# Thermodynamic Descriptions of the Quaternary Mg–Al–Zn–Sn System and Their Experimental Validation

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**Abstract**

A brief review on the thermodynamic descriptions of all the sub-binary and ternary systems in the Mg–Al–Zn–Sn system available in the literature was first performed, from which the most reliable ones were chosen. After that, thermodynamic description of the quaternary Mg–Al–Zn–Sn system was established via the direct extrapolation of the chosen thermodynamic descriptions of the sub-binary and ternary systems in the framework of CALculation of PHAse Diagrams (CALPHAD) approach. The reliability of the established thermodynamic database was finally validated through a comprehensive comparison of the model-predicted solidified microstructure characteristics and phase fractions in different quaternary alloys with the experimental ones.

**Keywords**

Mg–Al–Zn–Sn • CALPHAD • Thermodynamic assessment • Scheil simulation

## Introduction

The low density of magnesium alloys makes them an attractive material for lightweight components in industry, automobiles, and aerospace fields [1, 2]. For the past years, numerous researches have been carried out on different magnesium alloys [3, 4], among which the Mg–RE (rare earth)-based alloys show excellent mechanical properties and good corrosion resistance. However, the prices and reserves of RE elements limit the application of Mg–RE-based alloys in commercial domain. Therefore, the development of RE-free magnesium alloys is very crucial. However, the previous studies indicate the mechanical properties of the current RE-free magnesium alloys are still not exceedingly good enough, compared with Mg–RE-based alloys. Thus, the development of novel RE-free magnesium alloys is in urgent need. Nowadays, the computational thermodynamics based on the CALculation of PHAse Diagrams (CALPHAD) approach [5] become an efficient tool that supplies valuable information to guide the design of alloys and/or the optimization of preparation processing. The development cycle and costs of novel alloys can be then significantly reduced with the aid of the computational thermodynamics. The key point for the alloy design driven by the computational thermodynamics lies in the accurate thermodynamic database of the target alloy system. With the accurate thermodynamic database, the multicomponent phase equilibria at any composition/temperature/pressure can be easily obtained. Moreover, the solidification process of cast alloys of industrial relevance can also be predicted according to, i.e., the Scheil–Gulliver simulations.

In the field of RE-free magnesium alloys, the AZ (Mg–Al–Zn) and AT (Mg–Al–Sn) series magnesium alloys have recently attracted more and more research attention of researchers [6, 7] due to their low cost. Aluminum is a common alloy element in magnesium alloys. Al addition can improve the casting properties and mechanical properties of magnesium alloys. As a major additive in magnesium alloys, Zn can play a role in solution strengthening and second phase strengthening, thus improving the creep resistance of magnesium alloys. As a special alloy element, Sn additional in magnesium alloys can induce the $Mg_2Sn$ phase with high melting point that may suppress the slip of grain boundary and improve the mechanical properties of alloys. Therefore, if the optimal amounts of additional Al, Zn, and Sn in Mg alloys can be designed, the optimal mechanical properties of RE-free Mg–Al–Zn–Sn alloys can be achieved. However, most of the current researches on AZ and AT series magnesium alloys depends on trial-and-error experimental investigation [8], which is very difficult to fully exploit the potential of AZ and AT series alloys. In order to perform the computational thermodynamics-driven alloy design of the

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Mg–Al–Zn–Sn system, the accurate thermodynamic descriptions of quaternary Mg–Al–Zn–Sn system are the prerequisite, but still missing in the literature.

Consequently, the major research targets of the present paper are (i) to perform a comprehensive review on the thermodynamic descriptions of all sub-binary and ternary systems in the Mg–Al–Zn–Sn quaternary system, (ii) to construct a self-consistent set of thermodynamic descriptions of the Mg–Al–Zn–Sn quaternary system based on all sub-binary and ternary systems, and (iii) to validate the present thermodynamic database of the Mg–Al–Zn–Sn quaternary system by comparing the Scheil–Gulliver solidification simulation of two casting alloys with the experimental ones available in the literature.

## Review on Thermodynamic Descriptions for Binary Systems

### Mg–Al

The Mg–Al binary system is of particular importance to the magnesium and aluminum industry. The Mg–Al system consists of three solution phases (liquid, $(Mg)_{hcp}$, and $(Al)_{fcc}$) and three intermetallic compounds β ($Al_3Mg_2$), γ ($Al_{12}Mg_{17}$) and ε ($Al_{30}Mg_{23}$) phases. In 1977, the calculated phase diagram of Mg-Al system was firstly presented by Saboungi and Hsu [9]. In their work, the authors treated the γ phase as a stoichiometric compound, which is unreasonable in fact. The calculated eutectic temperature and compositions of $(Al)_{fcc}$ and β phases are inconsistent with the experimental ones. From the literature [10], some major issues were found in the work of Ludecke and Hack. The calculated results by Ludecke and Hack show that $Al_3Mg_2$ phase disappears at low temperatures. In addition, the calculated phase equilibria in Mg-rich side are not accurate. Murray [11] re-assessed the Mg–Al system in 1982. The author treated γ phase as two sub-lattice model, i.e., that one sub-lattice is occupied by Al and Mg and the other is occupied by Al and vacancies. It should be noted the γ phase owns an α-Mn structure with four sub-lattices without the vacancy occupation. Hence, such treatment for γ phase is inappropriate. Afterwards, the thermodynamic descriptions of Mg–Al system were reported by Saunders [10] and Zuo and Chang [12], respectively. In their work, the phase ζ not ε phase was considered in the Mg–Al system. However, the results of [13] indicated the ε phase is stable. Based on the experimental results of [13], Chartrand and Pelton [14] reviewed the Mg–Al system again. Later, Liang et al. [15] re-optimized this system based on the new experimental data [16]. The calculated results from [15] can well reproduce most of the reported experimental ones. Therefore, the thermodynamic parameters from Liang et al. [15] are adopted in the present work for construction of the Mg–Al–Zn–Sn quaternary system.

