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SUMMARY OF TITANIUM STUDIES IN SUPPORT OF FUSION ENERGY

Compiled by

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Materials/FUSION

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RADIATION DAMAGE IN TITANIUM ALLOYS*

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(Ti-6Al-4V)
(Ti-15V-3Sn-3Cr-3Al)

* Read & read
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1. Introduction

Titanium alloys are among materials being considered for the first wall and blanket structure of a fusion reactor. Titanium alloys are of interest because of their low long-term residual radioactivity and the attractive combination of thermophysical and mechanical properties which result in low thermal stresses high fatigue strength, and high fracture toughness. Previous studies^(1,2) of neutron irradiation effects in pure titanium indicate that at irradiation temperatures of 335-800°C and neutron fluences $\approx 10^{21}$ neutrons/cm², titanium is resistant to void formation and swelling. The early studies of neutron radiation damage in titanium alloys^[3,4] were performed at irradiation temperatures and fluences much lower than those of a fusion-reactor first-wall structure environment. In a recent investigation, Wilkes and Kulcinski^[5] studied the damage microstructure in mill-annealed Ti-6Al-4V irradiated with 17.5-MeV Cu⁺ ions at 250-450°C. The Cu⁺ ion irradiation produced nonequilibrium fine precipitates in the alpha phase in addition to the expected defect clusters, dislocation loops, and dislocation tangles. The first indication of void formation in titanium alloys was reported by Nolfi^[6] in both single-ion (2.5 MeV V⁺) and dual-ion (2.5-MeV V⁺ and 0.95-MeV ³He⁺) irradiated Ti-6Al-4V at temperatures greater than 540°C. Ion irradiation, which alters the local chemical composition of the alloy matrix in addition to producing displacement damage, may not be indicative of high-energy neutron irradiation. Preliminary results of irradiation creep studies of titanium alloys have been reported recently^[7], and radiation damage studies of titanium alloys irradiated to higher fluences are in progress. The crystallographic features of the neutron-radiation-induced defect structure, radiation-induced precipitation of nonequilibrium phases, and annealing of damage microstructure determined by transmission electron microscopic examination of variously heat-treated alpha-beta, alpha₂, and beta-titanium alloys irradiated to a fluence of 3×10^{21} neutrons/cm² ($E_n > 0.1$ MeV) are reported here.

2. Experimental Procedure

The compositions and heat treatments of the different titanium alloys studied are given in Table 1. Rectangular 50 x 6.4 x 1.0-mm cross-section specimens were prepared from the 1.0-mm sheet stock supplied by the alloy producers.

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The specimens were irradiated at $450 \pm 30^\circ\text{C}$ in Row VII of the EBR-II reactor to a fluence of 3×10^{21} neutrons/cm² ($E_n > 0.1$ MeV). The resulting damage in these alloys was 2.1 displacements per atom. Following irradiation, the specimens were chem-milled to 0.3-mm thickness in a solution of nitric acid, hydrofluoric acid, and water maintained at 0°C , and 3-mm diam discs were prepared from the chem-milled sheets. Specimens for optical metallographic examination were prepared by mechanical polishing of the 3-mm diam discs using 3- μm diamond abrasive. A twin-jet electrolytic thinning technique using methanol-butanol-perchloric acid electrolyte^[8] was used for preparing specimens for transmission electron microscopic examination. The temperature of the electrolyte during thinning was maintained below -15°C to prevent hydrogen pick-up and hydride formation. The thin foils were examined in a JEOL JEM 100B electron microscope operated at 100 kV. To quantify the irradiation-induced defect microstructure, grains of several different orientations were examined using bright-field, conventional dark field, and weak-beam dark-field techniques. The nature of dislocations and dislocation loops was determined by standard contrast experiments under two-beam conditions, and the small defect clusters were identified using the line-of-contrast criterion^[9] and black-white vector orientation criterion^[10,11]. The hardness values of unirradiated and irradiated 3-mm discs were determined using a Leitz microhardness tester with a 50-g load.

