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Section 5. Structural materials

Radiation-induced precipitation in V–(Cr,Fe)–Ti alloys irradiated at low temperature with low dose during neutron or ion irradiation

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Abstract

Effects of neutron irradiation damage on mechanical properties and microstructure were studied for V–4Cr–4Ti–0.1Si, V–3Fe–4Ti–0.1Si and vanadium binary alloys with three fluences between 0.01 and 0.1 dpa for 220°C and 340°C. Irradiation hardening appeared in V–(Cr,Fe)–Ti alloys at an early stage of irradiation. Microstructural analysis showed that the irradiation hardening in V–(Cr,Fe)–Ti alloys is caused by radiation-induced precipitates (RIPs). In order to investigate the behavior of RIPs, ion irradiations of highly purified vanadium alloys were performed. It is likely that the nucleation and growth processes in vanadium alloys containing titanium are independent of the impurity concentration during ion irradiation. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Vanadium alloys, especially those containing titanium have been regarded as candidate materials for fusion reactor application, mainly due to low induced-radioactivity, superior mechanical properties at high temperatures [1–3] and high swelling resistance [4]. However, some studies have reported that significant radiation hardening and embrittlement occurred in V–4Cr–4Ti irradiated by neutrons for 100–400°C below a few displacement per atom (dpa) [5–7]. Radiation-induced precipitates (RIPs) are considered to be an important factor for the degradation of vanadium alloys irradiated at low temperature with low exposure to neutrons. Recently, several studies have been done in order to investigate the characterization of RIP in V–Ti alloys and have reported that titanium oxide plays an important role. Rice and Zinkle reported that dislocation loops with a Burgers vector of $a/2\langle 110\rangle$ were formed below 300°C and $\{001\}$ defect clusters were formed above 300°C during HFBR irradiation [8]. Detailed information on the $a/2\langle 110\rangle$ loops is still lacking; however, the nature of the $\{100\}$ defect clusters has been determined. The $\{100\}$ defect clusters have been reviewed briefly by Gelles et al. [9] who determined them to be Ti(OCN). He noted that reflections from the precipitates occurred at the $2/3\langle 222\rangle$ position on the $\langle 110\rangle$-zone axis of the vanadium matrix, and at $3/4\langle 200\rangle$ on the $\langle 001\rangle$-zone axis in the diffraction patterns. Our preliminary work has determined that precipitates formed in V–5Ti irradiated in FFTF at 600°C up to 15 dpa were fcc type with a lattice parameter of $a_0 = 0.424$ nm and a crystallographic orientation of $(110)_p//(100)_m$ and $[011]_p//[001]_m$, where the p, m subscripts denote precipitate and matrix, respectively. Similar results of crystallographic analysis have been reported previously [10]. From this crystallographic analysis, 3/4(2 0 0) reflections arose from the (2 0 0) plane projected onto the $\langle 011\rangle$ direction for precipitates, and 2/3(222) reflections arose from the (0 2 2) plane projected onto the $\langle 111\rangle$ direction. These reflections from precipitates indicate the precipitates have an NaCl type of crystal structure. Parallel electron energy loss spectroscopy (PEELS) analysis showed that titanium and

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oxygen were enriched in the precipitates and no signal was obtained for nitrogen or carbon; these findings indicate that Ti(ONC) are mainly TiO and the anion lattice should be occupied mainly by oxygen. This paper reports the microstructure and mechanical properties of vanadium alloys following two series of neutron irradiations at 220°C and 340°C. In addition, ion irradiation experiments on vanadium alloys are reported in order to investigate the impurity effect, especially oxygen, for the nucleation and growth processes of precipitation in vanadium alloys containing titanium.

