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The effect of cycling through the hydride phase on isotherms for fcc Pd-rich alloys

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Abstract

The Pd–Ni, Pd–Co, Pd–Cr, Pd–Au, Pd–Rh, Pd–Mo and Pd–Pt fcc Pd-rich alloys have been found to exhibit large effects of cycling through the hydride phase. The effect of cycling Pd–Mo alloys is noticeable even at a composition of $X_{Mo}=0.02$ whereas for Pd–Rh alloys it is not significant until $X_{Rh}>0.10$. The dependence of the effect of the cycling on alloy composition will be reported here for the alloy systems Pd–Cr and Pd–Mo. The effect of cycling for a Pd–Ag alloy has also been determined. The temperature dependencies of the plateaux pressures of the cycled and the annealed alloy forms are reported for the $Pd_{0.95}Cr_{0.05}$ alloy.

Keywords: Isotherms; Pd-rich alloys; Hydride phase change

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1. Introduction

The plateau for hydride formation for the initial isotherm of the intermetallic compound $LaNi_5$ has a greater pressure than for the subsequent isotherms [1,2]. These AB_5 intermetallics undergo brittle fracture during the hydride phase change. Hydride formation and its accompanying abrupt volume change in Pd-rich alloys, which are ductile, does not lead to fracture. Isotherms for Pd-rich alloys, nonetheless, evolve with cycling [3,4]. In this research cycling refers to repetitions of hydride formation and decomposition at relatively moderate temperatures without intermediate annealing. Although both plateau pressures change as a result of cycling, the increase of the decomposition plateau pressure, p_d, generally is not as great as the decrease of the formation plateau pressure, p_f. Although there have been many studies of hydrogen absorption/desorption by substitutional fcc Pd-rich alloys [5–7], especially in the two phase plateau region where the cycling effects originate, cycling itself has not received much attention. One reason for this is that the decomposition plateau pressure is believed by some workers to represent the equilibrium state [8,9] and it does not change as much with cycling as the formation plateau pressure. In some cases, however, the decomposition plateau pressure also changes significantly. A factor in the apparent invariance of p_d is that the decomposition plateau is always measured after the hydride phase has been formed and therefore changes in p_d may have already occurred.

If isotherms are determined at different temperatures, changes of the plateau pressures due to cycling may accompany the inherent temperature variation of the plateau pressures and therefore erroneous thermodynamic parameters would be obtained from the van't Hoff plots. It should also be noted that the plateau pressures of pure Pd do not undergo significant changes with cycling [10]. Its plateau pressure for hydride formation increases slightly while that for decomposition does not change.

Fig. 1 is a schematic representation of the isotherms for a prototype Pd-rich alloy during cycling at ambient temperature where it can be seen that for the initial isotherm the plateaux slope markedly especially for hydride formation. Even Pd alloys which are known to be quite homogeneous often exhibit sloping plateaux; sloping is usually not as significant for the decomposition plateau (Fig. 1). For the second cycle, p_f decreases and p_d increases slightly, and the plateaux become more nearly horizontal. The third cycle continues this trend and then after 5 or 6 cycles, the cycling behaviour appears to level off, however, many more cycles could result in further changes such as the elimination of hysteresis; to our knowledge such exhaustive cycling of Pd-rich alloys has not been reported. (In this work we report cycling a $Pd_{0.90}Ag_{0.10}$ alloy 49 times). According to the phase rule, plateaux should be horizontal when the metal alloy behaves as single component, as expected at moderate

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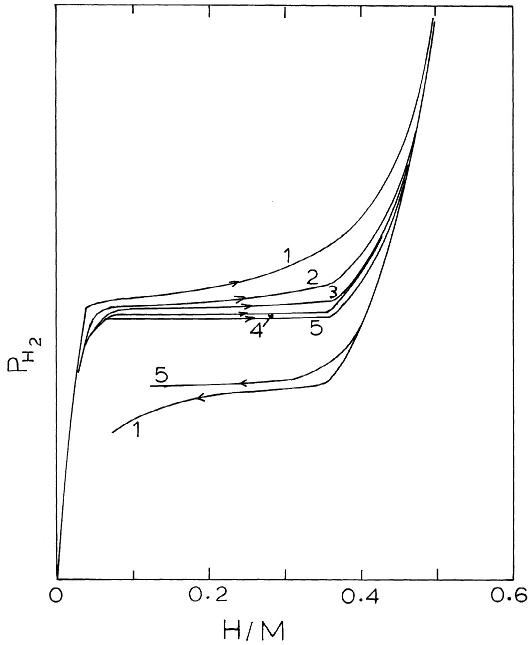

