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The Near Elimination of Hysteresis in Pd/Cr_2O_3 Composites

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Abstract

Although its value varies with the microstructure, hysteresis always accompanies hydride formation and decomposition in Pd(pure)-H, e.g., it is present even in nano-crystalline and thin films. Internal oxidation of $Pd_{0.93}Cr_{0.07}$ alloys leads to a pure Pd matrix containing nano-crystalline chromia precipitates. The characteristic hysteresis of Pd-H almost disappears in this form of Pd. The reasons for this are discussed.

Introduction

Hysteresis is an almost universal feature of first order solid state transitions [1]. Its presence means that when such a transition is reversed, it follows a different path than that taken in the forward direction leading to a loss of useful work. Hysteresis is, of course, a reflection of the irreversibility of the transition.

Hysteresis

For metal-hydrogen systems which form hydride phases in the region of co-existence of the dilute and hydride phases the phase rule predicts an invariant p_{H2}, the plateau pressure. The formation of the hydride phase can be written as

$$½\ H_{2(g)} + (b-a)^{-1}MH_a = (b-a)^{-1}MH_b \qquad (1)$$

where *a* and *b* are the H-to-metal atom ratios in the co-existing dilute and hydride phases, respectively. The reverse of this reaction is hydride decomposition.

The most common manifestation of hysteresis in metal-H systems is that the minimum plateau p_{H2} needed for hydride formation, p_f, i.e., the forward reaction of equation (1), is greater than that for hydride decomposition, p_d, the reverse of (1). Hysteresis is best evaluated quantitatively as either $RTln(p_f/p_d)^{1/2}$ J/ mol $^1/_2H_2$ or else as $RT§lnp^{1/2}dr$ J/ mol metal where r=(H-to-Pd) atom ratio. Hysteresis should be a minimum for applications of metal-hydrogen systems because it represents a loss of efficiency.

Hysteresis always accompanies hydride formation/decomposition in Pd-H. There have been reports of its absence but these are believed to be spurious [2]. It is clear, however, that the extent of hysteresis depends upon the microstructure of the Pd. Compared to bulk Pd, hysteresis for Pd black, nano-crystalline, and thin films are found to be reduced. Nonetheless, it is still appreciable even in these forms and, e.g., the change of hysteresis from bulk to Pd black is quite small [3]. For 50 nm Pd films hysteresis at 382 K is similar to bulk Pd but there is a significant decrease at 471 K which is attributed to critical temperature lowering [4]. Even for 3.1 nm Pd nano-clusters hysteresis has been reported [5].

An instance where hysteresis is significantly reduced is in tritium-charged Pd which has been aged allowing the T to decay into He–3 which subsequently accumulates into nano-sized bubbles within the lattice. The presence of these bubbles causes the isotherms to profoundly change resulting in a decreased plateau p_{H2} and hysteresis and sloping plateaux with a region of initial trapping [6].

It has been shown earlier that successive hydriding/dehydriding, cycling, of Pd alloys containing certain minimum solute compositions, the value of which depends upon the specific solute, causes significant decreases of p_f and usually smaller increases of p_d so as to decrease hysteresis [7,8,9,10]. For example, such cycling effects are found in binary Pd alloys with X_{Ni}=0.10, 0.15 and X_{Mo}=0.02 alloys. For the X_{Ni}=0.15 alloy repeated cycling lead to a complete disappearance of hysteresis [7]. On the other hand, for annealed Pd and very dilute alloys, e.g., X_{Ni}=0.01, cycling has the opposite effect, i.e., p_f increases slightly [11]. Tritium aging in 50 weight percent Pd on kieselguhr (silica), which causes an increasing He bubble content in the metal matrix, causes p_f and p_d depression [25]. As well, a Pd-Rh-Co alloy has shown loss of hysteresis upon tritium aging [26]. Cycling of tritium-aged La-Ni-Al alloys also results in recovery of the plateaus towards their original positions [27]. The present paper is, however, concerned with hysteresis in Pd and not in its alloys.

Internal Oxidation of Pd Alloys

Binary Pd alloys containing small amounts of readily oxidizable solute metals such as Al, Mg, Zr, can be internally oxidized to form essentially a pure Pd matrix phase with a second phase of nano-sized oxide precipitates [12,13]. After internal oxidation of, e.g., *Pd*–Al alloys, a composite forms consisting of nanocrystalline alumina precipitates within a matrix of Pd and, because of the great stability of alumina, the amount of unoxidized Al remaining after internal oxidation is negligible and hence the matrix can be regarded as pure Pd. The term *matrix* will be employed for the Pd in such a composite and the term *annealed* for pure, bulk Pd with the understanding that both the phases are pure and in the bulk form as distinguished from, e.g., thin films or nanopowders, and is some cases these forms will be cycled and will be referred to as cycled *annealed* or cycled Pd *matrix*.

