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Structural, hydrogen storage and thermodynamic properties of some mischmetal–nickel alloys with partial substitutions for nickel

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ABSTRACT

Mischmetal–nickel (Mm–Ni) alloys with single (Al) and multiple (Al, Co, Mn, Fe) substitutions for Ni are studied for their structural, hydrogen storage and thermodynamic properties. The alloys considered are $MmNi_5$, $MmNi_{4.7}Al_{0.3}$, $MmNi_{4.5}Al_{0.5}$, $MmNi_{4.2}Al_{0.8}$ and $MmNi_4Al$ for single substitution, and $MmNi_{3.9}Co_{0.8}Mn_{0.2}Al_{0.1}$, $MmNi_{3.8}Co_{0.7}Mn_{0.3}Al_{0.2}$, $MmNi_{3.7}Co_{0.7}Mn_{0.3}Al_{0.3}$, $MmNi_{3.6}Co_{0.6}Mn_{0.3}Al_{0.3}Fe_{0.2}$ and $MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$ for multiple substitutions. The XRD patterns of all the alloys show single phase with the reflection peaks related to the $CaCu_5$ hexagonal structure. All the multiple substituted alloys absorb and desorb hydrogen at sub-atmospheric pressures. The equilibrium pressure and hysteresis decrease, while enthalpy of formation (ΔH) and plateau slope increase with increase in unit cell volume, indicating an increase in the stability of the alloys.

1. Introduction

For low temperature hydrogen storage applications $MmNi_5$ has been suggested as a possible material. However, it forms an unstable hydride, requires high pressure for charging and exhibits a large hysteresis. Transition elements like Co, Mn, Fe, Cu, and elements like Al and Si are substituted partially in place of Ni to improve the hydrogen absorption and desorption characteristics of $MmNi_5$. A broad range of Pressure-Concentration Isotherms (PCIs) can be achieved with plateau pressure variation over as much as three orders of magnitude [1]. The investigations on $MmNi_{5-x}Al_x$ ($x = 0.25$–0.5) [2] and $MmNi_{5-y}Si_y$ ($0.4 \leq y \geq 0.8$) [3] have shown that the dissociation pressure of hydrogen decreases with increase in Al and Si substitution for Ni. The hydrogen desorption studies on $MmNi_{5-x}Fe_x$ ($x = 0.3$, 0.5, 0.7, 0.85, 1.0), prepared by arc melting, show that the substitution of iron for nickel causes a decrease in dissociation pressure of hydrogen [4]. Mungole et al. [5] synthesized and evaluated $MmNi_{5-x}Mn_x$ ($x = 0.4$ and 0.8) for hydrogen storage applications. The plateau pressure of absorption decreased with increasing Mn content. The maximum storage capacity was not affected till $x = 0.7$, but decreased considerably for $x > 0.7$. Studies on hysteresis during hydride formation and decomposition have shown that with partial substitution of Ni with Al, Mn and Sn resulted in the lowering of hysteresis for $MmNi_5$ [6]. The absorption–desorption characteristics of $MmNi_{5-x}Al(Mn)_{y-z}M_z$ and $MmNi_{5-x}Al(Mn)_yM_z$ (M = Co, Cr, Cu, Nb, Ti, V, Zr; $x = 0.3$–0.5; $y = 0.3$–0.5; $z = 0.05$–0.1) have revealed that the substitution or addition of element M reduces the hysteresis [7]. The hysteresis for $MmNi_{4.7}Al_{0.3}M_{0.1}$ decreased for substitution of M in the order of: Zr > Co > Cr > Ti, V > Cu. The hydrogen absorption and structural studies on $MmNi_{3.8}Al_{0.4}Fe_{0.4}Co_{0.4}$, $MmNi_{3.5}Al_{0.5}Fe_{0.5}Co_{0.5}$, $MmNi_{3.4}Mn_{0.4}Al_{0.4}Fe_{0.4}Co_{0.4}$, $MmNi_{3.368}Mn_{0.333}V_{0.333}Al_{0.3}Fe_{0.333}Co_{0.333}$ and $MmNi_3Mn_{0.333}V_{0.333}Al_{0.333}Fe_{0.333}Co_{0.333}Cu_{0.333}$ showed that the lattice constants and the unit cell volume increased, and the storage capacity of hydrogen decreased with substitution of Mn, V, Cu, Fe, Al and Co at the Ni sites in $MmNi_5$ [8].