Fig. 1. Schematic cycling behaviour for a prototype Pd-rich alloy which shows the effect of cycling at near ambient temperature. The numbers on the isotherms indicates the cycle number.

temperatures where the metal atoms are immobile. Cycling decreases the extent of hysteresis and hysteresis has been found to disappear completely for a $Pd_{0.85}Ni_{0.15}$ alloy after cycling ≤10 times [4]. Therefore after cycling, an isotherm for the alloy more closely follows a reversible, equilibrium pathway. It should also be noted from Fig. 1 that cycling does not influence the hydrogen capacity of the alloy, i.e. the limiting H content corresponding to the steep rise in p_{H_2}.

Fcc Pd-rich alloys have either expanded or contracted unit cells as compared to Pd. Generally for the former the enthalpies of hydrogen solution and hydride formation are more exothermic than for Pd and, for the latter, they are more endothermic. In this research both expanded, e.g. Pd–Ag, and contracted, e.g. Pd–Mo, Pd–rich fcc alloys will be examined in order to learn whether cycling affects both types of alloy similarly.

An attempt will be made to establish the generality of the effect of cycling for Pd-rich alloys and to also examine its temperature dependence. The cycling effect is dependent upon the existence of hysteresis and, if there is only a small hysteresis, the magnitude of the cycling effect is limited by this, however, in this case cycling may cause a relatively large reduction in hysteresis. The cycling effect will be examined for various forms of a given alloy, i.e. annealed, cold-worked and melt-spun. Cycling effects have been reported for Pd–Rh [3,11], Pd–Ni [4,10] and Pd–Pt alloys [12]. Van't Hoff plots for a $Pd_{0.91}Ni_{0.09}$ alloy in its cycled form and in its annealed, virgin form have been found to differ significantly [13].

2. Experimental

The alloys were all prepared by arc-melting the pure elements. The buttons from the arc-melting were annealed at 1133 K for 3 days and then rolled into foils (120 μm) and then reannealed at 1133 K.

3. Results and discussion

3.1. Pd–Cr alloys

The cycling behaviour for three compositions are shown in Fig. 2 (303 K) for the initially annealed alloys. No effect is seen for the $X_{Cr}=0.02$ alloy but a significant one is observed for the $X_{Cr}=0.05$ alloy. For the $X_{Cr}=0.09$ alloy there is only a small hysteresis and hence the plateau pressure's movement is limited but the relative change of hysteresis is significant, i.e., the value after cycling is ≈20% of the initial value. The cycling effect for annealed, cold-worked and melt-spun forms of the $X_{Cr}=0.05$ alloy have been determined and there is a similar, but not identical, cycling effect for each (303 K) (Fig. 3). Since the presence of a cycling effect is present for all the three

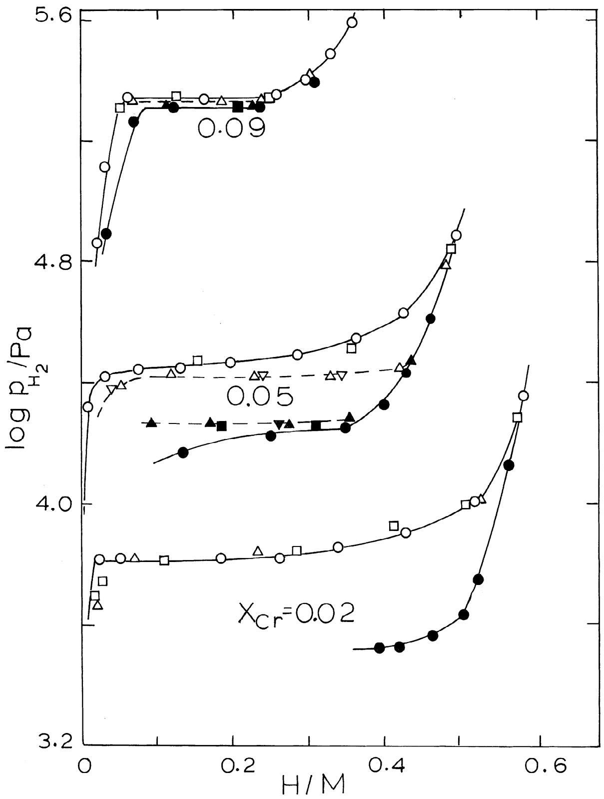

Fig. 2. Cycling of Pd–Cr alloys (303 K) which were originally in their annealed form. The atom fraction of Cr is shown on the figure. (○) first cycle; (□) second cycle; (▽) fourth cycle; (△) fifth cycle. The open and filled symbols represent absorption and desorption data, respectively.

