Thermodynamic assessment of the Al–Ca binary system using random solution and associate models

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Abstract

The thermodynamic properties of the binary Al–Ca system are investigated. The assessment is carried out by means of the computer program Thermo-Calc, using models for the Gibbs energy of individual phases. In the present study, both associate and random solution models are tested for the system to better reproduce the experimental data. The results from the two models are compared with each other and with experimental data in the literature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Al–Ca; Thermodynamics; Modeling; Phase diagram; Associates; Intermetallics

1. Introduction

In many binary systems containing alkali earth elements, stoichiometric intermetallic compounds often form with melting temperatures much higher than those of the constituent pure elements. Correspondingly, there is a deep valley in the enthalpy of mixing in the liquid phase. When the random solution model is used for the liquid phase with the Redlich–Kister polynomial [1], it is found that higher-order interaction parameters in the liquid are typically needed to reproduce the liquidsus around the high-melting-temperature intermetallic compounds, and it often results in a less satisfactory liquidus at other compositions. The Al–Ca binary alloy is one of these systems with a very high melting temperature compound (Al$_4$Ca) compared to those of pure Al and Ca. A short-range ordering tendency in the liquid state in this system is likely. The recent experimental studies [2,3] on the liquid Al–Ca alloys provide strong evidences for the existence of molecular-like Al$_4$Ca species, called associates.

In the present work, the thermodynamic properties of the Al–Ca system are modeled, and the two models for the liquid phase are considered, i.e., the random solution model [4] with the free Al and Ca atoms only and the associate model [5–7] with both free atoms and the Al$_4$Ca associates. There are four intermetallic phases in the system which are all treated as stoichiometric compounds. The results from the two models are compared with each other and with the available experimental data.

2. Experimental information

The experimental equilibrium phase diagram information for the Al–Ca binary system [8] was collected in several phase diagram compilations [9–11]. The phase diagram presented by Hansen and Anderko [12] with the two confirmed binary compounds, Al$_4$Ca and Al$_8$Ca, (after Refs. [13,14]) has been accepted as a complete phase diagram until now. Most recent studies [15,16], however, indicated that there exist two more compounds in the system, Al$_{14}$Ca$_{13}$ and Al$_{3}$Ca$_{8}$. Their crystal structures were investigated and well defined by X-ray analysis. The four binary compounds and their crystal structures are listed in Table 1. In this section, experimental thermodynamic and phase equilibrium data in the literature will be reviewed.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model</th>
<th>Crystal structure</th>
<th>Prototype and Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_4$Ca</td>
<td>(Al)$_4$(Ca)$_4$</td>
<td>b.c.t. (D1$_{2}$)</td>
<td>Al$_4$Ba [14]</td>
</tr>
<tr>
<td>Al$_8$Ca</td>
<td>(Al)$_8$(Ca)$_8$</td>
<td>f.c.c. (C15)</td>
<td>Cu$_2$Mg [13]</td>
</tr>
<tr>
<td>Al$<em>{14}$Ca$</em>{13}$</td>
<td>(Al)$<em>{14}$(Ca)$</em>{13}$</td>
<td>Monoclinic</td>
<td>– [15]</td>
</tr>
<tr>
<td>Al$_3$Ca$_8$</td>
<td>(Al)$_3$(Ca)$_8$</td>
<td>Triclinic</td>
<td>Ca$_3$In$_5$ [15,16]</td>
</tr>
</tbody>
</table>

