Thermodynamic description of the Al–Mg–Si system using a new formulation for the temperature dependence of the excess Gibbs energy

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\textbf{A B S T R A C T}

An exponential formulation was proposed to replace the linear interaction parameter in the Redlich–Kister (R–K) polynomial for the excess Gibbs energy of ternary solution phase. The theoretical analysis indicates that the proposed new exponential formulation can not only avoid the artificial miscibility gap at high temperatures but also describe the ternary system well. A thermodynamic description for the Al–Mg–Si system and its boundary binaries was then performed by using both R–K linear and exponential formulations. The inverted miscibility gaps occurring in the Mg–Si and the Al–Mg–Si systems at high temperatures due to the use of R–K linear polynomials are avoided by using the new predicted. Besides, the thermodynamic properties predicted with the new formulation confirm the general thermodynamic belief that the solution phase approaches to the ideal solution at infinite temperatures, which cannot be described with the traditional R–K linear polynomials.

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1. Introduction

Redlich–Kister (R–K) polynomial [1] is, among others [2–4], most widely used to describe the excess Gibbs energies of the solution phases. The interaction parameters in the form of the R–K polynomial usually take the linear dependence of temperature, such as \( L = a + bT \), where \( L \) is the interaction parameter and \( T \) is the temperature. Such a linear expression is usually valid within limited temperature and composition ranges. Extrapolating the description to very high temperatures, the linear expression sometimes leads to an inverted miscibility gap at high temperatures [5–7]. In addition, the thermodynamic properties calculated by using the R–K linear polynomial, such as enthalpy of mixing, are sometimes temperature independent. Those temperature independent thermodynamic properties are not consistent with a general thermodynamic belief that the behavior of any phase approaches to that of the ideal solution phase at infinite temperatures [8]. In order to solve the above problems in the binary systems, Kaptay proposed an exponential equation \( \exp(-bT) \) [8] to describe the binary interaction parameter. Since its publication, the exponential polynomial has been applied to several binary systems [7,9–18], reproducing the experimental phase diagram and thermodynamic data successfully. It is found that this exponential polynomial can avoid the inverted miscibility gap at high temperatures without enforcing any thermodynamic constraints [12,17].

To the best of our knowledge, so far excess Gibbs energies of ternary solution phases and multi–composition phases are almost always described with the R–K linear polynomial. When the R–K linear polynomial is applied to a ternary system, the calculations lead to an artificial miscibility gap in some systems [6,19–22]. Such a miscibility gap is either due to the unreasonable interaction parameters in the boundary binary system [6,19–22] or due to the introduction of ternary interaction parameters. In the later case, the problem can be solved by adding the thermodynamic constraints at high temperatures. However, for the complex systems with many solution phases, such as the Al–Fe–Si system, a thermodynamic optimization adding the thermodynamic constraints is time-consuming. As for the miscibility gap caused by the unreasonable binary interaction parameters, re-optimization for the binary side is usually required. Thus, it is of great interest to develop a new form to describe the excess Gibbs energy in the ternary system to avoid the artificial miscibility gap at high temperatures automatically without adding any thermodynamic constraint. It is also noted that so far no work has been done to verify if the thermodynamic behavior at infinite temperatures for the ternary solution phase described using R–K linear polynomial is consistent with the behavior of the ideal solution phase.

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The purposes of this study are (i) to propose a temperature-dependent formulation in the form of exponential equation to describe the excess Gibbs energy of the ternary solution phase, which can avoid the ternary artificial miscibility gap at high temperatures automatically; (ii) to apply the exponential formulation to the thermodynamic modeling of the Al–Mg–Si system with a desire to demonstrate the reliability of the new formulation to represent the excess thermodynamic properties at high temperatures.

