Thermodynamics of Hydrogen Absorption (Desorption) in Unoxidized and Internally Oxidized Pd–Ti Alloys.

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Abstract

Hydrogen isotherms have been measured from 273 K to 323 K in solid solution, low Ti content fcc *Pd*–Ti alloys over H content ranges available up to $p_{\text{H}_2} \approx 0.10$ MPa. ΔH_{H} and ΔS_{H} have been determined from the H_2 isotherms in the dilute phase region as a function of the H content of the alloys. Thermodynamic parameters have been determined for hydride formation and decomposition reactions from the temperature dependence of the plateau pressures. Hysteresis has been determined for the alloys up to $\text{Pd}_{0.94}\text{Ti}_{0.06}$; the $\text{Pd}_{0.92}\text{Ti}_{0.08}$ alloy does not form a hydride phase at $T \geq 273$ K. Alloys were internally oxidized to form Pd/TiO₂ composites and the H_2 solubilities re-determined. The isotherms indicate H trapping at the Pd/TiO₂ interfaces. The enthalpies for H trapping have been determined by reaction calorimetry for the internally oxidized $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy and the relative partial enthalpies for absorption are quite negative compared to H_2 solution in the dilute phase of pure Pd. These results probe the properties of metal/oxide interfaces which are important for a number of technological applications.

Keywords:

Pd–Ti alloys; thermodynamics of H_2 solution; internal oxidation; hysteresis

Introduction

Kandasamy and Lewis [1] examined the absorption of H_2 by some *Pd*–Ti alloys electrochemically and later Sakamoto *et al* [2] carried out a gas phase

investigation where the italics for Pd indicate that it is the majority element. Sakamoto *et al* [2] measured isotherms from 273 to 453 K for the Pd_{0.98}Ti_{0.02} Pd_{0.96}Ti_{0.04} and Pd_{0.94}Ti_{0.06} alloys and determined the fcc lattice parameters for the H-free, solid solution alloys. The fcc lattice parameters decrease with atom fraction Ti, X_{Ti} , only slightly from that of Pd. They characterized the two phase,(dilute + hydride), co-existence regions from measurements of the absorption plateau pressures but desorption isotherms were not measured and, consequently, hysteresis was not determined. In the present work desorption isotherms and hysteresis will be determined and the investigation will be extended to include the Pd_{0.92}Ti_{0.08} alloy.

In addition to measurement of the alloy isotherms, the alloys will be internally oxidized, IOed, and the H₂ isotherms of the IOed alloys will be measured. IO yields a Pd matrix containing nano-sized oxide precipitates, *i.e.*, TiO₂, in the present case. For IOed Pd alloys such as *Pd*-Al and *Pd*-Mg, dissolved H becomes trapped at the Pd/metal oxide interfaces [3]. The amount of trapping can be determined from the absorption isotherms which reflect the trapping region prior to solution in the dilute phase of the Pd matrix. After the trapping of H at the Pd/oxide interfaces, the completely IOed alloys should exhibit H₂ isotherms similar to pure Pd. Kirchheim and co-workers [3] investigated such trapping in IOed Pd-alloys employing electrochemically measured isotherms. More recently Flanagan and co-workers, *e.g.*, [4, 5, 6], determined the strongly trapped H from gas phase isotherms. Small angle neutron scattering, SANS, will be employed here to characterize the TiO₂ precipitates resulting from IO.

Previously reaction calorimetry was employed to characterize H trapping at Pd/alumina interfaces produced from IO of *Pd*-Al alloys [6]. It was found that ΔH_{H} markedly decreases in exothermicity from about -85 to about -10 kJ/mol H as r , H-to-metal, atom ratio, increases from about 0 to 0.008. Thus the trapping strength decreases markedly as H fills the trapping sites. Since the H trapping is much more exothermic than solution of H in the dilute phase of Pd, -10 kJ/ mol H [7], there are two regimes of H solution in the dilute absorption isotherms. H trapping at the Pd/TiO₂ interfaces will be characterized here for an IOed Pd_{0.98}Ti_{0.02} alloy by reaction calorimetry.

Experimental

The alloys were prepared in this laboratory by arc-melting the pure metals together under an Ar atmosphere. They were then annealed at 1273 K for several days. Some of the alloys were internally oxidized (IOed) in the atmosphere at

either 1083 K for 72 h or at 1273 K for 12 h. The percent IO was determined gravimetrically and, after oxidation for three days, the % oxidation was close to 100% TiO_2 (see below). The gravimetric results provided the evidence that TiO_2 is formed as the internal oxidation product. Further evidence that the IO was 100% is the H_2 isotherm after IO which, if it is the same as pure Pd, indicated 100% IO. It should be remarked that Pd and each of its alloys has a unique H_2 isotherm at a given temperature which provides experimental evidence of the composition and microstructure of the metallic phase. It has also been reported in the literature [8] that TiO_2 tetragonal precipitates form within Pd as a result of internal oxidation of Pd/Ti alloys. These workers investigated the faceted TiO_2 /Pd interfaces using high resolution electron microscopy. Since IO proceeds from the surface inwardly [9], partial IO yields alloys which are composed of an outer IOed alloy (Pd) and the inner un-oxidized alloy and the hydrogen isotherms of such partially IOed alloy should reflect both Pd and the inner, un-oxidized alloy. Therefore if the plateau pressure and the H content of the hydride phase are similar to that of pure Pd, it can be concluded that IO was complete. After IO, the alloys were quenched into ice/water baths to prevent further changes, *e.g.*, growth of the precipitates.

