Diffusion of Ag, Au and Cs implants in MAX phase Ti_3SiC_2

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ABSTRACT

MAX phases (M: early transition metal; A: elements in group 13 or 14; X: C or N), such as titanium silicon carbide (Ti_3SiC_2), have a unique combination of both metallic and ceramic properties, which make them attractive for potential nuclear applications. Ti_3SiC_2 has been considered as a possible fuel cladding material. This study reports on the diffusivities of fission product surrogates (Ag and Cs) and a noble metal Au (with diffusion behavior similar to Ag) in this ternary compound at elevated temperatures, as well as in dual-phase nanocomposite of Ti_3SiC_2 /3C-SiC and polycrystalline CVD 3C-SiC for behavior comparisons. Samples were implanted with Ag, Au or Cs ions and characterized with various methods, including x-ray diffraction, electron backscatter diffraction, energy dispersive x-ray spectroscopy, Rutherford backscattering spectrometry, helium ion microscopy, and transmission electron microscopy. The results show that in contrast to immobile Ag in 3C-SiC, there is a significant outward diffusion of Ag in Ti_3SiC_2 within the dual-phase nanocomposite during Ag ion implantation at 873 K. Similar behavior of Au in polycrystalline Ti_3SiC_2 was also observed. Cs out-diffusion and release from Ti_3SiC_2 occurred during post-implantation thermal annealing at 973 K. This study suggests caution and further studies in consideration of Ti_3SiC_2 as a fuel cladding material for advanced nuclear reactors operating at very high temperatures.

1. Introduction

Silicon carbide (SiC) and SiC/SiC composites have been proposed and tested as a cladding material for nuclear fuels (such as UCO and UO_2) in the tristructural-isotropic (TRISO) particle design [1-4], which consists of four layers of surface coatings, including a SiC layer of several to tens of microns in thickness. The SiC layer not only provides the mechanical strength for the fuel particle, but also acts as an impenetrable barrier for fission products, including metallic and gaseous species. The behavior of fission products in the TRISO-coated particles was studied up to 1573 K with high burn-up (up to 10%) [5]. Tests of the post-irradiated TRISO-coated fuel particles at accident temperatures of 1973 and 2073 K were also performed [6]. The results show that the irradiated fuel in the pre-heating test has a relatively large fractional release of $^{110\text{m}}\text{Ag}$ compared to other radionuclides, such as ^{137}Cs , ^{154}Eu and ^{85}Kr . Large cracks of the SiC layer was also found after annealing at the extremely high temperatures.

Experimental studies [7-11] of Ag diffusivity in both crystalline and amorphized SiC indicate that Ag is essentially immobile in SiC up to 1573 K. The concentration of implantation defects and even an

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amorphized state in SiC does not significantly affect the behavior of Ag immobility at and below 873 K [7]. First-principles calculations [12] suggest that Ag is immobile in the SiC bulk, but becomes mobile on SiC surfaces. A diffusion couple [13] consisting of a SiC cap layer on pyrolytic carbon film on a SiC substrate has been fabricated and used to explore diffusion mechanisms of fission products in pristine SiC without implantation damage. Although many fission products (Cs, Sr, Eu and I) remained immobile in SiC at 1373 K, Ag was found to escape through the SiC barrier layer, which was attributed to the presence of oxygen and nitrogen in the cap layer. A recent report [14] suggests the possibility that a void mediated Ag transport due to the change in microstructure of the 3C-SiC at elevated temperatures plays a role. This interpretation is consistent with the void formation due to mobile vacancies in neutron- or ion-irradiated SiC at similar high temperatures [15-17] for Ag diffusion. As a potential candidate for cladding material, SiC has a number of advantages, including good corrosion properties, great mechanical strength, and excellent dimensional stability at high temperatures; it also has a relatively low effective neutron absorption cross section. However, SiC is brittle, which can promote in-service failure. The cost, joining, and chemical stability with the fuel and coolant are also major issues confronting the development of SiC fuel cladding [18].

In order to improve fuel performance, more ductile cladding materials with extremely low diffusivities of fission products at reactor-relevant high temperatures need to be explored. MAX phases ($M_{n+1}AX_n$ with $n = 1, 2$, or 3 , where M is an early transition metal, A is mostly elements in group 13 or 14, and X is C or N) have a layered, hexagonally close-packed structure and share outstanding properties of both metals (machinable, ductile, highly thermally conductive, highly radiation-resistant, etc.) and ceramics (elastically stiff, highly corrosion resistant, thermal shock resistant, having a high melting point, etc.). As such, MAX phase materials are considered as hybrids of ceramics and metals. The unique combination of the properties may make them good candidates for use as structural materials in nuclear reactors. Titanium silicon carbide (Ti_3SiC_2), the most studied MAX phase to date, has fracture toughness about 3 times higher than SiC at ambient temperature [19] and this ternary compound has been considered as a possible fuel-cladding material [20-24]. To the best of our knowledge, there have been no diffusion studies of fission products in Ti_3SiC_2 or other MAX phases to date. It is of scientific interest and technological importance to investigate and understand the diffusion behavior of fission products in the potential cladding materials, especially at elevated temperatures. In this study, diffusion behavior of fission product surrogates (Ag and Cs) and a noble metal (Au) in polycrystalline Ti_3SiC_2 , CVD 3C-SiC, and a dual-phase nanocomposite of $Ti_3SiC_2/3C-SiC$ is studied as a function of annealing temperature (isochronal), duration (isothermal) and irradiation status (present or absent) using various methods, including x-ray diffraction (XRD), electron backscatter diffraction (EBSD), energy dispersive x-ray spectroscopy (EDS), Rutherford backscattering analysis (RBS), helium ion microscopy (HIM), and transmission electron microscopy (TEM).

