ELSEVIER

Journal of Nuclear Materials 307–311 (2002) 408–411

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Oxide formation of a purified V–4Cr–4Ti alloy during heat treatment and ion irradiation

H. Watanabe [a,*], M. Suda [b], T. Muroga [c], N. Yoshida [a]

[a] Research Institute for Applied Mechanics, Kyushu University, 6-1, Kasuga-kouenn, Kasugashi, Fukuoka, 816-8580, Japan
[b] Interdisciplinary Graduate School of Sciences, Kyushu University, 6-1, Kasuga-kouenn, Kasugashi, Fukuoka, 816-8580, Japan
[c] National Institute for Fusion Science, 322-6, Oroshi, Toki, Gifu, 509-5292, Japan

Abstract

To investigate the effect of oxygen on the titanium oxide formation in V–4Cr–4Ti during heat treatment and also under irradiation, oxygen was gettered by Zr foils. After annealing and copper ion irradiation at different temperatures, the microstructure was investigated by transmission electron microscopy. Titanium oxides were detected by annealing between 973 and 1173 K, but the number density and size of the oxides decreased with the oxygen concentration. The temperature range corresponds to the temperature where long-range migration of titanium will occur. Ion irradiation revealed that residual oxygen atoms are very effective to titanium oxide precipitates formation in the temperature range of 773–973 K.

1. Introduction

In the V–4Cr–4Ti alloy, it is well established that interstitial impurities such as oxygen and nitrogen play an important role for radiation effects such as microstructure change, irradiation hardening and embrittlement [1–3]. Among them, oxygen is regarded as the most effective atom. Recently, ion irradiation experiments on V–4Cr–4Ti alloys revealed that varying temperature irradiations have strong effects on the enhanced formation of small titanium oxide precipitates during irradiation [4]. To understand the radiation induced phenomena due to oxygen, not only the behavior of point defects but also oxygen and titanium must be considered. Usually, however, fair amounts of oxygen atoms exist in the alloy and the alloys are also easily picked up by the specimen surface at elevated temperatures. Oxygen pick-up remains as one of the major concerns for the V–4Cr–4Ti alloys, particularly in the case of welds. Grossbeck et al. [5] revealed that $Ti_{16}(O_3N_3C_2)$ was formed in gas tungsten arc welded V–4Cr–4Ti alloys after heat treating at 1223 K (2 h). After oxidation at 773 K, DiStefano et al. [6] noticed that a microstructure with ultrafine oxides were formed in the matrix and along grain boundaries. So, it is very important to do experiments with a sample whose oxygen content is well controlled.

In this study, the damage process and the role of oxygen atoms on the titanium oxide formation were examined by preparing the V–4Cr–4Ti alloys with different oxygen concentrations. In order to reduce the oxygen impurity in V–4Cr–4Ti alloys, the zirconium (Zr) foil method was used [7,8]. After purification, the mechanisms of titanium oxide formation under heat treatment and irradiation were examined.

2. Experimental procedure

Arc-melted V–4Cr–4Ti [8] (named ML–LP, hereafter) and a large scale heat of V–Cr–4Ti alloy [3] (named NIFS1–LP, hereafter) with different oxygen concentrations (namely, 389 and 219 wt ppm, respectively) were used in this study. To getter oxygen, a Zr foil of 2 μm thickness was jointed with a rolled V–4Cr–4Ti sheet with

* Corresponding author. Tel.: +81-92 583 7717; fax: +81-92 583 7690.
E-mail address: watanabe@riam.kyushu-u.ac.jp (H. Watanabe).

0022-3115/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(02)01097-8

a thickness of about 150 μm by annealing for 0.5 h at 1373 K. The sandwiched sample was annealed between the Zr foils at 1373 K for 2 h in vacuum. After the treatment, the oxygen concentration of ML–LP and NIFS1–LP was reduced to 56 (named ML–HP, thereafter) and 28 (named NIFS1–HP, thereafter) wt ppm, respectively. The detailed purification using a Zr foil has been reported in Ref. [7,8]. To investigate the oxide formation due to annealing, the samples were annealed under vacuum ($\simeq 1 \times 10^{-5}$ Pa) in the temperature range of 873–1273 K. A 2.4 MeV copper ion irradiation was carried out with the tandem accelerator at Kyushu University. The samples were irradiated at 473–1073 K up to 0.75 dpa. After irradiation, the area near the peak damage region (at about 700 nm) was electro-polished by the back thinning method. The damage rate and the implanted copper concentration in this region were 1.7×10^{-4} dpa/s and 10^{-3} at.% (at 0.1 dpa), respectively.