For IO in general it has been found that the extent of penetration of the IO front is proportional to the square root of the oxidation time [9]. The progress of IO for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy in the atmosphere (1083 K) is shown in Fig. 1 by a % IO *vs* $\sqrt{t}$ plot using IO data both for a single alloy which had been IOed at progressively longer times and also for other $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloys IOed for various times. The % IO was determined in all cases from the weight increases after IO. The square-root relation is seen to be followed and extrapolation to 100% IO suggests that IO for 72 h at this temperature would lead to 100% IO which is consistent with the results that the alloys IOed for 72 h at 1083 K were completely IOed as found by their weight increases and absorption isotherms.

SANS (small angle neutron scattering) was carried out at NIST and was employed to estimate the size of the precipitates. The $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy IOed at 1083 K for 72 h had an average Guinier radius of 3 nm and the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy IOed at 1273 K for 12 h had a much wider size distribution with an average Guinier radius of ≈ 10 nm and more precipitates formed along the grain boundaries than in the alloys which were IOed at the lower temperature. A more detailed discussion of SANS with respect to determining precipitate size is given in reference [10] and [11] gives the necessary background information. It is known that IO at higher temperatures yields larger oxide precipitates [9] which is consistent with the present results.

Table 1: $\Delta H_{\text{plat}}^{\text{f}}$, $\Delta H_{\text{plat}}^{\text{d}}$, $\Delta S_{\text{plat}}^{\text{f}}$ and $\Delta S_{\text{plat}}^{\text{d}}$ for *Pd*-Ti Alloys (273-323 K); the units of ΔH_{plat} and ΔS_{plat} are kJ/mol H and J/K mol H, respectively. The superscripts f and d refer to hydride formation (absorption) and decomposition (desorption), respectively, and the hysteresis evaluated, at 303 K, is in J/ mol H.

X_{Ti}	$\Delta H_{\text{plat}}^{\text{f}}$	$\Delta H_{\text{plat}}^{\text{d}}$	$\Delta S_{\text{plat}}^{\text{f}}$	$\Delta S_{\text{plat}}^{\text{d}}$	$RT \ln (p_{\text{f}}/p_{\text{d}})^{1/2}$
0	-18.7 [7]	19.5[7]	-46.3 [7]	46.2 [7]	1270 [7]
0.02	-17.2	18.8	-44.8	47.7	836
0.04	-14.8	17.5	-40.6	48.8	298
0.06	-14.4	15.3	-44.1	46.9	42

Table 2: $\Delta H_{\text{H}}^{\circ}$, $\Delta S_{\text{H}}^{\circ}$ (273-323 K) and g_1 (323 K) for *Pd*-Ti Alloys. The units of $\Delta H_{\text{H}}^{\circ}$ are kJ/mol H and those of $\Delta S_{\text{H}}^{\circ}$ are J/K mol H. The entropy changes have been evaluated using $\beta=1$ and $(1 - X_{\text{Ti}})^9$ and g_1 has also been evaluated using these two values of β and is in units of kJ/mol H.

X_{Ti}	$\Delta H_{\text{H}}^{\circ}$	$(\Delta S_{\text{H}}^{\circ})^*$	$(\Delta S_{\text{H}}^{\circ})^{*,*}$	g_1^*	$g_1^{*,*}$
0	-10.1 [12]	-53.7 [12]	-	-47.3 [12]	-
0.02	-10.7	-54.5	-53.0	-38.3	-38.1
0.04	-10.6	-56.0	-53.0	-34.8	-36.6
0.06	-11.2	-61.0	-56.0	-33.1	-35.9
0.08	-12	-69.0	-59.0	-31.3	-33.0

* $\beta=1.0$; *,* $\beta = (1 - X_{\text{Ti}})^9$

Results and Discussion

Un-oxidized *Pd*-Ti Alloys

Thermodynamics of H_2 Solution in Un-oxidized *Pd*-Ti Alloys

In the earlier investigation of H_2 solution in Pd-Ti alloys [2] dilute phase data were determined from 273 to 433 K [2] and therefore similar data determined here will not be reported in detail. Because only H_2 absorption data were determined previously [2], data for desorption (Figs 2-5) and, also, hysteresis are

reported (Table 1). The $\text{Pd}_{0.92}\text{Ti}_{0.08}$ alloy has not been investigated previously [2] and therefore more data will be shown for it than the other alloys.

Complete absorption/desorption isotherms are shown in Figures 2-5. Hysteresis is seen to disappear for the $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloy at 323 K. The $\text{Pd}_{0.92}\text{Ti}_{0.08}$ alloy (Fig. 5) does not have plateaux and therefore its critical temperature for the dilute $\rightleftharpoons$ hydride transition must be below 273 K. The plateau thermodynamic values are shown in Table 1 and the plateau van't Hoff plots are shown in Fig. 6; the plateau pressures for the van't Hoff plots have been taken as the mid-points of the plateaux (Figs. 2-5). It can be seen in Fig. 6 that the gaps between the $\ln p_f$ and $\ln p_d$ plots decrease with increase of X_{Ti} . It is also apparent that the magnitudes of the slopes of the plots are greater for hydride decomposition than for hydride formation, *i.e.*, the magnitudes of the ΔH_{plat} are greater for hydride decomposition as found for other Pd-alloy systems and for Pd itself [13]. The enthalpies for the $\text{Pd}_{0.96}\text{Ti}_{0.04}$ appear to have some experimental error; another indication of this is that the ΔS_{plat} magnitudes for this alloy are also quite different whereas they should be equal [13].

