The Hydrides of Palladium and Palladium Alloys

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In the second part of this article, concluded from the October issue of 'Platinum Metals Review', a short account is given of changes in the physical properties of palladium following absorption of hydrogen. The behaviour of certain palladium alloys is compared with that of palladium and alternative methods of approach towards an understanding of the constitution of the hydrides are briefly outlined.

Specimens of hydrided palladium for which equilibrium with gaseous hydrogen is inhibited can remain either in vacuo or in air for long periods without appreciable loss of absorbed hydrogen (8): very many of the physical measurements on palladium hydrides have been carried out under such conditions (2). However, particularly in the presence of oxygen, the loss of hydrogen may be subject to erratic behaviour and once begun can sometimes proceed very rapidly indeed (8). Although it is usual that, on completion of physical measurements, an analysis of the final hydrogen content is obtained either by using strong oxidising solutions (8, 9, 33) or by degassing in vacuo (10, 34, 36), this alone will give no absolute indication of the content at the time of measurement.

It is thus important in these circumstances that convenient, reliable and non-destructive physical measurements be developed to provide a continuous measurement of hydrogen content at all times.

Physical Properties of Palladium Hydrides

When compared to other solid systems the detailed measurement of physical properties as a function of hydrogen content is in principle especially convenient due to the ability of palladium to absorb large quantities of hydrogen without macro-disruption. How-ever, although scattered measurements have been reported on a variety of properties such as elastic constants, hardness, Hall coefficient and thermoelectric power (2, 29, 36, 37), the data available for most properties are generally not detailed over a wide range of hydrogen contents.

More complete studies have been made of changes in paramagnetism (12) which is found to decrease almost linearly with hydrogen content up to $H/Pd \sim 0.6$, and particular attention has been paid to changes of electrical resistance.

The salient features of the changes of relative electrical resistance, R/R_0 (R_0 is the initial, hydrogen-free, resistance) with hydrogen content (H/Pd, atomic ratio) at about 25°C are shown in Fig. 5. R/R_0 increases almost linearly with H/Pd until $H/Pd \sim 0.55$ with a definite change of slope at the termination of α-phase (10, 12). Beyond $H/Pd \sim 0.55$ there is enhanced disagreement between the results available (10): R/R_0 is believed to decrease (12, 14, 15) when the content exceeds $H/Pd \sim 0.7$.

Although a somewhat larger variation has recently been suggested (33), the R/R_0—H/Pd relationships appear to be almost independent of temperature (34), up to $H/Pd \sim 0.5$, within the range 0 to 100°C.

For reasons discussed in the first part of this article, electrolysis has often been em-

ployed to introduce hydrogen for resistance studies, and it is unfortunate that sources of error (31) in the measurement of hydrogen content have not been fully appreciated in many of the earlier and most detailed studies of the R/R_0–H/Pd relationships.

Errors in R/R_0 can also result from proton transfer effects (38, 39) during the application of the bridge (measuring) current in the relatively strong (1–2N) acid solutions which have generally been used as electrolyte and possible effects of *ab*sorbed oxygen (12, 40), which may be introduced during pre-annealing and activation of palladium must also be considered. Particularly since doubts that the removal of hydrogen is not always reflected by a change in R/R_0 now appear to be largely unfounded (10), resistance changes fulfil, in principle, several of the necessary requirements of a continuous analytical measure of absorbed hydrogen.

Palladium Alloy-Hydrogen Systems

Little work has so far been reported on alloys of palladium with a metal such as titanium or vanadium that is also capable of absorbing large quantities of hydrogen.

The information available has been largely restricted to the behaviour of alloys with metals which, by themselves, absorb very little hydrogen such as the other metals of Group VIII or silver or gold. (Although such alloys may form ordered lattices in certain composition ranges after prolonged annealing (40), the samples which have so far been used have almost certainly been in the form of supercooled solid solutions).

