

## 論文

### バナジウム表面における水素の解離反応速度の バルク中酸素濃度依存性

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### Sticking of H<sub>2</sub> on Oxygen-Covered Surface of Vanadium Doped with Oxygen to Various Bulk Concentrations

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#### Abstract

The sticking probability of H<sub>2</sub> on the surface of polycrystalline V covered with oxygen was examined as a function of oxygen concentration in the *bulk metal* (0.4 to 3.3 at.%) at specimen temperatures from 200 to 1000 °C. At all temperatures examined, the sticking probability was strongly dependent on the oxygen concentration in the bulk. Such correlation between the reaction rate of H<sub>2</sub> on the surface and the oxygen concentration in the bulk was attributed to the dependence of concentration of oxygen vacancies (holes in surface oxygen coverage) on the oxygen bulk concentration. The values of sticking probability were relatively high even at the oxygen bulk

concentration of 3.3 at.%; the oxygen coverage on vanadium was rather “holey” even at the oxygen concentration close to the solubility limit. The activation energy for H<sub>2</sub> dissociation on such holes in the coverage was evaluated to be 10 kJ/mol H<sub>2</sub>.

## 1. Introduction

Understanding of reaction mechanism of hydrogen on metal surfaces is important for the development of catalysts, hydrogen permeation membranes and storage materials, non-evaporable getters, low-outgassing materials and so on. The surfaces of these materials, however, are not necessarily clean but covered with nonmetallic impurities such as oxygen, sulfur and carbon in most cases. Therefore, one of the key issues to understand the reaction mechanism is to clarify the reaction centers on the metal surfaces covered with nonmetallic impurities.

If temperature of metal surface,  $T_S$ , is sufficiently high, the equilibrium is attained between the impurity on the surface and in the bulk. According to Langmuir-McLean equation [1], the correlation between the surface impurity coverage,  $\theta_O$ , and the impurity concentration in the bulk,  $C_O$ , is described as

$$\frac{\theta_O}{1-\theta_O} = k_O C_O \exp\left(-\frac{\Delta H_{\text{seg}}}{RT_S}\right), \quad (1)$$

where  $\Delta H_{\text{seg}}$  is the heat of surface segregation of the impurity, and  $k_O$  is the constant coefficient. Usually,  $\Delta H_{\text{seg}}$  takes large negative value, and hence  $\theta_O$  is comparable to unity even at very low  $C_O$ . Nevertheless, a certain portion of the surface,  $1-\theta_O$ , still remains free from the impurity at any  $T_S$  and  $C_O$ . In other words, even a *monolayer* coverage ( $\theta_O \approx 1$ ) contains a definite number of stochastically distributed *holes* (the

surface sites free from the impurity). One can consider two different concepts with regard to the reaction centers on the metal surface covered with nonmetallic impurities.

1. The “*Holes in the coverage*” concept: the surface sites free of impurity (holes in coverage) form active centers. This mechanism appears to be dominant at higher  $T_S$  where, according to Eq. (1), a considerable portion of clean surface opens up. Since  $1-\theta_O$  depends on  $C_O$ , bulk impurity concentration will govern reaction kinetics in this case as demonstrated by Hörz and Fromm [2,3] who reported the clear influence of the bulk concentrations of oxygen and nitrogen on the reactivity of polycrystalline Nb and Ta towards the decomposition of  $C_nH_m$  molecules at  $T_S > 1200$  °C. According to Eq. (1), however, the fraction of coverage holes,  $1-\theta_O$ , is negligible at lower  $T_S$ . For example,  $1-\theta_O$  should be in a range of  $10^{-5}$  at  $T_S \sim 200$  °C in the O–Nb system even at  $C_O$  as low as 0.1 at.% (with  $|\Delta H_{\text{seg}}| = 71$  kJ/mol [4]).

