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Hydrogen segregation to internal interfaces of Pd–yttria composite prepared by internal oxidation of Pd–Y alloys

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Abstract

Pd–Y alloys have been internally oxidized in the atmosphere at $T \geq 973$ K to form Pd–yttria composites. Dilute phase H_2 isotherms and reaction calorimetry have been used to characterize the trapping of dissolved H at the Pd–yttria interface. Although H_2 isotherm measurements have been used before for this purpose for other metal–oxide composites [1,2], this is the first report of reaction calorimetric measurements used to characterize H segregation to interfaces in Pd-based composites. The relative partial enthalpies for H_2 solution (303 K) in the internally oxidized $Pd_{0.98}Y_{0.02}$ alloy decrease in magnitude with $r = H/Pd$, i.e., $\Delta H_H = -85$ kJ/mol H, $r \rightarrow 0$, -60 kJ/mol H, $r = 0.004$, -40 kJ/mol H, $r = 0.0055$ and -20 kJ/mol H, $r = 0.0065$. After evacuation at 303 K, the enthalpies were found to be $\Delta H_H = -35$ kJ/mol H at $r \rightarrow 0$ and -15 kJ/mol H at $r = 0.0025$, i.e., some of the trapped H is not removed by evacuation (303 K). For H_2 solution in well-annealed Pd, $\Delta H_H = -10.3$ kJ/mol H at $r = 0$. The amounts of strongly and weakly trapped H at the interface are determined for *Pd*–Y alloys internally oxidized at different temperatures. Internal oxidation takes place by the inward movement of the internal oxidation front [3]. In contrast to other *Pd*–M alloys which have been partially internally oxidized such as *Pd*–Al [2], the inner, unoxidized *Pd*–Y region becomes hydrided before the outer oxidized zone because of its lower p_{H_2} for hydride formation; thus there is significant expansion on the inside of the sample before the outer zone becomes hydrided. The present results show that this does not affect the plateau pressure for hydride formation for the alloy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pd-yttria composites; Internal oxidation; Hydrogen solubility; Enthalpy; Hydrogen trapping; Metal-oxide interface

1. Introduction

Several *Pd*–M alloys, where M is a solute more readily oxidizable than Pd, have been internally oxidized to form Pd–oxide composites [1–3]. The total interfacial area produced in this way can be several m^2 per cm^3 of alloy [4]. A great advantage of this method of producing metal–oxide interfaces is that solute segregation to the interface can be studied with confidence because the interfaces are very clean. Dissolved H has been used as a probe for such metal–oxide interfaces [1] and in this investigation it will be extended to reaction calorimetric studies of the H segregation.

The probable internal oxidation product of *Pd*–Y alloys, yttria, is important in a variety of applications such as coating for refractors, as catalysts, laser crystals, phosphors, and as a stabilizer for zirconia in oxygen sensors and in solid state conductors. The investigation of Pd–yttria composites is therefore of interest.

Dilute phase H_2 solubility gives information about H trapping at the Pd–yttria interface; Huang et al. [1] suggested that, for internally oxidized *Pd*–Al and *Pd*–Mg alloys, H atoms become strongly trapped to oxygen atoms at the most densely packed oxygen planes at the interface, thereby forming O–H bonds [1]. The extent of the strong trapping was determined from the initial region of the isotherm where $p_{H_2} \approx 0$, i.e., there is a positive shift along the r (=H/M) axis such that the expected hydrogen solubility in the Pd matrix does not commence until the traps associated with the interface are filled.

Pd dissolves hydrogen to form two solid phases below the critical point of 564 K. The presence of two solid phases requires that the chemical potential of H be constant in this region. If H_2 is in equilibrium with the solid, p_{H_2} must also be constant across the two-phase, plateau region. *Pd*–M alloys also exhibit two phase regions. Pd alloy–H systems which have expanded unit cells with respect to Pd generally have lower plateau pressures than Pd–H while contracted alloys have higher plateau pressures [5]. *Pd*–Y alloys fall into the former category [6]. Before their internal oxidation, *Pd*–Y alloys have characteristic H_2 isotherms with plateau pressures

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lower than Pd–H and with markedly smaller H capacities. After complete internal oxidation, the plateau should change to one for Pd–H because the alloy will consist of yttria precipitates within a Pd matrix, i.e., a Pd–yttria composite. Partial internal oxidation should give an isotherm consisting of two plateaux, one for the unoxidized alloy–H and one for Pd–H.

