

# Features of elastic energy dissipation in the Pd–Ag–H system

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## Abstract

Studies of anelastic phenomena resulting from the introduction of hydrogen into palladium–silver alloys have been extended to include Pd<sub>73</sub>Ag<sub>27</sub> and Pd<sub>68</sub>Ag<sub>32</sub> alloy compositions. Results of measurements over 90–300 K at 3 kHz have been compared with features observed in earlier experiments with other Pd–Ag alloys. Changes with alterations of silver and hydrogen compositions in two anelastic relaxations associated with stress-assisted rearrangements of hydrogen interstitials have been discussed.

## 1. Introduction

In addition to relaxations associated with hydrogen–dislocation complexes (Snoek–Köster) [1–8] and with H long-range diffusion (Gorsky) [9, 10], previous anelastic studies of palladium alloy have been concerned with stress-induced rearrangements of hydrogen interstitials (Zener) [7–10].

A lower temperature peak designated H<sub>(1)</sub> had been found to be the dominant feature in the case of pure palladium. An analogous peak, again designated as H<sub>(1)</sub>, has again been found to be the dominant peak in the Pd<sub>90</sub>Ag<sub>10</sub> and Pd<sub>77</sub>Ag<sub>23</sub> alloys.

This peak has continued to be observed in the case of Pd<sub>60</sub>Ag<sub>40</sub>H<sub>n</sub> and Pd<sub>53</sub>Ag<sub>47</sub>H<sub>n</sub> systems but it was found to appear in conjunction with a second H peak designated as H<sub>(2)</sub>, appearing at higher temperatures than H<sub>(1)</sub> [8–14]. Comparisons of results at various hydrogen levels indicated that with increasing silver content there was clear evidence of an increasing dominance of the H<sub>(2)</sub> peak [8]. Confirmation of this trend was provided by the finding that the H<sub>(2)</sub> peak was the solely discernible peak in the Pd<sub>45</sub>Ag<sub>55</sub>H<sub>n</sub> alloy [8].

Initial objectives of the present investigation with Pd<sub>73</sub>Ag<sub>27</sub> and Pd<sub>68</sub>Ag<sub>32</sub> alloys had been to obtain consolidating experimental information concerning modifications of H<sub>(1)</sub> and H<sub>(2)</sub> peaks as functions of hydrogen concentration and alloy composition.

## 2. Experimental details

Sample preparation and acoustic measurement procedures employed in the present investigation were

analogous to those previously described [8]. Specimens were in the form of rectangular bars of dimensions 45.0 × 8.4 × 1.8 mm<sup>3</sup> (Pd<sub>73</sub>Ag<sub>27</sub>) and 42.0 × 6.8 × 1.8 mm<sup>3</sup> (Pd<sub>68</sub>Ag<sub>32</sub>). During simultaneous measurements of the resonant vibration frequency  $f$  and elastic energy dissipation coefficient  $Q^{-1}$ , the specimens were vibrated in a free–free mode at about 3 kHz. Before measurements the specimens were annealed *in vacuo* at 500 °C for 2 h. Loadings with hydrogen were made either by electrolysis at a current density of about 3 mA cm<sup>-2</sup> or by equilibration with hydrogen gas at a pressure of 30 bar and at temperatures ranging between 150 °C and 120 °C. Hydrogen contents were in either cases estimated by weight differences to an accuracy of 0.001 in the atomic ratio  $n = [H]/[Me]$ .

Acoustic measurements were performed *in vacuo* ( $p = 10^{-5}$  Torr) during either cooling or heating runs over the temperature range 90–300 K. Checks by re-weighing at the conclusion of the measurements showed that losses of hydrogen had been less than 1%.

## 3. Results

In Figs. 1–5 the temperature dependence between 90 and 300 K of the elastic energy dissipation coefficient  $Q^{-1}$  in the case of Pd<sub>73</sub>Ag<sub>27</sub>H<sub>n</sub> (Figs. 2 and 3) and Pd<sub>68</sub>Ag<sub>32</sub>H<sub>n</sub> (Fig. 4) are compared with analogous series of previously reported measurements for Pd<sub>77</sub>Ag<sub>23</sub> (Fig. 1) [13] and Pd<sub>60</sub>Ag<sub>40</sub> (Fig. 5) [8].

