EFFECTS OF INTERSTITIAL SOLUTES ON THE
MICROSTRUCTURES OF SELF-ION IRRADIATED VANADIUM

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EFFECTS OF INTERSTITIAL SOLUTES ON THE
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ABSTRACT: Vanadium and vanadium containing 0.1% C, 0.4% C, 1.0% N, and 1.0% O were irradiated with 3-MeV $^{51}\text{V}^+$ ions in the temperature range 650-880°C to a dose level of ~ 20 dpa. The results show that nitrogen is most effective in controlling the void swelling. Carbon and oxygen also suppress the swelling considerably when compared with unalloyed vanadium. Except for V-1.0% N, all compositions exhibit a fine platelet precipitate with {012} habit at 650°C. In the case of vanadium-carbon alloys, this phase persisted even at higher temperatures. Vanadium and V-1.0% O showed fine precipitation on dislocations and void surfaces at 880°C. V-0.1% C exhibited a metastable {013} carbide precipitate at 880°C, whereas V-0.4% C showed equilibrium V_2C phase with some {012} precipitates. This {012} precipitation was irradiation induced and was dependent upon the carbon concentration. V-1.0% N did not show any evidence of precipitation over the entire temperature range.

KEY WORDS: CTR wall materials, bcc metals, interstitial solutes, radiation effects, swelling, voids, dislocations, metastable precipitation.

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Introduction

Strong effects of interstitial solutes on the irradiation-induced microstructure of bcc metals and alloys have recently been demonstrated in ion-bombardment experiments. For example, a reduction in the void swelling of dilute niobium-oxygen alloys compared with pure Nb has been reported [1], and our preliminary studies indicated similar behavior in V-O alloys. The theoretical calculation of Schilling and Schroeder [2], based primarily on vacancy trapping by interstitial solutes in bcc metals, also predicts significant suppression of swelling with solute content. In addition, irradiation may produce precipitates in alloys which, under thermal equilibrium, would not contain precipitates. Such irradiation-induced precipitates have been observed in ion-irradiated vanadium [3,4], and are thought to arise from very low concentrations of interstitial impurities.

To determine the effects of these interstitial solutes on the void swelling as a function of temperature, we have prepared and irradiated dilute binary alloys of vanadium containing known amounts of carbon, oxygen, and nitrogen. In addition, our early results suggested a correlation between irradiation-induced precipitation and carbon content. Thus we also investigated a normally two-phase vanadium-carbon alloy. A dose level of ~20 dpa was selected on the basis of previous dose-dependence studies of swelling that indicated a maximum swelling in the vicinity of this dose level [3].

Experimental Procedure

Vanadium was obtained in the form of 0.02-cm sheet from Wah Chang, Albany. The supplier's analysis, an independent mass spectrographic analysis for substitutional elements, and vacuum-fusion analysis of interstitial elements are given in Table 1. As shown in Table 1, the carbon, oxygen, and nitrogen contents of the vanadium correspond to ~ 0.05 , 0.04 , and 0.01 at.% respectively. Sheets (20 by 0.4 by 0.02 cm) of vanadium containing an additional 0.1% and 0.4% carbon, 1.0% oxygen, and 1.0% nitrogen were made by reacting the vanadium at 1250°C with methane, oxygen, or nitrogen in an ultra-high vacuum system. In the case of carbon alloys, the residual hydrogen was removed by evacuating the system to $\sim 10^{-8}$ Torr before cooling the sheet. When possible, nominal compositions were checked by comparing sample weight gain based on the amount of gas reacted with those actually measured. These quantities agreed within 1% of the weight of solute added.

Specimens for irradiation were obtained by punching 3-mm disks from the sheet stock described above. One surface was polished by procedures described previously [5]. Hydrogen picked up during polishing was removed by final degassing for 15 m at 1050°C just prior to inserting the samples into the ultra-high vacuum irradiation chamber. Groups of specimens from each composition were clamped in a 4 by 5 array in a tungsten specimen holder and irradiated with 3.0-MeV $^{51}\text{V}^{+}$ ions in the ANL dual ion-irradiation facility [5]. A given array contained three disks of each alloy. The ion flux and fluence were typically $0.55 \mu\text{A cm}^{-2}$ and 4.0 mC cm^{-2} . One disk of each composition was shielded from the beam and acted as a control sample in that it experienced the same thermal treatment and gaseous environment as the irradiated specimens. The nominal irradiation temperatures were 650, 700, 750, 800, and 880°C . The temperature was controlled by thermocouples in the sample holder and individual

specimen temperatures were read using an infrared pyrometer calibrated for these materials and specimen-preparation procedures. Total gas pressures during the ~ 2 -h irradiation were in the low 10^{-8} Torr range, dropping to 10^{-9} Torr as the run proceeded. Residual gas-pressure measurement showed approximate partial pressures for H_2O of $\sim 3 \times 10^{-9}$ Torr and for combined N_2 and CO $\sim 5 \times 10^{-9}$ Torr.

