Bi-Directional Hydrogen Permeation through F82H under DEMO-Relevant Conditions*)

Haishan ZHOU, Yoshi HIROOKA[1)], Naoko ASHIKAWA[1)], Takeo MUROGA[1)] and Akio SAGARA[1)]

Department of Fusion Science, The Graduate University for Advanced Studies, Toki 509-5292, Japan
[1)]*National Institute for Fusion Science, 322-6 Oroshi, Toki 509-5292, Japan*

(Received 9 December 2012 / Accepted 1 April 2013)

Using a laboratory-scale plasma device, plasma-driven and gas-driven permeation of hydrogen through a ferritic steel alloy: F82H has been investigated under some of the DEMO-relevant conditions. The steady state plasma-driven permeation flux has been found to be strongly affected by the variation in upstream surface morphology resulted from plasma bombardment. The activation energy of permeability for gas-driven permeation has been estimated to be ~0.5 eV, which is close to the result of plasma-driven permeation. Gas-driven permeation can occur in the opposite direction of plasma-driven permeation, which then results in an increase in first wall recycling.

Keywords: plasma-driven permeation, gas-driven permeation, reduced activation ferritic steel, first wall, hydrogen plasma, Force-Free Helical Reactor

DOI: 10.1585/pfr.8.2402065

1. Introduction

In a number of recent DEMO reactor studies such as FFHR [1], the breeder serves as a coolant as well in the blanket structures. The first wall is defined as the plasma-facing surfaces of the blankets which are required to operate at elevated temperatures for an efficient heat exchange. Also, to reduce thermal stresses, the thickness of the first wall is often limited to less than 1 cm. In the case of FFHR, molten salt FLiBe has been employed as a self-cooled breeder and the tritium overpressure is $\geq 10^4$ Pa [2]. Under these conditions, the first wall will be subjected to bi-directional permeation of hydrogen isotopes: (1) one surface is to be exposed to the plasma, leading to plasma-driven permeation (PDP) of deuterium as well as tritium into blankets [3–8]; and (2) the other surface is to be exposed to bred tritium in blankets, depending upon its dissociation pressure, which can result in significant gas-driven permeation (GDP) of tritium back to the edge plasma [8–11]. If plasma-driven permeation dominates, deuterium flowing into the blanket will hinder the recovery of tritium and will probably necessitate isotope separation as well. On the other hand, if the opposite is true, gas-driven permeation will result in an increase in first wall recycling. Due to their critical importance to steady state reactor operation, these technical issues must be clearly addressed.

In our recent studies [7, 8], plasma-driven and gas-driven hydrogen permeation through a reduced activation ferritic steel alloy: H82H have been investigated by a laboratory-scale plasma device, VEHICLE-1 [12]. Both plasma-driven permeation and gas-driven permeation have been found to be essentially diffusion-limited. For a 5 mm F82H membrane, the PDP flux at ~500 °C and the GDP flux at ~350 °C have been measured to be of the orders of 10^{13} H/cm^2/s and 10^{15} H/cm^2/s, respectively.

In the present work, further experiments on PDP and GDP through F82H have been conducted, using a new heating setup. These separate PDP or GDP experiments are used to characterize the mechanism of hydrogen permeation through F82 H. To investigate the effect of GDP on first wall recycling, preliminary bi-directional hydrogen permeation experiment has also been run under some of the DEMO-relevant conditions.

2. Experimental

The experimental details for PDP or GDP have already been described in [7, 8]. Shown in Fig. 1 is a schematic diagram of the bi-directional permeation setup in VEHICLE-1. The F82H membrane has been fixed in such a way that the upstream surface is exposed to hydrogen plasma, while the other side is exposed to hydrogen gas with a pressure of ~100 to ~760 Torr, which is measured by an absolute pressure gauge. The sample membrane can be heated up to >500 °C by plasma bombardment and heat from a heater. The plasma-facing side of the membrane is monitored by an optical spectrometer. Plasma parameters are as follows: the plasma density is of the order of 10^{10} cm^{-3}, the electron temperature is around

author's e-mail: zhou.haishan@LHD.nifs.ac.jp
*) This article is based on the presentation at the 22nd International Toki Conference (ITC22).

