

## Pd-4 at%Pt 合金による水素吸収の動力学的研究

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## Kinetics of Hydrogen Absorption by Pd-4 at%Pt Alloy

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### ABSTRACT

The kinetics of hydrogen absorption by a Pd-4 at%Pt alloy was studied in the temperature range of 0 to 80 C and pressure from 0.1 to 10 Torr by using a vacuum microbalance. The absorption kinetics extending over the entire absorption curve could be analyzed by a diffusion model assuming notable contributions from dissociative adsorption of hydrogen molecules and associative desorption of adsorbed hydrogen atoms on the surface. The activation energies for absorption and desorption were determined to be 4.6 and 9.0 kcal/mol(H<sub>2</sub>), respectively. Based on these values, the heat of the hydrogen solution was evaluated to be -4.6 kcal/mol(H<sub>2</sub>), which is in good agreement with the value obtained by thermodynamic study. In addition, the activation energy for diffusion was determined to be 7.1 kcal/mol(H), causing slower hydrogen diffusion in the alloy than Pd.

### 1. Introduction

Mechanisms involved in the process of hydrogen absorption by palladium and its alloys have long been the subject of a number of investigations, and sophisticated studies can be found in literature published as early as 1930s. Various models with different physical bases have been proposed to describe the reaction between palladium and hydrogen as well as heavier hydrogen isotopes. The aim is to reveal the reaction mechanism and to specify the rate controlling step in order to predict the dependence of the reaction rate on the key parameters such as temperature, hydrogen pressure, surface and bulk conditions of the metal, as well as its hydrogenization history.

In contrast with the well-defined thermodynamic features of the reaction, however, kinetic results from different researchers with different experimental procedures show little agreement.

This can be attributed to the sensitivity of kinetic processes on working conditions, which have been proven to include a number of factors that are difficult to control. Therefore attempts to generalize kinetic models predicting the reaction rate under various conditions often encounter enormous difficulties; a satisfactory description of the reaction process is still far from being completed.

The pioneering work of Wagner[1] resulted in a simple model involving two successive steps, a rate determining chemisorption step followed by a transfer step of the adsorbed atoms into the lattice. Auer and Grabke[2] proposed a basically similar two-step mechanism, but the chemisorption step was suggested to involve a transition state with one atom of an adsorbed molecule entering an interstice, while the other remaining adsorbed. Bucur[3, 4] added a third step to the chemisorption process, which is a surface migration of adsorbed atoms between two distinct types of adsorption sites. The common point of all these models is that they proposed a surface controlled process, which is characterized by a first order kinetics with respect to hydrogen pressure.

On the other hand, in many instances first order behavior is not observed, suggesting a diffusion controlled transfer process from the adsorbed state on the surface to the absorbed state inside the lattice.

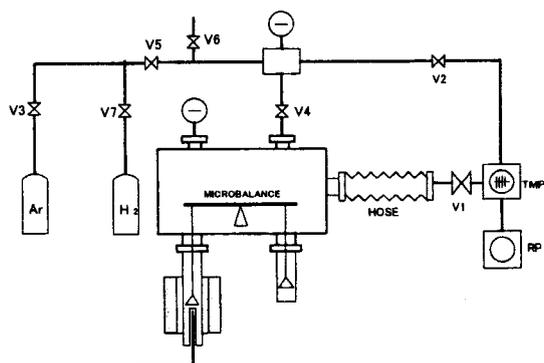
The perplexing state of the theoretical description is quite likely to cause problems in its application to engineering design; for example, surface property oriented modifications to materials may be futile if the process is actually controlled by a transfer process within the lattice. A general description depends strongly on the collection of reliable data under different material conditioning and working conditions. Recent efforts on Pd-H interaction studies have been mostly devoted to the surface physics on well-defined surfaces of only several layers thickness [5]. Such studies are worth while in obtaining information about the subtle surface processes such as surface relaxation due to hydrogen adsorption, but they are still far from being able to provide good predictions of the macroscopic kinetic features, which are the most important for technological applications.

