Hydrogen in Palladium and its Alloys

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A symposium organised by Professor E. Wicke and Professor T. B. Flanagan on the general topic of 'Hydrogen in Transition Metals' was held in July at the Institute für Physikalische Chemie of the University of Münster. Most of the papers presented were concerned with palladium or its alloys and a brief review of these contributions is given here.

The bulk of the subject material at this conference concerned the interaction of hydrogen with palladium and its alloys, although considerable attention was also paid to the nickel/hydrogen system and to the behaviour of the hydrides of vanadium, niobium and tantalum.

Dr H. Brodowsky of the University of Münster opened the symposium with a review of current attempts to account theoretically for the form of the (p-c-T) relationships between the non-stoichiometric hydrogen contents of palladium and palladium alloys and the equilibrium pressure of hydrogen as a function of temperature. He outlined the theoretical approach in which the non-ideal solution of hydrogen can be considered as associated with a combination of lattice strain and the filling of the electron bands of palladium and its alloys. Dr Brodowsky then discussed the extensions of this form of theoretical approach to account for the experimental form of low temperature specific heat data for the palladium/hydrogen system, and for the form of the p-c-T relationships of the vanadium, niobium and tantalum/hydrogen systems.

Sustained interest in Münster concerning diffusion of hydrogen in palladium was reflected in the contributions of H. Züchner and K. Meyer which dealt, respectively, with diffusion of hydrogen in the high (β-) and low (α-) hydrogen content phases of the palladium/hydrogen system. These talks revealed that there is now a high measure of agreement between diffusion coefficients obtained from several sources and by different techniques over a wide range of temperature. They also indicated the importance of considering chemical potentials rather than concentrations of hydrogen in calculations of diffusion coefficients. Meyer presented an analysis of problems of estimating the kinetics of surface processes in experiments in which oxygen and ethylene were reduced by hydrogen which was being continuously diffused through a palladium membrane.

F. A. Lewis of Queen's University, Belfast, presented a review of the development of knowledge concerning correlations between electrode potential measurements and the p-c-T relationships of palladium and palladium alloys. Attention was given to the derivation of these relationships from a knowledge of the kinetics of the absorption of molecular hydrogen from solution when this was governed by diffusion transport through the Brunner-Nernst interfacial layer.

Professor T. B. Flanagan of the University of Vermont reviewed the various techniques which have been employed in electrochemical methods for the measurement of coefficients of diffusion of hydrogen in palladium. He next gave a detailed analysis of a technique in current use at Münster which had an important advantage in that there was an effectively negligible flux of hydrogen into or out of specimens over the times of measurements. Professor Flanagan then presented recently determined values of the diffusion

coefficients of hydrogen in several series of palladium alloys as obtained by this technique, and discussed the form of the relationships between diffusion coefficient and alloy composition.

Professor B. Baranowski, of the Polish Academy of Sciences, Warsaw, gave a general review concerning experimental problems in the study of the nickel/hydrogen system. An outline was presented of the development at Warsaw of high pressure apparatus, capable of attaining pressures up to about 16,000 atmospheres, which was necessary for studying the form of equilibrium p-c-T relationships over a wide range of hydrogen contents. Professor Baranowski then discussed measurements of lattice constants, thermoelectric power and electrical resistance concerning the nickel/hydrogen systems, and also presented information concerning measurements of changes of the electrical resistance of hyrided palladium in equilibrium with hydrogen gas at very high pressures.

Professor G. Wedler of the University of Erlangen gave a review of experimental studies with ultra-high vacuum techniques of changes of heat of adsorption, electrical resistance and work function of evaporated nickel films resulting from the adsorption of hydrogen and deuterium. Results from experiments in which very small amounts of either isotope were successively adsorbed or desorbed, suggested that at all coverages some but not all of either adsorbed isotope was readily exchangeable. In an analysis in which the existence of different forms of available adsorption sites on different crystal faces was considered, it was concluded that differences in such respects were not sufficient to have a great influence on the differential heat of adsorption, in keeping with its observed behaviour up to complete monolayer coverage.

Dr R. Rubin, of the European Atomic Energy Research Centre at Ispra, discussed the experimental problems in obtaining diffusion information from measurements of the coherent scattering of low energy neutrons by hydrogen in low concentrations in palladium, niobium, vanadium and tantalum. This technique seems uniquely valuable in indicating favoured crystallographic directions for interstitial jumps.

M. Mahnig of the University of Münster reviewed recent experimental data obtained at Münster concerning the effect of hydrogen on the magnetic properties of palladium and several palladium alloys, and on the Mössbauer spectra of palladium/tin and palladium/iron alloys. Results were discussed in terms of changes of the electron band structure of palladium.

Dr H. J. Bauer of the University of Munich reported extensive experimental information concerning changes of the ferromagnetic behaviour of thin foils of nickel and nickel/copper alloys on absorption of hydrogen by electrolysis. Conjoint measurements had also been made of changes of the electrical resistance and lattice parameters of the foils. Photomicrographs of changes of the appearance of the nickel foils during electrolysis were also presented.

Hydrogen Diffusion through Rhodium-Palladium Alloys

Palladium alloys used for the purification of hydrogen by diffusion must not become deformed during the repeated thermal cycles to which they are subjected. Workers at the State Scientific Investigation and Planning Institute for the Rare Metal Industry, Moscow, have now shown (1) the effect of adding rhodium to stabilise alloys used in diffusion equipment by X-ray structural analyses of 1 per cent rhodium-palladium, 1 per cent rhodium-19 per cent silver-palladium and 10 per cent rhodium-palladium. Deformation of the two 1 per cent rhodium alloys after 20 to 800°C thermal cycles was shown to be due to an $\alpha \rightleftarrows \beta$ phase change, which altered their volume. 10 per cent rhodium-palladium, which is nearly as permeable to hydrogen as pure palladium, had no phase change, thus explaining its stability in such conditions. However, even 1 per cent rhodium addition significantly increased the stability of 20 per cent silver-palladium.

(1) A. A. Rodina, M. A. Gurevich and N. I. Doronicheva, *Zh. fiz. Khim.*, 1968, **42**, (7), 1822.