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Hydrogen-induced metal atom rearrangements in $Pd_{3+x}Mn_{1-x}$ alloys with $x \geqslant 0$ using transmission electron microscopy, electrical resistivities and H_2 solubilities

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Abstract

In this research we have characterized the products of the hydrogen-induced ordering of disordered and of $L1_{2-s}$ ordered $Pd_{3+x}Mn_{1-x}$ alloys with $x \geqslant 0$. The long-period superstructure ($L1_{2-s}$) form is produced by a heat treatment at a temperature of about 700 K *in vacuo*. An $L1_2$ ordered form can be prepared by exposing Pd–Mn alloys to hydrogen (1 MPa or above) at temperatures of 500 K or above; this ordering is induced by hydrogen under conditions where ordering does not occur in its absence. After the alloys have transformed to their $L1_2$ form, they remain in this form if the hydrogen is removed at moderate temperatures.,

Large dislocation densities appear from the hydrogen-induced ordering of the disordered alloys; the density of these dislocations appears to decrease with increase in x. Dislocations are also introduced by the disorder$\rightarrow L1_{2-s}$ transformation which occurs *in vacuo*.

The mechanism of the hydrogen-induced ordering is unknown but it must be related to the lattice expansion caused by the hydrogen. It should be noted that not very much dissolved hydrogen is needed to cause these transitions, *i.e.* a hydride phase does not form.

1. Introduction

When manganese is substituted into the palladium lattice, more hydrogen dissolves at low pressures than in pure palladium; however, the solubility at moderate pressures is smaller than in palladium [1]. The plateau pressures are smaller for these alloys than for palladium. This is a characteristic of "expanded" alloys, *i.e.* alloys whose unit cells are larger than pure palladium [2]. Phutela and Kleppa [3] showed that there is a decrease in hydrogen solubility as the ordered ($L1_{2-s}$) Pd_3Mn alloy is heated above its critical temperature T_c.

A long-period superstructure forms when Pd_3Mn is annealed below T_c, *e.g.* annealed at about 700 K. The $L1_{2-s}$ form has been recently shown to be of the Al_3Zr type [4] rather than the Ag_3Mg type previously reported [5, 6].

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A preliminary report has appeared concerning the hydrogen-induced ordering of Pd_3Mn [7]. Hydrogen ($p_{H_2} \geqslant 1$ MPa) induces ordering at temperatures where it does not occur over long time periods in the absence of hydrogen [7]. It has also been shown that the type of order induced by hydrogen is $L1_2$ in contrast with the long-period superstructure, $L1_{2-s}$, which results from slow cooling or annealing *in vacuo* below the critical temperature of 803 K. The two ordered forms of the alloy can be interconverted by the removal or addition of small amounts of dissolved hydrogen at 723 K [8]. In this paper we wish to amplify the preliminary reports of these results and to report results for the hypostoichiometric alloys, $Pd_{3+x}Mn_{1-x}$, $x > 0$. One goal of this research is to compare directly the hydrogen solubilities in the three forms of the alloy under comparable experimental conditions.

Hydrogen-induced metal atom mobility is of great general interest and the Pd_3Mn alloy system has proved to be excellent for examining this phenomenon in detail. This system has the following advantages.

(1) The hydrogen solubility is large enough to be conveniently measured under thermodynamically meaningful conditions, *i.e.* hydrogen activities in the metal phase are easily determined from measurement of the surrounding hydrogen fugacities.

(2) The changes which occur are not limited to the surface regions but occur throughout the alloy.

(3) The hydrogen-induced lattice changes can be easily detected by hydrogen solubility measurements and characterized by physical measurements such as electron diffraction and electrical resistivity.

2. Experimental details

The alloys were prepared by high frequency induction heating under an argon atmosphere or else by arc melting under argon. The buttons which formed were rolled into foils of thicknesses between 100 and 140 μm. The alloys were annealed at about 1200 K *in vacuo* for several days.

In order to disorder the alloys they were wrapped in titanium foil, sealed *in vacuo* in silica tubes and then heated to about 1200 K. They were then quenched into ice–water while simultaneously breaking the quartz vessel, resulting in a rapid quench.

The samples for electron microscopy were in the form of discs about 3 mm in diameter. These alloys were jet electropolished in a solution of 1 volume of perchloric acid to 4 volumes of acetic acid at 270 ± 5 K. The electron microscopy was carried out with a Hitachi-800 microscope.

X-ray diffraction with Cu Kα radiation was not very useful for the determination of order in these alloys because their superstructure reflections are weak. By contrast, electron diffraction showed these reflections; any splitting was very clear and it was therefore the preferred technique. X-ray diffraction was employed to determine the lattice parameters of the cubic cell, giving a_0 values of 0.3900 nm, 0.3901 nm and 0.3899 nm for the disordered, $L1_2$ and $L1_{2-s}$ forms where the latter form has a unit cell consisting of four collinear cubes; the value of a_0 reported is the average of $c_0/4$ and a_0.

Electrical resistance measurements were carried out *in vacuo* with a four-point contact method using a current of 50 mA. Hydrogen solubilities were determined from pressure changes in a system of known volumes. The pressures were measured with MKS diaphragm gauges.

3. Results and discussion

The various forms of the alloys and their methods of preparation will be described first; these different forms of the alloys have been established by electron diffraction [7–9].

3.1. *Disordered alloys*

The disordered $Pd_{3+x}Mn_{1-x}$ alloys were prepared by rapid quenching; an f.c.c. unit cell is found. There is some evidence for short-range order in the stoichiometric alloy, judging from the existence of faint superlattice reflections. Despite this likelihood of short-range order in the quenched alloys, for convenience, they will be referred to as disordered. Alloys with $x=0$, 0.2, 0.3 and 0.4 were also prepared in their disordered forms by quenching. The electron diffraction pattern of the quenched alloy ($x=0$) is shown in Fig. 1(a) where only the principal f.c.c. reflections can be seen.

