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A NEW PHASE IN PALLADIUM HYDRIDE TECHNOLOGY*

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ABSTRACT

Two plateaux are observed in both the absorption and desorption isotherms of palladium hydride. For the absorption isotherm, a change in plateau pressure is observed at a hydrogen-to-metal (H/M) ratio of about 0.35 for all temperatures studied. For the desorption isotherm, the change in plateau pressure appears to be a function of temperature, ranging from an H/M ratio of 0.18 at 80° C to 0.3 at 140° C. These data are interpreted as being experimentally observed boundaries to an equilibrium phase line located in the miscibility gap of the palladium/hydrogen phase diagram. This new phase does not appear to be a stoichiometric compound, but rather its composition seems to vary with temperature.

INTRODUCTION

The use of metal hydrides for storage, purification, isotope separation, pumping, and compression has proven to be an efficient and safe method for processing hydrogen isotopes.[1] However, when tritium is handled as a metal tritide, the radioactive decay product, ^{3}He, induces microstructural changes in the metal hydride lattice which do not occur for the protide or the deuteride. Because most of the helium generated by tritium decay in a metal tritide is retained in the solid,[2] the influence of helium on the behavior of metal tritides must be understood to design gas handling systems which use metal tritides for tritium storage and compression.[1] Studies necessary to successfully utilize metal hydrides in hydrogen handling systems also contribute to the fundamental understanding of the behavior of both helium and hydrogen isotopes in metals and metal hydrides.

The effect of helium from tritium decay on the gas-solid thermodynamics of palladium tritide for up to one year of exposure has been reported.[3] The effect is a lowering of only one of the observed two plateaux in the pressure-temperature-composition (P-T-C) region of the isotherm where a single plateau is normally reported. A protium isotherm also showed the two plateaux, and it was suggested that the existence of the dual plateau is intrinsic to palladium, and not because of some artifact of tritium or tritium decay.[3]

In this paper, the absorption and desorption protium isotherms for palladium powder are reported from 80° C to 140° C. These data were collected using palladium powder which had never been exposed to tritium gas or tritium contaminated equipment. They all show the dual plateau, again suggesting that the two plateaux are intrinsic to palladium.

EXPERIMENTAL

The palladium powder used in this study was purchased from Engelhard Industries, Inc., and is described elsewhere.[3] The experimental assembly and procedure are also described elsewhere.[4] In this case, isotherm data were collected immediately upon quantitative charging of protium to the sample. The error in the pressure measurements (10,000 Torr MKS Baratron® Capacitance Manometer 390H) in these studies is estimated based on calibration of the pressure transducer to be a maximum of ±2% of the reading at pressures equal to or less than 250 Torr and approximately 1.2% of the reading in the 500 to 1000 Torr range. Temperatures were measured inside the sample vessel.[4]

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RESULTS

The set of absorption isotherms for protium on palladium powder are shown in Fig.1, and the corresponding desorption isotherms are shown in Fig.2. The two plateaux for each temperature isotherm are clearly shown in both figures.

For the absorption isotherms, there appears to be an area around H/M = 0.3 to H/M = 0.4 where the transition to the upper plateau occurs. There is a slight temperature dependence to the transition point, but it does not appear to be regular. For example, at 140° C, the transition occurs at about H/M = 0.35; at 120° C and 110° C, at about H/M = 0.3; and at 100° C and 80° C the transition occurs at about H/M = 0.4. In all cases, the two plateaux are very flat.

For the desorption isotherms, the area of transition is shifted to lower H/M, and the temperature dependence is opposite to the absorption isotherm data. At 140° C, the transition to the lower plateau occurs at H/M = 0.28, whereas at 80° C the transition occurs at H/M = 0.18. Again, the two plateaux are very flat for all temperatures.

The change in the pressure from the lower to the upper plateau for both absorption and desorption isotherms at all temperatures is shown in Fig.3. There is an increase in the ΔPress with temperature for both absorption and desorption data.

