The Role of Al on the Thermodynamics of Hydrogen Absorption/Desorption by Some Ternary Pd-M-Al Alloys where M=Rh, Ni, Pt, Cr, Ag.

by
K. L. Shanahan
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

D. Wang
Chemistry Dept., University of Vermont
VT USA

T. B. Flanagan
Chemistry Dept., University of Vermont
VT USA

DOE Contract No. DE-AC09-96SR18500

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.
This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/support/index.html

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov
The Role of Al on the Thermodynamics of Hydrogen Absorption/Desorption by Some Ternary Pd-M-Al Alloys where M= Rh, Ni, Pt, Cr, Ag. (U)

D. Wang and Ted B. Flanagan
Chemistry Department, University of Vermont,
Burlington, VT 05405
and
Kirk L. Shanahan
Westinghouse Savannah River Company
Aiken, South Carolina 29802

Abstract

The solution of hydrogen and hydride formation in FCC substitutional solid solution Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ alloys have been examined. In contrast to some other Pd ternary alloys, a linear relation does not obtain between the H capacity and x for the Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ alloys investigated here where the H capacity of the alloys is estimated from the H content of the steeply rising part of the isotherms in the hydride phase regions. A linear increase of the dilute phase H solubility with x for these Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ alloys does, however, obtain for these alloys.

Although Pd-Rh binary alloys have broader plateaux than does Pd itself, small amounts of Al substituted into Pd$_{0.85}$Rh$_{0.15}$ or Pd$_{0.80}$Rh$_{0.20}$ alloys can reduce or eliminate the two phase regions, the plateaux; there is, however, not much effect on the dilute phase solubilities. For example, small amounts of Al substituted into the Pd$_{0.85}$Rh$_{0.15}$ or Pd$_{0.80}$Rh$_{0.20}$ alloys eliminate the plateaux. On the other hand, alloying Pd with Al to form binary alloys with X$_{Al}$=0.015 or 0.030 does not eliminate the plateaux which are present in these binary alloys up to X$_{Al}$=0.075 (298 K). Small amounts of Al substitution do not have such a dramatic effect on the plateau widths of the Pd$_{0.90}$Ni$_{0.10}$ and Pd$_{0.80}$Ni$_{0.20}$ alloys and similarly substitution of Al into Pd-Cr and Pd-Ag alloys does not introduce any anomalous effects into the isotherms.

Introduction

Pd alloys, like Pd itself, form hydride phases if the solute metal content is not too large. When the hydride phase forms by adding hydrogen to the dilute phase, the hydrogen pressure should be invariant at equilibrium because there are three phases and two components. This pressure, predicted to be invariant, is called the plateau pressure. The plateau pressures and H capacities are of the interest for possible applications of these
systems. When the system is on the plateau the reaction which takes place upon H₂ (g) absorption is:

\[(1/2)H₂ (g) + (1/(b+a)) MH_a \rightarrow (1/(b+a)) MH_b\]

where \(b\) and \(a\) are the H/M atom ratios of the co-existing hydride and dilute phases, respectively. Because of hysteresis, complete equilibrium is not attained and there is not a single plateau pressure but two, one for hydride formation and a lower one for decomposition.

The solution of hydrogen and hydride formation in binary solid solution Pd alloys have been examined for many different solutes \([1, 2]\) and interest has now been extended to ternary Pd-rich alloys partly because of the possibility of obtaining desired properties of hydrogen absorption by variation in the amounts of two rather than just one solute as for the binary alloys.

The solution of hydrogen in binary \(Pd\)-Rh alloys has been studied by several workers \([3-7]\). These alloys are of interest because they, and possibly \(Pd\)—Ni alloys, are the only Pd alloys where the H capacity increases with solute metal concentration. This may be because Rh itself absorbs hydrogen to form a hydride phase at \(P_{H₂}=3.8\) GPa \([8]\). The absorption of hydrogen by \(Pd\)-Al alloys has been studied by Sakamoto \textit{et al} \([9]\) who found that the plateau pressures increase because these are contracted fcc lattices compared to Pd and the H capacities decrease with Al content such that there is no plateau for the \(Pd_{0.90}Al_{0.10}\) alloy at 323 K \([9]\). The plateau pressures increase with % Al almost the same as with % Rh in the \(Pd\)-Rh system.

In this paper the effect of Al substitution on several Pd-rich alloys will be examined because it was observed in this laboratory that Al has a rather dramatic effect on the H capacity of several \(Pd\)-Rh alloys.

**Experimental**

The alloys were prepared by arc-melting the components under argon and then annealing them at 1133 K for 72 h. They were then rolled into thin foil and re-annealed at 1133 K for 24 h. In one series of experiments the compositions were chosen so that the Pd content was constant at \(X_{Pd}=0.90\) and the total solute atom fraction, \(X_{Rh} + X_{Al}\) was kept at 0.10. For another series of experiments, small amounts of Al were added to \(Pd\)-Rh binary alloys such that they can be described as, e.g., \((Pd_{0.85} Rh_{0.15})_{0.985}Al_{0.015}\) which indicates that the \(Pd_{0.85} Rh_{0.15}\) alloy is treated as one component of mol fraction 0.985 while Al is the other component with \(X_{Al}=0.015\). If the composition were to be represented as atom fractions for this ternary alloy, the composition would be \(Pd_{0.837}Rh_{0.148}Al_{0.0148}\) which is not as convenient as the other description.

**Results and Discussion**
Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ Alloys

Lattice Parameters

The lattice parameters for annealed Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ alloys were measured and the results are shown in Table 1. The parameters decrease with increase of x so that the alloys become more contracted as x increases and it would therefore be expected that $\Delta H_H^o$ and $\Delta H_{plat}$ for these “contracted” Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ alloys would decrease in magnitude with increase of x [1].

