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Hydrogen-induced rearrangements in Pd-rich alloys

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Abstract

Homogeneous fcc Pd alloys have been found to undergo lattice rearrangements such as phase separation in the presence of dissolved H. For Pd–Rh alloys the phase-separated form is the thermodynamic stable state but for others which have been investigated, for example, Pd–Ni, Pd–Pt, the binary homogeneous substitutional solutions are the thermodynamically stable state. Phase separation for the latter alloys is a consequence of a ternary (Pd+M+H) equilibrium. The rearranged lattices are metastable after evacuation of the dissolved H at a temperature where the recovery back to its homogeneous state does not take place at a measurable rate. These H-induced changes differ from the lattice rearrangements which accompany hydride formation in metals and alloys where the hydride phases are very stable and which have different structures from the parent alloy, e.g. the formation of dihydrides in Zr or Zr-based alloys such as Zr–Nb (5 at.%). These very stable hydride phases will return to their initial states after removal of H at the required elevated temperatures. By comparison, H can be removed at moderate temperatures from the fcc Pd-based alloys because H is not very strongly held in the lattices. The metastable, H-free phase-separated Pd alloys return towards their homogeneous state after annealing in vacuo at, for example, 673 K, demonstrating that the phase-separated *binary* alloy is metastable. Results of H-induced changes in Pd-rich alloys are discussed for different ranges of temperature and hydrogen pressure for several Pd alloy systems. A ternary-phase diagram is calculated using known thermodynamic parameters for hydrogen solution in the homogeneous binary alloys and the thermodynamics of mixing of the metals. Using the (Pd+Pt) system as an example, a ternary (Pd+Pt+H) equilibrium is shown to cause phase separation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

It has been known for some time that hydrogen can induce phase transitions in austenitic stainless steels [1–3]. It is also known to cause dislocation generation and motion in pure iron and nickel [4–9] which obviously has important implications for H embrittlement. This review will not consider these but will instead concentrate on Pd-based alloys because, in the authors' view, the effects of dissolved H are less ambiguous than in other alloys. In contrast to other alloy systems, H-induced lattice migration (HILM) occurs in Pd-rich alloys under relatively well defined thermodynamic conditions of p_{H_2} and temperature and the changes are not confined to the layers adjacent to the surface as they often are in Fe-based alloys.

The phenomenon of H-induced lattice migration (HILM) has important implications in materials science and metallurgy, e.g. alloys can be prepared which cannot

be in the absence of the H, phase diagrams may be established which cannot by other means, etc.

Dissolved H can enhance metal atom diffusion and also cause phase separation via a ternary (Pd+M+H) equilibrium. It will be shown that both roles of dissolved H can be important for the interpretation of the observed results in the Pd-rich alloys: Pd–Rh, Pd–Ni, Pd–Co, Pd–Ag and Pd–Pt. Of these, the phase-separated form is the thermodynamically stable state only for Pd–Rh, i.e. it is obtained by annealing in vacuo for a long time at an elevated temperature [10,11].

2. Changes resulting from the application of ultra-high p_{H_2}

2.1. Results of Ponyatovskii et al.

Pd alloys have been found to undergo lattice rearrangement in the presence of p_{H_2} in the GPa range [12]. The results of the exposure of homogeneous Pd alloys to

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ultra-high p_{H_2} appear to fall into two categories: alloys which order such as Pd–Ag [13] and Pd–Cu [14,15] and those which separate into Pd-rich and Pd-poor regions such as Pd–Pt [16] and Pd–Ni alloys [17]. An early study indicated that Pd–Au alloys did not fall into either category since evidence for H-induced lattice migration was not found [16]. From a study of the Mössbauer spectra after exposure of a Pd_{0.90}Au_{0.10} alloy to p_{H_2} in the GPa range at 598 K, however, Baier et al. [18] found regions with composition Pd_{0.5}Au_{0.5}. Segregation did not occur when the alloy was heated at 598 K in the absence of hydrogen. The authors did not know how, or if, this segregation is related to the short-range order and superstructure which has been reported for Pd–Au alloys at other compositions [19–21].

In order for lattice changes to take place in these Pd alloys, the Russian workers found that temperatures generally had to be ≥ 523 K. From their work it is clear that the large amounts of dissolved H resulting from ultra-high p_{H_2} at moderately high temperatures cause changes in the alloy lattices as a result of ternary (Pd+M+H) equilibria. The role of dissolved H in enhancing the rate of these lattice rearrangements was not considered explicitly.

