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Solution thermodynamics of hydrogen in the mischmetal–Ni_5 system with aluminium, manganese and tin substitutions

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Abstract

The thermodynamics of hydrogen solubility in $MmNi_5$ (where Mm denotes Indian mischmetal containing (wt.%) 43% Ce, 23% La, 18% Nd, 5% Pr, 3% Sm and 8% Fe) by partially replacing nickel with aluminium, manganese and tin has been studied using pressure–composition–temperature isotherms at 273, 278, 288, 298, 308 and 318 K. The compositions that were studied are $MmNi_5$, $MmNi_{4.6}Al_{0.4}$, $MmNi_{4.2}Al_{0.8}$, $MmNi_{4.6}Mn_{0.4}$, $MmNi_{4.2}Mn_{0.8}$ and $MmNi_{4.6}Sn_{0.4}$. The solubility of hydrogen in the systems initially varies linearly with the square root of partial pressure of hydrogen in the solution region. The relative partial molar enthalpy of solution as a function of hydrogen content has been obtained for all the systems. It has been found that the relative partial molar enthalpy of hydrogen in solution decreases with increasing hydrogen content for all the systems except $MmNi_{5-x}Mn_x$ ($x=0.4$ and 0.8). This behaviour has been explained by considering the geometric and electronic contributions to the partial molar enthalpy. The partial molar enthalpy of hydrogen at any fixed ratio H:M decreases with the substitution of aluminium, manganese and tin for nickel in $MmNi_5$. It also decreases with increasing amount of aluminium and manganese substitution. This decrease in enthalpy has been correlated with the increase in the volume of the unit cell of $MmNi_5$ with aluminium, manganese and tin substitutions.

1. Introduction

Large quantities of hydrogen can be absorbed by several metals, alloys and intermetallic compounds [1]. At present, attention is focused on the economical storage of hydrogen for energy purposes using the above-mentioned compounds. The rare earth compound $LaNi_5$, having the hexagonal $CaCu_5$-type structure, is a candidate material for rechargeable hydrogen storage [2, 3]. However, owing to the high cost of lanthanum, it has been replaced in $LaNi_5$ by mischmetal (Mm), a cheaper rare earth element mixture [4, 5].

$MmNi_5$ as such does not show favourable hydrogen storage properties such as easy activation, low plateau pressure for hydride formation, low hysteresis loss and large hydrogen storage capacity. For example, the equilibrium dissociation pressure of $MmNi_5$ (about 13 atm at 20 °C) is higher

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than that for $LaNi_5$ (about 2 atm at 20 °C) [6]. Currently, research is under way on $MmNi_5$ systems where nickel is partially replaced by several elements such as copper [5], aluminium [5, 6], manganese [5, 7], iron [5, 8], cobalt [9], chromium [10] and silicon [11]. These substitutions have been shown to lower the equilibrium dissociation pressure in $MmNi_5$ [5]. The maximum H:M obtainable with the $MmNi_{5-x}M_x$ ($M \equiv$ Cu, Al, Fe, Mn etc.) system (typically between 0.6 and 0.8) is lower than the maximum H:M of unity possible in the $LaNi_5$ system [5, 6, 12]. This has been attributed to the impurity content in $MmNi_5$. Several properties of interest, namely hydrogen solubility, hydride formation characteristics and the hysteresis effect of hydride formation, still need to be studied in the above systems.

Determination of the partial molar enthalpy $\Delta\bar{H}_H$ in the dilute solution region is important since it provides the behaviour of dissolved hydrogen in the system in the absence of the complications arising due to the H–H interaction when the hydrogen concentration is increased. The basic reaction considered in the solution region is

$$\tfrac{1}{2}H_2(g) \longrightarrow H(\text{solution}) \tag{1}$$

where the hydrogen from the gaseous phase is dissolved in the parent phase.

In equilibrium, the chemical potential of gaseous hydrogen, which is related to its partial pressure p, can be expressed in terms of the change in partial molar enthalpy $\Delta\bar{H}_H$ and the partial molar entropy $\Delta\bar{S}_H$ as follows [13]:

$$RT \ln p^{1/2} = \Delta\bar{G}_H = \Delta\bar{H}_H - T\Delta\bar{S}_H \tag{2}$$

Therefore, assuming that the heat capacity is constant over a given temperature range, the free energy is linearly related to the temperature, and hence the partial molar enthalpy and partial molar entropy of hydrogen in solution can be obtained.

