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Journal of Nuclear Materials 329–333 (2004) 411–415
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Influence of heat treatment on hydrogen ingress into V–4Cr–4Ti alloy

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Abstract

Specimens of V–4Cr–4Ti alloy were heated at 1273 K in vacuum, and the influence of this heat treatment on H_2 absorption was examined at temperatures from 523 to 1023 K under the presence of water vapor of 10^{-5} Pa. The rate of H_2 absorption was significantly reduced by the heat treatment in the temperature range examined. Such reduction in the absorption rate was ascribed to the surface segregation of Ti and increase in surface oxygen coverage caused by preferential oxidation of segregating Ti by water vapor. Comparison with data reported by other researchers [J. Nucl. Mater. 233–237 (1996) 376; Fusion Technol. 34 (1998) 868; J. Nucl. Mater. 233–237 (1996) 510] indicated the strong barrier effect of Ti oxide against hydrogen ingress.

1. Introduction

Vanadium alloys are recognized as promising candidate structural materials for fusion power plants [1–3]. Tritium inventory and permeation, however, are important problems because of the relatively high diffusivity and solubility of hydrogen isotopes in vanadium alloys [4]. The permeation and ingress rates of hydrogen isotopes in vanadium and its alloys are often limited by surface reactions such as dissociative absorption and recombinative release [5–8]. Therefore, it is necessary to accumulate kinetic data on these surface reactions.

The influence of surface impurity such as sulfur on recombination coefficients has been reported for pure vanadium [9,10]. In the cases of vanadium alloys, however, not only impurities but also the redistribution of constituent elements of the alloy could have a strong influence on the surface reactions of hydrogen isotopes. The present authors have examined the effects of heat treatment on surface composition and hydrogen absorption of V–4Ti alloy [8,11]. It was found that Ti segregated to the surface of V–4Ti alloy during vacuum heating at temperatures from 823 to 1273 K [11] and the hydrogen absorption rate radically decreased owing to this surface segregation of Ti [8]. Such reduction in the absorption rate was ascribed to the formation of Ti oxide on the specimen surface by preferential oxidation of segregating Ti. Water vapor present as an impurity was the source of the oxygen [8]. This observation indicated that a favorable barrier effect against tritium absorption and permeation could be obtained by appropriate heat treatment. Similar enrichment of Ti on the surface has been reported for V–4Cr–4Ti alloy by Shkolnik et al. [12] after heating in vacuum at 973 K. They also examined the permeation of hydrogen through V–4Cr–4Ti alloy membranes under this surface condition, but no data on surface reaction rates were given because they analyzed the results by assuming diffusion-limited permeation [12]. Romanenko et al. [7] have carried out permeation experiments for V–6Cr–5Ti

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doi:10.1016/j.jnucmat.2004.04.078

alloy membranes and derived the sticking and recombination coefficients of hydrogen. Their results, however, did not agree very well with the data for other vanadium alloys as stated by these authors, and the surfaces of their specimens were not analyzed [7].

In the present study, the influence of heat treatment on hydrogen absorption rate was examined for the V–4Cr–4Ti alloy, and the results obtained were compared with those for V–4Ti alloy to understand the effect of surface segregation of Ti. The permeation rate of hydrogen through a V–4Cr–4Ti alloy membrane in the surface-limited regime was evaluated from the values obtained for the absorption coefficient to compare with the data reported by Shkolnik et al. [12] and other researchers [7,13], and the influence of surface composition on the hydrogen permeation was discussed.

2. Experimental

Sheet specimens ($4 \times 14 \times 0.5$ mm^3) were cut from a plate of high purity V–4Cr–4Ti alloy (NIFS-HEAT-2) supplied from National Institute of Fusion Science (NIFS), Japan. The chemical composition of the specimen is given in [3]. Two types of surface treatments were carried out: (1) mechanical polishing with fine Al_2O_3 powder (0.06 μm), and (2) heating at 1273 K for 2 h in vacuum after polishing. The absorption experiments were carried out in the same apparatus after the heat treatment without exposing the specimens to air. The as-polished specimens are hereafter denoted as Specimen AP and the heat-treated ones as Specimen HT.