The purpose of our present effort is to undertake an investigation on the hydrogen absorbing behavior of palladium alloys, especially those in the form of powder, which is of great significance for applications such as isotope separation[6] and hydrogen storage.

## 2. Experimental

Palladium and platinum plates were purchased from Nilaco. Their purities were guaranteed

to be above 99.9%. The Pd-4at%Pt alloy was prepared from the raw materials by argon arc melting. Filings of the ingot below 200 mesh were used as the sample. Prior to use, the sample powder was examined with X-ray diffraction analysis and ICPS (Radio-Frequency Inductive Spectroscopy) to examine the crystallinity and the chemical composition, respectively. Gases used were purchased from Nihon Sanso with purities above 99.9999 and 99.999 % for H<sub>2</sub> and Ar, respectively.



**Fig. 1.** Block diagram of the experimental apparatus installed with a vacuum microbalance system

of the system can be seen in Fig.1 .

Alloy powder of mass 0.5249 g was put in the aluminum pan of the microbalance and the system was evacuated down to  $10^{-6}$  Torr at room temperature. Subsequently, the sample was heated to 300 C using an electric furnace, then soaked in 50 Torr of hydrogen for 5 hours and finally kept in vacuum of  $10^{-6}$  Torr for 12 hours for activation.

Subsequently, the sample was cooled down to a given temperature in the range from 0 to 80 C and then 10 Torr of pure argon was first introduced into the main chamber to damp the undesirable vibration of the microbalance owing to a sudden pressure change caused by hydrogen introduction. After the microbalance was stabilized in the argon atmosphere, the desired amount of hydrogen was introduced into the main chamber from the standard volume, where the hydrogen pressure was set in the range from 0.1 to 10 Torr. The sample temperature was controlled with an ice/water or water bath within  $\pm 0.5$  C. The temperature was measured with an alumel-chromel thermocouple attached to the outside wall of the sample tube. The weight gain was recorded by a two pen recorder.

### 3. Results and discussion

#### 3.1. Absorption curves

The X-ray diffraction analysis showed that the sample prepared had good crystallinity and

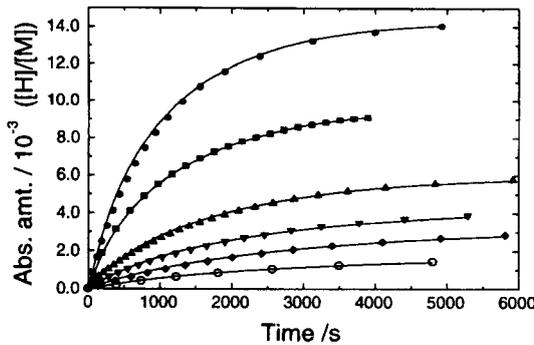
A Cahn-2000 microbalance with a sensitivity of 0.1 mg was used to measure weight gain of the sample by hydrogen uptake. The microbalance was installed in the main chamber of a high vacuum system equipped with a capacitance manometer, an ionization gauge, a standard volume and gas reservoirs. The system could be evacuated down below  $1 \times 10^{-6}$  Torr by turbomolecular and oil-sealed rotary pumps. A schematic description

gave the lattice constant of 3.889 Å. According to the ICPS analysis, the chemical composition was 3.88 at%Pt. Nevertheless, the sample will be denoted as Pd-4at%Pt in the present paper for simplicity. In addition, the specific surface area of the powder was determined to be 0.092 m<sup>2</sup>/g by the BET method using Kr.

