

The Hydrogen Absorption Kinetics in very thin Pd film(α phase)

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α 상 Pd박막의 수소 흡수 동역학

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Abstract

4-probe resistivity measurement technique was used to study kinetics of hydrogen absorption on Pd film (180Å thick) in the α phase. Hydrogen gas was introduced to the activated Pd film. For very low hydrogen concentration the following rate law is valid in α phase very thin Pd film

$$v = k \frac{1}{1+KX_H} P_{H_2} - k' \frac{KX_H^2}{1+KX_H},$$

which is similar to that of bulk. The activation energy of the forward reaction is 4.6kcal/mol H and of the backward reaction 8.4kcal/mol H, which yields the reaction enthalpy -3.8kcal/mol H in the temperature range between 25 and 40°C. The values of activation and enthalpy of thin film are rather smaller than that of bulk sample.

This may be due to surface area difference between bulk and film.

초록

α 상 영역에서의 Pd박막(두께 180 Å)의 수소흡수 동역학을 4극 전기비저항측정법을 이용하여 연구하였다. 기체상태의 수소를 Pd 박막에 흡수시켰다. α 상의 매우 낮은 농도 영역에서 수소 반응율이 다음과 같이 나타내어졌다.

$$v = k \frac{1}{1+KX_H} p_{H_2} - k' \frac{KX_H^2}{1+KX_H}$$

이는 덩어리 시료의 경우와 같다. 정방향반응의 활성화에너지는 4.6kcal/mol H이고 역방향반응의 활성화에너지는 8.4kcal/mol H이다. 반응엔탈피는 25에서 40°C 영역에서 -3.8kcal/mol H이다. 박막의 활성화에너지와 반응엔탈피값들은 덩어리의 경우에 비하여 조금 작았는데 이는 덩어리와 박막의 표면적의 차이에 의한것으로 추정된다.

1. INTRODUCTION

Most of bulk material of hydrogen absorption metal pulverize after several hydrogen absorption and desorption process(A-D process). Hydrogen absorption kinetics changes due to the pulverization, which changes physical properties of samples, i.e. surface area of particle and contact area between particles. But it is not easy to see pulverization in thin film metal-hydrogen system⁽¹⁾. We can observe size effect in hydrogen absorption kinetics due to difference of film thickness⁽²⁻⁴⁾.

Very thin(180 Å thick) Pd film was made by thermal evaporation for hydrogen absorption kinetics experiments. Hydrogen gas was introduced to the sample and measure hydrogen

concentration change in time by using resistivity measurement technique at the temperature range between 25 and 40°C. Activation energy and reaction enthalpy of hydrogen absorption process in the α phase were calculated by analyzing kinetics data of the sample.

2. THEORY

Most of previous articles of hydrogen absorption kinetics research did not deal forward reaction and backward reaction separately. In this work we analyze two reactions separately.

Reaction rate is given as $v = 1/A \frac{dn_H}{dt}$, where A is surface area, n_H is mol of hydrogen, t is time. The rate of the hydrogenation is given by the difference of the rates of the forward

and backward reaction. The forward reaction rate is a function of the hydrogen pressure and of the hydrogen concentration, backward reaction rate is only a function of the hydrogen concentration⁽⁵⁾

$$v = \vec{v}(P_{H_2}, X_H) - \overleftarrow{v}(X_H) \quad (1)$$

In the hydrogenation the forward and the backward reaction occur simultaneously. In the dehydrogenation the hydrogen pressure is virtually zero and only the backward reaction occurs. Thus we can calculate the forward reaction contribution in the hydrogenation by using equation (1). In the α -Pd the forward reaction and backward reaction rate are given as follows

$$\vec{v} = k P_{H_2} \frac{1}{1 + KX_H} \quad (2)$$

$$\overleftarrow{v} = k' \frac{KX_H^2}{1 + KX_H} \quad (3)$$

where X_H is the hydrogen concentration, P_{H_2} is the hydrogen pressure, k and k' are rate constants, K is the equilibrium constant for the adsorption equilibrium.

