

Thermodynamics of Hydrogen Solution and Hydride Formation in Binary Pd Alloys

Ted B. Flanagan and S. Luo

(Submitted October 24, 2006)

Some recent thermodynamic results for the solution of H₂ and hydride formation in fcc disordered Pd-rich alloys based on a combined equilibrium-calorimetric technique are reviewed in this paper. This dual approach is more powerful than employing only one of these techniques. Some interesting thermodynamic results connected with these systems are presented, such as minima in ΔH_H and ΔS_H as a function of the H content of the alloys.

Keywords metal-hydrogen, thermodynamics, hydrides

1. Introduction

Combined equilibrium-calorimetric measurements will be described for the determination of thermodynamic properties of H₂ absorption by random binary substitutional fcc Pd alloys. An earlier review covering this type of research was published by Kleppa^[1] in 1983 for a large series of Pd-rich alloys. Most data were obtained at $T \geq 555$ K, where the H₂ solubilities are small and hydride phases do not form. They did, however, carry out measurements for Pd-H at relatively high pressures over the temperature range, 518–623 K, where thermodynamic data for hydride phase formation was determined calorimetrically.^[2]

The research to be reviewed here uses the same dual approach employed by Kleppa and co-workers,^[1] where thermodynamic parameters are determined using calorimetry and equilibrium p_{H_2} measurements. This dual approach has advantages as compared to the usual technique of employing only equilibrium p_{H_2} measurements at a series of temperatures because the calorimetric data are unaffected by hysteresis in the dilute \leftrightarrow hydride two-phase region^[3] and it is more accurate in the phase transition regions while the equilibrium p_{H_2} measurement method is more accurate in the dilute phase.

This paper was presented at the Multi-Component Alloy Thermodynamics Symposium sponsored by the Alloy Phase Committee of the joint EMPMD/SMD of The Minerals, Metals, and Materials Society (TMS), held in San Antonio, Texas, March 12–16, 2006, to honor the 2006 William Hume-Rothery Award recipient, Professor W. Alan Oates of the University of Salford, UK. The symposium was organized by Y. Austin Chang of the University of Wisconsin, Madison, WI, Patrice Turchi of the Lawrence Livermore National Laboratory, Livermore, CA, and Rainer Schmid-Fetzer of the Technische Universität Clausthal, Clausthal-Zellerfeld, Germany.

Ted B. Flanagan and **S. Luo**, Materials Science Program and Chemistry Department, University of Vermont, Burlington, VT 05405, USA. Contact e-mail: ted.flanagan@uvm.edu

Based on their lattice constants relative to Pd, fcc Pd alloys fall into expanded or contracted categories and the former have a more exothermic and the latter, a less exothermic solution of H₂ than Pd. This classification does not work well for borderline cases where the lattice changes are small but, otherwise, it is reliable.^[4] Based on entropy changes it is generally agreed that some octahedral interstitial sites must be preferred to others.^[1,5,6] Wagner and co-workers^[7,8] have shown directly from Mössbauer measurements that H avoids interstices with Fe, Sn, Au, Pt, Co, etc., as nearest neighbors, however, it does not avoid interstices with Rh nearest neighbors.

Except for the Pd-Rh and Pd-Ni fcc substitutional alloys, all of the other Pd alloys have decreased miscibility gap widths as compared to Pd-H and all fcc, disordered Pd alloys have greater dilute/(dilute + hydride) phase boundaries (THS, terminal H solubilities) than that for Pd-H.

Another interesting feature are the minima found in plots of ΔH_H and ΔS_H against $H/(Pd_{(1-x)}M_x)$, mol ratio, = r for Pd alloys above their critical compositions, $X_{M,c}$. A minima is also found for Pd-H above its T_c .^[9] After the minima, there is a linear increase of ΔH_H with r (Fig. 1), which is consistent with the linear increase of $\log p_{H_2}$ in the hydride single-phase region.^[10]

Mohri and Oates^[11] have used the cluster variation method to calculate the phase diagram of Pd-H and have found that, in addition to the stress induced long-range attraction,^[12] there is a shorter range, chemical, configurational interaction. The integral internal energy of the former is positive, while the latter is negative but their sum is slightly negative.

For Pd-based alloys the $|\Delta S_{plat}|$ for hydride formation or decomposition are always $46 \text{ J/K} \pm 2 \text{ mol H}$ in the temperature range from about 273 to 373 K.^[13] This is presumably due to a cancellation of the configurational effects, although this has not been explicitly shown.

2. Experimental

The Pd-M alloys employed in the research to be described were prepared by arc-melting the pure compo-

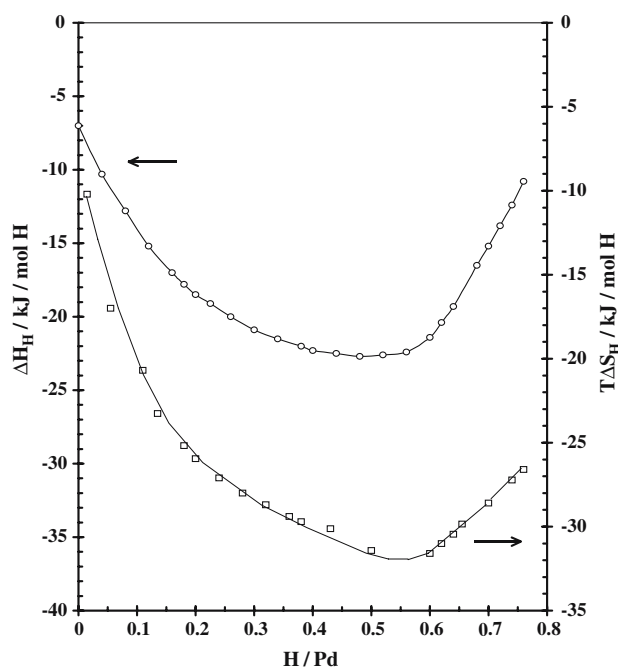


Fig. 1 Partial thermodynamic data for Pd-H from single phase data and from data above the critical temperature.^[9] ○, ΔH_H and □, $T\Delta S_H$

nents and then annealing the arc-melted buttons at 1173 K for 3 days. The buttons were then rolled into thin foil and re-annealed. The foils were cut into small pieces and mixed with an equal mass of Cu powder for purposes of heat conduction. The samples were then placed in the calorimeter vessel and evacuated. Equilibrium p_{H_2} against $H/(Pd_{(1-x)}M_x) = r$ relations (303 K) were determined from the changes of p_{H_2} in known volumes. H_2 uptake or evolution was generally rapid in the all-metal system at 303 K where the reaction calorimetry and equilibrium $p_{H_2} - r$ measurements were carried out. For small increments of H_2 added or removed from the alloy in single-phase regions, $(\delta q/\delta n_H)_T \approx \Delta H_H$ where $\Delta H_H = H_H - \frac{1}{2}H_{H_2}$ (g, 0.1 MPa).

