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Journal of Alloys and Compounds 218 (1995) 139–142

Journal of ALLOYS AND COMPOUNDS

The effects of hydriding–dehydriding cycles on the plateau pressures and van't Hoff plots for Pd–Ni alloys

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Received 14 July 1994

Abstract

Pd and its alloys that form hydride phases exhibit hysteresis. It has been observed that if Pd–Ni alloys have been hydrided and then dehydrided a number of times, "cycled", at moderate temperatures, the hysteresis is reduced. After the $Pd_{0.91}Ni_{0.09}$ alloy had been cycled until its isotherms no longer changed, isotherms at other temperatures were measured. It was found for the cycled alloy that hysteresis is appreciable at 273 K and small at 343 K. The van't Hoff plots are affected by this changing hysteresis and consequently the derived thermodynamic parameters are also affected. If, instead of employing an alloy that had been cycled, virgin alloys, i.e. annealed ones, are employed for each temperature, the hysteresis is more constant and the resulting van't Hoff plots are more linear. The enthalpy has also been measured by reaction calorimetry for comparison with the values from the van't Hoff plots.

Keywords: Hydriding–dehydriding cycles; Plateau pressures; Palladium; Nickel

1. Introduction

Thermodynamic data for metal hydrides are generally obtained from van't Hoff plots of their plateau pressures. Many hundreds of these have been made for the characterization of the many intermetallic compounds that have been prepared for their possible technological applications as hydrides. It is well known that the plateau pressures change for intermetallic compounds from the first hydriding (activation) to the second, and thereafter the plateaux change more slowly, essentially becoming repeatable after 3 or 4 cycles [1–3]; the hydride formation plateau is most affected by the cycling. This does not seem surprising in view of the fact that the initial hydriding causes brittle fracture of most intermetallic compounds, and only after several cycles do the particle sizes become reasonably constant.

It seems clear from these considerations that thermodynamic data for intermetallic compounds should be obtained from the temperature dependence of the isotherms only if the effects of the evolving isotherms are allowed for, either by employing hydrides only after reproducible behavior is obtained by cycling many times, or else by employing virgin alloy for each separate isotherm determination.

Because brittle fracture and disintegration do not accompany the hydriding of the ductile palladium and its alloys, a similar dependence of the isotherms upon cycling would be unexpected. Nonetheless, it has been found recently that the plateau pressures of Pd–Ni alloys, e.g. the $Pd_{0.9}Ni_{0.1}$ and $Pd_{0.85}Ni_{0.15}$ alloys, are affected by cycling [4]. (It is curious that such cycling effects have not been reported earlier, in view of the many studies of hydrogen uptake by palladium alloys.)

Thermodynamic data for the "plateau" reaction, i.e.

$$\tfrac{1}{2}H_2(g)+\frac{1}{(b-a)}\,MH_a \rightleftharpoons \frac{1}{(b-a)}\,MH_b \qquad (1)$$

where a and b are the $(H/M)=r$ ratios of the co-existing dilute and hydride phase boundaries respectively, can be derived from the temperature dependence of the plateau pressures. Thermodynamic data can also be obtained from reaction calorimetry, where the heat evolved or absorbed accompanying the "plateau" reaction is measured directly.

Because of hysteresis, the minimum plateau pressure needed for the forward reaction (1), hydride formation at p_f is greater than that for the reverse of reaction (1), hydride decomposition at p_d. Isothermal hysteresis for metal hydrides is best expressed thermodynamically as $\tfrac{1}{2}RT\,\ln(p_f/p_d)$, which is the work done on the system

SSDI 0925-8388(94)01404-3

(per $\frac{1}{2}$ mol H_2) and which is released to the surroundings as dissipated heat. Because of hysteresis, there are two different van't Hoff plots, one corresponding to the forward and one to the reverse reaction of (1). In these van't Hoff plots ln p_f or ln p_d is plotted against T^{-1}; the latter plot is expected to be steeper, i.e. have a larger value of $|\Delta H_{plat}|$ than the former. This is illustrated very well by the results obtained by Lässer and coworkers [5,6] for pure palladium–hydrogen. The p–c–T data obtained by these workers, which was restricted to the temperature range above about 300 K, is probably the most complete for this system. They found the values shown in Table 1. The enthalpy of reaction derived from the van't Hoff plot for p_d, $|\Delta H^d_{plat}|$, is 0.8 kJ per mol H larger than the value derived from their van't Hoff plot for p_f, $|\Delta H^f_{plat}|$. This is consistent with the measured hysteresis for this system, which is 800 J mol^{-1} H, i.e. the difference in enthalpies derived from the two van't Hoff plots is equal to the hysteresis, ≈ 800 J per mol H. From thermodynamic arguments it has been shown that this is the expected result when hysteresis is constant over the temperature interval of the study [7]. It has also been shown that the calorimetrically measured enthalpy for reaction (1) has the same magnitude for both directions and is equal to 19.2 kJ per $\frac{1}{2}$ mol H_2 [8] which is very close to the average of the two enthalpies (magnitudes) derived from the van't Hoff plots [5,6]. Thus for the palladium–hydrogen system the average of the enthalpies derived from the van't Hoff plots of p_f and p_d is very close to the true (calorimetric) value, a result that had been predicted from thermodynamic arguments [7].