2. Structure and Properties of MAX Phase Ti_3SiC_2

Titanium silicon carbide is one of the MAX phases in the group 312. MAX phases have a hexagonal, layered structure with space group $P6_3/mmc$ (194), combining M_6X octahedra with a single intercalating layer A. There are over 60 MAX phases currently known in 3 groups (211, 312 and 413) with different compositions and lattice parameters [19]. Fig. 1 shows the lattice structure of Ti_3SiC_2 with $a = 0.307$ nm, $c = 1.767$ nm and a theoretical density of 4.52×10^3 kg/m³ [19,25]. The close-packed Ti and Si layers are arranged in the sequence of Ti-Ti-Ti-Si-Ti-Ti-Ti-Si, with the C atom located at the center of the Ti_6C octahedron between the Ti layers. There are two polymorphs of Ti_3SiC_2 with stacking sequences of

$A\gamma BaB\gamma A\beta CaC\beta A\gamma BaB\gamma A$ (α - Ti_3SiC_2) and $A\gamma BcB\gamma A\beta CbC\beta A\gamma BcB\gamma A$ (β - Ti_3SiC_2), respectively, where the capital letters denote Ti layers, low-case letters Si layers, and Greek letters C positions. Since transformation from α - to β - Ti_3SiC_2 does not involve breaking the strong Ti-C bonds, the process has relatively low activation energy. The simulated diffraction patterns of the two polymorphs look similar, but can be readily distinguishable by the locations of their 100% reflection peaks ($2\theta = \sim 39.5^\circ$ for α - Ti_3SiC_2 and $\sim 42.5^\circ$ for β - Ti_3SiC_2) [19].

In general, MAX phases, including Ti_3SiC_2 , are considered as a hybrid of metals and ceramics because they have both metallic nature of the M-X bonds that are exceptionally strong and the elongated M-A bonds that are relative weak (especially in shear) in the layered structure, resulting in an unusual combination of physical and chemical properties. The ternary compounds are elastically stiff, yet relatively soft and readily machinable. They behave like a “ductile ceramic” with high fracture toughness and good thermal and electrical conductivities. The materials are the only polycrystalline solids that deform by a combination of kink and shear bands, together with the delamination of individual grains. Dislocations in MAX phases multiply and are mobile at room temperature, glide on the basal plane, and are arranged either in arrays or kink boundaries [19]. Ti_3SiC_2 combines mechanical anisotropy with thermal properties that are fairly isotropic ($\alpha_a = 8.6 \times 10^{-6} K^{-1}$ and $\alpha_c = 9.7 \times 10^{-6} K^{-1}$ [26]). It has a thermal conductivity ranging from $\kappa_{th} = 37 Wm^{-1}K^{-1}$ at 300 K to $32 Wm^{-1}K^{-1}$ at 1300 K, mostly from electronic contributions. Pure Ti_3SiC_2 is thermally stable up to at least 1973 K [19], but decomposes in vacuum between 1273 and 1473 K [27] due to low barriers to Si loss. Polycrystalline Ti_3SiC_2 can be oxidized in air over the temperature range between 1173 and 1673 K [28]. With the exception of HNO_3 , MAX phase Ti_3SiC_2 has a very low corrosion rate in many of the common acids and NaOH at room temperature [29]. It is also resistant to thermal shock [30,31] and creep [32,33], and is tolerant to mechanical damage [19] and irradiation-induced amorphization [21-24,34,35].

3. Experimental Details

Materials used in this study include dual-phase nanocomposite of $Ti_3SiC_2/3C-SiC$ (synthesized at the Pacific Northwest National Laboratory (PNNL)), polycrystalline CVD 3C-SiC (obtained from Dow Chemical Company), and polycrystalline Ti_3SiC_2 (obtained from Reade Advanced Materials). These three types of materials were cut into small samples that were subsequently mechanically and chemically polished. Three ion accelerators/implanters at different locations were used with beam rastering systems to achieve uniform implantation. Implantation under random ion-incidence geometry (as opposed to channeling directions) was used in all cases to minimize or avoid channeling effects. Implantation of 400 keV Ag^{2+} in $Ti_3SiC_2/3C-SiC$ and CVD 3C-SiC was conducted at Innovion Corporation with 7° off surface normal to ion fluence of $2.8 \times 10^{20} Ag^{2+}/m^2$ at 873 K. This geometry was used because some on-axis cut single crystals were included for implantation, but study of those single crystals is beyond the scope of this article. Polycrystalline Ti_3SiC_2 samples were not available when the Ag^{2+} ion implantation was performed. The maximum atomic percentage of the implanted Ag is 3.5 at.% in Ti_3SiC_2 and 3.7 at.% in SiC, according to SRIM03 full-damage cascade simulations [36], where the threshold displacement energies for the Ti, Si and C sublattices in Ti_3SiC_2 were rather arbitrarily assumed to be 40, 35 and 20 eV, respectively. The simulations also suggest a dose of 110 dpa at the damage peak (70 nm deep) in Ti_3SiC_2 and 84 dpa at the damage peak (87.5 nm deep) in SiC. For dual-phase nanocomposite of $Ti_3SiC_2/3C-SiC$, the values are slightly different, depending on the weight percentages.

Polycrystalline MAX phase Ti_3SiC_2 material was later obtained and used for an in-situ diffusion study as a function of implantation temperature. 2.0 MeV Au^{2+} ion implantation in Ti_3SiC_2 was performed at the

3.0 MV tandem ion accelerator within the Environmental Molecular Sciences Laboratory (EMSL) at PNNL. Normal incidence was used for the implantation to $1.0 \times 10^{20} \text{ Au}^{2+}/\text{m}^2$ at temperatures ranging from 230 to 873 K, corresponding to 0.81 at.% Au and 60 dpa at the peak maxima. The ion flux was on the order of $10^{16} \text{ Au}^{2+}/\text{m}^2/\text{s}$, which could lead to a temperature increase of ~ 15 K in this study. However, the sample temperature was controlled to be accurate within ± 5 K using an e-beam heater and a constant flow of liquid nitrogen. Similarly, the beam heating effects from Ag^{2+} ion implantation at 873 K and Cs^{13+} ion implantation at 673 K (see below) in this study were also not a major issue. Au was selected as a substitute for Ag in the in-situ diffusion study partly because the Ag^+ beam current was extremely low for implantation. Similar to Ag, Au rarely reacts with host atoms to form strong chemical bonds. The atomic diffusion of both Au and Ag in the solid materials is dominated by physical processes and their general diffusion behavior is expected to be similar. Two Ti_3SiC_2 samples of high-T (873, 773, 673 and 573 K) and low-T (473, 373, 300, and 230 K) were used for the implantation. Each sample had four quarter areas for implantation at different temperatures. The implantation was conducted in order of decreasing temperature starting from 873 to 573 K for the high-T sample and from 473 to 230 K for the low-T sample to minimize or avoid post-implantation thermal annealing effects. Each implantation took 2100 to 2400 s for the high-T sample and 1440 s for the low-T sample except for the 230 K area that took 5400 s for implantation. 1.0 MeV Cs^{13+} ions were also implanted into the polycrystalline Ti_3SiC_2 at 7° off normal to $5.7 \times 10^{20} \text{ Cs}^{13+}/\text{m}^2$ (4.0 at.% Cs and 239 dpa) at 673 K using a 320 kV high-voltage platform connected to an electron cyclotron source at the Institute of Modern Physics, Chinese Academy of Sciences. The elevated temperatures for ion implantation were applied to avoid full amorphization in the material. In-situ 1800 s isochronal annealing of the Cs^{13+} implanted Ti_3SiC_2 in vacuum (10^{-4} Pa) was performed over the temperature range from 723 to 1073 K; in-situ isothermal annealing at 1073 K was also conducted from 300 to 7200 s. Additional furnace annealing at 1173 K for 1800 s was carried out under flowing Ar gas conditions. The purity of Ar gas was 99.99%, but the quartz tube in the furnace could not be pre-pumped and had a partial pressure of oxygen. The thermal annealing was performed with a ramp-up time of 7200 s. The sample was taken out of the furnace at 390 K after 50400 s cooling to expose to ambient air. The ion implantation and thermal annealing parameters are summarized in Table 1.

