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The ion- and atom-driven transport of deuterium in Nb under the influence of surface impurities

K. Ohkoshi [a,*], V. Alimov [b], K. Yamaguchi [c], M. Yamawaki [a], A.I. Livshits [b]

[a] *Department of Quantum Engineering and Systems Science, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[b] *Surface Physics and Electronics Research Centre, Bonch-Bruyevich University, 61 Moika, St. Petersburg 191186, Russian Federation*

[c] *Nuclear Engineering Research Laboratory, University of Tokyo, Tokai-mura, Ibaraki-ken 319-1106, Japan*

Abstract

Atom- as well as ion-driven permeation behavior of deuterium in Nb was studied experimentally. The measurements were performed under two different vacuum conditions which resulted in contrasting surface compositions: one resulted in a surface rich in carbon (C) after atom beam irradiation and the other rich in sulfur (S) which was unaffected by the irradiation. The result of permeation measurements revealed that when the specimen surface was covered by sulfur the deuterium permeation rate weakly depended on the temperature, whereas when the surface was rich in carbon and oxygen it tended to decrease sharply for temperatures below ~700 K.

Keywords: Atomic hydrogen; Impurities; In situ AES; Niobium; Permeation

1. Introduction

Nb (niobium) is a possible candidate material for the membrane pumping in a fusion device [1], where it could provide selective pumping of hydrogen isotopes from plasma exhaust, owing to its high permeability. Under certain conditions, the permeation flux through some metals becomes almost equal to the incident flux; this is referred to as superpermeation [2]. It is widely accepted that the role of the surface impurities on hydrogen transport is of fundamental importance; the superpermeation phenomenon is considered to result from the presence of a surface impurity layer, although the details of the mechanism still remain to be made clear.

The interaction of atoms with solid surfaces is an area where the current database for fusion applications is lacking [3]. Hydrogen atoms produced through thermal dissociation process in an atomizer heated up to temperatures around 2350 K, have translational energies around 0.3 eV. Hence, in contrast to energetic ion beams, such a low energy of incidence will not produce defects in the specimen, and their transport may be affected by additional factors such as chemical interactions between adatoms and surface atoms. Many studies have been devoted to this subject. As an example, Kiriyama and Tanabe [4] studied reflection of atoms at surface of various metals and indicated some correlation between the reflection coefficient and solution energy. However, they did not refer to the possible effects due to surface conditions, in particular, surface impurities.

The purpose of the present study is to investigate the interaction of ionic and atomic deuterium with the surface of Nb, with particular emphasis on the effect of surface impurities on the observed deuterium transport. Measurements were made in an experimental device equipped with an in situ surface analyzer [5].

2. Experimental

As shown in Fig. 1, an atomic beam source (ABS) has been installed in our existing hydrogen permeation experimental device [5]. This facility has two quadrupole mass spectrometers (QMS) for dynamic measurement of

* Corresponding author. Tel.: +81 29 287 8434; fax: +81 29 287 8488; e-mail: ohkoshi@tokai.t.u-tokyo.ac.jp.

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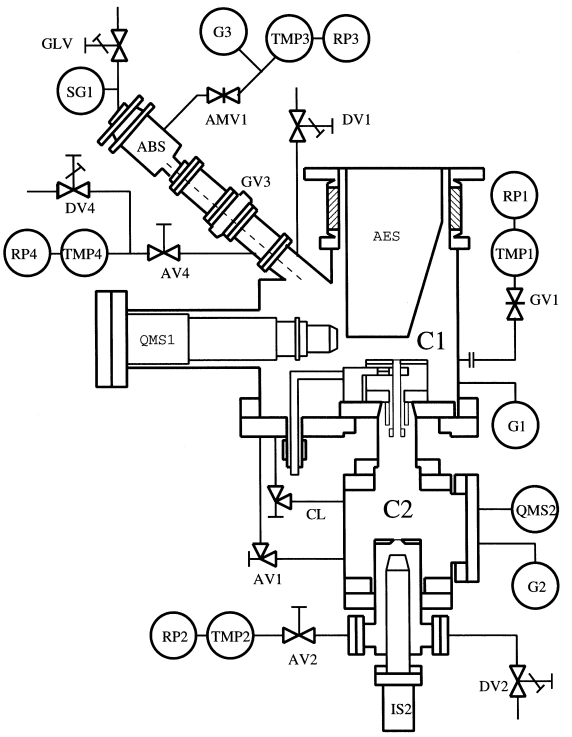

Fig. 1. Schematic drawing of experimental device (HYPA-IV): C1 and C2, vacuum chambers; AV1–AV4, valves; DV1–DV4, variable leak valves; GV1–GV3, gate valves; TMP1–TMP4, turbomolecular pumps; RP1–RP4, rotary pumps; G1–G3, Bayard–Alpert gauges; SG1, Schultz gauge; QMS1 and QMS2, quadrupole mass spectrometers; AES, Auger electron spectrometer; and IS2, ion source.

the deuterium fluxes (HD and D_2) in both the upstream-side and downstream-side chambers (indicated as C1 and C2 in the figure, respectively), together with AES (Auger electron spectroscopy) or SIMS (secondary ion mass spectrometry) analyzing systems.

