Thermodynamic modelling of the Mg–Ca, Mg–Sr, Ca–Sr and Mg–Ca–Sr systems using the modified quasichemical model

M. Aljarrah, M. Medraj*

Department of Mechanical Engineering, Concordia University, 1455 de Maisonneuve Blvd. West, H3G 1M8, Montreal, Canada

Abstract

In this work, a thermodynamic description of the Mg–Ca–Sr system is carried out using the modified quasichemical model. The three binary systems Mg–Ca, Mg–Sr and Ca–Sr have been reoptimized based on the experimental phase equilibria and thermodynamic properties available in the literature. Good agreement was obtained among the calculated phase diagrams, thermodynamic properties and the corresponding experimental data from the literature. Using the established database, the Mg–Ca–Sr phase diagram is calculated. Also, a comparison between the liquidus projection calculated using random solution model and the modified quasichemical model is presented. Since experimental data on the mutual solubility between Mg_2Ca and Mg_2Sr could not be found in the literature, the Mg–Ca–Sr phase diagram is calculated and compared for the two cases of limited and complete solubility between these two compounds.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Modified quasichemical model; Ternary phase diagram; Mg alloys; Mg–Ca–Sr system

1. Introduction

Strontium and calcium are two important additives used in magnesium alloys. The alloying effects of strontium on magnesium alloys, e.g. Mg–Al based alloys, have been found to display superior creep performance and excellent high-temperature properties [1]. Alloying magnesium with calcium, on the other hand, is suggested to improve the creep resistance and tensile strength, and to provide corrosion resistance comparable to commercial Mg-alloys with rare earth elements [2]. Moreover, calcium protects melt surface causing less slag formation and less additive loss.

To create an accurate thermodynamic model of a ternary system, it is necessary to have thermodynamic description of the three constituent binary systems first. In order to provide a good prediction for the thermodynamic properties of the Mg–Ca–Sr system, it is necessary to choose the suitable model that describes the excess Gibbs energy. If a model based on random mixing is used for the liquid phase, higher

order interaction parameters are needed to reproduce the liquidus around the intermetallic compounds, such as Mg_2Ca, and it often results in a less satisfactory liquidus at other compositions. According to Sommer [3] and Mishra et al. [4] there is a tendency for glass formation in the Mg–Ca system in the composition range between 50–74 at.% Ca and partial glass formation in the composition ranges of 10–50 and 74–85 at.% Ca. This indicates the tendency for short range ordering in the Mg–Ca liquid. To deal with short range ordering, the associates model was proposed in the literature. However, this model is not physically sound, since it assumes that some molecules occupy specific atomic positions. Furthermore, using random solution model to treat liquids with short range ordering continues to appear in the literature. In reality, a random solution model is only expected at very high temperature when the entropy term overwhelms any tendency for ordering or clustering of atoms. It follows that the configurational entropy of mixing should vary with temperature. The quasichemical solution model has a better treatment of configurational entropy that accounts for a non-random distribution of atoms. Therefore, no model based on the random mixing can properly describe the influence of short-range ordering, as they do not solve the problem of the configurational entropy. The description of short-range

* Corresponding author. Tel.: +1 514 848 2424x3146; fax: +1 514 848 3175.
  E-mail address: mmedraj@encs.concordia.ca (M. Medraj).
  URL: http://www.me.concordia.ca/~mmedraj (M. Medraj).

ordering can be taken into account with bond energy models by considering the interactions between atoms that extend beyond the nearest neighbours approximation. This problem has been treated using quasichemical model [5,6]. The model is so-called because it has a mass-action equation that is typical in chemical reaction theory.

No phase equilibrium, ternary compound or experimental thermodynamic data for the Mg–Ca–Sr system could be found in the literature, thus this work was initiated to critically evaluate the thermodynamic description of this system using the modified quasichemical model.

2. Experimental data

2.1. Mg–Ca system

Baar [7] determined the liquidus temperature for the Mg–Ca system. The starting materials in his work were of low purity. The melting point of the starting Ca was 808 °C, and for Mg was 632.6°C, compared to 842 °C and 650 °C [8] for pure Ca and Mg, respectively. Further work on this system was carried out by Paris [9] while he was studying the Mg–Ca–Zn ternary system. He stated that his results differ slightly from those of Baar [7]. However, Paris [9] did not report the purity of the starting materials. Haughton et al. [10] determined the liquidus temperature in the Mg-rich region in the composition range of 0 to 26 at.% Ca. They found that the liquidus temperatures in this composition range are in fair agreement with Vosskühler [11], and Klemm and Dinkelacker [12] but differ slightly from that given by Baar [7]. Haughton et al. [10] reported that the invariant reaction in the Mg-rich region occurs at 10.5 ± 0.5 at.% Ca and 517 °C, compared to Baar's results as 12.46 at.% Ca and 514 °C. Whereas, Klemm and Dinkelacker's [12] values are 10.5 at.% Ca and 516.5 °C which are in good accord with Haughton et al. [10].

Nayeb-Hashemi and Clark [13] critically assessed this system based on the liquidus temperatures and the eutectic reactions of Vosskühler [11], and Klemm and Dinkelacker [12]. However, they [13] placed the melting point of Mg₂Ca at 715 °C which is the average temperature measured by Baar [7] and Vosskühler [11]. Agarwal et al. [14] measured calorimetrically the enthalpy of mixing of liquid Mg–Ca alloy at 750 °C and heat contents of Mg₂Ca between 477 and 877 °C. They used these values together with the experimental phase equilibria from [10–12] to calculate the phase diagram of the Mg–Ca system. The enthalpy of mixing of Sommer et al. [15] was not used since it contradicts with their measurement. According to Agarwal et al. [14], their experiments were performed in an iron crucible and adding Ca to the melt resulted in creeping the crucible and producing less reliable measurements. Hence, the enthalpy of mixing measured by Sommer et al. [15] seems to be more reliable than the one published by Agarwal et al. [14] and it will be used in the current work.

Several researchers [10–12,16–18] measured the solubility of Ca in Mg. Among them Burke [16] and Vosskühler [11] who reported limited solubility and their results agree fairly well,

whereas other researchers reported larger solubility. Hence, the limited solubility will be adopted in this work.

Many efforts had been made to measure the heat of formation of the compound Mg₂Ca [14,19–26]. The average heat of formation reported in [21–23,26] will be used during the optimization in this work because these results are more reliable. Mashovets and Puchkov [27], and Sommer [28] determined the activity of Mg and Ca in Mg–Ca liquid at 807, 927 and 737 °C using vapour pressure measurement. Hultgren et al. [29] summarize the experimental work performed on this system. These data will be also used in this work.

2.2. Mg–Sr system

Nayeb-Hashemi and Clark [30] reviewed the Mg–Sr system and their article provides a comprehensive discussion of all the experimental results obtained by previous researchers [31–34]. Brown [33] used differential thermal analysis (DTA) and high temperature X-ray diffraction analysis to determine the (Sr) solidus and its allotropic transformations. Ray also [34] determined the (Sr) solidus by thermal analysis. According to Nayeb-Hashemi and Clark [30], despite the possibility of hydrogen contamination of Brown's [33] samples, the solidus temperatures he obtained were more realistic than those of Ray [34]. Thermal analyses and metallographic examinations indicated a very small solid solubility of Sr in Mg, less than 0.5 at.% Sr [33]. This was considered negligible in the optimization of the Mg–Sr phase diagram by Chartrand and Pelton [35]. On the other hand, a significant solid solubility of Mg in Sr was detected by Ray [34] using thermal and metallographic analyses which do not agree with Brown [33] who reported limited solubility. In the current evaluation, the experimental data of Brown [33] are used because they have better agreement with the limiting slope of the liquidus at $X_{Sr} = 1$, Eq. (1), than those of Ray [34]. If the solubility of Mg in Sr is negligible, the limiting slope is related to the enthalpy and temperature of fusion of Sr as shown by Eq. (1).

$$\left(\frac{dx_i}{dT}\right)^l_{X_i=1} - \left(\frac{dx_i}{dT}\right)^s_{X_i=1} = \frac{\Delta_{fus}H}{RT^2_{fus}}. \tag{1}$$

A tin solution calorimetry was used to measure the heat of formation of the congruently melting compound Mg₂Sr from solid Mg and Sr by King and Kleppa [36]. Sommer et al. [15] determined the enthalpy of mixing of the liquid alloys at 807 °C, using high temperature calorimetry. The thermodynamic activities of liquid alloys at 781 °C were determined by Sommer [36] using a modified Ruff boiling technique. These were the only thermodynamic data found for the system and they will be used in the current optimization.

