EXPERIMENTS ON HYDROGEN TRAPPING WITH ION BEAM ANALYSIS

Ikuji Takagi
Department of Nuclear Engineering
Kyoto University
Sakyo-ku, Kyoto 606-8501, Japan
+81 (75) 753-5838

ABSTRACT

Depth profiles of deuterium in nickel, continuously exposed to deuterium plasma, were observed by use of the nuclear reaction analysis. Trapping energy for deuterium in nickel bombarded with energetic ions was 0.24eV, which was determined under equilibrium between trapping and solution sites. From the shape of the depth profile and the trapping energy in cases of hydrogen and helium bombardment, the traps were considered to be associated with radiation damages. Experiments on kinetics of deuterium on metal surface were also conducted.

I. INTRODUCTION

Plasma-facing walls in fusion devices will be bombarded with energetic particles such as fast neutrons and helium ions, which would produce hydrogen trapping and increase tritium inventory in the walls. There have been many experimental works on trapping of hydrogen isotopes, in which transient methods such as thermal desorption[1] and isothermal annealing[2] are generally used.

We have developed an in-situ observation technique by use of ion beam analysis,[3] which is a kind of an equilibrium method. Experimental results on characteristics of the trapping site in nickel will be shown. Application of the technique to study on some rate constants of thermally activated processes for deuterium on metal surface will also be mentioned.

II. EXPERIMENTAL

Fig.1 shows schematic illustration of the experimental setup and its typical procedure. A sample membrane is set between two vacuum chambers of upstream and downstream. A lamp heats up the sample while the upstream side of the sample is exposed to deuterium rf-plasma. Permeation flux to the downstream is monitored.

After the permeation reaches at the steady state, an ion beam of helium-3 irradiates the plasma-exposed side at 45 degree to normal to observe a depth profile of deuterium by use of the nuclear reaction analysis (NRA) with a reaction of $D(^3He,p)^4He$.[4] In order to produce traps, the membrane is bombarded with energetic ions such as helium and hydrogen between the observation of NRA.

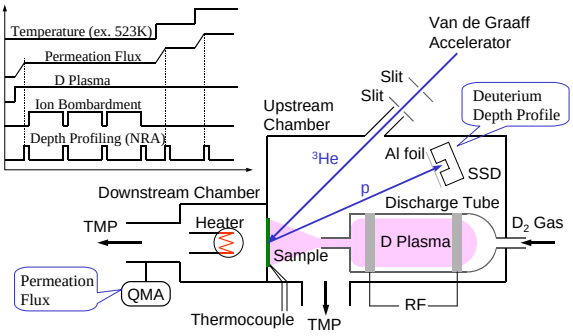

Fig.1 Schematic illustration for the experimental setup and its typical procedure

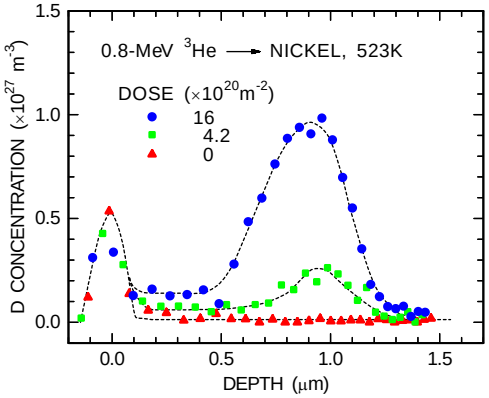

Fig.2 Depth profiles of deuterium in nickel before and after 0.8MeV-^{3}He bombardment.[5]

III. RESULTS

Depth profiles of deuterium in nickel bombarded with helium-3 are shown in Fig.2.[5] Before bombardment, deuterium exists only on the surface and little deuterium is observed in the bulk. After the bombardment, a broad peak

appears in the bulk and its height increases with bombarding dose because traps are produced by the bombarding ions.

As deuterium is absorbed on the surface, dissolved or trapped in the bulk, the depth profile of trapped deuterium can be estimated by substituting the profile before bombardment from that after bombardment, which is shown in Fig.3.[5]

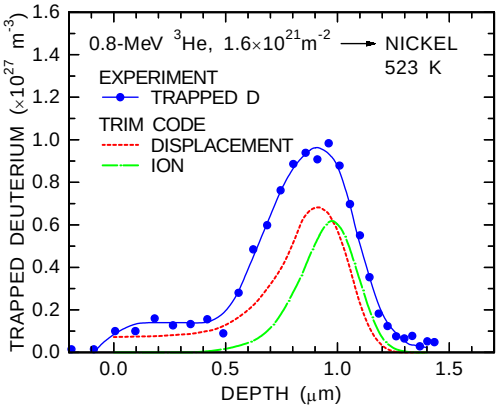

Fig.3 The depth profile of trapped deuterium obtained from the data shown in Fig.2.[5] Distribution of bombarding ions and atomic displacements are also shown.