The ABS consists of a tungsten (W) nozzle, surrounded by a thin cylindrical tantalum (Ta) heater, electrodes and water-cooled vessel. The hydrogen molecules passing through the nozzle are thermally dissociated ($T \simeq 2350$ K) and the atoms generated are emitted with translational energy $\geqslant 0.3$ eV. As shown in Fig. 1, the ABS is installed at an angle of 50 degrees from the surface normal. The flux density of incident atoms is evaluated from geometric consideration:

$$I_{\mathrm{m}}^{\mathrm{H}} = 2\eta \frac{1}{4} n_{\mathrm{a}}(T) v_{\mathrm{a}}(T) \pi \left(\frac{d_{\mathrm{a}}}{2}\right)^2 \pi \left(\frac{d_{\mathrm{m}}}{2}\right)^2 \frac{1}{\pi L^2}, \quad (1)$$

where $I_{\mathrm{m}}^{\mathrm{H}}$ is the atomic flow (s^{-1}), $n_{\mathrm{a}}(T)$ and $v_{\mathrm{a}}(T)$ are the density (m^{-3}) and the velocity ($\mathrm{m\ s}^{-1}$) of hydrogen molecules at temperature T (K), η is the dissociation probability which is also a function of T, d_{a} and d_{m} are the diameters (m) of the nozzle and the atomic beam (at the specimen surface), respectively, and L is distance between the nozzle and the specimen (m). The deuterium was employed as a source of the atomic beam, and the deuterium atomic flux, ϕ_{a} ($\mathrm{D\ m}^{-2}\ \mathrm{s}^{-1}$), to the specimen was thus evaluated to be 2.5×10^{17} $\mathrm{D\ m}^{-2}\ \mathrm{s}^{-1}$ at a nozzle temperature 2350 K.

The specimen employed in the present study is a Nb foil (supplied by Nilaco 0.1 mm$t$, 14 mmϕ, 99.9 at.% in purity), which was welded on the top of a cylindrical sample holder made of type 304 SS. The specimen was cleaned ultrasonically in acetone before being installed in the vacuum vessel. The AES or SIMS analyses were performed occasionally in order to monitor the surface impurities on the specimen, while the specimen temperature was varied from 600 to 1000 K.

3. Results and discussion

3.1. Analyses of surface impurity compositions

The impurity composition of the upstream-side surface of specimen as determined by AES is indicated in Fig. 2. The Nb specimen was annealed in vacuo at 1050 K for 10 min, while the residual pressure in the vacuum vessel was below 10^{-6} Pa. As seen in the figure, the surface concentration of Nb was larger than 50 at.%, while sulfur was evaluated to be ≈40 at.%. Other impurity elements were: carbon (C) < 10 at.% and traces of oxygen (O) and calcium (Ca). It should be noted that the surface compositions were essentially the same independent of the temperature. This seems to indicate that once sulfur segregates to the surface it provides thermally stable surface condition under ultra-high vaccum (above 600 K). The stability of this sulfur-rich surface was also examined by exposure to atomic deuterium. In some measurements the irradiation lasted more than

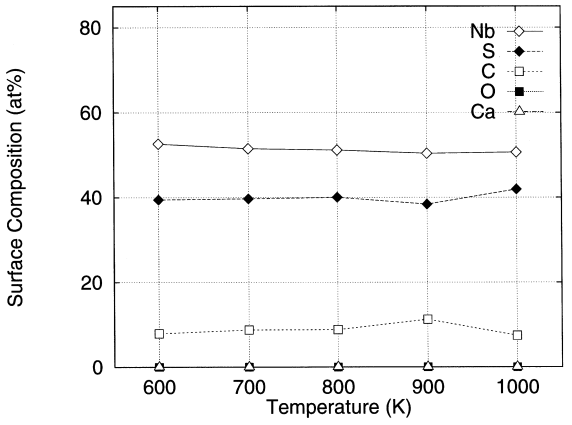

Fig. 2. Result of AES analysis on upstream-side surface of Nb specimen performed before irradiation by atomic deuterium.

about 40 h (total fluence; 6×10^{20} D m^{-2}), but the surface compositions remained unchanged.

