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Journal of Nuclear Materials 248 (1997) 60–63

journal of nuclear materials

Permeation behavior of deuterium implanted into Ti–6Al–4V alloy

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Abstract

Permeation of deuterium implanted into Ti–6Al–4V alloy has been studied using 0.5 keV D^+ ion beam in the temperature range of 323 to 753 K. Above 600 K, the ratio of steady state permeation flux/incident flux ranges from 3.3×10^{-3} at 633 K to 4.8×10^{-3} at 753 K. The activation energy of permeation is about 0.12 eV in this temperature range. At temperatures below 600 K, the permeation flux of deuterium decreases drastically. Deuterium implanted in the lower temperature range desorbed from the alloy by heating after implantation. Thus, the most of the implanted ions remain in the alloy at low temperatures. © 1997 Elsevier Science B.V.

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1. Introduction

To choose an optimum material for a vacuum chamber of a Tokamak D–T fusion reactor, hydrogen isotope behavior in several materials have been examined. Among such materials, Ti alloys have advantages of low electrical conductivity, high strength/weight ratio, low thermal expansion and, especially, low activation [1]. Ti–6Al–4V alloy possesses the above characteristics, and is one of the candidate materials for the next fusion experimental device of the Japan Atomic Energy Research Institute (JAERI) [2]. On the other hand, Ti alloys are prone to form hydrides which causes embrittlement of the alloys. Some studies have been carried out on the interactions of Ti alloys with hydrogen gas. However, there are few works on interaction between Ti alloys and plasma or energetic ions of hydrogen isotopes [3]. For safe handling of tritium in fusion reactors, it is important to know permeation behavior of implanted hydrogen isotope ions through the alloy. In the present work, permeation behavior of deuterium through Ti–6Al–4V alloy is studied under more realistic conditions for vacuum chambers of fusion reactors using a 0.5 keV D^+ ion beam.

2. Experimental

Ti–6Al–4V alloy disks of 34 mm ∅ and 0.1 mm thick were prepared by rolling and were annealed at 973–1063 K. The structure of the alloy was a mixture of α-Ti and β-Ti. The chemical composition of the alloy is shown in Table 1.

An experimental apparatus (tritium permeation apparatus) which was developed in the Tritium Engineering Laboratory of the JAERI [4] consists of an up stream (main) chamber equipped with an ion source and a down stream chamber with a quadrupole mass spectrometer (QMS) as shown in Fig. 1. The specimen target with an effective permeation area of about 25 mm in diameter separates two chambers. The duo-PIGatron ion source emits deuterium ion (D^+) beam with an energy range of 0.2–2.0 keV, and a flux range of $1.3–13 \times 10^{18}$ ions m^{-2} s^{-1}. The ions are implanted from the front side (up stream) of the specimen, and a halogen–tungsten lamp at the back side heats the sample up to about 760 K. The temperature of the specimen is measured by a thermo-couple spot-welded at the front surface (up stream side) of the specimen.

The up-stream chamber was evacuated by a cryo sorption pump and the pressure of deuterium in the chamber was kept 4.0×10^{-4} Pa during experiments. The down-stream chamber was evacuated by an ion pump, and the

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PII S0022-3115(97)00116-5

Table 1
Chemical composition of the Ti–6Al–4V sample

Ti	Al	V	Ca	Fe	Mg
bal.	6.12 (wt%)	3.87 (wt%)	9.2 ppm	304 ppm	4.71 ppm

pressure in the chamber was below 1.3×10^{-5} Pa with the specimen at room temperature. The permeated deuterium flux was estimated from the partial pressure of deuterium in the down-stream chamber measured by the QMS ($m/e = 4$). The QMS signal had been calibrated before the experiments, as follows. By installing an orifice of 1 mm Ø instead of a specimen, the QMS signal was measured at various differential pressures between the up stream and the down stream chamber. The deuterium flux through the orifice Q was calculated from the relationship of

$$Q = C_o(p_1 - p_2), \tag{1}$$

where C_o is the conductance of the orifice, and $p_1 - p_2$ the differential pressure between the two chambers. The values of p_1 and p_2 were measured by ionization gauges in the each chamber. The QMS signal was found to have a 1:1 relationship with $p_1 - p_2$, thus the QMS was calibrated comparing the QMS output signal and the above Q value.

