

Thermodynamic Model of the Mg-Ca-Zn System

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Abstract

A thermodynamic description of the ternary Mg-Ca-Zn system has been developed as a part of a multicomponent thermodynamic database for Mg alloys that includes most of the important alloying elements. The available thermodynamic and phase diagram data were critically evaluated for the binary subsystems. Optimized thermodynamic properties of the binary systems were then used to model the ternary system. The literature included contradicting information regarding the ternary compounds in this system. Therefore thermodynamic modeling of phase equilibria is used to determine the most likely description of this system and to exclude the self-contradicting experimental observations. The liquid phase is described by the modified quasichemical model while the intermediate solid solutions are modeled using the compound energy formalism. The resulting model predicted 7 saddle, 10 quasi-peritectic, 3 peritectic and 6 ternary eutectic points. The calculated results are in accord with the available experimental data from the literature.

Introduction

Among all the metals magnesium is the lightest as the basis of structural alloys. This entices the automobile and aerospace manufacturers to replace the denser material by magnesium based alloys in order to achieve higher fuel efficiency. However their use is limited to non critical parts in the automobile due to poor creep resistance of the conventional Mg alloys [1].

It was found that adding Ca to a basic casting system like Mg-Zn alloys can greatly improve the creep resistance [1]. On the other hand, alloying Ca with Mg can increase the strength, castability and corrosion resistance and at the same time the presence of Zn in the binary Mg-Ca alloy also enhances the precipitation hardening response [2].

Despite the high potential of the Mg-Ca-Zn system, a very limited amount of experimental work has been done on this system regarding the phase equilibrium diagram and thermodynamic properties. Recently, Brubaker and Liu [3] calculated the ternary Mg-Ca-Zn system mainly based on the work of Paris [4] and Clark [5]. They used sublattice model [6] to describe the liquid phase which is more suitable for the long range ordering in atoms whereas clear evidence of the short range ordering (SRO) in the liquid has been found in the literature for the constituent binaries of the Mg-Ca-Zn system [7,8]. In addition, they considered one of the two ternary compounds reported by Clark [5] and confirmed by Jardim *et al.* [9] who used melt-spun alloys which were under non-equilibrium condition. In the present work, the liquid phase in the Mg-Zn and Ca-Zn systems have been re-optimized using the modified quasichemical model [10] in order to account for the presence of short range ordering. The optimized Gibbs energy parameters of the third binary, Mg-Ca system, were taken from Aljarrah and Medraj [11] who

also used the modified quasichemical model for the liquid phase. The two ternary compounds reported by Clark [5] were considered during optimization as well.

Experimental Data Assessment

The Mg-Zn Binary System

Phase Diagram Data

The liquidus curve of the Mg-Zn binary system was evaluated by Grube [12], Bruni *et al.* [13], Bruni and Sandonnini [14] and Chadwick [15] using thermal analysis. Grube [12] firstly reported the intermediate phase MgZn_2 with a melting point of 595°C and this was endorsed by later investigators [13-15] but at a lower melting point. A new compound MgZn_5 discovered by Chadwick [15] was later replaced by $\text{Mg}_2\text{Zn}_{11}$ based on the more reliable X-ray diffraction analysis of Samson [16]. Afterward, Hume-Rothery and Rounsefell [17] studied the system in the composition range of 30 to 100 at.% Zn using thermal and microscopic analysis and their data agrees fairly well with those of [12] and [15]. They also reported another new compound MgZn which was later substituted with a stoichiometric ratio 12:13 by Clark and Rhines [18] using X-ray diffraction analysis. Takei [19] at first discovered the compound Mg_2Zn_3 which occurs by a peritectic reaction at $410 \pm 10^\circ\text{C}$ where the values of Anderko *et al.* [20] and Park and Wyman [21] were $410 \pm 5^\circ\text{C}$ and $416 \pm 1^\circ\text{C}$ respectively. Contradicting results regarding the peritectic formation of the Mg_7Zn_3 compound, which was discovered by Takei [19], were found in the literature. Later on, Higahsi *et al.* [22] resolved this issue by placing the compound on the hypo-eutectic side of the Mg rich eutectic after careful crystal structure determination using X-ray diffraction analysis. The solid solubility of Zn in Mg was measured by Schmidt and Hansen [23] using metallography, Grube and Burkhardt [24] using electrical resistance measurements, Schmid and Seliger [25] using X-ray diffraction and Park and Wyman [21] using X-ray diffraction and microscopic examination and their values agree well with each other. Besides Park and Wyman [21] also measured the Mg solidus curve according to whom the maximum solubility of Zn in Mg is 2.5 at.% Zn at $340 \pm 1^\circ\text{C}$. The narrow solubility of Mg in Zn was determined by Hume-Rothery and Rounsefell [17] applying metallographic analysis and reported that the maximum solubility of Mg in Zn is 99.7 at.% Zn at 364°C . The homogeneity range regarding composition and temperature for the intermediate solid solution MgZn_2 measured by Park and Wyman [21] was about a 1 at.%Zn, from 66 at.% Zn at 416°C to 67.1 at.%Zn at 381°C .

