

Symposium on Hydrogen in Metals

PALLADIUM CONTINUES TO FIND APPLICATION

The International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications (I.S.M.H.S.) was held at the Max-Planck Institute for Metal Research, Stuttgart, West Germany from 4th to 9th September 1988. Over 300 papers and posters were presented covering all aspects of metal-hydrogen behaviour. The symposium represented the unification of two, previously separate, conference series and the end of both the Hydrogen in Metals and the Metal-Hydride series of meetings. This review outlines some of the 30 to 40 papers that were concerned with the interaction of hydrogen with the platinum group metals.

Amorphous Alloys

The reported work on amorphous materials included a study by U.S. investigators of the palladium-containing Zr_2Pd alloy which absorbs hydrogen to form either an amorphous Zr_2PdH_x hydride or a separate crystalline phase (R. C. Bowman, D. R. Torgeson, R. G. Barnes, A. J. Maeland and J. J. Rush). The experimental data showed that the diffusion rates followed simple Arrhenius behaviour when the hydrogen atoms occupy only one specific interstitial site, for example the Zr_4 tetrahedra in $Zr_2PdH_{1.84}$. However, at higher hydrogen concentrations, where different interstitial sites are filled, considerably more complex behaviour was observed for both the crystalline and glassy hydrides. A thorough analysis of diffusion in both forms of the hydride has been carried out.

A paper by G. Driessen and K. W. Kehr of the Institut für Festkörperforschung der Kernforschungsanlage, Jülich, West Germany, and D. Richter, Institut Lave-Langevin, Grenoble, France, questioned the accepted view that the motion of hydrogen in amorphous $Pd_{1-x}Si_x$ alloy, as investigated by quasi-elastic neutron scattering (Q.N.S.), could be described by considering the hydrogen in interstitial sites of

energy given by a simple Gaussian distribution. In such treatments the saddle point energies are considered to be constant, but Driessen considers this to be inappropriate in view of the glassy structure. Instead he employed a modified model in which the PdSi alloy was described by a Gaussian distribution of saddle point energies. In a second paper on the $Pd_{1-x}Si_x$ alloy, G. Driessen, R. Hempelmann and D. Richter employed Q.N.S. for the direct observation of hydrogen motions on the time scale $10^{-8} < t < 10^{-11}$ seconds, and in the spatial range $< 50 \text{ \AA}$. This work revealed two distinct jump processes, slow and fast. Using an appropriate model, they proposed that these two regimes suggested the occupation of two types of interstice, these being the octahedral and tetrahedral sites.

A paper by B. Bogdanovic, S. Huckett, B. Spliethoff and U. Wilczok of the Max-Planck Institute reported the reaction of catalytically prepared MgH_2 or $Mg(CH_2CH_3)_2$ with certain palladium complexes to produce an amorphous compound which analyses as $MgPd$. So far this has been obtained only as a crystalline solid. The paper points to the interesting possibility of being able to prepare previously unknown amorphous alloys via a metal-hydrogen route, and also reports the existence of a previously unknown hydride Mg_2PdH_2 and the new metallic phase Mg_2Pd .

Order-Disorder Transformations

Another popular study which featured the platinum group metals was one detailing the influence of order-disorder transformations on the equilibrium and the kinetic behaviour of dissolved hydrogen.

In a paper by P. Ahlzen, Y. Andersson and R. Tellgren of the University of Uppsala, Sweden and Professor T. B. Flanagan of the University of Vermont, U.S.A., the Pd_3Mn alloy was studied. This orders to the Ag_3Mg

type structure at 803 K, and the ordered alloy was observed to absorb more hydrogen than the disordered alloy, a fact attributed to the alteration in the relative populations of different sites during the ordering process. In addition, hydrogenated Pd₃Mn was observed to undergo a hydrogen induced phase change, whereby an ordered structure of the type Cu₃Au formed at temperatures between 573 and 793 K.

Two platinum group metals were featured in a paper on ordering by B. Coluzzi, C. Costa, P. Marzola and F. M. Mazzolai of the University of Perugia, Italy. This paper concentrated on the stress induced ordering process in a single crystal of Pd_{0.85}Pt_{0.15}H_{0.29} as observed through ultrasonic elastic measurements.

The order-disorder systems Pd₃Fe and PdFe were prepared and electrolytically charged with hydrogen by C. U. Maier, M. Hirscher and Professor H. Kronmuller of the Max-Planck Institute. This group used magnetic after-effect measurements to follow single jumps in the hydrogen diffusion process. They found relaxation spectra composed of characteristic maxima and minima, the extent of the maximum being highly dependent on the degree of order within the alloy. Using the data obtained about the specific jumps in conjunction with a statistical model of the site distribution, they assigned the various jump processes to particular cell configurations, such as 6Pd, 5PdFe and 4Pd₂Fe, and thus fitted the hydrogen behaviour to the degree of order in the alloy.

