

The Hydrogen-Palladium System

THE ROLE OF X-RAY AND NEUTRON DIFFRACTION STUDIES

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Although the absorption of hydrogen by palladium has been studied for almost a century, interest in this system has not diminished. On the contrary, with the current realisation of the important role of nonstoichiometry in solid reactions, this system is receiving even more attention as an excellent example of a compound which exhibits a large degree of nonstoichiometry.

Lewis (1) has recently reviewed the hydrogen-palladium system in some detail and readers should refer to his series of articles for a general background. This article will be restricted to the key role that diffraction techniques have played in the understanding of this system.

Constitution of the System

Before the availability of X-ray diffraction methods Roozeboom (2) postulated on the basis of the shape of the isotherms that the palladium-hydrogen system consisted of two solid solutions separated by an interval of immiscibility. The pressure invariant region of the 100°C isotherm in Fig. 1, for example, was interpreted in terms of coexistence of two solid solutions. (This was, in fact, among the earliest applications of the phase rule). Some of the isotherms, however, did not conform to this idea in that the pressure did not remain absolutely invariant in the assumed two-phase region, for example, the 140°C isotherm. Since Roozeboom was unable to offer an explanation he was forced to leave the constitution of the system somewhat unsettled.

The constitution of the palladium-hydrogen system was unequivocally established by X-ray diffraction methods (3). McKeehan

confirmed Roozeboom's postulate of two solid phases and showed furthermore that both phases were f.c.c. like palladium itself. The hydrogen positions could not, of course, be established because of the large difference in scattering power between hydrogen and palladium, but the two phases were distinguished by their difference in lattice parameter. McKeehan's conclusions have since been verified many times and according to the most recent X-ray data we may summarise the system as follows (4, 5, 6): a small, but continuous, increase in lattice parameter occurs as hydrogen is absorbed into the palladium lattice. When H/Pd (atomic ratio) has reached $\alpha_{\max} \sim 0.02$ at room temperature (the lattice has expanded from 3.889 Å to 3.895 Å) a new phase, the β -phase, having a lattice constant near 4.025 Å appears. The two phases coexist until H/Pd = 0.58 (β_{\min}) at which composition the α -phase disappears entirely. Further hydrogen uptake causes a gradual expansion of the β -phase; the equilibrium value is 4.040 Å at 25°C, 1 atm. H₂ pressure, (H/Pd = 0.70). The α_{\max} composition changes to larger hydrogen contents with increasing temperature while β_{\min} moves to lower H/Pd ratios. At approximately 300°C there is a critical point; above this temperature only one homogeneous phase can exist. The changes in lattice parameters of α_{\max} and β_{\min} are summarised in Fig. 2 (6).

Complete Structure of the β -phase

With the development of neutron diffraction techniques it has become possible to determine the spatial distribution of protons in crystals of heavy atoms. Worsham *et al*

(7) have investigated the hydrogen-palladium system by this method and found the hydrogen atoms to be located in the octahedral interstices of the f.c.c. palladium lattice. If all these sites were filled, the composition would be PdH and the structure NaCl. However, since the limiting composition at room temperature (one atmosphere) is H/Pd ~ 0.7 only ~ 70 per cent of the interstitial holes are occupied and their distribution appears to be random (7). The value of H/Pd ~ 0.70 is therefore not associated with crystallographic saturation, but must have its origin elsewhere. The work of Worsham *et al* has since been repeated and confirmed by Bergsma and Goedkoop (8). It may be noted in passing that the sample used by Worsham *et al* was charged with hydrogen from the gas phase while that used by Bergsma and Goedkoop was charged electrolytically. This disproves the speculation (9) that there is a difference in structure between the hydride prepared from the gas phase and that obtained by electrolysis (8).