Thermodynamic Data

The enthalpy of mixing of the Mg-Zn liquid was measured by Pyka [26] using calorimetric measurement at three different temperatures showed temperature independence where the value of Agarwal and Sommer [27], using same technique, showed some deviation from the value of [26] at 660°C , especially in the Mg rich side. Terpilowski [7], Chiotti and Stevens [28], Moser [29] and Pogodaev and Lukashenko [30] measured the activity of Mg over Mg-Zn liquid at different temperature using electromotive force (EMF) technique. On the other hand, the activity of Zn in the liquid alloy was measured by Pogodaev and Lukashenko [30] at 800°C and Kozuka *et al.* [31] who used vapor pressure measurement at 670°C . The enthalpy of formation for the three intermediate phases $\text{Mg}_{12}\text{Zn}_{13}$, MgZn_2 and $\text{Mg}_2\text{Zn}_{11}$ was determined by

Schneider *et al.* [32] using reaction calorimetry, where the same property for the first two phases was measured by King and Kleppa [33] using tin solution calorimetry and for all the phases by Pedokand *et al.* [34] using EMF. These experimental data will be compared with the current thermodynamic calculations.

The Ca-Zn Binary System

Phase Diagram Data

A few works have been done so far on the Ca-Zn system. Among them the liquidus data of Messing *et al.* [35] suggested to be most reliable in terms of sample preparation and experimental methods. They performed differential thermal analysis (DTA) supplemented by X-ray diffraction analysis (XRD) and vapor effusion measurement to investigate the liquidus line. They reported accuracy of $\pm 5^\circ\text{C}$ and predicted eight intermediate stoichiometric compounds: Ca_3Zn , Ca_7Zn_4 , CaZn , CaZn_2 , $\text{Ca}_7\text{Zn}_{20}$, CaZn_5 , CaZn_{11} and CaZn_{13} . Apart from CaZn_2 , CaZn_5 and CaZn_{11} all compounds undergo peritectic decomposition. Later on, the compound Ca_7Zn_4 and $\text{Ca}_7\text{Zn}_{20}$ designated by [35] was replaced with Ca_5Zn_3 and CaZn_3 respectively based on the more accurate crystallographic investigations of Bruzzone *et al.* [36] and Fornasini and Merlo [37] and these were used in the present optimization.

Thermodynamic Data

Itkin and Alcock [38] evaluated the activity of Zn at 800°C during their assessment from the vapor pressure measurement data of Chiotti and Hecht [39] who used dewpoint method for samples containing greater than 50 at.% Zn and the Knudsen effusion method for lower Zn concentration. Delcet and Egan [40] determined the activity of Ca at 800°C using EMF measurement. No experimental data for the enthalpy of mixing of the liquid phase could be found in the literature.

The Mg-Ca-Zn Ternary System

Paris [4] for the first time investigated the Mg-Ca-Zn ternary system by measuring cooling curves of 189 different samples and reported one ternary compound $\text{Ca}_2\text{Mg}_5\text{Zn}_5$. Afterward, the isothermal section of the Mg-Ca-Zn system at 335°C was studied by Clark [5] using metallography and X-ray diffraction on seventy-six alloys. Clark [5] mentioned two ternary compounds, namely $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and $\text{Ca}_2\text{Mg}_5\text{Zn}_{13}$ which were stable at room temperature under equilibrium condition and disputed about the Paris' [4] composition of $\text{Ca}_2\text{Mg}_5\text{Zn}_5$.

