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Correlations between electrical resistance–hydrogen pressure relationships of the Pd/Pt/H system and alterations of structure with changes of hydrogen content in the Pd/H system

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Abstract

For higher Pt content alloys of the Pd/Pt series of alloys, relationships at 25 °C between hydrogen content, n, and incremental changes of specific electrical resistance, $\Delta\rho$, seem representable to a good approximation by a common curve, with a maximum of $\Delta\rho$ near $n=0.5$, of similar form to 'Nordheim' types of relationship between resistivity and composition appropriate to substitutional alloys. An attempt has been made to assess whether phase-transition-related deviations from this symmetrical form of $\Delta\rho$–n relationship in the cases of palladium itself and Pd/Pt alloys with lower Pt contents may provide useful guidance concerning the sequence of hydrogen occupation of interstitial sites in α and $\beta(\alpha')$ phases (domains) of these systems.

1. Introduction

In comparison with other series of binary palladium alloys, the Pd/Pt series presents some particular advantages for studies of hydrogen absorption and desorption over a wide range of compositions and experimental conditions. Although platinum is virtually twice as dense, it has an only slightly larger fcc lattice constant than its group partner palladium and alloys of the two metals represent a very close approximation to an uncomplicatedly continuous series of solid solution over their entire composition range [1, 2].

In regard to divisions of palladium alloys with reference to differences in patterns of p–n–T relationships [1–7], the Pd/Pt series represents a marginal example of an 'expanded' alloy series in correspondence with the small dimensional increases of the palladium lattice produced by added Pt. However, the Pd/Pt/H isothermal (*e.g.* 25 °C) p–n relations actually exhibit patterns of change that are more characteristic of a 'contracted' alloy series. Thus with increasing Pt there are corresponding gradual increases in values of the pressures $p_{\alpha,\beta}$ and $p_{\beta,\alpha}$ corresponding to the pressure invariant main regions of phase transition, accompanied by decreases of complementary ranges of hydrogen content, n, over these regions. Consequently, (with similarity to the sequence of changing forms of p–n isotherms of the Pd/H system with increasing temperature [3, 4, 6, 8]) with increasing Pt content, the p–n isotherm of each alloy in turn fits wholly within those of lower Pt content at all reference pressures. Hysteresis effects also simultaneously decrease and the critical temperature $T_c(\alpha, \beta)$ with respect to the $\alpha \rightleftharpoons \beta$ phase transitions reduces to 25 °C for an alloy composition of approximately $Pd_{85}Pt_{15}$.

1.1. *Hydrogen content–electrical resistivity relationships*

At 25 °C, the continuous increases on absorption of hydrogen by palladium of the relative parameter R/R_0 (R_0 representing initial resistivity ($n=0$)) with n (=H/Pd, atomic ratio) has been identified with the main part of the $\alpha\rightarrow\beta$ phase transition including an early change of slope associated with its onset [1, 3, 4, 6, 7]. In the case of the desorption relationship a 'hysteretic shoulder' has been identified with the onset of the $\beta\rightarrow\alpha$ transition [3, 7, 9]. A trend towards more pronounced hysteretic differences of R/R_0–n relationships has been found in studies over the temperature range up to 100 °C [10, 11] which in combination with indications from X-ray studies [12], have been interpreted as evidencing that α and β phase structures (now appearing essentially to differ from one another only in respect of densities of hydrogen occupation of the preferred octahedral interstitial sites [13, 14]) can also coexist together in 'subsidiary' regions of hysteresis loops (*e.g.* BC, DE, EG and HB in Fig. 1) adjacent to the more precisely pressure invariant regions of $\alpha\rightarrow\beta$ and $\beta\rightarrow\alpha$ transitions [3, 11, 15].

