involves the complicated dynamic evolution of He bubble and defects. Further work is necessary to clear it, and our work is ongoing to characterize the defects in detail.

In summary, we have studied the characteristics of defects and He bubbles in high damage environment in Ti_3AlC_2, which are created by 3.5 MeV Fe-ion irradiation and 500 keV He-ion implantation successively. Compared with single Fe-ion irradiation, (Fe+He) irradiation enhances damage dramatically, creating more serious structural distortion. However, Ti_3AlC_2 still retains the crystalline structure, without amorphization. A large number of He bubbles with mean radius about 0.62 nm appear in He depositional region. It seems that the relative low appmHe/dpa does not make an obvious influence on the growth of He bubbles compared with the high appmHe/dpa. However, the following He-ion implantation influences in part the pre-created defect configurations.

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