2.3. Ca–Sr system

Schottmiller et al. [37] determined the liquidus as well as the solidus of the Ca–Sr phase diagram over the entire range of composition using DTA. The melting point of the starting Ca was 843 ± 1 °C, and for Sr was 774 ± 1 °C, compared to 842 °C

and 776 °C [8] for pure Ca and Sr, respectively. They reported that the two-phase region liquid and solid is very narrow; never exceeds a range of 6 °C. They mentioned that there are three allotropies of Ca and Sr. Their proposed phase diagram was later redrawn by Elliott [38]. A more reliable report by Smith et al. [39], stated that there are only two allotropies occurring in both pure Ca and Sr. Schottmiller et al. [37] investigated the lattice parameter for fcc, hcp and bcc solid solutions using X-ray diffraction. They found a linear variation of lattice parameter with Sr content at room temperature for fcc solid solution obeying Vegard's law. Whereas, a positive deviation from Vegrad's law occurs in the Sr-rich region at 415 °C for bcc and hcp solid solutions. It should be noted that the work of Peterson and Fattore [41] for the Ca–H system indicated the nonexistence of hcp allotropy of Ca. King [42] determined the lattice parameters at room temperature for six samples in the Ca–Sr system using XRD. He reported a linear variation of the unit cell volume with Sr content obeying Vegard's law. In addition, Klemm and Mike [40] reported only little deviation from Vegard's law. Such behaviour is expected considering the similar atomic sizes and crystal structures of Ca and Sr. Further, the results of Schottmiller et al. [37], King [41], and Klemm and Mike [40] were analysed by Alcock et al. [43] who found that there is only little deviation from Vegard's law.

In this work, it is considered that Ca and Sr form a solid solution throughout the entire composition range. Both pure Ca and Sr have the same type of allotropic phase transformation from fcc to bcc at 443 °C and 556 °C [8], respectively. Predel et al. [44] determined the enthalpy of mixing for the liquid alloys at 870 °C using high temperature calorimetry. The excess entropy of mixing of the Ca–Sr liquid is relatively small and it is assumed to be zero by Predel et al. [44].

2.4. Mg–Ca–Sr system

No experimental thermodynamic data for the Mg–Ca–Sr ternary system could be found in the literature. Combining the computational thermodynamic with first principle approach, Mg–Ca–Sr system was evaluated by Zhong et al. [45]. In their evaluation, even though there is no experimental data to verify the mutual solid solubility between Mg$_2$Sr and Mg$_2$Ca, a complete solid solution has been assumed based on the similarity with other systems that contain Laves phases and on the fact that Sr and Ca are very similar in terms of crystal structure and atomic size. Their model is based on random mixing, which cannot properly describe the short-range ordering. Thus, this work was initiated to model this system using the modified quasichemical model. The phase equilibria will be established for this system based on the optimized binary subsystem.

3. Thermodynamic models

For a pure element with a certain structure φ, its Gibbs free energy, referenced at room temperature, is described as

$$
\begin{aligned}
{}^{\circ}G_A^{\varphi}(T) = {} & a + bT + cT \ln T + \mathrm{d}T^2 + eT^3 + fT^{-1} \\
& + gT^7 + hT^{-9}
\end{aligned} \tag{2}
$$

where the parameters a through h are assigned from the SGTE database [46].

Gibbs energy functions of the stoichiometric compounds are represented by Eq. (3):

$$
G^{\text{phase},\varphi} = x_i \, {}^{\circ}G_i^{\varphi} + x_j \, {}^{\circ}G_j^{\varphi} + \Delta G_f \tag{3}
$$

where ${}^{\circ}G_i^{\varphi}$ and ${}^{\circ}G_j^{\varphi}$ denote Gibbs free energy of element i and j in their standard state and $\Delta G_f = a + bT$ represents the Gibbs energy of formation of the stoichiometric compound, where a and b are the model parameters to be optimized using experimental data.

The Gibbs energy of a disordered solution phase is described by the following equation:

$$
G = x_i \, {}^{\circ}G_i^{\phi} + x_j \, {}^{\circ}G_j^{\phi} + RT[x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^{\phi} \tag{4}
$$

where Φ denotes the phase in question and x_i, x_j denote the mole fraction of component i and j, respectively. The excess Gibbs energy is represented using the Redlich–Kister equation:

$$
{}^{ex}G^{\phi} = x_i . x_j \sum_{n=0}^{n=m} {}^{n}L_{i,j}^{\phi}(x_i - x_j)^n \tag{5}
$$

with ${}^{n}L_{i,j}^{\phi} = a_n + b_n \times T$ $(n = 0, \ldots, m)$, where ${}^{n}L_{i,j}^{\phi}$ is the interaction parameters and a_n and b_n are model parameters to be optimized in terms of experimental phase diagram and thermodynamic data.

In this study, one terminal solid solution phase, that is the Mg-hcp phase, in the Mg–Ca system and two complete solid solutions, fcc and bcc, in the Ca–Sr system were modeled using random solution model.

The molar Gibbs energy for the liquid phase, derived from quasichemical theory [47], is described by Eq. (6):

$$
G^{\text{liq}} = n_i \, {}^{\circ}G_i^{\text{liq}} + n_j \, {}^{\circ}G_j^{\text{liq}} - T \Delta S^{\text{config}} + \frac{n_{ij}}{2} \Delta \, {}^{ex}G^{\text{liq}}, \tag{6}
$$

where n_i and n_j are the number of moles of the component i and j, n_{ij} is the number of $(i–j)$ pairs, ΔS^{config} is the configurational entropy of mixing given for randomly distributing the $(i–i)$, $(j–j)$, and $(i–j)$ pairs.

$$
\begin{aligned}
\Delta S^{\text{config}} = {} & -R[n_i \ln(x_i) + n_j \ln(x_j)] \\
& - R \left[n_{ii} \ln \left(\frac{x_{ii}}{y_i^2} \right) + n_{jj} \ln \left(\frac{x_{jj}}{y_j^2} \right) + n_{ij} \ln \left(\frac{x_{ij}}{2y_i y_j} \right) \right]
\end{aligned} \tag{7}
$$

where x_i and x_j are the overall mole fractions of the components i and j, respectively

$$
x_i = \frac{n_i}{n_i + n_j}. \tag{8}
$$

Pair fraction:

$$
x_{ii} = \frac{n_{ii}}{n_{ii} + n_{jj} + n_{ij}}. \tag{9}
$$

And the coordination-equivalent fractions

$$
y_i = \frac{Z_i n_i}{Z_i n_i + Z_j n_j} \tag{10}
$$

where Z is the coordination number.

The mass balance in the quasichemical model gives [48]:

$$Z_i n_i = 2n_{ii} + n_{ij} \tag{11}$$

$$Z_j n_j = 2n_{jj} + n_{ij}. \tag{12}$$

Substituting Eqs. (11) and (12) into Eqs. (9) and (10) gives:

$$
\begin{aligned}
y_i &= x_{ii} + \frac{x_{ij}}{2} \\
y_j &= x_{jj} + \frac{x_{ij}}{2}.
\end{aligned}
\tag{13}
$$

In Eq. (6), the expansion $^{ex}G^{liq}$ can be expressed as a polynomial in terms of the pair fraction x_{ii}, x_{jj}, x_{ij} as shown in Eq. (14) [6]:

$$\Delta\,^{ex}G^{liq} = \Delta g_{ij}^{\circ} + \sum_{\substack{i \geq 1 \\ m \geq 1}} g_{im}^{m\circ} x_{im}^{m} + \sum_{\substack{j \geq 1 \\ n \geq 1}} g_{nj}^{\circ n} x_{nj}^{n}. \tag{14}$$

The parameters, Δg_{ij}°, $g_{ij}^{i\circ}$ and $g_{ij}^{\circ j}$ are to be optimized using experimental data.

Chartrand and Pelton [7] modified the quasichemical model, in order to permit the coordination number to vary with compositions, as follows:

$$
\begin{aligned}
\frac{1}{Z_i} &= \frac{1}{Z_{ii}^{i}}\left(\frac{2n_{ii}}{2n_{ii}+n_{ij}}\right) + \frac{1}{Z_{ij}^{i}}\left(\frac{n_{ij}}{2n_{ii}+n_{ij}}\right) \\
\frac{1}{Z_j} &= \frac{1}{Z_{jj}^{j}}\left(\frac{2n_{jj}}{2n_{jj}+n_{ij}}\right) + \frac{1}{Z_{ji}^{j}}\left(\frac{n_{ij}}{2n_{jj}+n_{ij}}\right)
\end{aligned}
\tag{15}
$$

where Z_{ii}^{i} and Z_{ij}^{i} are the values of coordination number of i atom when all nearest neighbours are i's and j's, respectively.