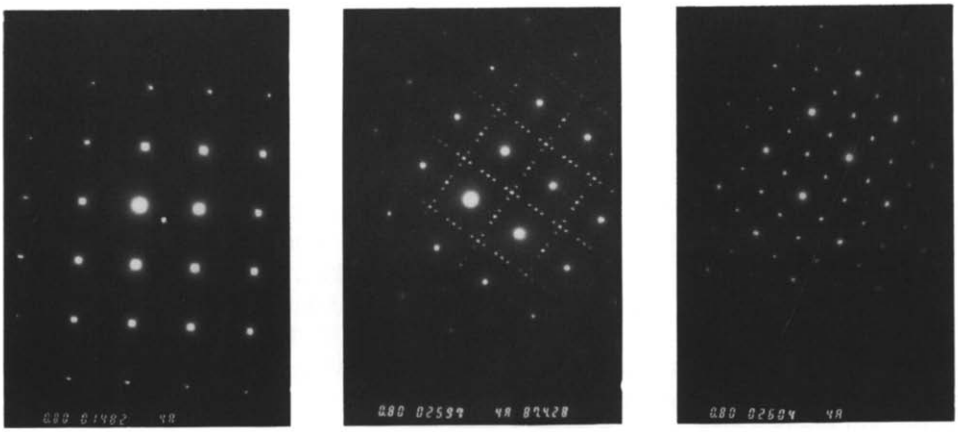

(a) (b) (c)

Fig. 1. (a) Electron diffraction pattern along [001] of the disordered, quenched alloy with $x=0$. (b) Electron diffraction pattern along [001] of the $L1_{2-s}$ form of the $x=0$ alloy prepared by slow cooling *in vacuo* from above T_c and then exposed to hydrogen at 5.0 MPa and 373 K for 24 h. (c) Electron diffraction pattern along [001] of the $x=0$ alloy prepared by exposure to hydrogen gas at 1 MPa and 726 K for 24 h.

3.2. *Long-period superstructures of the Al_3Zr type*

It is well known that the stoichiometric alloy Pd_3Mn, when ordered *in vacuo*, has a long-period superstructure [5]. It has been classified as belonging to the Ag_3Mg type but very recently it was found to belong to the Al_3Zr type [4]. This reclassification has to do with the recognition of the presence of a center of symmetry; the arrangement of the metal atoms with respect to each other are unaffected by this reclassification. This structure will be referred to here simply as the $L1_{2-s}$ form. Alloys with $x=0$, 0.2, 0.3 and 0.4 were also prepared in their $L1_{2-s}$ ordered forms by slow cooling *in vacuo* from above 800 K. Figure 1(b) shows the electron diffraction pattern for this form of the $x=0$ alloy where the splitting of the superlattice reflections of the $L1_2$ structure indicates that the unit cell has increased in size in one dimension. The pattern shown in Fig. 1(b) is for an $L1_{2-s}$ ordered alloy which was subsequently exposed to hydrogen at 5.0 MPa and 373 K for 24 h. It can be seen that there is no indication of any transformation to the $L1_2$ form after this relatively low temperature treatment.

There has been some controversy about the structures of the hypo-stoichiometric alloys resulting from annealing *in vacuo* [10]. For the bulk forms of these alloys, Sato and Toth [11] found that the structure of those with $0<x\leqslant 0.2$ was $L1_2$. Gjönnes and Olsen [12] similarly found this type of order for alloys with $x>0$. On the contrary, Iwasaki *et al.* [10] found that the alloys with $x>0.04$ exist only in the disordered f.c.c. structure. Krén and Kádár [13] also arrived at this conclusion.

3.3. *$L1_2$ (Cu_3Au type)*

3.3.1. *The stoichiometric alloy ($x=0$)*

The $L1_2$ structure has not been previously observed for the Pd_3Mn alloy; it has been found in this research that it can be prepared by exposure of either the disordered or the $L1_{2-s}$ forms to hydrogen gas (at 1 MPa or above) at 523 K or 726 K respectively. (The former temperature is one where ordering does not occur in the absence of the hydrogen and the latter temperature is where the $L1_{2-s} \rightarrow L1_2$ ordering transition readily occurs.) The amounts of hydrogen dissolved at these temperatures are relatively small, especially at 726 K, because the solution of hydrogen in these systems is exothermic and their solubilities decrease with increase in temperature. The solubility in the $L1_2$ form at 523 K and 1 MPa has been measured by exposing the alloy to these conditions, cooling it to liquid nitrogen and evacuating. The sample is then degassed; this gave a value of $[H]/[M]=0.1$. The solubility in the disordered form is really the more relevant quantity since this is the initial state of the system and the solubility in it will be much smaller since it is about one tenth of that in the $L1_2$ form.

Ordering to the $L1_2$ form from the disordered alloy, which occurs under conditions where the ordering does not occur in the absence of hydrogen, was first noted from hydrogen solubility studies [7]. The solubility in the ordered form is much greater than in the disordered form and the solubilities thereby provide a convenient tool for following the course of the ordering.

It was found that some ordering takes place at temperatures as low as 423 K in the presence of hydrogen at 5 MPa. It is possible that ordering would be observed at even lower temperatures if higher pressures of hydrogen were employed. The structure of this form is established from electron diffraction (Fig. 1(c)). Figure 1(c) shows the electron diffraction pattern of an initially disordered Pd_3Mn alloy which has been exposed to hydrogen at 1 MPa and 726 K. Unsplit superlattice reflections are seen which are indicative of the $L1_2$ structure.

It has been found here that at the temperatures and hydrogen pressures where the disordered$\rightarrow L1_2$ transition was observed the use of comparable pressures of helium instead of hydrogen did not lead to any transformation. This demonstrates that it is necessary for the hydrogen to dissolve in the solid in order to cause the transformation to the ordered phase via hydrogen-induced lattice mobility.