Dilute phase hydrogen isotherms (323 K) are shown in Fig. 7 along with an isotherm for Pd. At low p_{H_2} , the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy has a small increase of solubility compared to Pd but at larger X_{Ti} , the H_2 solubilities at a given p_{H_2} are smaller than for Pd and decrease with X_{Ti} which is mainly due to the decrease of the fraction of octahedral interstices which can be occupied because of their proximity to Ti atoms as discussed below. ΔH_{H} and ΔS_{H} are determined from the slopes and intercepts of plots of $R\ln p^{1/2}$ against $1/T$ at constant r where these relative parameters are for the overall reaction

and $[\text{H}]$ refers to H absorbed at a given r within the alloy. It should be pointed out that the amount of adsorbed H is small compared to the amount absorbed. Thermodynamic parameters at infinite dilution are shown Table 2; $\Delta H_{\text{H}}^\circ$ values were determined by extrapolation of the ΔH_{H} to $r=0$ and the $\Delta S_{\text{H}}^\circ$ were determined from extrapolation of $\Delta S_{\text{H}}^{\prime\circ}$ to 0 where $\Delta S_{\text{H}}^{\prime\circ} = \Delta S_{\text{H}} + R\ln[r/(\beta - r)]$. The values for alloys with $X_{\text{Y}}=0.02$ and 0.04 agree reasonably well with the previous ones [2] where there is a small increase in exothermicity of $\Delta H_{\text{H}}^\circ$ with X_{Ti} , however, this continues in the present data to $X_{\text{Ti}}=0.08$ whereas in the earlier investigation the $X_{\text{Ti}}=0.06$ alloy was reported to have a decreased exothermicity compared to Pd. The dependence of ΔH_{H} on r in the dilute region is shown in Fig. 8 for these Pd-Ti alloys where the extrapolations to $r=0$ to obtain $\Delta H_{\text{H}}^\circ$ values shown in Table 2 can be seen. The g_1 values (Table 1) appear in the

mean field expression for μ_{H} , *i.e.*,

$$\Delta\mu_{\text{H}} = \mu_{\text{H}} - \frac{1}{2}\mu_{\text{H}_2} = \text{RTln}p_{\text{H}_2}^{1/2} = \Delta\mu_{\text{H}}^{\circ} + \text{RTln}[r/(\beta - r)] + g_1 r, \quad (2)$$

where g_1 is the first order term in a polynomial expansion of the excess chemical potential. β is the fraction of octahedral sites which can be occupied by H.

The results for $\Delta S_{\text{H}}^{\circ}$ and g_1 in Table 2 are shown for both $\beta=1.0$ and for $\beta = (1 - X_{\text{Ti}})^x$ where $x=9$ gives the best agreement with the $\Delta S_{\text{H}}^{\circ}$ value for H in Pd. The assumption is that $\Delta S_{\text{H}}^{\circ}$ should be the same as that for pure Pd–H since the principal factor in determining the non-configurational entropy is the H vibrational frequency which is the same for H in Pd and for H in several Pd-rich alloys as determined from inelastic neutron scattering [14]. The value of $x=9$ was determined as an average from the values of ΔS_{H} in column 3 (Table 2) and the value of H in Pd, -53.7 J/K mol H. The value of 9 suggests that interstices with a Ti atom as a nearest neighbor or with Ti in about half of the next nearest neighbors are blocked for occupation by H. The $X_{\text{Y}}=0.08$ alloy follows the trend of increasingly negative $\Delta S_{\text{H}}^{\circ}(\beta=1.0)$. $\Delta S_{\text{H}}^{\circ}$ values using $\beta = (1 - X_{\text{Ti}})^9$ do not decrease as much with X_{Ti} as those employing $\beta=1.0$.

Re-arrangement of eq. (2), gives

$$\text{RTln}p^{1/2}(\beta - r)/r = \Delta H_{\text{H}}^{\circ} - T\Delta S_{\text{H}}^{\circ} + g_1 r. \quad (3)$$

Plots of the left-hand-side of eq. (3) against r gives $\Delta\mu_{\text{H}}^{\circ}=\Delta H_{\text{H}}^{\circ}-T\Delta S_{\text{H}}^{\circ}$ from the intercept and g_1 from the slope. This is illustrated by data for the $\text{Pd}_{0.92}\text{Ti}_{0.08}$ alloy in Fig. 9 where β is taken as $(1 - X_{\text{Ti}})^9$; the g_1 results shown in Table 2 for this alloy and the others at 323 K are from plots based on eq. (3) such as shown in Fig. 9. It is seen that g_1 decreases with atom fraction solute which is the same as found for other Pd-rich alloys [15].

Kinetics of H₂ Absorption by IOed Pd–Ti Alloys

It has been pointed out before [16] that partial or complete IO of Pd alloys containing solute metals more oxidizable than Pd, can enhance the kinetics of H₂ absorption. The purpose of the present experiments was to compare the rates of H₂ absorption of IOed Pd–Ti alloys with the rates for Pd and an IOed $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy and not to attempt to elucidate fundamental kinetics. The rates were determined from the time-dependence of the H₂ pressure decreases in a closed vessel (273 K) where the starting p_{H_2} was 0.33 bar and the final p_{H_2} at 273 K was ≈ 0.004 bar while the samples were within their two phase plateau

regions. Rates were examined for $\text{Pd}_{0.98}\text{Ti}_{0.02}$ and $\text{Pd}_{0.96}\text{Ti}_{0.04}$ alloys IOed at both 1083 and 1273 K. It was found that the alloys IOed at 1273 K had faster kinetics than those IOed at 1083 K. For the alloys IOed at 1273 K the initial absorption was fast while those IOed at 1083 K the initial rates were slow but after several cycles they became quite rapid and nearly equivalent to those of the $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy which is much faster than that for pure Pd. In some cases Cu powder was added to minimize the self-heating during absorption and this enhanced the rates slightly.

