Thermodynamic analysis of dehydrogenation path of Mg–Al–Li–Na alloys

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Abstract

A thermodynamic study on the Mg–Al–Li–Na–H system is conducted in this work in order to investigate its hydrogen storage properties. For that purpose, a thermodynamic database is constructed using the CALPHAD technique. In this work, Li is added to the previously studied Mg–Al–Na–H system and the related binaries (Li–Mg, Li–Na) and ternaries (Al–Li–Mg, Al–Li–H, Li–Mg–H) are reassessed using the Compound Energy Formalism (CEF) for the terminal solid solutions and the Modified Quasichemical Model (MQM) for the liquid phase. The quaternary hydride Na2LiAlH6 is assessed for the first time. The constructed database is used to calculate de/re-hydrogenation reaction pathways of MgH2–LiAlH4/Li3AlH6 composites in a wide temperature and pressure range. The results are analyzed and compared with the experimental data to better understand and predict the reaction mechanisms. It is shown that Al resulted from the decomposition of LiAlH4/Li3AlH6 hydrides destabilizes MgH2 by the formation of Mg–Al phases: β and γ, and that LiH does not contribute to these reactions. Only negligible amounts of hydrogen are released from LiH because of the limited solubility of Li (from LiH) in Mg at high temperatures. It is concluded that MgH2–LiAlH4 system has better reversibility than MgH2–LiAlH4 system and promising compositions (e.g. 37.09 mol% and 53.65 mol% MgH2 contents) are predicted. Also, a new destabilization reaction is predicted in the system. The MgH2 and Na2LiAlH6 hydrides destabilize mutually at 308.4 K (35.25 °C) and 1 bar because of the formation of MgNaH3. However, the hydrogen capacity is reduced. It is concluded that Na considerably reduces the hydrogen storage potential of the system.

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1. Introduction

The present work is a contribution to the search and development of new materials suitable for hydrogen storage applications. In fact, the storage of hydrogen is the most critical issue for the development of hydrogen energy, especially for mobile applications [1]. Significant attention has been devoted to magnesium and its alloys as potential materials for hydrogen storage because of their high hydrogen capacity [2]. Magnesium hydride, MgH2, can store as much as 7.0 wt% H2, but its thermodynamic stability is always the major problem in hydrogen storage systems. Among these systems, Mg–Al–Li–Na–H has been reported to be very promising and many researchers focus their efforts on trying to understand reaction mechanisms and finding the best additives/catalysts to improve their hydrogen storage properties [3–11]. A comprehensive thermodynamic study is needed to find the best compositions in this system and to show their potential and limitations for hydrogen storage applications.

Recently Abdessameud et al. [12,13] used thermodynamic modeling to construct a database that describes the Mg–Al–Na–H system for hydrogen storage application. In this work, this database is extended to include Li in the system. This work is composed of two main parts; the first one consists of the assessment of the different binaries and ternaries in this system using CALPHAD method and FactSage software [14]. The second part focuses on the analysis of hydrogen storage properties of this system in comparison with the available experimental data and on the prediction of the most promising compositions in this system.

2. Literature review

2.1. Thermodynamic properties of Mg–Al–Li–Na–H system

The Mg–Al–Na–H system was reviewed and modeled in our previous papers [12,13]. In this section, a review of the remaining...
subsystems of the Mg–Al–Li–Na–H is presented.

No ternary compounds have been reported in the literature for the Al–Li–Na, Li–Mg–Na, and Li–Na–H systems. Since this work is oriented toward hydrogen storage properties, these ternaries are extrapolated from the constituent binaries using the CALPHAD method and are not included in this review.

2.1.1. Al–Li

A critical literature review and thermodynamic modeling of Al–Li systems have been conducted by Saunders [15]. The phase diagram consists of liquid phase, terminal solid solutions fcc-Al and bcc-Li, a nonstoichiometric compound AlLi(η) and two stoichiometric compounds; Al2Li3 and Al4Li9. The liquid phase has been assessed using the substitutional solution model [15]. Harvey and Chartrand [16] used the Al–Li thermodynamic parameters published by Saunders [15] to predict the hydrogen solubility in liquid Al–Li alloys. They [16] found that the hydrogen solubility was overestimated and reassessed the Al–Li model parameters for the liquid phase used in this work.

Harvey [17] completed the assessment of the entire Al–Li system using the substitutional model for the terminal solid solutions fcc-Al and bcc-Li. Since the present work is dedicated to hydrogen storage applications, the fcc-Al and bcc-Li are remodeled in this work using the compound energy formalism (CEF), thus the model parameters published by Harvey [17] are changed accordingly. The thermodynamic model parameters for the compounds AlLi, Al2Li3 and Al4Li9 [17] are used in this work with minor changes in order to accommodate the newly modeled solid solutions; fcc-Al and bcc-Li. The calculated Al–Li phase diagram is presented in Fig. 1 and the parameters used are reported in Table 1.

2.1.2. Li–H

Harvey and Chartrand [16] assessed the Li–H system using the MQM for the liquid phase. The phase diagram consists of a gas phase, bcc-Li solid solution phase, a liquid phase with miscibility gap and a hydride phase, LiH. The model parameters used to describe the Li–H system by Harvey and Chartrand [16] are used in the present work except for the bcc-Li phase, which was remodeled using the CEF. The parameters used to describe the Li–H system are reported in Table 1 and the calculated Li–LiH phase diagram is presented in Fig. 2.

2.1.3. Li–Mg

Nayeb-Hashemi et al. [18] reviewed the literature on the Li–Mg system and only the literature experimental data found by these authors [18] are used in the present optimization. The phase diagram consists of three phases: Liquid, hcp-Mg and bcc-Li terminal solid solutions. In the assessed phase diagram by Nayeb-Hashemi et al. [18], the maximum solid solubility of Li in Mg was 17 at% Li, the maximum solid solubility of Mg in Li was 75.5 at% Mg; and a eutectic reaction (L→hcp-(Mg)+bcc-(Li)) occurred at 23 at% Li and 861 K. The equilibrium diagram of the Li–Mg system has been widely investigated using different techniques [19–24].

Thermodynamic properties of the Li–Mg system have been investigated by Sommer [25], who measured the heat of mixing in the liquid phase at 940 K and by Saboungi and Blander [26], who measured Li activity in the Li–Mg liquid phase at 670, 735, 830 and 887 K. Gasior et al. [27] determined Li activities in solid and liquid Li–Mg alloys between 638 and 889 K.