3. Results and Discussion

3.1 General Features of Pd-H and Pd-M-H Alloys

Pd-H has a miscibility gap separating the dilute and hydride phases with a critical temperature of 563 K.^[14] The Pd sub-lattice is the same in the dilute and hydride phases with an 11% volume expansion upon forming the hydride phase (298 K). Another variable appears for Pd-rich fcc alloys, the mol fraction of alloying element, X_M , and therefore three dimensions, p_{H_2} , X_M , r are needed for isothermal representations. Often, however, isotherms of p_{H_2} against r at constant X_M are made for a series of T values from which a $T-r$ phase diagram can be obtained, or else p_{H_2} is plotted against r at constant T for a series of X_M values giving a X_M-r phase diagram. Instead of

p_{H_2} , $\Delta\mu_H = RT \ln p_{H_2}^{1/2}$ can be employed at constant T . There is generally a critical composition, $X_{M,c}$, above which the hydride phase disappears in the X_M-r phase diagram at constant T and, in the $T-r$ phase diagram, there is a T_c where the co-existing phases disappear for a fixed X_M . For fcc Pd-Rh and Pd-Ni systems an $X_{M,c}$ does not exist because both Rh and Ni also form hydride phases isomorphous with Pd hydride.

We have carried out equilibrium p_{H_2} -calorimetric measurements for several contracted Pd alloys, i.e., Pd-Co,^[15] Pd-Fe^[13] Pd-6B metals,^[16] and Pd-Cu^[17] and for several expanded alloy systems, Pd-Sn, Pd-Au and Pd-Ag and Pd-Mn.^[18] It should be noted that the metal atoms in these alloys are “frozen” at the usual temperatures where the thermodynamic determinations are made. At higher temperatures and p_{H_2} it is possible that the metal atoms segregate according to a ternary equilibrium to form Pd-rich and Pd-poor phases with different H contents. This has been found for the Pd-Pt^[19] and Pd-Ni^[20] alloys. The Pd-Rh alloys have a miscibility gap, but the phase separation is very slow, e.g., 1 year at 873 K,^[21] however, it has been found that dissolved H accelerates the phase separation allowing it to be achieved in much shorter times.^[22] The temperatures of the thermodynamic investigations to be discussed here are too low for such segregation to occur but, nevertheless, the thermodynamic results should be viewed for the above alloys as states of meta-stable equilibrium. This “frozen” metal atom situation leads to hysteresis for the two-phase reaction which is usually characterized by different, meta-stable “equilibrium” p_{H_2} for hydride formation and for decomposition.

ΔH and ΔS , which will be designated here as ΔH_{plat} and ΔS_{plat} in the two solid-phase region and ΔH_H and ΔS_H in single phase regions and the latter partial values have been determined over a range of r accessible up to about $p_{H_2} = 0.5$ MPa. The Δ refers indicates a quantity relative to $1/2H_2$ (g, 0.10 MPa). Below its T_c a plot of ΔH_H for pure Pd shows discontinuities at the phase boundaries; however, the discontinuity at the (dilute + hydride)/hydride phase boundary is not as clear as for the lower boundary (Fig. 2).

3.2 Thermodynamic Quantities

In the single-phase regions ΔH_H can be measured calorimetrically as a continuous function of r by using small increments of H_2 . Relative partial molar entropies, ΔS_H , can be obtained isothermally from the calorimetrically measured enthalpies and corresponding equilibrium p_{H_2} using:

$$\Delta S_H = S_H - \frac{1}{2}S_{H_2}^c(1 \text{ bar}) = \Delta H_H/T - R \ln p_{H_2}^{1/2} \quad (\text{Eq 1})$$

The partial entropies relative to $\frac{1}{2}S_{H_2}(p_{eq})$, i.e., with respect to different equilibrium p_{H_2} at each r , are given by:

$$\Delta S_{H,eq} = S_H - \frac{1}{2}S_{H_2}(p_{eq}) = q/T = \Delta H_H/T \quad (\text{Eq 2})$$

In the two-phase plateau region the equilibrium entropy change is also given by Eq 2 with $\Delta H_H = \Delta H_{plat}$ and is unaffected by any assumptions about hysteresis whereas that

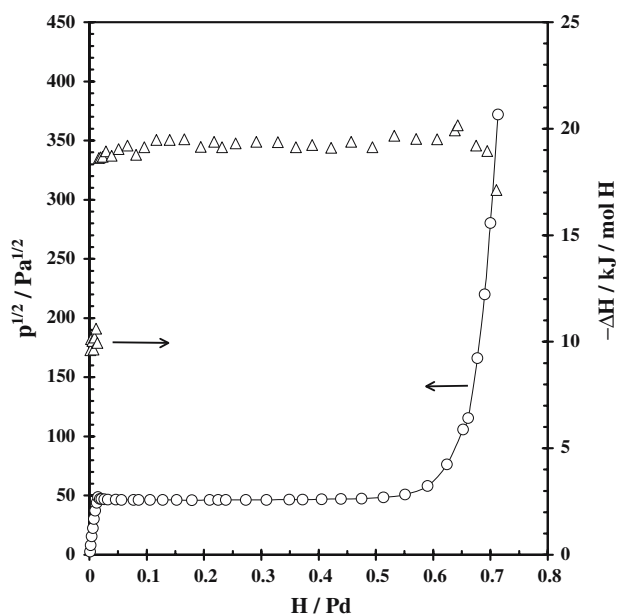


Fig. 2 Plot of ΔH_H data from reaction calorimetry for annealed Pd for H_2 absorption (303 K) which is below T_c . The discontinuity at the dilute/(dilute+hydride) phase boundary can be seen and also the start of the linear fall in ΔH_H at the end of the two-phase co-existence region. The accompanying isotherm (303 K) is shown. Δ , ΔH_H ; \circ , $p_{H_2}^{1/2}$

given by Eq 1 requires a plateau pressure, which can be taken as a mean value in an attempt to allow for hysteresis.^[3] ΔS_H or ΔS_{plat} values are almost universally employed for metal-H systems relative to 1 bar (0.1 MPa) H_2 , Eq 1, which has the advantage of focussing on the entropy changes of the H-containing solid phase.

Based on a regular interstitial solution model,^[23] the following equation can be employed for H in Pd and its alloys at low H contents:

$$\mu_H = \mu_H^\circ + RT \ln(r/(\beta - r)) + g_1 r \quad (\text{Eq 3})$$

where g_1 is the first term in a polynomial expansion of $\mu_H^E(r)$, the excess or non-ideal chemical potential, and β is the number of interstices available for occupation by H per metal atom. Combining this with the equation for $\mu_H(g)$, we can write:

$$\mu_H(g) = \frac{1}{2} \mu_{H_2}^\circ + RT \ln p_{H_2}^{1/2} = \mu_H^\circ + RT \ln(r/(\beta - r)) + g_1 r \quad (\text{Eq 4})$$

or, rearranging,

$$RT \ln p_{H_2}^{1/2} = \Delta \mu_H^\circ + RT \ln(r/(\beta - r)) + g_1 r$$

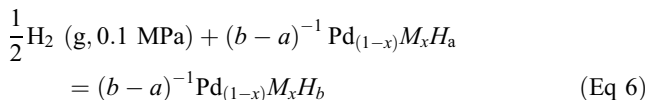
where

$$\Delta \mu_H^\circ = \mu_H^\circ - \frac{1}{2} \mu_{H_2}^\circ = \mu_H^\circ - T \Delta S_H \quad (\text{Eq 5})$$

The first order term in r of the excess partial free energy, g_1 , is a measure of the interaction of the H atoms and is

expected to be a good approximation at small r . The zero superscript refers to standard conditions of 0.1 MPa for ΔH_H° and ΔS_H° , i.e., infinite dilution of H and without the configurational term for the latter.

