ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 868–871

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Permeation of hydrogen through vanadium under helium ion irradiation

Yuji Hatano *, Yoshiyasu Nanjo, Ryo Hayakawa, Kuniaki Watanabe

Hydrogen Isotope Research Center, Toyama University, Gofuku 3190, Toyama 930-8555, Japan

Abstract

Hydrogen permeation through vanadium was examined under helium ion irradiation. The upstream surface of a vanadium membrane was exposed to hydrogen gas at 673 K and 640 Pa, and the downstream surface was irradiated with 5 keV helium ions. No significant variation in the permeation rate was observed in the initial stage of irradiation. The permeation rate, however, started to decrease at a helium ion dose of 10^{21} m^{-2} with further irradiation. In this region, the permeation rate dropped immediately by intermission of irradiation and shot up by resumption. These results were successfully explained with a model that helium bubbles act as trapping sites of hydrogen and detrapping is enhanced under irradiation.

1. Introduction

Permeation of tritium through structural materials is an important problem for safety assessment of fusion reactors. Neutron irradiation induces defects such as vacancies, dislocation loops and helium bubbles in the structural materials, and it has been pointed out that these defects act as trapping sites of hydrogen isotopes [1,2]. The trapping–detrapping and the permeation should be affected by displacement of constituent atoms at or near the trapping sites. Therefore, an in situ examination of the permeation is required for understanding dynamic trapping–detrapping processes under irradiation of high-energy particles. Takagi et al. [3–5] examined the plasma-driven permeation of deuterium through a nickel membrane under irradiation of 1.3 or 1.7 MeV helium ions, in which the deuterium concentration near the upstream surface was measured with nuclear reaction analysis. They reported that the deuterium concentration increased with increasing helium ion dose owing to trapping effect, but no significant change was observed in the permeation rate. Few studies, however, have been reported for other materials and irradiation conditions.

Vanadium alloys are widely recognized as candidates of the structural materials because of their low-induced radioactivity by neutron irradiation, and various properties of vanadium alloys have been extensively studied [6]. The permeation of hydrogen isotopes under irradiation, however, has not been clarified.

From these viewpoints, the present authors studied the permeation of hydrogen through a vanadium membrane under irradiation of 5 keV helium ions to understand the dynamic trapping–detrapping effect caused by radiation defects.

2. Experimental

Fig. 1 shows a schematic description of the apparatus used for permeation measurements. The apparatus consisted of two vacuum chambers, i.e., upstream and downstream chambers; they were separated from each other by the specimen membrane. Both chambers were evacuated with turbo-molecular pumps and oil-rotary pumps, and the base pressures were 1×10^{-7} Pa. The upstream chamber was equipped with a diaphragm gauge to measure hydrogen pressure. Hydrogen was introduced via a cold trap chilled by liquid nitrogen, and its pressure was adjusted with a variable-leak valve. A halogen lamp was installed in this chamber to heat up the specimen. The downstream chamber was equipped

* Corresponding author. Tel.: +81-764 456 928; fax: +81-764 456 931.

E-mail address: hatano@hrc.toyama-u.ac.jp (Y. Hatano).

0022-3115/00/$ - see front matter
PII: S0022-3115(00)00139-2

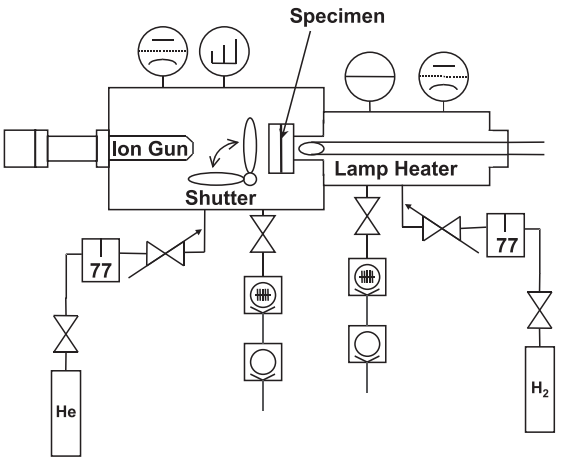

Fig. 1. Schematic description of permeation apparatus.