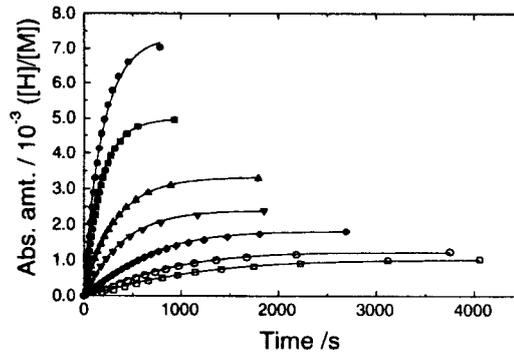
Weight gain was converted to atomic fraction by

$$X = \Delta W \cdot M_M / (W_0 \cdot M_H) \quad (1)$$

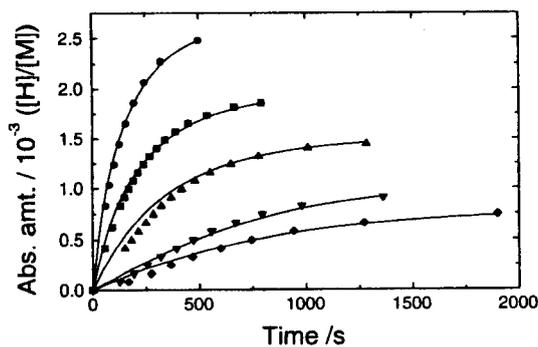
and plotted against reaction time to obtain hydrogen uptake curves, where  $X$  is the atomic fraction of hydrogen in the alloy,  $\Delta W$  the weight gain and  $W_0$  the original sample weight.  $M_M$  and  $M_H$  are the atomic weights of Pd-4%Pt and hydrogen, respectively, where  $M_M$  was taken as 108.39 g/mol.



**Fig. 2.** Hydrogen absorption curves at 0°C under different pressures (from the top down, 10.0, 5.0, 2.0, 1.0, 0.5 and 0.2 Torr)



**Fig. 3.** Hydrogen absorption curves at 40°C under different pressures (from the top down, 5.0, 2.0, 1.0, 0.5, 0.2 and 0.1 Torr)

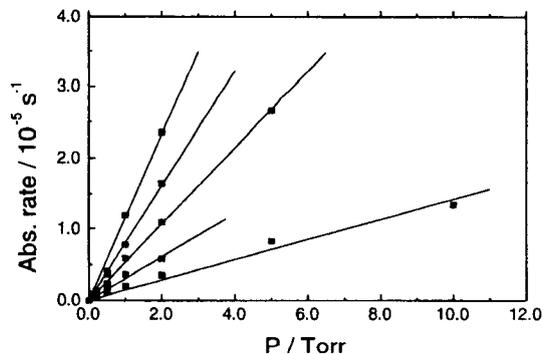


**Fig. 4.** Hydrogen absorption curves at 60°C under different pressures (from the top down, 2.0, 1.0, 0.5, 0.2 and 0.1 Torr)

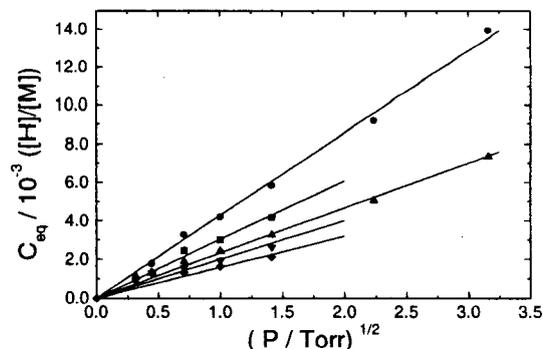
The hydrogen uptake by the sample was measured at 0, 20, 40, 60 and 80 C in the pressure range from 0.1 to 10 Torr. The absorption curves at 0, 40 and 60C are shown in Figs. 2 - 4, as an example. In spite of an appreciable weight gain of the sample, there was no measurable pressure change for each experimental run throughout the present study because of the small amount of sample in the relatively large volume of the experimental chamber.

Therefore, the hydrogen uptake vs time curves were obtained under constant pressures. The hydrogen uptake initially increased rapidly, then the uptake rate reduced gradually and eventually the uptake approached a final steady value for a given temperature and pressure. The uptake at the end of each experimental run was far larger than that expected by

adsorption on the surface. Therefore, the hydrogen uptake observed is due to absorption into the bulk and then the steady value of hydrogen uptake should correspond to the equilibrium concentration in Pd-4at%Pt alloy.



