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Asymmetric surface recombination of hydrogen on palladium exposed to plasma

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Abstract

Recombination coefficient of deuterium on either side of a palladium membrane was experimentally studied. Under conditions that one side of the membrane was continuously exposed to a deuterium plasma and the permeation flux was monitored on the other side, two experiments were conducted. One was to observe the transient behavior of the permeation when the incident flux from the plasma was quickly changed and the other was to observe the deuterium concentration by the nuclear reaction analysis. The permeation was limited by the second-order kinetics with respect to deuterium concentration, and the recombination coefficient k_u on the plasma-facing side was expressed by $k_u = 1.5 \times 10^{-27} \exp(-0.48\ \mathrm{eV}/kT)\ \mathrm{m}^4\,\mathrm{s}^{-1}$, which is explained by the Pick's model. The recombination coefficient k_d on the downstream side was the same as k_u at lower temperatures but showed different temperature dependence above 400 K. This can also be explained by the model but another process of the second-order kinetics may be present.

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Keywords: Plasma–wall interactions; Palladium; Hydrogen; Recombination; Nuclear reaction analysis; Coverage

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1. Introduction

The recombination of hydrogen, in which two atoms recombine to form a molecule, is often the rate-determining process for hydrogen desorption from surface, and hence the recombination coefficient is important for evaluating both hydrogen recycling and tritium inventory in plasma-facing materials. The recombination coefficient is a phenomenological constant and is generally a function of the rate constants for some surface processes [1–4]. It is difficult to predict actual values due to lack of sufficient information on the processes and investigation on recombination is still needed.

In the present work, the recombination coefficient on palladium, exposed to deuterium plasma, is experimentally studied by transient permeation measurement [5] and the in situ observation of concentration [6]. There have been reported some features in palladium, for example, a coverage-dependent recombination [7] and a difference of recombination between a hydrogen-facing side and a vacuum-facing side [8]. These features are expected to be examined by our experimental system and the results would help to understand a mechanism of the recombination phenomena. In addition, palladium is being employed for practical use such as separating hydrogen isotopes from mixed gas in fusion technology. The values of the recombination coefficient will be of use, but available data [8,9] are not so many.

2. Experiment

Two experiments on deuterium permeation through palladium were performed. One was an observation of the transient behavior of the permeation when incident flux of deuterium was quickly changed. The other was an in situ observation in which the permeation flux and

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the deuterium concentration were observed simultaneously. In both experiments, a palladium sheet with 0.1-mm in thickness and 99.95% in purity was used for samples.

In the transient permeation experiment, the sample was mounted between two vacuum chambers; one was an upstream-side chamber in which a discharge tube for deuterium plasma was located and the other was a downstream-side chamber in which a quadrupole mass analyzer was set to monitor the permeation flux. In order to observe the transient behavior of permeation, a mechanical shutter was installed between the sample and the discharge tube. The shutter had two areas, one with a large hole and the other with some small holes, to change the incident flux of deuterium from the plasma in a short time, typically 30 ms. Details of the experimental setup have been explained elsewhere [5].

In the in situ experiment, the components of the setup were essentially the same as above, except that a system for the nuclear reaction analysis (NRA) was installed instead of the shutter. A probing beam of 0.8-MeV $^3He^+$ ions from a 4 MV Van de Graaff Accelerator of Kyoto University irradiated the upstream side of the sample at 45° to the surface normal and protons produced by the reaction $D(^3He,p)^4He$ were detected by a solid-state detector located at a scattering angle of 174.3°. The energy spectrum of the protons was converted into a depth profile of deuterium [10] from surface to around 0.5 μm depth. Details of the in situ experiment have been explained elsewhere [6].

To minimize the effects of irradiation, the beam flux was restricted to 1×10^{16} m^{-2} s^{-1} and the beam dose per measurement was less than 1×10^{19} m^{-2}. During the NRA, the sample was continuously exposed to the plasma and the permeation flux was simultaneously monitored.

