Hydrogen in Palladium

AN INTERNATIONAL CONFERENCE IN BIRMINGHAM

An International Conference on hydrogen in metals was held at the University of Birmingham on January 5th and 6th under the auspices of the Faraday Division of the Chemical Society. Over forty papers were presented, many of them dealing with palladium and its alloys. These latter papers are reviewed briefly in this note.

The interaction of the smallest interstitial atom, hydrogen, with the metallic lattice continues to attract considerable interest from the scientific community, as was amply evidenced at the international meeting held recently in Birmingham. As may be expected, many of the papers featured the classical palladium-hydrogen system and related alloys. The rare earth metals and the Group VA elements vanadium, niobium and tantalum also commanded a good deal of attention.

The first paper of the conference dealing with palladium was presented by Professor T. B. Flanagan of the University of Vermont. In the work described, an unambiguous demonstration has been made of the effect of dislocations on the solubility of hydrogen in the low content α-Pd phase. Solubility enhancements up to 23 per cent were observed in palladium heavily cold worked by milling. A good correlation between this solubility increase and dislocation density was obtained. Almost identical enhancement was found for deuterium, in spite of the solubility of this isotope in α-palladium being significantly lower.

Internal Friction Measurements

Internal friction measurement is a searching technique for the determination of interstitial behaviour, and Dr F. A. Lewis of Queen's University, Belfast, presented one of several papers on this topic. His study involved a novel resonance vibration method using disc samples of palladium-silver alloys. From the discontinuities in the plots of vibration frequencies against temperature it was possible to construct the phase diagram of the Pd/Ag/H system showing the hydride transformation boundaries. The upper temperature limit of the two-phase region is reduced from 300°C for pure palladium to near room temperature for the 23 per cent silver alloy or to −120°C for the 40 per cent silver-palladium alloy.

The "50K transition" in PdH was also the subject of internal friction studies by Dr G. J. Zimmermann of Munich University, and by Professor F. D. Manchester of Toronto. In spite of extensive new data being available from specific heat, neutron diffraction, n.m.r. and other physical measurements, doubt still remains on the precise nature of the structural changes involved in the transformation.

Dr M. Mahnig and Dr G. Sicking, both of the Institute of Physical Chemistry, Munster, presented papers dealing with the electronic structures of palladium-hydrogen and other alloys. One of the few techniques available for obtaining quantitative information on the local densities of states is Appearance Potentional Spectroscopy. New data from this and other sources show good agreement with the model proposed.

A study of the absorption of hydrogen and deuterium by palladium sponge over the range 80 to 140°C was reported by Professor D. H. Everett of Bristol University. Detailed thermodynamic analysis of the data obtained has given new information on the enthalpies and entropies of absorption over the whole composition range.

The only paper of the conference dealing specifically with mechanical properties was from the University of Birmingham, presented by Dr M. L. H. Wise. Alloy solid solution softening in body-centred cubic metals is now a commonplace phenomenon but the hydrogen softening reported by the Birmingham investigators is unusual. Microhardness measurements on a series of palladium-rare earth alloys (Pd-Y, Pd-Gd, Pd-Eu and Pd-Ce) showed that, apart from pure palladium and a few dilute alloys, pronounced softening occurred in these materials when charged with hydrogen by electrolysis. The hardness of a particular binary alloy was correlated with the product of the lattice expansion, determined by X-ray methods, and the electron concentration. The softening on hydrogenation can be explained by a reduction in the shear modulus and the atomic mismatch factor resulting from the filling of the 4d states. A consequence of this finding is that fabrication of palladium alloys may be facilitated if the material is in the hydrogenated state.

Significant progress in extending the range of hydrogen contents in β-phase palladium was described by Dr J. P. Burger of the Université D'Orsay. By a low temperature electrolytic technique, PdH_x was obtained with x values near to unity. Studies of these high hydrogen content samples by electrical resistivity and magnetic susceptibility measurements suggests that the $x=1$ region is simpler than at $x=0.7$; the hydrogen atoms only occupy interstitial sites and the 50K transition is absent.

Dr H. Zuchner of the Institute of Physical Chemistry, Munster, discussed several variants of electrolytic methods for the study of metal-hydrogen systems. The poor interphase transfer at the electrolyte/metal boundary for most metals has now been overcome by coating with a thin evaporated palladium layer after an ultra-high vacuum cleaning operation. The versatility of the electrochemical method resides in the possibility of varying the boundary conditions, for example by constant current, pulse methods, etc. Diffusion constants, permeabilities and solubility data may all be derived from the measurements.

Transport Processess

Experiments on the mobility of interstitial atoms in metals by various transport processes constitute a powerful method for studying thermodynamic properties of such systems. Three such transport processes were analysed in detail by Dr H. Wipf of Munich University, the Gorsky effect (stress-induced transport), electrotransport and thermotransport. The magnitude and behaviour with time of the concentration changes were shown to depend on the applied forces, the diffusion coefficient and chemical potential of the hydrogen atoms. A comparison was made between these transport processes and microscopic techniques for determining hydrogen mobility, and Mössbauer spectroscopy was discussed as a new method of studying hydrogen diffusion.

Contributions to the conference of direct industrial significance were few and far between. An exception was the description by Dr S. C. Lawrence, of Lawrence Electronics Co, Seattle, of a new hydrogen detection gauge. This is based on a slightly modified thermionic valve (6V6) fitted with a hydrogen permeable membrane. The membrane may be either a 0.016 in thick 1020 (0.2%C) steel window or a silver-palladium tube attached to the metal envelope of the valve. Hydrogen permeating through these membranes may be measured from the ionisation current between the electrodes. Many measurements of practical importance are possible with the gauge including control of hydrogen embrittlement during plating, internal corrosion in oil-wells, chemical or nuclear reactors, and sorbed hydrogen during pickling or other similar processes.

The papers presented at Birmingham will be published in full in a special issue of the *Journal of the Less-Common Metals*.

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