Effect of helium irradiation on deuterium permeation behavior in tungsten

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Abstract

In this study, we measured deuterium (D) gas-driven permeation through tungsten (W) foils that had been pre-damaged by helium ions (He^+). The goal of this work was to determine how ion-induced damage affects hydrogen isotope permeation. At 873 K, the D permeability for W irradiated by 3.0 keV He^+ was approximately one order of magnitude lower than that for un-damaged W. This difference diminished with increasing temperature. Even after heating to 1173 K, the permeability returned to less than half of the value measured for un-damaged W. We propose that this is due to nucleation of He bubbles near the surface which potentially serve as a barrier to diffusion deeper into the bulk. Exposure at higher temperatures shows that the D permeability and diffusion coefficients return to levels observed for undamaged material. It is possible that these effects are linked to annealing of defects introduced by ion damage, and whether the defects are stabilized by the presence of trapped He.

Keywords: tungsten, hydrogen isotope permeation, helium irradiation, helium bubble

1. Introduction

Tungsten (W) is a promising candidate for plasma facing materials (PFMs) in future fusion reactors [1-2] due to low hydrogen isotope retention and high melting temperature. A comprehensive understanding of the behavior of hydrogen isotopes in W is crucial for evaluating the safety of future fusion reactors [3]. Hydrogen diffusion and permeation in un-damaged W has been studied since the late 1960's (Frauenfelder: [4-5]) and early 1970's (Zaharakov: [6]). For further details on more recent developments, we refer the reader to Ref. [7-9]. Investigations of high-flux plasma-driven permeation using tritium [10] are also planned in the near-future. However, for a variety of reasons, tritium-based measurements of this nature are quite complex. Experiments that use deuterium gas-driven permeation provide complementary information, and can operate at relevant temperatures to provide useful comparisons between different plasma-facing materials (including advanced alloys, as described in Ref. [11].)

When considering permeation measurements, it is important to keep in mind the complexity of the fusion environment. In addition to exposure to high-flux, low energy D+T plasmas, the PFMs will also be exposed both energetic helium (He) and 14 MeV neutrons that escape from the plasma. The damage introduced by this irradiation will strongly affect how hydrogen migrates through the material. In particular, He⁺ irradiation causes the formation of pressurized He bubbles. Prior temperature-programmed desorption and depth profiling measurements indicate that deuterium (D) diffusion into the W bulk is reduced considerably as a result of mixed species irradiation. The prevailing hypothesis is that the dense layer of He bubbles formed near the W surface [12-13] strongly influences this migration.

In our previous study [14], we examined the effect of He⁺ irradiation on D retention in W. We proposed that the higher thermal stability of He-trapped dislocation loops interfered with the complete recovery of damage at 1173 K. The growth of He bubbles

was remarkable above 1073 K and damage recovery was not possible even at 1173 K. Given these retention results, the next logical step (in the context of the effect of fuel behavior on fusion reactor operation) is to evaluate what effect He bubbles have on hydrogen isotope permeation. This is the focus of the present study, which includes a comparison of hydrogen permeation in both He⁺ irradiated and un-damaged W.

2. Experimental configuration

Fig. 1 shows a diagram of the gas-driven permeation instrument at Shizuoka University. This instrument includes a sample holder that can accommodate 10 mm diameter specimens secured with fittings for 6.35 mm VCR tubing. To create a tight seal, the specimen is sandwiched between two silver coated metal gaskets [15]. A thermocouple was introduced through the inner tubing and directly contacted the upstream side of the specimen to measure its temperature. The upstream D₂ gas pressure is regulated by a variable leak valve (V. L.V.) and monitored by capacitance manometers. The vacuum at the downstream side was maintained at $\sim 10^{-6}$ Pa by a turbomolecular pump (TMP) backed by a rotary pump (RP). The sample holder was contained within an evacuated quartz tube to reduce oxidation and prevent any adventitious signals arising from the D permeation to the surrounding environment during heating. The TMP and RP maintained a vacuum within the quartz tube of less than 10^{-4} Pa. Thereafter, D₂ gas was introduced to the upstream side. The D permeation to the downstream side was quantified by a MKS Microvision quadrupole mass spectrometer (QMS) to monitor mass 4 (D₂) and mass 3 (HD) peaks [16]. The D₂ sensitivity of the QMA was calculated by two standard leaks with different leak rates. The same sensitivity was assumed for the D₂ and HD peaks.