### Mg–Zn

As an important binary system, the Mg–Zn system has been experimentally and thermodynamically investigated by many groups. In this binary system, liquid, $(Mg)_{hcp}$, $(Zn)_{hcp}$, and five intermetallic compounds (i.e., $MgZn_2$, $Mg_2Zn_3$, $Mg_7Zn_3$, $Mg_{12}Zn_{13}$, and $Mg_2Zn_{11}$) exist. In 1988, a comprehensive thermodynamic assessment of Mg-Zn system was carried out by Clark et al. [17] based on the reported experimental data by Chadwick [18], Hume-Rothery and Rounsefell [19], and Park and Wyman [20]. Nevertheless, Higashi et al. [21] pointed that $Mg_7Zn_3$ phase was placed at the hypereutectic part in the Mg-rich side according to Clark et al. [17]. Afterwards, the thermodynamic descriptions of Mg–Zn system were performed by Agarwal et al. [22], Liang et al. [15], and Wasiur-Rahman and Medraj [23], respectively. Agarwal et al. [22] treated all the intermetallic compounds as stoichiometric compounds. However, Park and Wyman [20] and Massalski [24] reported that $MgZn_2$ phase owns a certain homogeneity range that has been considered in the assessment of Liang et al. [15] and Wasiur-Rahman and Medraj [23]. Besides, the liquid phase was described using the Bragg–Williams model by Agarwal et al. [22] and Liang et al. [15], while in the assessment by Wasiur-Rahman and Medraj [23], the modified quasi-chemical model (MQM) was employed to describe the liquid phase. Later, Ghosh et al. [25] re-assessed the Mg–Zn system based on the recently reported enthalpy of formation, entropy, and C*p* information of intermediate phases [26–29]. The thermodynamic descriptions by [15] have been used to establish the thermodynamic descriptions of Mg–Sn–Zn [30], Cu–Mg–Zn [31], Mg–Zn–Gd [32]. In consideration of the consistence of thermodynamic database, the thermodynamic parameters from [15] are selected in the present work.

### Mg–Sn

As a simple binary eutectic system, the Mg–Sn system includes two eutectic reactions and a congruently melting compound, $Mg_2Sn$. The phase equilibrium information of binary Mg–Sn system was crucially assessed by Nayeb-Hashemi and Clark [33]. In 1984, Fries and Lukas [34] re-optimized the Mg–Sn system based on the published experimental information. Afterwards, the thermodynamic descriptions of this binary system were performed by Jung et al. [35, 36] and Kang and Pelton [37], respectively. In the work of [35–37], the high temperature C*p* values of $Mg_2Sn$ were evaluated according to the assumption of

$Cp$ ($Mg_2Sn$) = 2$Cp$ (Mg) + $Cp$ (Sn). Recently, the thermodynamic descriptions of Mg-Sn binary system were updated by Meng et al. [30], who took into account the newly reported heat capacities and heat contents of $Mg_2Sn$ at low temperatures [38]. Later, Ghosh et al. [25] re-optimized the Mg–Sn system. The liquid phase was described with the MQM. It should be noted a better agreement between the experimental data and thermodynamic calculations from [30] is achieved, compared with previous ones [25, 33–37]. Therefore, the thermodynamic parameters of [30] are directly adopted in the present work.

### Al–Zn, Al–Sn, and Zn–Sn

Al and Zn are crucial alloy elements in the magnesium alloys. Hence, the investigation on the Al–Zn binary system is also necessary. There are two solid solution phases, i.e., $(Al)_{fcc}$ and $(Zn)_{hcp}$, and three invariant reactions. As early as 1973, Hultgren et al. [39] reviewed the thermodynamic properties and phase equilibria of the Al–Zn system. Later, the thermodynamic assessment of this binary system was carried out by Murray [40]. However, the calculated results by [40] are not in good agreement with the experimental data in the literature. Subsequently, Mey and Effenberg [41] thermodynamically updated this system. However, their calculated phase boundaries between $(Al)_{fcc2}$ and $(Al)_{fcc2}$ + $(Zn)_{hcp}$, as well as those for the miscibility gap of the $(Al)_{fcc}$ phase are obviously different from the reported experimental ones. Afterwards, thermodynamic assessment of the Al–Zn binary system was performed by Mey [42], Chen and Chang [43], and Mathon et al. [44], respectively. The thermodynamic descriptions by [42–44] give very similar results. Among the three assessments, the thermodynamic descriptions of Al–Zn system reported by Mey [42] have been applied to construct the thermodynamic databases for the Al–Mg–Zn [15], Al–Zn–Ti [45], and Al–Cu–Zn [46] systems. In consideration of the compatibility of thermodynamic database in multicomponent systems, the thermodynamic parameters of Al–Zn system by [42] were directly employed in the present work.

