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Potential energy diagram for hydrogen near vanadium surface

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Abstract

In order to examine the mechanism of the hydrogen recombination phenomenon, the potential energy diagram for hydrogen isotopes near a vanadium surface was experimentally studied. One side of a sample membrane was continuously exposed to deuterium plasma and the surface density and the bulk concentration of deuterium were measured by nuclear reaction analysis. At the same time, the permeation flux to the other side was monitored. The recombination coefficient on the plasma-exposed surface agreed well with the theoretical value for a clean surface. The activation energies for the recombination process and the jump process from the surface to the bulk were found to be 0.23 and 0.04 eV, respectively. There is a barrier potential of 0.29 eV on the vacuum-facing surface, which can be attributed to surface impurities.

1. Introduction

The recombination phenomenon in which two hydrogen atoms on a surface form a molecule to be desorbed is one step controlling the rate of hydrogen recycling between the edge plasma and the plasma-facing materials in a fusion reactor. The rate of desorption is generally expressed as the product of the square of the hydrogen concentration and the proportional constant, called the recombination coefficient. The recombination coefficient is a phenomenological constant [1–3], which consists of some rate constants for thermally activated processes such as jumping of an atom between the surface and the bulk, diffusion into the depths, and recombining of two atoms on the surface to form a molecule. For more insight into the recombination, these rate constants must be known.

In our previous works [4,5], the deuterium density on the surface which was exposed to plasma was directly observed by nuclear reaction analysis (NRA). As a result, the potential energy diagrams for the rate constants in nickel and copper have been obtained. The potential of the surface site is close to that in vacuum and larger than that of the solution site. The recombination rate can be reduced if impurities exist on the surface. These results support the recombination models [1–3].

Nickel and copper are endothermic metals in which the heats of hydrogen solution are positive. In the present work, the same experiment has been conducted with vanadium. Vanadium is an exothermic metal with the negative heat of solution, so different behavior from endothermic metals is expected.

2. Experimental

The experimental setup and the procedures have been described elsewhere [5] and will be explained briefly here. A sample of vanadium sheet with a thickness of 0.127 mm (99.8% metal basis; Johnson and Matthey GmbH) was placed between two vacuum chambers and heated up by a lamp. One side of the sample, called the upstream side, was continuously exposed to a deuterium rf-plasma produced in a discharge tube. Conditions of the discharge were a deuterium pressure of 1 Pa in the tube and the rf power of 20 W held constant during the experiment. A quadrupole mass analyzer (QMA) monitored the permeation flux to the other side, called the downstream side. The base pressure in the downstream was 1×10^{-5} Pa.

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The NRA was conducted during the plasma exposure. An analyzing beam of 1.7 MeV ^{3}He from a 4 MV van de Graaff accelerator of Kyoto University irradiated the upstream side and protons produced by the reaction D(^{3}He,p)^{4}He were detected. The energy spectrum of protons was converted into a deuterium depth profile near the upstream surface. The beam dose of each run was less than 2×10^{19} m^{-2}, to minimize radiation effects. The beam current of 10 nA was low enough to cause no increase in the sample temperature.

Two samples were used for the experiment. Sample A was mechanically polished with 50-nm alumina finish and sample B was used in the as received condition. Ranges of the sample temperature were 385–595 K for sample A and 418–558 K for sample B. The NRA for sample A was conducted when the permeation flux became constant. The elapsed time was 4 ks at most. The NRA for sample B was conducted after the elapsed time of 4 ks. So all the measurements were considered to be done at the steady-state permeation and concentration.

3. Results

Typical depth profiles observed by the NRA with sample B are shown in Fig. 1. Each profile can be divided into a peak at 0-depth and a flat plateau in the bulk. The peak and the plateau correspond to deuterium on the surface and that in the bulk, respectively. Due to the finite resolution of the detecting system, the peak broadens at negative depths. The probe depth is around 1.6 μm. Similar profiles were observed in the two samples in the whole temperature range.

The concentration deeper than 0.18 μm depth seems to be constant and the bulk concentration of deuterium, *C*, is taken as the average value for depths between 0.18 and 1.6 μm. The surface density of deuterium, *S*, and the bulk concentration contribute to the integrated value of the deuterium concentration from −0.18 to 0.18 μm. *S* is estimated by subtracting the areal density of *C* between 0 and 0.18 μm from the integrated value. The temperature dependence of *S* and *C* are shown in Fig. 2(a) and (b), respectively. In this temperature range, deuterium does not form any deuterides up to a concentration of 2×10^{27} m^{-3} [6]. This is much larger than the measured values of *C* so the deuterium atoms in the bulk are in solid solution.