The various implantation and annealing conditions were applied to study (1) diffusion behavior of Ag in Ti_3SiC_2 during Ag ion implantation at an elevated temperature (873 K), (2) dependence of Au diffusion in Ti_3SiC_2 on implantation temperature, and (3) thermal responses of Cs diffusion in Ti_3SiC_2 from both isochronal and isothermal annealing experiments. A JEOL 7600F scanning electron microscope equipped with a Nordlys camera and interfaced with the Oxford/HKL Channel 5 software package was used to characterize the three types of samples prior to ion implantation. Low-angle backscatter microstructural analysis, EDS and EBSD examinations were performed using an accelerating voltage of 20 keV. EBSD mapping of the CVD 3C-SiC sample was performed at a magnification of $250\times$ using a 500 nm step size. Due to the refined grain size of the polycrystalline Ti_3SiC_2 and dual-phase nanocomposite of $\text{Ti}_3\text{SiC}_2/\text{SiC}$ samples, the analytical magnification was increased to $850\times$ and EBSD maps were generated using a 100 nm pixel step size. Grain size histograms were generated using the EBSD inverse pole figure maps and binned at 0.25 μm . The intercept method was used to evaluate grain size and grain boundaries across the mapped region. An FEI Quanta scanning electron microscope, integrated with focused ion beam (FIB) capability, was used for TEM specimen preparation in this study. Both symmetric scan XRD and grazing-angle incidence XRD (GIXRD) were conducted to determine phase percentages and crystallite size using a Philips X'Pert multipurpose diffractometer with a fixed Cu anode ($\lambda_{\text{Cu}} = 0.154 \text{ nm}$) operating at 45 kV and 40 mA. 2.0 MeV He^+ RBS at a scattering angle of 150° was performed near room temperature to measure the depth profiles of the implanted Ag in the materials. 3.0 MeV He^+ RBS (and resonant backscattering) was also selected to resolve the peaks of the implanted Au and Cs from the host Ti_3SiC_2 .

spectra and to detect surface oxygen. Some of the RBS measurements were repeated under the same conditions to study the behavior of implants at different implantation or annealing temperatures. Micro-XRD measurements (beam spot size: $\sim 50\ \mu\text{m}$) were performed with a rotating Cr anode ($\lambda_{\text{K}\alpha} = 0.229\ \text{nm}$) and a 2D image plate detector to analyze each of the Au^{2+} ion implanted quarters of the polycrystalline Ti_3SiC_2 samples. In addition, the surface of the Au^{2+} ion implanted Ti_3SiC_2 and the cross section of the surface oxidized Ti_3SiC_2 were examined using HIM instrument (Carl Zeiss SMT) under the secondary electron mode at the He^+ ion energy of 30 keV. Compared to conventional scanning electron microscopy (SEM), HIM has demonstrated a better surface sensitivity, higher spatial resolution, larger depth of field, and sharper atomic number contrast. A Cs-corrected JOEL ARM 200cF transmission electron microscope with a probe corrector (0.9 Å spatial resolution) and an enhanced EDS system (JEOL silicon drift detector at a large solid angle of 0.98 steradians) was also used to examine the microstructures of different phases in polycrystalline Ti_3SiC_2 before and after Au^{2+} ion implantation at 230 and 300 K. Most the sample characterizations were performed using EMSL under a user proposal.

4. Results and discussion

4.1. Sample characterization prior to ion implantation

Materials used in this study were characterized using XRD, EDS and EBSD prior to ion implantation. Typical data from the XRD measurements for dual-phase nanocomposite of Ti_3SiC_2 /3C-SiC, CVD 3C-SiC and polycrystalline Ti_3SiC_2 are shown in Fig. 2. Quantitative Rietvelt analysis of the XRD data for the Ti_3SiC_2 /3C-SiC sample (Fig. 2a) suggests that the material has two major components of MAX phase $\alpha\text{-Ti}_3\text{SiC}_2$ and cubic phase 3C-SiC with weight percentages of 63 wt.% and 30 wt.% and average crystallite sizes of 54 and 19 nm, respectively. It should be noted that 3C-SiC ($a = 0.4359\ \text{nm}$) and cubic phase TiC ($a = 0.4327\ \text{nm}$) are essentially indistinguishable in the XRD pattern (Fig. 2a) because their corresponding diffraction peaks can hardly be resolved. The grain composition was determined by EDS. From Fig. 2a, there is an observable minor phase of orthorhombic TiSi_2 with 7 wt.% in the nanocomposite. The average crystallite size of TiSi_2 in the dual-phase nanocomposite has been determined to be 33 nm. Average crystallite size is the average inter-planar distance between the adjacent planar defects that discontinue the lattice periodicity in a crystalline grain. In principle, crystallite size should not be greater than a grain size that can be determined by microscopy methods (see below). Typically, the smaller the average crystallite size, the higher the defect concentration in a crystalline grain is. The XRD pattern in Fig. 2b suggests that the CVD 3C-SiC sample is a single-phase 3C-SiC; the composition of various grains has been confirmed by EDS. The small plateau near the (111) peak originates from the stacking faults in SiC [37]. Rietvelt analysis of the pattern suggests an average crystallite size of 33 nm. Similar analysis of the pattern in Fig. 2c indicates that the major phase in the polycrystalline Ti_3SiC_2 sample is MAX phase $\alpha\text{-Ti}_3\text{SiC}_2$ with 68 wt.% in weight percentage and 168 nm in average crystallite size. The material contained two secondary phases of cubic TiC and orthorhombic TiSi_2 with weight percentages of 24 wt.% and 8 wt.% and average crystallite sizes of 163 and 52 nm, respectively. The results for the three samples are summarized in Table 2.

