Exploring Lattice Defects in Palladium and Its Alloys Using Dissolved Hydrogen

PART I: HYDROGEN SOLUBILITY AND ITS SEGREGATION TO DISLOCATIONS AND VACANCIES

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The first part of this paper describes a combination of physical metallurgical techniques and hydrogen (H₂) solubilities employed to help in the characterisation of defects in palladium and its alloys. Cold working or hydride formation and decomposition introduce large dislocation densities into palladium and palladium alloys. These can be examined by transmission electron microscopy and correlated with hydrogen (H) segregation to the stress fields of the dislocations determined from H₂ solubilities. H atoms are strongly trapped by vacancies in the palladium lattice and evidence for vacancy trapping in cold-worked palladium is shown by deviations in H₂ solubility, different to that expected if H segregated only to the dislocation stress fields. The second part of this paper, to be published in the October 2001 issue, will be concerned with hydrogen segregation to defects introduced by the internal oxidation of palladium alloys or by treatment at moderately high temperatures and hydrogen pressures.

From Thomas Graham onwards (1), the sponge-like ability of palladium (Pd) for hydrogen gas (H₂) has long been a fascination for scientists. In recent years the investigation of H interactions with lattice defects has been an active research area. Myers *et al.* (2) have considered hydrogen interactions with defects in crystalline solids and more specifically, Kirchheim (3, 4) has reviewed H as a probe for defects, mainly in Pd.

At moderate temperatures and small pressures (p_{H2}) H₂ dissolves in the dilute α-phase of Pd, that is, the Pd state which contains very little H₂. As p_{H2} increases, the H₂ solubility also increases until the hydride phase appears. The minimum composition where it appears is the solvus or terminal hydrogen solubility in the metal phase for that temperature. When further hydrogen is absorbed the fraction of hydride phase increases relative to the dilute phase. According to the phase rule, such a system comprised of two solid phases should have a constant

hydrogen pressure, the so-called plateau pressure; this is shown by an isotherm for Pd-H in Figure 1.

Face centred cubic (f.c.c.) Pd-rich substitutional alloys also have plateau pressures where the dilute and hydride phases coexist. Except for *Pd*-Rh alloys and, possibly *Pd*-Ni alloys, all other binary Pd alloys have narrower plateau regions than Pd (the italics indicate that Pd is the majority element in the alloy). The plateau pressures for Pd alloys can be larger or smaller than for Pd-H depending, with a few exceptions, on whether the substitutional metal contracts or expands the Pd lattice (5). Alloys with contracted lattices relative to Pd cause increases in the plateau pressures, while those with expanded lattices cause decreases in the plateau pressures. It would be expected that it should be easier to insert H into alloys with expanded unit cells and these would consequently form more stable hydride phases. For analogous reasons the contracted alloys form less stable

hydride phases. The terminal hydrogen solubilities in Pd alloys are *always* greater than for Pd-H (5).

Hysteresis is a complication present in metal-H systems which leads to two plateau pressures instead of one; hydride formation is not reversible, see Figure 1. Hysteresis is observed in almost all solid state first order phase transitions and its presence means that there is a net loss of work during the cyclic phase change which corresponds to hydriding and dehydriding for metal-H systems (6). In metal-H systems hysteresis is undoubtedly related to the abrupt lattice expansion/contraction which takes place upon hydriding/dehydriding because it is absent in single phase regions where the lattice changes are continuous with H content.