The permeation of deuterium through the sample specimen during ion implantation was measured under a constant beam flux of 6.4×10^{18} ions m^{-2} s^{-1}, and beam energy of 0.5 keV at a specimen temperature range of 323–753 K.

In the temperature range below 473 K, no significant permeation of deuterium was observed during 3 h implantation of the ions. To confirm the existence of implanted ions in the alloy after low temperature implantation, the specimen was heated up to 673 K, and deuterium extracted from the back side of the specimen was measured. In order to check the effects of absorption and permeation of deuterium driven by the D_2 gas under the base pressure of the ion implantation experiments (4.0×10^{-4} Pa) upon the ion driven permeation, permeation test of deuterium during exposure to the D_2 gas with a succeeding thermal desorption was also performed. The schematic diagram of the experimental sequence is shown in Fig. 2.

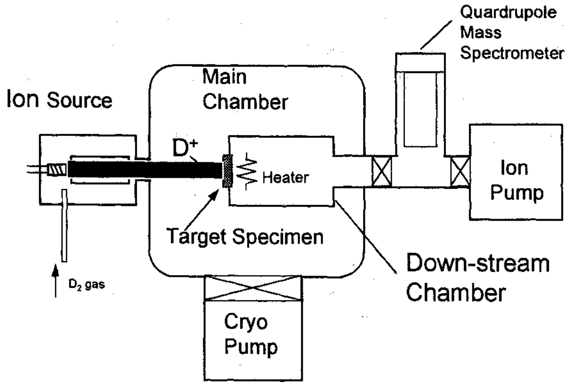

Fig. 1. Apparatus for permeation experiment.

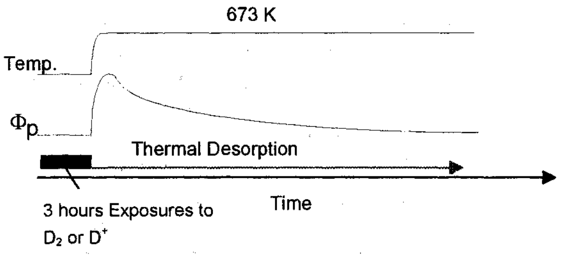

Fig. 2. Schematic diagram of the exposure and desorption test. After the specimen is exposed to D_2 or energetic D^+, the permeation flux of deuterium from the back surface is measured.

3. Results and discussion

Permeation fluxes under implantation of D^+ ions are shown in Fig. 3. The permeation of deuterium under ion implantation was not observed within the experimental period of 3 h at 473 K and below. Furthermore, at 323 K no permeation was observed by an implantation of 15 h. The results of the permeation driven by D_2 gas with a pressure of 4.0×10^{-4} Pa in the up-stream chamber is also shown. No gas driven permeation was observed at any temperature examined within this experimental period of 3 h. Above 473 K, permeation of implanted deuterium through the membrane was observed. The permeation flux increased both with the duration of ion implantation and with the increase in the specimen temperature. To attain a steady state permeation, a time much longer than 24 h might be needed at low temperatures.

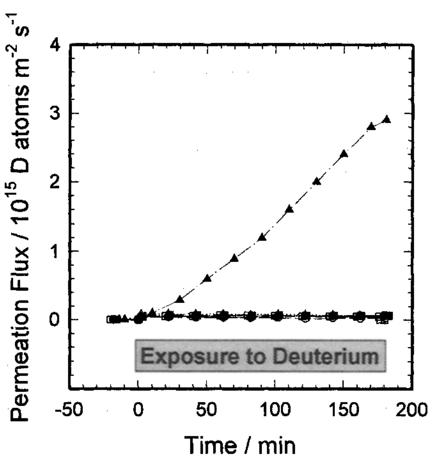

Fig. 3. Permeation curves for Ti–6Al–4V at various temperatures (■, □: 373 K; ●, ○: 473 K; and ▲, △: 573 K) during exposure to D_2 gas (open symbols) and D^+ ions (solid symbols).