Following irradiation, the specimens were sectioned to depths between 7100 and 8500 Å from the irradiated surface, then thinned from the back side to perforation. The section depth for a particular specimen was determined with an interference microscope and was used in computing the dose for that specimen. Deposited energy densities as a function of depth, calculated from Brice Codes RASE3 and DAMG2 [6], were converted to displacements per atom (dpa) using a threshold energy of 40 eV. For the 3-MeV V^+ irradiation, the depth of maximum displacement damage was 9300 Å, and an ion flux of $1 \mu A/cm^2$ corresponded to a displacement rate of 5.5×10^{-3} dpa/s. The void and precipitate microstructures were examined by procedures described previously [5].

Void and Dislocation Data

Comparisons of data for the void and dislocation microstructure of four interstitial doped alloys with those for unalloyed vanadium are given in Figs. 1 through 4. Plots show, respectively, void volume fraction, void number density, mean void diameter, and dislocation density plotted as a function of irradiation temperature. For the V, V-0.1% C, V-1.0% O, and V-1.0% N, the dose level of the transmission-electron microscopy specimens was $20 \pm 10\%$ dpa, whereas that of V-0.4% C was $16 \pm 10\%$ dpa. The curves on the plots show the trends in the parameters.

The temperature dependence of the void volume fraction for vanadium is consistent with previous data for Ni^+ ion irradiations at a dose level of

~50 dpa [7]. The swelling rises rapidly with temperature, peaks in the vicinity of 700°C, and drops off slowly on the high temperature side. Within limits of the present data set, it appears that the shape of the swelling curve for V-0.4% C is not strongly affected, although the magnitude of the swelling is significantly depressed. V-0.1% C exhibits swelling over the same temperature range as the vanadium. In V-1.0% O and V-1.0% N swelling is decreased over this temperature range, but for V-1.0% O it is increased at lower temperatures. A comparison of these swelling data with those obtained previously in a $^{58}\text{Ni}^+$ irradiation shows that, although the magnitude of the swellings are similar, the void number density was an order of magnitude lower in the self-ion irradiation. The void number density is strongly dependent upon the solute, although in all cases the density decreases rapidly as the temperature increases. Interstitial solutes cause large variations in void number density, particularly at the lower temperatures: oxygen appears to promote void nucleation, nitrogen depresses it, whereas carbon in solution exhibits an intermediate behavior closely paralleling that for unalloyed vanadium. However, only the void size tends to increase with irradiation temperature; V-0.4% C exhibits the more generally observed monotonic increase [8]. The variations in the other curves, although not presently understood, appear to be valid as they are well outside the limits of the relative error in the mean void diameters ($\pm 10\%$).

Micrographs showing the void structure of the various alloys after irradiation at 700°C are shown in Fig. 5. Nonrandomness in the void distributions can be seen in vanadium and the carbon alloys where the voids tend to form a network pattern and, to a lesser extent, the oxygen-doped alloy where a few void clusters are visible. However, at temperatures above and below 700°C, all specimens tended to exhibit more random void structures. A precipitate

structure can be seen in V-0.1% C (Fig. 5b), whereas the dislocation microstructure is visible in the oxygen- and nitrogen-doped alloys (Figs. 5c and 5d). In all the alloys, dense dislocation tangles were observed, the density of which decreased with an increase in the irradiation temperature (Fig. 4). Vanadium exhibited a significantly lower dislocation density than the other alloys, whereas in the 0.4% C alloy, the dislocation density at high temperatures was significantly greater than the other compositions. This is ascribed to the generation of additional dislocations by prismatic punching at V_2C particles [9].

Precipitation Phenomena

Under normal conditions of thermal equilibrium, all alloys investigated, except V-0.4% C, are single phase at the irradiation temperatures [10,11]. V-0.4% C contains the V_2C phase and a bcc solid solution, as described by Diercks and Wert [9]. These authors have demonstrated that formation of V_2C at temperatures $\geq 500^\circ C$ is preceded by a metastable carbide with {013} habit. Our V-0.4% C unirradiated control specimen from the $880^\circ C$ irradiation showed V_2C precipitates on the external surface and at a depth corresponding to the peak damage ($9300 \text{ \AA}$). The morphology and electron diffraction patterns from the internal V_2C phase were the same as those reported by Diercks and Wert [9].