Phase diagram calculations have been performed by Saboungi and Hsu [28], Nayeb-Hashemi et al. [18], Saunders [29], Gasior et al. [27], and most recently by Wang et al. [30]. In this work, the Li–Mg system is remodeled using the modified quasichemical model MQM for the liquid phase and CEF for the solid solutions for consistency with other systems in the same database. The results are discussed in more details in Section 4.1.1.

2.1.4. Li–Na

A critical review of the Li–Na system was reported by Bale [31]. This system exhibits extensive immiscibility in the liquid and the solid phases. A monotectic reaction takes place at 443.8 K and Na compositions 3.4 and 90.2 at% and a eutectic reaction at 365.3 K and 96.5 at% Na [31]. The consolute point has been calculated to be at 576.35 K (303.2 °C) and 35.7 at% Na. No thermodynamic data have been reported in the literature for the Li–Na system but the phase equilibria has been widely investigated using different techniques [31]. In the present study, the experimental data [32–39] selected by Bale [31] are used. Since no experimental evidence of solid solutions has been found in the literature, Li and Na mutual solubilities are considered negligible in the present work.

Pelton [40] and Zhang et al. [41] assessed the Li–Na system using substitutional solution model for the liquid and solid solution phases and using the critical review of Bale [31]. However, the system is re-modeled in this work using the MQM for the liquid phase and CEF for the solid solution for consistency with other binaries showing short range ordering. The modeling results of this system are discussed in Section 4.1.2.

2.1.5. Al–Li–Mg

Literature review of the Al–Li–Mg system was reported initially by Goel et al. [42] and Ghosh [43] and was then updated by Wang et al. [30]. Phase equilibria in this system were investigated by Schürmann and Voss [44] who designed a special apparatus to prepare Mg–Li–Al alloys. Phase analysis was performed by X-ray diffraction, optical metallography and electron probe micro-analysis. However, Schürmann and Voss [44] did not include the Al4Li9 phase in their analysis of the Mg–Al–Li system and reported a ζ-phase (Al11Mg10), which is not considered as stable phase according to the widely accepted Al–Mg phase diagram [13].

Enthalpy of mixing of the Al–Li–Mg liquid was determined by Moser et al. [45] in the 869–1031 K temperature range using an isothermal high temperature mixing calorimeter. Schürmann and Geissler [46] constructed Al–Li–Mg isothermal sections at 473, 573, and 673 K (200, 300 and 400 °C) below 60 at% Li. Only one ternary stable compound τ (Al53Li33Mg14) has been accepted in the literature [30,46]. Considerable solubility of Li in Al–Mg solid phases and of Mg in Al–Li solid phases has been reported in the literature [46,47]. In fact, Al–Mg compounds Mg3Al(γ), Mg2Al3(β), and
Table 1
Optimized model parameters for the different phases in the Mg-Al-Li-Na-H system (G, Δg, and L in J/mole).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model</th>
<th>Formula</th>
<th>Parameters</th>
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<tbody>
<tr>
<td><strong>Liquid phase (MQM)</strong></td>
<td></td>
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<tr>
<td>Z^{G}<em>{\text{Mg}} = Z^{G}</em>{\text{Li}} = 2, \Delta g^{G}_{\text{Mg}} = -25, 597.8 + 15.012T - 0.121771nT</td>
<td>This work</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td>\Delta g^{G}<em>{\text{Al}} = -1.2557; \Delta g^{G}</em>{\text{H}} = -14, 126.8 + 10.3702T</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z^{G}<em>{\text{Mg}} = Z^{G}</em>{\text{Li}} = 6, \Delta g^{G}<em>{\text{Mg}} = 3974.8 + 2.137T; \Delta g^{G}</em>{\text{Al}} = 0.698T</td>
<td>This work</td>
<td></td>
<td></td>
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<tr>
<td>Z^{G}<em>{\text{H}} = Z</em>{\text{Mg}}^{G} = 6, \Delta g^{G}<em>{\text{H}} = 3640.0; \Delta g^{G}</em>{\text{Al}} = 2698.68 - 3.033T; \Delta g^{G}_{\text{Li}} = 209.2</td>
<td>This work</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\Delta g^{G}<em>{\text{H}} = 7, 040.9 + 5.97T; \Delta g^{G}</em>{\text{Al}} = -55, 745</td>
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<td></td>
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<tr>
<td><strong>Terminal solid solutions (Compound energy formalism)</strong></td>
<td></td>
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<tr>
<td>hcp-(Mg) (Mg,Na,Al,Li)_{2}(H,Va)</td>
<td></td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>\text{hcp-H}<em>{\text{Mg}} = 2G(\text{hcp}) + 1/2G(\text{H}</em>{2}, \text{gas})</td>
<td>\text{bcc-Mg}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\text{bcc-Mg,H}<em>{\text{V}} = -13, 879.36; \text{hcp-Mg,Li}</em>{\text{v}} = 7, 832.64; \text{hcp-Mg,Al}_{\text{v}} = 7, 832.64</td>
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<tr>
<td>\text{hcp-Mg,Al}_{\text{v}} = 62, 836</td>
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<tr>
<td>\text{hcp-Mg}_{\text{v}} = 40000</td>
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<tr>
<td>bcc-(Na) (Na,Mg,Al,Li)_{3}(H,Va)</td>
<td></td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>\text{bcc-Mg,H}<em>{\text{V}} = 27, 000 + 8T; \text{bcc-Mg,Li}</em>{\text{v}} = 27, 000 + 8T; \text{bcc-Mg,Al}_{\text{v}} = 27, 000 + 8T</td>
<td></td>
<td></td>
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<tr>
<td>\text{bcc-Mg,Al}_{\text{v}} = 26, 163.199 + 9.67T</td>
<td></td>
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<tr>
<td>fcc-(Al,Mg,Na,Al,Li)_{3}(H,Va)</td>
<td></td>
<td>This work</td>
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<tr>
<td>\text{fcc-Mg,H}_{\text{v}} = 21G(\text{fcc})</td>
<td>\text{bcc-Al}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\text{bcc-Al,Li}<em>{\text{v}} = 21G(\text{fcc}) + 1/2G(\text{H}</em>{2}, \text{gas}) + 500, 000</td>
<td></td>
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<tr>
<td>\text{bcc-Al,Li}_{\text{v}} = -26, 163.199 + 9.67T</td>
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<tr>
<td><strong>Nonstoichiometric compounds</strong></td>
<td></td>
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<tr>
<td>G^{G}_{\text{Al,Mg}} = -41, 338 + 18.357T + G(\text{Al}) + G(\text{Mg})</td>
<td></td>
<td>[17]</td>
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</tr>
<tr>
<td>G^{G}_{\text{Mg,Li}} = 19, 816 + G(\text{Mg}) + G(\text{Li})</td>
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</tr>
<tr>
<td>G^{G}_{\text{Al,Li}} = -8, 405 + 10.257 + G(\text{Mg}) + G(\text{Li})</td>
<td></td>
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<tr>
<td>G^{G}_{\text{Al,Mg}} = 8, 368 + 2G(\text{Mg})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G^{G}_{\text{Al,Li}} = 8, 293.3 - 8.368T + G(\text{Al}) + G(\text{Li})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G^{G}_{\text{Al,Mg}} = G(\text{Mg})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G^{G}<em>{\text{Al,Li}} = 2, 000; G^{G}</em>{\text{Al,Li}} = -24, 414.4 + 9.58T</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>G^{G}<em>{\text{Al,Mg}} = 11, 632; G^{G}</em>{\text{Al,Mg}} = 20, 000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1 (continued)

