Thermodynamic modeling of the Na–Al–Ti–H system and Ti dissolution in sodium alanates

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ABSTRACT

Thermodynamic assessments were made to optimize thermodynamic models and parameter fits to selected experimental and first principles hypothetical predicted phase data within the Na–Al–Ti–H system. This enabled thermodynamic modeling of Ti solubility within the sodium alanates: NaAlH4 and Na3AlH6, and the relative stability of Ti-bearing phases. The modeling provides insights into the role of Ti originating from Ti-based activating agents commonly referred to as ‘catalysts’ in promoting reversibility of the Na–Al–H dehydrogenation and rehydrogenation reactions under moderate temperature and pressure conditions relevant to H storage applications. Preliminary assessments were made to evaluate H solubility in bcc-Ti and hcp-Ti, and stability of the hydride δ-TiH2. To model possible Ti dissolution in NaAlH4 and α-Na3AlH6, sub-lattice models were applied. A repulsive interaction is predicted by first principles calculations when Ti is dissolved in NaAlH4 or α-Na3AlH6, which becomes stronger with increasing temperature. Although Ti is virtually insoluble in NaAlH4 or α-Na3AlH6, a small addition of TiCl3 will induce a thermodynamic driving force for formation of TiH2 and/or TiAlH4. The addition of pure Ti shows a weaker effect than TiCl3 and leads to formation of TiH2 only. Based on a combined interpretation of present thermodynamic modeling and prior experimental observations, the TiAlH4 and TiH2 phases are ascribed to have a catalytic effect, not a thermodynamic destabilization effect, on the reversibility of the dehydrogenation/rehydrogenation reactions in the Na–Al–H system.

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1. Introduction

Titanium and other transition metal additives have shown great utility for tailoring the functional properties of ceramic components, including: microwave dielectrics, tunable solid-state lasers, thermo-optic devices, waveguide amplifiers, lithium ion battery electrodes, superconducting wires, semiconductors, stabilized and/or densified structural ceramics, and solid lubrication films. Recently, Ti and other transition metal activating agents have also been shown to significantly increase the kinetics of the dehydrogenation and rehydrogenation reactions of the complex covalent sodium alanate stoichiometric compounds, NaAlH4 and α-Na3AlH6, promoting their consideration to be one of the premier moderate temperature and pressure H storage material candidates [1–3]. Titanium additives also effectively enhance the kinetics of a wide range of other solid-state inorganic hydride H storage materials.

A number of experimental and theoretical studies have sought to elucidate the Ti activation mechanisms in the sodium alanates in order to lay a foundation for further H storage material development. Overall, it can be concluded from the summary in Ref. [4] as well from more recent reports [5–12], that these studies have hypothesized that Ti phases could affect the sodium alanate H cycling kinetics either by changing the dehydrogenation reaction products, altering the properties of the sodium alanate phases, and/or catalyzing surface reactions or solid-state transformations. Experimentally, Ti has been observed in Ti-activated sodium alanate samples as an ordered TiAl3 alloy [6,13–15], amorphous Ti–Al compounds [5,8,9,11,12,15–19], Ti-hydrides [12,20,21] and Ti interstitials in NaAlH4 [16]. The formation of these new phases incorporating Ti could shift the favorability of the sodium alanate reactions, akin to the destabilization of metal or covalent
Hydride dehydrogenation by metal or metal hydride additives [22],
to achieve lower temperatures for equilibrium H reversibility.
Titanium dissolution in sodium alanate phases, and modification
of these alanates caused by such dissolution has been investigated
both experimentally and theoretically. It has been interpreted from
these studies that the most favorable Ti substitution in the sodium
alanate structures, may be either on the Na sublattice [4,23–25], or
on the Al sublattice [26–30], albeit in some cases in a metastable
state and others a stable state. It has also been reported from some
studies that Ti may act as a heterogeneous catalyst on the reacting
phase surfaces, activating H recombination and H₂ gas desorption
upon dehydrogenation, H₂ gas dissociation and adsorption upon
rehydrogenation, and/or nucleation and growth of the associated
reaction products [5,9,11,12,31–34].

A recent study created ground state chemical potential maps of
the Na–Al–Ti–H system from first principles phase formation en-
thalpies and predicted favorable Ti substitution for Al under Al-
poor/H-rich conditions [35]. Thermodynamic methodologies can
be used to model the equilibrium distribution and behavior of
Ti-bearing bulk phases formed from Ti-activated sodium alanates
over an even wider range of temperature and pressure conditions.
This is accomplished in the present study by the thermodynamic
assessment of combined experimental measurements of known
phases and first principles finite temperature predictions of hy-
pothetical Ti-substituted phases. In the present work the ther-
modynamic mixing interactions of Ti with NaNH₂ or α-Na₃AlH₆
and the thermodynamic properties of the fully Ti-substituted hy-
pothetical end-member compounds are predicted with density
functional theory ground state minimizations and direct method
lattice dynamics. The CALPHAD (CALculation of PHase Diagrams)
methodology is used to simultaneously fit thermodynamic mod-
els to the large set of experimental and predicted data, where
the latter effectively reduces the number of fit parameters. The
Na–Al–Ti–H assessment is progressively built on increasing ele-
mental order, first establishing the unassessed binary Na–Ti and
Ti–H systems, then merging these with the other established rel-
vant binary and ternary assessments, and finally incorporating
the modeled quaternary interactions. A thermodynamic parameter
database constructed in this way for the Na–Al–Ti–H system en-
ables equilibrium thermodynamic modeling of Ti-doping in bulk
sodium alanates, the stability of sodium alanates, and the effect
of Ti on the formation of Ti–Al compounds and Ti-hydrides. This
methodology does not intend to address surface catalytic effects
on sodium alanate dehydrogenation/rehydrogenation kinetics; in-
stead it describes the ideal thermodynamic upper bound that can
be achieved for sodium alanate reversibility in the presence of Ti
additives.