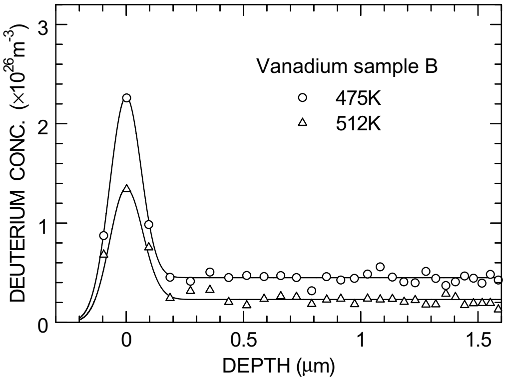

Fig. 1. Typical depth profiles of deuterium in vanadium near the plasma-exposed surface. Solid lines are guides for the eyes, not a fit to the data.

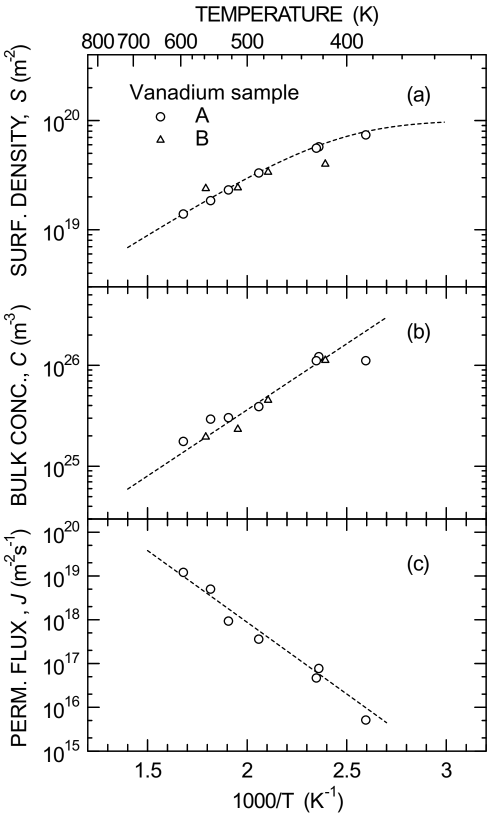

Fig. 2. Temperature dependence of (a) the surface density, *S*, and (b) the bulk concentration, *C*, near the plasma-exposed surface of the samples, and (c) the permeation flux, *J*, through sample A.

The permeation flux, *J*, was lower than the detection limit of 2×10^{15} m^{-2} s^{-1} for sample B while *J* was observed for sample A as shown in Fig. 2(c).

4. Discussions

At steady state, the incident flux of hydrogen atoms from the plasma, *F*, is balanced by the permeation flux *J* and the reemission flux *R* from the upstream side. The value of *F* was difficult to measure due to a large fraction of neutral atoms in the incident particles. It was estimated to be 6×10^{20} m^{-2} s^{-1} from our previous work

[7], where a palladium membrane was exposed to the same plasma as in the present work. For both samples, J was much smaller than F in the whole temperature range. In the following discussions, we assume that R is equal to F, in other words, there is quasi-equilibrium between the plasma and the sample.

With the recombination coefficient on the upstream side, k_u, R is expressed as

$$R = k_u C^2. \tag{1}$$

As F is independent of the sample temperature and equal to R, k_u is directly obtained as shown in Fig. 3. The data give the Arrhenius form of $k_u = 8 \times 10^{-27} \times \exp(-0.52\ \mathrm{eV}/kT)$ [m^4 s^{-1}]. A broken line expresses the theoretical recombination coefficient of $K_{ro}\exp(2E_s/kT)$ [2] for a clean metallic surface, where E_s is the heat of solution (−0.28 eV for V–D system [8]). The pre-exponential factor of K_{ro} is $\nu N^{-4/3}$ where N is the atomic density of vanadium and ν is the jump rate of the deuterium atom taken as 10^{13} s^{-1}. The data of k_u agrees with the theoretical value, indicating that the upstream surfaces of samples A and B were clean. Although some impurities may exist on the surface of vanadium [9], they were assumed to be removed by the deuterium particles from the plasma. The agreement also indicates that there were no intrinsic traps for deuterium since the traps would cause increase in C and hence decrease in the experimental result of k_u.