Analytical Description of The Thermodynamic Models

The Gibbs energy of pure element i ($i = \text{Mg}, \text{Ca}$ and Zn) in a certain phase, ϕ is described as a function of temperature by the following equation:

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

Where ${}^0G_i^\phi(T)$ the Gibbs energy at standard state and T is the absolute temperature. The value of the coefficient a to h are taken from the SGTE (Scientific Group Thermodata Europe) compilation by Dinsdale [41].

The Gibbs energy for stoichiometric compounds are described by the following equation:

$$G^\phi = x_i {}^0G_i^{\phi_1} + x_j {}^0G_j^{\phi_2} + \Delta G_f \quad (2)$$

Where x_i, x_j are the mole fraction of component i and j and ${}^0G_i^{\phi_1}, {}^0G_j^{\phi_2}$ represent the Gibbs energy in their standard state and $\Delta G_f = a + bT$ is the Gibbs energy of formation per mole of atoms of the stoichiometric compound where the parameters a and b are obtained by optimization using experimental results of phase equilibria and thermodynamic data.

Random solution model was used to describe the disorder terminal solid solution phases which can be expressed as:

$$G = x_i {}^0G_i^\phi + x_j {}^0G_j^\phi + RT[x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^\phi \quad (3)$$

The excess Gibbs energy ${}^{ex}G^\phi$, is expressed using the Redlich-Kister polynomial model [42].

The modified quasichemical model was selected to describe the liquid phases of the constituent binary systems. According to quasichemical theory [43] the molar Gibbs energy of the liquid is given by:

$$G^{liq} = (n_A {}^0g_A^{liq} + n_B {}^0g_B^{liq}) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB} \quad (4)$$

Where n_A and n_B are number of moles of component A and B , n_{AB} is the number of moles of $(A-B)$ pairs, ΔS^{config} is the configurational entropy of mixing given by random distribution of the $(A-A)$, $(B-B)$ and $(A-B)$ pairs.

Pelton *et al.* [8] made modification to equation 4 by expanding Δg_{AB} as a polynomial in terms of the pair fraction X_{AA} and X_{BB} as shown in equation 5

$$\Delta g_{AB} = \Delta g_{AB}^o + \sum_{i \geq 1} g_{AB}^{i0} X_{AA}^i + \sum_{j \geq 1} g_{AB}^{0j} X_{BB}^j \quad (5)$$

Where, Δg_{AB}^o , g_{AB}^{i0} and g_{AB}^{0j} are the model parameters to be optimized and can be expressed as functions of temperature ($\Delta g_{AB}^o = a + bT$)

The Gibbs energy of an ordered solution phase is described by the compound energy formalism [6] which can be expressed as:

$$G = G^{ref} + G^{ideal} + G^{excess} \quad (6)$$

$$G^{ref} = \sum y_i^l y_j^m \dots y_k^q {}^0G_{(i,j,\dots,k)} \quad (7)$$

$$G^{ideal} = RT \sum_l f_l \sum_i y_i^l \ln y_i^l \quad (8)$$

$$G^{excess} = \sum y_i^l y_j^l y_k^m \sum_{\gamma=0}^{\gamma} L_{(i,j):k} \times (y_i^l - y_j^l)^{\gamma} \quad (9)$$

Where $i, j, \dots k$ represent components or vacancy, l, m and q represent sublattices. y_i^l is the site fraction of component i on sublattice l . f_l is the fraction of sublattice l relative to the total lattice sites. ${}^0G_{(i,j):\dots k}$ represents the energy of a real or hypothetical compound (end member). ${}^{\gamma}L_{(i,j)}$ represents the interaction parameters which describe the interaction within the sublattice.

Results and Discussions

The Mg-Zn Binary System

Phase Diagram

The re-optimized Mg-Zn phase diagram is shown in figure 1, demonstrating reasonable agreement with the experimental data from the literature. From the same figure, it can be seen that there are two eutectic points, four peritectic points and all the compounds melt incongruently except MgZn_2 which melts congruently.