Hydrogen solubility in pure, annealed Pd metal reflects occupation by H of a nearly perfect sublattice of octahedral interstices within the f.c.c. Pd lattice. In such a perfect lattice there are no deviations from the ideal solubility relation $r = K_s p_{H_2}^{1/2}$ which is obeyed as $r \rightarrow 0$ where $r \equiv$ (H/Pd), the atom ratio of H to Pd, and K_s is a constant at a give temperature for each metal or alloy. The
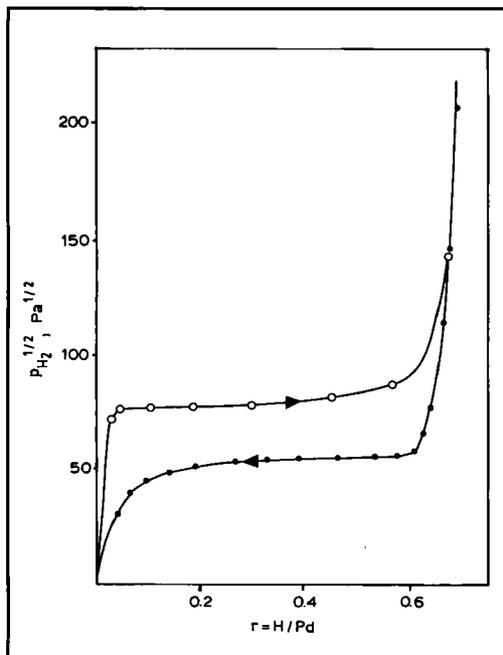

Fig. 2 Dilute phase H_2 isotherms (323 K) for Pd from unpublished research of Flanagan and Wang.
o   *solubility for well-annealed Pd;*
Δ   *solubility for cycled Pd;*
- - - *ideal dilute solubility behaviour*

square root dependence on pressure proves that H_2 dissociates upon entering the Pd lattice.

The ideal solubility of H_2 in Pd metal is shown by the dashed straight line in Figure 2. At higher r values the experimental data fall below the ideal solubility, due to H-H attractive interactions. Any deviations from the H_2 solubility behaviour in pure, annealed Pd metals (Figure 2) can be attributed to defects, such as vacancies, dislocations or large surface/volume ratios which act as traps for H, that is, sites which trap H more energetically than the normal interstice. (High temperature annealing of metals and alloys reduces the concentration of most defects to levels which do not measurably affect H_2 solubilities.)

Hydrogen solubilities in Pd alloys may also deviate from the ideal solubilities characteristic of annealed, randomly disordered substitutional f.c.c. alloys because of similar defects found in Pd and because of ordering or segregation of the alloys.

H Segregation to Dislocations

Solute atoms, which expand the lattice, are attracted to the tensile stress field around edge dislocations to form *Cottrell atmospheres*. Interstitial

Fig. 1 A H_2 isotherm for Pd foil (120 μm) at 323 K from unpublished work by Flanagan and Wang. Filled symbols are for desorption and open ones for absorption
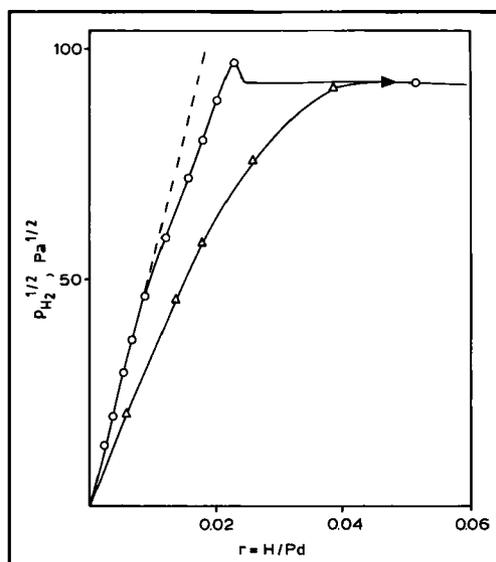
solutes, such as H, always expand metal lattices and are therefore attracted to the tensile stressed regions. Dissolved hydrogen and its isotopes are especially important in this regard because of their high diffusivity and the possibility, in contrast to other solutes, of forming *Cottrell atmospheres* at relatively low temperatures.

When the hydride phase forms from the dilute phase at moderate temperatures, the Pd lattice expands abruptly and requires dislocation creation in order to accommodate the volume change. Large dislocation densities, comparable to those introduced by heavy cold-working, are introduced into Pd by this hydride phase change (7, 8). It has been shown from TEM (transmission electron microscopy) that after cold-working Pd, dislocations are arranged in cell walls with only a few within the cells, but when dislocations are created by hydride formation and decomposition (cycling), they are distributed more uniformly and it is difficult to discern a cell structure (7, 9). A cell in this context refers to dense tangles of dislocations arranged in walls which enclose nearly dislocation-free regions. Cycling is therefore a convenient way to introduce large and relatively uniform dislocation densities into Pd. Large dislocation densities enhance H_2 solubility, relative to annealed Pd, due to the formation of *Cottrell atmospheres* of H. Figure 2 shows supersaturation before the plateau region for annealed Pd indicating difficulties in nucleation to form the hydride phase (10, 11). The isotherms measured after cycling shows no nucleation difficulties because of the high dislocation density.

