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論文

清浄 Nb 表面への水素の吸着と偏析

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Adsorption and Segregation of Hydrogen on Clean Nb Surface

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Abstract

Sticking coefficient of H_2, α, on a clean Nb surface was measured as a function of specimen temperature (25 – 477 °C) and hydrogen uptake. The initial value of sticking coefficient at negligible hydrogen uptake was ca. 0.25 and was independent of surface temperature. At any temperature examined, α showed a significant reduction with increase in hydrogen uptake, although the extent of reduction decreased with increasing temperature. Such reduction in α was ascribed to the increase in the surface coverage of hydrogen due to

surface segregation and was explained by a model assuming equilibrium partitioning of hydrogen between the surface and the solid solution phase in the bulk.

1. Introduction

Adsorption of hydrogen on a clean Nb surface has been examined by several researchers [1-8]. The results obtained by these researchers, however, were not fully interpreted. Johnson et al. [1] measured the sticking coefficient for dissociative adsorption of H_2, α, on a clean surface of polycrystalline Nb wire in a temperature range from 377 to 925 K. They reported that the initial value of α at negligible hydrogen coverage was 0.13 and was independent of the specimen temperature [1]. On the other hand, Pick [7] who measured α at ca. 340 – 500 K on a thin Nb foil preferentially having (110) plane on its surface observed significant temperature dependence of initial sticking coefficient and reported that there is a potential barrier (5.32 kJ/mol H) against dissociative sticking. Besides, Smith [5,6] and Strongin et al. [8] examined hydrogen adsorption on Nb (110) planes by means of photoemission spectroscopy and reported that the growths of hydrogen-induced photoelectron peaks were faster than that expected from a simple model assuming equilibrium partitioning of hydrogen between the surface and the solid solution phase in the bulk. In order to interpret such results, these authors proposed more complicated models assuming formations of "near-surface" distribution of hydrogen [6] or surface hydride [8]. The validities of these models, however, were not fully confirmed.

Niobium and other group 5 metals (V and Ta) are suitable materials for superpermeable membranes which can be used for particle control in edge plasma and tritium recovery in fusion devices [9]. From this viewpoint, the present authors have examined the interaction of atomic and molecular hydrogen with Nb [10-13]. In these studies, the surfaces of specimens were covered by non-metallic impurities such as oxygen, because the suppression of reemission by such impurities is essential for superpermeation under exposure to suprathermal hydrogen particles such as atoms and ions. The techniques developed in these experiments, however, can be applied for studies of clean surfaces.

In this paper, the sticking of H_2 molecules on a clean surface of Nb ribbon preferentially having (100) plane was examined in a temperature range from 25 to 477 °C by measuring the speed of H_2 pumping by the specimen. The initial sticking coefficient showed no significant temperature dependence; the dissociative sticking of H_2 was virtually non-activated process in the temperature range examined. The kinetics of hydrogen uptake was well described by a simple model assuming equilibrium partitioning of hydrogen between the surface and the solid solution phase in the bulk. The heat of surface segregation of hydrogen and that of adsorption were evaluated from the dependence of α on the specimen temperature and hydrogen uptake; the obtained value of the heat of adsorption was close to that reported in literatures [2,7].

2. Experimental

A ribbon of polycrystalline Nb ($7.2 \times 370 \times 0.1$ mm^3) was used as a specimen. In order to obtain uniform temperature distribution during ohmic heating described below, two Mo sheets ($7.3 \times 46 \times 0.2$ mm^3) were spot welded to the both ends of the specimen ribbon as shown Fig. 1. After polishing the surface with abrasive papers, the specimen was cleaned with acetone in a ultrasonic bath and then installed in an auxiliary chamber of an ultra-high vacuum apparatus described elsewhere [10] with an electric feedthrough as shown in Fig. 2. The pressure of residual gases in the chamber

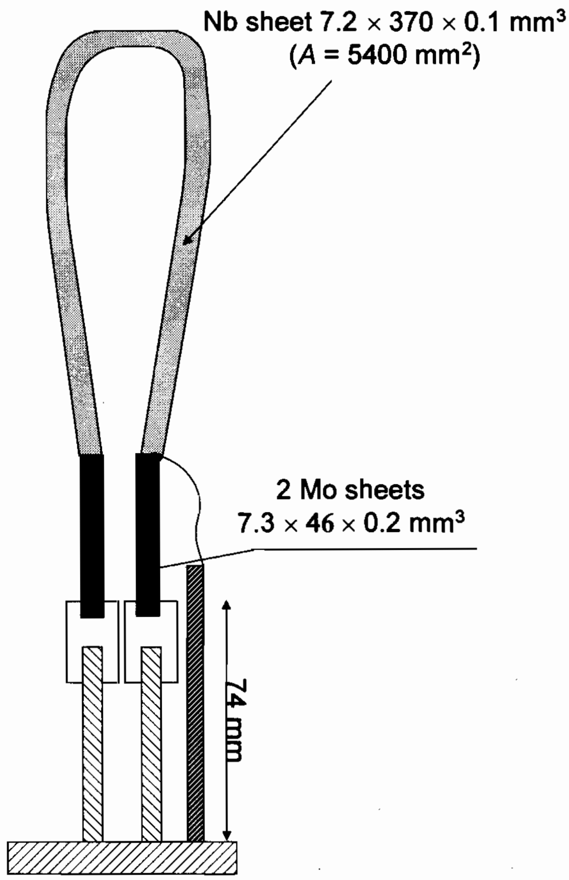

Fig. 1 Schematic description of specimen setup.

was below 1 × 10^{-7} Pa, and the main component was H_2.