2. Review of experimental data and modeling methodologies

2.1. Thermodynamic modeling and evaluation of binary systems

To model the quaternary Na–Al–Ti–H system, it is essential
to have thermodynamic descriptions of all six constituent binary
systems. The Al–H [36], Al–Na [37], and Na–H [38] systems were
evaluated by the present authors, while the Al–Ti system was
modeled by Ansara et al. [39]. Their phase diagrams are shown
in Figs. 1–4. Modeling of the Na–Ti system is not available from
literature and is conducted in the present work. There were several

Fig. 1. The Al–H phase diagram calculated at 1 atm from Ref. [36].

Fig. 2. The Al–Na phase diagram calculated at 1 atm from Ref. [37].

Fig. 3. The Na–H phase diagram calculated at 1 atm from Ref. [38].
Fig. 4. The Al–Ti phase diagram calculated from Ref. [39].

Fig. 5. The Na–Ti phase diagram calculated at 1 atm according to the present modeling.

attempts to evaluate the Ti–H system thermodynamically [40–
42]. Most recently, Königsberger and co-workers [42] modeled the
Ti–H and Zr–H systems using the CALPHAD approach. However,
they set interstitial sites as one per metallic atom for hcp, and 1.5
for bcc when modeling the metal–H interstitial solutions. Those
models could not be combined with the Na–Al–H system. As a
consequence, a new evaluation of the Ti–H system had to be made
in the present work.

A review on the Na–Ti system by Bale [43] in 1989 showed that
the published experimental data were not available. By analogy
with binary phase diagrams of alkali metal and Group IVa ele-
ments, Bale suggested that the Na–Ti system is almost completely
immiscible in both the solid and liquid states. Since Na and Ti have
extremely low mutual solubilities, a univariant

A term in Eq. (1) is the excess energy due to the interaction be-

between Na and Ti in the liquid, bcc, fcc, or hcp phases. The
interaction parameter \( L \) can be expressed as a linear function of
temperature, \( L = A + BT \), fitted to relevant experimental data. The
goal of the present modeling was to evaluate interaction parameters
for liquid, bcc, and hcp phases in order to reproduce reasonable phase diagram and solubility data. This was done using an optimization module in Thermo-Calc [47]. Due to the extremely low solubility, a strong positive interaction, i.e. a repulsive interaction, between Na and Ti should be expected for all the phases. From the preliminary optimizations it was found

that a temperature dependent parameter with an approximate
value of 75 J/mol/K was necessary for the liquid phase. On the other
hand, a constant interaction parameter is efficient for the bcc or hcp
solid solutions. With the present models and parameters, the Na–Ti
diagram was calculated as presented in Fig. 5. It shows almost no
mutual solubility in solid and liquid states, and each three-phase
equilibrium temperature is almost the same as the corresponding
transformation temperature of a pure element. It is worth noting
that similar thermodynamic descriptions would be expected when
modeling the Na–Sc, Na–Y, Na–Ce, Na–Zr, Na–Hf, Na–V, and Na–Nb
systems.

The Ti–H system is of importance to the present work since
titanium hydrides may be formed during dehydrogenation of
Ti–activated sodium alanates. The Ti–H binary system was
investigated experimentally several times. A literature review was
conducted by San-Martín and Manchester [48], who compiled
most of the experimental information on the Ti–H phase diagram,
H solubility in bcc-Ti and hcp-Ti, and thermodynamic properties
of the hydride \( \delta \)-TiH\(_2\). Hydrogen solubility in both the hcp and bcc
phases is very high. They are described together with vacancies
(Va) in the interstitial solution model, using \( (Ti)_1(H, Va)_3 \) for the
bcc phase and \( (Ti)_3(H, Va)_{0.5} \) for the hcp phase in the present work.

Accordingly, the Gibbs energy for one mole of formula unit of bcc
or hcp is given by

\[
G_m = \sum_j x_j \delta G_j + RT \left( \sum_j x_j \ln x_j + x_{H_2} x_{L_2} L \right) \tag{1}
\]

where \( x_j \) is the molar fraction of Na or Ti, and \( \delta G_j \) is the Gibbs
energy of pure elements in the liquid, bcc, or hcp phases, re-
ferred to the enthalpy of the so-called Stable Element Reference (SER)
at 298.15 K and 1 bar (same thereafter). The Gibbs energy of all
the pure elements are compiled in Ref. [46], and are also available
in the SGTE database [45]. The last term in Eq. (1) is the excess
energy due to the interaction between Na and Ti in the liquid, bcc,
fcc, or hcp phases. The interaction parameter \( L \) can be expressed
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bcc phase and \( (Ti)_3(H, Va)_{0.5} \) for the hcp phase in the present work.

Accordingly, the Gibbs energy for one mole of formula unit of bcc
or hcp is given by

\[
G_m = \sum_j x_j \delta G_j + cRT \left( y_{H_2} \ln y_{H_2} + y_{VA} \ln y_{VA} + y_{H_2} y_{VA} L \right) \tag{2}
\]

where \( c = 3 \) for bcc, and 0.5 for hcp. The variable \( y \) is the fraction
of occupied H atoms or vacancies in the second sublattice. The
quantity \( \delta G_j \) is Gibbs energy of the pure element bcc-Ti or hcp-
Ti, while \( \delta G_{H_2} \) is Gibbs energy of the hypothetical compounds
bcc-TiH\(_2\) or hcp-TiH\(_{0.5}\). These two quantities are evaluated from
experimental information using the following expressions

\[
\delta G_{Ti,H}(TiH_2) = a + b_1T + c_1T \ln T + \delta G_{hcp}(hcp) + 1.5 \delta G_{H_2}(gas) \tag{3a}
\]

\[
\delta G_{Ti,H}(TiH_{0.5}) = a_2 + b_2T + c_2T \ln T + \delta G_{hcp}(hcp) + 0.25 \delta G_{H_2}(gas). \tag{3b}
\]

The last term in Eq. (2) represents excess energy due to
interaction between H and vacancies in second sublattice. It is
determined from experimental data.