3. Results

In the temperature range of 973–1173 K, Ti-enriched plate-like precipitates lying on {0 0 1} habit plains were formed in ML–LP and NIFS1–LP by annealing in vacuum for 2 h. Bulk precipitates, which are also enriched in titanium of about 20 wt% in grain boundaries, were observed at the same annealing temperature. Judging from the titanium enrichment and their habit plains, these precipitates were titanium oxides with {0 0 1} habit plains. The width of the zone denuded of oxides adjacent to the grain boundary after annealing at 973 and 1073 K

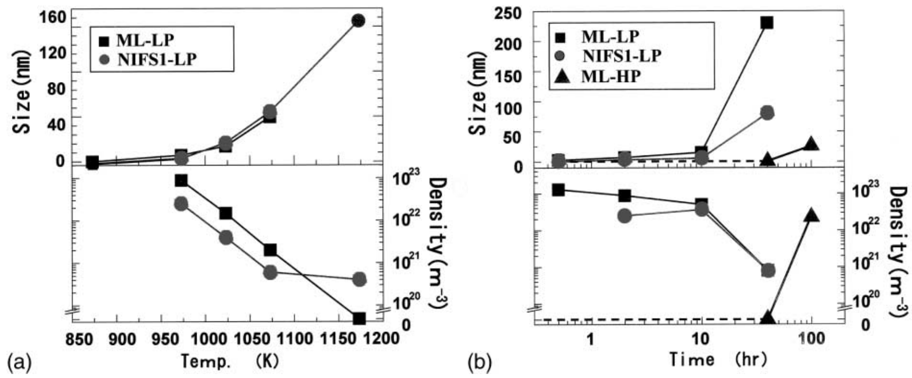

Fig. 1. Annealing temperature dependence of measured precipitate number density and size (a), corresponding annealing time dependence (b).

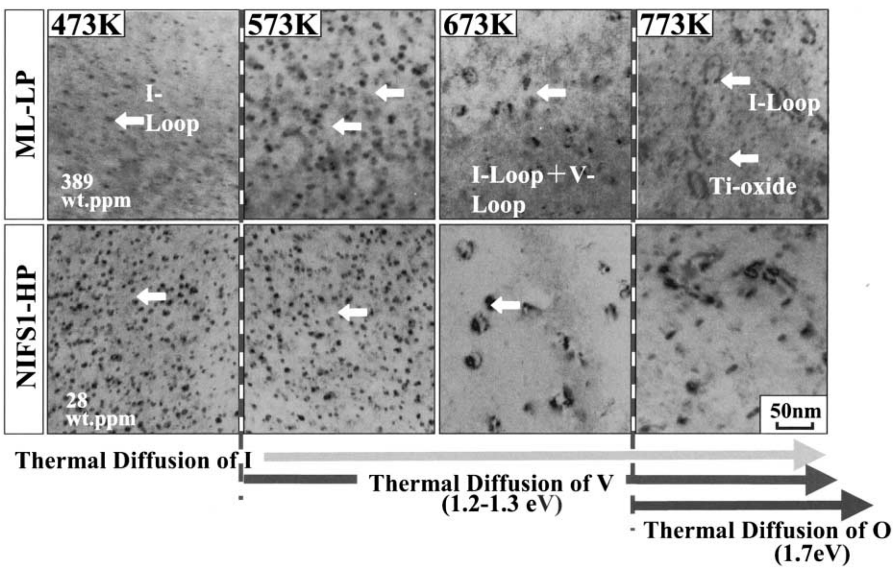

Fig. 2. Irradiation temperature dependence of microstructure (lower temperature case).

was 50 and 100 nm, respectively. The annealing time dependence of the alloys at 973 K revealed that the nucleation of titanium oxide was strongly influenced by the oxygen concentration. Small oxide precipitates were formed at the beginning of annealing in ML–LP (389 wt ppm oxygen) but they were not formed even after 100 h in NIFS1–HP (28 wt ppm oxygen). The dependence of oxide size and density on annealing temperature and annealing time at 973 K were summarized in Fig. 1.

