Thermodynamic assessment of the Mg−Zn−Sr system

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Abstract

The phase equilibria and thermodynamic properties of the Mg−Sr−Zn system were analyzed in this work for the first time and a thermodynamic description of the system was obtained using a computerized optimization procedure. The available thermodynamic and phase diagram data were critically assessed for the Mg−Sr, Mg−Zn and Sr−Zn binary systems. Optimized thermodynamic properties of the binary systems were then used to construct a database and calculate the ternary phase diagram. The excess terms of the liquid phase in the binary Gibbs energy equation, for all binaries, were described by the Redlich−Kister polynomial equation. The established database predicted 4 saddle points, 11 ternary quasi-peritectics, 1 ternary peritectic and 3 ternary eutectics. Lack of ternary experimental data led to the following assumptions: no ternary solid solution and/or compounds are present in the system and no ternary terms were added to the model parameters for the thermodynamic properties of the liquid. The calculated ternary phase diagram can be improved by the addition of new experimental data and can help in establishing Mg multi-component database.
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1. Introduction

Strontium and zinc 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 zinc, on the other hand, is suggested to improve creep resistance, strength and corrosion resistance of the alloy [2,3]. Hence, establishing the phase equilibria in the Mg−Sr−Zn system will help in understanding the alloying effects of Sr and Zn on the phase stability of magnesium alloys.

To create an accurate thermodynamic model of a ternary system, it is necessary to have thermodynamic descriptions of the three constituent binary systems first. The constituent binaries in the Mg−Sr−Zn system are: Mg−Sr, Mg−Zn, and Sr−Zn. For these binaries that bound the ternary system,

the Mg−Sr system was re-optimized in the present work, whereas the Sr−Zn and Mg−Zn binary systems were taken from Zhong et al. [4] and Liang et al. [5], respectively.

A ternary phase diagram calculation requires that the same model be used in all binary systems for each phase present in the ternary field [6]. The compatibility between these models is crucial because information from these systems is used to construct a database from which the ternary phase diagram is constructed [7]. For the liquid phase the Redlich−Kister model was used.

No ternary compound or thermodynamic data for the Mg−Sr−Zn ternary system has been reported in the literature, thus this work was initiated to evaluate the thermodynamic description of this system for the first time.

2. Experimental data

2.1. Mg−Sr system

Nayeb-Hashemi and Clark [8] reviewed the Mg−Sr system and provided a comprehensive discussion of all the experimental results obtained by previous works [9−12].

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A tin solution calorimetry was used to measure the heat of formation of the congruently melting compound Mg_2Sr from solid Mg and Sr (King and Kleppa [13]). Sommer et al. [14] determined the enthalpy of mixing of the liquid alloys at 1080 K, using high temperature calorimetry. The thermodynamic activities of liquid alloys at 1054 K were determined by Sommer [15] using a modified Ruff boiling technique. These were the only thermodynamic data found for the system and they will be used in the current analysis.

2.2. Mg−Zn and Zn−Sr systems

In the present work, the optimized parameters for Mg−Zn system, presented in Fig. 1, were obtained from Liang et al. [5]. The phase diagram of Zn−Sr shown in Fig. 2 was recalculated from Zhong et al. [4] who described the liquid phase using Redlich−Kister model. Since the minimum value for heat of mixing is ~ -5 kJ/mol, this justifies using Redlich−Kister model because the short range ordering is not evident in the liquid. This phase diagram varied from that of Bruzzone and Merlo [16], due to the misguided assumption made by the latter that the Sr-hcp phase was stable at high temperature, but according to the SGTE data for pure elements [17], Sr-bcc is the stable phase at high temperature.

