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Journal of Nuclear Materials 329–333 (2004) 420–424

journal of nuclear materials

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The precipitation behavior of ion irradiated V–4Cr–4Ti alloys at various oxygen and nitrogen levels

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Abstract

NIFS HEAT-1 and nine types of the V–4Cr–4Ti model alloys with different oxygen and nitrogen concentrations were irradiated with 2.4 MeV Cu^{2+} ions at 973 K up to doses of 3 dpa. Oxygen concentrations were 44–921 wppm and nitrogen concentrations were 11–1070 wppm, respectively. Fine Ti(O,N,C) precipitates were observed in all specimens. In low oxygen content specimens (<50 wppm), the number density of precipitates was lower than that of high content specimens. This was because the nucleation of precipitates, which resulted in irradiation hardening, was suppressed, especially on low damage level. On the other hand, nitrogen enhanced the hardening especially at low concentration. The total amounts of oxygen in precipitates, which were estimated from the density and size of precipitates at 0.75 and 3 dpa, were higher than that of matrix level before irradiation. The result suggests that oxygen diffuses from vacuum and other regions of the specimen to the irradiated region.

1. Introduction

A vanadium alloy V–4Cr–4Ti is recognized as candidate materials for structural components of fusion reactors, because of its low activation and high strength at elevated temperature [1–3]. However, change of mechanical properties by formation of the precipitates under irradiation at elevated temperature is key problem. Numerous experiments have been carried out to investigate the change of mechanical properties due to irradiation [4–6]. In recent studies, development of techniques to remove impurities shows improvement of the hardening due to precipitation under irradiation [7]. Therefore, detailed analysis on precipitation in relation to O and N impurities level is necessary. The correlation of oxygen and nitrogen concentration and the precipitation behavior of Ti(O,N,C) is studied in this paper. Furthermore, diffusion behavior of oxygen is also evaluated from microstructure.

2. Experimental

NIFS HEAT-1 and nine types of V–4Cr–4Ti model alloys with different oxygen and nitrogen concentrations, which were produced by National Institute for Fusion Science (NIFS), were used in this study. Oxygen concentrations were 44–921 wppm and nitrogen concentrations were 11–1070 wppm, respectively. Chemical composition of the interstitial impurities are shown in Table 1. From these samples, 3 mm diameter and 0.2 mm thick TEM disc were made for examination. All specimens were annealed at 1373 K in a vacuum of 1×10^{-4} Pa for 2 h for recrystallization. Irradiation was performed with 2.4 MeV Cu^{2+} ion at 973 K using a tandem type accelerator at RIAM Kyushu University. The depth in vanadium for peak irradiation damage due to 2.4 MeV Cu^{2+} ion irradiation was computed to be 550

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2004.04.076

Table 1
Impurity levels of V–4Cr–4Ti alloys

Composition (wppm)	Oxygen	Nitrogen
NH1	181	103
HP3	44	88
VA-O6	244	115
VA-O7	513	125
VA-N10	49	362
VA-N11	46	734
VA-N12	74	1070
VA-EB-1	309	14
VA-O9	599	11
VA-O10	921	16

nm by TRIM code [8]. The damage rate at damaged region was about 6.0×10^{-4} dpa/s.

After irradiation, the specimens were measured by Micro-Vickers hardness using nano-indenter, and then the area of peak damage was electropolished by a back-thinning method for TEM observation.

3. Results

Fig. 1 shows the microstructure of HP3, H1, VA-O6 and VA-O7 irradiated at 973 K up to 3 dpa. Fine Ti(O,N,C) precipitates oriented in ⟨0 0 1⟩ directions were formed in all specimens by the irradiation. In HP3, the number density of Ti(O,N,C) precipitate at 0.1 dpa was about an order less than that of other three specimens. The size of precipitates is constant up to 3 dpa, although the number density of precipitates increase with irradiation dose. In H1, VA-O6 and VA-O7, fine precipitates were formed at 0.1 dpa and grew with irradiation dose. On the other hand, number density decreased with irradiation doses. Two sizes of precipitates, large and fine ones were observed simultaneously at 0.75 and 3 dpa.

Fig. 2(a) shows the microstructure of EB-1, VA-O9 and VA-O10 irradiated at the same irradiation condition. These specimens content only 10 wppm nitrogen. In this case, the number densities of fine Ti(O,N,C) precipitates at 0.1 dpa were relatively high. In these alloys, two sizes of precipitates, large and fine ones were also observed at 0.75 and 3 dpa. The size of precipitate increase with oxygen level at 0.1 dpa, although this trend was not seen at high doses. The number densities of relatively large precipitates were decreased with irradiation doses.

