Critical assessment and thermodynamic modeling of Mg–Zn, Mg–Sn, Sn–Zn and Mg–Sn–Zn systems

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ABSTRACT

All available thermodynamic and phase diagram data of Mg–Zn, Mg–Sn and Sn–Zn are critically evaluated and most reliable data are incorporated to model each system. The binary liquid phases are modeled using the modified quasi-chemical model in order to incorporate the strong ordering in the Mg–Sn and Mg–Zn systems. The binaries are extrapolated to construct the Mg–Sn–Zn ternary using the symmetric Kohler geometric model without using any ternary interaction parameter. The calculated Mg–Sn–Zn ternary diagram shows very good consistency with the published experimental data.

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1. Introduction

Mg-alloys are widely used in structural application, automobile, electronics, aerospace and other industries because of their very interesting and advantageous properties which include outstanding strength to weight ratio, high stiffness to weight ratio; especially in wrought products, low machining cost, high creep resistance, ease of founding large and complex casting, good weldability, very good hot forming properties, good corrosion resistance properties, good dimensional stability are few of them [1,2]. Zn is one of the major alloying elements added to Mg to improve mechanical property and corrosion resistance. Recently, Mg–Sn based systems are investigated as an addition of Sn results in stable microstructure and better mechanical properties, especially at high temperature. Besides, Sn is a reasonably cheap material as compared to other alloying elements such as rare earths (RE).

Therefore the Mg–Sn–Zn ternary system is one of the important systems in the family of Mg-based alloys and it is worth studying in details. Bamberger [3] calculated the Mg–Sn–Zn ternary system from the extrapolation of the three binary sub systems using a commercial Mg-database but only compared the Mg-rich side of the phase diagram with experimental findings. Jung et al. [4] also calculated the Mg–Sn–Zn ternary system. However they did not report the parameters and the ternary system was not

compared with the experimental results of Otani [5] and Godecke and Sommer [6] in detail. Later on, Meng et al. [7] modeled the same system and compared their work with experimental findings of Otani [5] and Godecke and Sommer [6]. They used an associate solution model to describe the liquid phases. In their calculation, they added few ternary parameters but failed to achieve the consistency with the experimental results [5,6] near the Mg side of the Mg–Zn binary in the ternary. Kang and Pelton [8] suggested that the Modified Quasi Chemical model (MQM) is more physically realistic than the associate solution model. They also suggested that both models can provide very similar and equally good fits to the experimental thermodynamic and phase diagram data with approximately the same number of parameters but in ternary or higher order system MQM will give better consistency. Therefore, the present work is to re-optimize the Mg–Sn–Zn system using MQM model for liquid phase and incorporate the latest available thermodynamic and phase diagram data for the constituent binaries as well as the ternary. For example, the latest thermodynamic properties for the intermetallic compounds in the Mg–Zn system after Morishita et al. [9,10] are incorporated in the present modeling. All those details are discussed in the appropriate sections.

2. Binary systems

2.1. The Mg–Zn binary system

The liquidus curve for the whole composition range was first determined by Boudouard [11] by thermal analysis. However,

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his reported values are not very reliable due to a contamination problem and thus will not be used in this work. Later on, the liquidus line was investigated by Grube [12], Bruni et al. [13], Bruni and Sandonnini [14] and Chadwick [15] using thermal analysis and their reported values agree reasonably well with each other.

The solid solubility of Zn in Mg was first investigated by Chadwick [15] using microscopic examination of the quenched samples. However, his results suffer lack of reliability because of the higher content of zinc due to the presence of silicon as impurity. Afterward, the Mg-solvus curve was reported by several researchers such as Schmidt and Hansen [16] using metallography, Grube and Burkhardt [17] using electrical resistivity, Schmid et al. [18] using X-ray diffraction and Park and Wyman [19] using both XRD and microscopic examination and their values agree reasonably well with each other. Park and Wyman [19] also measured the Mg solidus curve and reported maximum solubility of Zn in Mg as 2.5 at.% Zn at 340 ± 1 °C. Hume-Rothery and Rounsefell [20] determined the limited solubility of Mg in Zn by metallographic analysis and reported that the maximum solubility of Mg in Zn as 0.3 at.% at 400 °C.

The intermediate phase $MgZn_2$ was first reported by Grube [12] with a melting point of 595 °C and this was later confirmed by other investigators with slightly lower melting point [13–15]. A narrow homogeneity range of 1 at.% (from 66 at.% at 416 °C to 67.1 at.% at 381 °C) for this phase is reported in the literature [19,21]. Another compound $MgZn_5$ was first discovered by Chadwick [15] and later on replaced by Mg_2Zn_{11} based on the more reliable X-ray analysis by Samson [22]. Hume-Rothery and Rounsefell [20] reported another compound MgZn which was later substituted by $Mg_{12}Zn_{13}$ by Clark and Rhines [23] based on their X-ray diffraction analysis. Takei [24] first reported the presence of Mg_2Zn_3 formed by a peritectic reaction at 410 ± 10 °C. Laves [25] identified this phase by metallographic and X-ray method. Takei [24] and Laves [25] also pointed out that Mg_2Zn_3 is at equilibrium with Mg terminal solid solution at room temperature which was proved wrong by Clark and Rhines [23]. They reported the presence of $Mg_{12}Zn_{13}$ instead and also pointed out clearly that the Mg_2Zn_3 phase is not in equilibrium with the Mg solid solution at any temperature. This was confirmed by Anderko et al. [26] and Park and Wyman [19] and the peritectic reaction temperature was reported as 410 ± 1 °C and 414 ± 1 °C, respectively. Clark and Rhines [23] also mentioned that at the Zn-rich side of the phase diagram, Mg_2Zn_3 is in equilibrium with $MgZn_2$ while on the Mg-rich side, Mg_2Zn_3 is in equilibrium with the liquid phase from 416 to 347 °C. The intermediate phase Mg_7Zn_3 was first reported by Takei [24] and Ishida [27] and confirmed by Laves [25], Urazov et al. [28], Koster and Muller [29], and Koster [30]. However, investigators [24,25,27–31] placed this compound at the hyper-eutectic side of the Mg-rich eutectic according to the following peritectic reaction:

$L + MgZn \leftrightarrow Mg_7Zn_3$. However, a careful crystal structure analysis by X-ray diffraction, Higashi et al. [32] replaced the Mg_7Zn_3 (30 at.% Zn) compound by $Mg_{51}Zn_{20}$ (28.169 at.% Zn) and placed it at the hypo-eutectic side of the Mg-rich eutectic

Pyka [33] and Agarwal and Sommer [34] measured the enthalpy of mixing of the Mg-Zn liquid using calorimetric method at different temperatures. The reported enthalpy of mixing values by Pyka [33] did not show any temperature dependence. However, Agarwal and Sommer [34] reported temperature dependency of the enthalpy of mixing of the liquid. This was attributed to the stabilization of one or more Mg-rich intermediate compounds and as an indication of short-range ordering in the liquid phase by Agarwal and Sommer [34]. Partial Gibbs energies of Mg for the Mg-Zn liquid were measured by Terpilowski [35], Chiotti and Stevens [36], Moser [37], Pogodaev and Lukashenko [38] and Pedokand [39] by EMF method. The partial Gibbs energy of Zn in

the Mg-Zn liquid was experimentally determined by Pogodaev and Lukashenko at 800 °C [38] and Kozuka et al. [40] at 670 °C. The same property was obtained by Terpilowski [35] using Gibbs-Duhem equation at 650 °C. Terpilowski [35] measured the partial enthalpy of mixing of Mg-Zn liquid using the EMF method whereas Agarwal et al. [41] measured it by calorimetric method.

The enthalpy of formation of $MgZn_2$, $Mg_{12}Zn_{13}$ and Mg_2Zn_{11} was measured by Schneider et al. [42] using reaction calorimetry at 25 °C whereas King and Kleppa [43] measured the same for the first two compounds using tin solution calorimetry. On the other hand Pedokand [39] reported partial Gibbs energy values of the Mg-Zn solid by EMF measurement. Very recently, Morishita et al. [9,10,44,45] measured the enthalpy of formation of $Mg_{12}Zn_{13}$, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11} in an acid solution calorimeter and simultaneously determined the heat capacity (Cp) of the compounds by a differential scanning calorimeter (DSC) above room temperature and relaxation calorimetry at low temperature. They also calculated and reported the standard entropy of formation and standard free energy of formation of these compounds through combining the measured enthalpy of formation and Cp data.

Many researchers investigated the Mg-Zn system both experimentally and thermodynamically over the years. An overall assessment of the Mg-Zn system was performed by Clark et al. [31] based on the experimental work by Chadwick [15], Hume-Rothery and Rounsefell [20], and Park and Wyman [19]. However, Clark et al. [31] placed the Mg_7Zn_3 ($Mg_{51}Zn_{20}$) compound at the hyper-eutectic side of the Mg-rich side of the phase diagram which was later corrected by Higashi et al. [32]. Agarwal et al. [41], Liang et al. [46] and Wasiur-Rahman and Medraj [47] performed the thermodynamic optimization of the system. All of them reported five intermetallic compounds (Mg_7Zn_3, $Mg_{12}Zn_{13}$, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11}) apart from two terminal solid solutions and the liquid phase. Agarwal et al. [41] modeled all the intermetallic compounds as stoichiometric phases however, Liang et al. [46] and Wasiur-Rahman and Medraj [47] modeled the $MgZn_2$ phase taking into account the homogeneity range reported by Park and Wyman [19] and Massalski [21]. Agarwal et al. [41] and Liang et al. [46] both used Bragg–Williams (B–W) model to describe the liquid phase while Wasiur-Rahman and Medraj [47] used the MQM to describe the liquid phase. However, Wasiur-Rahman and Medraj [47] did not take into account the recent enthalpy of formation, entropy and Cp data of the intermediate compounds reported by Morishita et al. [9,10,44,45]. The present study will re-optimize the Mg-Zn system in light of all the experimental data, both new and old, and will use the MQM to describe the liquid phase to take into account the short range ordering.