2. The “*Holes in the barrier concept*”: here, holes are regarded to be inherent to the *regular* surface sites covered with impurity [5], i.e. the holes are not the “stochastic” sites with the lack of impurity atoms but such area in *each* surface unit cell where the barrier is lower than in other parts for an incident molecule with particular orientation and internal state. For example, Eibl and Winkler [5,6] who measured the sticking coefficient of  $D_2$  molecules on V(111) covered with oxygen and sulfur at  $T_S = 77$  K and  $T_g = 300$  K, attributed rather large value of sticking coefficient,  $10^{-4}$ , to such holes in barrier ( $T_g$  indicates gas temperature).

In order to understand the type of dominant reaction centers at *relatively low*  $T_S$  where one should expect a virtually saturated coverage ( $\theta_O \approx 1$ ), the sticking probability of  $H_2$ ,  $\alpha_{H_2}$ , on O-covered Nb surface, was measured as a function of  $C_O$  in a wide temperature range including room temperature [7]. The sticking probability of  $H_2$ ,  $\alpha_{H_2}$ ,

was clearly dependent on  $C_O$  at all  $T_S$  examined. Namely,  $\alpha_{H_2}$  was proportional to  $1/C_O^2$ . Therefore, it was concluded that two adjacent oxygen vacancies played the role of reaction centers in  $H_2$  sticking on the O-covered Nb surface even at low  $T_S$ . Such dependence on  $C_O$  has been also observed for the rate constant of recombinative desorption of  $D_2$  from Nb [8].

Preliminary investigation on V containing oxygen showed that  $\alpha_{H_2}$  on the V surface is also dependent on  $C_O$  [9], but details of  $H_2$  reaction have not been understood. In the present study,  $\alpha_{H_2}$  on the V surface is examined in wide ranges of  $C_O$  (0.4 to 3.3 at.%) and  $T_S$  (200 to 1000 °C) by permeation techniques [7], and the mechanism underlying  $H_2$  sticking is discussed by comparing the obtained results with those for Nb acquired in the previous study [7].

## 2. Experimental

The specimen used was a membrane of polycrystalline V (0.1 mm thickness) in tubular shape fabricated from a sheet supplied by ESPI Metals Co., USA. Nominal purity of the specimen was 99.9 mass%.

The permeation experiments were performed in an ultra-high vacuum (UHV) apparatus separated into two chambers by the tubular membrane [7,10]. Both chambers were independently pumped by turbo-molecular pumps and sputter-ion pumps, and the pressure of residual gas was about  $10^{-8}$  Pa. The outside surface of the tubular membrane was exposed to  $H_2$  gas, H atoms or hydrogen plasma, depending on experimental requirements. In the case of exposure to  $H_2$  gas, the temperature of the gas was virtually close to room temperature due to collision with the chamber walls. The permeation flux of hydrogen was measured with a calibrated ionization gauge and a quadrupole mass

analyzer. The specimen was heated resistively, and its temperature was measured by a thermocouple inside the tubular membrane.

After the installation in the apparatus, the specimen surface was sputtered by hydrogen plasma at  $T_S$  in the range from 600 to 1000 °C. The surface analysis by Auger electron spectroscopy (AES) carried out in a different UHV apparatus showed that sulfur was a dominant segregated surface impurity in this temperature range before the sputtering. Nevertheless, long-term sputtering (15 hours) in this range of  $T_S$  resulted in the removal of sulfur, and oxygen became sole surface impurity. The oxygen concentration in the bulk of the specimen was 0.4 at.% after the sputtering treatment. Then oxygen was uniformly introduced into the specimen in a step-by-step manner up to 3.3 at.% by a gas absorption method and subsequent diffusion annealing in UHV. At each step of the oxygen doping, the permeation experiments were carried out by filling the outside chamber with  $H_2$  gas ( $10^{-3}$  to 10 Pa) at  $T_S$  from 200 to 1000 °C. Note that at  $T_S$  and  $C_O$  utilized in this work, oxygen was in solid solution phase [11].