2.2. The Pd–Rh system and the results of Fukai et al.

The Pd–Rh system has been shown experimentally to have a miscibility gap [10,11]; theoretical calculations [22–25] agree closely with the experimental phase diagram [10,11]. The metastable disordered fcc Pd–Rh alloys are stable from ambient to relatively high temperatures as based on the criterion of the appearance of reflections from two sets of fcc lattice parameters in the XRD pattern [10,11] and according to this criterion, phase separation of the Pd_{0.74}Rh_{0.26} alloy did not occur after 6 months at 873 K. It should be noted that the more sensitive H₂ solubility method shows that some phase separation takes place after heating at 873 K for very much shorter times [26].

Fukai et al. [27] have found two sets of lattice parameters after a Pd_{0.80}Rh_{0.20} alloy is exposed to ultra-high H₂ pressures at 873 K after ≤ 250 s. Although it was not noted by Fukai et al., their results must not correspond to the binary (Pd+Rh) miscibility gap but to a (Pd+Rh+H) ternary equilibrium. The enhanced metal atom diffusion needed for the phase separation was suggested to be due to a large vacancy concentration [27] estimated to be approximately $10^7 \times$ greater than expected for the equilibrium concentration in Pd (873 K). Fukai et al. had also reported that large vacancy concentrations form in pure Pd and Ni at 873 K at ultra-high H₂ pressures [28–31]. These results are obviously of great potential importance for materials science.

3. Lattice changes induced at moderate p_{H_2}

In contrast to the work at ultra-high p_{H_2} , Flanagan et al. have employed HHT (hydrogen heat treatment) on Pd alloys at moderate p_{H_2} at 423–873 K; they found that lattice changes took place in initially homogeneous Pd–Rh alloys. Ultra-high p_{H_2} is, therefore, not a requirement for significant HILM to take place leading to lattice rearrangement in Pd alloys.

After an alloy has undergone HILM at a given temperature, the dissolved H can be removed by evacuation at a lower temperature. The stable phase-separated H-free (Pd+Rh) alloys or the metastable phase-separated (Pd+Pt), (Pd+Ni) alloys can then be examined using various analytical techniques such as XRD, electron microprobe analysis, small angle neutron scattering (SANS), TEM, and any other appropriate physical metallurgical techniques. A technique, which differs from these physical metallurgical ones, has been extensively employed by Flanagan et al. to detect the occurrence of lattice changes in Pd-rich alloys. This utilizes H₂ solubilities, so-called diagnostic isotherms, before and after HHT at ambient temperature and low p_{H_2} where further HILM will not occur, i.e., the relationships between p_{H_2} , or the relative H chemical potential, $\Delta\mu_{\text{H}} = \mu_{\text{H}} - \frac{1}{2}\mu_{\text{H}_2}^{\circ}(g) = RT \ln p_{\text{H}_2}^{1/2}$, and the corresponding H content of the alloy. Since the μ_{H} vs. H content isotherm is unique for each alloy–H system, it serves as a convenient in situ tool for probing the lattice. Equilibrium is readily established between Pd alloys with relatively clean surfaces and gaseous H₂ because of the facile chemisorption and dissociation of the H₂ on the catalytically active Pd surface.

The use of hydrogen solubility as a means for detecting lattice changes in Pd and its alloys has not been generally appreciated by the materials science community despite a review article by Kirchheim [32] which describes its unique advantages for the characterization of lattice defects such as dislocations and grain boundaries.

3.1. Phase separation of the Pd–Rh alloys

3.1.1. Phase separation in vacuo

In a study of the phase separation of Cu–Co alloys Michaelson [33] found only a single set of XRD reflections for coherent Cu–Co layers of thickness ≤ 10 nm. For such thin multilayers of Cu–Co the observed XRD pattern corresponds to an average lattice spacing of the overall composition. Michaelson employed these multilayer structures to simulate the formation of phases from supersaturated solid solutions. This research makes it clear that conventional XRD cannot detect coherent phase formation when the dimensions of the phases are very small. This apparently is also the situation for the Pd–Rh system when it is cooled into, from above, the miscibility gap [11]. XRD

was, however, successful in characterizing the two phases after prolonged annealing [10] or else after HHT of the $\text{Pd}_{0.80}\text{Rh}_{0.20}$ alloy at moderate [34] or ultra-high p_{H_2} [27].