This is the first investigation of the internal oxidation of *Pd*–Y alloys and their subsequent interaction with hydrogen.

2. Experimental

The alloys were prepared by arc melting under argon, annealing (1133 K, 72 h) and rolling into foil (110 μm); they were then re-annealed to remove stress. After re-annealing, the alloys were then oxidized in air at different temperatures for various lengths of time. The samples were quenched to room temperature after the oxidation experiments to prevent the surface oxidation of Pd. Pd forms a stable surface oxide when exposed to oxidizing atmospheres at temperatures below about 1100 K [7]. Samples for TEM were prepared by jet polishing. The reaction calorimeter suitable for metal–H systems has been described elsewhere [8].

3. Results and discussion

3.1. Internal oxidation

Several different *Pd*–Y alloys were internally oxidized at different temperatures. The internal oxidation was followed by weight changes. After times sufficient for complete internal oxidation, seven separate determinations gave an average stoichiometry of Y_2O_3. The principal error arises from the stoichiometries of the alloys before their internal oxidation, i.e., they will not be exact, e.g., $Pd_{0.98}Y_{0.02}$. With consideration of the experimental error in the weight changes, it is reasonable to conclude that yttria, Y_2O_3, is the internal oxidation product.

After internal oxidation at 1100 K, TEM photomicrographs showed oxide precipitates which were faceted small crystals of sizes from about 10 to 30 nm. The dislocation density in the vicinity of the precipitates or elsewhere in the internally oxidized alloy was low.

The rate of internal oxidation was faster for the *Pd*–Y than for *Pd*–Al alloys [2]. For example, for foils of comparable thickness, internal oxidation was complete for the $Pd_{0.98}Y_{0.02}$ alloy after 8 h at 1073 K, whereas after internal oxidation for 12 h at 1073 K, a $Pd_{0.97}Al_{0.03}$ alloy was only about 50% internally oxidized [2]. It is not known why the internal oxidation of the Pd–Y alloys is faster because the slow step for internal oxidation is believed to be diffusion of oxygen through the lattice [3].

3.2. Dilute phase hydrogen solubilities

The amount of trapped H was determined from the intercept along the *r*-axis to the point where the dilute phase solubility starts; in the absence of traps the solubility intercepts the origin. The amounts of trapped H were determined from the intercepts after internal oxidation and then redetermined after evacuation (323 K). After the latter, the hydride phase was formed completely and decomposed (cycled) (323 K). The presence of small, closely spaced yttria precipitates is expected to increase the dislocation density produced from the cycling. This can be assessed from the enhancement of the dilute phase solubility due to segregation of dissolved H to the dislocation stress fields [9,10].

Fig. 1 shows results for the $Pd_{0.98}Y_{0.02}$ alloy after complete internal oxidation at 1273 K. The intercept and therefore the corresponding strongly trapped H is $r=0.003$, for the repeat solubility measurement it is 0.0007 and after cycling, the intercept is about 0.002. These measurements were repeated with another sample internally oxidized at 1273 K with slightly different results, i.e., the strongly trapped H was $r=0.002$, the repeat intercept $r=0$ and, after cycling, $r=0.001$. The same sequence of measurements was carried out for a $Pd_{0.98}Y_{0.02}$ alloy internally oxidized at 1073 K (72 h) (Fig. 1). The initial intercept corresponding to the strongly trapped H was $r=0.0035$, the repeat was 0.0005 and, after cycling, $r=0.002$.