The specimen was heated ohmically. Measurements of voltage-current (*V-I*) characteristics allowed the evaluation of specimen temperature from (1) resistivity [14], and (2) emissivity [14] by assuming that the inputted power was balanced against the emission. The values evaluated by these two methods were slightly different from each other below 500 °C as shown in Fig. 3, although fairly good agreement was obtained in higher temperature region. Hence, in the region below 500 °C, the specimen temperature was evaluated from the dashed line connecting data point for room temperature ($V = I = 0$) and that for 500 °C.

A clean surface was prepared by repeated heating of the specimen in ultra-high vacuum up to 2100 °C for durations of 10-30 s; the total heating time was ca. 10 ks. Such heat treatment in ultra-high vacuum is commonly employed to obtain a clean Nb surface [15]. The

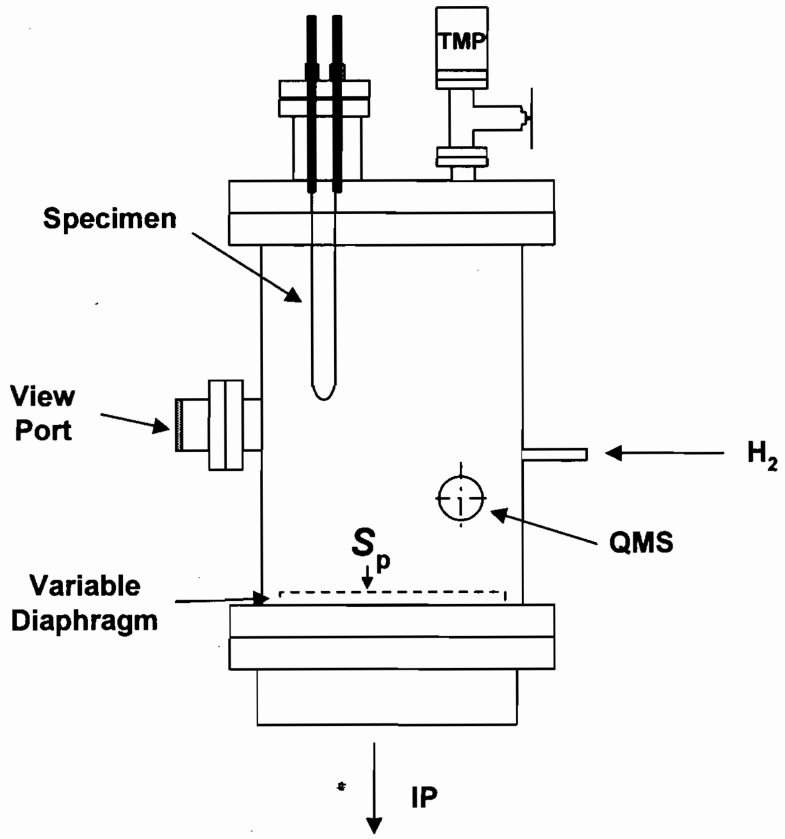

Fig. 2 Schematic description of vacuum chamber; TMP: turbo-molecular pump, and QMS: quadrupole mass spectrometer.

exposure of prepared clean surface to the residual gases led to no significant change in the sticking coefficient of H_2; the influence of surface contamination by residual gases was negligibly small under the present conditions.

The sticking coefficient of H_2, α, was measured by absorption experiment in the temperature region from 25 (controlled room temperature) to 477 °C in the following manner. First, pumping of the chambers was stopped by closing valves, and the surface was deactivated by the exposure to residual gases at rather high pressure (10^{-4} Pa) at room temperature. Then the chamber was evacuated to ultra-high vacuum again by a sputter-ion pump (IP), and H_2 gas was introduced through a variable-leak valve (VLV) at known flow rates (10^{-8} – 10^{-7} Pa·m^3/s) to pressures in the order of 10^{-6} Pa. After the establishment of stable pressure, the H_2 introduction was stopped by pumping the backside of the VLV, in which the opening of VLV was kept constant. Then, the clean surface was prepared by heating the specimen for a short period of time (activation). Hydrogen gas was introduced into the chamber at the same flow rate as before but in stepwise by supplying H_2 gas of the same pressure to the backside of VLV. The pressure of H_2 in the chamber did not reach the previous value due to H_2 absorption (i. e. pumping) by the specimen. The sticking coefficient α was estimated from this pressure difference.

