



Effect of the penetration of Li atoms into the Pd surface on thermodynamic properties of the Pd–H system

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Abstract

This study reports the effect of the penetration of Li atoms into the Pd surface on the pressure–composition–temperature relation of the Pd–H system and on the heats of reactions of hydrogen. A heat treatment of Pd in a 1 M LiOH solution induces the penetration of Li atoms into Pd even at 353 K. The marked enhancement about by 90–100% for the formation of hydrogen solid solution, and about by 29% for the formation of PdH_{1-x} hydride phase seems to be attributed to strong interactions of hydrogen with the Li atoms penetrated from the LiOH during the pretreatment. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In previous papers [1,2], we reported that alkaline atoms (Li, Na and K) penetrate into the surface region of the hydrogen storage alloys by the pretreatment of the alloys in LiOH, NaOH and KOH solutions. The presence of the alkaline atoms in the surface region including surface oxide layers were found to induce marked accelerations of the rate of initial activation of the alloys both in the hydrogen gas phase and electrolytic process [1–3].

Based on these facts, we examined the penetration of Li atoms into the surfaces of Pd. For the Pd–H system, a plenty of thermodynamic and kinetic studies have been made using electrolytic methods. However, the effect of the alkaline atoms of the electrolytic solutions on the equilibrium properties of the Pd–H system has not been considered. A long contact of the Pd surface with LiOH solutions may change the Pd surface condition, and this effect may not be neglected for small crystal grains or particles of Pd.

The aim of this study was to confirm whether or not the penetration of the Li atoms of LiOH solutions takes place and affects the thermodynamic properties of the Pd–H system.

2. Experimental details

2.1. The evaluation of heats of reactions

The heats of hydrogen solution and hydride formation of this system were calculated from the pressure–composition–temperature (*P–C–T*) relations measured for the Pd–H system using a Sieverts' type apparatus [4] in the ranges of hydrogen pressures from 10⁻⁴ to 10⁻¹ MPa, temperatures from 298 K to 373 K, and the hydrogen concentration from [H]/[Pd]=10⁻³ to 1.0 in atom ratio, respectively. The details of the measurement method of *P–C–T* relations are reported elsewhere [4].

2.2. Pd samples

The penetration of Li atoms into Pd was examined using a Pd (purity: 99.99%) plate (3 cm long×1 cm wide and a 0.05 mm thickness). The plate sample was degassed in a vacuum lower than 10⁻³ Pa at 973 K for 10 h. Subsequently, the sample was heated in a 1 M LiOH at 353 K either for 1 h and 3 h. The sample surfaces were analyzed using secondary ion mass spectroscopy (SIMS) at a sputter rate of 1.4 nm/s.

For the *P–C–T* measurements, Pd particle samples with two different sizes: 1 μm (Pd black) and 150 μm were used. The particle samples were subjected to the measurement with or without the heat pretreatment in a 1 M LiOH at 353 K for 1 h.

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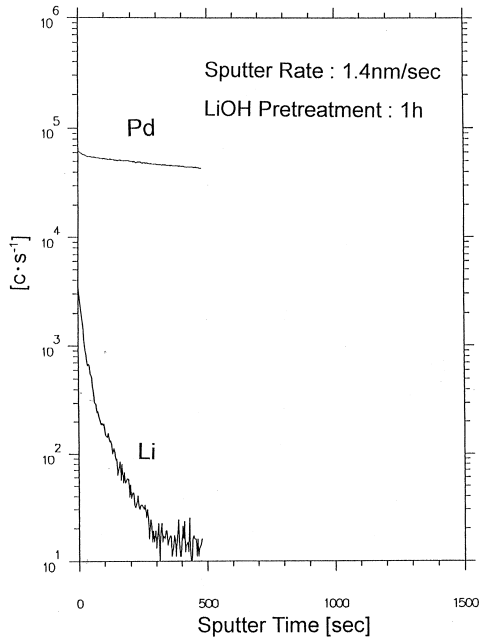


Fig. 1. The distribution of Li atoms in the Pd surface pretreated with 1 M LiOH at 353 K for 1 h.