3. Results

3.1. Transient permeation experiment

The transient behavior of the deuterium permeation was observed between 398 and 571 K. When the shutter was set to the large hole and the permeation flux J_i became constant, the shutter was quickly moved to the small holes at $t = 0$ and the decrease in the permeation flux $J(t)$ was monitored until it became constant, J_f. In this case of decrease evolution, $J_i > J_f$. A typical decrease curve of $J(t)$ at 452 K is shown in Fig. 1. An increase curve when the shutter was moved from the small holes to the large one ($J_i < J_f$) is also shown.

The permeation flux begins to change at $t = 0$ without any time-lag in each curve, which indicates the permeation is not limited by the diffusion process. When the desorption of deuterium from each side is limited by the second-order kinetics with respect to deuterium concentration, $J(t)$ is expressed as [11,12]

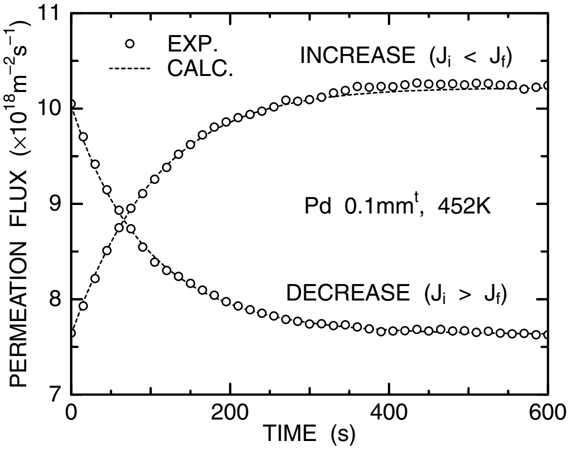

Fig. 1. Typical evolution curves in permeation flux of deuterium at transient state.

$$J(t) = J_f \left[\frac{A(t) - 1}{A(t) + 1} \right]^2, \tag{1}$$

$$A(t) = \frac{\sqrt{J_f} + \sqrt{J_i}}{\sqrt{J_f} - \sqrt{J_i}} \exp(\lambda t), \tag{2}$$

$$\lambda = \frac{2(k_u + k_d)\sqrt{J_f}}{L\sqrt{k_d}}, \tag{3}$$

where L is the sample thickness, k_u and k_d the recombination coefficients at the upstream and the downstream sides, respectively. The parameter λ has to be fitted to the evolution curve. The results of the calculation with these equations agree well with the experimental data as shown in Fig. 1. In the temperature range investigated, all the other data can also be well reproduced by the calculation. This confirms the assumption of the second-order kinetics.

In order to estimate k_u and k_d, a parameter y is introduced. It is a function of k_u and k_d and derived from Eq. (3) as

$$y = (k_u + k_d)/\sqrt{k_d} = L\lambda/2\sqrt{J_f}. \tag{4}$$

The temperature dependence of y is shown in the Arrhenius diagram of Fig. 2. The values of y do not form a straight line. This suggests that k_u and k_d are different from each other.

Fig. 3 shows the temperature dependence of the steady-state permeation flux J in case of the large hole. From the particle balance at the steady state, J is expressed as

$$J = F \cdot k_u/(k_u + k_d), \tag{5}$$

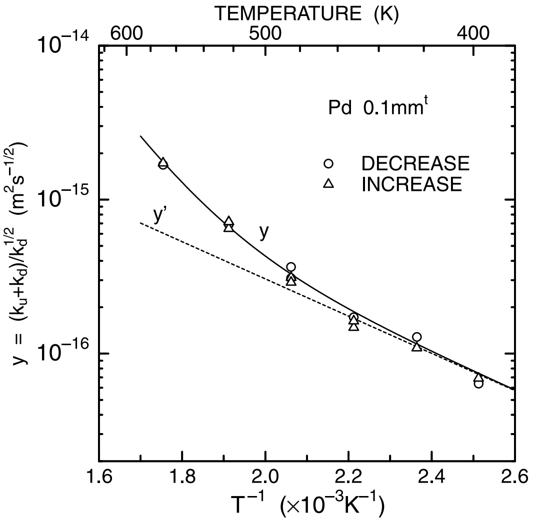

Fig. 2. Temperature dependence of a parameter y. y is a function of recombination coefficients and explained in the text.