The binary fcc Pd–Rh alloy system has a miscibility gap with a critical temperature of about 1200 K at $X_{\text{Rh}} \approx 0.5$ [10,11]. The kinetic difficulties in achieving phase separation have been described. Indications of phase separation were, however, found from the H_2 solubility differences between alloys which have been prepared by quenching from above the miscibility gap (or by melt–spinning) and or cooling relatively slowly in a furnace after annealing [26]. Greater compositional fluctuations indicative of incipient phase separation were found by electron microprobe analysis after the relatively slow furnace–cooling than after quenching or melt–spinning [35].

3.1.2. H-enhanced phase separation

$\text{Pd}_{0.80}\text{Rh}_{0.20}$ alloys were subjected to HHT in the p_{H_2} range 1.0–10.0 MPa and $T=773\text{--}873$ K [34]; these conditions resulted in significant changes in the diagnostic isotherms. Fig. 1 shows the dilute-phase solubilities at 303 K after HHT at $p_{\text{H}_2}=5.5$ MPa at a series of temperatures in the range 573–873 K for about the same time, $\approx 4\text{--}5$ h. Also shown are H_2 solubilities after annealing in the absence of H_2 using different cooling rates; the significant differences are due to different degrees of phase separation.

After HHT, large changes are also apparent in the complete isotherms for the $\text{Pd}_{0.80}\text{Rh}_{0.20}$ alloy. The isotherms change from ones having plateaux and relatively

large capacities to isotherms with lower plateau pressures and smaller capacities depending on the time application of the HHT (873 K and 12.3 MPa) (Fig. 2). These diagnostic isotherm results are consistent with separation into two phases, one richer and the other poorer in Pd relative to the initial homogeneous alloy. The latter phase will not absorb significant amounts of H at the p_{H_2} employed to measure the diagnostic isotherms because of the high plateau pressures of alloys with $X_{\text{Rh}} \geq 0.25$ [26].

In a further series of experiments HHT was employed on the homogeneous $\text{Pd}_{0.80}\text{Rh}_{0.20}$ and $\text{Pd}_{0.75}\text{Rh}_{0.25}$ alloys at higher p_{H_2} and lower temperatures, e.g. 100 MPa and 673 K. This resulted in more complete phase separation of the alloys than found in the experiments described immediately above. Evidence for phase separation came from ‘diagnostic’ isotherms measured before and after HHT at either 303 K or 273 K [34]. For example, after HHT at 673 K at 100 MPa, the complete diagnostic isotherm for the $\text{Pd}_{0.80}\text{Rh}_{0.20}$ alloy revealed that phase separation had occurred. High plateau pressures changed after HHT to a shorter plateau at quite low pressures (Fig. 3). The $\text{Pd}_{0.80}\text{Rh}_{0.20}$ and $\text{Pd}_{0.75}\text{Rh}_{0.25}$ alloys both have rather high plateau pressures in their initial, homogeneous forms but, after HHT, a well-defined plateau indicative of a Pd-rich phase, appeared at quite a low p_{H_2} as shown for the former alloy in Fig. 3. When this phase-separated alloy was subsequently annealed for 20 h in vacuo, its diagnostic isotherm did not change (Fig. 3) and it also did not change after an additional HHT at 30 MPa for 25 h. This proves that the phase-separated form is thermodynamically stable and that the ternary equilibrium (Pd+Rh+H) does not