In the present study, the thermodynamics of hydrogen in solution in the systems $MmNi_5$, $MmNi_{4.6}Al_{0.4}$, $MmNi_{4.2}Al_{0.8}$, $MmNi_{4.6}Mn_{0.4}$, $MmNi_{4.2}Mn_{0.8}$ and $MmNi_{4.6}Sn_{0.4}$ using Indian mischmetal containing cerium, lanthanum, neodymium, praseodymium, samarium and iron has been studied. The thermodynamics of hydrogen in solution in pure palladium [14, 15], titanium [16], niobium [17, 18], tantalum [17, 18], vanadium [17, 18] and $LaNi_5$ [19], in binary f.c.c. solid solutions of Pd–Ag [20–23], Pd–Au [20, 24], Pd–Cu [20, 25–27], Pd–Rh [28], Pd–Pt [29] and Pd–Ni [30], and in binary b.c.c. solid solutions of V–Co [31], V–Cr [32], Nb–Mo [33], Ti–Mo [34, 35] and Ti–Re [35] have already been studied. In this context, it must be noted that the $MmNi_5$–H system has not been studied in great detail regarding solution behaviour. No detailed study has been performed to elucidate the effect of a substitutional element M on the thermodynamic behaviour of hydrogen in solution in $MmNi_{5-x}M_x$ compounds. The thermodynamic property that will be addressed in the present study is the partial molar enthalpy of hydrogen in solution as a function of hydrogen addition, for the $MmNi_5$ system with nickel partially replaced by aluminium, manganese and tin.

Attention is not focused on the hydride formation behaviour, which is the subject of future work.

2. Experimental procedure

The Indian mischmetal used in this work was obtained from M/S Raw Flints Private, Rajkote-360002, India. The composition of the mischmetal was determined analytically and it contained (wt.%) 43% Ce, 23% La, 18% Nd, 5% Pr, 3% Sm and 8% Fe.

This was used in preparing $MmNi_5$, $MmNi_{5-x}Al_x$ ($x=0.4$ and 0.8), $MmNi_{5-x}Mn_x$ ($x=0.4$ and 0.8) and $MmNi_{5-x}Sn_x$ ($x=0.4$) compounds. The nickel, aluminium, manganese and tin used for making the compounds were 99.99% pure. Samples were prepared by arc melting using an argon gas atmosphere. Each sample was melted three times to ensure complete homogeneity. These samples were further annealed at 1000 °C for 24 h using a vacuum of 10^{-2} Torr. For pressure–composition–temperature (*PCT*) measurements, each sample (specimen diameter, 3–4 mm) was first activated at a hydrogen pressure of 3000 kPa using a 10 min cycle of pressurization and depressurization at 30 °C. The samples were found to be activated by 10 cycles. These activated samples were used for *PCT* measurements in a locally fabricated pressure system. System pressure was monitored by a pressure transducer (MKS, USA). The temperature of the sample was maintained constant using a water bath. *PCT* isotherms were obtained at 273, 278, 288, 298, 308, 318 and 328 K by equilibrium pressure measurements. For each isotherm, three regions in the curve were defined, namely the solution of hydrogen in the compound, the hydride formation region and the solution of hydrogen in the hydride. The present study focuses on the data obtained for the solution of hydrogen in the parent compounds.

X-ray diffraction (XRD) data were obtained at room temperature using monochromatic chromium radiation in a Rich-Siefert 2000 diffractometer. The hydrogen-free annealed samples were crushed and mixed with a finely powdered and annealed copper standard for the diffraction experiments. The diffraction patterns were analysed and precise lattice parameters a_0 and c_0 were obtained using a linear least-squares $\cos^2\theta$ extrapolation of the diffractometer data. No XRD analyses were attempted on the hydrogen-containing samples.