**Fig. 5.** Plots of initial absorption rate vs hydrogen pressure at different temperatures (from the top down, 80°, 60°, 40°, 20° and 0° C)



**Fig. 6.** Plots of equilibrium hydrogen concentration to square root of hydrogen pressure at different temperatures (from the top down, 0°, 20°, 40°, 60° and 80° C)

The absorption rate and the final total amount of absorption became larger with increasing hydrogen pressure at a given temperature. The final absorption amount at a given pressure decreased with increasing temperature, although the absorption rate increased with temperature. The absorption curves were first fitted by polynomial and/or exponential functions to evaluate the initial absorption rate and the equilibrium hydrogen concentration at a given pressure and temperature. These curves are shown in Figs. 5 and 6. Figure 5 shows that the initial rate is proportional to hydrogen pressure at a given temperature, indicating that the adsorption process is important in determining the initial absorption rate. The slopes of these lines give the rate constants for hydrogen adsorption at different temperatures. Figure 6 indicates that the equilibrium hydrogen concentration is proportional to the square root of hydrogen pressure, and expressed as

$$x = K\sqrt{p} = \left( \sqrt{p/p_0} \exp(\Delta S_s/kT) \exp(-\Delta H_s/kT) \right), \quad (2)$$

where  $x$  is the solubility of hydrogen,  $K$  a constant,  $p$  the equilibrium hydrogen pressure; the equation in the parenthesis is the generalized expression, where  $p_0$  is the standard pressure, and  $\Delta S_s$  and  $\Delta H_s$  are the entropy and the enthalpy change for hydrogen absorption, respectively. Sievert's law is conventionally described as

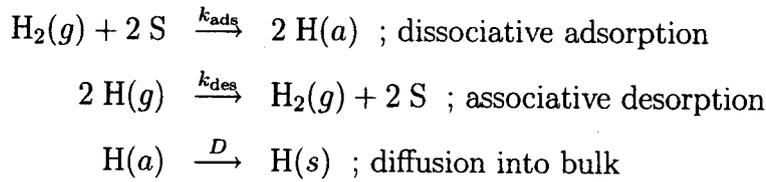
$$\sqrt{p} = K_s x, \quad (3)$$

where  $K_s$  is the Sievert's constant. Then the slope of a straight line in Fig. 6 gives the inverse of Sievert's constant at a given temperature. The reduction of the hydrogen concentration at

a given pressure with increasing temperature is a result of the exothermic nature of hydrogen absorption by this alloy.

### 3.2. Kinetic analysis

The characteristic features of the absorption curves mentioned above and preliminary data analysis indicated that the absorption curves could not be described by simple diffusion limited models nor adsorption limited processes. Instead, it was implied that the dissociative adsorption of hydrogen gas on the surface, its reverse reaction, namely the associative desorption of adsorbed hydrogen atoms, and diffusion into the bulk are all important to determine the absorption kinetics. The absorption process can be expressed as



where  $\text{H}_2(g)$ ,  $\text{H}(a)$  and  $\text{H}(s)$  denote gas, adsorbed and solute phase hydrogen, respectively, and  $\text{S}$  a surface adsorption site;  $k_{\text{ads}}$ ,  $k_{\text{des}}$  and  $D$  are the adsorption rate, desorption rate and diffusion constants, respectively.

Here, it is assumed that a powder particle was a sphere having a radius of  $r_d = d/2$ , where the diameter  $d$  was taken as the size of mesh, viz., 0.0074cm. Then, the absorption rate is described by the Fick's law,

$$\frac{\partial c(r, t)}{\partial t} = D \left[ \frac{\partial^2 c(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r, t)}{\partial r} \right], \quad (4)$$

with respective surface boundary and initial conditions.