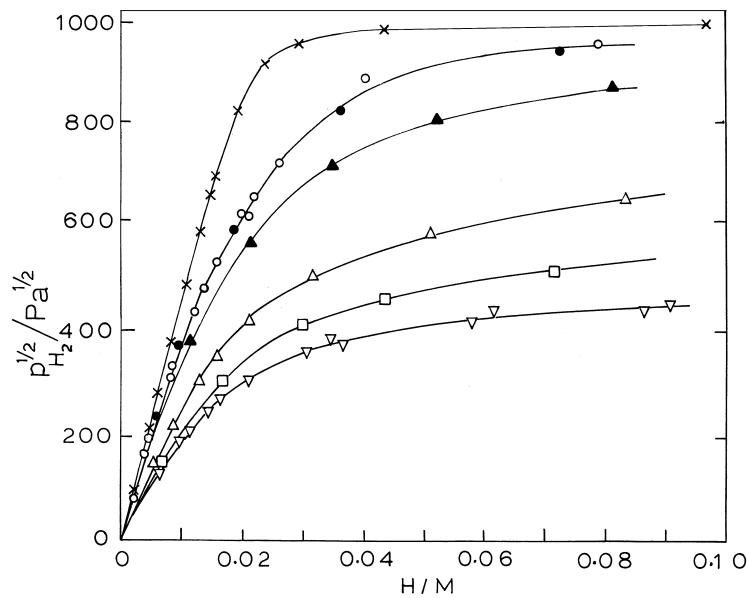


Fig. 1. Dilute phase H_2 solubilities (303 K) for the $\text{Pd}_{0.80}\text{Rh}_{0.20}$ alloy. \times , quenched; \circ , cooled rapidly but not quenched; \bullet , HHT, 5.5 MPa, 573 K; \blacktriangle , HHT, 5.5 MPa, 623 K; \triangle , HHT, 5.5 MPa, 673 K; \square , HHT, 5.5 MPa, 773 K; ∇ , HHT, 5.5 MPa, 873 K. The homogeneous alloys were subjected to HHT for about 4–5 h.

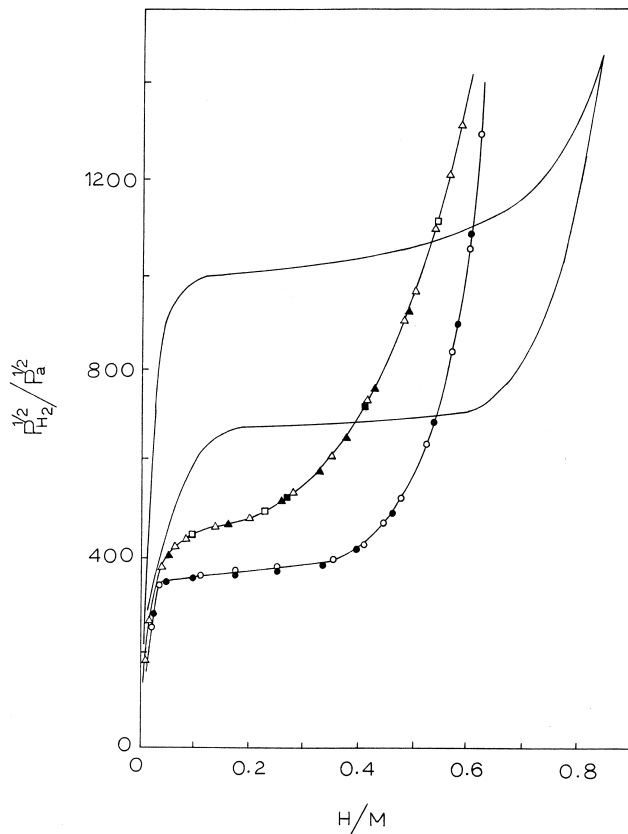


Fig. 2. H_2 diagnostic isotherms (303 K) for the $Pd_{0.80}Rh_{0.20}$ alloy. Solid curves without symbols, quenched alloy. Δ , HHT 4 h, 5.5 MPa, 873 K; \square , HHT 10 h, 5.5 MPa, 873 K; \circ , HHT 12 days, 5.5 MPa, 873 K. Open symbols are for absorption and closed symbols are for desorption.

significantly affect the metal atom compositions of the separated phases at these p_{H_2} and temperatures because, otherwise, the phase-separated $Pd_{0.80}Rh_{0.20}$ alloy would rearrange further on annealing in vacuo, i.e. from the compositions corresponding to the ternary equilibrium to those corresponding to the binary (Pd+Rh) equilibrium phase diagram. By contrast, when Pd–Pt alloys, which have become phase-separated via HHT, are annealed in vacuo they return towards the homogeneous state (see below). After HHT the plateau pressure of the $Pd_{0.80}Rh_{0.20}$ alloy (Fig. 3) corresponds to a homogeneous alloy of composition $X_{Rh} \approx 0.03$. This value cannot be quantitatively compared with the experimental binary-phase diagram which does not extend to such a low temperature but it is not an unreasonable value judging by extrapolation of the binary diagram [10,11].