3. Results

In the solution region, for all the six systems, the square root of the equilibrium pressure of hydrogen $p^{1/2}$ was linearly related to the H:M ratio. Figure 1, Fig. 2, Fig. 3, Fig. 4, Fig. 5 and Fig. 6 show this behaviour for $MmNi_5$, $MmNi_{4.6}Al_{0.4}$, $MmNi_{4.2}Al_{0.8}$, $MmNi_{4.6}Mn_{0.4}$, $MmNi_{4.2}Mn_{0.8}$ and

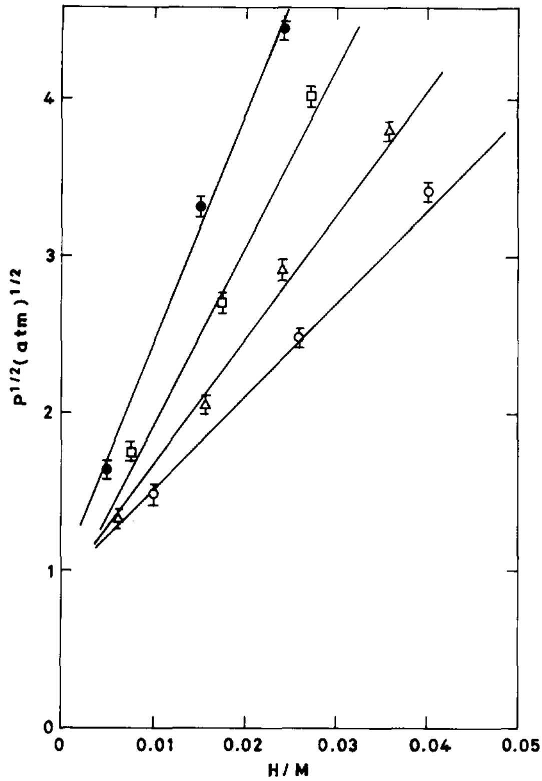

Fig. 1. *PCT* isotherms for $MmNi_5$ for the hydrogen solution region at 278 K (○), 288 K (△), 298 K (□) and 308 K (●).

$MmNi_{4.6}Sn_{0.4}$ respectively. In these figures, the square root of equilibrium hydrogen pressure is plotted as a function of the H:M ratio. The isotherms were obtained at 273, 278, 288, 298, 308, 318 and 328 K. Error bars are shown to indicate the experimental error in the measurement of pressure. These figures indicate that, in the range of H:M investigated, the square root of the hydrogen partial pressure varies linearly with H:M.

From the *PCT* isotherms (Figs. 1–6) of the six systems, the values of $p^{1/2}$ were obtained at different H:M ratios for each temperature. The plots of ln $p^{1/2}$ *vs.* $1/T$ were constructed for the different H:M ratios for each system. Least-squares fit lines were drawn for each H:M ratio and the partial molar enthalpies of solution $\Delta\bar{H}_H$ were obtained from the slopes. The results are shown in Figs. 7 and 8 for the six systems. In these figures, the partial molar enthalpy of hydrogen $\Delta\bar{H}_H$ is presented as a function of the H:M ratio. The curves in Figs. 7 and 8 were extrapolated to H:M = 0 to obtain the relative partial molar enthalpy of hydrogen in solution at infinite dilution $\Delta\bar{H}_H^0$. These values are tabulated in Table 1 along with the measured lattice parameters and unit cell volumes for the six systems.