The presence of the small yttria precipitates after internal oxidation can cause an enhanced solubility in the dilute phase due to thermal residual stress resulting from cooling the Pd–oxide composite from the internal oxida-

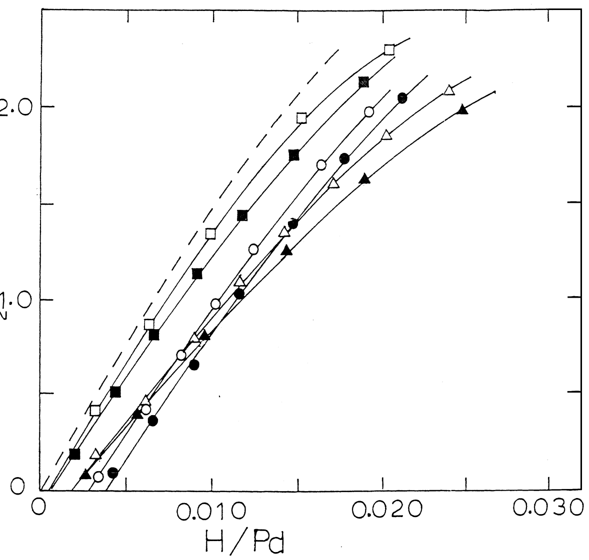

Fig. 1. Dilute phase H_2 solubility (323 K) for $Pd_{0.98}Y_{0.02}$. Dashed line, Pd; (○) initial solubility; (□) repeat solubility; (Σ) solubility after cycling. The open symbols are for the $Pd_{0.98}Y_{0.02}$ alloy after internal oxidation at 1273 K, 12 h and the filled symbols are for after internal oxidation at 1073 K for 72 h.

tion temperature [11]. These stresses result due to different thermal expansion coefficients for Pd and yttria. The solubility enhancement (r'/r), was 1.22 (at 1.2 kPa) which is larger than the value of 1.12 found for the alloy internally oxidized at 1273 K, where r' is the H–Pd atom ratio for the internally oxidized alloy after subtraction of the contribution of the strongly trapped H and r is the solubility in Pd at the same p_{H_2}. This solubility enhancement is somewhat smaller than found for internally oxidized *Pd*–Al alloys [11].

Solubility enhancements (323 K) caused by segregation to dislocations, produced by cycling, can also be evaluated. For the $Pd_{0.98}Y_{0.02}$ alloy internally oxidized at 1073 K and then cycled (323 K), $(r'/r)=1.51$ (323 K) where r' is after cycling and r is for annealed Pd–H at $p_{H_2}=1.2$ kPa. The corresponding value for cycled Pd is 1.35. The solubility enhancement for a cycled alloy which was internally oxidized at 1273 K is 1.40. Because the precipitate size decreases with decrease of temperature [3] and because dislocation movement is more effectively blocked by the smaller, closely spaced precipitates which are formed by internal oxidation at low temperatures, e.g., 1073 K, the dislocation densities and resultant solubility enhancements are larger after internal oxidation at lower temperatures (Fig. 1). This was shown to be the case for Pd–alumina composites prepared by internal oxidation and, in addition, it was shown that the dislocations formed by cycling after internal oxidation at 1073 K are very much more stable towards annealing than those from cycling an alloy internally oxidized at 1273 K [12].

The intercept, i.e., the trapping, for the internally oxidized $Pd_{0.98}Y_{0.02}$ alloy after cycling is about 50% of its initial value after internal oxidation, which is greater than the repeat value even though it was not heated during cycling above 323 K, the temperature employed for evacuation prior to the repeat solubility measurements (Fig. 1). For the internally oxidized *Pd*–Al alloys, the intercept for the cycled alloys is the same or greater than the initial intercept [13]. Cycling produces profound changes because dislocation formation and movement are needed to accommodate the volume changes on hydriding (and dehydriding) in Pd. The precipitates, which are barriers for dislocation movement, pin the dislocations, where they must affect the binding of the trapped H.

