Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 367–370 (2007) 505–510
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Effects of interstitial impurity on behavior of helium-defect complexes in vanadium studied by THDS

N. Nita *, K. Miyawaki, H. Matsui

Institute for Material Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

---

Abstract

The effects of helium on macroscopic mechanical properties in vanadium alloys have been studied rather extensively. However, the evolution processes of helium-defect complexes, especially during the early stage, is not clearly understood. This is mainly because of the complexity of helium behavior due to the large amount of interstitial impurities (C, N, O, etc.) in vanadium. THDS (thermal helium desorption spectrometry) was performed to examine the nature and behavior of helium-defect complexes. The observed desorption peaks were assumed to be concerned with vacancy type defects. In vanadium, most of vacancies are decorated by interstitial impurities, and implanted helium produces He_nV_nX-type defects ($X = C, N, O$). The desorption peaks of 570 K, 690 K and 940 K were assigned as He_nOV, He_nOV_2 and He_nOV_4, respectively. The population of these peaks increased with oxygen concentration. On the other hand, some peaks which were independent of impurity concentration were deduced as impurity free defect clusters such as He_nV_n.

---

1. Introduction

Vanadium alloys are considered to be one of the leading candidates for the fusion reactor blanket material [1,2]. Although vanadium has many attractive features for the fusion application, its use at high temperature will be limited by the helium embrittlement [3]. Another problem concerning helium, from a technical point of view, is the enhancement of nucleation and growth of cavities. It is well-known that helium atoms stabilize cavities, which affects microstuructural evolution such as swelling [4]. The effects of helium on the macroscopic mechanical properties have been studied rather extensively [5,6], but the evolution processes of helium-defect complexes, especially during the early stage, are not clearly understood. This is mainly because of the complexity of helium behavior due to the large amount of interstitial impurities (C, N, O, etc.) in vanadium. It has been reported that the impurities decrease the binding energy between helium and a vacancy type cluster in tungsten and molybdenum [7]. The objective of present paper is to investigate the effects of impurities on helium clustering behavior in vanadium at their early stage using THDS (thermal helium desorption spectrometry) which is one of the most effective techniques to study He–V–X ($X = C, N, O$, etc.) type complexes.

---

* Corresponding author. Tel.: +81 22 215 2068; fax: +81 22 215 2066.
E-mail address: nita@imr.tohoku.ac.jp (N. Nita).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.03.109

2. Experimental procedures

Specimens used were pure vanadium. Oxygen contents in samples were systematically controlled by regulating the atmosphere during annealing or by using a Zr-treatment technique [8]. Specimens whose nitrogen content was controlled by regulating the atmosphere during arc-melting were provided by NIFS. Table 1 shows the concentration of the major impurities in vanadium measured by the chemical analysis. Oxygen controlled samples and nitrogen controlled samples will be referred as VO_n and VN_n (n is the concentration of oxygen or nitrogen), respectively. Samples of 8 mm diameter were electropolished with electrolyte of sulfuric acid and methanol prior to THDS measurements because it is very sensitive to the surface condition [9]. The locally built THDS apparatus consists basically of an ion gun equipped with a $E \times B$ mass filter, accelerator, an electron beam heating system, a standard helium leak for calibrating the absolute helium desorption rate and a quadrupole mass analyzer in a UHV chamber. THDS was performed in the following manner to examine the nature and behavior of helium-defect complexes. First, helium implantation at the accelerating voltage of 1 keV was conducted up to 3.2×10^{17} ions/m^2 at room temperature, then the specimen was heated to 1800 K at a constant rate of 40 K/s while monitoring the release rate of helium gas with a quadropole mass spectrometer. Note that the 1 keV helium bombardments produce Frenkel pairs in vanadium. According to the SRIM calculation [10], the distribution of helium and vacancies was limited to within 20 nm from the surface.