The three samples were also characterized using EDS and EBSD. EBSD is a useful technique for microstructural analysis, having the ability to simultaneously assess grain structure and preferential orientation. When coupled with EDS, compositional information can also be obtained to provide a more complete characterization profile. EDS was performed for different grains in the three samples and the results (not shown) confirmed the compositions of all the crystal phases determined by XRD (Fig. 2). The

EBSD phase maps of $\text{Ti}_3\text{SiC}_2/\text{3C-SiC}$ and Ti_3SiC_2 as well as the EBSD grain orientation map of single-phase CVD 3C-SiC are shown in Fig. 3, where the black areas are the unindexed regions that include voids, grain boundaries, lattice distortions (strain), or a grain size below the step size. There are twin grains observed in the CVD 3C-SiC (Fig. 3c). Also included in Fig. 3 are the histograms binned at 0.25 μm for the grain size distributions obtained from 50-line intercepts of grain surfaces in the EDSB images. Individual phases are taken into account in the size analysis of the nanocomposite $\text{Ti}_3\text{SiC}_2/\text{3C-SiC}$ and polycrystalline Ti_3SiC_2 . Twin boundaries with a 60° rotation about $\langle 111 \rangle$ axis in the SiC sample were removed from the grain size calculation to allow for a more accurate determination of the size distribution. From the histograms, small grains are greatly outnumbered in each case. The average grain size $\bar{s}$ has been estimated using

$$\bar{s} = \sum n_i s_i / \sum n_i,$$

where n_i expresses the occurrence frequency of the intercept length s_i at sequence number i in a histogram. Estimation shows that $\bar{s}$ value is 1.1 μm for Ti_3SiC_2 , 0.43 μm for 3C-SiC, and 1.2 μm for TiSi_2 in the nanocomposite $\text{Ti}_3\text{SiC}_2/\text{3C-SiC}$. Similarly, $\bar{s} = 5.5 \mu\text{m}$ for the single-phase CVD 3C-SiC, and 2.2, 0.79 and 1.5 μm for phases Ti_3SiC_2 , TiC and TiSi_2 in polycrystalline Ti_3SiC_2 , respectively. These estimated sizes for the three samples are included in Table 2.

4.2. Ag^{2+} ion implanted CVD 3C-SiC and $\text{Ti}_3\text{SiC}_2/\text{3C-SiC}$

2.0 MeV He^+ RBS spectra before and after 400 keV Ag^{2+} ion implantation in CVD 3C-SiC and dual-phase nanocomposite of $\text{Ti}_3\text{SiC}_2/\text{3C-SiC}$ are shown in Fig. 4, where the Ag depth scale is estimated using the SRIM03 database for pure SiC ($3.21 \times 10^3 \text{ kg/m}^3$). The RBS spectrum for the unimplanted sample is statistically the same as that for the implanted one in each case except for the absence of the scattering yields from the Ag implants, as expected. Since the spectra of the host materials (SiC and $\text{Ti}_3\text{SiC}_2/\text{SiC}$) did not change before and after ion implantation, their compositions remained the same without significant surface oxidation or carbon accumulation. The implanted SiC is not expected to be fully amorphized because its critical temperature for amorphization (550 K for Au^{2+} ion irradiation [38]) is much lower than the implantation temperature (873 K), which is consistent with a previous report [7] for SiC irradiated with Ag^{2+} ions to a higher dose at 873 K. The Ag^{2+} ion implanted Ti_3SiC_2 at 873 K should also not be fully amorphized as its critical temperature for amorphization is slightly below 230 K (see below). The Ag peak in Fig. 4a for CVD 3C-SiC shows a Gaussian distribution that is well resolved from the SiC spectrum. The observed Ag peak position (120 nm) is close to the SRIM03 prediction (123 nm). The result suggests that noticeable Ag diffusion did not occur during implantation in polycrystalline CVD 3C-SiC at 873 K. This is an expected result and agrees well with previous observations of immobile Ag in SiC below the temperature of 1573 K [7]. In the Ag^{2+} ion implanted $\text{Ti}_3\text{SiC}_2/\text{3C-SiC}$ (Fig. 4b), however, the Ag profile consists of two convoluted peaks: a broad peak and a sharper one. The broad peak corresponds to immobile Ag in 3C-SiC as observed in the CVD 3C-SiC, while the sharper peak is attributed to Ag accumulation on the sample surface as a result of Ag outward diffusion in Ti_3SiC_2 within the nanocomposite during implantation at 873 K. Similar results for Ag diffusion in Ti_3SiC_2 have never been reported in the literature to the best of our knowledge. Considering the crystal structure of MAX phase Ti_3SiC_2 (Fig. 1), impurity diffusion may prefer to proceed along the relatively open basal plane, where the Si chemical bonds are not as strong. Presence of Si vacancies in the irradiated Ti_3SiC_2 is expected, which could assist the outward diffusion process. However, it remains to be further investigated

to develop diffusion mechanisms of impurities in MAX phases and understand the role of grain boundaries.

4.3. Au^{2+} ion implanted Ti_3SiC_2

Further in-situ diffusion studies were performed as a function of implantation temperature in polycrystalline Ti_3SiC_2 without the presence of SiC using 2.0 MeV Au^{2+} ions as Ag^+ beam was not available. Au was selected as a substitute for Ag because its general diffusion behavior is similar to that of Ag. Optically, the surface of the sample implanted at 230 K has an apparent change in the reflectivity of visible light, while the rest of the samples implanted at higher temperature from 300 to 873 K do not. The RBS spectra for polycrystalline Ti_3SiC_2 implanted at various temperatures, along with an unimplanted sample, are shown in Fig. 5, with elements on the sample surface indicated by arrows. Oxygen resonant backscattering (see next section) is not observed, indicating that the sample surface is not oxidized during the implantation in vacuum (10^{-4} Pa) at the elevated temperatures. The two vertical dashed lines show the depth region of the implanted Au and the horizontal dotted lines represent offsets for clarity. From Fig. 5, the Au peak position, width, and shape do not change up to 673 K, suggesting that observable Au diffusion in Ti_3SiC_2 does not occur up to this temperature. The Au atoms appear to start diffusing in Ti_3SiC_2 during implantation at 773 K, where the peak becomes slightly broader, but the peak position remains unchanged. There is an extensive Au out-diffusion in Ti_3SiC_2 during implantation at 873 K and Au accumulation on the surface is clearly visible. The result is similar to the extensive Ag outward diffusion observed in Ti_3SiC_2 within the dual-phase nanocomposite during ion implantation at 873 K (Fig. 4b). The RBS spectra do not suggest a composition change in the ternary compound during the Au^{2+} ion implantation at 10^{-4} Pa up to the highest applied temperature (873 K).