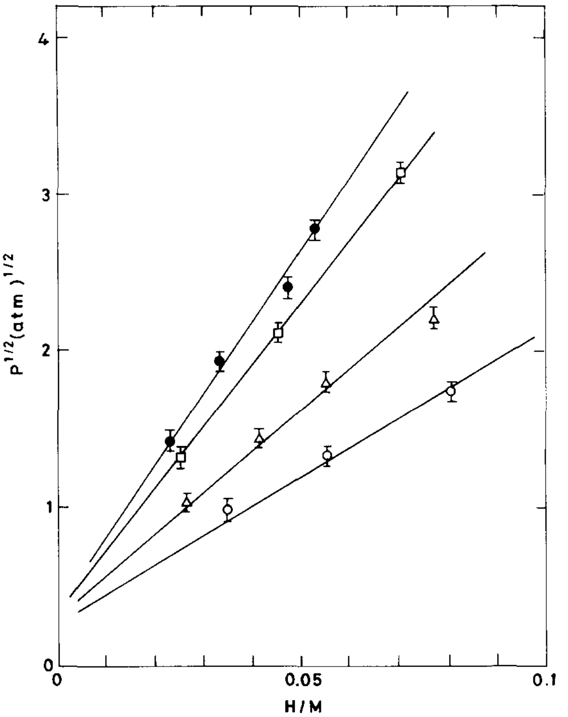

Fig. 2. *PCT* isotherms for $MmNi_{4.6}Al_{0.4}$ for the hydrogen solution region at 278, 288, 298 and 308 K (symbols as in Fig. 1).

4. Discussion

The results in Figs. 1–6 indicate that the solution region for $MmNi_5$ extends up to 16 atm. With the addition of aluminium, this region is reduced to 11 atm for $MmNi_{4.6}Al_{0.4}$ and to 3 atm for $MmNi_{4.2}Al_{0.8}$, in the temperature range 278–328 K. The addition of manganese has a similar effect. The solution region extends only up to 9 atm for the $MmNi_{4.6}Sn_{0.4}$ system. Similar reductions in the hydrogen solubility range with aluminium and manganese additions have been observed earlier [6, 7]. For example, the results of Osumi *et al.* [6] indicate that, with increasing aluminium additions in $MmNi_5$, the solid solubility range of hydrogen at 20 °C is reduced from 10 atm for $MmNi_5$ to 1 atm for $MmNi_{4.5}Al_{0.5}$. Sandrock's results [5] also show the same trend in that manganese and aluminium substitutions in $MmNi_5$ reduce the hydrogen solid solubility region. This type of behaviour is confirmed in the present study for the case of manganese and aluminium additions.

The variation of $\Delta\bar{H}_H$ with H:M for the six compounds reveals two important features. First, the solution reaction becomes more exothermic (*i.e.* $\Delta\bar{H}_H$ becomes more negative) with increasing hydrogen addition for $MmNi_{4.6}Al_{0.4}$, $MmNi_{4.2}Al_{0.8}$ and $MmNi_{4.6}Sn_{0.4}$ (Figs. 7 and 8), while the change is not significant for $MmNi_{5-x}Mn_x$ compounds. Secondly, substitution of

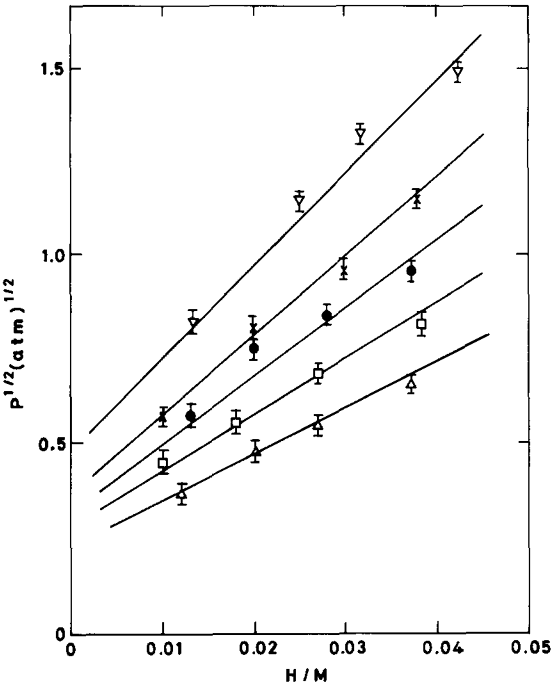

Fig. 3. *PCT* isotherms for $MmNi_{4.2}Al_{0.8}$ for the hydrogen solution region at 288 K (△), 298 K (□), 308 K (●), 318 K (×) and 328 K (▽).

aluminium, manganese or tin for nickel in $MmNi_5$ leads to a decrease in $\Delta\bar{H}_H$ at a fixed H:M ratio. The origin for these effects will now be explored.