3. Results and discussion

3.1. The distribution of Li atoms at the Pd surface

Figs. 1 and 2 show the results for the change in the distribution of Li atoms by SIMS analyses for Pd plate samples pretreated in a 1 M LiOH solution for 1 h and 3 h, respectively. These results clearly demonstrate the penetra-

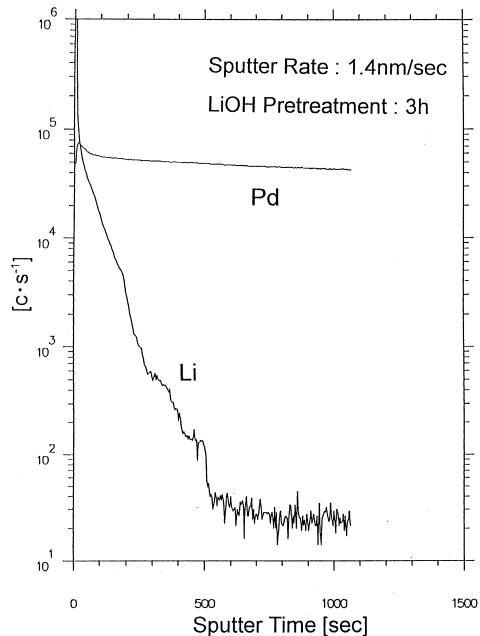


Fig. 2. The distribution of Li atoms in the Pd surface pretreated with 1 M LiOH at 353 K for 3 h.

tion of Li atoms from LiOH solution into the Pd surfaces. The concentration of Li atom at the Pd surface increases with the exposure time to the LiOH solution. The concentration of Li was found about $[Li]/[Pd] \geq 1$ in atom ratio at the surface and then decreased exponentially with depth. The depth profile of Li atoms in the Pd samples was calculated from the sputter rate, 1.4 nm/s, and this yielded that Li atoms penetrated up to about 400 nm after 1 h and 700 nm after 3 h of the pretreatment. These results indicate that Li atoms penetrate into Pd even at 353 K. Actually, this pretreatment temperature seems too low to induce these Li penetrations into Pd only by thermal diffusion. Though the phase relation of the Li–Pd system is reported [5], the precise mechanism of the penetration of Li atoms into Pd cannot be well understood at present. Our SIMS results indicate that Li atoms are located rather randomly at interstitial and substitutional sites in the Pd lattice. However, the phase diagram for the Li–Pd system [5] suggests the possibility of the local formation of Li–Pd intermetallics, too.

3.2. P – C – T relations

Figs. 3 and 4 show the P – C – T relations of the Pd–H system for Pd samples with particle sizes 1 μm and 150 μm , respectively. These results show that the Pd sample with a smaller particle size exhibits higher hydrogen solubilities than the larger sample. This might be attributed to the effect of subsurface [6] or the different volume expansibilities between small and large particles [7]. More precise consideration and discussion for this effect are reported from a thermodynamic viewpoint [8].

Figs. 5 and 6 show typical P – C – T relations for the Pd samples pretreated with a 1 M LiOH. The isotherms of the

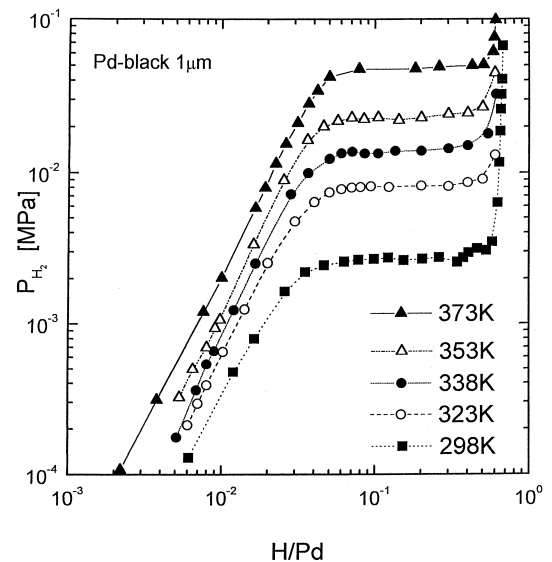


Fig. 3. P – C – T relations of the Pd–H system for a Pd black sample with a particle size of 1 μm .