As a simple eutectic binary system, the Al–Sn system consists of three solution phases, i.e., liquid, $(Al)_{fcc}$, and $(Mg)_{hcp}$. The Al–Sn system was first reviewed by Hayes [47]. Subsequently, the thermodynamic parameters from [47] were included in COST 507 database [48]. Afterwards, Kang and Pelton [37] thermodynamically reviewed the Al–Sn binary system by modeling the liquid phase with MQM. However, the groups of authors [37, 47] did not take into account the solubility of Sn in $(Al)_{fcc}$ during their thermodynamic assessments. It should be noted the calculated solubility of Sn in $(Al)_{fcc}$ by Hayes [47] is much larger than the reported experimental data. In addition, Flandorfer et al. [49] presented the new experimental data on the enthalpies of mixing in the liquid phase of this system. In the recent, the present authors [50] re-optimized the Al–Sn binary system by taking into account the new experimental information [49]. The calculated phase equilibria and thermodynamic properties from [50] show better agreements with comprehensive experimental data and have a significant improvement compared with previous assessments [37, 47]. Thus, the thermodynamic parameters by Cheng et al. [50] were directly employed in this work.

Similarly, the Sn–Zn is also a simple eutectic system, consisting of three solution phases, i.e., liquid, $(Sn)_{bct}$, and $(Zn)_{hcp}$. The Sn–Zn binary system was thermodynamically assessed by several groups [51–53]. Among them, Lee [51] comprehensively reviewed the Sn–Zn binary system based on the experimental data. The calculated results from Lee [51] can better reproduce the reported experimental data. Hence, the thermodynamic descriptions from [51] were employed in the present work.

All the calculated phase diagrams of the Mg–Al, Mg–Zn, Mg–Sn, Al–Zn, Al–Sn, and Sn–Zn binary systems according to the adopted thermodynamic descriptions from Refs. [15, 30, 42, 50, 51] are shown in Fig. 1, respectively.

## Review on Thermodynamic Descriptions for Ternary Systems

### Mg–Al–Zn

Because Al and Zn are basic alloy elements for a series of high-strength magnesium/aluminum alloys. Thus, the thermodynamic descriptions of Mg–Al–Zn are of importance and can serve as the basis for the quaternary and higher-order systems. For Mg–Al–Zn ternary system, there are two ternary phases, which named as $\phi$ with the nominal composition (Al, $Zn)_5Mg_6$ and T with the nominal composition (Al, $Zn)_{49}Mg_{32}$ (note that it was denoted τ in [15]), respectively. In addition, a ternary quasi-crystal phase named as Q was reported. The ternary Mg–Al–Zn system was initially assessed by Chen [54] using the technology from Chen and co-workers based on the PMLFKT program [55] for computing the phase equilibria. It should be noted that the models for $MgZn_2$ and T phases are different from those for their isotopic phases in the Al–Mg–Cu system [56]. Afterwards, Liang et al. [57] assessed the Mg–Al–Zn system based on the thermodynamic descriptions of the Mg–Al [12], Mg–Zn [22] and Al–Zn [43] binary systems. In their work, three different models (disordered solution phases, stoichiometric compounds, and semi-stoichiometric phases) are used to different phases in this system.

Subsequently, Liang et al. [15] experimentally and thermodynamically investigated the Mg–Al–Zn ternary system.

