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Journal of Nuclear Materials 290–293 (2001) 501–504

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Influence of hydrogen surface coverage on atomic particle reflection

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Abstract

Atomic reflection of deuterium on metal samples of nickel, palladium and type 304 stainless steel (SS-304) was observed by use of a permeation probe. The surface densities of deuterium on the sample materials, which were continuously irradiated by atomic deuterium particles, were measured by the nuclear reaction analysis (NRA). As a result, for each sample, the amount of reflected deuterium decreased with increasing the sample temperature and temperature dependence of the amount was very similar to that of the surface density of deuterium. This would be explained by the fact that atomic hydrogen is reflected as being atoms with a significant probability on hydrogen-covered surface but not reflected on hydrogen-free surface.

Keywords: Hydrogen atoms; Hydrogen reflection; Nuclear reaction analysis

1. Introduction

Reflection of energetic fuel particles from plasma-facing walls in fusion devices is one of the important processes in hydrogen recycling and many experimental works [1–3] have been conducted above keV energy region. At eV and lower energy region, however, a few experimental data are available and simulation works [4,5] have contributed to knowledge, that is, the particle reflection coefficient of hydrogen on clean metallic surface is very low and hydrogen atoms tend to form molecules when desorbed.

In our previous work [6], atomic reflection of hydrogen particles with a few eV on some materials was observed. The term atomic reflection used here means that hydrogen atoms are reflected as being atoms. As a result, a significant amount of atomic hydrogen was reflected and the amount was nearly independent of the reflector material. One possible reason for disagreement of our results with the simulation works would be that the reflection behavior is influenced by surface hydrogen coverage because the sample surface was continuously exposed to hydrogen plasma in our experiment. Time evolution of the amount of hydrogen atoms reflected on graphite suggested that atomic reflection became significant when the surface was covered with hydrogen.

Recently Vietzke et al. [7] have experimentally shown that the atomic reflection coefficient on graphite is very high, typically 0.7, and it is influenced by the surface modification.

In the present work, a reflection experiment was conducted in which a sample reflector was continuously exposed to a deuterium plasma and heated to decrease surface coverage of deuterium. Temperature dependence of surface density of deuterium on the reflector material was also observed by the nuclear reaction analysis (NRA). Influence of surface coverage of hydrogen (deuterium) on atomic reflection will be discussed from results of the two experiments.

2. Reflection experiment

A permeation probe [8], which was a palladium membrane with a thickness of 0.1 mm and diameter of 18 mm, was used to detect atomic deuterium. The

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0022-3115/01/$ - see front matter
PII: S0022-3115(00)00442-6

permeation probe is explained in detail elsewhere [6] and will be briefly reviewed here.

As atomic hydrogen isotopes can easily permeate through a palladium membrane while thermalized hydrogen molecules can scarcely, the membrane acts as a filter to block hydrogen molecules. Under our experimental conditions, deuterium permeation through the probe was limited by the recombination process, so the permeation flux J was proportional to the incident flux of atomic deuterium F. The proportionality constant a is expressed as

$$a = \frac{k_d}{k_u + k_d}, \tag{1}$$

where k_u and k_d are the recombination coefficients on the deuterium-incident side and the other side, respectively. The probe temperature was kept constant at 453 K to fix the value of a.

A schematic view of an experimental set-up is shown in Fig. 1(a). The system was separated into two vacuum chambers by the probe. A sample cylinder with 32 mm diameter and 86 mm length was located as a reflector between the probe and a discharge tube in one chamber. Due to a narrow nozzle of the tube, the pressure in the chamber of 7 mPa was much lower than that of around 1 Pa in the tube when deuterium gas was fed into. A deuterium rf-plasma was produced in the tube to expose atomic deuterium to the inner surface of the cylinder. Atomic deuterium particles incident to the probe permeated through it and recombined to form deuterium molecules on the opposite side, which were detected by a quadrupole mass analyzer located in the other chamber.