3. EXPERIMENTS

Thin Pd($1.0 \times 4.0 \text{ mm}^2$, 180 \AA thick) film was evaporated thermally on the glass substrate (Corning 2948) in ultra high vacuum (pressure = 10^{-7} torr) at room

temperature. The evaporation rate is about $1 \text{ \AA}/\text{sec}$ and the distance between the substrate and Pd source is about 20 cm. The thickness of the sample was monitored by quartz crystal thickness monitor. Ultrasonic wedge bonder was used to make connection lead ($25 \mu\text{m}$ diameter Al wire). Hydrogen gas (purity = 99.999%) was used for hydrogenation of the sample. The pressure was measured by pressure transducer (WIKA Model 1290). The 4-probe resistivity was measured by using DMM(Keithley Model 196) and temperature is measured by using PT-100 via DMM(Keithley Model 195A). All of the above data were collected by PC(IBM AT) via HP-IB interface card (HP Model 82335). To see the thermal annealing effect, the sample was heated under vacuum at 290°C . To see activation process the sample was hydrogenated upto 5 torr hydrogen pressure for 20 minute and dehydrogenated for 20 minute at 25°C . This process was repeated 27 times. The sample was hydrogenated upto 8 torr hydrogen pressure and dehydrogenated 27 times to measure hydrogen absorption kinetics in the temperature range between 25 and 40°C in the α phase.

4. RESULTS AND DISCUSSION

The resistivity of the sample(as made) was $85 \mu\Omega\text{cm}$ which is about 8 times larger than that of the bulk, $11 \mu\Omega\text{cm}$. But the resistivity of the sample was decreased to $40 \mu\Omega\text{cm}$ after annealing (at 290°C), which is still larger than

that of the bulk sample. This may be due to removing the defects from annealing. To see hydrogenation activation process, hydrogen was introduced upto 5 torr and removed by pumping sample chamber at room temperature. As you can see in the Fig. 1, the resistivity of the sample was decreased gradually to 12th A-D (about 0.5 %) and was about constant value after 12th A-D. This indicated that the sample was activated and ready for kinetics measurements. The change of resistivity of the activated sample was measured at 25, 30, 35, 40°C for various hydrogen pressure. The change of the resistivity of the Pd sample is linear to the change of the hydrogen concentration. But the rate of resistivity change of the bulk is not the same as that of the film. For 180Å thick Pd film hydrogen concentration can be calculated by $X_H = (11/3) \Delta R/R_0$, where R_0 is initial resistance, ΔR is $R - R_0$, R is resistance of the sample during hydrogenation [6].

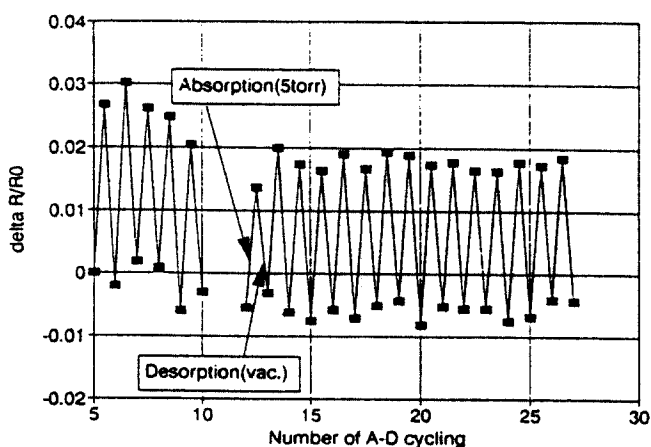


Figure 1. The $\Delta R/R_0$ vs. hydrogen A-D cycling for PdH_x film 180Å thick at 25°C.