A solubility enhancement for H can be defined as the ratio of the solubility of H_2 in dislocated Pd compared to its solubility in annealed Pd at the same p_{H_2}, $(r'/r)p_{H_2}$, where r' and r are the H/Pd ratios in the presence and absence of a significant dislocation density, respectively. The solubility enhancement can be measured accurately in Pd and Pd alloys because the $H_2 (g) = 2H_{dissolved}$ equilibrium is readily established for H in the normal interstices and those in the stress fields of dislocations and because the H_2 solubilities are substantial. With varying degrees of success, Flanagan *et al.* (12), Kirchheim (13), Tyson (14), Wolfer and Baskes (15), Park *et al.* (16) and Huang (17) have given quantitative accounts of the solubility enhancements in Pd, leaving no doubt that the origin of the effect is trapping in the dislocation stress fields. Although the H_2 solubility enhancements are not directly proportional to the dislocation densities, greater solubility enhancements do reflect greater dislocation densities (edge components). Negligible solubility enhancement at moderate temperature does not imply that the dislocation density is low, but rather that it is less than about 10^{14} m^{-2}. Hydrogen solubility enhancements serve as a convenient way of monitoring relative values of large dislocation densities (3, 12, 18) which is difficult to do by 'dislocation counting' in TEM photomicrographs.

Quantitative Considerations of H Segregation to Dislocations

The chemical potential of dissolved H, μ_H, in unstressed metals can be expressed as (19):

$$\mu_H = \mu^{\circ}_H + RT \ln (r/(1-r)) + \mu^E_H (r) \qquad \text{(i)}$$

where μ°_H is the chemical potential of an isolated H in the lattice, the second term on the right hand side of the equation is a configurational term arising from the number of ways to insert the H into the octahedral interstices and the factor of unity in its denominator indicates that there is one interstice available for H per metal atom, as is the case for Pd, and $\mu^E_H (r)$ is the non-ideal or excess chemical potential, that is, factors not covered by the other terms. Generally the chemical potential is a measure of the ability of a component, for example, H, to cause physical or chemical change and is defined as the partial derivative of the Gibbs free energy with moles of the component, for example, H, holding other variables, such as T, constant. The chemical potentials of H in the gas and solid phases must be equal at equilibrium:

$$\mu_H = \mu_H (g) = 1/2 \, \mu^{\circ}_{H_2} + RT \ln (p_{H_2})^{1/2} \qquad \text{(ii)}$$

and, from Equations (i) and (ii),

$$RT \ln (p_{H_2})^{1/2} = \mu^{\circ}_H - 1/2 \, \mu^{\circ}_{H_2} + \\ RT \ln (r/(1-r)) + \mu^E_H (r) \qquad \text{(iii)}$$

Pd-H will be used to illustrate H solubility enhancements due to dislocations. However, the

discussion applies to any metal or alloy which dissolves H. Dissolved H atoms are attracted to the tensile stressed region of the edge dislocations (Figure 3) and repelled from the compressive stress region. Stress affects the H chemical potential, μ_H, by an additive work term, that is, σV_H where σ, the hydrostatic stress, is positive for compressive stress and negative for tensile stress and V_H is the partial molar volume of the H, $(\partial V/\partial n_H)_{T,p}$, n_H being the moles of H atoms (20). The stress is not constant about an edge dislocation but is a function of both the distance (d) and angle (θ) from the core (Figure 3) (21). When uniaxial stress is applied to a Pd rod, μ_H changes with σ according to a one-dimensional stress term, $1/3\sigma V_H$, as proven experimentally by the changes of electrode potential with σ (22).