The various precipitate types observed in the irradiated specimens are shown in Fig. 6. Figure 6a shows a platelet precipitate that trace analysis confirmed had an {012} habit, henceforth called the {012} precipitate. This precipitate was previously observed by Agarwal and Taylor [3]. It is extremely thin, perhaps only one or two atom layers thick, as evidenced by profuse streaking along $\langle 012 \rangle$ in the electron diffraction patterns. Furthermore, it displays

well-developed displacement fringe contrast when inclined to the electron beam. Figure 6b shows irregular, three-dimensional precipitates identified as V_2C by electron diffraction. As previously stated, these are surrounded by dense tangles of dislocations. In addition to V_2C precipitates, Fig. 6c shows thin, disk-shape precipitates that are visible by displacement fringe contrast. Trace analysis of these precipitates showed a $\{013\}$ habit. They produced diffraction effects identical to the metastable carbide phase described by Diercks and Wert, Fig. 6 of their paper [9]. In the present case, this precipitate clearly forms heterogeneously on dislocations and void surfaces. The presence of precipitates along dislocations was also observed in vanadium at the highest irradiation temperatures (Fig. 6d). These precipitates are very thin disks of $\{013\}$ habit with an ~ 500 Å diameter. They frequently occur as parallel sets along the dislocations, e.g., the region labeled A. In other orientations visible in Fig. 6d, the overlapping strain contrast of these precipitates causes the fringed appearance of some portions of the dislocations.

Table 2 is a summary of the various kinds of precipitates observed as a function of irradiation temperature and alloy composition. The V-1.0% N alloy showed no precipitates over the entire temperature range investigated. Vanadium and V-1.0% O exhibited qualitatively similar behavior, namely a high density of $\{012\}$ precipitates at the lowest irradiation temperature only and precipitates on dislocations at the highest temperatures. The V-0.1% C and V-0.4% C also showed high densities of $\{012\}$ precipitates at 650°C. Unlike vanadium and V-1.0% O, the $\{012\}$ precipitate in the carbon alloys persisted to much higher temperatures ($\sim 800^\circ\text{C}$). This is demonstrated in the case of V-0.1% C in Fig. 7. This figure shows that the precipitates become less dense and coarser as the irradiation temperature increases. The $\{012\}$ precipitate was not observed

in samples irradiated at 880°C. However, these did show the metastable carbide phase described earlier (Fig. 6c), which is believed to form during cooling from the irradiation temperature.

Conventional thermal aging of V-0.4% C at temperatures above 600°C produced only V₂C precipitates, which was also the case for samples irradiated at 880°C. However, at 650°C no V₂C precipitate was observed in the irradiated specimen, but instead only a very high density of {012} precipitate (Fig. 6a). With an increase in temperature, the relative proportion of {012} precipitate decreased and that of V₂C increased (Fig. 6b). At 880°C, the presence of V₂C in the external surface of the irradiated V-0.4% C was noted, which was similar to the unirradiated control sample.

Discussion

The present investigation of the influence of interstitial solutes on the void microstructure of vanadium indicates systematic dependence of the microstructure upon the solute species. To a first approximation, possible effects due to impurity contamination from the vacuum environment during the irradiation have been limited by bombarding all alloy compositions simultaneously. Nitrogen doping produces the largest effect, in that both the void number density and the void swelling are lower than in the unalloyed vanadium. Alloying with oxygen reduces the swelling and causes a large increase in the observed void number density at the lowest temperature. In both oxygen and nitrogen alloys, an indication has been found that the swelling curve shifted to lower temperatures when compared with unalloyed vanadium. The lower carbon concentrations of 0.1 and 0.4% produce significant depressions in swelling mainly through reduction in void size. The origin of the irregularities in the

temperature dependence of the void size are not understood. Complications arising from segregation and precipitation of impurities and the temperature dependence of these effects require additional investigation.

The influence of oxygen concentration on swelling can be inferred from a comparison of the present data with some of our previous observations [12] of a V-5.0% O alloy that showed negligible swelling at 700°C, i.e., <0.001% because of the $\sim 10^{12} \text{ cm}^{-3}$ void density. Thus, a progressive decrease in swelling with an increase in oxygen content [1] is apparent.

The mechanism by which interstitial solute atoms inhibit void swelling is not clear. The Schilling and Schroeder [2] model, which involves vacancy trapping by immobile interstitial solutes, predicts a reduction in swelling, and a shift of the swelling-temperature curves to higher temperatures. A decrease in the swelling is observed. However, with the addition of interstitial solutes the direction of the shift in the peak swelling implied by the oxygen and nitrogen data is opposite that predicted by the Schilling and Schroeder model. Okamoto et al. [13] have developed a model consistent with the observed trends in our data.