Substituting Eq. (15) in Eqs. (11) and (12) gives:

$$
\begin{aligned}
n_i &= \frac{2n_{ii}}{Z_{ii}^{i}} + \frac{n_{ij}}{Z_{ij}^{i}} \\
n_j &= \frac{2n_{jj}}{Z_{jj}^{j}} + \frac{n_{ij}}{Z_{ji}^{i}}.
\end{aligned}
\tag{16}
$$

The coordination number of the pure elements in the metallic liquid solution, $Z_{CaCa}^{Ca} = Z_{MgMg}^{Mg} = Z_{SrSr}^{Sr}$, is set to be 6 which is the same coordination number used by Pelton and Chartrand [5], whereas, the coordination numbers of the pairs; Z_{MgCa}^{Mg}, Z_{CaMg}^{Ca}, Z_{MgSr}^{Mg}, Z_{SrMg}^{Sr}, Z_{CaSr}^{Sr} and Z_{SrCa}^{Ca} are chosen to permit the composition of maximum short-range ordering in the binary system to be consistent with the composition that corresponds to the minimum heat of mixing. The tendency to maximum short-range ordering near the composition 55 at.% Mg in the Mg–Ca system was obtained by setting $Z_{MgCa}^{Mg} = 5$ and $Z_{CaMg}^{Ca} = 4$. In the Mg–Sr system, the tendency to maximum short-range ordering near the composition 40 at.% Sr was obtained by setting $Z_{MgSr}^{Mg} = 4$ and $Z_{SrMg}^{Sr} = 6$. The positive heat of mixing in Ca–Sr system is reflecting the fact that formation of Ca–Ca and Sr–Sr pairs is more favourable than formation of Ca–Sr pairs. This indicates that the coordination number for Ca–Sr pairs should be small. Hence the parameters Z_{CaSr}^{Sr} and Z_{SrCa}^{Ca} are set to be 3 in this work.
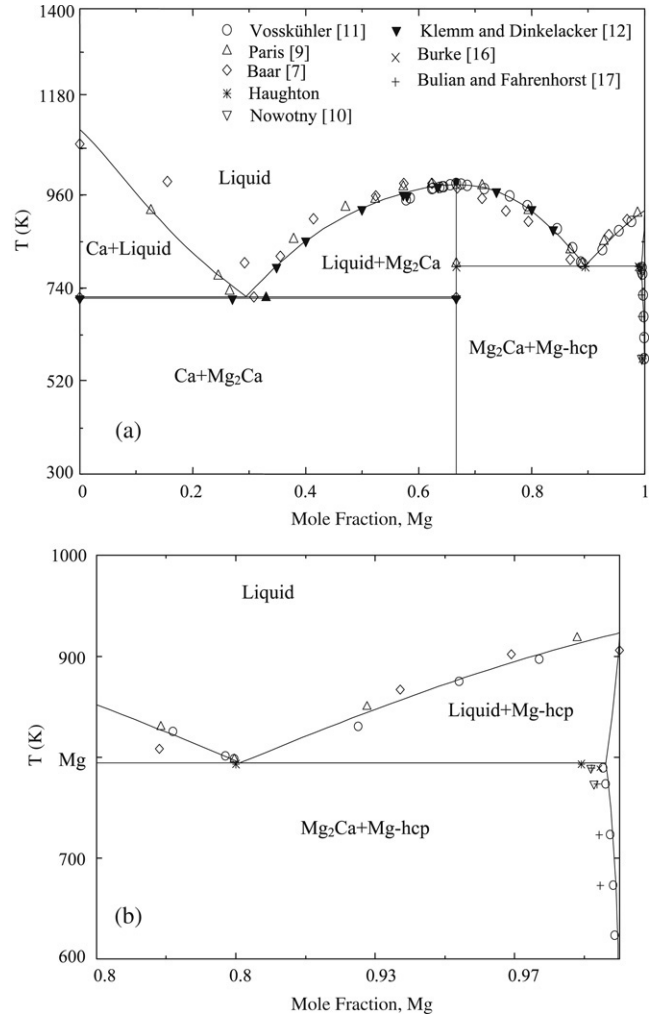

Fig. 1. (a) Reoptimized Mg–Ca System, (b) Mg-rich region of Mg–Ca system.

Thermodynamic optimization and calculation were performed in this work using FactSage program [49].

4. Results and discussions

4.1. Mg–Ca system

The re-optimized Mg–Ca phase diagram along with all experimental data from the literature is shown in Fig. 1. As can be seen from this figure the calculated liquidus and invariant points are in good agreement with the experimental data of Vosskühler [11], and Klemm and Dinkelacker [12] but differ slightly from the results of Baar [7]. A limited solid solubility of Ca in Mg is observed in the calculated phase diagram shown in Fig. 1(b). As can be seen from this figure the maximum solid solubility of Ca in Mg is 0.43 at.% at 517 °C, this agrees with the results of Vosskühler [11] who reported 0.50 at.% at 516.8 °C. Table 1 lists the thermodynamic model parameters obtained by optimization using the experimental thermodynamic and phase equilibrium data from the literature. The calculated invariant points in relation to the experimental data from the literature are presented in Table 2.

Table 1
Optimized thermodynamic parameters of the Mg–Ca, Mg–Sr and Ca–Sr systems (J/mol atom)

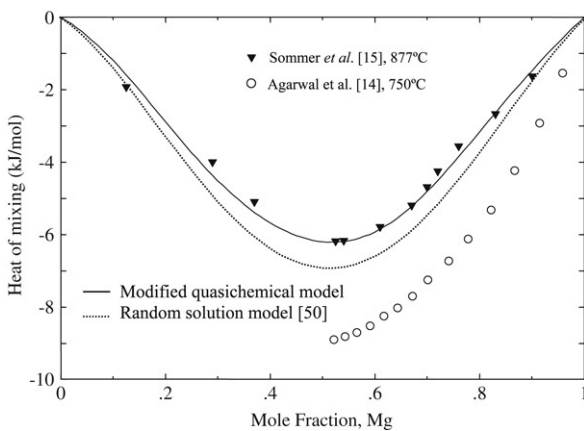|	The modified quasichemical model	Random solution model [50,51]
Phase	$\Delta^{ex}G^{liq} = \Delta g^{\circ}_{AB} + \sum_{i \geq 1} g^{i\circ}_{AB} x^{i}_{AA} + \sum_{j \geq 1} g^{\circ j}_{AB} x^{j}_{BB}$	$\Delta^{ex}G^{liq} = x_i \cdot x_j \sum_{n=0}^{n=m} {}^n L^{\phi}_{i,j} (x_i - x_j)^n$
Liquid (Mg, Ca)	$\Delta^{ex}G^{liq} = -706.33 + 0.37T + (323.40 - 1.20T)x_{Ca,Ca}$ $+ (508.82 - 0.89T)x_{Mg,Mg}$ $Z^{Mg}_{MgCa} = 5$ $Z^{Ca}_{CaMg} = 4$	$\Delta^{ex}G^{liq} = x_{Ca}x_{Mg}(-24\,018.6 + 1.94T) + x_{Ca}x_{Mg}(1785.73 + 4.47T)(x_{Ca} - x_{Mg}) + x_{Ca}x_{Mg}(14\,387.5 - 22.98T)(x_{Ca} - x_{Mg})^2$
Liquid (Mg,Sr)	$\Delta^{ex}G^{liq} = -447.89 + 0.15T + (-355.16 - 0.05T)x_{Sr,Sr}$ $+ (170.42 - 0.07T)x_{Mg,Mg}$ $Z^{Sr}_{MgSr} = 4$ $Z^{Mg}_{SrMg} = 6$	$\Delta^{ex}G^{liq} = x_{Sr}x_{Mg}(-19\,560 + 4.01T)$ $+ x_{Sr}x_{Mg}(-14\,250.02 + 6.03T)(x_{Sr} - x_{Mg})$
Liquid (Ca,Sr)	$\Delta^{ex}G^{liq} = 43.74 + 0.01T + 22.85x_{Ca,Ca} - 6.09x_{Sr,Sr}$ $Z^{Sr}_{CaSr} = 3$ $Z^{Ca}_{SrCa} = 3$	$\Delta^{ex}G^{liq} = x_{Ca}x_{Sr}(1682 + 0.59T) + x_{Ca}x_{Sr}(521.05 + 0.052T)(x_{Ca} - x_{Sr}) + -900x_{Ca}x_{Sr}(x_{Ca} - x_{Sr})^2$
Mg$_2$Ca	$G^{Mg_2Ca}_{Mg:Ca} = -13\,468.62 + 2.0T$	$G^{Mg_2Ca}_{Mg:Ca} = -12\,704.4 + 1.81T$
Mg$_2$Sr	$G^{Mg_2Sr}_{Mg:Sr} = -7950.79 + 0.03T$	$G^{Mg_2Sr}_{Mg:Sr} = -9385.8 + 0.115T$
Mg$_{38}$Sr$_9$	$G^{Mg_{38}Sr_9}_{Mg:Sr} = -12\,206.3 + 0.1T$	$G^{Mg_{38}Sr_9}_{Mg:Sr} = -12\,796.85 + 7.5T$
Mg$_{23}$Sr$_6$	$G^{Mg_{23}Sr_6}_{Mg:Sr} = -12\,125.28 + 0.2T$	$G^{Mg_{23}Sr_6}_{Mg:Sr} = -12\,680.89 + 6.96T$
Mg$_{17}$Sr$_2$	$G^{Mg_{17}Sr_2}_{Mg:Sr} = -12\,330.53 + 0.91T$	$G^{Mg_{17}Sr_2}_{Mg:Sr} = -13\,441.77 + 10.67T$
bcc	$G^{bcc}_{Ca:Sr} = 3770.03 + 0.01T$	$G^{bcc}_{Ca:Sr} = 3770.03 + 0.01T$
fcc	$G^{fcc}_{Ca:Sr} = 3770.03 + 0.11T$	$G^{fcc}_{Ca:Sr} = 3770.03 + 0.11T$

Fig. 2. Comparison between the calculated heat of mixing of Mg–Ca liquid at 877 °C using the modified quasichemical model and random solution model along with the experimental data [14,15].