3.3.2. The hypostoichiometric alloys

In order to prepare the $L1_2$ form of these alloys the disordered forms were subjected to hydrogen at 5.0 MPa for 24 h at 673 K. A lower temperature was employed for these alloys than for the stoichiometric alloy because their critical temperatures are lower (see below).

In contrast with the very weak electron diffraction patterns of the $L1_{2-s}$ structure after annealing *in vacuo*, the extra reflections corresponding to $L1_2$ obtained from hydrogen ordering of these alloys are well defined and strong for both the $x = 0.2$ and the $x = 0.3$ alloys.

3.4. Ordering of disordered $Pd_{3+x}Mn_{1-x}$ alloys in vacuo

3.4.1. The stoichiometric alloy ($x = 0$)

Ordering was followed by hydrogen solubilities, electrical resistivity changes, transmission electron microscopy (TEM) and electron diffraction. Figure 2 shows the electrical resistance of the disordered stoichiometric alloy during heating (2 K h^{-1} from 520 to 1030 K) and subsequent cooling at the same rate over the same temperature range. The resistance of the ordered alloy (shown by the full triangles) is slightly smaller than that of the disordered alloy at, for example, 400 K, but the difference is not very large compared with most order–disorder alloy systems.

A feature of considerable interest is the maximum in resistance which occurs during the heating in the range where ordering commences (Fig. 2). Electron diffraction patterns were taken of samples quenched from the temperatures indicated by the letters a to f. These diffraction patterns establish that ordering had not commenced at 592 K (a) but had at 663 K (b). At 726 K (c) the splitting of the superstructure spots are evident and at 778 K (d) the splittings are sharp. At 876 K (e) and 971 K (f) the superstructure spots have disappeared leaving only the fundamental reflections from the disordered f.c.c. lattice.

TEM photomicrographs were taken at 50 000× magnification and the dark field images at 726 K (c) revealed a very fine domain structure; the

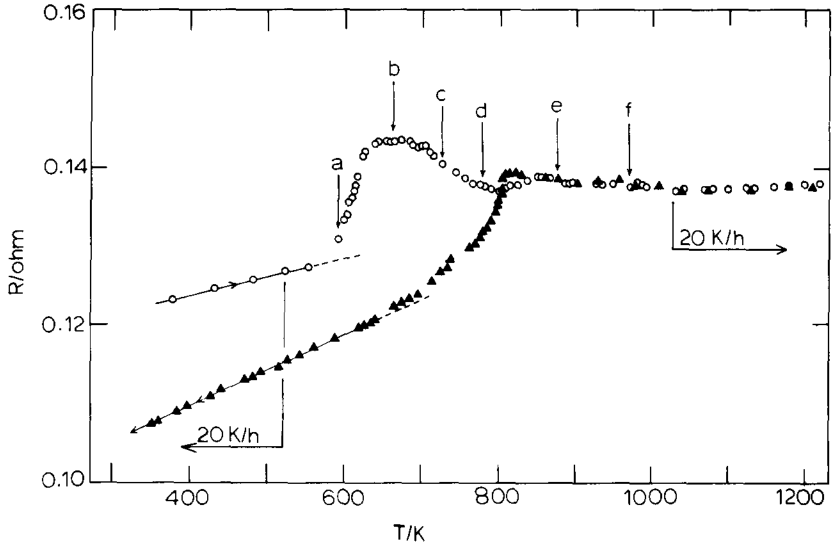


Fig. 2. Electrical resistance of Pd_3Mn ($x = 0$) during heating of initially a disordered sample, (○) and subsequent cooling from above T_c (▲). The letters labeling the heating curve indicate temperatures at which the sample was quenched and analyzed by electron diffraction. Between the two horizontal arrows labeled as 20 K h^{-1}, the heating and cooling rates were each 2 K h^{-1}.

domains had coarsened significantly with further heating (2 K h^{-1}) to 778 K (d). Electron diffraction and TEM observations were carried out during cooling of the sample from above T_c; it was found that at 778 K the order was very well established and the domains were large compared with those observed during heating, *i.e.* they are a factor of about 10 larger. The domains observed at 778 K during cooling are very similar in size to those shown in the paper of Gjönnes and Olsen [12]. The domain size does not change significantly during cooling below 778 K. The domains disappear above T_c and upon cooling they reappear in a much coarser form, *e.g.* at d during cooling the domains are many times larger than at the same temperature during heating.

T_c for ordering is found to be 850 K during heating (Fig. 2) and 803 K during cooling. The latter is more well defined than the former temperature. These values agree reasonably well with estimations from other methods [5, 11].

Cooling of the disordered alloy from above T_c is shown in Fig. 3 where it can be seen that, when it cools *in vacuo*, its resistance decreases non-linearly to about 700 K and then linearly with a further decrease in temperature. During reheating, the resistance of this ordered alloy clearly exhibits hysteresis in the transition, showing that it is first order.

