Fundamentals and Applications of Metal-Hydrogen Systems

INTERNATIONAL SYMPOSIUM ON RESEARCH INVOLVING PALLADIUM AND OTHER PLATINUM GROUP METALS

The fourth biennial International Symposium on Metal-Hydrogen Systems (Fundamentals and Applications) was held in the picturesque surroundings of Mount Fuji, in the Conference Centre, Fujiyoshida, near Tokyo, from the 6th to the 11th November 1994, under the joint Chairmanship of Professor Seijirau Suda of Kagakuin University and Professor Yuh Fukai of Chuo University. The direct involvement of the platinum group metals in this area of study was amply shown by the substantial amount of research that was reported, notably, by the amount of ongoing work on the phase and allied thermodynamic relationships of the palladium/hydrogen and palladium alloy/hydrogen systems.

Also prominent were studies relating to the high mobility of the large concentrations of associated hydrogen interstitials which could be potentially available over a wide range of conditions and could be used for various applications, such as hydrogen purification membranes or film coatings to improve the electrode surfaces in metal-hydride batteries. The latter focus of interest formed the basis of conference keynote talks from D. Noréus of Stockholm University and Y. Lei of Zhejiang University.

Almost two hundred papers were submitted to the Symposium and presented in approximately equal numbers of oral and poster contributions. Over thirty of these presentations were concerned with studies of hydrogen interactions with palladium or palladium alloyed with various elements – including other platinum group metals, particularly platinum and rhodium.

Hydride Formations and Structural Identification

The preparation of a new hydride, $CaPd_3H$, at relatively high temperatures (650 K) and pressures (40 bar) from the direct interaction of palladium and CaH_2, was reported by D. Noréus of the University of Stockholm and K. Kadir of the National Research Institute, Osaka. Structurally the hydride is closely related to the recently reported superconducting hydride, $NaPd_3H_2$, which has a transition temperature of 1.6 K, and was the subject of an electronic structure analysis reported by A. Switendick of the National Engineering Laboratories, Idaho Falls, U.S.A.

In allied studies at higher upper temperature limits (~ 900 K) and pressures (~ 2500 bar) performed by G. Auferrmann and W. Bronger of the Institute of Inorganic Chemistry, Aachen, Germany, the formation of alkali ternary hydrides was reported from interactions between hydrides of A (where A represented sodium, potassium, rubidium or caesium) with metallic sponges of palladium and platinum, to give new compounds $APtH_6$ and $APtH_4$, which were structurally analogous to $APtCl_6$ and $NaPdH_4$, respectively.

The successful use of diamond anvil techniques to reduce the upper limits of temperature and pressure required for the formation of hydrides of various transition metals, including rhodium, were reported by M. Tkacz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw.

Hydrogen Isotope Structural Studies

Studies of neutron powder diffraction concerned with the preferred interstitial positions in the Pd_9Si_2 structure which had been deuterated to a deuterium content corresponding to composition $Pd_9Si_2D_{0.26}$ were reported by Y. Andersson and colleagues of the Chemical Institute, University of Uppsala. Neutron diffraction measurements were also reported by E. Gray and colleagues, Universities of Brisbane, Sydney and Newcastle, and the Australian Nuclear Scientific and Technical Organisation, Menai, Australia, on deuteron ordering in β-phase palladium-deuterium compositions at low temperatures, close to a 50 K anomaly region of the palladium/deuterium system.

Certain palladium alloys seem to have shown particular attractions as materials for tritium storage. J. Hölder and J. W. Wermer from the Westinghouse Technical Center, South Carolina, presented results of studies performed on alloys with rhodium, nickel, cobalt and chromium that were indicative of improvements concerning irreversible ageing reductions of their tritium storage capacities, and related increases of the slopes of p-n relationships over the phase transition regions, which seemed to signify the formation and retention of the ^3He products from the decomposition of tritium.

Lattice Defect Influences

Influences of increases in surface to substrate ratios of palladium atoms within dispersed films and clusters continue to be reported as effecting modifications of phase relationships, and of physical and chemical characteristics.

These attempts to simulate the anticipated effects of estimated volume and surface area ratios of internal defects on the phase relationships of nanocrystalline clusters composed of 500 palladium atoms, were presented and compared with available experimental relationships by M. Leonard and R. Wolf of the Westinghouse Technical Center, South Carolina. The effects of controlled productions of dislocations at $\alpha \leftrightarrow \beta$-phase hydride transitions, and resultant formations of palladium-based materials with improved strength, special physical properties and also high plasticity, were reviewed by Professor V. A. Goltsov of the State Technical University, Donetsk, Ukraine.

