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Thermodynamic properties of hydrogen in fine Pd powders

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Abstract

The effect of Pd particle size on the thermodynamic properties of the Pd–H system was examined at 298 to 373 K. In this study, the pressure–composition(PC) isotherms were determined for Pd fine powders with around 0.2 μm in diameter of primary particle and derived thermodynamic properties were compared with values obtained for Pd sheet. In the solid solution region, the hydrogen solubility increased with reducing Pd particle size. This is similar to the case found for $LaNi_5$–H system. On the other hand, it was found that the plateau pressures on P–C isotherms increased with decreasing particle size at relatively low temperatures, which is the reverse to the case for $LaNi_5$–H system. This research demonstrates the difference in thermodynamic properties of hydrogen in between fine Pd powders and Pd sheet, well reflecting the difference in hydrogen solubility and plateau pressure on PC isotherms. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

A great number of studies have been concerned with measurements of the PC isotherms to obtain the thermodynamic properties of metal–hydrogen systems because determination of the pressure–composition–temperature (PCT) relation gives much more valuable information than any other ways. However, as pointed out in earlier studies [1–4], it is very difficult to determine the intrinsic thermodynamic properties for metal–hydrogen systems. In fact, in the case of $LaNi_5$ alloy, literature values of isotherms are widely scattered. This could imply that isotherms are strongly affected by the preparation history of samples for PCT measurements [2,4–6].

As well known, large volume expansion takes place during hydrogen uptake in metal lattices so that in many cases severe pulverization causes, especially once isotherms reach plateau pressures. In the case of $LaNi_5$–H system highly densified defects are created even in the hydrogen solid solution region [3]. The lattice defects act as hydrogen trapping sites so that hydrogen solubility in the hydrogen solid solution region increases with increasing the number of hydriding–dehydriding cycles [7]. Recently, Uchida et al. pointed out that $LaNi_5$ powdered samples exhibit higher hydrogen solubilities in the solid solution region because stress relaxation can easily occur in fine powders [3,4]. The effect of the particle size not only on the hydrogen solubility but also on the plateau pressure should be important to consider. As pointed out by Uchida and Naragaki [7], plateau pressure for $LaNi_5$–H system significantly decreases during first several hydriding–dehydriding cycles, implying that plateau pressure for fine powders is lower than that for block samples because hydriding/dehydriding process yields severe pulverization of $LaNi_5$ alloy.

In this study, we investigated the effect of Pd particle size on the hydrogen solubility and plateau pressure on PC isotherms because highly densified defects are not created in the solid solution region [8] and Pd does not pulverize even during hydride formation, although severe plastic deformation takes place.

2. Experimental

Both Pd sheets and powders (Pd black) with 99.99% of purity were supplied from Kojundo Chemical Co., Ltd. Preparation technique of fine Pd powders is a chemical reduction process from an aqueous solution. An SEM picture of Pd powders, shown in Fig. 1, indicates that each primary particle is more or less 0.2 μm in diameter but because of low particle dispersion, secondary particles larger than 20 μm exist. Before PCT measurements, Pd sheets (0.5 mm thick) were annealed at 1173 K for 12 h

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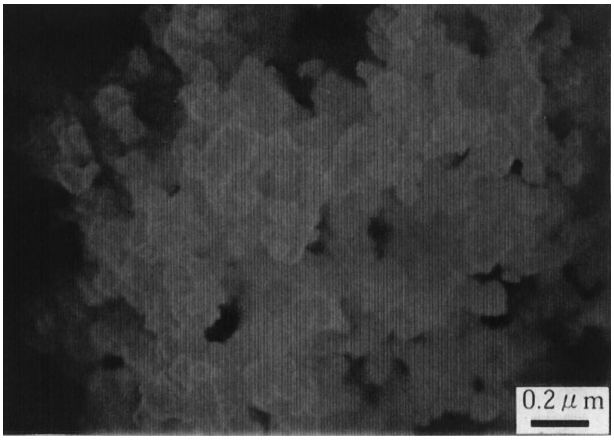

Fig. 1. SEM image of Pd fine powders.

under Ar atmosphere. In the case of Pd powders, they were not annealed at elevated temperatures to avoid proceeding coalescence of fine powders [9]. The PC isotherms for hydrogen absorption were measured using a Sieverts type of apparatus.