2. A new formulation for the temperature dependence of the excess Gibbs energy of a ternary solution phase

The Gibbs energy of a ternary solution phase $\varphi$ in a fictitious 1–2–3 ternary system is defined as:

$$ G_m^\varphi = \sum_{i=1}^{3} x_i \Delta G_i + \sum_{i<j}^3 x_i x_j \sum_{v=0}^{n} h_{ij} \exp \left( -\frac{T}{\tau_{ij}} \right) (x_i - x_j)^v + \varepsilon G $$

(1)

where $x_i$, $x_j$, and $x_k$ are the mole fractions of the constituents, $\Delta G_i$ is the Gibbs energy of pure element $i$, the second term is the contribution of the ideal mixing to the Gibbs energy, and $\varepsilon G$ is the excess Gibbs energy. In the literature, interaction parameters of the excess Gibbs energy for the ternary solution phases are almost always presented using R–K linear polynomial. In the present work, a new formulation for the temperature dependence of excess Gibbs energy of the ternary solution phase is proposed, which is based on the exponential equation for binary systems proposed by Kapany [8]. The expression is given by:

$$ \varepsilon G = \sum_{i=1}^{3} \sum_{j=i+1}^{3} x_i x_j \left[ \sum_{v=0}^{n} h_{ij} \exp \left( -\frac{T}{\tau_{ij}} \right) (x_i - x_j)^v \right] + x_1 x_2 x_3 \left[ \sum_{i=1,2,3} h_i \exp \left( -\frac{T}{\tau_i} \right) x_i \right] $$

(2)

where the first term is the summation of the binary excess Gibbs energy, while the second term is the ternary excess Gibbs energy. The exponential equation $h_{ij} \exp(-T/\tau_{ij})$ is the binary interaction parameter of components $i$ and $j$ with an order $v$, and $h_i \exp(-T/\tau_i)$ is the ternary interaction parameter. The parameters $h_{ij}$ and $\tau_{ij}$ are taken from the boundary binary systems, while $h_i$ and $\tau_i$ are optimized from the experimental phase diagram data and/or thermodynamic properties in the ternary system.

It is necessary to discuss the stability of a ternary solution phase at high temperatures using Eq. (2). The stability of a solution phase in one multicomponent system requires that the second derivative of the Gibbs energy ($d^2 G/dx^2$) at any direction is positive. The composition will have a fluctuation when the second derivative is negative, and this fluctuation leads to the instability of the phase [23]. As for the liquid phase at high temperatures, such a fluctuation will generate an artificial miscibility gap.

At very high temperatures, the exponential interaction parameters approach to zero. In this case, the solution phases described using Eq. (2) approach to ideal solution phase at infinite temperature. Therefore, the ternary liquid phase is stable at high temperatures, and the artificial miscibility gap will not appear when the excess Gibbs energies of the ternary liquid phase is described using the exponential formulation.