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2.1. Thermodynamic data

Kocherov et al. [17] utilized a conventional isothermal calorimeter with two different methods to measure the enthalpies of formation of Al–Ca alloys. In the first method, a self-sealing calorimetric bomb (also known as combustion method) was employed for the mixtures with compositions ranging from 20.0 to 46.0 at.% Ca. In the second method, the alloys and mixtures with compositions between 2.5 and 86.0 at.% Ca were dissolved in HCl. The results obtained for the compositions of 20.0 at.% Ca (Al(Ca) and 32.7 at.% Ca (mainly Al(Ca)) are:

\[ \Delta H_f (Al_{0.9}Ca_{0.2}, s, 298 \text{ K}) = -41.8 \pm 6.3 \text{ kJ/mol of atoms (combustion).} \]

\[ \Delta H_f (Al_{0.8}Ca_{0.2}, s, 298 \text{ K}) = -43.9 \pm 4.2 \text{ kJ/mol of atoms (dissolution).} \]

\[ \Delta H_f (Al_{0.67}Ca_{0.33}, s, 298 \text{ K}) = -71.1 \pm 6.3 \text{ kJ/mol of atoms (combustion).} \]

\[ \Delta H_f (Al_{0.67}Ca_{0.33}, s, 298 \text{ K}) = -73.2 \pm 4.2 \text{ kJ/mol of atoms (dissolution).} \]

In another more recent investigation by Notin et al. [18], the enthalpies of mixing of the Al-rich (<45 at.% Ca) intermediate phases were measured at 953 and 1038 K using calorimetry. Each calorimetric signal recorded corresponds to the enthalpy change during the addition of a solid Ca piece in each step to an Al melt in the crucible. From the measurements, Notin et al. [18] were able to determine the enthalpies of formations of Al(Ca) and Al_{2}Ca. The chemical reactions and their enthalpy values for the formation of these intermetallic compounds are:

\[ 0.8Al_{(l)} + 0.2Ca_{(l)} = Al_{0.8}Ca_{0.2(s)} \]

\[ \Delta H_f (Al_{0.8}Ca_{0.2}, s, 953 \text{ K}) = -27.2 \text{ kJ/mol of atoms} \]

\[ 0.67Al_{(l)} + 0.33Ca_{(l)} = Al_{0.67}Ca_{0.33(s)} \]

\[ \Delta H_f (Al_{0.67}Ca_{0.33}, s, 1038 \text{ K}) = -40.6 \text{ kJ/mol of atoms} \]

where the uncertainties were not given.

The most recent studies [15,16] show the existence of the two new compounds, Al_{14}Ca_{13} and Al_{2}Ca. The enthalpy of formation of the Al_{14}Ca_{13} phase was measured at room temperature by Kevorkov et al. [19] as:

\[ \Delta H_f (Al_{14}Ca_{13}) = -3.7 \pm 1.3 \text{ kJ/mol of atoms.} \]

For the Al_{14}Ca_{13} phase, there are no experimental enthalpy of formation data reported in the literature up to date. The reason for this is probably the sluggish formation kinetics of the phase and thus the difficulty of preparing an Al_{14}Ca_{13}-rich sample as reported by Kevorkov and Schmid-Fetzer [16], although they assumed the phase as AlCa instead of Al_{14}Ca_{13}.

The Gibbs energies and the entropies of formation of Al_{2}Ca and Al_{14}Ca were also determined by different techniques [20,21]. Notin et al. [20] used a solid electrolyte galvanic cell technique where they investigated the Ca(CaF_{2})(Al,Ca) cell between the temperature range of 750–900 K. The Gibbs energy and entropy values for the formation of AL_{2}Ca and Al_{14}Ca are:

\[ \Delta G_f (Al_{0.8}Ca_{0.2}, 800 \text{ K}) = -17800 \pm 140 \text{ J/mol of atoms.} \]

\[ \Delta G_f (Al_{0.67}Ca_{0.33}, 800 \text{ K}) = -28500 \pm 300 \text{ J/mol of atoms.} \]