All the compounds derived by substitution in $MmNi_5$ for Ni with single element [2–6], and with multiple elements [7,8] exhibit similar $CaCu_5$ hexagonal structure. However, there is no systematic study of hydrogen storage and thermodynamic properties of $MmNi_5$ based alloys with respect to unit cell volume. Hence in the present study, a series of alloys with single (Al) and multiple (Al, Co, Mn and Fe) substitutions for Ni in $MmNi_5$, in the order of increasing unit cell volume, are evaluated for lattice parameters, lattice volumes, plateau slopes, hysteresis, thermodynamic properties and absorption and desorption PCIs. The plateau pressure and thermodynamic properties are studied with respect to variation of lattice cell volume.

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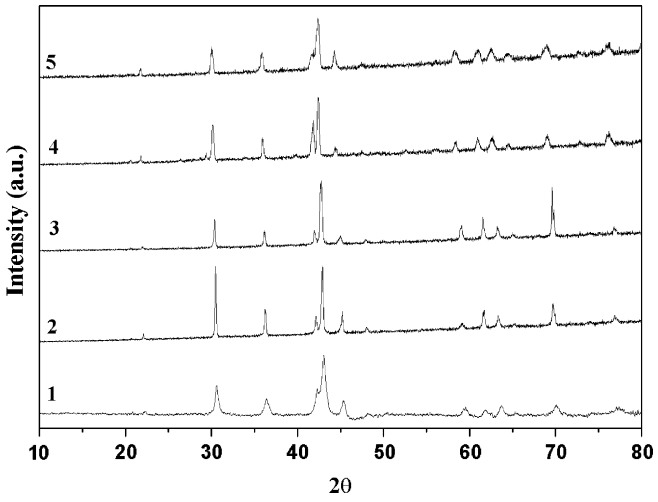

Fig. 1. XRD patterns for (1) $MmNi_5$, (2) $MmNi_{4.7}Al_{0.3}$, (3) $MmNi_{4.5}Al_{0.5}$, and. (4) $MmNi_{4.2}Al_{0.8}$, (5) $MmNi_4Al$.

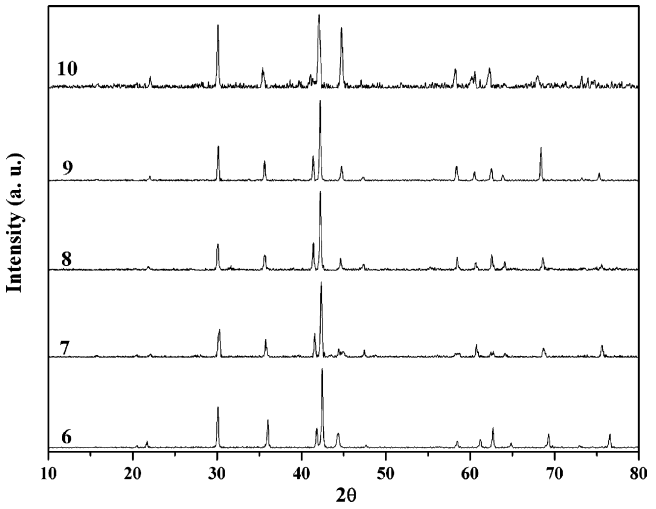

Fig. 2. XRD patterns for (6) $MmNi_{3.9}Co_{0.8}Mn_{0.2}Al_{0.1}$, (7) $MmNi_{3.8}Co_{0.7}Mn_{0.3}Al_{0.2}$,. (8) $MmNi_{3.7}Co_{0.7}Mn_{0.3}Al_{0.3}$, (9) $MmNi_{3.6}Co_{0.6}Mn_{0.3}Al_{0.3}Fe_{0.2}$, (10) $MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$.

Table 1
The unit cell constants and lattice volumes of Al substituted alloys.

S. No	Composition	a(Å)	c(Å)	Unit cell volume	$(\Delta v/v, \%)$
1	$MmNi_5$	4.953	4.005	85.07	–
2	$MmNi_{4.7}Al_{0.3}$	4.984	4.018	86.43	1.60
3	$MmNi_{4.5}Al_{0.5}$	4.999	4.029	87.22	2.53
4	$MmNi_{4.2}Al_{0.8}$	5.036	4.052	89.01	4.62
5	$MmNi_4Al$	5.051	4.057	89.64	5.37

Table 2
The unit cell constants and lattice volumes of multiple substituted alloys.