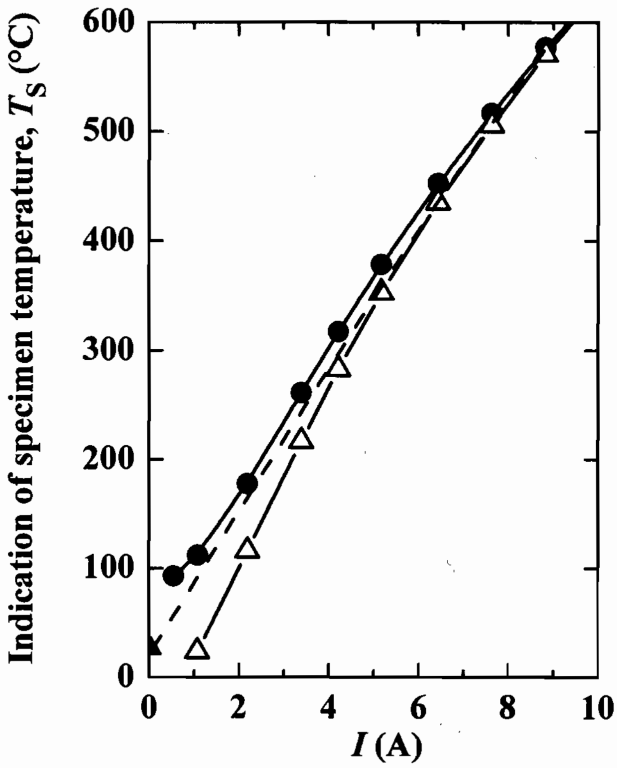

Fig. 3 Correlation between electric current, I, and specimen temperature evaluated from resistivity (△) and emissivity (●).

3. Results and discussion

The analyses by means of X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) showed that the specimen surface mainly consisted of Nb(100) plane (~90%) inclined at 0.8–1.9° to the surfaces, and also of Nb(211) (~10%) plane inclined at ~2.2°. Hence, the results described below mainly indicate the characteristics of Nb(100) plane.

A typical result of absorption experiments obtained at 25 °C is shown in Fig. 4. When H_2 gas was introduced into the chamber after the activation treatment, the pressure of H_2 immediately reached to 6.2×10^{-7} Pa, while that before the activation was 4.0×10^{-6} Pa at the same flow rate of H_2 gas. This difference in H_2 pressure was due to pumping by the specimen. The sticking coefficient α was evaluated from this extent of pressure difference with the following equation:

$$\alpha = \frac{S_P \sqrt{2\pi m}}{A\sqrt{RT_g}} \frac{P_1 - P_2}{P_2}, \quad (1)$$

where S_P is the pumping speed by IP typically controlled to be 0.12 m^3/s by adjusting the position of variable diaphragm shown in Fig. 2, m is the molar mass of H_2 molecules, A is the

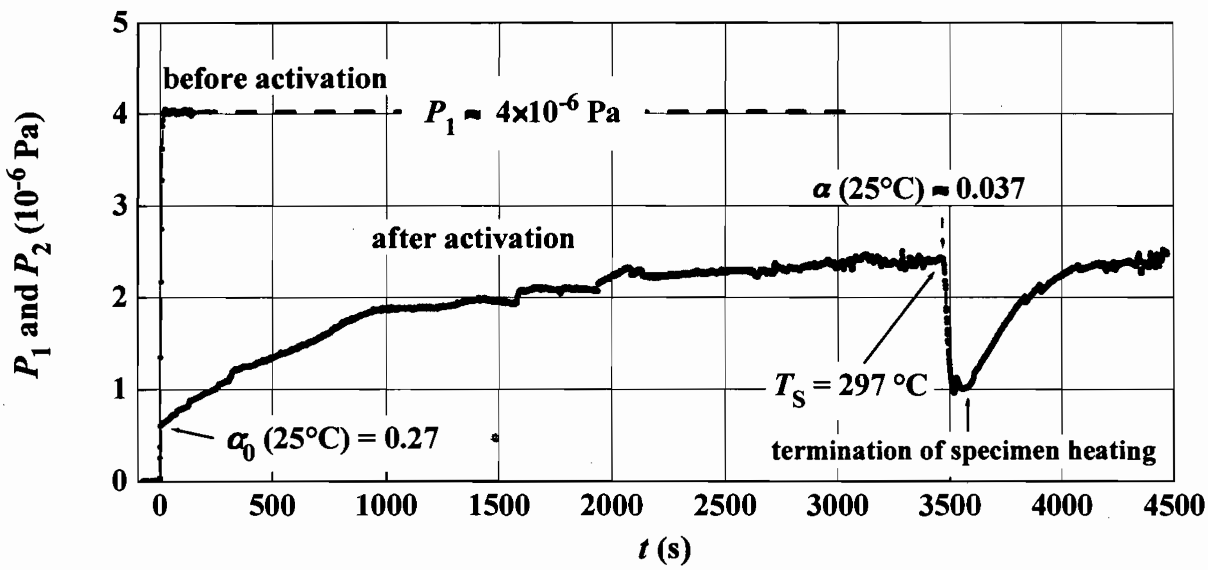

Fig. 4 Typical result of absorption experiment at 25 °C.