As an example of the rates in the plateau region a $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy was completely IOed at 1083 K for 72 h and then the rates were determined as a function of the number of cycles of hydriding/dehydriding and compared to that of an IOed $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy which is known to have enhanced kinetics after IO [16]. It is seen in Fig. 10 that the rate for the first cycle of an IOed $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy is faster than that for first cycle of a $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy. The initial H_2 absorption for the first cycle for IOed $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy does have better kinetics than that of pure Pd which had been cycled once (Fig. 10). It can be seen that the rates progressively increase with the number of hydriding/dehydriding cycles (Fig. 10) and after 6 cycles the rate closely approaches that of the IOed $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy. It can be seen that after several cycles, the rates of the IOed (1083 K) alloy are similar to that for the cycled $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy. It has been observed using SEM for other IOed Pd alloys [17] that cycling causes cracking and introduces a porous nature to the surface regions. It can be concluded that IO of Pd-Ti alloys leads to enhanced kinetics after cycling through the hydride phase change (323 K).

Calorimetric Studies of H trapping at Pd/TiO_2 Interfaces

A $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy was completely IOed (1083 K for 96 h) and then inserted into a twin-cell, heat-leak calorimeter which is employed at 303 K and which has been described earlier [18]. Relative partial molar enthalpies were determined by adding small amounts of hydrogen, dn_H , to the IOed alloy, so that r does not change appreciably, and measuring the heat evolved, dq , *i.e.*, conditions where $\text{dq}/\text{dn}_\text{H} \approx \Delta H_\text{H}$. Results are shown in Fig. 11 where the enthalpies for absorption are seen to fall in magnitude with increase of r from ≈ 90 kJ/mol H ($r=0$) to about 10 kJ/mol H at about $r=0.015$; the latter enthalpy is the same as that for pure Pd in the very dilute phase [19]. Figs. 11 and 12 should be viewed together because Fig. 12 shows the corresponding p_{H_2} changes for each of the $|\Delta H_\text{H}|-r$ determinations. The composition of $r=0.015$ where the ΔH_H becomes equal to that of Pd in the dilute region (Fig. 11) corresponds

to the onset of a linear region in the $p_{\text{H}_2}^{1/2}-r$ plot, or Sieverts' law portion, of the isotherm for this IOed alloy (Fig. 12). The extent of the strong H trapping is determined by extrapolation of the linear, Sieverts' law, portion of the initial isotherm to the r -axis. At smaller values of r before the linear region, the pressures are finite but do not correspond to the behavior of pure Pd because the ΔH_{H} is more negative than for Pd and, instead, reflects trapping at the Pd/TiO₂ interfaces.

The IOed alloy was then evacuated at 303 K for 12 h, and the enthalpies and pressures re-determined (Figs. 11, 12) and it can be seen that the enthalpies are much smaller in magnitude than the initial ones; the equilibrium pressures can be superimposed onto those of the initial absorption if the data is shifted along the r axis by $\Delta r=0.008$. This demonstrates that only some, $\approx 20\%$, of the trapped H can be removed by evacuation at 303 K. The IOed alloy was then evacuated for 12 h at 648 K and the subsequent $|\Delta H_{\text{H}}|-r$ and $p_{\text{H}_2}-r$ data determined and it can be seen from Figs. 11, 12 that more H has been removed and the $|\Delta H_{\text{H}}|$ values are greater than after the 303 K evacuation. The sample was then evacuated at 925 K (12 h) and the subsequent $|\Delta H_{\text{H}}|$ determined were greatly increased, however, they were still not as great as for the initial isotherm measurement.

The IOed alloy was hydrided/dehydrided (cycled) and evacuated at 303 K for 12 h. The subsequent $|\Delta H_{\text{H}}|-r$ relation was similar to that of the alloy after evacuation at 303 K following the initial absorption and, therefore, cycling and evacuation did not allow removal of the H in the strong trapping sites. After cycling, there was an appreciable solubility enhancement in the Pd-like region due to the formation of dislocations from cycling which serve as weak trapping sites where the solubility enhancement is the ratio of r values for the cycled IOed alloy and Pd at a given p_{H_2} [20].

H₂ Solubility in the Dilute Trapping Region of IOed Pd–Ti Alloys

Alloys were internally oxidized (IOed) at either 1273 K (12 h) or 1083 K (72 h) and typically the IO proceeded to $\approx 100\%$ TiO₂ judging from the weight increases. For example, after IO at 1083 K for 72 h the Pd_{0.98}Ti_{0.02} alloy gained weight corresponding to 103% TiO₂ formation, and after IO at 1273 K (12 h), a Pd_{0.94}Ti_{0.06} alloy gained weight corresponding to 100.8%. Another way to determine the % IO was to measure isotherms after IO, which, if they correspond closely to pure Pd, the IO had been $\approx 100\%$ IOed. This will be

seen to be the case following the IO conditions employed above from the H_2 isotherms which extended into the hydride phase.