with an ion gun for helium ion irradiation. A shutter was installed between the ion gun and the specimen membrane. Helium was introduced via a cold trap chilled by liquid nitrogen, and its pressure was adjusted with a variable-leak valve. A quadrupole mass analyzer was also installed to measure the permeation rate. The specimen membrane was held in a vacuum flange sealed with a copper gasket. Temperature of the specimen was measured with a thermocouple spot-welded on the edge of the specimen.

The specimen membrane was cut from a sheet of pure vanadium (99.9%). The diameter and the thickness of the specimen were 30 and 0.1 mm, respectively. The specimen was cleaned in an ultrasonic bath filled with acetone and then heated in vacuum at 773 K for 1 h after installation in the permeation apparatus to remove volatile impurities from the surfaces.

Permeation experiments were carried out under the following procedure. The upstream surface of the specimen was exposed to hydrogen gas at 640 Pa and 673 K to accomplish a steady state of permeation. Then, the downstream surface was irradiated with a broad helium ion beam. The kinetic energy and the flux of the ion beam were 5 keV and 2×10^{16} He m^{-2} s^{-1}, respectively. The range of helium ions is 30 nm under this condition [7]. The irradiation was repeatedly intermitted and resumed by switching off and on the ion gun or by closing and opening the shutter to examine the difference between the permeation rate under the irradiation and that in the absence of the irradiation.

3. Results and discussion

The permeation rate at 673 K was 3.2×10^{21} H m^{-2} s^{-1} before the irradiation. According to the literature, solubility [8–10] and diffusivity [11] of hydrogen in vanadium under the present experimental conditions are expected to be 2 at.% (1×10^{27} H m^{-3}) and 1.4×10^{8} m^2 s^{-1}, respectively. Therefore, if the permeation was controlled by bulk diffusion, the permeation rate should be 1×10^{23} H m^{-2} s^{-1}. The observed permeation rate is significantly lower than this estimated value. This indicates that the permeation rate was determined not by the bulk diffusion process but by the surface reaction process before the irradiation. The surface of a vanadium specimen was heated at 773 K in another vacuum chamber and examined by X-ray photoelectron spectroscopy. Although there appeared no appreciable chemical shift for the binding energy of V 2p photoelectrons, a large amount of oxygen was present; the atomic ratio of oxygen to vanadium was about unity. This implies that the rate of surface reaction was reduced by oxygen in the permeation measurements. But the permeability of 2×10^{-8} mol H m^{-1} s^{-1} $Pa^{-1/2}$ at 673 K, which was evaluated from the above-mentioned permeation rate, is higher than that reported by other investigators [12–14]. This suggests that the amount of surface impurities is smaller in the present study than in the others [12–14].

Fig. 2 shows the variation of permeation rate by the irradiation. No significant change was observed in the permeation rate in the initial stage of irradiation. It should be mentioned here that the helium ion irradiation resulting in sputtering did not vary the permeation rate in the initial stage. This observation suggests that the permeation was controlled by the dissociation process on the upstream surface and not by the recombination process on the downstream surface. It should be emphasized that the permeation rate started to decrease at 900 min corresponding to a dose of 10^{21} He m^{-2}. Mechanisms underlying the reduction in the permeation rate will be discussed later.

In the region of irradiation time below 900 min, the permeation rate did not show any response to the

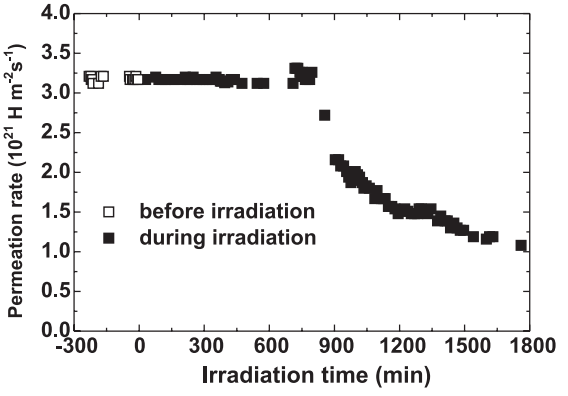

Fig. 2. Permeation rate of hydrogen through vanadium under helium ion irradiation.

