

Metal-Hydrogen Systems

A REVIEW OF PALLADIUM AND PALLADIUM ALLOYS

The second International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, was held from the 2nd to 7th September 1990, in Banff, Canada. This survey outlines a selection of the papers presented at the conference on work involving hydrogen interaction with the platinum group metals.

The chairman of the organising committee, Professor F. D. Manchester, opened the conference by commenting on the many new developments that have arisen within the field of metal-hydrogen studies since the 1988 Symposium in Stuttgart – perhaps most notably as a consequence of the “cold fusion” controversy which has brought many aspects of metal-hydrogen research to world attention.

Cold Fusion

As a reflection of this particular area of interest, a significant proportion of the papers were concerned with various aspects of cold fusion.

A group from Japan, K. Tsuchiya (Tokyo National College of Technology), K. Ohashi (Tamagawa University), Y. H. Ohashi and M. Fukuchi (Keio University) approached the question by estimating the nearest neighbour distance between two deuterium atoms in a f.c.c. palladium lattice using the Schrödinger equation, taking into account the electronic screening cloud. They estimated the D-D distance to be 0.66 Å, which is smaller than the molecular value of 0.74 Å.

Several researchers tackled the question of electrolytically induced cold fusion by using various techniques to determine the maximum possible deuterium content of palladium.

An in-situ X-ray diffraction observation of a palladium foil cathode during electrolysis of heavy water solution, particularly concentrating on the nature of the transformation into the deuteride (β -PdD_x) phase, was reported by T. Yamamoto, T. Oka and R. Taniguchi from the Osaka Prefectural Radiation Research Institute,

Japan. The lattice constants observed were converted into deuterium concentrations and potentials by the use of known data on the phase relation. A maximum deuterium content, expressed as an atomic ratio, D:Pd = 0.80 at room temperature was reported.

A limiting concentration of D:Pd = 0.78 was reported by P. R. Stonadge, M. J. Benham, S. M. Bennington, J. P. A. Fairclough and D. K. Ross from Birmingham University, who used time-of-flight neutron diffraction and concurrent resistivity measurements to investigate electrochemical charging of palladium rods.

On a positive note, an alternative approach taken by researchers H. Uchida, Y. Matsumura, T. Hayashi and M. Kawachi (Tokai University, Japan) was the use of GM- and NaI-scintillation counters to measure γ - or X-ray emissions from an electrolytically deuterided palladium electrode. They reported 20 to 35 per cent excess radiation during deuteriding of palladium wire in KOD solution at greater than 600 mA/cm² and 20 V but no excess radiation on hydriding of palladium in KOH at similar current and voltage input.

Negative results were again however reported by Y.-Q. Lei, Y.-L. Chen, D.-L. Sun, J. Wu and Q.-D. Wang from Zhejiang University, China; no excess heat or γ -ray emission higher than background were detected during a 290 hour electrolysis of deuterium oxide using a palladium bar cathode.

The subject of cold fusion was raised in debate again at the conclusion of the conference. Despite the huge number of negative results, and apparent irreproducibility of the effect, some delegates cautioned against complete dismissal of the phenomenon.

Electronic Structure

Electronic band structure calculations featured in several of the reported theoretical studies of metal hydride systems. In work motivated once

again by interest in cold fusion possibilities, A. C. Switendick from the Sandia National Laboratories in New Mexico, reported on the use of band structure and density of state calculations to determine the stability of the palladium deuterides PdD, PdD₂ and PdD₃. The only stable system was concluded to be PdD.

The use of density of state calculations to analyse the Pd-H, alkali metal-H and H-H interactions in the recently synthesised hydrides Na₂PdH₂ and Li₂PdH₂, was reported by M. Gupta (Université Paris-Sud, France) and W. M. Temmerman (Daresbury Laboratory, Warrington, UK). Since the pure intermetallic compounds cannot be synthesised in the absence of hydrogen, such calculations have provided a valuable insight into the role of hydrogen atoms in the lattice.

Order-Disorder Transformations

An area of study in which the platinum group metals featured prominently was that of order-disorder transformations. Professor T. B. Flanagan of the University of Vermont opened a session on this topic by reviewing literature evidence and presenting recent observations of how hydrogen can induce lattice mobility in metals, and lattice changes in disordered alloys. There is segregation of palladium-nickel alloys into palladium- and nickel-rich regions under conditions of ultra high hydrogen pressure and temperatures greater than 493 K, and there is also evidence that the palladium-rhodium-hydrogen system may be subject to segregation on a small scale. Under high pressures of hydrogen, disordered Pd_{0.6}Cu_{0.4} and Pd_{0.5}Ag_{0.5} transform to ordered tetragonal structures. At $p_{H_2} > 1$ MPa and $T > 450$ K, disordered Pd₃Mn transforms to an ordered form which has an increased hydrogen solubility. This can be seen as a variation on Le Chatelier's Principle; if a disordered alloy can dissolve more hydrogen by either ordering or segregating then the stress is reduced.