According to Ref. [48], \( \delta \)-TiH\(_2\) has a cubic structure similar to
CaF\(_2\) and is the only stable hydride in the Ti–H system. It exhibits a
considerable concentration range from 60 to 66 at.% H, but H never completely occupies all available tetrahedral vacancy sites. As a consequence, a two-sublattice model (Ti)\(_2\)(H, V\(_{\text{a}}\)\(_2\)) is applied to account for H deficiency in the vacancy sites, and its Gibbs energy is also expressed with Eq. (2). There are two quantities of Gibbs energy: one for hypothetical Ti with the same structure as TiH\(_2\), and another for the stoichiometric composition TiH\(_2\). The former is assumed to be equal to the Gibbs energy of metastable fcc-Ti given in Ref. [46]. The latter is modeled as a function of temperature with the following polynomial

\[ ^{0}G_{\text{TiH}_2} = a + bT + cT \ln(T) + dT^2 + eT^3 + f/T \]  

(4)

where the parameters \(a, b, c, \ldots\) are evaluated from experimental data. The liquid phase is modeled as a substitutional solution. However, model parameters cannot be evaluated due to the lack of relevant experimental information.

Experimental data compiled in Ref. [48] were used as input to optimize the model parameters for bcc, hcp, and δ-TiH\(_2\) through the optimization module in Thermo-Calc. These data include phase boundaries, pressure–composition data, and thermodynamic data of δ-TiH\(_2\). In addition, conditions are also introduced in the optimization to ensure the metastable status of hypothetical bcc-TiH\(_2\) and hcp-TiH\(_{0.5}\) when evaluating the coefficients in Eqs. (3a) and (3b). The condition for bcc-TiH\(_2\) was set as \(^{0}G_{\text{TiH}_2} > \) Gibbs energy of the mixture of TiH\(_2\) and gas, or, bcc and gas, at \(x_{\text{H}} = 0.75\); while the condition for TiH\(_{0.5}\) was set as \(^{0}G_{\text{TiH}_{0.5}} > \) Gibbs energy of the mixture of hcp, bcc, TiH\(_2\), and gas at \(x_{\text{H}} = 0.33\). During the optimization, it was found that a regular solution model was sufficient to describe H solubility in bcc-Ti and hcp-Ti. The final results were obtained when most experimental data were accounted for within the expected uncertainty limits by the calculations. All the model parameters are given in Appendix.

Using the present models and parameters, the enthalpy, entropy, and Gibbs energy of formation of δ-TiH\(_{1.6}\) and δ-TiH\(_{2.0}\) were calculated as a function of temperature, as shown in Figs. 6–8 in comparison with experimental data [49–55]. It is seen that the present modeling is in good agreement with most of the experimental data. Nevertheless, the enthalpy of formation of δ-TiH\(_2\) predicted from the present modeling differs somewhat from those by Arita and co-workers [49] based on analysis of experimental H dissolution in Ti. It is noted that their data are more negative than the other experiments [50–55] including their own previous data [50], as shown in Fig. 6. Obviously, it is impossible to fit their data and others simultaneously.

The Ti–H diagram calculated at 1 atm is presented in Fig. 9, where the symbols represent the experimental phase boundaries from literature compiled in Ref. [48]. It is seen from this diagram that the present calculations are in satisfactory agreement with experimental data on the equilibria between hcp and bcc, but some differences remain for the phase boundary bcc/bcc + δ-TiH\(_2\). A significant effort was made to improve the fitting by applying a subregular solution model to the bcc phase, but improvement could not be achieved. It is noted that the experimental phase boundary data are based on isothermal measurements of pressure–composition, and thus would bear some uncertainty.
The Ti–H phase diagram calculated at 1 atm according to the present modeling, where the symbols represent experimental phase boundaries from literature compiled in Ref. [48].

Fig. 10. Pressure–composition isotherms of the Ti–H system calculated at different temperatures, where the symbols represent experimental data from various investigators cited in Ref. [48].

The experimental data are from various investigators as cited in Ref. [48]. The agreement between the present calculations and experiments is reasonably good, which can be taken as an indication that the H solubility in bcc is modeled well at temperatures below 1000 °C. A potential diagram of the Ti–H system in Fig. 11 calculated from the present modeling shows the dissociation pressure of TiH₂.

2.2 Thermodynamic modeling and evaluation of ternary systems

The Na–Al–Ti–H system consists of four ternary systems, among which the Na–Al–H description encompassing the ternary sodium alanate stoichiometric compounds was previously developed by the present authors [37] and was the only ternary system incorporated in the present work. A potential diagram of the Na–Al–H system is presented in Fig. 12 to show the stability of various phases and their relationships. There are no ternary compounds with known crystal structures in the other three constituent ternary systems: Al–Ti–H, Al–Na–Ti, and Na–Ti–H. Hydrogen solubility in Ti-rich Ti–Al phases is on the order of ppm and decreases markedly with increasing Al content [56]. Therefore, thermodynamic evaluation of the three ternary systems would not affect the present modeling for the Na–Al–Ti–H system. Among the three ternary systems, it is worth to examine the effect of H₂ pressures on the stability of Ti–Al metallic compounds and hydrides. This is illustrated in Fig. 13 by a diagram of the Al–Ti–H calculated at 100 °C by combining all binary models from the present work and previous studies [36,39]. It is interesting to note that TiAl₃ can coexist with TiH₂ under H₂ pressure range of 0.0012–9293 bar at 100 °C, while TiAl₂ remains stable only at pressures below 0.0012 bar. Further calculations indicate that TiAl₃ still remains stable together with TiH₂ within the H₂ pressure range of 0.102–33299 bar at 200 °C.
Table 1