Consider two infinitesimal volumes at the same distance, d, from the origin, the core, of an edge dislocation but on opposite sides, for example, at $\theta = 1/2\pi$ and $3/2\pi$ (Figure 3); the stresses in these two volumes will be equal but opposite in sign because σ depends directly on sin θ. The μ_H values in these volumes will be modified at a given distance, d, by the additive terms $|\sigma|V_H$ at $\theta = 1/2\pi$ and $-|\sigma|V_H$ at $\theta = 3/2\pi$. The H solubilities in these stressed infinitesimal volumes, relative to the unstressed solubilities, can be derived from Equation (iii) modified by the stress terms at a given p_{H_2} under conditions where, because of the small H contents, μ^E_H (r) can be neglected, that is:

$$\ln (r_t/r) = |\sigma|V_H/RT \qquad \text{(iv)}$$

$$\ln (r_c/r) = -|\sigma|V_H/RT \qquad \text{(v)}$$

where r_t and r_c are the H/Pd atom ratios in the tensile and compressively stressed infinitesimal volumes, respectively, and r is the ratio in the unstressed region.

The incremental changes in the H contents in the tensile and compressive stressed infinitesimal volumes can be obtained from Equations (iv) and (v) as:

$$r_t - r = r (\exp(x) - 1) = r (y - 1) \qquad \text{(vi)}$$

$$r_c - r = r (\exp(-x) - 1) = r ((1/y) - 1) \qquad \text{(vii)}$$

where $x \equiv |\sigma(d)|V_H/RT$ and $y \equiv \exp x$.

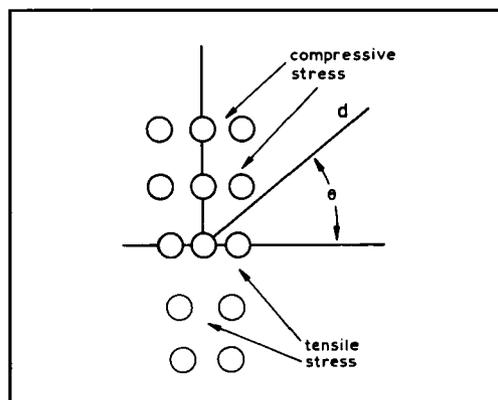Since $y > 1$, it follows from Equations (vi) and

Fig. 3 Diagram of an edge dislocation defining θ and d, the distance from the core

(vii), that more H is gained by the tensile stressed infinitesimal volume than lost by the corresponding compressively stressed one. As the system is an open one, the H which segregates to the dislocations is mainly obtained from the gas phase. At very small overall hydrogen contents, the increment of H lost from the compressively stressed regions, $r_c - r$, will be negligible and can be neglected. Therefore, in the presence of dislocations at small r, the solubility increment, $\Delta r = r' - r$, is mainly determined by the tensile stressed volumes.

Experimental solubility data for Pd-H in the dilute phase are shown in Figure 2 (323 K) for annealed Pd and for Pd containing a large dislocation density. The solubility enhancements at given p_{H_2} values can be obtained from the data (Figure 2) and are nearly constant with r as expected, since σ does not depend on r. However, they are no longer constant as the plateau is approached where processes other than dislocation-enhanced solubility may be a factor. The solubility enhancements decrease with increase of temperature because of the temperature dependence in Equation (v) and consequently, the solubility enhancement in Pd is negligible above about 373 K. The solubility enhancements from cycling (323 K) or from cold working (cold-rolling 90%) are comparable.