Neutron scattering of hydrogen nuclei is both coherent and incoherent. Coherent scattering leads to diffraction phenomena from which the position of the hydrogen atoms can be ascertained and in addition, information can be obtained about the lattice vibrational amplitudes. Incoherent scattering can yield detailed information about the vibrational spectrum of the lattice. From coherent scattering experiments Worsham *et al* (7) determined the root-mean-square amplitudes of palladium

Fig. 2 Lattice parameters of the α - and β -phases of the hydrogen-palladium system

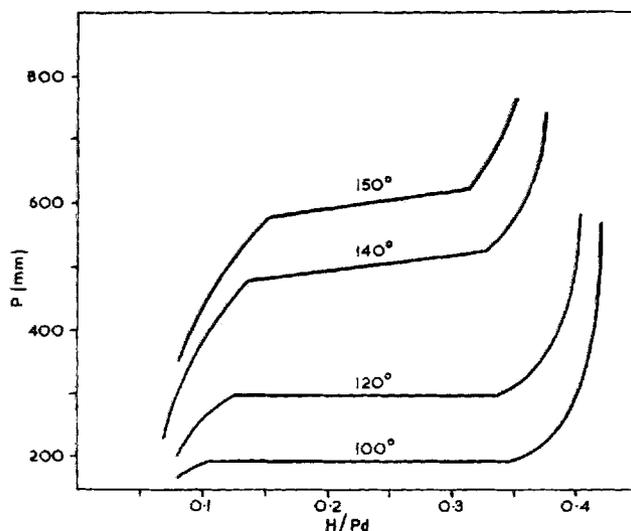
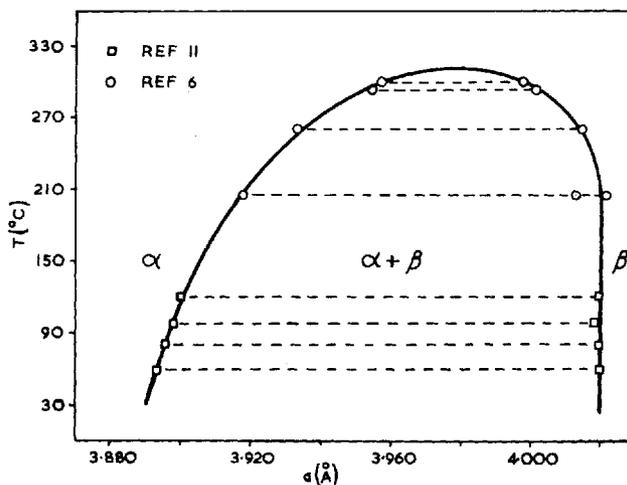


Fig. 1 Representative absorption isotherms of the hydrogen-palladium system

and hydrogen in PdH_{0.706} as 0.071 and 0.23 Å, respectively and Bergsma and Goedkoop (8) found values for these same quantities of 0.10 and 0.24 Å in PdH_{0.63}. From incoherent scattering of cold neutrons the latter workers observed a sharp proton fundamental vibration absorption of 0.056 eV, indicating that, to a good approximation the hydrogen motions in the lattice can be treated by the Einstein model.

Lattice Distortion

The X-ray reflections of palladium exhibit considerable line-broadening as hydrogen is absorbed to form the β -phase (10-14). If the



α -phase is formed from undistorted pure palladium, there is no line-broadening; however, if it is formed from removal of hydrogen from the β -phase, considerable line-broadening is present in the α -phase (11). Complete removal of hydrogen from β -phase at 250°C followed by prolonged heating at this temperature fails to remove the line-broadening. However, annealing at 450°C for four hours results in complete removal of broadening (11).

It is, in general, difficult to decide whether line-broadening indicates distortion of the lattice or the presence of finely dispersed microcrystallites. Owen (12) favours the latter explanation. However, recent research supports the former explanation (13, 14). During a series of studies of the effects of annealing on previously hydrogenated palladium specimens Sugeno and Kawabe (13) found asterism still present in Laue photographs after the grain growth occurring during the annealing of the specimens was almost complete. This shows that the distortion, which is distributed homogeneously throughout the sample, is present after the grains have attained their final form. Tiedema *et al* (14) have obtained X-ray photographs (Van Arkel mounting) of a single crystal of palladium charged with hydrogen. The formation of β -phase caused both deformation and disorientation of the single crystal. After partial hydrogenation of palladium, the α -phase showed well resolved lines but the β -phase showed characteristic, line-broadening. Since both the α - and β -phases would be expected to be finely dispersed in this experiment, both this research (14) and that of Sugeno *et al* (13) strongly support the view that distortion

rather than the presence of finely dispersed microcrystallites causes line-broadening.

