



Experiments on potential energy diagram for hydrogen isotopes on nickel surface

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Abstract

Activation energies for some processes concerned with hydrogen recombination were studied experimentally. One side of a nickel membrane was exposed to a deuterium plasma and the deuterium permeation flux J at a steady state was monitored. At the same time, the surface density S of deuterium on the plasma-exposed side was observed by nuclear reaction analysis. The results showed that both the data of S^{-2} and J/S fell on straight lines in Arrhenius diagrams. Considering the particle balance equations under the experimental conditions, two values of the activation energy for the rate constant were obtained: one for two atoms recombining and subsequently leaving from the surface of 0.40 eV and the other for one atom migrating from the surface to the bulk of 0.57 eV. From these values, the energy term in the conventional form of the recombination coefficient was found to be 0.08 eV. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Copper; Nuclear reaction analysis; Activation energy of desorption; Deuterium; Permeation; Recombination; Plasma irradiation

1. Introduction

Recombination coefficients of hydrogen isotopes are important parameters for the evaluation of hydrogen recycling between the edge plasma and the plasma-facing materials in fusion reactors. In the literature, numerous experimental works on hydrogen recombination on various materials, such as nickel [1–3] and copper [4–6], have been reported. According to theoretical works [7–9], the recombination coefficient is a phenomenological constant which consists of several rate constants such as recombining of two atoms on the surface, migration of one atom between the surface and the bulk, and so on. It is, therefore, important to know these rate constants which contribute to the recombination coefficient.

In our previous work [10], the surface density and the permeation flux of deuterium in copper were observed

simultaneously and activation energies for some rate constants were obtained. In the present work, the same experimental technique is used for nickel and the results are compared with those for copper.

2. Experiment

The feature of the present experimental work is that the surface density and the permeation flux of deuterium in a metal membrane are observed simultaneously. The experimental setup is shown in Fig. 1. A sample membrane, a 0.1 mm thick foil of nickel (99.997%; Johnson Matthey GmbH), was placed between two vacuum chambers; one placed upstream and the other downstream. A lamp heated up the sample, the temperature of which was monitored by a thermocouple. The upstream side of the sample was exposed to a deuterium rf-plasma, produced in a discharge tube in the upstream chamber. Conditions of the plasma were kept constant during the experiment, that is, the deuterium pressure in the tube was 1 Pa and the rf power fed to the coil was 20 W.

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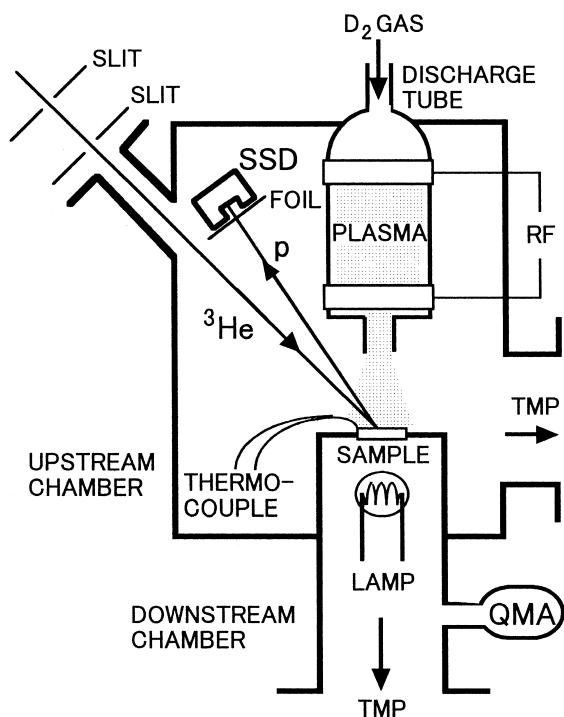


Fig. 1. Schematic view of the experimental setup.

The permeation flux of deuterium through the sample to the downstream side was monitored by a quadrupole mass analyzer (QMA). When permeation reached steady-state conditions, an analyzing beam of 1.3 MeV ^3He from the 4 MV van de Graaff accelerator of the Radiation Laboratory of Kyoto University irradiated the upstream side and protons produced by the nuclear reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$ were detected by a solid-state detector (SSD). The beam was collimated into 4 mm diameter by two slits 1 m apart from each other. The energy spectrum of the protons observed was converted into a deuterium depth profile near the surface by nuclear reaction analysis [11,12].

