The Palladium-Hydrogen System

A SURVEY OF HYDRIDE FORMATION AND THE EFFECTS OF HYDROGEN CONTAINED WITHIN THE METAL LATTICES
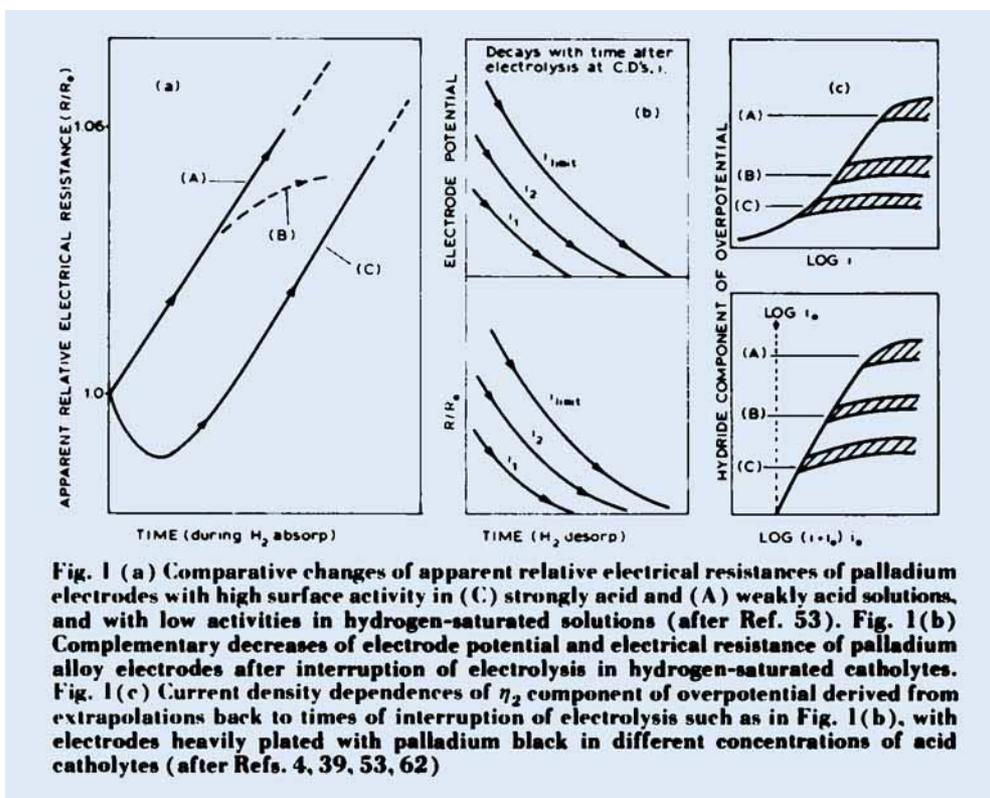
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A very substantial amount of additional information has been published concerning hydrides of the platinum group metals over the two decades since the hydrides of palladium and palladium alloys were the subject of an earlier review article in this Journal. In addition to the many articles in the general literature, the subject matter has formed a major part of the programmes of several scientific conferences and of a number of books and monographs appearing over this period. Furthermore, silver-palladium diffusion tubes are incorporated into hydrogen generators built by Johnson Matthey, and utilised for such diverse applications as the hydrogenation of edible oils, manufacture of semiconductors, annealing of stainless steel and the cooling of power station alternators. In view of the considerable interest being shown in both theoretical and technical aspects of these systems this unusually long review is presented, and will be published in parts during the year.

Over recent years there has been a substantial expansion of research activity in the field of study of metal-hydrogen systems. In addition to intrinsic academic interests, this expansion has also stemmed from aspects of technological importance such as the effects of hydrogen on the mechanical properties of metals, and of the purification and storage of hydrogen to be used as a general chemical reagent or as a fuel.

Although it can by no means be wholly separated from the fields of adsorption and catalysis [1], and although the term "transition metal hydrides" has been applied to include molecular complexes of transition metals which include hydrogen in their structures [2]—the subject area of metal-hydrogen systems seems most generally accepted to be concerned with the effects of the subsurface incorporation of hydrogen within metal lattices, either in solid solution, or in the formation of hydride phases. With regard to hydrogen systems of the six platinum metals and their companion elements, iron, cobalt and nickel, in terms of such a rough demarcation of area of interest, studies of the hydrides of palladium and its alloys have continued to dominate the field of investigation over the interval since an initial review article on these systems in *Platinum Metals Review* [3]. Publication of an expansion [4] of this review coincided quite closely with the appearance of a collection of articles [5] commemorating the centenary of the initial observations of the absorption of hydrogen by palladium; and with the appearance of other books concerning metal-hydrogen systems, which generally have included information about various aspects of the palladium-hydrogen system [6–11].