2.2. The Mg–Sn binary system

Two eutectic reactions and a congruently melting compound, Mg_2Sn, characterize the topology of the Mg-Sn system. The whole liquidus curve thus is divided into three parts; the (Mg) liquidus, Mg_2Sn liquidus and the (Sn) liquidus. The (Mg) liquids curve was determined by Grube [48], Kurnakow and Stepanow [49], Hume-Rothery [50] and Raynor [51] using thermal analysis whereas Nayak and Oelsen [52,53] measured the same using a calorimeter. The results of Grube [48], Hume-Rothery [50] and Raynor [51] are in fair agreement whereas Kurnakow and Stepanow [49] and Nayak and Oelsen [52] are at higher temperatures. The liquidus curve of the Mg_2Sn was determined by several researchers [48–55] and the melting point reported of Mg_2Sn as 770 °C ± (8–25 °C). The (Sn) liquidus curve was first measured by Heycock and Neville [56] and later on by other investigators [49,50,52,53,57,58]. Hume-Rothery [50] reported a bump in the (Sn) liquidus curve and

interpreted it as a slight liquid immiscibility. However, no other investigators [49,52,53,56–58] confirmed this phenomenon.

The (Mg) solidus curve was determined by Grube and Vosskuhler [59] and Vosskuhler [60] using resistivity technique, by Raynor [51] using metallography and by Nayak and Oelsen [53] using calorimeter. The solid solubility of Sn in Mg was reported by Stepanow [61] and Gann [62] and later by Grube and Vosskuhler [59], Vosskuhler [60], Raynor [51], Nayak and Oelsen [53] and Nishinura and Tanaka [63] by different methods. According to Nayeb-Hashemi and Clark [58] the solid solubility of Mg in Sn is infinitesimally small.

Eldridge et al. [64] and Caulfield and Hudson [65] reported a very narrow solid solubility range of Mg and Sn in Mg_2Sn at high temperature (few tenth of a percent [64] to 0.5 at.% [65]) and thus the Mg_2Sn is considered as a line compound in the current analysis.

Kawakami [66], Sommer [67] and Nayak and Oelsen [68,69] measured the heat of mixing of the Mg–Sn liquid with calorimetric method whereas Eremenko and Lukashenko [70], Steiner et al. [54], Eldridge et al. [64] and Sharma [71] calculated it from the EMF measurement. The heat of formation of the Mg–Sn solid were determined by Kubaschewski [72], Nayak and Oelsen [68], Sharma [71], Biltz and Holverscheit [73], Ashtakala and Pidgeon [74] and Borsese et al. [75]. According to Nayeb-Hashemi and Clark [58], Dobovisek and Paulin [76] calculated the heat of formation of the Mg_2Sn compound using the Pauling's rule and reported a value of −96.72 kJ/mol. The heat capacity of the Mg_2Sn compound was determined by Jelinek et al. [77] at low temperature (up to 27 °C) whereas Chen et al. [78] determined the same at much higher temperature (27–427 °C) using a differential scanning calorimeter.

The phase equilibrium and experimental phase diagram data are reviewed by Nayeb-Hashemi and Clark [58]. Nayeb-Hashemi and Clark [58] along with others like Egan [79], Eckert et al. [80], Pavlova and Poyarkov [81] optimized the phase diagram using measured thermodynamic data. Very recently, Jung et al. [82,83] and Kang and Pelton [8] optimized the same system and modeled the liquid phase by the MQM. Jung et al. [82,83] and Kang and Pelton [8] assumed the high temperature Cp value of Mg_2Sn as $Cp (Mg_2Sn) = 2Cp (Mg) + Cp (Sn)$. Recently, Chen et al. [78] measured and published the high temperature heat capacity of Mg_2Sn using a differential scanning calorimeter. In the present work the liquid phase will be modeled using the MQM to take into account the strong short range ordering exist in the liquid and all the experimental thermodynamic data reported in the literature will be critically taken into account. The results will be also compared with the earlier optimization by MQM.

2.3. The Sn–Zn binary system

The Sn–Zn phase diagram is a simple eutectic type phase diagram where three phases, namely liquid and two terminal solid solution phases exist [84]. A detail review of the experimental data and assessment of the phase diagram of this system was carried out by Moser et al. [85]. The experimental points on the liquidus by various investigators [85–91] showed very good agreement with one another in spite of the fact that different measurement methods were used. Tamman and Crone [92], Tamman and Rocha [93] reported 0.039 at.% eutectic solid solubility of Sn in HCP_Zn whereas Vnuk et al. [94] and Homer and Plummer [95] reported the maximum solubility of Zn in Sn as 0.6 at.%. The eutectic composition of the Sn–Zn liquid between 13.5 and 15.8 at.% Zn and a close temperature range of eutectic reaction (from 198 to 199 °C) was reported in the literature [86,87,96–99].

The enthalpy of mixing of the Sn–Zn liquid was measured by various researchers by different methods; for instance Kleppa [100], Oelson [86], Schurmann and Trager [87] and Moser

et al. [101] used calorimetry whereas Dobovisek and Straus [88], Genot and Hagege [102] and Itagaki and Yazawa [103] used thermal analysis. All experimental data show positive values of the enthalpy of mixing. The chemical potential of Zn in the Sn–Zn liquid was measured by EMF method [87,89,91,104–109], by vapor pressure method [110–112], by torsion effusion method [113,114] and also by atomic absorption spectroscopy [90].

The thermodynamic optimization of the system are carried out by Ohtani et al. [115], Lee [84] and by Fries et al. [116]. However, the above authors used different unary data in their assessments and there resulting phase boundaries also differ from each other as indicated by Vizdal et al. [117]. In the present work, the Sn–Zn liquid phase will be modeled using the MQM to be able to combine it with the other two binaries. All the other relevant experimental data will also be taken into account during modeling of this system.

2.4. The Mg–Sn–Zn ternary system

In 1933, Otani [5] experimentally determined the Mg–Sn–Zn phase diagram using thermal analysis and microscopic method over the whole concentration range. He reported two pseudo-binary sections and several invariant points. However, the existence of some of the Mg–Zn binary compounds was not known at that time and thus the ternary Mg–Sn–Zn system published by Otani [5] did not give a complete picture. Mingolo et al. [118,119] studied the cast structure of Mg–Sn–Zn alloys (alloy composition: $(Mg_{70}Zn_{30})_{100−x}Sn_x$, where x = 2.5, 5, 7.5, 10, 12.5 and 15) by the Mossbauer spectroscopy and X-ray diffraction methods and found out the presence of Sn with the terminal solid solutions of Mg and Zn and in Mg_2Sn compound and not in any other Mg–Zn compounds. This fact is later supported by Sirkin et al. [120]. Gladyshevsky and Cherkashin [121] determined the solubility of Sn in $MgZn_2$ at 400 °C as 3.6 mass% (1.6 at.%) whereas Godecke and Sommer [6] reported maximum solubility of Sn in $MgZn_2$ as 0.7 mass%. This indicates the fact that Sn has a very limited solubility in the Mg–Zn compounds. In 1994, Godecke and Sommer [6] studied in detail the Mg–Sn–Zn system in the Mg_2Sn–$MgZn_2$–Sn–Zn area by thermal analysis and microscopic method and taken into account the modern versions of the binary systems. They reported a number of vertical sections of the phase diagram, two pseudo-binary sections and the projection of the liquidus surface.

No ternary phase is reported in the system. The reported solubility of Zn in Mg_2Sn along the Mg_2Sn–$MgZn_2$ section is about 0.2 mass% and about 0.1 mass% along the Mg_2Sn–Zn section [6]. The reported solubility of Sn in $MgZn_2$ is 3.6 mass% (1.6 at.%) at 400 °C [121] whereas Godecke and Sommer [6] reported this as 0.6 mass% at 340 °C along the Mg_2Sn–$MgZn_2$ section and the maximum as 0.7 mass% at the eutectic temperature of 567 °C. Sn does not have any solubility in Mg_7Zn_3 ($Mg_{51}Zn_{20}$) and Mg_2Zn_3 as indicated by Mingolo et al. [118,119] and Sirkin et al. [120]. Solubility of Sn in other two Mg–Zn compounds ($Mg_{12}Zn_{13}$ and Mg_2Zn_{11}) was not reported in the published literature.

Rokhlin [122] reviewed and assessed the system in detail based on the earlier experimental results of the system [5,6] and reported the ternary equilibrium invariant points and the overall reaction scheme. He also re-constructed the liquidus surface of the system, the two pseudo binaries, an isothermal section at 250 °C and a few vertical sections based on published literature data [5,6]. Bambergar [3], Jung et al. [4] and Meng et al. [7] thermodynamically modeled the Mg–Sn–Zn system.

Bambergar [3] used ThermoCalc software and a commercial Mg database to model the ternary system. The liquid phase in the system was described by Bragg–Williams model using Redlich–Kister polynomial [123]. Bambergar [3] reported only the Mg-rich side of the isothermal section at 450 °C.

Jung et al. [4] thermodynamically modeled the Mg–Sn–Zn system using FactSage software. In their case, the Mg–Sn liquid was modeled by taking into account the short range ordering however, unlike the Mg–Zn liquid which was treated as a normal regular solution. They only reported the liquidus projection of the ternary system but did not publish the model parameters. They also did not report the experimental validation of the system except two experimental liquidus points on the liquidus surface.