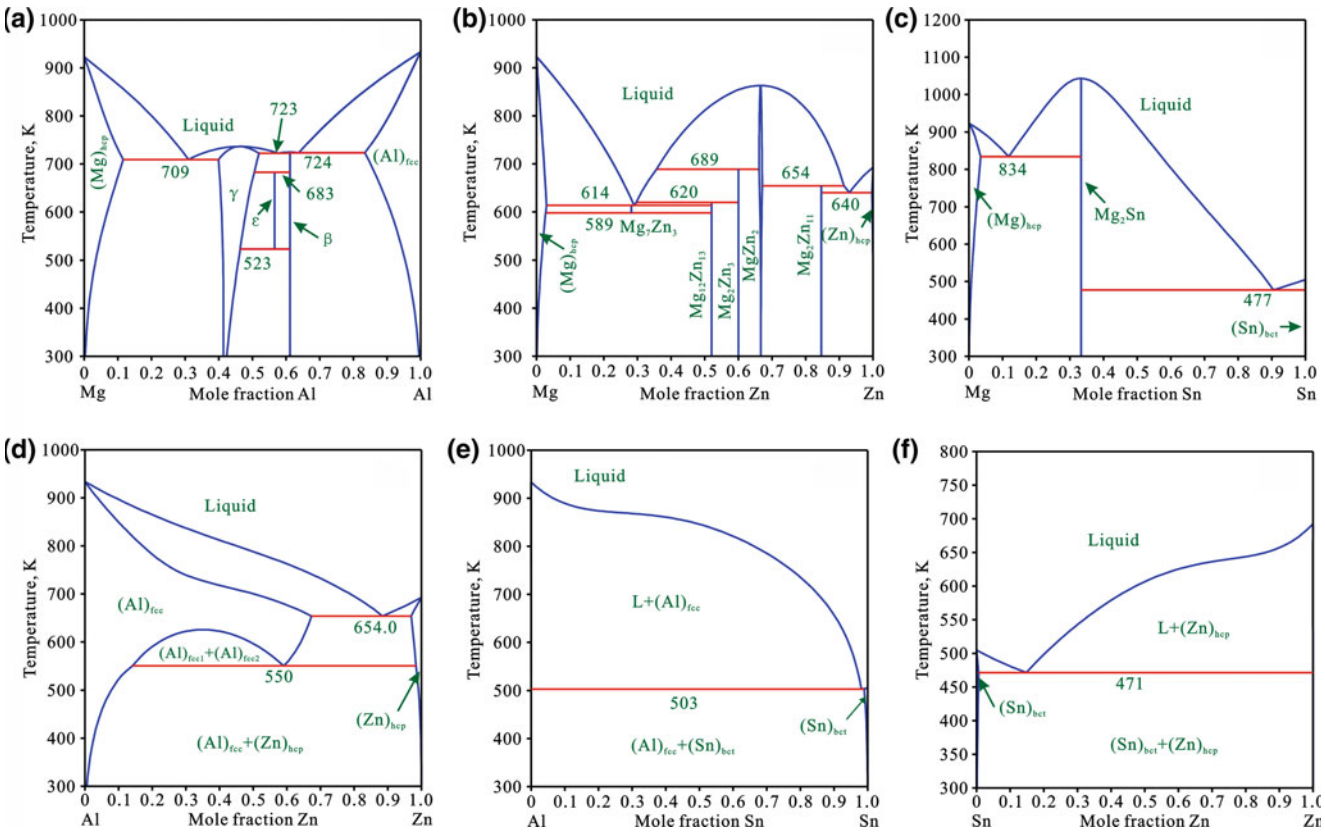


**Fig. 1** Calculated phase diagrams of **a** Mg–Al, **b** Mg–Zn, **c** Mg–Sn, **d** Al–Zn, **e** Al–Sn, and **f** Zn–Sn binary systems by Liang et al. [15], Meng et al. [30], Mey [42], Cheng et al. [50], and Lee [51], respectively

In their work, 34 ternary samples were annealed at 335 °C for 19 days. The phase equilibria were determined by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). In addition, the compositions of these phases were investigated by electron probe microanalysis (EPMA) and listed in the literature. The experiments were performed to provide the experimental information of the ternary solubilities of the Mg–Al and Mg–Zn phases, as well as to improve the cognitions of extensions of the homogeneity ranges of $\phi$ and T phases. These experimental data together with the constitutional, thermochemical, and crystallographic data from the literature were considered in their optimization. Moreover, the thermodynamic descriptions of Mg–Al–Zn system were established based on the thermodynamic descriptions of the Mg–Al [15], Mg–Zn [15], and Al–Zn systems [42], which have been discussed in detail in Sect. 3. The calculated results from [15] can well reproduce most of the experimental data. The calculated vertical and isothermal sections in ternary Mg–Al–Zn system from [15] are shown in Figs. 2 and 3, respectively.

## Mg–Al–Sn

In the Mg–Al–Sn ternary system, no ternary phase was reported, and no ternary solubilities of the binary intermetallic compounds were observed. In 2006, Doernberg et al. [58] experimentally and thermodynamically investigated the Mg–Al–Sn system. There are 9 samples placed in a Ta capsule which were melted in argon atmosphere. Seven samples are with high magnesium contents, with Mg content varying between 61.7 and 75 at.%. The other two contained 26 and 33.3 at.% Mg, respectively. The isothermal equilibration at 400 °C was performed for 3 weeks. The liquidus of different vertical sections was determined by DTA and DSC. The microstructure of those alloys was investigated by XRD and scanning electron microscope (SEM). The calculated phase diagrams from [58] are in good agreement with their own experimental results and reported experimental data from other literature. Afterwards, the thermodynamic descriptions of the Mg–Al–Sn ternary system were carried out by Kang and Pelton [37]. In their work, the short-range ordering was taken into account for the liquid phase. A series