<table>
<thead>
<tr>
<th>Stoichiometric compounds: 298.15 K &lt; T &lt; 1000 K (When not specified)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = 2G(Al_{2}H_{6}) + 3G(LiH) = -89, 690 + 33.96T$</td>
</tr>
<tr>
<td>$G_{\text{LiAlH}<em>{4}} = 4G(Al</em>{2}H_{6}) + 9G(LiH) = -438, 967.89 + 69.28T$</td>
</tr>
<tr>
<td>$G_{\text{LiH}} = -88, 297.32 + 153.52T - 22.86TlnT - 22.315 \times 10^{-3}T^2 - 5.89 \times 10^{-7}T^3$</td>
</tr>
<tr>
<td>$-2, 370\ln T$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = 53G(Al_{2}H_{6}) + 33G(LiH) + 14G(Mg_{8}Al_{17}) - 1, 324, 573.135 + 2, 729T$</td>
</tr>
<tr>
<td>$-8, 948, 200T^{0.5} - 298K &lt; T &lt; 500 K$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = -330, 533.6 + 4, 817.71T - 811.344TlnT + 1.23T^2 + 39.6 \times 10^{-5}T^3$</td>
</tr>
<tr>
<td>$+ 8, 948, 200T^{0.5}T^{0.5} - 298K &lt; T &lt; 500 K$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = -132, 001.66 + 206.9T - 38.11TlnT - 0.081T^2 + 1.42 \times 10^{-3}T^3 - 461, 924.05T^{-5} + 500$</td>
</tr>
<tr>
<td>$K &lt; T &lt; 800 K$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = -331, 337.95 + 674.277T - 110.34TlnT - 0.081T^2 - 1.77 \times 10^{-5}T^3$</td>
</tr>
<tr>
<td>$+ 446, 400T^{-1}$</td>
</tr>
<tr>
<td>$-7, 110\ln T$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = G(\text{LiH}) + G(\text{MgH}<em>{2}) + 3G(\text{AlH}</em>{3}) = 37, 221$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = G(\text{LiH}) + G(\text{MgH}<em>{2}) + G(\text{AlH}</em>{3}) - 1, 350$</td>
</tr>
<tr>
<td>$G_{\text{Li}<em>{2}AlH</em>{6}} = G(\text{LiH}) + G(\text{NaH}) + G(\text{NaAlH}_{4}) = 36, 124.41 + 47.91T$</td>
</tr>
</tbody>
</table>

Fig. 2. The calculated Li-LiH phase diagram at 1 bar.

Mg$_{23}$Al$_{3}$H$_{5}$ dissolves up to about 20 at% Li, 7 at% Li, and 0.8 at% Li, respectively [12,13]. LiAl(η) phase dissolves up to about 17 at% Mg [46,47].

Harvey [17] and Wang et al. [30] assessed the Al–Li–Mg system using the above-mentioned experimental data. Harvey [17] extrapolated the ternary liquid phase from the constituent binaries using mixed models (MQM for Al–Li and Al–Mg and substitutional solution model for Li–Mg) while Wang et al. [30] used substitutional solution model to extrapolate the liquid phase. In this work, the liquid phase is re-assessed using the MQM for all the binary liquids. No ternary interactions have been used in this work. The model parameters of Harvey [17] for the ternary compounds are used in this work with some modifications to attain consistency with the binary systems. The terminal solid solutions are re-modeled using the CEF.

2.1.6. Al–Li–H

Recently, Bodak and Perrot [48] conducted a literature review on the Al–Li–H system. Two ternary hydrides have been reported in the literature. LiAlH$_4$ (P121/1c space group [49]) is not stable at room temperature but has a theoretical hydrogen capacity of 10.6 wt% H$_2$. Li$_2$AlH$_6$ (R3̅(148) space group [50]) is, in turn, stable and has a theoretical hydrogen capacity of 11.2 wt% H$_2$. LiAlH$_4$ decomposes in three steps [51] through reactions (1)–(3): LiAlH$_4$ $\rightarrow$ 1/3 Li$_2$AlH$_6$ + 2/3 Al + H$_2$ 5.3 wt% H$_2$ (1) Li$_3$AlH$_6$ $\rightarrow$ 3LiH + Al + 3/2 H$_2$ + 2.6 wt% H$_2$ (2) 3LiH + 3Al $\rightarrow$ 3AlLi + 3/2 H$_2$ + 2.6 wt% H$_2$ (3)

Jang et al. [52] assessed the thermodynamic properties of the Al–Li–H hydrides using available experimental data [53–58]. These authors [52] presented two sets of thermodynamic parameters for Li$_2$AlH$_6$ because of the contradicting pressure composition iso-therm (PCI) data of Chen et al. [57] and Brinks et al. [58]. Later, Grove et al. [59] reassessed the thermodynamic properties of Li$_2$AlH$_6$ hydride using thermal analysis data of Claudi et al. [54] and first principle predictions [50,60,61]. The results published by Grove et al. [59] showed very good agreement with the PCI results of Chen et al. [57]. The parameters adopted by Grove et al. [59] are used in this work. The ternary liquid is extrapolated from the constituent binaries.

2.1.7. Li–Mg–H

Experimentally verified ternary phases in the H–Li–Mg system could not be found in the literature. Li et al. [62] predicted by means of density functional theory (DFT) the thermodynamic stability of two lithium magnesium hydrides: LiMgH$_3$ and Li$_2$Mg$_2$H$_4$ at 300 K. Recently, Meggloyaro et al. [63] predicted, using the same method, that these hydrides are metastable and spontaneously decompose to MgH$_2$ and LiH.

