

# Hydrogen Interstitial Structures in Palladium-Silver Membranes

## ELASTIC ENERGY DISSIPATION INDICATIONS OF DEVIATIONS FROM EXPECTED HOMOGENEITY

Initial reports that the palladium alloy Pd<sub>77</sub>Ag<sub>23</sub> was a convenient membrane material for hydrogen diffusion, with technical superiority to pure palladium (1), served effectively as a precursor for a widening interest in the results of interactions of hydrogen with a variety of palladium alloys. This in turn has resulted in the development of background information on a wide range of associated parameters concerning physical, physicochemical and structural properties (2).

A main objective in studying hydrogen permeation in palladium alloys has been to obtain as precise as possible values of hydrogen diffusion coefficients as functions of temperature and alloy composition. It is constructive to be able to consider these values in conjunction with the most detailed information available on hydrogen solubilities, corresponding to gaseous hydrogen pressures at both input and exit surfaces (3). In addition there has now been increased interest in effects on the permeation rates imposed by strain gradients produced by the lattice expanding effects of the permeating hydrogen interstitials. In this latter respect, the involvement of co-ordinated Gorsky and Diffusion Elastic Effects have recently been particularly well illustrated in studies with the still widely used Pd<sub>77</sub>Ag<sub>23</sub> alloy (4).

### Palladium Alloy Membranes

Various aspects of the extensive technological interest in palladium alloys have continued to be quite regularly monitored by this journal, as shown by a continuous series of important review articles (5). The latter four articles in this list may have particularly reflected the substantial research on this topic in the former Soviet Union – partly an indication of the plentiful resources of platinum which are available there, and which have encouraged the use

of relatively expensive component elements (6).

The primary technological advantage gained from using palladium alloys instead of pure palladium membranes, has centred around their improved resistance to irreversible dimensional deformation resulting from repeated cycles of hydrogen absorption and desorption which may occur during processes, such as hydrogen separation and purification. This particular advantage also has been associated with major decreases in hysteresis which accompany reductions in the extent of the  $\alpha \rightleftharpoons \beta$  phase transition regions; these are indicated in Figure 1b.

Such reductions in hysteresis effects have been matched by decreases of an associated critical temperature,  $T_c(\alpha, \beta)$ , from values of near 300°C, deduced for the palladium-hydrogen system (7), to values of around 25°C. These decreases have been found to be produced by alloying palladium with various other elements, in amounts of as low as 9 per cent in the case of several transition metals (8), up to amounts of about 23 per cent for silver in the palladium-silver-hydrogen system (9). Certain aspects of studies of internal friction in the palladium-silver-hydrogen(deuterium) system, involving in particular Pd<sub>60</sub>Ag<sub>40</sub> alloys (10), have also seemed to provide evidence of hydrogen distributions which correspond to “supercritical” regions of quasi  $\alpha$ - and  $\beta$ -phases coexistence in palladium-silver alloys containing silver contents substantially greater than 23 per cent.

### Elastic Energy Dissipation in the Pd-Ag-H System

Elastic energy dissipation (internal friction,  $Q^{-1}$ ) measurements in the palladium-hydrogen system, at vibration frequencies of about 3 kHz over a temperature range of 90 to 300 K, have revealed a main  $H_{(1)}$  peak at a temperature of about 106 K, see Figure 1(a). With hydrogen