S. No	Composition	a(Å)	c(Å)	Unit cell volume	$(\Delta v/v, \%)$
6	$MmNi_{3.9}Co_{0.8}Mn_{0.2}Al_{0.1}$	4.951	4.053	86.036	2.35
7	$MmNi_{3.8}Co_{0.7}Mn_{0.3}Al_{0.2}$	4.983	4.074	87.603	4.22
8	$MmNi_{3.7}Co_{0.7}Mn_{0.3}Al_{0.3}$	5.015	4.092	89.124	6.03
9	$MmNi_{3.6}Co_{0.6}Mn_{0.3}Al_{0.3}Fe_{0.2}$	5.019	4.108	89.615	6.61
10	$MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$	5.029	4.116	90.148	7.24

2. Experimental studies

2.1. Alloy preparation and activation

All the alloys were synthesized at the Defence Metallurgical Research Laboratory, Hyderabad and delivered as powder with an average particle size of 50 μm. The synthesizing procedure is given elsewhere [9]. Alloy samples of 20 g each are used for testing. The activation procedure for $MmNi_5$ with Al substitution for Ni was presented recently by the authors [10]. All the multiple substituted alloys are activated by evacuating to 0.001 mbar at 363 K and then supplying hydrogen at 40 bar. The plateau pressures of the hydrides formed by these compounds were found to be below atmospheric pressure. Since the properties of the alloys were not known initially, hydrogen was supplied at 40 bar for activation. The system was allowed to absorb for about 30 min, then it was cooled and maintained at room temperature for about 3 h. Then it was heated to 363 K and the cycle was repeated 20 times.

2.2. PCI measurements

In static PCI measurement, the amounts of hydrogen absorbed and desorbed are calculated based on mass balance of hydrogen. An experimental setup with an operating temperature range between 253 and 573 K and maximum pressure of 100 bar is used in static PCI measurements. The experimental setup and details of reactor, working procedure and data reduction are published in authors' recent paper [11]. The maximum error in calculating percent weight of hydrogen is ±3% and the errors for ΔH and ΔS are within ±6%.

3. Results and discussion

3.1. Structural analysis

X-ray diffraction (XRD) patterns were obtained by a powder diffractometer (Rigaku Minifelx) using a Copper Kα X-ray radiation source. The XRD scan rate was set at 1 s per step of 0.02° (2θ) and the range of all the measurements was restricted to 10–80° (2θ). XRD patterns of the series of $MmNi_5$ alloys are shown in Figs. 1 and 2. Single phase with the reflection peaks, related to the $CaCu_5$ hexagonal structure (JCPDS no. 65-3476), was observed for all the alloys. From the XRD patterns, cell parameters '*a*' and '*c*' were obtained, and from these parameters unit cell volumes were calculated using the equation $V = \frac{\sqrt{3}}{2}a^2c$. Cell parameters, unit cell volumes and relative change in the cell volumes for all the alloys are given in Tables 1 and 2. Since the atomic radius for Al (1.43 Å) is higher than that of Ni (1.24 Å), with increasing Al content cell volume also increases from 1 to 5 for the alloys. The aluminium substitution can only take place at 3 g sites where as manganese atoms can replace nickel at both 3 g and 2*c* sites leading to more disordered structure [12]. Thus, in multiple substitutions

Table 3
Storage properties of Al substituted alloys.

Composition	Storage capacity at 20 °C (wt%)	Mid plateau pressure at 20 °C (bar)		Plateau slope at 20 °C [d(ln *P*)/d(wt%)]	
		Absorption	Desorption	Absorption	Desorption
$MmNi_5$	1.44	49.6	18.5	0.4	0.4
$MmNi_{4.7}Al_{0.3}$	1.42	9.2	4.3	1.12	1.12
$MmNi_{4.5}Al_{0.5}$	1.36	4.5	2.2	1.42	1.26
$MmNi_{4.8}Al_{0.2}$	1.32	0.28	0.14	2.15	2.06
$MmNi_4Al$	1.30	0.22	0.12	2.42	2.42

