Journal of Alloys and Compounds, 184 (1992) 57–67
JALCOM 188

The kinetics of hydrogen-induced ordering in Pd_3Mn to the $L1_2$-type structure

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(Received October 30, 1991)

Abstract

A study of the kinetics of hydrogen-induced ordering from "as-quenched" and initially ordered ($L1_{2\text{-}s}$-type) states in Pd_3Mn to the $L1_2$-type structure has been carried out to examine the conditions necessary for the ordering, *i.e.* the hydrogen pressures, temperatures and times and to consider the ordering mechanism, using electrical resistance measurements. The ordering rate for the initially ordered alloy of the $L1_{2\text{-}s}$-type structure is slower than that for the initially "as-quenched" state. The hydrogen-induced ordering to the $L1_2$-type structure may occur from the periodic one-dimensional antiphase domain structure of the $L1_{2\text{-}s}$ type with a cubic fundamental cell, in which a step shift, $(\boldsymbol{a}_2+\boldsymbol{a}_3)/2$, is introduced at every two cells along the a_1 axis, by attaining a particular stress state due to the lattice expansion caused by the preferential occupation of hydrogen in the octahedral sites of six palladium nearest-neighbor atoms.

1. Introduction

Pd_3Mn, after slow cooling below its critical temperature T_c of about 803 K, forms a periodic one-dimensional antiphase domain structure with a domain size $M=2$, *i.e.* a long-period superlattice, which has been recently found to belong to the Al_3Zr type [1] rather than the previously accepted Ag_3Mg type but will be referred to here as a $L1_{2\text{-}s}$ type. Whereas on rapidly quenching into ice–water from high temperatures, *e.g.* 1193 K, it mainly forms a disordered f.c.c. structure, although electron diffraction shows a very faint superlattice reflection of the $L1_{2\text{-}s}$-type structure [2–4] which indicates that it is not possible to obtain the fully disordered alloy even with the rapid quenching technique. The solubility of hydrogen in the $L1_{2\text{-}s}$-type ordered state is much greater than in the "as-quenched" state as determined from solubility measurements below the order–disorder transition temperature [3, 4]. However, the diffusivity of hydrogen in the "as-quenched" state is greater than that for the ordered form [5].

When the initially "as-quenched" and the initially ordered (long-range order of $L1_{2\text{-}s}$-type) alloys of Pd_3Mn were exposed to hydrogen gas at elevated temperatures, *e.g.* at 523 K and $p_{H_2}=5$ MPa, they were both found to

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transform into another ordered structure, an $L1_2$ type (Cu_3Au type), with accompanying large dislocation densities [3, 6]. The hydrogen-induced $L1_2$-type structure is metastable below a temperature of about 650 K even in the absence of dissolved hydrogen; the electrical resistance in its hydrogen-free state is 13–17% lower than that of the $L1_{2\text{-}s}$-type structure at 550 K [7].

The detailed conditions necessary for hydrogen-induced ordering, *i.e.* the hydrogen pressures, temperatures and times, are not well established; information about the kinetics of these ordering processes is lacking. The mechanism for this hydrogen-induced ordering is also unknown but it must be a consequence of the lattice expansion accompanying the solution of hydrogen, *i.e.* the lattice expansion may allow the necessary metal atom rearrangement.

Recently it has been observed from a neutron diffraction study [1] that deuterium atoms in the ordered $L1_{2\text{-}s}$-type structure of Pd_3Mn occupy mainly the octahedral sites which have only palladium nearest-neighbor atoms and to a much lesser extent octahedral sites with one manganese and five palladium nearest-neighbor atoms. It should also be pointed out that the occurrence of the transition $L1_{2\text{-}s} \rightarrow L1_2$ when hydrogen gas is added to the system can be viewed as a consequence of LeChatelier's principle because more hydrogen dissolves in the $L1_2$ form than in the $L1_{2\text{-}s}$ form and the lattice rearrangement relieves the applied stress, *i.e.* the hydrogen pressure.

The aim of this study is to consider the ordering mechanism by obtaining more detailed information on the hydrogen-induced ordering using electrical resistance measurements to follow the kinetics of the changes.

