

HYDRIDING INFLUENCE OF INDIUM ON Pd-In ALLOYS<sup>①</sup>

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**ABSTRACT** Hydrogen absorption and desorption isotherms were measured in a microbalance in the pressure range between 0.001 MPa and 3.5 MPa and at seven temperatures between 381 K and 621 K on four Pd-In alloys between 3.6% and 15% (in atom) In as well as on pure Pd. The results are similar to those obtained on the analogous alloys Pd-Ag and Pd-Sn and are interpreted in the same manner. Indium has two opposing effects upon the solubility of H in the Pd alloys, increase of the Fermi energy upon the donation of valence electrons and a lattice dilatation. At valence electron concentrations below 0.5, the lattice dilatation predominates and the H solubility is increased with addition of In. At valence electron concentrations above 0.5, the influence of elevated Fermi energy predominates and the H solubility is lowered by addition of In. The molar enthalpy of Pd hydriding at infinite dilution is strongly increased with increasing In content, but the molar entropy is not much affected by In. The excess chemical potential of hydrogen at small hydrogen concentrations and at a given temperature increases with increasing In. The apparent H-H attractive interaction energy,  $w_{H-H}$ , is decreased by the presence of In.

**Key words** hydriding valence electrons lattice dilatation Fermi energy

## 1 INTRODUCTION

The absorption of hydrogen by palladium-silver alloys and palladium-tin alloys has been studied by Brodowsky H and Poeschel E<sup>[1]</sup>, Brodowsky H and Husemann H<sup>[2]</sup>. The hydrogen solubility in Pd-Ag alloys was measured in a concentration range of 10~40% (in atom) Ag in the temperature range 303~421 K. The measurements on Pd-Sn were carried out in the temperature range 323~498 K on five alloys between 2.5% and 15% (in atom) Sn. The authors evaluated the data in terms of the contribution of the Fermi energy and of the contribution of the lattice dilatation to the deviation from ideality. The purpose of this study is to determine the thermodynamic parameters for hydrogen solution at infinite dilution in Pd-In alloys of several indium contents, as well as the deviation from ideality at higher hydrogen concentrations.

## 2 EXPERIMENTAL

The alloys of Pd with 3.64, 7.78, 10.89,

and 14.53% (in atom) In for the pressure-composition-temperature ( $p$ - $c$ - $T$ ) measurements were prepared by induction melting under an argon atmosphere. The starting materials were of 99.8% (in weight) purity for Pd and 99.8% (in weight) purity for In supplied by Degussa and Ventron, Germany, respectively. After rolling to a thickness of about 0.2 mm the foils were subjected to a homogenizing anneal in the presence of zirconium as a getter material under a vacuum of  $1.5 \times 10^{-1}$  Pa at 1273 K for one week. The lattice parameters of the four alloys were 3.9049, 3.9191, 3.9298, and 3.9423 Å respectively. Prior to the  $p$ - $c$ - $T$  measurements, all the foil samples were chemically etched with a solution of about 5% HNO<sub>3</sub> in order to remove the oxide at the surface and then coated with a thin layer of Pd by cathodic dissolution of H in the samples and subsequently deposition of Pd in a solution of PdBr<sub>2</sub>. The coating acts as a hydrogen transition catalyst which greatly accelerates equilibration at low temperatures.

The equilibrium  $p$ - $c$ - $T$  data were deter-

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mined by a microgram balance in a vacuum system at temperatures between 381 K and 621 K and at hydrogen pressures up to 3.5 MPa. The samples weighed about 0.9 g. Counter weights of pieces of Au and Ag were made such that both mass and volume were closely equal to those of the sample. The weights were suspended on thin Al wires to minimize the buoyancy effects. The hydrogen pressures were measured by a precise quartz spiral (Texas Instruments). Samples were allowed to absorb a small amount of hydrogen at the temperature range chosen. Sample temperatures in the range 381 ~ 621 K were maintained using an electric furnace with a variation of the Pt-100 thermal resistor of  $\pm 0.15$  K. Desorption isotherms were done directly after the absorption isotherms. An allowance of 1 ~ 2 K for the thermal gradient between sample and thermal resistor has to be made.