According to the above mentioned reaction scheme, the boundary and initial conditions are described

$$-D \left( \frac{\partial c(r, t)}{\partial r} \right)_{r=r_d} = k_{\text{ads}} P N_s^2 [1 - c(r_d, t)]^2 - k_{\text{des}} N_s^2 c(r_d, t)^2, \quad (5)$$

$$-D \left( \frac{\partial c(r, t)}{\partial r} \right)_{r=0} = 0, \quad (6)$$

$$c(r, 0) = 0, \quad t = 0, \quad 0 \leq r \leq r_d \quad (7)$$

where  $c(r, t)$ ,  $P$  and  $N_s$  are the hydrogen concentration with respect to metal atoms, hydrogen pressure and number of adsorption sites per unit surface area. The set of equations was solved numerically by the Crank-Nicolson implicit method, where the diffusion constant was treated as the main fitting parameter.

The numerical calculation was carried out by adopting the apparent initial absorption rate and desorption rate constants as starting values. The former was determined from the initial absorption rate and the latter was evaluated from the equilibrium concentration and the dynamic equilibrium condition as

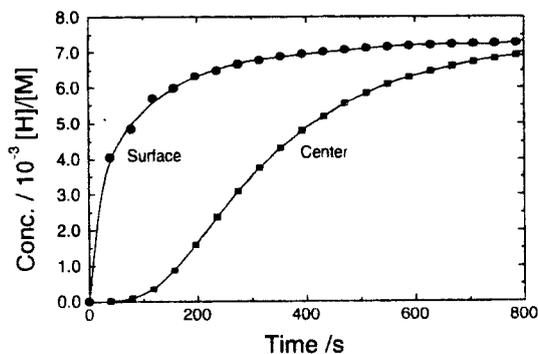
$$k_{\text{ads}}^{\text{app}} P [1 - c(r_d, t)]^2 = k_{\text{des}}^{\text{app}} c(r_d, t)^2, \quad (8)$$

$$\text{where } k_{\text{ads}}^{\text{app}} = k_{\text{ads}} N_s^2, \text{ and } k_{\text{des}}^{\text{app}} = k_{\text{des}} N_s^2.$$

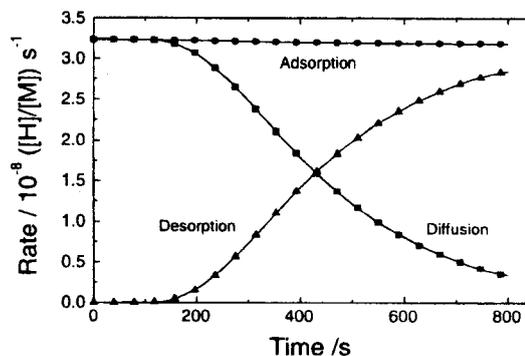
To compare the numerical calculation with the observations, the average hydrogen concentration in a sphere at time  $t$  was evaluated from the calculated hydrogen concentration distribution at  $t$ ,  $c(r, t)$ , as

$$\Theta_{\text{av}}(t) = \left( \frac{3}{4\pi r_d^2} \right) \int_0^{r_d} 4\pi r^2 c[r, t] dr, \quad (9)$$

where  $\Theta_{\text{av}}(t)$  is the average concentration,  $3/4\pi r_d^2$  the volume of a sphere of radius  $r_d$  and  $4\pi r^2$  the surface area of the sphere at the radius,  $r$ . The solid lines shown in Figs. 2 - 4 are the calculated absorption curves. It can be seen that the calculated absorption curves agree considerable well with the observed ones. Similar agreement between the calculated and the observed absorption curves was found at other temperatures. Therefore, the hydrogen absorption kinetics can be explained by this model.



**Fig. 7.** Changes in the hydrogen concentration at the surface,  $c(r_d, t)$ , and the center,  $c(0, t)$ , of the sphere with time, calculated for 40° C and 10 Torr



**Fig. 8.** Calculated adsorption, desorption and diffusion rates at 40° C and 10 Torr

Figure 7 shows the change in the hydrogen concentrations at the surface and the center of a sphere with time, calculated for the absorption at 40C and 10 Torr, as an example. It is seen that the surface concentration increases steeply first with time to attain an equilibrium concentration. On the other hand, the concentration at the center initially stays at zero and then approaches sigmoidally to the equilibrium concentration. It is also seen that the concentration at the surface increases much faster than the average concentration shown in Fig.