3. Application of the exponential formulation to the Al–Mg–Si ternary system

It is of theoretical interest to verify Eq. (2) by applying it to a real ternary system. For that purpose, the technologically important Al–Mg–Si system was chosen as the target. Before applying Eq. (2) to the Al–Mg–Si system, it is necessary to describe the excess Gibbs energies of three binary systems using the exponential equation because the parameters of the first term in Eq. (2) are taken from Al–Si, Al–Mg and Mg–Si boundary binary systems. Since the Mg–Si system has been optimized by means of the exponential equation in our research group [12], only the Al–Si and Al–Mg systems are needed to be considered in the first step. Subsequently, the exponential formulation is applied to describe the excess Gibbs energy of the liquid phase in the Al–Mg–Si system. In order to further check the reliability of the exponential formulation to describe the ternary phase diagram and thermodynamic properties, it is necessary to compare these calculated results with those using the R–K linear polynomial. Therefore, full assessments using R–K linear polynomial were also performed for the binary and ternary systems by using the same phase diagram and thermodynamic data as those using the exponential equation.
Table 2  
Summary of the optimized thermodynamic parameters in the Al–Si, Al–Mg, Si–Mg and Al–Mg–Si systems.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model</th>
<th>Optimized linear parameters</th>
<th>Optimized exponential parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Al, Si) Liquid</td>
<td>( G_{\text{Al, Si}}^0 ) = -13842.105 + 0.45733T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( G_{\text{Al, Si}}^{\text{f}} ) = 717.10348 – 0.20120T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Si)</td>
<td>( G_{\text{Al, Si}}^{\text{hcp}} ) = -9374.468 + 2.30827T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Mg)</td>
<td>( G_{\text{Al, Mg}}^{\text{fcc}} ) = 470.2715 – 0.12679T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Mg)</td>
<td>( G_{\text{Al, Mg}}^{\text{hcp}} ) = -66985.2876 + 16.6774T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si)</td>
<td>( G_{\text{Mg, Si}}^{\text{fcc}} ) = -30504.9231 + 17.0716T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si)</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = -35331.27 + 18.4009T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Mg, Si) fcc</td>
<td>( G_{\text{Al, Mg, Si}}^{\text{fcc}} ) = 16424.027 – 148.171T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Mg, Si) hcp</td>
<td>( G_{\text{Al, Mg, Si}}^{\text{hcp}} ) = -3377.335 \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si)</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = -6675.925 \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Mg) ( \beta )</td>
<td>( G_{\text{Al, Mg}}^{\text{hcp}} ) = -10371.1982 + 284.663T + 1400C_{\text{hcp}}^{\text{hcp}} + 890C_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al, Mg) ( \epsilon )</td>
<td>( G_{\text{Al, Mg}}^{\text{hcp}} ) = -211586.254 + 13.383T + 300C_{\text{hcp}}^{\text{hcp}} + 230C_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si) ( \gamma )</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = 20.640 + 12.709T + 240C_{\text{hcp}}^{\text{hcp}} + 50C_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si) ( \delta )</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = -108099.027 + 7.290T + 120C_{\text{hcp}}^{\text{hcp}} + 170C_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si) ( \theta )</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = 266234.875 – 22.381T + 120C_{\text{hcp}}^{\text{hcp}} + 170C_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg, Si) ( \kappa )</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = 158042.25 – 27.886T + 290C_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg, Si</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = -2603.0126 + 1.3656T \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg, Si</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = -85584.06 + 379.869T + 67.5778T ln(T) \</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg, Si</td>
<td>( G_{\text{Mg, Si}}^{\text{hcp}} ) = 6.6804 \times 10^{-7}T + 248961.78/T + 2H_{\text{hcp}}^{\text{hcp}} + H_{\text{hcp}}^{\text{hcp}} \</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \) means the exponential parameters from Yuan et al. [12].
The experimental information including phase diagram data and thermodynamic data in the Al–Si, Al–Mg and Al–Mg–Si systems up to 1992 was critically reviewed by Chakraborti and Lukas [21]. As a consequence, only the data for these systems after 1992 are listed in Table 1. As for the Mg–Si system, the experimental data used in the present assessment are the same as those utilized by Yuan et al. [12].

In principle, the values of the exponential interaction parameter in Eq. (2) are rather different from the previous linear ones. Since numerous binary systems have been assessed by using the R–K linear polynomial in the literature, it is necessary to estimate the starting values for the parameters expressed in the form of exponential function. In Appendix A, one method was proposed to estimate the starting values of the exponential parameters from the optimized linear ones. Such a method is successfully applied to the Al–Si, Al–Mg and Al–Mg–Si systems in the present work. Sets of optimized thermodynamic parameters using both the linear and exponential models are listed in Table 2.

### 3.1. Al–Si, Al–Mg and Mg–Si binary systems

For the present Al–Mg and Mg–Si descriptions, all the compounds (β-Al140Mg89, ε-Al30Mg23 and Mg2Si) are treated as stoichiometric phases except for γ-Al12Mg17, which is modeled as ((Mg)9(Al,Mg)12)(Al,Mg)12, as listed in Table 2. All the calculated invariant equilibria in the Al–Si, Al–Mg and Mg–Si systems are summarized in Table 3 along with the experimental data [24,30,33,36,37]. As shown in this table, the calculated temperatures and compositions agree quite well with those reported in the literature.