### 3 RESULTS AND DISCUSSION

Since H atoms occupy the octahedral sites of the lattice and In atoms substitute the Pd atoms, the appropriate concentration variables for calculation of thermodynamic parameters are the molar fraction,  $X_{\text{In}} = N_{\text{In}} / (N_{\text{In}} + N_{\text{Pd}})$  for In and the atom ratio  $n = N_{\text{H}} / N_{\text{Pd}}$  for H.

Fig. 1 (a) and (b) show the absorption isotherms at 381 K and desorption isotherms at 541 K for In alloys between 3.64% and 14.53% (in atom) as well as for pure Pd. In the high pressure part of the isotherms, the influence of In reduces the solubility of H in Pd in a very regular way. The same effect was observed in Pd+Ag and Pd+Sn alloys<sup>[1-3]</sup>. This reduction of solubility is attributed to the partial filling up of the 4d-band of Pd by In, Ag, or Sn.

At lower pressure, there occurs a crossing over of the alloy isotherms with the Pd isotherm, such that up to  $X_{\text{In}} = 0.1089$  additions of In actually increase the solubility of H. The behavior was also observed in Pd+Ag and Pd+Sn alloys and is attributed to the lattice expansion of the alloys with respect to pure Pd, which facilitates the dissolution of H in metal as long as the Fermi energy is still in the 4d-band.

The chemical potential of hydrogen dis-

solved in Pd can be set as<sup>[4, 5]</sup>:

**Fig. 1 Absorption and desorption isotherms**

(a) —absorption  $T = 381$  K

(b) —desorption  $T = 541$  K

$$\mu_{\text{H}} = \mu_{\text{H}}^0 + RT \ln [n / (1 - n)] + \Delta\mu_{\text{H}}^+ + \Delta\mu_{\text{e}}^- \quad (1)$$

where  $\mu_{\text{H}}^0$  is the standard potential,  
 $\Delta\mu_{\text{H}}^+$  is the excess potential as a contribution of the protons,  
 $\Delta\mu_{\text{e}}^-$  is the excess potential as a contribution of the hydrogen electrons

Owing to

$$\Delta\mu_{\text{H}}^+ = 12RT \ln [(2 - 2n) / (\beta + 1 - 2n)],$$

$$\beta = [1 + 4n(1 - n) (\exp(-w_{\text{H-H}} / RT) - 1)]^{1/2}$$

here  $w_{\text{H-H}}$  —interaction energy of H pair

$$\Delta\mu_{\text{e}}^- = 1050n_{\text{e}} - 4062n_{\text{e}}^2 + 34830n_{\text{e}}^3 - 75495n_{\text{e}}^4 + 68839n_{\text{e}}^5$$

$$(n_{\text{e}} < 0.655)$$

$$\Delta\mu_e^- = 19242(n_e - 0.492) \\ (n_e > 0.655)$$

and the valence electron concentration  $n_e$  is equal to  $n$  for H (namely  $n_H$ ) in pure Pd and equal to  $n + ZiXi$  for alloys (where  $Xi$  is the mole fraction and  $Zi$  the effective valency of the other alloy components<sup>[5]</sup>) e. g.  $Z_{Ag} = 1$ ,  $Z_{Sn} = 3.4$ .

Therefore we have:

$$\mu_H = \mu_H^0 + \mu_e^0 + \Delta\mu_H^+ + \Delta\mu_e^- + \\ RT \ln [n_H / (1 - n_H)]$$

In order to show the relationship of the nearest neighbor interactions to the other contributions of the chemical potential, the various parts of Equation (1) are schematically represented in Fig. 2.

$\mu_e^0 + \Delta\mu_e^-$  indicates the Fermi energy rise in the alloy. The transition from the moderate rise in the 4*d*-band regime to the steep rise in the 5*s*-band regime is shifted from about  $n_H = 0.5$  in Pd to about 0.3 in the 7.78% (in atom) In alloy, since part of the 4*d*-band gap has already been filled by the valence electrons of In. Pd-In and several other Pd alloys have this convenient feature of a concentration range and most other systems do not have. Also, many properties of Pd-In alloys change abruptly near the valence electron concentration  $n_e = 0.5$ .

