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Deuterium permeation through metals under hydrogen counter flow

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Abstract

Experiments on counter-permeation of deuterium (D) and hydrogen (H) through a nickel membrane were performed under diffusion limited condition, and transient between surface limited and diffusion limited condition. Deuterium permeation rates were measured as a function of upstream D_2 pressure, with hydrogen being permeated in the opposite direction by supplying H_2 gas at the downstream side of the membrane with respect to the D permeation. The deuterium permeation rate was found to decrease with increasing the counter H permeation. Significant deuterium permeation remained to be observed even when the deuterium upstream pressure was much lower than the downstream hydrogen pressure. These results are very similar to those observed for palladium (Pd) which showed surface limited permeation. The deuterium permeation rate under counter H permeation was reasonably well explained by a simple model based on surface limited permeation in which the ratios of the deuterium permeation rates with and without counter H permeation are proportional to the fractional concentration of deuterium in the surface layers. This implies that adsorption (absorption) of D_2 from the gas phase is inhibited, and also surface recombination of deuterium is blocked by hydrogen. This model can be extended from the surface limited permeation to diffusion limited one. The present model may be applied for energetic tritium (T) impinging case. Tritium permeation rate to the cooling channel can be estimated, when the surface concentration of the impinging tritium and hydrogen uptake at the cooling side are determined. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fuel recycling at the first wall and tritium (T) permeation to the environment are key issues for fusion reactor development. In most cases, only the tritium permeation from plasma side to the cooling side is considered [1–5]. At the cooling side, however hydrogen (H) uptake which is accompanied by water corrosion of the wall is not so small [6] that the dissolved H from the cooling side permeates to the plasma side. Accordingly deuterium (D) and T permeate through the wall under hydrogen counter flow.

In the previous work [7], the first experiments for counter-permeation of deuterium and hydrogen through a palladium (Pd) membrane (0.025 mm thick) under surface rate-limited condition [8] was performed. It was found that significant deuterium permeation occurred even when the deuterium upstream pressure was much smaller than the hydrogen downstream pressure. However, with increasing the counter H permeation, the deuterium permeation rate was found to be gradually reduced. These results were well represented by a simple model under following assumptions.

(i) The permeation is a surface limited process and no concentration gradient exists throughout the bulk.

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(ii) The bulk concentration of hydrogen (C_H) and deuterium (C_D) can be expressed by Sieverts' law [9].

(iii) The surface conditions are the same for both sides.

(iv) The surface areas available for D_2 and H_2 release are proportional to the fractions $C_D/(C_D + C_H)$ and $C_H/(C_D + C_H)$, respectively.

The applicability of this simple model to endothermic hydrogen occluder and under a diffusion limited condition is of current interest.

As a first step for the detail study of the counter-permeation mechanism of the three hydrogen isotopes (hydrogen, deuterium and tritium) and that of energetic impinging D and T, we need reliable data on the two component (H,D) counter-permeation by using a gas-driven permeation method. In the present work we have conducted the counter-permeation experiment in which deuterium and hydrogen permeate to the opposite directions. Nickel (Ni) was chosen for a sample membrane, because Ni, different from Pd, is an endothermic hydrogen occluder and shows diffusion limited permeation. In addition, this hydrogen permeation characteristics allowed us to simulate the phenomena in a stainless steel to be used for a fusion reactor.

2. Experimental

Fig. 1 shows the permeation apparatus. The system was separated into two vacuum chambers with a Ni membrane. Each chamber was evacuated by a rotary pump (RP) and turbo-molecular pump (TMP). The base pressure of the system was maintained below 1×10^{-6} Pa and was measured by an ionization vacuum gauge (IG). For convenience, the chambers are referred as "D side" and "H side", corresponding to the deuterium and the hydrogen gas injection side, respectively. The injected deuterium and hydrogen gas pressures in the chambers were monitored by ionization vacuum gauges (IG), a capacitance manometer (CM) and a quadrupole mass spectrometer (QMS). The relative sensitivity factor of the ionization vacuum gauge for hydrogen was calibrated to be 0.4, and the pumping speed of the system was 1.0×10^{-1} m^3 s^{-1} for both H_2 and D_2.