In the two-phase co-existence region (the plateau), the relative thermodynamic parameters are integral values represented by the reaction



where a and b are the dilute and hydride co-existing phase boundary compositions expressed as r and $Pd_{(1-x)} M_x$ is one mol of alloy. The plateau thermodynamic parameters, ΔH_{plat} and ΔS_{plat} are generally determined from van't Hoff plots of p_{plat} .

ΔH_{plat} and ΔS_{plat} have been determined for Pd-H(D) by the isothermal calorimetric-equilibrium p_{H_2} technique in early work in this laboratory,^[3] and as expected, the plateau thermodynamic parameters were found to be invariant along the two-phase co-existence region. In addition, their magnitudes were independent of the direction of Eq 6, i.e., unaffected by hysteresis.^[3] Van't Hoff plots in the plateau region are directly affected by hysteresis and therefore do not represent true equilibrium and different ΔH_{plat} values are obtained depending upon the direction of Eq 6. Recent calorimetric measurements of ΔH for Pd-H show the expected discontinuity at the dilute/(dilute+hydride) phase boundary and the start of a linear decline in the single hydride phase after traversing the two-phase co-existence region^[24] (Fig. 2).

The calorimetrically determined dilute phase values were not very accurate in the earlier investigation,^[3] but the values in the pure hydride single-phase region were accurate. The $|\Delta H_{H(D)}|$ values decrease almost linearly with r ($r = 0.65$ to 0.75) (298 K); $\log p_{H_2}$ also increases linearly with r as first pointed out by Wicke and Nernst for Pd-H.^[10] By carrying out reaction calorimetry from 223 to 298 K, Sakamoto et al.^[25] have shown that this linear dependence of ΔH_H on r extends to about $r = 0.86$. The linearity of $\log p_{H_2}$ and ΔH_H with r requires either that ΔS_H is linearly dependent upon r or else it is independent of r in this range.

3.3 Typical Results for fcc, disordered Pd-rich Alloys

Isotherms (303 K) for expanded, disordered Pd-Ag alloys recently measured in this laboratory are shown in Fig. 3^[26]. As expected, the plateau pressures decrease and the solubilities at low p_{H_2} increase with X_{Ag} whereas the solubilities at higher p_{H_2} decrease with X_{Ag} . The two-phase region disappears for alloys with $X_{Ag} > 0.24$ (303 K) and there is an extended region of solubility without a phase change for alloys with $X_{Ag} > 0.24$ but less than ≈ 0.35 (303 K). Partial thermodynamic parameters have been measured over a wide range of r values for these alloys.^[26] The THS is seen from Fig. 3 to increase with X_{Ag} .

Isotherms for contracted, disordered Pd-Rh alloys are shown in Fig. 4^[27] where the plateau H_2 pressures increase and the dilute phase solubilities decrease with X_{Rh} and, in

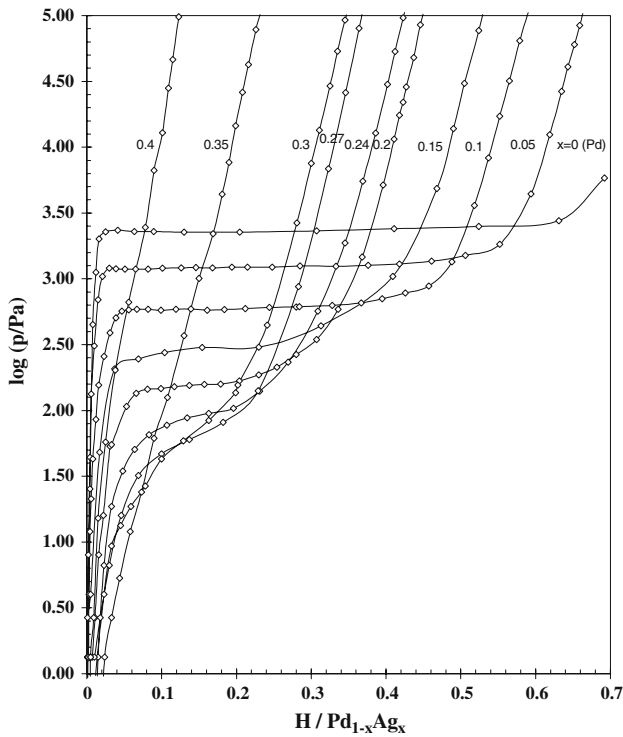


Fig. 3 Absorption isotherms for disordered Pd-Ag alloys (303 K)

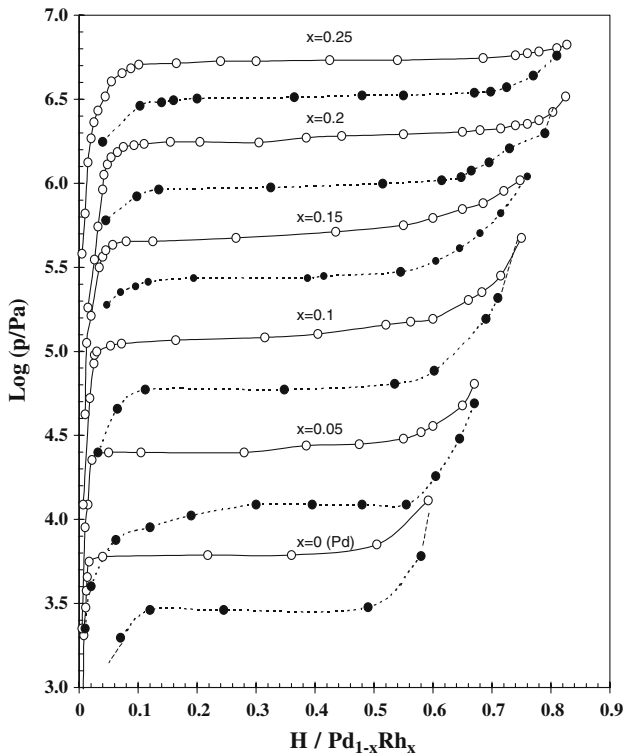


Fig. 4 Isotherms for Pd-Rh alloys (323 K). The open and filled symbols are for absorption and desorption, respectively