3. These features imply that the concentration gradient at the surface becomes progressively smaller with time, resulting in the reduction of hydrogen diffusion into the bulk.

Figure 8 shows the variations of the adsorption, desorption and diffusion rates, for hydrogen absorption at 40C and 10 Torr. The adsorption rate is kept almost constant. This is because the surface concentration,  $c(0, t)$ , is far less than unity, as shown in Fig. 7, and hence the term  $[1 - c(0, t)]^2$  does not change appreciably throughout the entire measurement under these conditions. On the other hand, the desorption rate is almost zero in the initial part of the absorption process and then increases gradually with time, eventually reaching the same rate as the adsorption, whereupon the net absorption rate becomes zero, corresponding the dynamic equilibrium condition. The diffusion rate varies conversely to the desorption rate. It is seen that the diffusion rate initially is the same as the adsorption rate, indicating that the adsorbed hydrogen atoms readily diffuse into the bulk; therefore the adsorption rate determines the net absorption rate at this stage. Subsequently the diffusion rate decreases with time because of the reduction in the concentration gradient, and hence the excess hydrogen atoms on the surface return to the gas phase via the associative desorption reaction.

### 3.3. Temperature dependence

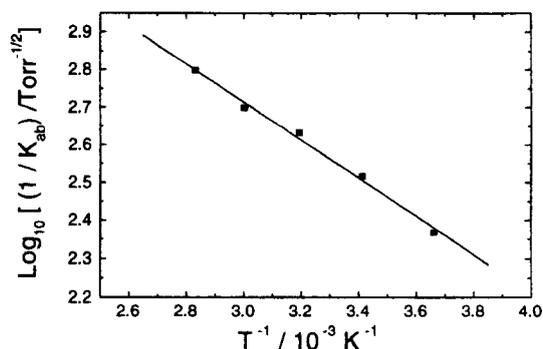


Fig. 9. Temperature dependence of Sievert's constant

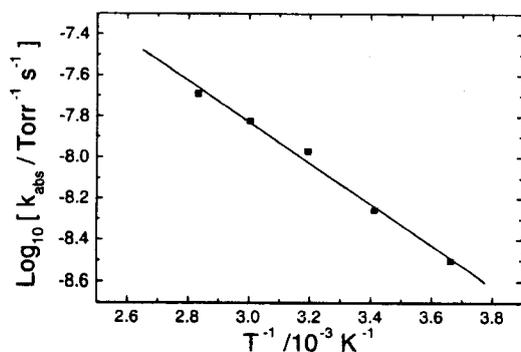


Fig. 10. Arrhenius plot of the adsorption rate constant evaluated by simulation

Figure 9 shows the temperature dependence of Sievert's constant determined from the slopes of straight lines shown in Fig.6. A good straight line was observed, which gave the heat of hydrogen solution of -4.6 kcal/mol. This value is in good agreement with that obtained by thermodynamic study (-4.30 kcal/mol) in a temperature range from 0 to 100C[7, 8], although the heat and the entropy of hydrogen solution at infinite dilution in the same alloy are temperature dependent. Furthermore, the heat of hydrogen solution in pure Pd is reported as -4.70[2], -4.72[9] and -4.50 kcal/mol[10], suggesting that the heat of hydrogen solution does not change appreciably by alloying with a small amount of Pt.

