(La, Mm)Ni_{5-x}Fe_xH_{6-7} Intermetallic Hydrides: Thermodynamic, Structural and Hydrogen absorption properties and Computer simulation studies of P–C–T Isotherms

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ABSTRACT:

Hydrides of the LaNi_5 -related alloys are widely used in different applications, including hydrogen storage, compression, H purification and separation, heat management and nickel–metal hydride batteries. This work is focused on synthesis, structural/microstructural characterization, hydrogenation behaviour and computer simulation studies of P-C-T isotherms La_{x} Mm_{1-x} Ni_{4.9}Fe_{0.1} (x=0.4, 0.6 and 0.8) alloys, where Mm denotes Ce-rich mischmetal. The alloys have been analysed using X-ray diffraction technique (XRD) and scanning electron microscope (SEM). A feasible mathematical model has been developed to simulate the P–C isotherms. The model describes the asymmetry of the ‘pressure–composition’ isotherms, temperature-dependent plateau slopes and smooth transitions between $\alpha$, $\alpha+\beta$ and $\beta$-regions. The above materials have been synthesized and their P–C isotherms, enthalpy and entropy change have been evaluated experimentally in order to have input data for simulation. Special software was developed to simulate the P–C isotherms using the said model. The simulated and experimental curves have been found to match closely. It is suggested that mathematical modeling is useful for predicting P–C–T behaviors when the hydride is used at different temperatures.

KEYWORDS: computer simulation, storage, hydrogenation
INTRODUCTION:

Hydrogen, the most abundant element on earth, scores over all renewable fuels regarding reversibility, energy density and compatibility with the environment. The interest in hydrogen as a fuel has grown dramatically and in order for hydrogen to be potentially used, hydrogen storage technologies must be significantly improved if a hydrogen storage based energy system for transport sector is to be established.

Many metals and intermetallic compounds are capable of reversibly absorbing large amounts of hydrogen. In the families of metal hydrides (AB, A₂B, A₂B₂, A₂B₃ and AB₅) alloys derived from LaNi₅ (AB₅) show some very promising properties including fast and reversible sorption with small hysteresis, plateau pressure of few bars at room temperature and good cycling life (>10³ cycle). To achieve cost reduction, La in AB₅ alloys is replaced by Mischmetal (Mm), natural mixture of the light rare earth metals, La, Ce, Pr and Nd. Chemical substitution of La by Mm and Ni by transition or non-transition elements significantly modifies the hydrogenation behaviour of LaNi₅. There is always an interest in finding some substitution, which lead to an increase in hydrogen storage capacity and reduce the cost of LaNi₅. Keeping in view the fact that one of the criterion for increasing the hydrogen storage capacity through substitution for Ni will be to bring a more electron attractive element in place of Ni [1]. It has been found that Fe substitution, because of the higher electron attractive power of the Fe when substituted in small concentration, leads to enhancement of the hydrogen storage capacity. Structural and Microstructural features has been explored through X-ray diffraction and scanning electron microscope to see their effects on hydrogen storage capacity. We have studied the synthesis and hydrogenation behaviour of the storage alloys Laₓ Mm₁₋ₓ Ni₄.9Fe₀.₁ (x = 0.4, 0.6 and 0.8). The lattice parameter, cell volume, thermodynamical Parameters and storage capacity of the alloys are given in Table 1.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Composition</th>
<th>Lattice Parameter</th>
<th>Cell Volume</th>
<th>Thermodynamical Parameter</th>
<th>Storage capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>(Å³)</td>
<td>ΔH₀ (KJ/moleH₂)</td>
</tr>
<tr>
<td>1.</td>
<td>La₀.₈Mm₀.₂Ni₄.₉Fe₀.₁</td>
<td>5.0211</td>
<td>3.9989</td>
<td>87.3109</td>
<td>-23.56</td>
</tr>
<tr>
<td>2.</td>
<td>La₀.₆Mm₀.₄Ni₄.₉Fe₀.₁</td>
<td>5.0084</td>
<td>4.0183</td>
<td>87.2910</td>
<td>-22.55</td>
</tr>
<tr>
<td>3.</td>
<td>La₀.₄Mm₀.₆Ni₄.₉Fe₀.₁</td>
<td>5.0089</td>
<td>4.0046</td>
<td>87.0117</td>
<td>-17.48</td>
</tr>
</tbody>
</table>