Hydrogen absorption was examined in the temperature range 523–1023 K with the apparatus described elsewhere [8]. Prior to the experiments, Specimen AP was heated at 673 K for 1 h in vacuum to remove so-called natural oxide film [8]. After adjusting the specimen temperature, the reaction chamber was isolated from the pumping system by closing valves. The main residual gas under this condition was water vapor (H_2O) and its pressure was 3×10^{-5} Pa. Then, hydrogen gas at 13.8 Pa was introduced into the reaction chamber. The pressure of hydrogen decreased with elapsed time owing to the absorption by the specimen. The rate of hydrogen absorption was determined from the pressure reduction. The conductance between the reaction chamber and pressure gauge was carefully checked prior to the measurements to avoid the underestimation of absorption rate.

3. Results and discussion

3.1. Absorption rate measurements

Fig. 1 shows typical examples of absorption curves obtained for Specimens AP and HT. In the cases of Specimen AP, the hydrogen pressure dropped rapidly and reached the values determined by respective equilibrium conditions. In the cases of Specimen HT, the pressure decreased slowly, and the period of time necessary for the attainment of equilibrium was significantly longer than the cases of Specimen AP; it took, for example, 10 h at 723 K. From equilibrium pressure, the solubility of hydrogen K_S was evaluated by Sieverts' law: $C_H = K_S P^{1/2}$ where C_H is the concentration of hydrogen in atomic ratio, H/V, and P the hydrogen pressure. The solubility K_S was independent of the surface conditions as expected and determined to be $K_S = 2.1 \times 10^{-6} \cdot \exp(32.6\ \mathrm{kJ\,mol^{-1}}/RT)$ where R is the gas constant and T the temperature. This value agreed well with the data for V–4Cr–4Ti alloy reported in the literature [14–16].

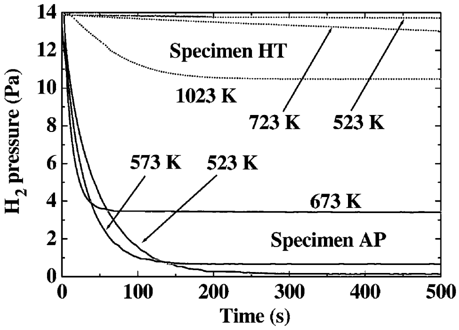

Fig. 1. Typical examples of hydrogen absorption curves for Specimens AP and HT.

The results shown in Fig. 1 indicate that the absorption was controlled by surface processes and not by bulk diffusion, even in the cases of Specimen AP. This is because a model calculation of diffusion-limited hydrogen absorption did not reproduce the absorption curves in this figure. Klepikov et al. [16] measured thermal desorption of hydrogen for V–4Cr–4Ti alloy and derived the diffusion coefficient D to be $D = 6.4 \times 10^{-8} \cdot \exp(-34\ \mathrm{kJ\,mol^{-1}}/RT)\ \mathrm{m^2\,s^{-1}}$. This value of D, however, was not employed in the model calculation for the reason described in Section 3.2. On the other hand, Tanaka and Kimura [17] have measured the diffusion coefficient of hydrogen in binary V–Ti and V–Cr alloys and reported that D decreased with increasing Ti concentration, while Cr had only a small influence on D. Hence, D for the present specimens appears to be comparable to that for binary V–4Ti alloy, which is evaluated to be $1.2 \times 10^{-8}\ \mathrm{m^2\,s^{-1}}$ at 573 K [17]. The model calculation using this value of D indicated that the equilibrium should be attained within 30 s. It is, however, apparent in Fig. 1 that a much longer time, about 150 s, was necessary for the attainment of equilibrium.