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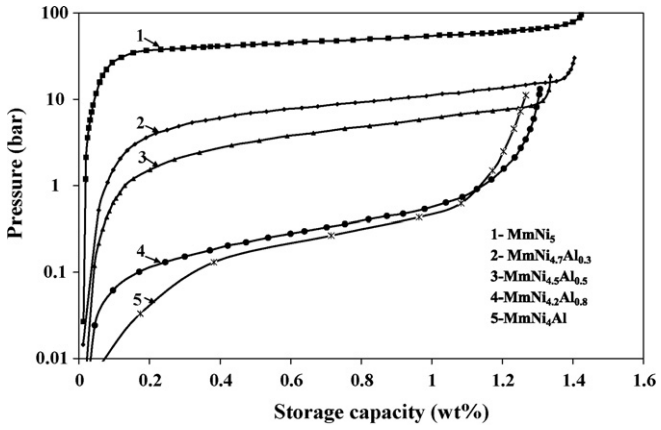

Fig. 3. Static absorption isotherms for Al substituted alloys at 293 K.

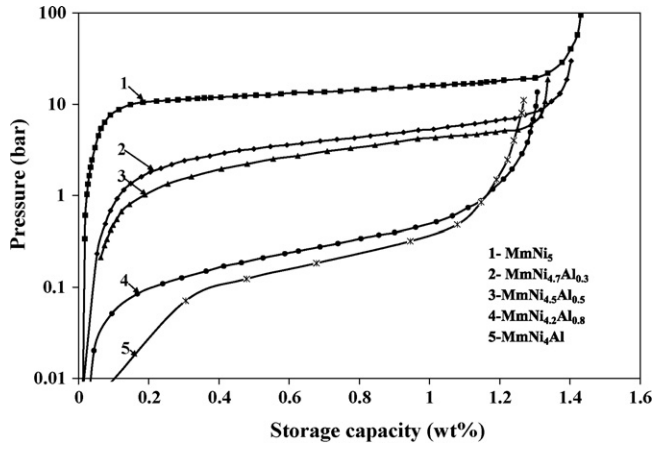

Fig. 4. Static desorption isotherms for Al substituted alloys at 293 K.

even though the Al content is less, the lattice volume is found to be more.

3.2. Hydrogen storage properties

The static absorption and desorption isotherms at 293 K for Al substituted alloys are shown in Figs. 3 and 4 while the storage properties are listed in Table 3. All the isotherms clearly show the three phases α (single phase solid solution), α + β (metal hydride formation) and β (second solid solution) with single sloping plateau. Plateau pressure and hydrogen storage capacity decrease, where as plateau slope increases with increase in Al substitution. For instance with 20% substitution of Al for Ni, the following changes are observed:

- Absorption and desorption mean plateau pressure decreased from 49.6 and 18.5 to 1.22 and 0.12 bar, respectively.

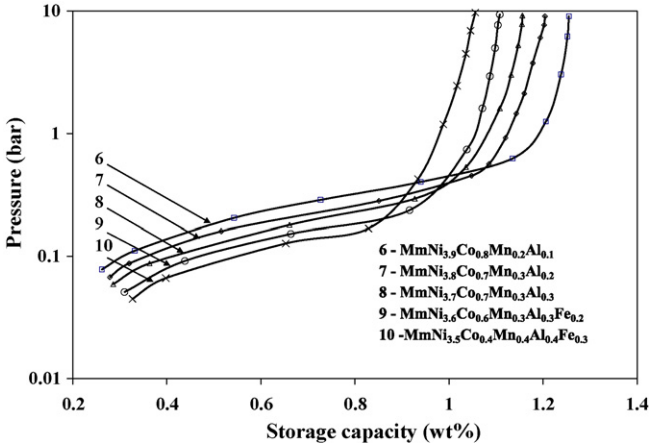

Fig. 5. Static absorption isotherms for multiple substituted alloys at 293 K.