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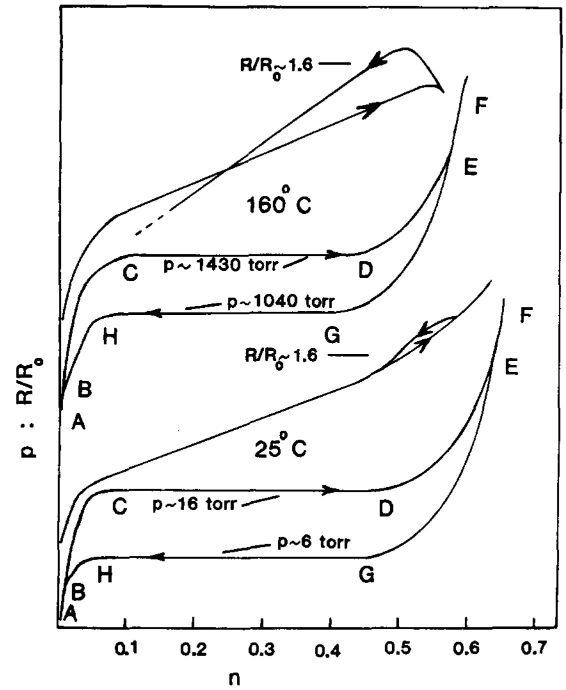


Fig. 1. Semi-diagrammatic comparison of 'hysteretic' differences between 'absorption' and 'desorption' hydrogen pressure–hydrogen content (p–n) and relative electrical resistance–hydrogen content (R/R_0–n) relationships for the Pd/H system at 25 °C and 160 °C.

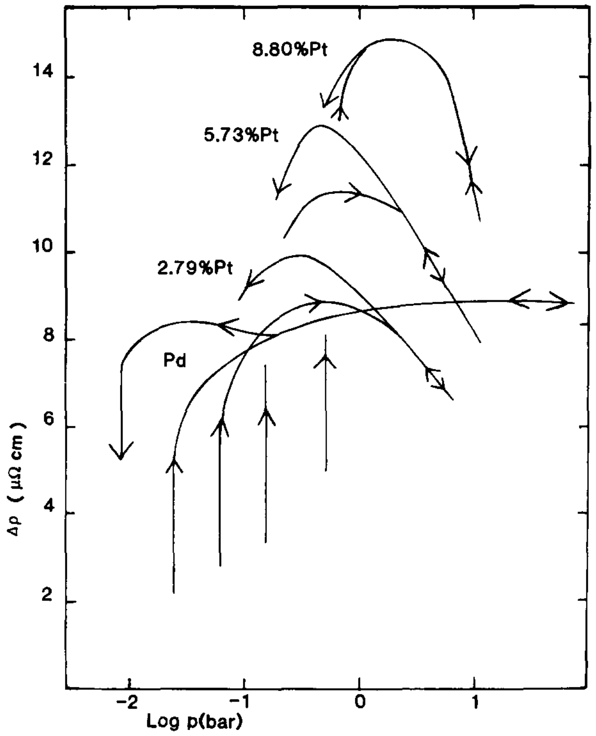


Fig. 2. 'Hysteretic' differences of 'absorption' and 'desorption' relationships between incremental changes of specific electrical resistance corresponding to equilibrium hydrogen pressures ($\Delta\rho$–n relationships) for the palladium–hydrogen and lower Pt content Pd/Pt alloy–hydrogen systems at 25 °C.

Still more prominent R/R_0–n hysteretic differences (Fig. 1) have been recorded in conjunction with the p-n relationships at 160, 180 and 200 °C in the important paper of Brüning and Sieverts [16] which would then seem likely to represent temperatures near to a point of turnover to a trend of reduction of hysteresis in p–n and other parameter relationships with n and p up to [3, 4, 6, 15, 17–19] and above [18–21] the critical temperature $T_c(\alpha, \beta)$ of approximately 300 °C.

This overall pattern of alteration of hysteretic differences between R/R_0–n (p) relationships with increasing temperature in the case of the Pd/H system would seem to have a counterpart (Fig. 2) in a similar trend of increase followed by decrease of hysteretic differences with increasing Pt content between absorption and desorption R/R_0–n relationships in the case of the Pd/Pt/H system at 25 °C over the course of the lower range of Pt contents extending up to approximately 15% Pt [1, 3, 15, 22].