Table 1. Lattice Parameters of the Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ Alloys

<table>
<thead>
<tr>
<th>Pd$<em>{0.9}$Rh$</em>{0.1}$</th>
<th>x=0.015</th>
<th>x=0.050</th>
<th>x=0.070</th>
<th>x=0.085</th>
<th>Pd$<em>{0.9}$Al$</em>{0.1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3882 nm</td>
<td>0.3880 nm</td>
<td>0.3877 nm</td>
<td>0.3876 nm</td>
<td>0.3877 nm</td>
<td>0.3874 nm</td>
</tr>
</tbody>
</table>

where the parameter for the Pd$_{0.9}$Al$_{0.1}$ alloy is from reference 9.

Dilute Phase Hydrogen Solubilities.

The hydrogen solubilities as $H/M= r \rightarrow 0$ for annealed Pd and its alloys are described by Sieverts’ law of ideal dilute solubility for a dissociating solute, $p^{1/2} = K_s r$. When solutes are substituted into Pd, the Sieverts’ law constants, $K_s$, either decrease or increase depending upon whether the lattice expands or contracts, respectively, upon alloying. From the variation of the Sieverts’law constants with temperature, the standard relative enthalpies $\Delta H_H^o$ and entropies $\Delta S_H^o$ can be obtained where standard refers to infinite dilution of $H$. Sakamoto and coworkers [9-13] have obtained such thermodynamic values for several ternary alloy systems.

Figure 1 shows the dilute phase solubilities for Pd$_{0.9}$Rh$_{0.1-x}$Al$_x$ alloys from x=0 to 0.10 (323 K). The slopes increase steadily with decrease of x in passing from Pd$_{0.9}$Al$_{0.1}$ (x=0.1) to Pd$_{0.9}$Rh$_{0.1}$ (x=0). This is due mainly to the change of $\Delta H_H^o$ with x. The dashed curve in Figure 1 was calculated for the composition Pd$_{0.9}$Rh$_{0.1}$ from the $H_2$ solubility in the Pd$_{0.9}$Al$_{0.1}$ alloy and the assumption that the only factor influencing the solubility is the enthalpy of solution in these two binary alloys; the values of $\Delta H_H^o$ for the two binary alloys were taken from the literature [6, 9]. The experimental error in these enthalpy data are enough to account for the deviation of the dashed line from the experimental solubility shown for the Pd$_{0.9}$Rh$_{0.1}$ alloy.

The Rh-rich alloys with x=0 and x=0.015 were quenched from the annealing temperature to room temperature in order to avoid phase separation during slow cooling [6]. It has been shown that the Pd$_{0.95}$Rh$_{0.05}$ alloy does not phase separate under these conditions [6]. Therefore, with the possible exception of the x=0.03 alloy, those with smaller Rh contents should not separate into two phases under these conditions.

A correlation can be made between log $K_s$, or equivalently, log $(p^{1/2}/\text{atm}^{1/2})$ at r=0.006, and x as shown in Figure 2. The correlation is quite linear except for the x=0.015 alloy which might have been on the line if a quenched alloy sample had been employed.
Some thermodynamic data were determined for the x=0.05 alloy in the dilute region using measured solubility relations from 303 K to 348 K (Fig. 3). Figure 4a shows a plot of $\Delta \mu_{H}/T$ against $r$ and the intercepts give $\Delta \mu_{H}^{0}/T$ values which have been used in Figure 4b to obtain the thermodynamic parameters at infinite dilution of H. $\Delta \mu_{H}$ is the relative chemical potential of dissolved H, i.e., $\Delta \mu_{H} = \mu_{H} - \frac{1}{2} \mu_{H^{2}}$, where the standard symbol on $\mu_{H^{2}}$ refers to 1 bar and $\Delta \mu_{H}^{0} = \Delta H_{H}^{0} - T \Delta S_{H}^{0}$. From these slopes and intercepts, $\Delta H_{H}^{0} = -9.1 \text{ kJ/mol H}$ and $\Delta S_{H}^{0} = -58 \text{ J/K mol H}$ (Figs. 3, 4); the corresponding values for Pd-H are $-10.2 \text{ kJ/mol H}$ and $-55 \text{ J/K mol H}$[14]. Hydrogen solution in the alloy is therefore not as exothermic as in Pd which is consistent with their greater plateau pressures.

Complete Hydrogen Isotherms.

An isotherm for the x=0.1 alloy has been measured at 323 K by Sakamoto et al [9] but because these results are rather crucial for the present research, an alloy was prepared in this laboratory and its isotherm measured at 323 K (Fig. 5). The agreement with the isotherm of Sakamoto et al is very good; there is no plateau or hysteresis for this alloy (323 K) although there is an inflection point in the isotherm indicative of supercritical behavior. Figure 5 also shows isotherms measured by Sakamoto et al [9] for the other Pd—Al alloys.