A $Pd_{0.98}Ti_{0.02}$ alloy was IOed at 1273 K for 12 h and the H_2 solubility was determined at 323 K (Fig. 13). The initial linear p_{H_2} increase characteristic of annealed Pd has been shifted from the origin by a small amount indicating some strong trapping, *i.e.*, strong enough so that $p_{H_2} \approx 0$; the shape of the isotherm after the small trapping region, is very similar to that of annealed Pd. Few dislocations have been introduced by the high temperature IO judging from the small solubility enhancement, *i.e.*, the H solubility at a given p_{H_2} as measured from the start of the linear region compared to that of Pd at the same p_{H_2} .

H_2 isotherms are shown in Fig. 14 at 323 K for $Pd_{0.96}Ti_{0.04}$ alloys IOed at 1083 K and 1273 K. For the alloy IOed at 1083 K, the intercept of the linear portion of the initial solubility is $r \approx 0.0075$ which is based on a line drawn through a single point parallel to that for this IOed alloy after its exposure to H_2 and evacuation at 323 K. This procedure to obtain the initial intercept is based on results where more data are available for the IOed (1083 K) $Pd_{0.98}Ti_{0.02}$ alloy (Fig. 12) and the IOed (1083 K) $Pd_{0.94}Ti_{0.06}$ alloy (Fig. 15). After exposure of this IOed alloy to H_2 and evacuation at 323 K, the intercept is $r = 0.0025$. After cycling (hydriding/dehydriding), the intercept of the alloy IOed at 1083 K appears to be nearly the same as the isotherm after evacuation at 323 K.

For a $Pd_{0.96}Ti_{0.04}$ alloy IOed at 1273 K the extent of the initial strong trapping at the Pd/TiO₂ interfaces is rather small, about $r = 0.0008$, compared to that found after IO at 1083 K (Fig. 14). The radii of the precipitates formed by IO at 1083 K and 1273 K, as determined from SANS, indicates, assuming spherical precipitates, that about 33 times as many precipitates are formed at 1083 K as at 1273 K which gives a total Pd/TiO₂ interfacial area of an alloy IOed at 1083 K as 3.3 times that of the alloy IOed at 1273 K. The ratio of the strong trapping for the two is found to be about 5 times for the IOed $Pd_{0.96}Ti_{0.04}$ alloy (Fig. 14) which is probably within the error margin because, *e.g.*, precipitates formed at the grain boundaries for the alloy IOed at 1273 K may behave somewhat differently in regard to H trapping than those which form in the bulk phase and there is a larger spread in the precipitate size for those resulting from IO at 1273 K. The H_2 solubility of the alloy IOed at 1273 K after the trapping region, closely resembles that of pure Pd while the alloy IOed at 1083 K is more sloping, indicative of trapping at dislocations introduced by the IO. It has been shown that dislocations are weak traps for H in Pd [20, 21]. The solubility enhancement after IO at 1083 K, as measured

by the isotherm after evacuation at 323 K, is 1.7 at 1 kPa which is greater than that for Pd which has been cycled through the phase change at ambient temperatures, *i.e.*, 1.4 [20]. The greater solubility enhancement of the IOed alloy compared to Pd is presumably due to the role of the nano-precipitates in dislocation creation during the formation of the hydride phase.

Figure 15 shows the isotherms (323 K) after IO at 1083 K of a $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloy. The kinetics of absorption were rather slow and there are not much data for this initial absorption but, nonetheless, the intercept is quite large. After evacuation at 323 K for 2 h, the solubility isotherm has a much smaller intercept. After evacuation at 623 K (2 h), the isotherm has a smaller intercept but a similar slope as the initial one. Finally after cycling and evacuation at 323 K, a dilute phase isotherm was re-determined and there is an appreciable solubility enhancement (Fig. 15).

To summarize this section: the amount of strong trapping is quite large for the alloys IOed at 1083 K and is similar for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ and $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloys which is surprising. The trapping for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ and the $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloys after IO at 1273 K is quite small, $r \leq 0.001$.

H₂ Absorption by IOed Pd–Ti Alloys into the Hydride Phase.

Fig. 16 shows absorption isotherms (323 K) which extend into the hydride phase for the $\text{Pd}_{0.96}\text{Ti}_{0.04}$ alloy IOed at 1083 K (72 h) and at 1273 K (12 h). This Figure shows the marked difference in isotherms of an alloy before and after IO. The important point is that the isotherm (323 K) of the IOed alloy is very similar to that of pure Pd with respect to the plateau pressures and the H contents of the hydride phases which indicates that complete IO has taken place at both temperatures. The unoxidized alloy has a smaller capacity and a greater plateau pressure than the IOed alloys (Fig. 16). Figure 17 shows detailed plots of the dilute→hydride transition region. The transition to the hydride phase is more gradual for the IOed alloy (1083 K) than for annealed Pd which exhibits supersaturation and then a transition to hydride phase. The transition to the hydride phase becomes quite gradual for the IOed alloy after it had been cycled through the hydride phase. The transition region is also shown for the alloy IOed at 1273 K along with that for pure Pd. The alloy IOed at 1273 K has a relatively sharp transition but without supersaturation. It is likely that the dilute→hydride transition becomes more gradual as the dislocation density increases. It has been suggested by Pundt and Kirchheim [21] that a hydride phase forms about the dislocation cores of edge dislocations

and this could be the reason for the gradual transition, *i.e.*, some hydride phase forms before the plateau.

Figure 18 shows complete absorption isotherms (323 K) for an IOed (1083 K, 72h) $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloy along with an isotherm for pure Pd and one for the unoxidized alloy. It is clear that the IO was virtually complete because the unoxidized isotherm differs markedly from the isotherms for the IOed alloy and Pd. The initial isotherm for the IOed alloy has a relatively sharp transition to the hydride phase but in succeeding ones the transition becomes progressively more gradual.