2. Experimental procedure

Several kinds of vanadium alloys were prepared; pure V, V–5 at.% Fe, V–5 at.% Nb, V–5 at.% Ti, V–4Cr–4Ti–0.1Si (VM9401) and V–3Fe–4Ti–0.1Si (VM9502). Transmission electron microscopy (TEM) disk specimens of 3 mm diameter were punched and annealed at 1100°C for 2 h. A series of neutron irradiations were performed at JMTR using a multi-section and multi-division controlled rig [11]. The rig allows the sub-capsule to be removed from the reactor core during reactor operation under temperature control by electric heaters. The time-dependence of radiation behavior in materials can be obtained with the same temperature and neutron flux during one reactor operation. Irradiation temperatures were 220°C and 340°C, and three different neutron doses were achieved; $7 \times 10^{22}, 4 \times 10^{23}, 1 \times 10^{24}$ n/m^2, which were converted into damage levels of dpa, 0.013, 0.061, 0.19 dpa, respectively. The atmosphere in the sub-capsule during neutron exposure was vacuum. Following the irradiation, positron annihilation lifetime measurements, Vicker's micro-hardness measurements and TEM observations were performed.

Several specimens were prepared for ion irradiation experiments: pure vanadium, V–5Ti, V–4Cr–4Ti–0.1Si, V–3Fe–4Ti–0.1Si and V–4Cr–4Nb. In order to reduce impurity concentration in these alloys, a zirconium foil gettering treatment (Zr-treatment) was employed. A sheet of an alloy with a thickness of about 1 mm was sandwiched with a pair of zirconium foils and rolled together in a single pass to form a Zr/V-alloy/Zr clad. The sandwiched specimens between zirconium were annealed at 1100°C for 2 h in vacuum. After annealing, the layer of zirconium was removed by chemical polishing. Disks 3 mm in diameter were punched out from the sheet and annealed at 600°C for 1 h in order to remove hydrogen picked up during chemical polishing [12]. The impurity concentration in vanadium alloys was reduced significantly, as shown in Table 1. The hardness of Zr-treated specimens was about 70% of the as-received specimens. Although chemical analysis was not done on the ternary alloy, it is likely from the reduction of hardness that the impurity concentration, especially oxygen, is significantly reduced. After heat treatment, the disks were cleaned by electropolishing to remove scale. Irradiation experiments were performed using the tandem accelerator in IMR, Tohoku University. The projectile ions are 4 MeV Cu ions. The irradiation doses were 0.1–1 dpa at the depth of 800 nm from the surface with the dose rate of 1×10^{-4}dpa/s. The irradiation temperatures were 400°C and 600°C. The irradiation environment was vacuum of 1×10^{-4} Pa. TEM observations were performed after the irradiation.

Table 1
The list of impurity concentration in pure V and V–5Ti before and after Zr-treated method

Composition (appm)	Oxygen	Carbon	Nitrogen
Pure V (as-received)	174	26	3
Pure V (Zr-treated)	15	7	1
V–5Ti (as-received)	406	51	21
V–5Ti (Zr-treated)	33	27	1

3. Results and discussion

3.1. Neutron irradiation

Fig. 1 shows the dose dependence of hardness changes for each vanadium alloy irradiated in JMTR. The hardness increased in pure V, V–5Fe and V–5Nb with irradiation dose. As the irradiation temperature increased, the hardness decreased in these specimens. These results agree with the general tendency in irradi-

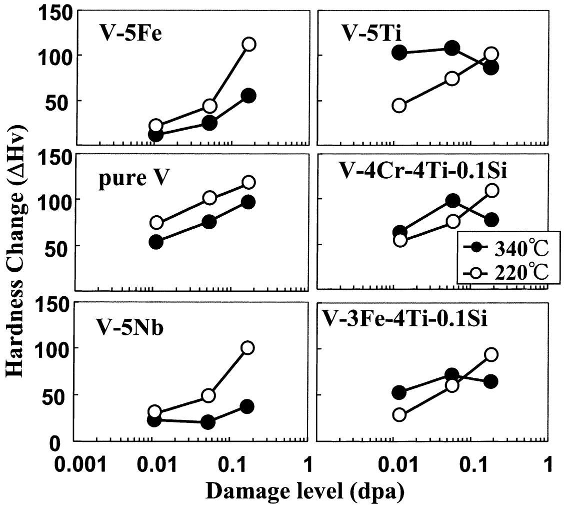

Fig. 1. The dose dependence of microhardness changes for V–5Fe, pure V and V–5Nb on the left column and V–5Ti, V–4Cr–4Ti–0.1Si and V–3Fe–4Ti–0.1Si on the right column.