Ikeda et al. [64] studied the formation of perovskite-type structure in the Li$_2$Na$_{1-x}$Mg$_x$H$_3$ (x = 0, 0.17, 0.33, 0.50 and 1) hydride synthesized by ball milling NaH, MgH$_2$, and LiH. They did not observe the formation of LiMgH$_3$. For x = 0, X-ray diffraction showed the diffraction peaks for the perovskite structure NaMgH$_3$, the position of these peaks shifted to higher angles indicating
partial substitution of Na by Li in the intermediate compositions (x=0.17, 0.33, and 0.50) but this shift disappeared after heat treatment of the samples [65]. These results [64,65] show that at equilibrium, Li cannot substitute Na in NaMgH2 and thus, no stable ternary hydride exists in the Li-Mg-H system. Therefore, in this study, the model parameters describing the Li-Mg-H system have been extrapolated from the constituent binaries and no ternary hydride has been included.

2.1.8. Quaternary phases

Three quaternary compounds, LiMg(AlH4)3, LiMgAlH6, and Na2LiAlH6, have been reported in the literature for the Al–Li–Mg–Na–H system [6,59,66–69]. Lithium–magnesium alanate, LiMg(AlH4)3, \( P2_1/c(14) \) [69] contains 9.7 wt% H2 and has been found to decompose in two steps between 373 and 453 K (100 and 180 °C) [68], Mamatha et al. [68] assumed that LiMg(AlH4)3 decomposes following Eqs. (4) and (5), where LiMgAlH6 (space group P321 [69]) is an intermediate product of the decomposition of LiMg(AlH4)3. This assumption was based on the amount of hydrogen released in each step.

\[
\text{LiMg(AlH}_4\text{)}_3 \rightarrow \text{LiMgAlH}_6 + 2\text{Al} + 3\text{H}_2 (4.8 \text{ wt% H}_2) \tag{4}
\]

\[
\text{LiMgAlH}_6 \rightarrow \text{LiH} + \text{MgH}_2 + \text{Al} + 3/2\text{H}_2 (2.4 \text{ wt% H}_2) \tag{5}
\]

Mamatha et al. [68] showed, using DSC, that reaction (4) is exothermic, then not reversible, with an enthalpy value of −5 kJ/mol H2 and reaction (5) is endothermic with an enthalpy of 8.7 kJ/mol H2. Tang et al. [6] reported an enthalpy of −5.5 kJ/mol H2 and of 13.1 kJ/mol H2 for reactions (4) and (5), respectively. Tang et al. [6] reported that the results for reaction (5) agree with the results of Mamatha et al. [68]. Since Mamatha et al. [68] reported this enthalpy to be 8.7 kJ/mol H2, this suggests that the value reported by Tang et al. [6] for reaction (5) (13.1 kJ/mol H2) might be in (kJ/mol LiMgAlH6). After dehydrogenation of LiMg(AlH4)3 to form MgH2, LiH and Al (reactions (4) and (5)), Tang et al. [6] attempted the rehydrogenation of the products at 353 and 373 K (80 and 100 °C) under 190 bar of hydrogen for 24 h. These authors [6] found that neither LiMgAlH6 nor LiMg(AlH4)3 form under these conditions.

Following the assessment of Grove et al. [59] for LiMg(AlH4)3 and LiMgAlH6 hydrides, the above experimental data are adopted in this work to assess these two hydrides.

Na2LiAlH6 takes an ordered perovskite structure (\( Fm\overline{3}m \) space group with a lattice constant of 7.4064(1) Å [67]) and decomposes reversibly to the binary hydrides following reaction (6) [66].

\[
\text{Na}_2\text{LiAlH}_6 \rightarrow 2\text{NaH} + \text{LiH} + \text{Al} + 3/2\text{H}_2 (3.5 \text{ wt% H}_2) \tag{6}
\]

The authors [66] investigated using DSC [70,71] and PCI [66,67,72,73] measurements during dehydrogenation reactions. No assessment of the Na2LiAlH6 hydride has been reported in the literature. All these experimental data are used in the current work to establish a self-consistent database for the Mg–Al–Li–Na–H system.

2.2. Hydrogen storage properties

Recently, the hydrogen storage properties of the Mg–Al–Li–H system have been widely investigated [74–83]. Zhang et al. [74] and Chen et al. [76] investigated the hydrogen storage properties and reaction mechanisms of ball milled MgH2–LiAlH4 composites (with different molar ratios) using thermogravimetry (TG), differential scanning calorimetry (DSC), and XRD. Zhang et al. [74] also investigated the non-isothermal dehydrogenation of the composites: MgH2–LiH, MgH2–Al, and MgH2–LiH–Al in comparison with MgH2–LiAlH4. The effect of additives on the hydrogen storage properties and reaction mechanisms of MgH2–LiAlH4 have been also investigated [77,78,81].

Liu et al. [75,79] investigated the MgH2–Li3AlH6 composites using ball milling method, XRD analysis, thermogravimetry TGA, DSC, SEM and TEM. For comparison purposes, Liu et al. [75] investigated the dehydrogenation of 4MgH2–LiAlH4 composite under the same conditions and showed that Li3AlH6 and LiAlH4 have the same destabilization effect on MgH2 (for 4:1 mol ratio of Mg to Al).

Recently, Yap et al. [82] and Juahir et al. [83] investigated the effect of dopants on the hydrogen storage properties and reaction mechanisms of 4MgH2–Li3AlH6 composites by the addition of 10 wt% of K2TiF6 and CoNiO. In all the reported results, the dehydrogenation temperatures in the mixtures, MgH2–LiAlH4 or MgH2–Li3AlH6, were lower than those of the components and the kinetics was significantly improved. Two stages of dehydrogenation of MgH2–LiAlH4 or MgH2–Li3AlH6 composites have been identified during the heating process:

\[
\begin{align*}
4.08\text{MgH}_2 + 0.92\text{LiH} &\rightarrow \text{Li}_0.92\text{Mg}_4.08 + 4.54 \text{H}_2 \\
17\text{MgH}_3 + 12 \text{Al} &\rightarrow \text{Mg}_{17}\text{Al}_{12} + 17\text{H}_2 \\
\text{MgH}_2 &\rightarrow \text{Mg} + \text{H}_2
\end{align*}
\]

The first route was proposed by Zhang et al. [74] who reported a mutual destabilization between MgH2 and LiH to form Li0.92Mg4.08 intermediate phase in addition to the effect of Al on the dehydrogenation process of MgH2 due to the formation of γ-phase (\( \text{Mg}_{17}\text{Al}_{12} \)). According to Zhang et al. [74] and many others [76,80–84], the second stage of dehydrogenation of MgH2–LiAlH4 or MgH2–Li3AlH6 composites occurs following reactions (7) and (8). Mao et al. [77] identified the Li–Mg intermediate phase that resulted from the interaction of MgH2 and LiH as Li1Mg6. In turn, Liu et al. [75,79] supported that LiH do not take part in the dehydrogenation reactions and the decomposition of MgH2 proceeds following reactions (8) and (9). These authors argued that LiH could not be detected in XRD results because of its small amount and amorphous structure.

