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Radiation hardening of V–C, V–O, V–N alloys neutron-irradiated to high fluences

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Abstract

Vanadium has a large affinity for interstitial impurities such as C, N and O. Mechanical properties and irradiation performance of vanadium alloys are affected by the impurities. Radiation hardening and defect microstructures of vanadium alloys doped with relatively large amounts of these interstitial elements were studied. Neutron irradiation was conducted in the Materials Open Test Assembly of the Fast Flux Test Facility (FFTF/MOTA-1F) to 47.9 dpa at temperatures of 679, 793 and 873 K. Irradiation hardening decreased with increasing irradiation temperature. Increase in hardness for the V–C alloy was relatively greater after irradiation at the low temperatures. Decorated dislocations and voids were observed depending on the alloying elements. The factors for irradiation hardening were different for each interstitial element in the alloys irradiated at 873 K to 47.9 dpa.

1. Introduction

Vanadium-base alloys, e.g., V–(4-5)Ti–(4-5)Cr type alloys, are considered promising candidate structural materials for fusion reactor components because of good mechanical properties at high temperature, low induced activity and good resistance to radiation damage [1]. However, the major deterrent to their use is the high affinity of vanadium for interstitial impurities such as C, N and O. Mechanical properties and irradiation performance for vanadium alloys are strongly affected by these interstitial elements [2]. Therefore, to develop an optimized vanadium alloy for use as structural materials in a fusion system, it is important to clarify the influence of interstitial impurities in heavy irradiation environments.

From a practical point of view, the concentration of interstitial impurities in current candidate vanadium alloys is less than 0.3 at.% [3]. However, it is important to clarify the influence of high concentration of interstitial elements on mechanical property change because vanadium can absorb considerable amount of interstitial impurities from the environment during fabrication, heat treatment processing and from the coolant materials of the reactor.

From a basic point of view, it is also interesting to study the effects of interstitial elements which cause the tetragonal strain and have relatively large diffusion coefficients compared with the substitutional elements. In the case of substitutional alloying elements, it has been shown that swelling in vanadium alloys could be explained in terms of the atomic size factor of solutes [4].

As for the influence of the interstitial elements on development of defect structures in vanadium during neutron irradiation, the influence of carbon and oxygen has been investigated [5–7]. But in those cases, neutron fluences were relatively low, so that the influence of high fluences is unknown. This paper describes the results of irradiation hardening and microstructural observations in vanadium alloys doped with relatively large amounts of interstitial elements.

2. Experimental

The alloys prepared in this work were V–0.9 at.% C, V–1.3 at.% N and V–1.2 at.% O in normal. Buttons of

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these alloys with each composition were made by arc-melting each mother alloy and electron-beam melted vanadium. Then ingots of about 10 mm in diameter were obtained by second arc-melting. These ingots were homogenized at 1773 K for 18 ks. Chemical analysis showed that concentrations of C, N and O were 0.93, 1.33 and 1.23 at.%, respectively. These ingots were sliced to about 0.35 mm in thickness and disk specimens were prepared from the slices by spark machining. After annealing at 1373 K for 3.6 ks, disk specimens of each alloy were neutron-irradiated in helium-filled capsules in the Materials Open Test Assembly (MOTA) during cycle 10 operation of the Fast Flux Test Facility (FFTF). The average irradiation temperatures and neutron fluences for the specimens were 679 K (8.19×10^{26} n/m^2), 793 K (8.30×10^{26} n/m^2) and 873 K (8.80×10^{26} n/m^2) [8]. These fluences correspond to 44.6, 45.2 and 47.9 dpa, respectively [9]. Micro Vickers hardness were measured at a load of 1.96 N at room temperature before and after neutron irradiation. The microstructures for each alloy irradiated at 873 K were also observed by transmission electron microscope (TEM), JEOL JEM-2010, operated at 200 kV. Thin foils were made by twin-jet electropolishing in a solution of 80% CH_3OH-20% H_2SO_4 at about 288 K.

3. Results

3.1. Irradiation hardening

Fig. 1 shows micro Vickers hardness for the V–0.9 at.% C, V–1.3 at.% N and V–1.2 at.% O alloys before and after neutron irradiation. The experimental errors in Vickers hardness were about ±2% for all specimens. Hardness depends on irradiation temperature and alloying elements. Compared with those of the V–1.3 at.% N and V–1.2 at.% O alloys, Vickers hardness number in unirrradiated condition of the V–0.9 at.% C alloy is low.