The present results shed new light on the {012} precipitate noticed in previous investigations [3]. This precipitate seems quite definitely associated with carbon in the vanadium. The {012} precipitate is present to higher irradiation temperatures than 650°C, when carbon is added to the vanadium. The presence of {012} at 650°C in the starting vanadium is probably due to small carbon concentration (~0.05%). Also, it competes with V₂C for the available carbon. At lower irradiation temperatures, where any irradiation-induced carbon segregation effect would be most noticeable, the {012} precipitate replaces V₂C observed under equilibrium thermal aging. At the higher temperatures

where irradiation-induced segregation would be less dominant [13], one observes the V_2C phase. Perhaps the {012} precipitate acts as a sink not only for carbon atoms but also for vacancies and/or self-interstitials [14].

Conclusion

1. The addition of the interstitial solutes nitrogen, oxygen, and carbon strongly suppress void swelling of vanadium induced by ion bombardment.
2. These solutes influence both the number density of voids and the mean void size.
3. Identical {012} metastable precipitates were observed in ion-irradiated vanadium and in V-0.1% C and V-0.4% C alloys. This precipitate replaces some of the V_2C phase observed in specimens of V-0.4% C alloy under thermal equilibrium.

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Table 1 - Chemical Analyses of Vanadium

Element	Supplier, wt ppm	Mass Spectrograph, wt ppm	Fusion Analysis, wt ppm
H	4	-	-
C	80	-	125
N	100	-	39
O	350	-	136
Al	80	<40	-
Cu	<40	2	-
Fe	90	33	-
Si	295	150	-
Remainder	-	<10	-

Table 2 - Summary of the precipitate microstructures observed in vanadium and vanadium alloys at various irradiation temperatures.

Irradiation Temperature, deg C	Vanadium	V-0.1% C	V-0.4% C	V-1.0% O	V-1.0% N
650	Very high density of {012} precipitates	Very high density of {012} precipitates	Very high density of {012} precipitates; no V ₂ C	High density of fine {012} precipitates	No precipitates
700	No precipitates	Dense {012} precipitates	V ₂ C + {012} precipitates	No precipitates	No precipitates
750	No precipitates	Low density coarse {012} precipitates	V ₂ C + {012} precipitates	No precipitates	No precipitates
800	Fine precipitation on dislocations	Coarse {012} precipitates	V ₂ C + some coarse {012} precipitates	No precipitates	No precipitates
880	Fine precipitation on dislocations and void surfaces	Metastable carbide exhibiting displacement fringe contrast	Fine V ₂ C on the surfaces of the specimen + V ₂ C in bulk + some metastable carbide	Fine precipitates on dislocations (similar to V)	No precipitates

Figure Captions

- Fig. 1 - Void volume fraction as a function of irradiation temperature.
- Fig. 2 - Void number density as a function of irradiation temperature.
(Arrows represent a +40°C temperature excursion for about 10 minutes in the beginning of the run. The total run time was about 2 hours.)
- Fig. 3 - Average void diameter as a function of irradiation temperature.
- Fig. 4 - Dislocation density as a function of irradiation temperature.
- Fig. 5 - Void microstructure in vanadium and vanadium alloys irradiated at 700°C.
- Fig. 6 - Various precipitate microstructures observed in vanadium and vanadium alloys irradiated in the temperature range 650-880°C [(100) foil].
- Fig. 7 - Coarsening of {012} precipitate in V-0.1% C as a function of temperature [(100) foil].

Fig. 1 - Void volume fraction as a function of irradiation temperature.

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Fig. 3 - Average void diameter as a function of irradiation temperature.

Fig. 4 - Dislocation density as a function of irradiation temperature.

- (a) VANADIUM
- (b) V-0.1C
- (c) V-1.0O
- (d) V-1.0N

Fig. 5 - Void microstructure in vanadium and vanadium alloys irradiated at 700°C.

- (a) V-0.4C AT 650° C
- (b) V-0.4C AT 800° C
- (c) V-0.1C AT 880° C
- (d) VANADIUM AT 880° C

Fig. 6 - Various precipitate microstructures observed in vanadium and vanadium alloys irradiated in the temperature range 650-880°C [(100) Fo11].

- (a) 650°C
- (b) 700°C
- (c) 750°C
- (d) 800°C

Fig. 7 - Coarsening of {012} precipitate in V-0.1% C as a function of temperature [(100) Foil].