2. Correlations of an approximately common solid solution R/R_0–n relationship for the Pd/Pt/H system with relationships involving regions of phase transition

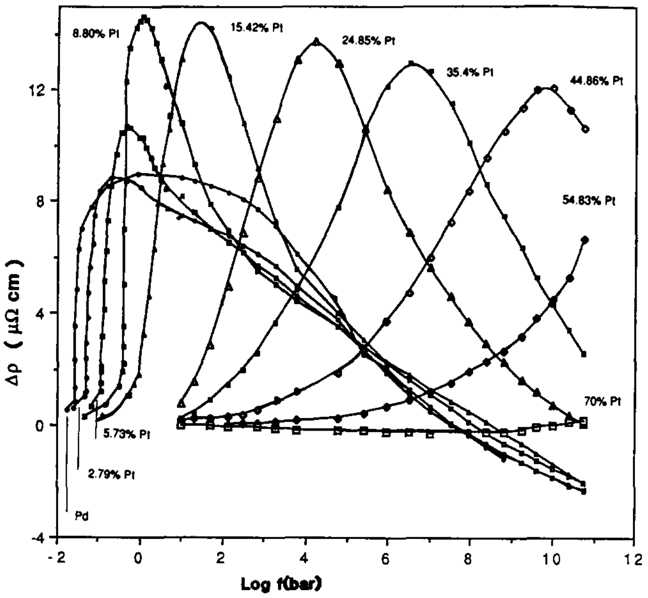


Fig. 3. 'Absorption' $\Delta\rho$–log f relationships between increments of specific electrical resistance and equilibrium hydrogen fugacities for palladium and Pd/Pt alloys with designated platinum contents in atomic percentages at 25 °C.

In Fig. 3 alterations of forms of resistivity/pressure(fugacity) relationships are preferentially represented [1] in terms of incremental changes (neglecting volume expansion corrections) of specific electrical resistivity ($\Delta\rho$) due to hydrogen introduction into each alloy in turn [1, 3, 15]. As salient features, it has been noted [1, 3] that the relationships of alloys with higher (more than 15%) Pt content alloys are coincident over sequences of increases and decreases of n (absorptions and desorptions), overlap one another in a consecutively similar way and have attained similar maximum values of $\Delta\rho$. On the other hand, the relationships for Pd and the alloys with 2.79, 5.73 and 8.8% Pt have asymmetric forms with lower maximum values of $\Delta\rho$ which increase from Pd up to $Pd_{91.20}Pt_{8.80}$, which would seem identifiable with regions of $\alpha \rightarrow \beta$ phase transition over which the β-phase regions have values of hydrogen content $n > 0.5$.

Analyses of high pressure studies have suggested that at pressures in the kilobar range, corresponding to substantially higher fugacities, the hydrogen content of palladium should asymptotically approach a value of $n = 1$ corresponding to a stoichiometric PdH composition with complete occupation of every octahedral site and so equivalent to a perfect sodium chloride structure [1, 3, 8, 11, 15, 23].

Similarity of derived forms of p–n relationships [1] for alloys with even 12.03% and 15.42% Pt to symmetrical forms with maximal values of $\Delta\rho$ at $n \sim 0.5$ combined with an appreciation of the essential structural similarity of α and β phases suggests that the $\Delta\rho$–n relationships for these and higher Pt content alloys could be quite closely approximated to by a common Nordheim type relationship in which incremental resistivity is proportional to n $(1-n)$ but in which the solute atoms are interstitial rather than substitutional in the case of a similarly symmetrical substitutional series such as the Pd/Pt series itself [1]. For a notional common maximum value of $\Delta\rho$ of 15 $\mu\Omega$ cm, slightly in excess of each of the curves in Fig. 1, such a relationship will take the particular form,

$$\Delta\rho = 60n(1-n) \qquad (1)$$

as plotted in Fig. 4.