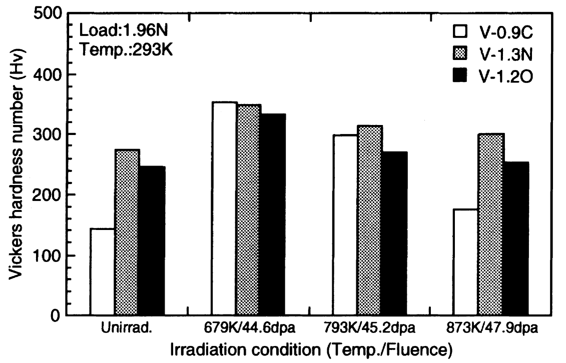

Fig. 1. Micro Vickers hardness of the V–0.9 at.% C, V–1.3 at.% N and V–1.2 at.% O alloys before and after neutron irradiation.

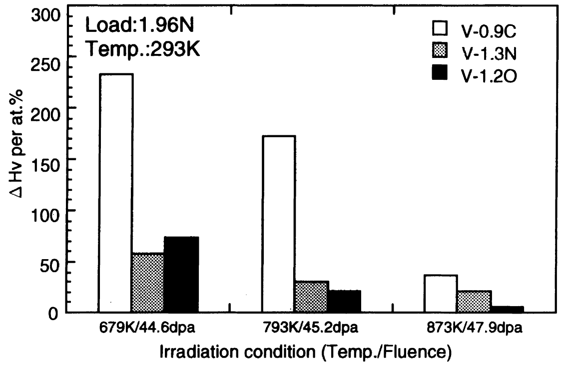

Fig. 2. Increase in hardness of the V–0.9 at.% C, V–1.3 at.% N and V–1.2 at.% O alloys after neutron irradiation.

The hardness for the V–1.3 at.% N and V–1.2 at.% O alloys before irradiation was almost the same as for the V–5Ti–5Cr–Si–Al–Y alloy [10], one of V–Ti–Cr–Si type alloys. The hardness is highest at the lowest irradiation temperature of 679 K and decreases with increasing irradiation temperature. For all irradiation conditions, the hardness of the V–1.3 at.% N alloy is larger than that of the V–1.2 at.% O alloy. While hardness of each alloy is not very different at 679 and 793 K, the hardness of the V–0.9 at.% C alloy at 873 K is very low.

Increases in hardness (ΔHv) per unit concentration of each interstitial element (at.%) are shown in Fig. 2. While the irradiation hardening of the V–0.9 at.% C alloy is relatively large in the range of low irradiation temperature, it decreases drastically with increasing temperature. The irradiation hardening of the V–1.3 at.% N alloy varies little with irradiation temperature. The relationship between the increases in hardness of the V–1.3 at.% N and V–1.2 at.% O alloys reverses at 793 K. In the case of irradiation at 873 K, hardening was relatively small compared with lower irradiation temperatures, especially in V–1.2 at.% O alloy.

3.2. Microstructural development

The microstructures of each alloy observed after irradiation at 873 K are shown in Fig. 3. Linear dislocations are observed in the V–0.9 at.% C alloy. Precipitates were observed along the dislocations with lengths of about 35 nm. Voids are distributed inhomogeneously and the average diameter is about 100 nm.

In the V–1.3 at.% N alloy, tangled dislocations are distributed uniformly. The void density for the V–1.3 at.% N alloy is much lower than that of the V–0.9 at.% C alloy, but the average diameter is almost the same as for the V–0.9 at.% C alloy.

In the V–1.2 at.% O alloy, dislocation microstructure was not observed. Large voids of about 150 nm in diameter are observed to be distributed homogeneously.