Table 1 Lattice parameters and unit cell volumes for Laₓ Mm₁₋ₓ Ni₄.9Fe₀.₁ (x=0.4, 0.6 and 0.8)
EXPERIMENTAL DETAILS:

High purity lanthanum (99.9%) nickel (99.99%) and cerium rich mischmetal are taken in correct stoichiometric proportions and pressed into cylindrical pellet by applying a pressure of \( \approx 1.5 \times 10^6 \) kg/m\(^2\). The cylindrical pellet (10gm by weight) of dimension nearly 1 cm in diameter & 3mm thickness was placed in a silica tube. Under continuous flow of argon (high purity), the pellet was melted using an RF induction furnace (18kW). The as-cast material was then homogenized through 3-4 times melting. To confirm the formation of desired alloy the melted materials (powder form) were analyzed using X-ray diffraction techniques employing a Phillips X-ray diffractometer. These alloys are then crushed mechanically and 3 gms of sample has been put into Sieverts type [2] hydrogenation reactor for P-C isotherm measurement. The sample is then evacuated to \( 10^{-6} \) torr and then hydrogenated at 60 atm pressure. After several activation cycle the P-C isotherm were plotted at different temperatures (325, 350 and 375K).

STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION:

Fig. 1 illustrates the XRD pattern of alloys La\(_{1-x}\)Mm\(_x\)Ni\(_{4.9}\)Fe\(_{0.1}\) (\(x = 0.4, 0.6\) and 0.8). The XRD results indicate that these alloys are all homogeneous with a single phase corresponding to hexagonal CaCu\(_5\) type structure. The lattice parameters a and c of La\(_x\) Mm\(_{1-x}\) Ni\(_{4.9}\)Fe\(_{0.1}\) (\(x = 0.4, 0.6\) and 0.8) and respective cell volumes are listed in table 1. It can be seen from the table that with the increase of Mm content, a and the cell volume decreases almost linearly.

Fig.1. XRD patterns of La\(_x\) Mm\(_{1-x}\) Ni\(_{4.9}\)Fe\(_{0.1}\) (\(x = 0.4, 0.6\) and 0.8) hydrogen storage alloys
Fig. 2(a and b) shows the XRD patterns of alloy \( \text{La}_{0.8}\text{Mm}_{0.2}\text{Ni}_{4.9}\text{Fe}_{0.1} \) as-synthesized and after hydrogenation / dehydrogenation through several cycles. XRD peak broadening can be seen in the fig. 2(b), which is the indication of reduced crystallite size. Crystallite sizes were estimated from FWHM using Scherer's equation. The crystallite size characterized by its FWHM of as-synthesized sample is ~45 nm which reduces to ~31 nm after 10 hydrogenation /dehydrogenation. This implies a decrease in crystallite size from 45 to 31 nm.

![X-ray diffractograms](image)

Fig. 2. X-ray diffractograms of the (a) as-synthesised and (b) dehydrogenated \( \text{La}_{0.8}\text{Mm}_{0.2}\text{Ni}_{4.9}\text{Fe}_{0.1} \) alloy.

In order to monitor the surface microstructure scanning electron microscopic (SEM) investigations were performed. Fig. 3(a) shows the as-synthesized sample, which has been crushed and loaded in the Sievert type apparatus. Fig. 3(b) shows the sample after 10-hydrogenation/dehydrogenation cycles on the same scale as in Fig. 3(a). It can be seen from the fig. 3(a, b and c) that pulverization due to hydrogenation/dehydrogenation has lead to reduce the average particle size from 50-150\( \mu \)m to 5-20\( \mu \)m. Close examination at higher magnifications 3(c and d) reveals that most of the large particles observed are severely cracked. These cracks are due to lattice expansion upon hydrogenation.
MATHEMATICAL MODEL FOR P-C ISOTHERMS:

Pressure Composition (P-C) isotherms of metal hydrogen systems can be modeled using some statistical thermodynamical parameters. These models can be used to simulate the P-C isotherms for several device applications where temperature or pressure changes. Lacher-type models [3-5] are the most frequently applied to describe the PCT diagrams. In the framework of Lacher theory, the real P-C-T diagrams are described as:

\[
\ln P = \ln P_o + 2 \ln \left( \frac{\theta}{1-\theta} \right) + 8z \left( \frac{1}{2} - \theta \right) \\
\]

Where \( z = \frac{T}{T_c} \); 

\[
\]
And \( \theta = \frac{C}{C_{\text{max}}} = \frac{1}{\sigma \sqrt{2\pi}} \int_{-\infty}^{+\infty} \vartheta(x-u) \exp\left( -\frac{u^2}{2\sigma^2} \right) \, du \), \hspace{1cm} (3)

Here \( \theta \) is the fraction of metal matrix filling with hydrogen atoms which corresponds to equilibrium hydrogen concentration \( C \) in a hydride; \( C_{\text{max}} \) is a maximal hydrogen concentration; \( P \) is the hydrogen equilibrium pressure; \( P_0 \) is the hydrogen equilibrium pressure at the plateau midpoint; \( T \) is a temperature; \( T_c \) is critical temperature at which the plateau cease to exist and \( \sigma \) is the dispersion of \( x \) argument.

The \( P_0 \) temperature dependence is expressed by the Vant-Hoff relation:

\[
\ln P_0 = -\frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT}
\] \hspace{1cm} (4)

Where, \( \Delta S \) and \( \Delta H \) are changes of standard entropy and enthalpy of hydride formation.

Lacher type isotherms are antisymmetrical in the coordinated \( \theta-\ln P \) with a midpoint. \( \theta_0 = 1/2 \) [3-8]. This model has been applied for simulating PCT isotherms for \( \text{AB}_2 \) & \( \text{AB}_5 \) type materials. The experimental isotherms are usually asymmetrical so the filling fraction \( \theta_0 \) in the plateau midpoint is usually smaller than \( 1/2 \).

Attractive and indirect H-H interactions mediated via the metal atoms has been presented in Lacher type eqn. [1]. H-H repulsion is an additional feature for interstitial H in the metal hydrides, especially at High H/M ratio. Applying the model of Hill –de Boer and consideration of adsorbate molecule in a condensed phase as a Vander Waal gas, the following expression is derived :

\[
\ln P - \ln P_0 = 2 \ln \left( \frac{\theta}{1-\theta} \right) - \frac{27}{2} \frac{T_c}{T} \theta + 2 \frac{\theta}{1-\theta}
\] \hspace{1cm} (5)

The relation between the values of \( \Delta S_0 \) and \( \Delta H_0 \) in Eq. and observed standard entropy and enthalpy (\( \Delta S^0 \) and \( \Delta H^0 \)) calculated from van’t Hoff dependencies of plateau pressure versus temperature are expressed as

\[
\Delta H^0 = \Delta H_0 - \frac{27}{2} R T_c \theta_{ov}
\] \hspace{1cm} (6)

\[
\Delta S^0 = \Delta S_0 - 2 R \left( \ln \frac{\theta_{ov}}{1-\theta_{ov}} + \frac{\theta_{ov}}{1-\theta_{ov}} \right)
\] \hspace{1cm} (7)
It can be seen that this model allows to improve the fitting of the experimental data compared to the Lacher-Kierstead model used in our earlier approaches [6-8]. It can be clearly seen in [7] that the $\alpha$-phase of the simulated isotherm deviates from experimentally observed isotherm for $\text{AB}_5$ type $\text{MmNi}_{5-x}\text{Fe}_x$ ($x=0.1, 0.3, 0.5$) alloys. However, in other regions the fits seem to be good in both cases.