3. Results

3.1 Post-Irradiation Microstructures of Titanium Alloys:

The microstructures of duplex annealed Ti-6Al-4V in the unirradiated and irradiated conditions are shown in Figs. 1a and 1b. The unirradiated microstructure (Fig. 1a) consists of large volume fractions of equiaxed 5-10 μm primary alpha grains and small volume fractions of Widmanstätten alpha-beta plates and intergranular beta. The microstructures of the irradiated specimens consist of a high density of small dislocation loops and dislocation debris along with 10-20 nm size ellipsoidal precipitates. The precipitates imaged in dark field with a precipitate reflection are shown in Fig. 2a. The precipitates, identified by selected-area electron diffraction (SAD) analyses (Figs. 2b and 2c) were body-centered-cubic beta phase with a lattice spacing of 0.302 nm. The orientations of the precipitates with respect to the alpha matrix conform to the Burgers orientation relationships of $\{0001\}_\alpha \parallel \{110\}_\beta$ and $\langle 11\bar{2}0 \rangle_\alpha \parallel \langle 111 \rangle_\beta$. The beta precipitates form preferentially along dislocation lines, low-angle boundaries, and grain boundaries. The post-irradiation microstructure of mill-annealed Ti-6Al-4V is similar to that of duplex annealed Ti-6Al-4V. The microstructure of irradiated beta-annealed Ti-6Al-4V shown in Fig. 3 indicates that the basic Widmanstätten structure is retained after irradiation, and the principal radiation-induced defect structure in the alpha phase is similar to that in mill-annealed and duplex-annealed Ti-6Al-4V.

Figures 4a and 4b are the electron micrographs of the defect structure in the irradiated near-alpha alloys. The defect structure consists of a high density of prismatic dislocation loops, small defect clusters, and c-component dislocations. In contrast with the extensive beta precipitation in Ti-6Al-4V, there was no indication of beta precipitation in the near-alpha alloys. The SAD patterns of the irradiated near-alpha alloys showed faint extra reflections coincident with Ti_3Al reflections, but well-defined contrast from

the Ti_3Al precipitates could not be obtained because of the small size of the precipitates. Ti_3Al formation may not be a radiation induced phenomenon because Ti_3Al precipitates have been observed in alpha-rich titanium alloys isothermally aged for long times at 400-500°C [12]

The defect structure imaged with a strongly excited (0002) reflection (Figs. 5a and 5b) shows a large number of defect clusters with black-white contrast. Although spherically symmetrical clusters and small dislocation loops show each black-white contrast under two-beam diffraction conditions, the black-white vector ($\mathbf{l}$) is always parallel to $\mathbf{g}$ for spherical strain centers. Examination of the defect clusters shown in Fig. 5a under different $\mathbf{g}$ vectors indicate that a significant number of the clusters are small dislocation loops with a c-component Burgers vector. Figure 5b taken with $\mathbf{g} = (0002)$ (thus rendering all the $a/3 [11\bar{2}0]$ dislocations out of contrast) shows dislocations with c-component Burgers vector detained at small dislocation loops.

The microstructure of unirradiated solution-treat-and-aged Ti-15V-3Sn-3Cr-3Al alloy shown in Fig. 6a consists of homogeneously distributed 40-100 nm size alpha precipitates in the beta matrix. After irradiation, the alpha precipitate density increases slightly, and the coarse elongated alpha precipitates acquire a globular morphology as seen at A in Fig. 6b. The substructure in the beta phase consists of a high density of defect clusters and prismatic loops, which are shown at location B in Fig. 6b. The details of the defect structure in the alpha phase were too fine to be resolved.

The effects of neutron irradiation on the microhardness of the alpha-beta and near-alpha alloys are shown in Fig. 7. Neutron irradiation results in an increase in hardness in both alpha-beta and near-alpha alloys. The irradiated alpha-beta alloy containing both defect clusters and fine precipitates shows a larger increase in hardness than the near-alpha alloys containing only defect clusters.

3.2 Post-Irradiation Annealing of Titanium Alloys:

The temperature dependence of annealing of the neutron-irradiation-induced defect structure was determined by transmission electron microscopic examination of annealed bulk specimens and specimens annealed in the heating stage of the electron microscope. In-situ annealing at 500°C for 10 min did not result in significant microstructural changes except for a limited amount of defect annihilation. Increasing the temperature to 560°C ($\sim 0.43 T_m$) resulted in a rapid annihilation of dislocations and dislocation loops and their coalescence into larger defects. Figures 8a and 8b show the same region of an irradiated duplex-annealed Ti-6Al-4V specimen after in-situ annealing for 10 min at 500°C and 560°C, respectively. In contrast with the continued presence of beta precipitates in the in-situ annealed sample, bulk annealing at 650°C resulted in complete annihilation of radiation induced defects and dissolution of beta precipitates by the alpha matrix (Fig. 9a). The difference between the bulk annealed and in-situ annealed specimens caused by surface effects and possible contamination of the specimen in the electron microscope suggest that care must be exercised in obtaining conclusions from in-situ annealing experiments. The radiation-induced-defect structure in the near-alpha alloy also anneals out at 650°C,

resulting in the formation of dislocation networks as shown in Fig. 9b.