For the absorption limited by surface processes, the absorption coefficient of H_2 molecules impinging on the specimen surface, α, can be evaluated from the rate of absorption in the initial stage where the reemission from the specimen is negligibly small. Namely, the absorption rate at the initial stage is described as

$$\left.\frac{dN}{dt}\right|_{t=0} = \alpha A \frac{P_0}{\sqrt{2\pi mRT}}, \tag{1}$$

where N is the number of hydrogen molecules absorbed, A the surface area of the specimen, P_0 the initial pressure of hydrogen, and m the mass of a H_2 molecule.

The temperature dependence of α determined by Eq. (1) is shown in Fig. 2 together with the α values for V–4Ti alloy obtained in the previous study [8]. The values of the sticking coefficient, equivalent to α in the present study, determined for V–6Cr–5Ti alloy by Romanenko et al. [7] are also plotted for comparison. The absorption coefficient α of Specimen HT was smaller than that of Specimen AP by 2–3 orders of magnitudes, and the activation energy for the former was three times as high as that of the latter. In addition, the values of α of both Specimens AP and HT were almost the same as those of V–4Ti alloy prepared in a similar manner in the previous study [8]. Therefore, it was concluded that the surfaces of Specimens AP and HT were identical to those of V–4Ti alloy prepared by mechanical polishing and by vacuum heating at 1273 K for 2 h after polishing, respectively. The concentration of Ti on the surface of V–4Ti alloy reached 50 at.% after heating at 1273 K [8,11]. Hence, the concentration of Ti on the surface of Specimen HT should be close to this value, 50 at.%. On account of the observation in the previous study [11] that preferential oxidation of Ti took place even at very low oxygen pressures, the significant reduction in α by heating at 1273 K was ascribed to the barrier effect of Ti oxide formed by preferential oxidation of segregating Ti, using the water vapor present in H_2 gas. The values of α reported by Romanenko et al. [7] were significantly smaller than those presently obtained. The mechanism underlying this difference is discussed in Section 3.2.

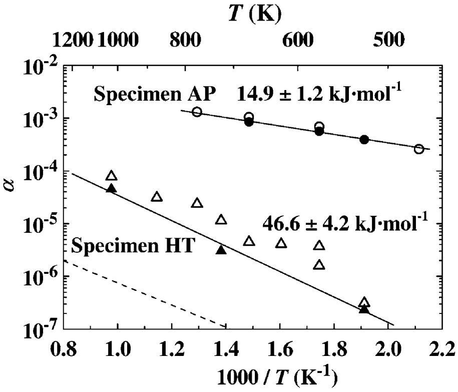

Fig. 2. Temperature dependence of absorption coefficient α. ●: indicates Specimen AP and ▲: Specimen HT. ○ and △: denote V–4Ti alloy specimens prepared in the same manner as Specimens AP and HT, respectively [8]. Dashed line shows the data reported by Romanenko et al. [7] for V–6Cr–5Ti alloy.