**RESULTS AND DISCUSSIONS:**

In our present investigations we have used the above given theoretical model simulating the P-C isotherms of $\text{La}_x\text{Mm}_{1-x}\text{Ni}_{4.9}\text{Fe}_{0.1}$ ($x=0.4, 0.6, 0.8$) hydrogen storage materials. The reason for using the theoretical model of Lototsky et al. [9] is its competence in terms of observed good fits. The simulated P-C isotherms determined by a set of $6m+1$ coefficients namely $C_{\text{max}}, \{g_i; T_c; \Delta S_i; \Delta H_i; \sigma_{Si}; \sigma_{Hi}\}$ $i=(1......m)$ are generated with the help of special software which has been developed by us. The integral

$$
\int_{-\infty}^{\infty} \theta(x) \exp\left(-\frac{(x-u)^2}{2\sigma^2}\right) \, du
$$

has been evaluated with the help of quadrature formulae of Gauss-Christophel type in the form of

$$
\int_{-\infty}^{\infty} \theta(x) \exp\left(-\frac{(x-u)^2}{2\sigma^2}\right) \, du \approx \frac{\exp\left(-\frac{x^2}{2\sigma^2}\right)}{\sqrt{\pi}} \sum_{j=1}^{n} \theta(2\sigma \xi_j) \exp\left(\frac{\sqrt{2x \xi_j}}{\sigma}\right) \eta_j
$$

(8)

Where, $\xi_j$ and $\eta_j$ are the roots and the weight coefficients of $n$-th degree Hermite polynomial respectively. Usage of the formula (6) at $n=10$ allows one to calculate filling fractions $\theta$ with the help of equation (1) with an absolute error not worse than 0.03.

The input parameters required for computer simulations correspond to $C_{\text{max}}, \Delta H_i, \Delta S_i, g_i, \sigma_{Si}, \sigma_{Hi}$. In order to evaluate these parameters for the type of hydrogen storage materials, the P-C-T curves have been plotted with the data obtained by the experimental techniques already described.

The simulated and experimental P-C-T curves are shown in the Fig. 5 for one of the composition. Vant Hoff plots were drawn from these curves to calculate the thermodynamic parameters, $\Delta H_o$ and $\Delta S_o$. Vant Hoff plot of one composition is shown in Fig. 4.
Fig. 4. Vant Hoff plot of La$_{0.4}$Mm$_{0.6}$Ni$_{4.9}$Fe$_{0.1}$ at T=325, 350 and 375 K;

Fig. 5. P-C-T curves of simulated and experimental data for La$_{0.4}$Mm$_{0.6}$Ni$_{4.9}$Fe$_{0.1}$ at T=325, 350 and 375 K;

\[ C_{\text{max}} = 1.39 \text{H/M}; \quad T_c = 521 \text{K}; \quad \Delta H_o = -17.48 \text{ KJ/mole H}_2; \quad \Delta S_o = -75.53 \text{ J/mole H}_2 \text{ K}; \quad \delta_\text{H} = 360 \text{ J/mole H}_2; \]

\[ \delta_\text{S} = 2.71 \text{ J/mole H}_2 \text{ K} \quad \rho_{\text{SH}} = 0.92; \quad \text{solid line} \quad \text{-- simulated data}; \quad \text{dotted line} \quad \text{-- experimental data} \]
The results obtained by the experimental data are tabulated in table 1, which are calculated from the Vant Hoff's plot using suitable formulas. Taking these data, we simulate the P-C isotherms at different temperatures (325K, 350K, and 375K). Figs. 5 show the experimental and corresponding computer simulated P-C-T graph of for La$_{0.4}$Mm$_{0.6}$Ni$_{4.9}$Fe$_{0.1}$. In the graph, it can be seen that the experimental and simulated data match closely. Thus it can be seen in the Fig.5 that, the model adapted in the present study successfully predicts the P-C isotherms of La$_x$Mm$_{1-x}$Ni$_{4.9}$Fe$_{0.1}$ (x=0.4,0.6 and 0.8) at different temperatures.

**CONCLUSIONS:**

(i) The series of AB$_5$ type materials has been synthesized and characterized for simulation studies.

(ii) The results shows that the theoretical model as envisaged in present study allow us to describe adequately the asymmetric P-C isotherms of AB$_5$ type hydrogen storage materials.

(iii) The desired P-C isotherm at a given temperature can be predicted from the data of measured P-C-T curves using the mathematical model. These studies are useful for predicting P-C-T hydride characteristics when the hydride is subjected to use at various temperatures.

**REFERENCES:**


