Effect of hydrogen on the stabilities of ordered structures in Pd$_3$Mn

Pragati Kumar, M. Hareesh, R. Balasubramaniam*

Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208016, India

Abstract

Thermodynamic stabilities of the ordered structures in Pd$_3$Mn have been theoretically evaluated, both in the presence and absence of hydrogen. The internal energies of the L1$_2$ and L1$_{2-s}$ structures of Pd$_3$Mn were found to be the same. The L1$_{2-s}$ phase is the stable phase at all temperatures, both in the presence and absence of hydrogen, according to the statistical thermodynamic calculations indicating that the hydrogen-induced ordering phenomenon from the L1$_{2-s}$ to the L1$_2$ structure could be due to stress-assisted motion of atoms as a result of hydrogen occupying interstitial sites in the L1$_{2-s}$ form. The difference in stabilities between the L1$_2$ and L1$_{2-s}$ structures is small for both of the cases. The difference in configurational entropies between the two ordered forms of Pd$_3$Mn decreases with increasing hydrogen concentration. The effect of configurational entropy on the stability of the L1$_2$ and L1$_{2-s}$ phases has been addressed.

Keywords: Hydrogen induced ordering; Statistical thermodynamics; Internal energy; Configurational entropy

1. Introduction

In the Pd–Mn system, the stoichiometric Pd$_3$Mn composition possesses a disordered f.c.c. structure above its critical temperature (803 K) [1–4]. The compound Pd$_3$Mn undergoes an order–disorder transformation below its critical temperature. The ordered Pd$_3$Mn structure is a long period structure (LPS) of the Al$_3$Zr type [5], referred to henceforth as the L1$_{2-s}$ structure in this presentation. The introduction of hydrogen at relatively low pressures (5 MPa) and high temperatures (500 K–726 K) below the critical temperature T_c induces ordering of the LPS to the ordered L1$_2$ structure [6]. The L1$_{2-s}$ and L1$_2$ structures of Pd$_3$Mn are shown in Fig. 1 and Fig. 2 respectively. Hydrogen-induced ordering to the L1$_2$ structure is also observed from the quenched and disordered f.c.c. structure below T_c in the presence of hydrogen [6].

In this presentation, we attempt to estimate theoretically and to compare qualitatively the stabilities of the L1$_{2-s}$ and L1$_2$ structures, with and without hydrogen. The observed stabilities of these ordered structures of Pd$_3$Mn have been earlier explained by other workers considering electronic effects on stability [4, 7]. In this
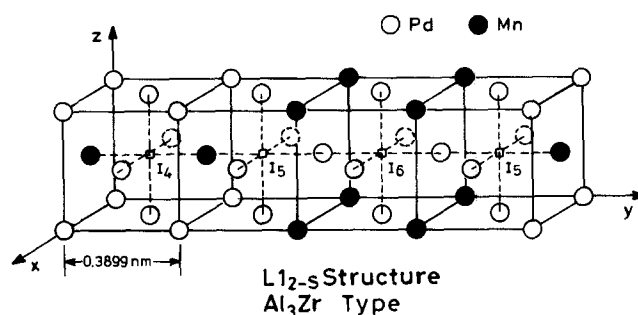

Fig. 1. Long period ordered L1$_{2-s}$ structure of Pd$_3$Mn. The I$_4$, I$_5$ and I$_6$ interstitial sites have been shown. Notice the coordination of Pd and Mn atoms in the structure.