This maximum shown for the heating of the disordered alloy in Fig. 2 is unexpected because ordering generally decreases the electrical resistance. There is, however, some precedence for this behavior in other systems which

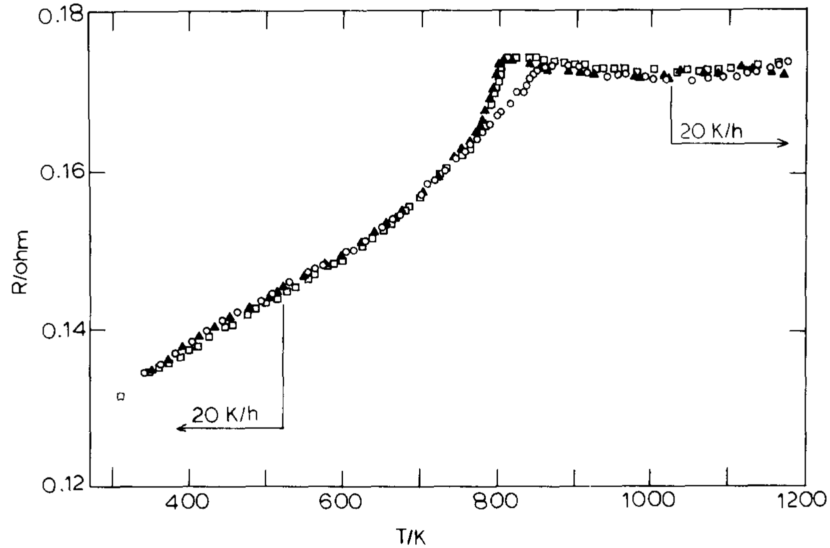


Fig. 3. Electrical resistance of Pd_3Mn ($x=0$) during cooling of an initially disordered sample from above T_c (▲) and subsequent heating to above T_c (○) and then recooled (□). Between the two horizontal arrows labeled as 20 K h^{-1}, the heating and cooling rates were each 2 K h^{-1}.

form $L1_{2-s}$ ordered structures; however, none of these other cases shows maxima as pronounced as those in Fig. 2. The maximum seen in Fig. 2 is due to the two opposing effects of (i) electron scattering from the domain boundaries and (ii) ordering within the domains.

Another feature of interest is that the electrical resistance of the disordered alloy shows very little change with temperature above the critical temperature. This behavior is characteristic of manganese alloys such as manganin and can also be seen to be characteristic of disordered Pd_3Mn.

The degree of order ($L1_2$) found in an initially disordered alloy (or $L1_{2-s}$) resulting from exposure to hydrogen at various temperatures and pressures was determined mainly by electron diffraction and TEM. Some results are summarized in Table 1. The relationship between the temperature and hydrogen pressure employed and the degree of $L1_2$ order attained by the initially disordered or $L1_{2-s}$ alloy represents a compromise between the diffusion rate of the metal atoms and the amount of hydrogen absorbed by the alloy. An increase in temperature leads to an increase in the former and a decrease in the latter at a given pressure. At a given pressure of hydrogen, both effects will depend exponentially on temperature with the diffusion term being larger in magnitude and dominant so that, at a given pressure of hydrogen, higher temperatures should be more effective in inducing $L1_2$ ordering.

Hydrogen solubilities were determined as a function of temperature during the heating *in vacuo* of the initially disordered alloy. Starting at the lowest temperature, about 350 K, solubilities were determined using small

TABLE 1

Summary of electron diffraction results for the hydrogen-induced formation of the $L1_2$ ordered form of Pd_3Mn

Reactant	T (K)	p_{H_2} (MPa)	Time (h)	Product
Disordered	523	5.0	6	Weak, $L1_2$ reflections
Disordered	523	5.0	24	Medium, $L1_2$ reflections
Disordered	523	5.0	48	Strong, $L1_2$ reflections
Disordered	523	5.0	168	Same as 48 h, $L1_2$ reflections
Disordered	523	1.3	24	Very weak, $L1_2$ reflections
Disordered	523	10.1	24	Strong, $L1_2$ reflections
Disordered	523	5.0	24	$L1_2$+trace $L1_{2-s}$
Disordered	473	5.0	24	$L1_2+L1_{2-s}$
$L1_{2-s}$	726	5.0	24	Strong $L1_2$ reflections

hydrogen pressures such that insignificant amounts of hydrogen dissolve (Fig. 4) and consequently there is negligible lattice mobility. The hydrogen solubility is simply used as a probe for the degree of order in the alloy and is not directly related to the hydrogen-induced ordering which requires high pressures of hydrogen. Data were obtained at a series of increasing temperatures such that, on average, the increase corresponded to about 2 K h^{-1}. The same procedure was employed during cooling. The time for each hydrogen solubility determination is relatively short, especially at the higher temperatures, and therefore during most of the heating period the sample was held *in vacuo* because the hydrogen was evacuated between each solubility determination.

The values of $\Delta\mu_H$ at infinite dilution of hydrogen are determined for the alloy at each temperature by extrapolation to $[H]/[M]=r=0$; these values are designated as $\Delta\mu_H^\circ$ and $\Delta\mu_H^\circ=\Delta H_H^\circ-T\,\Delta S_H^\circ$. This quantity reflects the partial free energy of solution of $\frac{1}{2}H_2$ without the configurational contribution to the entropy. The more negative $\Delta\mu_H^\circ$, the greater will be the hydrogen solubility at a given pressure in this region of very small hydrogen contents.

In Fig. 4 the values of $\Delta\mu_H^\circ/RT=\ln[p_{H_2}^{1/2}(1-r)/r]\approx R\ln(p^{1/2}/r)$ are plotted as a function of $1/T$ when the initially disordered alloy is heated and then cooled at the equivalent of 2 K h^{-1}. It can be seen that, during the initial heating, the plot is linear to about 530 K and then starts to deviate as ordering commences. In this sense the hydrogen solubility is a more sensitive probe for changes in structure in this system than are the resistance measurements because the latter do not show any changes until about 550 K; it should be emphasized that prolonged heating *in vacuo* at 523 K did not lead to appreciable ordering, judging from the electron diffraction patterns whereas similar heating in $p_{H_2}\geqslant 1$ MPa leads to diffraction patterns which show $L1_2$ reflections [7].

