

Metal-Hydrogen Systems and the Hydrogen Economy

SELECTIVE REVIEWS OF TWO RECENT CONFERENCES

Continuing interest in metal-hydrogen systems and in the advancement of the so-called hydrogen economy, has been demonstrated by two recent meetings, each attended by participants from some thirty countries. The first was at Uppsala University, Sweden during June, and the second was held in Paris later that month. At both it was evident that considerable research work involving the platinum group metals is taking place throughout the world.

The 1992 biennial **International Symposium on Metal-Hydrogen Systems**, fundamentals and applications, was held under the chairmanship of Professor S. Rundqvist of Uppsala University from June 8th to 12th, with some 300 participants. Many papers concerned hydrogen interactions with the platinum metals, the majority dealing with palladium.

Hysteresis Effects

A still incompletely resolved issue concerning the palladium-hydrogen system is that of "hysteretic" effects associated with regions of phase transition. These correspond to differences between values of the hydrogen content and steady state hydrogen pressures (and other experimental parameters) that are derived during sequences of increases and decreases of hydrogen content, respectively. This topic was discussed by B. Baranowski, Polish Academy of Sciences, Warsaw, who concluded that hysteresis was an inherent stress gradient dependent factor, with both absorption and desorption relationships representing effective equilibrium conditions.

Palladium Alloys

The influence of the relative sizes of alloying elements on the form of changes in the pressure-composition (p-n) and electrical resistance-composition relationships were reported by R.-A. McNicholl and F. A. Lewis of Queen's University, Belfast. Electrical resistance measurements of β -phase hydride composition

ranges for a wide variety of palladium alloys at low temperatures were discussed by A. W. Szafranski, Polish Academy of Sciences, Warsaw. Derivations of p-n relationships for palladium-indium and palladium-aluminium alloys, together with associated thermodynamic correlations, were reported by Y. Sakamoto, N. Ishimaru, M. Hasebe, E. Kakihisa and Y. Kinari from the University of Nagasaki. This group also reported studies on series of alloys: palladium-rhodium, palladium-nickel and palladium-lithium, acting as hydride electrodes in nickel/hydrogen (hydride) batteries. Studies of the effect of hydrogen on electrotransport and thermoelectric power in palladium-copper alloys were reported by J. Toth, K. Tompa and T. Tarnoczi, Central Research Institute for Physics, Budapest, while studies of the stability of β -phases in a series of palladium-zirconium, palladium-indium and palladium-iron alloys formed by electrolytic charging were reported by V. M. Christov, B. S. Sidzimov, St. D. Neov and L. Bozucov, Institute for Nuclear Research and Nuclear Energy, University of Sofia. An investigation of hydrogen site occupation in palladium-gold alloys by Mössbauer spectroscopy was reported by M. Baier, M. Karger, R. Ostermayer and F. E. Wagner, Technical University of Munich, H. J. Bauer and I. Dugandžić, University of Munich, V. E. Antonov, T. E. Antonova and V. I. Rashupkin, Russian Academy of Sciences, Chernogolovka, and S. M. Filipek, Polish Academy of Sciences, Warsaw. Some positron annihilation studies of

hydrogen in palladium-silver alloys were reported by E. Debowska, from the University of Wrocław, Poland.

Structural Information

With regard to structurally related measurements of the effects of hydrogen in palladium, M. Tkacz and B. Baranowski, Polish Academy of Sciences, Warsaw, reported X-ray evidence of a phase transition region appearing over certain ranges of high pressure for particular β -phase palladium:hydrogen ratios. Also in studies at high pressures V. A. Somenkov and I. N. Goncharenko, Kurchatov Institute, Moscow, reported results of neutron diffraction measurements of palladium:deuterium composition ratios. Considerations of structural alterations related to changes in electrical resistivity were discussed by J. P. Burger, University of Paris Sud. Studies by the small angle neutron diffraction technique, of trapped electrons in palladium were reported by D. K. Ross and K. L. Stefanopoulos, University of Salford, U.K., S. Forcey, Research Centre, Ispra, Italy and I. Iordanova, University of Sofia.