Similar measurements were performed with a different specimen (supplied by Daido Steel) under different vacuum conditions (residual pressure no better than 10^{-6} Pa). The results of AES measurement performed at 500 K are shown in Fig. 3. Although the surface compositions were initially the same, the carbon concentration increased after atom beam irradiation. The origin of carbon is not clear, but it may be probable that it was mixed with the deuterium source gas due to poor vacuum condition.

3.2. Dependence of permeation rate on surface compositions

In the preliminary runs with the ABS, it was observed that when the temperature of the nozzle was increased gradually, the deuterium permeation rate also increased. Assuming that the atomic flux is proportional to the dissociation probability (η in Eq. (1)), it was found that the permeation rate was directly proportional to the evaluated atomic flux.

The temperature dependence of steady state deuterium permeation rate was then measured in the temperature range between 600 and 1000 K, and the results are shown in Fig. 4. In this figure, the results of measurements performed under different vacuum conditions, corresponding to Figs. 2 and 3 are compared. A very weak temperature dependence of the permeation rate, with an apparent activation energy of 16.5 kJ mol^{-1}, which tends to saturate at higher temperatures, was observed in the case of the sulfur-rich surface (open symbols). In the case of the carbon-rich surface (closed symbols), a rather sharp decrease of permeation rate, with an apparent activation energy of 84.5 kJ mol^{-1}, was observed below 700 K.

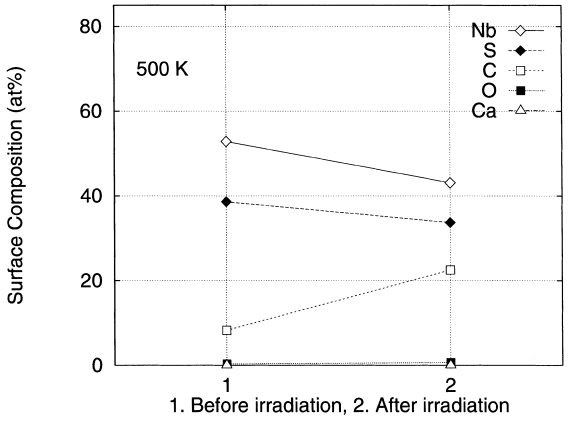

Fig. 3. Results from AES analysis on upstream-side surface of Nb specimen. The results before and after atomic deuterium irradiation are compared. Note that the measurements were performed under different vacuum conditions from those in Fig. 2.

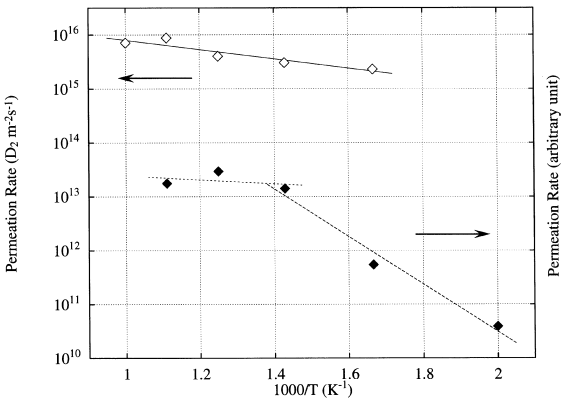

Fig. 4. Temperature dependence of atom-driven deuterium permeation rate from Nb. The measurements performed under different vacuum conditions, corresponding to Fig. 2 (open symbols) and 3 (closed symbols) are compared.

The observed phenomena may be explained as follows. Under steady state conditions, when the transport of hydrogen is limited by surface recombination at both sides, the molecular permeation rate, Φ_P (D_2 m^{-2} s^{-1}), may be expressed by

$$\Phi_P = \xi \frac{\alpha_2}{\alpha_1 + \alpha_2} \left(\frac{\phi_a}{2} \right), \tag{2}$$

where ξ is the 'retention' fraction of atoms on the surface, and α_1 and α_2 are the probabilities of dissociative adsorption at the upstream-side and downstream-side, respectively [2]. Since ξ is considered to be independent of temperature, T [2], the above equation would predict the permeation rate to be independent of T, assuming that the surface conditions are the same; i.e. $\alpha_1 \approx \alpha_2$.

Although Eq. (2) may be considered to be consistent with the experimental results in general, it does not predict the decrease of the permeation rate at lower temperatures in the case of the carbon-rich surface (closed symbols in Fig. 4). In order to be consistent with the experimental result one must assume that the deposition of carbon during atom beam irradiation has resulted in the decrease of ξ. It is unlikely that the surface composition of the downstream-side surface should change in the course of permeation, so that $\alpha_1 \approx \alpha_2$ may be assumed initially. Either due to the increase of surface potential barrier by carbon deposition, or to the increased retention by impurity layer, which is likely to become pronounced at lower temperatures, the entry of atomic deuterium into the bulk of Nb may have been limited.