Fig. 2(b) shows the case of VA-N10, VA-N11 and VA-N12. The oxygen levels of these alloys were only about 50 wppm. The number densities of precipitates increase with nitrogen level at 0.1 dpa and irradiation dose. Densities of the precipitates were drastically changed between the nitrogen levels of 362 and 734 wppm at 0.1 dpa.

Fig. 3 indicates the Micro-Vickers hardness of each specimen after irradiation. HP3 and VA-O10, which had a content of about 50 wppm oxygen, exhibited less hardening than other specimens, that showed hardening above 100 Hv at 0.1 dpa. In the case of VA-N11 and VA-O9, hardening saturated at 0.1 dpa. In other specimens, hardness increased with increasing irradiation dose. Fig. 4 compares the effect of oxygen and nitrogen levels on irradiation hardening. ΔHv increased with

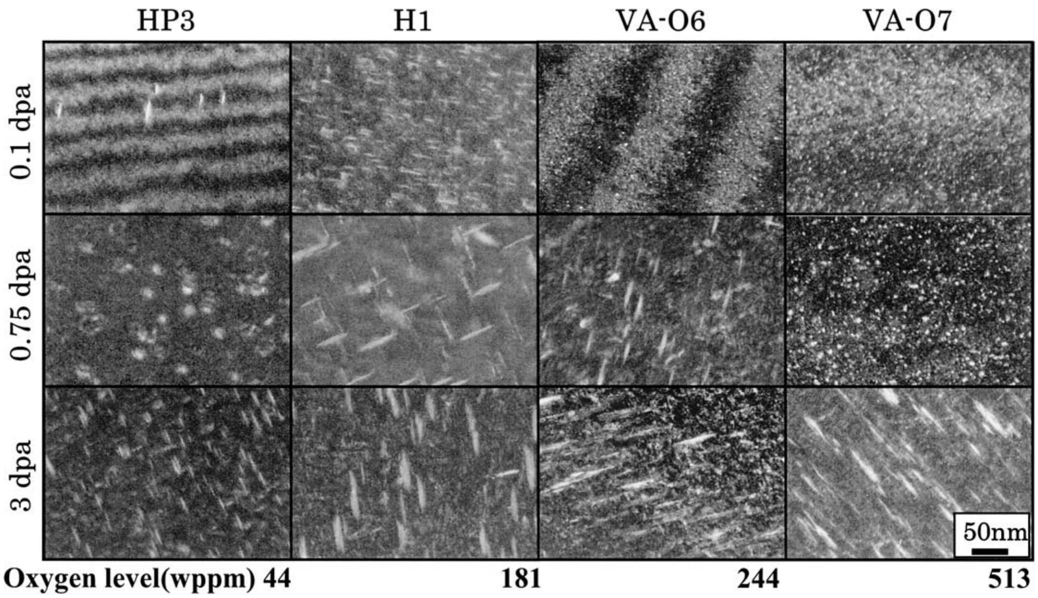

Fig. 1. The dark field image of V–4Cr–4Ti alloys after irradiation at 973 K. The nitrogen levels of these specimen are about 100 wppm.