The complete hydrogen isotherms for different x values are shown in Figure 6 (323 K). The results are quite dramatic in that the H capacities and degrees of hysteresis both decrease markedly while the plateau pressures do not change very much. The average plateau pressure of the x=0 alloy and the region where there is an inflection point in the isotherm for the x=0.10 alloy are quite similar. All of the plateaux and the inflection region for the x=0.10 alloy are contained within the absorption and desorption plateau pressures for the x=0.015 alloy. Although substitutional Al and Rh affect the plateau pressures similarly, Al reduces the plateau breadth whereas Rh does not and, in fact, Rh is the only element, aside possibly from Ni, which increases the breadth. Although changes of the plateau pressures with x are insignificant, the hydrogen capacity and hysteresis change very significantly. Figure 7 shows these changes where it can be seen that neither the capacity nor hysteresis are linear functions of x. There is a sharp fall of the hysteresis, $RT \ln \left( \frac{p_{f}}{p_{d}} \right)^{1/2}$, at a composition of about x=0.02; $p_{f}$ and $p_{d}$ are the plateau pressures for hydride formation and decomposition. The H capacities are smaller in the region of Al atom fraction 0.03 than predicted by a linear relation between x=0 and 0.1 where the latter is taken as the position of the change of slope in the supercritical region. Teter and Thoma [15] have indicated that the H capacities of the Pd$_{0.9}$Rh$_{0.1-x}$Co$_{x}$ ternary alloys can be described in terms of a summation of the descriptions for the binary alloys. This is not the case for the present alloys.

Plateau thermodynamic parameters have been determined for the x=0.05 alloy from van’t Hoff plots (Fig. 8) which give $\Delta H_{\text{plat}} = -15.8$ and $16.8 \text{ kJ/mol H}$ and $\Delta S_{\text{plat}} = -49.8$ and $-52.6 \text{ J/K mol H}$ for absorption and desorption, respectively. The enthalpies are smaller in magnitude than those for Pd-H and the entropies are larger. These values are
not as accurate as the dilute phase values because the hysteresis changes with temperature, i.e., there is hysteresis at 303 K but none at 348 K. The average plateau enthalpy of 16.3 kJ/mol H is about the same as the calorimetric value for the Pd0.90Rh0.10 alloy [6] but larger than found for either the Pd0.90Al0.10 or Pd0.95Al0.05 alloys [9].

(Pd0.85 Rh0.15)1-xAlx Alloys

The atom fractions of Al employed for the isotherm determinations of the (Pd0.85 Rh0.15)1-xAlx alloys were 0.01, 0.02 and 0.03 on the basis of the corresponding total transition metal fractions, X(Pd + Rh), of 0.99, 0.98, 0.97. When these are converted into atom fraction of each component, the Al fraction is almost unchanged but the Pd and Rh atom fractions decrease, e.g., for the (Pd0.85 Rh0.15)0.97Al0.03 alloy they are 0.825 and 0.146, respectively. Results for the dilute phase of the (Pd0.85 Rh0.15)1-xAlx alloys are shown in Figure 9 where there is seen to be very little difference in the dilute solubilities between the alloys including the binary Pd0.85 Rh0.15 alloy. Since the changes in the Al content are small and it has been found for Pd1-xAlx alloys that there is little change in the dilute solubilities from x=0 to about 0.050 [9], the result is not unreasonable.

Figure 10 shows complete isotherms (323 K) for the (Pd0.85 Rh0.15)1-xAlx alloys where there is a dramatic decrease in the plateau breadths with increase of Al content. At only 3 at% Al, the plateau disappears and hysteresis vanishes. Isotherms for the binary Pd—Al alloys do not show such large changes in plateau breadths with Al content [9] as shown by the inset in Figure 10 where the variation of the plateau widths with XAl are shown.

(Pd0.80 Rh0.20)0.985Al0.015

Figure 11 shows the effect of 1.5 at% Al on the plateau of the Pd0.80 Rh0.20 alloy (273 K). The plateau has vanished even though the Pd0.80 Rh0.20 alloy has a broader plateau than that of the Pd0.85 Rh0.15 alloy which in turn has a broader one than Pd [6]. Although there is no plateau in this alloy, its single phase H2 solubility is quite large, i.e., r≈0.6 at about 10 bar. Large single phase solubilities are desirable for certain applications such as for diffusion membranes where plastic deformation accompanying the abrupt hydride phase formation should be precluded.

From the results for the Al-substituted Pd0.90Rh0.1, Pd0.85 Rh0.15, and Pd0.80 Rh0.20 alloys, it can be concluded that the larger is the Rh content in the binary alloy, the greater is the effect of the substitutional Al on the breadth of the plateau even though the plateau breadth increases with XRh for these binary alloys.

(Pd0.0.90Ni0.10)0.985Al0.015, (Pd0.0.90Ni0.10)0.970Al0.030 and (Pd0.0.85Ni0.15)0.970Al0.030, (Pd0.0.80Ni0.20)0.970Al0.030 Alloys.
The alloys which are the most akin to the Pd-Rh alloys with respect to the plateau changes with X$_{\text{Ni}}$ are the Pd-Ni alloys because Ni does not progressively decrease the breadth of the plateaux and both elements Rh and Ni form fcc hydride phases with H/M equal to nearly 1.0 but at high H$_2$ pressures. It is therefore of interest to examine the effect of small amounts of Al on the plateaux of some Pd-Ni alloys. Dilute phase hydrogen solubilities are shown for (Pd$_{0.90}$Ni$_{0.10}$)$_{0.985}$Al$_{0.015}$ and (Pd$_{0.90}$Ni$_{0.10}$)$_{0.970}$Al$_{0.030}$ alloys in Figure 12 where the Al is seen to cause a progressive decrease in H$_2$ solubilities. The complete isotherms for these two alloys are seen in Figure 13 where Al is seen to decrease the breadth of the plateaux but not as much as it does for the Pd—Rh alloys (Figs. 10, 11). Al increases the plateau pressure and shortens the plateau for the (Pd$_{0.85}$Ni$_{0.15}$)$_{0.970}$Al$_{0.030}$ alloy but does not eliminate it or hysteresis (Fig. 14). When the Ni content increases to 0.20 as in the (Pd$_{0.80}$Ni$_{0.20}$)$_{0.970}$Al$_{0.030}$ alloy, the effect of the Al is still not very dramatic (Fig. 15) as for the Pd-Rh alloys, e.g., the (Pd$_{0.80}$Rh$_{0.20}$)$_{0.985}$Al$_{0.015}$ alloy where the plateau disappeared (Fig. 11). Thus the Pd-Ni alloys are not affected as much as the Pd-Rh alloys by small amounts of substitutional Al and the effect of Al does not increase with X$_{\text{Ni}}$.