The calculated Al–Si phase diagram based on the parameters of both linear and exponential polynomial along with the experimental data [24,25,38–57] are presented in Fig. 1. As shown in this figure, the calculations resulting from both models can reproduce the experimental data very well. The calculated enthalpies of mixing for the liquid phase at 1600 °C are presented in Fig. 2(a), which are consistent with experimental results of Rostovtsev and Khitrik [58]. The experimental data from Gizenko et al. [59] are not used in the present assessment and just used to compare with the present calculations. The calculated activities of Si in the liquid alloys at 1427 °C using the two kinds of parameters are depicted in Fig. 2(b), where the calculations agree well with the experimental data [60,61]. It is noted that the deviation between the calculated results using linear and exponential models is quite small.

The comparison between the calculated phase diagrams in the Al–Mg system using two kinds of parameters is shown in Fig. 3. An overall excellent agreement can be observed, but the solvus temperatures in the Mg–rich side calculated using exponential parameters (solid line) are slightly lower than those from the linear parameters (dashed line). Fig. 3 also shows the calculated phase diagram along with experimental data [36,62–78], where both the linear and exponential calculations are in good agreement with the reliable experimental data.

The calculated enthalpy of mixing at 674 °C and the activities of Mg at 807 °C in the liquid phase based on both the exponential (solid line) and linear (dashed line) parameters are shown in Fig. 4(a) and (b), respectively, compared with the corresponding experimental results [28,79–85]. The deviations between the calculated results and the experimental data are within the experimental uncertainties. The calculated activities of Mg in solid phase at 387 °C along
with the experimental data \[86\] are shown in Fig. 4(c). Again, the calculation reproduces the experimental data well.

As shown in Fig. 5, the Mg–Si phase diagram calculated using the linear polynomial can reproduce the previous exponential result \[12\] well in the temperature range below 1413.8 °C (melting point of pure Si). However, the liquid phase becomes unstable according to the calculations using the present linear parameters (dashed line), yielding an artificial miscibility gap at about 4420 °C.

### 3.2. The Al–Mg–Si ternary system

Since the Al–Mg–Si ternary system contains no ternary compound and the experimental information for the solid phase is limited, only the excess Gibbs energy of the liquid phase was described using the proposed formulation.

Table 4 presents the summary of the temperatures and compositions for the invariant reactions in the Al–Mg–Si ternary system. As shown in Table 4, the maximum difference between the calculated and the measured temperatures is within 3 °C. Besides, the discrepancy between the linear and the exponential calculations is quite small.

The calculated vertical sections along 2 mass% Si and 80 mass% Al using both exponential parameters (solid line) and linear parameters (dashed line) are shown in Fig. 6. In comparison with the experimental data \[6,87,92\], all the calculations show a satisfactory agreement for the liquidus. The solidus line shows a degree of the scatter between the calculation and experimental data \[92\] for the vertical section at 2 mass% Si. However, their measurements \[92\] were found to be inconsistent with solubility ranges in the binary systems. The calculated vertical sections at 5, 85, 90, and 95 mass% Al are also in good agreement with experimental data \[6,87,92\]. To conserve space, no diagrams are shown for these vertical sections.

In addition, the phase relations at low temperatures using the exponential parameters were computed. Figs. 1, 3 and 6 show that the liquid phase does not appear at low temperatures (0 °C) for the binary sides and the ternary system. Such a phenomenon is
Table 4

