Irradiation-induced disordering and amorphization of Al₃Ti-based intermetallic compounds

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An in situ ion-irradiation study, simultaneously examined using transmission electron microscopy, was performed to investigate irradiation-induced disordering and amorphization of Al₃Ti-based intermetallic compounds. Thin foil samples of two crystalline structures: D0₂₂-structured Al₃Ti and L₁₂-structured (Al,Cr)₃Ti were irradiated using 1.0 MeV Kr ions at a temperature range from 40 K to 573 K to doses up to \(4.06 \times 10^{15}\) ions/cm². The results showed that both the compounds underwent an order-disorder transformation under irradiation, where both Al₃Ti and (Al,Cr)₃Ti ordered structures were fully transformed to the disordered face-centered cubic (FCC) structure except at the highest irradiation temperature of 573 K. A slightly higher irradiation dose was required for order-disorder transformation in case of Al₃Ti as compared to (Al,Cr)₃Ti at a given temperature. However, their amorphization resistances were different: while the disordered FCC (Al,Cr)₃Ti amorphized at the irradiation dose of \(6.25 \times 10^{14}\) ions/cm² (0.92 dpa) at 40 K and 100 K, the Al₃Ti compound with the same disordered FCC structure maintained crystallinity up to \(4.06 \times 10^{15}\) ions/cm² (5.62 dpa) at 40 K. The critical temperature for amorphization of (Al,Cr)₃Ti under Kr ion irradiation is likely between 100 K and room temperature and the critical temperature for disordering between room temperature and 573 K.

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1. Introduction

Al₃Ti intermetallic compounds have been proposed as a potential high-temperature structure material because of their low density (3.36 g/cm³), relatively high melting temperature (>1623 K), and good oxidation resistance [1]. The main obstacle to employing Al₃Ti as a structural material is its brittleness that is intrinsically caused by a non-symmetrical (tetragonal) D0₂₂ crystal structure having insufficient independent slip systems for plastic deformation [2]. The D0₂₂-structured Al₃Ti can be transformed to the more symmetric L₁₂ structure by replacing some of the Al with transition metals [3–6]. The L₁₂ structure features improved ductility because the increased number of independent slip systems in the cubic structure improves tensile ductility when deformed at low temperatures [7].

Fig. 1 shows the unit cells of D0₂₂ and L₁₂ ordered structures. The tetragonal D0₂₂ structure is derived from the cubic L₁₂ structure by introducing an anti-phase boundary on every (001) plane. Under equilibrium conditions, Al₃Ti is stabilized into the relatively non-symmetrical D0₂₂ structure (instead of the more symmetrical L₁₂ structure) primarily due to the fact that the hybridization between Al p and Ti d electrons results in a strong directionality of bonding structure. The stability of D0₂₂ relative to L₁₂ varies depending on the c/a ratio, according to ab initio calculations performed using the augmented-spherical-wave (ASW) method [8]. The energy of the binary Al₃Ti compound with D0₂₂ structure was found to be lower than that with L₁₂ structure by about 0.05 eV/atom (4800 J/g-atom) when the c/a ratio was increased (relaxed) to 2.24, while, for the ideal c/a ratio of 2, L₁₂ was more stable than D0₂₂.

One possible application of Al₃Ti-based intermetallic compounds is in the fabrication of oxidation-resistant coatings for nuclear fuel cladding to enhance accident tolerance [9] as they show excellent oxidation resistance in high-temperature environments...
Prior to application in nuclear reactors, it is crucial to clarify the effect of irradiation on the properties of Al₃Ti-based intermetallic compounds. However, no work has been carried out on the effect of irradiation on phase stability of Al₃Ti-based alloys except that the D₀₂₂-structured Al₃Ti was reported to undergo amorphization at 1.3 dpa under 250 keV Kr ion irradiation at temperatures less than 40 K [12]. Moreover, L₁₂-structured Al₃Ti-based ternary alloys, which are more suitable for coating applications in the light of their higher ductility, are anticipated to show a different behavior under irradiation than D₀₂₂-structured binary Al₃Ti.