surface area of the specimen (5400 mm^2), R is the gas constant, T_g is the gas temperature, P_1 is the H_2 pressure before the activation and P_2 is that after the activation. The initial value of sticking coefficient α immediately after the stepwise introduction of H_2 was evaluated to be 0.27 in this case. The pressure of H_2 gradually increased to 2.4×10^{-6} Pa with time, t, as shown in Fig. 4. Such increase in H_2 pressure could be ascribed to either of (1) reduction in α due to saturation of surface sites, and (2) increase in reemission rate due to accumulation of hydrogen in the specimen. In order to understand the mechanism of this pressure increase, the specimen was heated to 297 °C at t = 3450 s. The increase in specimen temperature resulted in the reduction in H_2 pressure to 1.0×10^{-6} Pa. This reduction in H_2 pressure was ascribed to the increase in α due to reduction in surface hydrogen coverage caused by the enhancement of dissolution of hydrogen atoms from the surface into the bulk. Namely, this observation indicates that the increase in H_2 pressure with t was due to the reduction in α and not caused by the increase in reemission. The mechanism underlying the pressure increase with t was also examined by stopping the H_2 gas introduction (not shown in the figure). The pressure of H_2 immediately dropped to the background level after the interruption of H_2 introduction, indicating no significant hydrogen release from the specimen. The value of α corresponding to P_2 of 2.4×10^{-6} Pa was evaluated to be 0.037 by Eq. (1). Namely, the value of α was reduced by an order of magnitude.

Such change in α with t was measured in the same manner up to 200 °C. At higher temperatures, significant reemission of absorbed hydrogen was observed after accumulation of hydrogen in the bulk. Namely, H_2 pressure did not reach the background level when the introduction of H_2 gas was interrupted. Therefore, only *initial* values of α were obtained above 200 °C. The values of initial sticking coefficient, α_0, thus obtained are plotted against the specimen temperature, T_S, in Fig. 5. The value at the highest T_S (1520 °C) was evaluated from the rate of dissociation (atomization) [10]. Interestingly, α_0 showed no significant dependence on T_S in a very wide range of T_S. This observation agreed with the results obtained by Johnson et al. [1] in a narrower temperature range (377 – 925 K). Namely, in

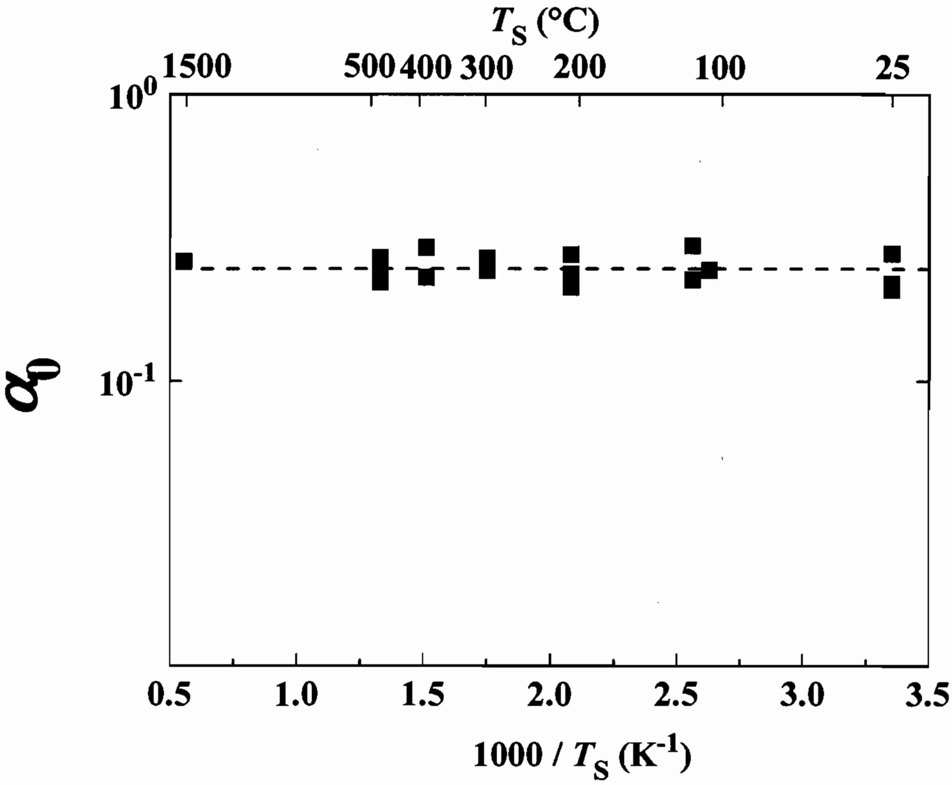

Fig. 5 Temperature dependence of initial sticking coefficient, α_0.

contrast to the study of Pick [7], no evidence for the presence of activation barrier was observed. The average value of α_0 was calculated to be 0.25 and was comparable to the value reported by Johnson et al., 0.13 [1].