3. Results

Fig. 1 shows the helium desorption spectra obtained for the oxygen content controlled vanadium with 1 keV helium ions up to 3.2×10^{17} ions/m^2. In all specimens, several peaks appeared at similar temperatures and increased their population with increasing dose. The peaks at 550 K and 730 K appeared from the lowest dose of 1×10^{16} ions/m^2, which may correspond to simple defect clusters as HeXV or HeXV$_2$. The peaks at higher temperatures appeared with increasing dose. Saturation of the 550 K and 730 K peaks at 2.4 ×

Table 1
Concentration of major impurities in vanadium

Specimen ID	O	N	C	Total (appm)
VO140	*140*	30	50	220
VO850	*850*	30	50	930
VO1600	*1600*	30	50	1680
VN30	140	*30*	50	220
VN430	130	*430*	300	860
VN620	160	*620*	340	1120
VN1700	130	*1700*	300	2130
VN2600	150	*2600*	321	3070

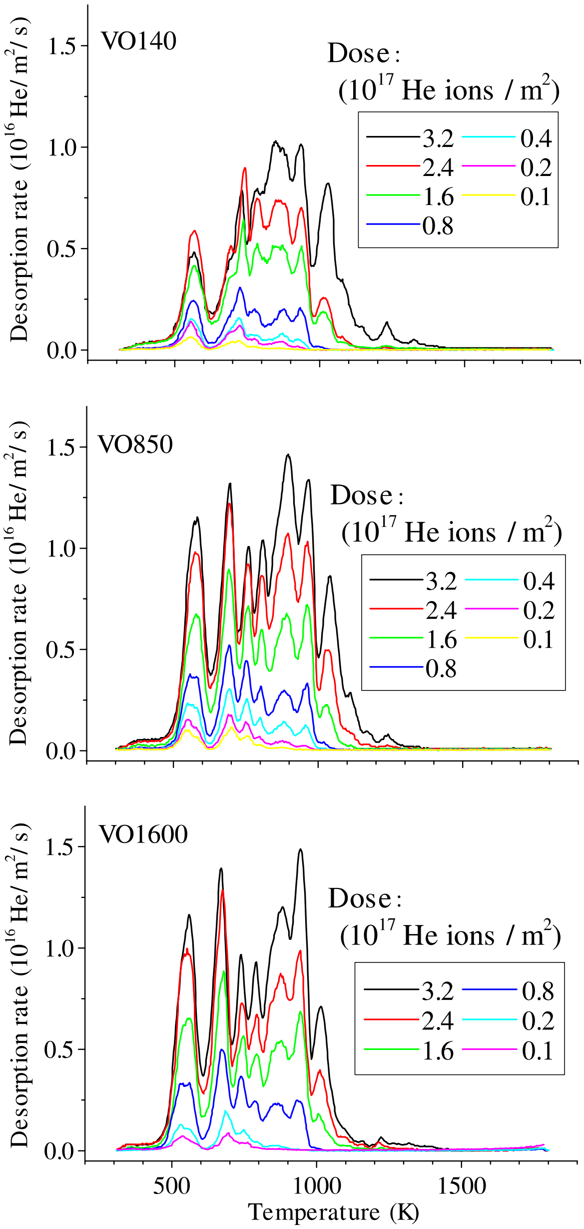

Fig. 1. Helium desorption spectra from the oxygen controlled vanadium.

10^{17} ions/m^2 was observed in VO140. Compared with VO140, prominent peaks appeared at 690 K in the sample with higher oxygen concentration (VO850, VO1600) and the 550 K peak was split into double peaks with increasing dose. The peak at 1230 K was observed at the dose of 3.2×10^{17} ions/m^2 whose population decreased with the impurity content.

Fig. 2 shows the helium desorption spectra obtained for the nitrogen content controlled vanadium with 1 keV helium ions up to 3.2×10^{17} ions/m^2. There were a lot of common trends in the spectra between the VO specimens and the VN specimens but peaks that were specific to VN specimens were not observed. Although there was a prominent peak at 690 K in VO specimens, population of the 690 K peak was relatively small in VN specimens. The 550 K peak was not split into double peaks even with the highest concentration of 2600 appm.

4. Discussion

The observed desorption peaks were assumed to be the result of vacancy type defects which are one of the effective trapping sites for helium in metals.