With the recombination coefficient on the downstream side, k_d, J is expressed as

$$J = k_d C'^2, \tag{2}$$

where C' is the bulk concentration of deuterium near the downstream side. J can be expressed in another way as $D(C - C')/L$ where D and L are the diffusion coefficient and the sample thickness, respectively. In case of the diffusion-limited permeation regime, C' is negligibly smaller than C and the apparent activation energy of D is estimated to be near 0.4 eV from the temperature dependence of J and C in Fig. 2. It disagrees with the actual value of 0.073 eV [10]. So C' should be close to C and we assume $C' = C$ in Eq. (2); that is, the concentration profile is uniform through the sample thickness. The values of k_d for sample A, as shown in Fig. 3, come from a straight line which is expressed as $6\times10^{-23}\exp(-1.1\ \mathrm{eV}/kT)$ [m^4 s^{-1}]. For sample B, the detection limit of the QMA and the observed concentration give that k_d was less than 2×10^{-37} m^4 s^{-1} in the temperature range.

Knowing the above results, the potential energy diagram for deuterium (hydrogen) near the surface can be drawn as shown in Fig. 4. The diagram and the rate processes are based on the recombination model [2]. The surface coverage θ is S/S_0 where S_0 is the density of the surface site. The relative bulk concentration c is C/N. Both θ and c are assumed to be much smaller than unity in the figure. f_i and k_i ($i = 2, 3, 4$) denote the flux of thermally activated process and the corresponding rate constant, respectively. The rate constant k_i is expressed in the form of $k_{i0}\exp(-E_i/kT)$ for $i = 3$, 4 and $k_{20}\exp[-2(E_i + E_c)/kT]$ where E_i is the activation energy and E_c is the barrier potential by the surface impurities. As the process of jumping of one atom from the bulk to the surface can be regarded as diffusion, E_4 is equal to the activation energy of diffusion, E_d.

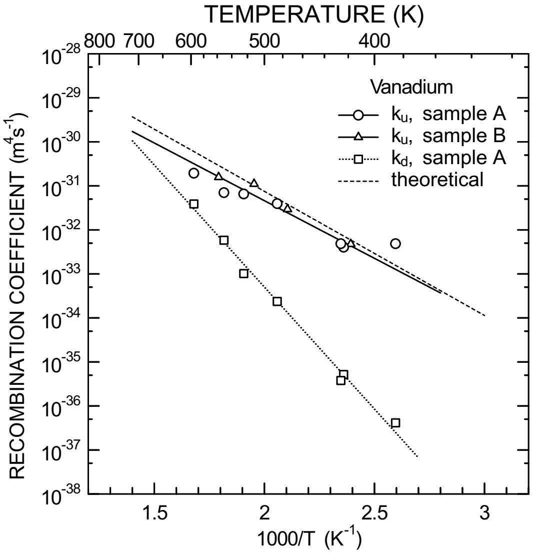

Fig. 3. Arrhenius diagram of the recombination coefficient of deuterium on the upstream surface k_u and the downstream surface k_d on vanadium.

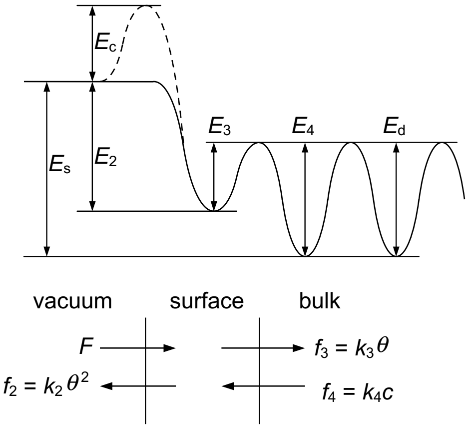

Fig. 4. Potential energy diagram for hydrogen near the surface of an exothermic metal and corresponding rate processes considered. Parameters are explained in the text.