Further evidence that after IO Pd-Ti alloys behave as Pd with respect to H_2 absorption is that $\Delta H_{\text{plat}}^{\text{f}}$ after IO (1083 K) of a $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy is -19.0 kJ/mol H as compared to -17.2 kJ/mol H for the un-oxidized $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy whereas that for annealed Pd is -18.7 kJ/mol H which can be considered to be within experimental error of that for the IOed alloy, -19.0 kJ/mol H.

A series of isotherms at higher temperatures are shown in Fig. 19 for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy after IO at 1083 K (72 h) and subsequent cycling. It can be seen that at the higher temperatures, in contrast to the lower temperature (Figs. 16, 18), the isotherms become more sloping and have smaller capacities and hysteresis than Pd. Earlier it was shown by Wang *et al* [22] that similar changes from the behavior of Pd occurred in IOed Pd-Cr alloys but to an even greater extent than for the Pd-Ti alloys. For example, some isotherms, which have not been shown elsewhere, for an IOed $\text{Pd}_{0.95}\text{Cr}_{0.05}$ alloy are shown in Fig. 20 as compared to isotherms for bulk Pd at the same temperatures. This IOed $\text{Pd}_{0.95}\text{Cr}_{0.05}$ alloy was hydrided/dehydrided (cycled) at 323 K four times prior to the isotherms shown in Fig. 20. It can be seen that hysteresis is reduced, the plateaux shortened and the isotherms become more sloping after IO and subsequent cycling. IOed Pd-Cr alloys have been examined by SEM and TEM [23] and there was found to be a high density of dislocation loops after IO and, after cycling the IOed alloys, a high density of dislocations appeared as dislocation cells and also subgrain boundaries were generated.

The effects of IO and cycling on the H_2 isotherms of IOed Pd-Ti and Pd-Cr alloys have some similarity to the effect of the size of Pd particles on the isotherms. For nano-sized Pd it has been shown by several workers *e.g.*, [24, 25], that the widths of the plateaux decrease, the slopes increase and there is a smaller hysteresis as compared to bulk Pd. It seems that large dislocation densities cannot be a factor in causing these effects on the isotherms in the IOed alloys because dislocations are not prevalent in nano-sized particles. Therefore it must be due to the small grain size in the IOed alloys after cycling. It seems that any explanation for this behavior which is applicable to nano-sized Pd

versus bulk Pd must also be able to explain this analogous behavior in these IOed alloys.

H₂ Solubility in an Pd_{0.93}Rh_{0.05}Ti_{0.02} Alloy before and after IO.

It is of interest to examine H₂ solubility in a ternary Ti alloy before and after IO; the Pd_{0.93}Rh_{0.05}Ti_{0.02} alloy was chosen because data exist for the Pd_{0.95}Rh_{0.05} alloy also because IOed *Pd*-Rh alloys exhibit interesting behavior with hydrogen [26]. An isotherm for the Pd_{0.93}Rh_{0.05}Ti_{0.02} alloy before IO is shown at 323 K in Fig. 21. The H content of the hydride phase is quite similar to that of the Pd_{0.98}Ti_{0.02} alloy at 323 K (Fig. 3) because the H content of the hydride phase does not change significantly as Pd is alloyed with Rh [27], however, the plateau pressures are greater due to the Rh. (Rh+H) itself is a miscibility gap system like (Pd+H), *i.e.*, Rh forms a monohydride phase within the fcc Rh lattice similarly to Pd but at much higher p_{H₂} [28].

Alloys were IOed at 1083 K and at 1273 K. It has been shown earlier that *Pd*-Rh alloys can be IOed at ≈ 1083 K to form precipitates of PdRhO₂, however, IO of *Pd*-Rh alloys in the atmosphere at 1273 K does not lead to IO because PdRhO₂ is unstable at this temperature [26]. It was also found that the oxide, PdRhO₂, formed at 1083 K can be reduced by exposure to H₂ at ≥ 573 K to form nano-precipitates of Rh within the Pd. Fig. 21 shows isotherms for Pd, un-oxidized Pd_{0.95}Rh_{0.05} and Pd_{0.93}Rh_{0.05}Ti_{0.02} alloys at 323 K which are compared to a Pd_{0.93}Rh_{0.05}Ti_{0.02} alloy IOed at 1083 K and then reduced in H₂ (573 K) and it can be seen that the isotherm for the reduced alloy is similar to that of pure Pd indicating that IO initially takes place to form TiO₂ and PdRhO₂ precipitates and then reduction of the PdRhO₂ precipitates gives Rh precipitates while the TiO₂ precipitates remain in the Pd matrix. The fact that the desorption plateau is the same as that of Pd-H confirms the identity of the metallic matrix because it is generally the same for different forms of Pd whereas the absorption plateau has been found to vary somewhat. The H capacity of the alloy after IO is somewhat smaller than that of Pd which is due to the fact that r in Fig. 21 has been calculated as H-to-total metal, however, if it is calculated instead as H-to-Pd, the agreement with the Pd isotherm is very good. This provides additional proof that the Rh is not alloyed with Pd after IO and reduction but appears as Rh precipitates within the Pd matrix as was found for IOed Pd-Rh alloys [26].