2. Experimental details

The Pd_3Mn alloy was prepared in a high frequency induction furnace under an argon atmosphere. The buttons were rolled into a foil of about 140 μm. Samples for the electrical resistance measurements were cut from the foil so that the dimensions were 2 mm × 30 mm and for electron microscopy the samples were trepanned from the foil into discs of 3 mm diameter.

The following two kinds of starting material were employed for these experiments on hydrogen-induced ordering: one was the initially "as-quenched" alloy, and the other was the initially "ordered" alloys. The former samples were prepared by rapid quenching from about 1193 K into ice–water, while simultaneously breaking the silica tubes which contained the samples wrapped in zirconium foil. The quenched samples were mainly in the disordered f.c.c. phase although, as noted above, electron microscopy observations showed very faint superlattice reflections due to the $L1_{2\text{-}s}$-type structure, *i.e.* some short-range order of the $L1_{2\text{-}s}$ type exists. The initially ordered samples of the $L1_{2\text{-}s}$-type structure were prepared by slow cooling *in vacuo* from about 1175 K to room temperature at a cooling rate of 2 K h^{-1}. All the samples were lightly abraded with fine emery paper and then chemically etched using a solution of 2:2:1 H_2SO_4:HNO_3:H_2O. The final thicknesses of the samples were about 110 μm.

The experimental procedure for following the kinetics of the hydrogen-induced ordering differs from the previous method employed [3, 4, 6] where the same samples, which were to be examined by electron diffraction and transmission electron microscopy, were placed in a stainless steel tube, evacuated to about 2×10^{-6} Torr at 323 K and then exposed to a given pressure of hydrogen gas at 323 K for 24 h. The temperature was increased to a given value in the hydrogen gas and held for a given period of time.

In the present experiments a reaction vessel was employed which was similar to that previously employed [3, 4, 6]. It contained the alloy sample which had leads spot welded to it for following the electrical resistance by the four-point method. The reaction vessel also contained small samples of an identical alloy which had been prepared for subsequent electron microscopy examination. In order to follow the ordering process the vessel containing these samples was first evacuated at room temperature and then rapidly heated by raising a pre-heated furnace around it; a time of approximately 4 min was needed to raise the sample to 623 K and 5 min for 673 and 726 K. (These times were determined from independent measurements using a nickel wire whose resistance–temperature behavior was known.) A given pressure of hydrogen gas was introduced at the elevated temperature and the electrical resistance of the alloy was followed as a function of time during the ordering using a strip-chart recorder.

After the sample had been exposed to hydrogen for a given period of time, the vessel was rapidly cooled by immersion into ice–water; the samples which had been prepared for electron microscopy were jet electropolished in a solution of perchloric acid and acetic acid (1:4 by volume) at a temperature between 263 and 278 K. Electron diffraction patterns and electron micrographs were obtained using a Hitachi H-800 electron microscope.

3. Results and discussion

3.1. *Effect of temperature on the ordering*

Figures 1 and 2 show the effect of temperature on the electrical resistance *vs.* time relationships for the exposure of the initially "as-quenched" and the $L1_{2\text{-}s}$ ordered alloys at a hydrogen pressure p_{H_2} of 1.0 MPa. The same figures also show the relationships obtained in a hydrogen-free environment at 726 K, *i.e. in vacuo*, for comparison. R_0 is the resistance just before exposure to hydrogen at each temperature, *i.e.* of the initial free state.

For both alloy samples it can be seen that from the moment that the hydrogen gas is introduced (Figs. 1 and 2) the electrical resistance increases very abruptly at each temperature and then the rate of increase gradually decreases until it eventually decreases, causing a maximum at the higher temperatures. The initial abrupt increase in electrical resistance upon introduction of hydrogen is mainly believed to be due to the effect of dissolved hydrogen on the electrical resistance of the samples. The solution process

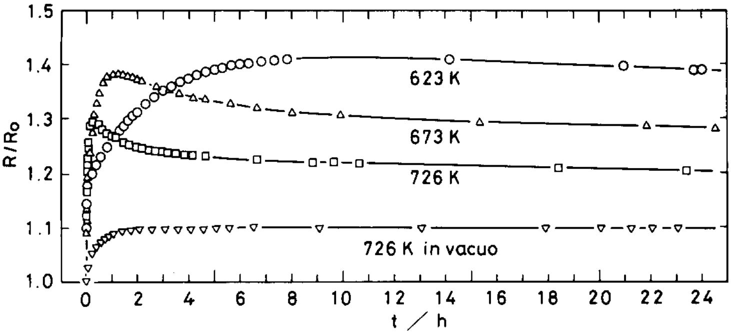

Fig. 1. Electrical resistance *vs.* time relationships at different temperatures under a hydrogen pressure of 1.0 MPa for a sample which was initially "as-quenched" Pd_3Mn.