The solubility increment, Δr, at a given p_{H_2} was measured for cold-worked Pd which was then cycled and re-measured. It had increased by an amount corresponding to that introduced only by the cycling of annealed Pd. This demonstrates that
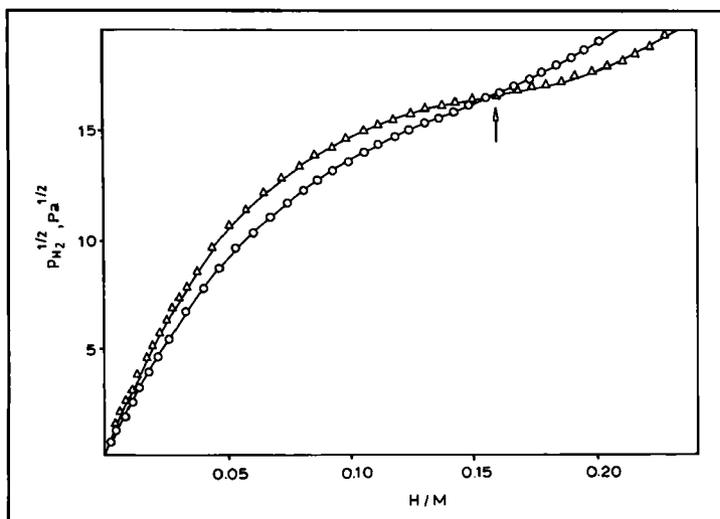
Fig. 4 H_2 solubilities in a $Pd_{0.75}Ag_{0.25}$ alloy (323 K).
Δ   solubility for well-annealed alloy;
o   solubility for the cold-worked (90%) alloy (25)

Solubility Enhancements in Cold-Worked Substitutional f.c.c. Pd Alloys

Kishimoto and coworkers (24–27) have measured H_2 solubility enhancements in cold-worked Pd-Ag, Pd-Ni and Pd-Pt alloys and some Pd-based ternary alloys with these same solute atoms. A $Pd_{0.75}Ag_{0.25}$ alloy does not have a two-phase region above about 273 K and therefore, in contrast to Pd-H, a solubility enhancement can be measured over a continuous range of r up to contents where it is no longer a good approximation to neglect the loss of H from the compressively stressed regions (25). Because of this loss, the solubility enhancement disappears at higher H contents for the cold-worked $Pd_{0.75}Ag_{0.25}$ alloy. At $r = 0.16$, $(r'/r) = 1$, and then for $r > 0.16$, the solubility enhancement changes to < 1, see Figure 4.

A simple model for the H_2 solubility enhancements in this cold-worked $Pd_{0.75}Ag_{0.25}$ alloy has been proposed whereby it is assumed that a given fraction of the alloy is under a uniform tensile stress and an equal fraction is under compressive stress of the same magnitude while the remainder is unstressed (25). Equation (i) can be applied to

each fraction with the appropriate stress terms. The total H_2 solubility at a given p_{H_2} is then the weighted sum of the three fractions. If all of the octahedral interstices are available for occupation, this model predicts a crossover in the solubility enhancement from > 1 to < 1 at $r = 0.5$, whatever fractions are chosen for the stressed regions, provided that the two oppositely stressed regions have equal fractions.