3. Results and discussion

3.1. Effect of particle size on isotherms

Fig. 2(a, b) shows PC isotherms for the Pd sheets and Pd fine powders at 298 K to 373 K. In order to discuss the detail of the effect of particle size on isotherms, isotherms at 298 K and 373 K in low hydrogen solubility region till $r(\mathrm{H/Pd})=0.1$ were reconstructed from Figs. 2, shown in Fig. 3. In Fig. 3 isotherms for coarser Pd powders, which are coalesced powders of more or less 1 μm (primary) in diameter, are added for comparison. At 298 K, significant particle size dependence of the hydrogen solubility can be seen. The hydrogen solubility increases with decreasing Pd particle size from sheet to 0.2 μm in powder. A similar effect has been reported on the $LaNi_5$–hydrogen system by Uchida et al [6,7]. As mentioned previously, metal lattice expands with absorbing hydrogen. The volumes of $LaNi_5$ and Pd expand respectively by 24% and 15% due to the hydride formation [10,11]. In the case of the Pd–H system, the volume expansion is almost proportional to the hydrogen solubility so that the volume expansion at the solubility limit of the solid solution, $r=0.02$ at 298 K, may be approximated to 0.5%. Equivalent value for $LaNi_5$ at $r=0.1$ is about 2%. Therefore, considering the ductilities and the above values of the volume expansion of Pd and $LaNi_5$, it may be concluded that severe plastic deformation is not yielded on Pd in the solid solution region compared to $LaNi_5$. In fact, as long as Pd is not exposed to hydrogen pressure higher than plateau pressures, the existence of defects and dislocations as trapping sites was not found even after absorption/desorption cycling [8].

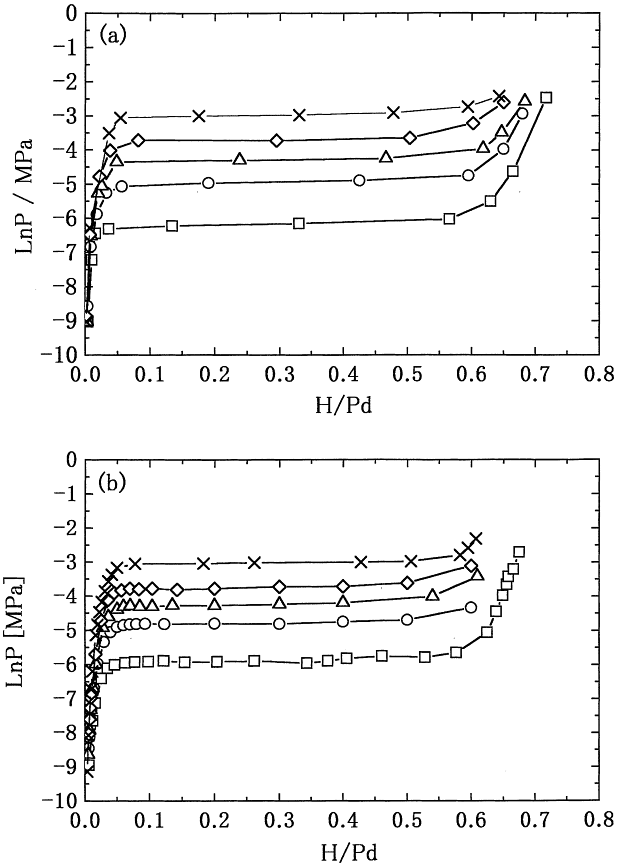

Fig. 2. Pressure–composition isotherms for Pd–H system for (a) sheet and (b) fine powders at temperatures (×) 373 K, (◇) 353 K, (△) 338 K, (○) 323 K and (□) 298 K.