Comparisons of relationships in Figs. 2 and 3 for comparable hydrogen contents have indicated that these relationships are essentially independent of which al-

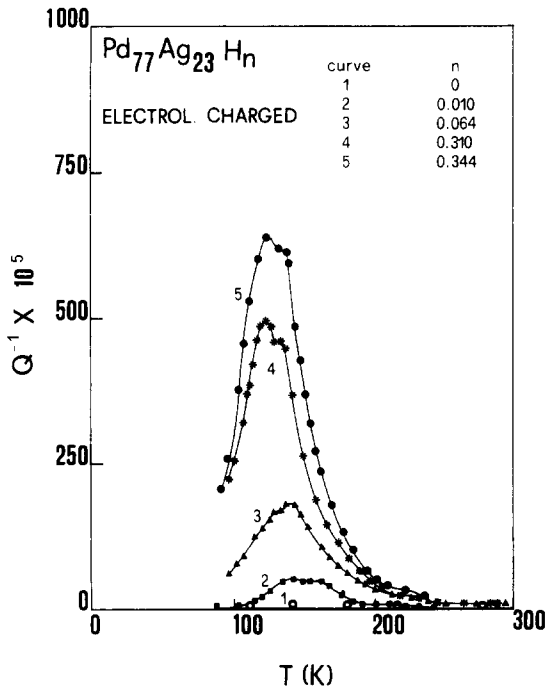


Fig. 1. Relationships between the elastic energy dissipation coefficient  $Q^{-1}$  and temperature for a series of hydrogen contents  $n = [H]/([Pd] + [Ag])$  during a sequence of measurements in a  $Pd_{77}Ag_{23}$  alloy [13].

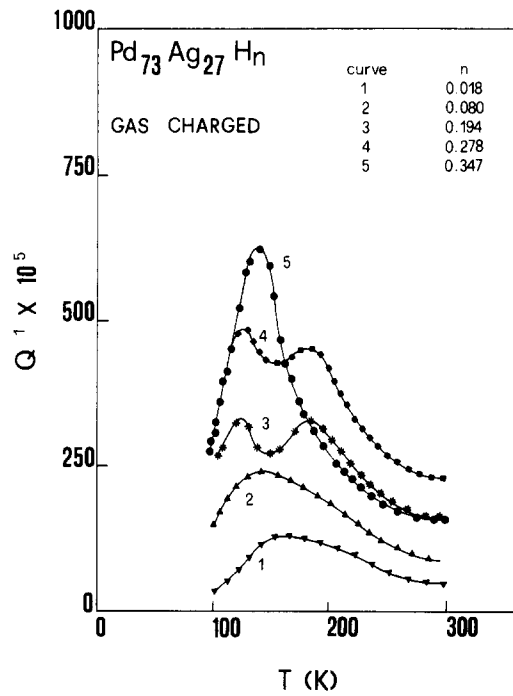


Fig. 3. Analogous measurements to those in Fig. 2 but after gas charging of the specimen.

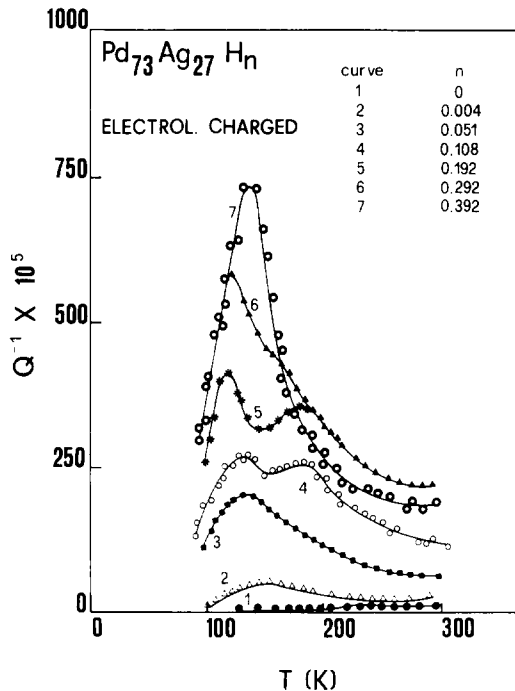


Fig. 2. Analogous measurements to those in Fig. 1 but for the alloy  $Pd_{73}Ag_{27}$ .