Direct evidence for phase separation was also found using XRD in the $Pd_{0.80}Rh_{0.20}$ alloy after HHT at $p_{H_2} = 100$ MPa for 3 h (673 K) [34]. The lattice parameters of Pd and Rh differ only slightly; the XRD evidence for phase separation was based on the appearance of a shoulder in the peaks reflecting a Rh-rich phase adjacent to the main reflection of the Pd-rich phase. The experimental asymmetrical XRD peak was successfully modeled using

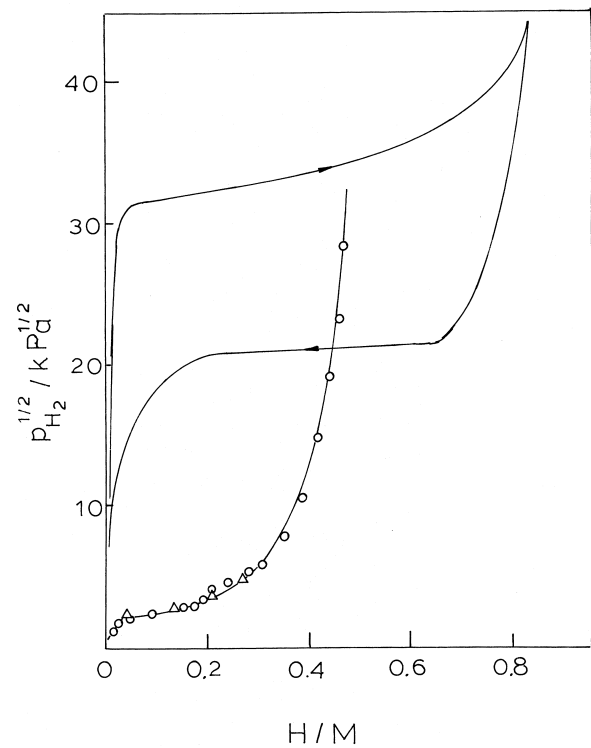


Fig. 3. H_2 diagnostic isotherms (303 K) for the $Pd_{0.80}Rh_{0.20}$ alloy. Solid curves without symbols, quenched alloy. \circ , HHT 3 h, 100 MPa, 673 K; Δ , after annealing the sample shown by \circ for 20 h in vacuo at 673 K. Only absorption points are shown.

Gaussian distributions for the Pd- and Rh-rich phase peaks [34].

3.2. H-induced phase separation of Pd–Pt alloys

Based solely on the melting point difference of Pd and Pt, Raub [36] suggested that there may be a miscibility gap for the fcc (Pd+Pt) alloy system but there has been no experimental verification and theoretical calculations indicate that there is no miscibility gap [24]; this is consistent with the enthalpies of formation which are slightly negative over the whole composition range [37].

As noted above, large amounts of dissolved H arising from p_{H_2} at several GPa caused phase separation of the Pd–Pt system at elevated temperatures [16]. It has been shown more recently that these alloys will also phase-separate at relatively moderate p_{H_2} [38,39]. The homogeneous $Pd_{0.80}Pt_{0.20}$ alloy does not form a hydride phase at $T \geq 273$ K and consequently does not dissolve large amounts of H_2 at moderate p_{H_2} . After HHT for 3 h (100 MPa, 673 K), a plateau appears in its subsequent diagnostic isotherm (273 K) which, according to its p_{H_2} , corresponds to an alloy with $X_{Pt} \approx 0.06$ (Fig. 4). The $H_2(g)$ solubility at 273 K and $p_{H_2} = 0.05$ MPa is $(H/M) = 0.275$