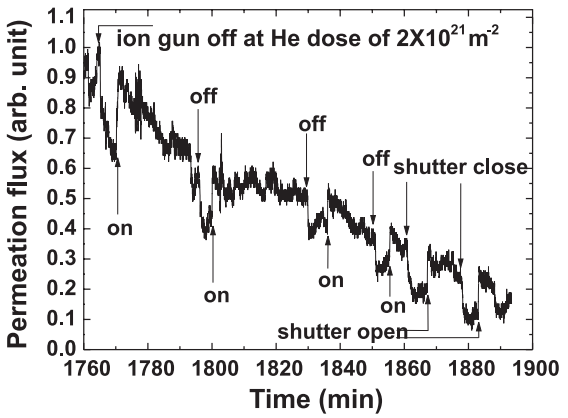

Fig. 3. Response of permeation rate to intermission and resumption of helium ion irradiation.

intermission and the resumption of the irradiation. In the region above 900 min, however, the permeation rate clearly responded to the intermission and the resumption as shown in Fig. 3. The permeation rate dropped promptly by the intermission and recovered by the resumption; the permeation rate under the irradiation was higher than that in the absence of irradiation.

Microstructural change induced by low energy ($\leqq$10 keV) helium ion irradiation has been investigated for nickel [15], molybdenum and tungsten [16,17] by transmission electron microscopy for a wide range of helium ion dose (10^{19}–10^{23} He m^{-2}). It has been reported that small defect clusters and dislocation loops are the dominant defects in the initial stage of irradiation, and helium bubbles become visible with a dose above 5×10^{20} m^{-2} [15–17]. In addition, it is well known that dislocations and helium bubbles act as trapping sites of hydrogen [1,2]. Those facts strongly suggest that the reduction in the permeation rate by the irradiation is caused by the change in the rate controlling process from the dissociation of hydrogen on the upstream surface to the transport process in a region around the range of implanted helium ions, where the transport is retarded by the trapping effect of accumulated radiation damages. The dose at which the permeation rate started to decrease in Fig. 2 (10^{21} m^{-2}) is close to the dose at which helium bubbles become visible in nickel, molybdenum and tungsten. Assuming vanadium behaves in a similar fashion, it can be proposed that helium bubbles make the dominant contribution to the reduction in the permeation rate. Consequently, the trapping energy should be higher for helium bubbles than for dislocations.

The high permeation rate under the irradiation shown in Fig. 3 can be ascribed to the radiation enhanced detrapping. Yoshida et al. [16] suggested that the recombination of a vacancy with a metal atom caused by a series of replacement collisions is the dominant mechanism for decomposition of a vacancy-helium cluster in a high dose region, and that helium atoms trapped by the vacancy are released by the decomposition of the cluster. Shrinkage and decomposition of helium bubbles resulting in the release of trapped hydrogen should take place through a similar mechanism under the present irradiation conditions. Namely, the detrapping of hydrogen from the helium bubbles is enhanced under the irradiation to increase the permeation rate.

The trapping of hydrogen by helium bubbles leads to buildup of hydrogen concentration. Therefore, the above-mentioned model can be confirmed by measuring the concentration distribution of hydrogen isotopes in an irradiated specimen. The present authors have developed a method to measure indestructibly the concentration distribution of hydrogen isotopes in solids by detecting X-rays induced by β-rays from tritium [18]. The measurement is now in preparation.