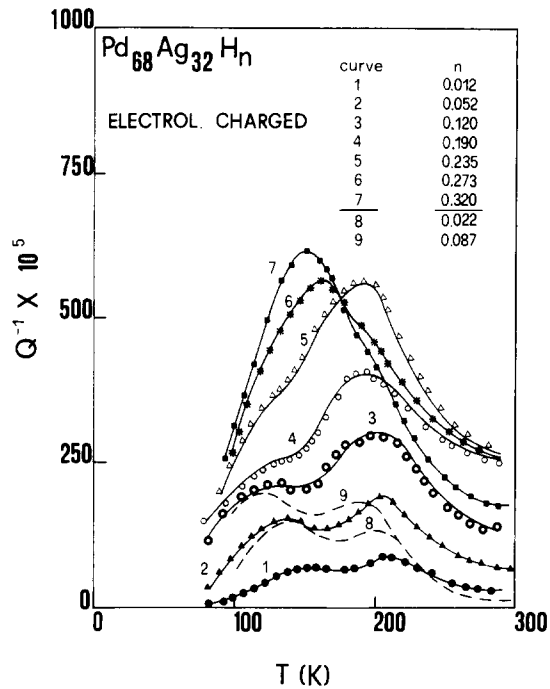


Fig. 4. Analogous measurements to those in previous figures after both electrolytic charging (curves 1-7) and gas charging (curves 8 and 9) of the  $Pd_{68}Ag_{32}$  alloy.

ternative means had been employed for hydrogen loading of the specimen before measurements. Such essential independence of relationships from the mode of hydrogen loading was also found in the case of the

concurrent measurements of resonant vibration frequencies (Fig. 6).

Taken overall, the feature changes exhibited in Figs. 1-5 seem to confirm those that had been indicated by the previously available series of measurements. For

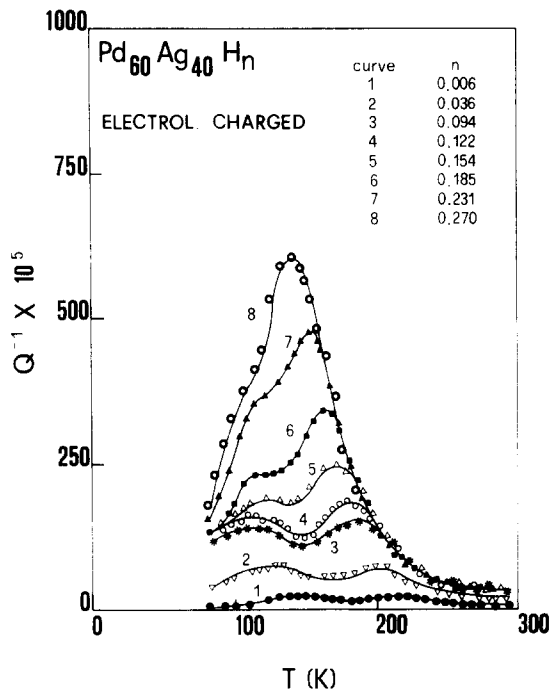


Fig. 5. Analogous measurements to those in Fig. 1 but for the alloy Pd<sub>60</sub>Ag<sub>40</sub> [8].