3. Thermodynamic models

For a pure element with a certain structure φ, its Gibbs free energy, SER, is described as:

$$^0G_A^\varphi(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \tag{1}$$
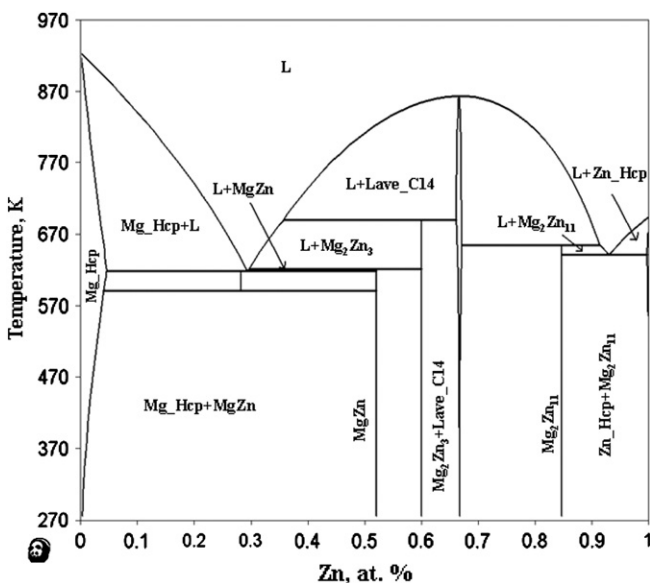

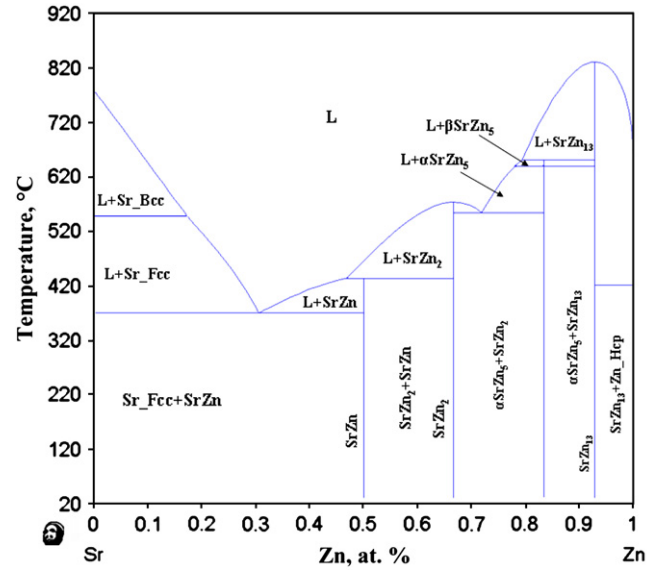Fig. 1. Calculated Mg−Zn from the database of Ref. [5].

Fig. 2. Optimized Sr−Zn system [4].

where the parameters a through h are assigned from the SGTE database [17]. In this study, only two terminal solid solution phases were modeled, these are the Mg-hcp and Zn-hcp phases in the Mg−Zn system. All other terminal phases are considered as stoichiometric and their Gibbs energy functions could be described by Eq. (1).

The molar Gibbs energy for the liquid phase, modeled as a substitutional solution, is described by Eq. (2).

$$G_{\text{liquid}} = x_i\,^0G_i^{\text{liq}} + x_j\,^0G_j^{\text{liq}} + RT\left[x_i\ln(x_i) + x_j\ln(x_j)\right] + {}^{ex}G^{\text{liq}} \tag{2}$$

where x_i and x_j are the mole fraction of the components i and j, respectively.

$$^{ex}G^{\text{liq}} = x_ix_j\sum_{n=0}^{m}\left[{}^nL_{i,j}^{\text{Liquid}}\left(x_i - x_j\right)^n\right] \text{ where } L \text{ is of the form:}$$

$$^nL_{i,j}^{\text{Liquid}} = a_n + b_nT \text{ and } n = 0, \ldots, m \tag{3}$$

Eq. (3) is the Redlich−Kister equation, its parameters, a_n and b_n are to be optimized using experimental data.