Meng et al. [7] calculated the Mg–Sn–Zn system using ThermoCalc software and CALPHAD method. They re-optimized the Mg–Sn system and used previously assessed Mg–Zn [46] and Sn–Zn [84] systems. As mentioned in Section 2.1, Liang et al. [46] modeled the Mg–Zn liquid phase as a substitutional solid solution using B–W model and this means that both Liang et al. [46] and Meng et al. [7] failed to consider the presence of short range ordering in the Mg–Zn system. Meng et al. [7] considered the ternary liquid phase to be consisted of four species; Mg, Sn, Zn and Mg_2Sn and subsequently described the liquid phase using the associated solution model. Their thermodynamically modeled Mg–Sn–Zn system could produce most of the equilibrium invariant points. However, there are discrepancies with the experimental findings [5,6,122] near the Mg-rich side of the Mg–Zn binary in the ternary. They reported a eutectic ternary reaction (mentioned as E1) and another ternary peritectic reaction (mentioned as U3) both at 341 °C. These reactions according to Meng et al. [7] are shown below:

$$L \leftrightarrow hcp(Mg) + MgZn + Mg_7Zn_3 \ (Mg_{51}Zn_{20}) \cdots\cdots\cdots E1 \ [7]$$

$$L + Mg_2Sn \leftrightarrow hcp(Mg) + MgZn \ (Mg_{12}Zn_{13}) \cdots\cdots\cdots U3 \ [7].$$
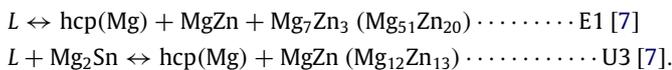
However, the eutectic reaction at that region does not involve the $Mg_{12}Zn_{13}$ compound and rather involves the Mg_2Sn as reported by Rokhlin [122]. The other reaction which is a peritectic reaction at that region does not involve hcp(Mg) according to Rokhlin [122] unlike what is reported by Meng et al. [7]. These reactions as reported by Rokhlin [122] are shown below:

$$L \leftrightarrow hcp(Mg) + Mg_2Sn + Mg_7Zn_3 \ (Mg_{51}Zn_{20}) \cdots\cdots\cdots E2 \ [122]$$

$$L + Mg_{12}Zn_{13} \leftrightarrow Mg_2Sn + Mg_7Zn_3 \ (Mg_{51}Zn_{20}) \cdots\cdots\cdots U4 \ [122].$$
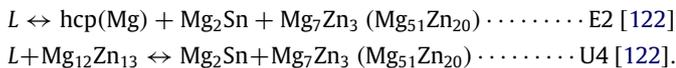
In this study, the Mg–Sn–Zn system is modeled considering the short range ordering exists in the Mg–Sn and Mg–Zn liquid phases. All the experimental data will be critically evaluated both in the binary and ternary systems to obtain a more consistent and reliable description of the system.

3. Thermodynamic models

3.1. Pure elements

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

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

where $^0G_i^\varphi(T)$ is the Gibbs energy at standard state and T is the absolute temperature. The values of the coefficient a to h are taken from the SGTE (Scientific Group Thermodata Europe) compilation by Dinsdale [124].

3.2. Liquid

The liquid phase in this current work is modeled using the MQM where the pair approximation is utilized to describe the short range ordering (SRO) exist in the liquid phase. It is observed that the alloy systems which show a strong compound forming tendency in the solid state (i.e. Mg–Zn, Mg–Sn etc.) display a pronounced minimum in the enthalpy of mixing of the liquid phase and this is caused due to the existence of short-range ordering [125]. The Bragg–Williams (BW) random-mixing model is not able to represent the binary solutions with short-range ordering (SRO) and thus unable to describe the enthalpy and entropy of mixing functions properly. The "associate" or "molecular" model [126] was also proposed to deal with the short-range ordering. However associate model assumes that some molecules occupy some of the atomic sites which is not physically sound. Another important weakness of the "associate" model is its inability to predict the correct thermodynamic properties of ternary solutions when the binary sub-systems exhibit short-range ordering [127]. The detailed description of the MQM can be found elsewhere [128–130].

3.3. Terminal solid solution

Random solution model is used to describe the disorder terminal solid solution phases and the excess Gibbs energy is expressed using Redlich–Kister polynomial [123] according to the following equation:

$$G = x_i^0 G_i^\varphi + x_j^0 G_j^\varphi + RT[x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^\varphi.$$

3.4. Intermetallic compound

All the intermetallic compounds in the system except $MgZn_2$ (Lave phase) are considered as stoichiometric. The Gibbs energy for stoichiometric compounds is described by the following equation:

$$G^\varphi = x_i^0 G_i^{\varphi 1} + x_j^0 G_j^{\varphi 2} + \Delta Gf$$

where φ denotes the phase of interest, x_i and x_j are the mole fraction of components i and j and $G_i^{\varphi 1}$ and $G_j^{\varphi 2}$ 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. The parameters a and b are obtained by optimization using experimental results of phase equilibrium and thermodynamic data.

The Laves phase $MgZn_2$ is modeled by Compound Energy Formalism (CEF) where two sublattices; $(Mg, Zn)(Mg, Zn)_2$ are used to describe the phase. The primary species in each sublattices are denoted by bold letters. The end members of this phase are Mg_3, $MgZn_2$, Mg_2Zn and Zn_3 where $MgZn_2$ is the stable phase. This model of two sublattices covers the whole composition range and therefore the homogeneity range of $MgZn_2$ (~66% to 67.1 at.% Zn) could be successfully reproduced. As $MgZn_2$ is the stable phase thus its standard Gibbs energy is set to actual Gibbs energy value whereas the Gibbs energies of the other hypothetical end members (i.e Mg_3, Mg_2Zn and Zn_3) are arbitrarily set to high positive values.

For this study the heat capacity of Mg_2Sn is taken from Chen et al. [78] whereas that of the Mg–Zn compounds are taken from Morishita et al. [9,10]

All the optimized model parameters of different phases in the Mg–Sn–Zn ternary system are summarized in Table 1.

4. Results and discussion

4.1. The Mg–Zn binary

Phase diagram

The calculated Mg–Zn phase diagram in relation to the experimental data points from the literature is shown in Fig. 1 whereas Table 2 summarizes the calculated and experimental invariant points of this system. Both of them show reasonable agreement with the experimental findings [12,14–20,131]. The maximum solubility of Zn in Mg is calculated as 2.5 at.% which

Table 1
Optimized model parameters of the Mg–Sn–Zn system.

Phase		Thermodynamic parameters
		Liquid phase (J/mol; J/mol K)
LIQUID	Mg–Zn Liquid	$Z_{MgZn}^{Mg} = 6$, $Z_{ZnMg}^{Zn} = 4$; $\Delta_{gMgZn}^{0} = -8326.2 + 3.19T$
		$\Delta_{gMgZn}^{10} = -4602.4 - 3.265T$, $\Delta_{gMgZn}^{01} = -62.76 - 3.7656T$
	Mg–Sn Liquid	$Z_{MgSn}^{Mg} = 3$, $Z_{SnMg}^{Sn} = 6$; $\Delta_{gMgSn}^{0} = -17819.7 - 4.10T$
		$\Delta_{gMgSn}^{10} = 1171.5$, $\Delta_{gMgSn}^{01} = -4184 - 2.092T$
	Sn–Zn Liquid	$Z_{SnZn}^{Sn} = 6$, $Z_{ZnSn}^{Zn} = 6$; $\Delta_{gSnZn}^{0} = 2384.88$;
		$\Delta_{gSnZn}^{10} = 2092 - 4.184T$, $\Delta_{gSnZn}^{01} = 5439.2 - 6.276T$
		Solid solution phases (J/mol; J/mol K)
(HCP)	Zn in Mg-hcp, Mg in Zn-hcp	${}^{0}L_{Mg,Zn}^{Mg-hcp,Zn-hcp} = -1200 + 6.5T$
	Sn in Mg-hcp	${}^{0}L_{Mg,Sn}^{Mg-hcp} = -62000$; ${}^{0}G_{Sn}^{Mg-hcp} = {}^{0}G_{Sn}^{Sn-bct} + 5000$
	Sn in Zn-hcp	${}^{0}L_{Sn,Zn}^{Zn-hcp} = 30000$; ${}^{0}G_{Sn}^{Zn-hcp} = {}^{0}G_{Sn}^{Sn-bct} + 5000$
(BCT)	Mg in Sn-bct	${}^{0}L_{Sn,Mg}^{Sn-bct} = -20000$; ${}^{0}G_{Mg}^{bct-Sn} = {}^{0}G_{Mg}^{hcp-Mg} + 8360$
	Zn in Sn-bct	${}^{0}L_{Sn,Zn}^{Sn-bct} = 6000 + 22.0T$; ${}^{0}G_{Zn}^{bct-Sn} = {}^{0}G_{Zn}^{hcp-Zn} + 4100$
MgZn$_2$ LAVE	(Mg3)	${}^{0}G_{Mg:Mg}^{Mg3} = 3G(Mg, Hcp\_A3) + 43.49 \times 10^3$
	(Zn3)	${}^{0}G_{Zn:Zn}^{Zn3} = 3G(Zn, Hcp\_Zn) + 20 \times 10^3$
	(Mg2Zn)	${}^{0}G_{Mg:Zn}^{Mg2} Zn = 2G(Mg, Hcp\_A3) + G(Zn, Hcp\_Zn) + 30 \times 10^3$
	(MgZn$_2$)	${}^{0}G_{Mg:Zn}^{MgZn2} = -55979.23 + 380.999T - 74T \ln T + 0.00085T^2 - 3.333 \times 10^{-6}T^3$
		${}^{0}\Delta H_{298.15 K}^{MgZn2} = -33815$; ${}^{0}S_{298.15 K}^{MgZn2} = 115.005$; Cp $= 74 - 0.0017T + 2 \times 10^{-5}T^2$
		${}^{0}L_{Mg,Zn:Mg}^{MgZn2} = {}^{0}L_{Mg,Zn:Zn}^{MgZn2} = {}^{0}L_{Mg:Mg,Zn}^{MgZn2} = {}^{0}L_{Zn:Mg,Zn}^{MgZn2} = 1.000000016$
		Stoichiometric compounds (J/mol; J/mol K)
Mg–Zn	Mg$_2$Zn$_{11}$	${}^{0}\Delta H_{298.15 K}^{Mg2Zn11} = -85820$; ${}^{0}S_{298.15 K}^{Mg2Zn11} = 499.65$; Cp $= 200 + 0.473T - 0.004T^2$
	Mg$_2$Zn$_3$	${}^{0}\Delta H_{298.15 K}^{Mg2Zn3} = -54950$; ${}^{0}S_{298.15 K}^{Mg2Zn3} = 183.725$; Cp $= 122 - 0.0311T + 0.0001T^2$
	Mg$_{12}$Zn$_{13}$	${}^{0}\Delta H_{298.15 K}^{Mg12Zn13} = -250500$; ${}^{0}S_{298.15 K}^{Mg12Zn13} = 885.3$; Cp $= 600.5 - 0.10875T + 0.0005T^2$
	Mg$_{51}$Zn$_{20}$	${}^{0}\Delta H_{298.15 K}^{Mg51Zn20} = 335000.355$; ${}^{0}S_{298.15 K}^{Mg51Zn20} = 2510$;
		Cp $= 51 \times$ Cp(Mg, Hcp $-$ A3) $+ 20X$ Cp(Zn, Hcp $-$ Zn)
Mg–Sn	Mg$_2$Sn	${}^{0}\Delta H_{298.15 K}^{Mg2Sn} = -85000$; ${}^{0}S_{298.15 K}^{Mg2Sn} = 111.75$; Cp $= 62.6 + 0.0208T - 4 \times 10^{-6}T^2$

is very close to the values of 2.5 and 2.4 at.% of Zn reported by Park and Wyman [19] and Schmidt and Hansen [16], respectively. However, the current results are away from 2.9 at.% Zn solubility reported by Grube and Burkhardt [17]. On the other hand a very limited solubility of Mg in Zn of around 0.25 at.% Mg is calculated in the present work which is also in good agreement with the reported value of 0.3 at.% Mg by Hume-Rothery and Rounsefell [20]. The calculated congruent melting temperature of MgZn$_2$ phase is 588 °C which agrees well with the value reported in most of the literature [14,15,19,20]. However this value is less than 595 °C as reported by Grube [12]. The homogeneity range is calculated as 66 at.% Zn at 415 °C to 67.3 at.% Zn at 381 °C which is also in good agreement with the reported values of 66 at.% Zn at 416 °C and 67.1 at.% Zn at 381 °C [19,21].