The surface morphologies of the Au^{2+} ions implanted Ti_3SiC_2 samples and an unimplanted sample were also examined using HIM under the secondary electron mode. The images for selected samples are shown in Fig. 6 with the same field of view (10 μm). Microstructurally, apparent fractures or microcracks are not observed in the implanted samples at the applied temperatures. The unimplanted sample (Fig. 6a) exhibits a flat surface with a sharp contrast for the grains and pores. The large grains are Ti_3SiC_2 , the major phase of the material. The smaller, brighter and darker particles are TiC and TiSi_2 , respectively, as determined by EDS and indicated in Fig. 6a, consistent with previous SEM studies [20,21]. The dark dots are pores that do not show preferred locations in the microstructure. Compared to the flat surface of the unimplanted sample (Fig. 6a), the 230 K implanted sample (Fig. 6b) appears to exhibit an uneven surface that is likely due to differential volume swelling among the different phases in the sample. Nappé *et al.* [21] used step-height method and determined volume swelling of 2.2% in Ti_3SiC_2 irradiated with Au^+ ions to a dose of 4.3 dpa at room temperature. The swelling was attributed to an increase in lattice parameter c [24]. However, there have been no reports on volume swelling in irradiation-induced TiC or TiSi_2 to date. As will be shown below, TEM and selected area electron diffraction (SAED) studies suggest that TiC is not fully amorphized, Ti_3SiC_2 nearly fully amorphized, and TiSi_2 completely amorphized under the irradiation conditions at 230 K. Full amorphization of crystals usually leads to a significant volume swelling. Observable volume swelling can also be induced by defect accumulation in the crystalline microstructure. Different compositions can have different disordering rates and simultaneous defect recovery efficiencies during ion implantation. The possible swelling effect is also visible at 300 K (Fig. 6c), but is less pronounced. The contrast gradually fades out with increasing irradiation temperature. It is generally expected that high-dose MeV ion implantation at a higher temperature (below the melting point) leads to a lower saturated defect concentration over a certain temperature range if complete amorphization does not occur.

In addition, micro-GIXRD at $\omega = 5^\circ$ for the Au^{2+} implanted samples was performed using Cr K_α irradiation ($\lambda = 0.229 \text{ nm}$). The data are shown in Fig. 7 with vertical offsets for clarity. The path length for the x-rays in Ti_3SiC_2 to attenuate its initial intensity to 10% and 50% is estimated to be 15 and 4.5 μm , respectively. For $\omega = 5^\circ$, the penetration depth (perpendicular to the sample surface) of the incident pathway corresponds to 1310 and 390 nm. Since the implantation damage band is extended to a depth of $\sim 600 \text{ nm}$ (see below), the data in Fig. 7 have considerable contributions from the unimplanted material. Micro-XRD at $\omega = 2^\circ$ was also attempted for comparison, but the reflection intensity was too small to achieve distinct diffraction patterns within a reasonable data collection time. As expected, three phases are identified with Ti_3SiC_2 as the major phase and TiC and TiSi_2 as minor phases, consistent with Fig. 2c. Although the size of the x-ray beam spot (an elliptical area with a short axis of 50 μm and a long axis of 570 μm due to 5° grazing angle incidence) is much larger than the average grain size in the sample, the weight percentage of TiSi_2 is relatively small (8%) (Table 2). The concentrations and orientations of the TiSi_2 grains could vary from spot to spot, resulting in different peak intensities in the XRD pattern, which can be seen from Fig. 7. The overall evolution of the XRD patterns with irradiation temperature suggests that the Ti_3SiC_2 grains have smaller residual damage produced at higher temperatures during ion irradiation. However, the change in the average crystallite size of Ti_3SiC_2 cannot be accurately determined from the XRD data due to weak peak intensities. Previous reports on some other nanocrystalline grains, such as SiC [39], ZrO_2 [40] and Fe_3O_4 [41], indicate grain growth with increasing dose at temperatures above the critical temperature for amorphization. How Ti_3SiC_2 nanoparticles would behave still remains to be investigated. At $2\theta \approx 92^\circ$ for Ti_3SiC_2 , the diffraction peak is hardly visible for implantation temperature at 230 K. This is an indication of the possible formation of a highly disordered lattice state at the sample surface due to ion implantation. The result is consistent with the TEM data (see below) and in a good agreement with a previous report [22] that showed heavy lattice damage in the structure of Au^+ ion irradiated Ti_3SiC_2 through nuclear interactions.