The depth profile consisted of two types of deuterium as described in our previous work [13]; one was deuterium absorbed on the surface showing a peak at 0-depth and the other was deuterium dissolved or trapped in the bulk showing a flat profile. The surface density of deuterium, S , was taken as the integrated value of the peak. As the trapped deuterium contributed to the profile in the bulk, the concentration of dissolved deuterium C was not determined from the profile. Knowing that the steady-state permeation was limited by the diffusion process in our experimental conditions [14], C was estimated from the permeation flux J using the following equation

$$J = DC/L, \quad (1)$$

where D is the diffusion coefficient of deuterium and L the membrane thickness.

3. Analytical model

There have been some models on the hydrogen recombination [7–9] and these models are based on the idealized potential energy diagram, as shown in Fig. 2, which is used for analyzing the data. In the figure, f and k represent the hydrogen flux and rate constant, respectively. Since the permeation is limited by the diffusion process, rate processes for the downstream surface are not considered.

The surface coverage of hydrogen θ is related to the observed surface density S by $\theta = S/S_0$, where S_0 is the saturated value of the hydrogen surface density and assumed to be constant. The relative concentration of hydrogen c is defined as the ratio of hydrogen concentration to the density of solution sites in the bulk, $c = C/hN$, where N is the atomic density of the host metal and h is the number of solution sites per host atom. For nickel, $N = 9.1 \times 10^{28} \text{ m}^{-3}$ and $h = 1$. From Eq. (1), a relation between c and J is obtained

$$c = JL/DhN. \quad (2)$$

The particle balance in the membrane at the steady state yields that $f_1 = f_2 + f_3$. The impinging flux f_1 is expressed by $F(1 - \theta)$, where F is the incident flux of atomic hydrogen from the plasma. In the experiment when the plasma was turned off, the permeation flux decreased by more than two orders of magnitude. Hence, the process of molecular sticking and subsequent dissociation is not considered. In the expression of the re-emission flux f_2 in Fig. 2, it is assumed that only the process of recombination of two hydrogen atoms and subsequent desorption from the surface contributes to the re-emission flux. So $f_2 = k_2\theta^2$. Other re-emission processes will be discussed later. The diffusion flux f_3 is equal to the permeation flux J .

Under the diffusion-limited permeation, the recombination flux f_2 should be much larger than the diffusion flux f_3 , which means there is quasi-equilibrium on the upstream surface. Hence, the particle balance equation is expressed by

$$F(1 - \theta) = k_2\theta^2. \quad (3)$$

Similarly, the particle balance in the bulk region is written as $f_3 = f_4 + f_5$, where f_3 and f_4 are fluxes from the surface into the bulk and from the bulk to the surface, respectively. The maximum value of c estimated from J by Eq. (2) in the experiment was 2×10^{-4} , which was much smaller than unity. So $k_3\theta(1 - c)$ of f_3 reduces to $k_3\theta$. As the diffusion flux f_5 would be much smaller

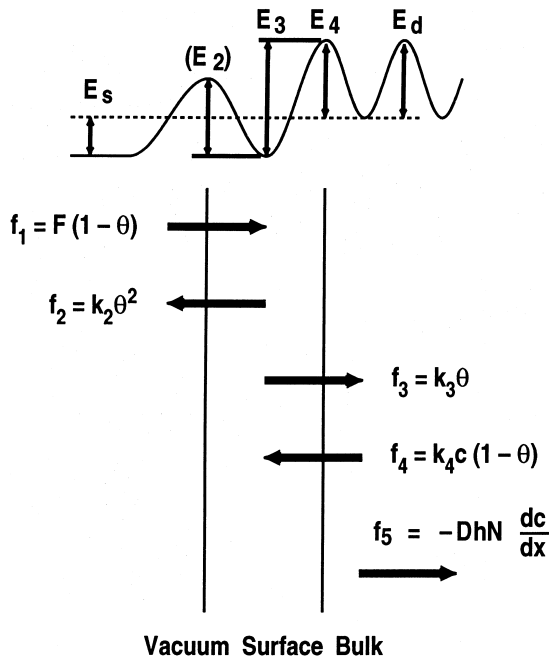


Fig. 2. Potential energy diagram for hydrogen near solid surface and corresponding rate processes considered. Parameters are explained in the text.

than f_4 and f_3 under the quasi-equilibrium condition, the particle balance equation is expressed by

$$k_3\theta = k_4c(1 - \theta). \tag{4}$$

Eqs. (3) and (4) are used for the analysis. As k_2 , k_3 and k_4 are the rate constants for thermally activated processes, these are expressed by

$$k_i = k_{i0} \exp(-E_i/kT) \quad (i = 2, 3, 4), \tag{5}$$

where E_i and k_{i0} are the activation energy and the pre-exponential factor, respectively.

