

# The Effects of Hydrogen on the Physical Properties of Palladium

## HYDROGEN-PHASE “NAKLEP” PHENOMENON DURING THE HYDROGEN TREATMENT OF PALLADIUM

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Palladium is not polymorphic, which is why the physical metallurgy of palladium and its alloys is quite poor in comparison with those of polymorphic metals (such as iron, titanium, and others). In recent years advances in the physical metallurgy of palladium and its treatment have been taking place. The changes are based upon the physical effects that hydrogen has upon palladium when it is taken into the metal (1). In Ukraine and Russia this has been called “hydrogen-phase naklep” and was first noted in 1972. This observation has led to an improved concept in materials science and engineering (1–5).

When palladium is saturated with hydrogen, it becomes a polymorphic material and hydride transformations may be induced in it by processes of heating ↔ cooling and/or saturation ↔ desaturation. As there are differences between the specific volumes of the  $\alpha$ -hydrogen solid solution and  $\beta$ -hydride phases in the palladium, these hydrogen-induced phase transformations cause internal plastic deformation (relaxation) and controllable strengthening of the palladium. Some basic changes of structure also occur: the density of dislocations grows, the size of the ‘mosaic’ blocks decreases while their number increases, the angle of their disorientation increases, and so on.

Unlike the internal cold work which occurs during the martensitic transformations in iron alloys, the structure changes mentioned above in palladium-hydrogen alloys are not only caused by internal plastic deformation but also by the development of some very specific processes of interactions of the solute hydrogen in the palladium, generating hydrogen-containing

phases and producing defects in the crystalline structure.

Because of the complex nature of this type of physical phenomenon, it has been described as “hydrogen-phase naklep” or the “HPN-phenomenon” (2, 5).

### Strengthening Effects

Annealed palladium has relatively poor mechanical properties, namely:

Ultimate strength	$\sigma_B = 180\text{--}200$ MPa;
Yield limit	$\sigma_{0.2} = 50\text{--}100$ MPa;
Relative elongation	$\delta = 20\text{--}25$ per cent.

An early noted HPN-phenomenon (1) was achieved by thermocycling specimens of palladium wire in hydrogen ( $20 \leftrightarrow 250^\circ\text{C}$ ), after which the wire specimens (diameter 0.5 mm) were fully degassed. During the hydrogen treatment the strength properties of palladium increased by a factor of 2–4, but the plastic properties of palladium decreased. It was consequently surmised that the HPN-treatment could be effectively used for strengthening palladium articles, *without noticeable changes to their dimensions and shape*.

### Superstrength Palladium Alloys: TRIP Alloys

Treating palladium alloys with hydrogen without immediate degassing can result in the formation of superstrength palladium-hydrogen alloys having high plasticities – the hydride TRIP-effect. (TRIP is transformation induced plasticity.)

The example shown in Figure 1 was achieved by a double (combined deformation-hydrogen)

treatment (3). First, 90 per cent of the possible plastic deformation of a palladium wire was induced, until it reached a specimen diameter of 0.5 mm. After this initial mechanical treatment, the palladium specimen had very high strength properties (points a and b) and very low plastic properties (point c). Samples were then HPN-treated. Hydride transformations,  $\alpha \rightarrow \beta \rightarrow \alpha$ , were effected by a number ( $n$ ) of pressure cycles (0.2 MPa  $\rightarrow$  1.33 Pa  $\rightarrow$  0.2 MPa) in a hydrogen atmosphere at 100°C. After this the specimens were not degassed and a new palladium hydrided material was obtained. From Figure 1 it is clear that this new hydrogen-containing material ( $n = 1-2$ ) is much stronger and has been found to be more plastic than the pure, annealed palladium.

The nature of HPN-strengthened metals having hydride TRIP-plasticity has been reviewed and detailed analysis of the hydrogen treatment of metals and metallic materials, based on hydrogen phase naklep has been more fully discussed (3, 4).

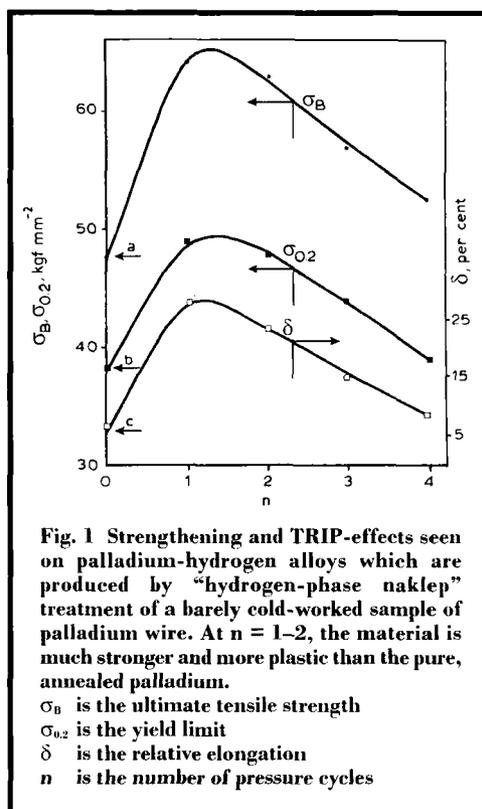
### Recrystallisation Treatment

HPN-strengthened palladium material has undergone recrystallisation annealing and its grain structure has been refined.

