MICROSTRUCTURAL DEVELOPMENT IN
IRRADIATED VANADIUM ALLOYSD. S. Gelles
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MICROSTRUCTURAL DEVELOPMENT IN IRRADIATED VANADIUM ALLOYS - D.S. Gelles,
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OBJECTIVE

The objective of this work is to provide further understanding of swelling response in vanadium alloys.

SUMMARY

Three simple vanadium alloys, V-5Al, V-1Ni, and V-2Ti-1Ni have been examined to determine the effects of fast neutron irradiation on microstructural evolution. Specimens were irradiated in EBR II at temperatures in the range 425 to 600°C to doses of 15 and 31 dpa. Each alloy responded very differently to irradiation. All V-5Al specimens were generally void-free and contained high densities of coherent precipitates, and moderate densities of network dislocations. Swelling was much higher in V-1Ni. Voids were uniformly distributed, but with widely varying shape and size. Precipitation of two types also developed. The response in V-2Ti-1Ni was intermediate to that of the other two alloys. Irradiation produced extensive precipitation of thin rods and a moderate density of large voids often associated with much larger precipitate particles. The dislocation structure strongly interacted with the rod precipitate particles.

PROGRESS AND STATUS

Introduction

Vanadium alloys are being seriously considered as candidate fusion reactor first wall materials based on inherent radiation damage resistance, low activation and high temperature refractory properties.^{1,2} However, recent results have demonstrated that vanadium alloys such as V-5Fe can lose radiation damage resistance.²⁻⁶ Swelling as high as 100% was observed in V-5Fe specimens following irradiation at 520 and 600°C to 52 dpa,³ and more recently 93.2% swelling was observed following irradiation at 600°C to 34.2 dpa.⁶ V-Cr alloys in the 10 to 15% Cr range with minor Al additions developed 40% swelling after irradiation at 600°C to approximately 80 dpa,⁴ V-5Cr developed 24.6% swelling after irradiation at 600°C to 34.2 dpa,⁶ and 27% swelling after irradiation at 600°C to 45 dpa,⁵ and V-2Si developed 35% swelling after irradiation at both 425 and 520°C to 45 dpa,⁵ and V-1Si developed 18.7% swelling following irradiation at 600°C to 34.2 dpa.⁶ Finally, V-12Ni developed 15% swelling following irradiation at 600°C to about 80 dpa.² The swelling rates that can be estimated from these results are summarized in Table 1. This high swelling response is in contrast to much lower swelling rates found in all other body centered cubic metal alloys. For example, a rate of 0.06%/dpa is the highest found in simple ferritic alloys.⁷

The effort described here is intended to study the effects of fast neutron irradiation on the microstructures of three simple vanadium alloys: V-5Al, V-1Ni, and V-2Ti-1Ni. Specimens were irradiated in the Experimental Breeder Reactor (EBR) II at temperatures in the range 425 to 600°C to

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doses of 15 and 31 dpa in order to expand our understanding of microstructural evolution in vanadium alloys not previously studied.

Table 1. Summary of high swelling rate response in vanadium alloys.

Alloy	Irradiation Temperature (°C)	Dose (dpa)	Swelling (%)	Swelling Rate (%/dpa)	Reference
V-5Fe	520	52	100	2.0	3
	600	34.2	93.2	2.7	6
V-Cr	600	80	210	0.5	4
V-5Cr	600	34.2	24.6	0.7	6
	600	45	27	0.6	5
V-2Si	425	45	35	0.8	5
	520	45	35	0.8	5
V-1Si	600	34.2	18.7	0.5	6
V-12Ni	600	80	15	0.2	2

Experimental Procedures

Specimens for transmission electron microscopy (TEM) (3 mm diameter x 0.25 mm thick) in the fully heat treated condition were obtained from P. Okamoto of Argonne National Laboratory and were included in an early fusion reactor materials irradiation experiment, designated AA XIV. A single specimen of each alloy condition was included in each of six helium filled stainless steel packets along with various other alloy specimens. Two packets were irradiated at each of three temperatures, 425, 500 and 600°C in gas gapped canisters of B7a design in EBR-II in Idaho Falls, ID. One packet irradiated at each temperature was removed after 15 dpa (doses are given based on displacement rates for stainless steel) and the second packet completed irradiation to 31 dpa. The irradiation temperature, dose and swelling (where measured by immersion density) for those specimens examined by TEM are summarized in Table 2.