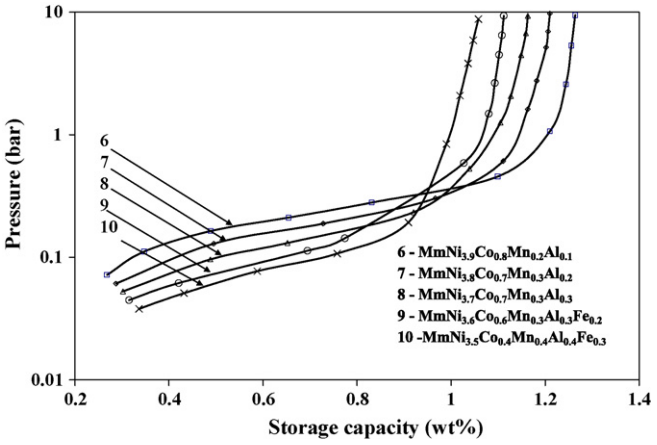

Fig. 6. Static desorption isotherms for multiple substituted alloys at 293 K.

- Maximum hydrogen storage capacity decreases from 1.44 to 1.3 wt%.
- Absorption and desorption plateau slopes increase from 0.4 to 2.42.

Figures 5 and 6 show the static absorption and desorption characteristics of multiple substituted alloys at 293 K. The storage properties are tabulated in Table 4. These alloys also reveal three phases with single sloping plateau. The absorption and desorption plateau pressures and maximum storage capacity decrease, and plateau slope increases with increase in unit cell volume. All these multiple substituted alloys absorb and desorb hydrogen at subatmospheric pressures. The mid-plateau pressures at 293 K are in the range of 0.21–0.1 bar. Maximum hydrogen storage capacity lies in between 1.26 and 1.05 wt.% at 293 K. In the range of 2.5–2.75 high plateau slope is observed.

Table 4
Storage properties of multiple substituted alloys.

Composition	Storage capacity at 20 °C (Wt%)	Mid plateau pressure at 20 °C (bar)		Plateau slope at 20 °C [d(ln *P*)/d(wt%)]	
		Absorption	Desorption	Absorption	Desorption
$MmNi_{3.9}Co_{0.8}Mn_{0.2}Al_{0.1}$	1.26	0.21	0.14	2.51	2.5
$MmNi_{3.8}Co_{0.7}Mn_{0.3}Al_{0.2}$	1.21	0.17	0.13	2.63	2.62
$MmNi_{3.7}Co_{0.7}Mn_{0.3}Al_{0.3}$	1.16	0.14	0.11	2.72	2.71
$MmNi_{3.6}Co_{0.6}Mn_{0.3}Al_{0.3}Fe_{0.2}$	1.11	0.12	0.1	2.74	2.73
$MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$	1.05	0.1	0.09	2.75	2.75

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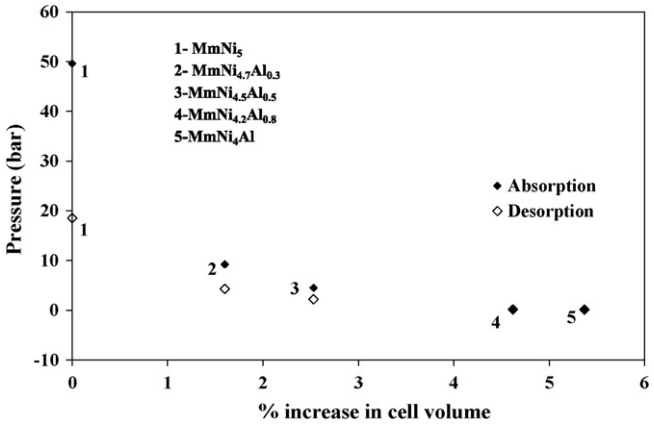

Fig. 7. Variation of plateau pressure at 293 K with unit cell volume for Al substituted alloys.

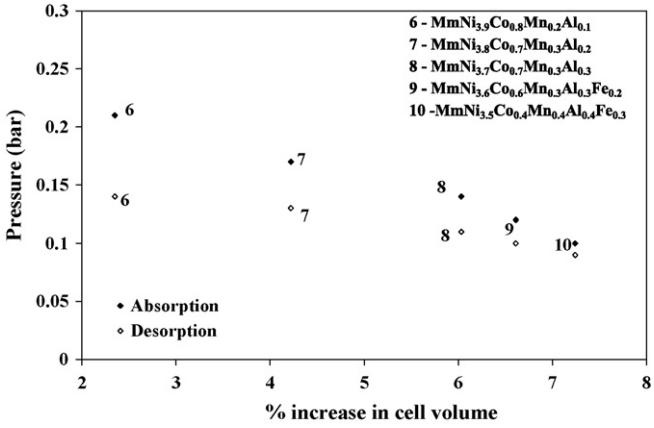

Fig. 8. Variation of plateau pressure at 293 K with unit cell volume for multiple substituted alloys.