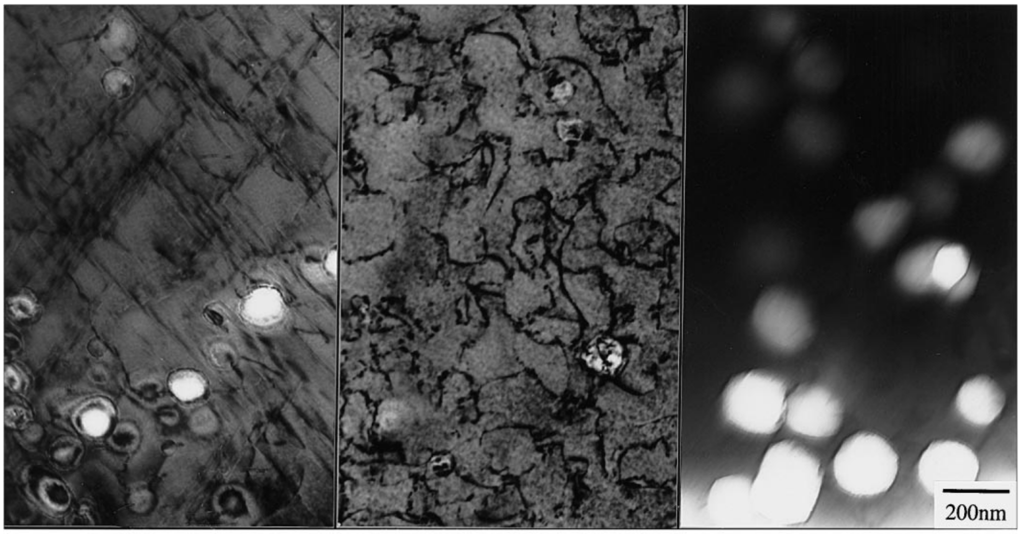

Fig. 3. Transmission electron micrographs of the V–0.9 at.% C, V–1.3 at.% N and V–1.2 at.% O alloys irradiated at 873 K to 47.9 dpa.

Precipitates were not observed in the V–1.3 at.% N and V–1.2 at.% O alloys.

The results of microstructural observation are summarized in Table 1. While the average void diameter for the V–1.3 at.% N alloy is slightly larger than for the unalloyed vanadium, the void density is relatively low, so that the void swelling is low. In the V–0.9 at.% C alloy, while void density is almost the same as for the unalloyed vanadium, the average diameter is large. In the case of the V–1.2 at.% O alloy, while the void density is lower than for the unalloyed vanadium, the average diameter is relatively large. Therefore, the swelling values of the V–0.9 at.% C and V–1.2 at.% O alloys are larger than for the unalloyed vanadium.

4. Discussion

4.1. Correlation between irradiation hardening and defect microstructure

The increase in hardness ($\Delta H\mathrm{v}_{\mathrm{cal}}$) for each alloy after neutron irradiation was evaluated from the increase in shear stress, $\Delta\tau$, by use of the following equations:

$$\Delta H\mathrm{v}_{\mathrm{cal}} \cong 3\Delta\sigma_y \quad (1)$$

$$\Delta\sigma_y = \overline{M}\Delta\tau = \overline{M}\Big(\alpha_{\mathrm{D}}\mu b\sqrt{\rho_{\mathrm{D}}} + \alpha_{\mathrm{V}}\mu b\sqrt{N_{\mathrm{V}}d_{\mathrm{V}}} + \alpha_{\mathrm{P}}\mu b\sqrt{N_{\mathrm{P}}d_{\mathrm{P}}}\Big), \quad (2)$$

where $\overline{M}$ is an orientation factor, α_{D}, α_{V} and α_{P} are interaction parameters of dislocations (D), voids (V) and precipitates (P), respectively. ρ_{D} is dislocation density, N is number density and d is average diameter. An orientation factor of 1.73 and an interaction parameter of 0.3 are used to a first approximation in this paper [11]. Also, μ is the shear modulus and b is the Burgers vector for vanadium with values of 4.67×10^4 MPa and 0.26 nm, respectively [11–13]. Based on the microstructural observations, the calculated values using Eqs. (1) and (2) for the increase in hardness for each alloy irradiated at 873 K are summarized in Table 2.

For the V–0.9 at.% C alloy, it is shown that contribution of voids to irradiation hardening is almost equal to that of dislocations. Since the precipitates may be present also in the unirradiated V–0.9 at.% C alloy, it is necessary to evaluate the contribution of precipitates in irradiated V–0.9 at.% C alloy based on that in

Table 1
Void parameter, dislocation density and precipitate size for the vanadium alloys and unalloyed vanadium neutron-irradiated at 873 K

Specimen	Damage level (dpa)	Void			Dislocation density (m^{-2})	Precipitate size (nm)
		Density (m^{-3})	Diameter (nm)	Swelling (%)		
V–0.9 at.% C		8.0×10^{19}	97.4	3.9	1×10^{13}	35
V–1.3 at.% N	47.9	1.4×10^{19}	91.2	0.55	1.0×10^{14}	–
V–1.2 at.% O		4.6×10^{19}	155	9.7	–	–
Unalloyed vanadium [11]	42.5	7.2×10^{19}	61.9	0.96	6.0×10^{12}	–

Table 2
Calculated values for the contribution of voids, dislocations and precipitates to the increase in hardness

Specimen	Voids	Dislocations	Precipitates	Calculation	Experiment
V–0.9 at.% C	10.2	11.5	13.6	(21.7)	33.1
V–1.3 at.% N	4.1	36.4	–	40.5	27.7
V–1.2 at.% O	9.7	–	–	9.7	6.0

unirradiated condition. Therefore, in the case of V–0.9 at.% C alloy, the calculated value within the parentheses means the sum of the calculated values for the contributions of defect structures except for precipitates.