When the upstream and downstream surfaces of membrane are identical, the permeation rate of  $H_2$ ,  $\phi_{H_2}$ , in steady state is expressed as

$$\phi_{H_2} = \frac{1}{2} \alpha_{H_2} \phi_{inc}, \quad (2)$$

where  $\alpha_{H_2}$  is the sticking probability of  $H_2$ , and  $\phi_{inc}$  is incident  $H_2$  flux onto the upstream surface. The incident flux is expressed as  $\phi_{inc} = P / \sqrt{2\pi mkT_g}$  where  $P$  is the pressure of  $H_2$  gas in the outside chamber,  $m$  is the mass of a  $H_2$  molecule, and  $k$  is Boltzmann constant. In this work, identity of upstream and downstream surfaces was confirmed by separate measurements of  $\alpha_{H_2}$  for upstream and downstream surfaces with

the H<sub>2</sub> absorption technique mentioned in Ref. [7]; the values of  $\alpha_{\text{H}_2}$  on upstream and downstream surfaces were always comparable with each other after oxygen doping.

### 3. Results

At all exposure conditions, the change in the permeation rate in a transient state after H<sub>2</sub> introduction in the upstream side showed that the permeation rate was controlled by surface processes (dissociative absorption and recombinative desorption) and not by bulk diffusion process. The diffusivity of hydrogen in V is rather high even at low  $T_S$ . For example, the diffusion coefficient is estimated to be  $1.0 \times 10^{-8}$  m<sup>2</sup>/s at 200 °C from the data recommended by Völkl and Alefeld [12]. Hence, the steady state should be attained within a time scale of few seconds provided that the permeation is controlled by the diffusion process. It took, however, several minutes or more to attain the steady state in the present study. Therefore, it was possible to evaluate the sticking probability,  $\alpha_{\text{H}_2}$ , from the permeation rate in the manner described in Section 2.

Fig. 1 shows the Arrhenius plot of  $\alpha_{\text{H}_2}$  at various oxygen bulk concentrations,  $C_{\text{O}}$ . In this case, the specimen was first heated to 1200 °C, and then  $T_S$  was reduced in a step-by-step manner; the specimen was kept at each temperature for 10 min. It should be noted that  $\alpha_{\text{H}_2}$  clearly decreased with increasing  $C_{\text{O}}$ . On the other hand, no significant change with  $C_{\text{O}}$  was observed in the temperature dependence; two characteristic bends in the plot were observed at around 500 and 300 °C at all  $C_{\text{O}}$  examined. The sticking probability  $\alpha_{\text{H}_2}$  showed weak temperature dependence in a range from 300 to 500 °C, and the slope in this region corresponded to the activation energy of 10 kJ/mol H<sub>2</sub>. A stronger temperature dependence was observed in the regions of  $T_S > 500$  °C and  $T_S < 300$  °C, corresponding to the activation energy of 30 –

35 kJ/mol (Fig. 1). Similar correlation between  $\alpha_{\text{H}_2}$  and  $C_{\text{O}}$  was observed also for a different membrane prepared from a sheet with different nominal purity (99.35 mass%). It was therefore concluded that the dependence of  $\alpha_{\text{H}_2}$  on  $C_{\text{O}}$  is a general property of V-O systems.

In order to check whether the data on  $\alpha_{\text{H}_2}$  shown in Fig. 1 pertain to definite values determined by  $T_{\text{S}}$  and  $C_{\text{O}}$ , the influence of thermal history of the specimen on  $\alpha_{\text{H}_2}$  was examined. That is definitely so in the range of sufficiently high  $T_{\text{S}}$  and  $C_{\text{O}}$  where there is an equilibrium between the surface and bulk oxygen. The establishment of such equilibrium, however, may be very slow at lower  $T_{\text{S}}$  and  $C_{\text{O}}$ , and it is practically never reached. In this range, oxygen coverage, and correspondingly  $\alpha_{\text{H}_2}$ , may be different at the same  $T_{\text{S}}$  and  $C_{\text{O}}$ , depending on thermal history. Figure 2 shows temperature dependencies of  $\alpha_{\text{H}_2}$  at  $C_{\text{O}} = 0.4$  and 1.3 at.% for two different measurement modes. Mode 1 corresponds to the method by which the data shown in