In terms of an uncomplicated sequence of stages of $\alpha \rightarrow \alpha + \beta \rightarrow \beta$ phase structures with increasing hydrogen content, it could be expected that all of the α phase structure converts to the corresponding β phase with a composition corresponding to point B in Fig. 4. The maximum value of $\Delta\rho$ can be expected to be lower than that if n had been reached at point B by following the general curve through $\Delta\rho = 15$. However, still further addition of hydrogen in a homogeneous β phase should then have produced an immediate decrease. On the basis of incomplete conversion of all regions of α phase with composition corresponding to A (Fig. 4), the increases of the resistivity over regions DE in Fig. 1 can be understood in terms of further continuing $\alpha \rightarrow \beta$ phase conversion and accompanying, possibly preferred, gradual occupation of the remaining interstitial sites in the residual α-phase regions—somewhat analogously to the preferential reversion to this mechanism proposed to account for changes in the magnitudes of Zener type internal friction peaks with increases of hydrogen content in the case of studies of the Pd/Ag/H system [3, 24]. Since values of p are again increasing with n in this region, the corresponding increases of n in the remaining α phase regions will specifically produce increases of $\Delta\rho$, although any further increases of the hydrogen content in the converted β phase regions, including regions undergoing additional conversions, should be expected to be producing decreases.

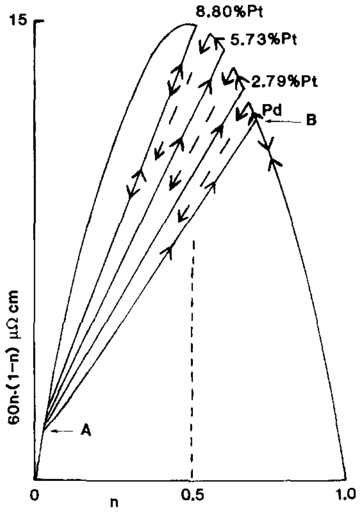


Fig. 4. Schematic representations of proposed sequences of alterations of incremental changes of specific electrical resistance ($\Delta\rho$) with increases and decreases of overall hydrogen contents (n) for Pd and designated Pd/Pt alloys at 25 °C.

Derivations of overall $\Delta\rho$–n relationships representing a continuing combination of α and β structures have been carried out on a basis of a continually pressure dependent alteration of relative combinations of the α and β phases that allow for pressure dependent changes in each of the phases separately according to the relationships

$$n_\alpha = k_1 p^{1/2} \qquad (2)$$

in α phase structures and

$$n_\beta = 0.70 + 1/k_2 \ln p \qquad (3)$$

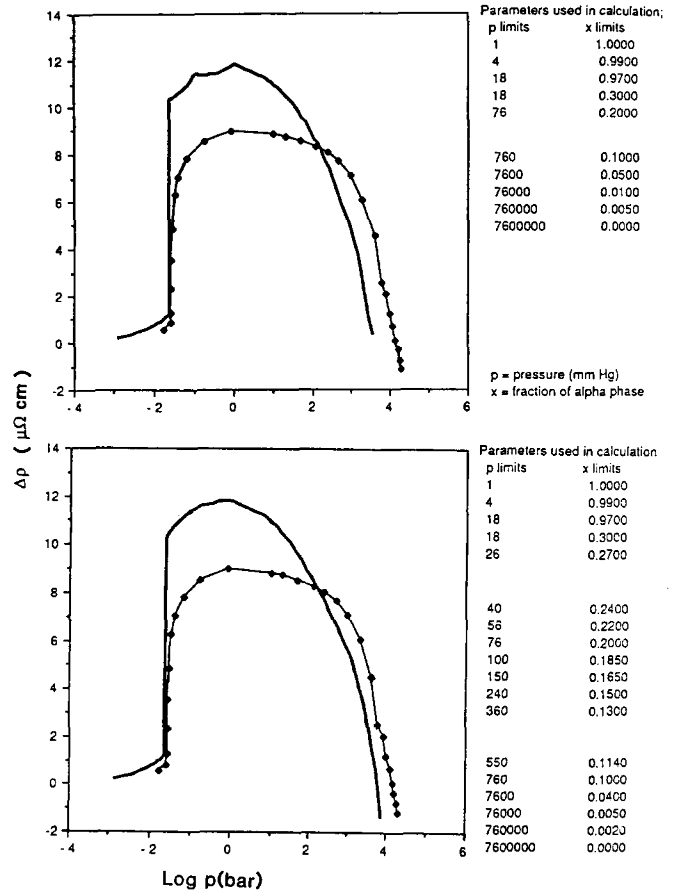
in β phase structures with values of $k_1 = 2.11\text{E-}3$ (25) and $k_2 = 38$ (26) (p in bar).