In Fig. 4, the pressure of H_2 was restored from 1.0×10^{-6} Pa to the previous value, 2.4×10^{-6} Pa, within 600 s after the termination of specimen heating, while it took more than 2700 s in the initial stage (i. e. from 250 to 3000 s). Namely, the duration of time required for the pressure increase was significantly reduced by the accumulation of hydrogen in the specimen bulk. This observation indicates that the surface concentration of hydrogen was determined by the surface segregation from the bulk and not by the incident flux of H_2 from the gas phase. According to the data on diffusion coefficient of hydrogen in Nb [16], the absorbed hydrogen atoms diffuse along a distance comparable to the specimen thickness within 1 s. Hence, it is appropriate to consider that the equilibrium is readily attained between hydrogen atoms on the surface and those in the bulk.

When the equilibrium is attained, and the bulk hydrogen concentration is enough low, the correlation between hydrogen concentration on the surface and that in the bulk can be expressed as follows:

$$\frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}} = C_{\mathrm{H}} K_0 \exp(\frac{\Delta H_{\mathrm{seg}}}{RT_{\mathrm{S}}}), \tag{2}$$

where θ_{H} is the surface coverage of hydrogen, C_{H} is the bulk concentration, K_0 is the entropy factor, and ΔH_{seg} is the heat of surface segregation. By assuming that two adjacent hydrogen-free surface sites act as the active center for H_2 adsorption, α on hydrogen-covered surface can be described as

$$\alpha = \alpha_0 (1-\theta_{\mathrm{H}})^2. \tag{3}$$

Hence, the value of θ_{H} can be obtained as

$$\theta_{\mathrm{H}} = 1-(\frac{\alpha}{\alpha_0})^{\frac{1}{2}}. \tag{4}$$

The specific amount of hydrogen taken up per unit surface area (H atoms/m^2), q_{ut}, is described as

$$q_{\mathrm{ut}} = \rho_{\mathrm{S}}\theta_{\mathrm{H}} + \rho_{\mathrm{b}}C_{\mathrm{H}} \times d/2, \tag{5}$$

in which ρ_{S} and ρ_{b} are areal density (9.2×10^{18} atoms/m^2 for (100) plane) and volume density (5.6×10^{28} atoms/m^3) of Nb, and d is the specimen thickness. The value of q_{ut} can be easily evaluated from Fig. 4 with the following equation:

$$q_{\mathrm{ut}} = \frac{2S_{\mathrm{P}}}{ART_{\mathrm{g}}}\int_0^t (P_1 - P_2(t))dt. \tag{6}$$

Typical examples of changes in q_{ut}, θ_{H} and C_{H} with t at 25 °C thus evaluated are shown Figs. 6 and 7. Although the pressure of H_2 was comparable, the development of θ_{H} was much slower than that shown by Strongin et al. (Fig. 1 in Ref. [8]), in which θ_{H} reached the maximum value within 200 s at 2×10^{-8} Torr (2.7×10^{-6} Pa). Two possible mechanisms can be proposed for this discrepancy; (1) the intensity of hydrogen-induced photoelectron peak examined in their study is not simply proportional to θ_{H} or (2) the characteristics of (100) and

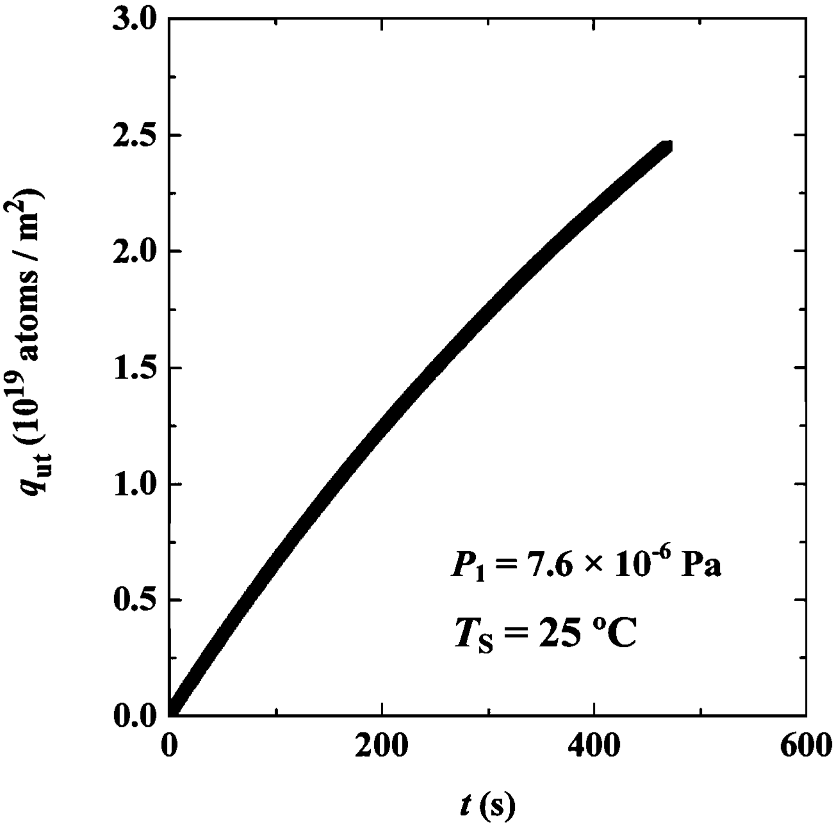

Fig. 6 Change in hydrogen uptake q_{ut} with time t at 25 °C.