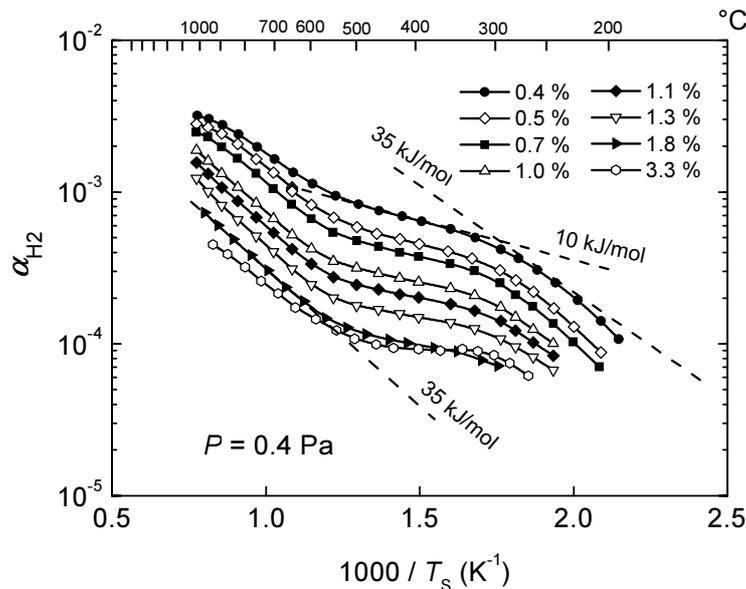


Fig. 1 Temperature dependence of sticking probability  $\alpha_{\text{H}_2}$  on V surface at different oxygen bulk concentration  $C_{\text{O}}$  indicated in the figure. Pressure of  $\text{H}_2$  gas in upstream side was 0.4 Pa.

Fig. 1 were acquired; the specimen was kept at each temperature for 10 min after heating in vacuum at 1200 °C. In mode 2, the specimen was kept at each temperature for much longer time (more than 1 h). No significant difference between the modes 1 and 2 was observed at low  $C_O$  (as shown in Fig. 2 for  $C_O = 0.4$  at.%). At  $1.0 \text{ at.\%} \leq C_O \leq 1.3 \text{ at.\%}$  and  $T_S \geq 800$  °C, however, the permeation rate first reached “quasi” steady state value within 10 min, and then gradually decreased with time to reach “new” stationary rate. Consequently, the value of  $\alpha_{H_2}$  measured in the mode 2 was smaller than those obtained in the mode 1 by ca. factor of 2 as shown in Fig. 2. Such gradual change in  $\alpha_{H_2}$  can be ascribed to gradual increase in the surface oxygen coverage by the segregation from the bulk. The sets of data obtained by the modes 1 and 2, however, showed similar temperature dependence. The difference between the modes 1 and 2 was not observed at  $C_O = 1.8 \text{ at.\%}$  and higher concentrations. It was therefore concluded that

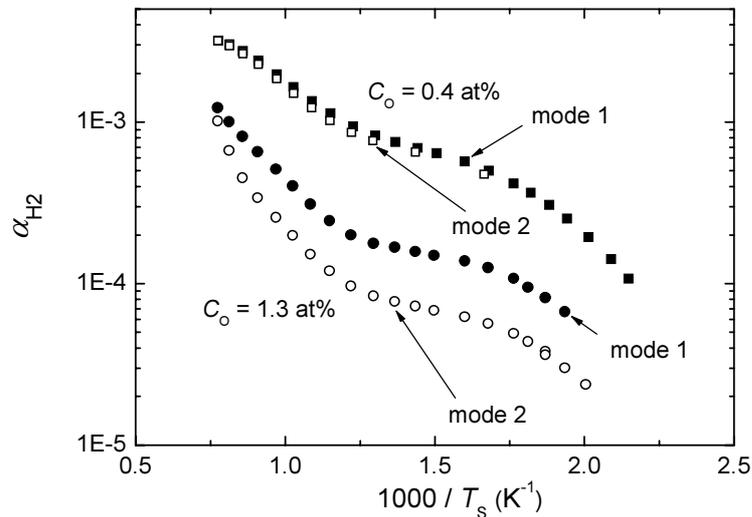


Fig. 2 Influence of thermal history of specimen on  $\alpha_{H_2}$ . Solid symbols refer to  $\alpha_{H_2}$  measured by keeping specimen at given temperatures for 10 min (mode 1), whereas open symbols refer to  $\alpha_{H_2}$  obtained by holding specimen for sufficiently long time (mode 2). Pressure of  $H_2$  gas in upstream side was 0.4 Pa.