Thermodynamic properties

Pyka [33] and Agarwal et al. [34] measured the enthalpy of mixing of the Mg–Zn liquid using calorimetric method at different temperatures. Pyka's [33] results did not show temperature dependence of the enthalpy of mixing obeying the Kopp–Neumann rule. However, Agarwal et al. [34] claimed to have a temperature dependency of enthalpy of mixing of liquid and later on incorporated, this by introducing a temperature dependent coefficient called '*c*' in the optimization of the Mg–Zn system [41]. The enthalpy of mixing measured by Kawakami [66] did not agree
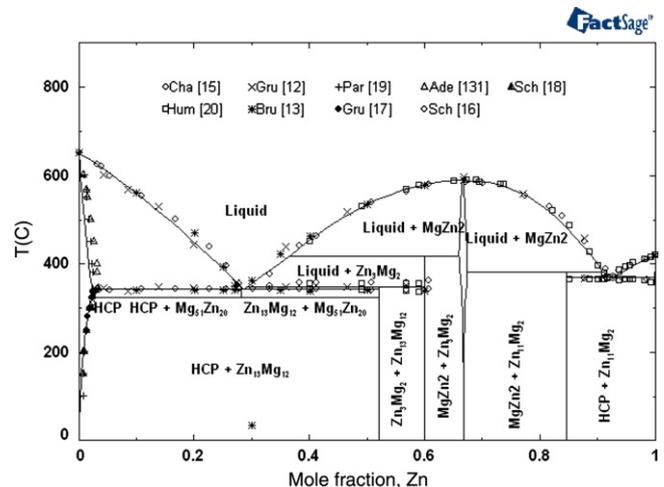
Fig. 1. Re-optimized Mg–Zn phase diagram with experimental data from the literature.

with the calculated value at 800 °C by Agarwal et al. [41]. However Kawakami's [66] results are closer to the measured values of Pyka [33]. The enthalpy of mixing values reported by Pyka [33]

Table 2
The calculated invariant points of the Mg–Zn system in comparison with the literature data.

Reaction type	Reaction	Composition (at.% Zn)	Temp. (°C)	Reference
Eutectic	$L \leftrightarrow Mg_{51}Zn_{20} + Mg_{12}Zn_{13}$	28.7	342	This work
		–	344	[12]
		28.7	340	[14]
		30.2	342.5	[15]
		28.1	340 ± 1	[19]
		30.0	343 ± 1	[26]
	$L \leftrightarrow Mg_2Zn_{11} + (Mg)\text{-hcp}$	93.1	369	This work
			368	[12]
		92.5	363	[13]
			368	[15]
		92.2	364	[19]
		92.2	364	[20]
Peritectic	$L + (Mg)\text{-hcp} \leftrightarrow Mg_{51}Zn_{20}$	28.3	341	This work
		28.3	342 ± 1	[19]
			346 ± 2	[26]
	$L + Mg_2Zn_3 \leftrightarrow Mg_{12}Zn_{13}$	52.1	346.2	This work
		51.5	347	[19]
	$L + (MgZn_2)\text{-LAVE} \leftrightarrow Mg_2Zn_3$	60.0	413.5	This work
			410 ± 10	[24]
			414 ± 1	[19]
			410 ± 1	[26]
	$L + (MgZn_2)\text{-LAVE} \leftrightarrow Mg_2Zn_{11}$	84.7	380	This work
			381	[19]
			380.5	[20]
Congruent	$L \leftrightarrow (MgZn_2)\text{-LAVE}$	66.7	587	This work
		66.7	595	[12]
		66.7	589	[14]
		66.7	585	[15]
		66.7	590	[20]
		66.7	588	[19]
Eutectoid	$Mg_{51}Zn_{20} \leftrightarrow (Mg)\text{-hcp} + Mg_{12}Zn_{13}$	28.1	321	This work
			325	[23]

showed a minima at around 60 at.% Zn which is also supported by Kawakami [66]. To the best of our knowledge, no experimentally measured Cp data of liquid Mg–Zn has been published in the literature till date. Thus the use of a c-coefficient (for non-zero heat capacity of mixing) seems to be unjustified as suggested by Lukas and Fries [132]. However just to obtain a steeper liquidus and to be compatible with the measured enthalpy of mixing of liquid by Pyka [33], Agarwal et al. [41] and subsequently Liang et al. [46] introduced the third term, the c-coefficient in the Gibbs energy function of the liquid phase [132]. This made their enthalpy of mixing of liquid at 800 °C very much away from the experimentally measured value by Kawakami [66]. However, in the present paper (as well as in Ref. [47]), this asymmetric nature in the enthalpy of mixing of liquid and the steeper liquidus have been accounted for by introducing short range ordering in the liquid using the Modified Quasichemical Model (MQM). Also MQM provides better representation of the partial properties of the ternary and higher order liquid phases [47,133]. The calculated integral and partial enthalpy of mixing of the Mg–Zn liquid in this study is shown in Fig. 2 along with the available experimental data from the literature and good consistency is achieved. The integral enthalpy of mixing (Fig. 2(a)) shows minima at 60 at.% Zn which is very close to the value suggested by Terpilowski [35], where maximum short range ordering takes place. Fig. 3 shows the calculated activities of Mg and Zn in the liquid phase at 650 °C in comparison with the literature values and both show good consistency. The heat of formation of the Mg–Zn compounds at 25 °C is shown in Fig. 4(a) along with experimental values reported in the literature [9,10,39,42–45] and also with the value used by Wasiur-Rahman and Medraj [47]. The calculated values show good agreement with most of the literature data. The enthalpy of formation values measured by Morishita et al. [9,10,44,45] has an uncertainty of

±3 kJ/mol and the present results are within this range. The calculated values show good agreement with the experimental values within the error limits. Fig. 4(b) shows the calculated S^0_{298} of the intermediate compounds with the experimental data from the literature in relation to the value reported by Wasiur-Rahman and Medraj [47]. Overall the current calculation shows good consistency with the literature data and much better consistency than Wasiur-Rahman and Medraj [47] especially for Mg_2Zn_{11} compound. Fig. 4(c) compares the calculated Cp values with the experimentally measured values [10] and show good consistency.

4.2. The Mg–Sn binary

Phase diagram

The calculated Mg–Sn phase diagram along with experimental data from the literature is shown in Fig. 5. Table 3 summarizes the calculated and the experimental invariant points of the system. Both show reasonable agreement with the experimental findings [48–54,56,57,59,60]. The maximum solubility of Sn in Mg is calculated as 3.41 at.% Sn which agrees well with the experimental findings by different investigators [51,53,59,60]. The eutectic temperature toward the Mg side is calculated as 567 °C which is well supported by the literature [48,50,51,54,60]. However, Kurnakow and Stepanow [49] reported a much higher eutectic temperature value of 581 °C at the Mg-rich side. The eutectic temperature at the Sn side is calculated as 199 °C at a liquid composition of 91.4 at.% Sn which agrees reasonably well with the values reported in the literature [49,50,53,54,57] except for Grube [48] who reported a higher temperature and lower Sn content in the eutectic liquid. Solid solubility of Mg in Sn is calculated negligibly small which is supported by Nayeb-Hashemi

Table 3
The calculated invariant points of the Mg–Sn system in comparison with the literature.

Reaction type	Reaction	Composition (at.% Sn)	Temp. (°C)	Reference
		10.7	567	This work
		11.6	564.8	[48]
		12	581	[49]
	$L \leftrightarrow Mg_2Sn + (Mg)\text{-hcp}$	10.5	561	[50]
		10.7	560.6	[51]
		11	561.2 ± 0.3	[54]
		10.7	567	[53]
Eutectic		–	561.5 ± 0.5	[60]
		91.4	199	This work
		89.0	209.4	[48]
		91.5	203.5	[49]
	$L \leftrightarrow Mg_2Sn + (Sn)\text{-bct}$	90.3	200	[50]
		90.4	203.5 ± 0.3	[54]
		91.4	198	[53]
			201.5 ± 1	[57]
		33.3	772.5	This work
		33.3	783	[48]
		33.3	795	[49]
Congruent	$L \leftrightarrow Mg_2Sn$	33.3	778	[50]
		33.3	770.5	[54]
		33.3	774 ± 1	[55]
		33.3	780	[52]
		33.3	778	[53]

Fig. 2. Calculated (a) enthalpy of mixing of Mg and Zn and (b) partial enthalpy of mixing of Mg at 650 °C in the Mg–Zn liquid with experimental data from the literature.

Fig. 3. Calculated activities of Mg and Zn (relative to pure liquid Mg and Zn) in the Mg–Zn liquid at 650 °C with experimental data from the literature.