The calculated heat of mixing of liquid Mg–Ca at 877 °C is plotted in Fig. 2 together with experimental values from the literature [14,15]. As can be seen in this figure, the calculated heat of mixing of liquid Mg–Ca agrees well with the experimental data of Sommer et al. [15], whereas, the measured heat of mixing by Agarwal et al. [14], which is twice as large as that measured by Sommer et al. [15], is not reliable. Fig. 2 shows that the minimum value of the heat of mixing is around 50 at.% Mg. Comparison between experimental heat of mixing of Mg–Ca liquid at 877 °C [14,15] and the calculations using the modified quasichemical model and random solution model is shown in Fig. 2. Although the experimental phase diagram was reproduced by both models and the same number of optimized parameters were used, as can be seen in Table 1, the quasichemical model resulted in better agreement with the experimental data of Sommer et al. [15]. The entropy of mixing of the Mg–Ca liquid at 807 °C calculated using the modified quasichemical model shows a minimum value near the composition 50 at.% Mg which corresponds to the composition where the enthalpy of mixing is minimum indicating a tendency for short range ordering in the Mg–Ca liquid as can be seen in Fig. 3. This is in agreement with the work of Sommer [3] and Mishra et al. [4] who reported a tendency for glass formation close to this composition. Also, it can be seen from this figure that the indication for short range ordering in the liquid is more obvious in the curve obtained by the modified quasichemical

Table 2
Comparison between calculated and experimental values of the invariant reactions in the Mg–Ca system

| Reaction	at.% Mg	at.% Ca	T (°C)	Reference	Reaction type
L ↔ Mg-hcp	100.00	0.00	650.0	[8]	Melting
	100.00	0.00	649.3	[This work]	
L ↔ Ca-bcc	0.00	100.00	842.0	[8]	Melting
	0.00	100.00	841.2	[This work]	
Ca-bcc ↔ Ca-fcc	0.00	100.00	443.0	[8]	Allotropic
	0.00	100.00	442.5	[This work]	
	27.00	73.00	442	[12]	
	26.58	73.42	460	[9]	
L ↔ Mg₂Ca + Ca-fcc	33.00	67.00	445	[10]	Eutectic
	30.86	69.14	446	[7]	
	29.44	70.56	445	[This work]	
	66.67	33.33	717	[11]	
	66.67	33.33	714	[9]	
L ↔ Mg₂Ca	66.67	33.33	725	[10]	Congruent
	66.67	33.33	721	[7]	
	66.67	33.33	714	[This work]	
	89.44	10.56	516	[11]	
	89.51	10.49	517	[10]	
L ↔ Mg₂Ca + Mg-hcp	88.95	11.05	525	[9]	Eutectic
	87.75	12.25	518	[7]	
	89.44	10.56	514	[This work]	
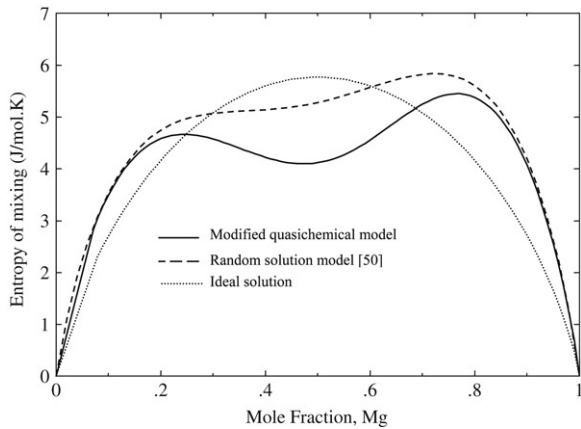
Fig. 3. Comparison between the calculated entropy of mixing of Mg–Ca liquid at 807 °C using the modified the quasichemical model and random solution model.

model. Fig. 4 presents the calculated activities of Ca and Mg in the liquid at 827 °C in relation to the experimental data obtained by [27,28]. As can be seen in Fig. 4(a) and (b), the calculated activities followed the general trend of the experimental data. The deviation is within the uncertainty limits of the measured values especially since these data were obtained by vapour pressure measurements which usually show large degree of scatter.

In this work, the calculated heat of formation of Mg₂Ca is −13.47 kJ/mol atom, which is in agreement with the heat of formation measured using tin solution calorimetry by King and Kleppa [26], and Davison and Smith [22] as −13.5 ± 1.25 kJ/mol atom and −13.17 ± 2.63 kJ/mol atom, respectively.
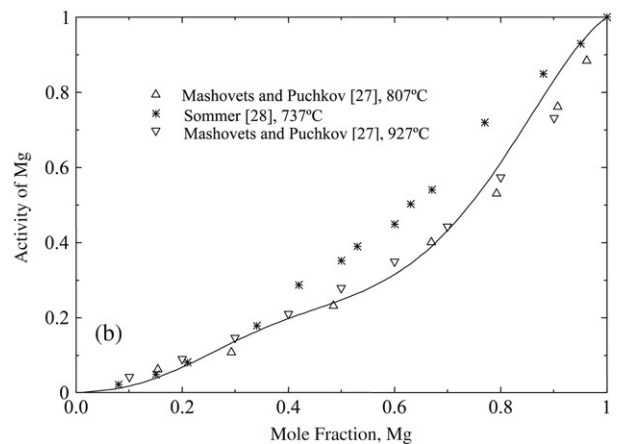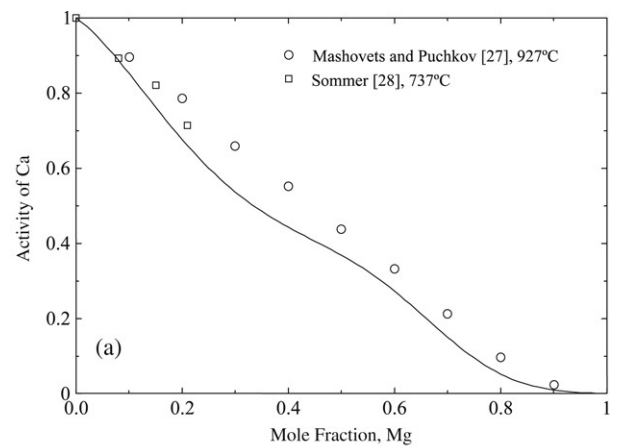

Fig. 4. Calculated activity of (a) Ca and (b) Mg in the Mg–Ca liquid at 827 °C (Reference state: Ca-liquid and Mg-liquid).

Table 3
Comparison between calculated and experimental values of the invariant reactions in the Mg–Sr system

Reaction	at.% Mg	at.% Sr	T (°C)	Reference	Reaction type
Sr-bcc ↔ Sr-fcc	0.00	100.00	547.0	[8]	Allotropic
	0.00	100.00	547.0	**[This work]**	
	35.00	65.00	842.0	[32]	
$L ↔ Mg_2Sr + Sr$-fcc	30.00	70.00	438.0	[34]	Eutectic
	29.60	70.40	426.0	[33]	
	30.56	69.44	426.0	**[This work]**	
	66.67	33.33	680.0	[32]	
$L ↔ Mg_2Sr$	66.67	33.33	680.0	[34]	Congruent
	66.67	33.33	689.0	[33]	
	66.67	33.33	676.6	**[This work]**	
	80.90	19.10	608.0	[34]	
$L + Mg_2Sr ↔ Mg_{23}Sr_6$	80.64	19.36	603.0	[33]	Peritectic
	79.31	20.69	600.7	**[This work]**	
	82.56	17.44	599.0	[34]	
$L + Mg_{23}Sr_6 ↔ Mg_{38}Sr_9$	82.50	17.50	598.0	[32]	Peritectic
	81.50	18.50	595.6	**[This work]**	
	84.90	15.10	592.0	[34]	
	84.50	15.50	587.0	[32]	
$L ↔ Mg_{17}Sr_2 + Mg_{38}Sr_9$	84.50	15.50	592.0	[31]	Eutectic
	83.40	16.60	599.0	[33]	
	84.90	15.10	592.4	**[This work]**	
	90.00	10.00	609.0	[34]	
	90.00	10.00	603.0	[32]	
$L ↔ Mg_{17}Sr_2$	90.00	10.00	606.0	[31]	Congruent
	89.47	10.53	604.0	[33]	
	89.47	10.53	595.4	**[This work]**	
	94.00	6.00	586.0	[34]	
	94.00	6.00	585 ± 2	[32]	
$L ↔ (Mg) + Mg_{17}Sr_2$	94.10	5.90	582.0	[31]	Eutectic
	93.55	6.45	585.0	[33]	
	93.34	6.66	586.8	**[This work]**	

4.2. Mg–Sr system

Experimental phase diagram, enthalpy of mixing and the activities of Mg and Sr in the liquid phase were used to optimize the thermodynamic model parameters of the liquid and the intermetallic compounds in this system. The optimized model parameters as well as the binary invariant points are given in Tables 1 and 3, respectively. The reoptimized phase diagram of the Mg–Sr system in relation to the experimental data from the literature is shown in Fig. 5. Good agreement between the reoptimized phase diagram and the measured liquidus points of [31–34] can be observed in this figure.

