Journal of Alloys and Compounds 404–406 (2005) 38–42

Journal of ALLOYS AND COMPOUNDS

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The near elimination of hysteresis in Pd/Cr_2O_3 composites

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Received 6 September 2004; received in revised form 22 October 2004; accepted 28 October 2004

Abstract

Although its value varies with microstructure, hysteresis always accompanies hydride formation and decomposition in Pd, 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. It is found that the characteristic hysteresis disappears in this composite of Pd at elevated temperatures and is quite small at moderate temperatures compared to pure Pd. Some possible reasons for this are discussed.

Keywords: Hysteresis; Metal/oxide composite; Hydrogen absorption

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1. 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.

1.1. Hysteresis

For metal-hydrogen systems which form hydride phases the phase rule predicts an invariant p_{H_2}, the plateau pressure, in the region of co-existence of the dilute and hydride phases. The formation of the hydride phase can be written as

$$\tfrac{1}{2}H_2(g) + (b-a)^{-1}MH_a = (b-a)^{-1}MH_b \qquad (1)$$

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_{H_2} needed for hydride formation, p_f, is greater than that for hydride decomposition. Hysteresis is best evaluated quantitatively as either $RT\ln(p_f/p_d)^{1/2}$/energy/mol $\frac{1}{2}H_2$ or, more accurately, as $RT\int \ln p^{1/2}\,dr$/energy/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.

Although there have been reports of the absence of hysteresis in Pd, 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 nano-clusters of Pd 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 change profoundly resulting in a decreased plateau p_{H_2} and hysteresis together with sloping plateaux with a region of initial trapping [6]. Tritium

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0925-8388/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2004.10.082

aging in 50 wt.% Pd on kieselguhr (silica) depresses both p_f and p_d [7]. As well, a Pd–Rh–Co alloy has shown loss of hysteresis upon tritium aging [8]. The present paper is, however, concerned with hysteresis in Pd and not in its alloys.

1.2. IO of Pd alloys

Binary Pd alloys containing small amounts of readily oxidizable solute metals such as Al, Mg, Zr, can be internally oxidized (IOed) to form essentially pure Pd matrix phases with second phases of nano-sized oxide precipitates [9,10]. After internal oxidation (IO) 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 IO 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 nano-powders.

Because alumina, which forms from IO of Pd–Al alloys is very stable, the Pd *matrix* is essentially pure and its H_2 isotherms would be anticipated to be similar to those of *annealed* Pd except in the very dilute phase where some H is trapped at or near the Pd/oxide interface [9–11]. Although the initial isotherms at moderate temperatures are similar to those of *annealed* Pd, after hydriding and dehydriding, cycling, IOed Pd–Al alloys, behave, especially at high temperatures, analogously [12] to the results to be reported here, but the trends are much more pronounced for the IOed Pd–Cr alloys. Any differences between the 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 the fact that small amounts of solute atoms ($\leq$0.5%) have negligible effect on the 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 IOed at the relatively low temperature of 998 K. The lower the temperature of IO, the smaller are the precipitates which form [13] and it will be shown that the smaller the precipitates, the greater the decrease of hysteresis. Small precipitates are also more effective in causing dispersion hardening of IOed alloys [13].

2. 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 × 0.3 cm × 110 μm. Pd–Cr alloys were IOed in the laboratory atmosphere in a tube furnace. Mainly results for the $Pd_{0.93}Cr_{0.07}$ alloy IOed at 998 K will be presented. The oxidation product of a number of Pd–Cr alloys were determined from their weight gains and these 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 IOed $Pd_{0.93}Cr_{0.07}$ alloy is brittle whereas a $Pd_{0.97}Cr_{0.03}$ alloy is not and, after repeated cycling of the IOed $Pd_{0.93}Cr_{0.07}$ alloy, it undergoes brittle fracture into small particles. Without any crushing these particles ranged from about 10 to 150 μm with the average size of about 30 μm.

An X-ray diffraction pattern of the finely divided IOed (998 K) $Pd_{0.93}Cr_{0.07}$ alloy showed that the alloy has been completely IOed because there is no evidence for any unoxidized alloy and the reflections correspond almost exactly with finely divided Pd, however, they are broader indicating lattice strain.

3. Results and discussion

3.1. Dilute phase

The dilute phase solubilities of the Pd/chromia composites for the initial absorption consist of a trapping region where $p_{H_2} \approx 0$ 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. The dilute phase solubilities of each are large, greatly exceeding that of annealed or cycled Pd and larger than any other IOed Pd–M alloy which we have examined. The positive intercept is caused by strong trapping at or near the interface [9,11]. 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 still not much greater than that for the initial cycle. The dilute phase behavior will, however, not be discussed in detail because it does not exhibit hysteresis.