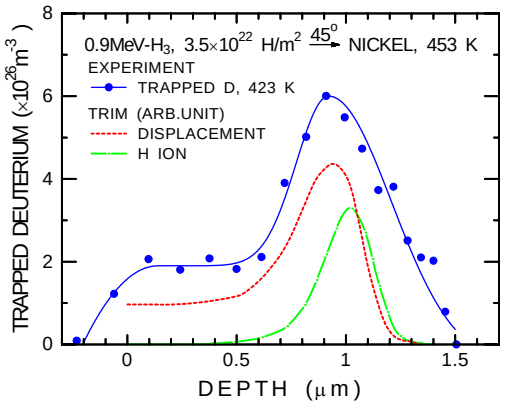

Fig.4 The depth profile of trapped deuterium in nickel bombarded with hydrogen ions.[7] Distribution of bombarding ions and atomic displacements are also shown.

Distributions of bombarding helium-3 ions and atomic displacements estimated by the TRIM code[6] are also shown in Fig.3. The depth profile is very similar to the distribution of the displacement rather than that of the ions.

Fig.4 shows a depth profile of trapped deuterium in nickel bombarded with 0.9MeV H_3 (equivalent to three 0.3MeV H) ions.[7] Also in this case, the profile is similar to the distribution of the displacement. These results indicate that the traps are associated with radiation damages, not with presence of the bombarding helium or hydrogen ions.

IV. DISCUSSIONS

A. Equilibrium Method

As the sample is continuously charged with deuterium from the plasma in the experiment, there would be equilibrium between the trapping and the solution sites. The equilibrium constant f can be expressed as

$$f = \frac{C_s}{hN - C_s}\frac{C_0 - C_t}{C_t} \tag{1}$$

where C_s and C_t are concentrations of deuterium in the solution sites and the trapping sites, respectively, hN the density of the solution sites and C_0 the density of the trapping sites. h is number of solution sites per host atom and N atomic density of host metal.

Analogy to chemical reactions, f is equal to $\exp(-\Delta G/kT)$, where ΔG is the difference in free energy between the trapping site and the solution site. When the difference in potential energy is defined as the trapping energy E_t, f is expressed as

$$f = f_0 \exp(-E_t / kT) \tag{2}$$

where $f_0 = \exp(\Delta S/k)$ and ΔS is the entropy difference.

Under our experimental conditions, the permeation is limited by the diffusion process. It has been confirmed from observation of transient behavior of permeation when incident flux from the plasma is quickly changed. In the diffusion-limited permeation, the permeation flux at the steady state, J, and C_s is directly related by the equation,

$$J = DC_s / L \tag{3}$$

where D and L are the diffusion coefficient and the sample thickness, respectively.

As a region from the surface to the depth to which the traps extend is much smaller than L, C_s can be regarded as uniform. C_s is much smaller than hN. Integration of Eq.(1) over the region yields,

$$f = \frac{C_s}{hN}\frac{S_0 - S_t}{S_t} \tag{4}$$

where S_t and S_0 are areal densities of trapped deuterium

and the trapping sites, respectively.

B. Trapping Energy

Fig.5 shows temperature dependence of (a) the concentration of dissolved deuterium, C_s, and (b) the areal density of trapped deuterium, S_t, respectively.[3] S_t increases with decreasing the sample temperature until it tends to be saturated. The saturated value is taken as the areal density of the trapping sites, S_0.