Films and Surfaces

Ways of utilising both the absorptive capacity and the relatively high catalytic activity of palladium were illustrated by studies of the electrical resistivity and Hall coefficients of palladium films coated on vanadium and niobium, by D. E. Azofeifa and N. Clark, University of Costa Rica; such surface films facilitated measurements of hydrogen diffusion coefficients in the aluminium substrate (H.-J. Schlüter and H. Züchner, University of Münster; R. Braun and H. Buhl, DLR, Köln). On the other hand the use of palladium as a substrate provided a means of determining hydrogen diffusion coefficients in MgH_2 (P. Spatz, H. A. Aebischer, A. Krozer and L. Schlapbach, University of Fribourg) and acted as a control on hydrogen adsorption levels, studied by colour changes of tungsten trioxide (J. Kleperis and A. Lūsis, Solid State Physics Institute, University of Latvia, Riga). Hall coefficient and also the magnetoresistance of hydrided palladium films were measured by

E. Flouda and C. Papastaikoudis, Institute of Materials Science, Athens.

Observations by LEED measurements of initial structures developed by hydrogen on palladium surfaces were reported by L. Stauffer, H. Ezzechar and H. Dreyse, Physics Laboratories, Mulhouse and Vandoeuvre-Les-Nancy, France. Activation of MgH_2 storage material by ruthenium and platinum co-deposited on charcoal was reported by H. Imamura and M. Nakamura, Yamaguchi University, Ube, Japan. Evidence of the production of hydrogen in atomic form during desorption from palladium films was indicated by its adsorption on gold (E. Nowicka, Z. Wolfram, W. Lisowski and R. Dús, Polish Academy of Sciences, Warsaw).

Diffusion: Lattice Expansion

Studies by NMR of hydrogen diffusion in Ti_3Ir were reported by D. Guthardt, D. Beisenherz and H. Wipf, Technische Hochschule (TH), Darmstadt, and of deuterium in Zr_3Pd_3 by L. P. Ferreira, University of Coimbra, Portugal and A. Baudry and P. Boyer, CEN, Grenoble. Nuclear resonance reaction measurements were used by B. Hjörvarsson, University of Uppsala, to estimate hydrogen profiles in a platinum-nickel single crystal. Gorsky Effect measurements of deuterium coefficients in β -phase palladium-deuterium at low temperatures were recorded by B. Coluzzi, C. Costa, A. Biscarini, B. Sobha and F. M. Mazzolai, University of Perugia and R.-A. McNicholl, Belfast. Hydrogen diffusion coefficients in palladium-yttrium alloys were studied by P. R. Stonadge, M. J. Benham and D. K. Ross, University of Salford, and measured in both cast and annealed palladium by Y. Q. Lei, D. L. Sun, Y. L. Chen, J. Wu and Q. D. Wang, Zhejiang University, Hangzhou, China.

The consequences of expansion and strain gradients produced by hydrogen on estimates of hydrogen diffusion coefficients in α -phase palladium hydride were treated in papers by J. Čermák and A. Kufudakis, Institute of Physics, Prague and F. A. Lewis, Belfast, and in α and $\alpha + \beta$ palladium hydride by Y. Sakamoto,

H. Tanaka, Nagasaki University, and F. A. Lewis and X. Q. Tong, Belfast. Allied studies with $\text{Pd}_{17}\text{Ag}_{23}\text{H}_n$ were reported by X. Q. Tong, K. Kandasamy, F. A. Lewis, Belfast and R. V. Bucur, University of Uppsala. The strain effects of hydrogen in dislocation networks on hydrogen solubilities in palladium were considered by R. V. Bucur, University of Uppsala and F. A. Lewis, Belfast. Studies of volume changes produced by hydrogen absorbed in CeRu_2 were reported by L. Severin and B. Johansson, University of Uppsala.