The Gibbs energy for an ordered binary solution phase is described in Eq. (4) [18].

$$G = G^{\text{Ref}} + G^{\text{Ideal}} + G^{\text{Excess}} \text{ where}$$

$$G^{\text{Ref}} = \sum y_p^i y_q^j \ldots y_s^l\, {}^0G_{(p:q:\ldots:s)}$$

$$G^{\text{Ideal}} = RT\sum_{i=1}^{l}f_i\sum_{p=1}^{m}y_p^i\ln\left(y_p^i\right)$$

$$G^{\text{Excess}} = \sum y_p^i y_q^i y_r^j\sum_{\gamma=0}^{}{}^\gamma L_{(p,q):r}\left(y_p^i - y_q^j\right)^\gamma \tag{4}$$

Table 1
Optimized thermodynamic parameters for the Mg–Sr system (J/mol atom)

Liquid (Mg,Sr)	$^0L_{Mg,Sr} = -19\,560 + 4.000T$
	$^1L_{Mg,Sr} = -14\,250 + 6.005T$
Mg$_2$Sr	$G^{Mg_2Sr}_{Mg:Sr} = -9385.8 + 0.115T$
Mg$_{38}$Sr$_9$	$G^{Mg_{38}Sr_9}_{Mg:Sr} = -12\,796.85 + 7.5T$
Mg$_{23}$Sr$_6$	$G^{Mg_{23}Sr_6}_{Mg:Sr} = -12\,680.89 + 6.96T$
Mg$_{17}$Sr$_2$	$G^{Mg_{17}Sr_2}_{Mg:Sr} = -13\,441.769 + 10.668T$

where,

- p, q, and r represent components or vacancy.
- i, j…l represent sublattices.
- y^i_p is the site fraction of component p on sublattice i.

- f_l is the fraction of the sublattice l with respect to the total lattice sites.
- $L_{(p,q):r}$ is the interaction parameter describing the interaction within the sublattice.

Gibbs energy functions for the stoichiometric compounds are represented by modifying Eq. (2) as:

$$G^{phase,\varphi} = x_i\,^0G_i^\varphi + x_j\,^0G_j^\varphi + \Delta G_f \tag{5}$$