3.2. Evaluation of permeation rate and comparison with literature data

The concentration ratio of Ti to V on the surface of Specimen HT is comparable to that on the surface of V–4Cr–4Ti alloy specimens prepared by Shkolnik et al. [12]. They reported that the surface of their specimen was heavily contaminated by carbon in the initial stage of experiments [12]. Hence, they heated the specimen first in O_2 at 873 K and then in vacuum at 973 K; the surface composition changed by this treatment from C 67.3 at.%, S 14.6 at.%, Ti 13.8 at.%, and V 4.3 at.% to C 14.9 at.%, S 47.9 at.%, Ti 18.6 at.%, and V 18.6 at.% [12]. Namely, the surfaces of their specimens were enriched in carbon and sulfur, whereas Ti oxide is believed to be formed on the surface of Specimen HT. Therefore, it is worthwhile to compare the reaction rates of hydrogen on these surfaces to understand the difference in the influences of carbon, sulfur and oxygen. Direct comparison is difficult, however, because Shkolnik et al. [12] analyzed their results of permeation experiments by assuming diffusion-limited permeation and no data on surface reaction rates were derived. Hence, the permeation rates for V–4Cr–4Ti alloy membranes under the surface conditions of Specimens AP and HT were evaluated from the presently obtained values of α by assuming surface-limited permeation, and they were compared with the permeation rates calculated from the data on permeability given by Shkolnik et al. [12]. The permeability data reported by other researchers for Pd-coated V–4Cr–4Ti [13] and V–6Cr–5Ti [7] alloys were also subjected to similar comparison. In the surface-limited regime, the permeation rate ϕ_P is expressed as $\phi_P = \alpha P_1 A/\sqrt{8\pi mRT}$, provided that the properties of upstream and downstream surfaces are identical, i.e. the membrane is symmetric. Here, P_1 is the pressure of hydrogen on the upstream side. The hydrogen pressure on the downstream side was assumed to be negligibly small. On the other hand, in the diffusion-limited regime, the permeation rate is expressed as $\phi_P = ADK_S P_1^{1/2}/L$ where L is the thickness of membrane; K_S should be in mol $H_2\,m^{-3}\,Pa^{-1/2}$. Here, DK_S is often described as permeability and given in Refs. [7,12,13]. The permeation rate was evaluated by applying $A = 1\ m^2$, $P_1 = 1$ Pa and L given in the corresponding papers [7,12,13].

The results of evaluation are summarized in Fig. 3. In this figure, the ‘theoretical’ permeation rate in the diffusion-limited regime evaluated from the presently obtained value of K_S and the above-mentioned value of D for V–4Ti alloy [17] is also plotted for comparison (Theoretical-1). In this evaluation, L was taken to be the same thickness as the membranes used by Shkolnik et al.

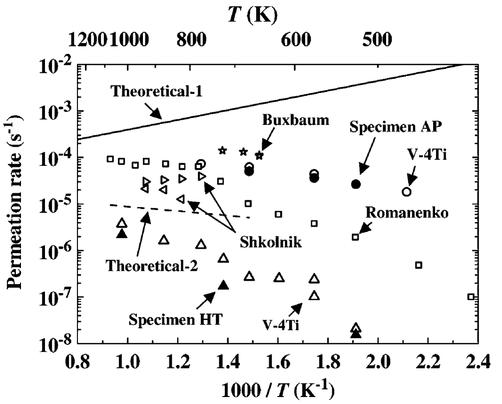

Fig. 3. Permeation rates evaluated from α obtained in the present and previous [8] studies and permeability data reported in the literature [7,12,13]. Details of evaluation are described in text. ● Specimen AP, ▲: Specimen HT. ○ and △: V–4Ti alloy specimens prepared in the same manner as Specimens AP and HT, respectively [8]. ◁: V–4Cr–4Ti alloy, C 67.3 at.%, S 14.6 at.%, Ti 13.8 at.%, V 4.3 at.% [12]. ▷: V–4Cr–4Ti alloy, C 14.9 at.%, S 47.9 at.%, Ti 18.6 at.%, V 18.6 at.% [12]. ☆: Pd-coated V–4Cr–4Ti alloy [13], and □: V–6Cr–5Ti alloy [7]. Solid line (Theoretical-1) indicates the 'theoretical' permeation rate in the diffusion-limited regime calculated from presently obtained K_S and D reported by Tanaka and Kimura [17] and dashed line (Theoretical-2) shows that evaluated from D and K_S reported by Klepikov et al. [16].