Fig. 22 shows the dilute phase solubilities (323 K) in Pd_{0.93}Rh_{0.05}Ti_{0.02} alloys IOed at 1273 K and 1083 K. The intercept of the latter does not correspond

H trapping in its IOed form because it has been already reduced with H_2 and evacuated at 673 K. The alloy IOed at 1273 K does reflect segregation to the metal/oxide interphases and it can be seen to be quite small as were those for the Pd -Ti alloys IOed at 1273 K, *e.g.*, Fig 14. The dilute phase isotherm for the alloy IOed at 1273 K has the same shape as that of the $Pd_{0.95}Rh_{0.05}$ alloy [26] suggesting that the Rh has not been oxidized to $PdRhO_2$ precipitates but remains alloyed with Pd. The dilute phase isotherm for the alloy IOed at 1083 K and then reduced has the same shape as that of Pd indicating that the Rh which has formed $PdRhO_2$ during IO has then been reduced to nano-sized Rh inclusions which do not absorb H_2 at the moderate pressures employed.

Hydrogen-Heat Treatment of the $Pd_{0.98}Ti_{0.02}$ Alloy.

It has been found the exposure of some Pd alloys to high pressures of H_2 at elevated temperatures leads to segregation of the alloys, *e.g.*, [10, 29]. The $Pd_{0.98}Ti_{0.02}$ alloy was subjected to high pressures of H_2 at elevated temperatures and the effect of this treatment was then determined from the subsequent H_2 isotherms after each treatment. Isotherms are a sensitive monitor of hydrogen induced changes, *e.g.*, hydrogen heat treatment can lead to markedly sloping isotherms in the region which corresponded to the plateau. The specific treatments were 1000 bar at 573, 673 and 773 K for 3-4 h and there was minimal effect of these treatments. It might be supposed that TiH_2 would form by segregation of the Ti but this was not the case and perhaps larger Ti contents are needed for segregation to occur.

Conclusions

Thermodynamic parameters for H_2 absorption/desorption have been determined for a series of low atom fraction Ti in Pd -Ti solid solution alloys. Hysteresis was determined and found to disappear at ≥ 273 K for the $Pd_{0.92}Ti_{0.08}$ alloy. Some investigations of internally oxidized Pd -Ti alloys were carried out, *e.g.*, relative partial enthalpies of H solution and trapping at the Pd/oxide interfaces were determined and the trapping was very exothermic compared to the occupation by H of octahedral interstices in Pd. IO of a $Pd_{0.93}Rh_{0.05}Ti_{0.02}$ alloy at 1273 K gives only precipitates of TiO_2 whereas IO at 1083 K gives TiO_2 and $PdRhO_2$ precipitates. Reduction of the ternary alloy in H_2 at 673 K gives precipitates of Rh within the Pd matrix which contains TiO_2 precipitates.

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Figure 1: Progress of internal oxidation of a Pd_{0.98}Ti_{0.02} alloy in the atmosphere at 1083 K.

Figure 2: Hydrogen isotherms for a Pd_{0.98}Ti_{0.02} alloy. $\triangle$, 273 K; $\circ$, 303 K; $\circ$ (red), 314 K, $\square$, 323 K. The open and filled symbols are for absorption and desorption, respectively.

Figure 3: Hydrogen isotherms for the $\text{Pd}_{0.96}\text{Ti}_{0.04}$ alloy. $\square$, 273 K; $\circ$, 303 K; $\triangle$, 323 K. The open and filled symbols are for absorption and desorption, respectively.

Figure 4: Hydrogen isotherms for the $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloy. $\square$, 273 K; $\circ$, 303 K; $\triangle$, 323 K. The open and filled symbols are for absorption and desorption, respectively.

Figure 5: Hydrogen isotherms the $\text{Pd}_{0.92}\text{Ti}_{0.08}$ alloy. $\square$, 273 K; $\triangle$, 303 K; $\circ$, 323 K;. The open and filled symbols are for absorption and desorption, respectively.

Figure 6: Van't Hoff plots of the plateau pressures for the Pd-Ti alloys. $\square$, $\text{Pd}_{0.98}\text{Ti}_{0.02}$; $\circ$, $\text{Pd}_{0.96}\text{Ti}_{0.04}$; $\triangle$, $\text{Pd}_{0.94}\text{Ti}_{0.06}$. The open and filled symbols are for absorption and desorption, respectively.

Figure 7: Dilute phase hydrogen isotherms for Pd -Ti alloys at 323 K. $\triangle$, Pd.

Figure 8: Plots of ΔH_H against r . $\bullet$, Pd; $\circ$, $Pd_{0.98}Ti_{0.02}$; $\triangle$, $Pd_{0.96}Ti_{0.04}$; $\square$, $Pd_{0.94}Ti_{0.06}$; $\diamond$, $Pd_{0.92}Ti_{0.08}$.

Figure 9: Plots of $RT \ln p^{1/2}(\beta - r)/r$ against r for the $\text{Pd}_{0.92}\text{Ti}_{0.08}$ alloy with $\beta=(1 - X_{\text{Ti}})^9=0.472$.

Figure 10: Kinetics of H_2 absorption at 273 K by the IOed (1083 K, 72 h) $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy, Pd and an IOed $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy. $\triangle$, Pd; $\circ$, initial absorption by IOed $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy; $\triangle$, 2nd cycle following the initial cycle for the IOed $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy; $\square$, 3rd cycle IOed $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy; $\odot$, 6th cycle IOed $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy; $\odot$, initial cycle for $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy completely IOed at 1083 K; $\triangle$, 2nd cycle for IOed $\text{Pd}_{0.97}\text{Al}_{0.03}$ alloy.