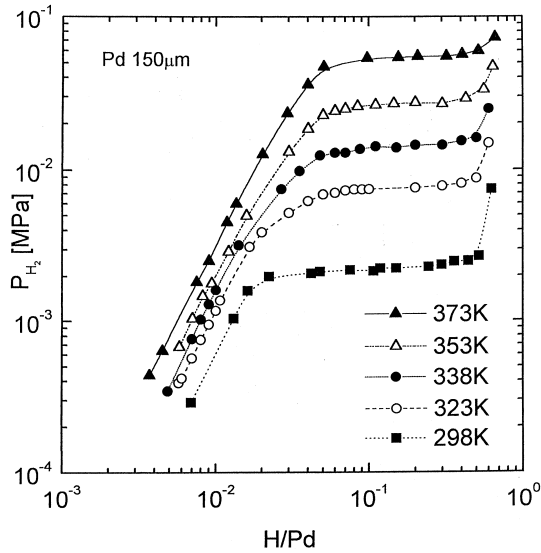


Fig. 4. P - C - T relations of the Pd-H system for a Pd powder sample with a particle size of 150 μm .

pretreated samples exhibit scattered data and much larger temperature dependence. This tendency was confirmed by the examination of the reproducibility of the P - C - T data. In the examination of the reproducibility, samples newly prepared with LiOH were subjected to each isotherm measurement. Any sample was reused after the P - C isotherm measurement. Each pretreated sample exhibited slightly different P - C isotherms even at a same temperature. When the fact that the Pd sample without pretreatment exhibit quite a high reproducible P - C isotherms is taken into account, the scattered data may be caused by different surface conditions of each Pd samples with different distributions of Li atoms.

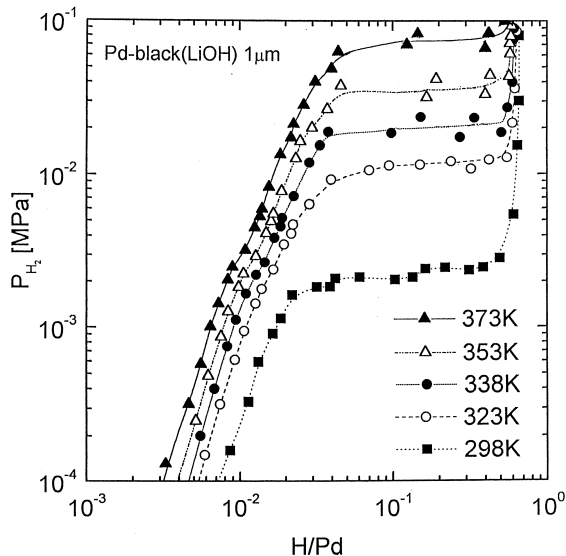


Fig. 5. P - C - T relations of the Pd-H system for a Pd black sample with a particle size of 1 μm with pretreated 1 M LiOH at 353 K for 1 h.

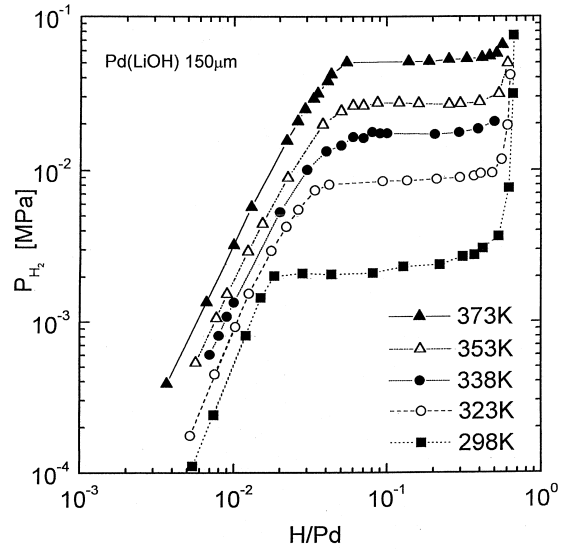


Fig. 6. P - C - T relations of the Pd-H system for a Pd powder sample with a particle size of 150 μm with pretreated 1 M LiOH at 353 K for 1 h.

3.3. The heats of reactions

From the temperature dependence of the equilibrium pressure, $\ln p$ vs. $1/T$, the partial molar enthalpies, ΔH , of hydrogen for hydrogen solution and hydride formation were calculated and are shown in Fig. 7.

The calculated heats of hydrogen solution at the hydrogen concentrations $[\text{H}]/[\text{Pd}] < 1 \times 10^{-2}$ are -9.5 ± 0.2 kJ/molH for the smaller samples (1 μm), and -10.4 ± 0.3 kJ/molH for the larger samples (150 μm), respectively. These values are in good agreement with a previously reported value [9]. However, the temperature dependence of the P - C isotherms for the pretreated samples resulted in higher ΔH values: about -20 kJ/molH for the smaller sample (1 μm), and about -12.5 kJ/molH for the larger sample (150 μm). The ΔH value for the pretreated samples are higher than those for the untreated samples by 90–100% for the small samples and by 15–26% for the large samples. These higher ΔH values are indicative strong interactions of hydrogen atoms with Li atoms in Pd.

