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Hydrogen-induced suppression of ordering to Pd$_7$M (M = Sm, Gd, Li) (Pt$_7$Cu-type superlattice)

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Abstract. It has been observed that the phase transition of α-Pd solid solution to the corresponding ordered Pd$_7$M (M = Sm, Gd, Li) phase in Pd–6.5 and 8.0 at.% Sm, Pd–10.0 at.% Gd and Pd–7.2 at.% Li alloys is suppressed by exposure to hydrogen pressures of > 20 bar. According to published phase diagrams the short-range ordered Pd$_7$M phase coexists with the α-Pd solid solution phase below the solid solubility limits of the solute metals, but at relatively high temperatures within the two-phase field the ordered phase has a tendency to disorder upon exposure to a hydrogen atmosphere (p_{H_2} > 20 bar) and subsequent slow cooling to room temperature with the pressure maintained. The suppression effect of ordering to Pd$_7$M structure may be due to the retardation of nucleation and growth of the Pd$_7$M ordered domain during cooling as a consequence of a weakening of Pd–M bonding by the dissolved hydrogen.

1. Introduction

Recently, Salomons *et al* [1] have observed from measurements of hydrogen solubility in a Pd$_{91}$Y$_9$ alloy that after annealing in hydrogen at 20 bar at 650 K, where the hydrogen content corresponds to about H/M = 0.3, the solubility isotherms for the alloy steepen; that is, the low-pressure hydrogen solubilities increase at temperatures between 413 K and 473 K and the high-pressure solubilities decrease. They also observed that the solubility isotherms are restored to their original shape following annealing of the sample in helium at a temperature of 650 K. This anomalous hydrogen solubility behaviour was attributed to the role of the dissolved hydrogen in suppressing the short-range order in the Pd–9 at.% Y alloy which was obtained in the absence of hydrogen at 650 K. This suppression was attributed to a weakening of the metal–metal interactions which lead to ordering. The authors [1] did not directly confirm their speculations about the suppression of the ordering by electron diffraction. Doyle *et al* [2] also observed anomalous solubility effects in a Pd–8 at.% Y alloy which probably have the same origins.

Recent studies on a series of Pd-rich Pd–RE (rare earth metal) alloys (RE = Ce [3–5], Y [6, 7], Sm [8], Eu [9], Gd [10], Dy [7], Ho and Er [11]) have shown that the presence of an ordered Pd$_7$RE phase, which is a Pt$_7$Cu-type superlattice [12], is observed both in electron diffraction and in electrical resistance measurements. The formation of the ordered Pd$_7$RE

phase has been found to be accompanied by a peritectoid reaction: α-Pd+Ll$_2$-type Pd$_3$RE (or Pd$_5$RE (RE = Ce [5], Sm [8] and Eu [9])) $\rightleftarrows$ Pd$_7$RE. In the more hypostoichiometric alloys of Pd$_7$RE, the order–disorder transitions of α-Pd $\rightleftarrows$ Pd$_7$RE correspond to the solid solubility limit of the solute metals.

According to the most recent phase diagram for Pd–Y [6,7], annealing of the Pd$_{91}$Y$_9$ alloy at 650 K as done in [1] exceeds the solid solubility limit of Y in the α-Pd phase solid solution, i.e. it is within the α-Pd+Pd$_7$Y mixed phase region. Salomons *et al* [1] regarded the alloy composition to be 'close to the mixed-phase region corresponding to the ordered Ll$_2$-type Pd$_3$Y structure', according to the earlier phase diagram of the Pd–Y system determined by Loebich and Raub [13] for Pd–Y alloys.

The ordered alloys of Pd-rich Pd–Ce [14, 15] and Pd–Y [2, 16] dissolve less hydrogen than the disordered alloys at low pressures but the diffusivity of hydrogen is much greater in the ordered alloys than in the disordered ones [17–20]. Doyle and Harris [16] have reported that the solubility decreases with an increase in size of the ordered domains in Pd–Y alloys.