ated bcc metals and alloys. From the hardness measurement and microstructural analysis, it is deduced that coarsening of dislocation loops reduced the hardness as the irradiation temperature increased. Voids were formed in V–5Fe at 340°C and grew with irradiation dose. Positron annihilation experiments showed that microvoids and voids were formed in pure V and V–5Fe. V–5Nb and vanadium alloys containing titanium did not have any microvoids but only single vacancies. However, the behavior of the vanadium alloys containing titanium was considerably different from pure V. The hardness for irradiated V–Ti alloys increased at 220°C with irradiation dose. But the hardness change of 340°C irradiation was higher than 220°C. It is likely that the hardness changes have saturated even at this low irradiation dose. Electron microscopy of V–4Cr–4Ti–0.1Si showed an increase in the density of defect clusters with increasing irradiation dose. The increase of hardness change is apparently caused by the increase in the density of defect clusters. In V–(Cr, Fe)–Ti alloys irradiated at 220°C, no fine diffraction spots from defect clusters were seen in the diffraction pattern. The nature of the defect clusters formed at 220°C is not clear, but they are very likely to be fine dislocation loops because of the absence of precipitate diffraction spots. The precipitates and dislocation loops can be seen in those vanadium alloys irradiated at 340°C even at lower irradiation doses. The precipitates were disk shaped with a {1 0 0} habit plane. As mentioned before, these precipitates have an NaCl crystal structure and their composition should be mainly TiO. Fig. 2 shows dark field images obtained from the diffraction spots from different variants of the precipitate. The projection direction was close to the [0 0 1] direction of the vanadium matrix. In addition to precipitates, large dislocation loops were also observed; the nature was *a*/2[1 1 1](1 1 1) prismatic loop, which was determined from contrast experiments. Fringes were observed inside the loops. The fringes are likely caused by the enrichment of iron or chromium inside the loops.

The hardness changes were estimated by from the microstructural changes using the well-known dispersed barrier hardening equation

$$\Delta\sigma_y = M\alpha\mu b(Nd)^{1/2}, \tag{1}$$

where $\Delta\sigma_y$ is the increase in strength from the unirradiated value, μ the shear modulus, b the magnitude of the *a*/2[1 1 1] Burgers vector of the dislocation loops, N and d the density and size of the defect clusters, respectively, and M is the Taylor factor, set to $M = 3$ after Rice and Zinkle [8]. The calculated value of the barrier strength for the dislocations was 0.35 from previous data revised by the $M = 3$ estimation. In order to determine

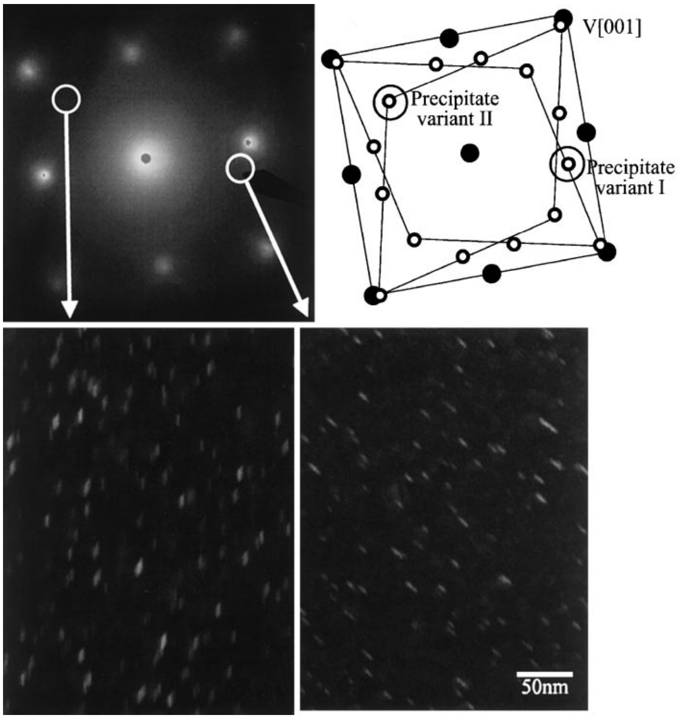

Fig. 2. Dark field images taken from precipitate spots and their diffraction pattern in V–3Fe–4Ti–0.1Si irradiated at 340°C with 0.19 dpa in JMTR. Two variants of precipitates can be seen from this diffraction pattern.