3.2. Two phase region

Before the initial cycle of hydriding/dehydriding at, e.g., 323 K, both p_f and p_d are lower for the IOed ($\leq$1100 K) Pd–Cr alloys, i.e., the Pd *matrix*, than for *annealed* Pd. After cycling, the formation plateau p_{H_2} decreases further while the decomposition p_{H_2} increases, to decrease hysteresis. The extent of these changes depends upon X_{Cr} and the IO temperature. These results differ from the differences between the plateaux of different forms of Pd, e.g., Pd black or thin film, where the average plateau pressures do not differ much from that of annealed Pd. In contrast to the Pd/chromia composites, some of the H capacities of these other forms are reduced compared to annealed Pd. The behavior of the IOed $Pd_{0.93}Cr_{0.07}$ alloy is closer to that of T-aged Pd [6] than to the forms of Pd mentioned above suggesting that the oxide precipitates play a similar role as the He bubbles in T-aged Pd.

Isotherms were measured at temperatures from 323 to 513 K for the 20× cycled, IOed (998 K) $Pd_{0.93}Cr_{0.07}$ alloy

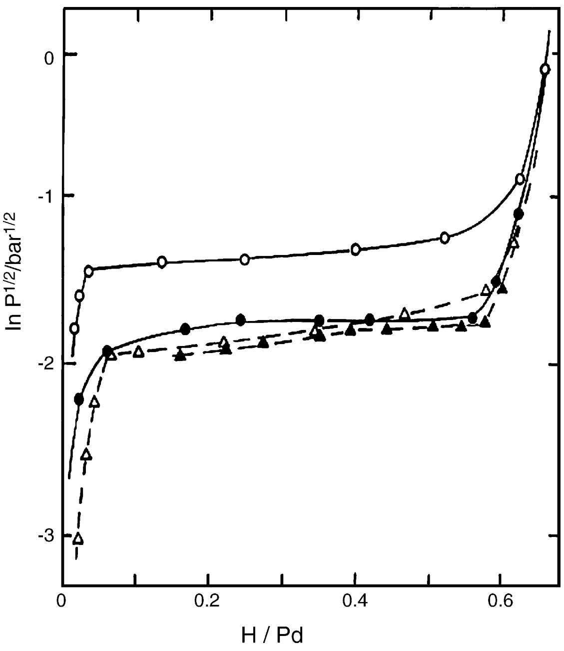

Fig. 1. Hydrogen isotherms at 323K. ○, *annealed* Pd, △, Pd *matrix* from IO of the $Pd_{0.93}Cr_{0.07}$ alloy. The filled and open symbols are for absorption and desorption, respectively.

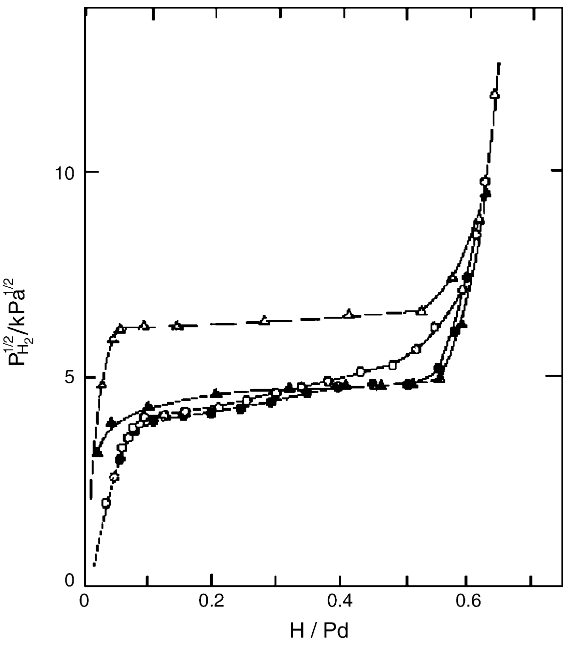

Fig. 2. Hydrogen isotherms at 373 K. △, *annealed* Pd; ○, Pd *matrix* from IO of the $Pd_{0.93}Cr_{0.07}$ alloy. The filled and open symbols are for absorption and desorption, respectively.

(Figs. 1–4) where it can be seen that there is an almost complete elimination of hysteresis at ≥493 K. Similar behavior is found for a $Pd_{0.95}Cr_{0.05}$ alloy IOed 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* and the *Pd matrix* from IO of the $Pd_{0.93}Cr_{0.07}$ alloy as evaluated at $r = 0.3$.