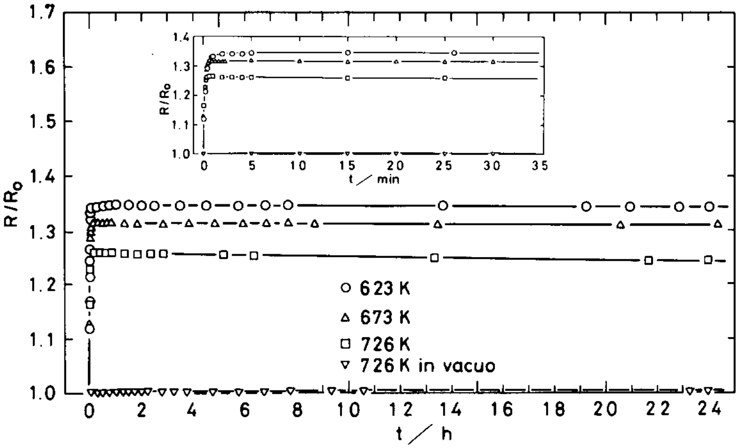

Fig. 2. Electrical resistance *vs.* time relationships at different temperatures under a hydrogen pressure of 1.0 MPa for a sample which was initially ordered ($L1_{2\text{-}s}$-type) Pd_3Mn. The inset is an enlarged version for smaller times.

is expected to be faster for the "as-quenched" alloy than for the $L1_{2\text{-}s}$ form because of the more rapid diffusion in the former form [5]. However, it is expected that the diffusion will be relatively rapid for both alloy forms at these elevated temperatures for the solution to occur nearly instantaneously on the time scale of Figs. 1, 2, 5 and 6.

The diffusion coefficients in both forms have been measured in a lower temperature range [5] and, if the activation energy and pre-exponential factors are appropriate, we can estimate the diffusion coefficients and the times needed for dissolving the hydrogen. For example, for the ordered alloy we obtain $D = 1.87 \times 10^{-11}$ m^2 s^{-1} at 623 K. Using the known solutions for diffusion from a constant pressure into a finite sheet [8], we find that after 4 min over 90% of the hydrogen should be dissolved into the sample assuming that surface steps are not slow which is reasonable for such elevated temperatures.

The resistance decrease and appearance of the maxima are most noticeable (*e.g.* Fig. 1) for the initially "as-quenched" samples which order in hydrogen to the $L1_2$ form. With increase in temperature the peak maxima shift to shorter times. The gradual increase in resistance with time for the "as-quenched" sample *in vacuo* is caused by the transition to the $L1_{2\text{-}s}$ form.

Figures 3(a)–3(e) show the [001] electron diffraction patterns after exposure to hydrogen for a series of different times at 726 K at $p_{H_2} = 1.0$ MPa for the initially "as-quenched" alloy; Fig. 3(f) shows the pattern for a similarly treated "as-quenched" alloy after being exposed to 1.0 MPa hydrogen pressure for 24 h at 623 K.

As early as after hydrogenation for 4 min (Fig. 3(a)), superlattice reflections characteristic of the hydrogen-induced $L1_2$-type structure can be seen, in addition to a faint reflection of $L1_{2\text{-}s}$ type structure. With an increase in hydrogenation time the reflections of the $L1_2$-type become clearer (Figs. 3(b)–3(e)). In particular, the sample after 24 h exposure to hydrogen (Fig. 3(e)) exhibits streaked spots which may be related to the stacking faults formed during the hydrogen-induced ordering. Figure 4 shows the diffraction patterns of the hydrogenated samples for the initially ordered ($L1_{2\text{-}s}$-type) alloys. It can be seen that the $L1_{2\text{-}s}$-type structure remains after 1 h exposure to hydrogen at 726 K, although superlattice reflections due to hydrogen-induced ordering appear for the samples exposed to hydrogen at the lower