Also, good agreement between the calculated enthalpy of mixing at 807 °C and the experimental data of Sommer et al. [15] can be observed in Fig. 6. As can be seen in this figure, the heat of mixing of Mg–Sr liquid at 807 °C calculated using the modified quasichemical model has better agreement with the experimental data than the random solution model. Fig. 7 shows the calculated activities of Mg and Sr in the Mg–Sr liquid at 827 °C along with the experimental data of [36]. The calculated activities show good agreement with the experimental data.

On the formation of an intermetallic compound from its components changes in the structure, bond type and strength occur. The Gibbs free energy of formation of the intermetallic compounds gives an indication of their stability. According to thermodynamic principles, the formation of an intermetallic compound results in small value of entropy of formation that ranges from −10 to 10 J/mol K which depending on the configurational and vibrational entropy of formation. Hence, unreasonable prediction of the entropy of formation creates less reliable value for the enthalpy of formation. In this work, the calculated heat of formation of Mg_2Sr is −7.95 kJ/mol atom, which is in agreement with the heat of formation measured from solid Mg and Sr using tin solution calorimetry by King and Kleppa [26] as −7.18 kJ/mol atom but different from Zhong et al. [45] value as −10.62 kJ/mol atom. Fig. 8 shows a comparison between the calculated enthalpy of formation from this work and Zhong's et al. [45] results. In this work, the calculated entropy of formation of Mg_2Sr is 0.038 J/mol K compared to Zhong's et al. [45] calculation as 3.03 J/mol K, this difference resulted in less reliable value for the heat of formation. The entropy of formation of other intermetallic
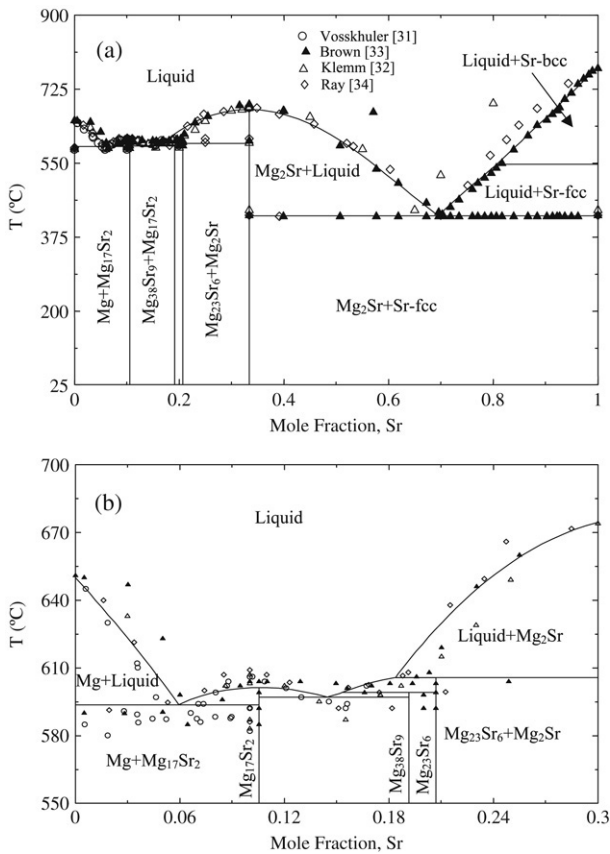
Fig. 5. (a) Reoptimized Mg–Sr system, (b) Mg-rich region of the Mg–Sr system.

Fig. 6. Comparison between the calculated heat of mixing of Mg–Sr liquid at 807 °C using the modified quasichemical model and random solution model along with the experimental data of [15].
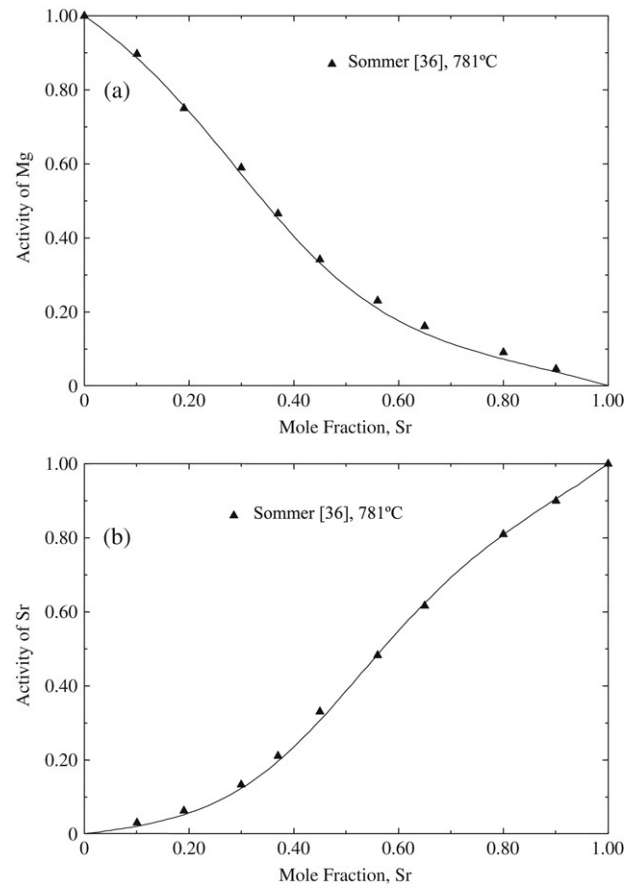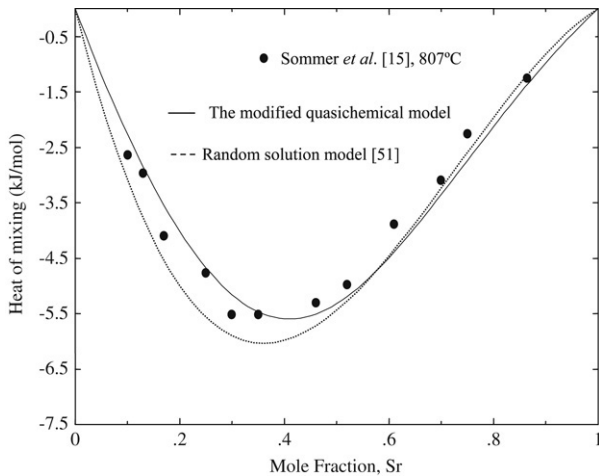

Fig. 7. Calculated activity of (a) Mg, (b) Sr in Mg–Sr liquid with the experimental data of [36] at 827 °C (Reference state: Sr-liquid and Mg-liquid).

Fig. 8. Heat of formation of different intermetallic compounds in the Mg–Sr system.

