

# A Selective Review of Metal-Hydrogen Technology in the Former U.S.S.R.

## ADVANCED PALLADIUM APPLICATIONS FEATURED

Substantial mineral wealth and a long metallurgical tradition have made the states of the former Soviet Union highly developed in terms of advanced metals technologies. One particularly well developed technology concerns the interaction of metals with hydrogen. The First International Conference on Diffusive-Cooperative Phenomena in Metal-Hydrogen Isotope Systems, held at the Donetsk Polytechnic Institute, Donetsk, Ukraine from 15th to 19th September 1992, provided an opportunity to review some of the recent developments and the main themes in metal-hydride technology in the Confederation of Independent States (CIS). The conference included around 200 papers from all states of the CIS, with around forty concerned specifically with the platinum group metals.

Topics covered during the conference included fundamental research concerning the nature of metal-hydrogen systems, their physical and electrical properties, and phase transformations. The detrimental effects of hydrogen on construction materials such as steel and materials associated with nuclear engineering were considered in a series of paper contributions. Some thirty papers on cold fusion testified to the persistent and perplexing nature of this phenomena. Reported applications of metal-hydrogen technology included: hydrogen processing of materials, hydrogen generation and storage and hydrogen purification technology based on palladium alloy membranes.

### Fundamental Physical Phenomena in Metal-Hydrogen Systems

Many of the contributions in this category were concerned with the changes brought about in the physical and mechanical properties of metals which can be brought about by successive hydrogenation-dehydrogenation cycles. V. A. Goltsov

of the Donetsk Polytechnic Institute has described this type of phenomenon using the Russian term "hydrogen phase naklep" (1).

### Hydrogen Phase Naklep

Much modern physical metallurgy is based on the polymorphism of metals. It is the polymorphic character of steel which allows the regulation of mechanical and physical properties via heat treatments. However, a large number of metals are not polymorphic and therefore only plastic deformation and subsequent re-crystallisation can be used to modify and control their properties.

The basic premise of hydrogen phase naklep is that a metal is charged with hydrogen electrochemically or under gas pressure to form the hydride phase. The metal is then cycled through several hydrogenation-dehydrogenation cycles during which the material undergoes repeated volume expansion and contraction. This results in the development of internal stresses and defect generation. Under controlled conditions the degassed material may be transformed into a new, state, characterised by high strength and with modified physical and mechanical properties. The conditions for hydrogen phase naklep will vary according to the metal. Strong hydride forming metals such as palladium, niobium, titanium and zirconium may only require fractions of a bar of hydrogen in order to be processed by hydrogen phase naklep. Metals which absorb hydrogen less readily will require higher hydrogen pressures in order to achieve similar results. In principle at least, hydrogen phase naklep should be applicable to all metallic elements.

The fact that a very large number of metals will reversibly absorb hydrogen offers the opportunity of using hydrogen phase naklep to modify their properties without recourse to working. An example of a material which can be readily processed by hydrogen phase naklep is palladium.

Palladium is not polymorphic but occludes hydrogen easily at room temperature. Hydrogen phase naklep applied to palladium (35 to 40 hydrogenation-dehydrogenation cycles) allows the ultimate tensile strength and yield limit to be increased by 1 to 3 times that of annealed palladium, which is equivalent to 80 per cent plastic deformation. A similar hydrogen treatment increases the microhardness of palladium by a factor of 2.5 compared to the annealed metal. Therefore, when applied to palladium, hydrogen phase naklep results in an increased strength, high plasticity state such that the ability of the material to withstand large deforming loads is significantly enhanced.

The effect of hydride transformations in palladium on electrical resistance was reported by A. P. Kusun, Donetsk Polytechnic Institute. An interesting conclusion of this work was that the effects of multiple saturation-degassing cycles do not simply accumulate in palladium. In fact after several cycles a very stable structure with an increased electrical resistance is formed.

Results detailing the kinetics and morphology of the  $\alpha$ - $\beta$  phase transformation in a series of palladium samples under a hydrogen pressure of 0.1 to 0.2 MPa and temperatures in the range of 20 to 300°C was presented by Yu. A. Artemenko, Donetsk Polytechnic Institute. One of the techniques utilised in this work involved the direct optical observation of palladium during the  $\alpha$ - $\beta$  phase transformation. Under isothermal (baric) conditions the phase transformation proceeds through "massive" precipitation. This is followed by a period of reduced growth before an explosion of "needles" heralds a further period of "massive" growth. This cyclic precipitate growth is a function of the diffusive flow of hydrogen towards the growing hydride phase. Migration of hydrogen towards the growing hydride occurs due to the stress field distribution produced by the volume differential between the hydride and solid solution phase.