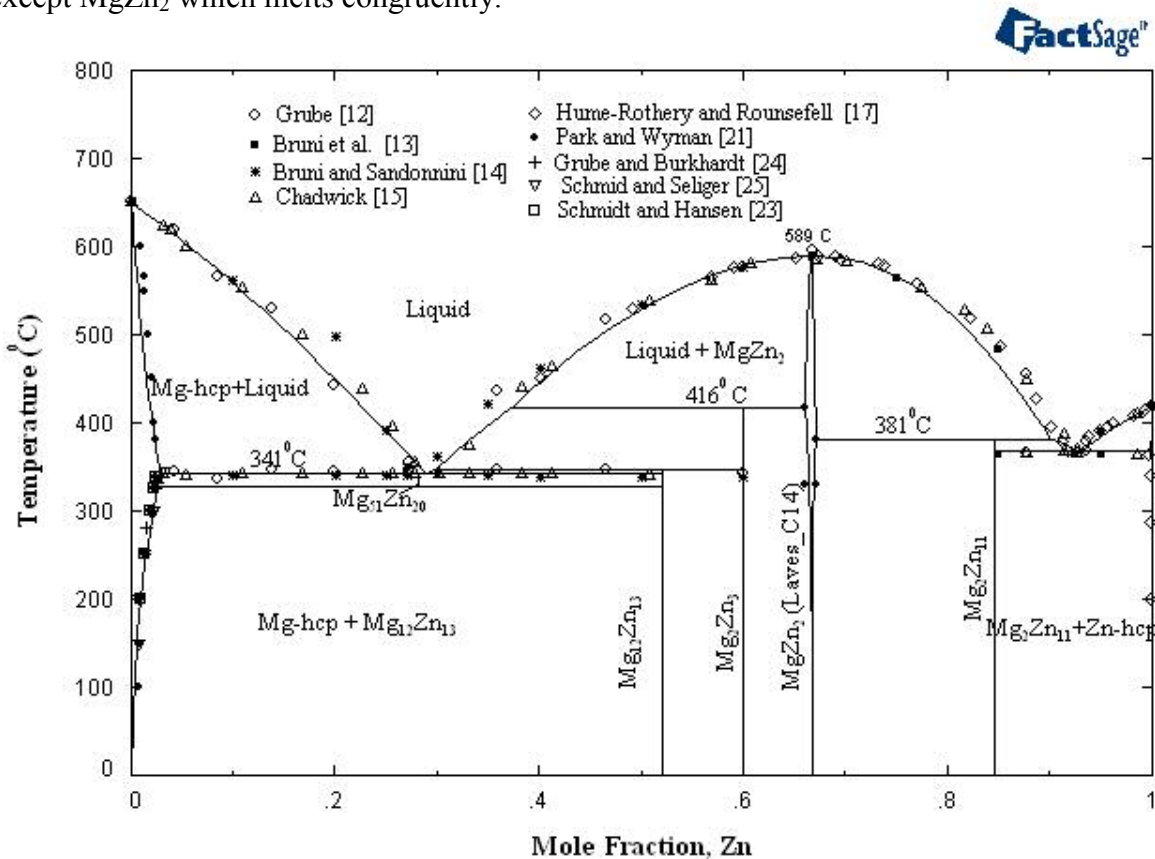


Figure 1 Re-optimized Mg-Zn system with the experimental data from literature

Thermodynamic Properties

Figure 2 shows that the enthalpy of mixing of the Mg-Zn liquid phase calculated at 708°C is in good agreement with the experimental data. It can be seen that Agarwal and

Sommers' [27] results at 660°C deviates than other values and this is probably due to the fact that, there were some errors during the experiment.