The oxide, alumina, which form in the internal oxidation of *Pd*-Al alloys is very stable and, consequently the *Pd matrix* is essentially pure, its H_2 isotherms would be anticipated to be very much like those of annealed Pd except in the very dilute phase where some H is trapped at or near the Pd/oxide interface [13,14]. Although the initial isotherms at moderate temperatures are similar to those of *annealed* Pd, after cycling internally oxidized *Pd*-Al alloys, their behavior, especially at high temperatures, is analogous [15], but much less pronounced, to the results to be reported here for internally oxidized *Pd*-Cr alloys. For internally oxidized *Pd*–Rh alloys the H_2 isotherms are similar to *annealed* Pd with have plateau pressures for hydride formation greater than for annealed Pd but the decomposition plateau pressures are almost the same [16]. Any differences which exist between H_2 isotherms for Pd/oxide composites and annealed Pd, must be attributed to the microstructural features of the *Pd matrix* caused by the nano-crystalline oxide precipitates and not to any atomic impurities such as unoxidized solute atoms in the Pd because of their negligible concentration and also because small amounts of solute atoms ($\leq 0.5\%$) have negligible effect on H_2 isotherms of Pd.

In the present investigation hysteresis will be shown to nearly disappear after cycling a $Pd_{0.93}Cr_{0.07}$ alloy which has been internally oxidized at the relatively low temperature of 998 K. The lower the temperature of internal oxidation, the smaller are the precipitates which form [17] and it will be shown that the smaller the precipitates, the greater the decrease of hysteresis upon cycling. Small precipitates are also more effective in causing dispersion hardening of internally oxidized alloys [17].

Experimental

Pd–Cr alloys were prepared by arc-melting the pure elements, annealing the buttons and then rolling them into foil of dimensions about 2 cm x 0.3 cm x 110 μm. *Pd*–Cr alloys were internally oxidized in the laboratory atmosphere in a tube furnace. Mainly results for the $Pd_{0.93}Cr_{0.07}$ alloy internally oxidized at 998 K will be presented. The oxidation product of a number of *Pd*–Cr alloys were determined from the weight gains and corresponded more closely to Cr_2O_3 than to other possible oxides although sometimes their weights exceeded that for Cr_2O_3, e.g., 110%.

The internally oxidized $Pd_{0.93}Cr_{0.07}$ alloy is brittle whereas an internally oxidized $Pd_{0.97}Cr_{0.03}$ alloy is not and, after repeated cycling of the internally oxidized $Pd_{0.97}Cr_{0.03}$ alloy, it undergoes brittle fracture changing the foils into small particles. Without any crushing, these particles ranged from about 10 to 150 μm with the average about size of about 30 μm. This range of particle size is somewhat larger than found for cycled ($20\times$) $LaNi_5$ [18].

An X-ray diffraction pattern was taken for the finely divided internally oxidized (998 K) $Pd_{0.93}Cr_{0.07}$ alloy and compared to finely divided Pd. The patterns show that the alloy has been completely internally oxidized because there is no evidence for any unoxidized alloy and the reflections for the oxidized alloy correspond almost exactly with the finely divided Pd, however, those for the composite are much broader indicating lattice strain.

Results and Discussion

Dilute Phase

The dilute phase solubilities of Pd/oxide composites for the initial absorption consist of a trapping region where p_{H2}~0 followed by a region where the solubility is enhanced to various extents as compared to *annealed* Pd depending on factors such as the oxidation temperature and the solute concentration [14]. The initial H_2 solubility of the internally oxidized $Pd_{0.93}Cr_{0.07}$ alloy (998 K) does not differ very much from that of the $Pd_{0.93}Cr_{0.07}$ alloy after internal oxidation at 1098 K. The dilute phase solubilities are both very large, greatly exceeding that of annealed Pd and larger than any other internally oxidized *Pd*–M alloy which we have examined [10,14]. The positive intercept is caused by strong trapping at the interface [12]. The dilute solubilities are shown to increase slightly after cycling and, after about 20 cycles, 10 of them at 273 K, the solubility is the largest which has been observed in this research although it is still not much greater than that for the initial cycle. The dilute phase behavior will not be discussed in detail here because it does not exhibit hysteresis.