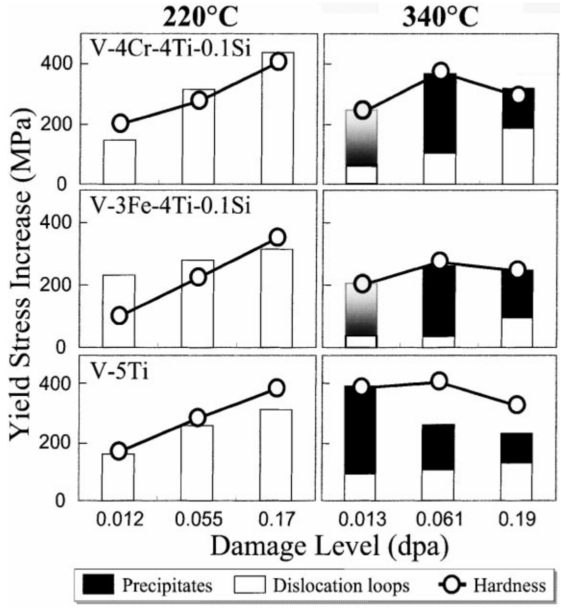

Fig. 3. The dose dependence of yield stress increases estimated from microhardness and microstructural analysis in V–5Ti, V–4Cr–4Ti–0.1Si and V–3Fe–4Ti–0.1Si irradiated in JMTR.

the applicable calculated value of the barrier strength for precipitates, simple linear algebraic equations were adopted. The value of the barrier strength for precipitates was obtained to be $\alpha \approx 0.2$. Fig. 3 shows the comparison of yield stress increases estimated from microhardness changes and microstructural analysis. At the lower irradiation dose for V–3Fe–4Ti–0.1Si and V–4Cr–4Ti–0.1Si, the size of the precipitates was too small to obtain reliable data. Mostly these analyses were in good agreement with the experimental hardness change data. It is suggested that significant hardening in V–Ti alloys at 340°C is caused by the precipitation of titanium oxide. The precipitation of titanium oxide should occur at an early stage of irradiations above 300°C. The suppression of precipitate nucleation should be effective in reducing the degradation of mechanical properties of vanadium alloys during neutron irradiation.

3.2. Cu ion irradiation

Cu ion irradiation experiments were performed on pure V, V–4Cr–4Nb and V–(Cr, Fe)–Ti alloys. Voids and precipitates were formed above 500°C irradiation in pure V, in good agreement with previous work [13]. V–4Cr–4Nb was selected in order to study the chemical effect of titanium in V–Cr–Ti alloys while keeping the atomic size factor about the same as Ti. Voids were formed in V–4Cr–4Nb irradiated at 400°C to 1 dpa. However, no voids were seen in V–4Cr–4Ti–0.1Si and V–3Fe–4Ti–0.1Si irradiated from 400°C to 600°C to 1 dpa. This result indicated that the effect of titanium in