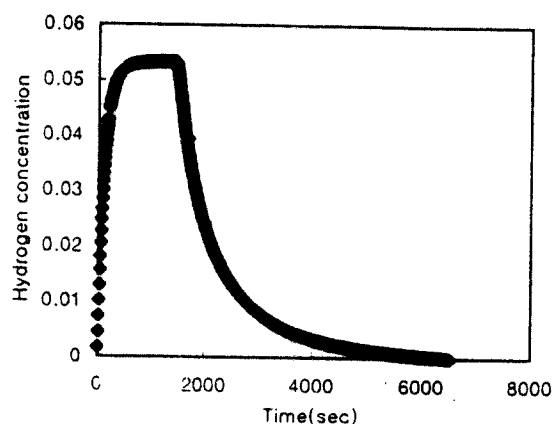


Figure 2. Hydrogen absorption and desorption on PdH_x(25°C, 1torr)

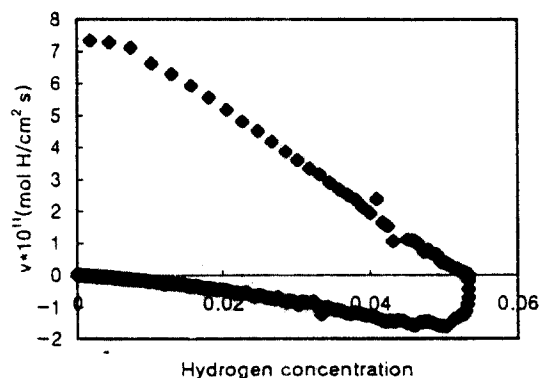


Figure 3. Plot of reaction rate vs. hydrogen concentration of PdH_x(25°C, 1torr)

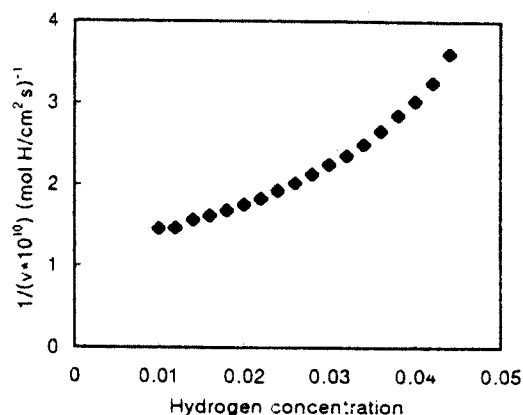


Figure 4. Plot of $1/v$ forward reaction rate vs. H concentration of PdH_x(25°C, 1torr)

Fig. 2 shows the typical hydrogen concentration change in time. The rate of reaction was calculated from hydrogen change curve (see Fig. 3). In the Fig. 3, the positive part of the v is v term and the negative part is v term in equation (1). Thus v can be obtained by $v + v$. To get v_0 value, which is v value when $X_H = 0$, equation (2) was rewritten as

$$\frac{1}{v} = \frac{K}{k P_{H_2}} X_H + \frac{1}{k P_{H_2}} \quad (2)'$$

v_0 was determined by extrapolating curve in the $1/v$ vs. X_H plot (Fig. 4). And initial forward reaction rate was given by $v_0 = k P_{H_2}$ (Fig. 5). The slope of the best fitted line in v_0 vs. P_{H_2} plot gives the k value. Plot of $\ln k$ vs. $1/T$ gives the activation energy of the forward reaction (Fig. 6). The activation energy was obtained $E_a = 4.6 \text{ kcal/mol H}$ for Pd film.

Equation (3) was rewritten for the analysis of backward reaction as follows

$$\frac{X_H}{v} = \frac{1}{k' K} \frac{1}{X_H} + \frac{1}{k'} \quad (3)'$$

k' was determined by extrapolating the line in the X_H/v vs. $1/X_H$ plot (Fig. 7). The Arrhenius plot gives the activation energy of the backward reaction. The activation energy was obtained as $E_a = 8.4 \text{ kcal/mol H}$. The difference of the activation energy of the forward and backward reaction is the enthalpy of reaction, which was -3.8 kcal/mol H for the Pd thin film (180 Å thick).