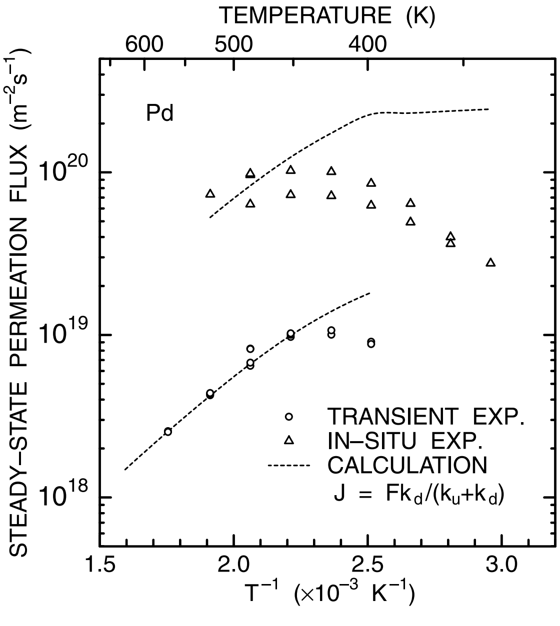

Fig. 3. Temperature dependence of the steady-state permeation flux in the transient permeation experiment (circles) and in the in situ observation experiment (triangles).

where F is the incident flux of deuterium. From Eqs. (4) and (5), the recombination coefficients can be derived. The incident flux from the rf plasma, however, is difficult to determine and is not always a constant value as will be discussed later. So k_u and k_d cannot be determined from the transient experiment only.

3.2. In situ observation

The temperature dependence of the steady-state permeation flux during the in situ observation is shown in Fig. 3. The sample was closer to the discharge tube than in the transient experiment, the permeation flux became higher and was observed at a very low temperature of 338 K.

A deuterium depth profile observed by the NRA showed a peak at the surface and a plateau in the bulk. This profile was a typical one that has also been observed in our previous works [13,14]. The peak area and the height of the plateau correspond to the areal density S of absorbed deuterium on surface and to the concentration C of dissolved deuterium in the bulk, respectively. Both S and C increased with decreasing temperature as shown in Fig. 4.

From C in Fig. 4 and J in Fig. 3, the recombination coefficient on the downstream side, k_d, can be directly obtained from the relation $J = k_dC^2$, assuming that C is uniform over the sample and all deuterium atoms are dissolved. The results are shown by circles in Fig. 5. In the experiment, the NRA was conducted twice at each temperature except for the highest and the lowest ones. If traps were produced by the probing beam, the apparent value of k_d at the first observation should be lager than that at the last one but the data showed no hysterisis. No traps contributed to the concentration. Some scattered data in Figs. 3 and 4 are attributed to instability of the plasma.

The value of k_u is estimated from Eq. (4) by substituting k_d and y. In the estimation, an asymptotic line, y' in Fig. 2, of y at lower temperatures is applied below 400 K. The results are shown by triangles in Fig. 5. Below

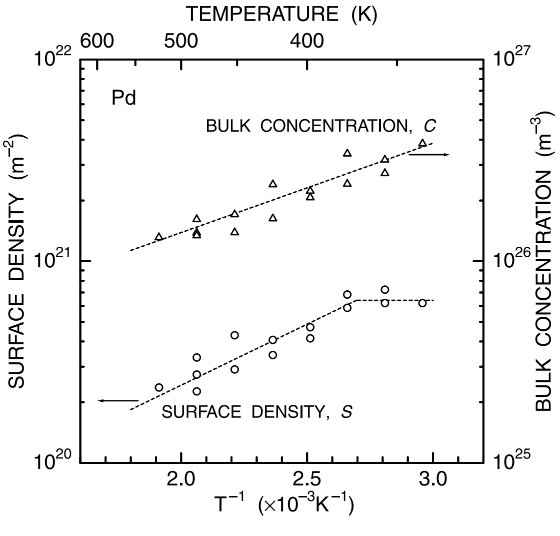

Fig. 4. Temperature dependence of the surface density S and the concentration in bulk C of deuterium observed by the NRA.

