Hydrogen Treatment of Materials

PALLADIUM STUDIES REPORTED AT A DONETSK CONFERENCE

Technological interest in the results of interactions of hydrogen with metals and with various other materials has been concerned with both destructive and advantageous structural alterations. This has been demonstrated by the contributions presented at the series of conferences held over recent years in Wyoming, U.S.A., organised by A. W. Thompson, N. R. Moody and I. M. Bernstein.

The programme of studies pursued by Professor V. I. Goltsov and his colleagues in Donetsk, Ukraine, has tended to concentrate on the advantageous consequences resulting from the interaction of hydrogen with various materials. Thus at the recent conference on Hydrogen Treatment of Materials, held from 20th to 22nd September, 1995, at the State Technical University in Donetsk, Professor Goltsov, in a keynote introductory address, highlighted the advantages of hydrogen treatment. In many instances this can provide competitive alternatives to straightforward mechanical treatment or to other means of processing materials.

Considering the rather specific subject matter of this conference, there was an encouraging attendance of approximately 100 participants, including representatives from France, Spain, Poland, China, Japan, South Korea, United Kingdom and United States of America, together with representation from ten of the Confederation of Independent States, with most contributors being from Ukraine and Russia.

In the historically-centred review by Professor Goltsov, mention was made of various areas where advantageous results occurring after hydrogen treatments had either been initiated or further developed. These included improvements achieved in some well investigated topics, such as in specific cases of structural damage and distortion, embrittlement and even softening of metals and alloys.

Another previously quite well investigated research area, included to emphasis its advantageous significance, concerned macroscopic fracturing and powdering together with subsequent reformulation. This topic was introduced with particular emphasis on the treatment of titanium, titanium alloys and analogous materials. However it was also discussed in terms of the beneficial incorporation of hydrogen treatments during the processing of intermetallic and electronic materials. These may have relevance to the solution of problems associated with hydrogen storage and energy generation, such as hydrogen batteries and shape memory devices. Improvements in kinetic parameters, including those of diffusion processes, order-disorder transformations and the formation of specifically selected products, resulting from hydrogen treatment were also discussed.

Further Studies with Palladium and Palladium Alloys

Contributions dealing with studies on palladium and palladium alloys were still focused largely upon their use as hydrogen purification membranes and in particular chemical processes where their specific catalytic advantages are utilised. In both of these areas the technological research had two objectives: improving the composition of membrane materials used for various combinations of experimental conditions, and avoiding the development of irreversible lattice dimensional and dislocation structural network damage, resulting from the $\alpha \leftrightarrow \beta$-phase hydride transitions.

The possibility of unwanted dimensional changes taking place within membranes during sequences of hydrogen absorption and desorption was again addressed. R. V. Kotelva and colleagues from the Technical University in Donetsk described changes in the shape of a palladium plate and discussed experimental procedures in some detail. A further report from Donetsk, presented by T. A. Ryumishina and colleagues, concerned the evolution of stresses during hydrogen diffusion processes in palladium. Associated
problems of kinetic and morphological peculiarities occurring during hydride phase transformations were reported by Yu. A. Artemenko and co-workers of Donetsk, while allied measurements of changes in the mechanical properties of the palladium/hydrogen system were presented by A. P. Kusin and colleagues, also from the same university.

Further quantitative and theoretical consequences of the effects of hydrogen expansion were discussed. The modelling of hydrogen-induced non-elastic deformations was reported by V. N. Madudin and co-workers, Chelyabinsk, Russia. A paper by Young-sui Cho, University of Kangwon, South Korea, considered the kinetics of hydrogen absorption - determined from measurements of changes in the electrical resistivity of thin palladium films.

The importance of stress/strain gradient behaviour to bulk lattice hydrogen diffusion processes, as shown by Gorsky and Diffusion Elastic Effect related phenomena, was reported in a paper by R. V. Bucur, Uppsala, Sweden, K. Kandasamy, Jaffna, Sri Lanka, Y. Sakamoto, Nagasaki, Japan, together with X. Q. Tong and F. A. Lewis, Belfast, Northern Ireland, with particular reference to apparent changing trends in the hydrogen diffusion coefficient, D_H, with the initial values of the hydrogen content.

Lastly, results of hydrogen isotope structure analyses by powder X-ray diffraction, for compositions approximating to PdH_x, PdD_y and PdT_z were reported by T. A. Beiter and J. S. Cantrell, of Miami University, Oxford, Ohio.

A number of the papers presented at this Donetsk conference will be published in a special issue of the International Journal of Hydrogen Energy.

Alkane Oxidation by Encapsulated Ruthenium Complexes

The oxidation reaction of alkanes by the usual metal complex catalysts eventually results in deactivation or catalyst degradation. Catalysts, such as porphyrin- or phthalocyanine-based complexes, can acquire improved stability by a halogenation treatment. However, these systems still eventually degrade. Encapsulating catalytic materials within other structures is now a routine operation, and has resulted in many interesting properties (see, for example, Platinum Metals Rev., 1994, 38, (2), 59) including enhanced catalytic activity. Therefore, isolating the phthalocyanine catalyst, to remove it from outside attack, by encasing it within zeolite pores was tried as a way to improve its lifetime. However, there are still drawbacks caused by the peroxide and iodosylbenzene oxidants.

Recent work has involved encapsulating an iron phthalocyanine, FePc, catalyst in zeolite within a polymer matrix, and this has been successful in producing a more active and stable catalyst. A perfluorinated FePc complex catalyst, however, was as sensitive to the oxidant as FePc.

Based on this researchers at the University of Texas at Dallas, U.S.A., (K. J. Balkus, M. Eissa and R. Levado, J. Am. Chem. Soc., 1995, 117, (43), 10753-10754) prepared a fluorinated ruthenium phthalocyanine catalyst, RuF_6Pc, and encapsulated it in zeolite NaX. It was used together with tert-butyl hydroperoxide oxidant for the oxidation of cyclohexane and cyclohexanol at room temperature.

Encapsulation prevented dimerisation of the complex and enhanced the activity. Even though the catalyst now contained less metal, it had over ten times the activity of the homogeneous catalyst. Cyclohexane was oxidised primarily to the ketone at a rate of almost 3000 turnovers/day and no deactivation was seen after over 20,000 turnovers. Placing the RuF_6Pc into the zeolite increased its selectivity towards cyclohexanone, compared with the homogeneous catalyst. The peroxide efficiency was also improved.

This system may be one of the best low-temperature peroxide-based oxidation catalysts.

Palladium Alloy Mechanical Properties

The mechanical properties of three structural forms of palladium-manganese alloy, containing 10 to 25 atomic per cent manganese, have been examined (D. Jonsen, A. Moss, J. Shenk, K. Rebeiz, S. Nesbit, R. Foley and A. Craft, Mater. Sci. Eng., 1995, A199, (2), 131-138). One form, with L1_2 structure, produced by the presence of hydrogen during heat treating the alloy, had markedly different properties to the other two forms; these included enhanced strength and hardness, reduced ductility and fatigue life. The differences are thought due to the formation of the L1_2 structure and a hydride phase in this alloy whose decomposition significantly affects the properties. The hydrogen-induced lattice rearrangement may be a way of manipulating the mechanical properties of alloys.

Platinum Metals Rev., 1996, 40, (1)