Further microstructural studies of the Au^{2+} ion implanted samples are performed using TEM, SAED and EDS. High-resolution EDS mapping of the implanted Au in Ti_3SiC_2 (data not shown) indicates the peak maximum of the Au profile is located at the depth of $\sim 380 \text{ nm}$, which is $\sim 100 \text{ nm}$ deeper than SRIM simulation predicts. This allows us to reasonably assume that the damage peak maximum is at $\sim 300 \text{ nm}$ from the surface based on SRIM prediction of $\sim 200 \text{ nm}$. Fig. 8 shows a bright-field TEM image of polycrystalline Ti_3SiC_2 implanted with 2.0 MeV Au^{2+} ions to $1.0 \times 10^{20} \text{ ions/m}^2$ at 230 K, which is one of the regions in the implanted sample that has three neighboring grains of hexagonal Ti_3SiC_2 , orthorhombic TiSi_2 and cubic TiC, as shown in the inset. A damage band is clearly visible, which extends to the depth of $\sim 600 \text{ nm}$. A thin crystalline layer ($\sim 5 \text{ nm}$ thick) on the sample surface is also observed, as shown in the inset of the upper left corner. The layer contains oxygen and titanium, as determined by EDS (data not shown). More data and discussion on the Ti_3SiC_2 surface oxidation are provided in the next section. A series of SAED patterns inside the damage band were taken using an aperture of 100 nm in diameter and some of the data are included in Fig. 8. On both sides of the band, bright diffraction spots in combination with Debye rings associated with intensity maxima are observed, indicating that single-crystal structure (long-range lattice order) of Ti_3SiC_2 is largely preserved with some defect concentrations that break the lattice periodicity and cause local crystalline zones to be misoriented by 3° to 5° . With increasing local dose in dpa (displacements per atom) up to the maximum value ($\sim 60 \text{ dpa}$) at the depth of $\sim 300 \text{ nm}$ (damage peak), the long-range order of crystallinity is gradually transformed into shorter-range order with further misorientation by 10° to 15° . The pattern between 300 – 400 nm evolves into predominant halos from the amorphized material and only very weak diffraction spots (in the innermost halo) from the remaining crystalline zones. The crystal is nearly, but not completely, amorphized at the damage peak. The results indicate that MAX phase Ti_3SiC_2 is very resistant to ion-irradiation-induced amorphization.

The critical temperature for amorphization in Ti_3SiC_2 is expected to be slightly lower than 230 K. Irradiation at 300 K to the same Au^{2+} ion fluence (1.0×10^{20} ions/ m^2) did not render the material fully amorphous (data not shown).

Fig. 9 shows a sequence of high-resolution TEM images taken at the depths of 100 and 300 nm of the same sample as in Fig. 8 for Ti_3SiC_2 , TiSi_2 and TiC grains. Also included in the figure are the SAED patterns and the fast Fourier transformation (FFT) results from the images, respectively. It is evident that at 100 nm, only the imaged TiSi_2 grain is fully amorphized. Lattice fringes from both the Ti_3SiC_2 and TiC grains in their TEM images are visible. Some orientation changes occur in individual crystalline zones of Ti_3SiC_2 , as the diffraction spots clearly become diverged ($\sim 5^\circ$) in the FFT pattern (inset of Fig. 9a). Only isolated defects appear in the TiC grain without loss of the crystal orientation as Debye rings are not observed in Fig. 9c. Near the damage peak (300 nm) where the dose is the highest, TiSi_2 is fully amorphized, as expected (Fig. 9e). The SEAD pattern in Fig. 9d shows some bright spots in the halo, suggesting that Ti_3SiC_2 crystal is not completely amorphized, which is consistent with the results in Fig. 8. The material is predominantly highly disordered with few remaining crystalline zones that are so small that the lattice fringes (overlapped with the contrast from the highly disordered structure) are not visible in the TEM image (Fig. 9d). However, the TiC grain still preserves a single-crystal structure, as shown in Fig. 9f. Apparently, TiSi_2 , Ti_3SiC_2 and TiC crystals are in order of increasing resistance to ion-beam irradiation induced amorphization.

4.4. Cs^{13+} ion implanted Ti_3SiC_2

The stable isotope ^{133}Cs was also implanted as a fission surrogate for ^{137}Cs to study its diffusion behavior in MAX phase Ti_3SiC_2 . 3.0 MeV He^+ ion RBS was used to measure the Cs depth profile in the as-implanted sample. Both isochronal and isothermal annealing experiments were followed to study Cs diffusion as a function of annealing temperature and duration using in-situ RBS methods. The data for the 1800-s isochronal annealing at temperatures from 723 to 1073 K are shown in Fig. 10a. Also included in the figure is the data for the as-implanted sample at 673 K. The Cs peaks are magnified by a factor of 3 for a better presentation of the fine structures. The RBS spectra of Ti_3SiC_2 did not change under the implantation conditions, suggesting that the material composition remained the same. In all cases, the Cs peaks in the spectra are well resolved and located in a low-background region. The Cs peak in the as-implanted Ti_3SiC_2 shows a Gaussian distribution, whose peak position is reasonably consistent with SRIM03 prediction. The result indicates that Cs is not very mobile in Ti_3SiC_2 during implantation at 673 K. The peak position, FWHM and shape of the implanted Cs hardly changed after thermal annealing up to 923 K. However, further annealing at 973 K leads to an abrupt change in the peak shape and a reduction in the peak intensity. The original Gaussian peak becomes at least two convoluted peaks, showing an overall Cs diffusion towards the surface at 973 K. However, Cs did not accumulate an observable amount on the surface at 973 K, but likely evaporated into vacuum (10^{-4} Pa) during the thermal annealing. About 36% of Cs was estimated to be released from the sample based on the reduction in the peak intensity. In contrast, Cs in SiC starts diffusing and escaping from the sample at a much higher temperature (~ 1473 K) without surface accumulation [42,43]. The Cs behavior is apparently different from that of Ag and Au whose surface accumulation was observed (Figs. 4b and 5). This may be associated with the sample temperature and the strength of chemical bonding with the surface atoms. Unlike Ag and Au in Ti_3SiC_2 during ion implantation at 873 K, the temperature for significant Cs diffusion is ~ 100 K higher. While chemical effects may be different for diffusion of Cs and Ag or Au in the sample, it is also possible that irradiation-enhanced diffusion may play a role. In general, an increase in temperature is not a big surprise because thermal processes usually take place at lower temperatures when ion irradiation is present. In

fact, ion irradiation can enhance diffusion processes through various mechanisms, including ionization-enhanced diffusion mechanism, Bourgoin mechanism, energy-release mechanism and recoil mechanism [44]. Further annealing of the sample at 1023 and 1073 K resulted in diminishing diffusion and loss of Cs, as shown in Fig. 10a, suggesting that Cs precipitation could occur in the matrix. At the end of the annealing at 1073 K for 1800 s, a total of ~50% Cs was released from the implanted Ti_3SiC_2 .