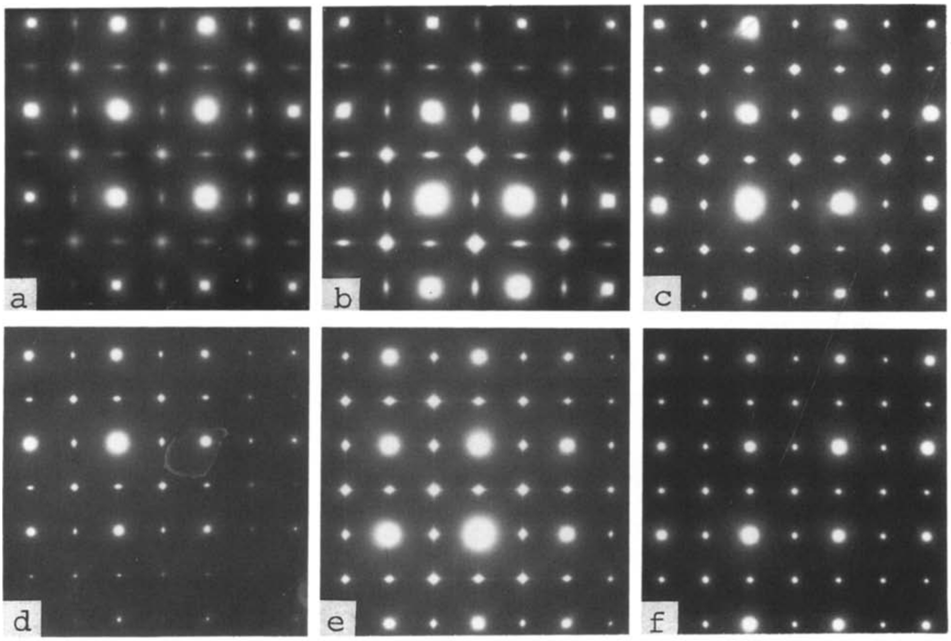

Fig. 3. Electron diffraction patterns, after exposure to hydrogen for different times (a)–(e) at 726 K and (f) at 623 K under a hydrogen pressure of 1.0 MPa for initially "as-quenched" Pd_3Mn (the beam is along [001]): (a) 4 min; (b) 1 h; (c) 5 h; (d) 10 h; (e) 24 h; (f) 24 h.

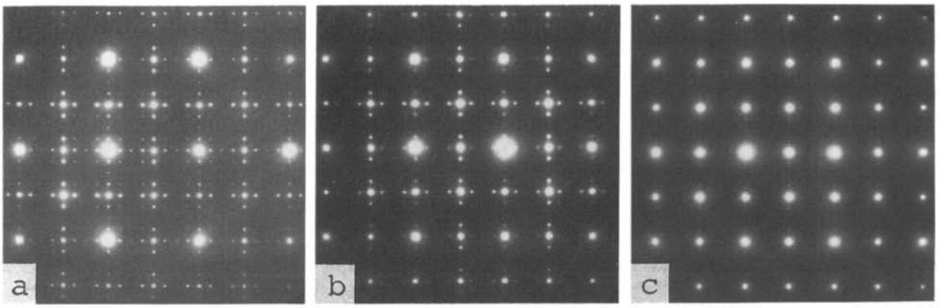

Fig. 4. Electron diffraction patterns, after exposure to hydrogen at various temperatures and times under a hydrogen pressure of 1.0 MPa for initially ordered ($L1_{2-s}$-type) Pd_3Mn (the beam is along [001]): (a) 1 h at 726 K; (b) 24 h at 673 K; (c) 24 h at 623 K.

temperatures of 623 and 673 K and for longer period of times (Figs. 4(b) and 4(c)).

From these results it can be concluded that the hydrogen-induced ordering to the $L1_2$-type structure is more difficult for the initially ordered samples than for the initially "as-quenched" samples. This is note worthy in view of the fact that the initially ordered sample dissolves more hydrogen than the "as-quenched" sample [3–5] although the diffusivity of hydrogen in the initially ordered state is smaller than that for the initially "as-quenched" form [5]. The driving force for ordering of the "as-quenched" alloy is presumably greater than for the $L1_{2-s} \rightarrow L1_2$ transition because the thermodynamic stability of the $L1_{2-s}$ structure must be greater than that of the "as-quenched" material, *i.e.* the mainly disordered form of the alloy.