<table>
<thead>
<tr>
<th>Phase-structure (Cell formula)</th>
<th>Ti substitution level (%)</th>
<th>(NaAlH4)</th>
<th>(Na2TiAlH6)</th>
<th>(Na2TiAlH6)</th>
<th>(Na2TiAlH6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlH4 H4/1/a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>α-Na3AlH6 P2_1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

2.3. Thermodynamic modeling and evaluation of Na–Al–Ti–H quaternary system

2.3.1. First principles predictions

Two atomic theoretical methodologies were used to predict the finite temperature thermodynamic properties of hypothetical Ti substitution in the NaAlH4 and α-Na3AlH6 phases. First, the periodic structures were predicted with the density functional theory Vienna ab initio simulation package (VASP) code [57, 58] full minimizations. The prediction used the standard Al and H, and hard valence Na and Ti projector augmented wave potentials [59] with the generalized gradient PW91 exchange correlation corrections [60]. The VASP parameters and approach used in the present study are given in detail in our previous work in Ref. [26]. The Materials Design Phonon module [61,62] was then used with VASP to calculate direct method lattice dynamics with the harmonic approximation for the minimised hypothetical Ti-substituted structures and to predict their finite temperature thermodynamic properties, following the methodology fully described in Refs. [37,38].

Our first principles predictions approximated the thermodynamic convention of referring to the elements in their standard states (SER), by referring the electronic enthalpies of formation of the Ti-substituted sodium alanates with respect to the standard state elemental phase structures, all simulated at the ground state. Following this approach, we previously determined the substitution of Ti on the Al sublattice to be more favorable than the substitution on the Na sublattice, regardless of whether the Ti formal charge state was varied from +1 to +4 by the introduction of vacancies [26]. Based on this premise, only the most favorable Ti interaction with the Al sublattices of the sodium alanate phases was simulated in this study, where one Ti atom was directly substituted for one Al atom effectively as the +3 formal charge state, in the absence of any vacancies. Various levels of Ti substitution for Al, given in Table 1, were simulated by changing the supercell size of the sodium alanate phases, where Ti was substituted into each supercell for the intermediate substitution stoichiometries. The interactions between the single Ti atoms in the periodic supercell were assumed to be negligible. Full Ti substitution was modeled as the hypothetical compounds, NaTiH4 and α-Na3TiH6, which were simulated as the structural analogs of NaAlH4 and α-Na3AlH6, respectively.

It has been shown in previous studies that spin polarization alters the ground state energetics of Ti-substituted NaAlH4 [4,39]. It can thus be expected that the use of non-restricted spin would have changed some of the results of the present study; we believe however that all the qualitative conclusions of this work are valid.

2.3.2. Thermodynamic modeling and evaluation

With thermodynamic modeling, the Gibbs energy of a compound is often expressed as a function of temperature with a polynomial form. Such a polynomial is quite acceptable in many cases and is often used in the CALPHAD approach. However, the polynomial cannot model heat capacity well at very low temperatures. On the other hand, Einstein’s model based on harmonic lattice vibrations can describe heat capacity reasonably well under normal conditions. In the present case, the heat capacity of NaTiH4 and α-Na3TiH6 is available from direct method predictions within the range from 0 K to 2000 K, see Fig. 14(a) and (b). To model heat capacity within the whole temperature range, it is necessary to combine Einstein’s model and the polynomial method, as demonstrated in our previous work [37,38]. The Gibbs energy per one mole of formula of NaTiH4 or Na3TiH6 is given by

\[ \Delta G_m = E_o + nRT \ln(\exp((0.5\theta_o/T) - \exp(-0.5\theta_o/T))/\theta_o) + \theta_o T^2 \quad \text{for} \quad 0 < T < 298.15 K \]

(5a)

\[ \Delta G_m = a + b T + c T \ln T + d T^2 + e T^3 + f T \]

for 298.15 K < T < 2000 K

(5b)

where \( \theta_o \) in Eq. (5a) is the Einstein temperature. The coefficients \( E_o \) and \( a \) in Eq. (5a) and \( b, c, d, e, f \) in Eq. (5b) are constants. The constant \( n \) in Eq. (5a) is equal to 3 for NaTiH4 and 6 for Na3TiH6. This choice is in line with the treatment in our previous work for NaAlH4 and α-Na3AlH6 [26]. The enthalpy, entropy, and heat capacity can be derived from the above equations using standard thermodynamic relations. As an example, the heat capacity \( C_T \) is given below:

\[ C_T = 3R \frac{\theta_o T^2}{[\exp(\theta_o/T) - 1]^2} + A_o T \]

for 0 K < T < 298.15 K

(6a)

\[ C_T = -c - 2dT - 6eT^2 - 2f/T^2 \]

for 298.15 K < T < 2000 K

(6b)

The first term in Eq. (6a) describes the harmonic lattice vibrations based on Einstein’s model, and the second term is used to account for electronic excitation and low-order anharmonic vibrations. We shall assess the properties of NaTiH4 and α-Na3TiH6 using the above models. The first step was to evaluate the coefficients \( \theta_o \) and \( A_o \) in Eq. (5a) and \( c, d, e, f \) in Eq. (5b) for the two compounds based on the heat capacity from the lattice dynamics.
predictions. To maintain a smooth variation of \( C_p \) around 298.15 K, a condition was applied in the optimization that the difference of Eqs. (6a) and (6b) at 298.15 K should be less than 0.1 J/mol/K. The next step was to evaluate coefficient \( E_o \) in Eq. (5a) and constants \( a \) and \( b \) in Eq. (5b) by best fitting to the Gibbs energy from first principles calculations, as shown in Fig. 15(a) and (b).