Two papers contributed by researchers B. Sobha, B. Coluzzi, C. Costa and F. M. Mazzolai of the University of Perugia, Italy, reported on a combined study of long range and short range

diffusion relaxation processes, by Gorsky relaxation and internal friction measurements, respectively, designed to compare the local motion of hydrogen in the ordered and disordered Pd₃Mn system. It was concluded that the relaxation processes appear to be due to stress assisted hydrogen interstitial reorientation processes.

A comprehensive study of hydrogen induced ordering in palladium-manganese alloys over the wider composition range 10 to 31 per cent manganese, investigated by metallography, X-ray and electron diffraction studies, and by electrical resistance measurements, was presented by K. Baba, Y. Niki and Y. Sakamoto from Nagasaki in collaboration with T. B. Flanagan.

Hydrogen Solubility and Diffusivity

The wide range of papers reporting on aspects of hydrogen solubility and diffusivity in palladium and palladium alloys again reflects continued special interest in the properties of this element among its congener elements in the platinum group, and indeed among other metals.

A paper by American workers, G. J. Thomas, S. E. Guthrie, (Sandia National Laboratory), R. W. Siegel and J. A. Eastman (Argonne National Laboratory) reported pressure-composition measurements on nanophase palladium, investigating the effects of high surface:volume ratio on hydrogen-metal interactions. It was found that in comparison with coarse grained materials, there is an increase in the α -phase solubility, but that the β -phase hydrogen:palladium solubility limit is decreased.

Thermodynamic parameters of hydrogen and deuterium absorption and desorption by palladium as derived by calorimetry were reported in a paper by W. J. Luo, J. D. Clewley and T. B. Flanagan of the University of Vermont. It was found that, within the limits of experimental error, the enthalpies of protide (deuteride) formation and decomposition were equal, and further that there is no evidence of any anomalous excess heat evolved in the PdD system as compared to PdH.

Although the stability of palladium hydride itself tends to be too high for convenient kinetic

study of its formation and decomposition, Z. Gavra, J. R. Johnson and J. J. Reilly of Brookhaven National Laboratory, New York, reported the use of $\text{Pd}_{0.85}\text{Ni}_{0.15}$ as a suitable substitute. Experiments carried out with the hydride particles suspended in *n*-undecane revealed the decomposition kinetics to be in accord with a phase controlled boundary model in which the rate limiting process is the phase transformation taking place at the interface between the unreacted hydride core and a hydrogen saturated metal product layer (shrinking core model). The model is to be tested in the future with other systems.

A poster by H. Züchner and T. Rauf from the University of Münster, Germany, reported derivation of pressure-composition isotherms for the palladium-hydrogen and palladium-silver-hydrogen systems by using an electrochemical bielelectrode charging method. This was found to be a simple and convenient technique provided certain specific conditions, such as using thin foils and low charging current densities, are adhered to in order to avoid anomalies in systems where phase transformations occur.

Solubilities and thermodynamic quantities of hydrogen in palladium-ytterbium solid solution alloys in the composition range 2.0 to 8.0 atomic per cent ytterbium, as determined from absorption pressure-composition isotherms between 273–473 K and hydrogen pressures up to 100 Torr were reported by F. L. Chen, M. Furukawa and Y. Sakamoto from Nagasaki University. Plateau pressures corresponding to the α/β phase equilibrium decrease with ytterbium content. Results were compared with previously studied palladium-rare earth alloy-hydrogen systems.

Pressure-composition and resistivity-composition relationships derived by an electrochemical technique at 298 K and 323 K for palladium alloyed with 1, 2 and 4 atomic per cent scandium were presented by R.-A. McNicholl and F. A. Lewis of the Queen's University, Belfast. In accordance with palladium-scandium being an expanded alloy, the absorption plateau pressures decrease with increasing alloy content but a somewhat unique invariance of the desorption plateaux was observed.

Also dealing with the same alloy system, U.S. investigators, T. J. Udovic, J. J. Rush (National Institute of Standards and Technology, Gaithersburg) and H. Schone (College of William and Mary, Williamsburg) in collaboration with I. S. Anderson from the Paul Scherrer Institut, Switzerland, reported on the use of inelastic neutron scattering in studying the effect of scandium impurity atoms on the vibrational density of states of hydrogen absorbed in palladium. Preliminary analysis of spectra obtained at 296 K and 80 K with hydrogen concentrations of 2 per cent and below, suggested hydrogen trapping of less than 1 per cent by the scandium atoms in a 2 per cent scandium alloy, and the existence of clusters looking like β -phase but modified by having a central scandium atom.