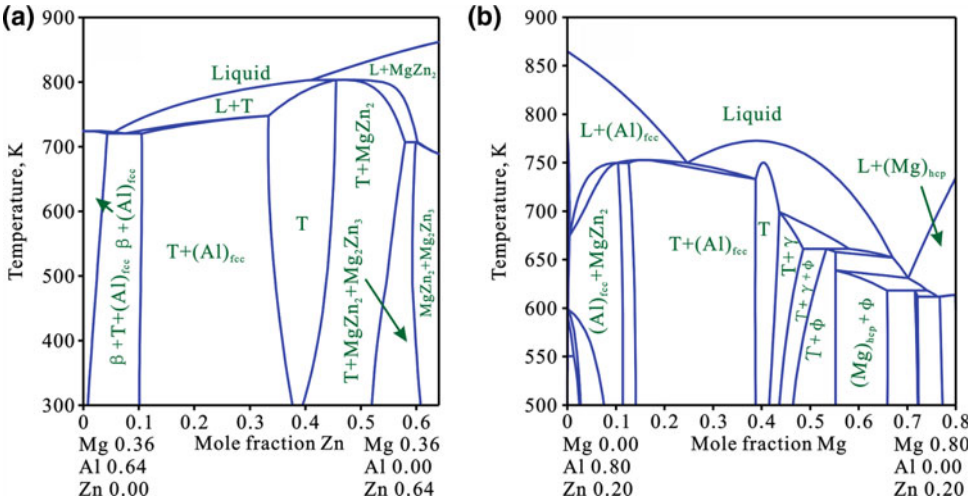


**Fig. 2** Calculated vertical sections in Mg–Al–Zn system along **a** 36 at.% Mg, and **b** 20 at. % Zn by Liang et al. [15]

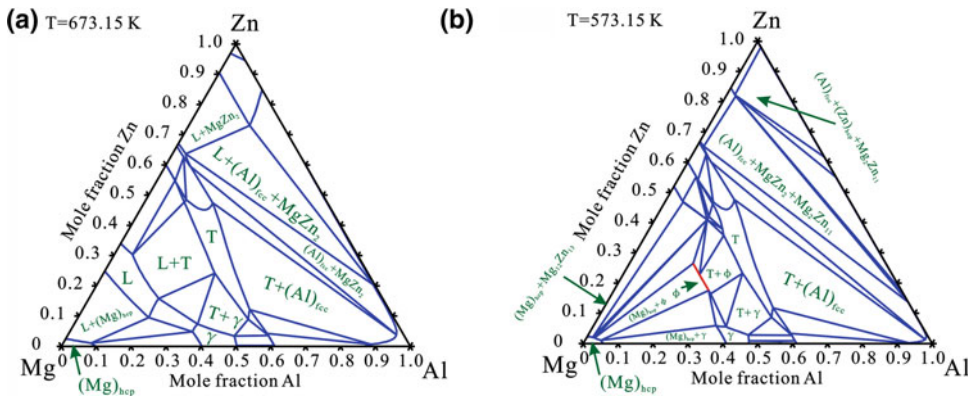


**Fig. 3** Calculated isothermal sections of the ternary Mg–Al–Zn system at 673.15 K and 573.15 K from Liang et al. [15]

of calculated vertical sections of Mg–Al–Sn were shown in their literature. The calculated results can well reproduce the experimental data. Recently, Cheng et al. [50] re-optimized the Mg–Al–Sn system and established a self-consistent thermodynamic database for this ternary system. In their work, the ternary liquid was described with associated solution model. A comprehensive comparison between the calculated phase equilibria/thermodynamic properties and the experimental data from the literature showed that their calculate results are in good agreement with these experimental information. Besides, the results of Scheil simulations furthermore validated the reliability of these thermodynamic descriptions. The vertical and isothermal sections due to [50] are shown in Figs. 4 and 5, respectively.

## Mg–Zn–Sn

For Mg–Zn–Sn ternary system, no ternary phase was reported in the previous investigations. In 2006, Bamberger [59] presented the calculated phase diagrams of Mg–Al–Sn system based on the commercial Mg database. However, only the isothermal section at 450 °C was shown. Jun et al. [60] assessed the Mg–Zn–Sn system. In their work, the authors did not report the thermodynamic parameters and only showed the liquidus projection. Moreover, the experimental validation for the calculated results did not take into account in their work.

The thermodynamic descriptions of Mg–Zn–Sn ternary system were performed by Meng et al. [30] using CALPHAD approach. In their work, the Mg–Sn system was updated and the thermodynamic parameters of Mg–Zn [15] and Sn–Zn [51] systems were directly adopted in their work. The associated solution model was applied for the Mg–Zn–Sn ternary liquid phase consisting of Mg, Zn, Sn, and $Mg_2Sn$. Meng et al. [30] showed that the calculated liquidus projection and vertical sections are in a reasonable agreement with most of reported experimental data. Afterwards, Ghosh et al. [25] re-optimized the ternary Mg–Zn–Sn system based on Mg–Sn, Mg–Zn, and Sn–Zn systems from their own work. Their calculated results are also consistent with the equilibrium invariant points. The typical vertical and isothermal sections due to [30] are shown in Figs. 6 and 7, respectively.