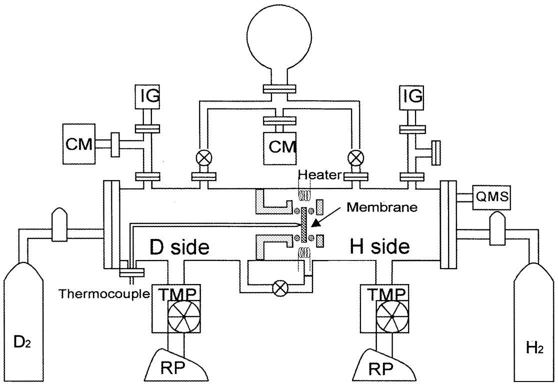

Fig. 1. Schematic diagram of the apparatus for counter-permeation measurements.

Experimental procedure of a 'counter-permeation' is as follows: (i) First, H_2 gas was introduced into the H side chamber to a fixed pressure to obtain a steady state permeation of hydrogen to the D side (where initially deuterium pressure was equal to zero), (ii) then D_2 gas was introduced into the D side, and the permeation D_2 flux to the H side was measured by QMS, and (iii) with the H_2 pressure being kept constant on the H side, the D_2 pressure on the D side was raised in a stepwise manner, and the resulting permeating D_2 flux to the H side was measured.

The deuterium permeation rate [$Q(t)$] through the membrane was determined from measurements of the partial pressure increment at the H side [$\Delta P_{D_2}(t)$] multiplied by the effective pumping speed of the system (S_{eff}):

$$Q(t) = \Delta P_{D_2}(t) \times S_{\mathrm{eff}}/(RT), \qquad (1)$$

where R and T are the gas constant and the gas temperature, respectively. The steady state permeation rate is given by,

$$J(\infty) = Q(\infty)/A, \qquad (2)$$

where A is the surface area of the membrane.

In the present work we could not determine the deuterium partial pressure on the H side directly. The permeated deuterium atoms may be equilibrated with H_2 at the Ni membrane surface and are released as D_2 ($m/e = 4$) and HD ($m/e = 3$). However the H_2 pressure on the H side was high enough to produce H_3 molecules ($m/e = 3$) in the ionizer of the QMS, several orders of magnitude larger than the observed HD. H_3 signal is by 3–4 orders of magnitude smaller than H_2 signal, but is still so large as to disturb the measurement of the permeation flux of HD. Therefore we estimated partial pressure of deuterium in the H side chamber from the D_2 signal ($m/e = 4$) in the QMS which was calibrated using a gas mixture of D_2 + H_2 in equilibrium in a separate system, assuming that the released D_2, HD and H_2 molecules were in equilibrium in the H side chamber. To confirm this assumption, we have conducted a "co-permeation" i.e. hydrogen and deuterium permeate simultaneously in the same direction. This procedure would give rise the maximum uncertainty of about 25% when deuterium pressure was at the minimum.

The Ni membrane (with a purity of 99.95%) was supplied by Nilaco, Japan. The thickness of the membrane was 0.01 or 0.1 mm with a surface area of 1.8×10^{-4} m^2. The membrane was fixed on a stainless steel sample holder using Cu gaskets without any vacuum leak, and was heated up to 1000 K by a molybdenum heater. The sample temperature was measured by a K-type thermocouple. Measurements were performed at a temperature of 800 or 950 K for D_2 pressure ranging from 7×10^{-4} to 10^3 Pa on the D side, with the H_2 pressure being set at 1.3×10^{-1}, 6.7×10^{-2} or 2.7×10^{-2} Pa.