From the resistance *vs.* time relationships shown in Fig. 1 for the initially "as-quenched" samples, the time τ was determined corresponding to the peak maxima at 623, 673 and 726 K, which are inversely proportional to the rate of hydrogen-induced ordering. The apparent activation energy Q for the ordering, determined from the plots of $\log(1/\tau)$ *vs.* $1/T$, was about 320 kJ mol^{-1}. It is interesting that the Q value is approximately equal to the sum of $Q_H = 33.6$ kJ mol^{-1} for hydrogen diffusion through the alloy [5] and $Q_{Mn} = 276$ or 281 kJ mol^{-1} for manganese diffusion in γ-Fe [9] or in nickel [10] respectively and/or $Q_{Pd} = 266$ kJ mol^{-1} for self-diffusion of palladium atoms [10]. Therefore the hydrogen-induced ordering process may be determined by the simultaneous diffusion of hydrogen and the migration of manganese and/or palladium atoms.

3.2. *Effect of hydrogen pressure on the ordering*

Figures 5 and 6 show the effect of hydrogen pressure on the electrical resistance *vs.* time relationships during exposure to hydrogen at 726 K of the initially "as-quenched" and the initially ordered alloys respectively.

It can be seen from Fig. 5 that generally, the higher pressure of hydrogen, the shorter is the time to reach the peak maximum. However, for the case of the lowest hydrogen pressure, the resistance only increases gradually; this

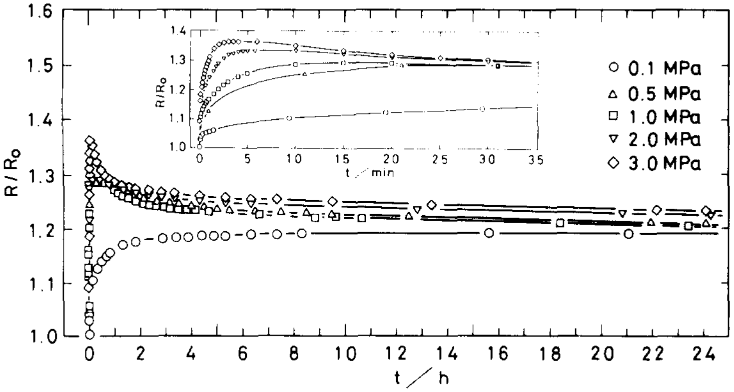

Fig. 5. Electrical resistance *vs.* time relationships at 726 K under different hydrogen pressures for initially "as-quenched" Pd_3Mn. The inset is an enlarged version for smaller times.

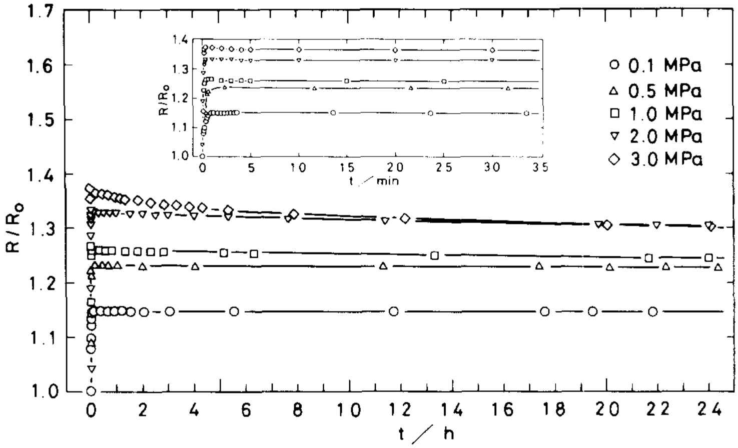

Fig. 6. Electrical resistance *vs.* time relationships at 726 K under different hydrogen pressures for initially ordered ($L1_{2\text{-}s}$-type) Pd_3Mn. The inset is an enlarged version for smaller times.

corresponds to the transition of the short-range to long-range order of the $L1_{2\text{-}s}$-type structure.