2.2. Phase equilibrium data

Hansen and Anderko [12] summarized the early experimental data on the Al–Ca system. Earlier studies [9,10] assumed that the phase Al_{14}Ca (25 at.% Ca) existed with a melting point at around 963 K. It was later shown by a comprehensive X-ray work [14] that the intermetallic phase with higher Al content is Al_{14}Ca but not Al_{14}Ca. Al_{14}Ca crystallizes in a b.c.t. structure with lattice parameters of \(a=4.36\ \text{Å}\) and \(c=11.09\ \text{Å}\) [14]. Al_{14}Ca melts incongruently at the peritectic reaction temperature (973 K) forming liquid (10 at.% Ca) and Al_{14}Ca (33 at.% Ca) [11]. The Al_{14}Ca phase has f.c.c. structure with a lattice parameter of \(a=8.038\ \text{Å}\) [13] and melts congruently at 1352 K. The recently discovered Al_{14}Ca phase [15,16] in the system is triclinic in crystalline nature and melts congruently at around 850 K. It has the lattice parameters of \(a=9.484\ \text{Å}, b=9.592\ \text{Å}, c=9.671\ \text{Å},\) and the unit cell with the
angles of $\alpha = 99.02^\circ$, $\beta = 101.13^\circ$ and $\gamma = 119.55^\circ$ [15]. The $\text{Al}_{14}\text{Ca}_{13}$ phase has monoclinic structure with lattice parameters of $a = 15.55$ Å, $b = 9.87$ Å and $c = 9.73$ Å, and the unit cell with the angles of $\alpha = 90^\circ$, $\beta = 108.09^\circ$ and $\gamma = 90^\circ$ [15]. It melts incongruently at the peritectic reaction temperature of about 906 K forming liquid (61.6 at.% Ca) and $\text{Al}_{14}\text{Ca}$ phases [16].

Comprehensive thermal and thermoresistometric investigations [11] were the basis of the Al–Ca equilibrium diagram. Matsuyama [11] found two eutectic reactions and determined most of the liquidus lines, as well. The eutectic point is determined precisely on the Al-rich side with the composition of 5.24 at.% Ca at 889 K. The other eutectic point found was on the Ca-rich side and approximately with the composition of 65 at.% Ca at 818 K [11]. Lately, it has been shown that there are two eutectic points on the Ca-rich side instead of one reported by Matsuyama [11]. These eutectic reactions occur at around 829 K and 833 K with the compositions of 66.2 and 79.5 at.% Ca, respectively [16]. The solid solubility of Ca in Al was found to be less than 0.03 at.% at 873 K [25].

3. Thermodynamic models

There are two types of phases in the system, i.e., solution phases and intermetallic compounds. The solution phases are modeled using one sublattice. The intermetallic compounds are modeled with two sublattices. The detailed expressions for the Gibbs energy of the phases will be presented below in terms of 1 mol of the formula unit.

3.1. Solution phases: liquid, f.c.c. and b.c.c.

The solution phases in the random solution model is treated as a substitutional solution, (Al, Ca), with the Gibbs energies expressed:

$$G_m^\Phi = x_{\text{Al}}^0 G_{\text{Al}}^\Phi + x_{\text{Ca}}^0 G_{\text{Ca}}^\Phi + RT(x_{\text{Al}} \ln x_{\text{Al}} + x_{\text{Ca}} \ln x_{\text{Ca}}) + \sum_{j=0}^{n} L_{\text{Al, Ca}}^j (x_{\text{Al}} - x_{\text{Ca}})^{j/j}$$

(1)

where $G_m^\Phi$ is the molar Gibbs energy of the pure element with the structure $\Phi$, from Dinsdale [26]. $\sum_{j=0}^{n} L_{\text{Al, Ca}}^j$ is the excess Gibbs energy, expressed in Redlich–Kister polynomials as follows:

$$\sum_{j=0}^{n} L_{\text{Al, Ca}}^j (x_{\text{Al}} - x_{\text{Ca}})^{j/j}$$

(2)

where $L_{\text{Al, Ca}}^j$ is the $j$th-order binary interaction parameter expressed as $A^j + B^j T$, and ‘A’ and ‘B’ are model parameters to be evaluated from experimental information.