In general, intermetallic compounds have been reported to undergo disordering and amorphization under irradiation [13,14] due to chemical and topological disordering [14]. The use of Al₃Ti-based intermetallic compounds in fuel claddings requires a due to chemical and topological disordering [14]. The use of Al₃Ti-based intermetallic compounds in fuel claddings requires a more fundamental understanding of the phase stability in the irradiation condition. It is crucial to clarify how Al₃Ti-based intermetallic compounds behave in terms of disordering, phase change, and susceptibility to amorphization under irradiation. The objective of this study is to investigate phase stability and susceptibility to amorphization under irradiation at various temperatures for Al₃Ti-based intermetallic compounds, with focus on the different response in terms of amorphization and disordering of the two crystal structures: D₀₂₂ and L₁₂.

2. Experimental procedure

Two types of Al₃Ti-based intermetallic compounds with different crystal structures were used in this study: Al₃Ti with D₀₂₂ and (Al,Cr)₃Ti with L₁₂. Ingots were manufactured by arc melting of mixtures with compositions of Al−25Ti and Al−25Ti−10Cr (at.%) followed by homogenizing at 1423 K for 48 h to obtain the desired crystal structures of D₀₂₂ for Al₃Ti and L₁₂ for (Al,Cr)₃Ti, respectively. Samples for in situ transmission electron microscopy (TEM) under ion irradiation were prepared by the following procedure: the homogenized ingots were cut into sheet-type specimens, mechanically polished down to a thickness of about 100 µm, punched out into 3 mm discs, and perforated by electro-polishing on both sides in a solution of 10% perchloric acid and 90% methanol at 253 K and 20 V.

The electron-transparent samples were irradiated with 1.0 MeV Kr ions at a dose rate of 6.25 × 10¹¹ ions/cm²-s using the IVEM-Tandem, a facility in the Electron Microscopy Center in the Argonne National Laboratory, in which a Hitachi 9000 transmission electron microscope is linked to an ion implanter. Ion irradiations were carried out at temperatures of 40 K, 100 K, 298 K (room temperature), and 573 K to examine the effect of temperature on the phase transformations of the crystal structure. The displacement damage distribution as a function of depth was calculated using the Monte Carlo software package SRIM [15]. Fig. 2 shows the SRIM calculation results for Al₃Ti and (Al,Cr)₃Ti using the Kinchin-Pease model [16] with a mean threshold displacement energy E_d = 28 eV for Al, Ti, and Cr. During the irradiation at each temperature, the changes in the material microstructures and diffraction patterns were observed in situ. Irradiations were systematically stopped at certain dose levels to acquire bright-field and dark-field images, and diffraction patterns using the Gatan Digital Micrographs software.

3. Results and discussion

Fig. 3 shows selected area diffraction patterns of Al₃Ti before and after irradiation with 1.0 MeV Kr ions at a rate of 6.25 × 10¹¹ ions/cm²-s at 40 K and room temperature, which, according to SRIM calculation, produces a displacement rate of approximately 5 × 10⁻¹⁶/s, proportionally divided between Al and Ti. Fig. 3a shows an Al₃Ti diffraction pattern taken before the irradiation which shows an ordered crystal structure of D₀₂₂ at 40 K. Both superlattice reflections and fundamental reflections were visible before the irradiation. The ratio of the intensity of the superlattice reflections to that of the fundamental reflections decreased as the irradiation dose increased to 6.25 × 10¹³ ions/cm² (0.09 dpa) (Fig. 3b), indicating that the irradiation caused disordering of the initially ordered crystal structure. The order-disorder transformation was found to be completed at the irradiation of 3.13 × 10¹⁴ ions/cm² (0.43 dpa) (Fig. 3c), as at that dose the superlattice reflections disappeared and the remaining fundamental reflections were identified as face-centered cubic (FCC). The disordered FCC structure was irradiated to a dose of 4.06 × 10¹⁵ ions/cm² (5.62 dpa) with no change in the diffraction pattern and in particular, no amorphization being observed (Fig. 3d).