In the quasi-equilibrium on the upstream side, F is equal to f_2 $(= R)$ and hence,

$$F = k_2\theta^2. \tag{3}$$

With the observed data, Eq. (3) is written as $k_2 = F(S_0/S)^2$. As E_c would be 0 for a clean surface, the data of S in Fig. 2(a) yield $E_2 = 0.23$ eV at higher temperatures. At lower temperatures, S seems to be saturated. This can be explained by assuming that the some incident particles were reflected due to deuterium occupation on the surface. In this case, the particle balance is expressed as $F(1 - \theta) = k_2\theta^2$. With the above values of F and E_2, the temperature dependence of S is fitted as shown by a broken line in Fig. 2(a). The values of S_0 and k_{20} are estimated to be 1×10^{20} m^{-2} and 2×10^{25} m^{-2} s^{-1}, respectively.

The flux of f_3 is equal to f_4 in the quasi-equilibrium between the surface and the bulk on the upstream side. For simplicity, the data at higher temperature, where θ is much smaller than unity, will be analyzed. In this case,

$$k_3\theta = k_4 c. \tag{4}$$

In another form of the experimental data, $k_3 = k_4 S_0 C/SN$. The activation energy E_3 is found to be 0.04 eV with temperature dependence of S and C when E_4 is taken as 0.073 eV. Combining Eqs. (1), (3) and (4), the energy term E_{k_u} of the recombination coefficient k_u is expressed as

$$E_{k_u} = 2(E_2 + E_d - E_3). \tag{5}$$

From the above data, $E_{k_u} = 0.52$ eV is obtained. It is close to the theoretical value of $-2E_s$ $(= 0.56$ eV). The small difference between the two values is attributed to the scattering of the data of C, probably due to some perturbation of the plasma.

On the downstream side, k_3 and k_4 should be the same as on the upstream side. Only the energy term E_{k_d} is different from E_{k_u} since the downstream side faced a vacuum and cleaning effects were not expected. So Eq. (5) for E_{k_u} can be replaced by

$$E_{k_d} = 2(E_2 + E_c + E_d - E_3). \tag{6}$$

As $E_{k_d} = 1.1$ eV, the barrier potential E_c is estimated to be 0.29 eV.

Based on the above results, the pre-exponential factors will be discussed. From Eqs. (1), (3) and (4), the pre-exponential factor k_{u0} of the recombination coefficient k_u is expressed as

$$k_{u0} = k_{20}(k_{40}/Nk_{30})^2. \tag{7}$$

As described ealier, k_{u0} is 8×10^{-27} m^4 s^{-1}. When the process for k_4 is assumed to be diffusion, k_{40} can be taken as $\nu N^{2/3}$ [2] (1.7×10^{32} m^{-2} s^{-1}). With these values, k_{30} is estimated to be 1×10^{29} m^{-2} s^{-1}. The value of k_{40} is about 10^7 times larger than k_{20} and about 10^3 times larger than k_{30}. The rate of one atom on the surface attempting to jump to the bulk would be different from that in the bulk attempting to jump to the surface, and from the rate of two atoms attempting to recombine to form a molecule. So it is not strange that the pre-exponential factors are different. On the downstream side, the pre-exponential factor k_{d0} is expected to be the same as k_{u0} but it is 6×10^{-23} m^4 s^{-1} as mentioned before, which is about 10^4 times larger than k_{u0}. The recombination models where all the pre-exponential factors are assumed to be the same as $\nu N^{2/3}$ cannot explain these discrepancies and further theoretical examination of the pre-exponential factors will be needed.

5. Summary

The potential energy diagram for deuterium (hydrogen) near a vanadium surface was determined as shown in Fig. 4 by the NRA observation. The results are the following. The activation energies E_2 and E_3 are 0.23 and 0.04 eV, respectively, when E_4 is taken as the activation energy of diffusion. On the upstream side, the barrier potential E_c is 0 but it is 0.29 eV on the downstream side, indicating a clean upstream surface and the presence of some impurities on the downstream surface. The pre-exponential factor k_{20} of the rate constant k_2 is estimated to be 2×10^{25} m^{-2} s^{-1}. The other factors of k_{30} and k_{40} are not determined independently but the relation $k_{30} = 7 \times 10^{-4} k_{40}$ is obtained. Although the theoretical value of the pre-exponential factor of the recombination coefficient agrees with the experimental data, it is clear that the constituent pre-exponential factors such as k_{20} and k_{30} will need to be further examined.

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