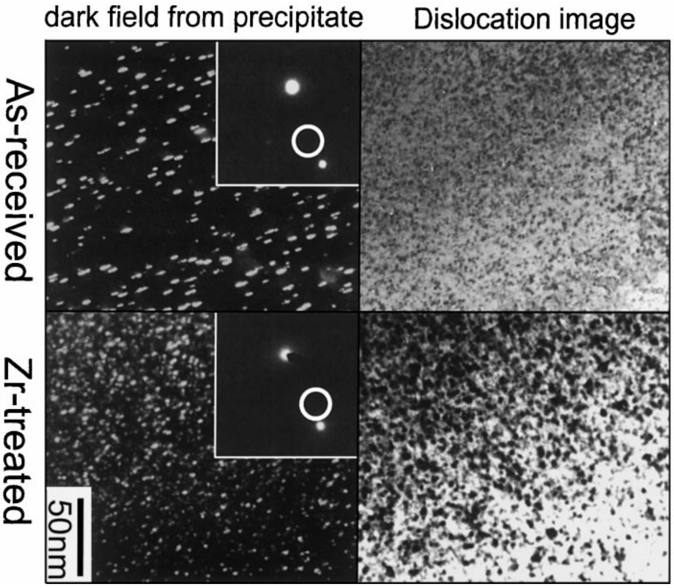

Fig. 4. A set of TEM images of V–3Fe–4Ti–0.1Si irradiated with 4 MeV Cu ions with damage levels of 0.1 dpa at 600°C. Top parts are bright images of $g = 110$ and bottom parts are dark field images taken from precipitates. The circles described in the inserted diffraction pattern show the positions of precipitate spots. Left part is an image of as-received specimen and right side is of Zr-treated specimen.

suppressing swelling is not primarily through its atomic size factor as an oversized solute atom, but that its chemical effect is important as well.

In order to investigate the effect of impurity concentration on nucleation and growth processes of defect clusters in vanadium alloys, highly purified vanadium alloys were used. No precipitates were found in V–4Cr–4Ti–0.1Si and V–3Fe–4Ti–0.1Si irradiated at 400°C with 1 dpa. However, a lot of fine precipitates were formed at 600°C. Fig. 4 shows the micrographs of V–3Fe–4Ti–0.1Si irradiated with 4 MeV Cu ions to 0.1 dpa at 600°C. The micrographs to the left show the as-received samples, and the ones on the right show the Zr-treated samples. There were many fine precipitates even at 0.1 dpa, as shown on the bottom of Fig. 4. These precipitates are identified as titanium oxides. From microstructural analysis, the densities of precipitates were extremely high even at 0.1 dpa and were three orders of magnitude higher than the density of dislocation loops with $b = a/2\langle 1\,1\,1\rangle$. The difference in microstructural evolution between the purified and original specimens is not very large. The number density and the average size of TiO formed during ion irradiation at 600°C, is $1\text{–}3 \times 10^{21}$ precipitates/m^3 and 5 nm, respectively. It was estimated that a few hundred appm of oxygen were contained as in the TiO precipitates even in the Zr-treated V–(Cr,Fe)–Ti alloys. Even though the impurity concentration of the Zr-treated V–(Cr, Fe)–Ti alloys is not clear at present, most of impurity is considered to be scavenged in TiO precipitates. The difference between the amount of oxygen amount contained in TiO and the oxygen concentration obtained by chemical analysis is not clear. Two possibilities are considered. First, the nucleation process of the precipitates may not need a high impurity concentration. Free oxygen atoms would migrate and bind with displaced titanium strongly during ion irradiation. But this does not explain why the size distribution of precipitates is unimodal and independent of the purification technique. Second, the oxide layer on the surface may dissolve during irradiation, and the dissolved oxygen atoms could migrate internally and bind with displaced titanium atoms. This would explain why precipitation is independent of the purification process for vanadium alloys; however, such behavior was not seen in any other vanadium alloys. In order to understand the intrinsic behavior in V–(Cr,Fe)–Ti alloys under ion irradiation, it is important to find out the origin of oxygen leading to precipitation.

4. Summary

Microhardness and microstructure of vanadium binary alloys and vanadium alloys containing titanium irradiated up to 0.1 dpa for 220°C and 340°C have been studied. The hardness changes of pure V and binary alloys increased when the irradiation dose increased and irradiation temperature decreased. However, vanadium alloys containing titanium showed more irradiation hardening at 340°C than at 220°C. The hardening in V–(Cr,Fe)–Ti alloys was caused by RIP of titanium oxides. The control of RIP is the key to improving the radiation resistance in the low temperature regime. In order to investigate the effect of impurities on the nucleation and growth processes of RIP, vanadium alloys containing titanium highly purified by Zr-treated methods have been used for Cu ion irradiations. The precipitation process in V–Cr–Ti and V–Fe–Ti alloys was not related to the purification technique during ion irradiation. The impurity concentration does not affect the nucleation process of RIP strongly, however, there are still unresolved issues.

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