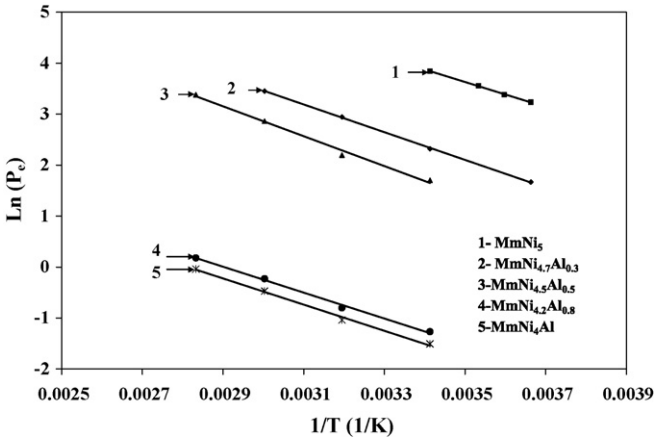

Fig. 9. Absorption van't Hoff plots for Al substituted alloys.

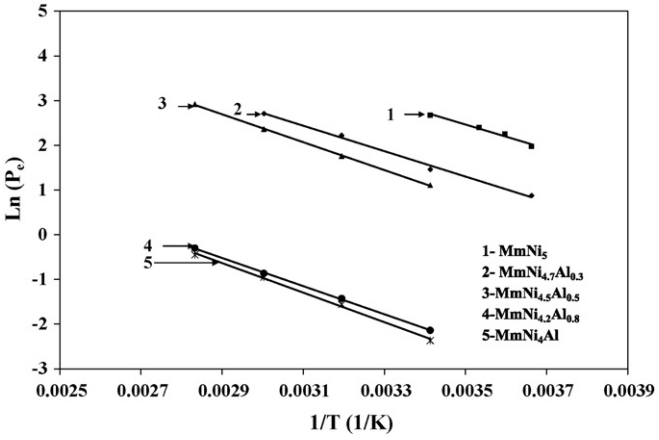

Fig. 10. Desorption van't Hoff plots for Al substituted alloys.

The decrease in mid-absorption and desorption plateau pressures with the various substitutions is attributed to the increase in cell volume as shown in Tables 1 and 2. Increase in unit cell volume decreases the strain energy necessary to accommodate the hydrogen atoms in interstitial sites. In both aluminium substituted alloys and multiple substituted alloys, the maximum hydrogen storage capacity decreases with decrease in Ni content. This can be attributed to the decrease in surface molecule dissociation activity. The increase in plateau slope with substitutions indicates that different parts of the material absorb and desorb hydrogen at different pressures due to surface inhomogeneities and stresses.

Variation of plateau pressure with cell volume for the substituted alloys is shown in Figs. 7 and 8. In general, the plateau pressure decreases exponentially with increase in cell volume. For Al substituted alloys the absorption and desorption plateau pressures decrease by as much as 225 times and 154 times respectively together with unit cell volume increase of 5.37%. For multiple substituted alloys the absorption and desorption plateau pressures decrease by 496 times and 205 times respectively with unit cell volume increase of 7.24%. In both systems of alloys, with increase in unit cell volume, decrease in absorption plateau pressure is larger compared to that of desorption plateau pressure, resulting in a decrease in hysteresis. The decrease in hysteresis with decrease in plateau pressure can be explained with the help of the theory proposed by Flanagan et al. [13] for high pressure alloys. The cause of hysteresis in metal hydride is believed to be due to the irreversible plastic work needed during hydriding to accommodate the volume changes. The energy needed for volume changes is proportional to dislocation formation which, in turn is proportional to the shear modulus. According to the regular interstitial model [14], the shear modulus for high pressure alloys is greater than that for low pressure alloys. Hence it follows that hysteresis also decreases

Table 5
Thermodynamic properties of Al substituted alloys.