On the other hand, in the associate model, the liquid phase is assumed to have three species (i.e., Al, Ca and $\text{Al}_2\text{Ca}$) based on the enthalpy of mixing in the liquid. The Gibbs energy of the liquid is written as:

$$G_m^L = y_{\text{Al}}^0 G_{\text{Al}}^L + y_{\text{Ca}}^0 G_{\text{Ca}}^L + y_{\text{Al}_2\text{Ca}}^0 G_{\text{Al}_2\text{Ca}}^L + RT(y_{\text{Al}} \ln y_{\text{Al}} + y_{\text{Ca}} \ln y_{\text{Ca}} + y_{\text{Al}_2\text{Ca}} \ln y_{\text{Al}_2\text{Ca}}) + \sum_{j=0}^{n} G_m^{L^j}$$

(3)

where ‘y’ shows the mole fractions of each species in the liquid. $G_m^{L^j}$ is again the excess Gibbs energy and expressed as follows:

$$G_m^{L^j} = y_{\text{Al}} y_{\text{Ca}} \sum_{j=0}^{n} L_{\text{Al, Ca}}^j (y_{\text{Al}} - y_{\text{Ca}})^{j/j}$$

(4)

3.2. Intermetallic phases

There are four stable intermetallic compounds in the Al–Ca system (see Table 1). They are modeled as stoichiometric compounds, and their Gibbs energy functions are written as:

$$G_m^{\text{Al}_{14}\text{Ca}_{13}} = A^\text{fcc} G_{\text{Al}}^{\text{fcc}} + B^\text{fcc} G_{\text{Ca}}^{\text{fcc}} + A^\text{Al}_{14}\text{Ca}_{13} + B^\text{Al}_{14}\text{Ca}_{13} T$$

(5)

for $\text{Al}_2\text{Ca}$, $\text{Al}_3\text{Ca}$, $\text{Al}_{14}\text{Ca}_{13}$ and $\text{Al}_4\text{Ca}_8$, respectively. $G_{\text{Al}}^{\text{fcc}}$ and $G_{\text{Ca}}^{\text{fcc}}$ are the molar Gibbs energies of the f.c.c. Ca and f.c.c. Al, respectively.

Fig. 1. Calculated phase diagram using random solution model, compared with experimental data by Donski [9], Bozza and Sonnino [10], Matsuyama [11] and Kevorkov and Schmid-Fetzer [16].
4. Evaluation of thermodynamic parameters and computational results

The model parameters (‘A’ and ‘B’) were evaluated using the Parrot module [27] in Thermo-Calc [28]. This program is able to take various kinds of experimental data in one operation. It works by minimizing an error sum with each of the selected data values given a certain weight. The weight is chosen and adjusted based upon the data uncertainties given in the original publications and upon the modeler’s judgment when examining all data simultaneously. All thermodynamic calculations are carried out