Thermodynamic properties

It is observed that there are some discrepancy exists in the reported thermodynamics properties of the Mg–Sn system, especially the enthalpy of mixing of the Mg–Sn liquid. Kawakami [66] first reported the heat of mixing at 800 °C for the Mg–Sn liquid by a direct reaction calorimeter in the composition range of 1.96–67.6 at.% Sn. They also reported the enthalpy for the rest of the composition range by extrapolation of their measured data. In 1980, Sommer et al. [67] determined the heat of mixing by high temperature calorimeter. The results of heat of mixing of the Mg–Sn liquid by Nayak and Oelsen [68,69] were less exothermic than the calorimetric measurement of Kawakami [66] and Sommer et al. [67] and the calculated values of Eremenko and Lukashenko [70], Steiner et al. [54] and Eldridge et al. [64]. On the other hand the calculated heat of mixing by Ashtakala and Pidgeon [74] was two to four times more exothermic than those of Beardmore et al. [54], Eldridge et al. [64], Kawakami [66], Sommer et al. [67] and Eremenko and Lukashenko [70]. Again the calculated values by Sharma [71] were less exothermic than Sommer et al. [67] for alloys less than 40 at.% Sn whereas more exothermic for alloys higher than 40 at.% Sn. Sharma [71] assigned an uncertainty of 1250–2100 J/mol in his measurement which was at-

and Clark [58]. A wide range of melting temperature of Mg_2Sn is reported in the literature [48,50,52,55]. For an example, Kurnakow and Stepanow [49] reported a value as high as 795 °C while Steiner et al. [54] reported a temperature around 770.5 °C. The congruent melting temperature of Mg_2Sn is calculated in the present study is around 772.5 °C which is within the temperature range reported in the literature.

a

c

$Mg_{12}Zn_{13}$

b

Mg_2Zn_3

Mg_2Zn_{11}

Fig. 4. Calculated (a) enthalpies of formation of the Mg–Zn compounds at 25 °C, (b) S^0_{298K} and (c) Cp values with experimental data from the literature.

tributed toward the temperature fluctuations and graphical inter-polations of the results. However, the reported values, especially by Sommer et al. [67] show a minimum at 33.33 at.% Sn which in-dicates the presence of short range ordering in the liquid. The en-thalpy of mixing of the Mg–Sn liquid at 800 °C calculated in this study in comparison with the literature values are shown in Fig. 6 and shows good consistency. Fig. 7 shows the calculated activity of Mg and Sn in the Mg–Sn liquid at 800 °C with respect to their liquid standard state along with experimental data points. Steiner et al. [54] and Nayak and Oelson [68] showed a positive devia-tion from Raoult's Law for alloys of less than 20 at.% Sn, whereas the results of the other investigators [70,64,71,79] showed a negative deviation for all compositions. In the present study, ac-tivity of both Mg and Sn show a negative deviation from Raoult's Law which is in agreement with the literature values [71]. Fig. 8(a) shows the calculated enthalpy of formation of solid Mg–Sn al-loys at 25 °C along with literature data. The reported values of Nayak and Oelson [68] are less exothermic than Borsese et al. [75] who determined this for the composition range of 0.3–0.7 at.% Sn. Apart from them, Sharma [71], Sommer et al. [67] and Beard-more [55] also reported the enthalpy of formation of Mg₂Sn which is at 0.33 at.% Sn while Dobovisek and Paulin [76] calculated the same from the electro-negativity of the two elements using the Pauling's Rule. In the present study, the calculated enthalpy of

formation of Mg_2Sn compound is close to the values reported by Sharma [71] and Beardmore [55], is slightly more exothermic than Sommer et al. [67] and less exothermic than Dobovisek and Paulin [76]. Overall, the enthalpy of formation values of the Mg–Sn solid reported in the literature is less negative than the calculated values in this study, except for those at the Mg_2Sn composition, but reasonably close within the error limits of the experiments. In this optimization the weight is given to the heat of formation value of the Mg_2Sn compound. The standard entropy of Mg_2Sn 111.75 J/K. mole is used in the present study which is higher than the value reported by Jelinek et al. [77] who has reported a value of 101.815 J/K. mole by low temperature Cp measurement using an adiabatic calorimeter. However, the present value is closer to the value used by Jung et al. [82]. Nevertheless, the present value and the value reported by Jelinek et al. [77] have a difference of 3.3 J/K. mole-atom. Considering the experimental set-up used by Jelinek et al. [77] in 1967, the difficulty in measuring the Cp val-ues at low temperatures and the extrapolation used to calculate S^0_{298}, the present value can be considered within the experimental error limit of the work of Jelinek et al. [77]. However, fresh mea-surement to determine the low temperature Cp values and sub-sequently S^0_{298} by reliable method (such as calorimetric method) for Mg_2Sn is recommended. The Cp value of Mg_2Sn above room temperature is taken from the measured value reported by Chen
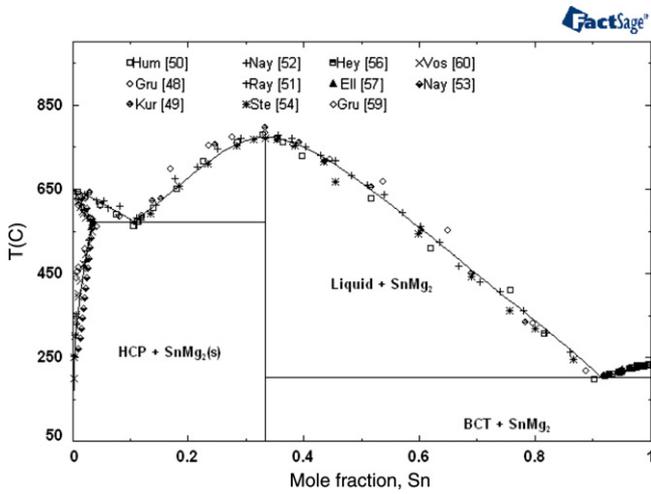
Fig. 5. Re-optimized Mg–Sn phase diagram with experimental data from the literature.
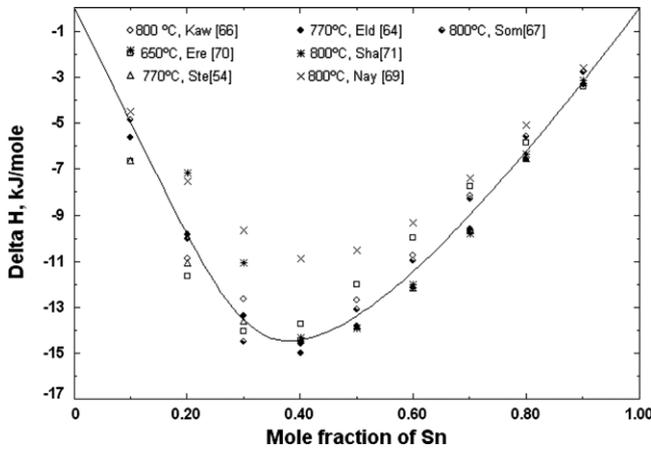
Fig. 6. Calculated enthalpy of mixing of Mg and Sn in the Mg–Sn liquid at 800 °C with experimental data points from the literature.
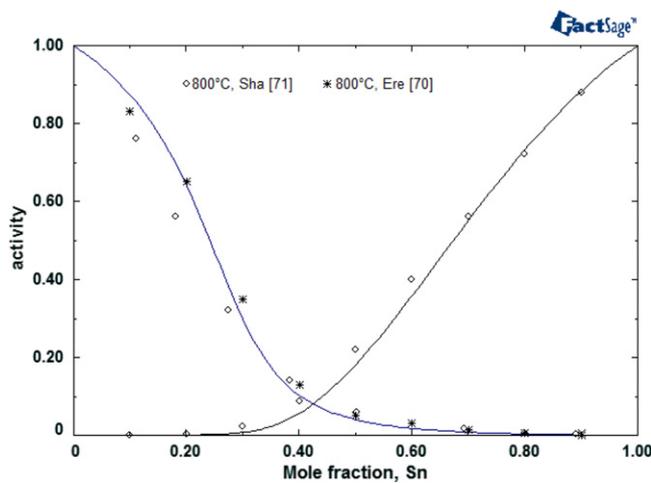
Fig. 7. Calculated activities of Mg and Sn (relative to pure liquid Mg and Sn) in the Mg–Sn liquid at 800 °C with experimental data from the literature.

et al. [78]. Fig. 8(b) shows the calculated Cp values along with the data from the literature [8,77,78,82,83,134], both experimental and calculated. This clearly indicates the present optimization is closer to the experimental results than the earlier optimizations [8,82,83].
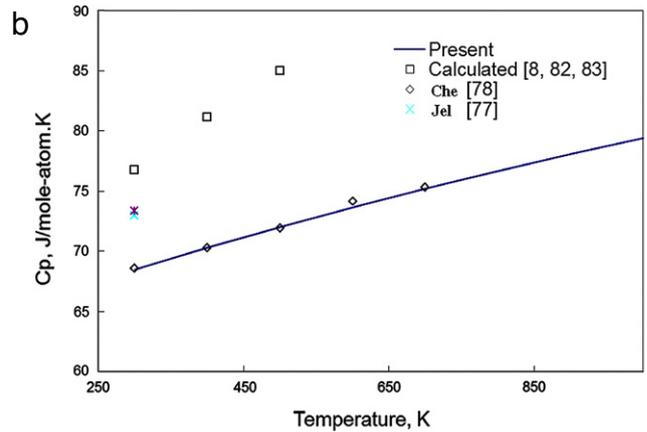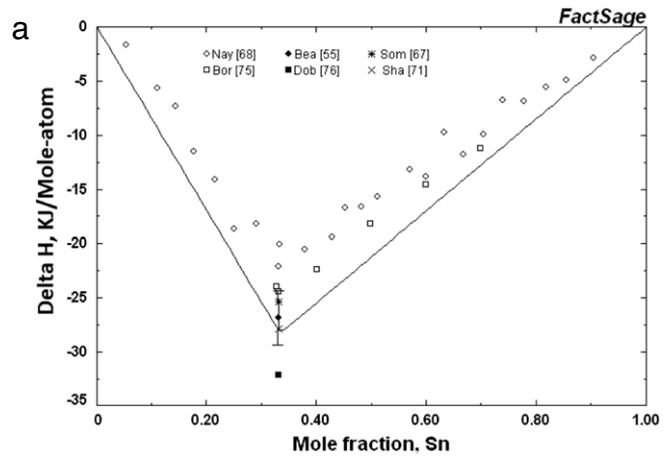
Fig. 8. Calculated (a) enthalpies of formation of the Mg–Sn solid at 25 °C with experimental data from the literature and (b) calculated Cp values with data from the literature.