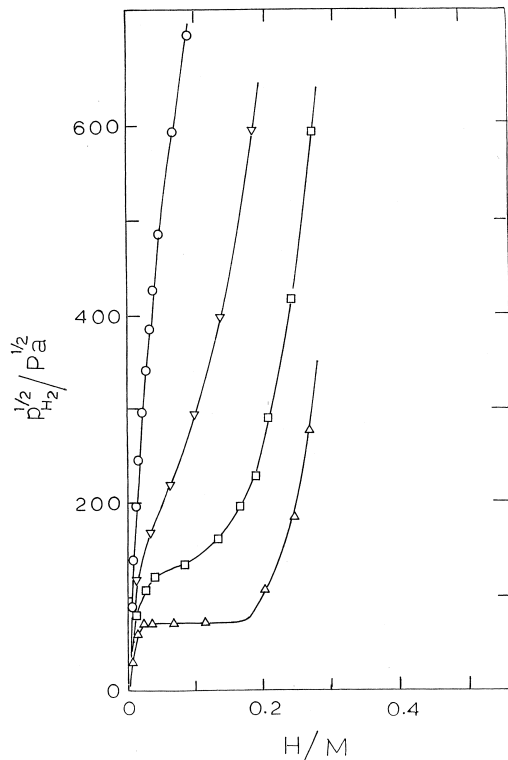


Fig. 4. H_2 diagnostic isotherms (273 K) for the $Pd_{0.80}Pt_{0.20}$ alloy. \circ , annealed alloy; Δ , HHT 3 h, 100 MPa, 673 K; \square , sample shown by Δ annealed in vacuo for 12.6 h at 673 K; ∇ , sample shown by Δ subjected to a further HHT for 12.6 h at 30 MPa (673 K).

after HHT but only 0.020 before HHT, i.e. a factor of 14 greater. The relatively short plateau found after this HHT (Fig. 4) is due to the fraction of the Pd-rich phase present after the phase separation and may also be due to the very small dimensions of the phases, i.e. 3 nm according to the SANS measurements [40]; the latter may lead to shortened plateaux similar to nanocrystalline Pd [41].

The conditions of 673 K and $X_{Rh}=0.20$ are within the miscibility gap predicted by Raub [36]. If a $Pd_{0.80}Pt_{0.20}$ alloy, which was phase-separated as a result of HHT at 673 K, is annealed in vacuo at 673 K, its resulting diagnostic H_2 isotherm (273 K) shows that it rearranged into an alloy of greater homogeneity (Fig. 4). This is strong evidence against the existence of a binary miscibility gap in this system. The only possibility for H-induced phase separation in this alloy is the onset of a ternary (Pd+Pt+H) equilibrium where the co-existing phases have different metal atom, and H, compositions. After such a phase separation via establishment of ternary equilibrium, removal of H at a moderate temperature results in a phase-separated metastable alloy. This interpretation of the phase separation is consistent with the results [38,39] that phase separation of Pd–Pt alloys does not occur at elevated temperatures where only small amounts of H_2 dissolve at $p_{H_2} \leq 100$ MPa, i.e. large amounts of H must dissolve in

order for the ternary equilibrium to cause significant metal atom separation. The Pd–Rh alloys exhibit contrasting behavior because they *do* phase-separate at elevated temperatures in the presence of small amounts of dissolved H or after long times in vacuo. This is expected from the existence of a binary miscibility gap in the Pd–Rh system.

The return towards the stable, homogeneous state of the phase-separated $Pd_{0.80}Pt_{0.20}$ alloy was found to be enhanced by smaller amounts of dissolved H than were needed for the large degree of phase separation (673 K) (Fig. 4). For example, at $p_{H_2}=30$ MPa the alloy, which had undergone phase separation at 100 MPa, returned towards its homogeneous state more completely than it did in vacuo (Fig. 4) which clearly demonstrates HILM. The equilibrium state at 30 MPa (673 K) lies between that of the homogeneous alloy and that which had been subjected to HHT at 100 MPa, 673 K.

3.2.1. Hydrogen-induced phase separation of Pd–Ni alloys

This alloy system forms fcc solid solutions over the whole composition range and there have been no suggestions of a miscibility gap [42]. The Russian workers found that Pd–Ni alloys underwent phase separation (473–623 K) at p_{H_2} in the GPa range [17]. Based on diagnostic isotherms measured before and after HHT and on SANS (small angle neutron scattering), phase separation has been observed in Pd–Ni alloys at moderate p_{H_2} values and at a temperature as low as 448 K [43].

Fig. 5 shows diagnostic isotherms (323 K) for a $Pd_{0.85}Ni_{0.15}$ alloy after various HHT and annealing treatments. After HHT at 100 MPa (673 K) for 3 h, it can be seen that the plateau pressure and the capacity have decreased as expected if the alloy separates into Pd-rich and Pd-poor phases. Judging from the plateau pressure after phase separation (Fig. 5), a Pd-rich phase is formed of $X_{Ni} \approx 0.07$ and the Pd-poor phase does not form a hydride phase at the p_{H_2} used for the diagnostic isotherm (Fig. 5). Hysteresis is nearly eliminated after HHT which is similar to the behavior of the Pd–Rh alloys. When this phase-separated alloy was subsequently annealed in vacuo at 673 K for 2 h, its diagnostic isotherm was found to undergo a small shift towards the isotherm for that of the homogeneous alloy (Fig. 5). If the phase-separated alloy (Δ , Fig. 5) is annealed at $p_{H_2}=25$ MPa (141 h), it recovers towards the homogeneous state much more dramatically (\times , Fig. 5) than does the same phase-separated alloy after similar annealing but in vacuo (∇ , Fig. 5). This shows that HILM also occurs in this system just as it does in the Pd–Pt system.