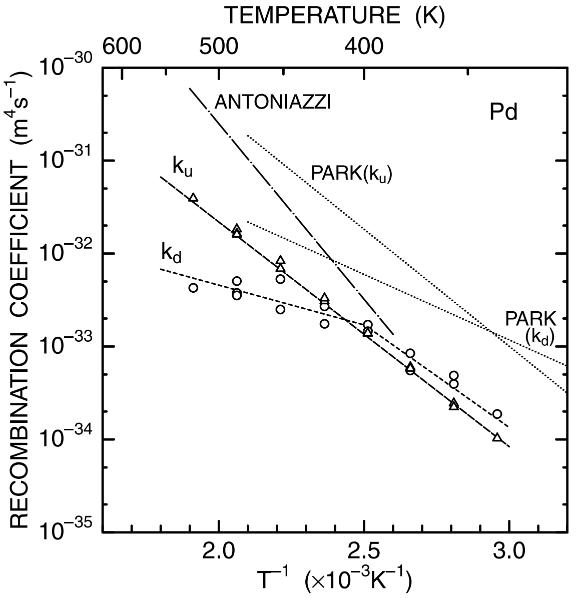

Fig. 5. Temperature dependence of the recombination coefficients k_u on the upstream side and k_d on the downstream side. Data for hydrogen by other researchers' works [8,9] are also shown.

400 K, k_d is very close to k_u but deviates at higher temperatures. From Fig. 5, k_u is found to be expressed by one Arrhenius relation of

$$k_u = 1.5 \times 10^{-27} \exp(-0.48\ [\mathrm{eV}]/kT) \quad [\mathrm{m^4\,s^{-1}}]. \tag{6}$$

The energy term in Eq. (6) is close to that for k_u by Park et al. [8] although absolute value of k_u is slightly different. Data by Antoniazzi et al. [9] agree with k_u of the present work below 500 K (see Fig. 4 in Ref. [9]).

4. Discussion

The permeation flux J estimated by Eq. (5) with k_u and k_d is shown by broken lines in Fig. 3, where constant values of F are assumed in both the cases in the transient and the in situ experiments. The data agree with the results of calculation at higher temperatures but largely deviate at lower temperatures, where k_u and k_d are nearly the same and hence J should be independent of temperature. It is likely attributed to saturation of deuterium on surface. The surface density S, which is proportional to the surface coverage θ of deuterium, seems to be saturated below 380 K as shown in Fig. 4. If θ is not negligible, the impinging flux is denoted by $F(1-\theta)$ because the incident atoms with a fraction of $(1-\theta)$ cannot find empty sites to be absorbed on surface. More quantitative analysis is difficult since the precise value of $(1-\theta)$ cannot be determined in case of θ being close to unity.

According to the Pick's model [3], the energy term in Eq.(6), E_{ku}, is $-2(E_s - E_c)$, where E_s and E_c are heat of solution and activation barrier for desorption, respectively. Although E_s depends on hydrogen concentration and temperature, it can be regarded as a constant value of around −0.08 eV [15] under our experimental conditions. If this model is applied, E_c is 0.16 eV. The pre-exponential factor k_{u0} of k_u is around $\nu N^{-4/3}/h^2$ [3,4], where ν, N and h are the attempt frequency, the atomic density of palladium and the number of solution sites per host palladium atom, respectively. The value of k_{u0} is estimated to be 3.6×10^{-26} $\mathrm{m^4\,s^{-1}}$ when $\nu = 10^{13}$ $\mathrm{s^{-1}}$ and $h = 1$. It can be said that this value is not so different from that in Eq. (6), if comparisons are made in terms of logarithmic scales.

From the above discussion, the value of k_u can be explained by the Pick's model but the surface processes do not seem to be fully understood as the followings: The model is based on some conditions that forming a molecule from two atoms on surface is the rate-determining process of desorption, the jumping rate of an atom from bulk to surface, $k_4C(1-\theta)/hN$, is approximately balanced to that from surface to bulk, $k_3\theta$, and the surface coverage θ is proportional to the concentration C in bulk. Parameters of k_3 and k_4 are rate constants for jumping from surface to bulk and jumping from bulk to surface, respectively. At higher temperature where $\theta \ll 1$, the last condition applies because $k_3\theta = k_4C/hN$. At lower temperature where θ becomes high, the condition would be no longer applicable but k_u can be expressed by one equation of Eq. (6) in the whole temperature range. The reason is not clear as long as the jumping rate from bulk to surface is expressed by $k_4C(1-\theta)/hN$ but not k_4C/hN in the model.