3. Results and discussion

3.1. Co-permeation

In order to examine the accuracy of the calibration method, co-permeation of hydrogen and deuterium experiments were conducted using Pd membrane at surface limited condition. Hydrogen and deuterium gases were introduced simultaneously in the upstream side, and permeated H_2, HD and D_2 species were measured by QMS. The D_2 pressure was varied from 7×10^{-4} to 1 Pa with the H_2 pressure being set at 1.4×10^{-1} or 6.3×10^{-2} Pa. Fig. 2 shows the results of co-permeation experiments in a $J(\mathrm{HD})^2/J(\mathrm{H_2}) \times J(\mathrm{D_2})$ relation. The linear relation in the figure gives

$$J(\mathrm{HD})^2 = 4J(\mathrm{H_2}) \times J(\mathrm{D_2}). \tag{3}$$

This corresponds to the relation among the partial pressures in the down stream side,

$$P(\mathrm{HD})^2/P(\mathrm{D_2}) \times P(\mathrm{H_2}) = 4, \tag{4}$$

indicating the establishment of the equilibrium

$$\mathrm{H_2} + \mathrm{D_2} = 2\mathrm{HD},$$

where the equilibrium constant at higher temperatures is 4. This is the base for the assumption that the isotopic equilibrium should be established in the downstream side chamber in the counter-permeation experiments.

There is another important message from the co-permeation. Pd membrane is often used for isotopic separation for hydrogen, which is owing to the isotope effect in the co-permeation. In the present co-permeation experiment conducted such a low pressure of below 1 Pa, no significant isotopic effect was observed, and deuterium permeation flux (D_2 + 1/2 HD) was only proportional to the fractional concentration $[C_\mathrm{D}/(C_\mathrm{D}+C_\mathrm{H})]$ in Pd. This indicates no interaction between isotopes, probably because the bulk hydrogen concentration is so small.

3.2. Counter-permeation

At first, normal deuterium gas-driven permeation experiments were conducted with no H_2 gas injection to the H side chamber. The dependence of the steady state D_2 permeation rates $[J_0(\mathrm{D})]$ on the deuterium pressure in the D side chamber, with the Ni temperature at 800 (open square) and 950 K (open circle) are shown in Fig. 3. At above 10 Pa, the permeation flux shows the $P^{0.5}$ dependence, indicating the diffusion limited process, whereas below 10 Pa the permeation flux deviates downwards and shows the relation of $P^{0.7\text{–}0.9}$, suggesting the transition from the diffusion limited to the surface limited condition. The results of the D_2 counter-permeation $J(\mathrm{D})$ where $P_{\mathrm{H_2}} = 2.7 \times 10^{-2}$ Pa on the H side, are also shown in the figure [closed square (800 K) and closed circle (950 K)]. When deuterium pressure was much higher than the H_2 pressure, no reduction was observed. For H_2 below 1 Pa, however, the deuterium permeation was clearly suppressed by the existence of H_2

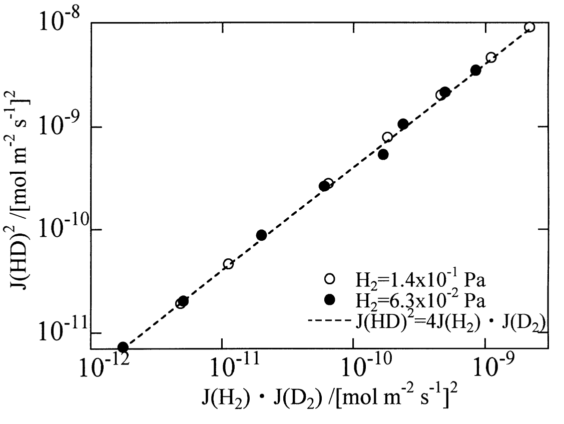

Fig. 2. The relation of co-permeation (H and D permeate to the same direction) flux of H_2, D_2 and H_D. $J(\mathrm{H_2}) \times J(\mathrm{D_2})$ vs. $J(\mathrm{HD})^2$.

