Formation of β-Phase Hydrides by Palladium–Cerium Solid Solutions

By William D. McFall, Trevor C. Witherspoon, and Frederick A. Lewis*
(*Chemistry Department, Queen's University, Belfast* BT9 5AG, *Northern Ireland*)

Summary Measurements are reported of the absorption of hydrogen by Pd–Ce alloys at 25 °C and results are discussed with reference to a model in which the forms of pressure–composition relationships are related to lattice strain effects.

It has recently been shown[1] that palladium can accommodate up to *ca.* 10 atomic % of cerium in the form of solid solution, and that Pd–Ce alloys have desirable characteristics as hydrogen diffusion membranes. Since cerium is a characteristic member of the inner transition elements which at any given reference pressure, absorb much higher equilibrium contents of hydrogen[2] than palladium,[3] it was of interest to obtain hydrogen pressure–composition relationships for these alloys.

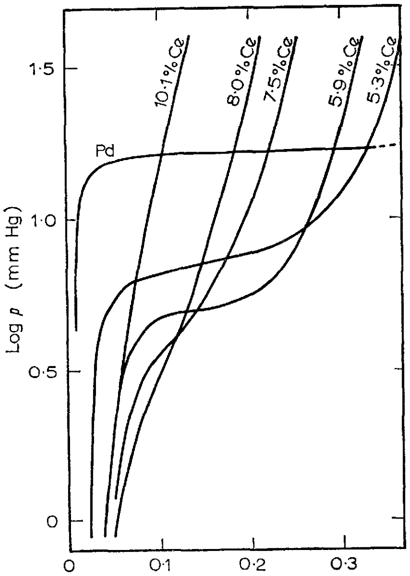

Figure 1. *Comparison of 'absorption' pressure–composition relationships for* Pd *and* Pd–Ce *alloys at* 25 °C.

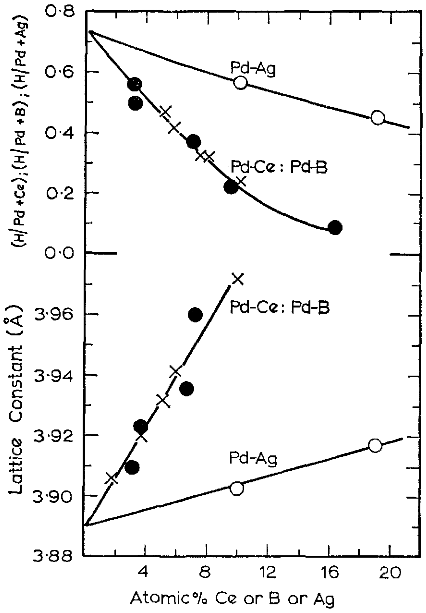

Figure 2. *Comparison of changes with alloy composition of lattice constants*[1,4,6] *and solubilities of hydrogen under* 1 *atm. pressure at* 25 °C. Pd–Ce, X; Pd–B, ●; Pd–Ag, ○.

Alloys were provided by Dr. I. R. Harris[1] and Johnson Matthey and Co. Specimens were thin strips 0·012 cm thick and *ca.* 10 cm long. Activation for absorption of molecular hydrogen from hydrogen-saturated dilute acid solutions was by electrodeposition of thin layers of palladium black.[4] Other experimental arrangements were also similar to those described previously.[4] Measurements were at 25° C. Concurrent measurements of changes with time of electrical resistance and electrode potential were made during absorption of hydrogen; and relationships between hydrogen content and hydride vapour pressure derived under conditions where the kinetics of hydrogen absorption were governed by diffusive transport through the Brunner Nernst layer.[4]