the data shown in Fig. 1 are definite values determined by  $T_S$  and  $C_O$  at  $1.0 \text{ at.\%} > C_O$  and  $C_O \geq 1.8 \text{ at.\%}$ , and the values at  $1.0 \text{ at.\%} \leq C_O \leq 1.3 \text{ at.\%}$  correspond to the surface states before the completion of oxygen segregation but show similar temperature dependence as “definite” values. The values of oxygen diffusivity in V reported in Ref. [13] indicated that the segregation should be completed within 1 min at  $C_O = 1.0 \text{ at.\%}$  and  $T_S = 800 \text{ }^\circ\text{C}$ . The rate-limiting step of oxygen surface segregation under the present conditions is not clarified at present.

The sticking probability  $\alpha_{H_2}$  at various  $T_S$  is plotted against  $C_O$  in Fig. 3. No systematic difference was observed at different  $T_S$ , and  $\alpha_{H_2}$  was roughly proportional to  $1/C_O$ . Figure 4 shows comparison of  $\alpha_{H_2}$  between V and Nb at selected  $T_S$ . The values of  $\alpha_{H_2}$  for V are significantly higher than those for Nb. Namely, the effects of oxygen were much weaker for V than for Nb. In the case of the Nb-O system,  $\alpha_{H_2}$  was proportional to  $1/C_O^2$  at  $T_S \geq 1000 \text{ }^\circ\text{C}$  and to  $1/C_O^{1.5}$  at  $T_S$  below  $1000 \text{ }^\circ\text{C}$  [7], while

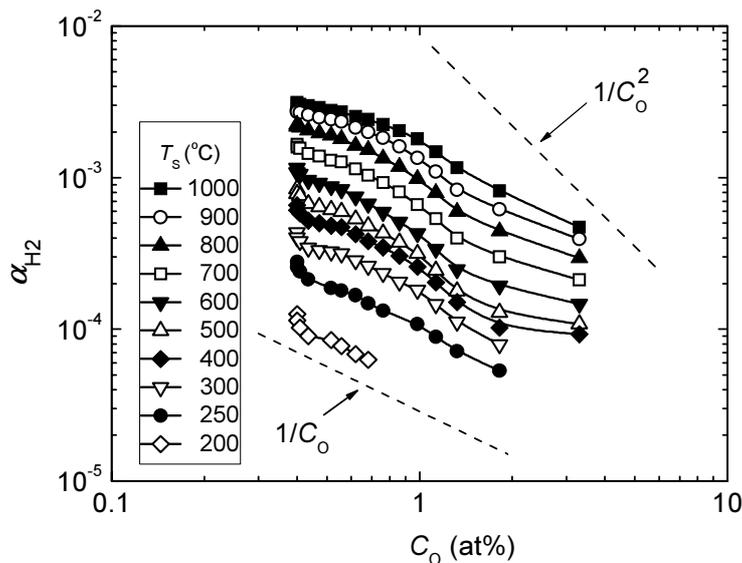


Fig. 3 Dependence of  $\alpha_{H_2}$  on  $C_O$  at various  $T_S$ . Pressure of  $H_2$  gas in upstream side was  $0.4 \text{ Pa}$ .

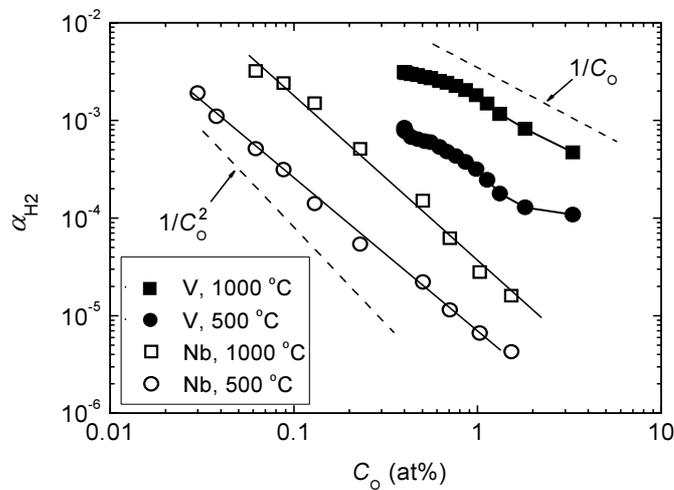


Fig. 4 Comparison of  $\alpha_{\text{H}_2}$  between V and Nb [7].