The aim of the present research is to compare the van't Hoff plots for a cycled Pd-Ni alloy with those obtained using a virgin, i.e. annealed, alloy for each separate isotherm. The enthalpies derived from these van't Hoff plots will be compared with those measured in this work directly from reaction calorimetry.

Table 1
A summary of effects of cycling on the thermodynamic parameters for $Pd_{0.91}Ni_{0.09}-H$ and also shown are previously obtained values for Pd. ΔH_{plat} is in kJ/$\frac{1}{2}$ mol H_2; ΔS_{plat} is in J/K $\frac{1}{2}$ mol H_2

X_{Ni}	ΔH^f_{plat}	ΔH^d_{plat}	ΔS^f_{plat}	ΔS^d_{plat}	Ref.
0	−18.7	19.5	−46.3	46.2	[5,6]
0 (cal)	−19.1	19.3	−46.6	46.6	[8]
0.092 (ann)	−14.2	16.2	−45	49.2	this work
0.092 (cycl)	−13.2	15.5	−40.6	47.0	this work
0.092 (cal)	−14.9	14.9	−46.1	46.1	this work

(ann) refers to the annealed, (cycl) to the cycled alloy and (cal) to enthalpies determined from calorimetry. ΔS_{plat} values for samples labeled (cal) are obtained from equation (3) and refer to 298 K; the other entropies are obtained from the intercept of the van't Hoff plots shown in Figure 3.

2. Experimental

The samples were in the form of thin foils. The Sieverts-type apparatus is a conventional, all-metal one capable of measuring pressures up to about 5 MPa. The calorimeter is a twin-cell, heat leak type which has been described elsewhere [9] and has proven to be very well suited for palladium [8] and its alloys [10].

3. Results and discussion

After cycling the $Pd_{0.9}Ni_{0.1}$ alloy through the hydride phase several times at 323 K [4], hysteresis was markedly reduced, but not eliminated, as it is for the $Pd_{0.85}Ni_{0.15}$ alloy at 323 K. In this research a $Pd_{0.91}Ni_{0.09}$ alloy was cycled at 303 K until repeatable behavior was found. A reduction in hysteresis was observed for this alloy at 303 K, which was somewhat smaller than previously observed at 323 K for an alloy of very similar composition [4]. Isotherms for the alloy, which was in the cycled condition, were then measured at several temperatures, and the results are shown in Figs. 1 and 2. After these isotherm measurements, the temperature was returned to 303 K and an isotherm remeasured in order to check that there had been no further changes with the ad-

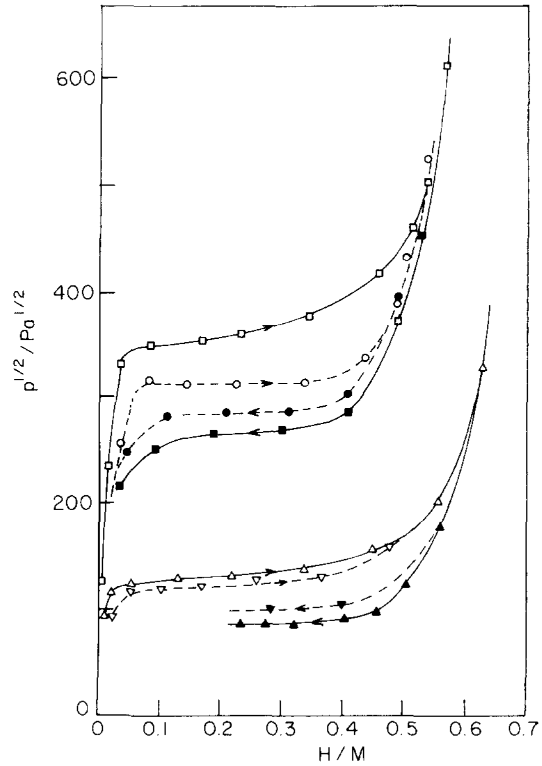

Fig. 1. Isotherms at 273 K and 323 K for $Pd_{0.91}Ni_{0.09}$ in the cycled and virgin annealed forms; the lower and upper set of data points are for 273 K and 323 K respectively. The continuous lines have been drawn through the latter data and the dashed lines through the former. Open symbols refer to absorption and filled symbols to desorption.

ditional cycling at the other temperatures, and it was found that this was indeed the case.