The increased exothermicity on hydrogen going into solution can be explained by considering the geometric and electronic contributions to the partial molar enthalpy. The relative attraction between metal and metal (M–M) and between metal and hydrogen (M–H) is first considered. The increase in the number of nearest M–H neighbours as hydrogen goes into solution and the simultaneous decrease in the number of M–M nearest neighbours results in lowering the M–M interactions and a corresponding increase in the H–M interactions. This leads to the hydrogen solution reaction becoming more exothermic with hydrogen addition.

The qualitative pair-bond model of Rudman [36] could also be applied to explain the increased exothermicity with hydrogen addition. According to this model, the M–H interactions increase with increasing hydrogen content due to the lattice dilation caused by the addition of hydrogen. Therefore, at low hydrogen concentrations, the partial molar enthalpy of hydrogen decreases because of this lattice expansion. In this regard, it is interesting to note that hydrogen causes a lattice expansion in nickel [37] and the partial molar enthalpy of hydrogen in nickel decreases with increasing hydrogen content [38]. At higher hydrogen concentrations, however, the H–H inter-

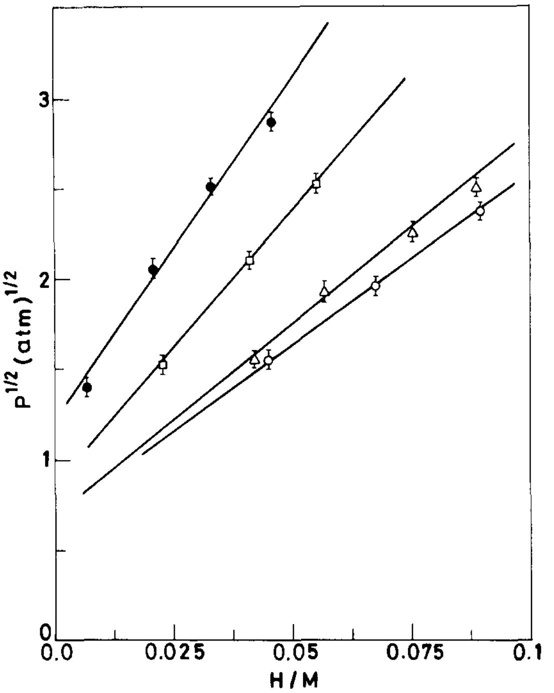

Fig. 4. *PCT* isotherms for $MmNi_{4.6}Mn_{0.4}$ for the hydrogen solution region at 273 K (○), 278 K (△), 288 K (□) and 298 K (●).

actions become increasingly repulsive due to shorter H–H distances and the enthalpy is expected to increase with increasing hydrogen content.

The present investigation does not address this region of high hydrogen concentrations. In the region of hydrogen concentrations studied, it is expected that hydrogen would cause a dilation of the $MmNi_5$ lattice (as has been observed in $LaNi_5$–H [39] and other M–H systems [40]) and this could explain the observed behaviour. The change in the lattice parameters as a function of hydrogen addition could not be obtained in the present study because of experimental difficulties.

The partial molar enthalpy is also affected by the electron density of states at the Fermi level. The screened-proton model states that the partial molar enthalpy of hydrogen in solution should decrease with increasing density of states [41]. It is known that the density of states at the Fermi level increases with hydrogen addition in $LaNi_5$ due to the additional electrons bought by hydrogen [39]. These electronic effects were indicated in earlier studies on $MmNi_{5-x}Al_x$ compounds through electrode potential [42] and magnetic measurements [43]. A similar behaviour can be expected in $MmNi_{5-x}M_x$ systems and this would also lead to the lowering of the partial molar enthalpy of hydrogen with hydrogen addition. The behaviour of the manganese-substituted $MmNi_5$ compounds is not clear at this time. The effect