To describe possible Ti dissolution in the sodium alanates, as mentioned earlier, it is assumed that Al in NaAlH\(_4\) and \( \alpha\)-Na\(_3\)AlH\(_6\) can be substituted by Ti. By applying the sublattice models, the Gibbs energy per mole of formula of \((Na)_{x}(Al, Ti)(H)_y\) is given by

\[
G_m = y_{Al}G_{NaAlH_y} + y_{Ti}G_{NaTiH_y} + RT(y_{Al} \ln y_{Al} + y_{Ti} \ln y_{Ti}) + y_{Al}y_{Ti}L
\]

(7)

where \( y_{Al} \) and \( y_{Ti} \) are site-fractions of Al and Ti in the second sublattice, and \( G_{NaAlH_y} \) and \( G_{NaTiH_y} \) are molar energies of Na\(_x\)AlH\(_y\) (NaAlH\(_4\) or \( \alpha\)-Na\(_3\)AlH\(_6\)) and Na\(_x\)TiH\(_y\) (NaTiH\(_4\) or \( \alpha\)-Na\(_3\)TiH\(_6\)), respectively, modeled with Eqs. (5a) and (5b). The parameter \( L \) represents the interaction between Al and Ti on the second sublattice, and can be evaluated from the mixing properties between NaAlH\(_4\) and NaTiH\(_4\) or between \( \alpha\)-Na\(_3\)AlH\(_6\) and Na\(_3\)TiH\(_6\) from first principles calculations at different temperatures.

3. Results and discussion

Using the present models and parameters, the heat capacity of hypothetical NaTiH\(_4\) and \( \alpha\)-Na\(_3\)TiH\(_6\) was calculated as a function of temperature, as shown in Fig. 14(a) and (b), respectively, in comparison with the lattice dynamics predictions. It is seen that the combination of modified Einstein’s model at low temperatures and polynomial at high temperatures is capable of describing...
(a) Na(Al, Ti)H₄ at lower temperatures. (b) Na(Al, Ti)H₄ at higher temperatures.

Fig. 16. Composition dependence of Gibbs energy of Na(Al, Ti)H₄ calculated at different temperatures according to the present thermodynamic modeling, in comparison with lattice dynamics predictions.

(a) Na₃(Al, Ti)H₆ at lower temperatures. (b) Na₃(Al, Ti)H₆ at lower temperatures.

Fig. 17. Composition dependence of Gibbs energy of α-Na₃(Al, Ti)H₆ calculated at various temperatures according to the present thermodynamic modeling, in comparison with lattice dynamics predictions.

the heat capacity very well within the whole temperature range. A comparison of Gibbs energy between the present modeling and lattice dynamics predictions is presented in Fig. 15(a) and (b), where the Gibbs energy is referred to the enthalpy of the Stable Element Reference (SER) at 298.15 K and 1 bar. For convenience of discussion, Gibbs energy of NaAlH₄ and α-Na₃AlH₆ was also plotted in Fig. 15(a) and (b). It is noted in these figures that the Gibbs energy of NaAlH₄ or α-Na₃AlH₆ predicted from thermodynamic modeling shows almost the same temperature dependence as the Phonon direct prediction within whole temperature range, but it slightly shifts towards more negative values. As explained in our previous work [37], this is because the thermodynamic model is intended to fit to experimental data rather than the data predicted from the Phonon direct method.

There is no experimental data available for the hypothetical NaTiH₄ and α-Na₃TiH₆ phases. The present thermodynamic models were used to fit the Gibbs energy predicted from the Phonon direct method. Compared to NaAlH₄ or α-Na₃AlH₆, thermodynamic modeling of NaTiH₄ or α-Na₃TiH₆ fit the Phonon direct predictions quite well within the whole temperature range, although some differences still remain.

With the thermodynamic descriptions of these stable and hypothetical compounds, it was possible to model the mixing properties between NaAlH₄ and NaTiH₄ and between α-Na₃AlH₆ and Na₃TiH₆. The Gibbs energy of Na(Al, Ti)H₄ and Na₃(Al, Ti)H₆ at different Ti contents was predicted as a function of temperature from the first principles calculations, and some results are plotted in Figs. 16 and 17 to show the composition dependence at different
Fig. 18. IsothermalsectionsoftheNa–Al–Tisystemcalculatedat100 °CtoshowequilibriumofTiAl3withdifferenthydridesunder(a)1atmH2,(b)25atmH2, and (c)100atmH2.

temperatures. The data for Na(Al, Ti)H4 in Fig. 16 shows almost a linear relation between the Gibbs energy of NaAlH4 and that of NaTiH4 at 0 K and 298 K, and then it deviates from the linear relation with increasing temperature. Nonlinear effects already exist for Na3(Al, Ti)H6 at 0 K and 298 K, as seen in Fig. 17, and its deviation from the linear relation also becomes stronger with increasing temperature. The deviation from the linear relation in Figs. 16 and 17 indicate a repulsive interaction when mixing NaAlH4 and NaTiH4, or mixing α-Na3AlH6 and Na3TiH6, and the repulsion becomes stronger with increasing temperature. In order to model such behavior, a temperature dependent interaction parameter has to be used for both Na(Al, Ti)H4 and Na3(Al, Ti)H6. With such interaction parameters, the mixing Gibbs energy of Na(Al, Ti)H4 and Na3(Al, Ti)H6 was calculated at various temperatures in comparison with the lattice dynamics predictions, as shown in Figs. 16 and 17. In general, the present thermodynamic model describes quite well the repulsive behavior between NaAlH4 and NaTiH4, or between α-Na3AlH6 and Na3TiH6, as predicted by the Phonon direct method.