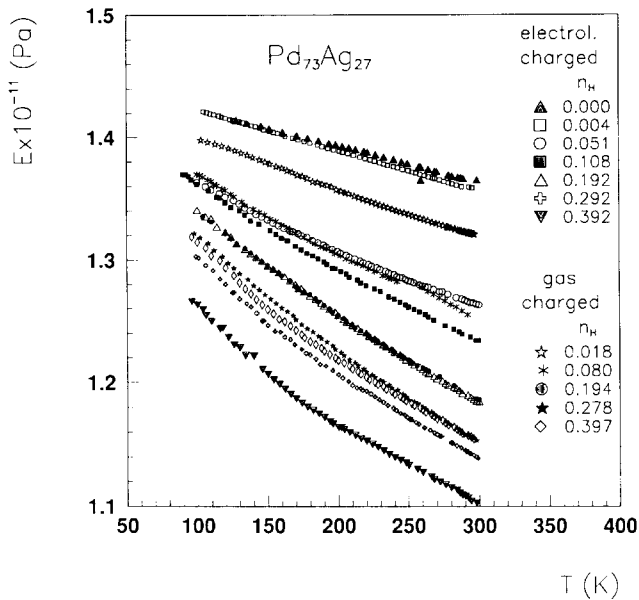


Fig. 6. Relationships of the Young modulus and temperature for both electrolytically charged and gas-charged Pd<sub>73</sub>Ag<sub>27</sub> alloy.

instance, while the pattern for Pd<sub>73</sub>Ag<sub>27</sub>H<sub>n</sub> in Fig. 2 indicates a retention of an overall dominance of the H<sub>(1)</sub> peak, similar to the case of Pd<sub>77</sub>Ag<sub>23</sub>H<sub>n</sub> in Fig. 4, there is also clear evidence of a well-separated H<sub>(2)</sub> peak for intermediate ranges of hydrogen content *n* even though, at the maximum values of *n*, it has reduced to a rather small shoulder on the high temperature side of H<sub>(1)</sub>.

As well as a gradual increase in the height of the H<sub>(2)</sub> peak with increasing content of silver, the series of measurements for Pd<sub>68</sub>Ag<sub>32</sub>H<sub>n</sub> exhibits at even the lowest values of *n* clearer evidence of a well-separated H<sub>(2)</sub> peak, which continues to be the dominant feature up to a value of *n* equal to 0.235, even though, beyond this value of *n*, a single amalgamated peak occurs.

The results for the Pd<sub>60</sub>Ag<sub>40</sub>H<sub>n</sub> alloy in Fig. 5, illustrative of a dominance of the H<sub>(2)</sub> peak, have been included to emphasize a trend that the present measurements have quite clearly shown already in the cases of Pd<sub>73</sub>Ag<sub>27</sub>H<sub>n</sub> and Pd<sub>68</sub>Ag<sub>32</sub>H<sub>n</sub>.

#### 4. Discussion and conclusions

In previous papers [8, 14] two alternative interpretations of H<sub>(1)</sub> and H<sub>(2)</sub> peaks have been proposed. The first attributed the H<sub>(1)</sub> peak to short-range order changes induced by stress within the concentrated α' hydride phase and H<sub>(2)</sub> to a similar mechanism occurring within the dilute H solid solution (α phase). It is difficult in this interpretation, however, to account for the occurrence of the two peaks at the lowest H contents in silver-rich alloys, where a single phase is expected to be present within the sample down to the lowest measurement temperatures.

The second interpretation was based on the assumption that at microscopic level the binary Pd–Ag alloy might present compositional fluctuations and, accordingly, that the two peaks might be Zener-type effects, occurring within palladium-rich (H<sub>(1)</sub>) and palladium-poor (H<sub>(2)</sub>) “domains”. In the absence of a direct proof of the occurrence of these compositional fluctuations the model remained speculative.

On the basis of recent analysis concerning the nature of interstitial sites in binary alloys [15], a more adequate interpretation of the two peaks is as follows. Hydrogen atoms in Pd–Ag alloys only occupy octahedral sites with six (I(6)) or five (I(5)) palladium atoms in their first shell of neighbours [16]. Peak H<sub>(1)</sub> would be essentially due to a stress-assisted redistribution of H over the I(6) type of sites, and H<sub>(2)</sub> to a similar process occurring over the I(5) type of sites. In this second case, apart from the Zener effect, a reorientation of the anisotropic I(5) elastic dipole should contribute at the lowest contents. Interplay of I(6) and I(5) site occupancies would lead to the amalgamation of the two peaks at the highest H contents, with the plausible consequence of an overall effect occurring at temperatures intermediate between those of the two individual peaks, as observed.

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