Surface condition effects on plasma driven permeation

M. Takizawa [a,*], K. Kiuchi [a], M. Okamoto [b], Y. Fujii [b]

[a] *Interfacial Studies Laboratory, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-11, Japan*
[b] *Research Laboratory for Nuclear Reactor, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan*

Abstract

Low energy plasma driven permeation (PDP) experiments were conducted with deuterium and a 10 μm type 304 SS membrane. Adsorbed non-hydrogen molecules like H_2O or D_2O on the upstream surface reduced the gas driven permeation (GDP) rate but enhanced the PDP rate. According to the steady state permeation model, this opposite role was evaluated by calculating recombination coefficients. The calculated values for different upstream surface conditions at 480 K were $K_{1A} = 1.4 \times 10^{-31}$ and $K_{1B} = 2.3 \times 10^{-33}$ (m^4/s). The former was obtained on condition that the water was eliminated and the latter that the water remained. In addition, K_{1B} was proved to have a larger activation energy. It indicates that such non-hydrogen molecules on the front surface obstruct dissociation and recombination there, which results in an enhanced PDP rate and a reduced GDP rate. © 1997 Elsevier Science B.V.

1. Introduction

The phenomena of large hydrogen permeation through a metal membrane exposed to hydrogen plasma have been paid attention to from the viewpoint of tritium leakage and superpermeable membrane pumps in fusion reactors. A lot of experiments for studying these phenomena have been carried out and several important factors to influence the permeation behavior have come to be recognized. The energy of upstream hydrogen and the surface condition are some of them. A wide range of hydrogen energy which should be taken into consideration for the surroundings of plasma in fusion reactors has been treated as the experimental conditions, e.g., gas, atom and ion [1,2]. Super-permeation, i.e., a quite high permeation probability (permeation rate is as large as injection rate) is achieved by reducing re-emission of dissolved hydrogen in the metal from the upstream surface. Low energy hydrogen tends to rise the permeation probability because it does not have enough energy to remove the non-metallic layer on the front surface which plays a role in obstructing the re-emission [3]. We have investigated PDP (plasma driven permeation) phenomena by using an ECR discharge device which produces low energy hydrogen plasma (~ eV) and can treat tritium. From the viewpoint that the surface condition leads tritium to permeate easily/hardly and to have large/small permeation probability, a lot of experiments have been conducted. In this paper, the experimental data of deuterium permeation rate through the austenitic stainless steel membrane in different upstream surface condition is shown, which gives fundamental and practical knowledge of hydrogen plasma and structural materials interactions in fusion reactors.

2. Theory

According to the permeation model which has been employed to describe the steady state when a hydrogen ion beam (> keV) is injected into the membrane, the permeation patterns are divided into four regimes, the RR-regime, RD-regime, DR-regime and DD-regime [4]. In the low energy case (< eV), only two regimes, the RR-regime and the RD-regime, will exist because the injection depth is nearly zero and the rate-determining step at the upstream side must be the recombination process. In this work, without treating high energy hydrogen, the description of these regimes is to be shortened as the R-regime and the D-regime.

* Corresponding author. Tel.: +81-29 282 6829; fax: +81-29 282 5922; e-mail: takizawa@sun2sarl.tokai.jaeri.go.jp.

Among permeation flux, J, implanted flux, ϕ, and re-emission flux, ψ, the following relationship is formed:

$$J = \phi - \psi. \tag{1}$$

The permeation flux, J, in the steady state of PDP is derived from Eq. (1):

R-regime

$$J = K_2\phi/(K_1 + K_2); \tag{2}$$

D-regime

$$J = D(\phi/K_1)^{0.5}/L. \tag{3}$$

K_1, K_2, D and L indicate the recombination coefficients of upstream and downstream surface, diffusion coefficient, and thickness of membrane, respectively. A small temperature dependence of the permeation rate is expected at the R-regime if K_1 and K_2 have nearly equal activation energy. The D-regime will have a large temperature dependence in the case that the activation energy of diffusion is much larger than that of recombination.