Composition	Enthalpy of formation at mid plateau (kJ/mol of H_2)		Entropy of formation at mid plateau (kJ/mol of H_2 K)		Difference in magnitude of enthalpy of formation (kJ/mol of H_2)
	Absorption	Desorption	Absorption	Desorption	
$MmNi_5$	−20.356	22.548	−101.43	−99.41	2.192
$MmNi_{4.7}Al_{0.3}$	−22.629	24.286	−96.68	−93.51	1.657
$MmNi_{4.5}Al_{0.5}$	−24.417	25.966	−97.04	−95.43	1.548
$MmNi_{4.8}Al_{0.2}$	−25.091	26.579	−80.05	−75.93	1.488
$MmNi_4Al$	−26.175	27.486	−79.90	−82.757	1.31

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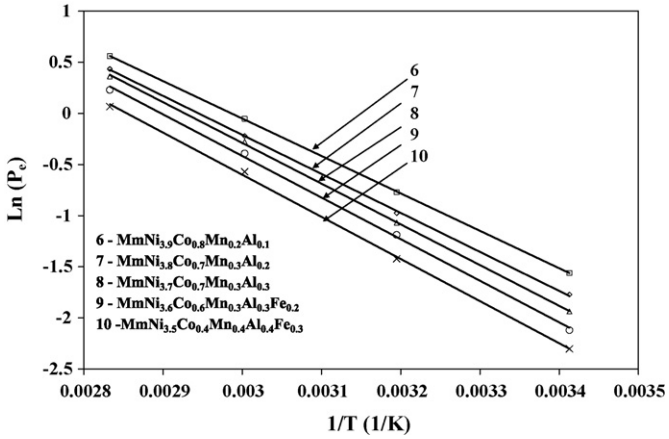

Fig. 11. Absorption van't Hoff plots for multiple substituted alloys.

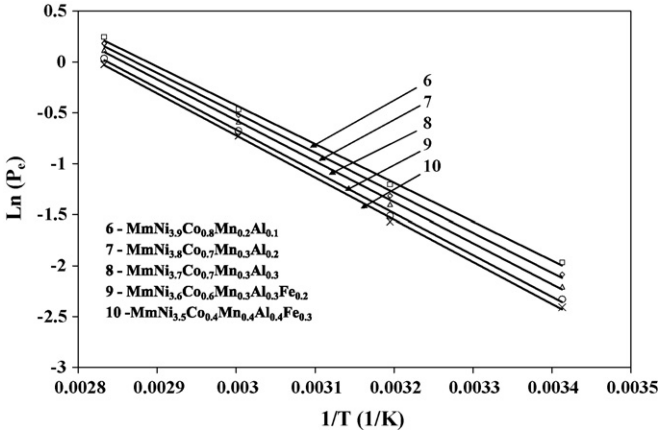

Fig. 12. Desorption van't Hoff plots for multiple substituted alloys.

as the plateau pressure decreases with increase in unit cell volume.

3.3. Thermodynamic properties

Figures 9 and 10 show absorption and desorption van't Hoff plots for Al substitutions. The ΔH and ΔS values are given in Table 5. Since absorption is an exothermic process, the ΔH is shown with negative sign whereas for desorption it is shown as positive. Van't Hoff plots are drawn in the temperature range of 273–293 K for $MmNi_5$, 273–333 K for $MmNi_{4.7}Al_{0.3}$ and 293–353 K for the remaining three alloys. The slopes of the van't Hoff lines increase with Al substitution causing the increase in enthalpy of formation. The magnitudes of absorption and desorption ΔH values increase from 20.356 and 22.548 kJ/mol for $MmNi_5$ to 26.175 and 27.486 kJ/mol for $MmNi_4Al$. Entropies of formation for both absorption and desorption are relatively constant at -90 ± 15 J/mol K.

The absorption and desorption van't Hoff plots for multiple substituted alloys are shown in Figs. 11 and 12 in the temperature range of 293–353 K. The ΔH and ΔS values are given in Table 6. The magnitude of absorption and desorption ΔH values increase from 30.453 and 31.658 kJ/mol for $MmNi_{3.9}Co_{0.8}Mn_{0.2}Al_{0.1}$ to 34.275 and 34.378 kJ/mol for $MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$. The change in entropy of formation for both absorption and desorption is not significant and has a value of 95 ± 5 J/mol K. As the value of ΔS is nearly constant, ΔH is usually considered to be more important in dealing with the thermodynamics of metal hydride [15].

