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EFFECT OF NICKEL AND NITROGEN ON VOID FORMATION IN ION BOMBARDED VANADIUM

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The objective of this study is to determine how both substitutional and interstitial solutes affect void formation in vanadium. Samples of high purity vanadium have been doped with 1% to 8% nickel, or with 1% nitrogen and irradiated with 14 MeV Cu ions to dose levels between 1 and 10 dpa at 6×10^{-4} dpa/sec. Swelling is observed at temperatures ranging from 450°C to 650°C in high purity vanadium at 2.5 dpa. The peak swelling temperature at this dose level is 550°C. The addition of >2% Ni to the high purity vanadium completely suppressed void formation at temperatures between 350°C and 650°C. Samples doped with 1% Ni exhibited extremely low void densities. In samples irradiated at 450°C, 550°C and 650°C nitrogen doping reduced the void density. This effect resulted in a generally decreased level of swelling in the V-1%N samples.

1. INTRODUCTION

The successful operation of commercial fusion reactors will require the development of advanced alloys that will combine favorable mechanical and nuclear properties with a strong resistance to radiation damage. Preliminary studies have shown that a number of vanadium base alloy systems have the potential of meeting this combination of requirements. The objective of this study is to determine how a substitutional addition (nickel) and an interstitial addition (nitrogen) affect void formation in vanadium.

A number of substitutional solutes have been studied as solid solution hardeners, including Ti, Nb, Ta, Cr, Mo, W, Fe, and Ni [1]. Using these alloying additions, it is possible to obtain a wide range of mechanical properties. However, the high temperature irradiation behavior has been studied in only a few of the possible substitutional solid solution alloys. The alloy systems that have been studied include the V-Ti [2-6], V-Cr [6] binary systems and the VANSTAR [6] series of alloys. All of these alloy systems have exhibited resistance to void formation.

The interstitial alloying additions of oxygen and nitrogen can also serve as matrix hardeners in vanadium. Both elements have terminal solubilities in excess of 1 atomic per cent at 500°C. The residual interstitial impurity content in "commercially pure" vanadium stock material is generally in excess of 0.3 atomic per cent. Consequently, in any study of vanadium alloys, it is necessary to carefully account for the effect of interstitial impurities. Studies by Agarwal, Potter, and Taylor [7,8] have shown that carbon, oxygen, and nitrogen all reduce void swelling in ion irradiated vanadium. However under neutron irradiation, oxygen may increase void swelling in vanadium [9].

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2. EXPERIMENTAL PROCEDURE

The base material used in this study was high purity vanadium containing less than 200 wt-ppm interstitial impurities and less than 10 wt-ppm substitutional impurities. The same material was used in a previously reported study of pure vanadium [10]. An alloy containing 1 atomic per cent nitrogen was prepared using the Sieverts apparatus at Argonne National Laboratory [11]. The vanadium-1% nickel alloy used in this study was also obtained from Argonne National Laboratory [12].

Prior to irradiation, the samples were mechanically polished to produce a flat surface and then electropolished to remove surface damage. The samples were then punched into 3mm discs, and given a one hour anneal at 1050°C in a high vacuum furnace (<2×10^{-6} Pa). The samples were then furnace cooled. This heat treatment produced a well-annealed structure devoid of precipitation.

All of these irradiations were performed on the University of Wisconsin Heavy Ion Irradiation Facility using 14 MeV Cu^{3+} ions. This facility, which has been described previously [13], provides a vacuum of less than 2×10^{-6} Pa at temperature, during irradiation. Post irradiation examination was performed by electropolishing to remove a 1 μm thick layer from the irradiated surface and then back thinning the foils for transmission electron microscopy. The amount removed from the irradiated surface was determined by using interference fringes in an optical microscope. Damage calculations were performed using the E-DEP-1 code of Manning and Mueller [14] assuming an effective displacement energy of 43 eV. The displacement rate in the region of examination was approximately 6×10^{-4} dpa/second.

3. RESULTS

3.1 Pure vanadium

Results of a series of irradiations at temperatures between 450°C and 650°C to 2.5 dpa are included in Table 1. In agreement with a previously reported study of void formation at 1 dpa [10], voids were observed over this entire temperature range. The peak in swelling, which occurred at 550°C results from a low density of extremely large voids. In Figure 1, a micrograph of pure V, V-7%Ni and V-1%N all irradiated at 550°C to ~2.5 dpa are compared. Even though voids were observed at 650°C, the void density was extremely low ($<5 \times 10^{11}$ voids/cm3). A low density of precipitates associated with the voids was also observed at 650°C. The swelling in the pure V is plotted as a function of temperature in Figure 2.