The values of k_d are essentially the same as those of k_u at lower temperatures but deviate at higher temperatures. A possible process for k_d at higher temperatures is the recombination of two atoms on surface and subsequent desorption without the barrier. The energy term of k_d at higher temperatures is around 0.17 eV and is nearly the same as $-2E_s$ of 0.16 eV. If it is adopted, another rate-determining process with the second-order kinetics would be required for k_u, since $E_c = 0$ is also expected to the upstream side, which is continuously cleaned by deuterium atoms. A possible process for k_u is that two atoms in the bulk just beneath the surface jump to form a molecule outside the bulk [16,17]. In this process the potential barrier for an atom would be the same as the activation energy for diffusion, E_d, and the energy term of the recombination coefficient is $2E_d$. As E_d is 0.21 eV for deuterium in palladium [18], the energy term is 0.42 eV, which is close to the value in Eq. (6). This process could explain temperature dependence of k_d at lower temperatures and k_u at the whole temperature range but no clear evidence is observed in the present work.

5. Summary

Concerned with the mechanism of hydrogen desorption from solid surface and practical requirement in fusion technology, the recombination coefficient of deuterium on either side of a palladium membrane was determined from two experiments. Under continuous exposure of the deuterium plasma to one side of the sample, transient behavior of permeation and the deuterium concentration near the plasma-facing surface were observed. As the results, the permeation was limited by the second-order kinetics of concentration and the recombination coefficient k_u on the plasma-facing side was expressed by one Arrhenius equation. The recombination coefficient k_d on the vacuum-facing side was essentially the same as k_u at lower temperatures but showed different temperature dependence above 400 K. Although the temperature dependence can be explained by the Pick's model with some activation barrier for desorption, another process of recombination of two atoms in the bulk just beneath the surface is suggested. Further investigation is worthwhile to understand the recombination phenomena comprehensively.

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References

[1] A.I. Livshits et al., Vacuum 29 (1979) 113.
[2] F. Waelbroeck et al., J. Nucl. Mater. 93&94 (1980) 839.
[3] M.A. Pick, K. Sonnenberg, J. Nucl. Mater. 131 (1985) 208.
[4] I. Takagi, H. Fujita, K. Higashi, J. Nucl. Mater. 266–269 (1999) 697.
[5] I. Takagi et al., Fusion Technol. 25 (1994) 137.
[6] I. Takagi, K. Yoshida, K. Shin, K. Higashi, Nucl. Instrum. and Meth. B 84 (1994) 393.
[7] W.B. Carter, J. Nucl. Mater. 111&112 (1982) 657.
[8] J. Park et al., J. Nucl. Mater. 220–222 (1995) 827.
[9] A.B. Antoniazzi, A.A. Haasz, O. Auciello, P.C. Stangeby, J. Nucl. Mater. 128&129 (1984) 670.
[10] D. Dieumegard, D. Dubreuil, G. Amsel, Nucl. Instrum. and Meth. 168 (1980) 223.
[11] I. Ali-Khan, K.J. Dietz, F.G. Waelbroeck, P. Wienhold, J. Nucl. Mater. 76&77 (1978) 337.
[12] I. Takagi, K. Toyoda, M. Katayama, H. Fujita, K. Higashi, J. Nucl. Mater. 258–263 (1998) 1082.
[13] I. Takagi, H. Kariyama, K. Shin, K. Higashi, J. Nucl. Mater. 200 (1993) 223.
[14] I. Takagi, H. Hashimoto, H. Fujita, K. Higashi, Fusion Eng. Des. 41 (1998) 73.
[15] J.D. Clewley et al., J. Chem. Soc. Faraday Trans. I 69 (1973) 449.
[16] P.M. Richards, J. Nucl. Mater. 152 (1988) 246.
[17] G. Comsa, R. David, Surf. Sci. Rep. 5 (1985) 145.
[18] Y. Fukai, The Metal-Hydrogen System, Springer, Berlin, 1993, p. 231.