The results of the irradiation-induced phase transformation at room temperature were similar to those observed at 40 K, except that the irradiation dose for the completion of order-disorder...
transformation increased up to $6.25 \times 10^{14}$ ions/cm$^2$ (0.86 dpa) (Fig. 3h). The ordered crystal structure of D0$_{22}$ became increasingly disordered with higher irradiation dose, which is confirmed by the fact that the intensity of the superlattice reflections became weaker as the irradiation dose increased from 0 up to $1.56 \times 10^{14}$ ions/cm$^2$ (0.22 dpa), eventually changing to the disordered FCC structure. The irradiation at room temperature was ended at $6.25 \times 10^{14}$ ions/cm$^2$ (0.86 dpa) when the ordered structure of D0$_{22}$ was fully transformed to the disordered FCC structure.

The irradiation-induced phase transformation was also investigated for the (Al,Cr)$_3$Ti sample which has a L1$_2$ crystal structure. Fig. 4 shows the selected area diffraction patterns (a, c, d, f) and the transmission electron micrographs (b, e) of (Al,Cr)$_3$Ti before and after irradiation with 1.0 MeV Kr ions at a rate of $6.25 \times 10^{11}$ ions/cm$^2$-s at 40 K. The diffraction pattern obtained before irradiation exhibited a fully ordered structure of L1$_2$ with both fundamental and superlattice reflections visible (Fig. 4a) and an absence of defects or imperfections (Fig. 4b). As the irradiation dose increased up to $6.25 \times 10^{13}$ ions/cm$^2$ (0.09 dpa), the intensity of superlattice reflections decreased (Fig. 4c), finally disappearing at a dose of $1.56 \times 10^{14}$ ions/cm$^2$ (0.23 dpa). In Fig. 4d, an amorphous ring is also visible together with the diffraction pattern on FCC, indicating that the ordered L1$_2$ structure has fully transformed to the disordered FCC structure before this dose level. Many defects are visible in the irradiated microstructure up to a dose of $1.56 \times 10^{14}$ ions/cm$^2$ (0.23 dpa) (Fig. 4e). The dose to the completion of order-disorder transformation was lower in (Al,Cr)$_3$Ti compared to Al$_3$Ti at 40 K. The disordered FCC (Al,Cr)$_3$Ti eventually amorphized as the irradiation dose increased up to $6.25 \times 10^{14}$ ions/cm$^2$ (0.92 dpa) (Fig. 4f), whereas Al$_3$Ti remained crystalline up to $4.06 \times 10^{15}$ ions/cm$^2$ (5.62 dpa).