<table>
<thead>
<tr>
<th>Invariant reactions</th>
<th>Reaction type</th>
<th>Experimental data</th>
<th>Calculated data (associate)</th>
<th>Calculated data (random solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid = Al + Al\textsubscript{5}Ca</td>
<td>Eutectic</td>
<td>$T$ (K) 884, 886, 889</td>
<td>at.% Ca in liquid 5.6, 6.4, 5.2</td>
<td>$T$ (K) 885.9, 886.0, 887.0</td>
</tr>
<tr>
<td>Liquid = Al\textsubscript{4}Ca\textsubscript{13} + Al\textsubscript{12}Ca\textsubscript{7}</td>
<td>Eutectic</td>
<td>$T$ (K) 818, 820, 829</td>
<td>at.% Ca in liquid 66.2</td>
<td>$T$ (K) 830.5, 831.0, 831.5</td>
</tr>
<tr>
<td>Liquid = Al\textsubscript{5}Ca\textsubscript{3} + βCa</td>
<td>Eutectic</td>
<td>$T$ (K) 818, 820, 833</td>
<td>at.% Ca in liquid 79.5</td>
<td>$T$ (K) 822.5, 823.0, 823.5</td>
</tr>
<tr>
<td>Liquid = Al\textsubscript{2}Ca</td>
<td>Congruent</td>
<td>$T$ (K) 1352, 1359</td>
<td>at.% Ca in liquid 33.3</td>
<td>$T$ (K) 1354.0, 1355.0</td>
</tr>
<tr>
<td>Liquid = Al\textsubscript{12}Ca\textsubscript{4}</td>
<td>Congruent</td>
<td>$T$ (K) 852</td>
<td>at.% Ca in liquid 72.7</td>
<td>$T$ (K) 852.0, 853.0</td>
</tr>
<tr>
<td>Liquid + Al\textsubscript{2}Ca = Al\textsubscript{12}Ca\textsubscript{13}</td>
<td>Peritectic</td>
<td>$T$ (K) 973, 973</td>
<td>at.% Ca in liquid 10.0</td>
<td>$T$ (K) 974.0, 975.0</td>
</tr>
<tr>
<td>Liquid + Al\textsubscript{5}Ca = Al\textsubscript{12}Ca\textsubscript{13}</td>
<td>Peritectic</td>
<td>$T$ (K) 906</td>
<td>at.% Ca in liquid 61.6</td>
<td>$T$ (K) 905.5, 906.0</td>
</tr>
</tbody>
</table>
using Thermo-Calc. A complete and self-consistent thermodynamic description for the Al–Ca binary system is thus obtained and listed in the Appendix for both the random solution model and the associate model. The reference state of the Gibbs energy of individual phases is the so-called standard element reference (SER), i.e., the enthalpies of the pure elements in their stable state at 298.15 K [26].

The optimization procedure starts with the liquid phase and its equilibria with the pure Al and Ca phases. The model parameters of the Al$_2$Ca phase were then evaluated because of the congruent melting of the phase and the extensive liquidus associated with the Al$_2$Ca phase. The thermodynamic parameters of the other phases were optimized one after another. Many iterations were necessary to reproduce all experimental data. Finally, the model parameters of all phases were optimized simultaneously with all experimental data included.

The calculated phase diagram using a random solution model for the liquid phase is shown in Fig. 1. The interaction parameters up to second order, $^{2L}_{\text{Al,Ca}}$, were used for the liquid (see Appendix A). In the associate model, the Gibbs energy for the formation of Al$_2$Ca species in the liquid is calculated using two optimizing

![Fig. 4. Gibbs energy of formation at 800 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [20] and Veleckis [21].](image)

![Fig. 5. Enthalpy of mixing as a function of Ca concentration in the liquid. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [18] and Sommer et al. [22].](image)
variables. In addition, the interactions among the free atoms and between these free atoms and the associates are considered using $I_{f,\text{Al},\text{Ca}}$, $I_{f,\text{liquid}}$, $I_{f,\text{Al}_2\text{Ca},\text{Ca}}$ and $I_{f,\text{liquid}}$, respectively (see Appendix A). The resulting phase diagram from the associate model is shown in Fig. 2. Both calculated and experimental temperatures, and Ca contents in a liquid phase at invariant equilibria are listed in Table 2.

During the optimization, interactions between the Al and Al$_2$Ca and between the Ca and Al$_2$Ca were tested and found less important than the interactions between the Al and Ca in the liquid. The amount of each species in the liquid is calculated and shown in Fig. 3. It is found that about 15% of the species in the liquid is Al$_2$Ca at compositions around 35 at.% Ca. All the other phases, i.e., the intermetallics, are treated as stoichiometric compounds. Each compound is described by the two model parameters and their values are listed in Appendix A.