4. Results and discussions

4.1. Rate constant k_2

The temperature dependence of the surface density S and the permeation flux J on deuterium is shown in Fig. 3. As Eq. (3) is rewritten by $S = S_0[F(1 - \theta)/k_2]^{1/2}$ and the data of S fall on a straight line in Fig. 3(b), it can be assumed that $\theta \ll 1$ within the examined temperature range.

From Eqs. (3) and (5),

$$S^{-2} = \frac{k_{20}}{S_0^2 F} \exp(-E_2/kT). \tag{6}$$

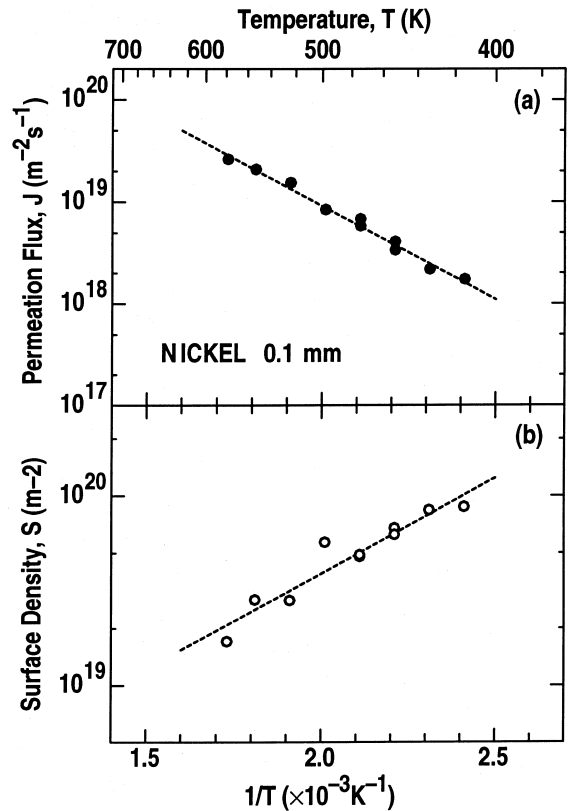


Fig. 3. Temperature dependence of (a) the permeation flux and (b) the surface density of deuterium at the steady state in the nickel sample.

Arrhenius plots of S^{-2} , shown in Fig. 4, yield $E_2 = 0.40$ eV.

Although the three models [7–9] indicate that $E_2/2$ is the potential energy for atoms on the surface relative to the potential peak between surface and vacuum, another explanation is possible. For example, E_2 may be the activation energy for atoms jumping to a neighboring site on the surface. In the present work, E_2 , as shown in parentheses in Fig. 2, is considered to express the activation energy for the recombination of two atoms and their subsequent desorption.

The maximum value of S is $8.8 \times 10^{19} \text{ m}^{-2}$, which exceeds the geometrical surface density $N^{2/3}$ of $2.0 \times 10^{19} \text{ m}^{-2}$. The reason would be that the saturated density S_0 is much larger than $N^{2/3}$ because of surface roughness [10]. Most hydrogen particles impinging on the membrane are neutral and the incident flux F cannot be measured. For the above reason, it is difficult to estimate k_{20} from the experiment.

Rough estimation of k_{20} would be possible from the theoretical consideration [8], that is, $k_{20} = \nu N^{2/3} = 2 \times 10^{32} \text{ m}^{-2} \text{ s}^{-1}$, where ν is the jumping rate of the hydrogen atom on the surface taken as 10^{13} s^{-1} .

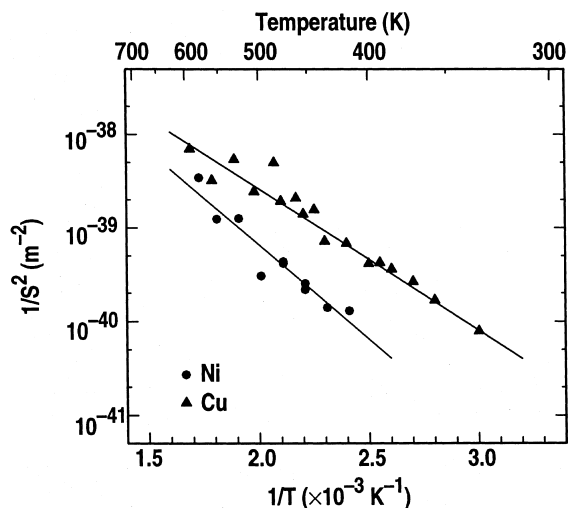


Fig. 4. Arrhenius plots of S^{-2} for the nickel sample (circles). The data for copper (triangles) observed in our previous work are also shown.