In Fig. 1 ln $p^{1/2}_{H_2}$ has been plotted K for the 20× cycled, IOed (998 K) $Pd_{0.93}Cr_{0.07}$ alloy rather than $p^{1/2}_{H_2}$ because ln $p^{1/2}_{H_2}$ represents hysteresis more directly and it is much smaller for the IOed $Pd_{0.93}Cr_{0.07}$ 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 phase boundaries especially the upper one (Fig. 3). This may indicate that there is a greater difficulty in the growth of either phase in their early stages than when about equal amounts are present. Nucleation will not be a problem, however, due to the large defect concentration in the cycled IOed alloy, e.g., there is no supersaturation of the dilute phase in Pd after it has been cycled whereas there is for uncycled *annealed* Pd.

Table 1
Hysteresis in units of J/$\frac{1}{2}$mol H_2 for the Pd matrix in IOed (998 K) $Pd_{0.93}Cr_{0.07}$ alloy and annealed Pd both evaluated at $r = 0.30$

T (K)	$\frac{1}{2}RT\ln(p_f/p_d)$ (*cycled*, Pd *matrix*)	$\frac{1}{2}RT\ln(p_f/p_d)$ (cycled, annealed Pd)
273	240	1030
323	122	935
343	97	900
373	68	940
493	~0	550

At all temperatures *both* the hydride formation and decomposition plateaux are lower near their midpoints, e.g., $r = 0.3$, for the Pd *matrix* than for *annealed* Pd, i.e., the equilibrium has been shifted and not just the degree of hysteresis. Although it appears as if the decreases of the plateau

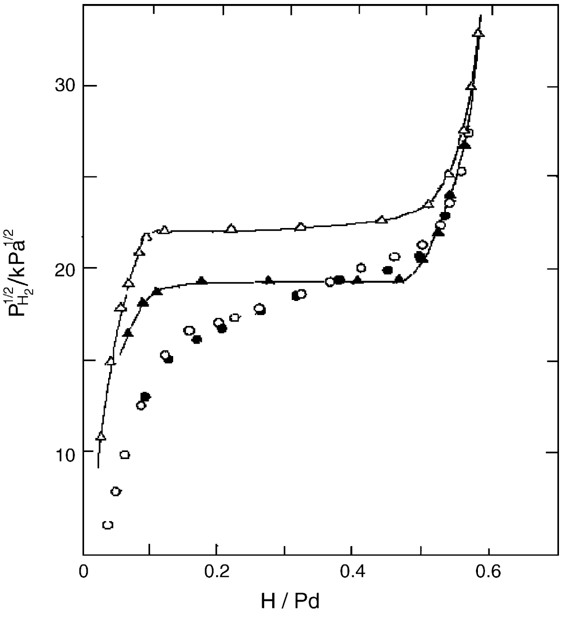

Fig. 3. Hydrogen isotherms at 473 K. △, *annealed* Pd; ○, Pd *matrix* from IO of the $Pd_{0.93}Cr_{0.07}$ alloy. The filled and open symbols are for absorption and desorption, respectively.

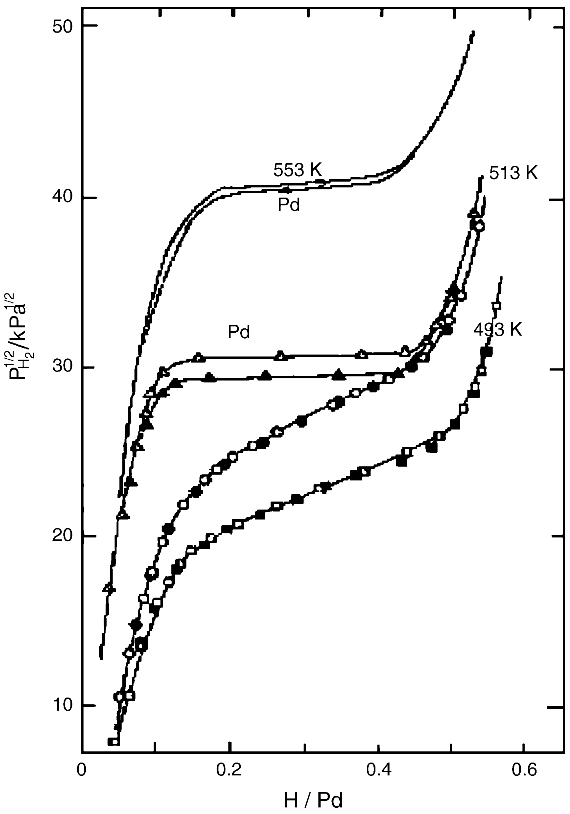

Fig. 4. Hydrogen isotherms at 493 K, 513 K and 553 K. Solid curves without symbols at 553 K, *annealed* Pd; △, *annealed* Pd at 513 K; ○, Pd *matrix* 513 K from IO of the $Pd_{0.93}Cr_{0.07}$ alloy; ⊡ , Pd *matrix* at 493 K from IO of the alloy. The filled and open symbols are for absorption and desorption, respectively.