presentation, the stabilities of the ordered structures in Pd$_3$Mn are compared from a statistical thermodynamics viewpoint. The aim is to compare the statistical free energies of the L1$_2$ and the L2$_{2-s}$ structures to provide information about the stable structure at ambient temperature, both in the presence and absence of hydrogen. The stability of the disordered f.c.c. phase is not considered in the present analysis because this phase is unstable below T_c. In fact, it has been shown that weak diffuse superlattice spots of the L1$_{2-s}$ structure are obtained from the quenched and disordered f.c.c. phase even after rapid cooling, indicating that it is
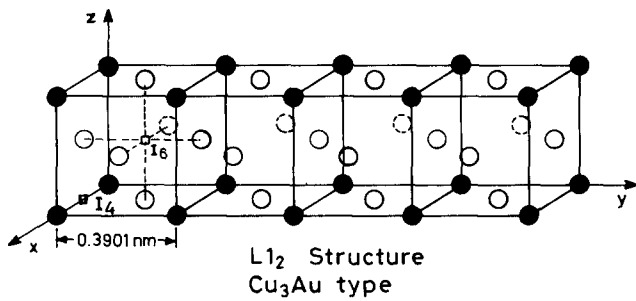
Fig. 2. Ordered $L1_2$ structure of Pd_3Mn. The Pd atoms occupy the face centres and the Mn atoms occupy the cube corners. The I_4 and I_6 interstitial sites have been indicated.

difficult to suppress the order–disorder transformation below T_c [1,2,6,8].

Earlier neutron diffraction studies have shown that hydrogen occupies octahedral interstices in palladium alloys, to which group Pd_3Mn belongs [9]. The occupation probabilities of hydrogen among the various interstitial sites in the $L1_2$ and $L1_{2-s}$ structures have been determined precisely at ambient temperature by neutron diffraction [5,10]. The statistical thermodynamics calculation performed is rigorous since the observed experimental probabilities of hydrogen occupancy in the different interstitial sites have been taken into account.

2. Stabilities of ordered structures in Pd_3Mn

The stability of a given structure is, in general, given by its free energy of formation. The Helmoltz free energy F of a structure at a given temperature T is given by

$$F = E - TS \tag{1}$$

where E is the internal energy and S the entropy of the structure. Statistical thermodynamics enables the determination of these parameters.

The internal energy is given in terms of the energies of the particles which constitute the system. Internal energy is composed of [11]

$$E = E_i + E_m \tag{2}$$

where E_i is the configurational energy of the system (determined by the assignment of the type of atom to each lattice site) and E_m is the part of internal energy that is independent of the configuration of atoms and depends only on the composition of the alloy.

The entropy of the structure is made up of three components: thermal entropy, configurational entropy S_i and electronic entropy. The electronic contribution to the stability of the ordered structures in Pd_3Mn has been earlier discussed by Iwasaki et al. [4], and Gjönnes and Olsen [7]. Thermal entropy arises from the number of ways the available thermal states of the system can

be shared among the constituent particles. Configurational entropy, on the contrary, arises from the number of ways in which the particles can be distributed over the space available to them. The configurational entropy is important in determining the stability of any structure and is given by [12]

$$S_i = k \ln \Omega \tag{3}$$

where k is the Boltzman constant (1.38×10^{-23} J mol^{-1} K^{-1}) and Ω, the number of configurational microstates available to the system, is generally referred to as thermodynamic probability.

3. Internal energy of ordered structures

The $L1_2$ and $L1_{2-s}$ structures have the same composition and hence E_m should be the same for both of them. Therefore, the configurational part of internal energy alone would be addressed below in calculating the internal energies.

The configurational component of the internal energy may be expressed in terms of the interaction energy of pairs of different atoms located at various separations. In this presentation we have used the nearest-neighbour approximation [13,14] for which E_i takes the form

$$E_i = N_{AA} \nu_{AA} + N_{BB} \nu_{BB} + N_{AB} \nu_{AB} \tag{4}$$

where ν_{AA}, ν_{BB} and ν_{AB} are the interaction energies of nearest pairs of neighbouring atoms A–A, B–B, and A–B respectively and N_{AA}, N_{BB} and N_{AB} are the number of A–A, B–B and A–B bonds in the structure respectively.