Figure 11: Calorimetric measurements of ΔH_H for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy IOed at 1083 K. ○, initial absorption; △, absorption after evac. at 303 K; ●, after evacuation for 12 h at 648 K; □, evac. 12 h at 925 K; △, after complete hydriding/dehydriding and evacuation at 303 K.

Figure 12: Isotherms (303 K) accompanying the calorimetric measurements for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy IOed (1083 K). $\circ$, initial absorption; $\triangle$, repeat absorption after evac. at 303 K; $\circ$, after evacuation at 648 K (12h); $\square$, after evac. 12 h at 925 K; $\triangle$, after complete hydriding/dehydriding at 303 K.

Figure 13: Dilute phase isotherms at 323 K for the $\text{Pd}_{0.98}\text{Ti}_{0.02}$ alloy IOed at 1273 K (12 h). $\circ$, initial absorption; $\bullet$, after evacuation at 323 K; $\circ$, after complete hydriding/dehydriding and evacuation at 323 K.

Figure 14: Dilute hydrogen isotherms at 323 K for IOed $\text{Pd}_{0.96}\text{Ti}_{0.04}$ alloys. $\circ$, initial absorption after IO at 1083 K. The kinetics were slow and only one point has been obtained in this linear region through which a line has been drawn parallel to the linear region of the isotherm after evacuation at 323 K; this procedure is based on the behavior of a similarly IOed $\text{Pd}_{0.94}\text{Ti}_{0.06}$ alloy; $\triangle$, an isotherm after evacuation at 323 K of the alloy IOed at 1083 K; $\square$, an isotherm following complete hydriding/dehydriding at 323 K. The various treatments are sequential, *e.g.*, an isotherm was first measured after IO without any pretreatment and then the sample was evacuated at 323 K and a dilute phase isotherm re-measured. $\circ$, initial absorption after IO at 1273 K (12 h); $\square$, after hydriding/dehydriding the alloy at 323 K which had been IOed at 1273 K;

Figure 15: Dilute phase isotherms at 323 K for the IOed Pd_{0.94}Ti_{0.06} alloy. $\circ$, initial absorption after IO at 1083 K (12 h); the kinetics were slow and a line has been drawn through the two highest p_{H_2} points which lies parallel to the isotherm after evacuation at 323 K; $\triangle$, after evacuating at 323 K; $\circ$, after evacuation at 623 K for 2 h; $\square$, absorption after hydriding/dehydriding at 323 K.

Figure 16: Hydrogen isotherms (323 K) over the full range of H contents up to the hydride phase for the IOed $\text{Pd}_{0.96}\text{Ti}_{0.04}$ alloy. ○, absorption after IO at 1083 K (72 h) but before forming the hydride phase; △, after the alloy IOed at 1083 K has been cycled through the hydride phase; ○, after IO at 1273 K. The solid line is annealed Pd and the upper isotherm is for the un-oxidized $\text{Pd}_{0.96}\text{Ti}_{0.04}$ alloy.

Figure 17: Hydrogen isotherms (323 K) showing the details of the dilute→hydride transition for the IOed Pd_{0.96}Ti_{0.04} alloy. ○, absorption before prior of formation of the hydride phase after IO at 1083 K (72 h); □, after IO at 1273 K (12 h); △, after cycling the alloy IOed at 1083 K; ○, isotherm for Pd annealed at 1373 K.

Figure 18: Hydrogen isotherms (323 K) over the full range of H contents to the hydride phase for the IOed Pd_{0.94}Ti_{0.06} alloy. ○, initial absorption isotherm after IO at 1083 K (72 h); △, 2nd cycle for alloy IOed at 1083 K; □, 3rd cycle for alloy IOed at 1083 K; continuous red line is an isotherm for annealed Pd and the upper isotherm is for the un-oxidized alloy.

Figure 19: High temperature hydrogen isotherms for the IOed Pd_{0.98}Ti_{0.02} alloy after IO at 1083 K (72 h); $\circ$, and the dashed lines showing negligible hysteresis at these temperatures are isotherms for pure Pd. The latter are from Blaurock [30] and the former from the present work. $\circ$, IOed Pd_{0.98}Ti_{0.02} alloy at the indicated temperatures. The open and filled symbols are for absorption and desorption, respectively.

Figure 20: Isotherms for the IOed $Pd_{0.95}Cr_{0.05}$ alloy after IO at 1083 K (72 h). The red symbols refer to pure Pd and similar symbols refer to the same temperature for the IOed alloy and Pd. The open and filled symbols are for absorption and desorption, respectively.

Figure 21: Hydrogen isotherms at 323 K. $\square$, $\text{Pd}_{0.93}\text{Rh}_{0.05}\text{Ti}_{0.02}$ alloy IO at 1083 K (72 h) and reduction in H_2 (523 K); $\square$, annealed Pd; $\circ$, un-oxidized $\text{Pd}_{0.93}\text{Rh}_{0.05}\text{Ti}_{0.02}$ alloy; $\triangle$, un-oxidized $\text{Pd}_{0.95}\text{Rh}_{0.05}$ alloy. Open and filled symbols are for absorption and desorption, respectively.

Figure 22: Dilute hydrogen isotherms at 323 K for $\text{Pd}_{0.93}\text{Rh}_{0.05}\text{Ti}_{0.02}$ alloys after IO at 1273 K and 1083 K (72 h) and reduction in H_2 at 573 K for the latter; isotherms for Pd and the $\text{Pd}_{0.95}\text{Rh}_{0.05}$ alloy are also shown as red symbols.