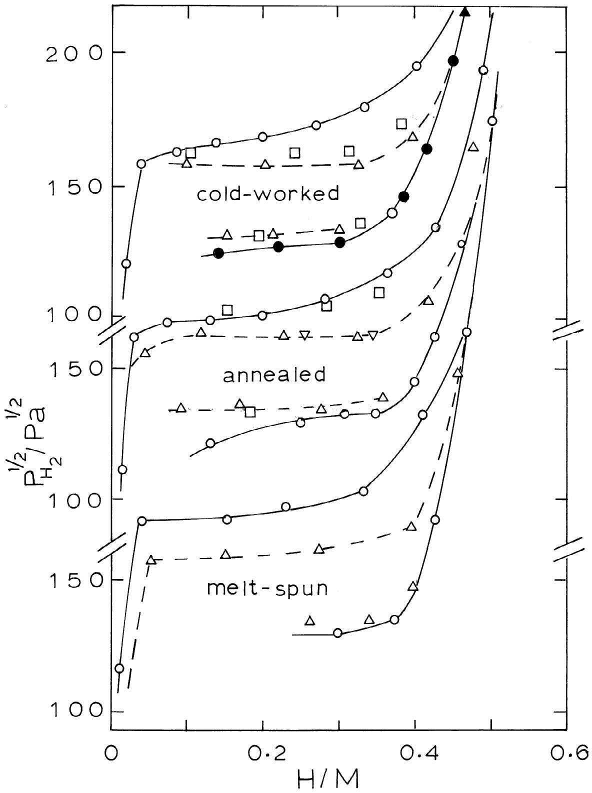

Fig. 3. Cycling isotherms (303 K) for the $X_{Cr}=0.05$ alloy in three different forms as labelled on the figure. (○) first cycle; (□) second cycle; (▽) fourth cycle; (△) fifth cycle. The upper symbols represent absorption data, and the lower symbols for each form represent desorption data.

forms (Fig. 3), its existence is independent of such factors as grain size and initial dislocation density.

3.2. Van't hoff plots for the $X_{Cr}=0.05$ alloy

Van't Hoff plots for the $X_{Cr}=0.05$ alloy have been made for the alloy which had been cycled at 303 K until no further changes appeared. Van't Hoff plots were also made for data at each temperature for the alloy in its virgin, annealed form. The results are shown in Fig. 4 where the van't Hoff plots for hydride formation are different for the two alloy forms but the decomposition plots are similar. Thermodynamic parameters derived from the annealed, virgin samples would appear to be the more reliable but are the more tedious to measure because of the need to employ a newly annealed sample at each temperature. For the two forms of the $Pd_{0.91}Ni_{0.09}$ alloy both the formation and decomposition plots differed markedly while the decomposition plots were more comparable [13].

3.3. Pd–Mo alloys

The cycling effect for three compositions of the Pd–Mo alloy system is seen in Fig. 5 where there is no effect for the $X_{Mo}=0.01$ alloy but an appreciable one for the $X_{Mo}=$

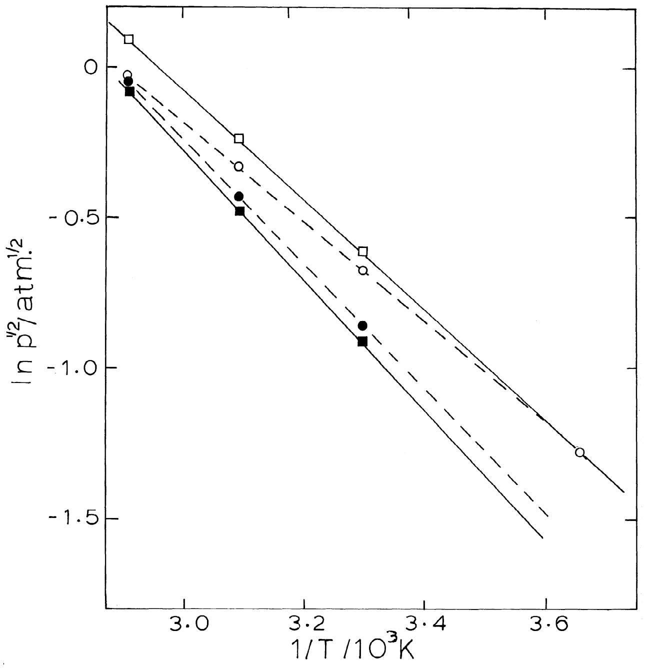

Fig. 4. Van't Hoff plots for the $X_{Cr}=0.05$ alloy. (□) virgin, annealed alloy employed for each temperature; (○) the same cycled alloy employed for each temperature. The open and filled symbols represent absorption and desorption data, respectively.