The hydrides formed by these alloys again show no tendency for macro-disruption. Regions of coexistence of α- and β-phase hydrides are still found at close to room tem-
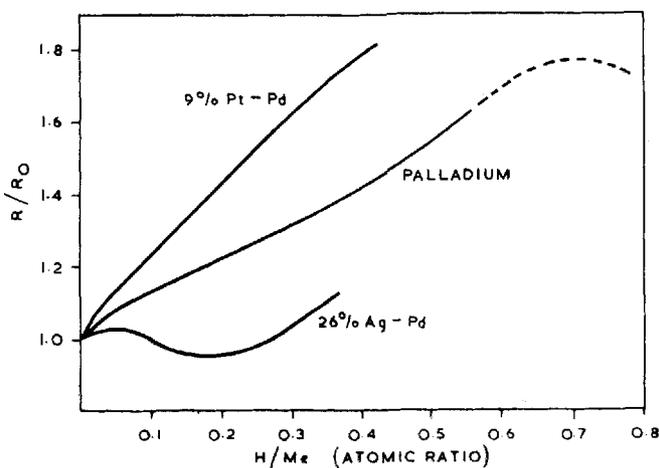

Fig. 5 Relationships between relative electrical resistance and hydrogen content

perature for the lower contents of alloying metal (2). Properties such as electrical resistance are altered by a similar order of magnitude to those of palladium although with minor differences. For example, with increasing platinum content (Fig. 5) R/R_0 increases more steeply (34) with hydrogen content than for pure palladium, and increases less steeply in the case of silver-palladium alloys (12, 41, 42). As is shown in Fig. 5 the resistance may actually decrease slightly with increasing hydrogen content over the region of α- and β-phase coexistence for certain silver alloys (42), cf. Fig. 7.

Aside from somewhat more complex behaviour found with the silver-palladium, and almost certainly with gold-palladium alloys, which are further discussed below, the general effect of a feebly absorbing metal is to reduce the equilibrium amount of hydrogen absorbed by the alloy to below the amount absorbed by pure palladium, when comparison is made at almost any temperature and pressure.

Apart from some early study by Sieverts (43) of the Pt-Pd-H, Ag-Pd-H, and Au-Pd-H systems (at temperatures of 138°C and above and at pressures up to one atmosphere), virtually no P-C-T data have been obtained for palladium alloy-hydrogen systems by direct equilibration with molecular hydrogen in the
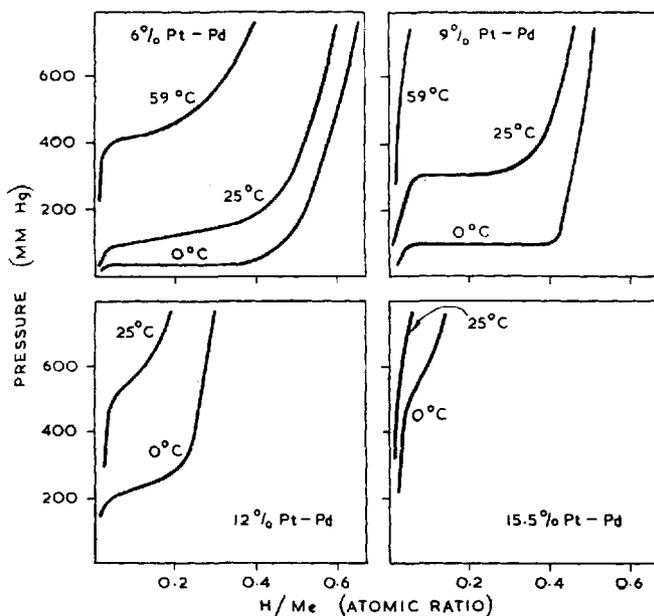
Fig. 6 Isotherms for a series of Pt-Pd-H systems

the chemical potential for the absorption of hydrogen, and by the use of the Clapeyron equation it has also been shown to reflect a decrease in the heat of absorption (44). In addition the P-C-T data indicates (Fig. 6) that the critical temperature and pressure for α and β-phase coexistence is also steadily reduced with increase of the platinum content of the Pt-Pd alloys (34, 44).