The relative chemical potential decreases above about 530 K as ordering takes place. At 750 K the solubility is about equal to that of the alloy during

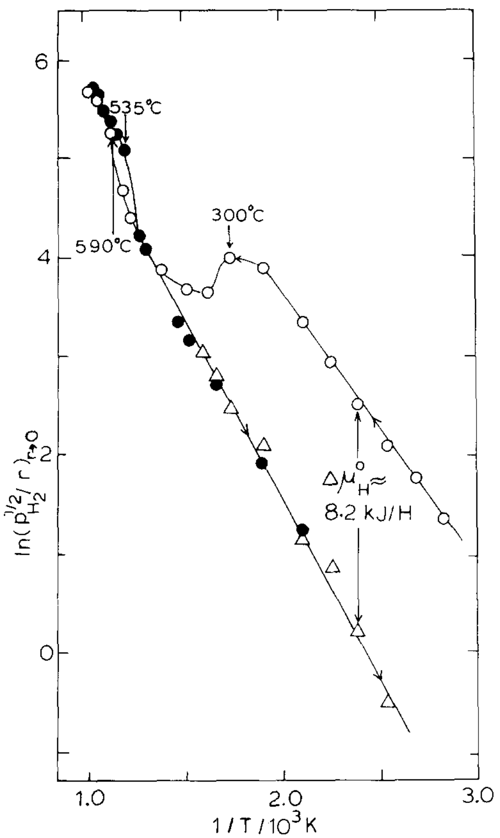


Fig. 4. The dependence of $\Delta\mu_{H}^{\circ}/T$ upon $1/T$ for the heating of initially disordered Pd_3Mn ($x=0$) (○) followed by its cooling from above T_c (●) and subsequent reheating (△). The slope of these relationships is the value of ΔH_{H}° and the intercept ΔS_{H}°.

cooling. Upon further heating the relative hydrogen chemical potential increases about linearly with decrease in $1/T$. Upon cooling, a transition at about 803 K occurs which corresponds to the onset of ordering. The remainder of the cooling behavior follows a straight line with a steeper slope than during the heating. The relative hydrogen chemical potential is seen to be consistently smaller for the ordered alloy ($L1_{2-s}$) than for the disordered alloy and hence the solubility is greater in the former. The slope of these plots leads to ΔH_{H}° and the intercept at $1/T=0$ equals $-\Delta S_{H}^{\circ}$. It can be seen that the value of ΔH_{H}° below the transition temperature during heating (the disordered form) is less exothermic than during subsequent cooling (the $L1_{2-s}$ form).

For this alloy system, hydrogen solubilities provide a sensitive and convenient tool for monitoring the ordering changes which occur (Fig. 4).

3.4.2. *Hypostoichiometric Pd–Mn alloys* ($x>0$)

The ordering of the quenched hypostoichiometric alloys was followed with the same techniques as for the stoichiometric alloy. The resistance changes during heating of a quenched alloy with $x=0.2$ ($Pd_{0.8}Mn_{0.2}$) are shown in Fig. 5. Following a linear increase in resistance with temperature, there is seen to be a more marked increase starting at about 575 K. This abrupt increase is complete at about 625 K and thereafter the increase with increasing temperature is relatively small. The cooling of the sample is shown and the subsequent reheating. (An electrical contact was broken after the first heating and, before the subsequent cooling and heating, the sample was reconnected and this accounts for the slight offset in resistance during heating and cooling.) The value of T_c is lower for this alloy than for the stoichiometric alloy (Fig. 5 and Table 2) which suggests that the structure of the hypo-

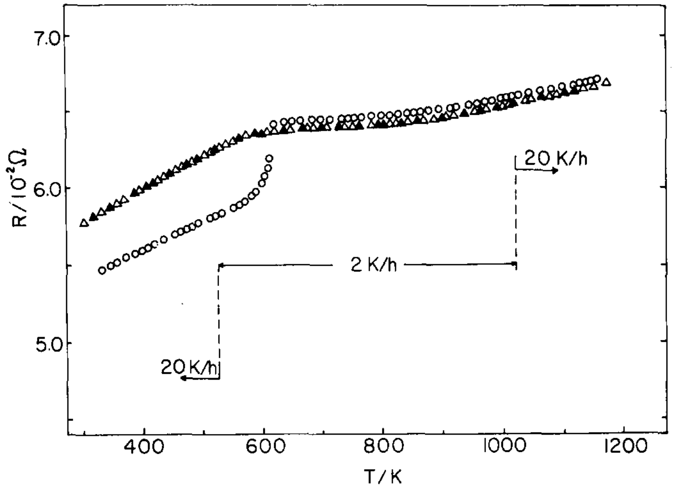


Fig. 5. Electrical resistance of $Pd_{0.80}Mn_{0.20}$ ($x=0.2$) during heating of the disordered alloy (○), subsequent cooling (▲) and reheating (△).

TABLE 2

Critical temperatures for ordering to $L1_{2-s}$ as estimated from resistivity and hydrogen solubility measurements

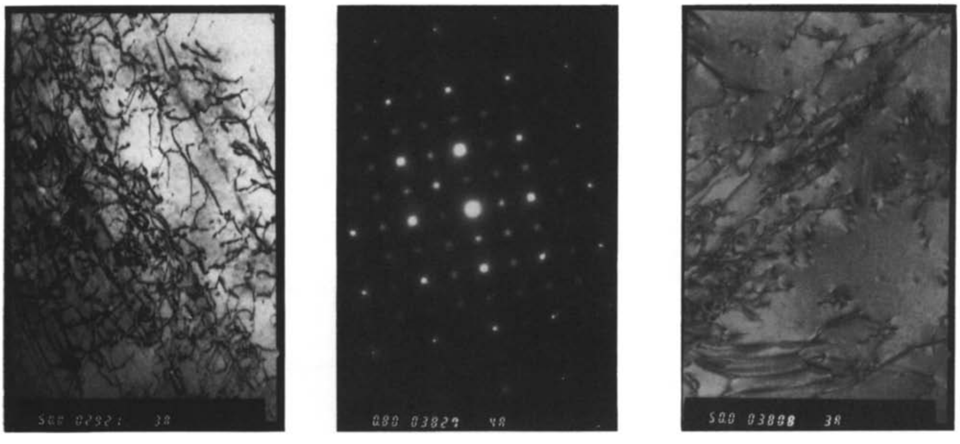
Alloy	T_c (heating) (K)	T_c (cooling) (K)
H solubility		
Pd_3Mn ($x=0$)	853	799
$Pd_{0.8}Mn_{0.2}$ ($x=0.2$)	773	725
$Pd_{0.85}Mn_{0.15}$ ($x=0.4$)	650	616
$Pd_{0.9}Mn_{0.1}$ ($x=0.6$)	555	–
Electrical resistivity		
Pd_3Mn	850	803
$Pd_{0.8}Mn_{0.2}$	–	–
$Pd_{0.85}Mn_{0.15}$	660	615
$Pd_{0.9}Mn_{0.1}$	550	550