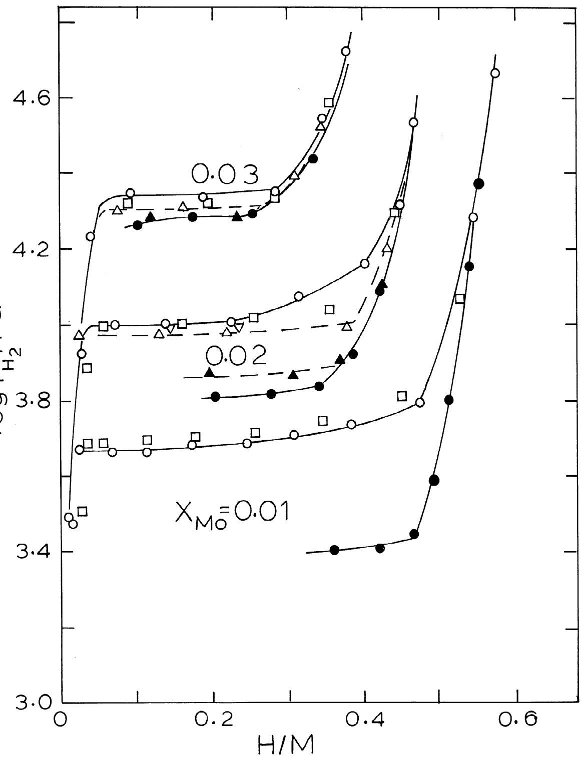

Fig. 5. Cycling of Pd–Mo alloys (303 K) originally in their annealed form. The atom fraction of Mo is indicated on the figure. (○) first cycle; (□) second cycle; (▽) fourth cycle; (△) fifth cycle. The open and filled symbols represent absorption and desorption data, respectively.

0.02 alloy, i.e. comparable to that for the $X_{Cr}=0.05$ alloy (Fig. 2). There is a large fractional reduction of hysteresis for the $X_{Mo}=0.03$ alloy but, because of the small hysteresis, the actual changes of the plateau pressures are small. The large effect on the hydrogen solubility of small amounts of Mo should also be noted in agreement with the results given by Ura et al. [14].

3.4. Pd–Au and Pd–Ag alloys

These alloys were cycled at T≥353 K because their low plateau pressures made it inconvenient to measure decomposition pressures at ambient temperatures. Since the plateaux were originally rather horizontal for the $Pd_{0.90}Au_{0.10}$ alloy at 353 K, there was not much change with cycling in this aspect of the isotherms but the plateau pressures changed significantly and hysteresis fell from 240 to 60 J mol^{-1} $\frac{1}{2}H_2$ after 6 cycles at 353 K.

The $Pd_{0.90}Ag_{0.10}$ alloy was cycled at both 348 and 373 K and a similar effect of cycling was found at each temperature and the effect was similar to that found for the $X_{Au}=0.10$ alloy. This $Pd_{0.90}Ag=0.10$ alloy was cycled 49 times, which is the largest number of cycles performed in this work; a small difference was observed between the 49th and the 21st cycles for p_f but none for p_d.

3.5. Recovery of a cycled $Pd_{0.90}Ag_{0.10}$ alloy

Dilute phase data for the $Pd_{0.90}Ag_{0.10}$ alloy were measured (Fig. 6) and the effect of cycling appears to saturate after about the fourth cycle. After cycling the alloy 49 times, it was annealed in vacuo at progressively higher temperatures, 623 K (13 h), 723 K (17 h), and at 823 K(4 h); after each annealing the recovery was monitored by the dilute phase solubility (323 K) (Fig. 6). The cycled alloy partially recovers after annealing at the rather low temperature of 623 K. The recovery was found to be complete after annealing at 823 K. The recovery was also monitored by the plateau pressure values, p_f, which were found to parallel the recovery monitored by the dilute solubilities (inset, Fig. 6). The dilute phase solubility enhancement of Pd and its alloys has been shown to be due mainly to dislocation trapping of the H [15,16] and therefore the observed parallel recovery of the dilute and plateau regions strongly suggests that cycling is also a dislocation-related effect. A high density of dislocations assists the phase change in both directions, thereby reducing hysteresis for Pd-rich alloys; the solute atoms play a significant role in the cycling effect. It is known that solute atoms are important for various dislocation phenomena such as solid solution hardening so that it is not surprising that the cycling effect is solute dependent.