Structural Rearrangements

A keynote paper was presented by T. B. Flanagan and H. Noh, both from the University of Vermont, which dealt with the influences of experimental pressurised hydrogen atmospheres and annealing conditions on the rearrangement of lattice structures in palladium alloys, including associated phase transitions.

"Superabundant vacancy" formation in palladium that resulted from annealing in hydrogen at ~ 800°C was reported by Professor Y. Fukai of Chuo University, Tokyo. Together with K. Watanabe, also of Chuo University, Y. Hayashi of Kyushu University, Fukuoka and Y. Sakamoto of the University of Nagasaki, Professor Fukai also reported on the separation of a $Pd_{80}Rh_{20}$ alloy into palladium-richer and rhodium-richer regions after heating at ~ 550 to 600°C also in very high pressures of hydrogen. Essentially analogous findings of the separation of a $Pd_{90}Pt_{10}$ alloy into preferentially palladium-rich and rhodium-rich regions after heating at temperatures between 448 and 573 K in atmospheres of hydrogen, were reported by Y. Sakamoto with H. Noh and T. B. Flanagan.

In contrast to these general findings of enhancement in compositional ordering after annealing in a hydrogen atmosphere, Sakamoto with K. Takao of the University of Nagasaki and T. B. Flanagan, reported experimental effects produced by the dissolved hydrogen acting usually to suppress ordering of palladium-rare earth solid solutions compositionally corresponding to Pd_3Gd(Sm, Eu) alloy structures.

Defect and Phase Relationship Anelastic Effects

Internal friction (elastic energy dissipation) measurements associated with interaction effects related to hydrogen and dislocations in vibrating reeds made of nanocrystalline palladium, containing 2 and 4 atomic per cent hydrogen, were reported by H. Wipf and colleagues of the Universities of Darmstadt and Saarbrücken, and were compared with corresponding data for palladium in single crystal and coarse particle forms.

Measurements of internal friction over comparable temperature ranges (~ 90 to 300 K) and vibration frequency, (~ 3 kHz) were reported by F. M. Mazzolai and colleagues from the Universities of Perugia and Belfast, in studies with an extensive series of palladium-silver alloys covering wide ranges of hydrogen content. Results were correlated with corresponding gradual changes in phase relationships and complementary structural interpretations of the palladium-silver-hydrogen system.

Diffusion Related Studies

Studies of muon spin relaxation effects in hydrogen-loaded Zr_3Pd were reported by R. V. Havill and colleagues, University of Sheffield, measured over the temperature range 10 to 300 K. Results were discussed in terms of a muon tunnelling control mechanism changing to hydrogen diffusion control with increasing temperature. Studies of hydrogen permeation through palladium foils during modulations in imposed hydrogen pressure difference were discussed in a contribution from A. Altunogl and N. Braithwaite of the Open University Research Unit, Oxford. These techniques were represented as attractive methods for identifying control mechanisms between various alternative choices of surface and bulk processes.

Electrolytically Supplied Hydrogen

Studies related to cold fusion possibilities performed by M. Alquero and colleagues, University Autonoma Madrid, concerned electrolytic loading and hydrogen diffusion arising from measurements of pressures of deuterium and hydrogen gases evolved at palladium cathodes in closed cell systems. In similar studies made in conjunction with measurements of electrical resistivity, K. Kunimatsu and colleagues, IMRA Japan Co. Ltd., Sapporo, also reported pressure measurements in closed cells of hydrogen and deuterium gas evolved at palladium and palladium-rhodium alloy cathodes.

Palladium Coatings

The advantages of using a combination of palladium and nickel coated surfaces in a complex mischmetal-nickel based negative electrode, for producing improvements in hydrogen storage capacities and battery discharge rates of nickel-metal hydride batteries, were reported by M. Ganz of the Central Iron and Steel Research Institute, Beijing. A composite palladium/titania film bielectrode, in conjunction with surface impedance measurements, was used in studies of hydrogen permeation through titania films, reported by S. I. Pyun and colleagues of the Korea Institute of Science and Technology, Taejon. Measurements of the permeation of "ion-gun implanted" hydrogen through layers of palladium sputtered onto iron surfaces at 295 to 610 K, were reported by Y. Hayashi and colleagues of Kyushu University, Fukuoka, in work directed towards investigating conditions for hydrogen permeation through iron membranes.