\textbf{Pd-Pt-Al Alloys.}

By contrast with the Pd-Ni and Pd-Rh binary alloys, substitution of Pt in Pd causes the plateaux to decrease in breadth rather sharply. Like Rh and Ni substitution, Pt increases the plateau pressures in binary Pd alloys [16]. Complete isotherms for the (Pd$_{0.95}$Pt$_{0.05}$)$_{0.985}$Al$_{0.015}$ and (Pd$_{0.95}$Pt$_{0.05}$)$_{0.970}$Al$_{0.030}$ alloys are shown in Figure 16 where there is a significant decrease in the H capacity but the plateaux are still present as is hysteresis. The greater amount of Al in the latter alloy causes a significantly greater decrease in the plateau widths. The dilute phase solubility is slightly greater for the former alloy. In the inset data for four cycles of the (Pd$_{0.95}$Pt$_{0.05}$)$_{0.985}$Al$_{0.015}$ alloy are shown on an expanded scale and there is an anomalous looping in the third and fourth cycle isotherms as has been observed for Pd-Cr alloys [17].

The higher Pt content alloy (Pd$_{0.90}$Pt$_{0.10}$)$_{0.975}$Al$_{0.025}$, does not have a plateau and hysteresis has vanished (Fig. 17). There is a relatively large range of single phase hydrogen solubility which may be useful for an alloy where such a large range of H content is needed without the plastic work generated by hydride formation/decomposition.

\textbf{(Pd$_{0.95}$Cr$_{0.05}$)$_{0.975}$Al$_{0.025}$ Alloy.}

The isotherm for a (Pd$_{0.95}$Cr$_{0.05}$)$_{0.975}$Al$_{0.025}$ alloy is shown in Figure 18 (323 K) where it can be seen that there is still a plateau and the effect of Al is the expected one of increasing the plateau pressures and slightly shortening the plateau. The increase of $\text{RT} \ln p^\frac{1}{2}$ in passing from the Pd$_{0.95}$Cr$_{0.05}$ alloy to the (Pd$_{0.95}$Cr$_{0.05}$)$_{0.975}$Al$_{0.025}$ alloy is 850 J/ mol H which is almost exactly the same as going from Pd to Pd$_{0.975}$Al$_{0.025}$. 

6
(Pd_{0.90}Ag_{0.10})_{0.970}Al_{0.03} Alloy.

All of the above binary Pd/M alloys can be classified as “contracted” alloys because their lattice parameters decrease with increase of substitutional M in Pd and consequently the plateau pressures all increase with increase of M. The substitution of Al increases the plateau pressures further. It was of interest to learn the effect of substitutional Al on the capacity of an “expanded alloy” that is, one whose unit cell is greater than Pd. The alloy chosen for this investigation was the Pd_{0.90}Ag_{0.10} alloy which has a plateau pressure lower than for that for Pd since it is an expanded alloy. The (Pd_{0.90}Ag_{0.10})_{0.970}Al_{0.03} alloy was prepared and this increased the plateau pressure relative to the binary alloy and decreased the plateau breadth (Fig. 19) similar to the changes which took place in the (Pd_{0.90}Ni_{0.10})_{0.970}Al_{0.03} alloy (Fig. 13). There seems to be no difference between the contracted and expanded alloys with regard to their behavior with substitutional Al.

Predicted Effects of Al on the Plateaux of Some Pd—M Alloys Based on Linear Relationships between the Constituent Binary Alloys.

Table 2
Calculated and Experimental Values of $P_f$ and (b-a) due to Al Substitution in $Pd$—M Alloys (323 K).

<table>
<thead>
<tr>
<th></th>
<th>$P_f$/bar(exp)</th>
<th>$P_f$/bar(calc)</th>
<th>(b-a)(exp)</th>
<th>(b-a)(calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pd_{0.85}Rh_{0.15})<em>{0.980}Al</em>{0.02}</td>
<td>4.7</td>
<td>7.5</td>
<td>0.20</td>
<td>0.39</td>
</tr>
<tr>
<td>(Pd_{0.90}Ni_{0.10})<em>{0.970}Al</em>{0.03}</td>
<td>3.2</td>
<td>3.7</td>
<td>0.23</td>
<td>0.31</td>
</tr>
<tr>
<td>(Pd_{0.95}Pt_{0.05})<em>{0.970}Al</em>{0.03}</td>
<td>0.64</td>
<td>0.68</td>
<td>0.23</td>
<td>0.31</td>
</tr>
<tr>
<td>(Pd_{0.95}Cr_{0.05})<em>{0.975}Al</em>{0.025}</td>
<td>1.2</td>
<td>1.1</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>(Pd_{0.91}Ag_{0.09})<em>{0.970}Al</em>{0.03}</td>
<td>0.03</td>
<td>0.03</td>
<td>0.22</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The change of log $p_f$ with $X_{Al}$ is linear for $Pd$-Al alloys (323 K) and therefore the value of $p_f$ for any composition up to $X_{0.10}$ can be determined from this linear relation. If it is assumed that the ternary alloys’ values of log $p_f$ change by the same amount with Al as the binary alloys, then the log $p_f$ for the ternary alloys can be calculated from the following equation

$$\text{plateau } p_f(\text{binary Al})/p_f(\text{Pd}) = p_f(\text{ternary Al})/p_f(\text{binary})$$

where $p_f(\text{ternary Al})$ is the unknown. Some of the predicted plateau pressures are shown in Table 2 in comparison to the experimental values. The agreement is quite good except for the (Pd_{0.85}Rh_{0.15})_{0.980}Al_{0.02} alloy.