The data for a copper membrane observed in our previous work [10] are also shown in Fig. 4. The pre-exponential factors of S^{-2} for nickel and copper are $7.1 \times 10^{-36} \text{ m}^{-4}$ and $2.8 \times 10^{-36} \text{ m}^{-4}$, respectively. The plasma conditions were not changed and hence F would be the same for the nickel and copper cases. The atomic density N of copper is nearly the same as that of nickel. So a slight difference in the pre-exponential factor would be attributed to the jumping rate and the surface roughness.

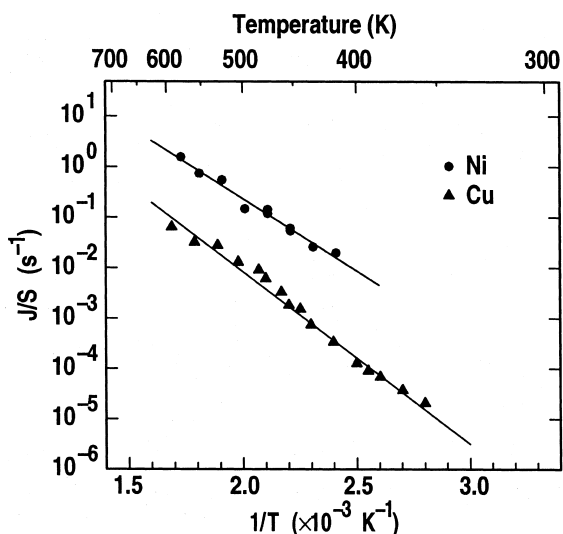


Fig. 5. Arrhenius plots of J/S for the nickel sample (circles). The data for copper (triangles) observed in our previous work are also shown.

4.2. Rate constant k_3

Substitution of Eq. (2) into Eq. (4) yields that

$$\frac{J}{S} = \frac{k_3}{k_4} \frac{DhN}{S_0L}. \quad (7)$$

As k_3 , k_4 and D are expressed by the Arrhenius equation, the data J/S are expected to fall on a straight line in an Arrhenius diagram, which is shown in Fig. 5. Assuming that E_4 is equal to the activation energy E_d for the diffusion coefficient, Eq. (7) is rewritten by

$$\frac{J}{S} = \frac{k_{30}D_0hN}{k_{40}S_0L} \exp(-E_3/kT), \quad (8)$$

where D_0 is the pre-exponential factor of D . Using Eq. (8), the activation energy E_3 is found to be 0.57 eV from Fig. 5.

According to Pick's model [8], $k_{20} = k_{30} = k_{40} = vN^{2/3}$. As S_0 is larger than the maximum value of S ($8.8 \times 10^{19} \text{ m}^{-2}$), substituting the data shown in Fig. 5, k_{40} and D_0 [14] into Eq. (8) yields that $k_{30} > 6 \times 10^{30} \text{ m}^{-2} \text{ s}^{-1}$. It is not so far from the value of $vN^{2/3}$ ($2 \times 10^{32} \text{ m}^{-2} \text{ s}^{-1}$) and the validity of $vN^{2/3}$ would be confirmed.

The data of J/S for copper observed in our previous work [10] are also shown in Fig. 5. As in the case of S^{-2} in Fig. 4, the pre-exponential factor of J/S for nickel ($1.2 \times 10^5 \text{ s}^{-1}$) is close to that for copper ($6.0 \times 10^4 \text{ s}^{-1}$). It is because of the same values of L and nearly the same values of N and D_0 [14,15] for nickel and copper. A slight difference would be attributed to the jumping rate and the surface roughness.

4.3. Other re-emission processes

Chorkendorff et al. [16] have suggested that when a surface is saturated with hydrogen, a hydrogen atom emerging from the bulk recombines with another hydrogen atom on the surface. This flux is expressed by $k_6c\theta$. Fig. 3(b) indicates that the surface was not saturated ($\theta \ll 1$) as described above, hence this process is not considered.

Another desorption process is the direct emerging of two atoms from the bulk to recombine, which has been suggested by Comsa et al. [17]. The flux f_8 is expressed by k_8c^2 . If f_8 is much larger than f_2 , Eq. (3) is replaced by $F = k_8c^2$ and substitution in Eq. (2) yields $k_8 = F(DhN/JL)^2$. The energy term for k_8 , estimated from the experimental data of J , is 0.1 eV. This process would not be dominant in our experiment, since the potential barrier for hydrogen in the bulk to jump to the surface should be much larger, probably close to E_d of 0.41 eV.