4.3. Ca–Sr system

The experimental data of Schottmiller et al. [37], and Predel and Sommer [44] are used to reoptimize the Ca–Sr system. The stable phases in the present optimization of this system are liquid, fcc and bcc. Fig. 9 shows the reoptimized phase diagram with the experimental data of Schottmiller et al. [37]. The reoptimized Ca–Sr system agrees well with the experimental

compounds in Mg–Sr system calculated by Zhong et al. [45] are also different from this work; the entropy of formation of $Mg_{38}Sr_9$, for example, is 54.73 J/mol K compared to 0.16 J/mol K calculated using the modified quasichemical model. Therefore, this difference in the entropy of formation between the two works resulted in different values for the heat of formation as can be seen in Fig. 8.
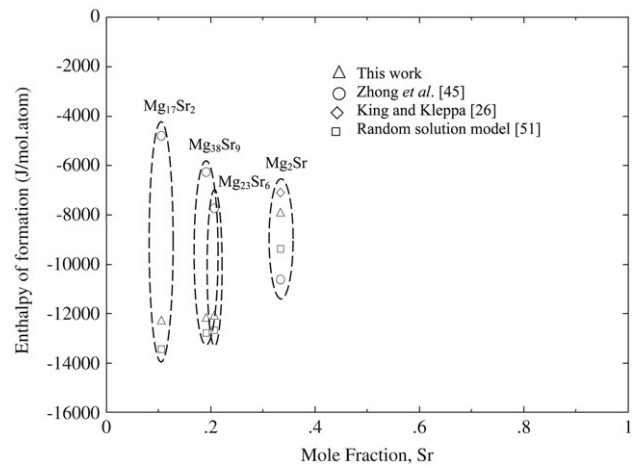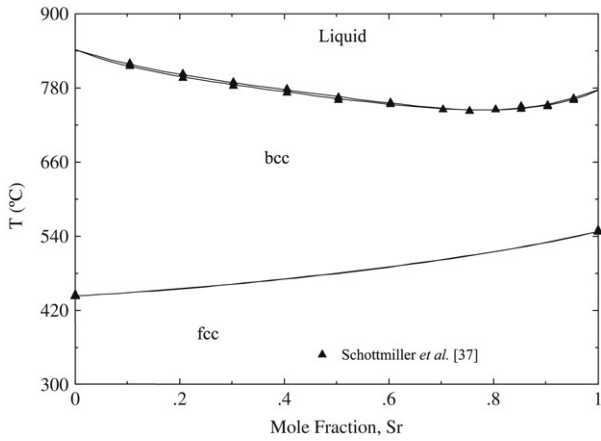
Fig. 9. Re-optimized Ca–Sr system.
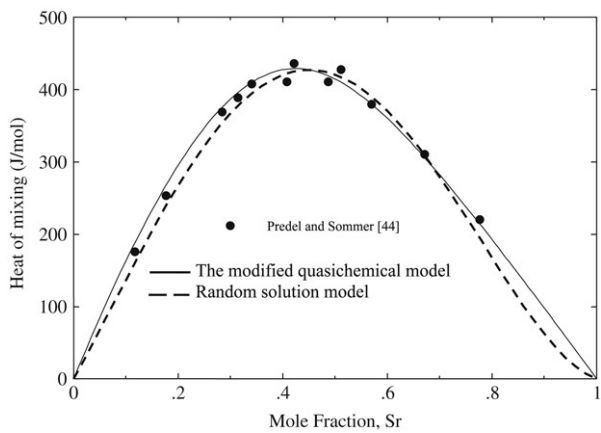
Fig. 10. Calculated heat of mixing of Ca–Sr liquid alloys at 827 °C.

Fig. 11. Ternary liquidus projection of Mg–Ca–Sr in weight fraction with invariant points calculated using the modified quasichemical model and limited solubility between Mg$_2$Ca and Mg$_2$Sr is assumed.

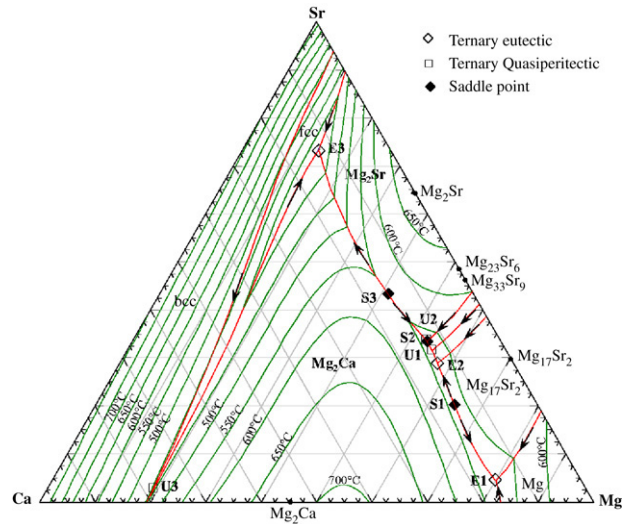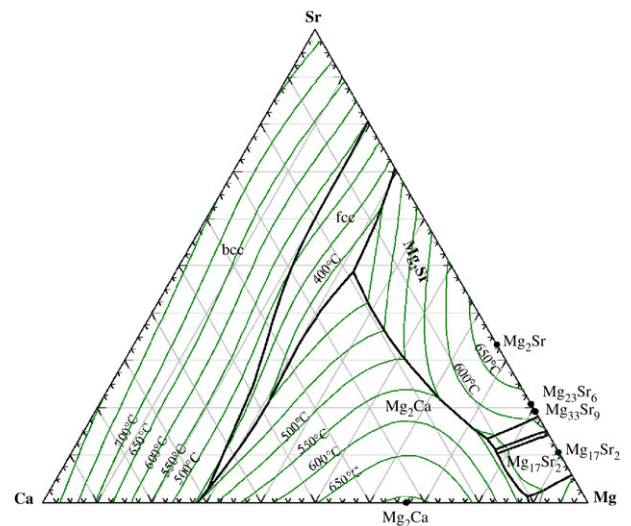Fig. 12. Ternary liquidus projection of the Mg–Ca–Sr system in mole fraction calculated using the modified quasichemical model and limited solubility between Mg$_2$Ca and Mg$_2$Sr is assumed.

data. Fig. 10 shows good agreement between the calculated heat of mixing and the experimental data of [44]. As can be seen in this figure, the heat of mixing of Ca–Sr liquid at 827 °C calculated using the modified quasichemical model has better agreement with the experimental data than the random solution model. Physically, the positive heat of mixing is reflecting the fact that formation of Ca–Ca and Sr–Sr pairs is more favourable than formation of Ca–Sr pairs. In this work, the excess entropy of mixing of the liquid alloys is relatively small with maximum value of +0.02 J/mol K which is in agreement with the evaluation of Alcock et al. [43].

Due to the lack of experimental data for the Ca–Sr system, its thermodynamic description was predicted based on the experimental work of Schottmiller et al. [37], and Predel and Sommer [44] only.

4.4. Mg–Ca–Sr system

The thermodynamic properties of the liquid were estimated from the optimized binary parameters using Kohler extrapolation [52]. No ternary adjustable terms were added since experimental phase equilibrium and thermodynamic data for the Mg–Ca–Sr system could not be found in the literature. The database was then used to calculate polythermic projections of the liquidus surfaces shown in Figs. 11 and 12. The Mg–Ca–Sr

ternary system is presented as a projection using Gibbs triangle at various temperature and constant pressure. The calculated liquidus projection is divided into eight primary crystallization fields: (Mg), Mg$_{17}$Sr$_2$, Mg$_2$Sr, Mg$_{23}$Sr$_6$, Mg$_{38}$Sr$_9$, fcc, Mg$_2$Ca, and bcc. The crystallization fields of Mg$_{23}$Sr$_6$ and Mg$_{38}$Sr$_9$ are more extended in the ternary diagram than these predicted in the work of [45]. Liquidus surfaces of bcc and Mg$_2$Ca dominate the phase diagram. The model predicted three saddle points, three peritectics, three quasiperitectic and three ternary eutectics. The respective reactions of these points are listed in Table 4. A comparison between liquidus projections calculated using random solution model and the modified quasichemical model is presented in Fig. 13. The two models predicted slightly different liquidus projection for the Mg–Ca–Sr system.

Table 4
Ternary invariant points of the Mg–Ca–Sr system for the case of no solid solubility between Mg_2Ca and Mg_2Sr (wt.%)

Reaction	wt.% Mg	wt.% Ca	wt.% Sr	T (K)	Reaction type[a]
$L \leftrightarrow Mg_2Ca + Mg + Mg_{17}Sr_2$	79.96	15.45	4.59	792.2	E1
$L \leftrightarrow Mg_{17}Sr_2 + Mg_{38}Sr_9 + Mg_2Ca$	57.40	13.68	28.92	809.9	E2
$L \leftrightarrow Mg_2Ca + fcc + Mg_2Sr$	13.77	13.02	73.21	622.5	E3
$L + Mg_{23}Sr_6 \leftrightarrow Mg_2Ca + Mg_{38}Sr_9$	54.99	13.40	31.61	819.64	U1
$L + Mg_2Sr \leftrightarrow Mg_2Ca + Mg_{23}Sr_6$	52.89	13.36	33.75	814.02	U2
$L + bcc \leftrightarrow Mg_2Ca + fcc$	19.17	78.02	2.81	718.6	U3
$L \leftrightarrow Mg_2Ca + Mg_{17}Sr_2$	64.73	14.98	20.29	813.4	S1
$L \leftrightarrow Mg_2Ca + Mg_{23}Sr_6$	53.21	13.32	33.47	811.8	S2
$L \leftrightarrow Mg_2Ca + Mg_2Sr$	41.25	15.37	43.38	839.0	S3