Although log $p_f$ is directly proportional to a thermodynamic quantity, $\Delta G_{\text{plat}}$ for the formation of the hydride phase, the plateau breadth is not directly proportional to a single thermodynamic parameter but is a more complex function of the thermodynamics of the system. The widths of the plateaux, (b-a), for the $Pd$-Al alloys are almost directly
proportional to \( X_{Al} \) up to 0.10 where \( a \) and \( b \) are the lower and upper phase boundary compositions which are estimated from the isotherms. The plateau breadths are predicted by assuming that for the ternary alloys they are decreased by the same percentage as for the \( Pd-Al \) alloys. It can be seen from Table 1 that the agreement of the predicted with the experimental values is not very good indicating that the plateau breadth is reduced more by the substitution of \( Al \) to form binary alloys than it is reduced by the substitution of \( Al \) in pure \( Pd \). The \( (Pd_{0.80}Rh_{0.20})0.98Al_{0.02} \) plateau breadth is reduced the most and \( (Pd_{0.95}Cr_{0.05})0.975Al_{0.025} \) the least, by \( Al \) substitution.

Possible Origin for the Large Effect of \( Al \) on the Plateaux of \( Pd—Rh \) Alloys.

**Thermodynamics of \( Pd-H \)**

The magnitudes of \( \Delta H^o_H \) and \( \Delta S^o_H \) do not affect the plateau breadth which is determined by \( r \)-dependent contributions to the \( H \) chemical potential. The \( r \)-dependent terms are the configurational entropy, the \( H-H \) interaction, and the influence of how band-filling by electrons donated from \( H \) influences the enthalpy of \( H_2 \) solution or, stated in a more general way, how the dissolved \( H \) affects the electronic structure of the alloy and how it, in turn, affects the enthalpy of \( H_2 \) solution. It seems necessary to first consider the thermodynamic origins of two phase formation in \( Pd-H \) and then in \( Pd-Rh-H \) alloys.

Figure 20a shows the various contributions to \( \Delta \mu_H=\mu_H-\frac{1}{2} \mu_{H_2}^o \) as a function of \( r \) for the \( Pd-H \) system at 300 K where the necessary data were taken from reference [14]; for convenience in this plot \( \Delta \mu_H^o \) is taken as zero which does not affect the two phase boundaries. The equation for \( \Delta G_{plat} \) is

\[
RT\ln p_{\text{plat}}^{1/2} = \Delta G_{plat} = \Delta \mu_H^o + \left[ RT/(b-a) \right] \left[ b \ln b - a \ln a + (1-b) \ln (1-b) - (1-a) \ln (1-a) \right] + \Delta \mu_E \quad (1)
\]

where \( \Delta \mu_E \) is taken as:\( (b-a) \int_a^b \mu_H^E(r) dr \), \( \Delta \mu_H^o=\mu_H^o-(1/2) \mu_{H_2}^o \) and \( \mu_H^o \) is the value at infinite dilution of \( H \) [17]. The presence of two solid phases is shown by the loops in the \( \Delta \mu_H-r \) relation where the rule of equal areas can be employed to determine the plateau pressure and phase boundary compositions. The value of \( \Delta H_{plat} \) is determined by the position of the horizontal line which satisfies: \( (b-a)\Delta H_{plat}=\int_a^b \Delta H_H \)dr as shown in Figure 20b where a value of -22 kJ/ mol \( H \) is obtained for \( \Delta H_{plat} \) by this method which is somewhat too large since the calorimetric value at 300 K is -19.2 kJ/ mol \( H \) [18] and the discrepancy must be due to some errors in the data of [14].

**Thermodynamics of \( Pd-Rh-H \)**

\( \mu_H^E \) is determined by the non-ideal configurational entropy and other \( H \)-dependent contributions to the entropy and enthalpy. \( Rh \), like \( Pd \), forms an almost stoichiometric \( RhH \) hydride within the fcc metal, although \( P_{H_2}=38 \) GPa is needed to form \( Rh \) hydride. The high \( P_{H_2} \) needed for \( Rh \) is mainly due to the \( |\Delta H_H^o| \) term. The \( H \)-dependent terms such as the configurational entropy and the \( H—H \) interactions might be expected to be qualitatively rather similar for \( Pd \) and the \( Pd-Rh \) alloys since their plateau breadths are similar. There is experimental evidence that their \( |\Delta H_E| \) relations have similar shape for the alloys as for \( Pd \) [6,18] because the \( |\Delta H_E| \) values both increase as \( r \) increases from 0.
and decrease with \( r \) in the hydride phase. The \( |\Delta H_H(r)| \) relationships for the \( Pd-Rh \) alloys must be consistent with the measured values of \( |\Delta H_{\text{pl}}| \) which are smaller than those for \( Pd-H \) and decrease with \( X_{Rh} \) and also the plateaux are somewhat broader than for \( Pd-H \). These two requirements mean that the \( |\Delta H_H(r)| \) against \( r \) relation must be somewhat flatter with smaller \( |\Delta H_H(r)| \) values than for \( Pd-H \), a tendency which must increase with \( X_{Rh} \). Experimentally the difference between \( |\Delta H_{\text{pl}}| \) and \( |\Delta H_H^o| \) decreases with \( X_{Rh} \) [6] and, in fact this may be characteristic of all \( Pd \) alloys because the solvus compositions always increase relative to \( Pd-H \) [1]. With reference to Figure 20b, this difference for \( Pd-H \) is represented by the distance between the horizontal dashed line indicating \( |\Delta H_{\text{pl}}| \) and \( |\Delta H_H| = 10.2 \text{ kJ/mol H} \); for the \( Pd-Rh \) alloys this distance becomes progressively smaller with increase of \( X_{Rh} \). The smaller differences for the alloys require that the \( |\Delta H_H(r)| \) relations are flattened as \( X_{Rh} \) increases compared with \( Pd-H \).