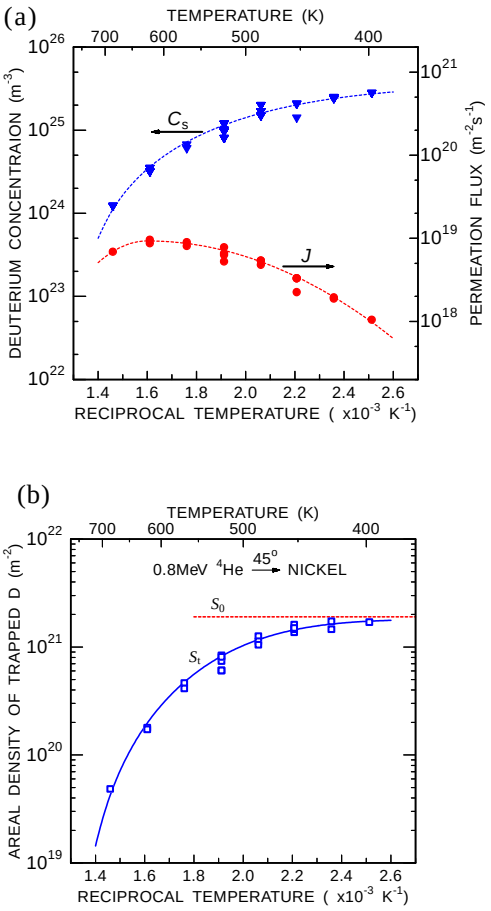

Fig.5 Temperature dependence of (a) the concentration of dissolved deuterium and (b) the areal density of trapped deuterium in nickel bombarded with ^{4}He.[3]

Values of f, estimated from Eq.(4) with the above experimental data and plotted in an Arrhenius diagram in Fig. 6[7], come on straight lines, which indicates that one kind of the traps is observed in the experiment. The trapping energies E_t are 0.24 eV for helium bombardment and 0.22 eV for hydrogen bombardment. The traps in both the cases would be the same.

The trapping energy obtained in the present work should be compared with those in other researchers' works. It is, however, difficult because the models used for analysis of the experimental data are different from each other.[8] The most important issue in the models would be the pre-exponential factor f_0 in Eq.(2). In some works, f_0 has been assumed to be unity, that is, the difference in free energy is taken as the trapping energy. On the contrary, f_0 in the present work is much larger than unity. The entropy term is considered to be important for evaluation of the tritium inventory.

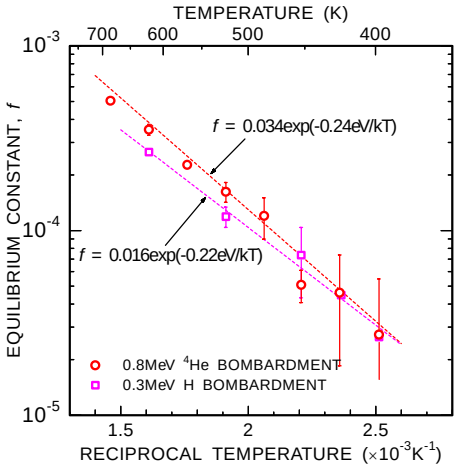

Fig.6 Arrhenius diagram of the equilibrium constant in nickel in cases of ^{4}He and H bombardment.[7]

C. Trap Density

Fig.7 shows evolution of the areal density of the traps as a function of atomic displacement.[9] The trap density was nearly proportional to the displacement in cases of helium-3 and hydrogen bombardment. The rate of the traps to the displacement in helium-3 case was about three times larger than that in hydrogen case. This is probably because helium ions produce larger collision cascades in which many defects survive a short-time annealing process.

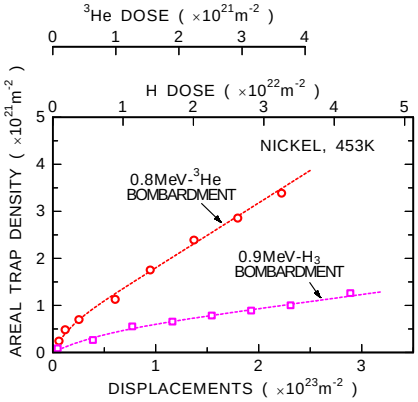

Fig.7 Evolution of the trap density with atomic displacement in nickel.[9]

V. KINETICS OF HYDROGEN ON SURFACE

A. Experimental

There is a peak at the 0-depth in the observed depth profile as shown in Figs. 2 and 8.[10] The peak would represent absorbed deuterium on surface. The peak area is taken as the surface density of deuterium, S, here. S is directly related to the deuterium surface coverage θ by $\theta = S/S_s$, where S_s is the saturated deuterium density. The concentration of deuterium just beneath the surface, C, is known from the permeation flux J as described before and the relative concentration, c, is defined here by $c = C/hN$.