One motive of this research was to compare the isotherms for the cycled alloy with those for a virgin alloy, i.e. one that had been annealed at 1125 K for 3 days between each isotherm measurement. Isotherms for the virgin alloy are also shown in Figs. 1 and 2, where it can be seen that there is a very large effect of the cycling, especially at the higher temperatures. Hysteresis for the cycled alloy decreases markedly over this limited temperature range. It can also be seen that the plateaux become much more horizontal after cycling so that it is clearer where the $(\alpha+\beta)/\beta$ and $\beta/(\alpha+\beta)$ boundaries are located. Hysteresis also decreases with temperature for the virgin alloy, but it still remains appreciable at 343 K (Fig. 2).

Van't Hoff plots have been obtained from the plateau pressures for both hydride formation and decomposition from these isotherms (Figs. 1 and 2) and these plots are shown in Fig. 3. It can be seen that the plots of $\ln p_f$ and $\ln p_d$ appear to converge for the cycled alloy at a temperature somewhat greater than 343 K. The plots for the cycled alloy are not very linear because they are affected by the change of hysteresis over this small temperature range. Best straight lines have been drawn through these data, and the resulting thermodynamic parameters are given in Table 1. The van't Hoff plots for the annealed alloy are more linear (Fig. 3), and its derived thermodynamic values should therefore be more meaningful (Table 1).

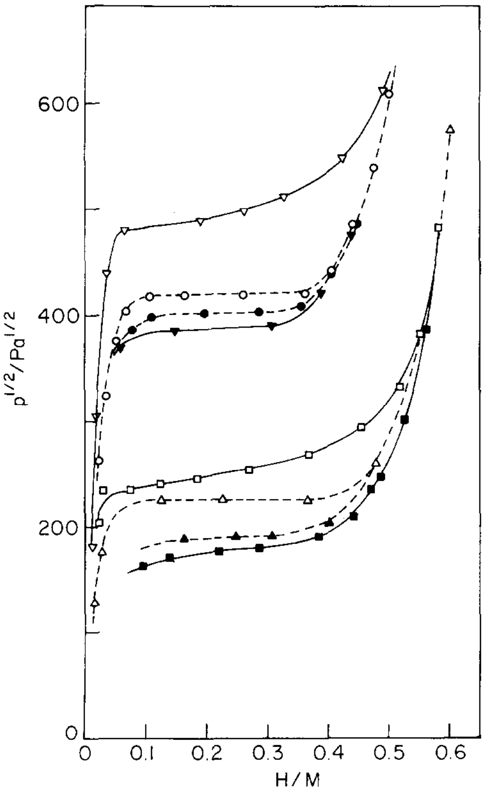

Fig. 2. Isotherms at 303 K and 343 K for $Pd_{0.91}Ni_{0.09}$ in the cycled and virgin annealed forms; the lower and upper set of data points are for 303 K and 343 K respectively. The continuous lines have been drawn through the latter data and the dashed lines through the former. Open symbols refer to absorption and filled symbols to desorption.

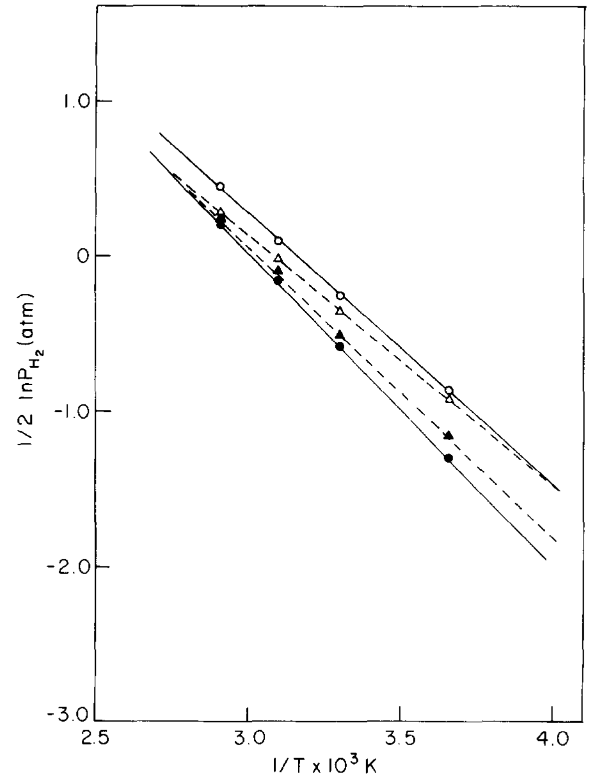

Fig. 3. van't Hoff plots for cycled and virgin annealed forms of $Pd_{0.91}Ni_{0.09}$. The dashed lines refer to the cycled alloy data and the continuous lines to the virgin annealed alloy data.