3.2 Vanadium-nickel

Two series of V-Ni alloys were irradiated. The first series was doped prior to irradiation with one atomic per cent nickel. The second series of samples contained 1.5 to 8% nickel. The nickel contents given in Table 1 for the second series of Ni specimens were determined by energy dispersive X-ray analysis in a post irradiation study.

The void densities observed in the samples containing 1 atomic per cent Ni irradiated at 550°C to 1 dpa and at 650°C to 1 and 5 dpa were extremely low. These low void densities resulted in negligible swelling levels. In the second series of samples, which contained larger amounts of nickel, void formation was completely suppressed.

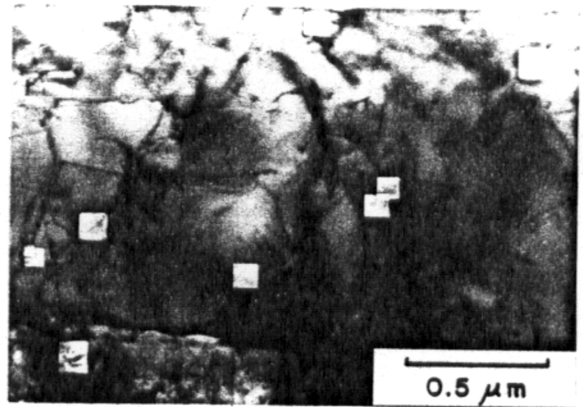
Evidence of solute segregation to dislocations occurs in V-1%Ni samples irradiated at 650°C and 550°C. The onset of precipitation was observed as large regions of strain contrast in the transmission electron microscope. Evidence of coherent precipitation was also observed in the sample irradiated to 5 dpa at 650°C.

3.3 Vanadium-nitrogen

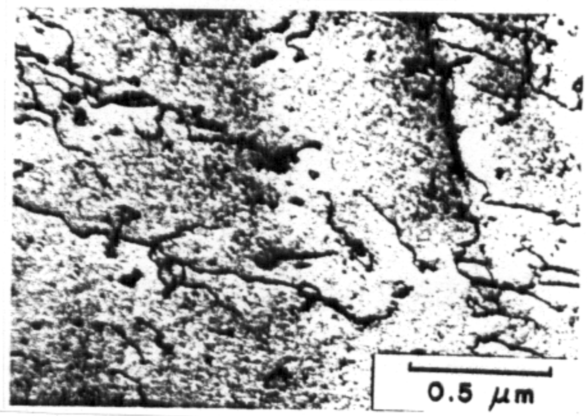
Samples of V-1%N were also irradiated at 450°C, 550°C, and 650°C to doses between 1 and 10 dpa. The results of these irradiations are presented in Table 1. The addition of nitrogen reduced swelling in vanadium at those temperatures, as illustrated in Figure 2, where the swelling levels in vanadium-nitrogen specimens irradiated to 2.5 and 10 dpa are compared to swelling levels in pure vanadium irradiated to 2.5 dpa. In general this reduction appears to be due to lower void densities in the nitrogen doped specimens.

4. DISCUSSION

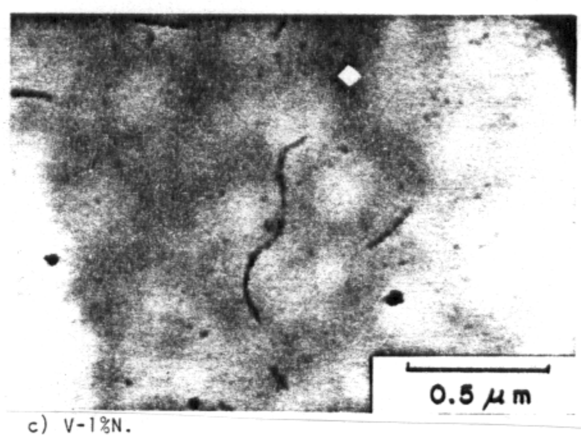
4.1 Pure vanadium



a) Pure V.



b) V-7%Ni.



c) V-1%N.