Hydrogen Isotopes in Palladium Electrodes

A review of recent information on the possibility of fusion of electrolytically discharged deuterium in palladium was reported by D. Lewis, Royal Institute of Technology, Stockholm. Consolidation measurements of hydrogen contents in palladium electrodes corresponding to effective pressures of hydrogen generated electrolytically were provided by F. A. Lewis, S. G. McKee and R.-A. McNicholl, Belfast. Similarly, for studies partly initiated by the possibility of cold fusion, R. N. Kuz'min, A. P. Kuprin and P. O. Revokatov, M. V. Lomonosov Moscow State University, reported on accumulations of electrolytically discharged tritium in palladium cathodes. A model for determining the concentration profiles during electrolytic charging and discharging of hydrogen by palladium was presented by Y. Sakamoto and N. Ishimaru, Nagasaki University. A discussion of electrochemical hydrogen discharge processes was presented by G. Jerkiewicz, Sherbrooke University, Canada. The effects of current density and of prior cold working of palladium cathodes on radioactive emissions were reported by H. Uchida, Y. Hamada, Y. Matsumura and T. Hayashi, Tokai University, Kanagawa, Japan.

Hydride Complexes of Platinum Group Metals

Considerable research activity was reported in regard to complexes of the platinum metals X-ray structural analyses of alkali metal com-

plexes such as NaPd_3H_4 were reported in three papers by the group of D. Noréus, University of Stockholm. Results of examining structurally related hydrides, such as $\text{Na}_2(\text{K}_2)\text{PtH}_4$, were presented by G. Auffermann and W. Bronger and by W. Bronger, K. Jansen, G. Ridder, G. Auffermann and P. Müller, Institute of Inorganic Chemistry, TH Aachen, and included a description of a method of high pressure preparation; and by F. Bonhomme and K. Yvon, University of Geneva and P. Fischer, ETH Zürich, for the deuterated complex Mg_2RuD_3 .

Structures of analogous compounds of cerium and gadolinium together with measurements by SEM and DSC were reported by Y.-G. Kim and J.-Y. Lee, Korea Advanced Institute of Science and Technology, Taejon; while structures of mixed Group II and Group III compounds $[\text{Sr}_{2-x}\text{Eu}_x]\text{RuH}_6$ and their magnetic behaviours were studied by R. Lindsay, R. O. Mayer, W. Strange, D. F. Storey, W. H. Clapp and J. R. Knapp, Trinity College, Hartford, Connecticut. Generalised problems of hydrides, including those of the platinum metals, were dealt with in contributions by M. M. Jakšić, University of Belgrade, J. K. Nørskov, Technical University, Lyngby, Denmark, and W. A. Oates, Institut für Festkörperforschung, KFA Jülich, Germany.

The papers presented at the Uppsala Symposium will be published in the *Zeitschrift für Physikalische Chemie* and subsequently gathered into a volume of proceedings under joint editorship with Professor E. Wicke.

The next meeting in this series is planned to be organised in Japan by Professor S. Suda, Department of Chemical Engineering, Kogakuin University, Tokyo.

The Ninth World Hydrogen Energy Conference was held in Paris from 22th to 25th June, 1992, under the co-chairmanship of Dr. C. Dérive and Dr. J. Pottier. As for previous conferences, a central objective has been to effect advancement of hydrogen as an environmentally acceptable source of energy. Primary conference topics have included the

means of hydrogen production, methods of purification and ways of increasing the utilisation of hydrogen.

Membranes of Palladium Alloys

In addition to the main established means of hydrogen production – such as the various processes of interaction of water (steam) with methane or other carbonaceous materials – significant volumes of hydrogen can also be abstracted from residues of other processes and purified by passage through palladium alloys membranes, such as those reported as developed by N. I. Timofeev, F. N. Berseneva and V. M. Makarov, Russian Academy of Sciences, Ekaterinburg, and recently reviewed here by V. Z. Mordkovich, Yu. K. Baichtock and M. H. Sosna (*Platinum Metals Rev.*, 1992, 36, (2), 90–97).