Figure 10 shows the temperature dependence of the adsorption rate constant determined from the

simulation. The plot shows a linear relationship with  $1/T$ , leading to an activation energy of 4.6 kcal/mol. The temperature dependence of the desorption rate constant determined by simulation is shown in Fig.11. From the slope of the straight line, the activation energy for desorption was determined as 9.0 kcal/mol. The activation energy for adsorption by the Pd-4at%Pt alloy is a little smaller than that reported for Pd of 6.8 kcal/mol[2]. As to the activation energy for hydrogen desorption from Pd, Auer et al. reported 11.5 kcal/mol[2], whereas a smaller value of 8.5 kcal/mol was also reported by others[11]. It is noted, however, that the former was determined from absorption and desorption measurements in a flow of He carrier gas, whereas the latter was evaluated by means of thermal desorption spectroscopy in a high vacuum system. On comparison of experimental conditions, the present results are best compared with the results by Auer et al. Therefore, alloying with Pt appears to cause the reduction of the activation energies for adsorption and desorption.

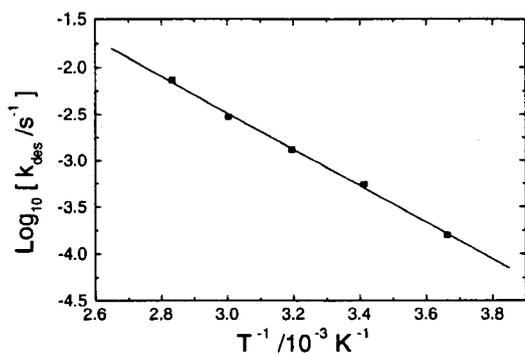


Fig. 11. Arrhenius plot of the desorption rate constant evaluated by simulation

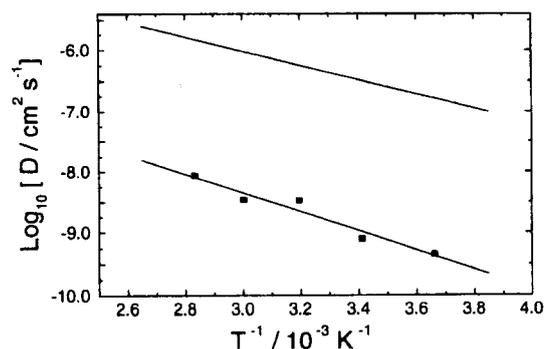


Fig. 12. Arrhenius plot of the diffusion constant evaluated by simulation. The upper solid line is for pure Pd[12]

Figure 12 is the Arrhenius plot of the diffusion constants determined by simulation. A reasonable straight line was observed, and the activation energy was evaluated to be 7.1 kcal/mol. This value is a little higher than that reported for Pd (5.30 kcal/mol)[12]. Moreover, the frequency factor for the alloy ( $2.0 \times 10^{-4} \text{ cm}^2/\text{sec}$ ) was about 15 times smaller than that for Pd ( $2.90 \times 10^{-3} \text{ cm}^2/\text{sec}$ ). With regard to the activation energy for hydrogen diffusion, similar alloying effects have been observed; for example, the increase in the activation energy was observed by alloying Re (Pd-5%Re)[2], Ag (Pd-50%Ag)[13]. Similarly, it can be concluded that the alloying of 4 at%Pt into Pd causes a decrease in the diffusion constant of hydrogen through the increase in the activation energy and a reduction of the frequency factor.

#### 4. Conclusions

Hydrogen absorption by Pd-4at%Pt alloy powder was studied using a vacuum microbalance in the range of temperature from 0 to 100C and of pressure from 0.1 to 10 Torr. The equilib-

rium hydrogen concentration in the alloy was proportional to the square root of the hydrogen pressure, obeying Sievert's law, and the heat of hydrogen absorption was determined to be -4.6 kcal/mol. Although the initial absorption rate obeyed the first order kinetics with respect to hydrogen pressure, the entire absorption curve could not be simulated well with simple models assuming surface reaction or diffusion limited processes. However these curves could be reproduced well with a diffusion model including extensive contributions from dissociative adsorption of hydrogen molecules and associative desorption of hydrogen atoms on the surface. The activation energies were determined to be 4.6 kcal/mol for adsorption and 9.0 kcal/mol for desorption. Also the activation energy for diffusion was determined to be 7.1 kcal/mol. The apparent trend is that this alloy shows slightly smaller activation energies for adsorption and desorption, but a larger value for diffusion in comparison with pure Pd.

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