In the case of the $L1_2$ structure (Fig. 2), each Pd atom is surrounded by 8 Pd atoms at a distance of $a/\sqrt{2}$ and 4 Mn atoms also at a distance $a/\sqrt{2}$ (a is the lattice parameter), while each Mn atom is surrounded by 12 Pd atoms. Thus the coordination number of either Pd or Mn in the structure is 12. In order to determine the internal energy in the framework of nearest-neighbour approximation [13,14], the number N_{Pd-Pd} of Pd–Pd, the number N_{Mn-Mn} of Mn–Mn and the number N_{Pd-Mn} of Pd–Mn bonds are given by

$$N_{Pd-Pd} = \tfrac{1}{2} (12N_{Pd} - N_{Pd-Mn}) \tag{5}$$

$$N_{Mn-Mn} = \tfrac{1}{2} (12N_{Mn} - N_{Pd-Mn}) \tag{6}$$

If the total number of atoms in the structure is N, then

$$N = N_{Pd} + N_{Mn}$$

where N_{Pd} is the total number of Pd atoms and N_{Mn} is the total number of Mn atoms. The stoichiometry of Pd_3Mn provides

$$N_{Pd} = \frac{3N}{4} \text{ and } N_{Mn} = \frac{N}{4}$$

and since $N_{Mn-Mn} = 0$ for the L1$_2$ structure (Fig. 3), using Eq. (5), we obtain

$$N_{Pd-Mn} = N_{Pd-Pd} = 3N$$

The configurational part of the internal energy is then given by Eq. (4) as

$$E_i = 3N(\nu_{Pd-Mn} + \nu_{Pd-Pd})$$

In the case of the L1$_{2-s}$ structure (Fig. 1), it can be shown in a similar manner that

$$N_{Pd-Pd} = N_{Pd-Mn} = 3N$$

Therefore, the configurational internal energy of the L1$_{2-s}$ structure is also given by

$$E_i = 3N(\nu_{Pd-Mn} + \nu_{Pd-Pd})$$

The configurational internal energies of both the structures are the same. In fact, the enthalpies of formation of the L1$_{2-s}$ and L1$_2$ structures (calculated using Miedema's enthalpy model) were found to be the same, further validating the calculations.

4. Entropy of the ordered structures in the absence of hydrogen

The corner sites of the cubic structure (of L1$_2$ and L1$_{2-s}$) are denoted as type I sites and the face centre sites as type II sites. If N is the total number of atoms per cell in the close-packed structure, then the total number of octahedral interstitial sites is N. The numbers of type I and type II sites (in L1$_2$ and L1$_{2-s}$) are $N/4$ and $3N/4$ respectively.

For the case of the L1$_{2-s}$ structure, the distribution of Pd and Mn atoms among the type I and type II sites is presented in Table 1. The thermodynamic probability Ω of arranging the Pd and Mn over the sites they occupy is then given by

$$\Omega = C\left(\frac{3N}{4'}\frac{N}{8}\right)C\left(\frac{N}{4'}\frac{N}{8}\right)$$

Table 1

Distribution of Mn and Pd atoms in the type I (cube corner) and type II (face centre) sites in the L1$_2$ and L1$_{2-s}$ ordered structures of Pd$_3$Mn (N is the total number of atoms per unit cell)

Structure	Element E	Number of E atoms per unit cell	Number of E atoms on type I sites	Number of E atoms on type II sites
L1$_2$	Pd	3N/4	0	3N/4
	Mn	N/4	N/4	0
L1$_{2-s}$	Pd	3N/4	N/8	5N/8
	Mn	N/4	N/4	N/8

where $C(n,r)$ denotes the number of ways in which n indistinguishable atoms can be assigned to r type I sites and n-r type II sites. Mathematically,

$$C(n,r) = \frac{n!}{r!(n-r)!}$$

Using this value of Ω in Eq. (3) and invoking Stirling's approximation (ln $x! = x$ ln $x - x$), the configurational entropy of the L1$_{2-s}$ structure, in the absence of hydrogen, is

$$[S_i]_{L1_{2-s}} = k(0.5112N) \tag{7}$$

The sitewise distribution of Pd and Mn atoms among the type I and type II sites in the L1$_2$ structure is also presented in Table 1. In this case

$$\Omega = C\left(\frac{3N}{4'}\frac{3N}{4}\right)C\left(\frac{N}{4'}\frac{N}{4}\right) = 1$$

and therefore

$$[S_i]_{L1_2} = 0 \tag{8}$$

This is the expected result for an ordered structure.