By combining the Na–Al–H system [37] with the modeling of all the binary systems, it is possible to examine the phase stability of alanates in the Na–Al–Ti–H system and effect of temperature and pressures through thermodynamic calculations. To illustrate possible formation of Ti–Al compounds and Ti-hydride during the dehydrogenation of NaAlH4 and α-Na3AlH6 doped with Ti, isothermal sections of the Na–Al–Ti system were calculated at 100 °C under various pressures of H2, as shown Fig. 18(a), (b) and (c). It is very interesting to see that α-Na3AlH6 is in equilibrium with NaH and TiAl3 at 1 atm, Fig. 18(a). At 25 atm α-Na3AlH6 is in equilibrium with NaH and TiH2, while NaAlH4 is in equilibrium with α-Na3AlH6 and TiAl3, Fig. 18(b). At 100 atm, TiH2 is in equilibrium with both α-Na3AlH6 and NaAlH4, Fig. 18(c). Since the pressure will vary during the dehydrogenation process, it is possible to form both TiAl3 and TiH2 at different stages. This is consistent with experimental observation [14,15]. The formation of TiAl3 and/or TiH2 will also depend on kinetic conditions such as surface energy, nucleation, etc. Any amorphous Ti–Al compounds might be early forms of TiAl3 precipitation. The formation of TiH2 may be taken as an indication of H loss as observed in practice. From Figs. 16 and 17 it is seen that the dissolution of Ti in NaAlH4 or α-Na3AlH6 will increase Gibbs energy and thus is thermodynamically unfavorable. The present thermodynamic
calculation indicates that Ti is virtually insoluble in NaAlH₄ or α-Na₃AlH₆ under normal conditions. It has been shown in previous predictions, however, that the stability of the substitution is higher near the surface [26]. Thus, we should expect that any inclusion of Ti in the alanate sublattice is close to the surface.

Although the mechanism of Ti or TiCl₃ as a catalyst is not well known for the dehydrogenation processes, it is very interesting to examine reactions of Ti or TiCl₃ with NaAlH₄, especially during ball milling. If a typical amount of 2.5 mol % Ti or TiCl₃ additive is combined with NaAlH₄, the possible reactions that could occur:

\[
\text{NaAlH}_4 \rightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \quad (8a)
\]

\[
\text{NaAlH}_4 + \frac{1}{40} \text{Ti} \rightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{1}{40} \text{TiH}_2 + \frac{2}{3} \text{Al} + \frac{29}{40} \text{H}_2 \quad (8b)
\]

\[
\text{NaAlH}_4 + \frac{1}{40} \text{Ti} \rightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{1}{40} \text{TiAl}_3 + \frac{71}{120} \text{Al} + \frac{1}{2} \text{H}_2 \quad (8c)
\]

\[
\text{NaAlH}_4 + \frac{1}{40} \text{TiCl}_3 \rightarrow \frac{37}{120} \text{Na}_3\text{AlH}_6 + \frac{3}{40} \text{NaCl} + \frac{1}{40} \text{TiH}_2 + \frac{83}{120} \text{Al} + \frac{21}{20} \text{H}_2 \quad (8d)
\]

\[
\text{NaAlH}_4 + \frac{1}{40} \text{TiCl}_3 \rightarrow \frac{37}{120} \text{Na}_3\text{AlH}_6 + \frac{3}{40} \text{NaCl} + \frac{1}{40} \text{TiAl}_3 + \frac{74}{120} \text{Al} + \frac{43}{40} \text{H}_2 \quad (8e)
\]

A necessary condition for each reaction to proceed is an energy decrease. The more the energy decreases, the higher driving force for a reaction to proceed. Since thermodynamic models for all phases are now available, it is possible to calculate Gibbs energy of each phase at different temperatures, and plot energy change for each reaction at 1 bar. This is illustrated in Fig. 19(a). It is seen that the reaction equations (8d) and (8e) show a considerable energy decrease relative to reaction equation (8a) due to addition of 0.025 mol TiCl₃ in one mole of NaAlH₄. The reaction equations (8d) and (8e) have a much higher driving force, and thus both reactions are possible. As a consequence, TiH₂ and TiAl₃ can be reaction products depending on the kinetic competition between reaction equations (8d) and (8e). Reaction equation (8d) has a slightly higher driving force than reaction equation (8e). On the other hand, a small addition of Ti will promote reaction equation (8b) to a certain extent, which produces TiH₂, but not reaction equation (8c) with TiAl₃ as a reaction product.

Similarly, we can examine the energy change for possible reactions of Na₃AlH₆ with Ti or TiCl₃:

\[
\text{Na}_3\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \quad (9a)
\]

\[
\text{Na}_3\text{AlH}_6 + \frac{1}{40} \text{Ti} \rightarrow 3\text{NaH} + \frac{1}{40} \text{TiH}_2 + \text{Al} + \frac{59}{40} \text{H}_2 \quad (9b)
\]

\[
\text{Na}_3\text{AlH}_6 + \frac{1}{40} \text{Ti} \rightarrow 3\text{NaH} + \frac{1}{40} \text{TiAl}_3 + \frac{37}{40} \text{Al} + \frac{3}{2} \text{H}_2 \quad (9c)
\]

\[
\text{Na}_3\text{AlH}_6 + \frac{1}{40} \text{TiCl}_3 \rightarrow \frac{117}{40} \text{NaH} + \frac{3}{40} \text{NaCl} + \frac{1}{40} \text{TiH}_2 + \text{Al} + \frac{121}{80} \text{H}_2 \quad (9d)
\]

\[
\text{Na}_3\text{AlH}_6 + \frac{1}{40} \text{TiCl}_3 \rightarrow \frac{117}{40} \text{NaH} + \frac{3}{40} \text{NaCl} + \frac{1}{40} \text{TiAl}_3 + \frac{37}{40} \text{Al} + \frac{123}{80} \text{H}_2 \quad (9e)
\]