[a] E denotes ternary eutectic reaction; U denotes ternary quasiperitectic reaction and S denotes saddle point.
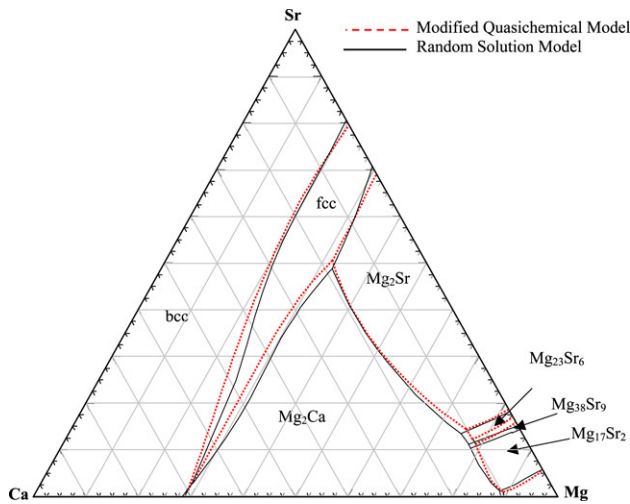

Fig. 13. Ternary liquidus projection of the Mg–Ca–Sr system in mole fraction calculated using random solution model and the modified quasichemical model.
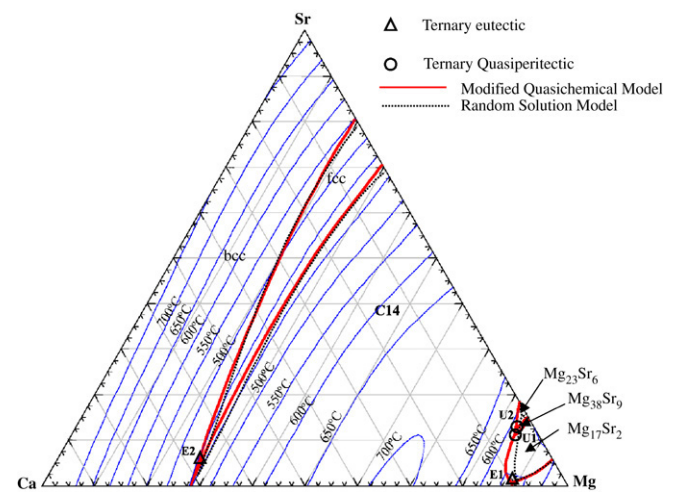

Fig. 14. Ternary liquidus projection of the Mg–Ca–Sr in mole fraction calculated using the modified quasichemical model assuming mutual solubility between Mg_2Ca and Mg_2Sr.

Since there is no experimental data to prove the existence of unlimited solubility between Mg_2Ca and Mg_2Sr, mutual solubility between Mg_2Ca and Mg_2Sr in the ternary phase diagram is considered. C14 is modelled with two sublattices with Mg atoms occupying the first sublattice. In view of the fact that atomic size and crystal structure of Ca and Sr are similar, these two elements replace each other and their mixing is allowed on the second sublattice.

The Gibbs energy of C14 is modelled using compound energy formalism as shown in Eq. (17).

$$G^{C14} = y_{Ca}G^{0,C14}_{Mg:Ca} + y_{Sr}G^{0,C14}_{Mg:Sr} + y_{Ca}G^{0,C14}_{Va:Ca}$$
$$+ y_{Sr}G^{0,C14}_{Va:Sr} + \frac{2}{3}RT(y_{Ca}\ln y_{Ca} + y_{Sr}\ln y_{Sr})$$
$$+ y_{Ca}y_{Sr}L^{0,C14}_{Ca,Sr:Mg}, \qquad (17)$$

where $G^{0,C14}_{Mg:Ca}$ and $G^{0,C14}_{Mg:Sr}$ are the Gibbs energy of formation of Mg_2Ca and Mg_2Sr compounds in the binary Mg–Ca and Mg–Sr systems. $G^{0,C14}_{Va:Ca}$ and $G^{0,C14}_{Va:Sr}$ represent the Gibbs energy of formation of the metastable end members of the solid solution and they were given high positive values (10^5 J/mol). $L^{0,C14}_{Ca,Sr:Mg}$ describes the ternary interaction parameter within the sublattice which is assumed to be negligible due to lack of the experimental data for this system.

The liquidus projection for the mutual solubility between Mg_2Ca and Mg_2Sr is drawn in Fig. 14. The model predicted two quasiperitectic and two ternary eutectics. Comparison between the calculated invariant points in this analysis and the work of [45] is listed in Table 5. Isothermal section of the Mg–Ca–Sr system at 450 °C using the modified quasichemical model for the mutual solubility between Mg_2Ca and Mg_2Sr is drawn in Fig. 15. Including mutual solubility between Mg_2Ca and Mg_2Sr resulted in different liquidus projection and invariant points. This demands experimental investigation in order to verify the mutual solubility and the invariant points.

5. Summary

A self-consistent thermodynamic database has been constructed for the Mg–Ca–Sr system using the modified quasi-chemical model. The model parameters are evaluated by incorporating all experimental data available in the literature. The phase diagrams and thermodynamic properties of all the three binaries show good agreement with the experimental data. The ternary phase diagram of the Mg–Ca–Sr system is calculated by combining the databases of the three constituent binaries. Two cases of limited and complete solubility between Mg_2Ca and Mg_2Sr were presented in this work. In the case of limited solubility, the established database for this system predicted three

Table 5
Ternary invariant points of the Mg–Ca–Sr system for the case of complete solid solubility between Mg_2Ca and Mg_2Sr (at.%)

Reaction	at.% Mg	at.% Ca	at.% Sr	T (K)	Reference	Reaction type[a]
$L \leftrightarrow C14 + Mg + Mg_{17}Sr_2$	88.95	8.43	2.75	783.90	[45]	E1
	89.05	10.20	0.75	792.97	**This work**	
$L + Mg_{38}Sr_9 \leftrightarrow Mg_{17}Sr_2 + C14$	83.32	3.60	13.08	841.90	[45]	U1
	84.34	4.61	11.05	852.66	**This work**	
$L + Mg_{23}Sr_6 \leftrightarrow C14 + Mg_{38}Sr_9$	81.95	1.95	16.10	859.50	[45]	U2
	83.83	3.74	12.43	858.07	**This work**	
$L \leftrightarrow C14 + fcc + bcc$	29.24	69.23	1.53	717.00	[45]	E2
	27.53	68.61	3.86	718.29	**This work**	

[a] E denotes ternary eutectic reaction; U denotes ternary quasiperitectic reaction.
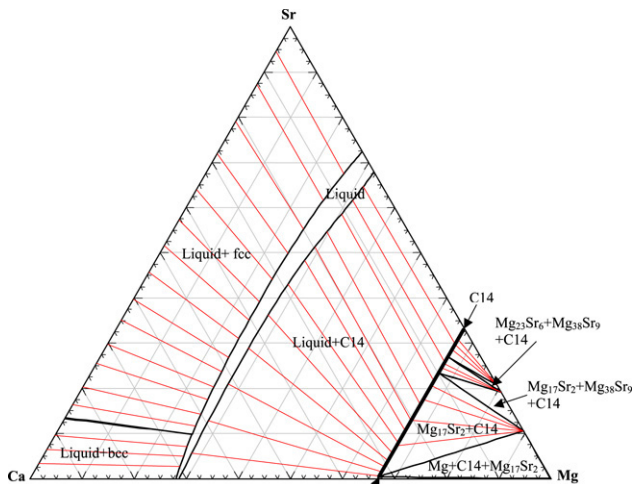

Fig. 15. Isothermal section of the Mg–Ca–Sr system in mole fraction at 450 °C calculated using the modified quasichemical model assuming mutual solubility between Mg_2Ca and Mg_2Sr.

saddle points, three quasiperitectics, and three ternary eutectics. However in the case of complete solubility, a significantly different Mg–Ca–Sr system was predicted with two quasiperitectic and two ternary eutectics. A comparison between the calculated liquidus projection using random solution model and the modified quasichemical model is presented. This is the first attempt to construct the ternary phase diagram of the Mg–Ca–Sr system using the modified quasichemical model. Since this model is more physically sound than the random mixing and associates models, this work lays down the foundation for more developed evaluation.

Acknowledgments

References

[1] E. Baril, P. Labelle, M.O. Pekguleryuz, Elevated temperature Mg–Al–Sr: creep resistance, mechanical properties, and microstructure, J. Miner. Metals Mater. Soc., JOM 55 (11) (2003) 34–39.

[2] M.O. Pekguleryuz, J. Renaud, Creep Resistance in Mg–Al–Ca casting alloys, in: Magnesium 2000 Symposium, J. Miner. Metals Mater. Soc., TMS, 2000, pp. 279–84.

[3] F. Sommer, Association model for the description of thermodynamic functions of liquid alloys II. Numerical treatment and results, Z. Metallkd. 73 (2) (1982) 77–86.