Such palladium membranes were also reported as being incorporated into a regenerative fuel cell using alkali metal hydride technology by P. Roy and S. A. Salamah, General Electric Company, San José, California, and were also suggested for encapsulation of hydrogen storage electrodes by F. A. Lewis, R.-A. McNicholl and K. Kandasamy, Belfast, and R. V. Bucur, University of Uppsala and Y. Sakamoto, University of Nagasaki. Impedance techniques for studying diffusion coefficients at the surfaces of palladium alloy membranes were discussed by C. G. Chen, R. Durand, R. Faure, ENSEEG, St Martin d'Herès, France and G. Jorge, School of Chemistry, UCV, Caracas.

Hydrogen Storage: Hydrides

In a measure of correlation with the Uppsala Symposium, one section of the Paris programme concerned developments of metal hydrides for hydrogen storage and paid attention to increasing utilisation in nickel-hydrogen batteries.

Granular composites of palladium and palladium-aluminium alloys were employed as reference materials in considerations of mass and heat transfer in storage compounds by A. Perevezentsev, A. Kroglov and B. Andreev, Mendeleev Institute, Moscow. Kinetic improvements by additions of catalytically assisting pal-

ladium to the hydrogen storage compound MgH_2 were reported by D. K. Slattery and R. Zidan, Solar Research Centre, Cape Canaveral, Florida. Thermodynamic aspects of hydride heat pump operation in platinum catalysed cycles of hydrogenation and dehydrogenation were discussed for acetone/2-propanol (Y. Yamashita, E. Ito and Y. Souto, University of Tokyo) and for cyclohexane/benzene (R. G. Sarmurzina, of the Kazakhstan Academy, Alma-Ata). Developments of polyhydride complexes containing rhodium and iridium as storage materials were outlined by K. R. McKinley, R. E. Rocheleau, P. K. Takahashi, Hawaii Natural Energy Institute; E. J. Bylina, Pacific Biomedical Research Center and C. M. Jensen, University of Hawaii. Problems concerning site energies in regard to hydrogen occupation by metals including palladium-platinum alloys were examined by Z. A. Matysina, B. Yu. Zaginichenko and O. S. Pogoralova, University of Dnepropetrovsk, Ukraine.

Hydrogen from Solar Energy

Methods of solar energy conversion for hydrogen production have become increasingly investigated. Platinum group metal, or compound, assisted photochemical dissociation of water, or other hydrides produced by irradiation of semiconductor materials such as silicon, (N. Getoff, G. Li, H. Stockenhuber, University of Vienna and K. Kotchev, Bulgarian Academy of Sciences, Sofia); or cadmium sulphide (C. A. Linkaus, T. E. Mingo and N. Z. Muradov, Solar Energy Center, Cape Canaveral) or Bi_2O_3 (P. Maruthamuthu, K. Gurunathan, E. Subramanian and M. V. S. Sastri, University of Madras) have been exemplified by platinum in cases of cathodic reactions (hydrogen evolution) and by oxides, such as RuO_2 , in cases of anodic reactions (oxygen evolution). Additionally or alternatively, initial photochemical activations of ruthenium complexes that have been utilised to effect electron transfer oxidation state changes may be either heterogeneously or homogeneously catalysed by suggested rhodium compounds (R. Bauer and C. Königstein, Technical University, Vienna;

K. S. Chandra Babu, R. N. Pandey and O. N. Srivastava, Banaras Hindu University, Varanasi, India). Platinum group catalysts have been somewhat analogously utilised in studies of bacterial and biochemically induced aqueous dissociation (C. L. K. Tennakoon, R. G. Bhardwaj and J. O'M. Bockris, Texas A and M).