The Gibbs energy change for each reaction at 1 bar was calculated as a function of temperature, as presented in Fig. 19(b). It is noted that the energy decrease is very small for reaction equation (9a) around 100 °C, and this reaction would hardly proceed, as is observed in practice. Nevertheless, an addition of 0.025 mol TiCl₃ in one mole of Na₃AlH₆ will result in considerable energy decrease, as in reaction equations (9d) and (9e) which yield TiH₂ or TiAl₃. The addition of Ti will induce a limited driving force for reaction equation (9b) with TiH₂ as a reaction product, but not for reaction equation (9c) with TiAl₃ as a reaction product. This is consistent with experimental observation that an addition of Ti powder usually results in formation of TiH₂ instead of TiAl₃ [63].

The present thermodynamic phase stability and reaction modeling reinforces hypotheses that Ti-bearing phases enhance dehydrogenation and rehydrogenation of the Na–Al–H phases by surface-mediated catalysis and not by a destabilization mechanism. Since the most favorable proposed reaction equations (8d), (8e), (9d) and (9e) of NaAlH₄ or α-Na₃AlH₆ with TiCl₃ are not reversible under reasonable conditions, the possible reactions of the Na–Al–H phases with the resulting favorable TiH₂ or
were more favorable than those of the pure NaAlH4 and Na2AlH6 phases given by reaction equations (8a) and (9a), respectively. However, increases in dissociation pressure have not been observed experimentally to support the occurrence of a destabilization effect. Indeed, our previous compilation [37] of predicted and experimental dissociation data for NaAlH4 and Na2AlH6 phases did not show evidence for destabilization or change in dissociation pressure by Ti-doping. True catalysis of NaAlH4 or Na2AlH6 dehydrogenation by the TiAl3 or TiH2 products cannot involve destabilization or the change in reaction energy. Also, a catalytic mechanism, not destabilization, could explain the observed benefit of Ti-additives improving the kinetics of dehydrogenation reactions, the reverse of reaction equations (8a) and (9a).

4. Conclusions

The Ti–H system was evaluated using thermodynamic models, and model parameters were optimized by best fitting to selected experimental data, including H solubility in bcc-Ti and hcp-Ti, and stability of the hydride δ-TiH2. To model possible Ti dissolution in sodium analates, NaAlH4 and α-Na2AlH6, sublattice models were applied. Thermodynamic properties of the hypothetical compounds NaTiH4 and Na2TiH6, as well as their mixing properties with NaAlH4 or α-Na2AlH6 were predicted from first-principles calculations based on density functional theory ground state minimizations and direct method lattice dynamics. The predictions have proved very effective for thermodynamic modeling. As predicted by the first principles calculations, a repulsive interaction is also described with the model when Ti is dissolved in NaAlH4 or α-Na2AlH6. The repulsion becomes stronger with increasing temperature. As predicted by the modeling, Ti is virtually insoluble in NaAlH4 or α-Na2AlH6 under normal conditions. On the other hand, a small amount of added TiC13 in NaAlH4 or α-Na2AlH6 will result in a considerable driving force for the formation of TiH2 and/or TiAl3. A small addition of Ti induces a limited driving force for the formation of TiH2 only. Based on a combined interpretation of present thermodynamic modeling and prior experimental observations, the TiAl3 and TiH2 phases are ascribed to have a catalytic effect, not a destabilization effect, on the reversibility of the dehydrogenation/rehydrogenation reactions in the Na–Al–H system.

Acknowledgements

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During the preparation of this work the authors did not see the work by Ukitake and co-workers [64] who modeled thermodynamically the Ti–H and Zr–H systems. It is interesting to note that their model for δ-TiH2 is same as what we used in our work, and their prediction of enthalpy of formation at the stoichiometric composition is also very close to our evaluation. On the other hand, their models for the solution phases bcc and hcp are different from ours.

Appendix

Summary of thermodynamic parameters describing the Na–Al–Ti–H system. Values are given in SI units (Joule, mole, Kelvin, and Pa) and correspond to one mole of formula units of the phases. The parameters marked with an asterisk (*) were evaluated in the present work. Gibbs energy for pure elements and gas can be found in [46].

Liquid with formula (Al, H, Na, Ti)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_\text{NaAlH}_4^{\text{liq}}$</td>
<td>$= 8035 + 257 + 27 \ln(T) + 0.5 \Omega_{\text{gas}}^{\text{H}_2}$</td>
</tr>
<tr>
<td>$G_{\text{Al},H}^{\text{liq}}$</td>
<td>$= 50942 - 11.1007T$</td>
</tr>
<tr>
<td>$G_{\text{Al},Na}^{\text{liq}}$</td>
<td>$= 14130 + 56.0985T - 1827(x_{\text{Al}} - x_{\text{Na}})$</td>
</tr>
<tr>
<td>$G_{\text{Al},Ti}^{\text{liq}}$</td>
<td>$= -108250 + 38T + (-6000 + 5T)(x_{\text{Al}} - x_{\text{Ti}}) + 15000(x_{\text{Al}} - x_{\text{Ti}})^2$</td>
</tr>
<tr>
<td>$G_{\text{Na},Na}^{\text{liq}}$</td>
<td>$= -70264 + 45.2458T + (-56577 + 21.8825T)(x_{\text{H}} - x_{\text{Na}})$</td>
</tr>
<tr>
<td>$G_{\text{Na},Ti}^{\text{liq}}$</td>
<td>$= 22520 + 75T$ (*)</td>
</tr>
</tbody>
</table>