Invariant equilibria in the Al–Mg–Si ternary system from different sources.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Composition (at.%) in the liquid</th>
<th>T (°C)</th>
<th>References</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Al]-fcc + Mg$_2$Si</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L \leftrightarrow$ (Al)-fcc + Mg$_2$Si</td>
<td>85.71</td>
<td>10.46</td>
<td>3.83</td>
<td>594.75</td>
</tr>
<tr>
<td></td>
<td>85.61</td>
<td>10.31</td>
<td>4.08</td>
<td>593.65</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>595.00</td>
</tr>
<tr>
<td></td>
<td>87.10</td>
<td>8.30</td>
<td>4.60</td>
<td>593.00</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>–</td>
<td>3.90</td>
<td>597.00</td>
</tr>
<tr>
<td></td>
<td>85.30</td>
<td>10.80</td>
<td>3.90</td>
<td>594.00</td>
</tr>
<tr>
<td></td>
<td>80.66</td>
<td>5.49</td>
<td>13.85</td>
<td>560.45</td>
</tr>
<tr>
<td></td>
<td>80.68</td>
<td>5.47</td>
<td>13.85</td>
<td>559.35</td>
</tr>
<tr>
<td>$L \leftrightarrow$ (Al)-fcc + (Si) * Mg$_2$Si</td>
<td>82.30</td>
<td>5.10</td>
<td>12.60</td>
<td>560.00</td>
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<tr>
<td></td>
<td>81.10</td>
<td>4.80</td>
<td>14.10</td>
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<td>80.50</td>
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<tr>
<td></td>
<td>81.50</td>
<td>5.40</td>
<td>13.10</td>
<td>557.00</td>
</tr>
<tr>
<td>$L \leftrightarrow$ γ + Mg$_2$Si</td>
<td>45.76</td>
<td>54.20</td>
<td>0.04</td>
<td>460.05</td>
</tr>
<tr>
<td></td>
<td>46.19</td>
<td>53.78</td>
<td>0.03</td>
<td>460.35</td>
</tr>
<tr>
<td></td>
<td>46.10</td>
<td>53.80</td>
<td>0.10</td>
<td>462.50</td>
</tr>
<tr>
<td>$L \leftrightarrow$ β + Mg$_2$Si</td>
<td>61.14</td>
<td>38.84</td>
<td>0.02</td>
<td>451.15</td>
</tr>
<tr>
<td></td>
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<td>38.84</td>
<td>0.02</td>
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<td>36.40</td>
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<td>34.50</td>
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<td></td>
<td>66.03</td>
<td>33.90</td>
<td>0.07</td>
<td>448.00</td>
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<tr>
<td></td>
<td>64.00</td>
<td>36.30</td>
<td>0.10</td>
<td>450.00</td>
</tr>
<tr>
<td>$L \leftrightarrow$ γ + Mg$_2$Si</td>
<td>57.95</td>
<td>42.04</td>
<td>0.01</td>
<td>449.95</td>
</tr>
<tr>
<td></td>
<td>58.12</td>
<td>41.86</td>
<td>0.02</td>
<td>450.35</td>
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<td>57.40</td>
<td>42.50</td>
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<td>449.00</td>
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<td>29.52</td>
<td>70.43</td>
<td>0.05</td>
<td>438.25</td>
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<td></td>
<td>30.15</td>
<td>69.80</td>
<td>0.05</td>
<td>438.25</td>
</tr>
<tr>
<td></td>
<td>32.30</td>
<td>67.50</td>
<td>0.20</td>
<td>434.00</td>
</tr>
<tr>
<td></td>
<td>30.00</td>
<td>69.90</td>
<td>0.10</td>
<td>436.00</td>
</tr>
<tr>
<td></td>
<td>30.90</td>
<td>69.00</td>
<td>0.10</td>
<td>435.60</td>
</tr>
</tbody>
</table>

also indicated for the previous assessment of the Fe–Zn system using the exponential parameters [17]. Besides, the enthalpies of mixing at 0 °C of in the boundary binary systems and Al–Mg–Si system were shown in Figs. 2(a), 4(a) and 9(b), respectively. It shows that the deviations between the linear and exponential model are small at low temperatures. Other thermodynamic properties, such as $\alpha G$ and $\alpha S$, are also computed and compared at 0 °C. The results show that the thermodynamic values computed by means of exponential interaction parameters are close to those resulting from linear interaction parameters at 0 °C. Consequently, it can be concluded that the exponential parameters are able to avoid the re-stabilization of the liquid phase and describe its thermodynamic properties reasonably at low temperatures.