These specimens were not examined until the recent results on V-5Fe were obtained, and it became apparent that further understanding of the high swelling in vanadium alloys was required. Specimens from the 15 dpa irradiations were first examined by TEM, and following those examinations, specimens irradiated to 31 dpa were measured for density change and then examined by TEM. TEM specimens were prepared following routine jet electropolishing procedures using a solution of 20% sulfuric acid in methanol at 10 to 15°C and about 60 V at high pump speed. Examinations were performed on a JEOL 1200EX operating at 120 KeV. Compositional overchecks using analytical electron microscopy confirmed that the respective alloying additions of Al, Ni and Ni plus Ti were present in the irradiated specimens.

Table 2. Compositions and irradiation conditions for vanadium alloy specimens in this study.

Alloy Composition	Heat Treatment	Specimen ID	Irradiation Temperature (°C)	Dose (dpa)	Swelling (%)
V-5Al		5AJ1	425	15	NA
"		5AJ2	500	15	NA
"		5AJ3	600	15	NA
"		5A92	500	31	0.13
V-1Ni		5BJ2	500	15	NA
"		5B03	600	15	NA
"		5B92	500	31	3.37
V-2Ti-1Ni		5EJ1	425	15	NA
"		5EJ2	500	15	NA
"		5E92	500	31	0.72

NA - not available, never measured for density.

Results

V-5Al

Specimens of V-5Al were examined following irradiation at 425, 500 and 600°C to 15 dpa and at 500°C to 31 dpa. The samples were remarkably free of voids. Only the specimen irradiated at 600°C was found to contain any voids, and those were nonuniformly distributed in regions near grain boundaries and associated with large precipitate particles. The dislocation structure formed a network in all conditions with highest dislocation densities occurring at the lowest irradiation temperatures and doses. Comparison of $\bar{g} = 200$ and 110 images of the same area following irradiation at 600°C indicated that the primary Burgers vector is $\frac{a}{2} \langle 110 \rangle$. Associated with the dislocation structure was a high density of precipitate particles. In general, precipitates were smaller and at higher density for the lower irradiation temperatures.

Microstructures of V-5Al are presented in Figure 1. Figures 1 a) through c) show dislocation and precipitate structures in V-5Al irradiated to 15 dpa as a function of increasing temperature. The precipitates in 1 c) appear largest. Figure 1 d) provides a precipitate dark field image using $\bar{g} = \frac{3}{4}(200)$ of the region in 1 b); comparison of the two images indicates a close to one-to-one correspondence of particles. Figure 1 e) gives examples of voids associated with large precipitate particles near grain boundaries shown at a lower magnification following irradiation at 500°C. Figures 1 f) through h) provide examples of V-5Al following irradiation at 500°C to 31 dpa. Figure 1 f) shows the dislocation structure, and Figures g) and h) provide comparison of precipitate structures under bright and dark field ($\bar{g} = \frac{3}{4}(200)$) imaging conditions. Therefore, Figures 1 b) and d) can be compared to 1 f) and h) to demonstrate dislocation evolution and precipitate growth with increasing dose at 500°C.

Figure 1. Microstructures in V-5Al following irradiation to 15 dpa at 425 in a), at 500°C in b), and at 600°C in c) with d) showing precipitates at 500°C in dark field contrast, at lower magnification for the 600°C condition in e) and following irradiation to 31 dpa at 500°C in dislocation contrast in f) and in bright and dark field precipitate contrast in g) and h).

V-1Ni

Specimens of V-1Ni were successfully examined following irradiation at 500 and 600°C to 15 dpa and at 500°C to 31 dpa. All specimens contained extensive void swelling and precipitation. The lower irradiation temperature produced voids and precipitates on a finer scale, as expected. Voids produced at 500°C were often of unusual shape due to association with precipitates, but voids produced at 600°C were generally cuboidal. The dislocation structure produced at 500°C consisted of an unfaulted network and faulted regions on (100) planes believed to be associated with precipitate structure, whereas following irradiation at 600°C, a dislocation network was created with few connections to precipitates and voids. Comparison of $\bar{g} = 200$ and 110 images of the same area following irradiation at 600°C indicated that the primary Burgers vector is $\frac{a}{2}\langle 110 \rangle$. However, irradiation to higher dose at 500°C resulted in disappearance of the faulted structure and a very unusual dislocation contrast indicative of helical coiling of the dislocations.

The microstructures of V-1Ni following irradiation are provided in Figure 2. Figures 2 a) and b) show dislocation, void, and precipitate structures in V-1Ni irradiated at 500 and 600°C, respectively, to 15 dpa using $\bar{g} = \langle 110 \rangle$. Two precipitate types can be identified in Figure 2 a): dark, blocky, equiaxed particles uniformly distributed and occasionally associated with voids; and plate-like features apparently on (100) planes and often containing stacking fault features. Figure 2 b) indicates voids and blocky precipitates are much larger following irradiation at the higher temperature. Note that the specimen irradiated at 600°C contains a surface contaminant that formed bubbles under the electron beam; those circular bubble features should be ignored.