Figures 7 and 8 show the [001] electron diffraction patterns, after exposure to hydrogen at 726 K for 24 h under various hydrogen pressures for the initially "as-quenched" and the initially ordered alloys respectively. In the case of the lower hydrogen pressures, *e.g.* $p_{H_2}=0.1$ and 0.5 MPa, the relatively sharp and intense superlattice reflections characteristic of the $L1_{2\text{-}s}$-type structure can be still seen even after 24 h exposure to hydrogen. It is especially obvious that the initially ordered alloy remains in the $L1_{2\text{-}s}$ form. However, in the case of higher hydrogen pressures, superlattice reflections due to hydrogen-induced ordering are clearly observed. Therefore the necessary pressure of hydrogen for hydrogen-induced ordering at 726 K seems to be above about 0.5 MPa for the initially "as-quenched" sample, and above about 1.0 MPa for the initially ordered alloy. The hydrogen-induced

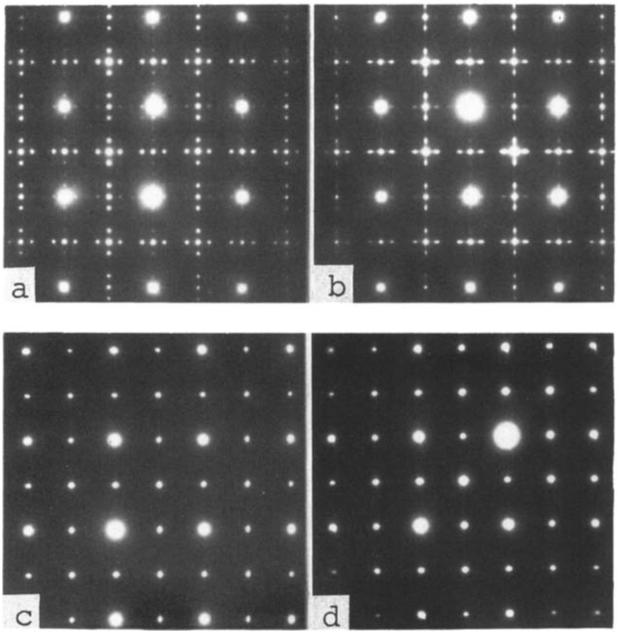

Fig. 7. Electron diffraction patterns, after exposure to hydrogen at 726 K for 24 h under different hydrogen pressures for initially "as-quenched" Pd_3Mn (the beam is along [001]): (a) 0.1 MPa; (b) 0.5 MPa; (c) 2.0 MPa; (d) 3.0 MPa.

ordering at higher temperatures requires greater pressures of hydrogen because the solubility of hydrogen is smaller than at lower temperatures. Conversely low temperatures are also unfavorable for ordering because the rearrangement of the metal atoms becomes more difficult.

Figure 9 shows the electron micrographs of the hydrogen-induced $L1_2$-type ordered samples. Figures 9(a)–9(c) are the dark field images taken with reflection around the (010) plane, and Figs. 9(d) and 9(e) are the bright field images for the same samples corresponding to Figs. 9(b) and 9(c) respectively. The dark field images show that the hydrogen-induced ordered domains obtained from the initially "as-quenched" samples under a high pressure of hydrogen (Fig. 9(b)) are relatively larger than those obtained under lower hydrogen pressures (Fig. 9(a)), and that the ordered domains obtained from the initially ordered ($L1_{2\text{-}s}$-type) sample (Fig. 9(c)) under the same hydrogen pressure are larger than that from the initially "as-quenched" sample (Fig. 9(b)). From the bright images (Figs. 9(d) and 9(e)) there can be observed relatively uniform slip bands running like a tweed pattern over the surface. These superlattice dislocations may have moved with little interaction with neighboring dislocations; they consist of two pairs of partial dislocations held together by the antiphase domain boundaries.

Ahlzén *et al.* [1] have observed that deuterium preferentially occupies the octahedral interstices with six palladium atoms as nearest neighbors. Since these sites are adjacent to the antiphase domain boundaries (Fig. 10),