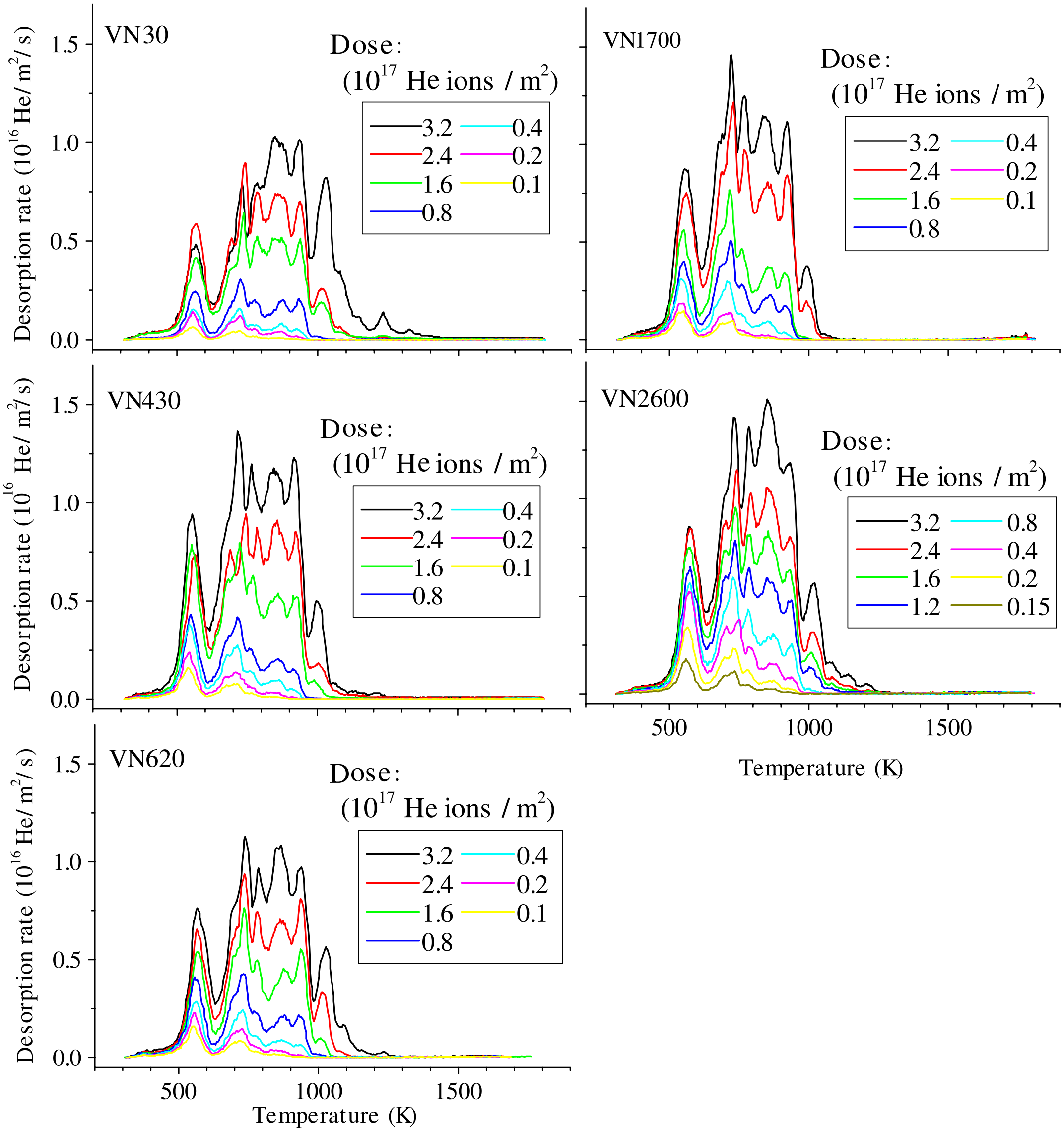

Fig. 2. Helium desorption spectra from the nitrogen controlled vanadium.

A single helium atom trapped by a mono-vacancy is the simplest helium cluster in metals. In vanadium, however, it has been reported in earlier papers [11] that most of vacancies are decorated by interstitial impurities, mainly oxygen, and implanted helium produces He_nV_nX-type defects ($X = C$, N, O). THDS measurements coupled with annealing at certain temperatures were performed to determine the number of vacancies in a He_nV_nX-type cluster. The desorption peaks at 550 K, 690 K and 940 K were assigned to He_nOV, He_nOV_2 and $He_nOV_{m>1}$, respectively.