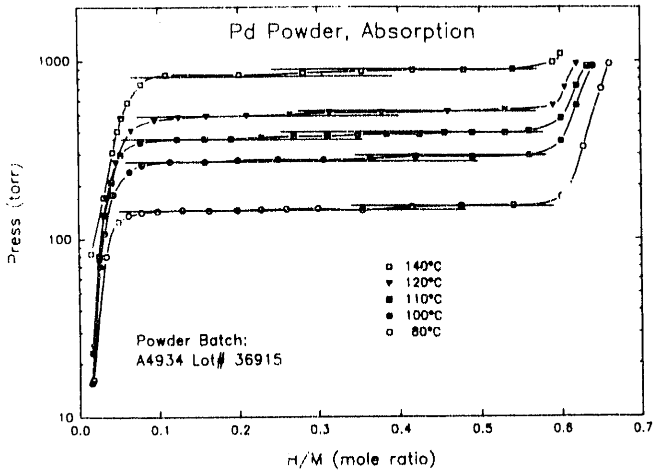

Figure 1. Absorption Isotherms for Palladium Powder

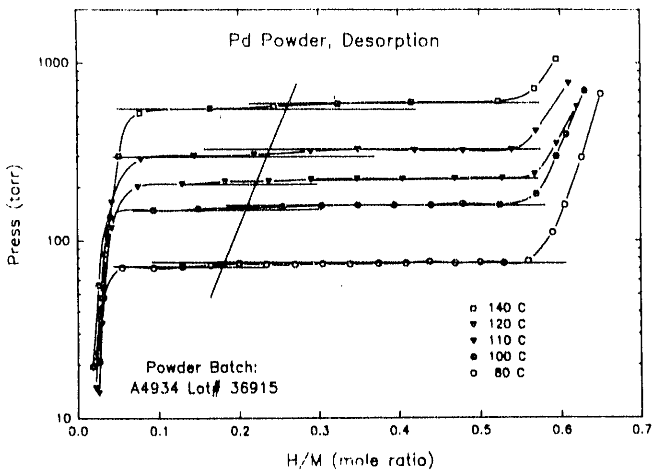

Figure 2. Desorption Isotherms for Palladium Powder

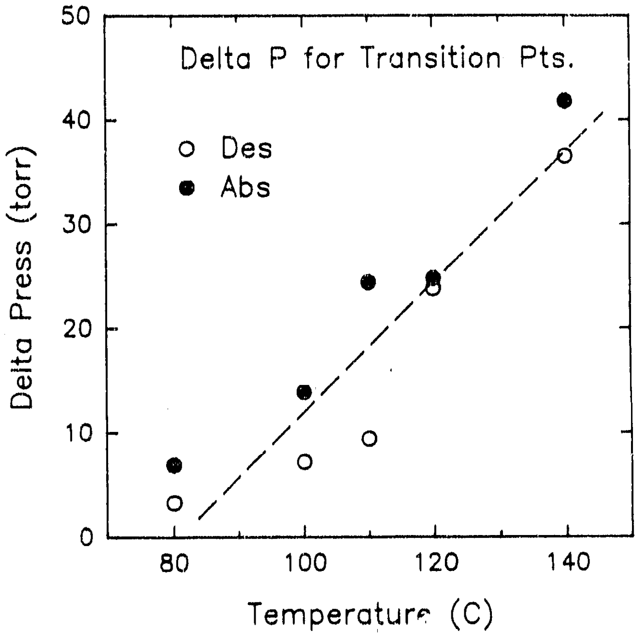

Figure 3. The change in pressure for both absorption and desorption isotherms with temperature