Subsequently the palladium-hydrogen area of research has formed the major part of the programmes of relatively small and informal conferences in Europe [12], which later developed into a series of more extensive and comprehensive meetings [13–16]. An important series of review articles concerning metal-hydrogen systems has been published quite recently [17], including one dealing specifically with aspects of palladium- and palladium alloy-hydrogen systems to which further reference

Fig. 1 (a) Comparative changes of apparent relative electrical resistances of palladium electrodes with high surface activity in (C) strongly acid and (A) weakly acid solutions, and with low activities in hydrogen-saturated solutions (after Ref. 53). Fig. 1(b) Complementary decreases of electrode potential and electrical resistance of palladium alloy electrodes after interruption of electrolysis in hydrogen-saturated catholytes. Fig. 1(c) Current density dependences of η_2 component of overpotential derived from extrapolations back to times of interruption of electrolysis such as in Fig. 1(b), with electrodes heavily plated with palladium black in different concentrations of acid catholytes (after Refs. 4, 39, 53, 62)

will be made below. Significant numbers of papers concerning the palladium-hydrogen and allied systems also have been included in programmes of other conferences centred on metal-hydrogen systems in which the major emphases have been those of low temperature phenomena (18) embrittlement and fracture, or of hydrogen utilisation and storage (19).

The various studies of the palladium-hydrogen system have been concerned both with improvements and extensions of knowledge concerning experimental parameters which had already been extensively studied, as well as with new types of experimental measurements. Significant increases also have been made in the quantity and variety of information concerning various palladium alloy-hydrogen systems; and this has seemed to be a valuable source of guidance with regard to possibilities of, and/or explanations of hydride formation by the remainder of the platinum group and by other transition metals.

Determining the Hydrogen Contents of Palladium and Palladium Alloys

In all aspects of measurements, the problems of being able to obtain as exact as possible a knowledge of the hydrogen content of the specimens of palladium and palladium alloys have continued to be most important considerations.

For measurements involving establishments of equilibria with gaseous hydrogen, contents have continued to be calculated from accurately determined changes of volume and pressure (20–24) and have quite recently been extended up to very high pressure ranges (25) which present particular experimental difficulties.

Direct measurements of weight changes also have been applied relatively recently in such pressure-composition studies (26,27). Determinations of hydrogen content from direct weighings of specimens also recently have been applied conveniently in measurements of
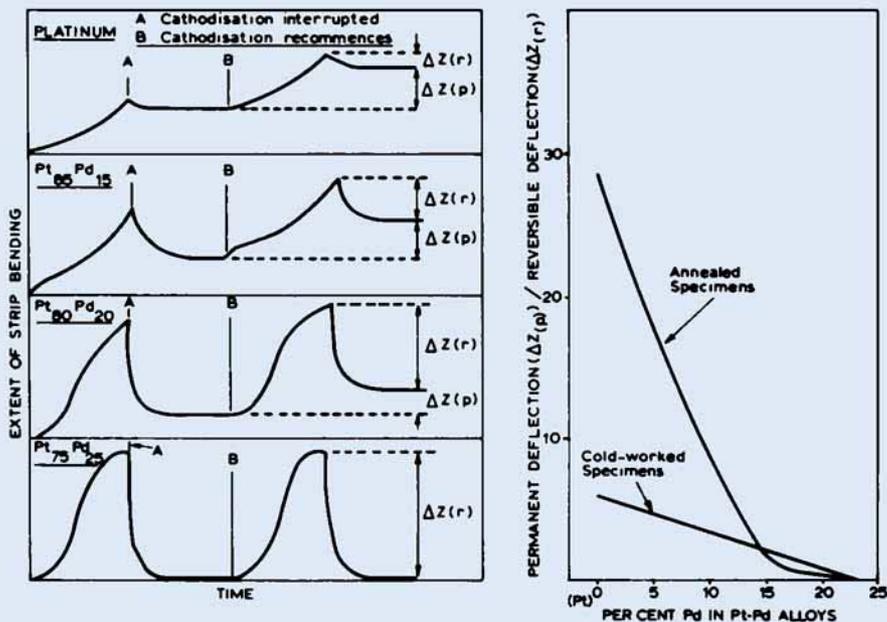
Fig. 2 Comparative extents of reversible $\Delta Z_{(r)}$ and irreversible $\Delta Z_{(p)}$ components of bending of strip cathodes (after Ref. 59)

physical properties—particularly in studies with relatively large specimens which can be conveniently handled and removed from their connections as, for example, in certain studies related to structural, elastic and anelastic properties (28–34).