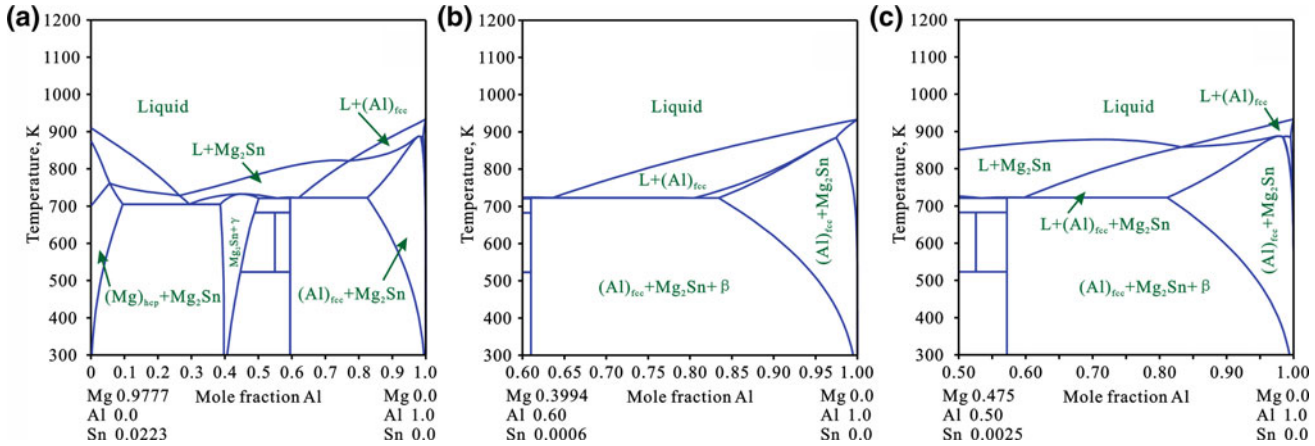


**Fig. 4** Calculated vertical sections close to the Mg–Al side of ternary Mg–Al–Sn system: **a** $Mg_{0.9777}Sn_{0.0223}$—Al, **b** $Mg_{0.9985}Sn_{0.0015}$—Al, and **c** $Mg_{0.95}Sn_{0.05}$—Al according to Cheng et al. [50]

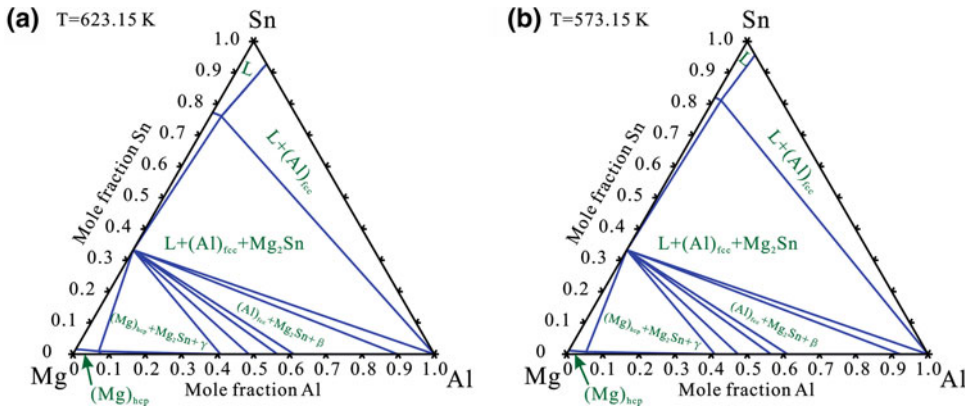


**Fig. 5** Calculated isothermal sections of the ternary Mg–Al–Sn system at 623.15 K and 573.15 K according to Cheng et al. [50]

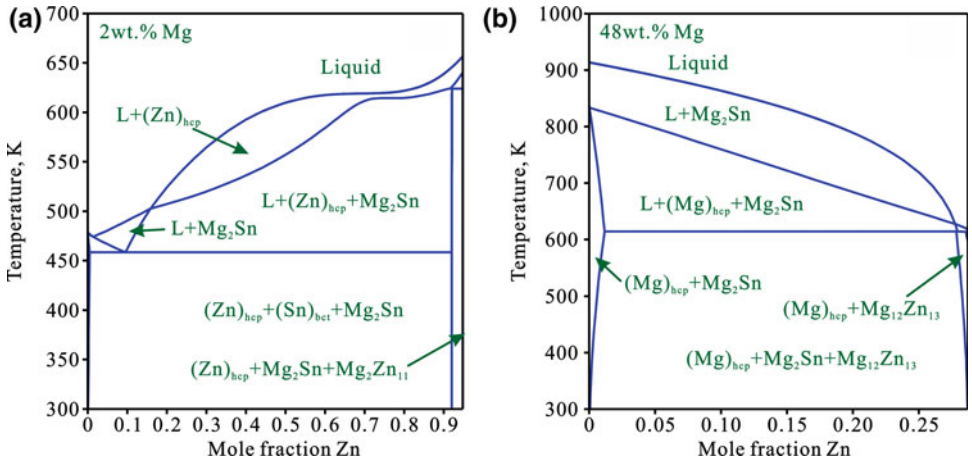


**Fig. 6** Calculated vertical sections in Mg–Zn–Sn system along **a** 2 wt% Mg, and **b** 48 wt % Mg by Meng et al. [30]