\[
\Delta \mu_{\text{pl}}^E = \Delta G_{\text{pl}} - \Delta \mu_H + \text{[ideal configurational term]},
\]

is almost equal for \( Pd \) and all the \( Pd-Rh \) alloys which is consistent with the expectation that the \( H \)-dependent terms in \( \mu_H \) be similar for \( Pd \) and \( Rh \). Figure 21 shows a plot of \( \Delta G_{\text{pl}} \) plotted against \( \Delta \mu_H \) and the intercept is equal to \( \Delta \mu_{\text{pl}}^E + \text{[ideal configuration term]} \). Such a plot is not linear for \( Pd \) alloys where the plateau widths decrease markedly with \( M \) which includes most \( Pd \) binary alloys. The corresponding values of \( \Delta S_{\text{pl}}^E \) and \( \Delta H_{\text{pl}}^E \) were determined (Table 3) and there are compensating changes of \( -T\Delta S_{\text{pl}}^E \) and \( \Delta H_{\text{pl}}^E \) with \( X_{Rh} \) which keeps \( \Delta \mu_{\text{pl}}^E \) constant. The values of \( -T\Delta S_{\text{pl}}^E = -T(b-a)^{-1} \int_a^b S_H^E(r) \text{d}r \) decrease with \( X_{Rh} \) while \( \Delta H_{\text{pl}}^E \) increases. The calculation of these excess plateau values depends on the values of \( \Delta H_H^o \) and \( \Delta S_H^o \) which were determined elsewhere earlier [6]. The values of \( \Delta S_H^o \) appear to be somewhat anomalous because they become increasingly negative with \( X_{Rh} \) (Table 3) and, for this reason, values for a typical alloy, \( X_{Rh} = 0.20 \), were redetermined in this work. The results (Table 3) are in good agreement with the earlier data. It is difficult to explain large negative values because they normally indicate that some interstices are excluded from occupation as for \( Pd-Ag \) alloys where \( H \) apparently avoids \( Ag \) nearest neighbors [19]; it seems unlikely for \( H \) to avoid \( Rh \) nearest neighbors in \( Pd-Rh \) alloys because such excluded interstices in the dilute phase must be occupied in the hydride phase because of the large \( H \) contents. Another possibility for large negative \( \Delta S_H^o \) values are an increase in the contribution of \( S_{\text{el}}^H \) [20] to the entropy because the electronic heat capacity should of the alloys should increase with \( X_{Rh} \). The heat capacities of \( Pd-Rh \) alloys increase with \( Pd \) [21] and therefore if \( H \) also acts to donate electrons to the d-band of \( Rh \), in the same way as \( Pd \), then the partial electronic entropy due to \( H \) should be positive and this could cause \( \Delta S_{\text{pl}}^E \) to increase with \( X_{Rh} \).
Table 3. Thermodynamic Properties of Pd/Rh Alloys from reference 6 and the last three Columns were Calculated here from the Earlier Data. Enthalpies and free energies are in kJ/ mol H and entropies are in J/K mol H.

<table>
<thead>
<tr>
<th>XRh</th>
<th>ΔG_{plat}</th>
<th>ΔH_{plat}</th>
<th>ΔS_{plat}</th>
<th>Δμ_{H}</th>
<th>ΔH_{H}</th>
<th>ΔS_{H}</th>
<th>ΔG_{E}</th>
<th>ΔH_{E}</th>
<th>ΔS_{E}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-4.3</td>
<td>-19.5</td>
<td>-46.0</td>
<td>7.2</td>
<td>-10.2</td>
<td>-54.0</td>
<td>-9.3</td>
<td>-9.3</td>
<td>-0.8</td>
</tr>
<tr>
<td>0.05</td>
<td>-2.3</td>
<td>-17.7</td>
<td>-47.8</td>
<td>9.1</td>
<td>9.1</td>
<td>-56.5</td>
<td>-8.9</td>
<td>-8.6</td>
<td>0.9</td>
</tr>
<tr>
<td>0.10</td>
<td>0.12</td>
<td>-16.1</td>
<td>-49.1</td>
<td>11.0</td>
<td>-8.5</td>
<td>-60.3</td>
<td>-9.3</td>
<td>-7.6</td>
<td>4.0</td>
</tr>
<tr>
<td>0.15</td>
<td>1.75</td>
<td>-14.2</td>
<td>-49.4</td>
<td>12.6</td>
<td>-7.9</td>
<td>-63.4</td>
<td>-9.6</td>
<td>-6.3</td>
<td>7.2</td>
</tr>
<tr>
<td>0.20</td>
<td>3.42</td>
<td>-12.8</td>
<td>-50.3</td>
<td>14.0</td>
<td>-7.3(-7.5)</td>
<td>-66.0(-66.3)</td>
<td>-9.6</td>
<td>-5.5</td>
<td>10.9</td>
</tr>
<tr>
<td>0.25</td>
<td>5.00</td>
<td>-11.2</td>
<td>-50.0</td>
<td>15.6</td>
<td>-6.6</td>
<td>-68.7</td>
<td>-9.5</td>
<td>-4.6</td>
<td>14.5</td>
</tr>
</tbody>
</table>

The values in parenthesis have been determined in this research and Δμ_{H} and ΔS_{H} have been evaluated assuming that all of the interstices are available for occupation.