Figs. 2 and 3 show the irradiation temperature dependence of the microstructure at lower and higher temperatures, respectively. The irradiation dose is 0.75 dpa. Two V–4Cr–4Ti alloys with different oxygen concentration were compared in the figures. The upper and lower micrographs show the case of ML–LP (389 wt ppm oxygen) and NIFS1–HP (28 wt ppm oxygen), respectively. The average temperature range of thermal diffusion of interstitials, vacancies and oxygen were described in Fig. 2. As shown in the figure, interstitial type dislocation loops were only formed at 473 K. With increasing irradiation temperature, the density of interstitial type dislocation loops decreased and small vacancy type dislocation clusters (at 673 K) and titanium oxides (at 773 K) were observed in both specimens. As shown in Fig. 4, the measured number density of interstitial type dislocation loops of ML–LP and NIFS1–HP is almost the same. At 873 K, the number density of titanium oxide (5×10^{22} m^{-3}) of ML–LP was ten times higher than that (5×10^{21} m^{-3}) of NIFS1–HP (see Fig. 3). Above 973 K, titanium oxides were detected in both samples. The irradiation temperature dependence of measured size and number density of oxide precipitate and interstitial type dislocations were shown in Fig. 4(a) and (b), respectively.

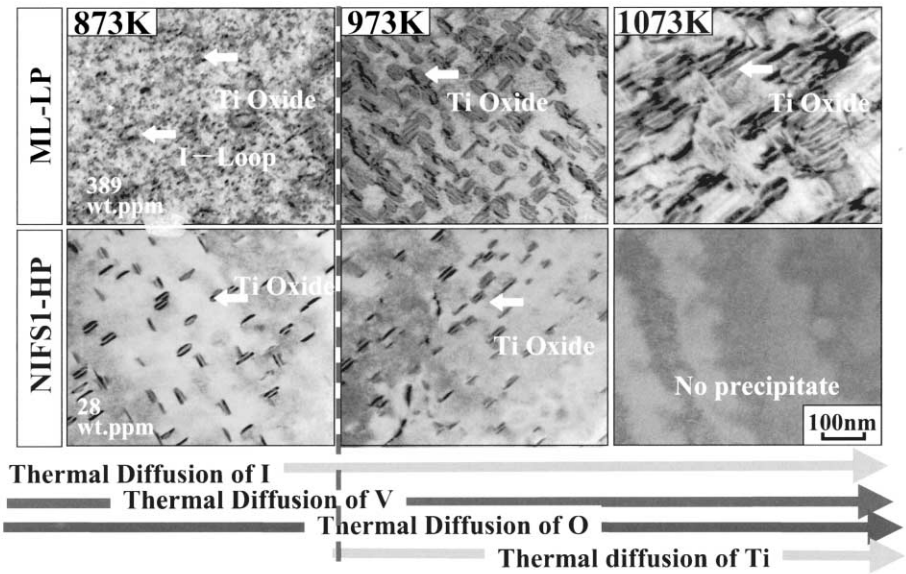

Fig. 3. Irradiation temperature dependence of microstructure (higher temperature case).

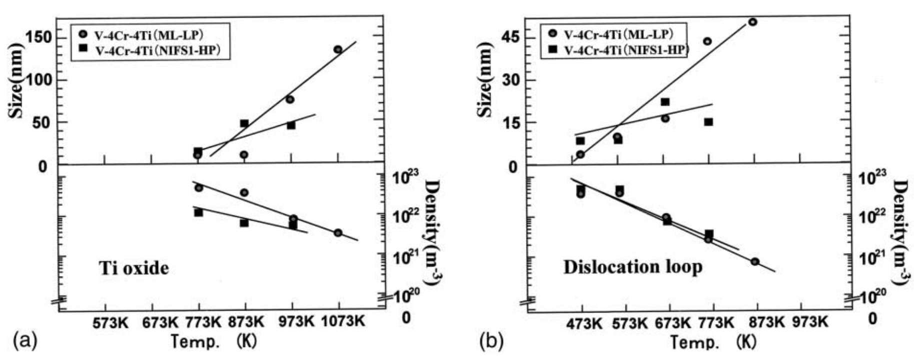

Fig. 4. Irradiation temperature dependence of measured titanium oxide size and number density (a), corresponding temperature dependence of interstitial type loop (b).