5. Entropy of ordered structures in the presence of hydrogen

The thermodynamic probability Ω' in the presence of hydrogen is given by

$$\Omega' = \Omega\Omega_H \tag{9}$$

where Ω is the thermodynamic probability of the given structure in the absence of hydrogen and Ω_H is the contribution of hydrogen to the thermodynamic probability.

It is assumed that N_H hydrogen atoms are introduced into the structure. The atomic fraction n of hydrogen is defined as follows:

$$n = N_H/N \tag{10}$$

Hydrogen occupies the octahedral interstitial positions in the L1$_2$ and L1$_{2-s}$ structures [9]. In these structures, the octahedral interstices are denoted by I$_i$, where the subscript i refers to the number of nearest Pd atoms surrounding that particular site. It must be remembered that the total number of octahedral interstitial sites in these face-centred close-packed structures is N, as there is one octahedral interstitial site per atom in close-packed structures.

In the L1$_{2-s}$ structure (Fig. 1), for total number of N atoms (Pd and Mn), there would be 5N/8 I$_4$ octahedral interstices, $N/4$ I$_5$ octahedral interstices, and N/8 I$_6$ octahedral interstices. Let us denote by N_i as the number of I$_i$ interstitial sites in the structure. If P_i denotes the probability of occupancy of site I$_i$ by hydrogen, then

the number N_{Hi} of hydrogen atoms occupying any site I_i is given by

$$N_{Hi} = P_i N_H$$

From Eq. (10), the above equation can be rewritten as

$$N_{Hi} = n P_i N$$

Therefore, the contribution of hydrogen to thermodynamic probability (Ω_H) for the $L1_{2-s}$ structure is given by

$$\Omega_H = \prod_{i=4}^{6} C(N_{i9} n P_i N) \tag{11}$$

Earlier neutron diffraction studies have shown that, in the $L1_{2-s}$ structure, there is preferential occupation of hydrogen in the I_6 sites (occupancy probability $P_6 = 0.85$) and to a lesser extent in the I_5 sites ($P_5 = 0.15$) at ambient temperature [5]. Using $P_4 = 0$, $P_5 = 0.15$ and $P_6 = 0.85$, the configurational entropy in the presence of hydrogen (S_i') for the $L1_{2-s}$ structure is

$$[S_i']_{L1_{2-s}} = k \ln \Omega' = k(\ln \Omega + \ln \Omega_H)$$

Using Eqs. (7) and (11) and invoking Stirling's approximation, we obtain

$$[S_i']_{L1_{2-s}} = kN\{0.5112 + 0.25 \ln(0.25n) + 0.125$$

$$\times \ln(0.125N) - (0.15n) \ln(0.15nN)$$

$$-(0.25 - 0.15n) \ln[(0.25 - 0.15n)N]$$

$$-0.85n \ln(0.85nN) - (0.125 - 0.85n)$$

$$\times \ln[(0.125 - 0.25n)N]\} \tag{12}$$

The above expression is valid in the domain

$$0 < n < 0.147$$

as all the I_6 interstitial sites in the $L1_{2-s}$ structure are filled up at $n = 0.147$ and remaining hydrogen atoms now occupy the I_5 sites. We are limiting our analysis up to only $n = 0.147$ because Sobha et al. have shown that it is very unlikely that hydrogen solubility exceeds 0.147 in the $L1_{2-s}$ structure [15]. It is to be noted that the value of n cannot exceed 0.375 because hydrogen occupies only the I_6 and I_5 sites.