The fully annealed, homogeneous $Pd_{0.85}Ni_{0.15}$ alloy was subjected to HHT for 24 h at 673 K at 25.0 MPa causing p_{plat} of its diagnostic isotherm to shift to slightly lower values (\circ , Fig. 5) and, in a separate experiment, the phase-separated (HHT at 100 MPa, 673 K for 3 h) was

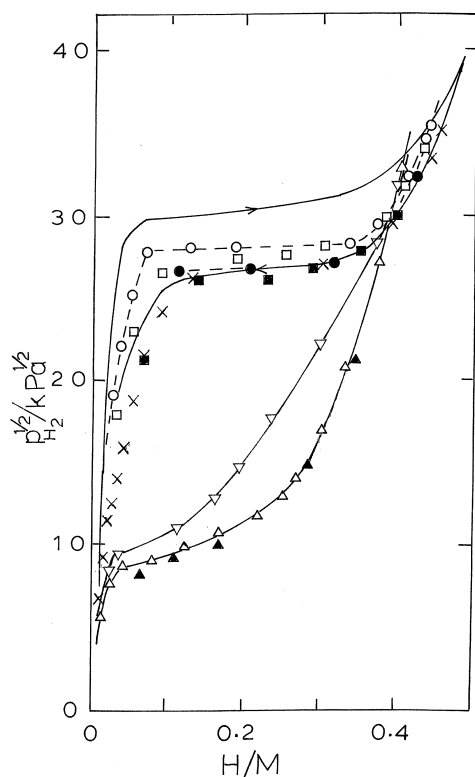


Fig. 5. H_2 diagnostic isotherms (323 K) for the $Pd_{0.85}Ni_{0.15}$ alloy. Solid lines without data points, annealed alloy. Δ , HHT 3 h, 100 MPa, 673 K; ∇ , phase-separated alloy shown by Δ annealed in vacuo for 2 h (673 K); \times , phase-separated alloy shown by Δ subjected to further HHT at 25 MPa for 2 h (673 K); \circ , homogeneous alloy subjected to HHT at 25 MPa (673 K); \square , phase-separated alloy shown by Δ treated at 25 MPa for 141 h (673 K). Open symbols are for absorption and closed symbols are for desorption.

annealed at the same temperature and p_{H_2} for 141 h and, after this, its p_{H_2} (\square , Fig. 5) increased to close to, but below, that of the initially homogeneous alloy. It can be concluded that subjecting both the already phase-separated and homogeneous alloys to the same p_{H_2} and temperature of HHT leads to the same ternary equilibrium state characteristic of 673 K and $p_{H_2} = 25$ MPa. Since the same state is approached from either direction, this demonstrates that an equilibrium obtains, characteristic of the (Pd + Ni + H) ternary alloy at 25.0 MPa, 673 K. By comparison of SANS patterns after annealing (673 K) the phase-separated alloy in H_2 and in vacuo, HILM is clearly established in this alloy system [43] as in the Pd–Pt alloy system.

3.3. The effects of HHT on Pd–Ag alloys

After HHT at $p_{H_2} \leq 100$ MPa, its only effect at either 473 or 673 K was a change from a rather sloping to a horizontal plateau for the $Pd_{0.90}Ag_{0.10}$ and the $Pd_{0.85}Ag_{0.15}$ alloys. Thus, under HHT conditions (673 K, $p_{H_2} \leq 100$ MPa), where the other alloys which have been investigated showed marked changes of capacity and

plateau pressure in the diagnostic isotherms, the Pd–Ag alloys are relatively unaffected.

3.4. Possible origin of hydrogen-induced lattice rearrangements in Pd alloys

Both kinetics and equilibrium play vital roles in some of the results described here:

1. The kinetic role concerns the enhancement of the rate of metal atom diffusion by the presence of dissolved H (HILM).
2. The equilibrium role concerns the ternary (Pd + M + H) equilibrium reached by the system which can be accompanied by phase separation into phases of different metal atom, and H composition.