Table 1 Summary of the PDP experiments.

Thickness (mm)	ECR power (W)	Membrane temperature (°C)	T_e (eV)	N_e (cm^{-3})	Estimated net implantation flux ($H{\cdot}cm^{-2}{\cdot}s^{-1}$)	Measured permeation flux ($H{\cdot}cm^{-2}{\cdot}s^{-1}$)	Steady state PDP flux ratio
5	~550	~520	3.5	3.0×10^{10}	2.0×10^{16}	3.9×10^{13}	1.9×10^{-3}
2			3.4	2.7×10^{10}	1.8×10^{16}	3.5×10^{13}	1.9×10^{-3}
1			3.3	3.1×10^{10}	1.9×10^{16}	8.5×10^{13}	4.5×10^{-3}
5	~300	~220	2.6	1.0×10^{10}	5.2×10^{15}	3.6×10^{12}	7.0×10^{-4}
2			2.4	9.6×10^{9}	4.6×10^{15}	7.7×10^{12}	1.7×10^{-3}
1			2.7	1.1×10^{10}	5.9×10^{15}	2.2×10^{13}	3.8×10^{-3}

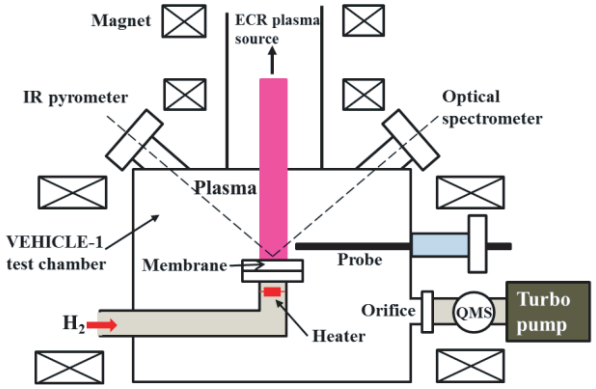

Fig. 1 A schematic diagram of the bi-directional permeation setup in VEHICLE-1.

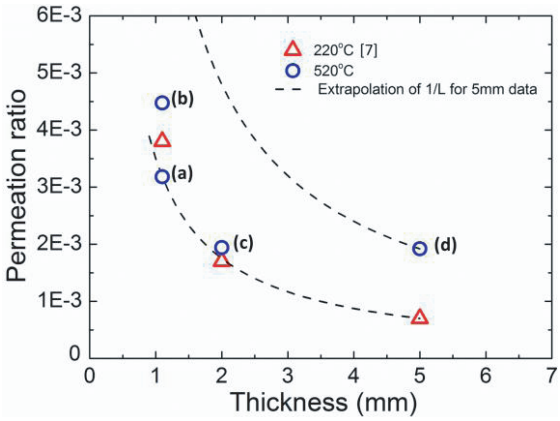

Fig. 2 F82H membrane thickness dependence of steady state PDP flux ratio. The surface morphologies of the membranes after PDP experiments at ~520 °C are shown in Fig. 3.

10 eV and the neutral hydrogen pressure is of the order of 10^{-4} Torr. A relatively high electron temperature is set so that hydrogen released from upstream surface can be ionized more easily, increasing the sensitivity of H_α measurement. The diameter of the cylindrical plasma column is ~70 mm. An orifice with a 2 mm diameter hole has been installed so that a quadrupole mass spectrometer (QMS) can be used to measure H_2 partial pressure within the operational pressure. Under such experimental conditions, if the recycling condition of the membrane surface changes, variation in H_α intensity and hydrogen partial pressure are expected to be detected.

The membrane surface before and after permeation experiment is analyzed by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) as a routine procedure. The XPS analysis is performed after ~10 s Ar^+ sputtering at 4 kV to remove contamination from the air [13].