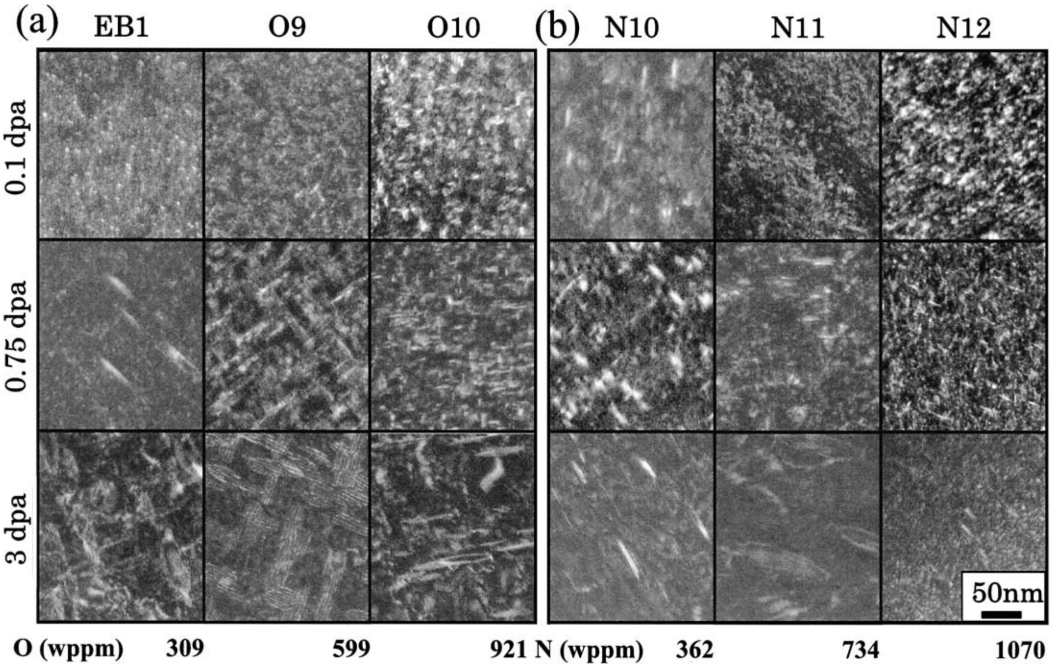

Fig. 2. The dark field image of V–4Cr–4Ti alloys after irradiation at 973 K. Nitrogen levels are about 10 wppm in (a), and oxygen levels are about 50 wppm in (b).

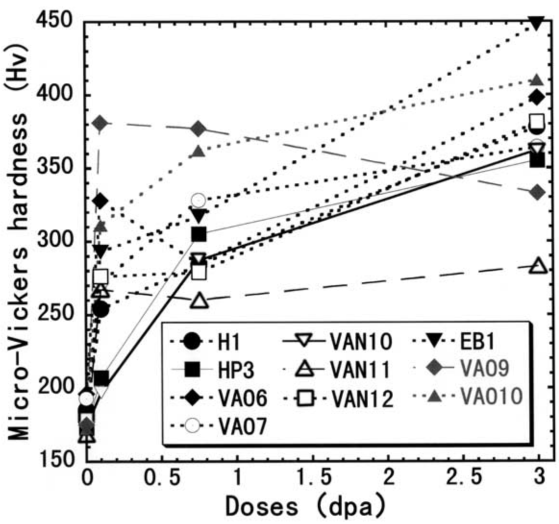

Fig. 3. The dose dependence of Micro-Vickers hardness for V–4Cr–4Ti alloys.

increasing oxygen level at all irradiation dose. The effect of oxygen, which enhances hardening, is clear at low irradiation dose. In nitrogen, irradiation hardening is enhanced especially by low nitrogen concentration below 10 wppm. In the case of nitrogen, the difference of its level is not significant at high concentration for irradiation hardening.

4. Discussion

The relationship between oxygen levels in V–4Cr–4Ti alloys and irradiation hardening was proportional as shown in Fig. 4(a). Especially, the tendency was remarkable on the low irradiation doses. When oxygen concentration is high, hardening, which follows Orowan mechanism, is progressed by the increase in number density of precipitate, because high oxygen level enhances the nucleation of precipitates.

On the other hand, decreasing of nitrogen concentration enhances irradiation hardening at 10 wppm as shown in Fig. 4(b). Muroga and coworkers reported that Ti-rich blocky precipitates, which were composed of Ti, C, N and O, were observed in NIFS HEAT-1 [3,9]. It is thought that this blocky precipitates, which were formed in the initial fabrication process, scavenge impurities such as O, N and C, and decrease impurity levels in the matrix. If nitrogen concentration is extremely low, it is possible that formation of blocky precipitates is prevented and the oxygen level of the matrix is kept relatively high. Thus, a high density of precipitates formed. For nitrogen level, further research is required.

For oxygen, its concentration in Ti(O,N,C) precipitates was estimated. Ti(O,N,C) has an NaCl crystal structure. Half of the site, which to be occupied by impurities such as O, N and C, contain vacancies [10]. Here, all impurities, which are contained in Ti(O,N,C) were assumed to be oxygen. The amount of oxygen in