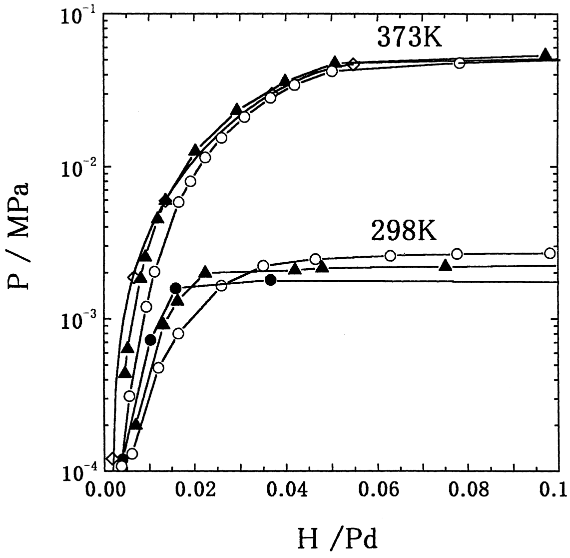

Fig. 3. Pressure–composition isotherms for Pd–H system for (●) sheet, (▲) coarse powders and (○) fine powders at low hydrogen concentrations.

Not only the hydrogen solubility but also the plateau pressure and solubility limit in solid solution are affected by the particle size. Plateau pressure and the solubility limit increase with decreasing particle size at 298 K. As previously mentioned that in the case of the $LaNi_5$–H system, plateau pressure is expected to decrease with decreasing particle size because plateau pressure for the second absorption is remarkably lower than that for the first absorption [7]. This opposite behavior could be related to the pulverization of $LaNi_5$ during hydride formation. Pd is not pulverized even though hydride formation yields large plastic deformation. It should be pointed out that this particle size dependence of plateau pressure disappears at elevated temperatures, see Figs. 3 and 4.

3.2. Thermodynamic properties

The chemical potential of hydrogen in gas and Pd, μ_{H_2} and μ_H, are given by

$$1/2\mu_{H_2} = 1/2\ \mu^0_{H_2} + RT \ln P^{1/2}_{H_2} \tag{1}$$

$$\mu_H = \mu^0_H + RT \ln (r/(1-r)) + \mu^E_H \tag{2}$$

where $r=$(mol H/mol Pd), $\mu^0_{H_2}$ is the chemical potential of hydrogen gas at 1 atm, μ^0_H is the chemical potential of hydrogen in the hypothetical infinitely dilute solution and μ^E_H is the excess chemical potential of hydrogen. From Eqs. (1) and (2) at equilibrium between metal and hydrogen gas, we obtain

$$RT \ln \left\{P^{1/2}_{H_2}((1-r)/r)\right\} = \Delta\mu^0_H + \mu^E_H \tag{3}$$

where $\Delta\mu^0_H = \mu^0_H - 1/2\mu^0_{H_2}$ which is the chemical potential of hydrogen at $r=0$. The hydride formation for the Pd–H system takes place in the miscibility gap type of transformation so that each thermodynamic parameter in Eqs. (1)–(3) varies continuously with temperature and/or hydrogen concentration. From Eqs. (2) and (3), the hydrogen solubility and plateau pressure may change if either $\Delta\mu^0_H$ or μ^E_H varies with particle size at a given temperature, expecting that the more negative these values are, the lower the plateau pressure is. Figs. 5 and 6 show thermodynamic properties, $\Delta\mu^0_H$ and W_H at solid solution region for both Pd sheet and powder, calculated from plotting the left hand side of Eq. (3) against r, where W_H is obtained from the approximation that $\mu^E_H = W_H \cdot r$ at low r.