Two papers from Professor I. R. Harris, M. L. Doyle and R. Wileman of the University of Birmingham, U.K., reported the marked influence of lattice order in palladium-12.5 per cent yttrium and palladium-8 per cent yttrium systems on their hydrogen dissolving and diffusing properties, respectively. This work showed that the formation of the ordered Pd₃Y superlattice, from the disordered solid solution, caused a significant decrease in hydrogen solubility, a fact which was ascribed to a rearrangement in site population and to a small change in lattice parameter. The second paper reported the extremely high permeation rates which could be obtained using a palladium-8

per cent yttrium alloy, and associated the sensitivity of the permeation process with the thermal history of the sample. Interesting isotope effects were also presented.

A poster presentation from Professor V. A. Somenkov, V. Glazkov, A. Iroova, I. Kurchatov (Institute of Atomic Energy), V. Antonov, and E. Ponyatovskii (Institute of Solid State Physics), U.S.S.R., detailed a hydrogen induced ordering process in a palladium-silver alloy, whereby the injection of hydrogen at high pressures caused the ordering of the metal atoms at temperatures around 420 K. The work also raised the possibility of producing ordered binary alloys which might not be available by normal routes.

Hydrogen in Catalysis

Two papers reported on the importance of hydrogen and platinum group metals as catalysts. In the first, Z. Paal of the Hungarian Academy of Sciences, examined the role of hydrogen in various hydrocarbon reactions which are promoted by a platinum catalyst. The effect of a hydrogen pre-treatment on the platinum catalyst showed that the size of crystallites was affected by the particular sintering temperatures, and he noted that a heat treatment in a hydrogen atmosphere may also influence the effectiveness of the catalyst, by changing the concentration of other elements present in the platinum. In addition to the role of hydrogen in pre-treating the catalyst, the paper reported that during the use of the catalyst, marked maxima were produced in the yields of various model hydrogenation reactions (such as n-heptane, n-hexane and alkylcyclopentanes) as a function of hydrogen pressure. This was interpreted as being due to the hydrogen influencing the dissociation of active intermediates during the catalytic process, so that at high hydrogen pressures less dehydrogenation species are produced. The role of hydrogen in the deactivation of the catalyst and the possible reactivation of a catalyst using hydrogen were also discussed.

A second paper also dealing with catalysis analysed the process of hydrogenation of

cyclopolyolefines (5 to 12 carbon atoms) using a palladium-6 per cent ruthenium catalyst. This work by Professor V. M. Gryaznov, M. M. Ermilova and N. V. Orekhova of the Institute of Petrochemical Synthesis, Moscow, showed that if a mixture of hydrogen and cyclopolyene vapour was introduced above the surface of the alloy the reaction would only start, and be sustained, if a definite amount of hydrogen was absorbed by the catalyst. If the catalyst was employed in a membrane configuration then the hydrogen:palladium ratio critical to the continuing reaction could be made to remain constant, rather than decrease as the reaction proceeds; which was the case when the inert gas mixture was fed over the alloy.

Superconductivity

A poster presented by I. T. Belash, V. E. Antonov, O. V. Zharikov, A. I. Latynin and A. V. Palnichenko of the Institute of Solid State Physics, Moscow, reported that developments in high pressure hydrogenation (pressures in the GPa range) enabled a number of superconducting hydride phases which are unstable under normal conditions to be synthesised. Among these phases were RuH_x where the incorporation of hydrogen caused the superconducting transition temperature of the pure metal to fall from 0.495 to 0.455 K. The addition of hydrogen to rhodium, with a superconducting temperature of 3.25×10^{-4} K, resulted in no superconductivity being detected within the limits of their determination.

Palladium-Hydrogen Systems

The unique properties of palladium metal among the platinum group metals, and indeed within the whole periodic table, ensured a broad representation of papers on palladium-hydrogen and palladium alloy-hydrogen systems.

Joint work by Czechoslovakian and Belfast researchers examined the diffusion characteristics of the palladium-hydrogen system in the α -phase using the diffusion elastic technique. F. A. Lewis, Queen's University, Belfast, analysed the effect of additions of

titanium, zirconium, niobium and cerium on the plateau pressures of various palladium alloy hydrogen systems and concluded that there is a direct link between the expansion and contraction of the lattice and the corresponding shape of the hydrogen isotherms.

Professor H. Brodowsky and Y. Chen of the University of Kiel, West Germany, showed the isotherms of a series of palladium-indium alloys, containing between 3.5 and 14 atomic per cent indium. An interpretation of the shape of the isotherms, based on well understood principles of increasing lattice dilation and decreasing density of states at the Fermi level as the hydrogen content of the alloy increases, was successful in modelling this system.