The opposite influence of In on H in Pd, increasing the solubility in the 4*d*-band regime and lowering it in the 5*s*-band regime or high pressure regime, is readily understood in terms of band filling and lattice dilatation effects. The absorption isotherms in a number of Pd-In alloys and in Pd at 381 K of Fig. 1(a) serve to illustrate these effects.

Introducing Sieverts' constant

$$K = \exp[(\mu_H^0 - \frac{1}{2}\mu_{H_2}^0)/RT] \quad (2)$$

into eqn. (1) yields

$$\ln \sqrt{p_{H_2}} = \ln [K \cdot n / (1 - n)] + \\ (\Delta\mu_H^+ + \Delta\mu_e^-) / RT \quad (3)$$

At vanishing concentrations, both  $\Delta\mu_H^+$  and  $\Delta\mu_e^-$  approach zero, and  $1 - n$  approaches 1. In that case, eqn. (3) simplifies the behavior in the ideal solution state, i. e., Sieverts' law. The values of  $K$  and  $w_{H-H}$  can be obtained from the  $p$ - $c$ - $T$  isotherms measured. According to  $\ln K = -(\Delta H^0 / 2RT) + (\Delta S^0 / 2R)$  and from the temperature dependence of  $K$ , values of the molar enthalpy  $\Delta H^0$  and the standard molar entropy  $\Delta S^0$  of absorption and desorption of hydrogen at infinite dilution can be determined from the slope and the intercept of a plot  $\ln K$  vs  $T^{-1} \times 10^3$  shown in Fig. 3(a) and (b). Fig. 4 shows the comparison of  $\ln K$  vs  $T^{-1} \times 10^3$  plots for several Pd alloys.

The difference of the standard potentials of dissolved and gaseous hydrogen,  $2\mu_H^0 - \mu_{H_2}^0 = -\Delta H^0 + T\Delta S^0 = 2RT \ln K$ , can be determined by known  $\Delta H^0$  and  $\Delta S^0$  or from  $\ln K$ . The difference of the standard potentials of hydrogen in

**Fig. 2 Constituent parts of the chemical potential of H in Pd and in a Pd- 7.78% (in atom) In alloy**

The standard potential  $\mu_H^0$  in Equation (1) has been split up into electronic and protonic contributions  $\mu_e^0$  and  $\mu_H^0$  respectively. In Fig. 2 the electronic and protonic parts have been lumped together with their corresponding excess potential  $\Delta\mu_e^-$  and  $\Delta\mu_H^+$ . The dashed line marked

**Fig. 3 Comparison of  $\ln K - T^{-1}$  for Pd-In alloys**

(a) —absorption; (b) —desorption  
 ■ —Pd; ● —Pd-In(96.36–3.64);  
 ▲ —Pd-In(92.22–7.78);  
 □ —Pd-In(89.11–10.89)

both absorption and desorption of the four Pd-In alloys due to increasing In content from  $X_{\text{In}} = 0.0364$  to  $X_{\text{In}} = 0.1453$  can be summarized as follows: (1) The molar enthalpies  $\Delta H^\circ$  for both absorption and desorption increase over than 4 times, and the molar entropies  $\Delta S^\circ$  increase 1.9 times. (2) The excess chemical potentials of hydrogen,  $\Delta \mu_{\text{H}}^0$ , for absorption and desorption increase 5.6 times and 5 times, respectively. (3) The apparent H-H attractive interaction energies,  $\omega_{\text{H-H}}$ , for absorption and desorption decrease 4 times and 3.5 times, respectively.