3. Results and Discussion

3.1 Plasma-driven permeation

Plasma-driven permeation experiments have been conducted with 1, 2 and 5 mm thick F82H membranes at 220 °C and 520 °C, respectively. To heat the membrane to > 500 °C, a higher ECR power is used. The details of the experiments are summarized in Table 1. Shown in Fig. 2 are the hydrogen permeation data taken from PDP experiments. At 220 °C, the steady state permeation flux ratio of F82H is inversely proportional to the membrane thickness, which agrees with prediction by the steady state permeation model for diffusion-limited PDP [5, 7]:

$$\frac{J_+}{J_0} = \frac{D}{L\sqrt{K_0 J_0}} \tag{1}$$

where J_+ is the permeation flux; J_0 is the net implantation flux; D is the diffusion coefficient; L is the membrane thickness and K_0 is the upstream recombination coefficient.

However, at a higher temperature (~520 °C) and higher plasma fluxes, the plasma-driven permeation flux has been found to be strongly affected by the surface condition of the membrane. Figure 3 shows the SEM images of the F82H membranes before and after PDP experiments at a sample temperature of ~520 °C. The surface morphologies of these membranes differ from each other because unfortunately the total plasma exposure times for the four samples are not well controlled. In the present PDP experiments, hydrogen reemission from the upstream is generally controlled by molecular recombination [7, 8]. The

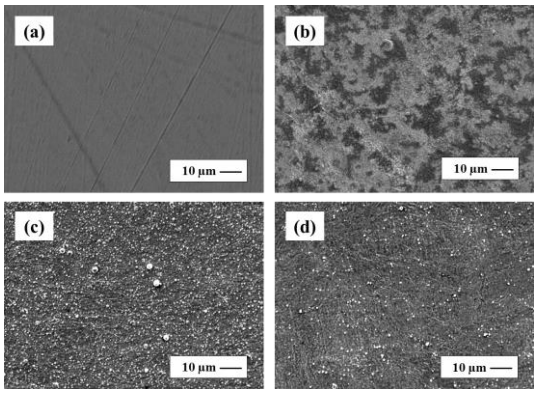

Fig. 3 SEM images of the upstream surface: (a) before and after a few hours of experiment; (b) 1 mm thick membrane after ~ 112 hours PDP+GDP; (c) 2 mm thick membrane after ~ 27 hours PDP+GDP and (d) 5 mm thick membrane after ~ 30 hours PDP+GDP.

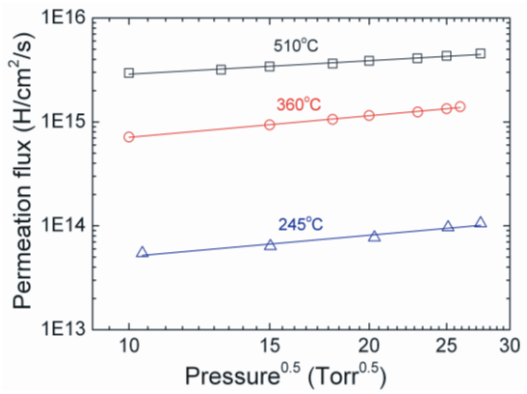

Fig. 4 Steady-state hydrogen GDP flux through a 1 mm thick F82H membrane at temperatures of ~ 245 °C, ~ 360 °C and 510 °C.

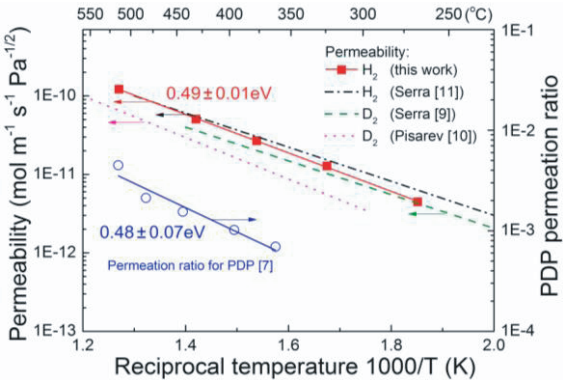

Fig. 5 Permeability for GDP and permeation ratio for PDP through a 1 mm thick F82H membrane. The experimental condition for the PDP experiment can be found in table 1.

change in surface area resulted from plasma bombardment would lead to a variation in hydrogen desorption at the upstream [14].