Although both R–K linear and exponential interaction parameters can describe the experimental phase diagram and low-temperature thermodynamic properties reasonably, noticeable discrepancies exist between the two formulas for the calculated phase diagrams at high temperatures.

The isothermal sections at 4600, 4800 and 5000 °C are calculated using linear parameters, as presented in Fig. 7, showing a miscibility gap near the Mg–Si boundary system. As shown in this figure, the higher the temperature, the larger the miscibility gap. This implies that the miscibility gap is an inverted one and the ternary liquid phase becomes unstable at high temperatures. On the contrary, when the exponential parameters are used for calculations, such an inverted miscibility gap does not appear. It is thus demonstrated that the exponential formulation is efficient to ensure the stability of the ternary liquid phase and remove the artificial miscibility gap at high temperatures.

To test the reliability of the optimized thermodynamic parameters, it is also of considerable interest to compare the model-predicted properties with the experimental data, which are not
used in the optimization. Fig. 8 compares the model-predicted activity Mg with the limited experimental data [93]. As shown in this figure, the calculations using exponential parameters agree well with the experimental data. Fig. 8 provides a further check on the reliability of the assessments using Eq. (2).

3.3. Excess thermodynamic properties at very high temperatures

The calculated phase diagrams and thermodynamic properties using the obtained linear and exponential thermodynamic parameters can reproduce the available experimental data satisfactorily. However, these two kinds of parameters show different behaviors for the liquid phase at high temperatures. The excess thermodynamic properties of liquid phase for the Al–Mg–Si ternary system at high temperatures using these two formulas are discussed in this section.

In a real system, as temperature increases, the interaction (attraction or repulsion) between the atoms becomes weaker. At infinite temperatures, it is expected that the liquid phase approaches to the ideal solution. Thus, the excess thermodynamic properties were expected towards zero at very high temperatures.

Fig. 9(a) represents the calculated excess Gibbs energy of the liquid phase in Al–Mg–Si at three temperatures (1050, 2500 and 4000 °C) along the Al<sub>0.5</sub>Si<sub>0.5</sub>–Mg vertical section. The discrepancies of the excess Gibbs energy for liquid phase between exponential (solid line) and linear (dashed line) expressions are tiny at the low temperature (1050 °C). Such small discrepancies imply that the exponential formulation can describe the ternary phase diagram as good as those using the R–K linear polynomial. As shown in Fig. 9(a), the calculations using the R–K linear polynomial show the positive values in the Mg-rich side at 4000 °C. If this effect is more predominant than the effect of the ideal mixing $RT\sum_{i} x_{i} \ln(x_{i})$ $(I = Al, Mg, Si)$ to the Gibbs energy, the liquid will become unstable, leading to the formation of an inverted miscibility gap. However, the calculations using the exponential formulation show that all the values have the same sign, and the excess Gibbs energies decrease with increasing temperature.

The enthalpies of mixing for the liquid phase along the Al<sub>0.5</sub>Si<sub>0.5</sub>–Mg section at 0, 1050, 2500 and 4000 °C were calculated using both exponential (solid line) and linear (dashed line) parameters, as shown in Fig. 9(b). The enthalpies calculated using linear parameters remain constant, as presented in this figure. On the
4. The ability of the exponential formulation to describe the ternary stable miscibility gap

According to the above application of Eq. (2) to the real Al–Mg–Si system, it shows that the exponential formulation can only describe the ternary phase diagram and thermodynamic properties well, but also be able to ensure the stability of a liquid phase at high temperatures and avoid the formation of the liquid at low temperatures. It is also of interest to discuss some other feature of this new ternary formulation. The ability of Eq. (2) to describe the stable miscibility gap within the finite temperature range will be discussed in this section.

Fig. 7. Calculated isothermal sections at 4600, 4800 and 5000 °C using the linear parameters in the Al–Mg–Si system.