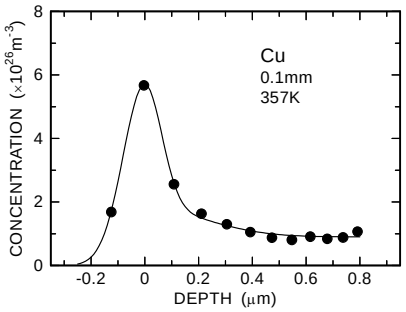

Fig.8 A typical depth profile of deuterium in a copper membrane exposed to deuterium plasma.[10]

From both the values of θ and c, some rate constants for thermally activated processes of hydrogen on metal surface would be estimated. These constants are required for evaluation of surface recombination coefficients.

B. Model

A model used here is based on particle balance as schematically shown in Fig.9. f_1 is the incident flux to the surface, f_2, the desorption rate from the surface, f_3, the jumping rate from the surface to the bulk, f_4, the jumping rate from the bulk to the surface and f_5, the diffusion flux.

Particle balance between on the surface and the bulk just beneath the surface yields $f_1 + f_4 = f_2 + f_3$ and $f_3 = f_4 + f_5$, respectively. In the diffusion-limited permeation, there would be quasi-equilibrium near the surface and f_5 should be much smaller than f_3 and f_4. Then,

$$F(1-\theta) = k_2\theta^2 \qquad (5)$$

$$k_3\theta = k_4 c(1-\theta) \qquad (6)$$

are obtained, where $c << 1$ is taken into account.

B. Results and Discussions

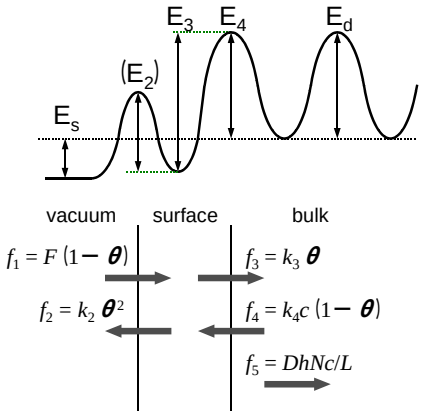

Fig.9 Schematic showings of potential energy diagram and rate processes of hydrogen near metal surface.

Fig.10 shows temperature dependence of $1/S^2$ for nickel and copper membranes.[11] Data come on straight lines in both the cases. These suggests that θ is much smaller than unity in each case and Eq.(5) can be rewritten by $k_2 = FS_s^2/S^2$. The activation energies E_2 for the rate constant k_2 are found to be 0.40 eV for nickel and 0.30 eV for copper.

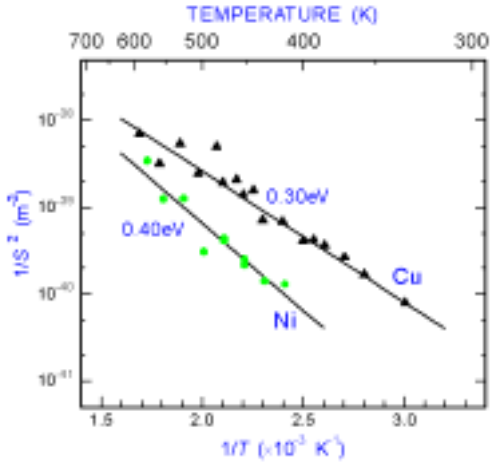

Fig.10 Temperature dependence of $1/S^2$ on nickel and copper membranes.[11]

When $\theta << 1$, Eq.(6) is rewritten by $k_3\theta = k_4 c$. Assuming that the activation energy E_4 for the rate constant k_4 is the same as that E_d for the diffusion coefficient, k_3 is expressed as $(k_{40}LS_s/D_0hN)(J/S)$, where k_{40} and D_0 are the pre-exponential factors of k_4 and D, respectively. Fig.11 shows temperature dependence of J/S,[11] from which the values of E_3 are found to be 0.57 eV for nickel and 0.68 eV for copper.

The recombination coefficient K_r is a phenomenological

constant and would be expressed as $k_2k_4^2/(hNk_3)^2$, according to the above model, where θ<<1 and hence k_4c << k_3 are assumed. The energy term E_r for K_r in the expression form of $K_{r0}\exp(-E_r/kT)$ can be estimated from the above experimental results and the activation energy for diffusion in other works.[8,12] They are 0.08 eV for nickel and -0.29 eV for copper. It should be noted that E_2 is not proper to materials but strongly depends on the surface conditions. So the important result is that the activation energy of E_3 is experimentally determined in the present work.