The sample sheets used in the present work were rinsed in organic solvent and distilled water before the experiments. As the surface of the samples was continuously cleaned by deuterium plasma, its conditions except for deuterium coverage would not be changed during the experiments.

In the arrangement shown in Fig. 1(a), both the flux F_d of atomic deuterium directly coming from the plasma and the flux F_r of atomic deuterium reflected on the cylinder contributed to the permeation flux J_1, that is,

$$J_1 = a(F_d + F_r). \tag{2}$$

In order to know F_d, J_2 and J_3 in the cases shown in Figs. 1(b) and (c), respectively, were measured. A disk in Fig. 1(c) was so located between the probe and the discharge tube as to fully block the direct flux F_d. Then,

$$J_2 = a(F_d + F_s) \tag{3}$$

for the arrangement in Fig. 1(b) and

$$J_3 = aF_s \tag{4}$$

in Fig. 1(c), where F_s was attributed to atomic reflection on the inside wall of the vacuum chamber. F_s in Eq. (4) was assumed to be the same as that in Eq. (3) because atomic deuterium reflected on the disk and subsequently on the chamber would not so much contribute to F_s due to a small solid angle to the disk. Eqs. (1)–(3) yield

$$F_r = (J_1 - J_2 + J_3)/a. \tag{5}$$

Temperature dependence of F_r is shown in Fig. 2. F_r is expressed as a relative value to the direct flux F_d which would be constant during the experiment. The sample materials were nickel, palladium and type 304 stainless steel (SS-304). At room temperature, F_r was around twice as large as F_d for each material. This indicated that atomic reflection was significant at lower temperature.

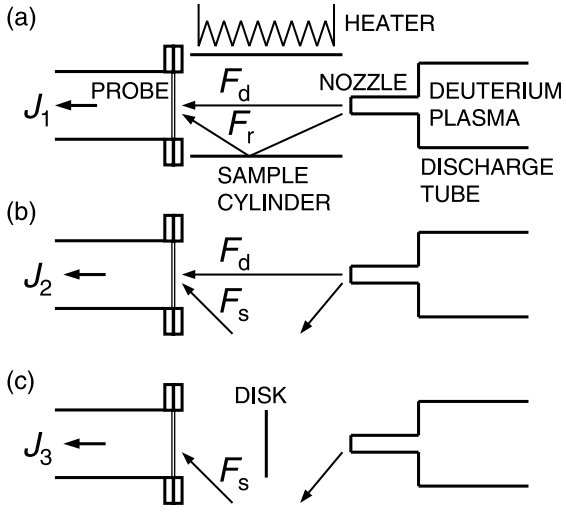

Fig. 1. Schematic showings of reflector arrangements in the reflection experiment.

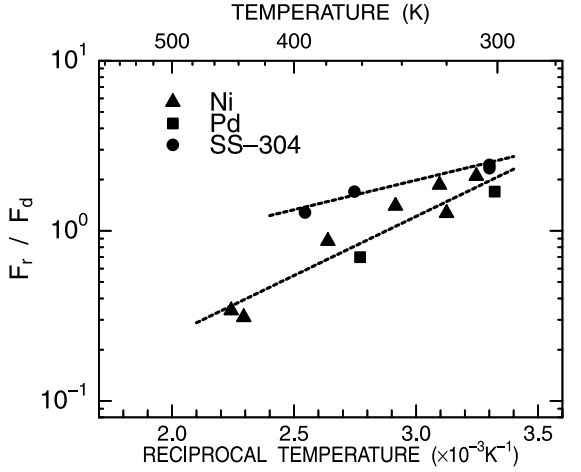

Fig. 2. Temperature dependence of the reflection flux F_r for nickel, palladium and SS-304. F_r is expressed as a relative value to the direct flux F_d. Broken lines are guides for eye.