Fig. 5 shows selected area diffraction patterns of (Al,Cr)$_3$Ti before and after irradiation with 1.0 MeV Kr ions at a rate of $6.25 \times 10^{11}$ ions/cm$^2$-s at 100 K. As the irradiation dose increased up to 2.19 $\times 10^{14}$ ions/cm$^2$ (0.32 dpa), the intensity of superlattice reflections decreased (Fig. 4c), finally disappearing at a dose of $1.56 \times 10^{14}$ ions/cm$^2$ (0.23 dpa). In Fig. 4d, an amorphous ring is also visible together with the diffraction pattern on FCC, indicating that the ordered L1$_2$ structure has fully transformed to the disordered FCC structure before this dose level. Many defects are visible in the irradiated microstructure up to a dose of $1.56 \times 10^{14}$ ions/cm$^2$ (0.23 dpa) (Fig. 4e). The dose to the completion of order-disorder transformation was lower in (Al,Cr)$_3$Ti compared to Al$_3$Ti at 100 K. The disordered FCC (Al,Cr)$_3$Ti eventually amorphized as the irradiation dose increased up to $6.25 \times 10^{14}$ ions/cm$^2$ (0.92 dpa) (Fig. 4f), whereas Al$_3$Ti remained crystalline up to $4.06 \times 10^{15}$ ions/cm$^2$ (5.62 dpa).
finally amorphizing at 6.25 \times 10^{14} \text{ ions/cm}^2 (0.92 \text{ dpa}). The trend of the phase transformation observed in Fig. 5 was, in general, similar to the behavior shown in Fig. 4 except that the irradiation dose for the completion of the order-disorder transformation increased from 1.56 \times 10^{14} \text{ ions/cm}^2 (0.23 \text{ dpa}) to 2.19 \times 10^{14} \text{ ions/cm}^2 (0.32 \text{ dpa}) with the increase of the irradiation temperature from 40 K to 100 K. The critical dose to amorphization could not be precisely detected at 40 K and 100 K although it is clear that amorphization was complete at an irradiation dose of 6.25 \times 10^{14} \text{ ions/cm}^2 (0.92 \text{ dpa}) at both temperatures.

When the irradiation temperature was increased to room temperature, the irradiation dose to the order-disorder transformation of (Al,Cr)_3Ti increased up to 2.50 \times 10^{14} \text{ ions/cm}^2 (0.37 \text{ dpa}) (Fig. 6b). It can be noted that the L1_2-structured (Al,Cr)_3Ti was not amorphized by the Kr ion irradiation up to 3.13 \times 10^{15} \text{ ions/cm}^2 (4.60 \text{ dpa}) at room temperature. In the irradiation experiment at 573 K, although some irradiation-induced disordering of (Al,Cr)_3Ti was observed when the material was subjected to a dose of 3.13 \times 10^{15} \text{ ions/cm}^2 (4.60 \text{ dpa}), the transformation was not complete. The superlattice reflections were still prominent in the diffraction pattern shown in Fig. 6f, even though the relative intensity of superlattice reflections to the fundamental ones became weaker compared to that for the unirradiated specimen.

Fig. 7 shows a summary of the results of the experiments conducted in a plot of irradiation dose (ions/cm^2) versus irradiation temperature for Al_3Ti and (Al,Cr)_3Ti. Both compounds become
chemically disordered at all temperatures but the highest temperature (573 K). At low temperatures (40 and 100 K), \((\text{Al,Cr})_3\text{Ti}\) becomes amorphous after irradiation to roughly twice the dose needed for chemical disordering, while \(\text{Al}_3\text{Ti}\) resisted amorphization even to a dose ten times as much that for chemical disordering. This indicates that chemical disordering is not sufficient to cause amorphization in these compounds, and further accumulation of damage might be required. It also appears that the damage accumulation processes at low temperatures are more efficient for \((\text{Al,Cr})_3\text{Ti}\) than for \(\text{Al}_3\text{Ti}\). Finally, the critical temperature for amorphization for \((\text{Al,Cr})_3\text{Ti}\) is likely between 100 K and room temperature while the critical temperature for disordering for \((\text{Al,Cr})_3\text{Ti}\) is likely between room temperature and 573 K.

In a previous study [12], \(\text{Al}_3\text{Ti}\) was reported to be completely amorphized at around 1.3 dpa by 250 keV Kr ion irradiation at temperatures less than 40 K. In this study, however, \(\text{Al}_3\text{Ti}\) was not amorphized when irradiated with 1.0 MeV Kr ions to a higher dose level, 5.62 dpa, at 40 K. The irradiation condition was similar in both experiments apart from a higher ion energy in the current study. The different resistance to amorphization found in the two experiments is difficult to understand in terms of the irradiation conditions only. The susceptibility to amorphization could be influenced by the materials’ chemical homogeneity, which might be altered in the two experiments due to the different manufacturing conditions.