where $^0G_i^\varphi$ and $^0G_j^\varphi$ denote Gibbs free energy of elements i and j in their standard state and $\Delta G_f = a + bT$ represents the Gibbs energy of formation of the stoichiometric phase,
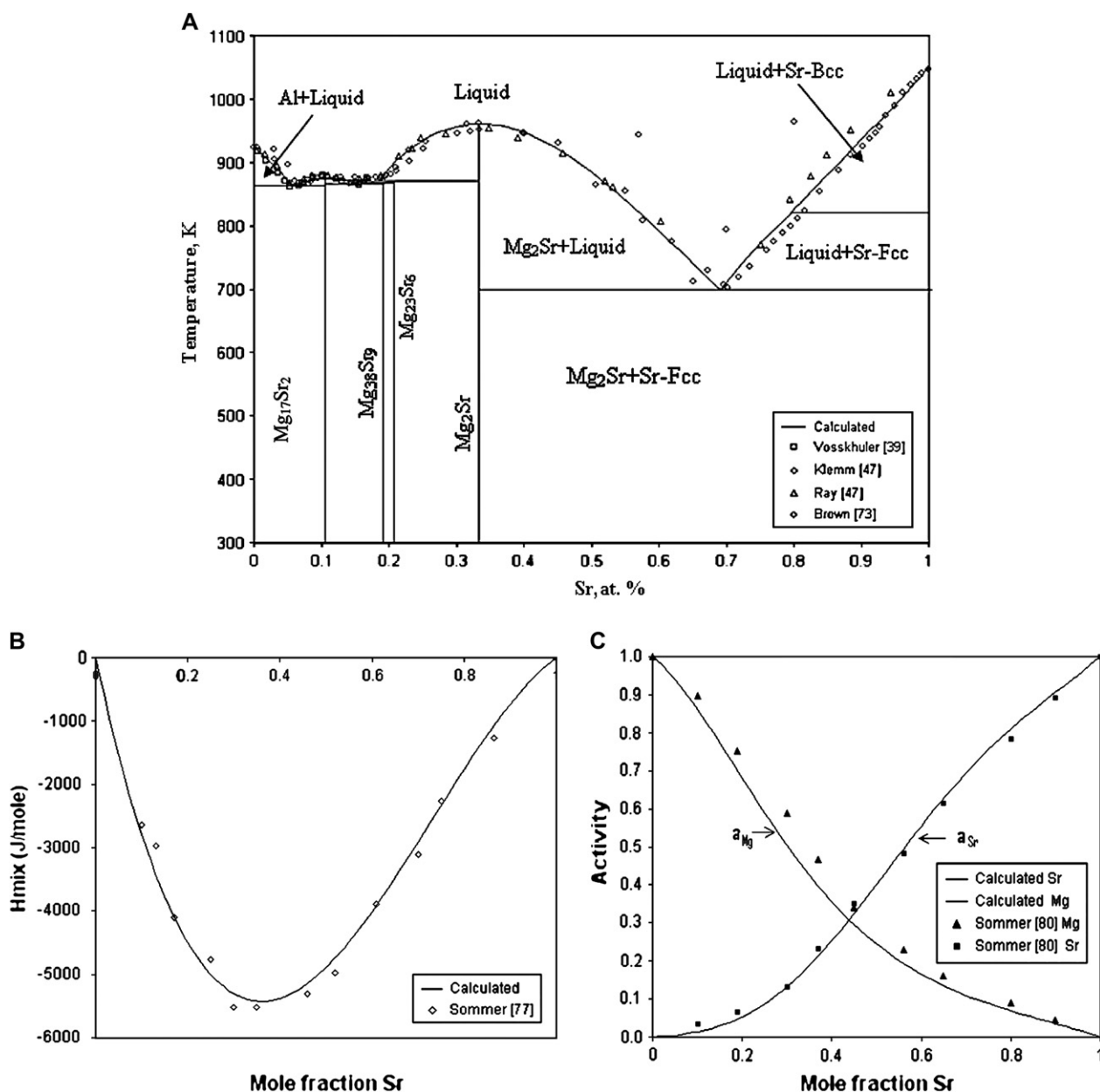

Fig. 3. (a) Re-optimized Mg–Sr system in relation to experimental results from the literature, (b) calculated heat of mixing of Mg–Sr liquid alloys at 1080 K, and (c) calculated activity of Mg and Sr in liquid compared with experimental data from the literature.

'a' and 'b' are the model parameters to be optimized using experimental data.

4. Results and discussion

4.1. Mg–Sr system

The Mg–Sr system was re-optimized using the Redlich–Kister polynomial to model the liquid phase. This was done to maintain the consistency with the other binaries Mg–Zn and Zn–Sr. Table 1 lists the thermodynamic model parameters that were obtained by optimization with the experimental thermodynamic and phase equilibrium data from the literature for the liquid and stoichiometric compounds in the Mg–Sr system. The optimization was done using WinPhaD [19].

The calculated phase diagram using the present thermodynamic description of Mg–Sr system in relation to the experimental data from the literature is shown in Fig. 3(a), the calculated liquidus and invariant reactions are in agreement with the experimental data.

Comparison between the calculated enthalpy of mixing of the Mg–Sr liquid phase with the experimental data of Sommer et al. [14] is shown in Fig. 3(b). The minimum of the enthalpy of mixing curve is between 34 and 38 at.% Sr. King and Kleppa [13] measured the enthalpy of formation of Mg$_2$Sr from solid Mg and Sr using tin solution calorimeter as −21.35 kJ/mol [13], and the calculated, in this work, is −20.9 kJ/mol, which is in good agreement.