At elevated temperature, F_r for all the materials decreased with increasing temperature. F_r decreased more rapidly for nickel and palladium than for SS-304. Assuming that F_r is expressed in a temperature-dependent form of $\exp(-E/kT)$, where k is the Boltzmann constant, the values of the energy term E were -0.07 eV for SS-304 and -0.15 eV for nickel and palladium.

It is difficult to know the reflection coefficient from F_r since there is lack of data on the angular distribution of reflected atoms and the source flux from the plasma. It would be noted that the reflection coefficient had a correlation with F_r and increased with decreasing temperature, which will be discussed later.

3. NRA measurement

Depth profiles of deuterium in the sample materials were observed by the NRA with a reaction of D(^{3}He, p)^{4}He [9]. Essential parts of an experimental set-up such as the discharge tube and the vacuum chamber were the same as the reflection experiment. The sample sheet was set with a holder to be normally faced to the nozzle of the discharge tube as shown in Fig. 3. A lamp heater was located behind the sample. While the sample was continuously exposed to the deuterium plasma of which conditions were the same as those in the reflection experiment, an analyzing beam of 0.8 MeV ^{3}He from the 4-MeV Van de Graaff accelerator of Kyoto University irradiated the sample at 45° to the surface normal. Protons produced by the nuclear reaction were detected by a solid-state detector (SSD), located at 174.3° to the direction of the beam, with a standard NIM system.

The depth profile of deuterium, converted from the energy spectrum of protons, showed a sharp peak at the surface, from which the surface density of deuterium, S, was obtained [10]. The surface coverage θ of deuterium is defined as S/S_0, where S_0 is the saturated value of the deuterium surface density. S represents a relative value of θ.

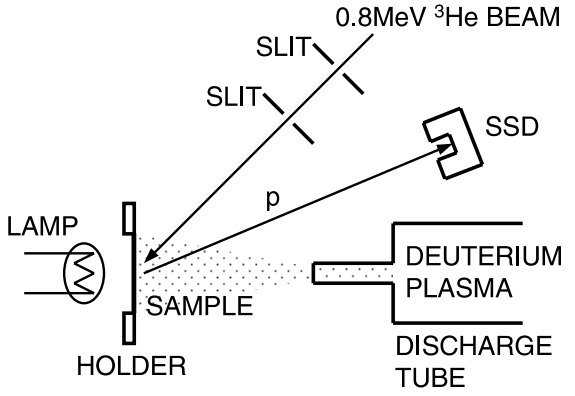

Fig. 3. An experimental set-up for depth profiling of deuterium by the NRA.

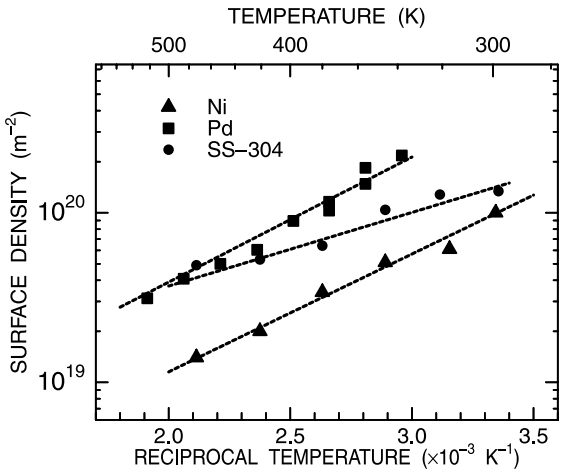

Fig. 4. Temperature dependence of the surface density of deuterium on the sample materials exposed to a deuterium rf-plasma.

Temperature dependence of the surface density S is shown in Fig. 4. For each sample, S decreased with increasing the sample temperature and data of S fell on straight lines in an Arrhenius diagram. The values of the energy term E in the best fitted lines of the form of $\exp(-E/kT)$ were -0.086 eV for SS-304, -0.14 eV for nickel and -0.15 eV for palladium.

4. Discussion

From Figs. 2 and 4, it seems that there is a good correlation between the reflection flux F_r and the deuterium surface density S, in other words, between the atomic reflection coefficient and the surface coverage of deuterium θ.