In order to help assess the significance of the thermodynamic parameters from these van't Hoff plots for the different sample forms, enthalpies were measured directly by reaction calorimetry and the following value was found for the plateau region: $|\Delta H_{plat}| = 14.9 \pm 0.2$ kJ per ½ mol H_2. Aside from the signs of the enthalpies, there was no apparent difference whether they were measured during hydride formation or decomposition. The calorimetrically measured value is believed to be close to the true value because it is not directly influenced by hysteresis [7].

These calorimetric results for the alloy appear to be reasonable by comparison with calorimetric data for pure Pd–H_2(g) because the difference between the enthalpies for pure palladium–H and the palladium alloy–H systems, −4.2 kJ per ½ mol H_2 (Table 1), is within experimental error of that derived from the ratio of the plateau pressures at 298 K, i.e.

$$\tfrac{1}{2}RT \ln\left(p_f(\mathrm{Pd})/p_f(\mathrm{alloy}) = \frac{2026\ \mathrm{Pa}}{47200\ \mathrm{Pa}}\right)$$
$$= -3.9\ \mathrm{kJ\ per}\ \tfrac{1}{2}\ \mathrm{mol}\ H_2 \qquad (2)$$

This agreement means that the plateau entropies must be similar for the alloy–hydrogen and pure palladium–hydrogen systems. The average magnitude of the enthalpies from the van't Hoff plots for p_f and p_d for the virgin alloy form is 15.2 kJ per $\frac{1}{2}$ mol H_2 (Table 1), which is close to the calorimetrically determined $|\Delta H_{plat}|$. For palladium–hydrogen the difference in the plateau values is closely equal to the hysteresis (Table 1). This is not true for the alloy because hysteresis also decreases for the virgin form of the alloy over the temperature interval from 273 to 343 K. This causes an $|\Delta H_{plat}|$ apparent increase of hydride decomposition and a decrease for hydride formation. The difference between the magnitudes of the formation and decomposition values for the annealed alloy is greater than the hysteresis, ≈800 J per $\frac{1}{2}$ mol H_2, at 303 K.

In contrast to Pd–H (Table 1), the entropies for the alloy derived from the van't Hoff plots are not equal in magnitude, and this may also be attributed to the changing hysteresis with temperature. The entropies can be calculated from the calorimetrically measured enthalpy, which should be independent of temperature over this small range from 273 to 343 K, and the average of the plateau pressures, $p_{plat}^{av}=\sqrt{p_f p_d}$, of the different isotherms (Figs. 1 and 2) using the following equation

$$\Delta S_{plat}=\frac{\Delta H_{plat}}{T}-\tfrac{1}{2}R\ln p_{plat}^{av} \tag{3}$$

The entropies calculated from Eq. (3) are found to be quite similar over the temperature interval, e.g. 45.5 (273 K) and 46.0 (343 K), and they are also close to the value for palladium–hydrogen (Table 1). These values for the alloy are believed to be most nearly correct because the other values for the alloy are quite different for formation and decomposition (Table 1). The entropy values shown in the last row of Table 1 are from Eq. (3) but the plateau pressures were measured in the reaction calorimeter.

4. Conclusions

This research demonstrates that the difference between the isotherms for a $Pd_{0.91}Ni_{0.09}$ alloy that has been cycled and the virgin form is significantly greater at 343 K than at 273 K. The cycled alloy has a hysteresis that is only 17% of the virgin one at 343 K and at 273 K it is 60% of the virgin one (Figs. 1 and 2). It should be emphasized that these values are quite reproducible once the alloy has been cycled. The reason for the greater effect of cycling at the higher temperatures is unknown.

It seems clear from this research that experimental uncertainties could be introduced by cycling into the van't Hoff plots for this alloy and very probably for other Pd alloys. A possible scenario leading to an erroneous van't Hoff plot would be that the first isotherm would be measured on a virgin sample and then the subsequent isotherms measured with the same alloy without any annealing treatment. It should be appreciated that this would lead to an erroneous van't Hoff plot for both hydride formation and decomposition because of the shifting plateau pressures with the various stages of cycling. It should be noted that while p_f is affected more than p_d by cycling, the latter is also affected (Figs. 1 and 2).

When the virgin alloy form was employed for an isotherm measurement at each different temperature, more linear van't Hoff plots were obtained (Fig. 3). The average magnitude of the enthalpy derived from the van't Hoff plot for the virgin alloy form closely agrees with that from reaction calorimetry. Although it is laborious, it seems that under the circumstances where the hysteresis for the cycled alloy changes markedly with temperature, a freshly annealed alloy must be employed at each temperature for the van't Hoff plot.

Acknowledgements

The authors are grateful to Los Alamos National Laboratory and the N.S.F. for the financial support of the research on palladium alloys.

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