In Equation (i), the factor of unity in the denominator of the ln term is appropriate when all of the octahedral interstices are accessible to H as in Pd. However, if some are unavailable, as in Pd-Ag alloys where H avoids those with nearest neighbour Ag atoms (28), it must be replaced by the fraction of available interstices, $\beta < 1$. The model then predicts the crossover point to be $r < 0.5$ as found experimentally for cold-worked $Pd_{0.75}Ag_{0.25}$ alloy (25) (Figure 4). The fraction of interstices with only Pd nearest neighbours in a completely random solid solution $Pd_{0.75}Ag_{0.25}$ alloy is 0.177. Using the proposed model with $\beta = 0.20$, and assuming that the fractions of the sample under tensile and compressive stress are each 0.25 and the remaining fraction is unstressed, a crossover point of $r = 0.13$ is calculated which is reasonably close to the experimental value (Figure 4). While this model is not quantitatively correct, it is reasonable and predicts the crossover in solubility enhancements as seen for cold-worked $Pd_{0.75}Ag_{0.25}$.
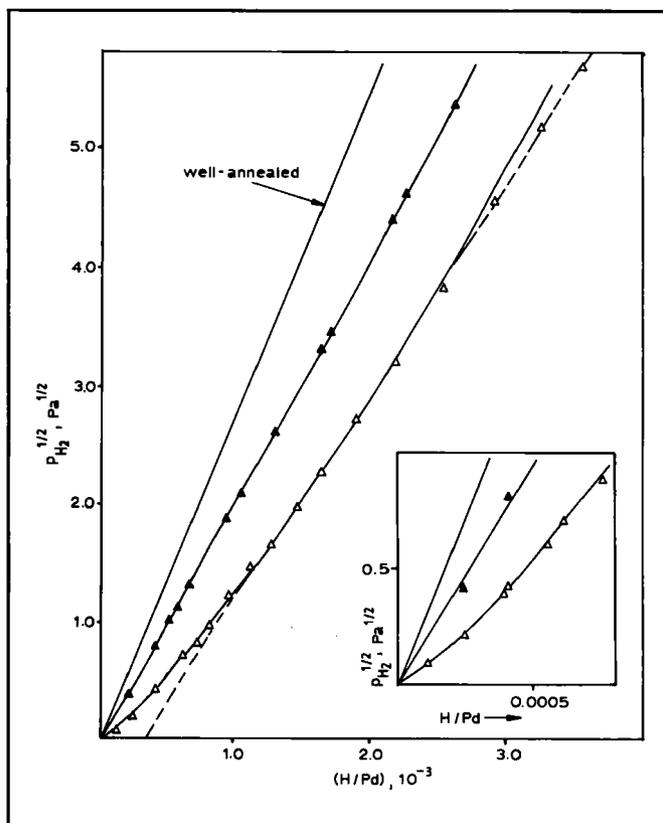
For cold-worked *Pd*-Ag alloys the H₂ solubility enhancements are found to decrease with increase of atom fraction of Ag in the alloy, X_{Ag} (26, 27). This can be explained by assuming that during cold working the larger Ag atoms move to occupy the tensile stressed regions about edge dislocations (27). This requires some mobility of the metal atoms at moderate temperatures during the cold working. Evidence supporting this is the observed destruction of long-range order by the cold working of ordered alloys (29). An enrichment of Ag atoms in the tensile stressed regions will reduce the number of interstices surrounded by only nearest neighbour Pd atoms thereby decreasing the H solubility enhancement. This model is supported by the finding that the solubility enhancement of cold-worked *Pd*-Ni alloys *increases* with increase of X_{Ni} (30). Since nickel (Ni) atoms are smaller than Pd atoms, they will be repelled from the tensile stress regions during cold working, increasing the fraction of interstices with Pd-only nearest neighbours.

Vacancy Trapping of H

H atoms and vacancies can be implanted into Pd using proton beams and the implanted H atoms diffuse to and occupy the vacancies. From the temperature at which the vacancy-trapped H is evolved, a trapping enthalpy, $|\Delta H^t_H| = 32.0$ kJ (mol H)⁻¹, was obtained (31) where the reference state is taken here to be $1/2H_2$ (g) rather than the untrapped, dissolved H as in (31). A theoretical trapping enthalpy of $|\Delta H^t_H| = 26$ kJ (mol H)⁻¹ has been calculated from effective-medium theory (32).

Hydrogen solubilities at the relatively low temperature of 273 K were measured some time ago by Flanagan and Kishimoto (33) employing a large Pd sample (21 g) which increased the accuracy of the data in the very dilute range. The solubilities deviated from the linear behaviour expected for only H-dislocation stress field interactions because the enhancements were anomalously large as $r \rightarrow 0$ (Figure 5).

Other than dislocations, the principal defects generated by heavy cold working which can trap H are Pd vacancies, that is, missing Pd atoms in the lattice. Although smaller in number than the

dislocation 'traps', vacancies trap H more strongly and therefore the observed deviations shown in Figure 5 are consistent with vacancy trapping. The extent of the vacancy trapping is $\Delta r \approx 0.0003$ (Figure 5) which is not unreasonable since vacancy concentrations following heavy cold work are estimated to be in this range (34). By fitting the experimental data to a two-state model (H trapped in vacancies and untrapped H), the enthalpy for $1/2\,H_2$ (g) solution into vacancies was found to be $|\Delta H^t_H| = 24$ kJ (mol H)$^{-1}$ (33) which is close to the theoretical value.