3.2 Gas-driven permeation

The steady state GDP data have been taken for F82H membranes at temperatures between ~ 245 °C and ~ 510 °C. Shown in Fig. 4 are the GDP data in which one can find a linear relation between GDP flux and the square-root of upstream pressure at all the temperatures examined in this work. These experimental data agree with the theoretical prediction for the steady state diffusion-limited GDP flux given by:

$$J_{\mathrm{GDP}} = D(T)K_{\mathrm{S}}(T)\frac{(P_{\mathrm{h}}^{0.5} - P_{\mathrm{l}}^{0.5})}{L} \qquad (2)$$

where J_{GDP} is the steady state GDP flux, K_{S} is Sieverts' constant, P_{h} and P_{l} are the hydrogen pressures on the high and low pressure sides, respectively. In our experiment, $P_{\mathrm{l}} = 0$ is assumed. Notice that the experimental data lines don't appear to intersect the zero point at $P_{\mathrm{h}} = 0$, which is presumably due to the desorption of residual hydrogen from previous experiments.

The permeability can be estimated by

$$\Phi(T) = D(T)K_{\mathrm{S}}(T) = J_{\mathrm{GDP}}L/P_{\mathrm{h}}^{0.5}. \qquad (3)$$

Figure 5 shows the temperature dependence of permeability for F82 H. Some literature data are also shown for a comparison in which one can find that our data is in good agreement with Serra's. From the Arrhenius plot the activation energy of permeability, E_{GDP}, is estimated to be 0.49 eV, which is very close to the result (indicated with E_{PDP}) obtained from our previous PDP experiment [7]. These data suggest that the rate-limiting steps in these PDP and GDP experiments could be the same. According to Eq. (3) E_{GDP} can be given by $E_{\mathrm{GDP}} \approx E_{\mathrm{D}} + E_{\mathrm{Ks}}$, where E_{D} and E_{Ks} are the activation energies of diffusion and solution. On the other hand, for PDP taking place in the RD-regime, E_{PDP} is related to the activation energies for surface recombination (E_{K0}) and diffusion as $E_{\mathrm{PDP}} \approx E_{\mathrm{D}} - 0.5E_{\mathrm{K0}}$. In the present PDP and GDP experiments, the temperature dependent data are taken by continually reducing the heater power, in which case residual hydrogen always exists inside the membrane. Under such condition the effect of upstream surface recombination or solution on hydrogen permeation would be less significant and diffusion will be the main driving force in downstream hydrogen release for both PDP and GDP.

For the blankets employing FLiBe as the self-cooled breeder, the tritium overpressure is ~ 100 Torr at a temperature around 500 °C [2]. Under this condition, the steady state GDP flux through a 1 mm thick F82H membrane has been measured to be $\sim 2.9 \times 10^{15}$ H·cm^{-2}·s^{-1}, which is about one order of magnitude larger than that of PDP. This result suggests that gas-driven permeation could dominate the hydrogen isotope transport through the first wall of FLiBe-employed blankets.

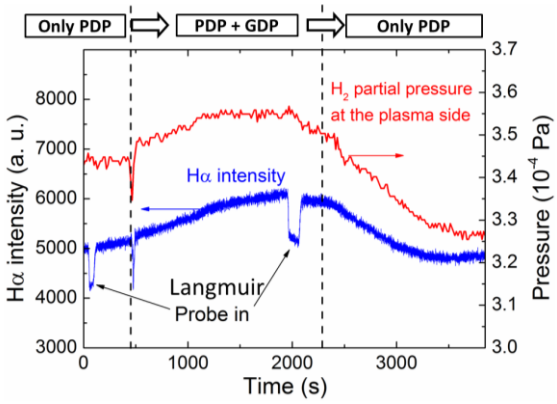

Fig. 6 H2 partial pressure and H_α intensity at the plasma side for a 1 mm thick F82H membrane. The sample temperature during the experiment is ~ 570 °C.