that on V was proportional to  $1/C_{\text{O}}$  as mentioned above. Namely, the dependence of  $\alpha_{\text{H}_2}$  on  $C_{\text{O}}$  observed for the V-O system was also significantly weaker than that for the Nb-O system.

#### 4. Discussion

The clear dependence of  $\alpha_{\text{H}_2}$  on  $C_{\text{O}}$  indicates that surface defects related to oxygen vacancies play dominant roles of active centers in  $\text{H}_2$  dissociation on the V surface covered with oxygen. Properties of such defects can be understood through the detailed analysis of dependence of  $\alpha_{\text{H}_2}$  on  $T_{\text{s}}$  and  $C_{\text{O}}$ . The Arrhenius plot of  $\alpha_{\text{H}_2}$  (Fig. 1) showed characteristic bends at 500 and 300 °C as mentioned above. Change in slope similar to the bend at 500 °C was also observed in the Arrhenius plot of  $\alpha_{\text{H}_2}$  for the Nb surface (Fig. 3 in Ref. [7]). Hence, the mechanism underlying the high temperature bend in Fig. 1 can be understood by the approach made in the previous study [7].

According to Eq. (1),  $\theta_O \approx 1$  at any  $C_O$  if  $T_S$  is sufficiently low. At certain  $T_S$ ,  $\theta_O$  should start to decrease with increasing temperature. Here, the temperature where  $\theta_O$  starts to decrease,  $T_S^*$ , rises as  $C_O$  increases. In reality, situation when  $\theta_O \approx 1$  is not necessarily reached even at sufficiently low  $T_S$  when  $C_O$  is low. The previous studies for the Nb-O [4, 7, 14] and the Ta-O [14] systems showed that the saturation level of  $\theta_O$  at sufficiently low  $T_S$  decreased with decreasing  $C_O$ . Nevertheless, at higher  $T_S$ ,  $\theta_O$  started to decrease with increasing  $T_S$  as expected from Eq. (1), and  $T_S^*$  rose with  $C_O$ .

The sticking probability  $\alpha_{H_2}$  can be expressed as

$$\alpha_{H_2} = (0.1 - 1) \sigma \exp\left(-\frac{2E_b}{kT}\right), \quad (3)$$

where a multiplier factor of (0.1 - 1) is a typical range of kinetic coefficient (conditioned, e.g., by the preferential sticking of molecules having certain orientations [15]),  $\sigma$  is the active portion of the surface, and  $2E_b$  is the activation energy for sticking on the active centers. Here,  $T$  indicates gas and/or surface temperature controlling the reaction rates, and  $T = T_S$  in the present case. If the active portion of surface,  $\sigma$ , is determined by the sites free from impurity (oxygen in the present case),  $\sigma$  cannot be independent of  $T_S$ : the number of oxygen-free sites,  $1 - \theta_O$ , depends on  $T_S$  (and  $C_O$ ) as described above.

Arrhenius plot of  $\alpha_{H_2}$  for the Nb-O system demonstrated the bend coincided with  $T_S^*$  [7]. Therefore, the sharp increase in  $\alpha_{H_2}$  with  $T_S$  at  $T_S > T_S^*$  was attributed to increase in  $\sigma$ . At  $T_S > T_S^*$ ,  $\alpha_{H_2}$  was proportional to  $1/C_O^2$  as shown in Fig. 4. This observation indicates that the active centers for  $H_2$  sticking are two adjacent oxygen vacancies whose concentration is expressed as  $(1 - \theta_O)^2$ . Namely,  $\sigma = (1 - \theta_O)^2$  in this case. Substitution of Eq. (1) in Eq. (3) by assuming  $\theta_O / (1 - \theta_O) \approx 1 / (1 - \theta_O)$  gives the activation energy for sticking as  $2|\Delta H_{seg}| + 2E_b$ . On the other hand, the oxygen coverage

was constant at  $T_S < T_S^*$ , and the activation energy observed in this region corresponded to  $2E_b$ . The mechanism underlying the correlation of  $\alpha_{H_2} \propto 1/C_O^{1.5}$  at  $T_S < T_S^*$  was discussed in Ref. [7] and is not repeated here.