The behaviour of the Ag-Pd-H system is, however, somewhat more complex. For example, with increase in silver content, at about 25°C, the ratio of hydrogen atoms to the total number of metal atoms (H/Me) in the β-phase hydrides (over the region of α and β-phase coexistence) becomes progressively less than for pure palladium (H/Pd~0.57). Nevertheless, again over the corresponding ranges of α and β-phase coexistence, the equilibrium vapour pressure steadily diminishes with increase in silver content up to about 30 per cent (42, 45) (Fig. 7).

As a result, although with increasing silver content at about 25°C the amount of hydrogen, absorbed under a pressure of one atmosphere, decreases continuously from the amount absorbed by pure palladium, more hydrogen is retained by the alloys with up to 30 per cent silver when the pressure is reduced to about 16 mm. (Roughly the minimum vapour pressure for existence of the β-phase hydride of palladium at 25°C (42, 45).) It now seems clear that a consolidation of these data will give a complete thermodynamic justification for the experimental findings of Sieverts (43), that at higher temperatures (≥ 138°C) the amount of hydrogen absorbed by alloys with up to 30 per cent silver exceeds the amount absorbed by pure palladium, when compared at a pressure of one atmo-

gas phase. For the bulk of the experimental work which has been carried out the hydrogen has been introduced into the alloys by electrolysis: since, until recently, electrode potentials were not generally measured in conjunction it is not surprising that there has been disagreement between the results obtained (12). There has been particular controversy with regard to the behaviour of the Ag-Pd-H system (12).

Certain of the difficulties appear to have been resolved by some further P-C-T data which has more recently been derived from electrode potential measurements. Although the electrochemical data have so far been obtained only over a rather narrow temperature range around 25°C, it has been sufficient to indicate that the family of isotherms for each alloy that absorbs hydrogen have a similar general appearance to those of the Pd/H system (34, 44).

For the Pt-Pd-H system at 25°C it has been found that increase of platinum content is paralleled by a steady increase in the equilibrium hydrogen vapour pressure over regions where α and β-phase hydrides coexist (Fig. 6). This reflects a corresponding decrease in

sphere. In view, for example, of the complex Ag-Pd-H behaviour, it is important not to overgeneralise when discussing these alloy-hydrogen systems. However, it seems that the minimum atomic percentage of feebly absorbing metal which has to be added to palladium so that the resultant alloy does not absorb hydrogen with the evolution of heat (exothermic absorption) appears to be roughly correlated with oxidation number. For example, exothermic absorption appears to be unlikely for alloys with >35 atomic per cent platinum (44) (the most common oxidation states of Pt are +2 and +4). The minimum percentage of nickel or rhodium (for which +2 oxidation states are common) that has to be added to produce a non-exothermally absorbing alloy is somewhat higher than 35 per cent (46, 47) and about 70 per cent of either gold (with oxidation states of +1 and +3) or silver (with a common +1 oxidation state) have to be added to palladium to achieve the same purpose (12, 44). It has been suggested (44) that alloys which do not form β-phase hydrides within experimentally convenient pressure ranges at room temperature, but which can still exothermally absorb appreciable amounts of hydrogen in α-phase, may prove to have advantages over palladium for application as diffusion membranes.

Constitution of the Hydrides

It appeared from the results of experiments by Coehn and co-workers (12, 41) that, under an electrical potential gradient, hydrogen was transferred from the positive to the negative pole of a specimen of palladium hydride. It was, therefore, concluded that the hydrogen was present in the solid in the form of protons.