For GDP, the permeation flux J in the steady state can be written as

R-regime

$$J = K_1 K_2 S^2 P_1/(K_1 + K_2), \tag{4}$$

D-regime

$$J = DSP_1^{0.5}/L. \tag{5}$$

S and P_1 mean solubility constant and upstream pressure respectively. If K_2 is much larger than K_1, which is called the R_1-regime, the permeation rate J becomes $K_1 S^2 P_1$, and in the reverse case, the R_2-regime, $K_2 S^2 P_1$.

The transport parameter W defined by Brice and Doyle [4] is written as

PDP

$$W = L(\phi K_1)^{0.5}/D, \tag{6}$$

GDP

$$W = LK_1 SP^{0.5}/D. \tag{7}$$

Physically W is regarded as the ratio of characteristic diffusion time and characteristic recombination response time.

3. Experimental condition

The experimental apparatus used in this work can produce ECR discharge plasma whose character is, for example, $T_e < \sim 10$ eV, $n_e < \sim 5 \times 10^{16}/m^3$, and $T_i \sim$ room temperature [5]. The arrangement of the apparatus is shown in Fig. 1. PDP and GDP experiments can be done with or without discharging. A test membrane is isolated electrically and the energy of ion or electron impinging to the membrane can be controlled by giving bias voltage between the plasma and the membrane. In this work no bias voltage was added (the plasma potential was $< \sim 5$

A: Quadrupole Mass Spectrometer   H: Micro-wave Guide
B: Ionization Vacuum Gauge   I : Micro-waveGenerator
C: Capacitance Manometer   J : Turbo MolecularPump
D: Test Membrane   K: Thermo Couple
E: Magnet (0.0875T)   L: Lead-wire for Bias
F: Hydrogen Isotope Gas FeedInlet   M: Plasma Chamber
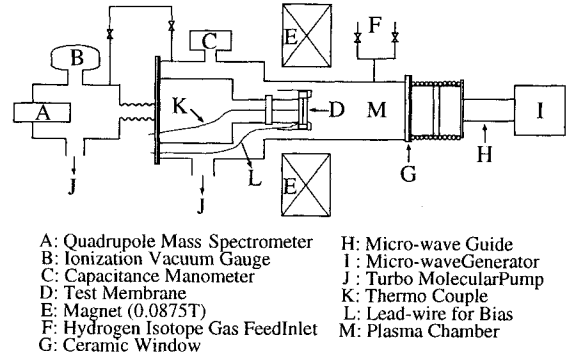G: Ceramic Window

Fig. 1. Arrangement of the experimental apparatus.

V). By calculation the main hydrogen particle form implanted to the membrane is considered to be the neutral atom in PDP experiments of this work. Type 304 SS with a thickness of 10 μm was used as a test membrane. The thickness was chosen because of the limit of detection sensitivity to measure the GDP rate around 70 Pa of the upstream pressure. The membrane temperature was measured and controlled by means of a thermocouple and a mantle heater. Preconditioning of the membrane, maintained at $\sim 10^{-5}$ Pa, 370 K for 9 h and exposed to hydrogen plasma for 1 h, was carried out to eliminate impurities on the surfaces. Baking of the device body for 9 h was also done. The surface condition is regarded as always equal after preconditioning because the permeation rate through the preconditioned membrane is reproducible. H_2O or D_2O exists in H or D plasma in this apparatus [6] and it cannot be easily pumped out even if the baking is fully carried out. The downstream side always maintained a high vacuum; not existing detectable water. So the upstream surface of the test membrane is considered to be covered with water as well as hydrogen. In this work, permeation experiments were conducted in two kinds of surface conditions. One was conducted just after the preconditioning and the other was one night after that, i.e., the test membrane was maintained in the highly vacuous and 'moist' plasma chamber. The latter results in more adsorbed water on the front surface remaining. In both cases, deuterium gas was introduced to the plasma chamber (the pressure was 66.6 Pa) and the permeation rate of deuterium through the test membrane was measured by a mass spectrometer.