Above 600 K, the steady state permeation was attained within 24 h of implantation. Fig. 4 shows the temperature dependence of the steady state permeation flux under the implantation of 6.4×10^{18} ions m^{-2} s^{-1}, at 0.5 keV. The steady state permeation flux ranged from 2×10^{16} atoms m^{-2} s^{-1} at 633 K to 3×10^{16} atoms m^{-2} s^{-1} at 753 K, which correspond to ratios of permeation/incident flux of 3×10^{-3} and 5×10^{-3}, respectively. The activation energy of the ion-driven permeation of deuterium through the alloy is estimated to be 0.12 eV from the Arrhenius plot of the permeation flux.

In the temperature range up to about 473 K, no significant permeation during implantation was observed within 3 h. To know how much implanted ions exist in the alloy, the specimen which was ion-implanted at 373, 473, and 573 K was heated to 673 K and the deuterium desorbing from the back side of the specimen was measured. The fraction released from the front side of the specimen could not be measured due to the apparatus construction. Fig. 5 shows the deuterium extraction curves during the heating to 673 K after ion implantation at various low temperatures. As shown in Fig. 5 with label 'GAS', which corresponds to the extraction curve after the exposure only to D_2 gas, no significant desorption peak is found. A small increase of QMS output in these curves seems to be due to deuterium degassing from the chamber walls by heating. This implies that deuterium, absorbed during the D_2 gas exposure, is negligible. The total desorbed deuterium from the back side of the specimen estimated from the integration of peak area is shown in Table 2.

The fluence of incident ion during 3 h implantation was 6.9×10^{22} ions m^{-2}. A part of the incident D^+ ions might be released from the front surface during implantation. The deuterium was desorbed both from the front and the back side of the specimen by heating up to 673 K. For all the cases in which the specimen was implanted at 373–573 K, about one or two percent of implanted deuterium desorbed from the back side of the membrane by the heating.

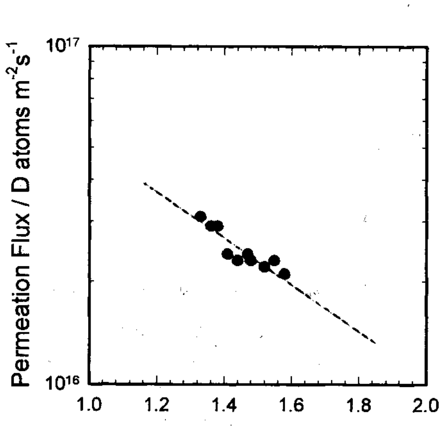

Fig. 4. Temperature dependence of permeation flux through Ti–6Al–4V at steady state.

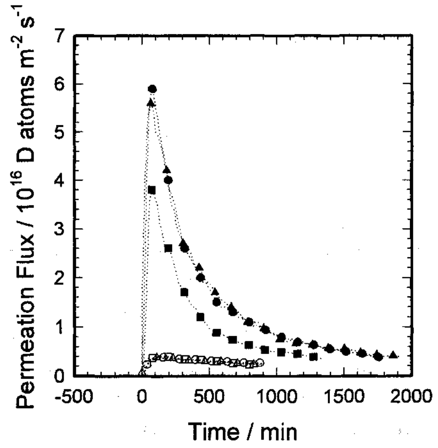

Fig. 5. Thermal desorption curves of deuterium for Ti–6Al–4V at 673 K after exposure to D_2 gas (open symbols) and D^+ ions (solid symbols) at various temperatures (■, □: 373 K; ●, ○: 473 K; and ▲, △: 573 K).

The desorbed deuterium from the back side of the membrane by heating increased with the specimen temperature during implantation. In our experiments, a little amount of deuterium permeated through the specimen within 3 h at temperatures above 573 K, but the amount of permeated deuterium in this period was negligible compared to that of the thermally desorbed deuterium. Wilson and Pontau [3] measured the deuterium re-emission rate under implantation of deuterium ion (10 keV/D_3^+) to Ti–6Al–4V at temperatures ranging from 300 to 800 K, and concluded that no thermal desorption of implanted deuterium took place from the implanting surface during bombardment below 600 K, and that the exothermic heat of solution of hydrogen in these metals acted as a potential energy barrier to the desorption from the surface. In our study, the release of deuterium from the front surface is negligible during implantation at low temperatures. In the subsequent heating, deuterium inside the alloy migrates quickly to; and desorbs from, both the front and the back, because the diffusion becomes more prominent at higher temperatures. Higher implantation temperature may cause the migration of deuterium from the implanted range near the front surface much deeper into the bulk of the alloy. So