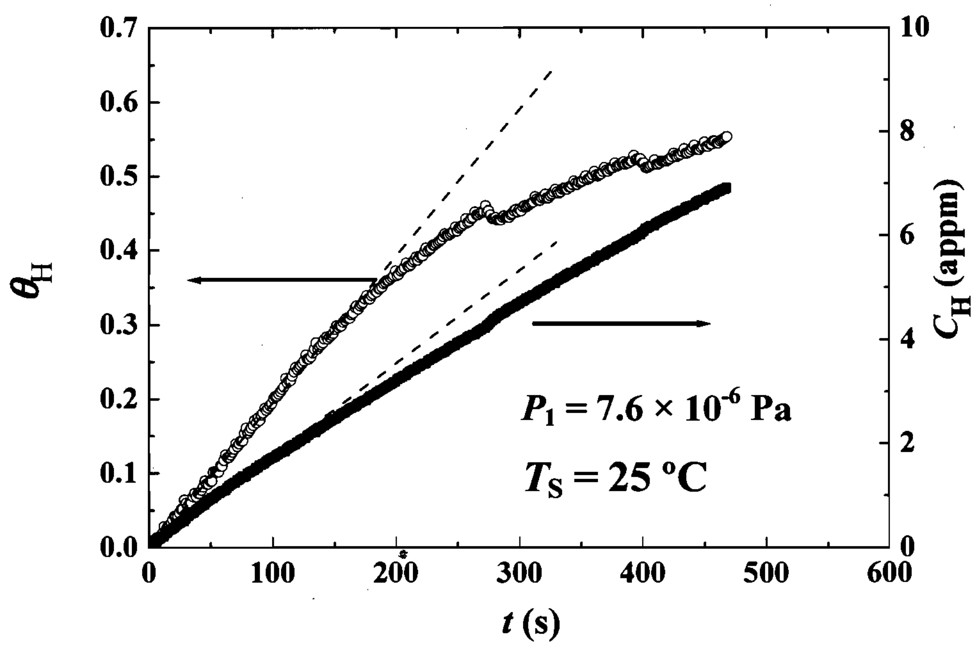

Fig. 7 Changes in θ_H and C_H with t at 25 °C.

(110) planes are different from each other. Final conclusion, however, has not been derived.

According to the present model, the rate of hydrogen uptake, dq_{ut} / dt, can be expressed as follows:

$$\frac{dq_{ut}}{dt} = \frac{2\alpha_0(1-\theta_H)^2}{\sqrt{2\pi mRT_g}} P_2(t). \tag{7}$$

Namely, the rate of hydrogen uptake, dq_{ut} / dt, should be proportional to $(1-\theta_H)^2 \cdot P_2(t)$. In order to check the validity of the present model, (dq_{ut} / dt) is plotted against $(1-\theta_H)^2 \cdot P_2(t)$ in Fig. 8 which clearly shows that (dq_{ut} / dt) is in proportion to $(1-\theta_H)^2 \cdot P_2(t)$. It was therefore concluded that the sticking of H_2 could be described by the above-mentioned simple model assuming the equilibrium partitioning of hydrogen between the surface and the solid solution phase in the bulk under the present conditions.