Fig. 5 shows a plot of  $RT \ln[\sqrt{P} \cdot (1-n)] /$

**Table 1 Experimental thermodynamic values of H in Pd and Pd-In alloys at 501 K**

$X_{\text{In}}$	$\Delta H^0 /$ ( $10^4 \text{ J} \cdot \text{mol}^{-1}$ )	$\Delta S^0 /$ ( $10^{-3} \text{ J} \cdot (\text{K} \cdot \text{mol})^{-1}$ )	$w_{\text{H-H}} /$ ( $10^3 \text{ J} \cdot \text{mol}^{-1}$ )	$\mu_{\text{H}}^0(X_{\text{In}}) - \mu_{\text{H}}^0(\text{Pd}) /$ ( $10^3 \text{ J} \cdot \text{mol}^{-1}$ )
(Desorption at 381~621K)				
0	1.74	100	-2.88	-
0.0364	1.79	92	-2.71	4.73
0.0778	2.87	105	-2.61	9.20
0.1089	5.01	134	-1.86	15.92
0.1453	7.56	176	-0.82	23.86
(Absorption at 381~621K)				
0	1.71	100	-2.75	-
0.0364	1.72	92	-2.83	4.31
0.0778	2.93	105	-2.64	10.12
0.1089	4.81	130	-2.04	16.29
0.1453	7.90	176	-0.68	24.14

**Fig. 4 Comparison of  $\ln K - T^{-1}$  for several Pd alloys**

palladium and in Pd alloys at 501 K,  $\mu_{\text{H}}^0(X_{\text{In}}) - \mu_{\text{H}}^0(\text{Pd})$ , is given in Table 1. From Table 1 the changes of thermodynamic data of

**Fig. 5  $RT \ln[\sqrt{P} \cdot (1-n)] / n] - \Delta \mu_{\text{e}}^0$  vs  $n_{\text{H}}$  for Pd-In alloy ( $X_{\text{In}} = 0.0778$ )**

$n] - \Delta\mu_e^-$  vs  $n_H$  for the Pd - In alloy ( $X_{In} = 0.0778$ ). Fig. 6 shows some electronic excess potentials determined experimentally for palladium with varying amounts of indium, silver, tin, and lead. In this evaluation of experimental data, indium is roughly three times as effective as silver in filling up the  $4d$ -band while tin and lead are about four times as effective<sup>[6,7]</sup>. A more realistic effective valency for this is  $Z_{In} \approx 2.9$  and  $Z_{Sn} \approx 3.4$ .

**Fig. 6 Electronic excess potential of hydrogen in Pd and Pd alloys**

The Fermi energy is strongly influenced by In, which donates its valence electrons to  $4d$ - $5s$  bands of the alloys, leaving fewer or no  $4d$ -band holes to be filled by hydrogen. In the alloy in Fig. 6, containing about 3.64% (in atom) In, the steep rise of the  $5s$ -band regime occurs at a smaller H concentration than in pure Pd but with the same slope. Fig. 6 more directly demonstrates the filling of the  $4d$ -band and the rise of Fermi energy in  $5s$ -band by electronic excess potential  $\Delta\mu_e^-$  of H in Pd-In alloy.

## 4 CONCLUSIONS

(1) Like alloying elements Ag and Sn, In has two opposite effects upon the Pd hydriding.

At low hydrogen concentrations, the solubility is usually increased and at high hydrogen concentrations, it is decreased by addition of In. These effects are explained in terms of a rise of the Fermi energy upon the donation of valence electrons, and a lattice dilatation. In general, at valence electron concentrations below 0.5, the lattice dilatation predominates and the H solubility is increased with addition of In. At valence electron concentrations above 0.5, the influence of the elevated Fermi energy predominates and the H solubility is lowered by addition of In.

(2) The molar enthalpy of absorption and desorption of hydrogen at infinite dilution is strongly increased with increasing In content, but the molar entropy is not nearly as much affected by In. The excess chemical potential of hydrogen at small hydrogen concentrations and at given temperature increases with an increase of In content. The apparent H-H attractive interaction energy,  $\omega_{H-H}$ , is decreased by the presence of In. The trend is also similar to that found for the Pd-Ag-H and Pd-Sn-H system.

(3) The effective valency of indium is roughly 3 (more realistically 2.9) in its effect on the Fermi energy and on the electronic part of the excess potential of hydrogen.

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