For the case of the $L1_2$ structure (Fig. 2), the number of I_4, I_5 and I_6 sites are $3N/4$, 0 and $N/4$ respectively. Neutron diffraction studies have shown that in the $L1_2$ structure all the hydrogen atoms occupy I_6 interstitial sites [10]. Thus we use $P_4 = P_5 = 0$ and $P_6 = 1$ for calculating the contribution of hydrogen to thermodynamic probability Ω_H in the $L1_2$ structure:

$$[S_i']_{L1_2} = k(\ln \Omega + \ln \Omega_H) \tag{13}$$

Since $\Omega = 1$ for $L1_2$, we obtain

$$[S_i']_{L1_2} = k \ln \Omega_H \tag{14}$$

Using Eqs. (11) and (14), and invoking Stirling's approximation, the configuration entropy in the presence of hydrogen for the $L1_2$ structure is

$$[S_i']_{L1_2} = kN[0.25 \ln(0.25N)$$

$$-n \ln(nN) - (0.25 \text{-} n) \ln(0.25N \text{-} nN) \tag{15}$$

6. Results and discussion

As the internal energies are the same for the $L1_2$ and $L1_{2-s}$ structures, configurational entropy could decide the stability of the structures (Eq. (1)). The structure possessing greater entropy would represent the stable phase of Pd_3Mn.

The values of configurational entropies for varying hydrogen concentration in the $L1_2$ and $L1_{2-s}$ structures, as calculated from Eqs. (12) and (15), are presented in Fig. 3. The figure shows that the $L1_{2-s}$ structure is more stable than the $L1_2$ structure at all temperatures in the absence of hydrogen. This has been experimentally verified for the stoichiometric Pd_3Mn composition in a number of studies [4]. The difference in the stabilities of the two structures in the presence of hydrogen is also small. Moreover, it should be noticed from Fig. 3 that, with increasing hydrogen content, the difference between the configurational entropies of $L1_{2-s}$ and $L1_2$ structures decreases. The results reveal that the $L1_{2-s}$ phase should also be thermodynamically stable in the presence of hydrogen. This indicates that hydrogen induces ordering of the $L1_{2-s}$ to the $L1_2$ form [6] and the stabilization of the $L1_2$ phase in the presence of hydrogen is not due to thermodynamic consideration. This implies that the ordering phenomenon is most probably due to stress-assisted displacements of atoms
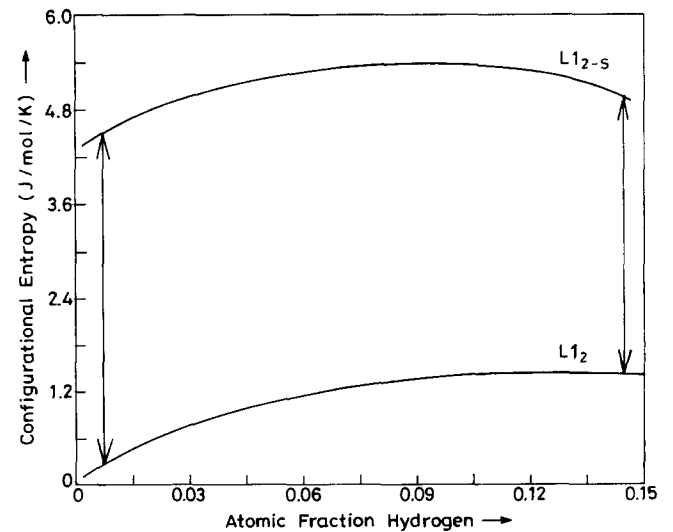

Fig. 3. Variation in configurational entropy with hydrogen concentration in the $L1_2$ and $L1_{2-s}$ ordered structures of Pd_3Mn.

around hydrogen-occupied interstitial sites in the $L1_{2\text{-s}}$ structure [16]. Stress-assisted motion of atoms to stabilize the $L1_2$ structure is possible since the difference in configurational stabilities between the $L1_2$ and $L1_{2\text{-s}}$ structures is extremely small and this difference, moreover, decreases with increasing hydrogen. In fact, the decrease in entropy difference between the $L1_{2\text{-s}}$ and $L1_2$ structures could be one of the driving forces for the observed transition from the $L1_{2\text{-s}}$ to the $L1_2$ structure in the presence of hydrogen.