The permeability (P) is expressed by:

$$P = \frac{xJ}{AP_D^n} \quad (1),$$

where J is steady-state permeation flux, x is sample thickness, A is surface area and P_D is the deuterium driving pressure. A pressure exponent n is calculated by measuring the permeation fluxes at different driving pressures as follows,

$$J \propto P_D^n \quad (2).$$

The permeation controlled by diffusion-limited regime satisfies the equation with $n = 0.5$. Likewise, when the permeation rate is limited by surface processes, the exponent of the deuterium driving pressure P_D is unity ($n = 1$). In addition, the time evolution of the permeation flux can be used to determine the diffusion coefficient D analytically using the following equation:

$$t_{\text{lag}} = \frac{x^2}{6D} \quad (3).$$

Here t_{lag} is determined by where a line fit to the asymptotic region of the permeation flux intersects the time axis[17].

The test specimens consisted of rolled W foils (Nilaco Co. Ltd) cut into discs (10 mm dia. $\times$ 0.035 mm thick) with snips. They were cleaned in ultrasonic bath with ethanol and preheated at 1173 K for 30 min under ultrahigh vacuum ($<10^{-6}$ Pa) to remove impurities and residual damage. Furthermore, an additional set of 3 mm dia. discs were thinned by pierce punch and electrolytic polishing for transmission electron microscopy (TEM) examination.

The W samples were then exposed to varying He^+ irradiation conditions to cover a range of energies and ion fluences. For the first set of experiments, 1.0 or 3.0 keV He^+ was implanted into the sample at room temperature (flux : $3.0 \times 10^{17} \text{ He}^+ \text{ m}^{-2} \text{ s}^{-1}$, fluence : $3.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$). Additional W samples were exposed to a fixed He^+ energy of 3.0 keV, with the fluence ranging between 0.03 and $9.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$. Following the pre-irradiation step, each sample was then installed into the gas-driven permeation instrument and exposed to D_2 pressures ranging between 10.00 - 120.0 kPa. We then measured permeation fluxes over a temperature range of 873 - 1173 K in each case.

To correlate the permeation results with the defect structure created by He^+ damage (and ameliorated by heating), we used transmission electron microscopy (TEM) (JEM 2000EX, JASCO Inc.) In addition, D depth profiles of He^+ irradiated W after exposure to D_2 gas at 873 K and 1173 K for 2 hours were also evaluated by the Glow Discharge-Optical Emission Spectroscopy (GD-OES) (GD-Profilier 2, HORIBA Ltd.) measurements at the University of Toyama.

3. Results and discussion

3.1 He^+ energy dependence

Fig. 2 shows D depth profiles of He^+ irradiated W after exposure to D_2 gas at 873 K and 1173 K measured by GD-OES. Irradiated He profiles calculated by SRIM are shown for comparison with the dashed lines and provide an indication of how displacement damage was distributed throughout the material. For both samples exposed to 1.0 keV He^+ irradiation, D was concentrated within the first 10 nm of the surface. These data are consistent with the expected profile shape for diffusion-limited release [17]. In the case of 3.0 keV He^+ irradiation followed by permeation at 873 K, the D profile reaches a maximum at ~ 20 nm from the surface. This suggests D trapping coincides with point defects introduced by He^+ irradiation, and the recovery of this damage had not fully completed. Now consider the profile associated with the specimen exposed at 3.0 keV He^+ followed by permeation at 1173 K. This temperature is still too low to prevent the annealing of He bubbles, but unlike the case at 873 K no additional D was accumulated. This suggests that point defects (e.g. vacancies) were recovered by the annealing process and He bubbles did not trap D [14], at least within the sensitivity of our GD-OES instrument.