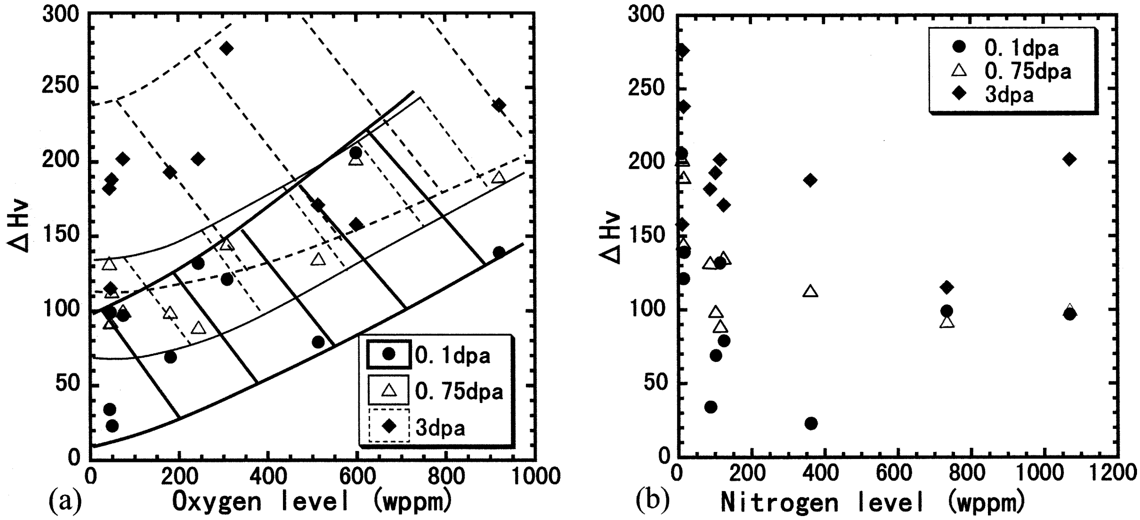

Fig. 4. Oxygen level dependence of irradiation hardening (a), corresponding nitrogen level dependence (b).

Ti(O,N,C) was calculated based on the precipitate's density and size. These parameters were obtained by TEM observation. Fig. 5 indicates the relation between the concentration of oxygen in the precipitates and irradiation doses in HP3, VA-O6 and VA-O7. In all specimens, the oxygen concentration, which exists in the precipitates at 0.1 dpa, is lower than that in matrix before irradiation. However, for 0.75 dpa or more doses, the oxygen concentration of precipitates has exceeded the oxygen levels, that existed in the matrix before irradiation. It suggests that oxygen diffuses from outside of irradiation region to irradiated region. In this region free oxygen atoms bind strongly with titanium, which was enhanced diffusion by irradiation, and formed Ti(O,N,C) precipitates. The flux of oxygen from vacuum to surface region of specimens was measured as oxidation rate [11]. The value in our study is 2×10^{-8} (mg/m^2h). If, the amount of oxygen, which is consumed by the growth of precipitate at unit time exceeds this flux, it may suggest that oxygen diffuses not only from vacuum but also from inside of the specimens. It is thought that the diffusion of oxygen caused hardening, which does not occur in the oxygen levels of the original matrix at high irradiation doses. Thus, it is necessary that evaluating the precipitation behavior of Ti(O,N,C) should be carried out at low irradiation doses and consideration of the diffusion behavior of oxygen.

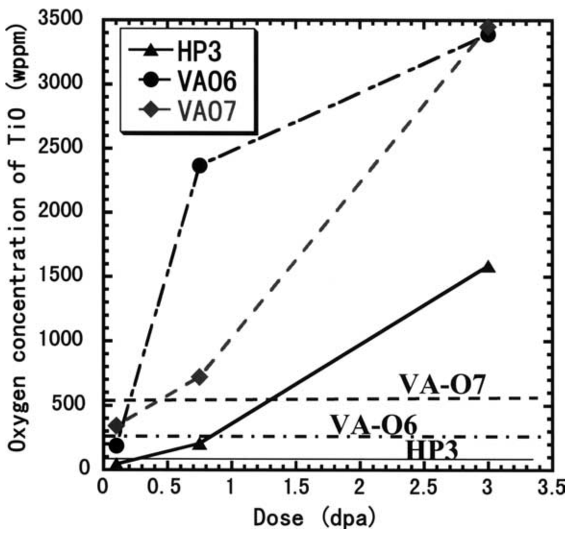

Fig. 5. The dose dependence of precipitate's oxygen concentration for HP3, VA-O6 and VA-O7. Under lines indicate the oxygen levels in matrix before irradiation.

5. Conclusion

To investigate the effect of oxygen and nitrogen levels on microstructure and hardness of V–4Cr–4Ti alloys, ion irradiation experiments were carried out at 973 K. Results may be summarized as follows:

(1) It is suggested that oxygen diffused from vacuum to damage regions and formed Ti(O,N,C) precipitates during ion irradiation in this study. Therefore, evaluation of microstructure and hardness should be performed at low irradiation doses such as 0.1 dpa, since it is possible that the microstructure did not correspond the concentration of impurities before high dose irradiation.
(2) In oxygen, purify of this element prevents precipitate's nucleation and hardening due to irradiation. The hardness increases with oxygen level.

(3) When nitrogen concentration was extremely low, the high density precipitates were formed, and contributed remarkable hardness rise.
(4) The conditions of the oxygen and nitrogen level, which controls the hardening most, are considered in oxygen to be 50 or less wppm and about 100 wppm of nitrogen, respectively.
(5) It is necessary that evaluating the precipitation behavior of Ti(O,N,C) should be carried out at low irradiation doses and considered about diffusion behavior of oxygen.

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