Two Phase Region

For the initial cycle of hydriding/dehydriding at, e.g., 323 K, both p_f and p_d for the internally oxidized ($\leq$1100 K)*Pd*–Cr alloys are lower than those for *annealed* Pd. After cycling, the formation plateau p_{H2} decreases further while the decomposition p_{H2} increases slightly thus decreasing hysteresis. The extent of these changes depends upon X_{Cr} and the internal oxidation temperature. These results differ from the small changes seen for the plateaux of different forms of Pd, e.g., Pd black or thin film, where the average plateau pressures do not change much from that of *annealed* Pd but in some cases the capacities are reduced, i.e., the H content at the end of the plateau. The behavior of the internally oxidized $Pd_{0.93}Cr_{0.07}$ alloy is closer to that of T-aged Pd [6] than to the other forms of Pd mentioned above suggesting that the oxide precipitates play a similar role as the He bubbles which form in T-aged Pd.

It is of interest that the plateau pressures change with cycling but the dilute phase solubilities are not much affected by cycling. This indicates that the dislocation arrays evolve with cycling but their total density, which is a large factor in determining the dilute phase solubility enhancements, does not change significantly. Dislocation loops are observed around the precipitates from TEM and these may give rise to some solubility enhancement.

Isotherms were measured at temperatures from 323 to 513 K for the 20× cycled, internally oxidized (998 K) $Pd_{0.93}Cr_{0.07}$ alloy (Figs. 1-4). Several features of interest emerge including the nearly complete elimination of hysteresis at $\geq$493 K. Similar behavior is found for a $Pd_{0.95}Cr_{0.05}$ alloy internally oxidized at 1098 K but the decrease of hysteresis is greater for the $Pd_{0.93}Cr_{0.07}$ alloy and therefore most attention will be given to it. Table 1 gives values of hysteresis at different temperatures for *annealed* Pd and the *Pd matrix* from internal oxidation of the $Pd_{0.93}Cr_{0.07}$ alloy as evaluated at r =0.3 using hysteresis= $RT\ln(p_f/p_d)^{1/2}$ J/ $\frac{1}{2}molH_2$.

In Figure 1 $\ln p_{H_2}^{1/2}$ has been plotted instead of $p_{H2}^{1/2}$ as in Figures 2-4; the former represents hysteresis more directly than employing the other ordinate. Hysteresis is much smaller for the internally oxidized $Pd_{0.93}Cr_{0.07}$ alloy than for annealed Pd at all temperatures (Table 1). At 473 K, hysteresis has disappeared at r =0.30 but there is still some indication of it near the two phase boundaries especially the upper one (Fig. 3). This may indicate that there is a greater difficulty in the formation of either phase in their early stages than for their growth when about equal amounts are present. Nucleation will not be a problem, however, due to the large defect concentration in the cycled internally oxidized alloy, e.g., there is no supersaturation of the dilute phase in Pd if it has been cycled whereas there is for uncycled *annealed* Pd, but, nonetheless, it appears in Figure 3 as if there is hysteresis in the early stages of growth.

At all temperatures *both* the hydride formation and decomposition plateaux for the *Pd matrix* are lower near their midpoints, e.g., r =0.3, than either plateau for *annealed* Pd; equilibrium has been shifted and not just the degree of hysteresis. Although it appears as if the decreases of the plateau p_{H_2} are greater as the temperature increases, the decrease of $\Delta\mu_H = RT\ln(p_f/p_d)^{1/2}$ J/ $\frac{1}{2}molH_2$, is greater (Figs. 2-4) at the low temperatures. From the data shown in Figure 1 at 323 K, $RT\int \ln p^{1/2} dr$ =720 J/mol Pd and 125 J/ mol Pd for *annealed* Pd and the cycled Pd *matrix* in the internally oxidized alloy, respectively, and $RT\ln(p_f/p_d)^{1/2}$ =1010 J/ $\frac{1}{2}molH_2$ and 95 J/$\frac{1}{2}molH_2$ for *annealed* Pd and the cycled Pd *matrix*, respectively, reflecting the larger decrease of hysteresis in the center of the plateau. This hysteresis at 323 K for Pd does not agree with that shown for a different sample in Table 1 illustrating that hysteresis varies somewhat even for *annealed* Pd.

Besides hysteresis being small or zero for the Pd *matrix* at elevated temperatures in the Pd/chromia composite, its isotherms become very sloping while the H capacities remain unchanged. The sloping increases with increase of temperature (Figs. 2-4). The same phenomena hold for the internally oxidized $Pd_{0.95}Cr_{0.05}$ alloy except that a small hysteresis is present at 513 K whereas it has disappeared at this content for the $Pd_{0.93}Cr_{0.07}$ alloy internally oxidized at 998 K.