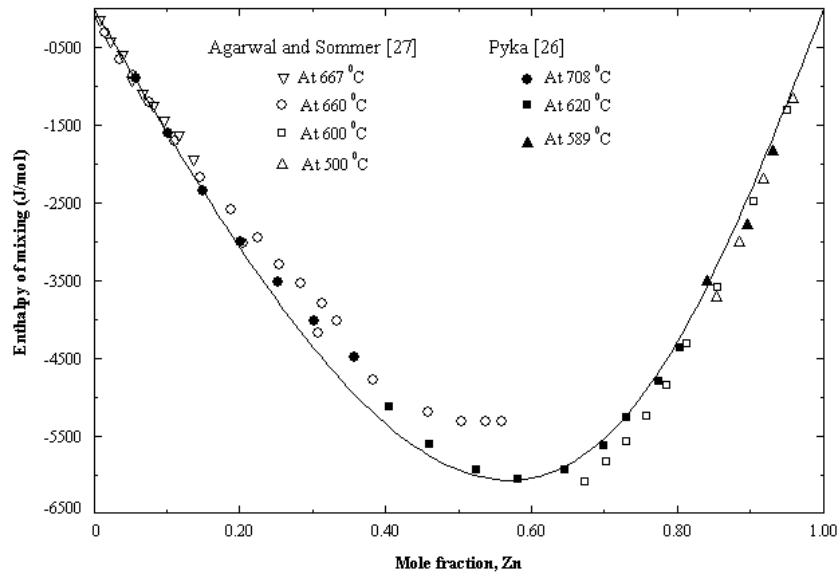


Figure 2 Calculated enthalpy of mixing in the Mg-Zn liquid at 708°C in comparison with experimental data

Figure 3 shows the activities of Mg and Zn in the liquid phase at 650°C and 800°C, respectively. The activity of Mg shows reasonable consistency with the experimental points whereas the activity of Zn deviates especially from the results of [30] and [31] but shows good agreement with the value of [7]. Activities of both components exhibit negative deviation from ideality which is an indication of compound formation in the solid state.

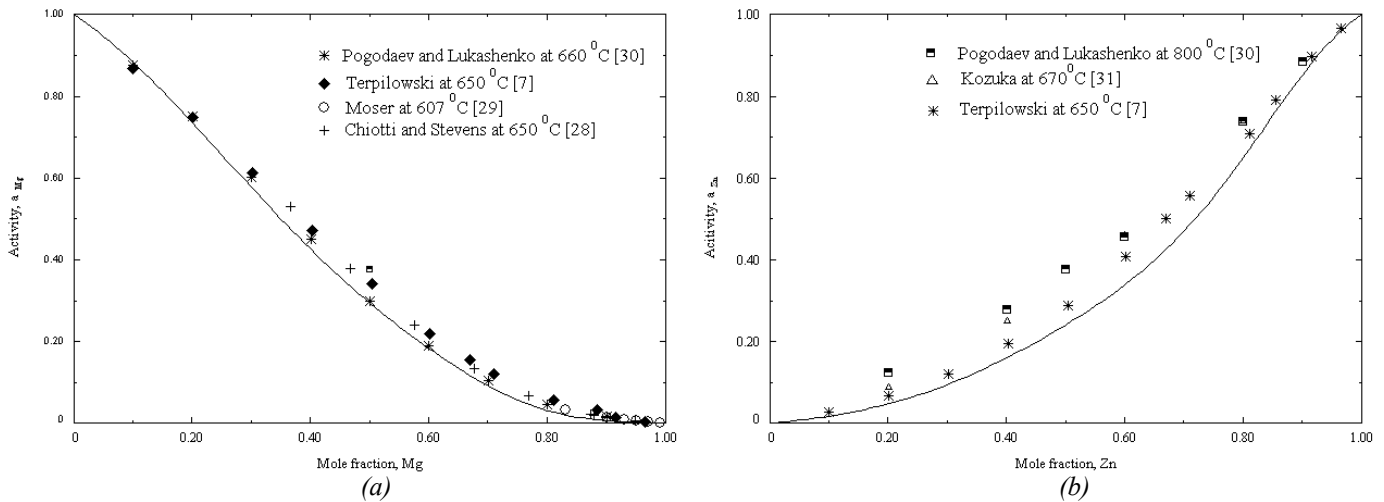


Figure 3 Calculated activity of (a) Mg at 650°C and (b) Zn at 800°C in the Mg-Zn liquid in comparison with experimental data

The enthalpy of formation of the intermediate phases in relation with the experimental data is shown in figure 4. The calculated values are consistent with the experimental values within the error limits.