Although detailed evaluation of the oxygen coverage for the V-O system by AES was impossible due to overlapping of oxygen peak (510 eV) with vanadium peak (511 eV), analogy to the Nb-O system indicates that  $T_S^* \approx 500$  °C for the V-O system. The activation energy at  $T_S > T_S^*$  (30 – 35 kJ/mol) is determined by  $|\Delta H_{\text{seg}}|$  and  $E_b$ , and that at  $T_S < T_S^*$  (10 kJ/mol H<sub>2</sub>) corresponds to  $2E_b$ . This value of  $2E_b$  is close to the activation energy for H<sub>2</sub> sticking on active centers on the O-covered Nb surface [7]. Reduction in  $\alpha_{H_2}$  with increasing  $C_O$  at 300 °C  $< T_S < 500$  °C can be ascribed to an increase in the saturation level of  $\theta_O$  with  $C_O$ . It is implausible that the steeper slope at  $T_S > 500$  °C is due to the activation of H<sub>2</sub> sticking on regular surface sites covered with oxygen because  $\alpha_{H_2}$  was clearly dependent on  $C_O$  even in high  $T_S$  region. In addition, *rapid* cooling from high temperature (1200 °C) resulted in significantly larger values of  $\alpha_{H_2}$  at sufficiently low  $T_S$  (e.g. 200 °C). Such change in  $\alpha_{H_2}$  is possible when the concentration of active centers increased at high  $T_S$  by reduction in  $\theta_O$  and then it was *frozen* by rapid cooling.

The Arrhenius plot of  $\alpha_{H_2}$  for Nb showed only one bend, and the slope was constant at  $T_S < T_S^*$  down to room temperature. Namely, the bend at 300 °C in Fig. 1 was observed only for the V-O system. In order to understand the mechanism underlying this low temperature bend, the pressure dependence of  $\alpha_{H_2}$  was examined. As shown in Fig. 5, no noticeable pressure dependence of  $\alpha_{H_2}$  was observed at  $T_S > 300$  °C. At  $T_S$  below 300 °C, however,  $\alpha_{H_2}$  clearly decreased with increasing H<sub>2</sub> pressure. These observations suggest that the sticking of H<sub>2</sub> at the holes in oxygen

coverage was affected by adsorbed hydrogen or impurities contained in  $H_2$  gas at  $T_S < 300$  °C. Details mechanisms underlying this pressure dependence, however, have not been clarified yet.

The sticking probability  $\alpha_{H_2}$  on the Nb surface was proportional to  $1/C_O^2$  at  $T_S > T_S^*$ , and this observation indicated that two adjacent oxygen vacancies make up active centers for  $H_2$  dissociation. In contrast to Nb,  $\alpha_{H_2}$  on V was proportional to  $1/C_O$ . This correlation suggests that  $\alpha_{H_2}$  was in proportion to  $(1 - \theta_O)$  (Eqs. (1) and (3)). Namely,  $\sigma = (1 - \theta_O)$ . Such correlation may mean that hydrogen molecules dissociates on a single oxygen vacancy. Alternative explanation is that oxygen vacancies on the V surface form clusters, and the total area of those clusters is proportional to  $(1 - \theta_O)$ . Further investigation is required to derive conclusion on this point.