The purpose of the present work is to examine whether or not there is hydrogen-induced suppression of the ordering to the Pd$_7$RE ordered state in other Pd–RE (RE = Sm, Gd) alloys, and also in Pd$_7$Li [21], by electron diffraction and electrical resistance measurements. This paper will be limited to the experimental results concerning the phase transitions of α-Pd solid solution to Pd$_7$M (M = Sm, Gd, Li) phases during cooling in a hydrogen atmosphere. The results of the effect of hydrogen exposure on the peritectoid reaction of α-Pd+Ll$_2$-type Pd$_3$RE (for Pd$_5$RE) $\rightleftarrows$ Pd$_7$RE will be reported in a subsequent paper.

2. Experimental details

The alloy samples were prepared as previously described [8, 10, 21]. The compositions used in this study were as follows: Pd–6.5 and 8.0 at.% Sm, Pd–10.0 at.% Gd and Pd–7.2 at.% Li alloys. After rolling the alloy buttons into thicknesses of about 100–200 μm, discs of diameter 3 mm were trepanned from the foils for use in electron microscopy. In order to obtain information about the reverse transformation from the disordered state, stabilized by dissolved hydrogen, to the original one during heating, electrical resistance measurements were carried out *in vacuo*, as the initial hydrogenated samples are heated and subsequently cooled at a rate of 50 K h^{-1}. The samples for electrical resistance measurements were cut from the foils with dimensions of about 2 mm $\times$ 25 mm.

All the samples were annealed *in vacuo* before hydrogenation by cooling from about 1123 K to room temperature at 50 K h^{-1} in order to assure that the samples used are in two-phase coexistence of α-Pd solid solution and Pd$_7$M (M = Sm [8], Gd [10], Li [21]). Hydrogenation was carried out in a Hastelloy tube vessel.

According to the previously determined phase diagrams of the Pd–Sm [8], Pd–Gd [10] and Pd–Li [21] systems, the temperatures for some of the hydrogen exposure treatments were chosen to correspond to a disordered state of α-Pd phase solid solution, i.e. at temperatures above the limiting solid solubility curves. Hydrogen exposure treatments of Pd–8.0 at.% Sm, Pd–10.0 at.% Gd and Pd–7.2 at.% Li alloys were also carried out at specified temperatures below the solid solubility limits of the solute metals, i.e. in the two-phase region of α-Pd solid solution and Pd$_7$M (M = Sm, Gd, Li). As an example, the hydrogen exposure temperatures employed for Pd–Sm alloys are shown in a partial phase diagram [8] in figure 1.
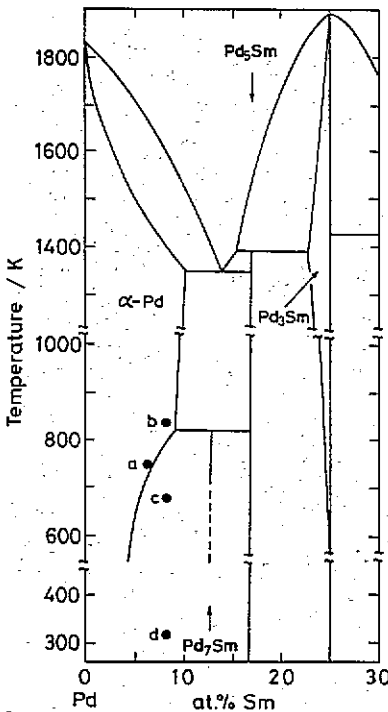
Figure 1. Partial phase diagram of the Pd–Sm system [8]. The temperatures for hydrogen exposure: a, 743 K for 6.5 at.% Sm, b, 843 K, c, 673 K and d, 323 K for 8.0 at.% Sm.

After evacuating the annealed, untreated samples at specified temperatures, e.g. those shown in figure 1, the samples, which were employed for electron microscopy and electrical resistance measurements, were exposed to a given hydrogen pressure, i.e. 10, 20, 30 and 50 bar, and held at the specified temperature for 1 h, and then cooled to room temperature at a rate of 50 K h^{-1}, while the pressure was maintained. The samples for electron microscopy were jet-electropolished in a solution of one volume perchloric acid to four volumes of acetic acid.

