

# Current Research on the Palladium-Hydrogen System

PAPERS AT THE SECOND INTERNATIONAL CONGRESS

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*Activity in the field of study of hydrogen in metals continues to increase, and there has been a complementary sustained interest in both practical and theoretical aspects of the high solubility and diffusivity of hydrogen in palladium and certain of its alloys. This article reviews some of the relevant papers presented at the conference on "Hydrogen in Metals" held in Paris in June.*

In recent years the upsurge of interest in the possible future use of hydrogen as a major practical energy source has been paralleled by increased activity in the field of research of hydrogen in metals. Preliminary notice was given in Paris of a number of further conferences that had been planned for the next two years, and the number of papers presented at the June Congress (1) was almost double the number given at the first Paris Congress in 1972.

Although a major proportion of these papers were again concerned either directly or indirectly with the, often damaging, effects of hydrogen on the mechanical properties of iron and steels, there was also a significant increase in the number of papers dealing with the absorption of hydrogen by other metals—including those known to form crystallographically distinct hydride phases. Of these papers, approximately twenty dealt with various aspects concerning the absorption of hydrogen by palladium or palladium alloys. These taken together with papers presented at the 1976 Birmingham conference (2, 3) represent a broad cross-section of current research effort in this area of study which, in earlier years has been one of the central topics both in small informal conferences (4, 5) and

in the much larger international conference held at Jülich in 1972 (6).

## Diffusion of Hydrogen in Palladium and Palladium Alloys

The rapid diffusion of hydrogen in palladium and its alloys continues to be of interest both from mechanistic and practical standpoints. Paper 1C7 by V. A. Goltsov, V. V. Latyshev, V. I. Koshel and N. I. Timofeyev (Donetsk) and paper 1C1 by V. A. Goltsov and L. I. Smirnov dealt with both aspects. For practical hydrogen diffusion membranes, an important object of alloying palladium with other metals is to reduce the critical temperature governing hydride phase transformations, and so effectively eliminate hysteretic effects which produce dimensional changes and deformation in cycles of absorption and desorption of hydrogen.

As recently reviewed by Knapton (7) it is also desirable to retain high values of hydrogen solubilities and diffusion coefficients combined with high surface catalytic efficiency and satisfactory mechanical properties in regard to both manufacturing and working conditions. It was clear from Paper 1C7 that commercial alloys may now consist of complex combinations of several alloying elements. In

view of the concerted effort in this area by the Donetsk group, it is not surprising that attention should also have been paid to mechanistic aspects of the diffusion process in Paper 1C1. Here, quasi-liquid behaviour of some of the hydrogen interstitials was proposed to account, among other features, for the frequent finding in these systems that the deuterium diffusion coefficient can exceed that of hydrogen at relatively low temperatures.

The direction of electromigrative diffusion of hydrogen within palladium under a potential gradient has long been a central issue in discussions concerning the relative protonic or anionic nature of hydrogen in palladium. A. Hérol, J. C. Rat and J. F. Mareché (Nancy) have reported in Paper 1C2 the reverse effect of the development of a potential difference as the result of diffusion of hydrogen along a palladium foil at 600°C; and in Paper 1C9 have reported the results of an extensive series of measurements of the electromigrative diffusion of both hydrogen and deuterium in a series of Pd-Ag alloys over the temperature range 200 to 800°C.

Within the last decade, anelastic phenomena, such as internal friction and elastic after-effect measurements, have been applied for measurements of hydrogen diffusion coefficients and for the study of stress dependent lattice rearrangements (2, 3). Paper 1C4 by H. A. Goldberg and F. D. Manchester (Toronto) has suggested how anelastic knowledge in regard to the critical point regions of the Pd-H, Pd-D and Pd-T systems, can be applied in a device designed to detect very small concentrations of the heavier isotopes in isotopic mixtures.

### **Thermodynamic Parameters and Problems of Lattice Structure**

Also in recent years, a considerable volume of increasingly detailed information has been obtained concerning hydrogen pressure-composition relationships combined with determinations of heats, entropies and free energies of hydrogen adsorption as a function of the hydrogen content of both pure pal-

ladium and many palladium alloys. Paper 1C3 by T. B. Flanagan, G. Gross and J. D. Clewley (Vermont) concerning the derivation of thermodynamic functions at vanishingly small hydrogen contents for the Pd-Fe-H system, was a further addition to several previous allied studies from this source in which special attention has been paid to errors in lattice solubilities which can arise from additional hydrogen solubility in dislocation networks (3). Measurements of magnetic susceptibilities and activation energies for hydrogen diffusion were also reported in 1C3.

The general increase in detailed thermodynamic equilibrium solubility information has been accompanied by continued parallel efforts to account for the information in terms of structural models which take consideration both of changes of electronic structure and of the energies of often localised lattice expansion in the non-stoichiometric structures (8). In Paper 2A7 R. B. McLellan (Houston) discussed evidence which was indicative of effects resulting from significant conjoint hydrogen occupation of octahedral and tetrahedral sites in the palladium lattice. The need to take into account the probability of varying degrees of order in palladium alloys, and a sequential measure of preferred interstitial site occupation by hydrogen, was the subject of Paper 2A11 by W. A. Oates and R. Ramathan (Newcastle, N.S.W.) which was particularly concerned with the well documented Pd-Ag-H system as a special case.