pressures are greater as the temperature increases, the decrease of $\Delta\mu_H = RT\ln(p_f/p_d)^{1/2}$ is greater (Figs. 2–4) at the low temperatures. From the data shown in Fig. 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 IOed alloy, respectively, and $RT\ln(p_f/p_d)^{1/2} = 1010$ and 95 J/$\frac{1}{2}$mol H_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 for the Pd/chromia composite, the isotherms are very sloping while the H capacities remain unchanged. The sloping increases with increase of temperature (Figs. 2–4) for the alloy IOed at 998 K. Since there is no hysteresis and the “plateau” region is very sloping at ≥493 K, it can be asked if there are still two phases 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 indicating the phase boundaries closely match those for *annealed* Pd at each temperature. In addition, the van’t Hoff plots evaluated at $r = 0.2$, 0.30 and 0.45 at $T = 400$ K, 493 K and 513 K all have similar slopes for the Pd *matrix* as in the lower temperature range where there are obviously two phases and hysteresis for the composite. If the Pd *matrix* were single phase, i.e., above its critical temperature, it would be expected that its thermodynamic parameters would differ at $r = 0.45$ and 0.20. Two phase regions do not exist for H in amorphous materials due to the spectrum of interstitial site energies [14,15], however, the Pd/chromia composite is not amorphous because its X-ray diffraction pattern proves its crystallinity and, furthermore, the lattice parameter of the matrix is identical to pure Pd.

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 that horizontal plateaux have large hysteresis whereas sloping plateaux exhibit smaller hysteresis in this system, however, this is not true generally and large hysteresis plus sloping has been found for some inhomogeneous Pd alloys. 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.

3.3. Thermodynamics

The thermodynamic parameters for the composite were determined from plateau pressures from 273 K to 373 K at $r = 0.30$. The van’t Hoff plots (Fig. 5) give ΔH of hydride formation and decomposition for the Pd/chromia composite of −20.9 and 21.5 kJ/mol$\frac{1}{2}H_2$, respectively, as compared to −18.6 and 20.3 kJ/mol$\frac{1}{2}H_2$ for *annealed* Pd. The sum of the magnitudes of the two plateau enthalpies for *annealed* Pd is 19.4 kJ/mol$\frac{1}{2}H_2$ and for the Pd matrix of the composite it is 21.2 kJ/mol$\frac{1}{2}H_2$. The former is close to the calorimetric value of 19.2 kJ/mol$\frac{1}{2}H_2$ [16]. 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 [17]. $|\Delta H_{av,plat}|$ is 1.8 kJ/$\frac{1}{2}$mol$\frac{1}{2}H_2$ greater for the Pd matrix than for *annealed* Pd. The larger enthalpy magnitude 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.

3.4. Possible origin of hysteresis reduction

Hysteresis is nearly eliminated at 323 K after cycling the IOed (998 K) $Pd_{0.93}Cr_{0.07}$ alloy (Fig. 1), i.e., it falls to about one sixth of the value for *annealed* Pd evaluated as the area of the loop, i.e., per mol Pd. Although it contains a second phase of nanocrystalline oxide precipitates, this can still be considered to be a marked reduction of hysteresis for Pd because the *matrix* is a pure phase. *Both* plateaux pressures decrease after IO but before any cycling. It should be kept in mind that large dislocation densities are formed from cycling

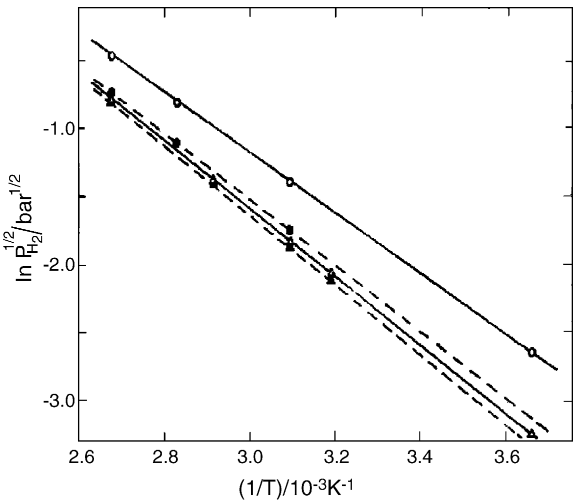

Fig. 5. Van't Hoff plots for plateau pressures; ○, hydride formation and △, decomposition for *annealed* Pd and the corresponding filled symbols are hydride formation and decomposition for the Pd *matrix* from IO of the $Pd_{0.93}Cr_{0.07}$ alloy. The plateau pressures have been evaluated at $r = 0.30$ for both. The solid lines are for annealed Pd and the dashed lines for the Pd matrix from IO.