## Al–Zn–Sn

For the Al–Zn–Sn ternary system, no ternary compound was observed. The thermodynamic assessment of Al–Zn–Sn system was initially performed by Hayes [47] by means of CALPHAD method. Later, many groups [61–66] investigated the experimental enthalpies of mixing of the liquid phase, activities of Al in the liquid and phase equilibria information. In consideration of these new experimental data, Cheng and Zhang [67] thermodynamically re-assessed the Al–Zn–Sn system based on the thermodynamic descriptions of Al–Sn [50], Al-Zn [42], and

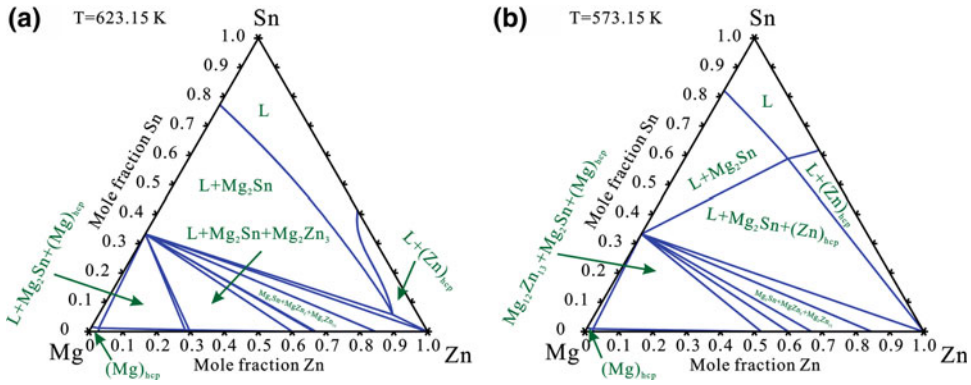


**Fig. 7** Calculated isothermal sections of the ternary Mg–Zn–Sn system at 623.15 K and 573.15 K from Meng et al. [30]

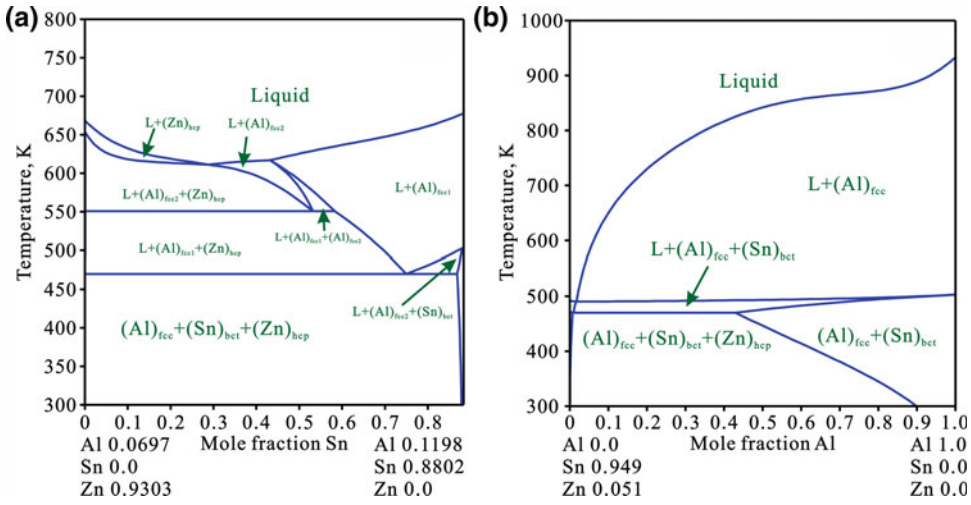


**Fig. 8** Calculated vertical sections in Al–Zn–Sn system along **a** $Al_{0.0697}Zn_{0.9303}$—$Al_{0.1198}Sn_{0.8802}$ and **b** $Sn_{0.949}Zn_{0.051}$—Al by Cheng and Zhang [67]

Sn–Zn [51] binary systems. The thermodynamic descriptions from [67] are very consistent with most of the experimental data. The calculated vertical sections and isothermal sections from [67] are shown in Figs. 8 and 9, respectively.

## Thermodynamic Models

The thermodynamic parameters of the pure elements Mg, Al, Zn and Sn were directly taken from SGTE compilation of Dinsdale [68].