### **Low Temperature Studies and Electronic Structure**

Despite the complications arising from localised lattice expansion effects, estimates of the changes in the electronic band structure of palladium as a consequence of hydrogen adsorption, continues to be an active area of elegant experimentation and theoretical argument. From the results of calculations of Fermi Surfaces based on measurements of de Haas—van Alphen oscillations of magnetic torque as a function of magnetic field at 1.3K,

R. Griessen, W. J. Venema, J. K. Jacobs and F. D. Manchester (Amsterdam and Toronto) have suggested in Paper 2C7 that electrons which may be donated at low values of the atomic ratio, H-Pd, do not enter the 4d electron band of palladium.

Interest continues in the measurement and interpretation of the electrical conductivities of palladium and palladium alloys containing high contents of hydrogen, with some particular emphasis on studies of superconductivity and residual resistivity at low temperatures. Correlations between the critical temperature  $T_c$  corresponding to superconducting transitions and surface impedance measurements have been reported in Paper 2C12 by C. Alquié, B. Rivière, A. Kreisler and J. P. Burger (Paris). In Paper 1D11, B. N. Ganguly (Webster) had discussed the likely importance of both anharmonicity of phonon frequencies due to the presence of hydrogen, and of tendencies towards superlattice ordering in palladium alloys, with reference to the known variation of  $T_c$  in various palladium alloy/hydrogen (deuterium) systems.

A method of introducing large contents of hydrogen by a low temperature electrolysis technique which was employed for the studies reported in 2C12, was also used by B. Souffaché and J. P. Burger (Paris) in studies of changes with hydrogen content of the electrical resistance and magnetic properties of Pd-Fe, Pd-Ni, Pd-Pt and Pd-Ag alloys, which were reported in Paper 2A8. The same method of hydrogen leading was also used by S. Senoussi and J. P. Burger who have reported measurements in Paper 2A9 of residual and Kondo resistivities at temperatures down to below 2K for palladium alloys with low (0.1 per cent) contents of iron, cobalt and nickel but with high contents of hydrogen.

Large hydrogen contents may be homogeneously introduced into palladium by using high hydrogen pressures (9). In studies of electrical resistivities down to 20K reported by A. Gorska, A. Gorski, J. Igalson, A. J.

Pindor and L. Sniadower (Warsaw) in Paper 2A10, the pressures had an upper limit of only 1600 atmospheres, but specimens containing up to  $\text{PdH}_{0.909}$  could then be cooled in situ during the resistivity measurements, which were designed to obtain information concerning the relative importance of optical and acoustical phonon-electron interactions.

### **Use of Palladium in Counteracting Hydrogen Embrittlement**

Two papers were presented which had relevance to the recent interest in the improved resistance of steels to hair-line cracking or flaking, which is effected by addition of palladium (10). In Paper 4A2, L. A. Chigirinskaya, G. P. Chernova and N. D. Tomashov (Moscow) have reported substantial reduction of the penetration of electrolytically evolved hydrogen into steels, which either contained palladium as an alloying additive, or had been plated with palladium. In Paper 1C8, A. Sawatzky and G. A. Ledoux (Pinawa, Manitoba) have discussed the thermodynamic and kinetic considerations which govern the promising possibility of preventing serious hydrogen embrittlement of zirconium tubes, by plating palladium on to the surface remote from hydrogen entry.

### **Studies of Hydrided Palladium Surfaces**

A general recent trend has been towards the use of increasingly pure and defect-free experimental specimens. Using carefully annealed palladium single crystals in a study of the  $\beta \rightarrow \alpha$ -phase transition with high resolution electron microscopy, E. Ho, H. A. Goldberg, G. C. Weatherley and F. D. Manchester (Toronto) have shown, amongst other features reported in Paper 2B3, the topographical growth of  $\alpha$ -phase dendrites along crystallographic directions which seemed in keeping with considerations of the stresses involved.

Interest also continues in the study of hydrided palladium electrode surfaces (5, 11).

In Paper 1C6 by J. P. Dalbera, C. Hinnen, P. Lengler and A. Rousseau (Meudon-Bellevue) the potentiodynamic sweep measurements of this group have been augmented by spectrophotometric studies and it has been shown that this latter technique can be employed as a useful indicator of changes of hydrogen content. In regard to components of hydrogen overpotential at palladium cathodes, there now seems fairly general acceptance that the  $\eta_2$  components of overpotential at highly active cathode surfaces, represents an overall surface hydrogen chemical potential governed by the diffusive transport of dissolved hydrogen molecules through the interfacial layer of solution. There is, however, much less general agreement concerning the origin of the  $\eta_1$  component (12). In Paper 5A2 by F. A. Lewis (Belfast) attention was drawn to experiments which suggested that the  $\eta_1$  component might partly be attributed to high localised values of surface hydrogen chemical potentials. Local cell hydrogen transfer effects, arising from a heterogeneity of surface hydrogen chemical potentials, were suggested to be an important factor in determining the values of electrolytic isotopic separation factors; and attention also was drawn in 5A2 to the means of estimating

surface hydrogen chemical potentials by using electrical resistance measurements to determine hydrogen chemical potentials in the bulk of the electrode.

Problems arising from heterogeneity of surface activity also were discussed in a study of rates of hydrogen penetration through a palladium bielectrode, reported in Paper 1C12 by I. Hristova (Sofia).

### References

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## Hydrogen Generators for Meteorology

A new range of hydrogen generators developed by Johnson Matthey Metals was introduced at the recent Meteorex '77 equipment exhibition held in Hamburg to coincide with two important international meteorological conferences organised by the World Meteorological Organisation. These generators, which have been designed specifically for civilian use, have lower rates of output than the military generators which were the subject of an earlier article in this Journal, although the method of hydrogen production and its purification using a palladium-silver diffusion unit are the same. Capable of working in environments not suitable for some other types of generator, these units can produce hydrogen at a cost which in many situations is considerably cheaper than other sources.