Diffusion Coefficients and Strain Gradient Developments

Problems in electrolytically based methods for determining hydrogen diffusion coefficients, D_H, in palladium were discussed in a review by R. V. Bucur and colleagues of the Universities of Uppsala, Nagasaki and Belfast, in which attention was drawn to influences on permeation rates of lattice strain gradients associated with "uphill effects". Evidence of such "uphill effect" transfers, from lower to higher concentrations of lattice expanding hydrogen interstitials, had encouraged proposals advanced in a report by X. Q. Tong and colleagues, Universities of Birmingham, Nagasaki and Belfast, that analogous strain gradient and Gorsky Effect mechanisms might also provide a basis of explanation of hysteresis phenomena in p-c(n)-T relationships of the palladium-hydrogen and allied metal-hydrogen systems.

Observations of further "uphill effects" in the palladium-cerium-hydrogen system, recorded during electrochemical galvanostatic studies on palladium-cerium alloy membranes, were reported by Y. Sakamoto and colleagues, from Nagasaki, Belfast and Birmingham Universities.

Palladium Alloy-Hydrogen Systems

The modifying effects of alloying elements on the p-c(n)-T relationships and other characteristics of the palladium-hydrogen system, continue to be active areas of study.

Information about phase relationships, associated thermodynamic parameters and structural determinations for the hydrogen systems of the intermetallic compounds $PdLi_{0.94}$ and $Pd_2Li_{1.04}$ were reported by Y. Sakamoto and colleagues of the University of Nagasaki. Measurements were reported by A. Percheron-Guegan and colleagues (CNRS Meudon and CEA Bruyères le Chatel), of p-c(n) isotherms of deuterium pressure/deuterium content for series of palladium-platinum, palladium-rhodium and palladium(rhodium, platinum) alloys recorded over the temperature range 10 to 100°C. An increased $\alpha \leftrightarrow \beta$-phase deuteride transition pressure was noted with increasing alloying element content of up to ~ 10 per cent.

Electrical Resistivity

Results from 7.5 to 20 K of electrical resistivity, after hydrogen loading at 1 GPa pressure, of palladium, alloyed with nickel, ruthenium, rhodium, platinum and silver, were reported by A. Szafrański, Polish Academy of Sciences, Warsaw. Forms of the resistivity-temperature relationships were consistent with examples of Kondo Effect and spin-glass behaviour. Summaries and discussions of combined measurements of electrical resistivity-hydrogen content and p-c(n) relationships of hydrogen systems of palladium alloys with respective *4d* and *5d* elements paired in the same transition metal sub-group, were presented by R.-A. McNicholl and colleagues, Universities of Belfast, Jaffna and Beijing.

Permeation Membranes

Differences between the forms of p-c(n) isotherms of palladium alloy-hydrogen systems have significance for the potential utilisation of the alloys as hydrogen permeation membranes. A paper that was presented by Professor V. A. Goltsov dealt particularly with these aspects, presenting diagnostic diagrams which suggested the relative suitabilities of alternative alloying elements from the characterisation of their hydrogen solubilities and diffusion coefficients, under various combinations of hydrogen gas pressures, temperatures and problems caused by potential catalytic poisoning and corrosion.

Alloys of palladium with elements, such as silver, having larger atomic volume than palladium, have proved to be advantageous compositions when used for hydrogen permeation membranes.

A paper by Y. Sakamoto and colleagues from the University of Nagasaki, reported on extensive comparative studies of palladium-rich "expanded" ternary alloys of types palladium-yttrium(gadolinium)-silver and palladium-yttrium-indium(tin, lead), and complementary examinations of the influence of methane additions to input hydrogen permeation gas.

It is planned that the refereed papers presented at the symposium will be published in forthcoming volumes of the *Journal of Alloys and Compounds.*

The next symposium of the series will be held during 1996 in Switzerland at a venue still to be finalised and will be under the Chairmanship of Professor L. Schlapbach of the University of Fribourg.

F.A.L.

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The Russian contribution to our knowledge of the platinum metals is incalculable; early research by gifted individuals led to the formation of the Institute for the Study of Platinum and Other Noble Metals at Petrograd, and in turn the first journal devoted exclusively to the platinum metals was founded to publish the research results of this Institute. Indeed, until its demise in 1955, this periodical was unique.

In 1993 a new Russian journal, entitled *Rhodium Express*, was launched to report on the co-ordination chemistry of rhodium. Although the majority of the papers published to-date have reported Russian work, enabling readers to gain an early insight of topics currently being studied there, the number of contributions from other countries is increasing with time.

Further information about this useful addition to the literature can be obtained from The Editor: Yuri S. Varshavsky, P.O.B. 77, 198013 St. Petersburg, Russia; E-mail Yuri@vniisk.spb.su; Fax: +7 (812) 251 4813.