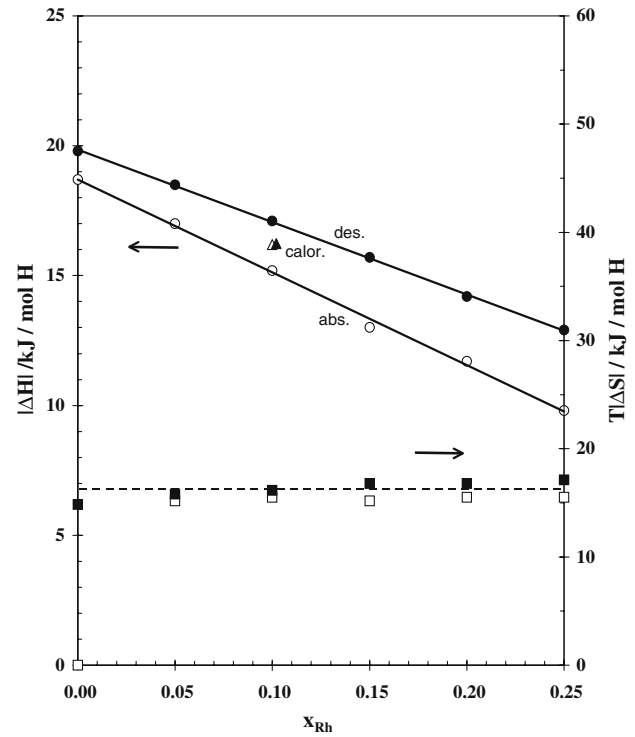


Fig. 5 $|\Delta H_{\text{plat}}|$ and $|\Delta S_{\text{plat}}|$ for Pd-Rh alloys. \circ , $|\Delta H_{\text{plat}}|$ from van't Hoff plots; Δ , $|\Delta H_{\text{plat}}|$ from calorimetry; \square , $T|\Delta S_{\text{plat}}|$, from van't Hoff plots. The open and filled symbols are for absorption and desorption, respectively

contrast to Pd-Ag and to most other Pd alloys, the plateau breadths do *not* decrease with X_{Rh} . Desorption isotherms are also shown and it can be seen that hysteresis is significant.

Figure 5 shows ΔH_{plat} and ΔS_{plat} for Pd-Rh alloys for reaction (6) obtained from slopes of van't Hoff plots. There is a ≈ 3 kJ/mol H difference between the $|\Delta H_{\text{plat}}|$ for absorption and desorption for the $X_{\text{Rh}} = 0.25$ alloy which is significant. Calorimetric data are available only for the $X_{\text{Rh}} = 0.10$ alloy^[27] and the ΔH_{plat} values obtained for both absorption and desorption for this alloy lie between the two van't Hoff plots for absorption and desorption. The $T\Delta S_{\text{plat}}$ values are shown to be almost the same for the various Pd-Rh alloys and independent of hysteresis (Fig. 5), where ΔS_{plat} has been calculated using Eq 1 with $p_{\text{plat}} = (p_{\text{f}}p_{\text{d}})^{1/2}$ where f and d refer to hydride formation and decomposition plateau pressures and ΔH_{plat} is taken as an average of the ΔH_{plat} magnitudes from the Van't Hoff plots.

3.4 Selective Occupation of Octahedral Interstices

Every octahedral site is accessible to H in Pd as $r \rightarrow 0$ and the maximum occupation is therefore $r = 1.0$, or $\beta = 1.0$ in Eq 3 and 4; however, for Pd-rich alloys this may not be true because interstices adjacent to metal solute atoms may be less favorable for H occupation than those surrounded by only Pd nearest neighbors. There is direct evidence of this from Mössbauer spectroscopy^[7,8] and

indirect evidence from thermodynamics.^[6] The latter evidence is that the ΔS_H° values calculated from Eq 7 are significantly more negative for some alloys than ΔS_H° for Pd-H:

$$\Delta S_H^\circ(\text{alloy}, \beta = 1.0) = \Delta S_H^\circ + R \ln r/(1-r) \quad (\text{Eq 7})$$

where the ΔS_H° for Eq 7 is obtained from intercepts of plots of $\ln p_{1/2}$ against $1/T$ at constant r or else from Eq 1 with calorimetric ΔH_H values. ΔS_H° values are then obtained by extrapolation of $\Delta S_H^\circ(r)$ values to $r = 0$. Flanagan and Lynch^[5] and Kleppa and co-workers^[11] have concluded that for alloys such as Pd-Ag, Pd-Au and Pd-Cu there is selective occupation of interstices as $r \rightarrow 0$. If the non-configurational contributions to ΔS_H are the same for the alloys as for Pd, then the entropy differences between Pd and the alloys must be configurational in origin. Some evidence that the non-configurational entropies are the same is that the vibrational frequency of H in a Pd_{0.80}Ag_{0.20} alloy and in Pd are very similar.^[28] In view of this, it seems that that the implications of $\Delta S_H^\circ(\beta = 1.0) < \Delta S_H^\circ(\text{Pd})$ are unambiguous reflecting $\beta \neq 1.0$ for some alloys.

All $\Delta S_H^\circ(\text{alloy}, \beta = 1.0)$ values for Pd alloys available up to 1995 are plotted against ΔH_H° in Fig. 6, where it can be seen that most of the entropies are more negative than $\Delta S_H^\circ(\text{Pd})$. The Gallagher-Oates (G-O) linear plots of ΔS_H°

against ΔH_H° are for pure metals for octahedral interstice occupation (fcc and hcp metals) and for tetrahedral occupation (bcc metals).^[29] The rationale of the linearity of the G-O plots is that the non-configurational entropy of H should decrease as its binding in the lattice becomes stronger which also means that ΔH_H° will be more negative. It can be seen in Fig. 6 that Pd-rich alloys do not follow the G-O fcc-hcp correlation, and therefore deviations of the alloys from the ΔS_H° of Pd-H, are not due to the non-configurational contribution to the entropy, but must be due to configurational effects, suggesting that certain interstices are excluded as $r \rightarrow 0$.

Sakamoto et al.^[30] have considered that in some alloys for the interstices to be occupied by H, Pd atoms must be both nearest and next nearest neighbors as $r \rightarrow 0$. To allow for this they employed the following equation:

$$\Delta S_H^\circ(\text{alloy}) = \Delta S_H^\circ(\text{Pd}) + R \ln \beta = \Delta S_H^\circ(\text{Pd}) + R \ln (1 - X_M)^z \quad (\text{Eq 8})$$

where z is the number of Pd atoms around a given interstice, e.g., if $z = 6$ only nearest neighbor atoms need to be Pd, Pd₆, but if the next nearest neighbors must also be Pd, Pd₁₄, then $z = 14$, etc.