3. Results and discussion

Figures 2(a) to (m) show comparisons of electron diffraction patterns between as-annealed (*in vacuo*) forms and their hydrogen-treated counterparts for Pd–6.5 at.% Sm (a, b), Pd–8.0 at.% Sm (c–g), Pd–10.0 at.% Gd (h, i) and Pd–7.2 at.% Li (j–m) alloys.

It can be seen that when these alloys were exposed to hydrogen atmosphere at pressures of more than about $p_{H_2} = 20$ bar (e, k) at temperatures above the solid solubility limits of the solute metals, i.e. in disordered states, and then slowly cooled to room temperature with the pressure being maintained, a suppression of ordering to the Pd$_7$M (M = Sm, Gd, Li) (Pt$_7$Cu-type superstructure [12]) is observed. After this hydrogen suppression of ordering,
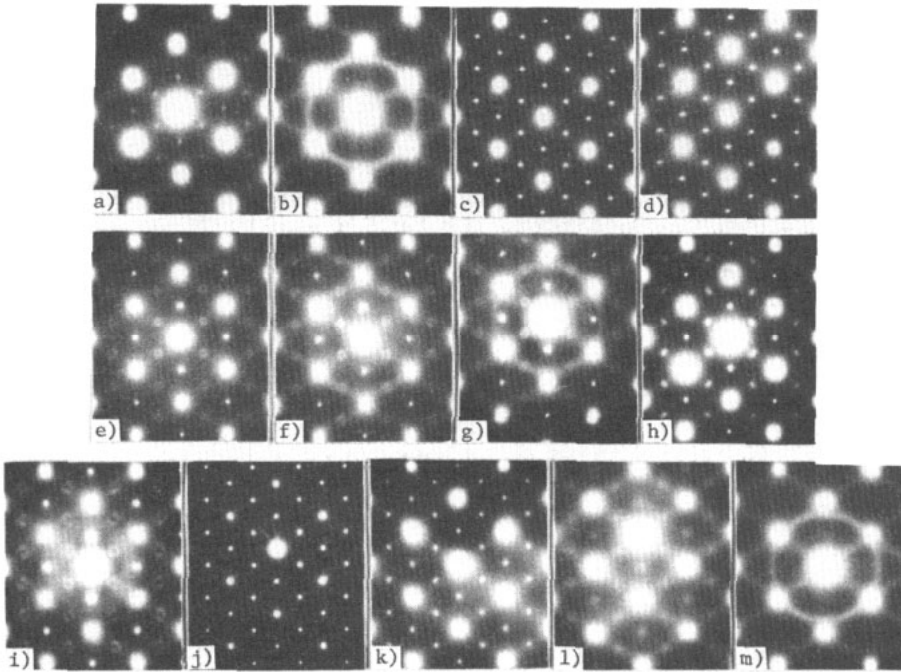
Figure 2. Electron diffraction patterns with [110] incidence for as-annealed samples *in va* and their hydrogen-treated counterparts. The time of hydrogen exposure of all the samples ur a given hydrogen pressure and at each temperature is 1 h. Pd–6.5 at.% Sm; a: as-annealed hydrogenated under $p_{H_2} = 30$ bar at 743 K. Pd–8.0 at.% Sm; c: as-annealed, d: hydrogena under $p_{H_2} = 10$ bar at 843 K, e: hydrogenated under $p_{H_2} = 20$ bar at 843 K, f: hydrogena under $p_{H_2} = 30$ bar at 843 K, g: hydrogenated under $p_{H_2} = 50$ bar at 843 K. Pd–10.0 at.% h: as-annealed, i: hydrogenated under $p_{H_2} = 30$ bar at 813 K. Pd–7.2 at.% Li; j: as-annea k: hydrogenated under $p_{H_2} = 20$ bar at 993 K, l: hydrogenated under $p_{H_2} = 30$ bar at 99: m: hydrogenated under $p_{H_2} = 30$ bar at 1023 K.

the reflection spots at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ due to the Pd_7M (M = Sm, Gd) structure, appear to be split, unclear and weak. In the case of exposure of $p_{H_2} = 10$ bar for 8.0 at.% Sm (d), the suppression effect is not as clearly observed, the difference in the degree of hydrogen suppression of ordering for $p_{H_2} = 20$ bar (e), 30 bar (f) and 50 bar (g) is not marked. After the hydrogen exposure treatments, many dislocations due to formation of β-hydride during the cooling were observed, especially for Pd–7.2 at.% Li.