[4] P.P. Mishra, M. Milanarun, N. Jha, A.K. Mishra, Thermodynamic properties of liquid glass-forming Ca–Mg alloys, J. Alloys Compounds 340 (1–2) (2002) 108–113.

[5] A.D. Pelton, P. Chartrand, The modified quasi—chemical model: Part II. Multicomponent solutions, Metall. Mater. Trans. A 32A (6) (2001) 1355–1360.

[6] A.D. Pelton, S.A. Degterov, G. Eriksson, C. Robelin, Y. Dessureault, The modified quasi-chemical model I—Binary solutions, Metall. Mater. Trans. B 31B (4) (2000) 651–659.

[7] N. Baar, On the alloys of molybdenum with nickel, manganese with thallium, and calcium with magnesium, thallium, lead, copper, and silver, Z. Anorg. Allg. Chem. 70 (1911) 362–366 (From British Library www.bl.uk, 'Ca–Mg (Calcium–Magnesium)', Landolt-Bornstein Series IV/5c, pp. 22–25).

[8] M.W. Chase, Heat of transition of the elements, Bull. Alloy Phase Diagr. 4 (1) (1983) 123–124.

[9] R. Paris, Contribution on the ternary alloys, Publ. Sci et Tech Ministére Air (France) 45 (1934) 39–41.

[10] J.L. Haughton, Alloys of magnesium. Part 6—The construction of the magnesium-rich alloys of magnesium and calcium, J. Inst. Met. 61 (1937) 241–246.

[11] H. Vosskühler, The Phase diagram of magnesium-rich Mg–Ca alloys, Z. Metallkd. 29 (1937) 236–237.

[12] W. Klemm, F. Dinkelacker, On the behavior of magnesium with calcium, strontium, and barium, Z. Anorg. Chem. 255 (1947) 2–12.

[13] A.A. Nayeb-Hashemi, J.B. Clark, The Ca–Mg (calcium–magnesium) system, Bull. Alloy Phase Diagr. 8 (1987) 58–65.

[14] R. Agarwal, J. Lee, H. Lukas, F. Sommer, Calorimetric measurements and thermodynamic optimization of the Ca–Mg system, Z. Metallkd. 86 (2) (1995) 103–108.

[15] F. Sommer, B. Predel, D. Assmann, Thermodynamic investigation of liquid alloys in the systems Mg–Ca, Mg–Sr, and Mg–Ba, Z. Metallkd. 68 (5) (1977) 347–349.

[16] E.C. Burke, Solid solubility of calcium in magnesium, J. Met. Trans. AIME 203 (1955) 285–286.

[17] W. Bulian, E. Fahrenhorst, Solubility of calcium in magnesium, Metallforschung 1 (1946) 70.

[18] H. Nowotny, E. Wormnes, A. Mohrnheim, Investigation on the Al–Ca, Mg–Ca, and Mg–Zr systems, Z. Metallkd. 32 (1940) 39–42.

[19] W. Biltz, G. Hohorst, Contributions to the Systematic Study of Affinity. XV. the Heats of Formation of the Compounds of Metallic Magnesium with Metallic Zinc, Cadmium, Aluminium and Calcium', Z. Anorg. Allg. Chemie 121 (1) (1922) 1–24.

[20] J.F. Smith, R.L. Smythe, Vapor pressure measurements over calcium, magnesium, and their alloy and the thermodynamics of formation of $CaMg_2$, Acta Metall. Mater. 7 (1959) 261–267.

[21] P. Chiotti, R.W. Curtis, P.F. Woerner, Metal hydride reaction, II. Reaction of hydrogen with $CaMg_2$ and $CaCu_5$ and thermodynamic properties of the compounds, J. Less-Common Met. 7 (1964) 120–126.

[22] J.E. Davison, J.F. Smith, Enthalpy of formation of $CaMg_2$, Trans. Metall. Soc. AIME 242 (10) (1968) 2045–2049.

[23] G.J. Gartner, Application of an Adiabatic Calorimeter to the Determination of the Heats of Fusion and Heats of Formation of Several Metallic Compounds, Thesis, Iowa State University, Ames, Iowa, 1965.

[24] J.E. Davison, J.F. Smith, Low temperature heat capacity and high temperature enthalpy of $CaMg_2$, Trans. Metall. Soc. AIME 242 (10) (1968) 2051–2054.

[25] B.P. Burylev, Thermodynamic properties of calcium based alloys, K.V. Astakhov (Ed.), Termodin Termokhin Konstanty Izd. Nauka, Moscow, USSR, 1970, pp. 32–39.

[26] R.C. King, O.J. Kleppa, A thermodynamic study of some selected laves phases, Acta Metall. Mater. 12 (1964) 87–97.

[27] V.P. Mashovets, L.V. Puchkov, Vapour pressure over molten alloys in the system Mg–Ca, Zhurnal Prikl. Khimii 38 (5) (1965) 1009–1014.

[28] F. Sommer, Thermodynamic activities of liquid alloys in the system Ca–Mg using a modified ruff method, Z. Metallkd. 70 (8) (1979) 545–547.

[29] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, OH, 1973.

[30] A.A. Nayeb-Hashemi, J.B. Clark, The Mg–Sr (magnesium strontium) system, Bull. Alloy Phase Diagr. 7 (2) (1986) 149–155.

[31] H. Vosskuehler, The structure of the magnesium-rich alloys of magnesium and strontium, Metallwirtschaft 18 (1939) 377–378.

[32] W. Klemm, F. Dinkelocker, Alloys of magnesium with calcium strontium and barium, Z. Anorg. Chem. 255 (1947) 2–12.

[33] J.W. Brown, The Strontium–Magnesium Phase System, Ph.D. Thesis, Syracuse University, NY, 1973.

[34] J.P. Ray, The Strontium-Magnesium Equilibrium Diagram, Ph.D. Thesis, Syracuse University, NY, 1947.

[35] P. Chartrand, A.D. Pelton, Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the Al–Mg, Al–Sr, Mg–Sr, and Al–Mg–Sr systems, J. Phase Equilibria 15 (6) (1994) 591–605.

[36] F. Sommer, Determination of thermodynamic activities of liquid alloys in the systems Mg–Sr and Ba–Mg, Z. Metallkd. 71 (7) (1980) 434–437.

[37] J.G. Schottmiller, A.J. King, F.A. Kanda, The calcium–strontium metal phase system, J. Phys. Chem. 62 (1958) 1446–1449.

[38] R.P. Elliott, Constitution of Binary Alloys, first supplement, McGraw-Hill Book Comp., New York, 1965.

[39] J.F. Smith, O.N. Carlson, R.W. Vest, Allotropic modification of calcium, J. Electrochem. Soc. 103 (1956) 409–413.

[40] W. Klemm, G. Mika, Interactions of the alkaline earth metals, Z. Anorg. Allg. Chemie 248 (1941) 155–166.

[41] D.T. Peterson, V.G. Fattore, Calcium–calcium hydride phase system, J. Phys. Chem. 65 (1961) 2062–2064.

[42] A.J. King, X-ray study of the calcium–strontium alloy series, J. Am. Chem. Soc. 64 (1942) 1226–1227.

[43] C.B. Alcock, V.P. Itkin, The Ca–Sr (calcium-strontium) system, Bull. Alloy, Phase Diagr. 7 (5) (1986) 455–457.

[44] B. Predel, F. Sommer, Thermodynamic investigations of the systems calcium–strontium, calcium–barium, and strontium–barium, Phys. Condens. Matter 17 (4) (1974) 249–265.

[45] Y. Zhong, J.O. Sofo, A.A. Luo, Zi Kui Liu, Thermodynamic modeling of the Mg–Sr and Mg–Ca–Sr systems, J. Alloys Compounds 421 (1–2) (2006) 172–178.

[46] A.T. Dinsdale, SGTE data for pure elements, CALPHAD 15 (4) (1991) 317–425.

[47] M. Blander, J. Braunstein, Quasilattice model of molten reciprocal salt systems, Ann. New York Acad. Sci. 79 (1960) 838–852.

[48] R.H. Fowler, E.A. Guggenhim, Statistical Thermodynamic, Cambridge University Press, Cambridge, UK, 1939, pp. 350–366.

[49] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J Melançon, A.D. Pelton, S. Petersen, FactSage thermochemical software and databases, CALPHAD 26 (2) (2002) 189–228.

[50] F. Islam, M. Medraj, Thermodynamic modeling of the Mg–Al–Ca system, Can. Metall. Q. 44 (4) (2005) 523–536.

[51] M. Aljarrah, U. Aghaulor, M. Medraj, Thermodynamic assessment of the Mg- Zn-Sr system, Intermetallics 15 (2) (2007) 93–97.

[52] F. Kohler, Estimation of the thermodynamic data for a ternary system from the corresponding binary systems, Mon. fuer Chemie 91 (1960) 738–740.