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A Method for the Prediction of the Hydriding Thermodynamics of Ternary Pd-Based Alloys

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A method has been developed to calculate the hydriding thermodynamics of ternary Pd-X-Y systems, where X and Y are substitutional alloying elements, by using the properties of the binary Pd-X and Pd-Y systems. Experimental data was collected on the Pd-Rh-Co system to test the validity of this method. Hydrogen pressure-composition isotherms of several binary Pd-Rh and Pd-Co alloys and Pd-Rh-Co ternary alloys were measured to determine the thermodynamics of hydrogen absorption, hydride formation and decomposition, and hydrogen capacity. Good agreement between the calculated and measured values for the ternary Pd-Rh-Co system, in the dilute alloying regime (< 10 at.% total alloying additions), was obtained using our method. Examining literature results on other ternary Pd-X-Y systems checked the universality of this method. Again, the method succeeds in predicting the hydriding thermodynamics for both lattice contracted and lattice expanded alloy systems, Pd-Ni-Rh and Pd-Ag-Y respectively.

Keywords: palladium (Pd), rhodium (Rh), cobalt(Co), hydrogen (H), hydrides, thermodynamics

1. Introduction

The thermodynamics of palladium-based alloys with hydrogen has been extensively studied and has been the subject of recent reviews[1, 2]. Both of these papers present a dependence of the relative chemical potential of dissolved hydrogen at infinite dilution, $\Delta\mu^\circ_H$, as a function of the lattice parameter of the alloy. As the lattice parameter of the alloy increases relative to pure Pd, $\Delta\mu^\circ_H$ decreases; and hence the hydrogen solubility increases as would be expected from a geometrical consideration. Similarly the standard free energy change for β-hydride formation at 298K, ΔG°_{plat}, decreases as the lattice parameter increases relative to pure Pd. In other words, alloys with "expanded" lattices have hydriding plateau pressures lower than pure Pd. Conversely, alloys with "contracted" lattices have hydriding plateau pressures greater than pure Pd. Even though these trends were observed, no capability was presented to predict the hydriding thermodynamics of the binary or ternary Pd alloys.

In a recent paper by Teter and Thoma[3], a method was developed to calculate the hydriding thermodynamics of Pd-Rh-Co alloys based upon the measured thermodynamics of the binary Pd-Rh and Pd-Co alloys.

In this paper, we summarize the approach and results used in our previous paper[3] and show its applicability to other ternary Pd-based systems in particular the lattice contracted system, Pd-Ni-Rh, and the lattice expanded system, Pd-Ag-Y. Also the system, Pd-Ni-Ag with alloying elements that both expand and contract the lattice, will be modeled.

2. Experimental

Data for the binary and ternary Pd-based alloys come from the following sources: Pd-Ni [4], Pd-Rh[3], Pd-Co[3, 5], Pd-Ag[6], Pd-Y[7], Pd-Ni-Rh[8], Pd-Ni-Ag[9], Pd-Y-Ag[6]Pd-Rh-Co[3]. Samples were foils with thicknesses ranging from 75 to 100 µm. The procedures for measuring the pressure-composition isotherms are given in each of these references and are essentially the same. Samples are exposed to aliquots of hydrogen in a constant volume system. Pressure changes indicate the amount of hydrogen absorbed/desorbed by the sample.

3. Dilute Phase Hydrogen Solubility

The first thermodynamic property modeled is the dilute phase solubility of hydrogen into the metal. The solution of hydrogen in the α phase at infinite dilution can be expressed as:

$$\tfrac{1}{2}H_2(g) + M \Leftrightarrow MH_\alpha \tag{1}$$

from which one obtains the thermodynamic relation[10]:

$$\Delta\mu_H = \tfrac{1}{2}RT\ln p_{H_2} = \Delta H_H - T\Delta S_H$$
$$= \Delta H^o_H - T\Delta S^o_H + RT\ln\left(\frac{r}{1-r}\right) + \mu^E_H(r) \tag{2}$$

where $\Delta\mu_H$ is the relative chemical potential of hydrogen, μ^E_H is the excess chemical potential, ΔH°_H and ΔS°_H are the relative enthalpy and entropy of the solution of hydrogen at infinite dilution, and r is the hydrogen-to-metal ratio. Rearranging equation 2 gives:

$$\Delta\mu_H = RT\ln\left(\frac{p_{H_2}^{1/2}(1-r)}{r}\right) = \Delta\mu^o_H + \mu^E_H(r) \tag{3}$$

where $\Delta\mu^\circ_H$ is the relative chemical potential of dissolved hydrogen at infinite dilution. The excess chemical potential term vanishes in the limit of infinite dilution, i.e. as r → 0. Therefore plots of $\Delta\mu_H$ against r gives $\Delta\mu^\circ_H$ at r=0 and the non-ideal interaction term is obtained from the slope. The values of $\Delta\mu^\circ_H/T$ are then plotted against 1/T to obtain ΔH°_H and ΔS°_H.