Figures 3(a) to (c) show the diffraction patterns of hydrogenated samples of 8.0 at.% Sm (a), 10.0 at.% Gd (b) and 7.2 at.% Li (c) alloys which were exposed to a hydrogen pressure of 30 bar at 673 K, 600 K and 600 K, respectively, for 1 h, where these temperatures are below the solid solubility limits of the solute metals; they were also subsequently slowly cooled while maintaining the pressure. It can be seen that even in the cases of the samples initially consisting of two phases, α-Pd and Pd_7M (M = Sm, Gd, Li), after exposure to a hydrogen atmosphere, the ordered Pd_7M phases have a tendency to disappear rather than to separate into two phases, as expected according to the phase diagrams [8, 10, 21].

Hydrogen exposure at the relatively low temperature of 323 K under the same pressure of

Figure 3. Electron diffraction patterns with {110} incidence for hydrogenated Pd–8.0 at.% Sm (a), 10.0 at.% Gd (b) and 7.2 at.% Li (c) alloys, which were initially in the two-phase coexistence of α-Pd and Pd₇M (M = Sm, Gd, Li). The temperatures for hydrogen exposure: a, 673 K, b and c, 600 K under p_{H_2} = 30 bar for 1 h.

30 bar for 1 h did not lead to the disappearance of the ordered Pd₇M phases. The suppression of the ordering therefore requires a moderately high temperature and a sufficiently high hydrogen pressure to dissolve an appreciable amount of hydrogen in order to induce the mobility of the metal atoms.

Figures 4(a) and (b) show the results of electrical resistance measurements for initially hydrogen-treated alloys of 8.0 at.% Sm and 7.2 at.% Li. Similar changes in resistance *versus* temperature behaviour are observed as has been reported for the hydrogen-induced Ll₂ ordered structure of Pd₃Mn [22, 23]. The alloys show an abrupt decrease in electrical resistance from about 353 K to 473 K for 8.0 at.% Sm, and from about 393 K to 433 K for 7.2 at.% Li during heating which is due to the loss of the hydrogen introduced during the hydrogen treatment.

Figures 5(a) to (d) show electron diffraction patterns for the 8.0 at.% Sm and 7.2 at.% Li alloys as the initial as-hydrogenated samples were heated and then quenched from the following temperatures during the electrical resistance measurements (figure 4): 583 K (a), 693 K (b) and 773 K (c) for 8.0 at.% Sm alloy, and from 533 K (d) for 7.2 at.% Li. Weak superlattice reflections characteristic of the suppressed Pd₇M (M = Sm, Li) structure can still be seen for the 8.0 at.% Sm alloy quenched from both temperatures of 583 K and 693 K, and for the 7.2 at.% Li alloy quenched from 533 K.

It can be seen from comparisons of the resistance *versus* temperature behaviour shown in figure 4 and the previously determined resistance *versus* temperature relationships for initially quenched Pd–8.0 at.% Sm [8] and Pd–7.2 at.% Li [21] alloys (hydrogen-free disordered forms) that the Pd₇M (M = Sm, Li) structures in these alloys are largely suppressed even in the absence of dissolved hydrogen in the temperature range from about 473 K to 693 K for the 8.0 at.% Sm and in the temperature range from about 433 K to 600 K for the 7.2 at.% Li.

With further heating (figure 4) ordering to the Pd₇M form occurs due to thermal equilibration at about 763 K for 8.0 at.% Sm and at about 623 K for 7.2 at.% Li, and these ordered phases start to show disorder again at about 793 K for 8.0 at.% Sm, and at about 723 K for 7.2 at.% Li.