The binary phase diagram for Ti–Al system indicates that \(\text{Al}_3\text{Ti}\) is a line compound, suggesting that \(\text{Al}_3\text{Ti}\) is not stable under irradiation conditions. Nakayama et al. reported that the L12 phase field in the isothermal section at 1273 K of the A1-Ti-Cr ternary phase diagram is very narrow with about 1 at% radius and its center at Al–25Ti–8Cr, and the extent of the L12 phase field increased toward higher content of Cr and Ti at 1423 K [3]. This suggests that...
the L12 phase is not stable at the irradiation temperatures used in this study even though the L12 phase was obtained in this study by annealing at 1423 K for 48 h. From this point of view, L12-(Al, Cr)3Ti is more likely to transform to another phase under irradiation compared to D022-Al3Ti, which maintains a stable line compound in the temperature range used in this study before irradiation.

The free energy increase by irradiation should be higher than the difference between the initial ordered phase and disordered or amorphous phase in order for the transformation to take place. A certain amount of energy needs to be stored in the lattice during the irradiation, though most energy can be dissipated as heat. Two most commonly accepted forms for accumulation of energy are chemical disordering (anti-site defect) and topological disordering (point defect). Chemical disordering is accepted as the major energy storage form [17], but point defects also contributes to the energy storage [18,19]. Tolerance to radiation damage is a material’s inherent ability to accommodate atomic lattice disorder under irradiation [20] and its damage annealing rate. This ability is closely associated with the increase of free energy by irradiation-induced defects. When the energy change by defect formation is large, the materials can undergo an order-disorder transformation or amorphization.

The current study showed that Al3Ti is much more resistant to amorphization under irradiation compared with (Al, Cr)3Ti. The resistance to amorphization is enhanced if the stored energy due to the accumulation of irradiation-induced defects is reduced. Intrinsically disordered materials tend to remain disordered throughout the irradiation process. A low energy for the order-disorder transformation helps the materials accommodate disorder more easily [20]. L12-(Al, Cr)3Ti is a more disordered structure compared to D022, considering that Al and Cr atoms can share face-centered lattice positions in the L12 unit cell as shown in Fig. 1. The current study, however, revealed that (Al, Cr)3Ti was more susceptible to amorphization. The consideration of chemical disordering only is not sufficient to explain the difference of susceptibility to amorphization between Al3Ti and (Al, Cr)3Ti under ion irradiation. Topological disordering needs to be considered together with chemical disordering to analyze the results obtained in this study. It is suggested that the addition of alloying elements promote the anti-site defect formation, which leads to an increase of the free energy. A previous study [21] showed that the critical dose to amorphization and the critical temperature varied according to the alloy type. This suggests that alloying elements play a critical role in defect accumulation under irradiation.

4. Conclusion

Samples of Al3Ti and (Al, Cr)3Ti were irradiated in situ with 1.0 MeV Kr ions at a rate of 6.25 x 1014 ions/cm²-s at 40 K and 573 K to doses up to 4.06 x 1015 ions/cm² to investigate the irradiation-induced disordering and amorphization of these compounds. The dose for completion of the irradiation-induced order-disorder transformation increased with increase in irradiation temperature, irrespective of the crystal structure, with both Al3Ti and (Al, Cr)3Ti ordered structures being fully transformed to the disordered FCC. Al3Ti showed a higher irradiation dose to order-disorder transformation compared to (Al, Cr)3Ti at a given temperature. However, the same disordered FCC structure showed a different tolerance to amorphization depending on the alloy. The disordered FCC-structured (Al, Cr)3Ti amorphized at the irradiation dose of 6.25 x 1015 ions/cm² (0.92 dpa) at 40 K and 100 K. However, Al3Ti with the disordered FCC structure maintained crystallinity up to an irradiation dose of 4.06 x 1015 ions/cm² (5.62 dpa) at 40 K.

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