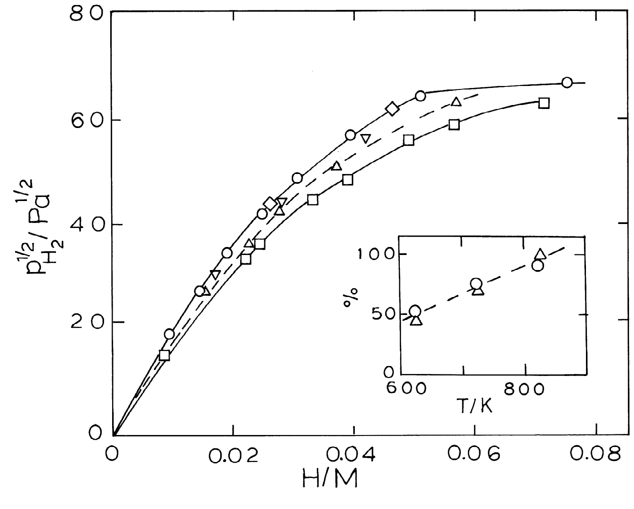

Fig. 6. Dilute phase hydrogen solubility in $Pd_{0.90}Ag_{0.10}$ alloy at 348 K. (○) solubility in the annealed alloy; (□) solubility in alloy cycled 49 times; (△) cycled alloy annealed at 623 K for 12.7 h; (▽) cycled alloy annealed at 723 K for 17 h; (◇) cycled alloy annealed at 823 K for 4 h. The inset illustrates the course of the annealing as a function of temperature of annealing where the course of the annealing is expressed as percent recovery; (○) the dilute phase solubility; (△) plateau pressure for hydride formation.

3.6. Physical examination of cycled alloys

The $Pd_{0.91}Ni_{0.09}$ alloy was cycled 6 times at 303 K and twice at 273 K. It was then examined by small angle neutron scattering (SANS); the SANS pattern showed no evidence for any phase separation as a result of the cycling. The cycled alloy was also examined by TEM and compared to Pd which had also been cycled. Before cycling both samples had been annealed at 1373 K and, after cycling, they were both found to have very large dislocation densities but the density was significantly lower for Pd than for the $Pd_{0.91}Ni_{0.09}$ alloy.

4. Conclusions

Both contracted, e.g. Pd–Ni, and expanded, e.g. Pd–Au, Pd-rich alloys exhibit similar cycling effects. Since pure Pd and very low solute Pd-rich alloys do not exhibit significant cycling effects, it seems clear that it is related to the presence of the solute. It is not clear why, for example, Pd–Mo alloys show significant effects of cycling at $X_{Mo}=0.02$ whereas they are not found for the Pd–Rh alloys until $X_{Rh}>0.10$; similarly cycling effects are not significant until $X_{Ni}>0.05$ but for the Pd–Cr a significant effect is found for $X_{Cr}=0.05$. Substitution of small amounts Mo or Cr in Pd, e.g. $X_M=0.02$, also have dramatic effects on the hydrogen solubilities whereas Ni or Rh do not. The lattice parameter changes of the solvent Pd lattice when binary alloys are formed of composition $Pd_{0.90}M_{0.10}$ are $\Delta a_{\circ}=-4.0$, -13.0, -24.0 and -8 nm × 10^{-4} for $M=$Mo, Cr, Ni or Rh [7]. Thus there is no correlation of the cycling behaviour with unit cell size. Furthermore it is difficult to understand the connection between the effect of these solutes on the cycling behaviour and the thermodynamics of their hydrogen solution.

One aspect of cycling which should be answered is the question of whether or not the cycling effect will be greater the lower the temperature at which the cycling is performed. This has not been examined systematically because it is difficult to carry out cycling at low temperatures due to the slow rates. Related to this question is whether the apparent merging of the van't Hoff plots at low temperatures (Fig. 4) is an artifact due to cycling at 303 K instead of, e.g. 263 K, or whether it has fundamental significance. Such an apparent merging is also noted for the Pd–Ni alloys [10].

It seems that the cycling effect has its origins in dislocation arrays whose behaviours are dependent on the solute concentration. Its elimination in the $Pd_{0.85}Ni_{0.15}$ alloy [13] may provide clues to the origin of hysteresis. Further work is needed to provide a detailed explanation of the cycling effect in these ductile alloys.

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