Fig. 1. Effect of nickel and nitrogen on void formation in vanadium irradiated at 550°C with 14 MeV Cu^{3+} ions. a) Pure vanadium sample irradiated to 2.5 dpa. Foil normal (100), b) V-7%Ni sample irradiated to 2 dpa (g=[110], c) V-1%N sample irradiated to 2.5 dpa. Foil normal (100).

Table 1. Irradiation and Void Parameters for Vanadium Alloys

Irradiation Temperature (°C)	dpa	Alloy Elements (atom %)	Void Density (cm^{-3})	<d> (Å)	ΔV/V%	Precipitation
			High Purity Vanadium			
450	2.5	Negligible	2×10^{14}	120	0.03	None
550	2.5	Negligible	7×10^{12}	1000	0.70	None
650	2.5	Negligible	4×10^{11}	330	~0	None
			Vanadium-Nickel			
550	1	1%Ni	$<10^{12}$	--	~0	Segregation
650	1	1%Ni	$<10^{11}$	--	~0	Segregation
650	5	1%Ni	$<10^{11}$	--	~0	Coherent
450	2	1.5%Ni	0	--	0	Sheet
550	2	7%Ni	0	--	0	None
650	2	8%Ni	0	--	0	None
			Vanadium-Nitrogen			
450	1	1%N	0	--	0	None
450	2.5	1%N	0	--	0	None
450	10	1%N	$<10^{11}$	--	0	None
550	1	1%N	2×10^{12}	310	0.004	None
550	2.5	1%N	$<10^{11}$	--	~0	None
550	5	1%N	0	--	0	None
550	10	1%N	8×10^{12}	410	0.04	Small black spots
650	1	1%N	1×10^{13}	300	0.02	None
650	2.5	1%N	0	--	0	None
650	5	1%N	10^{12}	350	0.003	Small black spots
650	10	1%N	$<10^{12}$	--	~0	Small black spots

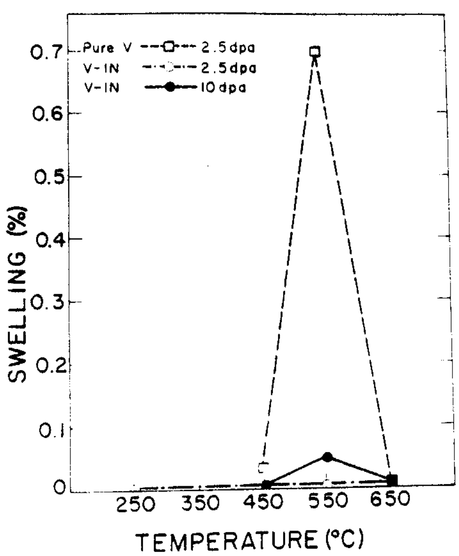


Fig. 2. Swelling as a function of temperature for pure vanadium and vanadium-1% nitrogen specimens. All irradiations performed on the University of Wisconsin Heavy Ion Irradiation Facility using 14 MeV Cu^{3+} ions.

The peak swelling temperature of 550°C observed in this study represents a shift of 175°C from the peak swelling temperature 725°C previously reported by Agarwal et al. [7] in ion irradiated vanadium. This shift can be attributed to the differences in dpa rates in the two experiments. For two different dpa rates, K_1 and K_2, a shift in the irradiation temperature from T_1 to T_2 is required to obtain equivalent swelling behavior. It has been shown [15] that for temperatures below the peak swelling temperature an estimate of this effect may be obtained using the relation:

$$\frac{D_v(T_1)}{K_1} = \frac{D_v(T_2)}{K_2} \tag{1}$$

where $D_v(T)$ is the diffusion coefficient for vacancy motion at temperature T. The dpa rate in the sample irradiated in this study at 550°C was 6×10^{-4} dpa/sec, while the dpa rate reported by Agarwal et al. [7] was 3×10^{-3} dpa/sec. Using a vacancy migration energy of 0.6 eV, an approximate temperature shift of 190°C is predicted. This is in reasonable agreement with the observed temperature shift of 175°C. In Figure 3, Agarwal et al's. results have been normalized and adjusted to equivalent swelling temperatures at 6×10^{-4} dpa/sec using equation 1 and compared to the normalized results of this study. Although this adjustment is only approximate at temperatures above the peak, the agreement is within experimental error over the range

500°C to 700°C.