Fig. 3(c) shows the calculated activities of Sr and Mg in the liquid at $T = 1000$ K in relation to the experimental data from the literature. This figure shows that the calculated activities agree well with the experimental data.

4.2. Mg–Sr–Zn system

The Mg–Sr–Zn system has been modeled and thus provides a foundation for future experimental investigations. A self-consistent database was constructed for this system by combining the binary thermodynamic properties of Mg–Sr, Mg–Zn and Sr–Zn. The database was then used to calculate the polythermic projections of the liquidus surfaces.

The Mg–Sr–Zn ternary system is presented as a projection using Gibbs triangle, at various temperatures and at atmospheric pressure in Fig. 4. This figure shows that the Mg$_2$Sr is clearly the dominating phase in this system. The model predicted 4 saddle points, 11 ternary quasi-peritectic points, 1 ternary peritectic and 3 ternary eutectic points in this system. The respective reactions of these points are listed in Table 2.

5. Summary

This is the first time that the Mg–Sr–Zn ternary system has been thermodynamically modeled. Optimized parameters for different phases in the Mg–Zn and Sr–Zn binaries were obtained from the literature. The Mg–Sr system has been re-optimized in this work in order to have a consistent thermodynamic description with the other two binaries where the disordered phases were described by the Redlich–Kister
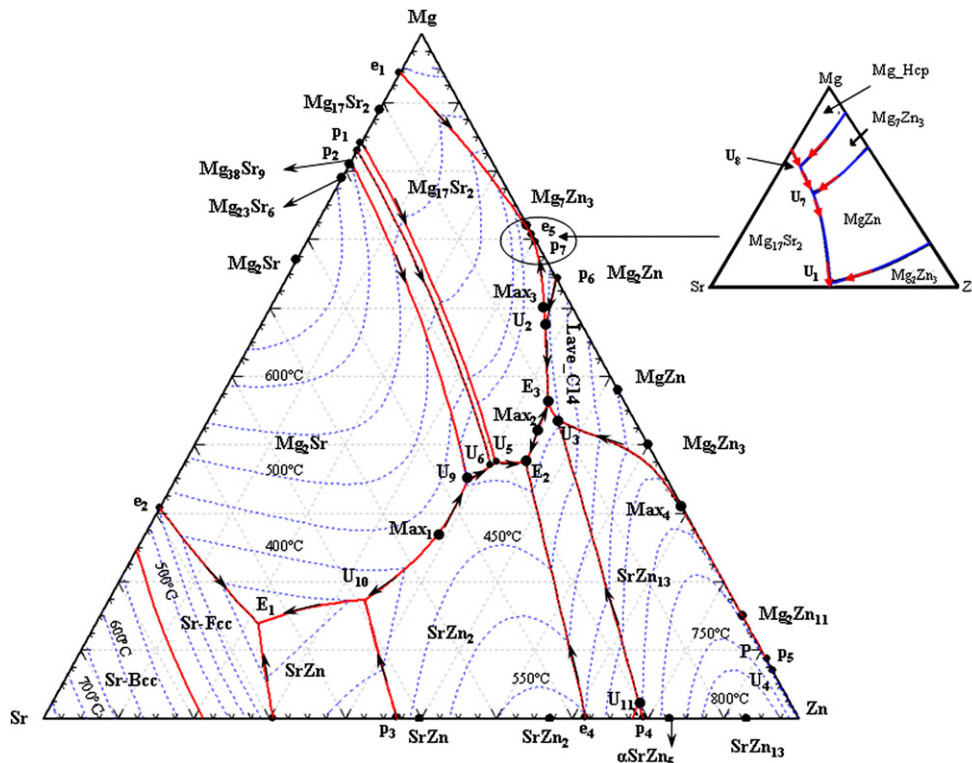

Fig. 4. Ternary phase diagram of Mg–Sr–Zn system with invariant points (based on mole fraction).