Figures 13 and 14 show the variation of ΔH with increase in cell volume for single and multiple substituted alloys respectively. ΔH increases by 5.82 and 4.94 kJ/mol with an increase in unit cell volume of 5.37% for absorption and desorption, respectively. In multiple substituted systems, the absorption and desorption ΔH increase by 3.82 and 2.72 kJ/mol with an increase in unit cell volume of 7.24%. In both Al substituted and multiple substituted

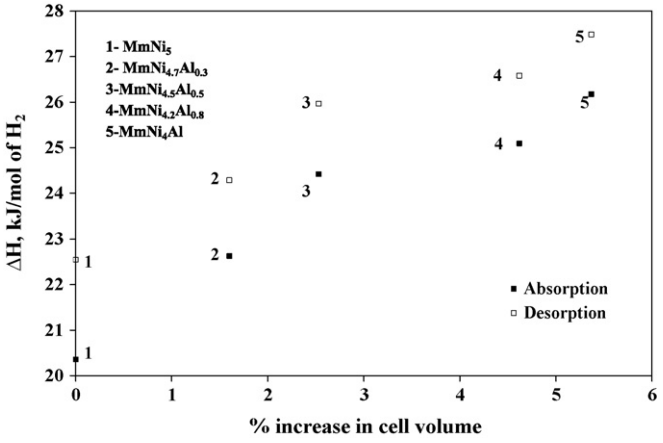

Fig. 13. Variation of ΔH with unit cell volume for Al substituted alloys.

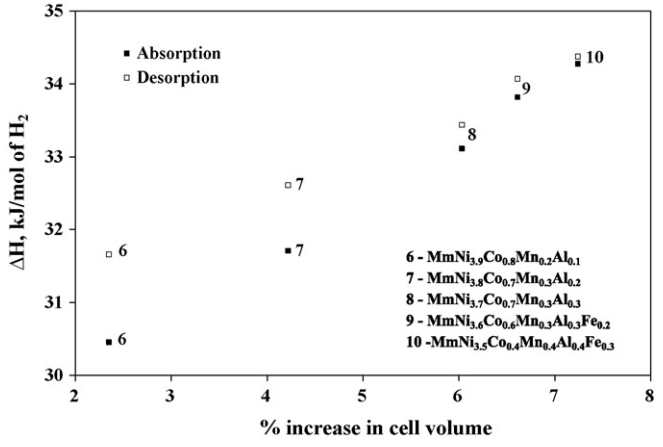

Fig. 14. Variation of ΔH with unit cell volume for multiple substituted alloys.

Table 6
Thermodynamic properties of multiple substituted alloys.

Composition	Enthalpy of formation at mid plateau (kJ/mol of H_2)		Entropy of formation at mid plateau (kJ/mol of H_2 K)		Difference in magnitude of enthalpy of formation (kJ/mol of H_2)
	Absorption	Desorption	Absorption	Desorption	
$MmNi_{3.9}Co_{0.8}Mn_{0.2}Al_{0.1}$	−30.453	31.658	−90.94	−91.43	1.205
$MmNi_{3.8}Co_{0.7}Mn_{0.3}Al_{0.2}$	−31.709	32.609	−93.38	−93.67	0.9
$MmNi_{3.7}Co_{0.7}Mn_{0.3}Al_{0.3}$	−33.112	33.439	−96.94	−95.55	0.327
$MmNi_{3.6}Co_{0.6}Mn_{0.3}Al_{0.3}Fe_{0.2}$	−33.817	34.071	−97.98	−97.98	0.254
$MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$	−34.275	34.378	−97.83	−97.12	0.103

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alloys the desorption ΔH is found to be more than the absorption ΔH for a given composition and the difference in magnitude decreases with increase in cell volume similar to the variation of hysteresis.

4. Conclusions

Many hydriding alloys with substitutions for Ni in $MmNi_5$ have been studied. The structural, hydrogen storage and thermodynamic properties data are presented leading to the following observations:

- Unit cell volume increased with substitutions.
- Plateau pressure decreased over a wide range of Al substitution and also with multiple substitutions.
- Substitutions also resulted in increased enthalpy of formation indicating higher stability of hydrides.
- Hysteresis decreased with increase in unit cell volume.

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