The subsequent cooling relationships for both alloys are almost the same as the previously examined relationships for the hydrogen-free alloys [8, 21]. It was confirmed that the electron diffraction patterns of the samples cooled slowly to room temperature exhibit reflections due to the ordered Pd₇M (M = Sm, Li) phase, as shown in figures 2(c) and (j). The electrical resistance *versus* temperature curves for other alloy compositions exhibited similar changes as shown in figures 4(a) and (b).
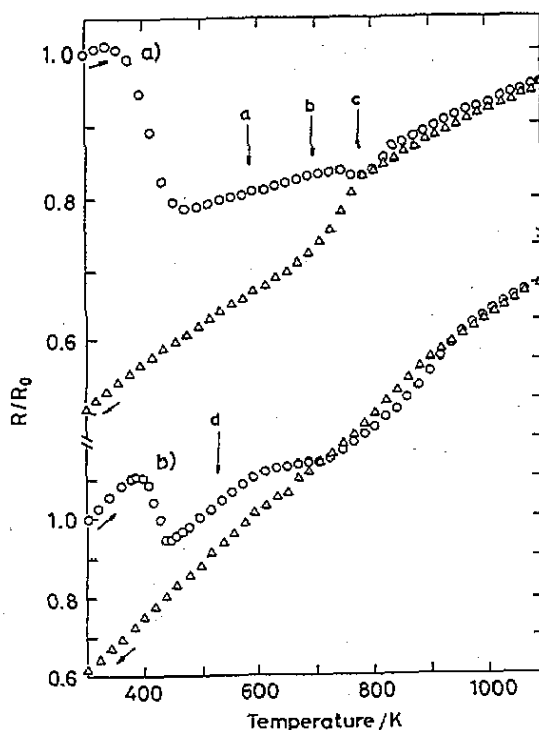
Figure 4. Electrical resistance *versus* temperature relationships for initially hydrogenated Pd–8.0 at.% Sm (a) at 843 K under p_{H_2} = 30 bar for 1 h and also hydrogenated Pd–7.2 at.% Li (b) at 993 K under p_{H_2} = 30 bar for 1 h. ○, heating; △, subsequently cooling. The heating and cooling rates, 50 K h^{-1}. The arrows with letter labels in the heating curves indicate the temperatures at which the samples were quenched and analysed by electron diffraction.

From the above results it can be concluded that the phase transition of α-Pd solid solution to Pd_7M (M = Sm, Gd, Li) is suppressed by the presence of dissolved hydrogen during cooling of the alloys. Similarly interstitial hydrogen tends to eliminate the short-range ordered Pd_7M (M = Sm, Gd, Li) phases which coexist with the α-Pd solid solution phase at relatively high temperatures.

This suppression of ordering may be related to the preferential occupation by hydrogen of the octahedral interstices surrounded entirely by nearest-neighbour Pd atoms. This may act to weaken the Pd–M attractive interaction which leads to ordering. In the alloys investigated in this research the substitutional metal, M, especially Sm and Gd, strongly reduces the ability of palladium to absorb hydrogen.

This also suggests a strong Pd–M attractive interaction which does not like to be disrupted by interstitial hydrogen and hence the solubility of hydrogen in these alloys is low. This is consistent with the picture of the suppression of order in these alloys by interstitially dissolved hydrogen.
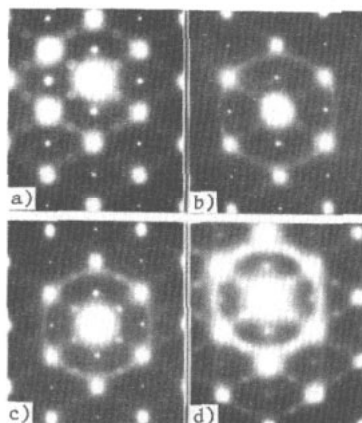
Figure 5. Electron diffraction patterns with [110] incidence for Pd–8.0 at.% Sm (a to c) and Pd–7.2 at.% Li (d) alloys, as the initially hydrogen-treated samples were heated and quenched from 583 K (a), 693 K (b) and 773 K (c) for 8.0 at.% Sm, and from 533 K (d) for Pd–7.2 at.% Li alloy (see figure 4).

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