We next measured the permeation flux dependence on D_2 gas pressure at 873 K and 1173 K using W specimens irradiated by 3.0 keV He^+ . These data, shown in Fig. 3,

reveal that for both cases the D permeation flux was proportional to $\sqrt{P_D}$ and consistent with diffusion-limited release [17]. This is also the case for un-damaged W.

Fig. 4 summarizes our measured D permeabilities and diffusion coefficients for W damaged by 1.0 keV and 3.0 keV He⁺. For comparison, this is accompanied by measurements using un-damaged W, as well as other published experimental results within the temperature range of 873 – 1173 K [12]. Our D permeabilities for un-damaged W are in good agreement with Zakharov's results in the temperature range of interest here [6]. Pre-irradiation with 1.0 keV He⁺ decreased both the permeability and diffusion coefficient to about 1/3 and 1/4 of that for un-damaged W at 873 K, respectively. No accumulation of D was found by GD-OES as mentioned above 873 K, indicating that irradiation defects did not trap sufficient D as observed by GD-OES [12-13]. Therefore, we propose that He bubbles act as a diffusion barrier, leading to the aforementioned reduction of the D permeabilities and diffusion coefficients. The atomic ratio of W and He calculated by SRIM was 1:10 at the implantation range of 1.0 keV He⁺. This suggested that the decreased atomic concentration of W in the implantation region was not sufficient to account for the changes in the D permeability and diffusion coefficients that we observed.

The D permeabilities and diffusion coefficients for 3.0 keV He⁺ irradiated W were approximately 1-2 orders of magnitude lower than those for un-damaged W at 873 K. This difference diminished as the temperature increased, but was still present even at the highest temperature considered here (1173 K). Additional reduction of D permeabilities (by a factor of 0.2) and diffusion coefficients (by a factor of 0.05) were found at 873 K for 3.0 keV He⁺ irradiated W. GD-OES measurements detected D accumulation at 873 K but not at 1173 K. Therefore, it is possible that the D permeability and diffusion coefficient are mainly affected by D trapped at point defects at temperatures < 973 K. To verify this hypothesis, we performed the same measurements at 873 K using a specimen that had been previously heated to 1173 K. For both the permeability and

diffusion coefficient, this reduced the difference between the irradiated and un-damaged W by more than 50%. The permeability for 3.0 keV D_2^+ implanted into W was also reduced [15], but eventually reached the same value that was measured for un-damaged W as the sample was heated up to 1173 K [13]. Taking these results into consideration, it is possible that He bubbles worked as a diffusion barrier at higher temperatures (e.g. above 1073 K) [12-14]. Recovery of the D diffusion path through annealing is thought to be quite different, due to the differences in the nature of defects and/or whether the defects are stabilized by the presence of trapped He.

3.2 He^+ irradiation fluence dependence

TEM images for the 3.0 keV He^+ irradiated W specimens at various ion fluences (3.0 and $9.0 \times 10^{21} He^+ m^{-2}$) are shown in Fig. 5 as a function of heating temperature up to 1173 K. The density of dislocation loops, apparent in the images as black dots, increased with He^+ fluence. A similar trend was noted for the size of He bubbles, visible as white circles in the TEM images. The He bubbles became faceted as He^+ fluence increased.

We also considered the dependence of permeation flux on the D_2 gas pressure. Consider Fig. 6, which illustrates this dependence for the W specimen irradiated with He^+ to a fluence of $9.0 \times 10^{21} He^+ m^{-2}$. The permeation flux is proportional to the square root of D_2 gas pressure, indicating that the permeation is controlled by diffusion-limited release even in cases where extensive He^+ damage is present.

