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The diffusion behaviors of interstitial impurities in V–4Cr–4Ti alloys under ion irradiation

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Abstract

NIFS HEAT-1 and four types of the V–4Cr–4Ti alloys with different oxygen and nitrogen content were irradiated with Cu^{2+} ions at 973 K up to dose of 10 dpa. In this irradiation condition, the flux of oxygen, which through the surface is estimated about $2\text{–}4 \times 10^{16}\,(\mathrm{s\,m^2})^{-1}$, and the oxygen levels in specimens are calculated by finite difference method. In the cases of high purity specimens, oxygen diffused from the surface into the irradiated region. Moreover, oxygen diffused from the back of the irradiated surface into the irradiated region and enhanced the precipitations at the irradiated region. It is shown that the initial impurity level and flux of oxygen, which diffused from the atmosphere, essentially limited the precipitation behavior.

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1. Introduction

Vanadium alloys have been identified as candidate materials for structural components of fusion reactors, because of their low activation, good resistance to neutron irradiation and high strength at elevated temperature [1–3]. However, the change of mechanical properties by the formation of precipitates under irradiation at elevated temperature is a key issue. Recently high purity heats (NIFS HEAT-1 and 2) were fabricated and purified by advanced techniques to control solution hardening [4]. However precipitation hardening at elevated temperature during irradiation was not controlled adequately. In recent studies it was pointed out that the diffusion of oxygen, which comes from the atmosphere contributes to precipitation [5]. Therefore, the effect of diffusion of interstitial impurities such as oxygen and nitrogen on the precipitation behavior and oxygen flux at surface are studied quantitatively in this paper.

2. Experimental

NIFS HEAT-1 (NH1) and four types of the V–4Cr–4Ti alloys with different oxygen and nitrogen

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

Composition (wppm)	Oxygen	Nitrogen
NH1	181	103
NH1HP	28	27
HP3	44	88
VA-O6	244	155
VA-O7	513	125

levels, which were produced by National Institute for Fusion Science (NIFS) were used in this study. Oxygen levels were 28–513 wppm and nitrogen levels were 27–125 wppm, respectively. Chemical composition of the interstitial impurities is shown in Table 1. NH1 was purified by Zr treatment. Details of the treatment using Zr foil have been reported in Ref. [6]. From these samples, 3 mm diameter and 0.15 mm thick TEM discs were made for examination. All specimens received solution annealing at 1373 K in a vacuum-encapsulated quartz tube for 2 h. Irradiation was performed with 2.4 MeV Cu^{2+} ion at 973 K using a tandem type accelerator at Kyushu University. The depths in vanadium for peak irradiation damage during 2.4 MeV Cu^{2+} ion irradiation was computed to be 550 nm by the TRIM code. The damage rate in this region was about 6.0×10^{-4} dpa/s.

In NH1 and NH1HP, annealing was also carried out up to 100 h at 973 K. Then microstructures were observed by TEM at depths of 500 nm and 75 μm. The ion irradiation and annealing were carried out at a reduced-pressure of 1×10^{-6} Pa.

3. Results and discussion

3.1. Precipitation behavior and oxygen diffusion in annealing

In annealing at 973 K, the precipitation behavior is different between a depth of 500 nm and the center of specimens (the depth from surface is 75 μm). Fig. 1 shows the microstructure of NH1 and NH1HP. In NH1 fine Ti(O,N,C) precipitates oriented in ⟨0 0 1⟩ directions were observed from 2 h annealing at the both depths. While, in NH1HP, precipitate were not observed at the center of specimen for 100 h annealing, because the impurity concentrations are lower than that of supersaturation. However, precipitation occurred near the specimen surface for 3 h. This result shows that the oxygen infiltrates into the specimen from the atmosphere, increases the impurity concentrations for 2 h and enhances precipitation. Therefore, the oxygen concentration at the depth of 500 nm was increased about 100 wppm for 2 h.