4. Discussion

Ti-enriched plate-like precipitates lying on the {0 0 1} habit plain were observed in the temperature range 973–1173 K, which corresponds to the temperature where long-range migration of titanium will occur. To understand the oxide formation in the matrix, not only the oxygen concentration in the matrix but also the oxygen diffusion from the specimen surface must be considered. Using oxygen diffusivity data in vanadium alloys [9], the diffusion distance of oxygen during annealing at 973 K (2 h) is about 70 μm. The value is almost half of the thickness of TEM samples used in this study. Moreover, a higher oxygen diffusivity is expected along the grain boundaries. However, as described in Section 3, the nucleation of titanium oxide at 973 K strongly depends on the oxygen concentration in the matrix. In the case of NIFS1–HP (28 wt ppm oxygen), oxides were not detected even after annealing at 100 h. Judging from the oxide denuded zone near the grain boundaries and the formation at the grain boundaries, it is very reasonable to believe that the oxide formation in the matrix is mainly controlled by the oxygen concentration in the matrix. It is known that the titanium oxide formation, which is considered to be an important factor for the degradation of the V–4Cr–4Ti alloy, is enhanced by irradiation. The present study again revealed that a decreasing oxygen concentration is essential.

During ion irradiation, as shown in Figs. 2 and 3, residual oxygen atoms do not play an important role for interstitial loop nucleation in the temperature range of 473–673 K, but the number density of titanium oxide is increased with increasing oxygen concentration in the higher temperature regime of 773–973 K. The results are not consistent with the ion irradiation experiment at 873 K (0.1 dpa) on a highly purified V–3Fe–4Ti–0.1Si alloy by the Zr-treatment method [10]. In the case of ion irradiation experiments, the peak of the damaged region (about 700 nm depth in this study) is very close to the specimen surface. Moreover, as described in the previous section, titanium oxides are formed in the temperature range where the effect of thermal formation of vacancies is prominent. Further studies are needed to clarify the mechanisms of the oxide formation under irradiation.

5. Conclusions

To understand the effects of oxygen on the microstructure, oxygen gettering and annealing experiments as well as ion irradiation were carried out. The main results are summarized as follows:

(1) The oxygen concentration in 150 μm-thick V–4Cr–4Ti alloys can be reduced by the Zr foil joint technique from 389 to 56 or from 219 to 28 wt ppm.

(2) Titanium oxide precipitates were detected between 973 and 1173 K, but the number density and size of the oxide precipitates decrease with the oxygen concentration. The temperature range corresponds to the temperature where long-range migration of titanium will occur.

(3) During irradiation, residual oxygen atoms do not play an important role for the interstitial loop nucleation in the temperature range of 473–673 K, but they do effect the titanium oxide formation in the temperature range of 773–973 K.

Acknowledgements

The Japan/US collaborative JUPITER program on fusion materials research supported the study. The authors would like to cordially thanks to Professor Matsui of Tohoku University for providing high purity vanadium alloys used in the study.

References

[1] D.L. Smith, B.A. Loomis, D.R. Diercks, J. Nucl. Mater. 135 (1985) 125.
[2] S.J. Zinkle, H. Matsui, D.L. Smith, A.F. Rowcliffe, E. van Osch, K. Abe, V.A. Kazakov, J. Nucl. Mater. 258–263 (1998) 205.
[3] T. Nagasaka, H. Takahashi, T. Muroga, T. Tanabe, H. Matsui, J. Nucl. Mater. 283–287 (2000) 816.
[4] H. Watanabe, T. Arinaga, K. Ochiai, T. Muroga, N. Yoshida, J. Nucl. Mater. 283–287 (2000) 286.
[5] M.L. Grossbeck, J.F. King, D.J. Alexander, P.M. Rice, G.M. Goodwin, J. Nucl. Mater. 258–263 (1998) 1369.
[6] J.R. DiStefano, B.A. Pint, J.H. DeVan, H.D. Roehrig, L.D. Chitwood, J. Nucl. Mater. 283–287 (2000) 841.
[7] K. Abe, K. Toma, H. Yoshinaga, S. Morozumi, J. Less-Common Met. 23 (1971) 213.
[8] K. Fukumoto, T. Morimura, T. Tanaka, A. Kimura, K. Abe, H. Takahashi, H. Matsui, J. Nucl. Mater. 239 (1996) 170.
[9] H. Nakajima, S. Nagata, H. Matsui, S. Yamaguchi, Philos. Mag. A 67 (1993) 557.
[10] K. Fukumoto, H. Matsui, Y. Candra, K. Takahashi, H. Sasanuma, S. Nagata, K. Takahiro, J. Nucl. Mater. 283–287 (2000) 535.