**Thermodynamics of Pd-Rh-Al-H**

It is difficult to understand why Al reduces the plateau widths of the Pd-Rh alloys so dramatically and why the effect increases with XRh. Substitutional Al in Pd-Rh alloys must alter the electronic structure rather markedly because, for example, although the plateau of a Pd_{0.80}Rh_{0.20} alloy is wider than for Pd itself [6], it disappears in the (Pd_{0.85}Rh_{0.15})_{0.97}Al_{0.03} and (Pd_{0.80}Rh_{0.20})_{0.985}Al_{0.015} alloys (Figs. 10, 11) where the fractions of Al are quite small. Δμ_{E plat} does not stay nearly constant with Al content for Pd_{0.90}Rh_{(0.1-x)}Al_{x} alloys as it does for the Pd-Rh alloys. The amounts of Al in these alloys are too small to significantly affect the fraction of available interstices and therefore the effect must be related to non-configurational entropy. By contrast, larger amounts of Al do not lead to plateau disappearance in Pd or the Pd_{0.90}Rh_{0.10} alloy.

Al donates 3 electrons to the d-band of Pd judging from magnetic susceptibility changes of Pd-Al alloys [22]. On the basis of this research, Al greatly suppresses two phase formation in alloys where the solutes also have holes in their d-bands such as Pd-Rh but the effect of Al on the plateaux of alloys such as Pd-Ag or Pd itself, it not unusual. It seems that the origin of the effect is in the changing of the electronic structure of the alloys but the details are not known at present.

**Conclusions**

The capacities of most of the Al-containing ternary alloys are smaller than predicted from the effect of Al on the capacities in binary Pd-Al alloys and the capacity of a Pd-Rh alloy is most decreased by Al. The plateau pressures are reasonably well predicted by the changes of pf with Al in the binary Pd-Al alloys. The most striking results are for the (Pd_{0.85}Rh_{0.15})_{0.97}Al_{0.03} and (Pd_{0.80}Rh_{0.20})_{0.97}Al_{0.03} alloys. It would be of interest to measure the electronic heat capacities of these alloys where the plateau has disappeared.

**Acknowledgements**

The authors wish to thank J. D. Clewley for help in sample preparation, etc.
References

Figure Captions

Figure 1. Dilute phase H₂ solubilities in Pd₀.₉₀Rh₀.₁₋ₓAlₓ (323 K). Solid curve without points, Pd; ○, Pd₀.₉₀Al₀.₁₀; •, Pd₀.₉₀Rh₀.₀₁₅Al₀.₀₈₅; △, Pd₀.₉₀Rh₀.₀₃Al₀.₀₇; ▼, Pd₀.₉₀Rh₀.₀₅Al₀.₀₅; ▽, Pd₀.₉₀Rh₀.₀₇Al₀.₀₃; ▼, Pd₀.₉₀Rh₀.₀₈₅Al₀.₀₁₅; □, Pd₀.₉₀Rh₀.₁₀.

Figure 2. Dilute phase solubilities (323 K) as indicated by log p½ at r=0.006 as a function of x.

Figure 3. Dilute phase solubilities of the Pd₀.₉₀Rh₀.₀₅Al₀.₀₅ alloy at: △, 303 K, ○, 323 and ▽, 348 K.

Figure 4. (a) Plots of (∆µ_H)/RT (=ln p½(1-r)/r against r at several temperatures for the Pd₀.₉₀Rh₀.₀₅Al₀.₀₅ alloy. (b) Plots of the intercepts at r=0, ∆µ_H/T, of the plots shown in (a) as a function of 1/T.

Figure 5. An isotherm for the x=0.₁₀ alloy (Pd₀.₉₀Al₀.₁₀) along with isotherms at 323 K for other Pd—Al alloys from reference 9. ○, present absorption data; •, present desorption data; △, from reference 9.

Figure 6. Complete isotherms (323 K) for the Pd₀.₉₀Rh₀.₁₋ₓAlₓ alloys. Open symbols are for absorption and filled symbols for desorption. The numbers on the curves indicate atom fraction Al.

Figure 7. Plots of the degree of hysteresis and β_min which is the r value at the upper end of the plateau for the Pd₀.₉₀Rh₀.₁₋ₓAlₓ alloys (323 K) as estimated from Figure 6.

Figure 8. Van’t Hoff plots for the plateau pressures evaluated at r =0.₂₀ for the Pd₀.₉₀Rh₀.₀₅Al₀.₀₅ alloy. ○, absorption data; •, desorption data.

Figure 9. Dilute phase solubilities for (Pd₀.₈₅Rh₀.₁₅)(1-x)Alₓ alloys (323 K). ○, for x=0; △, x=0.₀₁; ▽, x=0.₀₂; □, x=0.₀₃.

Figure 10. Complete isotherms for the (Pd₀.₈₅Rh₀.₁₅)(1-x)Alₓ alloys (323 K). ○, x=0; △, x=0.₀₁; ▽, x=0.₀₂; □, x=0.₀₃. The open symbols for absorption and filled ones for desorption. The inset shows the extent of the plateaux for these alloys and the Pd-Al alloys. ○, Pd-Al alloys. △, (Pd₀.₈₅Rh₀.₁₅)(1-x)Alₓ alloys.