It has been claimed that it is possible to remove all of the hydrogen at room temperature from the β -phase without causing the lattice parameter to return to the value of hydrogen-free palladium (15). The method of desorption was either aerial oxidation or ionic bombardment *in vacuo*. Unfortunately it appears that the amounts of hydrogen desorbed were not measured quantitatively and the results are therefore open to question. Also recent results obtained by Barton *et al* (16) seriously question such a claim. These workers found that when hydrogen was removed by oxidation at room temperature, the lattice parameter, electrical resistance and magnetic susceptibility all returned to values little different from those of pure palladium.

Hysteresis

Below approximately 260°C the hydrogen pressure over palladium in its two-phase region is found to be greater during absorption than during desorption. An isotherm illustrating this behaviour (hysteresis) is shown in Fig. 3. It is apparent that the limiting compositions of the α - and β -phase differ between the absorption and the desorption cycles. This has been confirmed by X-ray studies, that is, the lattice parameters

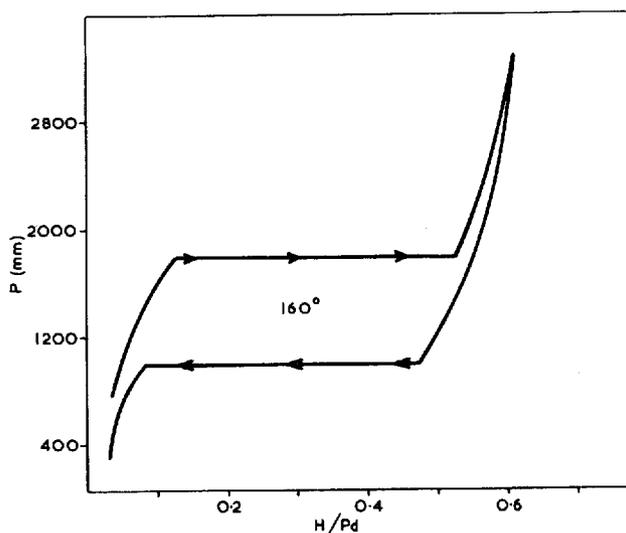


Fig. 3 Absorption and desorption branches of a typical hydrogen-palladium isotherm

reflect the difference in the limiting compositions of the two-phases during absorption and desorption. In addition, X-ray studies have shown that during an absorption or desorption cycle the parameters of α and β change slightly as the two-phase region is traversed (11, 12); these observations have not been confirmed in later work (4); however, there seems to be no reason to doubt Owen's results and it can be tentatively concluded that the presence or absence of a detectable change in lattice parameter as the two-phase region is traversed may be dependent upon the history and type of specimen employed. The fact that Owen's absorption isotherm was not pressure invariant in the two-phase region, whereas in the later work (4); it was closely pressure invariant, may also be an indication of differences between the specimens employed.

It is clear that hysteresis is connected with strain introduced into the lattice as a consequence of the different lattice parameters of the α - and β -phases. As to whether absorption (17), desorption (18, 19) or either (20) represents equilibrium we refer the reader to the literature of this rather controversial subject (17-23).

Future Problems for Diffraction Techniques

Since only a small amount of hydrogen is contained in the α -phase at room temperature (Pd/H \sim 0.02), attempts to determine by neutron diffraction the location of hydrogen in this phase have been unsuccessful (7). The hydrogen concentration in the α -phase may, however, be increased by raising the temperature and the pressure. The neutron diffraction determination may therefore be possible if the experiment is conducted at elevated temperature and pressure; for example, at 200°C and 4 atm.H₂ pressure H/Pd \sim 0.1. An alternative approach would be to employ an alloy of palladium with either silver or gold. The α -phase in an alloy of 20 atom per cent silver or gold, for example, extends to H/M \sim 0.1 at room temperature

and the corresponding pressure is of the order of a few millimetres. It is reasonable to assume that the positions of the hydrogen in the α -phase of these alloys are not different from those in the α -phase of pure palladium.

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