BCC_A2 with formula (Al, Na, Ti)1(H, Na)3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{Al},Al}^{\text{BCC}}$</td>
<td>$= 200000 + 0.2\Omega_{\text{Al}}^{\text{H}_2}$</td>
</tr>
<tr>
<td>$G_{\text{Na},Al}^{\text{BCC}}$</td>
<td>$= 215965 + 38T \ln[\exp(0.5 \times 2157)] - 0.00951132T$</td>
</tr>
<tr>
<td>$G_{\text{Ti},Al}^{\text{BCC}}$</td>
<td>$= 206754 + 2582187 - 42.90288T \ln(T) - 0.00404772T + 1.889 \times 10^{-7}T^3 + 696968/T$</td>
</tr>
<tr>
<td>$G_{\text{Al},Na}^{\text{BCC}}$</td>
<td>$= 118000$ (*)</td>
</tr>
<tr>
<td>$G_{\text{Al},Ti}^{\text{BCC}}$</td>
<td>$= 124220 - 233.89557 + 56.18337 \ln(T)$</td>
</tr>
<tr>
<td>$+ 0.5\Omega_{\text{H}<em>2}^{\text{hcp}} + 1.5\Omega</em>{\text{gas}}^{\text{H}_2}$ (*)</td>
<td></td>
</tr>
</tbody>
</table>

FCC_A1 with formula (Al, Na)1(H, Va)1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{Al},Al}^{\text{FCC}}$</td>
<td>$= 100000 + 0.5\Omega_{\text{Al}}^{\text{H}_2}$</td>
</tr>
<tr>
<td>$G_{\text{Na},Al}^{\text{FCC}}$</td>
<td>$= 1307 + 0.5\Omega_{\text{Na}}^{\text{H}_2}$</td>
</tr>
<tr>
<td>$G_{\text{Ti},Al}^{\text{FCC}}$</td>
<td>$= -45805 + 56.4302T$</td>
</tr>
<tr>
<td>$G_{\text{Al},Ta}^{\text{FCC}}$</td>
<td>$= -6210 + 76.4864T$</td>
</tr>
</tbody>
</table>

HCP_A3 with formula (Al, Na, Ti)1(H, Va)1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{Al},Al}^{\text{HCP}}$</td>
<td>$= 64310 - 766.9133T + 103.9079T \ln(T) + 0.25\Omega_{\text{H}_2}^{\text{hcp}}$</td>
</tr>
<tr>
<td>$G_{\text{Al},Ti}^{\text{HCP}}$</td>
<td>$= -133500 + 39T + 750(y_{\text{Al}} - y_{\text{Ti}}) + 17500(y_{\text{Al}} - y_{\text{Ti}})^2$</td>
</tr>
<tr>
<td>$G_{\text{Al},Va}^{\text{HCP}}$</td>
<td>$= 102025$ (*)</td>
</tr>
<tr>
<td>$G_{\text{Ti},Va}^{\text{HCP}}$</td>
<td>$= -21155$ (*)</td>
</tr>
</tbody>
</table>

AlH3 with formula (Al)1(H)3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{Al},Al}^{\text{H}_{3}}$</td>
<td>$= -28415 + 213.712933T - 41.75632T \ln(T) - 0.014548469T^2 + 446400/T$</td>
</tr>
</tbody>
</table>
NaH with formula (Na)$_1$(H)$_1$

$\Delta G_{\text{NaH}} = -66593 + 3RT \ln[\exp(0.5 \times 268/T) - \exp(-0.5 \times 268/T)] - 0.0188755T^2$

for $0 < T < 298.15$ K

$= -75768 + 293.7188T - 48.69355T \ln(T) - 2.614 \times 10^{-4}T^2$

+ $1.8048 \times 10^{-8}T^3 + 632658/T$

for $298.15$ K $< T < 2000$ K

$\delta$-TiH$_2$ with formula (Ti)$_1$(H, Va)$_2$

$\Delta G_{\text{TiH}} = 6150 - 0.29657T + F110327$ (*)

$\Delta G'_{\text{Ti,Va}} = 6000 - 0.17 + \alpha_{\text{G}}$ (*)

NaAlH$_4$ with formula (Na)$_3$(Al, Ti)$_1$(H)$_4$

$\Delta G_{\text{NaAlH}} = -128890 - 0.10258T + 3RT \ln[\exp(0.5 \times 220/T) - \exp(-0.5 \times 220/T)]$

for $0 < T < 298.15$ K

$= -150434 + 592.2826T - 99.6077T \ln(T) - 0.018466T^2$

+ $1.0858 \times 10^{-6}T^3 + 1091420/T$

for $298.15$ K $< T < 2000$ K

NaH with formula (Na)$_3$(Al, Ti)$_1$(H)$_4$

$\alpha$-Na$_3$AlH$_8$ with formula (Na)$_3$(Al, Ti)$_1$(H)$_8$

$\Delta G_{\text{NaAlH}} = -267960 - 0.17245T + 6RT \ln$

[exp(0.5 \times 217/T) - \exp(-0.5 \times 217/T)]

for $0 < T < 298.15$ K

$= -309621 + 1122.1777T - 187.247T \ln(T)$

- $0.02267T + 1.3138 \times 10^{-6}T^3 + 2200845/T$

for $298.15$ K $< T < 2000$ K

$\beta$-Na$_3$AlH$_8$ with formula (Na)$_3$(Al, Ti)$_1$(H)$_8$

$\Delta G_{\text{NaAlH}} = 3497 - 6.65877T + \alpha_{\text{G}}$

$\Delta L_{\text{Al, Ti, H}} = 46100 + 220T$

for $298.15$ K $< T < 2000$ K

References


180–186.


151917–1–3.


2475–2479.