[12] and Romanenko et al. [7], 1 mm, and hence direct comparison is possible. Similar evaluation was also carried out with the data on D and K_S reported by Klepikov et al. [16] (Theoretical-2). The characteristic points of this figure are:

1. Permeation rates for Specimen AP are comparable with those for Pd-coated V–4Cr–4Ti alloy reported by Buxbaum et al. [13], indicating that the surface of Specimen AP is rather clean;
2. Permeation rates for Specimen HT are significantly smaller than those for Specimen AP and for the data reported by other researchers [7,12,13];
3. The data of Shkolnik et al. [12] provide comparable permeation rates with Specimen AP, although Ti was enriched on the surfaces of their specimens;
4. Permeation rates for the data of Romanenko et al. [7] fall between those for Specimens AP and HT although the α values were significantly smaller than those of Specimen HT as mentioned in Section 3.1;
5. Theoretical-1 has a negative temperature dependence;
6. All data approach Theoretical-1 in the high temperature region;
7. Theoretical-2 is smaller than the permeation rates calculated from experimentally obtained permeability data [7,12,13].

The negative temperature dependence of the 'theoretical' permeation rate, Theoretical-1, is due to a large negative heat of solution of hydrogen ΔH_S In the diffusion-limited regime, the activation energy for permeation E_P is expressed as $E_P = E_D + \Delta H_S$ where E_D is the activation energy for diffusion. Here, E_D is 12 kJ mol^{-1} according to Tanaka and Kimura [17], whereas ΔH_S was determined to be −32.6 kJ mol^{-1} as mentioned above. Hence, E_P was estimated to be −20.6 kJ mol^{-1}. Such negative temperature dependence was experimentally observed by Shkolnik et al. [12] as shown in Fig. 3. On the other hand, E_P should be positive in the surface-limited regime because it is determined by the activation energy for dissociative absorption E_a which was 14.9 ± 1.2 kJ mol^{-1} for Specimen AP and 46.6 ± 4.2 kJ mol^{-1} for Specimen HT as shown in Fig. 2. The permeation rate takes the maximum value in the 'pure' diffusion-limited regime, and hence the approach of all data to this 'theoretical' permeation rate indicates the validity of this treatment. The activation energy for permeation E_P appears to become smaller as ϕ_P increases. This observation was ascribed to the smaller E_a or to the change in the permeation mechanism from the 'pure' surface-limited regime to that intermediate between surface- and diffusion-limited regimes by increase in ϕ_P. The small permeation rate for D and K_S reported by Klepikov et al. [16] (Theoretical-2) suggests that D value obtained by their desorption measurements was underestimated, because K_S agreed with presently obtained values and those reported by other researchers [14,15] as mentioned in Section 3.1. This is the reason that their D value was not employed in the model calculation of diffusion-limited absorption in Section 3.1.

The agreement between the permeation rates for the permeability data of Romanenko et al. [7] and those for the presently obtained α suggests that both of their permeation experiments and present absorption experiments were reliable and the surface properties of V–6Cr–5Ti and V–4Cr–4Ti alloys are similar. Hence, the disagreement in α shown in Fig. 2 can be ascribed to the evaluation method of α employed by Romanenko et al. [7].

Although the surfaces of the specimens used by Shkolnik et al. [12] were enriched in Ti and contaminated by carbon and sulfur, the permeation rates evaluated for their specimens were comparable with those for Specimen AP, the surface of which appears to be rather clean as described above. The negative temperature dependence of permeation rates observed for the data of Shkolnik et al. [12] indicates that the reaction rate of hydrogen on their specimen surfaces was rather high and consequently the permeation was controlled by bulk diffusion process in part. Hence, it is appropriate to consider that the influence of sulfur and carbon on hydrogen permeation is rather small. In addition, these results indicate that the surface segregation of Ti itself does not provide a barrier effect. Namely, oxidation of

Ti plays an essential role for the barrier effect observed for Specimen HT as proposed in the previous section. The partial pressure of water vapor in the present experimental conditions was rather low, 3×10^{-5} Pa. This level of oxygen containing impurities such as O_2, CO_2 and water vapor can be present in hydrogen isotope gases used to fuel fusion devices and could help to provide the barrier effect against hydrogen ingress. Further investigation on this barrier effect is necessary from the viewpoints of isotope effects and the influence of impurity levels to understand the tritium permeation and ingress for the expected conditions of fusion devices.