If the metal atoms are randomly distributed in the fcc lattice, the fraction of Pd₆ or Pd₁₄ interstices can be

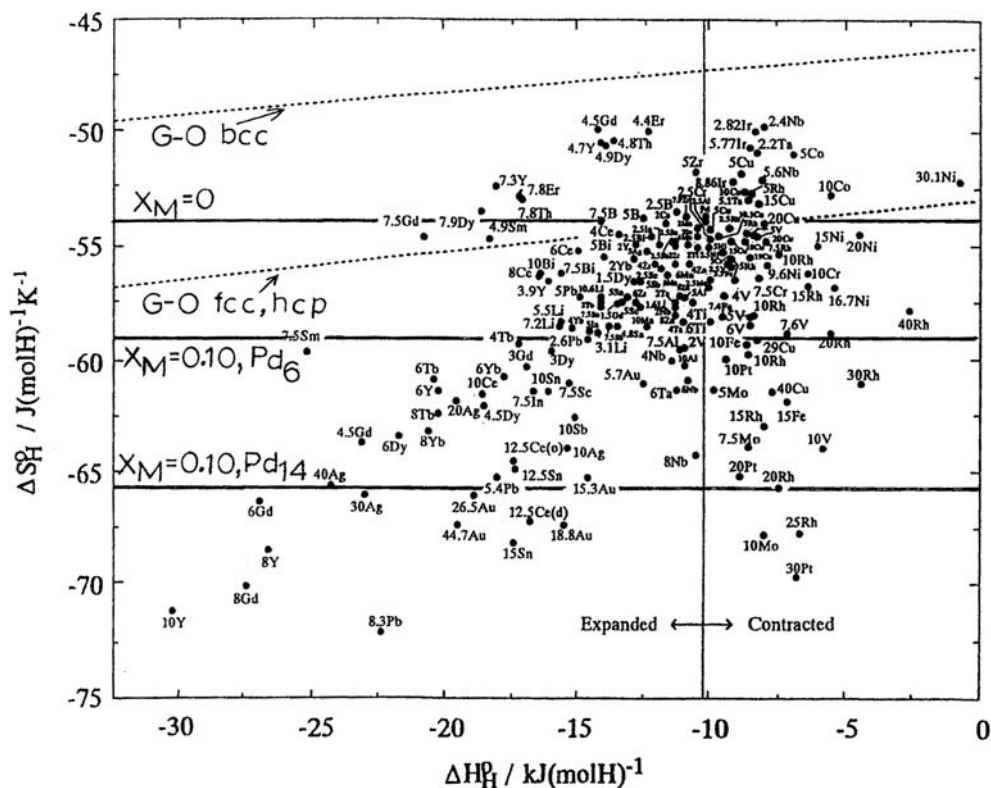


Fig. 6 A plot of ΔS_H° against ΔH_H° for Pd-rich alloys (300-400 K) modified from Ref 4. The sloped dashed lines are correlations given by Gallagher and Oates^[27] for pure metal-H systems. The horizontal solid lines are ΔS_H° values for pure Pd, ($X_M = 0$) and for alloys with $X_M = 0.10$ calculated from Eq 8 using $\beta = (1 - X_M)^6$, i.e., where only the Pd₆ interstices can be occupied and $\beta = (1 - X_M)^{14}$ for alloys where only Pd₁₄ interstices are occupied. The references for each point have been omitted because of their large number; however, these can be seen in the original figure^[4]

calculated using the binomial theorem. If H occupies only the Pd₆ or only the Pd₁₄ interstices as $r \rightarrow 0$, it would be expected that for a given X_M the deviations from $\Delta S_H^\circ(\text{Pd})$ would be characteristic of the occupation of either type of interstice. As shown in Fig. 6, this does not seem to be the case because there seems to be a continuous distribution between $z = 6$ or 14. For some alloys z may be >14 and for others all the octahedral interstices may be available, e.g., Pd-Rh. There can be appreciable experimental error in the $\Delta S_H^{\circ[4]}$ because they have been determined in different ways with various degrees of precision and this may be reflected by the data in Fig. 6. It appears, however, that the use of $z = 6$ or 14 cannot account for the data in Fig. 6.

3.5 Maxima and Compensation Effects for ΔH_H and ΔS_H as a Function of r

For solute contents $X_M > X_{M,c}$ at a given T , ΔH_H and ΔS_H are continuous functions of r , and these partial thermodynamic parameters often exhibit minima. Minima for the Pd_{0.875}Mn_{0.125} alloy are shown in Fig. 7 and 8.^[18] Such minima (Fig. 7, 8) have been found for other Pd-rich alloys and it has been found before that there are minima in $H_H^E(r)$ and $S_H^E(r)$ for Pd-H^[9] where these are excess properties, e.g., $\Delta H_H = \Delta H_H^\circ + H_H^E(r)$. In view of the known negative g_1 for Pd-H, the minimum in ΔH_H is not surprising, but the minimum in $\Delta S_H(r)$ is surprising (Fig. 1). $\Delta H_H(r)$ and $-T\Delta S_H(r)$ tend to compensate each other on each side of the minimum so as to minimize increases of $\Delta\mu_H$ with r as illustrated in Fig. 9 for the Pd_{0.875}Mn_{0.125} alloy.^[18]

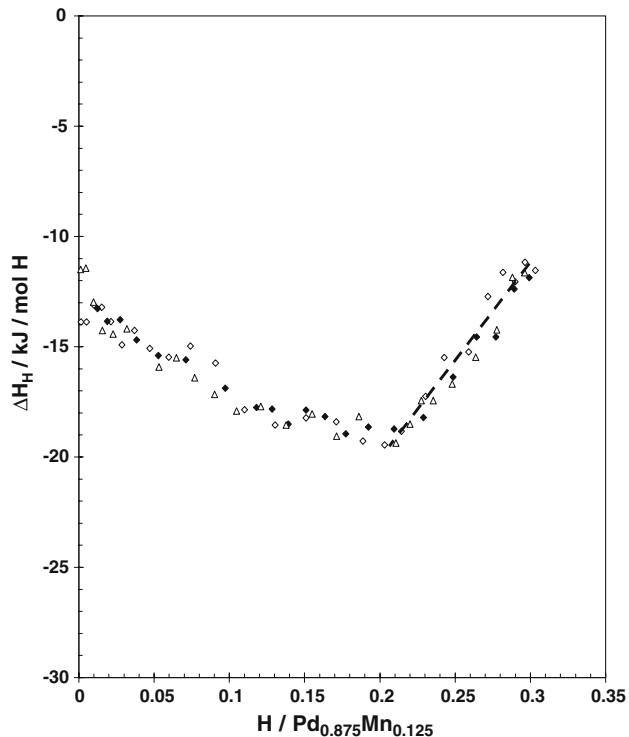


Fig. 7 Plot of ΔH_H from reaction calorimetry as a function of r for the Pd_{0.875}Mn_{0.125} alloy where the different symbols are for different series of determinations