4.3. The Sn–Zn binary

Phase diagram

Fig. 9 shows the calculated Sn–Zn phase diagram in comparison to the literature data. Table 4 summarizes the calculated and experimental invariant points of this system. The position of the calculated eutectic point is 14.1 at.% Zn and 199 °C which are good agreement with the values reported in the literature [86,87,96–99]. The calculated mutual solubilities of Zn in Sn and Sn in Zn are 0.6 at.% and 0.015 at.%, respectively. The reported solubility of Zn in Sn is 0.6 at.% [94,95] and that of Sn in Zn is 0.039 at.% [92,93] which agree well with the calculated values in this study.

Thermodynamics properties

The calculated enthalpy of mixing of the Sn–Zn liquid alloy at 600 °C in comparison with literature data is shown in Fig. 10. The calculated value is positive at all temperatures and does not show temperature dependence which is also supported in the literature [84]. The calculated enthalpy of mixing is in fair agreement with the experimental values from the literature [84,86, 100]. The calculated activity of Zn in the Sn–Zn liquid is shown in Fig. 11 in comparison with the experimental data from literature. Activity of Zn in the Sn–Zn liquid shows positive deviation from Raoult's law which is consistent with the literature findings.

4.4. The Mg–Sn–Zn ternary

All the calculated isothermal sections, liquidus projection and different vertical sections are calculated, critically compared

Table 4
The calculated invariant points of the Sn–Zn system in comparison with the literature data.

Reaction type	Reaction	Composition (at.% Zn)	Temp. (°C)	Reference
Eutectic	$L \leftrightarrow$ (Sn)-bct + (Zn)-hcp	14.1	199	This work
		15.8	198	[96]
		15.2	198	[86]
		14.6	198	[87]
		13.5	199	[97]
		13.9	199	[98]
		14.6	199	[99]
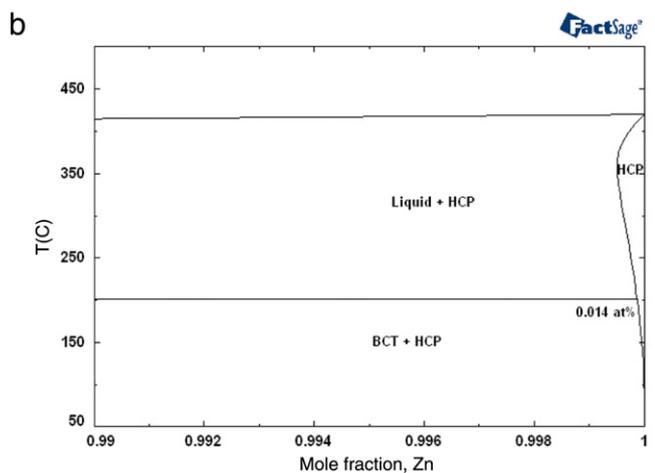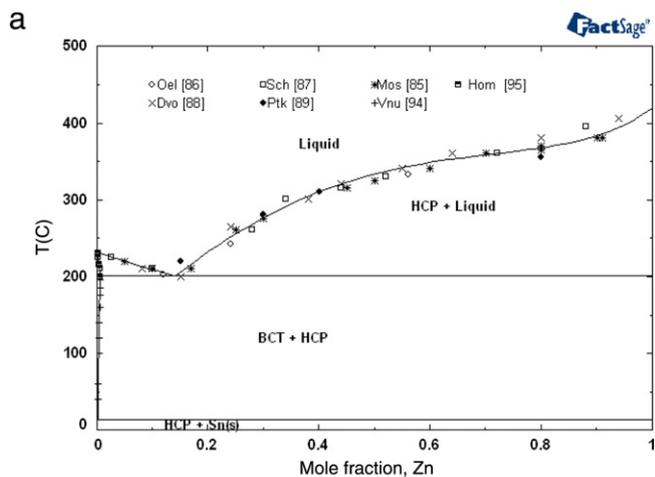
Fig. 9. Re-optimized (a) Sn–Zn phase diagram with experimental data from the literature and (b) Zn rich portion of the diagram.

Fig. 10. Calculated enthalpy of mixing of Sn and Zn in the Sn–Zn liquid with experimental data from the literature at 600 °C.
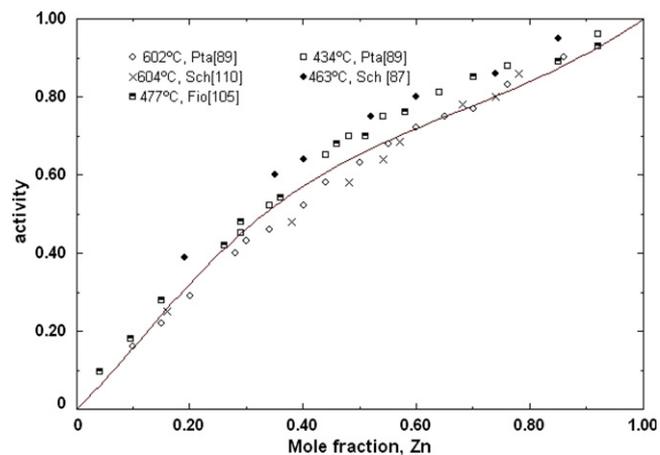
Fig. 11. Calculated activity of Zn in the Sn–Zn liquid (relative to pure liquid Zn) at 600 °C with experimental data from the literature.

with the published literature [5–7,122] and discrepancies, if any, found are addressed. However, no thermodynamic properties of this system could be found in the literature, except by Ogawa et al. [135] who studied experimentally the Mg–Sn–Zn liquid in the temperature range from 427 to 527 °C using a mass spectrometer. Neither experimental values of activities of the components nor excess Gibbs energy of the liquid were determined in their work. Furthermore, their composition of alloys samples was changed due to the evaporation of Zn and thus their experimental information is not reliable as pointed out by Meng et al. [7]. Thus no comparison is possible to make between the ternary thermodynamic properties from this work and the literature.

Isothermal section

Two calculated isothermal sections at 500 and 340 °C are shown in Fig. 12 along with experimental data points from the literature [6]. It can be seen that the present diagrams successfully

replicate the data points of the experimental isothermal sections reported by Godecke and Sommer [6]. The isothermal sections also show the other regions of the phase diagram where no experimental data points could be found in the published literature.

Liquidus projection

The calculated liquidus projection of the Mg–Sn–Zn system is shown in Fig. 13 and the four phase invariant reactions are listed in Table 5 along with the experimental values from the literature [6,122]. The present calculation yields all the seven invariant reactions reported in the literature [6,122] and shows good agreement both in terms of temperature and composition. Meng et al. [7] is the only one who published a complete work on the thermodynamic modeling of this Mg–Sn–Zn system. In

Table 5
The calculated invariant points of the Mg–Sn–Zn system in comparison with the literature data.

Reaction	$T(°C)$	Type	Liquid composition (at.%)			Reference
			Mg	Sn	Zn	
$L \leftrightarrow MgZn_2 + Mg_2Sn$	570.9	e_6	37.2	4.2	58.6	This work
	567		38.6	4.8	56.6	[6]
$L + MgZn_2 \leftrightarrow Mg_2Zn_3 + Mg_2Sn$	413.6	U_1	63.8	0.7	35.5	This work
	414		64.1	1.7	34.2	[6]
$L + MgZn_2 \leftrightarrow Mg_2Zn_{11} + Mg_2Sn$	375.8	U_2	9.95	2.03	88.02	This work
	368		9.7	3.9	86.4	[6]
$L \leftrightarrow Mg_2Sn + (HCP)$	358	e_7	7.9	4.3	87.8	This work
	355		8.9	4.2	86.9	[6]
$L \leftrightarrow Mg_2Zn_{11} + Mg_2Sn + (HCP)$	356.9	E_1	7.93	3.91	88.16	This work
	353		9.2	3.9	86.9	[6]
$L + Mg_2Zn_3 \leftrightarrow Mg_{12}Zn_{13} + Mg_2Sn$	346.0	U_3	70.8	0.3	28.9	This work
	346		69.1	0.6	30.3	[6]
$L + Mg_{12}Zn_{13} \leftrightarrow Mg_{51}Zn_{20} + Mg_2Sn$	342.5	U_4	71.2	0.28	28.52	This work
	341		71.0	0.3	28.7	[6]
$L \leftrightarrow Mg_{51}Zn_{20} + Mg_2Sn + (HCP)$	342.3	E_2	71.32	0.25	28.43	This work
	339		71.5	0.2	28.3	[6]
$L \leftrightarrow (BCT) + Mg_2Sn + (HCP)$	181.5	E_3	6.93	82.12	10.96	This work
	183		7.4	81.1	11.5	[6]
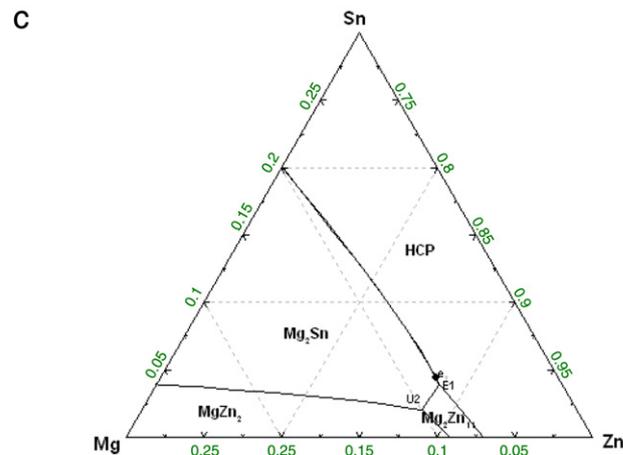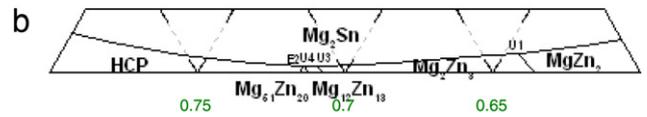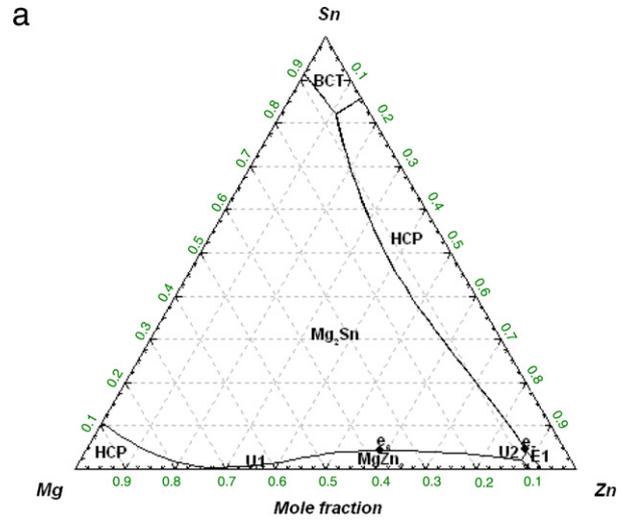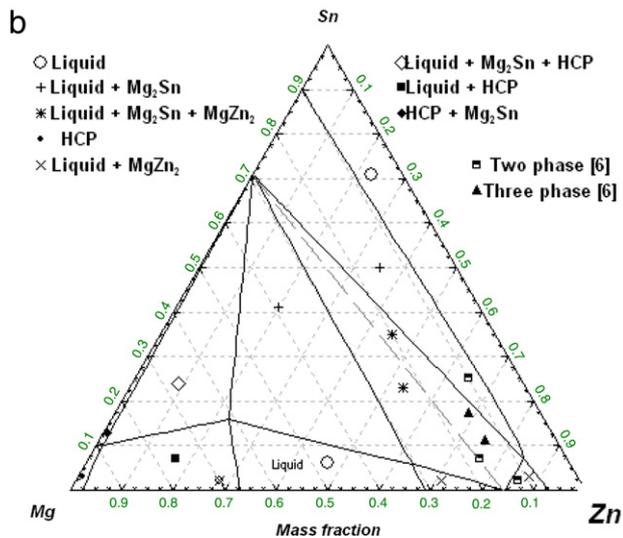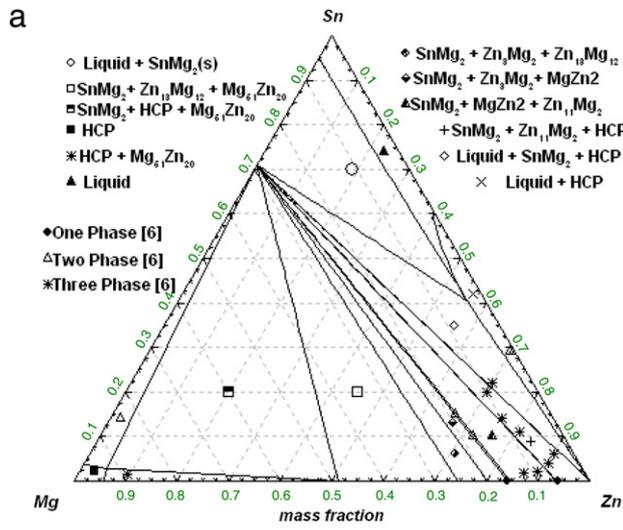
Fig. 12. Calculated isothermal section at (a) 340 °C and (b) 500 °C with experimental data from the literature.