Since  $\alpha_{H_2}$  was totally determined by the dissociation on active centers, no direct information was available from the present results on the dissociation on regular surfaces sites covered with oxygen atoms. Nevertheless, the minimum value of

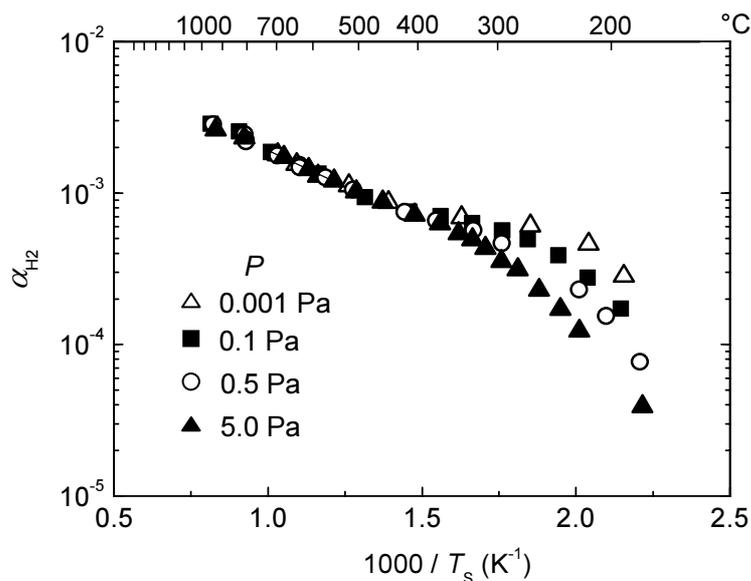


Fig. 5 Temperature dependence of  $\alpha_{H_2}$  on V surface at various  $H_2$  pressures ( $C_O = 0.4$  at.%).

activation energy can be evaluated. Beutl et al. [16] measured the sticking probability of H<sub>2</sub> and D<sub>2</sub> on the clean V surface and reported that the probability was 0.35 for molecules with translational energy corresponding to room temperature. By taking this value as kinetic coefficient in Eq. (3) and  $\sigma \approx 1$ , the sticking probability on regular surface sites,  $\alpha_{\text{H}_2}^{\text{reg}}$ , can be expressed as  $\alpha_{\text{H}_2}^{\text{reg}} = 0.35 \exp(-\frac{2E_{\text{b}}^{\text{reg}}}{kT_{\text{S}}})$ , where  $2E_{\text{b}}^{\text{reg}}$  is the activation energy for the dissociation on regular surface sites. The value of  $\alpha_{\text{H}_2}$  at  $T_{\text{S}} = 1000$  °C and  $C_{\text{O}} = 3.3$  at.% is  $4.5 \times 10^{-4}$ . Since  $\alpha_{\text{H}_2} \gg \alpha_{\text{H}_2}^{\text{reg}}$ ,  $2E_{\text{b}}^{\text{reg}}$  should be significantly larger than 70 kJ/mol H<sub>2</sub>. The activation energy for H<sub>2</sub> sticking on O-covered sites is larger than that on active centers by at least 7 times.

Eibl and Winkler [5] examined angular and energy distributions of D<sub>2</sub> flux desorbing from V(111) covered with oxygen and sulfur at  $T_{\text{S}} = 950$  K, and reported that desorption flux contains both thermal and hyperthermal contributions. They ascribed this observation to a corrugated potential energy surface. The presence of coverage holes, however, can be alternative interpretation of their results.

## 5. Conclusions

The sticking probability of H<sub>2</sub>,  $\alpha_{\text{H}_2}$ , on the V surface covered with segregated oxygen was examined as functions of the oxygen bulk concentration,  $C_{\text{O}}$ , and the specimen temperature,  $T_{\text{S}}$ . At all  $T_{\text{S}}$  examined,  $\alpha_{\text{H}_2}$  decreased with increasing  $C_{\text{O}}$ . This observation indicates that the main channels of H<sub>2</sub> dissociation was oxygen-free sites inherent to the segregated oxygen coverage. The activation energy for the H<sub>2</sub> sticking on

such active centers was evaluated to be 10 kJ/mol H<sub>2</sub>. The sharp increase in  $\alpha_{\text{H}_2}$  with  $T_s$  was observed at  $T_s > 500$  °C due to increase in portion of oxygen-free sites. The effects of oxygen presently observed for V were much smaller than that for Nb examined in the previous study [7].

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