Since there is no hysteresis and the “plateau" region is very sloping at $\geq$493 K, it can be asked if there are still two phases present in the plateau region of the Pd *matrix*. The answer to this is positive because the locations of the most marked changes of slope in the isotherms closely match those for *annealed* Pd at each temperature. In addition, the $\ln p_{plat}$ data evaluated at r =0.2, 0.30 and 0.45 at T=400 K, 493 K and 513 K all have similar van’t Hoff plot slopes for the Pd *matrix* as for the lower temperature range where there are obviously two phases and hysteresis. If the Pd *matrix* were single phase, e.g., above its critical temperature, it would be expected that its thermodynamic parameters would correspond to the plateau values only at the critical composition, e.g., $\approx$0.30, and not at, e.g., r =0.45 or 0.20.

On the basis of the above arguments it can be concluded that hysteresis completely disappears for the composite at ≥ 493 K and is replaced by very sloping plateaux. It seems as if there is a trade-off between horizontal plateaux/hysteresis and sloping plateaux/no hysteresis, however, a large hysteresis and very sloping plateaux have been observed for some inhomogeneous Pd alloys [21] so it does not appear to be a general correlation. For Pd films [4] there is a critical point lowering where the breadth of the plateau decreases and T_c is lowered for very thin films, 50 nm.

Thermodynamics

The thermodynamic parameters for the composite were determined from plateau pressures from 273 K to 373 K at $r = 0.30$ using liquid constant temperature baths for good heat transfer and control. The van't Hoff plots (Fig. 5) give the enthalpies of hydride formation and decomposition for the Pd/chromia composite –20.9 and 21.5 kJ/ $\mathrm{mol}\frac{1}{2}\mathrm{H}_2$, respectively, as compared to –18.6 and 20.3 $\mathrm{kJ/mol}\frac{1}{2}\mathrm{H}_2$ for *annealed* Pd. The sum of the magnitudes of the two plateau enthalpies for *annealed* Pd is 19.4 $\mathrm{kJ/mol}\frac{1}{2}\mathrm{H}_2$ and for the Pd *matrix* of the composite it is 21.2 $\mathrm{kJ/mol}\frac{1}{2}\mathrm{H}_2$. The former value is close to the calorimetric value of 19.2 $\mathrm{kJ/mol}\frac{1}{2}\mathrm{H}_2$ [19]. It has been shown that the average of the magnitudes of the van't Hoff plots should, to a first approximation, be the same as the calorimetric value [20]. $|\Delta H_{\mathrm{av,plat}}|$ is 1.8 kJ/ $\frac{1}{2}\mathrm{mol}\frac{1}{2}\mathrm{H}_2$ greater for the Pd *matrix* than *annealed* Pd. This is somewhat greater than the difference of ΔG_{plat} values at $r = 0.3$ indicating that there is also a difference in the ΔS_{plat} values. In any case, the larger enthalpy magnitude for the phase transition in the Pd matrix than for annealed Pd largely causes the plateau pressure decrease. This may be due to the internal stresses which assist both hydride formation and decomposition in analogy to a cyclic deformation assisted by the Bauschinger effect.

Table 1. Hysteresis in units of $\mathrm{J}/\frac{1}{2}molH_2$ for the Pd *Matrix* in Internally Oxidized (998 K) $\mathrm{Pd}_{0.93}\mathrm{Cr}_{0.07}$ Alloy and *Annealed* Pd both Evaluated at $r = 0.30$.

T/K	**1/2RTln(p_f/p_d)** **(*Pd matrix*)**	**1/2RTln(p_f/p_d)** **(*cycled annealed Pd*)**
273	240	1030
323	122	935
343	97	900
373	68	940
493	~0	550

Origin of Hysteresis Reduction

Hysteresis is nearly eliminated at 323 K after cycling a $\mathrm{Pd}_{0.93}\mathrm{Cr}_{0.07}$ alloy which had been internally oxidized at 998 K (Fig. 1); to be precise, it falls to about one sixth of the value for *annealed* Pd evaluated as the area of the loop, i.e., per mol Pd. The Pd *matrix* is a pure phase albeit it contains a second phase of nanocrystalline oxide precipitates.

Therefore it is clearly a reduction of hysteresis for a pure Pd phase. *Both* plateaux pressures decrease after internal oxidation before any cycling. It should be kept in mind that large dislocation densities are formed from cycling Pd through its hydride phase change due to the large lattice expansion/contraction of the volume, 11%, in the ductile metal, Pd [22,23]. It is known that small, coherent precipitates interact strongly with dislocations indeed this is the basis of dispersion hardening [24]. Therefore the cycling of Pd containing nanocrystalline sized chromia precipitates, will be affected by interaction of the dislocations with the precipitates. These phenomena are believed to be analogous to the changes observed after cycling some Pd–rich alloys. In both cases there are disturbances in the lattice, the solute atoms or oxide precipitates, which interact with the moving dislocations generated by cycling. In may be that the resulting dislocations cause internal stresses which aid in nearly eliminating hysteresis and in decreasing plateau pressures.