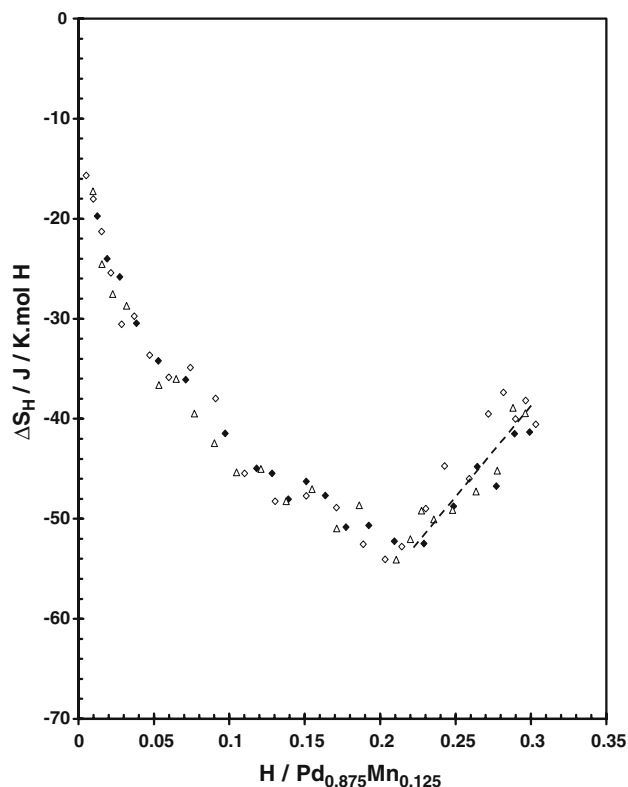


Fig. 8 Plot of ΔS_H from (Eq 1) using ΔH_H values from reaction calorimetry as a function of r for the Pd_{0.875}Mn_{0.125} alloy where the different symbols are for different series of determinations

On the low r side of the minima, the decrease of $\Delta H_H(r)$ with r is due to H-H attractive interactions while $\Delta S_H(r)$ decreases mainly because there are fewer interstices available for occupation with increase of r . On the high r side of the minimum, both $\Delta H_H(r)$ and $\Delta S_H(r)$ increase with r , but the origin of these changes is not as obvious as those for the lower r side. The increase of $\Delta H_H(r)$ may be due to a combination of the occupation of more, but less favorable, interstices and to H-H repulsions. The increase of $\Delta S_H(r)$ may be related to an occupation of more, but less favorable interstices and to a breakdown in the H-H correlations. In any case, the minima and partial compensation effects seem to be a common feature of H₂ solution in Pd-rich alloys.

3.6 THS of Disordered, fcc Pd-Rich Alloys

The universal increase of the terminal hydrogen solubility, THS, of disordered Pd alloys relative to pure Pd-H is illustrated by Fig. 10 which has been amended from Ref. 4. It has been shown that some non-Pd based alloys, such as Nb-Ta, also have very large TSH compared to the constituent elements,^[31] however, the explanation by Oates et al.^[32] which depends on formation of hydride phases with different structures is not applicable to disordered fcc Pd-alloys.

Figure 10 shows that the partial interaction free energies, g_1 , (Eq 4), of almost all Pd alloys are less negative than for

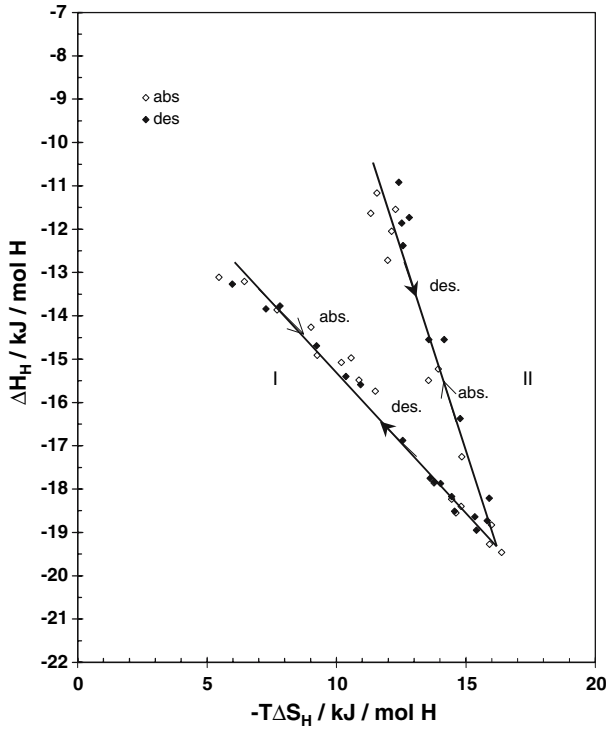


Fig. 9 Plot of ΔH_H against $-T\Delta S_H$ for the $\text{Pd}_{0.875}\text{Mn}_{0.125}$ alloy from data in Fig. 7 and 8. It can be seen that there are two regions of compensation. In region I, ΔH_H and $T\Delta S_H$ both become more negative with r . After the minimum, both become more positive with increase of r . Increases and decreases of r occur during absorption and desorption, respectively

Pd-H and the few which are slightly more negative (Fig. 10) are believed to be due to experimental error. It is therefore concluded that the increase of THS and the decrease in the magnitude of the apparent H-H interaction free energy are related,^[4] as would be expected from the regular interstitial solution model.^[23]

The increase of THS with alloying is illustrated by schematic plots of $\Delta\mu_H$ and $\Delta\mu_{\text{plat}}$ against X_M at constant T (Fig. 11a, b) where the dashed iso-H concentration lines of different r are shown in the single phase regions, while the heavy straight lines show the dependence of $\Delta\mu_{\text{plat}}$ on X_M . Figure 11 illustrates alloys where $\Delta\mu_H$ and $\Delta\mu_{\text{plat}}$ increase with X_M such as Pd-Rh (a) or decrease, e.g., Pd-Ag (b). The α and β phases refer to the dilute and hydride phases, respectively.

The THS values are given by the intersections of the iso-H content lines with the plateau-phase boundary lines (Fig. 11a, b). The H contents of the iso-concentration lines must be such that, $r_1 < r_2 < r_3 < \dots$, etc. for the dilute (α) and $r'_1 > r'_2 > r'_3 > \dots$, etc. for the hydride (β) phase in order to satisfy the thermodynamic stability requirement^[33] that $(\partial\mu_H/\partial r)_{X_M, T} > 0$; and therefore vertical lines in Fig. 11 of increasing μ_H at constant X_M must intersect tie lines at increasing r values. The iso-H concentration lines must not cross and they have been drawn to be linear for convenience (Fig. 11a, b). At the critical solute composition shown here as $X_{M,c} = 0.8$, above which two phases no longer form, the single-phase iso-H-concentration lines must merge, i.e., $(\partial\mu_H/\partial X_M)_{r,c,T} = (\partial\mu_{\text{plat}}/\partial X_M)_T$ which requires that all three tie lines converge at the critical concentration. If, on the other hand, the iso-concentration lines were to slope so that the THS decreases with X_M , there would then be problems