3.3 Preliminary data on bi-directional permeation

If the hydrogen isotope transport through the first wall is dominated by gas-driven permeation, first wall recycling will be increased when GDP happens. To verify such a prediction, a bi-directional hydrogen permeation experiment has been conducted. Shown in Fig. 6 is the result of bi-directional hydrogen permeation through a 1 mm thick F82H membrane at a temperature of ~ 570 ° C. The membrane is first exposed to a hydrogen plasma, in which case only PDP occurs. Then hydrogen is introduced from a gas cylinder into the closed volume to a pressure of 760 Torr, shown by the shaded area in Fig. 1. Langmuir probe measurements are performed before and after introducing hydrogen into the GDP volume. The plasma density is found to increase from 4.4×10^9 cm^{-3} to 5.7×10^9 cm^{-3}, while the electron temperature decreases from 11.5 eV to 9.8 eV. After the H_α signal becomes stable, hydrogen is pumped out again. A significant decrease of H_α intensity can be observed after pumping. These data indicate that GDP can occur in the opposite direction of PDP and increase in first wall recycling. From the extrapolation of the temperature dependent data, at a temperature around 570 °C the permeation fluxes through a 1 mm thick F82H membrane for PDP and GDP have been estimated to be $\sim 1\times10^{14}$ H·cm^{-2}·s^{-1} and $\sim 1\times10^{16}$ H·cm^{-2}·s^{-1}, respectively.

After this bi-directional permeation experiment the plasma-facing surface of the F82H membrane has been found to be oxidized. Energy dispersive X-ray spectroscopy shows there is no major impurity on the surface. In the following XPS analysis, the C, O, Cr, Fe and W peaks have been detected and the atomic composition is: C = 8.04 at.%, O = 49.02 at.%, Cr = 9.72 at.%, Fe = 26.10 at.% and W = 7.12 at.%. Oxygen should come from the residual water in the vacuum chamber.

4. Conclusion

Hydrogen permeation driven by plasma and gas has been investigated experimentally with VEHICLE-1 for F82H membrane under some of the DEMO-relevant conditions. Plasma-driven permeation can be reduced by modifying upstream surface condition. Gas-driven permeation may occur in the opposite direction of plasma-driven permeation, which then results in an unwanted increase in edge plasma density. However, details on bi-directional permeation are still unclear, especially on exchange of hydrogen isotopes inside the first wall and the effects of plasma bombardment on GDP which warrant more work on this subject.

Acknowledgement

The author would like to thank Mr. J. Yagyu, Dr. M. Sato, Dr. T. Nakano and Dr. A. Sakasai of JAEA, Naka for their material preparation.

[1] A. Sagara *et al.*, Fusion Technol. **39**, 753 (2001).
[2] S. Fukada *et al.*, Fusion Eng. Des. **83**, 747 (2008).
[3] R.A. Causey *et al.*, J. Nucl. Mater. **145-147**, 284 (1987).
[4] R.A. Kerst *et al.*, J. Nucl. Mater. **122&123**, 1499 (1984).
[5] B.L. Doyle *et al.*, J. Nucl. Mater. **111&112**, 628 (1982).
[6] M. Takizawa *et al.*, J. Nucl. Mater. **248**, 15 (1997).
[7] H. Zhou *et al.*, "Hydrogen plasma-driven permeation through a ferritic alloy F82H", Fusion Sci. Technol., in press (2013).
[8] Y. Hirooka *et al.*, "Plasma- and gas-driven hydrogen isotope permeation through the first wall of a magnetic fusion power reactor", Fusion Sci. Technol., in press (2013).
[9] E. Serra *et al.*, J. Nucl. Mater. **245**, 108 (1997).
[10] A. Pisarev *et al.*, Phys. Scr. **T94**, 121 (2001).
[11] E. Serra *et al.*, Mater. Sci. Technol. **14**, 573 (1998).
[12] Y. Hirooka *et al.*, J. Nucl. Mater. **337-339**, 585 (2005).
[13] N. Ashikawa *et al.*, "Edge-plasma interactions with low-activation ferritic steel alloys", Paper presented at the 22nd International Toki Conference, Toki, Japan, Nov. 19th - 22nd, 2012.
[14] Y. Hirooka *et al.*, Nucl. Instrum. Methods Phys. Res. **B23**, 458 (1987).