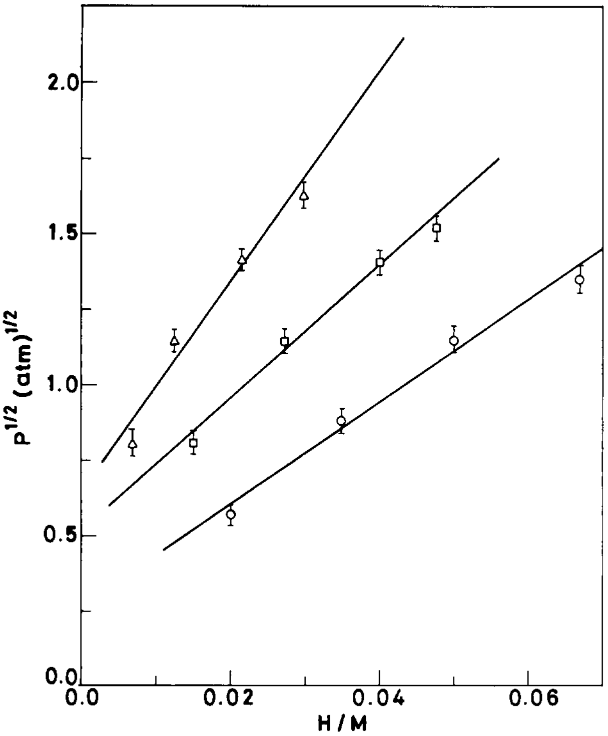

Fig. 5. *PCT* isotherms for $MmNi_{4.2}Mn_{0.8}$ for the hydrogen solution region at 288 K (○), 298 K (□) and 308 K (△).

of manganese substitution on the density of states needs to be determined to explain the observed behaviour.

The variation of $\Delta\bar{H}_H$ with aluminium, manganese and tin substitutions could also arise due to geometric and/or electronic factors. The geometric factor attributed to the partial molar enthalpy changes is the lattice dilation or contraction due to the addition of the substitutional element. This will be discussed in detail after considering the electronic effects.

The electronic contribution to the partial molar enthalpy is difficult to establish because of the lack of specific heat coefficient data (which is related to the electron density of states at the Fermi level) as a function of aluminium, manganese and tin substitutions in $MmNi_5$. It must nevertheless be noted that the electronic contribution to the partial molar enthalpy could be significant compared with geometric factors, as has been found for b.c.c. alloys [44]. In fact, it has been shown that the partial molar enthalpy becomes more negative with decreasing electron-to-atom ratio (e/a) and less negative with addition of elements that increase the value of e/a for binary vanadium alloys [31]. This treatment cannot be applied to the present $MmNi_{5-x}M_x$ systems since the density of states in the aluminium-, manganese- and tin-substituted $MmNi_{5-x}M_x$ compounds is not precisely known. However, an increase in the density of states in $MmNi_{5-x}Al_x$ compounds over that in

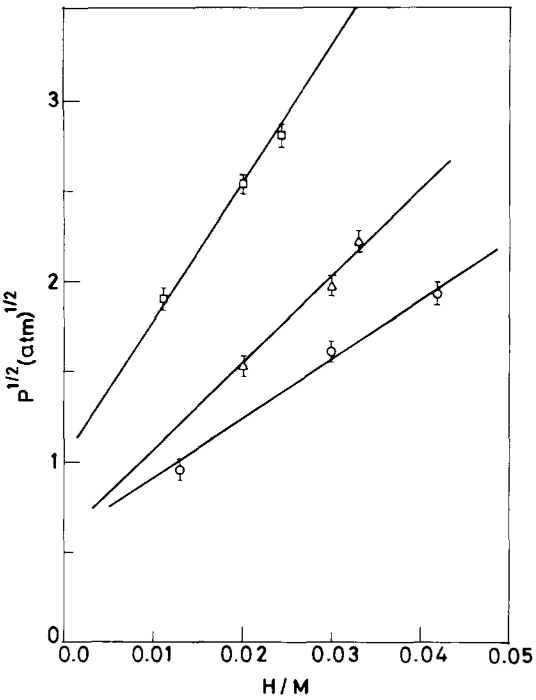

Fig. 6. *PCT* isotherms for $MmNi_{4.6}Sn_{0.4}$ for the hydrogen solution region at 278 K (○), 288 K (△) and 298 K (□).

$MmNi_5$ is indirectly indicated by earlier studies through electrode potential [42] and magnetic measurements [43]. The substitution of nickel should affect the density of states because it has been reported that the Ni d electron contribution to the density of states at the Fermi level is significant compared with the contribution due to rare earths in rare earth–Ni_5 compounds [39]. The determination of the electronic specific heat coefficients for the $MmNi_{5-x}M_x$ systems would shed more light on the electronic contribution to the partial molar enthalpy of hydrogen in these systems.