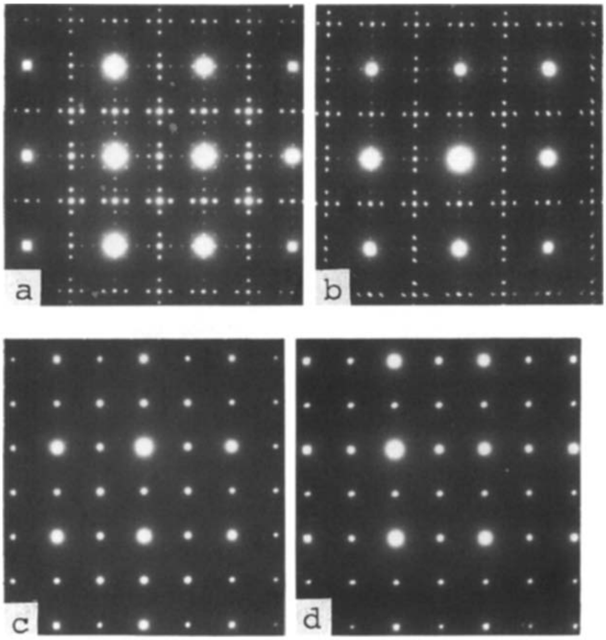

Fig. 8. Electron diffraction patterns, after exposure to hydrogen at 726 K for 24 h under different hydrogen pressures for initially ordered ($L1_{2-s}$-type) Pd_3Mn (the beam is along [001]): (a) 0.1 MPa; (b) 0.5 MPa; (c) 2.0 MPa; (d) 3.0 MPa.

it is possible that the occupation of these interstices and the accompanying lattice expansion in the $L1_{2-s}$ form assists the step shift, $(\boldsymbol{a}_2+\boldsymbol{a}_3)/2$, which is required for the $L1_{2-s} \rightarrow L1_2$ transition. This transformation introduces superlattice dislocations consisting of two pairs of partial dislocations joined by a stacking fault: $(a/2)[011] \rightarrow (a/6)[\bar{1}12]+(a/6)[121]$ with a Burgers vector of $(a/2)[011]$ on the $\{111\}$ plane (Fig. 10). The slip bands introduced by these dislocations are seen in Fig. 9(e).

A mechanism for the ordering of the "as-quenched" alloy is more difficult to formulate because the structure of this form of the alloy probably is mainly disordered with some small regions where $L1_{2-s}$ has formed. The ordering of this form occurs more easily than the $L1_{2-s} \rightarrow L1_2$ transition and, as noted above, this may be due to the greater driving force for this transition, *e.g.* the activation energy for the mobility of the metal atoms needed for the rearrangement may be less because of the greater stability of the final than the initial form of the alloy.

4. Conclusions

The hydrogen-induced ordering to $L1_2$-type structure from the initially "as-quenched" and the initially ordered (long-range order of $L1_{2-s}$-type) Pd_3Mn has been examined at different temperatures and various hydrogen pressures