In a further analysis of the palladium-platinum-hydrogen system F. A. Lewis, S. G. McKee and R.-A. McNicholl (Queen's University, Belfast) reported that relationships between increment of specific resistivity and hydrogen content, *n*, for the higher platinum content alloys seemed representable to a good approximation by a common curve of similar type to "Nordheim" forms of relationships between resistivity and composition appropriate to substitutional alloys. Assessments were made as to how far deviations from the common curve in the case of palladium and the lower platinum content alloys could be accounted for in terms of coexistence of phases with differing levels of hydrogen occupation.

A paper presented by R. V. Bucur and N. O. Ersson from the University of Uppsala, Sweden, with the help of X. Q. Tong (Belfast), reported work on $\text{Pd}_{17}\text{Ag}_{23}$ and pure palladium samples designed to investigate the dual influence of foreign atoms and defects in a host palladium lattice on the diffusivity and solubility of hydrogen.

Amorphous Alloys

The work reported on amorphous alloys included a study by investigators K. Tanaka, T. Araki and T. Abe (Nagoya Institute of Technology, Japan) of thermal desorption spectra of hydrogen on glassy and crystalline Zr_2Pd alloys. By simulation analysis using plural Gaussian curves to reproduce the different possible

site energy distributions of the hydrogen atoms (which are dependent on their metal atom environments), they deduced that in the glassy alloy, hydrogen atoms sit on Zr_4 , Zr_3Pd and Zr_2Pd_2 type sites, whereas in the crystalline alloy, they sit only on the Zr_4 sites at low hydrogen contents.

O. Yoshinari from Nagoya Institute of Technology, Japan and R. Kirchheim from Max Planck Institute, Stuttgart reported that the solubility of hydrogen in amorphous $Pd_{73.2}X_{8.8}Si_{18}$ (X = silver, copper, chromium, iron or nickel) alloys decreased in comparison with solubility in amorphous $Pd_{82}Si_{18}$. Diffusion coefficients were quite different in various ternary palladium-silicon alloys but this could be attributed to differing activation energies when a constant reference diffusivity was assumed.

Instrumental Techniques

A number of papers dealt with the use of various instrumental techniques for exploring aspects of metal-hydrogen interactions. A paper by D. H. W. Carstens and P. D. Encinias (Los Alamos National Laboratory, New Mexico) involved the use of Laser-Raman Spectroscopy for studying hydrogen isotopic exchange over palladium metal. A joint U.S. group from Washington University, St. Louis and Iowa State University, Ames (D. B. Baker, M. S. Conradi, R. E. Norberg, D. R. Torgeson and R. G. Barnes) presented a paper on novel measurements of nuclear spin cross-relaxation in metal hydrides using NMR. D. K. Ross, M. W. McKergow and D. G. Witchell (University of Birmingham) with J. K. Kjems (Riso National Laboratory, Denmark) reported the use of diffuse neutron scattering to monitor super lattice reflections as the deuterium atoms order at the 50 K anomaly in palladium-deuterium.

Applications

Promising practical applications involving the platinum metals were proposed in a number of papers presented. A group from the Max Planck Institute in Stuttgart (H. H. Uchida, H.-G. Wulz and E. Fromm) have observed remarkable enhancement of hydrogen dissociation if nickel,

iron or palladium, acting as catalysts, are present on the surface of oxidised titanium or intermetallic storage materials. This may prove a significant advance in the development of poisoning-resistant hydrogen storage systems. A promising material for a hydrogen separation membrane was reported by M. Amano, M. Komaki and C. Nishimura (National Research Institute for Metals, Tokyo, Japan). Palladium plated vanadium-15 atomic per cent nickel alloy membranes show good resistance to hydrogen embrittlement while having superior hydrogen permeability compared to palladium.

Concluding Remarks and Future Developments

The conference concluded with a rapporteur session in which it was agreed that while some aspects of metal-hydrogen research have reached maturity, the future holds many openings and scope for development of new areas of study particularly, for example, examination of bonding theories including the idea of pairing interactions, and exploring the realm of new intermetallic materials.

Proceedings of the Symposium will be published in the *Journal of Less-Common Metals* in Spring 1991. The next International Symposium on Metal Hydrogen Systems is to be held in Uppsala, Sweden from 8th to 13th June 1992.

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Palladium Membrane Reactors

The oxidative dehydrogenation of cyclohexane can take place with high yield when a palladium membrane is used to divide the reactor into reaction and separation sections. In order to establish the effect of the gas flow patterns when a sweep gas is used to remove the permeated hydrogen, five ideal flow models have been analysed and compared by N. Itoh, Y. Shindo and K. Haraya of the National Chemical Laboratory, Tsukuba, Japan (*J. Chem. Eng. Jpn.*, 1990, 23, (4), 420-426).

Concurrent, counter current, plug-mixing, mixing-plug and mixing-mixing models were considered. It was found that the highest performance was shown by the second of these, where the feed gas on one side of the palladium membrane flows in the opposite direction to the sweep gas on the other.