A poster by Professor B. Baranowski (Polish Academy of Sciences), F. A. Lewis and S. G. McKee (Belfast) and K. Kandasamy (University of Jaffna, Sri Lanka), investigated the changes in pressure within tubular membranes of palladium alloy following abrupt changes in the hydrogen contents of the outer surfaces of the tube walls. These changes were attributed to a strain-induced Gorsky effect transfer of hydrogen within the tube walls as the membrane bends.

T. Greber and L. Schlapbach, the University of Fribourg, Switzerland, provided a poster on the possible photogeneration of hydrogen from water at a palladium-cerium interface, the reaction being driven by the cyclic oxidation and reduction of the Ce ion.

The newly discovered hydride Na_2PdH_2 was examined by D. Noreus of the University of Stockholm, Sweden, who showed that at 400°C the hydride became molten. This property of melting prior to disintegration of the hydride is unique among ternary metal hydrides. To date the efficiency of heat pumps has been limited by the poor thermal conductivity of conventional solid powder reaction beds, therefore this material offers the possibility of more efficient heat pumps.

Many other papers concerned with palladium were presented including two papers on hydrogen trapping at dislocations in pure palladium and on the isotopic effects associated

with hydrogen, deuterium and tritium dissolved in palladium-silver alloys. The effects of hydrogen in palladium on Hall coefficients and thermoelectric power was also covered. In addition the behaviour of hydrogen in thin film and single crystal palladium was reported.

The Future

This survey reports briefly on only some of the platiniferous papers presented at the Stuttgart conference. The amount of work reported demonstrates continued interest in the interaction of platinum group metals with hydrogen, from both a fundamental and an applied viewpoint. The full conference pro-

ceedings will be published early in 1989 in the journal *Zeitschrift für Physikalische Chemie Neue Folge*.

The continuation of the I.S.M.H.S. conference series is to be held in the first week of September 1990 at Banff, Alberta, Canada. For details contact Professor F. D. Manchester, Department of Physics, University of Toronto, Canada. In the interim, a Gordon Conference on metal-hydrides is to be held 10th to 14th July 1989 at Tilton School, New Hampshire, U.S.A. A programme description, contact address and application details for this conference will appear in the March 1989 issue of the publication, *Science*. M.L.D.

A Durable Catalyst for Sealed Gas Lasers

Carbon dioxide transversely excited atmospheric pressure (TEA) lasers emit ultra-short pulses of infrared radiation in narrow, nearly parallel beams. The optical gain occurs in a pulsed, uniform electric discharge in a mixture of carbon dioxide, nitrogen and helium. To achieve maximum peak power output per unit discharge volume, a high concentration of carbon dioxide is required. In sealed operation, however, the carbon dioxide dissociates into carbon monoxide and oxygen, and even low concentrations of the latter cause the discharge to degenerate into localised arcs. Therefore it is necessary to ensure that the carbon monoxide and oxygen are recombined just as rapidly as the carbon dioxide is produced.

When the prolonged operation of a sealed carbon dioxide laser was first reported some ten years ago a thin platinum wire heated to a temperature of 1100°C was used to catalyse the recombination of the carbon monoxide and the oxygen. However, for some applications a hot platinum wire was too fragile, consumed too much power and created a cooling problem.

The need for lasers with much higher pulse repetition frequencies further increased the requirement for a catalyst with substantially greater activity at ambient temperature, and the use of finely dispersed platinum group metals supported on porous stannic oxide was reported to be capable of continuously recombining the carbon monoxide and oxygen generated in sealed carbon dioxide TEA lasers (1).

Now a communication from the Royal Signals and Radar Establishment reports the first use of a platinum/Fecralloy catalyst in a

long-lived sealed carbon dioxide TEA laser (2). Fecralloy steel is the Registered Trade Mark of the U.K. Atomic Energy Authority for a specific range of alloys developed at Harwell, and its use as a support for platinum group metals catalysts developed for automotive emission control and catalytic combustion has been described here previously (3). This metallic support is a ferritic steel containing chromium, aluminium and yttrium which can be heat treated to form an alumina-rich surface layer to which the platinum metals can be applied, using a proprietary technique.

As oxygen is the main cause of arcing in sealed carbon dioxide TEA lasers, if a laser is to achieve a prolonged life it is necessary to remove any oxygen at the same rate as it is produced by dissociation. Now platinum/Fecralloy has been shown to be an active catalyst for carbon monoxide oxidation. In the basic laser gas mixture, at a total pressure of one atmosphere, the removal rates of oxygen and carbon monoxide increase, up to a point, with the power input to the catalyst. For a given power input, platinum/Fecralloy recombines these two gases five times faster than a hot platinum wire does. The durability of the former is an additional advantage for use in compact, sealed carbon dioxide TEA lasers.

References

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