Figure 2 c) shows the microstructural features following irradiation at 500°C to 31 dpa using the same imaging condition as in Figure 2 a). Comparison of Figures 2 a) and c) reveals that irradiation to higher dose creates a major change in the dislocation structure, so that dislocations evolve into helical arrays and display unusual contrast, indicative of solute segregation effects. Figures 2 d), e), and f) show the same area as in 2 c) using precipitate dark field contrast to show the blocky precipitate in various orientations. At least three different orientations can be identified. Figures 2 g) and h) provide low magnification examples of grain boundary migration following irradiation at 500°C to 15 dpa. The grain boundary moved vertically in Figure 2 g) and toward the lower right in 2 h). Note enhanced void nucleation in the latter case.

Figure 3 was prepared to provide understanding of the dislocation structures in irradiated V-1Ni. Figures 3 a) and b) show V-1Ni irradiated at 500°C to 31 dpa using $\bar{g} = 110$ and 002 near a (110) orientation. The horizontal dislocations at the upper left and lower center in both images indicate a Burgers vector of type $\frac{a}{2}\langle 111 \rangle$. The helical diagonal images also appear in both images, but these images are not typical of dislocations. Therefore, strain in $\langle 111 \rangle$ directions is again indicated, but precipitation due to solute segregation at dislocations is thought to be the cause. Note that similar diagonal images are developing in association with the horizontal dislocations, suggesting that those $\frac{a}{2}\langle 111 \rangle$ dislocations are beginning to climb into helical configuration.

Also of interest is the wide variation in void shape in this micrograph series. Based on the geometries displayed, these voids are cuboidal with (110) or dodecahedral truncation, but the degree of truncation on the specific truncation planes varies widely from void to void. Wide variations in truncation are often due to associated precipitation or solute segregation. Figures 3 c) and d) show V-1Ni irradiated at 600°C to 15 dpa using $\bar{g} = 110$ and 200 near an (001) orientation. Because all dislocation images in 110 contrast also appear in 200 contrast, $\frac{a}{2}\langle 111 \rangle$ Burgers vectors are again indicated. However, the tendency for solute segregation appears to be reduced at the higher irradiation temperature.

Figure 2. Microstructures in V-1Ni following irradiation to 15 dpa at 500°C in dislocation contrast in a), and at 600°C in dislocation contrast in b), to 31 dpa at 500 in dislocation contrast in c) and in precipitate dark field contrast in d), e) and f), and to 15 dpa at 500°C showing grain boundary migration in g) and h).

Figure 3. Examples of dislocation contrast in V-1Ni following irradiation at 500°C to 31 dpa in a), and b), and at 600°C to 15 dpa in c) and d).

V-2Ti-1Ni

Specimens of V-2Ti-1Ni were examined following irradiation at 425 and 500°C to 15 dpa and at 500°C to 31 dpa. All specimens contained extensive precipitation, but precipitate morphologies were very different at the two irradiation temperatures. Moderate swelling was found following irradiation at 425°C, but following irradiation at 500°C, voids were only found in association with grain boundary structure and only at the higher dose. Therefore, additions of titanium completely altered the microstructural evolution when 1% nickel was present.

Examples of V-2Ti-1Ni microstructures are provided in Figure 4. Figures 4 a) and b) show void and precipitate structures in V-2Ti-1Ni that was irradiated to 15 dpa at 425 and 500°C. Precipitates are highly elongated in $\langle 100 \rangle$ directions following irradiation at 425°C, whereas after irradiation at 500°C, they are smaller and more equiaxed. Voids formed at 425°C are cuboidal with (100) faces, whereas no voids were observed following irradiation to 15 dpa at 500°C. Figures 4 c) and d) provide higher magnification examples of the structure formed following irradiation at 425°C. Figure 4 c) shows an area in absorption contrast to reveal precipitates and voids, and Figure 4 d) shows the same area in $\vec{g} = 200$ contrast to show the dislocation structure. The dislocation structure in Figure 4 is difficult to interpret, consisting of short line segments connected to precipitate particles.

Figure 4. Microstructures in V-2Ti-Ni following irradiation to 15 dpa at 425 in a), and at 500°C in b), at higher magnification to 15 dpa at 425°C in c) and in dislocation contrast in d) and at 500°C to 31 dpa in dislocation contrast in e) and f) and in precipitate contrast in g), and showing voids at grain boundaries in h).