To estimate the flux of oxygen at the surface, we calculated the oxygen level in NH1HP during annealing at 973 K. In our model, the flux of oxygen was treated as a constant. Diffusion of oxygen in the specimens was calculated by the one dimensional finite difference method. The diffusion was based on Fick's Law:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial^2 x}, \qquad (1)$$

where D is the oxygen diffusion coefficient and c is the oxygen concentration. Hasegawa et al. reported the diffusion coefficient of oxygen in V–5Ti [7]. We obtained $D = 8 \times 10^{-10}$ (cm^2/s). The diffusion of nitrogen is not considered for simplification. Fig. 1 indicates that the increase of the oxygen concentration is very small at the center of the specimen compared with the surface. Fig. 2 shows the time dependence of oxygen concentration at different oxygen fluxes from surface at 973 K. In oxygen fluxes of 2×10^{16} and 2×10^{17} n/s m^2 the oxygen level at the depth of 500 nm was increased about 40 and 300 wppm, respectively for 2 h. The concentration increase of 300 wppm is an overestimate, because the supersaturated concentration is between 28 wppm and 181 wppm. Therefore, the oxygen flux is estimated to be on the order of 10^{16} n/s m^2 in this experiment. This value agrees with the experimental result of Ref. [8].

3.2. Oxygen diffusion under ion irradiation

Fig. 3(a) shows the dose dependence of precipitate's oxygen concentration for HP3, VA-O6 and VA-O7. Here, we calculate the oxygen concentrations during irradiation. Calculations are carried out with the same diffusion model as used in annealing. The amount of oxygen, which trapped precipitates in unit time is based on the gradient of the plot in Fig. 3(a). Initial oxygen level dependence of oxygen concentration during irradiation is shown in Fig. 3(b) and (c). Here the flux of oxygen was assumed to be 2×10^{16} n/s m^2. In HP3, some of the oxygen is trapped by precipitates, which grow in the irradiated region, but most of the oxygen diffused into the inner region. Thus, precipitation is controlled by the flux of oxygen, which infiltrates from the atmosphere into the specimen. However, in

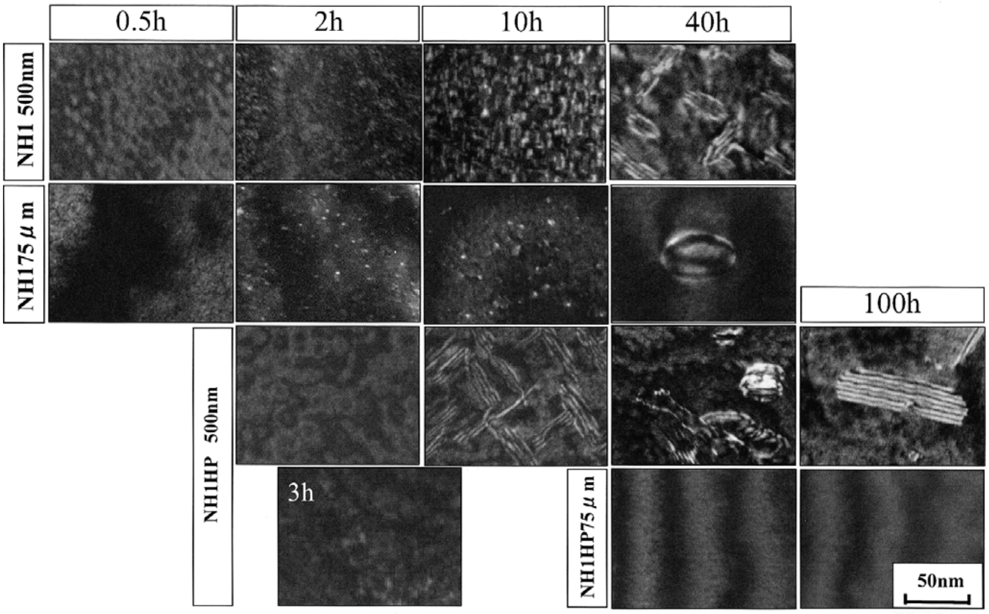

Fig. 1. Microstructure of NH1 and NH1HP annealed in a reduced-pressure of 1×10^{-6} Pa at 973 K. The depths from surface are 500 nm and 75 μm.