The effects of post-irradiation annealing on the hardness of the alloys are shown in Fig. 10. The decrease in hardness with increasing annealing temperature is in agreement with the recovery of radiation-induced microstructure determined by transmission electron microscopy.

4. Discussion

The most prominent microstructural modifications resulting from neutron irradiation of titanium alloys to a damage level of 2.1 defects per atom are the production of a high density of defect clusters, dislocation loops, and dislocations with nonbasal slip vectors in all alloys, and precipitation of fine beta phase in the alpha-beta alloy. The general characteristics of the defect structure are similar to those observed in other alloy systems (13-15) irradiated with high-energy neutrons, and the crystallographic features of defects in the alpha phase of the irradiated near-alpha and alpha-beta alloys are in agreement with the operative slip systems in binary Ti-Al alloys (16-18). Although both a-type slip, $(a/3\{10\bar{1}0\}\langle 11\bar{2}0\rangle)$, and c-component slip have been observed in binary Ti-Al alloys, the predominant deformation mode is the a-type slip in alloys deformed at 25-700°C. Because the $\{10\bar{1}0\}$ planes are the close-packed planes in Ti-Al alloys, the point defect clustering into dislocation loops of $a/3\langle 11\bar{2}0\rangle$ Burgers vector should readily occur in $\{10\bar{1}0\}$ planes. The dislocation loops seen in the irradiated Ti alloys are in agreement with the expected $a/3\{10\bar{1}0\}\langle 11\bar{2}0\rangle$ loops, and similar results have been reported in zirconium (19-20). However, in contrast with the exclusive a-type dislocation loops reported in irradiated zirconium, neutron irradiation of titanium alloys results in a significant number of c-component dislocations and dislocation loops (Fig. 8).

The defect clusters produced by neutron irradiation act as thermally activated barriers to dislocation motion and increase the yield stress of the alloy. Examples of dislocations held at point defect clusters are seen in Figs. 2, 6, 7 and 8. The stress (τ) necessary to overcome the point defect cluster barriers is given by (21)

$$\tau = \alpha \mu b / Nd$$

where α is a constant, μ is the shear modulus of the matrix, b is the Burgers vector of the dislocation, N is the number of defect cluster barriers, and d is their average size. The increase in hardness in the irradiated alloys (shown in Fig. 15) is in qualitative agreement with the strengthening expected from the defect clusters.

The dominant feature of the radiation-induced damage microstructure in the alpha-beta alloy is the dense precipitation of fine beta precipitates. The absence of such precipitation in isothermally annealed, unirradiated, Ti-6Al-4V alloys and the dissolution of the precipitates upon high-temperature annealing of the irradiated alloy indicate that beta precipitation occurs by radiation-induced solute segregation to point defect clusters rather than by radiation enhanced diffusion in the supersaturated alpha matrix, as was suggested by Nygren (7). Because vanadium in titanium has negative misfits of -3% on the a-axis and -6% on the c-axis, the segregation of vanadium to radiation-induced point defects is facilitated, and the solute enrichment of defect clusters is further enhanced by increased diffusion rates in the

irradiated alloy. When the localized vanadium segregation exceeds the solubility limit, beta precipitates nucleate. Local enrichment of undersized atoms and depletion of oversized atoms at defect sinks and the consequent formation of nonequilibrium precipitates and precipitate-free zones have been observed in Ni-Si and Ni-Al (23-24). The preferential precipitation of beta phase at vacancy sinks such as dislocation lines, low-angle boundaries, and high-angle boundaries (Fig. 3) indicates that the precipitation is caused by radiation-induced solute enrichment, with other radiation induced/enhanced phenomena such as changes in the free energies of alpha and beta phases and enhancement of diffusion rates by a large supersaturation of vacancies aiding the precipitation.

The compositions determined by x-ray energy dispersive analyses of alpha and beta phases of Ti-6Al-4V annealed at 700-900°C and slowly cooled to room temperature revealed no appreciable supersaturation of vanadium in alpha. Furthermore, the equilibrium volume-fraction of beta phase in Ti-6Al-4V is significantly lower at the irradiation temperature of 450±30°C than at the temperatures at which the alloy was annealed prior to irradiation. These results, coupled with the observation that dissolution of beta precipitates in irradiated Ti-6Al-4V occurs at 650°C, discount the possibility of equilibrium precipitate formation by enhanced diffusion in the supersaturated alpha matrix of Ti-6Al-4V.