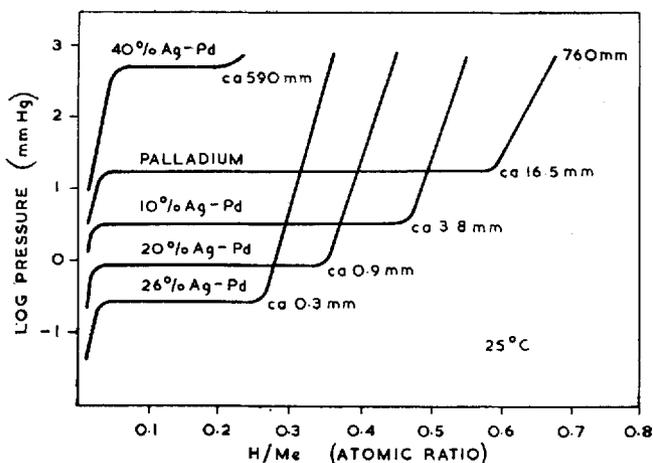These results could be conveniently incorporated into a simple picture of the Pd/H

Fig. 7 Isotherms for Ag-Pd-H systems at 25°C

system in terms of the electron band theory of solids. For example, if the electrons lost by the hydrogen atoms were accepted into vacancies which exist in the '4d' band of palladium, a plausible explanation could also be given of the seemingly linear decrease of the paramagnetic susceptibility of palladium up to H/Pd ∼ 0.55 (2, 48). As an extension of this picture it has been suggested that for H/Pd > 0.55 the electrons donated by hydrogen could be incorporated into the '5s' band of palladium (49).

As further support for this 'free proton' theory, a good matching of the experimental P-C-T data, including the region near to the critical temperature for α and β-phase coexistence, was obtained by a statistical thermodynamic analysis (49) which considered the interaction energy between the protons as a function of their concentration.

On the other hand, Coehn's interpretations of his experimental results have not gone unchallenged (39), and it may be claimed that similar changes of magnetic properties would result from other more usual forms of chemical union (37). It has also been pointed out that the 'free proton' theory has not allowed for any alteration of the electron bands of palladium which should result from the interatomic expansion when β-phase hydride is formed (50).

Since a system of resonating hydrogen bridge bonds has been suggested to account for certain features of uranium hydrides, this has helped to encourage a proposal (3) that the chemical binding in the Pd/H system may be of a more covalent type at temperatures below 0°C. Although the covalent model is advanced (3) as being complementary to the free proton model at higher temperatures a λ type specific heat anomaly observed at around 70°K has been suggested (3) to indicate local ordering to covalently bonded molecular units with a formula PdH_4. It is of interest to note that marked electrical resistance changes have also recently been reported (37) over the same temperature range as the specific heat anomaly.

An approach more diametrically opposed to the free proton theory is to consider the β-phase hydrides as ionic structures in which the hydrogen is present as negative ions. Some attention to this approach seems warranted if for no other reason than to examine any possible correlation between the hydrides of palladium and its alloys and other broad groups of solids.

Pressure-concentration isotherms of many chemical systems, including a number which comprise a transition metal and a more electronegative element such as oxygen and sulphur, show similarities with the Pd/H isotherms (51). The solid phases of these systems are likewise found to show marked divergence from stoichiometry and to exhibit considerable electronic conductance. Although detailed explanations are often complex, such behaviour is generally dealt with in terms of lattice vacancies or interstitial species in a reference stoichiometric crystal (51). There appears to be an increasing amount of evidence that the hydrides of other transition and rare earth metals can be included in this general group (52).

The Pd/H system has generally been somewhat set apart, even from the other 'exothermic' transition metal hydrides. This seems due both to the apparent success of the 'proton gas' model and to the superior resistance of palladium to disruption by hydrogen. It does appear, however, that the similarities of features such as the P-C-T data and electrical properties to those of the remainder of the transition metal hydrides may be at least as important a consideration. It is thus of interest to note that interatomic distances in several transition metal hydrides are compatible with the hydrogen being present as negative ions (53, 54, 55).

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