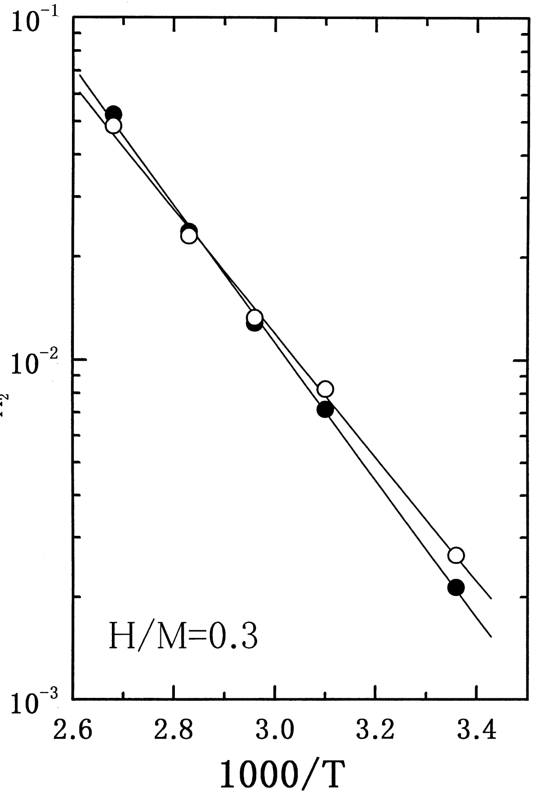

Fig. 4. Van't Hoff plots of the plateau pressures for (●) Pd sheet and (○) fine powders at H/Pd=0.3.

As shown in Fig. 5, at lower temperatures $\Delta\mu^0_H$ for Pd sheet is more positive than for Pd powder, i.e., $\Delta\mu^0_H$ (sheet)$-\Delta\mu^0_H$ (powder)$=0.8$ kJ/mol H at 298 K. However, $\Delta\mu^0_H$ (powder) increases more steeply with temperature than $\Delta\mu^0_H$ (sheet) and exceeds the value of $\Delta\mu^0_H$ (sheet) at 373 K. As shown in Fig. 6, the W_H value for Pd sheet, as expected, becomes more positive with increasing temperature. On the other hand, the W_H value for Pd fine powders is insensitive to temperature, corresponding to the fact that the solubility limit of the solid solution for Pd powder does not change with temperature because the solubility limit should be only affected by W_H. As shown in Fig. 6, W_H (sheet) is approximately 25 kJ/mol H more negative than W_H (powder) at 298 K but 7.5 kJ/mol H more positive at 373 K. From the above discussion, it

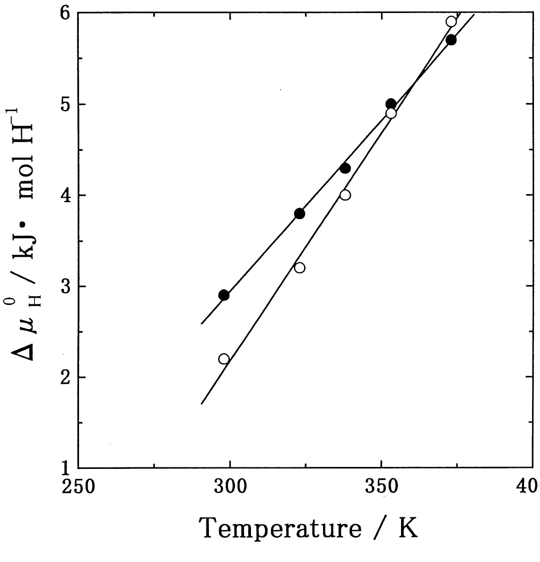

Fig. 5. Plots of $\Delta\mu^0_H$ against H/Pd determined from isotherms: (●) Pd sheet, (○) fine powders.