The initial hydride formation plateau after internal oxidation of the $Pd_{0.93}Cr_{0.07}$ alloy is reasonably horizontal (323 K) but after cycling, it becomes increasingly sloping in the region reflecting the latter half of conversion to the hydride. The pronounced sloping cannot be related to impurities in the Pd matrix but must be due to stresses which develop during cycling. The decomposition plateau is more horizontal than the formation plateau but it also slopes to some extent in the plateau region where the hydride phase fraction becomes small. It seems clear that the near elimination of hysteresis is facilitated by stresses from the microstructures which develop after cycling the internally oxidized alloys.

Conclusions

The most important points for the internally oxidized $Pd_{0.93}Cr_{0.07}$ alloy are that both plateau pressures decrease below those for annealed Pd and that hysteresis decreases significantly compared to annealed Pd.

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Figure Captions

Fig. 1 Hydrogen isotherms at 323 K. □ , *annealed* Pd; ⊔ , Pd *matrix* from internal oxidation of the [Trial mode] alloy. The filled and open symbols are for [Trial mode] absorption and desorption, respectively.

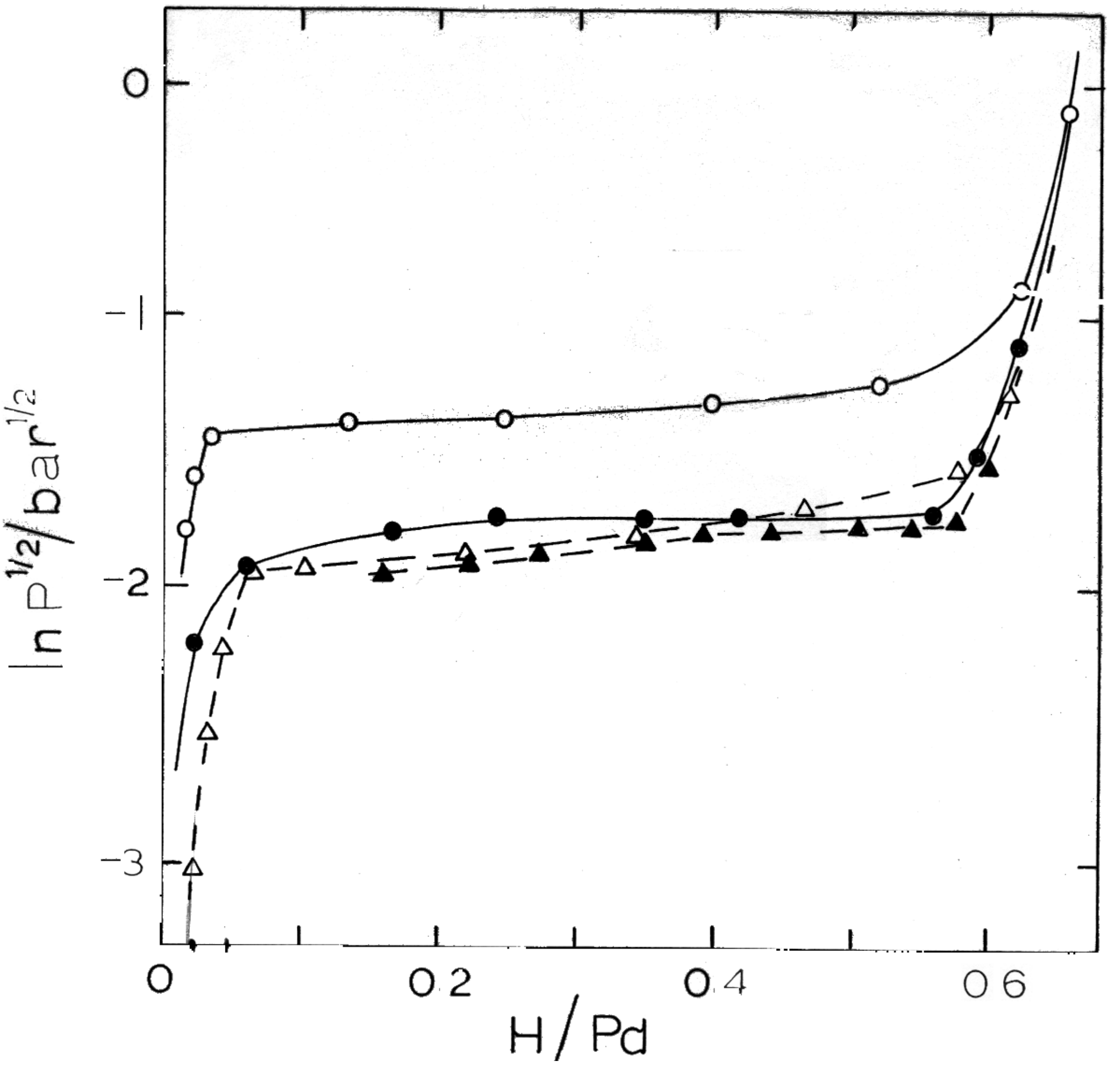
Fig. 2 Hydrogen isotherms at 373 K. [Trial mode], *annealed* Pd; [Trial mode],Pd *matrix* from internal oxidation of the [Trial mode] alloy. The filled and open symbols are for [Trial mode] absorption and desorption, respectively.