At elevated temperature, θ decreases as shown in Fig. 4. When atomic deuterium impinges to the surface not covered with deuterium, it would be scarcely reflected but absorbed on the surface. Absorbed deuterium atoms are desorbed in time as thermalized molecules but not detected by the probe. Atomic deuterium impinging to the deuterium-covered surface, on the contrary, would be reflected as being atoms with a significant probability that does not depend on temperature. This is a possible explanation of that the temperature dependence of F_r is very similar to that of S.

In order to make more quantitative discussion, we introduce an apparent reflection coefficient of atomic deuterium, R_a, in the case of θ being unity. It is expressed as

$$R_a = F_r/F_i, \tag{6}$$

where F_i is the source flux of atomic deuterium at the nozzle of the tube. Although R_a depends on the reflector arrangement and the angular distribution of the source flux, it is considered to express characteristics of atomic reflection.

When the surface is partly covered by deuterium with θ, Eq. (6) would be rewritten as

$$F_r = F_i \theta R_a. \tag{7}$$

Eq. (7) could explain the result that the temperature dependence of F_r is close to that of S ($= \theta S_0$) in each sample since R_a and F_i does not depend on the sample temperature.

Validity of Eq. (7) will be discussed below. The value of θ in the NRA measurement was probably different from that in the reflection experiment because of the sample position to the plasma. Moreover, θ on the inner surface of the sample cylinder would not be uniform because of the distance from the nozzle. The in situ observation on S and the deuterium concentration dissolved in the bulk just beneath the surface with some considerations of particle balance [10] have indicated that there was a quasi-equilibrium between the surface and the bulk and hence, temperature dependence of S was not changed by the amount of F_i under our experimental conditions. So the value of θ, which was taken as the averaged value for the sample in the reflection experiment, would be proportional to S in Fig. 4.

In Eq. (7), contribution of atomic deuterium which is reflected more than twice is not taken into account. For the sake of simplicity, an assumption is made that a probability R of atomic reflection and subsequent incidence to the probe is uniform over the reflector surface. Then $F_r = F_i(R + R^2 + R^3 + \cdots) = F_i R/(1 - R)$ for $\theta = 1$ and $F_r = F_i(\theta R + \theta^2 R^2 + \theta^3 R^3 + \cdots) = F_i \theta R/(1 - \theta R)$ for $\theta < 1$. Comparing the former equation with Eq. (6), $R = R_a/(1 + R_a)$ is derived and the latter equation is rewritten as

$$F_r = F_i \theta R_a/(1 + R_a - \theta R_a). \tag{8}$$

As R would be much smaller than unity because of a limited solid angle of the probe, $R_a \ll 1$. It was difficult to know the absolute value of S_0, which would depend on surface characteristics such as surface roughness, but the surface density of around 10^{20} m^{-2} on nickel as shown in Fig. 4 was considered to be far saturated with deuterium [10,11]. So Eq. (8) is approximately equivalent to Eq. (7).

In the present work, a good correlation between the atomic reflection and the surface coverage of deuterium was experimentally shown. Further data such as energy dependence of reflection and angular distribution of reflected atoms are needed to know the reflection behavior of hydrogen atoms at low energy region.

5. Summary

Atomic reflection of deuterium on some metals, which were continuously exposed to the deuterium plasma, was observed by the permeation probe. The surface densities of deuterium on the same materials were measured by the NRA. As a result, temperature dependence of the amount of deuterium atoms reflected on each material was very close to that of the surface density of deuterium. This could be explained by the fact that atomic hydrogen is reflected as being atoms with a significant probability on hydrogen-covered surface but not reflected on hydrogen-free surface.

This result would be important for evaluation of hydrogen recycling in fusion devices if plasma-facing walls, whose temperatures are low enough to be covered with hydrogen are located.

Acknowledgements

This work is supported by a grant-in-aid for scientific research from the Ministry of Education, Science, Sports and Culture, Japan.

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