Finally, the measured D permeabilities for W damaged with varying fluences of He^+ are plotted in Fig. 7 in Arrhenius coordinates. For the lowest He^+ fluence considered here ($0.03 \times 10^{21} He^+ m^{-2}$), the permeability was agreed well with our measurements for un-damaged W within the uncertainty of our measurements. The D permeability began to diminish as the He^+ fluence increased up to $3.0 \times 10^{21} He^+ m^{-2}$. Beyond this, no large difference was observed up to $9.0 \times 10^{21} He^+ m^{-2}$. One possible explanation is that the

concentration of He bubbles and defects were not saturated at the lowest fluence considered here. The main effect from the He^+ exposure was the production of displacement damage in the form of point defects (e.g. vacancies). However, increasing the He^+ fluence eventually led to self-trapping, and the nucleation of a network of He bubbles near the surface [18]. Therefore, the He bubble density increased, leading to no additional reduction of permeability at higher He^+ fluence. Heating to 1173 K enhanced the D permeability for all cases (except for the W specimen exposed to a fluence of $0.03 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$), although not quite to the level observed for un-damaged W. We propose that the presence of He bubbles is closely related to the reduction of available D diffusion pathways through the material [14]. The D permeabilities at 873 K also decreased with increasing He^+ fluence.

Based on the above observations, the D permeability was reduced with increasing He^+ fluence due to the increase of the amount of He bubbles and defects at the fluence of less than $3.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$. However, no large difference of D permeabilities was found for W with the fluence of 3.0 and $9.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$ due to competition between the formation of defects and He bubbles.

4. Conclusions

In this study, W specimens were damaged by He^+ irradiation (over a range of energies and fluences). D gas-driven permeation measurements at various temperatures were then performed to evaluate the hydrogen isotope permeation in the presence of He bubbles.

D permeabilities and diffusion coefficients for He^+ irradiated W were lower than those for un-damaged W. This difference diminished as the test temperature was increased, but never fully recovered to its original value even when heating to 1173 K. This is thought to be due to the presence of He bubbles, which cannot be annealed out at these temperatures. Up to fluences of $3.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$, the D permeability decreased with

increasing He^+ dose, which we attribute to an increased concentration of He bubbles and defects. However, no large difference in D permeability was found for measurements up to $9.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$. By this point, He bubbles are thought to dominate diffusion within the near surface region; displacement damage is thought to only minimally contribute to this effect. By heating at 1173 K, the D permeability for W with higher He^+ irradiation was still remained lower than un-damaged W. Several factors associated with the presence of He bubbles could contribute to this observation including: (a) the reduction of the available of D diffusion pathways within the near-surface due to the high density of the He bubble network, and (b) the contribution of surface reactions (e.g. enhanced recombination) due to the bubble surface area. Therefore, we can conclude that the existence of He bubbles and stability of defects clearly reduce the D permeability and increase the contribution of surface reactions.

In comparison to W damaged by low energy D_2^+ implantation, the recovery mechanism of the D diffusion pathways is thought to be quite different, due to the nature of defects (i.e. whether they are vacancies, bubbles, etc.) and whether the defects are stabilized by the presence of trapped He.

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Fig.1 The diagram of the gas-driven permeation measurement instrument

Fig. 2 D and He depth profiles for each sample by GD-OES measurement and SRIM calculation, respectively.

Fig. 3 The D₂ gas pressure dependence of permeation flux for 3.0 keV He⁺ irradiated W with a fluence of $3.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$

Fig. 4 (a) The D permeabilities and (b) the D diffusion coefficient for 1.0 keV and 3.0 keV He^+ irradiated W, as compared with un-damaged W and other published experimental results.

Fig. 5 TEM images of the microstructures for the He^+ irradiated W at various fluences and as function of heating temperature up to 1173 K.

Fig. 6 The D₂ gas pressure dependence of permeation flux for 3.0 keV He⁺ irradiated W with a fluence of $9.0 \times 10^{21} \text{ He}^+ \text{ m}^{-2}$

Fig. 7 The D permeability for He⁺ irradiated W with various fluence

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