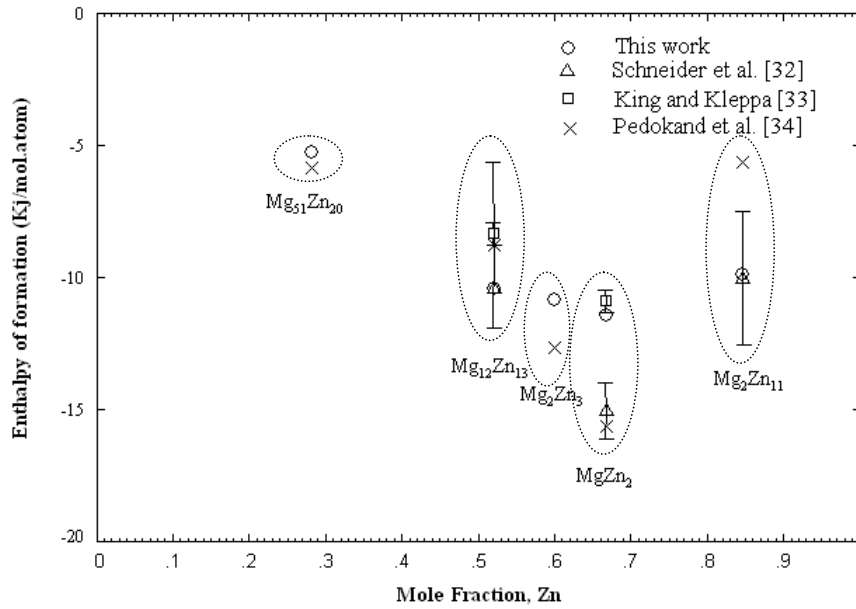


Figure 4 Calculated enthalpy of formation of the intermediate compounds at 25°C with experimental results

The Ca-Zn Binary System

Phase Diagram

The calculated phase diagram of the Ca-Zn system in comparison with the work of Messing *et al.* [35] is shown in figure 5 where reasonable consistency has been achieved.