3. Thermodynamic modeling

The Mg–Al–Li–Na–H system is modeled in the current work using FactSage software [14]. The Gibbs energy functions of the pure elements (Al, Li, Mg, Na) are taken from the compilation of Dinsdale [85]. The Gibbs energy function of liquid monoatomic hydrogen estimated by Ransley and Talbot [86] is used in this work.

The liquid phase of the different binary systems is modeled using the modified quasichemical model MQM. Binary liquid parameters have been interpolated using the asymmetric Kohler–Toop technique where H is singled out as the asymmetric component [12,13]. No ternary parameters have been added to the liquid model.

Since hydrogen atoms occupy the interstitial positions in the terminal solid solutions fcc-Al, hcp-Mg, and bcc-Li/Na, these phases are modeled using the compound energy formalism. As discussed in
our previous papers [12,13] two sublattices: (AlLiMg), (H,Va), (MgAlLiNa)(H,Va), and (NaLiAlMg)(H,Va) are used to describe these solid solutions, respectively, where Mg, Al, Li, and Na atoms mix randomly in the first sublattice to allow their mutual solubility and H atom and vacancy mix in the second sublattice.

The model parameters of the compounds: Al2Li3, MgH2, Mg(AlH4)2, NaH, NaMgH4, NaHAlH4, Na3AlH6 have been cited in our previous papers [12,13] and those of the compounds: LiH [17], AlLi13 [17], AlLi15 [17], Al3Li23Mg14 [17], LiAlH4 [59], Li3AlH6 [59] have been taken from the literature. LiMg(AlH4)3, LiMgAlH4, and Na3LiAlH6 are modeled in this work as stoichiometric compounds based on literature data that are found reliable [6,59,66–69].

The nonstoichiometric compounds: β (AlMg3), γ (Al12Mg17), and AlLi are taken from Harvey [17] where they have been described by the sublattices: (Mg,Li)10(Al,Mg)24(Al,Mg)24, (Al)19(Al,Mg,Li)2(Mg,Li)12, and (AlLiMg3)2(Li,Mg,Va), respectively.

The gases: Al, H2, AlH3, AlH4, Mg, H2, MgH2, MgH, Na, NaH, and NaH are included in this work and are considered ideal gases [12,13] because the non-ideal contribution of the pressure to the Gibbs energy, in the pressure range of interest, is very small. Gibbs energy functions of all the gases are taken from FactPS database [14].

When present in the assessed phase diagram, the gas phase refers to all the gases that form in the considered system and cited above. The pressure reported in all the figures is the total pressure of the system.

Thermodynamic equations used to model the different phases along with the model parameters of the Mg–Al–Na–H system have been reported in our previous papers [12,13]. The additional model parameters assessed in the current work are listed in Table 1.

4. Results and discussion

4.1. Thermodynamic properties of Mg–Al–Li–Na–H system

4.1.1. Li–Mg

Fig. 3 shows the calculated Li–Mg phase diagram in comparison with experimental data. Good agreement can be seen between the calculated phase diagram and the selected experimental data except for the calculated solubilities of magnesium in bcc-Li which were lower than those measured by Freeth and Raynor [21]. This result was also found in the previous Li–Mg phase diagram calculations [18,27–30] and it was not possible, in this work, to find a set of parameters that reproduce the results of [21]. Freeth and Raynor [21] reported that quenching of a sample with bcc-Li phase at higher temperature causes the precipitation of the hcp-Mg phase and this might be the source of error in the determination of the boundary (hcp-Mg + bcc-Li)/(bcc-Li). General agreement exists between the calculated phase diagram in this work and in the assessment of Saunders [29]. In the Li-rich region of the liquidus in Fig. 3, the results by Henry and Cordiano [19] Grube et al. [20], and Feitsma et al. [22] have been chosen in this work for their close agreement and especially the resistivity measurements of Feitsma et al. [22] who determined the liquidus temperatures at 1 K intervals using high purity alloys.

The calculated Li solidus region of the phase diagram is in very good agreement with the results of Grube et al. [20]. As stated by Nayeb-Hashemi et al. [18] the lower solidus of Henry and Cordiano [19] has been caused by the segregation present in the alloys containing relatively high Li content.

The calculated heat of mixing for the liquid phase at 940 K is presented in comparison with the experimental data in Fig. 4. Better agreement exists between the calculated and the measured heat of mixing [25] than the results of Saunders [29], presented in dotted line in Fig. 4, with lower number of parameters. The calculated Li activities in the liquid phase at 670, 735, 830, and 887 K (not shown here) are very similar to the assessment of Saunders [29]. Both calculations show very good agreement with the experimental data [26].

4.1.2. Li–Na

The calculated Li–Na phase diagram is presented in Fig. 5 where good agreement with the experimental data from the literature is shown. Since, no thermodynamic data have been found in the literature for this system, the model parameters have been selected to reproduce the liquid miscibility gap and the bcc (Li and Na) miscibility gap. The results obtained in this work are comparable to those obtained by Zhang et al. [41] and deviate slightly from those of Pelton [36]. In fact, the calculations of Zhang et al. [41] showed better agreement with the experimental data especially near the consolute point compared to the work of Pelton [40].

4.1.3. Al–Li–Mg

The parameters used to model the Al–Li–Mg system are given in Table 1. As discussed in Section 2.1.5, Harvey [17] extrapolated the ternary liquid phase from the constituent binaries using the MQM for Al–Li and Al–Mg and substitutional solution model for Li–Mg. In this work, only the MQM is used; the model parameters of Harvey [17] for Al–Li and Al–Mg binary systems have been adopted and Li–Mg has been modeled using the MQM in this work. As discussed in Section 2.1.5, the parameters used by Harvey [17] for the ternary compound τ (Al12Li3Mg14) and the binary compounds (where solid solubility of the third element was considered) have been adopted in this work. The terminal solid solutions fcc-Al, hcp-Mg, and bcc-Li/Na have been modeled using the CEF. The results (not shown here) are in reasonable agreement with experimental data and comparable to those obtained by Harvey [17] for the heat of mixing of liquid and Al–Li–Mg phase diagram. As discussed in Section 4.1.1, the calculated heat of mixing of Li–Mg liquid (using the MQM) show better agreement with the experimental data than the calculations done by Saunders [29] (which was used by Harvey [17] to extrapolate the ternary liquid in the assessment of Al–Li–Mg system). In this work, no improvement is shown with respect to the heat of mixing for the ternary liquid calculated by Harvey [17] because the available experimental data [41] covered only a small composition range.