For each binary Pd-X alloy, the enthalpy and entropy of the solution of hydrogen at infinite dilution are plotted as a function of alloying amount in at.%. For each of the binary systems examined, ΔH°_H shows a strong linear dependence. The entropy, ΔS°_H, does not vary significantly with alloying content, but was fit as though the dependence was linear. As will be shown later, this does not have a significant effect of the result. The fits were made according to the following relation:

$$\Delta H_H^o = -10.0 + m * (at.\%X)$$

$$\Delta S_H^o = -54.0 + m * (at.\%X) \qquad (4)$$

where m is the slope given in Table 1 for alloying element X. The intercepts of these equations were forced to be a constant with the values for pure Pd as measured by Sakamoto et al[11]. The results of the linear regressions are given in Table 1 for the binary systems examined in this paper. To calculate the thermodynamics properties of the ternary, Pd-X-Y systems, the slopes obtained for the binary systems are then used in the following relation:

$$\Delta H_H^o = -10.0 + m_X * (at.\%X) + m_Y * (at.\%Y)$$

$$\Delta S_H^o = -54.0 + m_X * (at.\%X) + m_Y * (at.\%Y) \qquad (5)$$

where m_X and m_Y are the slopes given in Table 1 for alloying elements X and Y respectively. If the total alloying additions being examined are less than 10%, then a linear dependence of the ternary system derived from the binary systems can be expected.

Very good agreement between the measured enthalpy and the calculated enthalpy for the ternary Pd-X-Y systems exists as is shown in Figure 1. The error bars represent a 10% error. All alloys, except one, fall within this 10% error. This approach works well for both lattice contracted alloys, Pd-Rh-Co and Pd-Ni-Rh, lattice expanded alloys, Pd-Y-Ag, and mixed alloys containing both lattice expanding and lattice contracting alloying additions, Pd-Ni-Ag.
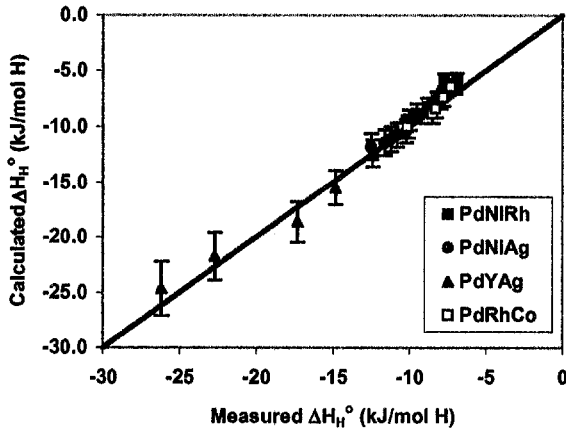

Figure 1: Comparison of the calculated and measured enthalpy of solution of hydrogen at infinite dilution.

4. α + β Plateau Thermodynamics

As the alloy exceeds the solubility limit, the solid solution alpha phase transforms to the beta hydride phase. The gas pressure in equilibrium with the alpha and beta phases remains constant as the hydrogen content of the alloy increases and the alpha phase transforms into the beta phase. This is known as the plateau region. The plateau chemical reaction can be written as:

$$\tfrac{1}{2}H_2(g) + \frac{1}{\beta - \alpha} MH_\alpha \Leftrightarrow \frac{1}{\beta - \alpha} MH_\beta \qquad (6)$$
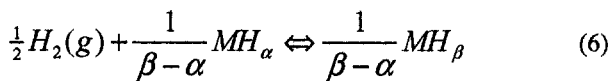
where α and β are the solid solution α-phase and β-hydride phase boundary compositions at a given temperature. The thermodynamics can be determined by examining the temperature dependence of the plateau pressures for this

reaction. The standard free energy change for β-hydride formation from the saturated α-phase with reference to (½)H_2(1 atm, g) is given as[12]:

$$\Delta G_{plat}^o = RT \ln p^{1/2} = \Delta H_{plat}^o - T\Delta S_{plat}^o . \qquad (7)$$