stoichiometric alloy is not a two-phase mixture of ordered Pd_3Mn and a disordered phase but a partially ordered single non-stoichiometric phase. The lower T_c suggests that the stability of this ordered phase is less than that of the stoichiometric compound.

An unexpected feature of behavior of this alloy is that the resistance of the quenched disordered form is less than that for the ordered form. This must be partly due to the imperfect order within the domains of these alloys ($L1_{2-s}$ form). This would cause electron scattering from the disordered regions and from the domain boundaries.

The dislocation array introduced into the initially well-annealed alloy upon slow cooling from above $T > T_c$ is shown in Fig. 6(a). This dislocation array is similar to that observed in the stoichiometric alloy following the same treatment; it indicates that ordering has occurred. Although the lattice parameters of the ordered and disordered phases are very similar, dislocations are introduced; they must arise from the domain growth.

When the disordered $x = 0.2$ alloy is heated in vacuum for 67 h at 523 K, the dislocation densities observed are minimal and no superlattice reflections are noted. When this same alloy is heated at the same temperature and for the same time in hydrogen at 5 MPa, rather strong superlattice spots are observed corresponding to the $L1_2$ structure (Fig. 6(b)). It is interesting that these reflections are much stronger than those found from the formation of the $L1_{2-s}$ structure resulting from cooling this alloy from above T_c in vacuum. The dislocation array resulting from heating in hydrogen at 5 MPa and 523 K for 67 h is shown in Fig. 6(c) where it can be seen that the dislocation



(a) (b) (c)

Fig. 6. (a) A TEM bright field image of $Pd_{0.80}Mn_{0.20}$ ($x = 0.2$) which has been slowly cooled *in vacuo* from above T_c; the dislocation arrays have been introduced by the ordering. (b) An electron diffraction pattern along the [001] direction for initially disordered $Pd_{0.80}Mn_{0.20}$ ($x = 0.2$) which has been ordered in hydrogen at 5.0 MPa and 523 K for 67 h. (c) A TEM bright field image of $Pd_{0.80}Mn_{0.20}$ ($x = 0.2$) which has been ordered in hydrogen at 5.0 MPa and 523 K for 67 h. The dislocation density does not appear as great as for (a). (Magnifications: (a), (c) 35 000×).

density is significant but not as great as for the slow cooling in vacuum (Fig. 6(a)) where the $L1_{2-s}$ form is produced.

There is no maximum in electrical resistance during the heating of the $Pd_{0.8}Mn_{0.2}$ ($x=0.2$) alloy as for the stoichiometric alloy (Fig. 2) The resistivity behavior of a series of hypostoichiometric alloys is shown in Fig. 7. For the alloys with $x \geqslant 0.5$ (*i.e.* 12.5 at.% Mn or less) there is only a small change in slope which indicates that ordering of the disordered alloy may occur.

This section again concerns the following of the disorder → $L1_{2-s}$ transition *in vacuo* where the progress of the ordering is followed by solubility changes as described for the stoichiometric alloy (Fig. 4). The hydrogen solubilities were followed during heating of the disordered alloys at the equivalent of 2 K h^{-1}. As for the stoichiometric alloy, low hydrogen pressures were employed and consequently they did not cause any ordering to the $L1_2$ form. The hydrogen solubility served only as a technique to follow the progress of the ordering *in vacuo.*

The results are shown in Figs. 8–10 where $\Delta\mu_{\mathrm{H}}^{\circ}/T$ is plotted against $1/T$ during heating and subsequent cooling. (For the $Pd_{0.9}Mn_{0.1}$ alloy, instead of data from its subsequent heating, data for heating of this alloy which had been previously ordered *in vacuo* are plotted. These data should be similar to the subsequent heating data for the same alloy specimen.) It can be seen that, in contrast with the less-sensitive electron diffraction and electrical resistance results, an effect due to ordering is quite marked for the $x=0.2$, 0.3 and 0.4 alloys, again demonstrating the superiority of the hydrogen solubility technique for the Pd–Mn system for following changes in the metallic lattice.

The temperature for the onset of ordering appears to be independent of alloy composition but T_c appears to decrease with increase in x, the extent of the deviation from the stoichiometric composition. Table 2 shows

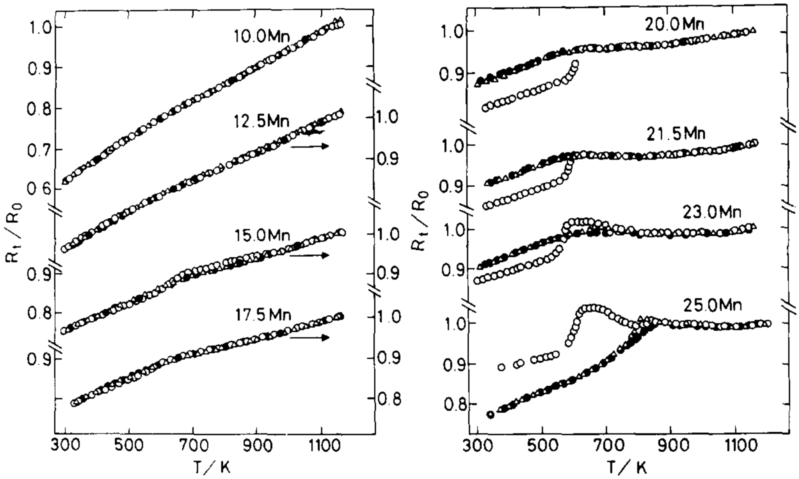


Fig. 7. Electrical resistance of a series of initially disordered Pd–Mn alloys as they are heated (○), then cooled from about 1200 K (△) and then reheated (●).