Electrolysers

Modern forms of electrolysers represent important sources of hydrogen generation powered by various physical sources, including water, wind and solar energy. Platinum group metals and compounds have been utilised as catalyst materials for both cathodic and anodic processes, for various forms of electrolysers which are incorporated into generalised hydrogen energy programmes, such as in Saudi Arabia (H. Steeb, H. Aba-Oud and W. Seeger, D.L.R. (German Aerospace Research Establishment), Stuttgart and K.A.C.S.T., Riyadh, Saudi Arabia); in China (D. Z. Chen and J. Y. Huang, Jiaotang University, Xian) and in Brazil (L. G. de Lima, University of Uberlandia and T. N. Veziroglu, Clean Energy Research, Coral Gables, Florida). An electrolyser with an RuO₂ activated anode has been proposed for preparation of methanol from carbon dioxide and hydrogen (M. Specht, A. Bandi and C. U. Maier, Solar and Hydrogen Energy Research Center, Stuttgart and University of Stuttgart). Platinum silicide has been suggested for electrodes (A. K. Vijh, Institut de Recherche d'Hydro-Quebec).

In principle the currently interesting nickel/hydrogen batteries can be regarded as a class of electrolysers in which the discharged hydrogen is temporarily stored rather than evolved as gas. One proposed form of hydride electrode (G. Crepy and Y. Borthomieu, Alcatel and Saft Research Groups, Marcoussis and Romainville, France) is that of platinum dispersed within a charcoal matrix.

Catalysis

From an environmental standpoint, the employment of platinum metals in catalytic converters would seem likely to be continued, as

hydrogen is introduced into dual fuel engines with gasoline (A. Sheipak and E. Isayev, Motor Car Construction Institute, Moscow) with diesel oil (H. C. Watson and S. M. Lambe, University of Melbourne; H. B. Mathur, L. M. Das and T. N. Patro, Indian Institute of Technology, New Delhi) or with kerosene (G. W. Dahl and R. Eising, Fachhochschule Aachen).

Even in conditions of solely hydrogen combustion, platinum catalysts still seem to be required for the conversion of nitrogen oxides, as indicated by several papers (A. Schmolz and W. Boegner, Daimler Benz, Stuttgart; Y. Ninomiya, Y. Hosono, H. Hashimoto, N. Hiruma and S. Furuhashi, Musashi Institute of Technology, Tokyo; D. Reister and W. Strobl, BMW, Munich; R. Wurster, L.B.S.T. Ottobrunn, M. Bracha, Linde A.G., Hollriegelskreuth; J. Braedt, B.S.M.L.U., Munich; H. Knorr, MANN. A.G., Nürnberg and W. Strobl, BMW, Munich; H. Blank and A. Szyszka, Solar Hydrogen G.m.b.H., Munich and K. Ledjeff and J. Gieshoff, Fraunhofer Institute, Freiburg).

Fuel Cells

The discharge stage of nickel/hydrogen batteries could be regarded as a special case of hydrogen fuel cell operation. In the more usual operating circumstances of gaseous hydrogen fuel, platinum metals and compounds have been employed as electrode catalysts, somewhat analogously to their uses in electrolysers, both in general (A. J. Appleby, Texas A and M University; P. Hoogeveen, Air Products, Netherlands, B. G. Marcenaro, Ansaldo Research, Italy; L. Vermeeren, Elenco, Belgium and J. P. Cornu, Saft, France; M. Ghose, H. Aba-Oud, M. Ba-Junaid, M. Al-Garni and M. I. Quadri, Solar Products, Riyadh, Saudi Arabia) and in the particular cases of phosphoric acid fuel cells (L. E. van Bibber, W. A. Summers and J. M. Ferret, Westinghouse Electric Corp., Madison, Pennsylvania) alkali fuel cells (A. N. Arshinov, Urals Electrochemical Plant, Ekaterinburg, Russia) polymer electrolyte fuel cells (N. V. Korovin, Moscow Power Engineering Institute, Moscow, P. Staiti, Z.