The general form of the pressure–composition relationships shown in Figure 1 is similar to those of the Pd–Ag–H[3,5,6] and Pd–B–H[3,4,7] systems, in that with increasing cerium content, there is a decrease of the steady state pressure over the pressure invariant ranges of hydrogen contents corresponding to an $\alpha \rightarrow \beta$-phase hydride transformation.[3] Figure 1 also shows, in keeping with X-ray results of Wise, Farr, and Harris,[1] that with increasing cerium content there is a continuous narrowing of the transition (two phase) region. These systems will therefore exhibit maxima[4,6] in relationships between hydrogen solubility and alloy composition at reference pressure below that corresponding to the $\alpha \rightarrow \beta$-phase transformation for the Pd–H system. However when comparisons are made at higher reference pressures, addition of cerium is shown to have effected a rather sharp reduction of the solubility of hydrogen which closely parallels the effect of added boron—despite the fact that over a wide range of reference pressures, (including those relevant to Figure 1) cerium itself absorbs considerably higher contents of hydrogen than palladium.[2,3]

Although cerium and boron are formally in the same periodic group, the marked differences in their physical properties and general chemistry (particularly in regard to the forms of their products of combination with hydrogen) make it highly unlikely that they would behave equivalently in terms of any donation of electrons to the palladium band structure.

An increase of the lattice constant of the Pd–Ce alloys with increasing cerium content shown in Figure 2 is compatible with its substitutional presence as a basically atomic (metallic) entity and not the much smaller tripositive ion.[2] Evidence however suggests that boron forms an interstitial alloy with palladium,[8] and difficulties in reconciling the behaviour of the Pd–B–H system with an electron band model have already been pointed out.[4]

Although there is increasing general evidence[2] that most alloying elements (rhodium now seeming a probable exception[9–11]) adversely affect the absorption of high concentrations of hydrogen, it seems reasonable[12] that alloying elements giving rise to expansive straining of the palladium lattice will cause a decrease in the volume of adjacent interstices and so make their occupation by hydrogen more difficult from steric and mechanical standpoints.

A good correlation between decreasing hydrogen solubility and increasing lattice parameter—anticipated as reflecting a summation of strain—is indicated in Figure 2 for alloy series where the hydrogen pressure over the $\alpha \rightarrow \beta$-phase transformation is lower than for pure palladium, and so for which a comparison of solubilities at one atmosphere pressure may be regarded as reasonably equivalent.

Because of the initial 'supplementary' strain introduced by alloying elements which produce an increased averaged lattice parameter, it can be suggested that a reduced amount of additional strain will be required from the absorbed hydrogen to initiate an $\alpha \rightarrow \beta$-phase transformation.[13] It therefore seems possible to account on this basis for the lower chemical potentials of hydrogen at which such phase transformations occur in these alloy systems.

(*Received*, 5*th May* 1972; *Com.* 762.)

[1] I. R. Harris and M. Norman, *J. Less Common Metals*, 1968, **15**, 285; J. P. G. Farr and I. R. Harris, B.P. Appl. 25512/70; M. L. H. Wise, Ph.D. Thesis, Birmingham 1971; J. P. G. Farr, I. R. Harris, and M. L. H. Wise, to be published.

[2] *Cf.* W. M. Mueller in 'Metal Hydrides,' ed. W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, Academic Press, New York, 1968, p. 384.

[3] *Cf.* F. A. Lewis, 'The Palladium/Hydrogen System,' Academic Press, London and New York, 1967.

[4] *Cf.* R. Burch and F. A. Lewis, *Trans. Faraday Soc.*, 1970, **66**, 727, which also gives references to other experimental detail.

[5] H. Brodowsky and E. Poeschel, *Z. physik. Chem. Neue Folge*, 1965, **44**, 143.

[6] A. W. Carson and F. A. Lewis, *Trans. Faraday Soc.*, 1967, **63**, 1453.

[7] H. Husemann and H. Brodowsky, *Z. Naturforsch.*, 1968, **23a**, 1693.

[8] K. D. Allard, T. B. Flanagan, and E. Wicke, *J. Phys. Chem.*, 1970, **74**, 208.

[9] J. C. Barton, J. A. S. Green, and F. A. Lewis, *Trans. Faraday Soc.*, 1966, **62**, 960.

[10] H. Brodowsky and H. Husemann, *Ber. Bunsengeselleschaft Phys. Chem.*, 1966, **70**, 626.

[11] T. B. Flanagan, B. Baranowski, and S. Majchrzak, *J. Phys. Chem.*, 1970, **74**, 4299.

[12] *Cf.* C. Wagner, *Acta Met.*, 1971, **19**, 843.