4. Results

Fig. 2 shows the comparison of GDP and PDP rates observed under the different upstream surface condition at 66.6 Pa of upstream pressure. Case A is the result of the experiment just after the preconditioning mentioned above and case B is the result of one night after that. The PDP rate is larger than the GDP rate by one or two orders of

magnitude because of ionization or atomization of hydrogen molecules by means of plasma discharge. An apparent difference in temperature dependence is observed in PDP at about 480 K. This suggests that the permeation mechanisms are changed at the temperature. The effects of surface condition are that the apparent activation energies of GDP and PDP in case B are lower than those in case A, and that the GDP rate becomes lower but the PDP rate rises up in case B compared with case A. Similar experimental results and theoretical interpretations concerning this remarkable phenomenon have been reported, e.g., [7–9]. In this paper these surface condition effects on PDP and GDP will be estimated quantitatively as well as qualitatively with calculating recombination coefficients in the following.

5. Discussion

5.1. Rate-determining steps in PDP and GDP

The difference in temperature dependence in PDP between below and above about 480 K shown in Fig. 2 is considered to be caused by different rate-determining steps. Eq. (6) indicates that higher temperature condition makes W smaller when the activation energy of D is larger than half that of K_1 and austenitic stainless steel is in this case [10]. According to the definition of W, W becoming smaller brings about the R-regime. In addition, a small or large temperature dependence of permeation rate should appear as expected from Eqs. (2) and (3). So PDP above 480 K is interpreted to be governed by the R-regime and that below 480 K by the D-regime. We suppose GDP to be

rate-determined as R-regime since the apparent activation energies of permeation rate in both cases are smaller than that of the permeability for austenitic stainless steel, which disagree with the D-regime's requirement.

5.2. The roles of adsorbed water on the surface in GDP and PDP

The surface condition effects on hydrogen permeation in this work, i.e., the opposite role of adsorbed water on GDP and PDP shown in Fig. 2, can be considered qualitatively. The difference between GDP and PDP is the process of hydrogen's entrance into metal, that is with or without the dissociation of molecules on the front surface. Non-hydrogen molecules like H_2O or D_2O on the surface obstruct hydrogen molecules' dissociation and dissolution into the membrane in GDP. On the other hand, they block the recombination and re-emission of hydrogen atoms under the upstream surface in PDP. So the adsorbed water acts upon decreasing the concentration of hydrogen under the upstream surface in GDP but increasing that in PDP. There is a positive correlation between this concentration and the permeation rate in both GDP and PDP. Similar considerations have been reported from the point of view of superpermeable condition, e.g., [8,11,12].

5.3. Estimation of recombination coefficient

The opposite role mentioned above can be evaluated by calculating the recombination coefficients. In Fig. 2, PDP rate is considered to be given by Eqs. (2) and (3) above/below 480 K. In this case, we suppose that the both equations give the same value at 480 K because the transition gap is small and the difference of the PDP rate between case A and case B is caused by the change of K_1 only, because D, K_2 and ϕ can be regarded as constant even if the upstream surface condition varies. In addition we regard implantation probability as constant and roughly 1. With the reference value of diffusion coefficient (m^4/s) for type 304 SS [1],

$$D = 3.50 \times 10^{-8} \exp\left(-42.4 \times 10^3/RT\right),　(8)$$

the following values at 480 K are estimated:

$$K_2 = 2.4 \times 10^{-32} \left(m^4/s\right),　(9)$$

$$K_{1A} = 1.4 \times 10^{-31} \left(m^4/s\right),　(10)$$

$$K_{1B} = 2.3 \times 10^{-33} \left(m^4/s\right).　(11)$$

These mean the adsorbed water on the front surface reduces the value of recombination coefficient at 480 K. The implanted flux ϕ is given as

$$\phi = 6.3 \times 10^{18} \left(D/m^2 s\right).　(12)$$

Since ϕ does not change at any membrane temperature, activation energy of recombination coefficient can also be
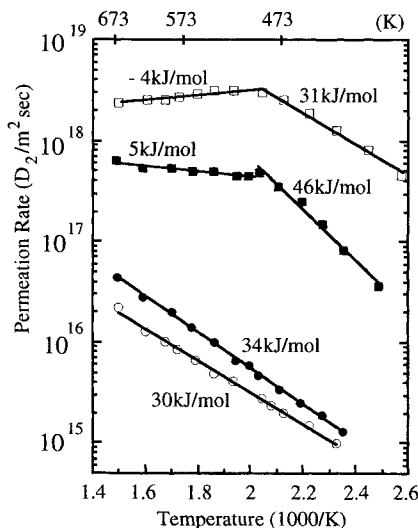
Fig. 2. PDP and GDP rate at different surface conditions. Upstream pressure: 66.6 Pa. ■: PDP in case A; □: PDP in case B; ●: GDP in case A; ○: GDP in case B.