Isothermal annealing at 1073 K in vacuum (10^{-4} Pa) was also performed for durations ranging from 300 to 7200 s. The in-situ RBS data are shown in Fig. 10b. The as-implanted sample shows a small peak that is barely seen in Fig. 10a, which could originate from a minor amount of surface Cs at 673 K. There is a small change in the Cs depth profile after 300 s annealing. It appears that Cs tends to diffuse towards the surface, but accumulation of Cs on the surface is not evident, which is consistent with the data in Fig. 10a. The overall reduction in the peak intensity or Cs loss is ~10% at 300 s. A more significant Cs loss of ~30% relative to the total implanted Cs occurred at 900 s, followed by a total Cs loss of ~40% at 1800 s, which is statistically not very different from the percentage (~50%) of Cs released after 1800 s isochronal annealing at 1073 K (Fig. 10a). Also similar is the shape of the Cs profile that consists of convoluted peaks. Further annealing for longer durations up to 7200 s does not lead to a significant change in the Cs depth profile. Again, this could be due to Cs precipitation in the sample. It should be noted that the Cs profiles in Fig. 10 show multiple peaks once significant Cs diffusion occurs (at 973 K for 1800 s and at 1073 K for 900 s), indicating that the Cs diffusion is non-Fickian and involves multiple activated processes at the same time with different activation energies. This complex process does not allow us to derive a single activation energy from the current Cs data. However, the parameter is critically important to support modeling efforts. Further specially designed experiments are warranted to determine the activation energy and the migration energy as well.

In addition, the Cs^{13+} ion implanted Ti_3SiC_2 sample was annealed in a furnace at 1173 K for 1800 s with flowing Ar gas. The data from the 3.0 MeV He^+ ion RBS/non-RBS (resonant RBS) measurement of the annealed sample is shown in Fig. 11, along with a spectrum for as-implanted sample. There is an oxygen peak at the surface from the strong $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ resonance centered at $E = 3.03$ MeV [45,46], indicating that the sample surface was oxidized during the thermal annealing step. In spite of the flowing Ar gas during thermal annealing, the quartz tube in the furnace had a partial pressure of oxygen that reacted with the hot Ti_3SiC_2 surface. The result suggests that MAX phase Ti_3SiC_2 is susceptible to oxidation at 1173 K. From Fig. 11, significant Cs diffusion and loss occurred during the annealing process. However, there is still an observable amount of Cs retained in the material. Inward Cs diffusion into the bulk is also evidenced. The data also suggest that there is a high Ti concentration starting from the surface. The overall RBS spectrum suggests that the MAX phase Ti_3SiC_2 decomposed upon oxidation and the surface of the annealed sample contains mainly titanium oxide. Further studies of the annealed sample were performed using GIXRD and cross-sectional HIM, and the data are shown in Figs. 12 and 13, respectively. The GIXRD data ($\omega = 5^\circ$) in Fig. 12 clearly indicates that in addition to a minor phase of anatase (TiO_2), crystalline rutile (TiO_2) was nucleated and grown to an average crystallite size of 44 nm during the oxidation process. The cross-sectional view of a freshly cleaved surface of the surface-oxidized Ti_3SiC_2 in Fig. 13 shows two distinct layers of nanocrystals and amorphous materials (with inclusion of small grains) on crystalline Ti_3SiC_2 . Clearly, Ti_3SiC_2 crystal prefers to cleave along basal planes at room temperature. The top surface layer consists of nanocrystals with grain sizes ranging from <100 to ~500 nm. From the XRD data in Fig. 12, these nanocrystals must be rutile, consistent with the RBS data in Fig. 11. The buried amorphous layer, showing a rather flat cleaved cross section, has a thickness of ~500 nm. According to the chemical reaction that occurs during oxidation of Ti_3SiC_2

the main composition of the amorphous layer should be SiO_2 , which is not visible in the XRD pattern (Fig. 12). It should be noted that previous oxidation studies of MAX phase Ti_3SiC_2 [28,47] showed the formation of an outer pure TiO_2 (rutile) layer and an inner mixed layer comprising crystalline TiO_2 and amorphous SiO_2 (silica) on sample surface annealed in air at 1373 K for 1296000 s. It was attributed to an inward diffusion of oxygen and a simultaneous outward diffusion of titanium in TiO_2 , while Si atoms were oxidized in situ [19]. Bellucci, *et al.* [48] presented evidence that the oxidation started with O ions diffusing through TiO_2 layer at the TiC/TiO_2 interface, substituting for C and releasing C as an interstitial that then diffused through the TiO_2 layer and was ultimately oxidized on the TiO_2 surface. The results shown in Figs. 11 to 13 confirm the previous observations and provide some detailed features about the gradient character of Ti concentrations in oxide layers, microstructures of the rutile nanocrystals, morphology of the amorphous SiO_2 layer with crystalline TiO_2 grains, and anatase as a minor phase. As a result of the material decomposition and oxidation, the Cs was no longer in the MAX phase Ti_3SiC_2 and its diffusion behavior could become very different. This could be an interesting topic for future studies.

4. Conclusions

The results from this study indicate that diffusion of Ag, Au and Cs in MAX phase Ti_3SiC_2 occurs at relatively low temperatures (773 – 973 K) compared to diffusion of species in 3C-SiC. Although the mechanisms for fast diffusion of these species in this ternary MAX phase have not yet been established, one hypothesis is that the layered crystal structure may play a significant role in determining impurity diffusion rates in MAX phases. The implanted species are observed to escape from the sample at the diffusion temperatures. It has also been found that TiSi_2 , Ti_3SiC_2 and TiC crystals in the sample show an increasing order of resistance to ion-beam irradiation induced amorphization. The critical temperature for amorphization in Ti_3SiC_2 is found to be slightly below 230 K. Significant surface oxidation of Ti_3SiC_2 takes place at 1173 K, leading to formation of a top layer of TiO_2 (rutile) nanocrystals and a buried layer of amorphous SiO_2 with TiO_2 inclusions. Because these temperatures are relatively low for advanced high-temperature reactor designs, this study suggests some caution in using Ti_3SiC_2 as a fuel cladding material for advanced nuclear reactors operating at very high temperatures. Further studies of impurity transport in the related materials may be warranted based on the results of this study.

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Table 1

Ion implantation and thermal annealing conditions for the study samples of dual-phase nanocomposite $\text{Ti}_3\text{SiC}_2/3\text{C-SiC}$, CVD 3C-SiC and polycrystalline Ti_3SiC_2 .