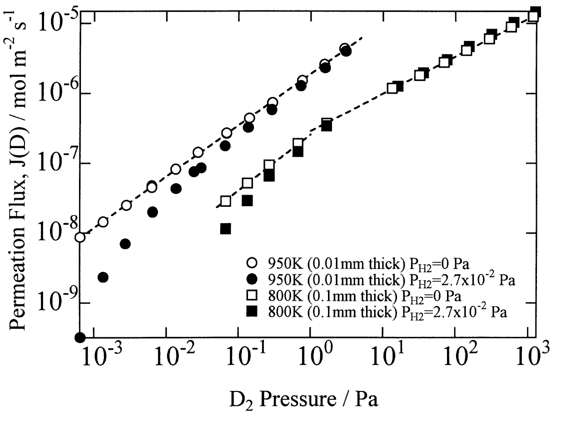

Fig. 3. Deuterium pressure dependence of the steady state deuterium permeation flux with H_2 ($P_{\mathrm{H_2}} = 2.7 \times 10^{-2}$ Pa, closed symbols) and without H_2 ($P_{\mathrm{H_2}} = 0$, open symbols) on either side at $T = 800$ (square symbols) and $T = 950$ K (circle symbols).

on the H side. In the following, we will focus on the 950 K results.

Fig. 4 shows sequential changes of deuterium permeation rates [J(D)] against D_2 pressure with a fixed H_2 pressure in the H side chamber. The rates were normalized by the J_0(D) measured without the counter H_2 permeation (i.e. $P_{H_2} = 0$, and shown as open circles in Fig. 3). Although the deuterium permeation was obviously suppressed by the existence of H_2 in the H side chamber, a significant amount of deuterium still permeated even when the H_2 pressure (on the H side) was higher than the D_2 pressure on the D side ($P_{D_2} < P_{H_2}$). These results are very similar to those observed for Pd [7]. This implies that the basic physics of the counter-permeation is the same in Ni (endothermic) and Pd (exothermic hydrogen occluder).

Therefore we have tried to apply a simple model which was very successful to describe the counter-permeation in Pd as demonstrated in the previous work [7]. The model is based on the assumption that the permeation rate is a surface limited process and no concentration gradient exists throughout the bulk. The concentration of hydrogen can be expressed as

$$C_H \propto S_H P_{H_2}^{1/2} \quad \text{and} \quad C_D \propto S_D P_{D_2}^{1/2}, \tag{5}$$

with S_H and S_D being the solubility for H and D, and P_{H_2} and P_{D_2}, the hydrogen pressure for H and D, respectively [9]. Suppose that the surface conditions are the same for both sides and the surface area available for H_2 and D_2 release are blocked by the fractions $C_D/(C_D + C_H)$ and $C_H/(C_D + C_H)$, respectively. Then, the permeating D_2 flux under the existence of H would be suppressed as

$$J(D)/J_0(D) = C_D/(C_D + C_H). \tag{6}$$

For the same reason, hydrogen permeation in the opposite direction should be reduced as

$$J(H)/J_0(H) = C_H/(C_D + C_H), \tag{7}$$

but this was not measured in the present work. Substituting Eq. (5) into Eq. (6), yields

$$J(D)/J_0(D) = P_{D_2}^{1/2}/[P_{D_2}^{1/2} + (S_H/S_D) \times P_{H_2}^{1/2}]. \tag{8}$$

Experimental values were compared with the simple model (Eq. (8)) in Fig. 4 (dotted line). A solubility ratio of H and D, S_H/S_D, is 1.2 at 950 K as has been given by Hawkins [10]. It is evident that Eq. (8) predicts the experimental data quite well, though the permeation in Ni is not fully in the surface limited but in the transient condition ($P^{0.7-0.9}$), probably because, interaction between the isotopes in the bulk is very small, as was observed in the co-permeation in Pd. Thus the suppression of deuterium surface concentration by the hydrogen in solution, or surface blocking by H atoms is very likely. This means the permeation is controlled simply by sub-surface concentrations. And also, if C_D and C_H are sub-surface concentrations, Eq. (8) can be applied for diffusion limited permeation. Of course, if the hydrogen pressure is significantly large, deviation from Eq. (8), that originates from H–D interaction in the bulk and/or in the diffusion process as appeared in the isotope effect in Ni membrane, shall be observed.