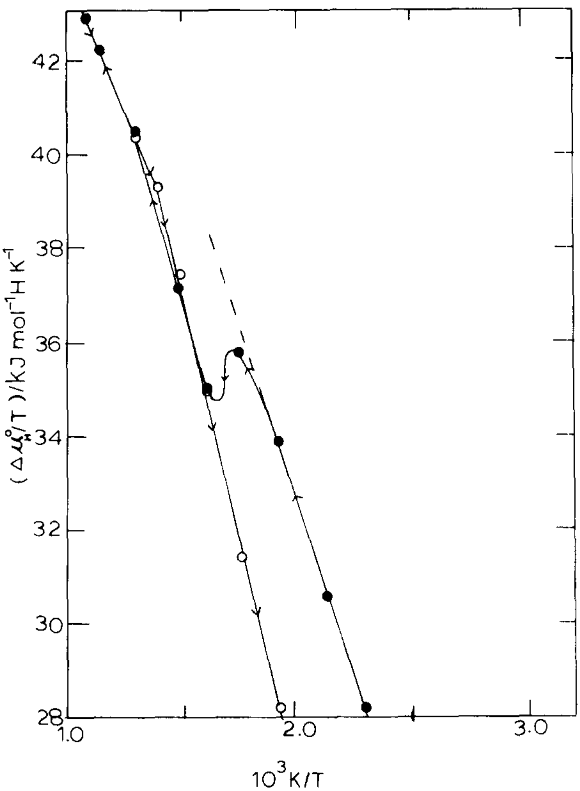


Fig. 8. Plot similar to Fig. 4 but for $Pd_{0.8}Mn_{0.2}$ ($x=0.2$): ●, heating of initially disordered alloy; ○, cooling of alloy after heating above T_c.

the critical temperatures for ordering to the $L1_{2-s}$ form as estimated from resistivity and hydrogen solubility measurements.

The solubility behaviors of all the alloys, including the stoichiometric alloys, are qualitatively similar. The relative standard hydrogen chemical potential starts to decrease, relative to the values extrapolated to low temperatures, at about 575 K and this is followed by an S-shaped behavior (Figs. 4, 8 and 9). The S shape is not so apparent for the $x=0.6$ alloy. It is of interest to correlate this solubility behavior with the electrical resistance changes during the same ordering process. It seems that, generally, changes become apparent in the solubilities before the resistance changes are detected. For example, the maximum in resistance of the stoichiometric alloy occurs at about 650 K and at this temperature the solubility behavior approaches that of the ordered alloy. The electric resistance is influenced by both the degree of order within domains and the number of domain boundaries, whereas the solubility is determined only by the former.

3.5. $L1_2 \rightarrow L1_{2-s}$ *transformation of the stoichiometric alloy*

The electrical resistance as a function of temperature corresponding to a change in order is shown in Fig. 11 where the $L1_2$ ordered form is heated

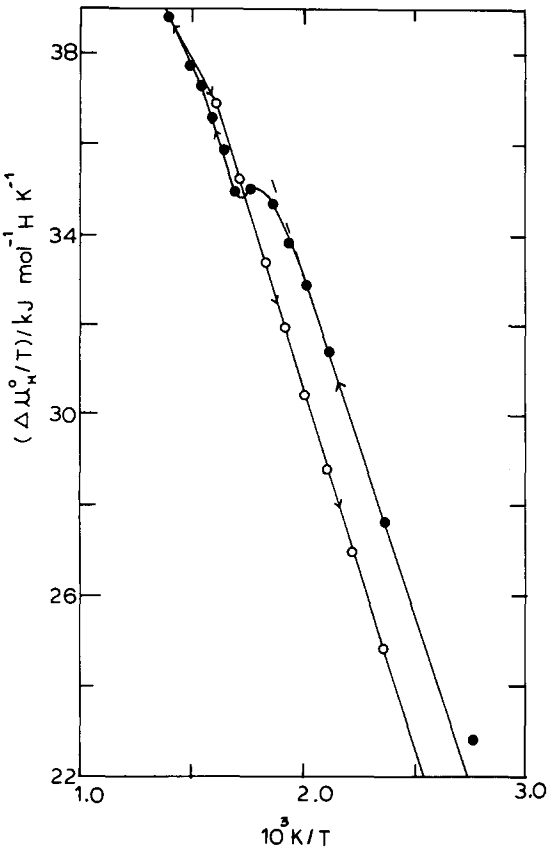


Fig. 9. Similar to Fig. 8 except for $Pd_{0.85}Mn_{0.15}$ ($x=0.4$): points are labeled in the same way as in Fig. 8.

in vacuo starting from a low temperature. (Some data below 500 K have been omitted because these changes in resistance were caused by the loss of hydrogen which had been introduced in the preparation of the $L1_2$ form.) Relative resistance against temperature data are shown for an alloy originally in the $L1_2$ form which had been prepared by exposure of the $L1_{2-s}$ form of the alloy to hydrogen at 5 MPa and 726 K. The electrical resistance of the $L1_2$ form is approximately 15% lower than that of the $L1_{2-s}$ ordered form at about 550 K, indicating the disappearance of the antiphase domain boundaries. At temperature a the alloy was quenched and shown to still be in the $L1_2$ form. Its resistance increases linearly with temperature to about 700 K and then undergoes an abrupt increase as the $L1_2 \rightarrow L1_{2-s}$ transformation occurs. At temperature b the sample was quenched and its electron diffraction pattern corresponded to $L1_{2-s}$. It is of interest that the $L1_2$ form is stable up to about 700 K *in vacuo* even though the thermodynamically stable form under these conditions is $L1_{2-s}$. The lowest temperature where the $L1_{2-s}$ form will convert into the $L1_2$ form in the presence of hydrogen has not