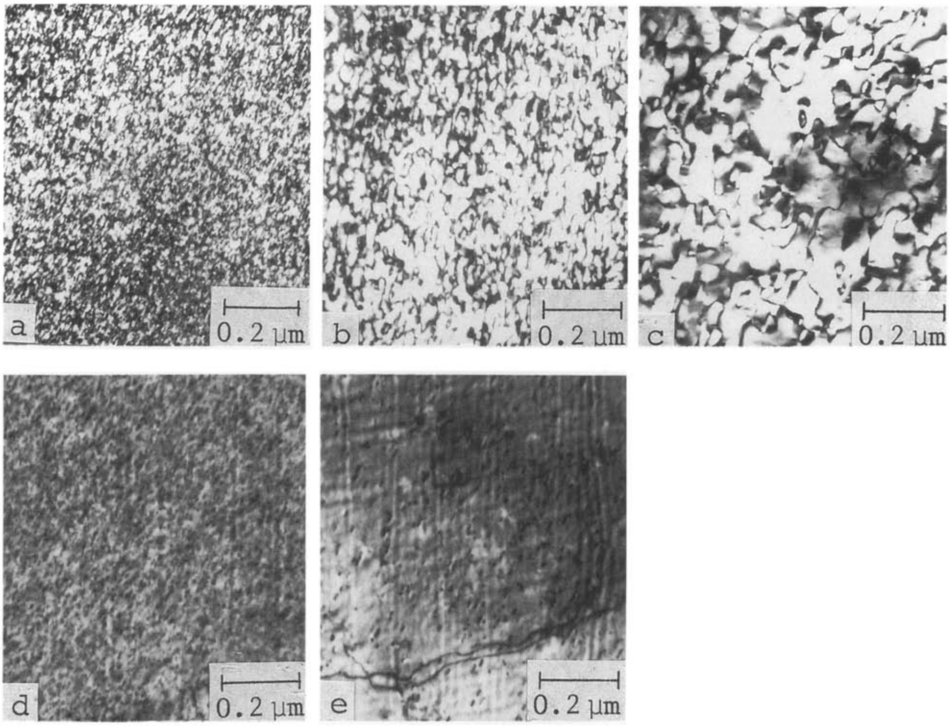

Fig. 9. Electron micrographs of the hydrogen-induced $L1_2$-type ordered samples: (a)–(c) the dark field images taken with reflection around the (010) plane for the ordered samples which were obtained from (a), (b) initially "as-quenched" Pd_3Mn under (a) $p_{H_2} = 1.0$ MPa and (b) $p_{H_2} = 3.0$ MPa at 726 K for 24 h and obtained from (c) initially ordered ($L1_{2\text{-}s}$-type) Pd_3Mn under $p_{H_2} = 3.0$ MPa at 726 K for 24 h; (d), (e) the bright field images of the same samples corresponding to (b) and (c) respectively.

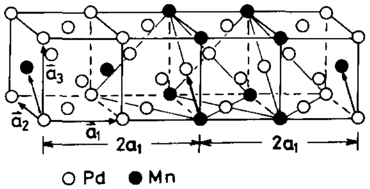

Fig. 10. Atomic arrangement of the one-dimensional long period ordered $L1_{2\text{-}s}$-type Pd_3Mn.

by following the ordering kinetics using electrical resistance measurements and by electron microscopy observations.

The resistance increases abruptly as soon as the hydrogen gas is introduced and thereafter attains a peak maximum for the initially "as-quenched" alloys; the resistance decreases gradually with progress of the hydrogen-induced ordering. The ordering rate for the initially ordered alloy of the $L1_{2\text{-}s}$-type structure is slower than that for the initially "as-quenched" state. The reason may be because the alloy is originally in a long-range ordered $L1_{2\text{-}s}$-type structure which is more stable towards the metal atom rearrangement because of hydrogen solution than the disordered form ("as quenched"). With respect to the effects of temperature and hydrogen pressure on the ordering, the conditions of greater hydrogen pressures and temperatures are favorable for the ordering. However, at high temperatures, higher pressure are needed, because the solubility of hydrogen decreases.

The hydrogen-induced ordering to the $L1_2$-type structure may occur from the periodic one-dimensional antiphase domain structure of the $L1_{2\text{-}s}$ type with a cubic fundamental cell, in which a step shift, $(\boldsymbol{a}_2 + \boldsymbol{a}_3)/2$, is introduced at every two cells along the a_1 axis by attaining a particular stress state due to the lattice expansion caused by the preferential occupation of hydrogen in the octahedral sites consisting of six palladium nearest-neighbor atoms.

Acknowledgment

T.B.F. wishes to thank the National Science Foundation for financial support.

References

1 P. J. Ahlzén, Y. Andersson, R. Tellgren, D. Rodic, T. B. Flanagan and Y. Sakamoto, *Z. Phys. Chem. N.F.*, *163* (1989) 213.

2 D. Watanabe, *Trans. Jpn. Inst. Met.*, *3* (1962) 234.

3 T. B. Flanagan, A. P. Craft, T. Kuji, K. Baba and Y. Sakamoto, *Scr. Metall.*, *20* (1986) 1745.

4 K. Baba, Y. Sakamoto, T. B. Flanagan, T. Kuji and A. P. Craft, *Scr. Metall.*, *21* (1987) 299.

5 K. Baba, Y. Sakamoto and T. B. Flanagan, *J. Chem. Soc., Faraday Trans. I*, *84* (1988) 459.

6 K. Baba, Y. Niki, Y. Sakamoto, T. B. Flanagan and A. P. Craft, *Scr. Metall.*, *21* (1987) 1147.

7 K. Baba, Y. Niki, Y. Sakamoto, A. P. Craft and T. B. Flanagan, *J. Mater. Sci. Lett.*, *7* (1988) 1160.

8 J. Crank, *The Mathematics of Diffusion*, Oxford University Press, Oxford, 1956.

9 W. Hume-Rothery, *The Structure of Alloys of Iron — An Elementary Introduction*, Pergamon, Oxford, 1966.

10 Japan Institute of Metals, *Metals Data Handbook*, Maruzen, Tokyo, 1974.