The effect of hydrogen treatments on the physical and mechanical properties of several palladium-molybdenum alloys was reported by F. Berseneva and colleagues at the Ural Department of the Russian Academy of Sciences,

Ekaterinburg, Russia. The hydride phase was only detected in alloys with less than 6 atomic per cent molybdenum. Alloys containing larger amounts of molybdenum formed only dilute solid solutions with hydrogen. Those containing up to 10 atomic per cent molybdenum were strengthened during the initial stages of hydrogen charging, with the largest increase in strength occurring in alloys in which hydride formation took place. As the strength of the palladium-molybdenum alloys increased, alloys in which no hydride phase was formed became more plastic while hydride forming compositions became severely embrittled.

### **Hydrogen Processing of Metals**

Observations of various metal-hydrogen interactions show that large changes can be wrought in the structures of metals by their reaction with hydrogen. In addition to the modified structures produced by hydrogen phase naklep, hydrogen has been shown to be capable of promoting and suppressing order-disorder phenomena in metals, and causing phase separation in some alloys (2). The accompanying changes in physical and mechanical properties resulting from the interaction of metals with hydrogen illustrates the potential for hydrogen as a useful tool for processing titanium and aluminium-silicon, for example.

### **Hydrogen Storage and Generation**

Interesting technology for the storage and production of hydrogen was presented by R. G. Sarmurzina of the Chemical and Metallurgical Institute, Academy of Science, Kazakhstan. Sarmurzina proposed a two-stage process in which multi-component alloys based on aluminium are first used to release hydrogen from water, with the residue from the reaction being later used as a dehydrogenation catalyst for the production of further hydrogen from hydrocarbon feedstocks. The result is a near wasteless process for hydrogen generation from water and from hydrocarbons, such as cyclohexane.

The process begins with an alloy of aluminium with gallium, indium and platinum. This material reacts spontaneously with water to evolve

hydrogen and produce aluminium hydroxide phases. Sarmurzina presented a wealth of data detailing the hydrogen evolution process. The by-product of the hydrogen evolution reaction of the aluminium alloy with water is a mixed pseudo-boehmite and beyerite material impregnated with gallium, indium and platinum. The relative composition of the hydroxide phases appears to depend on the platinum content of the initial alloy. After calcining the mixed product, a platinum-gallium-indium on alumina catalyst is formed which is highly active for dehydrogenation of organics. Catalysts with 0.5 to 1 weight per cent platinum yielded 96 to 98 per cent benzene from cyclohexane, the dehydrogenation beginning at around 250°C. The reaction is entirely selective and at 350°C conversion reaches 99.9 per cent. The high activity of the catalyst prepared in this way, from the reaction of a bulk alloy with water, was due to highly dispersed platinum promoted by gallium and indium on the developed alumina surface.

### **Hydrogen Purification by Diffusion through Palladium Alloy Membranes**

Another technology which has reached an advanced state of development in the CIS is hydrogen purification using palladium alloy membranes. Although commercial examples of palladium alloy membranes exist outside the CIS these are generally limited to very small scale units passing between 1 and 50 cubic metres of hydrogen per hour. A recent publication in this journal highlighted a diffusion membrane plant developed by The State Nitrogen Industry (Moscow), capable of a hydrogen throughput of around 2000 cubic metres per hour (3). This represents a rare example of a medium-large scale application of palladium alloy membranes.

One of the striking aspects of palladium membrane development in the CIS is the attention which has been paid to alloy development. Whereas most membrane units outside the CIS use the standard palladium-23 per cent silver alloy, the range of materials used in the CIS is more diverse, centred around the so called B-series alloys (4). The B-alloys are a range of multi-component alloys often containing 4 to 6 ele-

ments, each composition designed for a particular set of operational requirements. Examples of the B-series of alloys include: B1(Pd-Ag-Au-Pt-Ru-Al), B2(Pd-Ag-In-Y), B4(Pd-Ag-Y-Yb) and B6(Pd-Au-Fe). Alloys B2 and B4 have a high hydrogen capacity and hence a high hydrogen permeability, alloys B3, B9 and B11 are designed for high operating temperatures, while alloys B1, B5, B9 and B11 are capable of withstanding large pressure drops. Alloys B1, B4, B5, B9 and B11 are relatively resistant to cycling, alloys B1, B4 and B5 have increased resistance to poisoning and alloys B1, B2 and B5 show the largest isotope effects, useful for separating protium, deuterium and tritium. The alloys B2 and B3 are both capable of being strengthened in use, by hydrogen phase naklep (5).