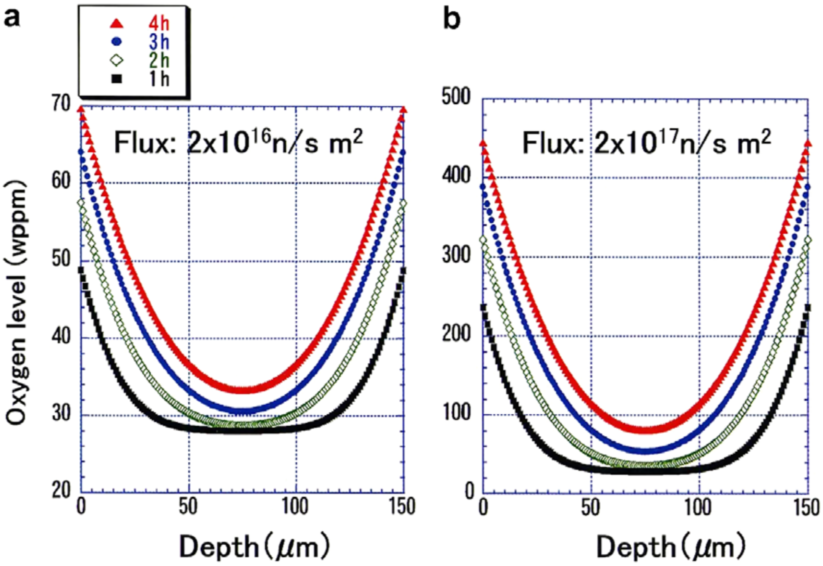

Fig. 2. The time dependence of oxygen level at different oxygen flux (2×10^{16} and 2×10^{17} n/s m^2) from surface at 973 K.

VA-O7, precipitates trap not only the oxygen, which diffuses from the surface of the irradiated side but also the oxygen which diffuses from the unirradiated region. Therefore, the precipitation of ion irradiated specimens is limited by the flux of oxygen, which diffuses from the surfaces and by the initial oxygen level.

3.3. Effect of oxygen in precipitation behavior of NIFS HEAT-1

Fig. 4 shows the dark field image of NH1 alloy after irradiation at 973 K up to 10 dpa. Fine Ti(O,N,C) precipitates were observed at 0.1 dpa. Then the size of the precipitates increase with irradi-

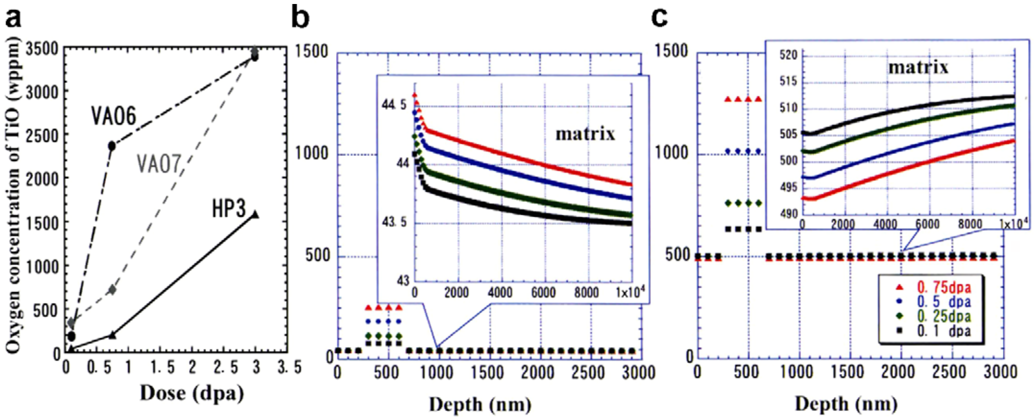

Fig. 3. The dose dependence of precipitate's oxygen concentration for HP3, VA-O6 and VA-O7. Under lines indicate the oxygen levels in matrix before irradiation (a). Calculated initial oxygen level dependence of oxygen concentration during ion irradiation in HP3 (b) and VA-O7 (c). Oxygen flux is $2 \times 10^{16} (\mathrm{s\,cm^2})^{-1}$, and the amount of oxygen, which is trapped by precipitates is estimated from experiment.

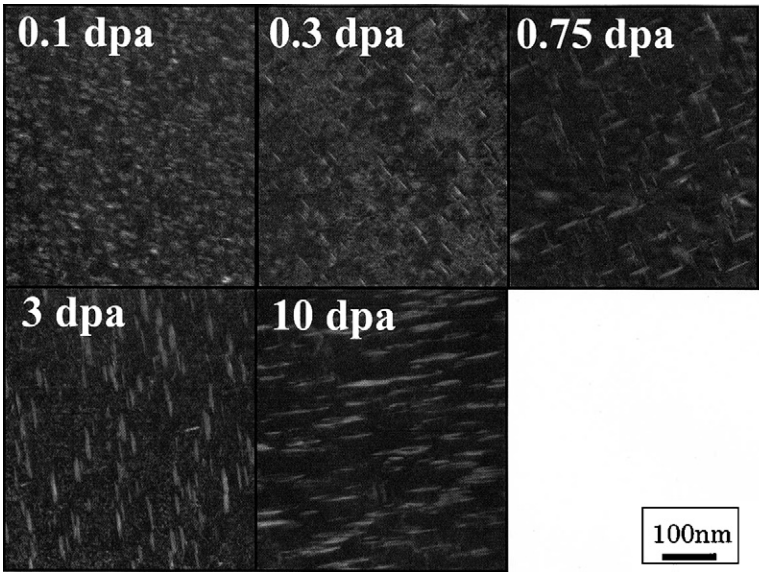

Fig. 4. The dark field image of NIFS HEAT-1 alloy after irradiation at 973 K.