On the other hand, the geometric factor can be used to explain the changes in the partial molar enthalpy of hydrogen with aluminium, manganese and tin substitutions in $MmNi_5$. The addition of aluminium, manganese and tin leads to an increase in the volume of the unit cell of $MmNi_5$ (Table 1). The increase in the volume is greater for larger additions of aluminium and manganese. Sandrock observed a similar increase in the volume of the unit cell of $MmNi_5$ with increasing aluminium substitution [5]. This lattice expansion could lead to increased M–H interactions and a corresponding decrease in the partial molar enthalpy of hydrogen.

The relationship between the lattice expansion or contraction and enthalpy changes in binary palladium-based solid solutions is addressed for the purpose of comparison. There is a lattice dilation and a corresponding decrease in the experimental partial molar enthalpy of hydrogen (measured at constant

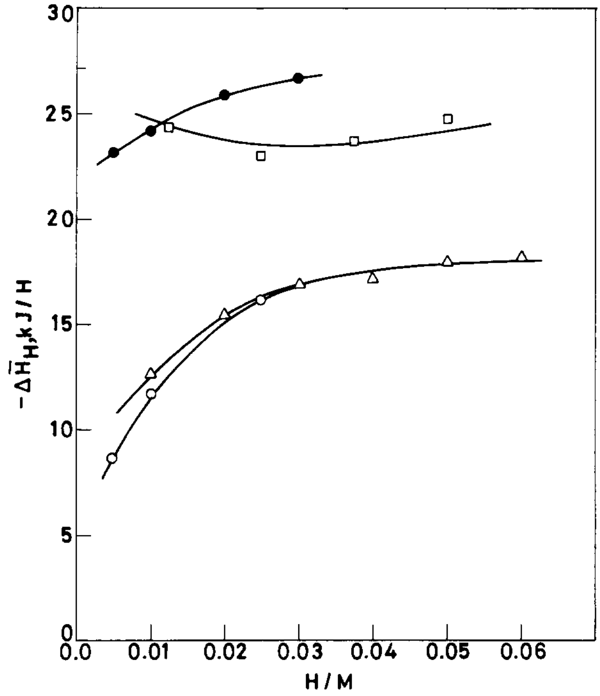

Fig. 7. Variation of partial molar enthalpy of solution $\Delta\bar{H}_H$ (kJ (mol H)$^{-1}$) with H:M ratio for $MmNi_5$ (○), $MmNi_{4.6}Al_{0.4}$ (△), $MmNi_{4.6}Mn_{0.4}$ (□) and $MmNi_{4.6}Sn_{0.4}$ (●).

pressure) with the addition of silver [20–23] and gold [20, 24] to palladium. On the other hand, there is a lattice contraction and a corresponding increase in the experimental partial molar enthalpy of hydrogen with the addition of copper [20, 25–27] and nickel [30] to palladium. For the case of Pd–Cu solid solutions, the partial molar enthalpy decreases initially till about 7 at.% Cu and then increases [26, 27] and this has been explained by considering the electronic contribution to the M–H interaction [27]. The correlation between lattice contraction or expansion and enthalpy changes has also been observed in binary b.c.c. alloys. For example, the addition of molybdenum to niobium and molybdenum to titanium leads to a decrease in the unit cell volume of niobium and titanium, respectively, and a corresponding increase in the partial molar enthalpy of hydrogen with molybdenum addition to niobium [33] and titanium [34, 35]. The lowering of the partial molar enthalpy of hydrogen with aluminium, manganese and tin substitution in $MmNi_5$ can be viewed as arising due to the lattice dilation caused by the substitution. This effect is also manifested in two other ways. The pressure (for a fixed H:M) decreases with increasing aluminium, manganese and tin substitutions compared with pure $MmNi_5$. This implies that the partial molar enthalpy is smaller for aluminium and tin substitutions, which, in fact, is the observed behaviour (Figs. 7 and 8). Secondly, the extrapolated enthalpy values at H:M = 0 (*i.e.* the relative partial molar enthalpy at infinite dilution) decrease