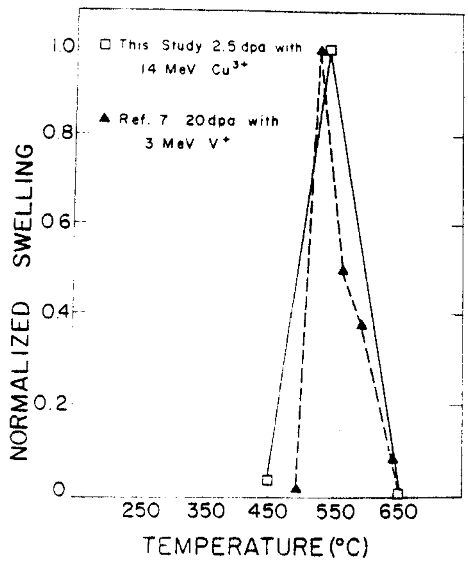


Fig. 3. Comparison of swelling results in heavy ion irradiated vanadium. ANL results have been adjusted to compensate for temperature shift due to differences in dose rates.

4.2 Vanadium alloys

These results show that nickel, like the other substitutional hardeners (Ti and Cr), suppreses void swelling in vanadium. Carlander, Harkness and Santhanam [2] suggest three possible mechanisms by which Ti may work to suppress void formation. They are: (1) the scavenging of interstitial impurities necessary for void nucleation; (2) the enhancement of point defect recombination at solute atom trapping sites; and (3) the formation of a high density of coherent precipitates to accommodate excess vacancies. The wide range of alloying elements (Ti, Zr, Ni, N) that may be used to suppress void swelling in vanadium suggests that the mechanism responsible for suppressing void swelling does not strongly depend on a specific chemical effect of the alloying addition. This would indicate that the scavenging of interstitial impurities is not primarily responsible for suppressing void formation. The scavenging hypothesis is also contradicted by the results obtained in the V-1%N alloy, which indicate that nitrogen retards rather than enhances void nucleation. Similar results have been obtained by Agarwal, Potter, and Taylor [7].

The suppression of void swelling by point defect trapping requires vacancy-impurity trapping energies which are far greater than the 0.05 eV typical of recent measurements of vacancy trapping energies [16]. Calculations made by Agarwal et al. [8] show that for an impurity concentration of 1%, a vacancy-impurity binding energy of 0.6 eV is required to get significant suppression of the void growth rate.

The precipitation phenomenon observed in the Ni doped samples could be responsible for the suppression of void swelling by increasing the density of unbiased sinks and thereby inducing recombination which reduces the concentration of excess vacancies in the matrix. In the nitrogen doped specimens, small black spot damage, which may correspond to precipitation was observed only at the higher doses. It is also possible that alloying additions retard void nucleation by increasing the surface energy of the void embryo. It might be expected that this would be a more universal phenomemon explaining the effects of both nickel and nitrogen on void swelling in vanadium. However, we have no direct evidence for either of those mechanisms.

Evidence of a radiation enhanced precipitation phenomenon is also observed in the V-1%Ni alloy. The solubilities and phase relationships have not been determined in the V rich region of the V-Ni phase diagram below 800°C, because the kinetics of precipitation become prohibitively slow. The sluggish rate of this reaction could have been accelerated by radiation enhanced diffusion.

5. CONCLUSIONS

The results of this study have produced the following conclusions.

1. The peak swelling temperature in pure vanadium irradiated to 2.5 dpa at a dose rate of 6×10^{-4} dpa/second is 550°C. Calculations of the temperature shift due to differences in dose rate show that this result is consistent with the peak swelling temperature of 725°C at 3×10^{-3} dpa/second reported by researchers at Argonne National Laboratory [7].

2. Void swelling in vanadium is suppressed at low doses by the addition of nickel. No voids were observed in specimens containing more than 1.5%Ni, irradiated to 2 dpa at temperatures between 450°C and 650°C. In a 1%Ni alloy, the maximum void density observed was less than 10^{12} voids/cm^3.

3. The void densities observed in nitrogen doped vanadium specimens irradiated at 550°C and 650°C are significantly lower than void densities observed in pure vanadium irradiated under the same conditions.

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