Table 2
Ternary invariant points (mole fraction)

Transformation		T (K)	Composition (mole fraction)		
			X[Mg]	X[Sr]	X[Zn]
Saddle points					
Max$_1$	Liquid ↔ Mg$_2$Sr + SrZn$_2$	688.75	0.270	0.343	0.387
Max$_2$	Liquid ↔ Mg$_{17}$Sr$_2$ + SrZn$_5$	645.49	0.418	0.137	0.445
Max$_3$	Liquid ↔ Mg$_{17}$Sr$_2$ + Mg$_2$Zn$_3$	658.38	0.596	0.039	0.365
Max$_4$	Liquid ↔ SrZn$_{13}$ + Lave_C14	861.44	0.319	0.003	0.678
Ternary quasi-peritectic					
U$_1$	Liquid + Mg$_2$Zn$_3$ ↔ Mg$_{17}$Sr$_2$ + MgZn	619.33	0.702	0.00168	0.297
U$_2$	Liquid + Mg$_2$Zn$_3$ ↔ Mg$_{17}$Sr$_2$ + Lave_C14	657.83	0.571	0.050	0.379
U$_3$	Liquid + SrZn$_{13}$ ↔ Lave_C14 + αSrZn$_5$	663.61	0.436	0.101	0.462
U$_4$	Liquid + SrZn$_{13}$ ↔ Mg$_2$Zn$_{11}$ + Zn–Hcp	640.38	0.070	1.77E−10	0.930
U$_5$	Liquid + Mg$_{38}$Sr$_9$ ↔ Mg$_{17}$Sr$_2$ + SrZn$_2$	658.47	0.374	0.214	0.412
U$_6$	Liquid + Mg$_{23}$Sr$_6$ ↔ SrZn$_2$ + Mg$_{38}$Sr$_9$	661.96	0.369	0.223	0.408
U$_7$	Liquid + MgZn ↔ Mg$_{17}$Sr$_2$ + Mg$_7$Zn$_3$	617.01	0.704	0.00141	0.294
U$_8$	Liquid + Mg–Hcp ↔ Mg$_{17}$Sr$_2$ + Mg$_7$Zn$_3$	617.09	0.701	0.00137	0.293
U$_9$	Liquid + Mg$_2$Sr ↔ SrZn$_2$ + Mg$_{23}$Sr$_6$	672.62	0.347	0.265	0.388
U$_{10}$	Liquid + SrZn$_2$ ↔ Mg$_2$Sr + SrZn	628.18	0.173	0.488	0.339
U$_{11}$	Liquid + SrZn$_{13}$ ↔ βSrZn$_5$ + αSrZn$_5$	909.54	0.024	0.200	0.775
Ternary peritectic					
P	Liquid + Lave_C14 + SrZn$_{13}$ ↔ Mg$_2$Zn$_{11}$	654.39	0.087	4.77E−10	0.913
Ternary eutectic					
E$_1$	Liquid ↔ Mg$_2$Sr + SrZn + Sr-Fcc	567.19	0.138	0.646	0.216
E$_2$	Liquid ↔ Mg$_{17}$Sr$_2$ + αSrZn$_5$ + SrZn$_2$	640.88	0.374	0.174	0.452
E$_3$	Liquid ↔ Mg$_{17}$Sr$_2$ + Lave_C14 + αSrZn$_5$	640.33	0.460	0.102	0.438

polynomial model and the intermetallic compounds were modeled as stoichiometric. The phase diagram and thermodynamic properties of the Mg–Sr system show good agreement with the experimental data from the literature.

The liquidus projection was obtained from the database that was obtained by combining the optimized model parameters of the constituent binaries. From this database the ternary phase diagram was calculated and the characteristic points were predicted. The Mg–Sr–Zn ternary system was observed to contain four saddle points, eleven ternary quasi-peritectic points, one ternary peritectic and three ternary eutectic points. There are no ternary experimental data for this system in the literature, therefore comparison was not possible.

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