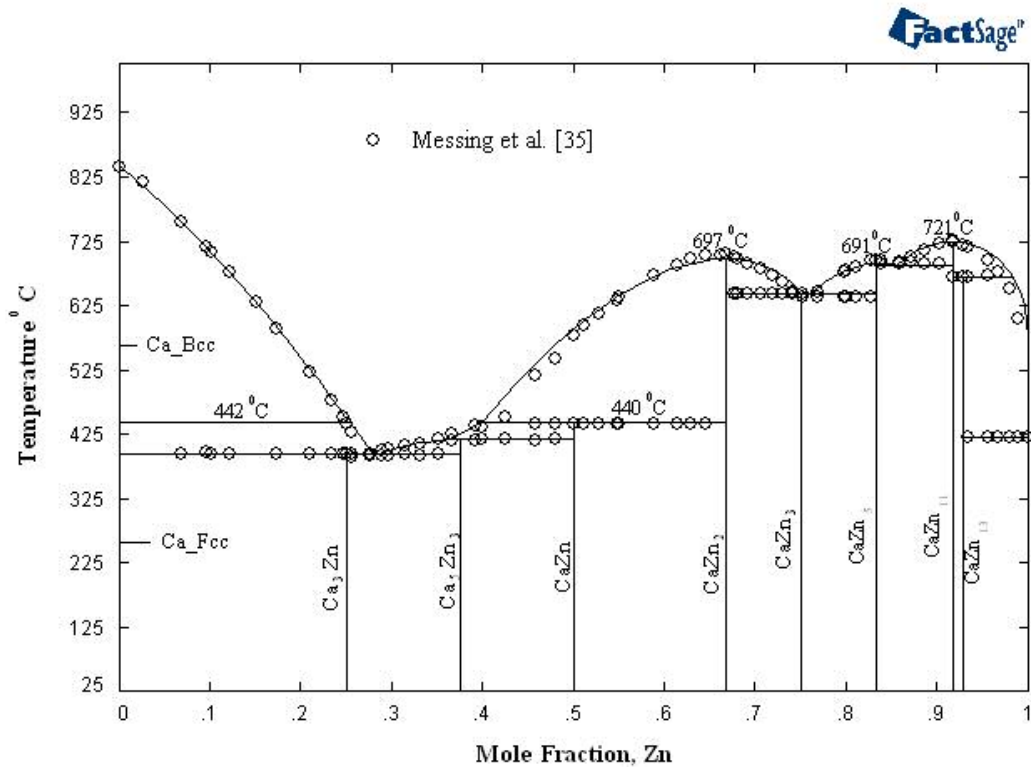


Figure 5 Re-optimized Ca-Zn system with the experimental data from literature

Thermodynamic Properties

The calculated activities of Ca and Zn in the Ca-Zn liquid at 800°C are shown in figure 6 which is in good agreement with the experimental results of [39] and [40]. It can be seen from the same figure that the activities of both components show negative deviation from ideality.

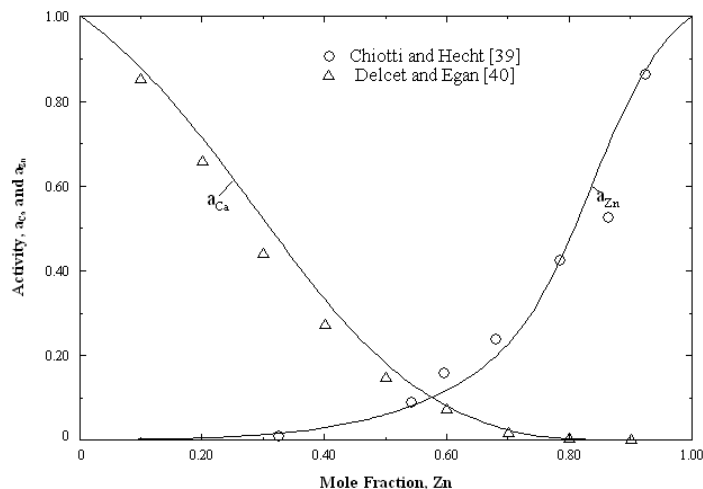


Figure 6 Calculated activities for Ca and Zn at 800°C in the Ca-Zn liquid in comparison with experimental data

The Mg-Ca-Zn Ternary System

A self-consistent thermodynamic database for the Mg-Ca-Zn system has been constructed by extrapolating the three constituting binaries Mg-Zn, Ca-Zn and Mg-Ca. The polythermal projection of the Mg-Ca-Zn ternary system in comparison with experimental data is shown in figure 7.