Samples of palladium wire were annealed in vacuum (about  $10^{-1}$  Torr) for 6 hours at 900°C. A metallographic investigation of the samples was then undertaken. The samples were found to have extremely large grains (generally, only two or three grains in the 0.5 mm cross section of the wire). Their size was in the range 0.25 to 0.15 mm.

The samples were then HPN-treated and metallographic investigation showed them to have the same grain size as did the annealed samples. Annealings at 100 and/or 200°C did not significantly change the microstructure or the character of the high angle boundaries.

However, for samples annealed at 300°C, the development of first-stage recrystallisations may be seen. Small, newly crystallised grains could be seen near the boundaries of the initially large grains. The dimensionally smallest of these newly changed grains was of the order of 15  $\mu\text{m}$ ; but



others may be 3-5 times larger. Annealing twins have also been observed. Annealing at 400°C led to further development of these recrystallisation effects, while above 500°C the grain sizes became significantly larger (by about 7-10 times).

### Conclusion

HPN is the experimentally observed phenomena of the transitions of metals and alloys, in particular palladium, into controllable high strength states with special physical properties during courses of charging with hydrogen and transformation of  $\alpha$ -phase solid solution  $\leftrightarrow$   $\beta$ -phase hydride. Therefore, HPN-phenomena may form the basis for the hydrogen treatment of palladium materials aimed at improving their structure and properties without noticeably affecting their dimensions and shape. Based on this treatment, novel advanced palladium alloys have now been made (5).

## References

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## Platinum 1999

During 1998 the world supply of platinum increased by 9 per cent to reach 5.4 million oz, while demand increased by 4 per cent to 5.35 million oz. Demand was higher mainly due to the increased fabrication of jewellery in China and the U.S.A. However, industrial demand weakened slightly. Supplies of platinum from South Africa declined slightly, but supplies from Russia, despite a four month suspension of exports during the first four months of 1998, rose by 400,000 oz to reach a record 1.3 million oz. These are just some of the facts contained in the latest Johnson Matthey annual market survey of the platinum group metals, "Platinum 1999". The review covers the supply, mining and exploration, and demand for the platinum group metals during 1998, with most emphasis being on platinum and palladium.

The major industrial use of platinum is in catalytic converters, and in 1998 this was unchanged at 1.83 million oz, supported by a rising use of platinum for diesel engines. Demand in Europe rose by 5 per cent, due to increased sales of diesel cars. In North America demand for platinum rose by only 1.25 per cent as consumers showed a preference for larger sized gasoline vehicles which carry palladium-based catalyst systems. The implementation of tighter emissions standards and the selection by U.S. manufacturers of palladium to meet hydrocarbon limits caused a 50 per cent surge in palladium sales.

An increase in the use of platinum for the hard disks of personal computers, which incorporate a platinum-cobalt layer to improve data storage, outweighed a lower demand for thermocouples. In total,

demand from the electrical sector increased by 15,000 oz to 320,000 oz.

Sales for platinum investment products rose by 75,000 oz to 315,000 oz in 1998, with higher demand for the platinum American Eagle coins in the U.S.A. and large investment bars in Japan.

Consumption of platinum by the chemical industry rose by 30,000 oz to 265,000 oz, with demand for platinum process catalysts being strong. Typical of this was the platinum used for the rising production of silicones for sealants and adhesives for the construction industries of North America and Europe.

Fuel cells accounted for only a small part of platinum consumption in electrical applications but the prospects for significant demand in the future is improving. Several car manufacturers have demonstrated fuel cell cars, but further work is required.

Demand for palladium rose to 8.19 million oz in 1998, while supplies rose to 8.4 million oz. Greatest demand was from the auto industry which reached 4.47 million oz, an increase of 1.27 million oz compared with 1997.

"Platinum 1999" contains two special features on platinum in hard disks and on developments in automotive emissions legislation which describes the increasingly strict controls over vehicle emissions in Europe, Japan and the U.S.A.

Readers of *Platinum Metals Review* who wish to receive a free copy of "Platinum 1999" are invited to contact Ms Emma Johnson at Johnson Matthey PLC, 40-42 Hatton Garden, London EC1N 8EE; e-mail: johnse@matthey.com; fax: +44-(0)20-7269-8389.