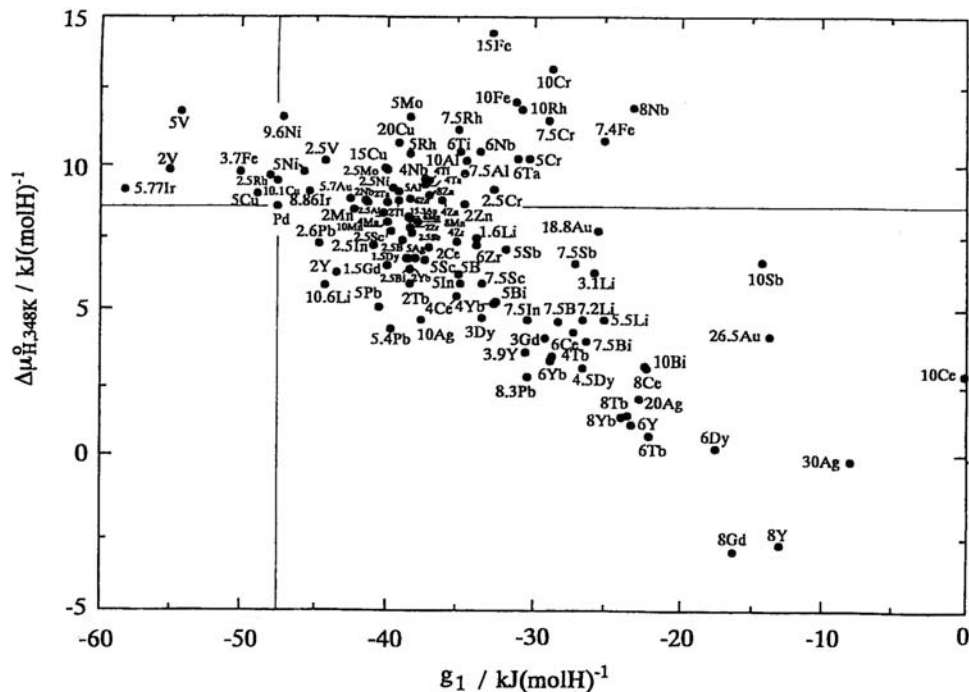


Fig. 10 Plot of $\Delta\mu_H^0$ against g_1 for disordered, fcc Pd alloys. The references for each point have been omitted because there are so many; however, these can be seen in an earlier version of the figure in Ref. 4

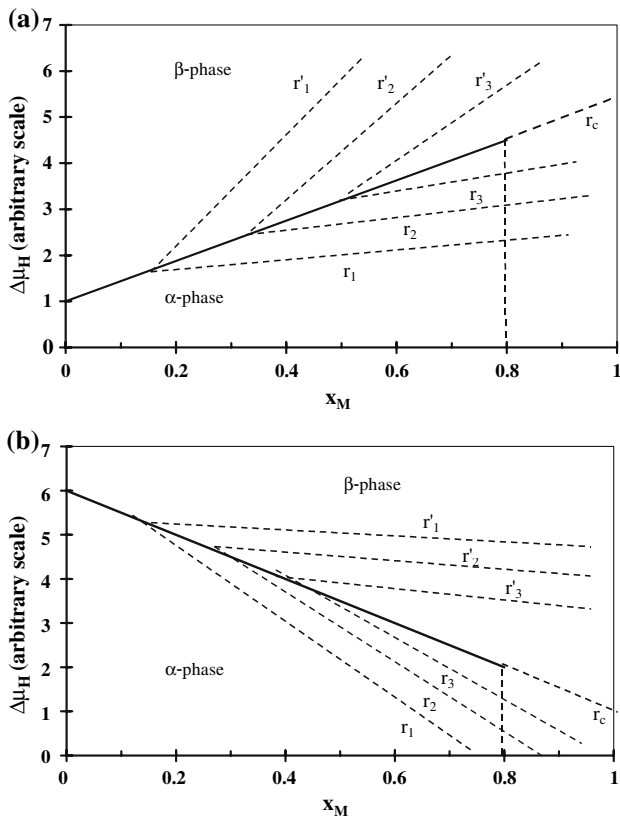


Fig. 11 Schematic isothermal plots of alloys where $\Delta\mu_H$ and $\Delta\mu_{\text{plat}}$ increase (a) and where they decrease (b) with X_M . The heavy lines represent $\Delta\mu_{\text{plat}}$ which ends at critical compositions, $X_{M,c}$. The dashed lines are iso-H concentration lines where, $r_1 < r_2 < r_3 < \dots$ for the dilute phase and $r'_1 > r'_2 > r'_3 > \dots$, etc. and for the single-phase hydride region and r_c is r at the critical composition where M is the solute metal mol fraction

with merging and non-crossing if the two-phase line is linear as in Fig. 11.

The following equation describes the tie lines in Fig. 11a, b:

$$(d\mu_H/dX_M)_{T,\text{plat}} = (\partial\mu_H/\partial M)_{T,\text{sp}} + (\partial\mu_H/\partial r)_{T,X_M}(dr/dX_M)_{T,\text{pb}} \quad (\text{Eq 9})$$

where the subscripts pb and sp refer to the phase boundaries and adjacent single phases, respectively. The schematic diagrams satisfy Eq 9 even though the $\Delta\mu_H$ and $\Delta\mu_{\text{plat}}$ change in opposite directions with X_M in the two figures. For example, for the $\alpha/(\alpha + \beta)$ boundary in Fig. 11(a) the term on the left-hand side and the first term on the right-hand side of Eq 9 are both positive, and since $(\partial\mu_H/\partial r)_{T,X_M} > 0$ because of the thermodynamic stability requirement,^[33] it follows that $(dr/dX_M)_{T,\text{pb}} > 0$; similar arguments leading to that $(dr/dX_M)_{T,\text{pb}} > 0$ can be made for 11(b).

A possibility different from that shown in Fig. 11(a) and (b) which would lead to a decrease of THS with X_M would be if the plateau co-existence lines were to bend upwardly; i.e., the X_M-r phase diagram would be very skewed with the lower boundary decreasing with X_M from the THS of pure

Pd. The hydride phase boundary must decrease sharply to reach the THS of the dilute phase at $X_{M,c}$. This seems very unlikely for a miscibility gap system and will not be discussed further here.

The ordered ($L1_2$) Pd₃Mn alloy has a smaller THS than Pd and also a more negative interaction, g_1 .^[18] This is not an exception to the above, however, because it is not a disordered alloy. It is of interest, however, that structure plays such an important role as shown by the small H₂ solubility and absence of hydride formation by the disordered form of this alloy with the same stoichiometry as the ordered one which has a large solubility and forms a hydride phase.

4. Conclusions

The dual approach of determining the thermodynamics of alloy-H systems via calorimetry and equilibrium p_{H_2} measurements is shown to be quite useful. Some interesting features of these systems have been described such as minima in partial thermodynamic parameters when plotted against r and the greater THS for the disordered alloys than for Pd.

Acknowledgments

Dr. H. Noh is thanked for obtaining some of the data and Dr. Alan Oates for his important and generous contributions to my research over many years.