Figures 4 e) through 4 h) give examples of the microstructure in V-2Ti-1Ni following irradiation at 500°C to 31 dpa. Figures 4 e), f), and g) show the same area under different contrast conditions. Figure 4 e) uses $\vec{g} = 110$ and f) uses 200 for a foil near (001). However, the dislocation images in these figures are very difficult to compare due to precipitate images that also appear. Figure 4 g) shows the precipitate particles in $\frac{5}{8}(200)$ dark field contrast, although other precipitate reflections showed similar images. From this figure, it is apparent that particle sizes vary from 3 to 6 nm, with some as large as 10 nm. Figure 4 h) shows one of several examples where a few voids are found in the vicinity of grain boundaries. The voids vary considerably in shape and size. Precipitate particles are also present (based on the mottled background contrast), so precipitate denuding due to grain boundary migration does not explain the presence of the voids.

Discussion

It has been proposed that the high swelling of vanadium alloys can be interpreted in terms of the atomic size effect of the alloying elements.⁶ Solute atoms that are smaller in size will diffuse by an interstitial mechanism and be preferentially segregated to point defect sinks such as dislocations and voids, and there, may significantly alter the sink bias for point defects.⁶ Based on a relative atomic size measurement from extrapolation of the lattice constant data for the alloy, it was shown that additions of Fe, with a relative atomic size of 0.86, developed higher swelling than did addition of Si (0.88) and Cr (0.93), which in turn developed higher swelling than pure V (1.00) and pure Mo (1.04). The present results suggest that Ni additions may produce swelling intermediate between Cr and V, and that Al and Ti additions produce response similar to Mo. However, if one uses the metallic radii estimates by Asaroff,⁸ the order of atomic size (in Å) is Si:1.17, Fe:1.24, Ni:1.24, Cr:1.25, V:1.31, Mo:1.36, Al:1.43, and Ti:1.44. Therefore, a different measure of the tendency for solute segregation is created that predicts the strongest effect with Si additions; next in potency would be Fe, Ni, and Cr and then pure V, Mo, Al, and Ti.

A large number of simple vanadium alloys have now been examined following neutron irradiation, and the present study adds to that list. Microstructural examinations have previously been reported for pure V,^{6,10} V-5Fe,^{2,6} V-1Si,⁶ V-10 to 15Cr(-.2Al),^{6,9} V-5 to 22Ti,^{9,11,12} V-5 to 15Cr-5 to 25Ti,¹³⁻¹⁵ V-4 to 5Mo,^{6,9} and V-8.6W.⁹ Those studies have shown that V-5Fe swells rapidly because of rapid void growth and rapid dislocation evolution.^{3,6} It was assumed that the cavities also developed an iron-rich surface layer. Rapid void growth can also occur with Si additions at low irradiation temperatures (410°C) and with Cr additions at 600°C (although only to half the level obtained with Fe).⁶ The present results for void growth in V-1Ni at 600°C are similar to those for V-5Cr. A value of about 150 nm following irradiation at 600°C in EBR-II to 31 dpa, whereas Nakajima and coworkers found a mean cavity size of 200 nm following irradiation at 600°C in the Fast Flux Test Facility to 34 dpa.⁶

Additions of Ti, Mo, and W have previously been shown to reduce swelling.^{6,9} The present studies have shown that Al, and Ti additions to V-1Ni have a similar effect. However, the mechanism that controls the reduction of swelling that can be identified from the present work is fine scale precipitation, similar to the mechanism proposed for V-15Cr-5Ti¹³ and ascribed to Ti₅Si₃,¹⁴ and similar to the previous observations on V-10Ti.⁹ The present work has indicated that dislocation movement would be inhibited by the precipitation in these systems. Therefore, a means for prevention of swelling in vanadium alloys may be precipitation rather than a high relative atomic size of solute additions.

CONCLUSIONS

The effects of solute additions of Ni, Al and Ti/Ni to vanadium have been studied based on microstructural examination of alloys V-5Al, V-1Ni, and V-2Ti-1Ni following irradiation in EBR-II in the temperature range 425 to 600°C. Based on these examinations, Ni additions promote swelling and precipitation on a coarse scale similar to but not as effectively as Cr additions, whereas additions of Al and Ti/Ni inhibit swelling and promote precipitation on a fine scale.

Therefore, solute additions of a small relative size are confirmed to promote swelling in vanadium alloys, and solute additions of a large relative size inhibit swelling.

FUTURE WORK

This work will be continued when suitable specimens become available.

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