3.3. Isotherms for the plateau, two-phase region

Fig. 2 shows the dramatic changes in the p_{H_2} isotherms (323 K) of the $Pd_{0.98}Y_{0.02}$ alloy as a result of internal oxidation. It can be seen that after complete internal oxidation at either 1073 or 1273 K, the isotherms, except for the very dilute trapping region, are very similar to Pd–H in both H capacity and plateau pressures. This is important because it proves that most of the characteristic features of p_{H_2} absorption are independent of whether Pd is in its pure form or is a matrix of a metal–oxide composite.

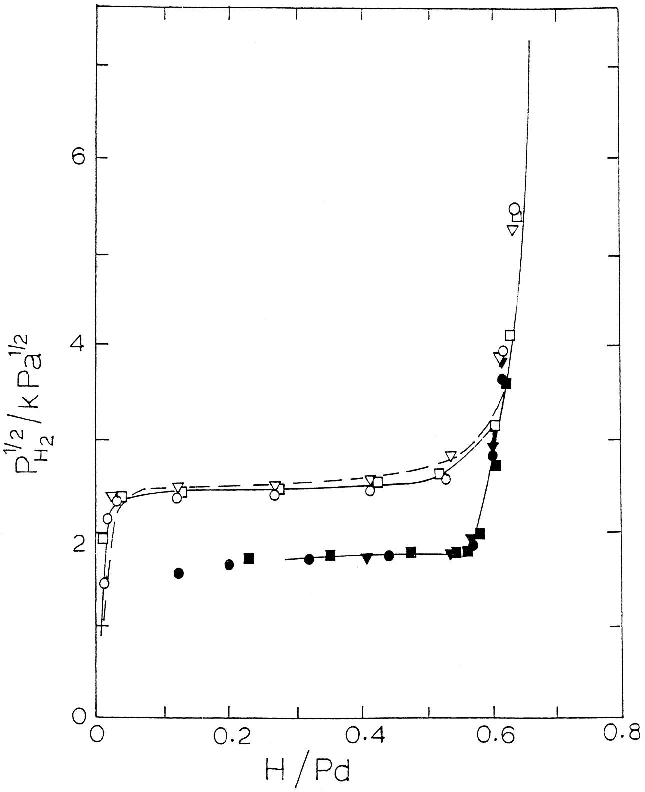

Fig. 2. Isotherms (323 K) after complete internal oxidation. Continuous line, annealed Pd initial cycle; dashed line, Pd second cycle; (○) initial isotherm after internal oxidation at 1073 K (72 h); (▽) second cycle after internal oxidation at 1073 K; (□) initial cycle after internal oxidation at 1273 K. The open symbols are for absorption and the closed symbols for desorption.

Partial internal oxidation of a $Pd_{0.97}Al_{0.03}$ alloy results in an isotherm with two plateaux: one corresponding to Pd–H, the internally oxidized portion, and the other corresponding to the $Pd_{0.97}Al_{0.03}$ alloy, the unoxidized portion [2]. The presence of the two plateaux attests to the interfacial nature of internal oxidation. The % of material internally oxidized can be conveniently calculated from the relative lengths of the two plateaux. When a partially internally oxidized $Pd_{0.97}Al_{0.03}$ alloy is hydrided, the outer internally oxidized fraction of the partially internally oxidized alloy is hydrided first and then the inner part, i.e., the hydride–dilute phase interface proceeds inwards from the surface in the usual way. For partially internally oxidized *Pd*–Y alloys, however, the situation is reversed because the Pd in the internally oxidized zone has a higher plateau p_{H_2} than the inner, unoxidized $Pd_{0.98}Y_{0.02}$ alloy and the latter will therefore be hydrided first. It is of interest to learn if hydriding the inner part of the alloy first causes any changes in its plateau pressure because of stresses generated due to its expansion against the outer unhydrided fraction.