3.5. Kinetics of H-induced lattice migration

The most favored explanation for the enhanced kinetics given in the literature is an increase of vacancy concentration due to H-vacancy complex formation [27,44–46]. Calculations based on H-vacancy complex formation have so far underestimated the enhanced vacancy concentrations which would be needed for the observed H-enhanced diffusion [45]. It seems that a lowering of the activation energy for diffusion by distortion of the environment of the diffusing metal atom by an adjacent H may be an important factor. The origin for the H-enhanced diffusion will not be considered any further in this review but, instead, we will concentrate on the equilibrium aspects.

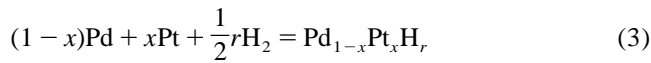
3.6. Thermodynamics of (Pd + M + H) ternary equilibrium

For phase separation to occur in a binary alloy, the enthalpies of mixing should be positive. For the Pd–Pt and Pd–Ni alloys the enthalpies of mixing are negative [37,47] and phase separation is, therefore, improbable in the binary systems. Since phase separation does take place in the presence of dissolved H, it must be concluded that when H is present, the enthalpies of mixing of the metals in the presence of dissolved H change sign causing phase separation. It is clear from the experimental results that non-stoichiometric ternary hydrides can form because the equilibrium compositions depend on p_{H_2} .

Although such phase diagrams for (Pd + M + H) systems are not available in the literature, some information about the ternary phase (Pd + Pt + H) diagram has been determined here. Some features of the (Pd + Pt + H) ternary equilibrium have been calculated by Park and Flanagan [48] using known thermodynamic data for:

$$(1-x)Pd + xPt = Pd_{1-x}Pt_x \quad (1)$$

$$Pd_{1-x}Pt_x + \frac{1}{2}rH_2 = Pd_{1-x}Pt_xH_r \quad (2)$$



The sum of the free energy changes of the first two reactions gives the desired free energy change for the overall process (3) for a given x . The evaluation of the free energies for the mixing of the pure metals (1) can be carried out for different compositions from the known enthalpies and entropies of mixing of the binary alloys [37,47]. The free energies for reaction (2) can be evaluated from pressure–composition isotherms for homogeneous alloys using the Gibbs-Duhem equation and $d\mu_{\text{H}}$ which can be obtained from $d\mu_{\text{H}} = RT \, d \ln p_{\text{H}_2}^{1/2}$. The detailed evaluation of the free energy for reaction (2) is shown elsewhere [48]. The free energies for reaction (3) are then evaluated from those for (1) and (2) for different values of x allowing construction of a ΔG vs. x relationship. If a straight line with common tangents can be drawn on this ΔG vs. x curve, then phase separation should occur. Such common tangent lines can be drawn for the experimental conditions where phase separation is shown to occur in the (Pd+Pt+H) alloy system [48].

Similar considerations for the Pd–Ag system [49] indicate that phase separation should *not* occur over the experimental range where HHT was applied. The difference in H-induced lattice changes between the Pd–Pt and Pd–Ag alloys can be understood by the different behavior of their plateau pressures with X_{M} . As the Pt content increases in the Pd–Pt alloys, the plateau pressures increase and, for the Pd–Ag alloys, as the Ag content increases the plateau pressures decrease. Thus, the Pd–Ag alloy hydrides are more stable than Pd hydride and consequently decomposition of the H-containing Pd–Ag alloys into Pd-rich and Pd-poor regions would not be expected.

4. Summary

It is shown that under certain conditions dissolved H in some Pd alloys will become a part of a ternary (Pd+M+H) equilibrium which may be accompanied by phase separation leading to two phases of different metal atom and H compositions. By removal of the H by evacuation, an alloy consisting of two phases of different metal atom compositions can be obtained which will be metastable at moderate temperatures. The reverse process of the return of the metastable alloy to a homogeneous state has been shown to be accelerated by the presence of dissolved H. The forward process of the establishment of the phase-separated ternary equilibrium must, therefore, also be accelerated by dissolved H. A thermodynamic analysis of the ternary (Pd+Pt+H) equilibrium supports separation into two phases under the experimental conditions.

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