4. Conclusions

(1) The heat treatment of V–4Cr–4Ti alloy at 1273 K in vacuum resulted in significant reduction in absorption coefficient of H_2, α.
(2) The reduction in α by the heat treatment was ascribed to the surface segregation of Ti and its preferential oxidation by water vapor present as an impurity in H_2 gas.
(3) The permeation rates of H_2 estimated for the heat-treated specimen from measured α values were radically smaller than those reported by other researchers [7,12,13], indicating the strong barrier effect of Ti oxide against hydrogen ingress.

Acknowledgements

The authors would like to express their sincere thanks to Professor T. Muroga and Dr T. Nagasaka of National Institute for Fusion Science for supply of NIFS-HEAT-2 specimens. This study is supported in part by a Grant-in-Aid for Scientific Research (B) of Ministry of Education, Culture, Sports, Science and Technology of Japan, No. 14380218.

References

[1] H. Matsui, K. Fukumoto, D.L. Smith, H.M. Chung, W.v. Witzenburg, S.N. Votinov, J. Nucl. Mater. 233–237 (1996) 92.
[2] R.J. Kurtz, K. Abe, V.M. Chernov, V.A. Kazakov, G.E. Lucas, H. Matsui, T. Muroga, G.R. Odette, D.L. Smith, S.J. Zinkle, J. Nucl. Mater. 283–287 (2000) 70.
[3] T. Muroga, T. Nagasaka, K. Abe, V.M. Chernov, H. Matsui, D.L. Smith, Z.-Y. Xu, S.J. Zinkle, J. Nucl. Mater. 307–311 (2002) 547.
[4] R. Lässer, Tritium and Helium-3 in Metals, Springer, Berlin, Heidelberg, 1989.
[5] E.H. Van Deventer, T.A. Renner, R.H. Pelto, V.A. Maroni, J. Nucl. Mater. 64 (1977) 241.
[6] T. Namba, H. Miyaguchi, M. Yamawaki, M. Kanno, J. Nucl. Mater. 150 (1982) 318.
[7] O.G. Romanenko, I.L. Tazhibaeva, V.P. Shestakov, A.Kh. Klepikov, Y.V. Chikhray, A.V. Golossanov, B.N. Kolbasov, J. Nucl. Mater. 233–237 (1996) 376.
[8] R. Hayawaka, Y. Hatano, A. Pisarev, K. Watanabe, Phys. Scr., in press.
[9] M. Yamawaki, T. Namba, K. Yamaguchi, T. Kiyoshi, Nucl. Instrum. and Meth. B 23 (1987) 498.
[10] K. Yamaguchi, S. Tanaka, M. Yamawaki, T. Namba, Fusion Eng. Des. 10 (1989) 337.
[11] R. Hayakawa, Y. Hatano, K. Fujii, K. Fukumoto, H. Matsui, K. Watanabe, J. Nucl. Mater. 307–311 (2002) 580.
[12] I.V. Shkolnik, T.V. Kulsartov, I.L. Tazhibaeva, V.P. Shestakov, Fusion Technol. 34 (1998) 868.
[13] R.E. Buxbaum, R. Subramanian, J.H. Park, D.L. Smith, J. Nucl. Mater. 233–237 (1996) 510.
[14] A.G. Zaluzhnyi, V.N. Tebus, N.N. Riazantseva, V.N. Kopytin, L.A. Voloshin, D.I. Torubarov, M.V. Chered-nichenko-Alchevski, Fusion Eng. Des. 41 (1998) 181.
[15] R.E. Buxbaum, D.L. Smith, J.H. Park, J. Nucl. Mater. 307–311 (2002) 576.
[16] A.Kh. Klepikov, O.G. Romanenki, Y.V. Chikhray, I.L. Tazhibaeva, V.P. Shestakov, G.R. Longhurst, Fusion Eng. Des. 51&52 (2000) 127.
[17] S. Tanaka, H. Kimura, Trans. JIM 20 (1979) 647.