Fig. 3. Hydrogen isotherms at 473 K. [Trial mode], *annealed* Pd; [Trial mode], Pd *matrix* from internal oxidation of the [Trial mode] alloy. The filled and open symbols are for [Trial mode] absorption and desorption, respectively.

Fig. 4. Hydrogen isotherms at 493 K, 513 K and 553 K. *Annealed* Pd, Solid curves without symbols at 553 K; [Trial mode], annealed Pd at 513 K; [Trial mode], Pd *matrix* from internal oxidation of the [Trial mode] alloy. Pd *matrix* from internal oxidation of the [Trial mode] alloy at 513 K and [Trial mode], Pd *matrix* at 493 K. The filled and open symbols are for [Trial mode] absorption and desorption, respectively.

Fig. 5 Van't Hoff plots for plateau pressures. [Trial mode], [Trial mode], hydride formation and decomposition for *annealed* Pd and filled [Trial mode], [Trial mode], hydride formation for the Pd *matrix* from internal oxidation of the [Trial mode] alloy. The plateau pressures have been evaluated at [Trial mode]=0.30 for both. The filled and open symbols are for [Trial mode] absorption and desorption, respectively.

Figure 1.



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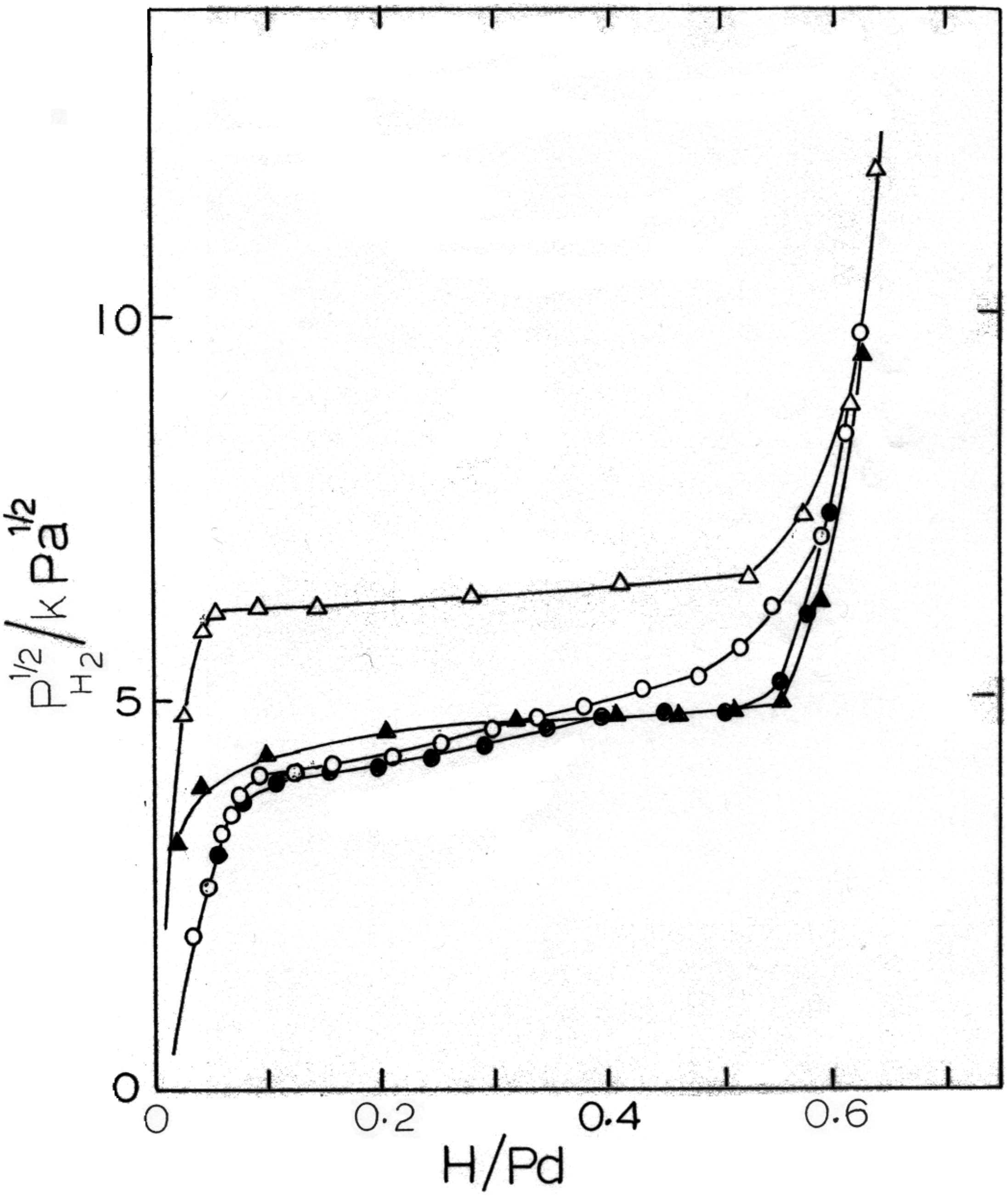