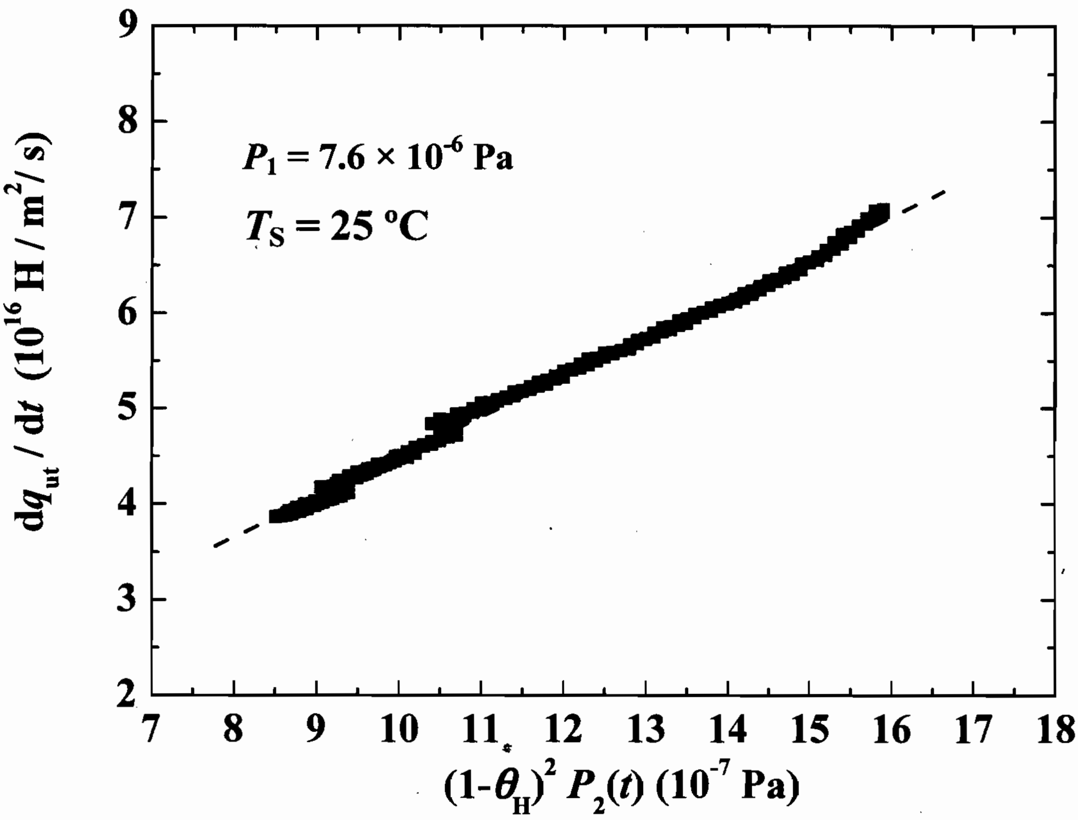

Fig. 8 Correlation between the rate of hydrogen uptake, q_{ut} / dt, and $(1-\theta_H)^2 \cdot P_2(t)$ at 25 °C.

Here, Eqs. (2) and (5) yield

$$\Delta H_{\mathrm{seg}} = RT_{\mathrm{S}} \times \ln\left[\frac{q_{\mathrm{ab}} - \rho_{\mathrm{S}}\theta_{\mathrm{H}}}{\rho_{\mathrm{b}} d/2}\left(\frac{1}{\theta_{\mathrm{H}}} - 1\right)\right]. \quad (8)$$

The values of ΔH_{seg} evaluated with Eqs. (4) and (7) by assuming $K_0 = 1$ are plotted against θ_{H} in Fig. 9; ΔH_{seg} was determined to be 29 kJ/mol at 25 °C and to be ca. 38 kJ/mol at higher temperatures. Slight reduction in ΔH_{seg} with increasing θ_{H} was observed at elevated temperatures, while no significant dependence on θ_{H} was observed at 25 °C. Such distinct tendency observed at 25 °C may be due to the surface reconstruction such as ordering of adsorbed hydrogen atoms, but the mechanism underlying this difference has not been fully clarified.

Figure 10 shows the correlation between α and q_{ut} at 25 °C as an example. The sticking coefficient α started to drop at $q_{\mathrm{ut}} = 10^{18}$ H/m^2 and became 1/10 of initial value at 2×10^{19} H/m^2. According to Eq. (4), α_0/α becomes 0.1 at $\theta_{\mathrm{H}} = 0.684$ and consequently at $\rho_{\mathrm{S}}\theta_{\mathrm{H}} =$

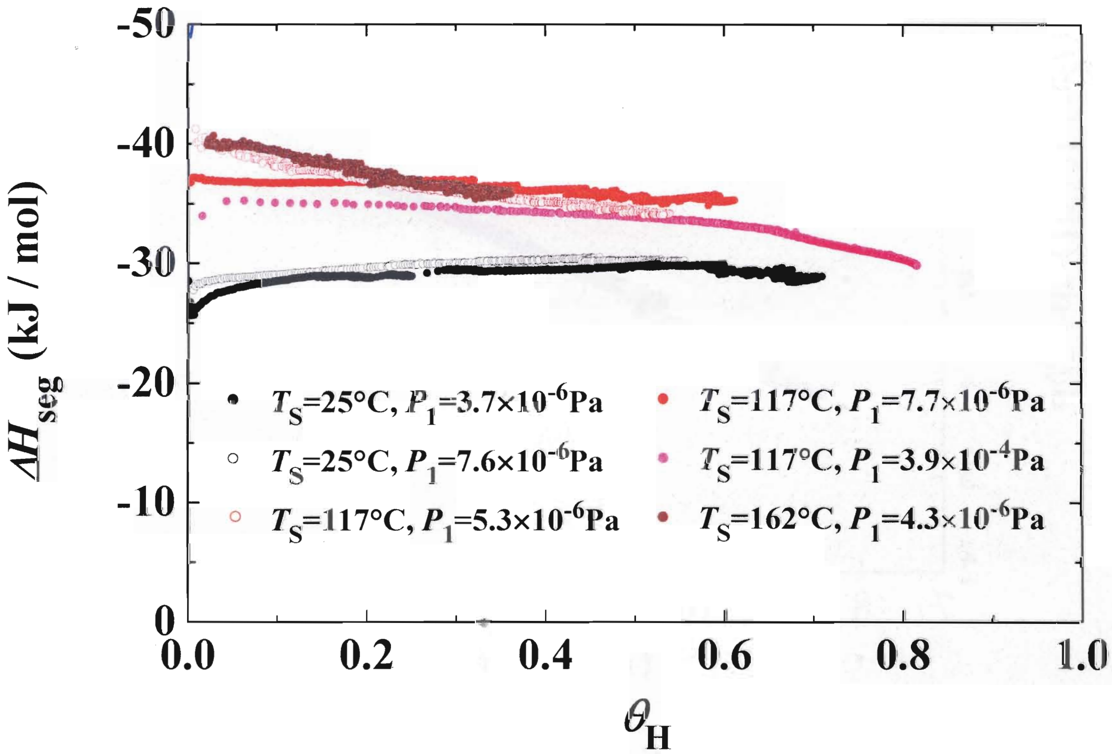

Fig. 9 Correlation between ΔH_{seg} and θ_{H} obtained under various conditions.