Changes of hydrogen content and particularly continuous changes during experiments also have continued to be determined from conjoint measurements of a suitable parameter which is an already known function of the content. Such parameters have included equilibrium pressure (35), dimensional changes (36), integrals of time dependent functions of electrode potential (37–39) and electrical resistivity (37–40).

Electrical resistivity measurements have continued to be found useful for following the kinetics of absorption and desorption of hydrogen (41–43) but in gas phase studies (44) a piezoelectric technique (45) has been recently applied in which changes of content have been followed by variations in vibration frequency of a palladium-coated quartz crystal which can be related to changes of weight.

For certain studies however it has continued to be impractical continuously to monitor hydrogen contents in the course of experimental measurements. Examples include measurements at very low temperatures and with particularly high contents of hydrogen which, in addition to electrolytic techniques discussed below, have been introduced under high pressures or else by ion implantation techniques (46). In these cases the contents of hydrogen during the measurements have been estimated by reduction of standard solutions of oxidising agents (37,47) or by vacuum outgassing at the conclusion of experiments (4,31,33,45,46,48,49). For this to be possible, the hydrogen contents of such specimens have to be temporarily maintained by an inhibition of the surface kinetics, and this may be deliberately aided by surface platings with metals such as copper or gold (50), or in some instances by adsorption of iodine

(33,40,51–53), which has the advantage of being quite readily removed again.

Electrolytic Studies Involving Aqueous or Alcoholic Solutions

Electrolytic methods have continued to be used in a number of instances as convenient means both of hydrogen introduction and also for effecting gradual reductions of hydrogen contents (34,55). Surface conditions of very different levels of catalytic activity for the formation and dissociation of hydrogen molecules have been employed in the various studies.

For specimens into which it may have been desired to introduce and retain high contents of hydrogen, either no surface activation procedure at all has been employed (34), or indeed inhibitors (56) of surface hydrogen combination reactions have been added to the electrolyte (3,40,45,50,57–60). Electrolysis in alcoholic solutions (49,61) at quite low temperatures has effected the introduction of particularly high hydrogen contents into palladium. In the case of such catalytically inhibited surfaces, it does not seem to be possible (4,39,45) accurately to relate components of electrode potential with hydrogen chemical potential, although estimations of hydrogen chemical potentials within surface-inhibited electrodes of palladium alloys have been derived from measurements of electrical resistivity (39,62). A series of studies of the open circuit potential of palladium electrodes following cathodisation in solutions containing surface inhibitors however, has been published recently (60). Nevertheless it has been a continued finding in electrochemical studies (4,39) that electrode potentials, which can be reliably equated with hydrogen chemical potentials, are only measureable under experimental conditions where surface kinetics are sufficiently rapid for the transport of dissolved molecular hydrogen to and from the electrode surface to be kinetically governing the values of electrode potential. This conclusion appears to be endorsed by recently reported results of studies in a series of acidified alcohols (63) in which particularly high hydrogen solubilities can be attainable. Such a sufficiently high surface activity can be obtained by the temporary formation of an easily reducible oxide layer, produced either by anodisation or relatively low temperature heating in oxygen (4,39,53). Often a highly active surface can be attained more reliably and conveniently by the electrodeposition of a thin layer of palladium black (4,37–39,47,62–65). Even thin layers have been found to retain a sufficiently high activity for a whole series of experiments (47,63) over which hydrogen can be absorbed several times to β-phase concentrations followed by its removal in oxygen-saturated solutions.