At selected pressures, the specific hydrogen contents, n_α and n_β corresponding to notional proportions of the two phases present at that pressure, were calculated through relations (2) and (3). The particular contributions to $\Delta\rho$ of each phase at n_α and n_β was then calculated through relation (1). A value of total $\Delta\rho$

was then obtained by summation of the assumed fractional contributions according to $n_\alpha + n_\beta = n$.

A computer programme has been prepared to allow comparisons of $\Delta\rho$–n relationships derived with gradually altering assumptions concerning proportions of the two phases present at particular equilibrium pressures. Examples of the form of derived relationships in the case of 'absorption' $\Delta\rho$–n relationships of the Pd/H system are shown in Fig. 5. It may be seen that the fit to the general form of the experimental relationships can be improved by using increasingly graduated changes of the fractions of α and β phases over narrower limits of pressure.

A point which follows from this line of argument and from the good degree of fit to the form of the experimental relationship, is that the existence of the flat maximum in the $\Delta\rho$–n relationships implies that a small fraction of α phase regions is still present in the Pd/H system at 25 °C up to pressures of approximately 50–100 bar which is thus out of precise keeping [8] with the assumptions that purely β phase regions are present at pressures greater than 1 bar, implied in utilisations of relationships such as eqn. (3).



Parameters used in calculation;

p limits	x limits
1	1.0000
4	0.9900
18	0.9700
18	0.3000
76	0.2000
760	0.1000
7600	0.0500
76000	0.0100
760000	0.0050
7600000	0.0000

p = pressure (mm Hg)
x = fraction of alpha phase

Parameters used in calculation

p limits	x limits
1	1.0000
4	0.9900
18	0.9700
18	0.3000
26	0.2700
40	0.2400
56	0.2200
76	0.2000
100	0.1850
150	0.1650
240	0.1500
360	0.1300
550	0.1140
760	0.1000
7600	0.0400
76000	0.0050
760000	0.0020
7600000	0.0000

Fig. 5. Comparisons of experimentally determined $\Delta\rho$–log p relationships (represented by symbols) between incremental changes of electrical resistance and equilibrium hydrogen pressures for the Pd/H system at 25 °C and plots generated by a computer programme based on proposed combinations of α and β phase regions as discussed in the text.

3. Hysteresis of electrical resistance–hydrogen content–hydrogen pressure relationships

Decreases towards a value of $n \simeq 0.5$ of hydrogen contents in β-phase regions over pressure invariant ranges would also seem to provide analogous underlying origins of patterns of trends illustrated in Figs. 1 and 2, in regard to R/R_0–n relationships exhibiting higher maximum desorption than absorption values of R/R_0. Thus, either in the case of the Pd/H system with increasing temperature (Fig. 1) or (for isothermal comparisons) with Ni, Rh [3, 15, 22] or Pt alloy contents (Fig. 2)—in both cases the value of n_β over the course of $\beta \rightarrow \alpha$ transitions will be lower than over the course of corresponding $\alpha \rightarrow \beta$ transitions and thus will tend to reduce more towards a value of $n = 0.5$ and correspondingly higher complementary values of resistivity.

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