Table 2
Extract amount of deuterium from Ti–6Al–4V

Implantation temperature (K)	Extract (D atoms m^{-2})
373	9.1×10^{20}
473	1.6×10^{21}
573	1.7×10^{21}

the extracted amount of deuterium from the back side of the specimen during the heating at 673 K is affected by the temperature during implantation. For the specimen implanted at 373 K, more deuterium was released from the front surface compared with that implanted at higher temperatures. This supports the results of the thermal desorption experiment.

To investigate the structural change with deuterium ion implantation, the X-ray diffraction spectra of the specimens before and after the ion-driven permeation experiments were measured using a monochromated Cu Kα (1.5405 Å) line. The specimen was irradiated by 0.5 keV, 6.4×10^{18} D^+ ions m^{-2} s^{-1} for 15 h at 323 K. All diffraction peaks obtained showed that the peak widths at half height broadened to a lower 2θ angle by the D^+ implantation. This suggests that crystal lattice of Ti alloy is enlarged by interstitial D atoms. Similar effects have been reported for the α-phase of pure Ti [5]. Since there are no new diffraction peaks, no drastic phase change is induced by the ion implantation. No evidence of Ti deuterides (TiD, TiD_2) is seen in the XRD. The sample after ion implantation has no macro defect. Thus, no considerable hydrogenation has occurred by deuterium ion implantation under the above mentioned experimental conditions.

Pontau et al. studied properties of pure Ti and its alloys implanted with deuterium ion (10 keV D_3^+, 10^{21}–10^{22} D^+ m^{-2}) [6,7]. The D/Ti ratio of about 1 was found near the surface, and deuteride formed in the α-phase of Ti and the alloy. On the other hand, in a mixed α,β-phase alloy (Ti–6Al–4V), no deuteride formed near the surface. The fluence of incident D^+ in 15 h implantation was above 10^{23} D^+ m^{-2} in the present work, and the X-ray diffraction study suggested no considerable hydrogenation. This agrees with the results of Pontau et al. The phase diagram of Ti and hydrogen shows the hydrogen solubility limit less than 10% in α-phase and about 50% in β-phase [5]. Thus the existence of β-phase would be the reason for the difficulty of the hydride formation in the alloy.

In the case of applying Ti–6Al–4V alloy for an actual vacuum vessel, tritium inventory and macro defects would be able to occur under long time and high fluence operation, since the implanted atoms would remain in the alloy. In this aspect, it is important to use a material with some tritium barrier, for example, surface coatings.

Permeation flux of hydrogen isotopes through the wall depends on the rate limiting process of the permeation. However, it is still difficult to conclude that the permeation of deuterium through the alloy is controlled either by diffusion in the alloy or by recombination at the surface from the present results. Thus, further investigation is required to clear this point.

4. Summary

The behavior of deuterium implanted into Ti–6Al–4V alloy was studied under the conditions of 0.5 keV, 6.4×10^{18} D^+ ions m^{-2} s^{-1}, up to 760 K. The conclusions of this study are as follows.

(1) The ratio of permeation/incident flux ranges from 3.3×10^{-3} at 633 K to 4.8×10^{-3} at 753 K for the steady state permeation (≥ 600 K). The activation energy of the ion-driven permeation of deuterium is 0.12 eV in this temperature range.

(2) Below 573 K, most of the implanted ions were estimated to remain in the membrane.

(3) No hydrides are formed under these experimental conditions. Under long time and high fluence operation of the fusion reactor, however, tritium inventory would be an important problem.

Acknowledgements

The authors would like to thank Dr M. Kikuchi, Dr N. Toyoshima, and Dr N. Miya (Tokamak Program Division of Department of Fusion Plasma Research, JAERI) for supplying the Ti–6Al–4V samples and discussions on the manuscript. The acknowledgment should also be expressed to Dr W.M. Shu (Toyama University) for the helpful comments.

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