The present model can be applied for energetic tritium T or deuterium D impinging case using Eq. (8), if its near surface concentration can be estimated. For example, IDP (ion-driven permeation) and PDP (plasma-driven permeation) are considered. Here, assuming that hydrogen counter flow is supplied by the gas injection at the downstream surface. Energetic T and D injected in the sub-surface are not necessarily equilibrated in the bulk and easily penetrate to the both surfaces. However, the release of T and D are likely blocked by hydrogen at the downstream surface as observed in this work. As a result, T and D recombination flux to the upstream side may be enhanced. Of course, this effect depends how

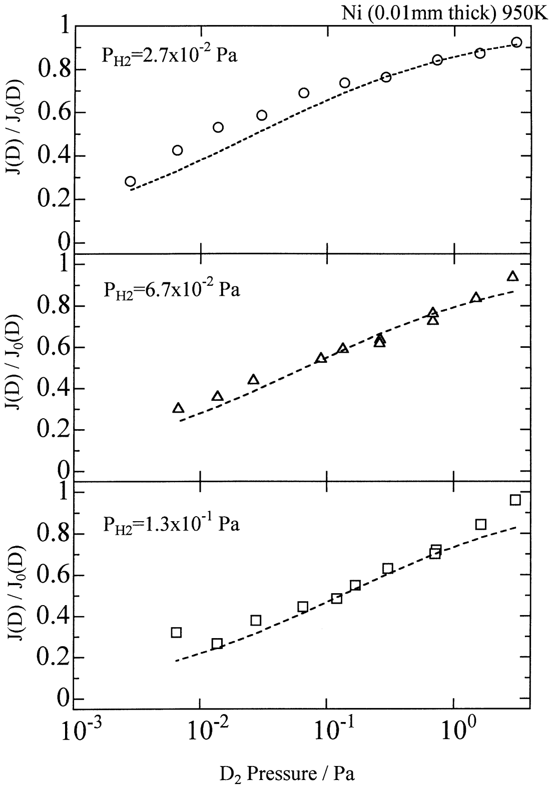

Fig. 4. Normalized deuterium permeation rates as a function of D_2 pressure with counter hydrogen permeation (i.e., D_2 on the D side and H_2 on the H side). Dotted line is estimated values by the simple model given by Eq. (8).

much hydrogen is taken up at the downstream surface and, therefore, the estimation of hydrogen uptake which is accompanied by water corrosion of the wall at the cooling side is important.

4. Conclusion

The counter-permeation experiment through nickel membrane was conducted by using a new experimental system in which deuterium (D_2) and hydrogen (H_2) permeate to the opposite directions. In the present experimental conditions, deuterium permeation through Ni was found to be diffusion limited (>10 Pa) or to be near surface limited condition (<1 Pa). Deuterium permeation rate was observed to decreased with increasing hydrogen counter flow (increase of H_2 pressure at the H side). However the counter deuterium permeation was remained to be observed, even if deuterium pressure in the D side was much lower than hydrogen pressure in the H side. These results are very similar to those observed for Pd.

It was found that the deuterium permeation rates with and without the counter H permeation was proportional to the fractional concentration of deuterium $[C_D/(C_H + C_D)]$ in the bulk. This relation was derived from a simple model in which the permeation is surface limited and there is no difference in the concentration of hydrogen at both surfaces, and successfully applied to Pd. The permeation in Ni was not completely in surface limited condition. Nevertheless, the results fit very well to the model. Probably because, the interaction between both isotopes in the bulk is very small, as observed for the co-permeation through Pd. This implies that adsorption (absorption) of D_2 from the gas phase is inhibited, and also surface recombination of deuterium is blocked by hydrogen.

The present model can be applied for energetic tritium T and deuterium D impinging case if the near surface concentration can be estimated. And T and D recombination flux to the upstream side may be enhanced, if hydrogen solution at downstream surface is comparably large with T and D injection. Therefore, the estimation of hydrogen uptake which is accompanied by water corrosion of the wall at the cooling side will be important.

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