DISCUSSION

The unit cell for palladium has four palladium atoms (f.c.c.) with four octahedral and eight tetrahedral interstitial sites. At an H/M ratio of one, there are four hydrogen atoms per unit cell. Therefore, at an H/M ratio of about 0.25, there is one atom of hydrogen per unit cell, on average. This is the vicinity in the plateau region of the P-T-C isotherm where the second plateau is developed. It appears that when hydrogen concentrations greater than about H/M ≈ 0.25-0.3 are achieved during absorption, the lattice sites of lowest energy for hydrogen occupancy change. On desorption, when hydrogen concentrations less than H/M = 0.3-0.18 are achieved, a relaxation occurs which returns the system back to the more stable hydrogen site locations. Also, at least one extra peak in the x-ray diffraction pattern for palladium hydride has been reported to have a lattice parameter about midway between the bulk α-and β-phases, assuming this peak is a (422) reflection of f.c.c. hydride phases other than α- and β-phases.[5] As with the two plateau observation, this new peak occurs in the vicinity of the isotherm where the second plateau is developed.

An attempt to describe the lower plateau hydrogen site occupancy will be made, followed by a description of the upper plateau. A hysteresis argument is used to describe the apparent temperature dependences of the transition points on the absorption and desorption isotherms.

1. Upper and Lower Plateaux

The lower plateau spans the palladium isotherm from about H/M = 0.03 up to about H/M = 0.4. In the region of the lower plateau there is only one hydrogen atom per unit cell on average. An occupied unit cell appears to be less available for additional hydrogen occupation than is an unoccupied unit cell. An average hydrogen-hydrogen distance is established which is determined by the hydrogen-hydrogen and palladium-hydrogen interactions. The palladium-hydrogen interaction is very dominant here, caused by the distribution of one hydrogen atom per unit cell, which determines the site energy and thus the equilibrium pressure for hydrogen observed as the plateau pressure.

The upper plateau spans the palladium isotherm from about H/M ≈ 0.25-0.3 to about H/M ≈ 0.6. The pressure of this plateau is reported in the literature as the plateau pressure for palladium hydride at each temperature, not the lower plateau. Also, as reported previously the helium effect for palladium tritide does not alter the upper plateau for about one year of tritium exposure.[3] Hydrogen is occupying sites in unit cells where a hydrogen atom already resides, and the hydrogen-hydrogen interaction becomes less attractive. The average hydrogen-hydrogen distance has decreased, and the repulsion among the two hydrogen atoms in the same unit cell is accommodated by an adjustment which distorts the local interstitial sites. This may be the cause of the extra peak in the x-ray data.[5] It is this hydrogen-hydrogen interaction which is determining the site energy and thus the equilibrium pressure of the upper plateau.

From the above, the lower plateau pressure appears to be determined by hydrogen-palladium interactions of a single hydrogen atom in a unit cell. The upper plateau likewise results from hydrogen-hydrogen interactions which cause the hydride to be less stable than at lower hydrogen concentrations; the palladium-hydrogen interaction is reduced by the hydrogen-hydrogen interaction. It appears that the interstitial sites which are associated with the upper plateau are less affected by the nature of the palladium than the sites associated with the lower plateau.