The permeation probability, $\chi \equiv 2\Phi_P/\phi_a$, was estimated to be $\approx$0.07, which is smaller than the values

generally reported by Livshits et al. [2]. The reason may be due to the fact that the angle of incidence was 50° in the present study, resulting in an increase of the particle reflection coefficient. However, it should be noted that the interaction of low energy incident particles with solid surfaces is the area where the fundamental database is incomplete. Unfortunately, the QMS signals were not calibrated in the case of the carbon-rich surface, so it is not possible, at present, to compare the absolute values of the permeation rates. Thus, the dependence on surface compositions is yet to be clarified.

3.3. Comparison with ion-driven permeation measurement

The experiments on ion-driven deuterium permeation in Nb were performed using the same experimental device [6–8]. Again, a very weak dependence of steady state permeation rate on temperature was observed above 873 K (see Fig. 5). This was considered to be a consequence of surface-limited processes taking place at both surfaces. In such a case,

$$\chi = \frac{k_2}{k_1 + k_2}, \tag{3}$$

where k_1 and k_2 are known as 'phenomenological' recombination rate coefficients. Since k's can be related to α's in Eq. (2) [2,9], these two equations are similar in terms of temperature dependence, ξ in Eq. (2) can be considered to be temperature-independent only because the impinging atoms are initially not in equilibrium with the surface temperature. This is considered to be the origin of the similarity between ion- and atom-driven permeation.

It is interesting to note in Fig. 5 that at lower temperatures the permeation rate also tends to decrease. However, the interactions due to atoms and ions are expected to be different, because the energies of incidence differ by orders of magnitude. Therefore, different mechanisms should be responsible for the observed results. In contrast to the probable role of surface impurities on the incident deuterium atoms as mentioned in Section 3.2, the energetic deuterium ions would induce physical sputtering of non-metallic surface impurities, which would lead to increase of k_1 in Eq. (3). Such an effect is more pronounced at lower temperatures, for the segregation rate of impurities from the bulk to counterbalance the loss by sputtering would be smaller. The above-mentioned effect cannot be expected in the case of atom-driven deuterium.

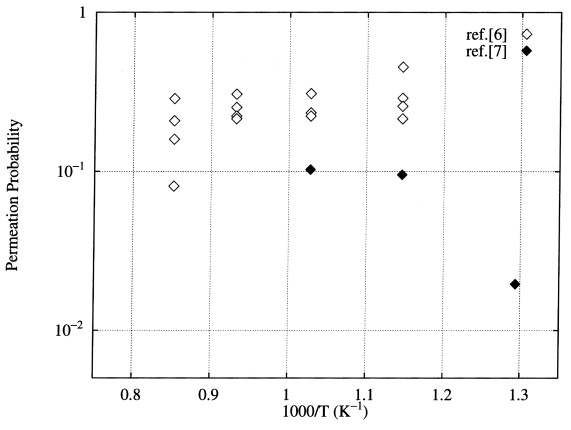

Fig. 5. Temperature dependence of ion-driven deuterium permeation rate from Nb [8]. The data series indicated with open and closed symbols means two different experimental sessions.

As expected the values of χ was considered to be larger for the ion-driven case than atom-driven case, although the precise calibration is yet to be performed in the atom-driven case. Furthermore, due to the lack of knowledge on ξ, 'phenomenological' recombination rate coefficients, corresponding to α's in Eq. (1), were not evaluated in the present study. If this becomes possible, then k's obtained from ion- and atom-driven experiments can be compared.

4. Conclusion

Atom- as well as ion-driven permeation behavior of deuterium in Nb was studied experimentally. An atomic beam source was installed in the current permeation experimental setup, thus making it possible to study the interaction of atoms with a solid surface, with in situ surface analysis. The measurements were performed under two different vacuum conditions, which resulted in contrasting surface compositions: one surface became enriched in carbon (C) after atom beam irradiation while both specimen surfaces had a large sulfur (S) content. The result of permeation measurements revealed that when the specimen surface was covered predominantly by sulfur the deuterium permeation rate weakly depended on the temperature, exhibiting the characteristic features of surface-limited transport. The surface composition was found to be unaffected by the atomic deuterium beam. On the other hand, when the surface was relatively rich in carbon and oxygen the permeation rate tended to decrease sharply when the temperature was below ~700 K. The above observations on the atom-driven experiment showed some similarities with the results of ion-driven experiment in terms of temperature dependence. Whereas the sputtering of surface impurities is considered to be responsible for the reduction of permeation rate at lower temperatures in the case of ion beam irradiation, such an effect cannot be expected in the case of atom beam irradiation. Some kind of effects by surface impurities which would inhibit the entry of atomic hydrogen was implied by the present study, but further experiments with more elaborate and

active control of surface impurity compositions, with the help of in situ surface analysis, are necessary in near future.

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