Van't Hoff plots of ln $p^{1/2}$ against 1/T will produce the standard enthalpy change, ΔH_{plat}^o, and the standard entropy change, ΔS_{plat}^o. In this work, the plateau pressure used to obtain the thermodynamics is interpolated from the data and calculated at a hydrogen composition of H/M = 0.30.
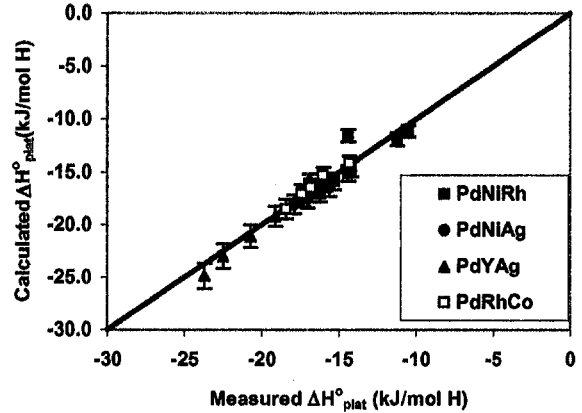

Figure 2: Comparison of the calculated and measured enthalpy of hydride formation from the plateau reaction for Pd-X-Y alloys.

A similar linear regression is made for the plateau thermodynamic properties as was made for the infinite dilution properties. The slopes obtained for the binary Pd-X alloys are given in Table 1. The ternary, Pd-X-Y, plateau thermodynamic properties are calculated as before by combining the relations obtained for the binary systems. The equations for the ternary Pd-based systems are:

$$\Delta H_{plat}^o = -18.5 + m_X * (at.\%X) + m_Y * (at.\%Y)$$

$$\Delta S_{plat}^o = -46.0 + m_X * (at.\%X) + m_Y * (at.\%Y) \qquad (8)$$
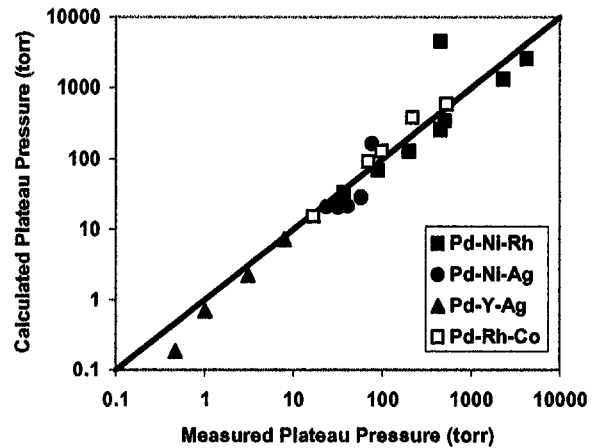

Figure 3: Comparison of the calculated plateau pressures evaluated at 300 K for the Pd-X-Y alloys.

again where m_X and m_Y are the slopes given in Table 1 for alloying elements X and Y respectively. The constant intercepts for pure Pd are from Sakamoto et al.[11]. Figure 2 shows the comparison of the measured and calculated enthalpies for hydride formation. Again very good agreement exists between the measured and calculated values for both lattice expanded and contracted alloys. The calculated entropies for the plateau reaction do not agree very well with the measured values with errors in the range of 25%. Application requirements are usually based on the plateau pressure and hydrogen storage capacity. Given the

enthalpy and entropy of the plateau reaction, the plateau pressure can be calculated from Equation 5. Since poor agreement exists for the prediction of the entropies, the measured entropy will be used for each plateau pressure calculation. The pressure comparison will be based only on the differences in the enthalpies of the plateau formation. Figure 3 shows that the calculated plateau pressures at 300K correlate well with the measured plateau pressures.

Table 1: Fitted slopes for the hydrogen-alloy thermodynamic properties.

	ΔH_H° (kJ/molH)	ΔS_H° (J/mol H*K)	ΔH_{plat}° (kJ/molH)	ΔS_{plat}° (J/mol H*K)
Pd-Ni	0.242	-0.116	0.475	0.174
Pd-Rh	0.236	-0.276	0.308	-0.180
Pd-Co	0.484	0.216	0.580	-0.420
Pd-Ag	-0.480	-0.240	-0.120	0.260
Pd-Y	-1.941	-1.574	-1.181	-1.305

5. Conclusions

The hydrogen absorption and hydriding thermodynamics of dilute (<10 at.% additions) ternary Pd-X-Y alloys can be successfully predicted based upon the thermodynamic properties of the binary alloys. This method should equally hold true for higher-order Pd-based alloys. In concept, this method may also be successful in predicting the thermodynamics of intermetallic hydrogen storage alloys.

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