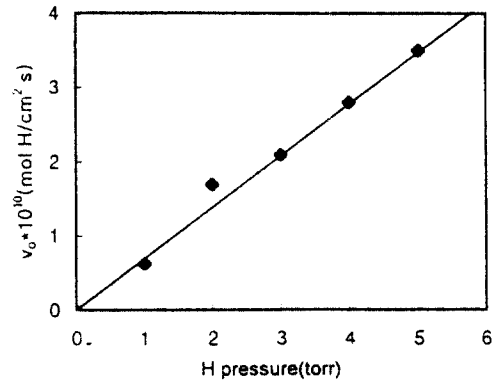


Figure 5. Plot of initial forward reaction rate vs. H pressure for PdH_x at 25°C (180 Å thick)

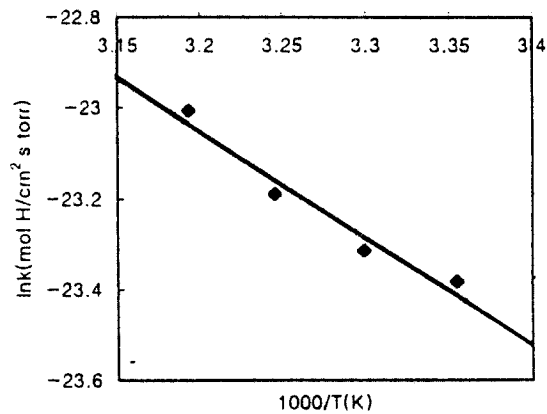


Figure 6. Arrhenius diagram for the rate constant of forward reaction on PdH_x (180 Å thick)

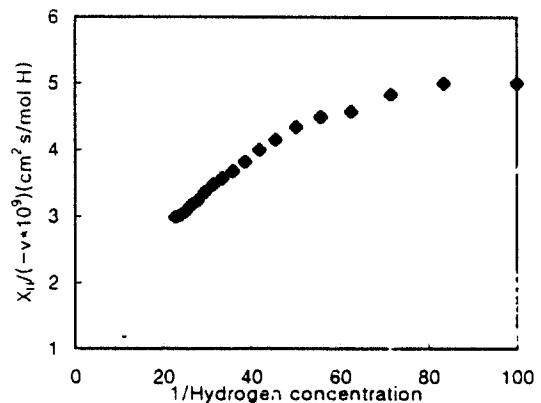


Figure 7. Plot of X_H/v vs. $1/X_H$ of Pd film (25°C, 1 torr \rightarrow vac.)

This is rather smaller than that of the bulk(Pd foil -4.7kcal/mol H [5]), which may be due to surface area difference between bulk and film.

5. CONCLUSION

The measurement of the resistivity change of the Pd film was very easy and useful tool to monitor of the hydrogen concentration change. The activation energy of the forward and backward reaction, and reaction enthalpy are rather smaller than that of the bulk sample. Future work will be focused on the dependance of film thickness on the activation energy in order to investigate the present experiment results.

ACKNOWLEDGEMENTS

Authors thank Sang-rok Kim and Sung-rae Lee for sample preparation. This work was supported by Korea Sanhak Foundation Fund, 1996. Authors are grateful to the fund.

REFERENCES

1. H. Sakaguchi, N. Taniguchi, H. Nagai, K. Niki, G. Adachi, and J. Shiokawa, *J. Phys. Chem*, **89**, 5550-5552, 1985.
2. M. Lee and R. Glosser, *J. Appl. Phys*, **57**, 5236-5239, 1985.
3. H. Sakaguchi, Y. Yagi, N. Taniguchi, G. Adachi, and J. Shiokawa, *J. of Less-Common Metals*, **135**, 137-146, 1987.
4. R. Feestra, G. J. de Bruin-Hordijk, H. L. M. Bakker, R. Griessen, D. G. de Groot, *J. of Phys. F*, **13**, L13-L18, 1983
5. W. Auer and H. J. Grabke, *Berichte der Bunsen-Gesellschaft*, **78**, 58-67, 1974
6. R. Feenstra, private communication.