A $Pd_{0.98}Y_{0.02}$ alloy was partially internally oxidized (1073 K, 2.5 h) where, as expected, there are two plateaux in the isotherm (Fig. 3). The lower plateau one is for the

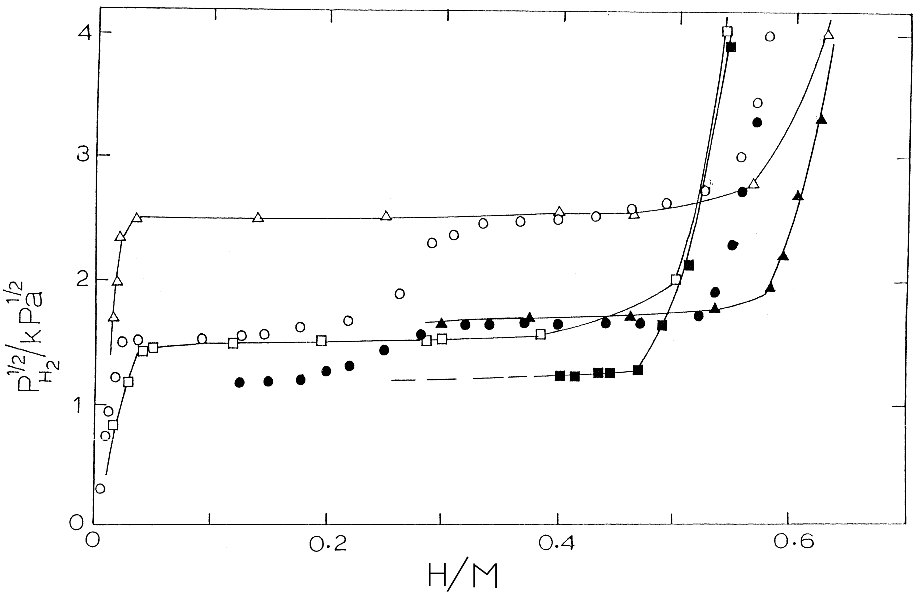

Fig. 3. Isotherm (323 K) for: (○) partially internally oxidized $Pd_{0.98}Y_{0.02}$ alloy (1073 K, 2.5 h); (△) annealed Pd; (□) annealed $Pd_{0.98}Y_{0.02}$ alloy. The open symbols are for absorption and the closed symbols for desorption.

inner, unoxidized alloy and the higher one for pure Pd in the internally oxidized outer fraction. The hydride formation plateau pressure of the inner unoxidized $Pd_{0.98}Y_{0.02}$ alloy is not affected significantly by stresses which may arise from its expanding against the outer internally oxidized fraction. Such an effect would perhaps be observed for a different geometry, e.g., cylindrical.

Recently, Poyser et al. measured a D_2 isotherm for a $Pd_{0.90}Y_{0.10}$ alloy where they found a small plateau-like region centered around 0.3 bar (333 K) which exhibited hysteresis (Fig. 3 in Ref. [14]). They suggested that the plateau was caused by an H-driven order–disorder transition involving the Y atoms. In earlier research, a $Pd_{0.90}Y_{0.10}$ alloy was cooled in H_2 from above the known ordering temperature [15,16] and there was no indication of a small plateau region introduced by dissolved H and no hysteresis. There is a known ordered Pd_7Y phase but dissolved H *suppresses* its formation in *Pd*–Y alloys [16] and also in other Pd–RE alloys [17].

The plateau pressures and hysteresis observed by Poyser et al. [14] correspond quite closely to Pd–D_2 [18] which could have resulted from a small amount of internal oxidation of the $Pd_{0.90}Y_{0.10}$ alloy during alloy preparation. They argued [14] that the observed plateaux, which have a continuous change of lattice parameter with D/M, differ from the usual metal–H_2 systems which have two distinct lattice constants in the plateau region. However according to the length of the observed plateaux, only a very small fraction of their alloy would have been internally oxidized, and therefore the lattice constants would reflect the majority phase of the unoxidized alloy, whose parameters *would* change continuously with D/M. They also note that their plateaux slope, in contrast to Pd–D(H), but often plateaux for Pd slope depending upon the sample geometry. We suggest that their evoking of an order–disorder process involving the Y atoms is open to question unless internal oxidation in their samples can be definitely ruled out.