Poltarzewski, V. Alderucci, G. Maggio and N. Giordano, CNR Institute, Messina, Italy) as well as in cases of methanol fuel cells (B. Ganser and B. Hohlein, Forschungszentrum Jülich).

Hydrogen Isotope Separation and General Information

Platinum metal activated electrode surfaces were among those examined by D. L. Stojic, S. S. Miljanic, T. D. Grozdic and M. M. Jakšić, University of Belgrade, within a study of electrolytic separation of protium and deuterium, and information available for palladium concerning hydrogen isotope exchange processes has been utilised for the development of a method to abstract tritium from tritium polluted water (B. Andreev, Y. Sakharovskij, A. Perevezentsev and M.

Rosenkovich, Mendeleev Institute of Chemical Technology, Moscow).

Articles which concerned the availability of information within general areas of study were presented by R. Fromageau, E.N.S.C., Paris and by V. A. Goltsov, C. Droniou and M. Rubinstein, L. F. Goltsova and V. A. Garkusheva, Polytechnic Institute, Donetsk.

Presented papers have been collected into a proceedings volume, "Hydrogen Energy Progress IX", edited by T. N. Veziroglu, C. Derive and J. Pottier and printed by M.C.I., Paris on behalf of the International Association for Hydrogen Energy. The next World Hydrogen Energy Conference will be held in Orlando, Florida during 1994 under the chairmanship of Dr David L. Block of the Florida Solar Energy Center, Cape Canaveral. F.A.L.

Platinum and Iridium Intermetallic Films

Carbon-carbon composites have high strength but their structural use is restricted by their rapid degradation in oxidising environments at temperatures as low as 500°C. For demanding aerospace applications such as for rocket nozzles and jet engine combustion chambers, where temperatures in excess of 2000°C may be encountered, a coating that would provide oxidation-resistance for even a short time would be advantageous.

As part of a programme to develop high-temperature, oxidation-resistant coatings for carbon-carbon composites researchers at GenCorp Aerojet Electronic Systems Division, in Azusa, California, investigated a closed-shell molecule, the Engel-Brewer compound zirconium triplatinide, $ZrPt_3$ (1). This material was selected because its melting point is in excess of 2190°C and it can be formed by heating a mixture of the two elements at temperatures above 2500°C.

An electron-beam evaporation procedure was used to build up a multilayered structure of zirconium and platinum on both pyrolytic graphite and phenolic resin/graphite samples. Three layers of each metal were deposited to give a total thickness of either 0.5 or 2.0 μm , the relative thicknesses of the individual layers being determined by the amounts calculated to yield stoichiometric $ZrPt_{33}$, when homogenised. Preliminary results demonstrated that the zirconium/platinum multilayers were adherent and provided oxidation-resistance to the underlying substrate. The metallic layers react together

at high temperatures, either during a preparatory annealing stage or in high temperature operation, to form the stable oxidation-resistant $ZrPt_3$ compound. Also, the highly reflective nature of the coating reduced the heat load on the substrates for short-time and high-temperature applications.

A more recent paper from the same laboratory reports the results of an investigation of the reaction mechanisms of oxygen, hydrogen and water vapour with $ZrPt_3$ and also $HfIr_3$ as a function of temperature and under ultra high vacuum conditions (2). The effect of hydrogen on the oxidation reaction is considered to be particularly relevant as hydrogen is present in rocket exhaust emissions.

The results indicate that these compounds only partially react with oxygen and water vapour, forming a surface oxide layer with a maximum thickness of 35Å. Vacuum annealing and hydrogen dosing prior to oxidation inhibit any subsequent oxidation of $ZrPt_3$, while exposure to hydrogen after oxidation reduces the surface oxide.

These materials show promise as oxidation-resistant coatings, providing they completely cover the carbon substrate.

References

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