Pd through its hydride phase change because of the large lattice expansion/contraction, 11%, in the ductile Pd [18]. It is known that small, coherent precipitates interact strongly with dislocations; this is the basis of dispersion hardening [13]. These phenomena are analogous to the changes observed after cycling some Pd-rich alloys [19,20]. In both cases the disturbances in the lattice 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. A MgH_2–Cr_2O_3 composite prepared by ball-milling has been shown to increase the rates of absorption/desorption [21] compared to MgH_2. It seems that chromia composites may prove to be useful for hydrogen storage systems.

The initial hydride formation plateau after IO of the $Pd_{0.93}Cr_{0.07}$ alloy is reasonably horizontal (323 K) but after cycling, it becomes increasingly sloping especially in the region where hydride conversion is >50%. The pronounced sloping is not due 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 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 precipitate-containing IOed alloys.

4. Conclusions

The most important results of this research with the composites resulting from the IO of a $Pd_{0.93}Cr_{0.07}$ alloy are that both plateau pressures decrease below those for annealed Pd and that hysteresis is significantly smaller than for annealed Pd. Other metal/chromia composites may prove to have reduced hysteresis which would be useful for hydrogen storage purposes.

Acknowledgements

The authors acknowledge Westinghouse Savannah River Corporation for partial financial support of this research.

References

[1] T.B. Flanagan, W. Oates, C.-N. Park, Prog. Solid State Chem. 23 (1995) 291–363.
[2] F. Lewis, The Palladium–Hydrogen System, Academic Press, N.Y., 1967.
[3] H. Frieske, E. Wicke, Ber Bunsen. Phys. Chem. 77 (1973) 50.
[4] E. Salomons, R. Feenstra, D. DeGroot, J. Rector, R. Griessen, J. Less-Common Met. 130 (1987) 415.
[5] A. Pundt, C. Sachs, M. Winter, M. Reetz, D. Fritsch, R. Kirchheim, J. Alloys Compd. 293–295 (1999) 480.
[6] S. Guthrie, W. Wulfer, J. Alloys Compd. 172–174 (1991) A35.
[7] K.L. Shanahan, J.S. Holder, J.R. Wermer, J. Alloys Compd. 293–295 (1999) 62–66.
[8] K.L. Shanahan, J.S. Holder, J. Alloys Compd. 348 (2003) 72–75.
[9] X. Huang, W. Mader, R. Kirchheim, Acta Metall. Mater. 39 (1991) 893.
[10] H. Noh, T.B. Flanagan, R. Balasubramaniam, J. Eastman, Scripta Met. Mater. 34 (1996) 863.
[11] D. Wang, H. Noh, S. Luo, T.B. Flanagan, J. Clewley, R. Balasubramaniam, J. Less-Common Met. 339 (2002) 76.
[12] D. Wang, H. Noh, T.B. Flanagan, R. Balasubramaniam, J. Alloys Compd. 348 (2002) 119.
[13] J. Meijering, in: H. Herman (Ed.), Advances in Materials Research, vol. 5, Wiley, New York, 1971, p. 1.
[14] R. Griessen, Phys. Rev. B 27 (1983) 7575.
[15] P.M. Richards, Phys. Rev. B 220 (1984) 5183.
[16] T.B. Flanagan, W. Luo, J. Clewley, J. Less-Common Met. 172–174 (1991) 42.
[17] T.B. Flanagan, J. Clewley, T. Kuji, C. Park, D. Everett, J. Chem. Soc. Faraday Trans. I 82 (1986) 2589.
[18] F.A. Lewis, The Palladium–Hydrogen System, Academic Press, London, 1967.
[19] H. Noh, T.B. Flanagan, Z. Gavra, J. Johnson, J. Reilly, Scripta Met. Mater. 25 (1991) 2177.
[20] T.B. Flanagan, D. Wang, H. Noh, J. Alloys Compd. 253–254 (1997) 216.
[21] Z. Dehouche, T. Klassen, W. Oelerich, J. Goyette, T. Bose, R. Schulz, J. Alloys Compd. 347 (2002) 319.