Examples of results with such specimens of studies of relationships between current densities of electrolysis, i, and the hydride component of hydrogen overpotential are shown in Figure 1(c). Values of this component (η_2) of overpotential have been calculated (4,39) from extrapolations of plots against time of open circuit electrode potentials and electrical resistivities following interruption of electrolysis, such as those shown in Figure 1(b). The linear plots in Figure 1(c) against the function log i + i_o are diagnostic of a control of η_2 by the rate of transport of evolving hydrogen molecules from the cathode—and limiting upper values of η_2 are found to correspond with the onset of general hydrogen bubble evolution (4,39) which for specimens coated thickly with palladium black, have shown a strong dependence on the acid strength of the catholyte (39,62). These findings have led to the development of explanations based on initial discharge of hydrogen at preferred sites and on an importance of the role of local cell hydrogen transfer processes in equalising surface hydrogen chemical potentials (39,62). Consideration of these concepts also has been found to provide explanations of the extents of electrolytic separation of hydrogen and deuterium isotopes by palladium electrodes and of the activity of palladium surfaces for isotope exchange reactions with the surrounding solution (39,53). For example, somewhat higher efficiencies in these regards have been related to apparent decreases of the electrical resistivities of palladium wires in acidic catholytes, of which
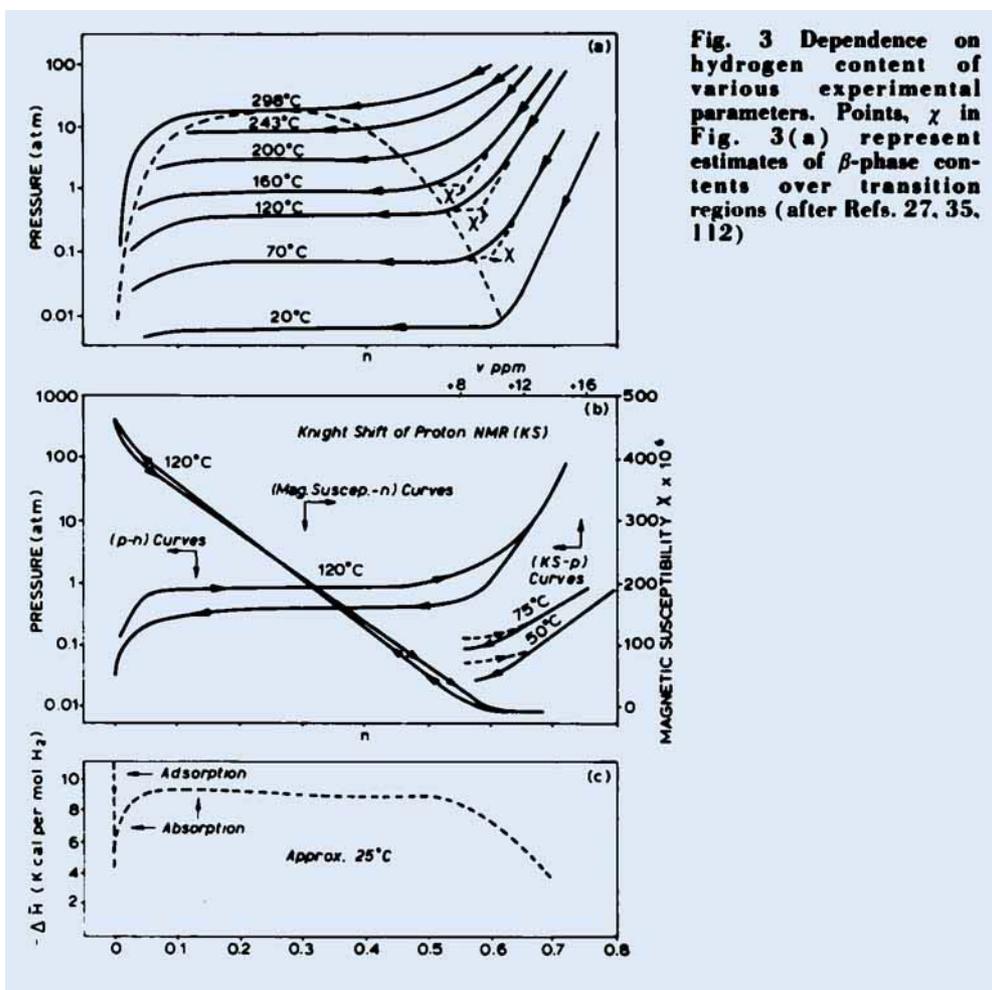
an example is illustrated in Figure 1(a), and which have been associated (4) with conditions of low impedances for local cell hydrogen transfer processes.