As mentioned in Section 1, Takagi et al. [3–5] reported that no significant change was observed in the permeation rate of deuterium through nickel under helium ion irradiation. They also reported that the permeation was controlled by the bulk diffusion process before and under the irradiation. The disagreement between the present study and theirs can be explained as follows. A membrane irradiated by helium ions has a double-layer structure, i.e., an implanted layer and an un-implanted layer. The diffusion coefficients of hydrogen isotopes should be lower in the former than in the latter owing to the trapping effect. The thickness of the former, however, is significantly thinner than that of the latter since helium ions can be implanted into a shallow region. The permeation of hydrogen isotopes is controlled by the diffusion process in the implanted layer provided that D/X of the implanted layer is smaller than that of the un-implanted layer. Here, D is the diffusion coefficient and X the thickness. The diffusion coefficients of hydrogen isotopes are markedly smaller in nickel than in vanadium, and hence D/X of the un-implanted layer was small in their study. Therefore, significant influence of irradiation was not observed in the permeation under their experimental conditions.

In the case of neutron irradiation, trapping sites are uniformly induced in a thick material. Therefore, the permeation should be influenced by the trapping sites.

4. Conclusions

The permeation behavior of hydrogen through a vanadium membrane was examined at 673 K under 5 keV helium ion irradiation. No significant variation in the permeation rate was observed in the initial stage of irradiation. Above a dose of 10^{21} m^{-2}, however, the permeation rate started to decrease with further irradi-

ation. In this region, the permeation rate under irradiation was higher than that in the absence of irradiation. These results were successfully explained by a model that helium bubbles act as trapping sites for hydrogen diffusion and detrapping from helium bubbles is enhanced under irradiation.

References

[1] C.A. Wert, in: G. Alefeld, J. Völkl (Eds.), Hydrogen in Metals II, Springer, Berlin, 1978 and references therein.
[2] S.M. Myers, P.M. Richards, W.R. Wampler, F. Besenbacher, J. Nucl. Mater. 165 (1989) 9.
[3] I. Takagi, J. Nucl. Sci. Technol. 29 (1992) 947.
[4] I. Takagi, H. Fujita, K. Shin, K. Higashi, J. Nucl. Mater. 191–194 (1992) 1313.
[5] I. Takagi, K. Yoshida, K. Shin, K. Higashi, Nucl. Instrum. and Meth. B 84 (1994) 393.
[6] H. Matsui, K. Fukumoto, D.L. Smith, H.M. Chung, W. van Witzenburg, S.N. Votinov, J. Nucl. Mater. 233–237 (1996) 92.
[7] J.F. Ziegler, Helium: Stopping Powers and Ranges in All Elemental Matter, Pergamon, New York, 1977.
[8] E. Veleckis, PhD thesis, Illinois Institute of Technology, 1960.
[9] R. Griffiths, J.A. Pryde, A. Righini-Brand, Trans. Faraday Soc. 68 (1972) 2344.
[10] T. Eguchi, S. Morozumi, J. Jpn. Inst. Met. 38 (1974) 1025 in Japanese.
[11] J. Völkl, G. Alefeld, in: G. Alefeld, J. Völkl (Eds.), Hydrogen in Metals I, Springer, Berlin, 1978.
[12] R.R. Heinrich, C.E. Johnson, C.E. Crouthamel, J. Electrochem. Soc. 112 (1965) 1071.
[13] E.H. Van Deventer, T.A. Renner, R.H. Pelto, V.A. Maroni, J. Nucl. Mater. 64 (1977) 241.
[14] T. Namba, H. Miyaguchi, M. Yamawaki, M. Kanno, J. Nucl. Mater. 105 (1982) 318.
[15] W. Jäger, J. Roth, J. Nucl. Mater. 93&94 (1980) 756.
[16] N. Yoshida, E. Kuramoto, K. Kitajima, Bull. Res. Inst. Appl. Mech. 57 (1982) 577 (in Japanese).
[17] H. Iwakiri, H. Wakimoto, H. Watanabe, N. Yoshida, J. Nucl. Mater. 258–263 (1998) 873.
[18] M. Matsuyama, K. Watanabe, K. Hasegawa, Fusion Eng. Des. 39&40 (1998) 929.