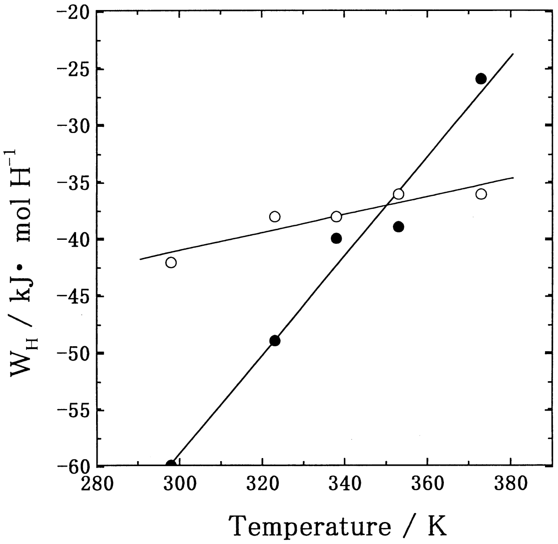

Fig. 6. Plots of W_H against H/Pd determined from isotherms: (●) Pd sheet, (○) fine powders.

could be concluded that at 298 K the large negative value of W_H (Pd sheet) yields lowering of the plateau pressure but at higher temperatures more positive values of $\Delta\mu_H^0$ (Pd powder) is compensated by more negative values of W_H (powder). As a result, the difference in plateau pressure between Pd sheet and powder disappears at higher temperatures.

As mentioned previously, in the case of Pd fine powders smaller than 1 μm, coalescence of the powders may occur even at 298 K [9]. This means that the surface energy of powder should be considered in the viewpoint of powder metallurgy. Considering the surface energy of Pd powder, the chemical potential of hydrogen in fine powder with radius of r_d written as $\mu_H(r_d)=\mu_H(\infty)+2V_H\gamma/r_d$, where $\mu_H(\infty)$ corresponds to the chemical potential of hydrogen for $r\to\infty$, V_H is the partial molar volume of hydrogen and γ is the surface energy/unit area. However, the calculated value of $2V_H\gamma/r_d$ is smaller than 10 J/mol H for 0.2 μm of Pd powder, concluding that the surface energy did not work on the difference in thermodynamic properties between Pd sheet and fine powders.

As Alefeld first pointed out [12], a substantial contribution to the negative value of W_H at low r comes from the volume interaction energy on the basis of the continuum model proposed by Eshelby [13]. According to a model based on an isolated isotropic defect in an isotropic medium, the volume interaction energy can be given by

$$W_H(\text{vol}) = -\nu B V_H^2/V_S \tag{4}$$

Where ν is $1-B/C_{11}$, B is the bulk modulus, V_H is the partial molar volume of hydrogen and V_S is the total volume per mole of Pd [14]. In the case of the $LaNi_5$–H system, we have been obtained V_H (powder)>V_H (block) [4]. If this relation in V_H can be applied for the Pd–H system, the difference in the νB value in Eq. (4) between Pd sheet and powder should create the difference in the thermodynamic properties. The ν value is more or less 0.2 and the B value for Pd fine powder might be much smaller than that for Pd sheet because as mentioned previously, sintering temperature of Pd fine powders is expected to be much lower than Pd sheet [9], implying lowering B value. At the moment, however, quantitative discussion is very much difficult due to the lack of physical values of ν and B.

Conclusions

In the Pd–H system, the hydrogen solubility in the solid solution region and plateau pressure are dependent upon Pd particle size. The thermodynamic discussions imply that a large negative value of W_H for Pd sheet is a dominant contributor to lowering plateau pressure for Pd sheet than that for Pd powders at lower temperatures. However, $\Delta\mu_H^0$ (powder) is more negative than $\Delta\mu_H^0$ (sheet) so that at lower temperatures this difference can not be compensated in the solid solution by more positive value of W_H for Pd powders. As the results, hydrogen solubility and plateau pressure for Pd powders is higher than those for Pd sheet at lower temperatures. These differences in the above thermodynamic properties should be related with the volume interaction energy but at the present time quantitative discussion is almost impossible. At higher temperatures, the hydrogen solubility difference remains but the difference in plateau pressures vanishes.

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