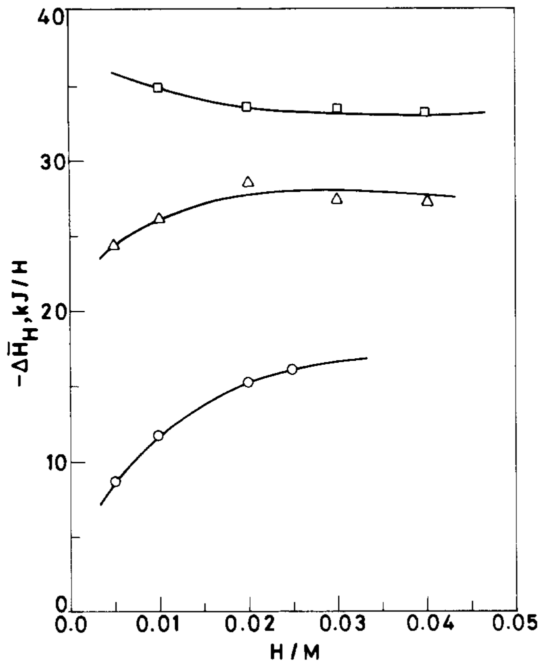

Fig. 8. Variation of partial molar enthalpy of solution $\Delta\bar{H}_H$ (kJ (mol H)$^{-1}$) with H:M ratio for $MmNi_5$ (○), $MmNi_{4.2}Al_{0.8}$ (△) and $MmNi_{4.2}Mn_{0.8}$ (□).

TABLE 1

The partial molar enthalpy of hydrogen in solution at infinite dilution $\Delta\bar{H}_H^0$ (extrapolated), lattice parameters a_0 and c_0, and unit cell volumes for the six systems

System	a_0 (Å)	c_0 (Å)	Volume (Å^3)	$-\Delta\bar{H}_H^0$ (kJ mol^{-1})
$MmNi_5$	4.9335	3.9898	84.0992	5
$MmNi_{4.6}Al_{0.4}$	4.9508	4.0169	85.2653	8
$MmNi_{4.2}Al_{0.8}$	4.9670	4.0451	86.4267	22
$MmNi_{4.6}Mn_{0.4}$	4.9421	4.0196	85.0230	26
$MmNi_{4.2}Mn_{0.8}$	4.9562	4.0699	86.5004	38
$MmNi_{4.6}Sn_{0.4}$	4.9695	4.0296	86.1823	22

with increasing unit cell volumes (Table 1). The extrapolated partial molar enthalpy at infinite dilution for $MmNi_{4.6}Mn_{0.4}$ and $MmNi_{4.2}Mn_{0.8}$ may not be very accurate because of the scatter of the data points in Figs. 7 and 8. Nevertheless, the trend of decreasing partial molar enthalpy at infinite dilution with increasing manganese addition must be noted.

In conclusion, this study shows that the solubility of hydrogen in $MmNi_{5-x}Al_x$, $MmNi_{5-x}Mn_x$ ($x=0$, 0.4 and 0.8) and $MmNi_{5-x}Sn_x$ ($x=0.4$) varies linearly with the square root of pressure at low hydrogen concentrations. The partial molar enthalpy of hydrogen in solution decreases with hydrogen addition in $MmNi_{4.6}Al_{0.4}$, $MmNi_{4.2}Al_{0.8}$ and $MmNi_{4.6}Sn_{0.4}$. The partial molar enthalpy of solution does not change significantly with hydrogen addition in $MmNi_{4.6}Mn_{0.4}$ and $MmNi_{4.2}Mn_{0.8}$. The partial molar enthalpy (at any fixed H:M ratio) also decreases with the substitution of aluminium, manganese and tin in $MmNi_5$, and with increasing amount of substitution. The addition of aluminium, manganese and tin leads to a dilation of the unit cell of $MmNi_5$ and this could explain the observed decrease in $\Delta\bar{H}_H$ with aluminium, manganese and tin substitutions. The possible role of the electronic contribution in affecting these changes has been discussed.

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