Fig. 13. Calculated liquidus projection of the Mg–Sn–Zn system, (a) overall, (b) near Mg–Zn side and (c) near Zn rich corner.
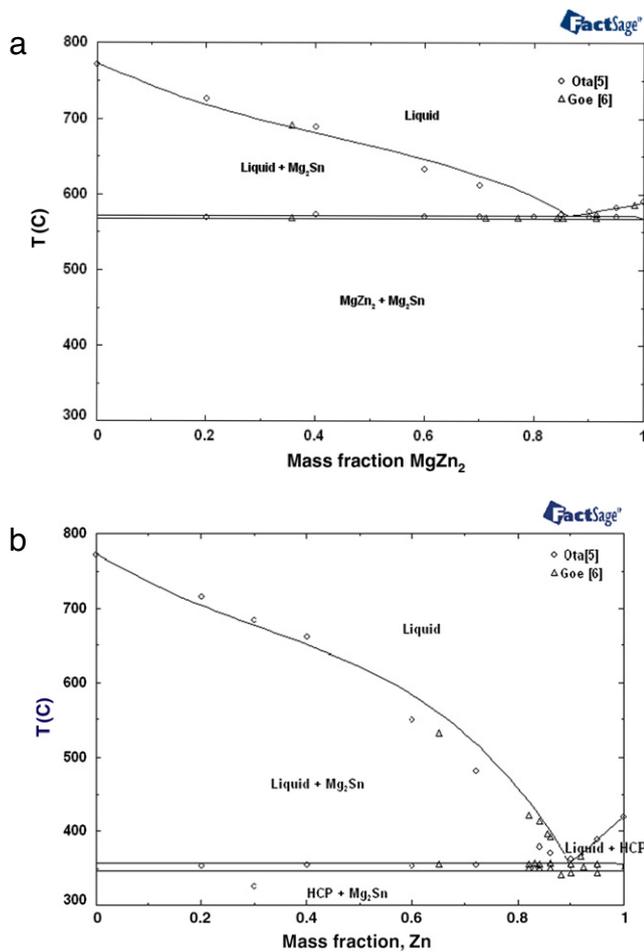
Fig. 14. The calculated vertical sections along with the experimental data points from the literature [5,6]; (a) Mg_2Sn–$MgZn_2$ and (b) Mg_2Sn–Zn.

their calculation, Meng et al. [7] could successfully re-produce the invariant reactions in the Mg_2Sn–$MgZn_2$–Sn–Zn part, however failed to maintain the consistency with the experimental findings of the Mg_2Sn–$MgZn_2$–Mg in the literature [6,122]; even after using ternary parameters. However, this present study results better consistency with the literature findings than Meng et al. [7], though no ternary parameters are added in the calculation.

Vertical sections

The calculated vertical sections of Mg_2Sn–$MgZn_2$ and Mg_2Sn–Zn are shown in Fig. 14. These two sections are actually pseudo-binary sections and match quite well with the experimental data published in the literature [5,6]. The eutectic point in the Mg_2Sn–Zn pseudo-binary section is calculated as 89.6 mass% Zn at 356 °C whereas that for Mg_2Sn–$MgZn_2$ is calculated as 72.8 mass% Zn at 570 °C; both of which match very well with the literature reported values [5,6]. In Mg_2Sn–$MgZn_2$ vertical section, a very small three phase region is calculated between 567 and 570 °C whereas in Mg_2Sn–Zn vertical sections three phase region consists of Liquid + Mg_2Sn + HCP exist between 347 and 356 °C. However, the calculated amount of liquid is very small (<0.02 mass%). Present calculation shows presence of Mg_2Zn_{11} in Mg_2Sn–Zn vertical section below 116 °C (not shown in the Figure) where no experiment data could be found in the published literature. However, the calculated amount of Mg_2Zn_{11} in this region varies from as low as 0.000002 mass% to a maximum of 0.0002 mass%. It is reported that upon cooling the formation of Mg_2Zn_{11} is suppressed sometimes due to difficulty in nucleation of the complex cubic structure of the phase [31] itself.
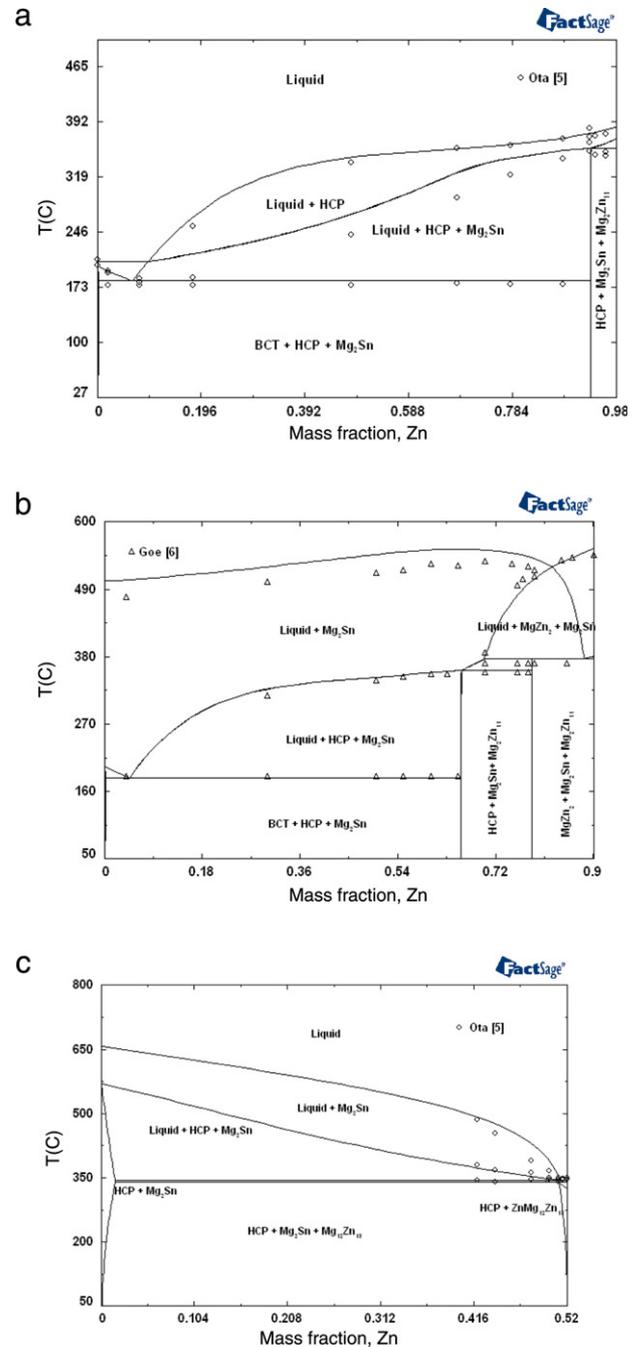
Fig. 15. The calculated vertical sections for (a) 2, (b) 10 and (c) 48 mass% of Mg along with experimental data points from literature.