It sometimes happens that a stable miscibility gap appears within a finite temperature range, and it ends at a critical point \( T_{\text{Cmax}} \). Such a stable miscibility gap is common, especially in the liquid phase \([94,95]\). The ability of the exponential interaction parameter to describe such a miscibility gap in the binary system was demonstrated by Kaptay \([96]\) using two examples. In this section, the ability of the exponential formulation to describe the stable miscibility gap in the ternary system was deduced.

Let us expand the exponential term \( \exp(-T/\tau) \) using a third-order Taylor series \( (1 - (T/\tau) + (1/2 !(T/\tau)^2 - (1/3 !(T/\tau)^3 + \ldots) \). In most case, the value of \( \tau \) is larger than 3000 K, which is much larger than maximum \( T \) below which there are experimental data. Thus, the higher order term is negligible. Considering the zero and first-order Taylor series and merging the similar terms, the second
derivatives of the Gibbs energy, which is presented in Eq. (1), can be rewritten as follows:

\[
\frac{\partial^2 G}{\partial x_2 \partial x_3} = \frac{1}{x_1 x_2 x_3} \left( A(x_2, x_3) + B(x_2, x_3) T \right) \tag{3a}
\]

\[
\frac{\partial^2 G}{\partial x_1 \partial x_3} = \frac{1}{x_1 x_2 x_3} \left( C(x_2, x_3) + D(x_2, x_3) T \right) \tag{3b}
\]

\[
\frac{\partial^2 G}{\partial x_1 \partial x_2} = \frac{1}{x_1 x_2 x_3} \left( E(x_2, x_3) + F(x_2, x_3) T \right) \tag{3c}
\]

where \( A, B, C, D, E \) and \( F \) are the polynomials of the \( x_2, x_3, h \) and \( \tau \) (\( h \) and \( \tau \) are the binary and ternary interaction parameters, respectively). The expressions for \( A \) and \( B \) are presented as follows, and the expressions for \( C, D, E \) and \( F \) are given in a similar way.

\[
A = 2(1 - x_2 - x_3)x_2x_3[-h_{12} + x_3(3x_2 - 2 + 2x_3)h_1
+ x_3(1 - 3x_2 - x_3)h_2 - x_3^2h_3] \tag{4a}
\]

\[
B = x_3(1 - x_3)R + 2(1 - x_2 - x_3)x_2x_3 \left[ \frac{h_{12}}{\tau_{12}} - x_3(3x_2 - 2 + 2x_3)\frac{h_1}{\tau_1} - x_3(1 - 3x_2 - x_3)\frac{h_2}{\tau_2} + x_3^2\frac{h_3}{\tau_3} \right] \tag{4b}
\]

Because \( x_2, x_3 \) and \( x_2 + x_3 \) are always in the range of \( 0 \)–\( 1 \), and the values for \( h \) and \( \tau \) are fixed, the values for these six polynomials \( \{A, B, C, D, E, F\} \) are finite. The stability function according to Hillert [23] can be written as follows:

\[
\left( \frac{\partial g_3}{\partial x_3} \right)_{g_2} = \frac{1}{x_1 x_2 x_3} \left[ \frac{(A + BT)(C + DT) - (E + FT)^2}{(A + BT)} \right] \tag{5}
\]

where \( g_2 \) is the notation for \( \langle \partial G_m^c / \partial x_2 \rangle_{T_2} \). Over the finite temperature range it is possible to find a series of parameters \( \{\tau, h\} \) to obtain negative \( \langle \partial g_3 / \partial x_3 \rangle_{g_2} \) in Eq. (5). In this case, a fluctuation in composition appears which will lead to the occurrence of a miscibility gap. Consequently, the proposed ternary formulation is able to describe the stable miscibility gap in the ternary system.

5. Conclusions

- A temperature-dependent formulation in the form of exponential equation was proposed to describe the excess Gibbs energy of solution phases in the ternary system, which can avoid the ternary artificial miscibility gap at high temperatures. The theoretical analysis of this new formulation was performed to demonstrate the stability of the liquid phase at high temperatures and the ability to describe the stable miscibility gap within the finite temperature range.