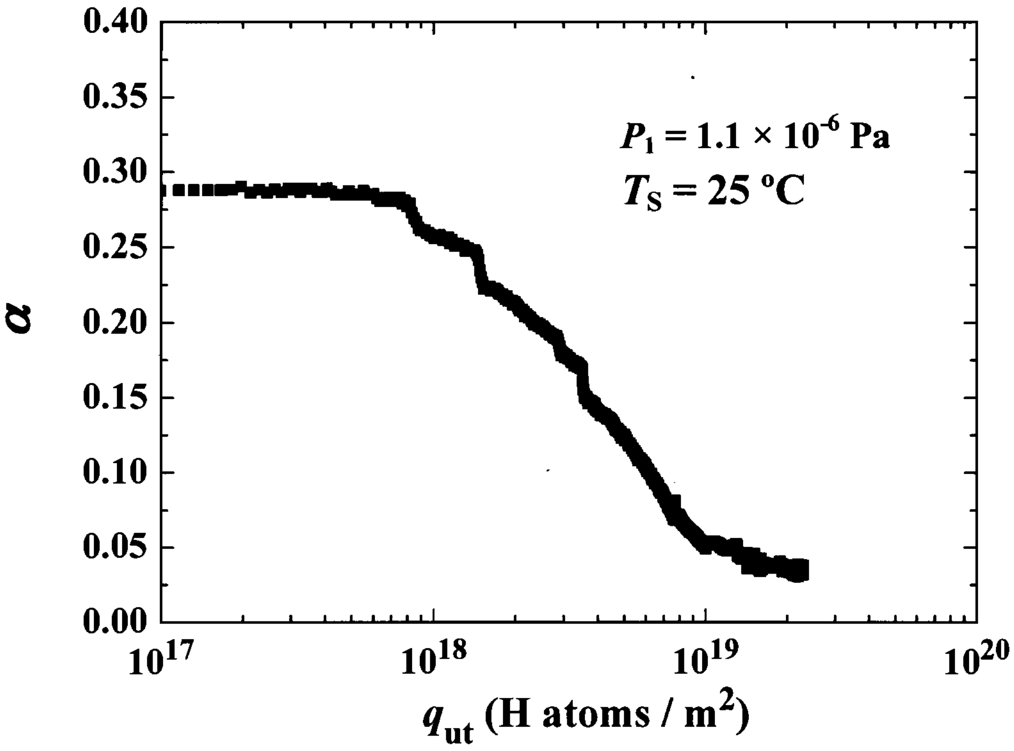

Fig. 10 Change in q_{ut} with θ_H at 25 °C.

6.3×10^{18} H/m^2. Hence, $\rho_b C_H \times d / 2 = 1.4 \times 10^{19}$ H/m^2 (Eq. (5)) where C_H is determined to be 5 appm. On the other hand, according to Eq. (2), θ_H becomes 0.684 at C_H = 5 appm when ΔH_{seg} = 32 kJ/mol. This value of ΔH_{seg} is close to that determined by Eq. (8), i. e. 29 kJ/mol. This consistency also shows the validity of the present model.

The heat of surface segregation ΔH_{seg} corresponds to the enthalpy difference between adsorption state on the surface sites and dissolution state in the bulk interstitial sites. On the other hand, the heat of solution ΔH_{sol} which is reported to be 34 kJ/mol for H-Nb system [17] is defined to be the enthalpy difference between hydrogen atoms in the state of H_2 molecule and the dissolution state. Therefore, the heat of adsorption ΔH_{ad} corresponding to the enthalpy difference between the state of H_2 molecule and the adsorption state is obtained as $\Delta H_{ad} = \Delta H_{sol} + \Delta H_{seg}$ = 72 kJ/mol H (elevated temperatures) or 63 kJ/mol H (25 °C). These values are comparable to that reported by Hagen and Donaldson [2] (56 kJ/mol H), and Pick [7] (56.6 kJ/mol H).

4. Conclusions

(1) Initial value of sticking coefficient of H_2, α_0, on a clean Nb surface obtained at gas temperature of 25 °C and specimen temperature of 25 - 280 °C was about 0.25 and was independent of surface temperature; no evidence for the presence of activation barrier against sticking was observed.

(2) The sticking coefficient, α, significantly decreased with increasing hydrogen uptake, and this reduction in α was well described by a simple model assuming the equilibrium partitioning of hydrogen between the surface and the bulk.

(3) The heat of surface segregation of hydrogen was evaluated to be 29 kJ/mol at 25 °C and 38 kJ/mol at elevated temperatures.

(4) The value of heat of adsorption of hydrogen obtained from the heat of surface segregation and that of solution agreed with a value reported in literatures [1,7].

Acknowledgements

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