Figure 11. Isotherm for the (Pd₀.₈₀Rh₀.₂₀)₀.₉₈₅Al₀.₀₁₅ alloy compared to the Pd₀.₈₀Rh₀.₂₀ alloy (273 K). ○, annealed Pd₀.₈₀Rh₀.₂₀ alloy; △, (Pd₀.₈₀Rh₀.₂₀)₀.₉₈₅Al₀.₀₁₅ alloy. Open symbols are for absorption and filled ones for desorption.

Figure 12. Dilute phase data (323 K) for Pd₀.₉₀Ni₀.₁₀ and (Pd₀.₉₀Ni₀.₁₀)₁₋ₓAlₓ alloys. □, Pd₀.₉₀Ni₀.₁₀; △, (Pd₀.₉₀Ni₀.₁₀)₀.₉₈₅Al₀.₀₁₅ alloy; ○, (Pd₀.₉₀Ni₀.₁₀)₀.₉₇Al₀.₀₃₀ alloy.
Figure 13. Complete isotherms (323 K) for the Pd$_{0.90}$Ni$_{0.10}$ and (Pd$_{0.90}$Ni$_{0.10}$)$_{1-x}$Al$_x$ alloys. ---, Pd$_{0.90}$Ni$_{0.10}$; o, (Pd$_{0.90}$Ni$_{0.10}$)$_{0.985}$Al$_{0.015}$ alloy; Δ, (Pd$_{0.90}$Ni$_{0.10}$)$_{0.97}$Al$_{0.030}$ alloy. Open symbols are for absorption and filled ones for desorption.

Figure 14. Complete isotherms (323 K) for the Pd$_{0.85}$Ni$_{0.15}$, Δ, and Pd$_{0.85}$Ni$_{0.15}$)$_{0.97}$Al$_{0.03}$, o, alloys. Open symbols are for absorption and filled ones for desorption.

Figure 15. Complete isotherms (323 K) for the Pd$_{0.80}$Ni$_{0.20}$, ----, (Pd$_{0.80}$Ni$_{0.20}$)$_{0.97}$Al$_{0.03}$, o, alloys. Open symbols are for absorption and filled ones for desorption.

Figure 16. Complete isotherms (323 K) for the Pd$_{0.80}$Pt$_{0.05}$ and (Pd$_{0.95}$Pt$_{0.05}$)$_{1-x}$Al$_x$ alloys. ---, Pd$_{0.95}$Pt$_{0.05}$; Δ, (Pd$_{0.95}$Pt$_{0.05}$)$_{0.985}$Al$_{0.015}$ alloy (1st cycle); □, (Pd$_{0.95}$Pt$_{0.05}$)$_{0.97}$Al$_{0.030}$ alloy. The insert shows more detailed behavior with anomalous isotherm behavior, i.e., “van der Waal”-like loops, for the (Pd$_{0.95}$Pt$_{0.05}$)$_{0.985}$Al$_{0.015}$ alloy. Δ, 1st cycle, ▽, 2nd cycle, □, 3rd cycle, x, 4th cycle. Open symbols are for absorption and filled ones for desorption.

Figure 17. Complete isotherms (323 K) for Pd$_{0.90}$Pt$_{0.10}$ and the (Pd$_{0.90}$Pt$_{0.10}$)$_{0.975}$Al$_{0.025}$ alloys. Δ, Pd$_{0.90}$Pt$_{0.10}$; o, (Pd$_{0.90}$Pt$_{0.10}$)$_{0.975}$Al$_{0.025}$.

Figure 18. Complete isotherms (323 K) for the Pd$_{0.95}$Cr$_{0.05}$, Δ, and (Pd$_{0.95}$Cr$_{0.05}$)$_{0.975}$Al$_{0.025}$, o, alloys. Open symbols are for absorption and filled ones for desorption.

Figure 19. Complete isotherms (323 K) for the Pd$_{0.91}$Ag$_{0.09}$, Δ, and the (Pd$_{0.91}$Ag$_{0.09}$)$_{0.97}$Al$_{0.03}$, o, alloys.

Figure 20. Upper figure, plots of the various contributions to $\mu_H$ for Pd—H (300 K) using data from reference 14. The value of $\mu_H^o$ is assumed to be 0 for convenience, $\mu_H^E$ is the excess chemical potential of H due to non-ideal terms and $\mu_H^{id, config}$ is the ideal configurational chemical potential. The sum of the various curves has loops as shown and the rule of equal areas locates the co-existing phase boundaries and plateau pressure. The lower figure is a plot of $\Delta H_H$ as a function of $r$ [14]. $\Delta H_{plat}$ is located by the equivalence of the areas from $a$ to $b$ of the continuous plot and the rectangular area $(b-a)\Delta H_{plat}$.

Figure 21. Plot of $\Delta^o\mu_H$ against $\Delta G_{plat}$ for Pd-Rh alloys (323 K).
Figure 1.
Figure 2.

\[ \log\left(\frac{p^{1/2}}{\text{bar}^{1/2}}\right) \text{ at } r=0.0006 \]
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Figure 7.
Figure 8.
Figure 9.
Figure 10.
Figure 11.
Figure 12.
Figure 13.
Figure 14.
Figure 15.
Figure 17.
Figure 18.
Figure 19.
Figure 20.

\[ \mu_{\text{H}, \text{id, config}} = RT \ln \left( \frac{r}{n-r} \right) \]
Figure 21.