Considerations of various aspects of surface heterogeneity have received increasing attention in regard to studies of the kinetics of hydrogen absorption by palladium from the gas phase (1,43) and have also produced interest (39,54,64) as to the extents to which total hydrogen overpotentials may contain contributions associated with high hydrogen chemical potentials at the initial discharge sites. Allied interest also has continued in the general area of study of low voltage hydrogen concentration cells, analogous in operation to surface local

cells, as a means of hydrogen storage (65,66) and of hydrogen isotope separation (67).

Electrolysis with Platinum and High Platinum Alloys: Blistering

Plots in Figure 1(c) correspond with the finding that for catalytically highly active cathode surfaces, the upper limiting values of the hydride component of overpotential corresponding to the general onset of hydrogen bubble evolution effectively limits hydrogen chemical potentials to equivalent hydrogen pressures of about 100 atmospheres. The reduction of surface activity by inhibitors as mentioned above, can however lead to development of internal hydrogen chemical potentials

equivalent to some thousands of atmospheres (39,50,62). In the case of platinum at temperatures near 25°C, studies with Pd-Pt alloys (45,50,68,69) have indicated that even such high pressures are likely to introduce only very small contents of hydrogen into the platinum bulk lattice. These low contents have however been sufficient to permit calculations of hydrogen diffusion coefficients either by permeation techniques (57) or from dilation-induced "diffusion-elastic" bending effects produced by hydrogen entry at one side of metal strips (58,59). Figure 2 shows, however, that in addition to the small "reversible" bending associated with bulk lattice hydrogen solubility, there is an accompanying irreversible distortion of platinum strips. This is associated with the development of "blisters" (59) resulting from equivalent high pressures of hydrogen gas developed within voids. Figure 2 also illustrates how the irreversible distortion, and accompanying blistering (59), is reduced by alloying additions of palladium—which also lead to increases in the reversible component of the bending, associated with complementary higher lattice hydrogen solubilities (50,68,69).

Catalytically Active, Hydrogen Transmitting Palladium Layers

In addition to providing an activated surface for palladium itself, electrodeposited layers of palladium black also have been effectively applied to further series of palladium alloys (4,37,70–83) in order to provide an intermediate region for transmission of hydrogen at closely similar chemical potentials to the substrate. Direct electroplating of palladium on to other hydride-forming metals is complicated by the presence of oxide layers, although for example an efficient contact to zirconium (84) seems to have been effected by subsequent high temperature annealing. Alternatively layers of palladium or palladium alloys have been contacted to niobium and tantalum by shock impact (85) or by vacuum evaporation after flash cleaning (86–88). These palladium overlayers, on which a further layer of palladium black may then be deposited, have enabled

hydrogen diffusion coefficient measurements in the substrates (86,89), and determination of pressure-composition (p–n) relationships (38).

Equilibrium Hydrogen Pressure versus Composition Relationships

Several further studies of equilibrium hydrogen pressure (hydrogen chemical potential) against composition (p–c(n)) relationships of the palladium-hydrogen(deuterium)(tritium) system have been reported in recent years for specimens in a wide variety of forms, including: powders (23,25,27,35), sponge (90), evaporated and support-dispersed films (91–93), pellets (35), chips, strips, foils and sheets (21,22,24,26,27, 94), wires, rods and bars (20,24,36).

In continuation of an important earlier series, a further extensive sequence of p–n (hydrogen:palladium atomic ratio) relationships has been reported by Frieske and Wicke (27) at temperatures up to 300°C and pressures of up to 140 atmospheres, over the course of increases (absorption) and decreases (desorption) of hydrogen content. Examples of the desorption series are shown in Figure 3(a), and a further extension up to 350°C has very recently been reported by Wicke and Blaurock (27). Studies in this range of temperatures and pressures are of interest in regard to estimation of the critical temperature and pressure with respect to regions of hydrogen content where α and β hydride phases coexist and a related set of p–n isotherms in good agreement have been derived by de Ribaupierre and Manchester (36). Also in this range of experimental parameters measurements have been reported by Picard, Kleppa and Boureau (22) at pressures up to 34 atm, at 245–352°C. Another study of p–n relationships was made for $Pd_{90}Ag_{10}H_n$ (26) where an analogous region of seeming criticality for α and β phase coexistence occurs over lower temperature and pressure ranges (4,37,95–98).

In the next issue of this journal Dr. Lewis' review of the relationship between equilibrium pressure and composition will be concluded, and other aspects of the hydrogen-palladium system will then be introduced and considered.

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