The sequential appearance and growth of the number of peaks was clearly observed in THDS spectra. For further analysis, THDS spectra were fitted using a theoretical equation based on the one order desorption mechanism [12] and deconvolution of the peaks was carried out. The desorption rate is given by

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -N_0 v \exp\left(-\frac{E_{\mathrm{diss}}}{kT}\right) \exp\left\{-\frac{vkT}{\beta E_{\mathrm{diss}}} \exp\left(-\frac{E_{\mathrm{diss}}}{kT}\right)\right\}, \tag{1}$$

where N_0 is the initial number of traps, v the frequency, E_{diss} the dissociation energy, k the Boltzmann constant, T the absolute temperature and β the heating rate. Fig. 3 shows one example of deconvolution of the THDS spectrum from VO1600 into 15 first-order desorption transients. Each component peak will be referred to as P1, P2, through, P15 from lower temperature in order. The dashed curves are the theoretical component peaks, the full curve is their sum and the dotted curve is the experimental spectrum. Excellent fits were obtained except for P15 (1230 K) which might not be explained with the first-order desorption mechanism. It is noted that the 550 K peak which might

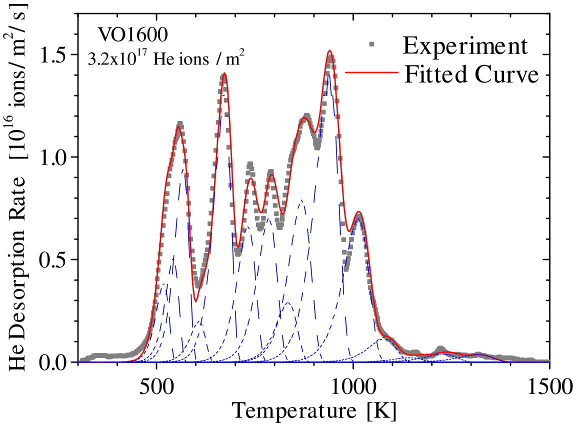

Fig. 3. Deconvolution of spectrum from VO1600 into 15 first-order desorption transients. The dashed curves are the theoretical component peaks, the full curve is their sum and the dotted curve is the experimental spectrum.

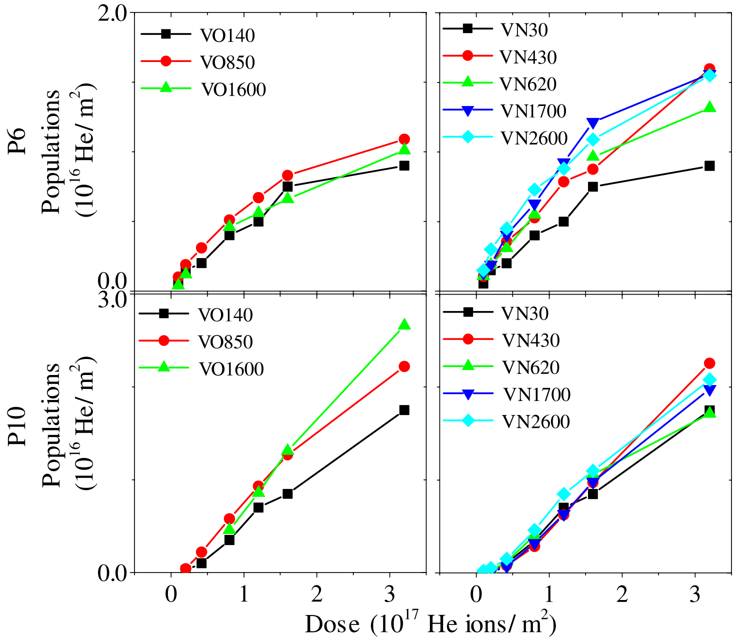

Fig. 4. The peak populations as a function of dose.

appear to be a single peak was deconvoluted into three compound peaks (P1, P2 and P3).

The peaks that depended on the impurity level were successfully separated from the peaks independent of the impurity. Fig. 4 shows the peak populations as a function of dose, in which P6 and P10 were chosen as typical examples. The population of P6 increased with nitrogen concentration while there was little dependence on oxygen concentration. This peak can be assigned to the dissociation from the defect clusters containing nitrogen. On the other hand, the population of P10 showed the opposite tendency, which leads to the assumption that this peak is due to the defect clusters which are related to oxygen. Some peaks which were independent of both oxygen and nitrogen concentration were concluded to be impurity free defect clusters such as He_nV_n.

Concerning the growth of peaks, populations of peaks below 790 K rose linearly with dose and the peaks at higher temperatures increased with the power law of dose. According to the simple model based on chemical rate theory [13], the desorption peaks at higher temperatures were considered to be the result of defect clusters which contain multiple numbers of vacancy and helium. Table 2 shows the summary of identification of the major desorption peaks observed in the present work.