In Fig. 4, Gibbs energies for the formation of the two compounds, i.e., Al$_2$Ca and Al$_3$Ca, are calculated and compared with the experimental results [20,21]. The comparison of the enthalpy of mixing data in the liquid phase [18,22] at 1453 K with our calculations (using both random solution and associate models) is illustrated in Fig. 5. There is a very deep valley in the enthalpies and a trend that the minimum of the curve in the Fig. is shifted

![Fig. 6. Enthalpy of mixing at 953 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [18].](image)

![Fig. 7. Enthalpy of mixing at 1038 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [18].](image)
towards the Al side. This shows stronger interactions between the atoms in the liquid at compositions around that of the Al₂Ca phase. Enthalpy of mixing data [18] at lower temperatures (1038 and 953 K), where liquid and solid two-phase regions exist at some compositions, are also compared with our calculations in Fig. 6 and Fig. 7. Each change of slope in the figures shows the formation of a new phase as the composition changes. The experimentally measured Al activities in liquid [23,24] are compared in Fig. 8 with the calculations performed at 1600 K. The calculated enthalpy of mixing at 298.15 K is also shown in Fig. 9 using both models.

5. Summary

A self-consistent thermodynamic description for the Al–Ca system is obtained with critically reviewed thermochemo-physical and phase diagram data. Four binary phases are considered and their individual Gibbs energies are evaluated. Based on the experimental observation, the associate
model was tested for the liquid phase, in addition to the random solution model for the liquid phase. Both models yield satisfactory agreement with the experimental data.

Acknowledgements

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Appendix A. Thermodynamic descriptions for the Al–Ca system (all in S.I. units)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Sublattice model</th>
<th>Evaluated description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random Liquid (Al, Ca)</td>
<td></td>
<td>( u_{i_{Al,Ca}} = -85332 + 25.066 T )</td>
</tr>
<tr>
<td>model</td>
<td></td>
<td>( u_{i_{Al,Ca}} = -28447 + 15.332 T )</td>
</tr>
<tr>
<td>Al_{1}Ca</td>
<td></td>
<td>( G_{Al,Ca} = 4 G_{Al} + G_{Ca} - 98238 + 16.809 T )</td>
</tr>
<tr>
<td>Al_{1}Ca</td>
<td></td>
<td>( G_{Al,Ca} = 2 G_{Al} + G_{Ca} - 96554 + 20.848 T )</td>
</tr>
<tr>
<td>Al_{1}Ca_{13}</td>
<td></td>
<td>( G_{Al,Ca_{13}} = 14 G_{Al} + 13 G_{Ca} - 670753 + 94.203 T )</td>
</tr>
<tr>
<td>Al_{1}Ca_{38}</td>
<td></td>
<td>( G_{Al,Ca_{38}} = 3 G_{Al} + 8 G_{Ca} - 141129 - 5.983 T )</td>
</tr>
<tr>
<td>Associate Liquid</td>
<td></td>
<td>( u_{i_{Al,Ca}} = -68842 + 25.372 T )</td>
</tr>
<tr>
<td>model</td>
<td></td>
<td>( u_{i_{Al,Ca}} = -30351 + 2.939 T )</td>
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<td>Al_{1}Ca_{13}</td>
<td></td>
<td>( G_{Al,Ca_{13}} = 2 G_{Al_{13}} + G_{Ca_{13}} - 77214 + 46.424 T )</td>
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<tr>
<td>Al_{1}Ca_{38}</td>
<td></td>
<td>( G_{Al,Ca_{38}} = 14 G_{Al_{38}} + 13 G_{Ca_{38}} - 666156 + 112.227 T )</td>
</tr>
<tr>
<td>Al_{1}Ca_{52}</td>
<td></td>
<td>( G_{Al,Ca_{52}} = 3 G_{Al_{52}} + 8 G_{Ca_{52}} - 142722 - 0.194 T )</td>
</tr>
</tbody>
</table>

References