In the two phase region (hydrogen solid solution and PdH_{1-x} hydride phases), the pretreated small samples (1 μm) exhibits the highest heat of hydride formation, about -22.5 kJ/molH, which is higher than -17.5 kJ/molH for the untreated small samples. The LiOH pretreatment markedly enhanced the heat of formation of palladium hydride by 29%. The large samples (150 μm) exhibit similar ΔH values, about -19.5 kJ/molH, at hydrogen concentrations $[\text{H}]/[\text{Pd}] < 10^{-1}$ in the two phase region. However, the ΔH of the pretreated large particle sample declines to more positive values, -17.5 kJ/molH at hydrogen concentrations $[\text{H}]/[\text{Pd}] > 10^{-1}$. For the large particle samples, the effect of the bulk volume should be more effective than that of the surface volume. The total

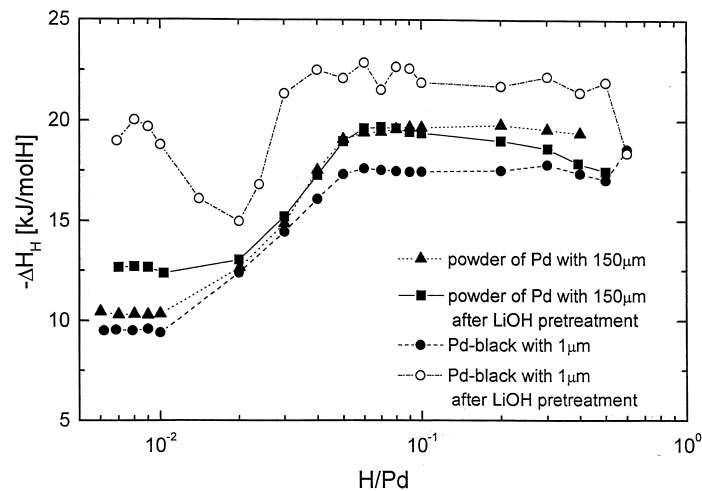


Fig. 7. The Change in relative partial molar enthalpy ΔH_{H} for H_2 dissolution and PdH_{1-x} hydride formation as a function of hydrogen concentration.

ΔH value may reflect rather the characteristics of bulk than those of surface though the surface was pretreated with LiOH. At the initial stage of the hydride precipitation in the two phase region, relatively low densities of defects such as microcracks and dislocations may be formed. Therefore, the ΔH value may be similar to that for the untreated large particle samples. As the formation of defects proceeds with increasing amount of hydride phase, the ΔH value may become rather to those for the untreated small particle samples because of high densities of defects inside the large particles (see Fig. 7). As another reason for that, the decrease of ΔH as the hydrogen concentration increases may also be due to the slope of the plateau near the hydride phase rather than to a change in thermodynamic properties.

The heat of LiH hydride formation is lying about -80 to -90 kJ/molH [9], which is higher than that for PdH_{1-x} hydride by factors eight to nine. Therefore, strong interactions of the Li with hydrogen atoms seems strongly responsible for the remarkably enhanced heats of reaction for the Pd samples with penetrated Li atoms by the LiOH pretreatment.

4. Conclusions

The heat treatment of Pd with a 1 M LiOH solution induces the penetration of Li atoms into the surface region of Pd even at 353 K. The longer treatment enhances the Li concentration along depth. For smaller particles of Pd, the Li penetration effect is more profound in the enhancement of the heats of reactions the heat of hydrogen solution by 90–100% and the heat of formation of PdH_{1-x} hydride by about 29% in comparison with those of the untreated Pd samples.

In a long electrolytic hydriding of a large Pd sample with LiOH, the Li atoms of the LiOH electrolytic solutions

may penetrate into the grain boundaries and then inside the grains. In such a case, the measured thermodynamic data may include the effect of the Li atom penetration at the surface region of each grain. The possibility of the Li inclusion into Pd or the formation of Li–Pd intermetallics at the Pd surface should be examined.

Acknowledgements

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