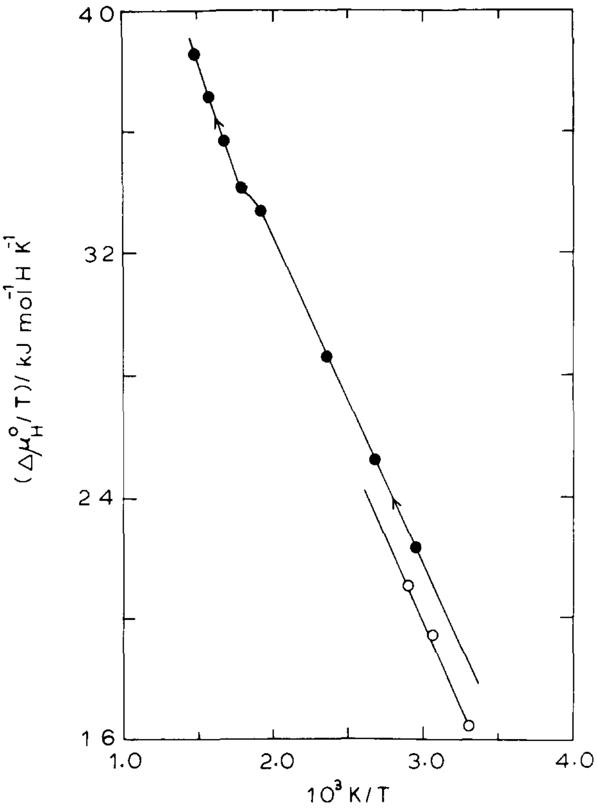


Fig. 10. Similar to Fig. 8 except for $Pd_{0.9}Mn_{0.1}$ ($x=0.6$): points are labeled in the same way as in Fig. 8.

been established experimentally; it may occur at about the same temperature where the reverse transformation occurs *in vacuo*. At temperature c, the alloy was still in the $L1_{2-s}$ form but, at d, only some very weak $L1_{2-s}$ reflections remain together with the strong principal reflections. This may indicate some residual order remaining above T_c.

The stability of the $L1_2$ form *in vacuo* was also investigated using hydrogen solubilities. A sample of $L1_2$ was annealed *in vacuo* for 24 h periods at increasing increments of 25 K starting from 573 K. After each period of heating, the sample was quenched to 523 K where the hydrogen solubility was measured in the low content region. By comparing these solubilities with the solubilities observed for pure $L1_2$ and $L1_{2-s}$ at 523 K, it was found that the $L1_2 \rightarrow L1_{2-s}$ transition commenced at approximately 660 K. The most completely ordered $L1_{2-s}$ alloy was obtained by annealing the $L1_2$ form at 700 K for 24 h; above this temperature, some disordering appeared judging from the solubility behavior at 523 K. If the resistance results are examined (Fig. 11), it can be seen that deviations from linearity commence at about 670 K; a temperature of 700 K falls into the region

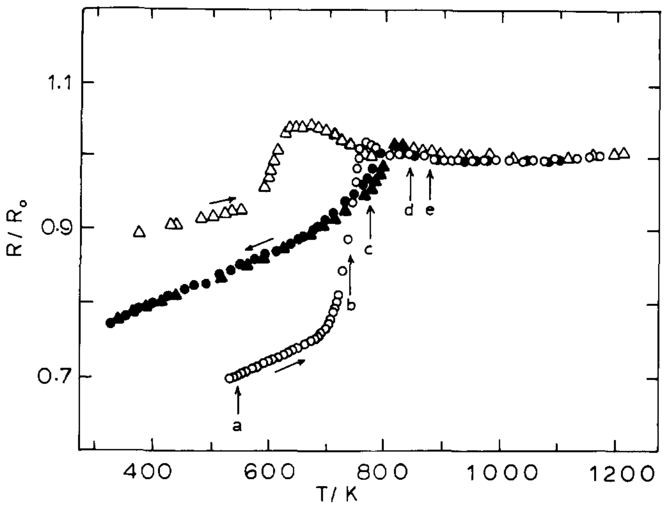


Fig. 11. Electrical resistance against temperature relationships for Pd_3Mn ($x=0$) starting heating from the $L1_2$ form (○), and then its subsequent cooling from above T_c (●). For comparison the behavior of the initially disordered alloy is shown during heating (△), and subsequent cooling (▲) from above T_c.

where the resistance undergoes rapid changes which must be partially connected with disordering.

3.6. *Conclusions*

This is the first time that the $L1_2$ ordered form of Pd_3Mn has been prepared [7] and this illustrates the potential for employing hydrogen in the preparation of materials which may not be obtained by other synthetic methods. It is possible that this approach could be employed in the preparation of technologically useful materials. It should be noted that these hydrogen-induced syntheses should occur at relatively low temperatures and this may prove advantageous. For example, certain changes could be induced by hydrogen *in situ* in microstructural components which could not be accomplished by conventional methods.

It should also be noted that this is an unambiguous example of hydrogen-induced lattice mobility where the resulting changes have occurred throughout the lattice and have been clearly identified by their electron diffraction patterns.

This report also shows that the disordered $L1_2$ and $L1_{2-s}$ forms can exist for $0.6 \geqslant x \geqslant 0$ and that partially ordered $L1_{2-s}$ results from annealing *in vacuo*, in disagreement with earlier work [10–13].

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