The calculated isothermal sections at 473, 573, and 673 K (200, 300, and 400 °C) are in good agreement with the experimental data [46] and comparable with the results of Harvey [17].

Fig. 3. Calculated Li–Mg phase diagram in comparison with experimental data from literature.
calculated isothermal section at 673 K (400 °C) is shown in Fig. 6.

4.1.4. Al–Li–H

LiAlH₄ and Li₂AlH₆ hydrides are considered as stoichiometric compounds. The calculated pressure-temperature diagram and reaction path of LiAlH₄ composition are presented in Fig. 7. It should be noted that "Gas" phase in Fig. 7a refers to all the gases cited in Section 3 including H₂ whereas Fig. 7b shows the amount of released hydrogen. Fig. 7a shows that LiAlH₄ is not stable and do not form even at very high pressures. Jang et al. [52] reported that, according to their calculations, Li₂AlH₆ could absorb hydrogen to form LiAlH₄ at pressures above 10³ bar. However they [52] did not include AlH₃ hydride in their calculations. According to Fig. 7b, reaction (1) is spontaneous and Li₂AlH₆ decomposes reversibly according to reaction (2) to form LiH, fcc-Al, and H₂ at 69.9 °C and 1 bar. Some of the LiH decomposes at 573.6 °C accompanied with the formation of AlLi and H₂ according to Eq. (3). Based on the current work, the remaining LiH and AlLi both melt at around 674 °C forming two immiscible liquids. Liquid LiH (Liquid 2 in Fig. 7) decomposes gradually to form liquid phase at about 701 °C. Al and Li contents in fcc-Al, AlLi and Liquid phases are presented in Fig. 7b in dashed and dotted lines, respectively, in the same color as the corresponding phase. It shows that the gradual decrease in the amount of LiH is accompanied by an increase of the Li content in fcc-Al and of the released hydrogen when the temperature is increased. This proves that there is a destabilization effect between Al and LiH because of the solubility of Li in fcc-Al which reaches its maximum at 573.6 °C where AlLi forms. It can be seen in Fig. 7b that the amount of the formed AlLi and Li dissolved in it increase with temperature while the amount of Al dissolved in AlLi is constant and the amount of the remaining LiH decreases. This shows that AlLi destabilizes LiH because of the solubility of Li in AlLi.

4.1.5. Li–Mg–H

As discussed in Section 2.1.7, no experimentally confirmed ternary hydrides have been found in the Li–Mg–H system. However, some researchers reported a destabilization effect between Mg and LiH with the formation of Mg–Li compound Li₀.₉₂Mg₄.₀₈ as mentioned in Section 2.2.

The calculated Li–Mg phase diagram presented in Fig. 3 shows that the system is composed of only bcc-Li and hcp-Mg solid solutions, and that the solubility of Li in hcp-Mg is about 20 at% Li. The Mg–Li compound Li₀.₉₂Mg₄.₀₈ cited in the literature [74] has the same crystal structure as hcp-Mg solid solution and its composition approaches the solid solubility limit of Li in hcp-Mg, which suggests that, when mixed with Mg, Li from LiH hydride starts dissolving in Mg until its solubility limit of about 20 at%.

In order to investigate the effect of Mg on LiH, the calculated LiH-Mg phase diagram at 1 bar is shown in Fig. 8. Fig. 8 shows that LiH in the LiH–Mg mixture starts releasing hydrogen at 580.55 K (307.4 °C) and the produced Li is dissolved in hcp-Mg. As the temperature increases, the solubility limit of Li, stemming from LiH, in hcp-Mg increases (following the phase boundary hcp-Mg/hcp-Mg + LiH) until it reaches a maximum of 8.3 at% LiH at 891.65 K (618.5 °C). Fig. 8 shows that LiH hydride is too stable; only a very small amount decomposes because of the solubility of the produced Li in hcp-Mg.

4.1.6. Quaternary hydrides

The quaternary compounds, LiMg(AlH₄)₃, LiMgAlH₆, and Na₂LiAlH₄ are considered in this work as stoichiometric compounds and their thermodynamic parameters are reported in Table 1. The assessment of LiMg(AlH₄)₃ and LiMgAlH₆ hydrides is performed based on the work of Grove et al. [59] and using the
The calculated \( \text{MgH}_2 - \text{LiAlH}_4 \) phase diagram at 1 bar is presented in Fig. 11a. It shows that \( \text{LiAlH}_4 \) decomposes spontaneously and the mixture is initially composed of fcc-Al solid solution, \( \text{MgH}_2 \), and \( \text{Li}_3\text{AlH}_6 \). At 343.03 K (69.9 °C), \( \text{Li}_3\text{AlH}_6 \) decomposes to
form LiH and fcc-Al. The remaining phase transitions concern the decomposition of MgH2–Al mixture, which depends on the atomic ratio of Mg and Al as discussed in our previous paper [13]. The phase diagram MgH2–LiAlH4 (not presented here) is similar to the phase diagram of MgH2–LiAlH4 with respect to phase relations which proves that dehydrogenation of Al–Li hydrides in the mixture is not affected by MgH2 and that only the Al produced following their decomposition destabilizes MgH2. Fig. 11a also shows that LiH does not take part in the dehydrogenation process of MgH2. As discussed in Section 2.2, many authors have reported a destabilization effect between MgH2 and LiH and claimed that this was due to the formation of Li–Mg compounds Li0.92Mg4.08 and Li3Mg7. However, Li0.92Mg4.08 and Li3Mg7 are not compounds in the widely accepted Li–Mg equilibrium phase diagram. In fact, Zhang et al. [74] identified, using XRD, two dehydrogenation stages in the 4MgH2–LiAlH4 composites. The first stage was attributed to the two steps decomposition of LiAlH4 (reactions (1) and (2)) and the second one to the decomposition of MgH2 (reactions (6) and (7)) which means that the composite was composed of Li0.92Mg4.08 and γ phases. However, Zhang et al. [74] could detect LiH peaks in the XRD results of dehydrogenated state at 773 K (500 °C) for all the MgH2–LiAlH4 composites that they investigated. Ismail et al. [84] reported Mg as rehydrogenation product at 773 K (500 °C) besides Li0.92Mg4.08 and γ-phase for the same composite; 4MgH2–LiAlH4 with the peaks of Li0.92Mg4.08 and Mg overlapping in the XRD patterns. Similar results have been reported by Chen et al. [76] for the MgH2–LiAlH4 composites with molar ratios 2.5:1 and 4:1 after dehydrogenation at 623 K (350 °C). For the composites with molar ratio 1:1, Chen et al. [76] reported that the peaks of Li0.92Mg4.08 or Mg could not be observed in the XRD results. In TiF3–MgH2–LiAlH4 (0.05:1:1) composites, Mao et al. [77] identified γ as a dehydrogenation product at 673 K (400 °C), and since no LiH was detected, they [77] identified Mg5Li2 as a possible product; they claimed that its peaks overlap with those of γ-phase in the XRD patterns.