Table 2
Identifications of the major desorption peaks

Defect complex	T_{peak} (K)	E_{diss} (eV)
He_n OV, He_nNV	530	1.3
He_n OV, He_nCV	550	1.4
He_nOV	570	1.5
He_nOV_2	690	1.7
He_nNV_2, He_nCV_2	740	1.9
He_nV_2	790	2.0
He_nV_3	870	2.2
He_nOV_4	940	2.4
He_nV_5	1010	2.6
$He_nXV_{m>5}$	>1090	>2.8

Fig. 5 shows the trapped fraction, namely, the ratio of the helium amount released from the sample during linear heating to the amount of implanted helium. Retention of helium in both VO and VN specimens was about 30–50% at high dose levels. In VO specimens, retention of helium increased about 10% with increasing oxygen concentration from 140 to 850 ppm and did not change by further addition of oxygen. The effect of nitrogen concentration on the helium retention was also kept within 10% although the saturation of impurity effect was not clear.

5. Conclusion

The helium desorption studies on pure vanadium presented in this paper provide the following conclusions:

(1) HeV clusters which are impurity-free-defect-complexes were detected in vanadium.
(2) Major peaks in THDS spectra were successfully identified as He_nXV_m complexes.
(3) Desorption peaks corresponding to He_nNV_m were observed, which means that nitrogen, as well as oxygen, can affect the formation of helium vacancy complexes.
(4) The effect of impurities on the retention of helium was about 10% of trapped fraction.

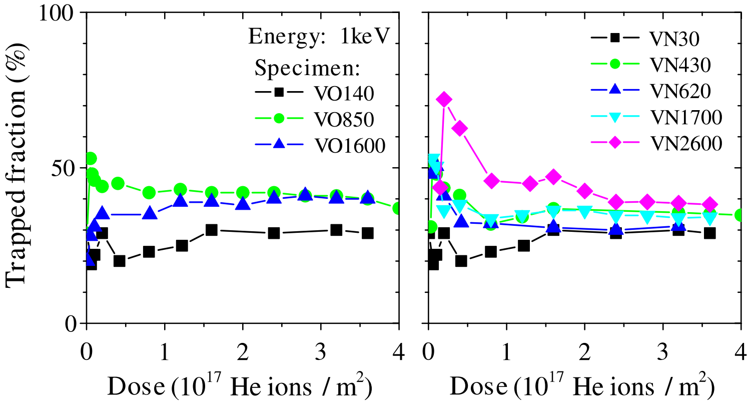

Fig. 5. The trapped fraction as a function of dose.

(5) The effect of oxygen concentration on the formation of He_nOV_m type complexes was saturated at 850 appm.

Acknowledgements

The authors would like to thank M. Tanno, Y. Kimura and Dr Y. Abe for their continuous efforts of building and assessing a self made TDS machine.

References

[1] T. Muroga, Mater. Trans. 46 (2005) 405.

[2] N. Nita, T. Yamamoto, T. Iwai, K. Yasunaga, K. Fukumoto, H. Matsui, J. Nucl. Mater. 307 (2002) 398.

[3] H. Matui, M. Tanaka, M. Yamamoto, J. Nucl. Mater. 191 (1992) 919.

[4] T. Iwai, N. Sekimura, F.A. Garner, J. Nucl. Mater. 239 (1996) 157.

[5] S.J. Zinkle, Fusion Sci. Technol. 47 (2005) 821.

[6] H.M. Chung, B.A. Loomis, D.L. Smith, J. Nucl. Mater. 233 (1996) 466.

[7] H.A. Filius, A. van Veen, J. Nucl. Mater. 144 (1987) 1.

[8] M. Koyama, K. Fukumoto, H. Matsui, J. Nucl. Mater. 329 (2004) 442.

[9] L.M. Caspers, A. vvan Veen, Phys. Status Solidi A 68 (1981) 339.

[10] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon, New York, 1985.

[11] A. van Veen, H. Eleveld, M. Clement, J. Nucl. Mater. 215 (1994) 287.

[12] E.V. Kornelsen, A.A. van Gorkum, Vaccum 31 (1980) 99.

[13] E.V. Kornelsen, Radiat. Eff. 13 (1972) 227.