3.4. Reaction calorimetric measurements of H trapping

Reaction calorimetric measurements (303 K) were carried out with an internally oxidized (1023 K, 144 h) $Pd_{0.98}Y_{0.02}$ alloy. The ΔH_H values shown in Fig. 4 are all for absorption and are therefore exothermic. The initial H trapping has a very exothermic $\Delta H_H \approx -85$ kJ/mol H as $r \to 0$ (Fig. 4) and the ΔH_H values fall in magnitude with r to reach about -20 kJ/mol H at $r=0.0065$. The strongly trapped H corresponds to about 0.0055 which is somewhat greater than for the isotherm data reported above; the differences are likely to be due to the lower internal oxidation temperature employed for the sample used for calorimetry. After evacuation at 303 K for 12 h, ΔH_H values were re-measured and are less exothermic than for the initial H trapping, i.e., ≈ -35 kJ/mol H at $r \to 0$ and ΔH_H falls to -20 kJ/mol H at $r=0.002$. If the $\Delta H_H - r$ relation for these re-measured values is shifted along the r axis by $\Delta r=0.005$, they can be superimposed on the initial $\Delta H_H - r$ relationship (Fig. 4). This shows that the strongly trapped H is not removed by evacuation at 303 K because only a much smaller amount of H can be re-trapped.

The sharp fall-off in the $|\Delta H_H|$ values with r for the initial H trapping by the internally oxidized $Pd_{0.98}Y_{0.02}$ alloy (Fig. 4) indicates that there is not just one type of trap with a constant energy of interaction but a spectrum of trap energies. Thus it seems unlikely that the trapping is due to dissolved H reacting with O atoms at the interface,

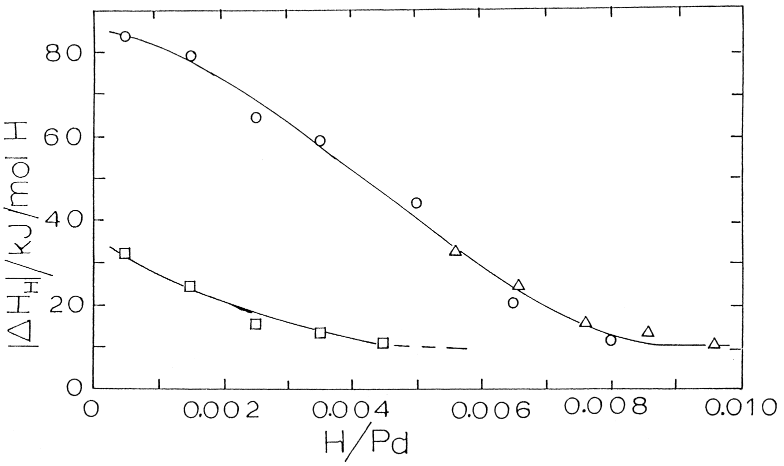

Fig. 4. ΔH_H values for an internally oxidized $Pd_{0.98}Y_{0.02}$ alloy determined at 303 K. (○,△) Initial determinations for two different samples; (□) repeat determination after evacuation at 298 K for 12 h.

as suggested by Huang et al. [1] for internally oxidized *Pd*–Al and *Pd*–Mg alloys, because it would then be expected that the enthalpies would be nearly constant until the O atoms have all reacted with H. There is no doubt, however, that the irreversible hydrogen trapping takes place at or near the interface since this is the major perturbation of the Pd lattice.

4. Conclusions

FCC *Pd*–Y solid solution alloys can be internally oxidized to form Pd–yttria composites. H is trapped at the internal Pd–yttria interfaces with a spectrum of energies. Aside from the very small amount of H trapped at the interface, the H_2 absorption–desorption isotherms of the composite are very much like those of pure Pd–H. For partially internally oxidized alloys, the unoxidized *Pd*–Y alloy core is hydrided first before the outer Pd–yttria composite, whereas for partially internally oxidized *Pd*–Al alloys, the core is hydrided last. The plateau pressure for the inner, unoxidized $Pd_{0.98}Y_{0.02}$ alloy is, however, unchanged from that of a homogeneous $Pd_{0.98}Y_{0.02}$ alloy.

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