Material	Sample Tilt (deg.)	Ion	Energy (MeV)	Fluence; Dose (10^{20} ions/m ² ; dpa)	Irradiation Temp. (K)	Ann. Temp./Time/Environment
$\text{Ti}_3\text{SiC}_2/3\text{C-SiC}$ CVD 3C-SiC	7°	Ag^{2+}	0.4	2.8; 110	873	None
Ti_3SiC_2	0°	Au^{2+}	2.0	1.0; 60	230, 300, 373, 473, 573, 673, 773, 873	None
Ti_3SiC_2	7°	Cs^{13+}	1.0	5.7; 240	673	(a) 1073 K: 300, 900, 1800, 3600, 7200 s, 10^{-4} Pa; (b) 1800 s: 723, 773, 823, 873, 923, 973, 1023, 1073 K, 10^{-4} Pa; (c) 1173 K, 1800 s, Ar

Table 2

Weight percentage, average crystallite size and average grain size of each phase in the three study samples prior to ion implantation.

Phase	PDF Number	X-ray Density (10^3 kg/m^3)	Nanocomposite Ti ₃ SiC ₂ /3C-SiC wt.%; C (nm) / G (μm) *	Polycrystalline CVD 3C-SiC wt.%; C (nm) / G (μm) *	Polycrystalline Ti ₃ SiC ₂ wt.%; C (nm) / G (μm) *
Ti ₃ SiC ₂	059-0189	4.528	63; 54 / 1.1	0; 0 / 0	68; 168 / 2.2
3C-SiC [#]	029-1129	3.216	30; 19 / 0.43	100; 33 / 5.5	0; 0 / 0
TiC [#]	032-1383	4.911	0; 0 / 0	0; 0 / 0	24; 163 / 0.79
TiSi ₂	033-1384	4.076	7; 33 / 1.2	0; 0 / 0	8; 52 / 1.5

[#]Minor phases of TiC and 3C-SiC are not distinguishable by XRD; the grain compositions were identified by EDS.

* C (nm) / G (μm) is the average crystallite size and average grain size in nm and μm , determined by XRD and EBSD, respectively.

Figure Captions

Fig. 1. A close-packed hexagonal structure of α - Ti_3SiC_2 , showing the atomic stacking sequence and Ti_6C octahedra.

Fig. 2. Symmetric scan XRD patterns for (a) dual-phase nanocomposite of Ti_3SiC_2 /3C-SiC with a secondary phase of TiSi_2 , (b) polycrystalline cubic phase of 3C-SiC and (c) polycrystalline MAX phase of Ti_3SiC_2 with secondary phases of TiC and TiSi_2 .

Fig. 3. (a) and (b) EBSD phase map and histograms for the grain size distributions in dual-phase nanocomposite of Ti_3SiC_2 /3C-SiC, (c) and (d) EBSD inverse pole figure Z-direction map and histogram for the grain size distribution in CVD 3C-SiC, and (e) and (f) EBSD phase map and histograms for the grain size distributions in polycrystalline Ti_3SiC_2 .

Fig. 4. 2.0 MeV He^+ RBS spectra for (a) polycrystalline CVD 3C-SiC and (b) dual-phase nanocomposite of Ti_3SiC_2 /3C-SiC implanted 7° off normal with 400 keV Ag^{2+} to 2.8×10^{20} ions/ m^2 at 873 K. RBS spectra for the unimplanted materials are also included.

Fig. 5. A sequence of in-situ 3.0 MeV He^+ RBS spectra for polycrystalline Ti_3SiC_2 implanted with 2.0 MeV Au^{2+} to the same ion fluence of 1.0×10^{20} ions/ m^2 at various temperatures. RBS spectrum for the unimplanted material is also included.

Fig. 6. A series of HIM micrographs of polycrystalline Ti_3SiC_2 before and after 2.0 MeV Au^{2+} ion implantation to the same ion fluence of 1.0×10^{20} ions/ m^2 at various temperatures. All images have the same scalar bar.

Fig. 7. A sequence of micro-beam GIXRD patterns ($\omega = 5^\circ$) for polycrystalline Ti_3SiC_2 implanted with 2.0 MeV Au^{2+} to the same ion fluence of 1.0×10^{20} ions/ m^2 at various temperatures. The pattern for the unimplanted material is also included.

Fig. 8. Bright-field TEM micrograph of Ti_3SiC_2 implanted with 2.0 MeV Au^{2+} ions to 1.0×10^{20} ions/ m^2 at 230 K, showing a damage band and a thin surface oxide layer. Insets show a low-resolution image of the FIB sample and a high-resolution image of the surface oxide layer, respectively. A series of SAED patterns are also shown, which were taken from the 6 circled regions within the damage band in Ti_3SiC_2 with an aperture diameter of 100 nm.

Fig. 9. High-resolution TEM micrographs with corresponding FFT results and SAED patterns taken at 100 nm in (a) Ti_3SiC_2 , (b) TiSi_2 and (c) TiC and at 300 nm (near the damage peak) in (d) Ti_3SiC_2 , (e) TiSi_2 and (f) TiC , implanted with 2.0 MeV Au^{2+} ions to 1.0×10^{20} ions/ m^2 at 230 K.

Fig. 10. A sequence of in-situ 3.0 MeV He^+ RBS spectra for polycrystalline Ti_3SiC_2 implanted with 1.0 MeV Cs^{13+} to an ion fluence of 5.7×10^{20} ions/ m^2 at 673 K, followed by (a) 1800 s isochronal annealing at various temperatures and (b) 1073 K isothermal annealing for various durations. The Cs peak is magnified by a factor of 3 for clarity.

Fig. 11. 3.0 MeV He^+ RBS/non-RBS spectrum for polycrystalline Ti_3SiC_2 implanted with 1.0 MeV Cs^{13+} to an ion fluence of 5.7×10^{20} ions/ m^2 at 673 K and annealed at 1173 K for 1800 s.

Fig. 12. GIXRD pattern for polycrystalline Ti_3SiC_2 implanted with 1.0 MeV Cs^{13+} to an ion fluence of 5.7×10^{20} ions/ m^2 at 673 K and annealed at 1173 K for 1800 s.

Fig. 13. (a) Cross-sectional HIM micrograph ($\sim 82^\circ$ off surface normal) of an oxidized Ti_3SiC_2 surface containing a crystalline rutile nanoparticle layer and an amorphous SiO_2 layer with TiO_2 grain inclusions on polycrystalline Ti_3SiC_2 implanted with 1.0 MeV Cs^{13+} to an ion fluence of 5.7×10^{20} ions/ m^2 at 673 K and annealed at 1173 K for 1800 s, and (b) a magnified micrograph of the oxidized surface layers in (a) (c: crystalline; a: amorphous).

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Figure9

Figure10

Figure11

Figure12

Figure13