The state of development of membrane technology in the CIS was illustrated at the Donetsk conference by more than a dozen papers.

The technological problems associated with the use of palladium alloy diffusion membranes for large scale applications were examined by V. M. Makarov, Ural Department of the Russian Academy of Sciences, Ekaterinburg, Russia. A crucial aspect of this technology is the selection of the membrane alloy. Makarov found complex alloys of palladium with other platinum group metals effective both in terms of high hydrogen throughput and high strength and durability.

The influence of local inhomogeneities, impurity elements and defects which alter the performance and durability of membrane systems was discussed by V. G. Sorokin of the St. Petersburg Technical University, Russia. In particular the segregation, accumulation and re-arrangement of small amounts of impurity elements such as potassium, calcium, magnesium, silicon, sulphur, titanium, iron and copper to the grain boundaries was seen as contributing to the early failure of membranes.

Shortcomings of the widely used palladium-20 to 25 per cent silver diffusion membrane alloy, in terms of its low strength and tendency to coarsen its structure during long term operation was discussed by N. I. Timofeev and co-workers at the Ekaterinburg Plant for the Treatment of Non-Ferrous Metals, Russia. Multi-component

alloys based on palladium-silver and palladium-platinum alloys were reported to show considerable improvements in their mechanical characteristics compared with the simple binary systems.

The influence of hydrogen dilation on the deformation and early cyclic failure of palladium alloy membrane elements has been examined by A. I. Berezin and colleagues at the State Technical University of Chelyabinsk, Russia. In particular, non-homogeneous hydrogen concentrations led to differential expansion within membrane elements and the resultant high stress states caused early membrane failure.

Three stages of production of tubular and flat foil membrane elements, namely alloy preparation and working; heat treatment; and welding were described by V. A. Kon'kova of the Ural Plant of Chemical Engineering, Ekaterinburg, Russia. Membrane elements manufactured by the methods outlined are currently being operated on an industrial scale. A large amount of data for these membranes under industrial conditions, were presented.

Eugene P. Chistov and co-workers of the State Scientific and Industrial Enterprise "Quantum", Moscow, presented a compact hydrogen purification membrane based on the B1 alloy. The device was of sheet construction with a number of individual "flag" membrane elements stacked together to give a hydrogen flow of up to 30 cubic metres per hour, at 500°C and 10 bar pressure.

A report of an examination of the behaviour of two membrane alloys, palladium-6 per cent ruthenium and B1, in a coke gas mixture was presented by V. A. Kurakin, Lugansk Engineering Institute, Ukraine, and colleagues from the Ekaterinburg Plant in the Treatment of Non-Ferrous Metals, Russia. The work was aimed at studying the passivation processes which occur when membranes are exposed to impure gas streams.

Both alloy membranes suffered a decrease in permeation performance after 16 hours exposure to the coke gas at 0.1 MPa pressure and a temperature of 550°C. A higher surface activity was noted for the palladium-6 per cent ruthenium alloy, confirming the beneficial effect of ruthenium on the catalytic activity of palladium.

A second presentation on the separation of pure hydrogen from coke gas was made by A. P. Kusin, Donetsk Polytechnic Institute. The report stressed that while many of the problems of construction and use of palladium alloy membranes have been solved, the application of this technology to impure gas streams is not yet well studied. Within the CIS groups were working on this problem and specifically looking at "off-gases" such as coke gas. An important conclusion of this early work was that although impure gas streams slow down the flow of hydrogen, these membranes do remain permeable to hydrogen.

Two reports focused on the effects of carbon films formed on palladium alloy diffusion apparatus as a result of hydrogen separation from hydrocarbon containing gas streams (I. E. Gabis et al, Physics Research Institute, St. Petersburg University, Russia). Experiments were carried out on films produced by the decomposition of natural gas on the B1 alloy. Graphite-like coatings, which formed under the conditions in which the purifiers operated, tended to slow down the permeation process. A model was developed to help optimise the operation of palladium alloy elements under such conditions.