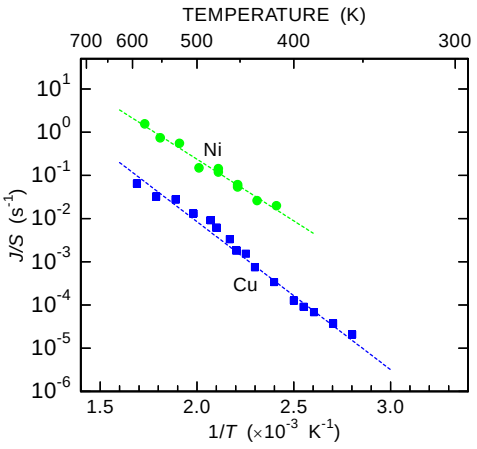

Fig.11 Temperature dependence of J/S in nickel and copper membranes.[11]

For better understandings of the recombination phenomenon, the pre-exponential factors of k_2, k_3 and k_4 are necessary to be known from experiments although they have been estimated from theoretical consideration.[13] The values, however, cannot be obtained in the experiment because the incident flux F and the saturated density S_s are uncertain. Determination of F and S_s remains as the issue of the present work.

VI. SUMMARY

The in-situ observation technique has been shown to be useful for studying thermal behavior of hydrogen in materials. As samples are continuously charged with hydrogen from plasma, there would be equilibrium of hydrogen between surface and bulk, the solution sites and the trapping sites. The samples would not suffer from damages or sputtering because particles from plasma have no sufficient energy and the energy of the analyzing beam is so high that the damage production and sputtering do not occur effectively. Both the studies on hydrogen trapping in the bulk and hydrogen kinetics near the surface are in progress and further results would be expected in future works.

REFERENCES

1. S. M. Myers et al., "Defect Trapping of Ion-implanted Deuterium in Fe," *J. Appl. Phys*., **50**, 5710 (1979).
2. Y. Muto and K. Morita, "Isothermal Re-Emission of Hydrogen Implanted into Isotropic Graphite," *J. Nucl. Sci. Technol*., **29**, 980 (1992).
3. I. Takagi et al., "A Combined Technique of Nuclear Reaction Analysis and Plasma-driven Permeation for a Quantitative Study on Deuterium Trapping," *Nucl. Instr. Meth*. **B84**, 393 (1994).
4. D. Dieumegard and D. Dubreuil, "Analysis and Depth Profiling of Deuterium with the D(^{3}He,p)^{4}He Reaction by Detecting the Protons at Backward Angles," *Nucl. Instr. Meth*. **166**, 431 (1979).
5. I. Takagi et al., "Depth Profiles of Trapped Deuterium in Nickel Bombarded with Helium-3," *J. Nucl. Mater*., **200**, 223 (1993).
6. J. F. Ziegler, J. P. Biersack and U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon Press, New York (1985).
7. I. Takagi et al., "Determination of Trapping Energy for Deuterium in Hydrogen-bombarded Nickel," *J. Nucl. Mater*, **220-222**, 908 (1995).
8. I. Takagi, "Diffusive Behavior of Deuterium in Nickel under Irradiation of Helium-3," *J. Nucl. Sci. Technol*., **29**, 947 (1992).
9. I. Takagi et al., "Observations of Trapped Deuterium in Nickel Bombarded with ^{3}He and Hydrogen Ions at an Elevated Temperature," *J. Nucl. Mater*., **212-215**, 1411 (1994).
10. I. Takagi et al., "An Experimental Study on the Potential Energy Diagram for Hydrogen Isotopes on Copper Surfaces," *Fusion Eng. Des*., **41**, 73 (1998).
11. I. Takagi et al., "Experiments on Potential Energy Diagram for Hydrogen Isotopes on Nickel Surface," *J. Nucl. Mater*., **266-269**, 697 (1999).
12. W. Eichenauer et al., "Loslichkeit und Diffusions-geschwindigkeit von Wasserstoff und Deuterium in Einkristallen aus Nickel und Kupfer," *Z. Metallkde*., **56**, 287 (1965).
13. M. A. Pick and K. Sonnenberg, "A Model for Atomic Hydrogen-metal Interactions - Application to Recycling, Recombination and Permeation," *J. Nucl. Mater*., **131**, 208 (1985).