Deviations from the linear solubility relation, which are attributed to vacancy trapping, were eliminated after annealing at a relatively low temperature, for instance, 447 K for 12 hours, as shown in Figure 5; however, segregation of H into the dislocation stress fields was not reduced proportionally. After annealing, a linear solubility, r versus $p^{1/2}$ relation is obtained with a significant solubility enhancement (Figure 5). The observed deviations from linearity at low r found before the annealing treatment cannot therefore be attributed to trapping by dislocation cores. The annealing temperature, 447 K, is in a range expected for the annihilation of vacancies in Pd (35).

More recently, Kishimoto *et al.* (28) carried out similar H_2 solubility experiments in the very dilute range using a $Pd_{0.8}Ni_{0.2}$ alloy. From plots of $\ln p_{H_2}$ against $1/T$, evaluated at a series of constant r values in the range from 2.7 to 4.9×10^{-4}, a value for $|\Delta H^t_H| = 30$ kJ (mol H)$^{-1}$ was obtained which is close to the trapping enthalpy determined from the ion-beam implantation experiments (31).

The partial molar volume of H, V_H, in bulk Pd is found to be 1.7 cm^3 mol^{-1} from lattice parameter measurements (36), but surprisingly, at very small H contents, negative values were found for cold-worked Pd (37). This was attributed to a local attraction between the H and the surrounding Pd

atoms in the relatively large vacancy volume as compared to the usual octahedral interstice volume where the local interaction is repulsive. Negative partial molar volumes were also found in amorphous *Pd*-Si alloys (38), which were also attributed to the occupation of vacancies. Thus, there is direct (ion implantation results) and indirect evidence for vacancy-trapping of H in Pd.

Conclusions

Hydrogen solubility relationships in Pd are well-established for the dilute phase for 'defect-free' Pd, that is, annealed Pd. It is shown that Pd which contains substantial concentrations of defects, such as dislocations and vacancies, measurably affect the hydrogen solubilities. The differences of the hydrogen solubilities between Pd with defects and 'defect-free' Pd can be used to obtain information about the nature of defects. In the presence of large dislocation densities the dilute phase solubilities increase but, after annealing at 477 K, the linear relation between $p_{H_2}^{1/2}$ and r is maintained. Pd vacancies trap H more strongly than dislocations. This is shown by an initial, nonlinear solubility indicating the strong trapping. Dislocations in cold-worked Pd alloys also trap H and in some alloys the trapping is greater than in Pd while in others the trapping is weaker because of suggested segregation of the solutes during the cold working.

Part II of this article, to be published in the October 2001 issue of this Journal, will discuss H_2 solubilities in internally oxidised Pd alloys, the effects of H on the phase separation in Pd alloys and crystallite size effects on hydrogen solubility.

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Sonochemical Preparation of Nano Platinum and Palladium

Ultrasound offers an attractive route for preparing metal nanoparticles: rapid reaction rate and very small particle formation. Ultrasound can create acoustic cavitation (formation, growth, and implosion of bubbles) in a liquid. When cavitation bubbles collapse areas of high pressure and high temperature (hot spot > 5000 K) are generated. This can decompose the molecules in the bubbles. The hot-spot temperature depends on the properties of the gases inside the bubble – another gas may produce a different effect. Nanoparticles prepared by sonochemical reduction generally have wide size distributions. Attempts at controlling particle size and size distribution have used different metal concentrations, surfactant types and coexisting alcohol types.

Researchers in Japan have now investigated the effect of different atmospheric gases on the particle size distribution of Pt and Pd nanoparticles prepared by the sonochemical reduction of H_2PtCl_6 or K_2PdCl_4 solutions, respectively (T. Fujimoto, S. Terauchi, H. Umehara, I. Kojima and W. Henderson, *Chem. Mater.*, 2001, 13, (3), 1057–1060). Poly(N-vinyl-2-pyrrolidone) was the protecting agent. A smaller, sharper size distribution was achieved for Pt particles prepared under Xe. Pd nanoparticles prepared under N_2 had a sharp size distribution. An optimum sonication time is necessary for preparing single-dispersion nanoparticles. The reaction rate, depending on the hot-spot temperature, is controlled by changing the dissolved gas.