ation dose. The amount of oxygen, which is contained in Ti(O,N,C) precipitates, was given by these microstructures. Fig. 5 shows the relationship between irradiation dose and oxygen concentration, which exists in Ti(O,N,C) precipitates. The time evolution of the oxygen concentration obeys a parabolic law. This result suggests that most of the oxygen that has diffused from the irradiated surface is trapped in the Ti(O,N,C) precipitates in the irradiation area, and the growth process is limited by diffusion of impurities. Fig. 6 shows the oxygen concentration during irradiation. Because each precipitate traps a large amount of the oxygen with the aid of the irradiation, the oxygen concentration in the irradiation

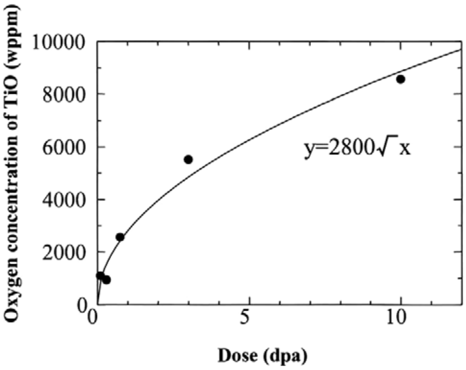

Fig. 5. The dose dependence of oxygen concentration of precipitates in NH1. Where x is dose and y is oxygen concentration of precipitates.

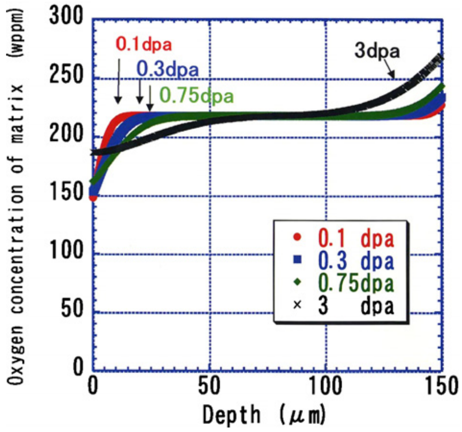

Fig. 6. Calculated dose evolution of the oxygen distribution in NIFS HEAT-1 up to 3 dpa at 973 K. The oxygen flux is 4×10^{16} n/s m^2.

region is rapidly decreased with decreasing dose. The oxygen concentration of the irradiated region recovers when irradiations increase up to 3 dpa, and the decrease of oxygen concentration is seen up to depth of 50 μm. It is shown that the change of oxygen concentration is small in the center of the sample up to 3 dpa. In an actual fusion reactor, the dose rate would be lower than that of this ion irradiation. Therefore, precipitation behavior will be similar to that produced by annealing. Precipitation will at first occur near the surface, and the precipitation region will progress inward with increasing dose. To control the precipitation, purifying of the alloys and preventing diffusion of oxygen from the reduced-pressure atmosphere into the materials are essential.

4. Conclusions

To investigate the effect of oxygen diffusion on precipitation behavior of V–4Cr–4Ti alloys, ion irradiation experiments and modeling were carried out at 973 K. Results can be summarized as follows:

(1) The flux of oxygen, which infiltrates from the reduced-pressure atmosphere at 973 K is estimated to be about 2–4 × 10^{16} n/s m^2.
(2) In the case of high purity specimens, the oxygen concentration decreases with the depth of specimen. However, in low purity specimens, the matrix of the irradiated region has a lower concentration than the center of specimen.
(3) The oxygen concentration, in Ti(O,N,C) precipitates obeys a parabolic law under irradiation.
(4) To control precipitation, purification of alloys and prevention of diffusion of oxygen from the reduced-pressure atmosphere into the materials are essential. Precipitation hardening in an actual fusion reactor is expected to be smaller than that of ion irradiation because the hardening, which is enhanced by diffused oxygen is overestimated.

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