The radiation-induced beta precipitates in Ti-6Al-4V impart additional strengthening to the alloy as evidenced by a larger increase in hardness in Ti-6Al-4V than in the near-alpha alloys irradiated to identical fluences. The precipitates could also significantly reduce swelling by capturing the defects and reducing the flux of vacancies to voids, an attractive feature from an alloy design viewpoint.

5. Summary and Conclusions

High-energy neutron irradiation of Ti-6Al-4V results in extensive defect clusters, prismatic loops along with fine, ellipsoidal, 10-20 nm beta precipitates with orientation relationships $\{0001\}_\alpha \parallel \{110\}_\beta$ and $\langle 1120 \rangle_\alpha \parallel \langle 111 \rangle_\beta$. The beta precipitates redissolve upon annealing the irradiated alloy at 650°C. The causes of beta precipitation were identified to be radiation-enhanced diffusion and radiation-induced segregation of the undersized beta stabilizing element, vanadium, to the defect clusters. The radiation-induced defect structure in the near-alpha alloys consists of a high density of defect clusters, $a/3\langle 1120 \rangle$ prismatic dislocation loops, and c-component dislocations and vacancy loops with no indication of beta precipitation. The increase in hardness as a result of irradiation is greater in Ti-6Al-4V than in the near-alpha alloys because of the precipitation strengthening by radiation-induced, fine, beta precipitates. The radiation damage of the alloys anneals out completely at 650-750°C.

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Table 1 Chemical composition, alloy type and heat treatment of the irradiated titanium alloys.

Alloy composition	Alloy type	Alloy designation	Heat treatment
Ti-6Al-4V	Alpha + Beta	Ti-6-4(MA)	Mill anneal; 730°C/2 h, Air cool to 25°C
Ti-6Al-4V	Alpha + Beta	Ti-6-4(DUP)	Duplex anneal; 940°C/10 min, argon quench to 25°C + 675°C/4 h, air cool to 25°C
Ti-6Al-4V	Alpha + Beta	Ti-6-4(BA)	Beta anneal; 1040°C/30 min, air cool to 25°C + 730°C/2 h, air cool to 25°C
Ti-6Al-2Sn-4Zr-2Mo-0.09Si	Near-Alpha	Ti-6242S(DUP)	Duplex anneal; 900°C/30 min, air cool to 25°C + 790°C/15 min, air cool to 25°C
Ti-5Al-6Sn-2Zr-1Mo-0.2Si	Near-Alpha	Ti-5621S(DUP)	Duplex anneal; 950°C/15 min, air cool to 25°C + 600°C/2 h, air cool to 25°C
Ti-15V-3Cr-3Al-3Sn	Beta	Ti-15-3-3-3(STA)	Solution-treat-and-age; 760°C/15 min, air cool to 25°C + 510°C/16 h, air cool to 25°C

Figure 1. Microstructures of duplex-annealed Ti-6Al-4V; (a) unirradiated and (b) after neutron irradiation to a fluence $\approx 3 \times 10^{21} \text{ n/cm}^2$.

Figure 2. Morphology and orientation of nonequilibrium precipitates in irradiated duplex-annealed Ti-6Al-4V; (a) dark-field electron micrograph of precipitates,

Figure 3. Microstructures of beta-annealed Ti-6Al-4V; (a) unirradiated, showing Widmanstätten α - β platlets and (b) irradiated, showing a high density of defects and precipitates in the α plates.

Figure 4. Defect microstructure in irradiated Ti-5Al-6Sn-2Zr-1Mo-0.2Si; (a) low-magnification micrograph and (b) high-magnification micrograph showing the details of dislocation loops.

Figure 5. Defect structure in Ti-5Al-6Sn-2Zr-1Mo-0.2Si imaged with $g = (0002)$; (a) dislocation loops showing black-white contrast and (b) c -component dislocations detained at defect clusters.

Figure 6. Microstructures of Ti-15V-3Cr-3Al-3Sn; (a) unirradiated, showing the equilibrium α precipitates in the solution-treat-and-aged condition and (b) irradiated, showing additional α precipitates and spheroidization of α at B.

Figure 7. Effect of neutron irradiation on the hardness of titanium alloys.

Figure 8. Microstructures of irradiated duplex-annealed Ti-6Al-4V after *in situ* annealing (a) at 500°C for 10 min and (b) at 560°C for 10 min.

Figure 9. Microstructures of irradiated titanium alloys annealed at 650°C for 24 h; (a) Ti-6Al-4V and (b) Ti-6Al-2Sn-4Zr-2Mo-0.09Si.

Figure 10. Influence of annealing on hardness of irradiated titanium alloys.