### **Catalyst Membrane Technology**

The use of palladium alloy membranes in catalytic devices is another technology developed within the CIS which has been the focus of international attention. An impressive body of literature exists largely due to V. M. Gryaznov and co-workers, A. V. Topchiev Institute of Petrochemical Synthesis, Moscow (6). The metals-orientated nature of the Donetsk meeting probably deterred many catalyst scientists from attending. However, the possible use of palladium metal membranes as catalytic devices was reported by B. Yu. Nogerbekov et al (Institute of Organic Catalysis and Electrochemistry, Alma-Ata, Kazakhstan). The absorption of hydrogen into a palladium membrane was achieved electrolytically from a 0.1 M sulphuric acid solution. The atomic hydrogen thus produced was used in the hydrogenation of various classes of organic compounds including acetylene spirits, benzoquinone and also aromatic nitrogen

compounds, with the catalytic activity dependent on the polarising current density.

## Conclusion

This conference provided an excellent opportunity for the international community to examine the extent of the development of metal-hydrogen technology within the CIS. Hydrogen phase naklep, diffusion membrane and membrane catalysis technology based on palladium are examples where work carried out in the CIS constitutes the "state of the art". These areas therefore appear likely to continue to attract growing international attention in the future.

## Reduction of Nitrogen Oxides by Hydrocarbons PERFORMANCE OF PLATINUM METALS CATALYSTS INVESTIGATED

The removal of nitrogen oxides present in the gases emitted from sources such as electric power generation boilers, stationary internal combustion engines and gas turbine engines—all of which are likely to use excess oxygen to achieve maximum fuel efficiency—can be achieved by a selective reduction process using ammonia as the reducing agent, the reaction being carried out over a base metal oxide catalyst. It had been considered that hydrocarbons were ineffective for this reaction but recent work has indicated that with suitable catalysts it may be possible to use them in a process which removes nitrogen oxides from the exhaust gases of both diesel and lean-burn gasoline-fuelled engines. For practical application, high activity under high space velocity and also high selectivity would be required.

The activity and durability of a variety of catalysts have been investigated, but to-date there has been only little interest in using the platinum metals as catalysts for this purpose. Now, however, a team at the National Institute for Resources and Environment, Tsukuba, Japan, have investigated the performance of platinum, palladium, rhodium, iridium and ruthenium supported on  $\gamma$ -alumina as catalysts for this application (A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno and H. Ohuchi, "Performance of Platinum-Group Metal Catalysts for the Selective Reduction of Nitrogen Oxides by Hydrocarbons", *Appl. Catal. B: Environ.*, 1993, 2, (1), 71–80).

The addition of some hydrocarbons to the exhaust is necessary to compensate for the greater amount of nitrogen oxides generally emitted from combustors operating under net-oxidising conditions, and the properties of

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propene favour its use as the reducing agent. With both model mixtures and real diesel exhaust gases it was found that platinum-rhodium/ $\gamma$ -alumina displayed high activity for nitrogen oxides conversion, at 200 to 350°C. These catalysts are similar to the three-way catalysts used for controlling emissions from gasoline fuelled engines. It is concluded that platinum metals catalysts will find practical usage for this purpose, especially if their selectivity to nitrogen is improved.

## Nanoscale Platinum Technology

As microelectronic device and computer components are reduced to sub-micron size there is a need for metal features of nanometre thickness. At the Naval Research Laboratory, Washington, a method has been developed for fabricating platinum patterns of varied geometry which may be as little as 20 nm thick and with heights of up to 700 nm. These are produced by thermal decomposition of a platinum precursor molecule, tetrakis-(trifluorophosphine)-platinum, onto the surface of a contoured substrate. A detailed description of the fabrication process, and an analysis of the properties and morphology of the platinum film structures have recently been published (D. S. Y. Hsu, N. H. Turner, K. W. Pierson and V. A. Shamamian, *J. Vac. Sci. Technol. B*, 1992, 10, (5), 2251–2258).

The substrate is amorphous silicon, fabricated by lithographic techniques suitable for large scale processing, and this permits a very thin polycrystalline platinum film to be deposited, which in turn makes possible the production of ultranarrow patterns with 20 nm linewidths. It is suggested that further reduction in linewidth is possible by improving various parameters.