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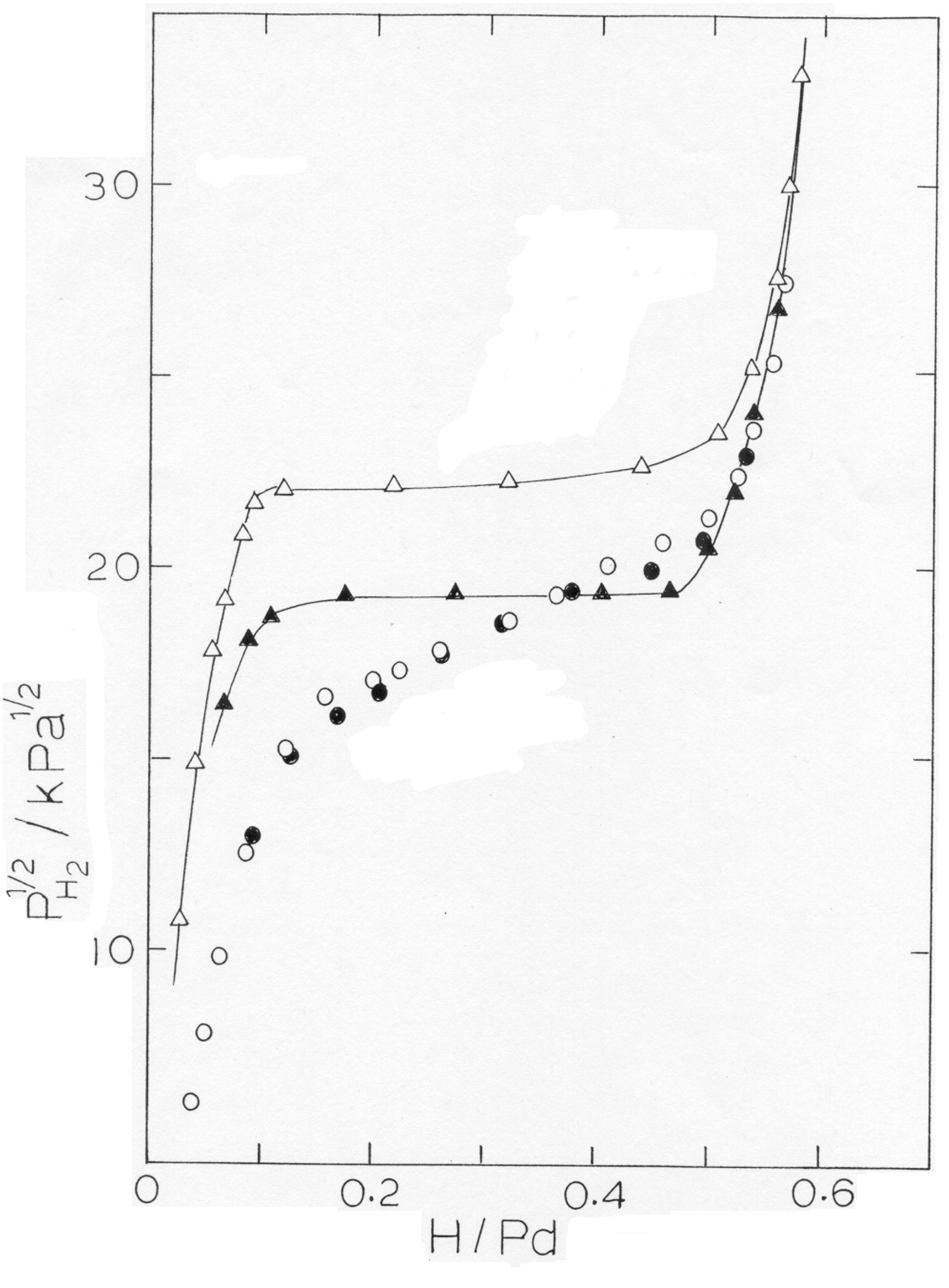