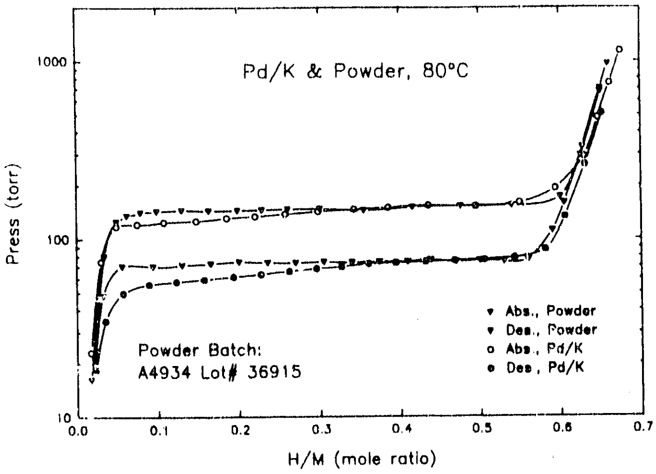

Figure 4. Isotherms for Pd/k and Palladium Powder

A test of this hypothesis is made when palladium is coated on kieselghur (Pd/k). Fig. 4 shows a comparison of the protium absorption and desorption isotherms for Pd/k and palladium powder at 80° C. The upper plateaux are coincident but the lower plateaux show a slope for the Pd/k isotherm at less pressure than the powder isotherms. By altering the nature of palladium the lower plateau was altered. Constraint of palladium by the kieselghur, variation in thickness or grain size, and variation in crystallite size all could be contributing to this change. Since the upper plateau is dominated by the hydrogen-hydrogen interaction, the nature of palladium has no effect on the plateau pressure; it is the same as the palladium powder upper plateau.

2. Hysteresis and the Transition Points

For the palladium powder absorption isotherms, the transition points are all at higher H/M values than the corresponding transition points for the desorption isotherms. Also, the difference in the absorption/desorption transition point for a given temperature isotherm increases with decreasing temperature. This is a type of hysteresis that is temperature dependent at the temperatures used in these experiments. This is not the normal absorption desorption hysteresis described for most metal hydride systems. The hysteresis referred to here is the $\Delta H/M$ between the transition points at each temperature for a given absorption-desorption isotherm pair.

Increasing the temperature at which the isotherms are measured increases the plateau pressure of gas phase. The higher plateau pressure indicates that the hydride is less stable at higher temperatures (decreased chemical potential). There is also a larger change in pressure between the upper and lower plateau pressures for a given absorption or desorption isotherm with increasing temperature. Neither of these effects by themselves explain the observed temperature dependence of the transition points.

From consideration of elastic and plastic accommodation effects on metal-hydride solubility, M. P. Puls describes a hysteresis of the terminal solid solubility (TSS) of hydrogen in metal hydrides.[6] He finds that undercooling is required to overcome the barrier to nucleation of the hydride from the solid solution and that it contributes significantly to the total shift between the TSS data measured on heating and on cooling. Heating is associated with the dissolution of the hydride phase, and cooling is associated with the precipitation of the hydride phase. The conclusion is that the hysteresis between the activation energies of the heat-up and cool-down TSS is approximately equal to the elastic accommodation energy.

Perhaps there is an equivalent misfit associated with the transition points between the upper and lower pressures observed on the palladium hydride plateaux in this work.

If upon absorption (cool-down) the transition point is associated with increased hydrogen-hydrogen interaction, then the observed temperature dependence is understood by an undercooling argument. Undercooling causes the TSS to be observed at higher hydrogen contents than at equilibrium hydrogen concentrations.[6] An undercooling argument for the family of absorption isotherms requires a greater hydrogen concentration for the observed transition point as temperature decreases. This rearrangement associated with the transition point is identified then as a rather coherent transition which is constrained by elastic energy as described for the TSS. This elastic energy appears to increase with temperature because the change in pressure across the transition point increases with temperature (Fig.3). The upper plateau pressures indicate a less stable hydride caused by the metal lattice distortions observed in the x-ray data.[5] If the pressure change is increasing, the distortion must be increasing and hence the elastic energy constraining the distortion must be increasing with temperature.

Upon desorption (heat-up), the matrix relaxes at the transition point; by analogy this is a good approximation to the stress-free TSS.[6] At higher temperatures, the hydride is less stable and the relaxation occurs at higher hydrogen concentrations because the elastic energy which is returned is larger. At the lower temperature, the metal hydride is more stable, and the elastic energy returned by relaxation is less; therefore more hydrogen must be removed from the hydride before the system can relax.

In summary, it appears that the desorption isotherm transition points are a better measurement of the equilibrium phase line than the absorption isotherm transition points. They show a very regular temperature dependence and are associated with a relaxation of elastic energy constraining the metal matrix when the less stable hydrogen interstitial sites are formed. Also, the upper plateau pressures appear to result from hydrogen-hydrogen interactions which reduce the palladium-hydrogen interactions. This gives the appearance of hydrogen interstitial sites which are less sensitive to the form of palladium.

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