estimated with Eqs. (2) and (3) fitted to the PDP rate in Fig. 2:

$$E_{1A} \sim -7 \ (kJ/mol), \tag{13}$$

$$E_{1B} \sim +22 \ (kJ/mol), \tag{14}$$

$$E_2 \sim 0 \ (kJ/mol). \tag{15}$$

The estimated large value of E_{1B} proves that the adsorbed water on the upstream surface obstructs the dissociation and the recombination there which results in the water's opposite role in PDP and GDP, and accords to the discussion in Section 5.2.

From the results of the GDP rate, the solubility constant of hydrogen for type 304 SS can be calculated with Eq. (4) by using K_1 and K_2 estimated above. The surface condition in case B would vary and could not be reproducible because discharging plasma during PDP experiments removes water on the upstream surface by degrees, which means K_{1B} in the PDP and GDP experiments may be a little different. Here we estimated S with K_{1A} and K_2.

$$S = 4.1 \times 10^{24} \exp(-17.3 \times 10^3 / RT). \tag{16}$$

This is within the scattered reference values [13–16], which means Ks which are used for Eq. (16) are appropriately evaluated.

6. Conclusions

To investigate the surface condition effects on low energy plasma driven permeation, permeation experiments for 10 μm type 304 SS membrane were conducted with ECR discharge plasma. Adsorbed non-hydrogen molecules,

D_2O on the upstream surface which play an opposite role on GDP and PDP, are evaluated by calculating the recombination coefficients. These molecules enlarge the activation energy of recombination, which indicates the adsorbed water on the front surface obstructs dissociation and recombination and results in enhancement of PDP rate and reduction of GDP rate.

References

[1] H.K. Perkins, T. Noda, J. Nucl. Mater. 71 (1978) 349.
[2] T. Tanabe, J. Nucl. Mater. 191 (1992) 444.
[3] R.A. Kerst, W.A. Swansiger, J. Nucl. Mater. 122&123 (1984) 1499.
[4] D.K. Brice, B.L. Doyle, J. Vac. Sci. Technol. A5 (4) (1987) 2311.
[5] M. Okamoto, T. Yoshida, M. Takizawa, M. Aida, M. Nomura, Y. Fujii, Fusion Technol. 14 (1988) 689.
[6] Y. Fujii, T. Yoshida, M. Nomura, M. Okamoto, Vacuum 40 (1990) 453.
[7] A.I. Livshits, Sov. Phys. Tech. Phys. 21 (2) (1976) 187.
[8] A.I. Livshitz, Vacuum 29 (1979) 103.
[9] M. Yamawaki, K. Yamaguchi, T. Kiyoshi, T. Namba, J. Nucl. Mater. 145 (1987) 309.
[10] B.L. Doyle, D.K. Brice, Radiat. Eff. 89 (1985) 21.
[11] A.I. Livshits, M.E. Notkin, A.A. Samartsev, J. Nucl. Mater. 170 (1990) 79.
[12] A.I. Livshits, M.E. Notkin, A.A. Samartsev, I.P. Grigoriadi, J. Nucl. Mater. 178 (1991) 1.
[13] N.R. Quick, H.H. Johnson, Metall. Trans. A10 (1979) 67.
[14] H.G. Nelson, J.E. Stein, NASA Rep. TND-7265 (1972).
[15] M.R. Louthan Jr., J.A. Donovan, G.R. Gaskey Jr., Nucl. Technol. 26 (1975) 192.
[16] J.R. Phillips, B.F. Dodge, AIChE J. 14 (1968) 392.