Although the interaction energies between Pd–H and Mn–H in the corresponding interstitials sites have not been considered (as the necessary interaction energies were unavailable) in the present analysis, their effect on stabilities of $L1_2$ and $L1_{2\text{-s}}$ phases has been elucidated by Sobha et al. [15]. They showed that the partial molar enthalpy of hydrogen (which is related to the interaction energies) initially decreases with increasing hydrogen content for both the ordered forms of Pd_3Mn, thereby indicating long-range attractive M–H interactions at dilute hydrogen contents in both of the structures [17]. Moreover, their study also revealed that the partial molar enthalpy of hydrogen in the $L1_{2\text{-s}}$ structure increases after a certain hydrogen content in the system, in contrast to the partial molar enthalpy of hydrogen in the $L1_2$ structure which always decreases with increasing hydrogen. This indicates that repulsive M–H interactions are more important in the $L1_{2\text{-s}}$ form than the $L1_2$ form.

The electronic effects should also be considered while discussing the stabilities of the $L1_2$ and $L1_{2\text{-s}}$ phases. These effects have been discussed in detail by Iwasaki et al. [4] and Gjönnes and Olsen [7]. Finally, the strain energy contribution to stabilities has been neglected in the present analysis. Elastic strain energies develop in the system when hydrogen occupies interstitial sites in the structures, and they should increase with increasing hydrogen content. However, the strain energy contribution can be neglected since the hydrogen-induced ordering phenomenon is observed only between 500 K and 700 K. Above this temperature range, hydrogen does not dissolve in the $L1_{2\text{-s}}$ and $L1_2$ structures as the solution of hydrogen in these structures is exothermic. At lower temperatures, rearrangement of atoms by diffusional transport is difficult and the hydrogen induced ordering phenomenon has not been observed below 500 K. At these relatively high temperatures, the strains (and, hence, the strain energy) generated in the system by hydrogen in solution would be relaxed owing to atomic diffusion. Therefore, strain energies should not affect stabilities in the temperature range where the hydrogen-induced ordering phenomenon is observed and has been neglected in the analysis. Moreover, the elastic strain energy contribution would be similar for both of the phases because hydrogen would distort the lattices similarly as the lattice parameters

of the $L1_2$ and $L1_{2\text{-s}}$ structure are similar (Figs. 1 and 2).

The study reveals that thermodynamic stabilities cannot be used to explain hydrogen-induced ordering of the $L1_{2\text{-s}}$ to the $L1_2$ structure and that kinetic factors are involved [16]. In fact, this kinetic effect (stress-induced motion of atoms due to hydrogen occupying interstitial sites [16]) may be crucial because the hydrogen-induced ordering phenomenon is only observed at high temperatures and the apparent activation energy of ordering from the $L1_{2\text{-s}}$ structure is composed of activation energy required for hydrogen diffusion and that for Pd or Mn diffusion in the alloy [8].

7. Conclusions

The thermodynamic stabilities of the ordered structures in Pd_3Mn have been evaluated, both in the presence and absence of hydrogen. Hydrogen occupation probabilities in the octahedral interstitial sites of the ordered structures have been taken into account in the calculations. The $L1_{2\text{-s}}$ structure of Pd_3Mn is stable considering configurational stabilities, both in the presence and absence of hydrogen, compared with the $L1_2$ form at all temperatures. The difference in the stabilities of the two ordered forms of Pd_3Mn decreases with increasing hydrogen concentration. This indicates that the $L1_2$ structure is not stabilized as a result of thermodynamic considerations but for kinetic reasons, i.e. by stress-assisted diffusion of atoms around hydrogen-occupied interstitial sites [17].

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