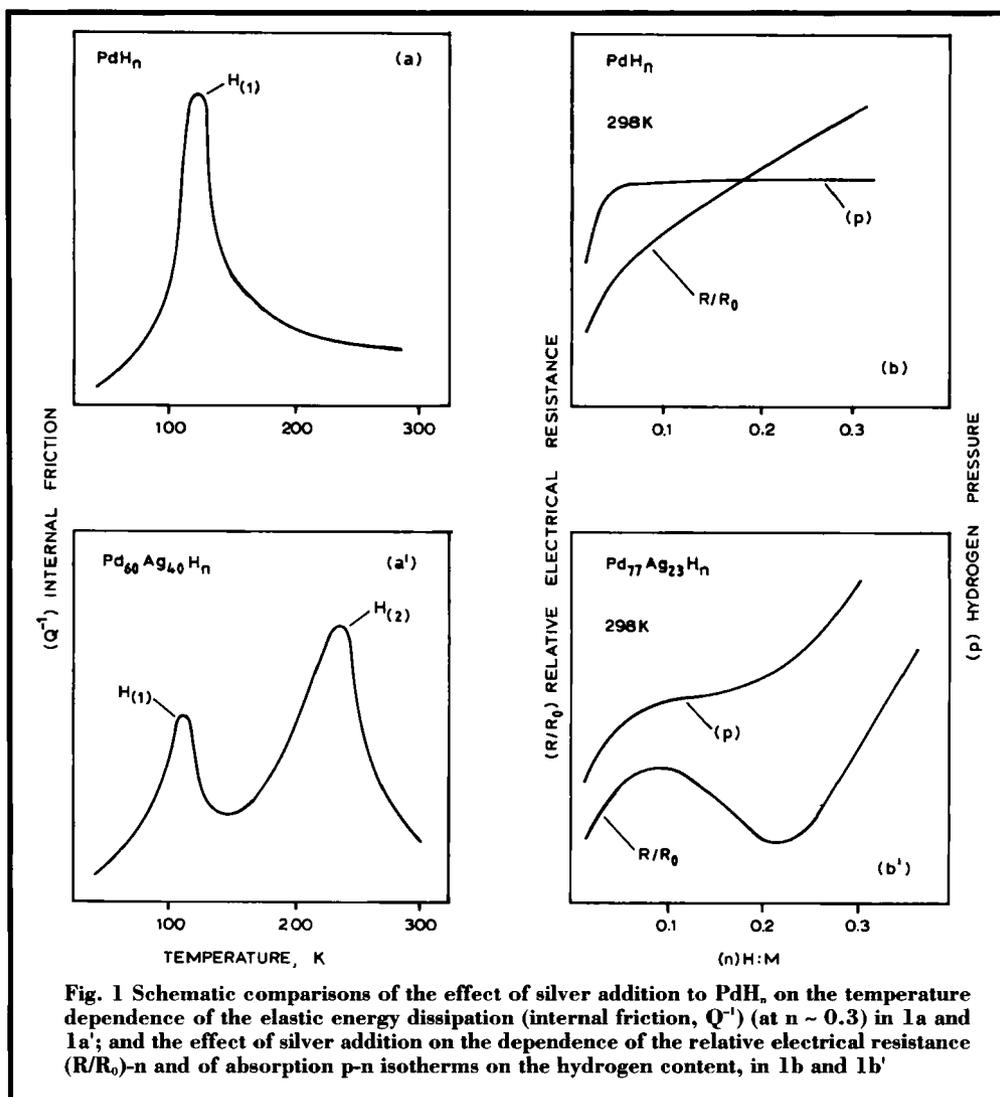


Fig. 1 Schematic comparisons of the effect of silver addition to PdH, on the temperature dependence of the elastic energy dissipation (internal friction,  $Q^{-1}$ ) (at  $n \sim 0.3$ ) in 1a and 1a'; and the effect of silver addition on the dependence of the relative electrical resistance ( $R/R_0$ )- $n$  and of absorption  $p$ - $n$  isotherms on the hydrogen content, in 1b and 1b'

contents (H:M, the ratio of hydrogen to metal atoms, generally represented by  $n$ ) of 0 to 0.3, this  $H_{(1)}$  peak seems to be attributable to a Zener type mechanism of stress-induced rearrangements of hydrogen interstitials, and could be considered to indicate the continued presence of the  $\beta$ -phase structures that had been introduced into specimens at around 298 K.

However, in analogous studies with  $Pd_{60}Ag_{40}$  and subsequently  $Pd_{33}Ag_{67}$  and  $Pd_{45}Ag_{55}$  alloys (11) there was clear evidence of the emergence of an additional  $H_{(2)}$  peak at higher tempera-

tures, see Figure 1a'. This peak became increasingly dominant relative to  $H_{(1)}$  with increasing silver content in the alloys.

### Rome Conference on Internal Friction

In order to obtain a more complete picture of internal friction phenomena in the palladium-silver-hydrogen system analogous measurements using alloys of intermediate composition:  $Pd_{27}Ag_{73}$  and  $Pd_{32}Ag_{68}$ , have been carried out. The results were reported in a paper by R.-A.

McNicholl and F. A. Lewis (Queen's University Belfast) and A. Biscarini, B. Coluzzi, C. Costa and F. M. Mazzolai (University of Perugia), which was presented at the 10th International Conference on Internal Friction and Ultrasonic Attenuation in Solids, recently held in Rome from 6th to 9th September 1993; the proceedings of which will be published in a special issue of the *Journal of Alloys and Compounds*.

The results provided further examples of  $H_{(1)}$  and  $H_{(2)}$  peaks occurring together and were also consistent with a view that the  $H_{(2)}$  peaks were associated with a Zener mechanism for hydrogen interstitial rearrangements within the  $\alpha$ -phase hydride regions.

Equally significant, however, was confirmatory evidence of the continuing presence of  $H_{(1)}$  peaks which gradually decreased in prominence with increasing amounts of the silver alloying content. These results, combined with those from the earlier measurements, appeared to consolidate inferences that could be drawn from the overall dependence on the hydrogen content of the relative heights of the  $H_{(1)}$  and  $H_{(2)}$  peaks; the inferences are that regions of incipient  $\beta$ -phase structures may still have been introduced at 25°C into alloys with silver contents substantially higher than those in  $Pd_{77}Ag_{23}$  and which may even approach the silver content of  $Pd_{50}Ag_{50}$ .

Such indications from elastic energy dissipa-

tion measurements of the relatively extended regions of quasi  $\alpha$ - and  $\beta$ -phase coexistence, would not seem to be out of keeping with evidence from a recent analysis of the relationship between electrical resistivity and hydrogen pressure for the palladium-platinum-hydrogen system (12). This analysis examined extensions of the limits of  $\alpha$ - and  $\beta$ -phase coexistence into regions of seemingly complete reversibility of absorption and desorption p-n relationships (where p is the equilibrium hydrogen pressure).

The indications also have a direct parallel with the unusual longstanding established pattern of gradual alterations in the relationship between the relative electrical resistance ( $R/R_0$ ) and the hydrogen content (n) in the palladium-silver-hydrogen system with alloy composition (13) and in the analogous palladium-gold-hydrogen system (14). In these cases a region of increasing  $R/R_0$  with increasing n, associated with  $\alpha$ - and  $\beta$ -phase coexistence in the  $PdH_n$  system, as indicated in Figure 1b, gradually alters its gradient with increasing silver or gold content to a region of decreasing  $R/R_0$  with n, as in the case of the  $Pd_{77}Ag_{23}$  alloy, see Figure 1b' (15). This remains as an enduring feature as corresponding values of n are gradually reduced for further increases of silver or gold content up to compositions approaching  $Pd_{50}Ag_{50}(Au)_{50}$ . This also could suggest some retained phase transition connotation.

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