For the V–1.3 at.% N alloy, the major contribution to irradiation hardening is from dislocations, and the calculated value is appreciably larger than the experimental value. In the V–1.2 at.% O alloy, only voids contribute to irradiation hardening, and the calculated value is close to the experimental value. Since the solubility of nitrogen and oxygen in vanadium is high [14], both are considered to form complete solid solutions with vanadium. In addition, there is little difference in irradiation hardening between the two alloys after irradiation at 679 and 793 K. Nevertheless, a large difference in irradiation hardening between the two alloys appears at 873 K. It is interesting that dependence of irradiation hardening on the irradiation temperature is different between the V–1.3 at.% N and V–1.2 at.% O alloys. The reason is remained to be clarified. For the V–1.3 at.% N alloy, the calculated value is appreciably larger than the experimental value. It is possible that an interaction parameter of 0.3 is too large.

At 679 and 793 K, the defect structure may be different from that at 873 K. While irradiation hardening in the V–1.3 at.% N and V–1.2 at.% O alloys is almost the same, that for the V–0.9 at.% C alloy is considerably large. That is attributed to the influence of precipitates, and it is possible that number density and distribution of the precipitates are different at 873 K.

4.2. Influence of interstitial elements on development of defect structure

The influence of the interstitial elements on development of defect structures in vanadium due to neutron irradiation were reported previously. According to Bressers et al. [5], void swelling was suppressed in vanadium with oxygen content of less than 850 appm irradiated at temperatures from 673 to 863 K to relatively low fluences (0.7–4.2 dpa). In the present study, however, both oxygen concentration and neutron fluence are more than ten times higher, while the temperature range is almost the same, and growth of voids cannot be suppressed.

Hasegawa et al. observed defect microstructures in the V–O and V–C alloys containing various concentrations of each interstitial elements irradiated in several irradiation conditions [6,7]. According to the results, for the V–O alloys after neutron irradiation at 703 K to fluences up to 1×10^{20} n/cm^2, the void density increased with increasing oxygen content up to 690 appm, while the void radius decreased with increasing oxygen content. For oxygen contents higher than 690 appm, however, the void radius increased with increasing oxygen content, while the density decreased with increasing oxygen content. For oxygen content higher than 1000 appm, both the void radius and density vary little with increasing oxygen content. Comparing with the previous reports [5–7], the development of defect structures in present vanadium alloys irradiated to high fluences is very different from that in the alloys irradiated to lower fluences. Although the influence of C, N and O on development of defect structure depends on irradiation temperature and neutron fluences, linear behavior is not observed.

Expanding lattice strain introduced by the interstitial elements is similar to that from oversized substitutional elements. In addition, the average lattice strain per unit concentration of the interstitial element such as C, N, O in bcc structure is larger than that from substitutional elements. However, interstitial elements cannot suppress swelling, while swelling is suppressed in vanadium alloys containing the oversized substitutional alloying elements [4]. This is likely due partly to the influence of large diffusion coefficients of interstitial elements in comparison with substitutional elements, and partly to the difference in type of the strain for substitutional and interstitial elements, i.e., isotropic and tetragonal strain. It is important to examine the development of defect structure in interstitial alloys, whose mechanism may be different from that in substitutional alloys.

4.3. Effect of the interstitial elements from a practical viewpoint

Irradiation hardening of the V–0.9 at.% C alloy is considerably larger, especially at temperatures less than 793 K. Since vanadium alloys containing such large amounts of carbon is supposed to become brittle due to irradiation hardening in this temperature range, an excess of carbon content must be reduced.

Althogh oxygen had the effect of suppressing void swelling at low dpa at about 850 K [5], such an effect does not exist at high dpa at 873 K. Because the effect varies with the level of dpa and irradiation temperature, it is necessary to control the variation in oxygen level according to the required conditions.

It is difficult to evaluate the effect of nitrogen compared with different conditions, because there is little information for the V–N alloys after neutron irradiation. Present work suggests that nitrogen can suppress void swelling.

It is also noted that the irradiation hardening in vanadium due to interstitial elements per unit concentration is larger than that from substitutional elements.

5. Conclusion

Hardness depended on irradiation temperature and alloying elements. Irradiation hardening decreased with increasing irradiation temperature. However, the increase in hardness for the V–0.9 at.% C alloy was relatively larger after irradiation at lower temperatures. In the alloys irradiated at 873 K to 47.9 dpa, large voids, dislocations and precipitates were observed. The factors for irradiation hardening were different for each interstitial element. Relatively large amounts of interstitial element could not suppress the void swelling at high neutron-fluence, contrary to the effect of interstitials at low neutron-fluence.

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