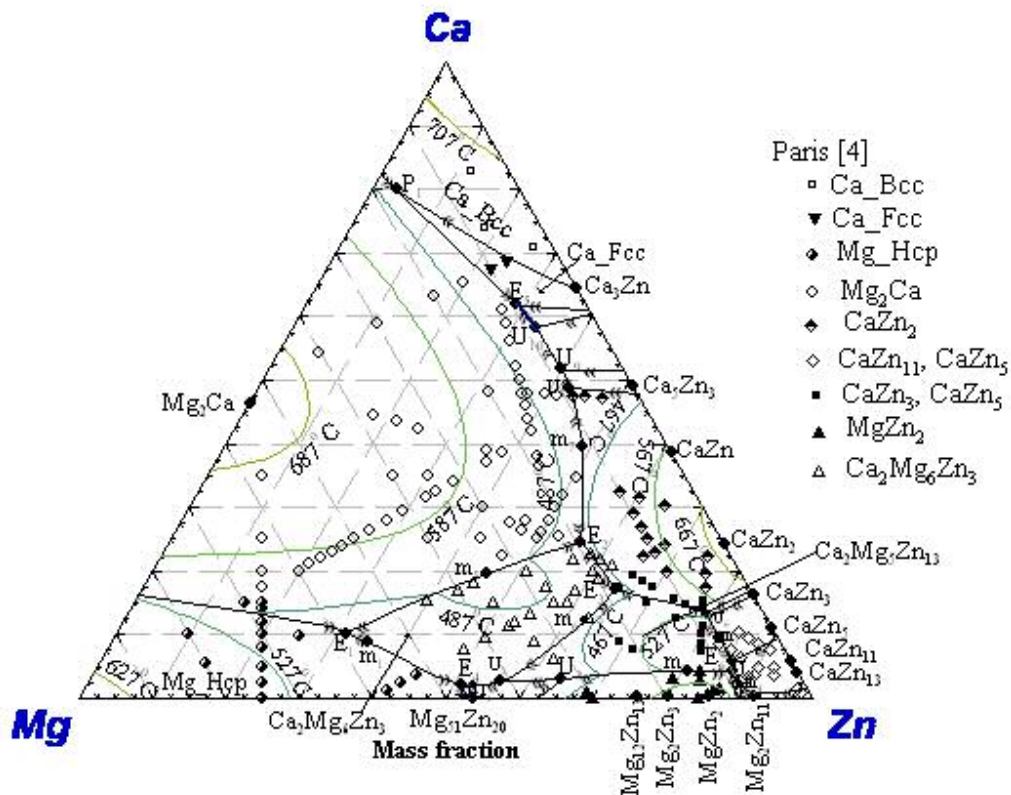


Figure 7 Polythermal projection of the ternary Mg-Ca-Zn system with experimental data

For extrapolation, the symmetric Kohler model [44] was used since none of the constituent binaries show extreme dissimilarity in their thermodynamic properties. Figure 8 shows the calculated isothermal section at 335°C which illustrates a reasonable agreement with the experimental data.

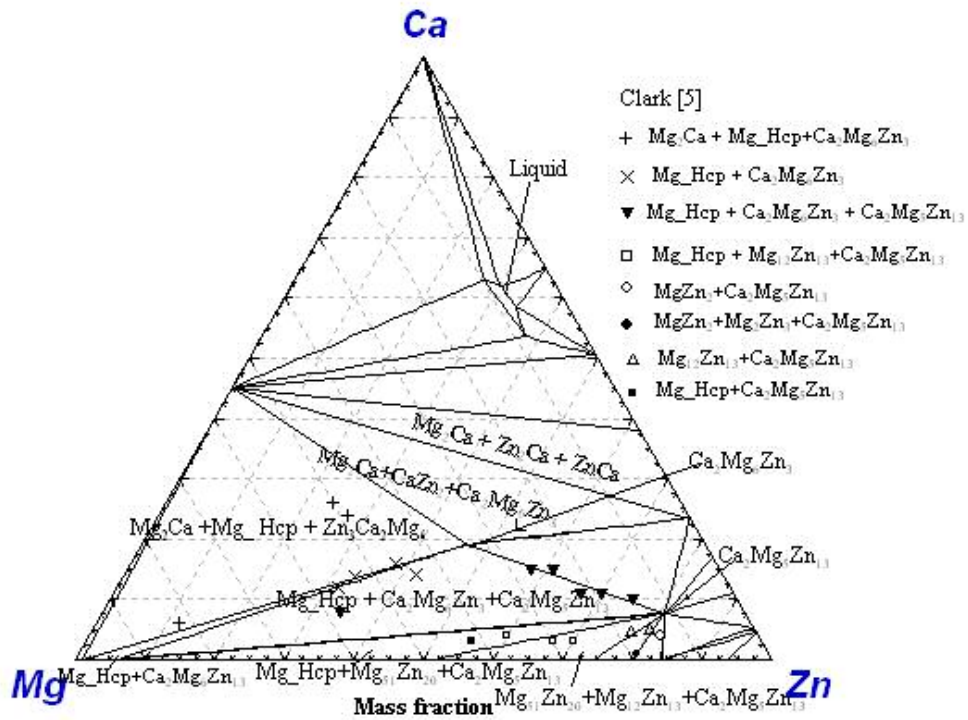


Figure 8 Isothermal section of the ternary Mg-Ca-Zn system at 335°C with experimental data from literature

Summary

An inclusive description of the Mg-Ca-Zn ternary system was carried out based on the computational thermodynamics approach. The modified quasichemical model was used to describe the liquid phase. The constituent binary systems show good consistency with the experimental data in terms of phase diagram along with the different thermodynamic properties. Good agreement was accomplished during calculation of the liquidus projection and the isothermal section of the ternary Mg-Ca-Zn system by considering two ternary compounds. However, additional experimental study is required to obtain more information about the ternary compounds regarding their melting points and the enthalpies of formation.

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