The calculations shown in Fig. 11 are compared to the abovementioned experimental data [74,76,77,84]. MgH2–LiAlH4 (4:1) and (2.5:1) composites correspond to 80 and 71.4 mol% MgH2, respectively, in Fig. 11a, which shows that the dehydrogenation products of these composites at 673 K (400 °C) are γ, hcp-Mg, and LiH. For MgH2–LiAlH4 (1:1) composite, Fig. 11a shows that the dehydrogenation products are γ and LiH only.

The fact that the reported Li0.92Mg4.08 compound has the same crystal structure as hcp-Mg and its XRD peaks coincide with those of magnesium [76,84], suggests that the phase indexed as Li0.92Mg4.08 compound might be actually hcp-Mg solid solution and that, except the small solid solubility of Li (from LiH) in hcp-Mg (as discussed in Section 4.1.5), there is no destabilization effect between MgH2 and LiH (reaction (6)). This suggestion is supported by the results of Chen et al. [76] who reported that neither Li0.92Mg4.08 nor hcp-Mg were detected after dehydrogenation of MgH2–LiAlH4 (1:1) composite which is in very good agreement with the calculations shown in Fig. 11a. Also, the assumption of Mao et al. [77] concerning Mg5Li2 compound as a possible product (with XRD peaks overlapping with those of γ-phase) after dehydrogenation of MgH2–LiAlH4 (1:1) composite cannot be supported only by the fact that LiH peaks could not be detected in XRD results. In addition, Liu et al. [75,79] did not report any Mg-Li

### Table 2

<table>
<thead>
<tr>
<th>ΔH (kJ/mol H2)</th>
<th>ΔS (J/K mol H2)</th>
<th>Experiment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.75</td>
<td>145.1</td>
<td>–</td>
<td>This work</td>
</tr>
<tr>
<td>62.8</td>
<td>–</td>
<td>DSC</td>
<td>[70]</td>
</tr>
<tr>
<td>52.3</td>
<td>–</td>
<td>PDSC (2 bar H2)</td>
<td>[71]</td>
</tr>
<tr>
<td>63.8</td>
<td>152.1</td>
<td>PCI</td>
<td>[72]</td>
</tr>
<tr>
<td>60.7 ± 0.9</td>
<td>146.5 ± 1.9</td>
<td>PCI</td>
<td>[72]</td>
</tr>
<tr>
<td>56.4 ± 0.4</td>
<td>137.9 ± 0.7</td>
<td>PCI</td>
<td>[72]</td>
</tr>
<tr>
<td>53.5 ± 1.2</td>
<td>132.1 ± 2.4</td>
<td>PCI</td>
<td>[67]</td>
</tr>
</tbody>
</table>

* These values were found excluding the data point measured at 443 K.

**Fig. 10.** The calculated Van’t Hoff plot (solid line) for the dissociation of Na2LiAlH6 (reaction (6)).

**Fig. 11.** (a) Calculated MgH2–LiAlH4 phase diagram at 1 bar. (b) Calculated reaction path of 4MgH2–LiAlH4 composite at 1 bar.
phase in the dehydrogenation process of MgH₂-LiAlH₄/LiAlH₆ composites. These authors [75,79] argued that peaks of LiH are not detected in XRD results due to its small amount in comparison to Mg-related phases, its lower atomic number and amorphous structure. In fact, almost all the experimental data for MgH₂-LiAlH₄ composites reported that LiH is produced after rehydrogenation of the composites but its XRD peaks are hardly detected or overlapped by those of Al. Also, Zhang et al. [74] conducted isothermal dehydrogenation of MgH₂-LiH composite at 773 K (500 °C) and reported LiMg₂ and Li₉.₅Mg₄ as the decomposition products. However the hydrogen released from the sample did not exceed 6 wt% H₂ [74] that is well below the hydrogen capacity of the composite (8.82 wt% H₂) and no other amorphous or unknown phases have been reported as other reaction products [74]. A reason for this inconsistency may be that only MgH₂ has decomposed (hcp-Mg could be indexed as Li₉.₅Mg₄) as reported by Zhang et al. [74].

With increasing temperature from 556.45 K to 784.25 K (283.3 °C to 511.1 °C), 0.14 wt% H₂ is released gradually from the mixture. Finally at 899.55 K (626.4 °C), all the LiH has decomposed and a total amount of 8.57 wt% H₂ is released from the composite. After rehydrogenation at 673 K (400 °C) and 4 MPa (40 bar), Zhang et al. [74] showed that the MgH₂-LiAlH₄ composite contains MgH₂, LiH, and Li₂Mg₁₂ (β-phase). These authors [74] concluded that only MgH₂ is reversible in this composite with a loss in the hydrogen capacity because of the formation of β-phase. In turn, Chen et al. [76] reported that only MgH₂ and LiH can be reformed after rehydrogenation at 623 K (350 °C) and 10 MPa (100 bar) in the 4MgH₂-LiAlH₄ composite. Liu et al. [75] showed that the mixture 4MgH₂-LiAlH₄ is composed of MgH₂, Al, and LiH after rehydrogenation under 523 K (250 °C) and 2 MPa (20 bar) H₂. To analyze these different experimental results, the Pressure–Temperature (P–T) diagrams of the 4MgH₂-LiAlH₄ composites are calculated in this work and presented in Fig. 12. The P–T diagrams of 4MgH₂-LiAlH₄ and 4MgH₂-LiSAlH₅ are similar. Fig. 12 predicts the conditions (pressure and temperature) for the reversibility of the hydriding process of the composites 4MgH₂-LiAlH₄/LiAlH₆. It can be seen that the calculations agree very well with all the cited experimental results [74-76] and give the conditions for the reversibility of the 4MgH₂-LiAlH₄ composite. All the reported data for the undoped MgH₂-LiAlH₄ [74,76] and MgH₂-LiSAlH₅ [75] show that the dehydrogenation kinetics and temperatures of these composites were improved in comparison with the composing hydrides and related these improvements to mutual catalytic effects between the hydrides. According to this work, MgH₂ does not affect the thermodynamics of LiAlH₄ and Li₂AlH₆ hydrides’ decomposition and then, we can conclude that the improved reactions might be due to a catalytic effect of MgH₂. However, the improvement in MgH₂ decomposition is related to its destabilization by the resulting Al to form Mg–Al compounds, which with LiH might play a catalytic role on the decomposition of MgH₂.