4.4. Recombination coefficient

The recombination coefficient k_r , defined by f_2/C^2 , is expressed as

$$k_r = k_2 \left(\frac{k_4}{hNk_3} \right)^2, \quad (9)$$

from Eqs. (3) and (4). When k_r is expressed by $k_{r0} \exp(-E_r/kT)$ in the conventional form, the energy term E_r is $E_2 + 2(E_4 - E_3)$. It is 0.08 eV assuming that $E_4 = E_d$.

The pre-exponential factor k_{r0} cannot be determined from the experimental data because S_0 and F are unknown. So k_{r0} is estimated, as in the case of k_{20} , to be $2.4 \times 10^{-26} \text{ m}^4 \text{ s}^{-1}$. The recombination coefficient is shown in Fig. 6 with results from other experimental works [1–3,18,19] and theoretical ones [8]. Since there seems to be quasi-equilibrium on the surface and Eq. (9) would be held in their experiments, the difference is due to the difference in the activation energy E_2 , which would depend on the amount of impurities on the surface.

The heat of solution E_s of deuterium in nickel, indicated in Fig. 2, is 0.15 eV [15] and very close to an energy difference of $E_3 - E_4$ (= 0.16 eV). This means that the potential of one hydrogen atom on the surface is

nearly equal to that of a half of a hydrogen molecule in the gas phase, which have been suggested by theoretical works [8,9]. In the case of copper, $E_3 = 0.68 \text{ eV}$ from Fig. 5 and $E_d = 0.39 \text{ eV}$ [15], hence $E_3 - E_4 = 0.29 \text{ eV}$ assuming that $E_d = E_4$. It is difficult to compare this energy difference to the value of E_s in copper because the literature data are rather scattered, for example, 0.39 eV(H) [15], 0.41 eV(D) [15], 0.32 eV(H) [20] and 0.51 eV(H) [21].

Although it was not confirmed that $E_s = E_3 - E_4$ for copper, a large value of E_3 in copper is considered to be the main reason why J in copper was much lower than that in nickel, typically by two orders of magnitude, under the same conditions of the plasma, sample thickness and temperature in the present work.

5. Summary

The permeation flux J and the surface density S of deuterium were observed simultaneously in a nickel membrane exposed to a deuterium plasma. Both S^{-2} and J/S fell on straight lines in Arrhenius diagrams. Using the particle balance equations, the experimental results were analyzed and two activation energies were obtained; 0.40 eV for the recombination of two atoms and subsequent desorption and 0.57 eV for the jumping of one atom from the surface to the bulk. From these values, the energy term E_r in the conventional form for the recombination coefficient was estimated to be 0.08 eV and it was found that the potential of one hydrogen atom on the surface was nearly equal to that of a half of a hydrogen molecule in the gas phase.

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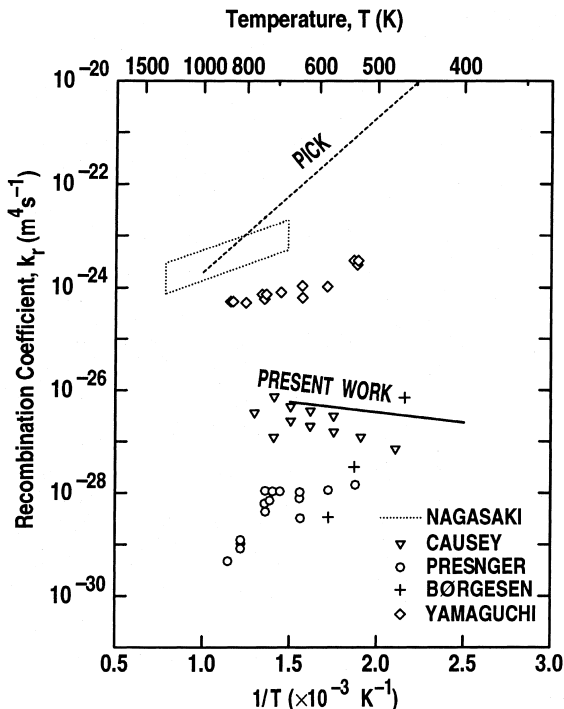


Fig. 6. Recombination coefficient of deuterium on nickel (solid line) with other experimental works (symbols). A broken line represents theoretical values for hydrogen on a clean surface.

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