- A thorough thermodynamic description of the Al–Mg–Si system and its boundary binaries was performed by using both R-K linear polynomials and the exponential formulation. Most of the experimental data including phase diagram and thermodynamic properties are well accounted for by both formulations. The advantage of the exponential formulation is that it can avoid the inverted miscibility gaps in the Mg–Si and the Al–Mg–Si systems at high temperatures due to the use of R-K linear polynomials. The calculations also show that the exponential formulation can yield reasonable thermodynamic properties at low temperatures, avoiding the formation of liquid phase at low temperatures.

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Appendix A. One method to estimate the starting values of the exponential parameters from the optimized linear parameters

If the identical phase diagram and thermodynamic data are used for the assessment using Eq. (2), the starting values can be estimated from the previous assessment using linear interaction. For the sake of clarity, the liner and exponential interactions are
presented with parameters specified as \( h_{\text{lin}}, h_{\text{exp}}, \tau_{\text{lin}} \) and \( \tau_{\text{exp}} \)
\((\text{lin} = \text{linear}, \text{exp} = \text{exponential})\):

\[
L_{\text{lin}} = h_{\text{lin}} \left( 1 - \frac{T}{\tau_{\text{lin}}} \right) \quad \text{(A1-a)}
\]

\[
L_{\text{exp}} = h_{\text{exp}} \exp \left( -\frac{T}{\tau_{\text{exp}}} \right) \quad \text{(A1-b)}
\]

In order to get the exponential function fit to the linear function well within \( T_{\text{min}} \) to \( T_{\text{max}} \) (\( T_{\text{min}} \) and \( T_{\text{max}} \) are the minimum and maximum temperatures of measured thermodynamic data), some constraints for Eq. (A1-a) should be satisfied in order to obtain a successful fit. To begin with, according to Kaptay’s assumption \[8\], it requests that \( \tau_{\text{lin}} \) of Eq. (A1-a) should be positive. Moreover, it is impossible for the exponential equation to have \( L_i \) with different signs. Thus, another constraint: \( \tau_{\text{lin}} > \tau_{\text{max}} \) is proposed to make \( L \) calculated by Eq. (A1-a) to have the same sign in the limited temperature range. In conclusion, Eq. (A1-a) should satisfy the following constraint in order to get a successful transition:

\[
\tau_{\text{lin}} > \tau_{\text{max}} \quad \text{(A2)}
\]

If the previously optimized linear parameters satisfy the above constraint Eq. (A2), the starting values can be obtained according to the following procedure, as shown in Fig. 10.

To begin with, one gets the logarithm of Eq. (A1-a):

\[
L'_{\text{lin}} = \ln(L_{\text{lin}}) \quad \text{(A3-a)}
\]

\[
L'_{\text{lin}} = \ln \left( h_{\text{lin}} \left( 1 - \frac{T}{\tau_{\text{lin}}} \right) \right) \quad \text{(A3-b)}
\]

Then, with a temperature step, one gets a series of points \((T, L'_{\text{lin}})\) from Eq. (A3-b) in one temperature range, and one then fits these points using the following linear function:

\[
L'_{\text{lin}} = m + nT \quad \text{(A4-a)}
\]

where \( m \) and \( n \) are parameters to be fitted. One can rewrite interaction \( L_{\text{lin}} \) as follows:

\[
L_{\text{lin}} = \exp(m) \exp(nT) \quad \text{(A4-b)}
\]

Comparing Eq. (A4-b) to Eq. (A1-b), the values of \( h_i \) and \( \tau_i \) are calculated to be:

\[
h_{\text{exp}} = \exp(m) \quad \text{(A5-a)}
\]

\[
\tau_{\text{exp}} = -\frac{1}{n} \quad \text{(A5-b)}
\]

The calculated values using Eq. (A5-a) and (A5-b) can be used as the staring values of the exponential parameters.

**References**