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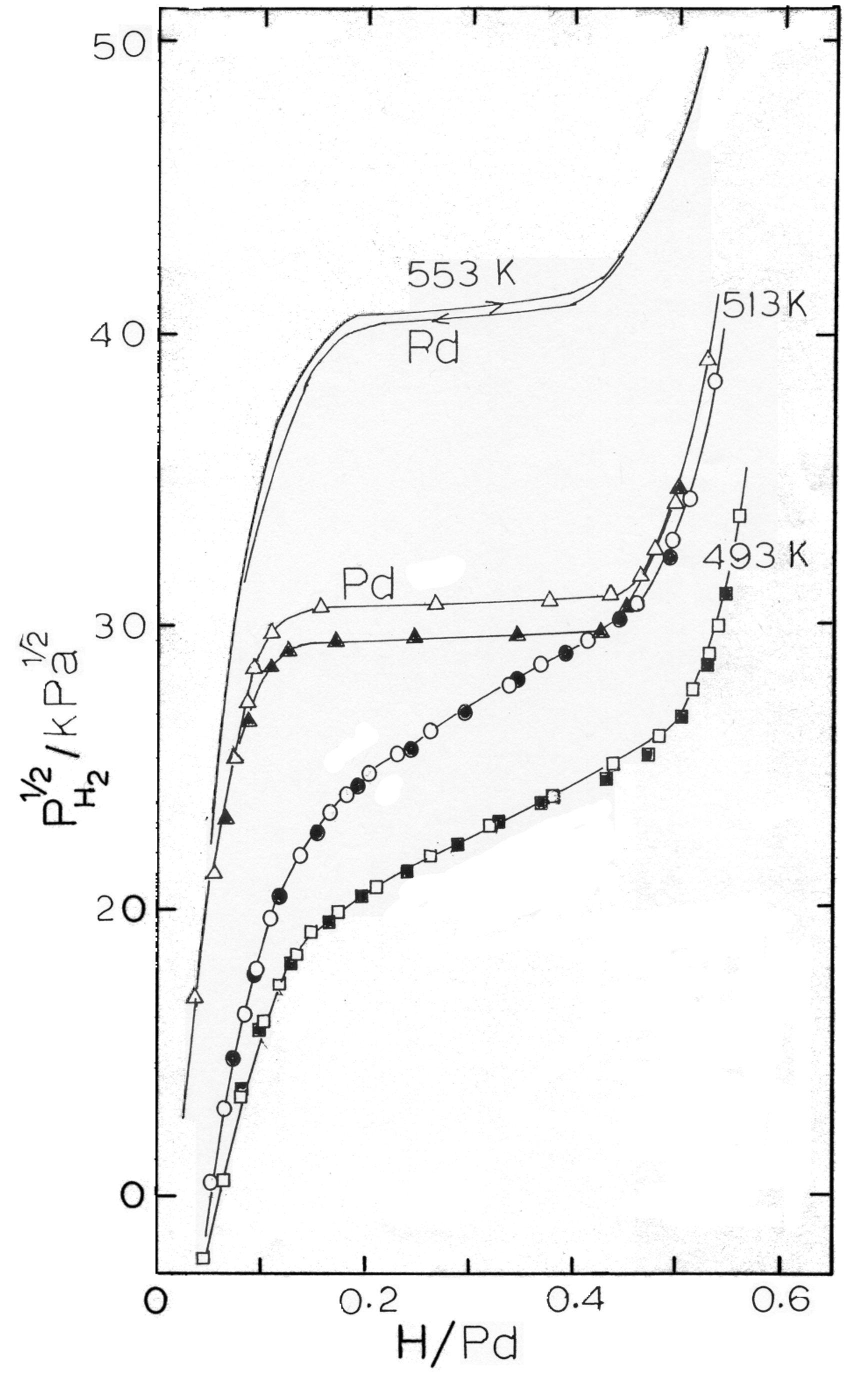

Figure 5.