References

1. O. Kleppa, High Temperature Thermodynamics of Solution of Hydrogen and Deuterium in Palladium and its Alloys, *Ber. Bunsenges Physik. Chem.*, 1983, **87**, p 741-749
2. C. Picard, O. Kleppa, and G. Boureau, A Thermodynamic Study of the Palladium-Hydrogen System at 245-352 °C and a Pressures up to 34 atm, *J. Chem. Phys.*, 1978, **69**, p 5549-5556
3. T. Flanagan, W. Luo, and J. Clewley, Calorimetric Enthalpies of Absorption and Desorption of Protium and Deuterium by Palladium, *J. Less-Comm. Mets.*, 1991, **172-174**, p 42-55
4. Y. Sakamoto, F. Chen, M. Ura, and T. Flanagan, Thermodynamic Properties for Solution of Hydrogen in Palladium-Based Binary Alloys, *Ber. Bunsenges Physik. Chem.*, 1995, **99**, p 807-820
5. T. Flanagan and J. Lynch, Partial Excess Entropies of Hydrogen in Palladium Alloys, *Metall. Trans.*, 1975, **A6**, p 243-246
6. W. Oates and T. Flanagan, The Solution of Hydrogen in Transition Metals and their Alloys, *Prog. Solid State Chem.*, 1981, **13**, p 193-283
7. M. Karger, F. Probst, B. Schuttler, and F. Wagner, *Metal Hydrogen Systems*, T. Veziroglu, ed. Pergamon Press, Oxford, 1982, Chap. 3, p 187
8. F. Wagner, M. Karger, F. Probst, and B. Schuttler, *Electronic Structure and Properties of Hydrogen in Metals*, P. Jena and C. Satterthwaite, eds. Plenum Press, New York, 1982, p 581

9. T. Kuji, W. Oates, B. Bowerman, and T. Flanagan, The Partial Excess Thermodynamic Properties of Hydrogen in Palladium, *J. Phys.F: Met. Phys.*, 1983, **3**, p 1785-1800
10. E. Wicke and G. Nernst, Zustandsdiagram und Thermodynamisches Verhalten der Systeme Pd/H und Pd/D bei Normalen Temperaturen: H/D Trenneffekte, *Ber. Bunsenges. Physik. Chem.*, 1964, **68**, p 235, in German
11. T. Mohri and W. Oates, CVM-based Calculation of the Pd-H Phase Diagram in the High Temperature Range, *Trans. Mater.*, 2002, **43**, p 2656-2661
12. G. Alefeld, Phase Transitions of Hydrogen in Metals due to Elastic Interaction, *Ber. Bunsenges Physik. Chem.*, 1972, **76**, p 746-755
13. W. Zhang, S. Luo, and T. Flanagan, Hydrogen Solution in Homogeneous Pd-Fe Alloys, *J. Alloys Compounds*, 1999, **293-295**, p 1-6
14. E. Wicke and J. Blaurock, Equilibrium and Susceptibility Behavior of the Pd/H System in the Critical and Supercritical Region, *Ber. Bunsenges Physik. Chem.*, 1981, **85**, p 1091-1096
15. D. Wang, K-Y. Lee, S. Luo, and T. Flanagan, The Thermodynamics of Hydrogen Absorption/Desorption by Pd-Co Alloys, *J. Alloys Compounds*, 1997, **252**, p 209-218
16. D. Wang, J. Clewley, S. Luo, and T. Flanagan, Thermodynamics of H₂ Absorption/Desorption for Pd-group 6B Alloys and Some Anomalous Isotherms, *J. Alloys Compounds*, 2001, **325**, p 151-159
17. T. Flanagan, S. Luo, and J. Clewley, Calorimetric Enthalpies for the Reaction of H₂ with Pd-Cu Alloys, *J. Alloys Compounds*, 2003, **356-357**, p 13-16
18. S. Luo and T. Flanagan, Thermodynamics of Hydrogen Solution and Hydride Formation in Pd-Mn Alloys. I. Disordered Alloys and a Correlation Effect, *J. Phys. Chem. B*, 2006, **110**, p 8080-8086
19. T. Flanagan, H. Noh, J. Clewley, J. Barker, and Y. Sakamoto, Hydrogen-Induced Lattice Migration in Pd-Pt Alloys, *Acta Mat.*, 1998, **46**, p 2173-2183
20. T. Flanagan, H. Noh, J. Clewley, and J. Barker, Evidence from SANS and H₂ Solubilities for H-Enhanced Metal Atom Diffusion, *Scripta Mat.*, 1998, **39**, p 1607-1611
21. E. Raub, H. Beeskow, and D. Menzel, Palladium-Rhodium Legierungen und Allotropieverhältnisse beim Rhodium, *Z. Metallkde.*, 1959, **50**, p 428-431, in German
22. H. Noh, J. Clewley, T. Flanagan, and A. Craft, Hydrogen-Induced Phase Separation in Pd-Rh Alloys, *J. Alloys Compounds*, 1996, **240**, p 235-248
23. W. Oates and T. Flanagan, Thermodynamic Properties of Regular Interstitial Solutions, *J. Materials Sci.*, 1981, **16**, p 3235-3243
24. S. Luo and T. Flanagan, Supersaturation and Hydride formation in the Dilute Phase of Pd-H and Pd-Mn-H Alloys, *J. Alloys Compounds*, 2006, **419**, p 110-117
25. Y. Sakamoto, M. Imoto, K. Takai, T. Yanaru, and K. Ohshima, Calorimetric Enthalpies for Palladium-Hydrogen(deuterium) Systems at H(D) Contents up to About (H(D)/Pd) = 0.86., *J. Phys.: Condens. Matter*, 1996, **8**, p 3229-3244
26. T. Flanagan, S. Luo, W. Wang, The Thermodynamics of Pd-Ag-H Systems Determined by Calorimetry and Equilibrium Techniques (to be submitted)
27. H. Noh, W. Luo, and T. Flanagan, The Effect of Annealing Pretreatment of Pd-Rh Alloys on their Hydrogen Solubilities and Thermodynamic Parameters for H₂ Solution, *J. Alloys Compounds*, 1993, **196**, p 7-16
28. M. Chowdbury and D. Ross, Neutron Scattering Study of the Vibrational Modes of H in the β Phases of Pd-H and Pd-Ag-H, *Solid State Comm.*, 1973, **13**, p 229-234
29. P. Gallagher and W. Oates, Partial Excess Entropies in Metals, *Trans. Met. Soc. A.I.M.E.*, 1969, **245**, p 179-182
30. Y. Sakamoto, K. Kajihara, Y. Fukusaki, and T. Flanagan, Hydrogen Solubility in Palladium-Yttrium Alloys, *Zeit. Physik. Chem.*, 1988, **159**, p 61-74
31. D. Westlake and J. Miller, Terminal Solubility of Hydrogen in Niobium-Tantalum Alloys and Characterization of the Solid Solutions, *J. Less-Common Mets.*, 1979, **65**, p 139-154
32. W. Oates and T. Flanagan, The Terminal Solubility of Hydrogen in Niobium-Tantalum Alloys, *Acta Met.*, 1985, **33**, p 693-697
33. J. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*. McGraw-Hill, N.Y., 1961