Figs. 15–17 show the calculated vertical sections at the different compositions for Mg, Zn and Sn, along with experimental data points from the literature [5,6]. The vertical section for 2 mass% Mg Fig. 15(a) is in very good agreement with the published experimental data [5]. In case of 10 mass% Mg (Fig. 15(b)) vertical section, very good agreement is observed with the published experimental data except for the liquids which is slightly higher than the experimental reported values. The same has been observed for 48 mass% Mg vertical section too. The vertical sections for 3, 70 and 90 mass% Zn are shown in Fig. 16(a)–(c). The calculated vertical sections at 3 and 70 mass% Zn (Fig. 16(a)–(b)) agree very well with the published experimental findings. However, slight discrepancy is observed in 90 mass% Zn vertical section in the range of 5–6 mass% Sn. In this region
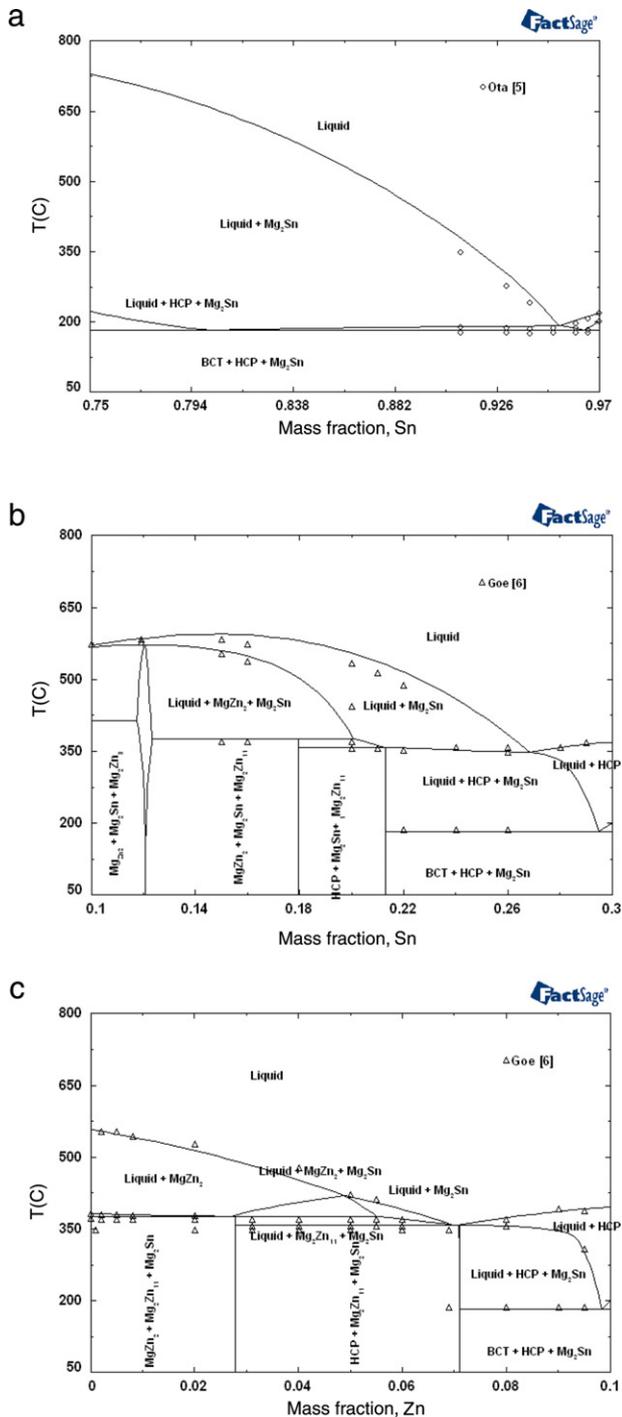
Fig. 16. The calculated vertical section for (a) 3, (b) 70 and (c) 90 mass% Zn with experimental data points from the literature.

absence of one three phase region consists of $L + MgZn_2 + MgSn_2$ and one two phase region consists of $L + Mg_2Sn$ (Fig. 16(c)) is observed in the literature [6] findings. However, no experimental data points regarding the phase relation in these regions are reported in the literature [6]. Apart from these phase boundaries, the phases reported in this section are an absolute match with the current findings where experimental data points are shown in the literature [6]. As no data of other investigator could be found in this region apart from Godecke and Sommer [6], this region should be looked experimentally in more detail. Meng

et al. [7] have also reported similar observation. Fig. 17(a)–(d) shows the calculated vertical sections for constant Sn. Overall all the calculated vertical sections match very well with the experimental findings of Otani [5] and Godecke and Sommer [6]. However, 2 mass% Sn vertical section (Fig. 17(a)) shows slight difference from the experimental findings [6]. First of all, Godecke and Sommer [6] mentioned the primary recrystallization phase as Mg_2Sn which is probably a typographical mistake and should be $MgZn_2$ as calculated in this work and also by Meng et al. [7]. Apart from that the boundary between $L + MgZn_2$ (mentioned as $L + Mg_2Sn$ in [6]) and $L + MgZn_2 + Mg_2Sn$ went only up to 84 mass% Zn whereas in the present calculation this boundary goes up to 88.7 mass% Zn. The other three constant vertical sections (10, 40 and 85 mass% Sn) show almost similar match with the experimental diagrams [5,6].

5. Conclusions

All the three binary sub-system are re-optimized using the CALPHAD method taking into account all the experimental findings, including the recent results and a set of self-consistent parameters for the binary Mg–Zn, Mg–Sn and Sn–Zn are obtained. These are used to satisfactorily reproduce most of the experimental data points, both in terms of phase diagrams and thermodynamics properties. The liquid phase is modeled using the MQM to take care of the short range ordering exist in the Mg–Zn and Mg–Sn liquids. These binaries then extrapolated to construct the ternary diagram which agrees well with the experimental findings and almost all the experimental phase relations and phase-fields are successfully re-produced, even without using any ternary parameters. Any discrepancies while noticed between experimental and calculated findings are addressed and the need for further experimental investigations is pointed out. For an example, making the enthalpy of mixing of the Mg–Sn liquid more negative than what has been calculated in this study will make the ternary diagrams (vertical sections, pseudobinary sections, liquidus projections, etc.) more consistent with the experimental ones. Specially 10 and 48 mass% Mg constant sections and two pseudobinaries (Mg_2Sn–Zn and Mg_2Sn–$MgZn_2$). There is inconsistency in the published literature data on thermodynamic properties of the Mg–Sn system, especially the heat of mixing of the liquid and it is strongly recommended to reinvestigate this system in detail. Also, being a very important system in the field of Mg-alloys, no reliable thermodynamic properties of the Mg–Sn–Zn ternary system are reported in the published literature. Thus future research on the Mg–Sn–Zn system should concentrate on these aspects and should be compared with the present findings.

Appendix. Supplementary data

Supplementary material related to this article can be found online at doi:10.1016/j.calphad.2011.10.007.
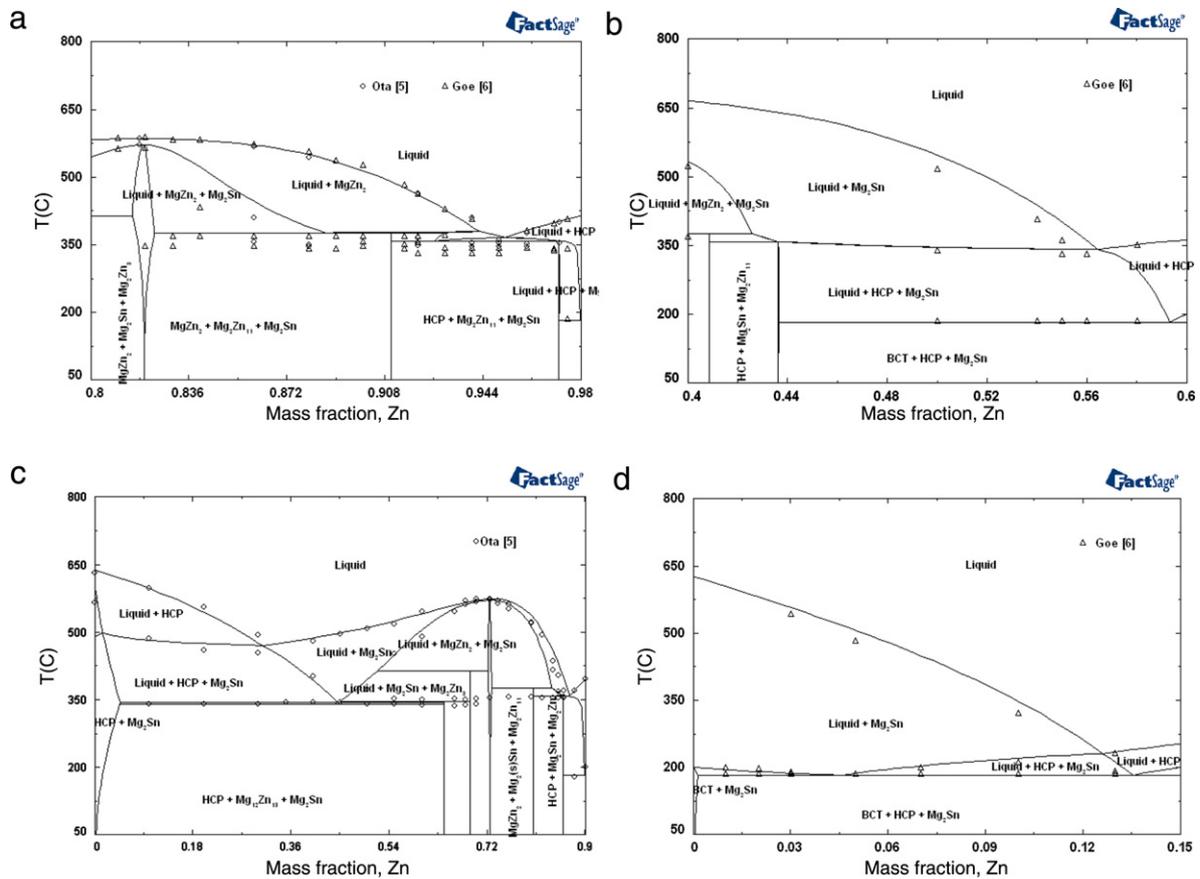
Fig. 17. The calculated vertical section for (a) 2, (b) 10, (c) 40 and (d) 85 mass% Sn with experimental data points from the literature.

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