The constructed database for the Mg–Al–Li–Na–H system allows predicting the dehydrogenation reaction mechanisms for all the possible composites in the system. According to our previous paper [13], MgH₂ dehydrogenation occurs following reaction (10). It has been already proved [13] that destabilization of MgH₂ is due to the effect of Al. In the MgH₂-LiAlH₄/LiAlH₆ composites, Al is produced from the decomposition of LiAlH₄/LiAlH₆ and MgH₂ decomposition route depends on the ratio of Mg to Al atoms [2]. Since LiAlH₄ is metastable, Li₃AlH₆ is preferable as Al source for its reversibility, its hydrogen content and low decomposition temperature. The dehydrogenation of Li₃AlH₆ proceeds according to reaction (11).

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Fig. 11a shows that for Mg composition of 37.1 mol%, MgH₂ reacts with Al to form β-phase and releases all its hydrogen (6.07 wt% H₂) at 507.25 K (234.1 °C). For Mg composition of 53.7 mol%, MgH₂ reacts with β-phase to form γ-phase and releases all its hydrogen (6.36 wt% H₂) at 531.05 K (257.9 °C). It can be concluded that at these compositions, the maximum amount of hydrogen is released from the destabilized MgH₂. Reaction path of MgH₂-LiAlH₄ composites with MgH₂ content of 37.1 mol% and 53.7 mol% is calculated in this work at 1 bar and presented in Fig. 13.

\[ \text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2 \] (10)

\[ \text{LiAlH}_6 \rightarrow \text{LiH} + \text{Al} + 1.5 \text{H}_2 (5.6 \text{wt% H}_2), \Delta H = 33.90 \text{kJ/mol H}_2 \] (11)

We have already shown for the Mg–Al–Na–H system [13] that in MgH₂–NaAlH₄/Na₃AlH₆ composites, the component hydrides destabilize mutually and spontaneously to form a more stable hydride, MgNaH₅, which reduces significantly the hydrogen storage potential of the system.

As discussed in Section 4.1.6, there is only one stable quaternary hydride in the Mg–Al–Li–Na–H system, Na₃LiAlH₆, whose decomposition path and properties are given by reaction (12).

\[ \text{Na}_3\text{LiAlH}_6 \rightarrow \text{Na}_2\text{LiAlH}_5 + 2\text{NaH} + \text{LiH} + 1.5 \text{H}_2 (3.52 \text{wt% H}_2), \Delta H = 61.83 \text{kJ/mol H}_2 \] (12)

Reaction (12) shows that this hydride might contribute to the destabilization of MgH₂ because of its decomposition products.
According to the current thermodynamic modeling, MgH₂ and Na₂LiAlH₆ destabilize mutually at 308.4 K (35.25 °C) to form MgNaH₃. The maximum amount of hydrogen released at 308.4 K from MgH₂/Na₂LiAlH₆ composites is for MgH₂ content of 2/3 mol fraction. The reaction path of this composite at 1 bar is presented in Fig. 13. It shows that 1.45 wt% H₂ is released from the composite at 308.4 K (35.25 °C) where MgNaH₃, Li₃AlH₆, and fcc-Al form. A total of 2.19 wt% H₂ is released from the composite at 443.02 K (69.9 °C) following the decomposition of Li₃AlH₆. It can be concluded that even though MgH₂ and Na₂LiAlH₆ destabilize mutually and the decomposition temperature is reduced, the formation of MgNaH₃ reduces the hydrogen storage potential of the system.

As a result of this work and our previous results [12,13], it can be concluded that the addition of Na to Mg–Al–Li–H system leads to the formation of MgNaH₃ and thus reduces the potential of the system for mobile application according to the recommendation of DOE [88], and that more work is needed to improve the hydrogen storage properties of Mg–Al–Li–H system.

5. Conclusion

Thermodynamic modeling is used in this work to construct a database that describes the Mg–Al–Li–Na–H system in order to study its hydrogen storage properties. Since Mg–Al–Na–H system was studied before, only Li related binaries and ternaries are reassessed in this paper. MQM and CEF are used to describe the liquid and the solid solution phases, respectively. Reaction pathways for MgH₂–LiAlH₄/Li₃AlH₆ composites are calculated and compared to the experimental data from the literature. A very good agreement has been found except for Li–Mg compounds reported in the literature. It is concluded that the reported Li₀.₉₂Mg₄.₀₈ is actually hcp-Mg, because the reported XRD peaks of this compound are identical to those of hcp-Mg and no compounds exist in the accepted Li–Mg phase diagram. Also, it is found that LiH is very stable and does not contribute to the decomposition reactions of MgH₂. Nevertheless, at high temperatures, a very small amount of Li from LiH dissolves in hcp-Mg and produces a negligible amount of H₂. In the composites MgH₂–LiAlH₄/Li₃AlH₆, Al produced from the decomposition of LiAlH₄/Li₃AlH₆ destabilized MgH₂ by the formation of β- and γ-phases. It is found that the re/dehydrogenation of the composites MgH₂–LiAlH₆ is reversible and that for MgH₂ content of 37.1 mol% and 53.7 mol%, 6.07 wt% H₂ (at 507.25 K (234.1 °C)) and 6.37 wt% H₂ (at 531.05 K (257.9 °C)) is released from the composite, respectively. A new destabilization reaction is predicted in this work between MgH₂ and Na₂LiAlH₆. These hydrides destabilize mutually at 308.4 K (35.25 °C) and 1 bar because of the formation of MgNaH₃. It is concluded that Na reduces considerably the hydrogen storage potential of the system.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [http://dx.doi.org/10.1016/j.calphad.2016.06.001](http://dx.doi.org/10.1016/j.calphad.2016.06.001).

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