In Mg–Sn binary system, the short-range ordering was taken into account for the liquid phase that was described using the associated model [69]. Hence, the associated model, which is possible to be integrated with the substitutional solution model, was also adopted for the liquid phase in the Mg–Al–Zn–Sn quaternary system. The liquid phase was treated as five species (i.e., Mg, Al, Zn, $Mg_2Sn$, and Sn) and four elements (i.e., Mg, Al, Zn, and Sn), among which $Mg_2Sn$ is the associated cluster. The $(Mg)_{hcp}$, $(Al)_{fcc}$, $(Zn)_{hcp}$, and $(Sn)_{bct}$ were described as completely disordered solutions. For Mg-Al-Zn-Sn quaternary system, the molar Gibbs energy of the solution phase (i.e., liquid, $(Mg)_{hcp}$, $(Al)_{fcc}$, $(Zn)_{hcp}$, and $(Sn)_{bct}$) can be expressed as follows [70]:

$$G_m^{\phi} = \sum_i x_i {}^0G_i^{\phi} + RT\sum_i x_i \ln x_i + {}^EG_m^{\phi} \tag{1}$$

where $R$ is the gas constant, $\phi$ represents the solution phase, $x_i$ and ${}^0G_i^{\phi}$ denote the mole fraction and the molar Gibbs energy of the elements $i$ ($i$ = Mg, Al, Zn, $Mg_2Sn$, or Sn for the liquid phase while $i$ = Mg, Al, Zn, or Sn for the solid solution phases), and ${}^EG_m^{\phi}$ represents the excess Gibbs energy, which can be expressed by the Redlich–Kister polynomial:

$${}^EG_m^{\phi} = \sum_{i\neq j} x_i x_j L_{i,j}^{\phi} + \sum_{i\neq j\neq k} x_i x_j x_k L_{i,j,k}^{\phi} + \sum_i \sum_{j>i} \sum_{k>j} \sum_{l>k} x_i x_j x_k x_l L_{i,j,k,l}^{\phi} \tag{2}$$

with

$$L_{i,j}^{\phi} = \sum_{j>i,v=0}^{n} {}^vL_{i,j}^{\phi}(x_i - x_j)^v \tag{3}$$

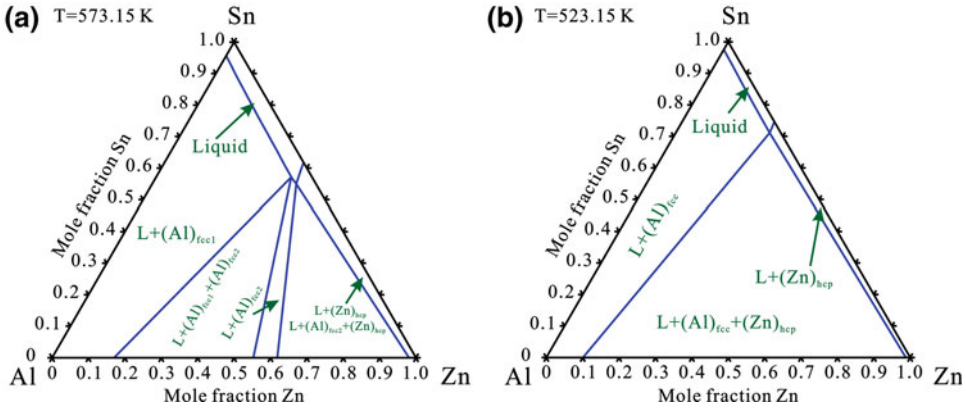


**Fig. 9** Calculated isothermal sections of the ternary Al–Sn–Zn system at 573.15 K and 523.15 K from Cheng and Zhang [67]

$$L_{i,j,k}^{\phi} = {}^{i}L_{i,j,k}^{\phi}\left(x_i + \eta_{i,j,k}\right) + {}^{j}L_{i,j,k}^{\phi}\left(x_j + \eta_{i,j,k}\right) + {}^{k}L_{i,j,k}^{\phi}\left(x_k + \eta_{i,j,k}\right) \quad (4)$$

$$\eta_{i,j,k} = \left(1 - x_i - x_j - x_k\right)/3 \quad (5)$$

${}^{v}L_{i,j}^{\phi}$ ($i$, $j$ = Mg, Al, Zn, $Mg_2Sn$, or Sn for the liquid phase, while $i$, $j$ = Mg, Al, Zn, or Sn for the solid solution phases, and $i \neq j$) and ${}^{i/j/k}L_{i,j,k}^{\phi}$ ($i$, $j$, $k$ = Mg, Al, Zn, $Mg_2Sn$, or Sn for the liquid phase, while $i$, $j$, $k$ = Mg, Al, Zn, or Sn for the solid solution phases, and $i \neq j \neq k$) are the binary and ternary interaction parameters, respectively. These parameters are usually expressed as $a + b$T. The $a$ and $b$ represent the interaction coefficients.

## Thermodynamic Descriptions for Mg–Al–Zn–Sn Quaternary System

Up to now, no accurate thermodynamic descriptions for Mg–Al–Zn–Sn quaternary system have been reported. In the present work, all the sub-binary and ternary systems were comprehensively reviewed in the above sections. Based on the above assessment, the thermodynamic parameters of Mg–Al–Zn, Mg–Al–Sn, Mg–Zn–Sn, and Al–Zn–Sn systems due to [15, 30, 50, 67] were directly employed in this work. Through the CALPHAD approach, a thermodynamic description of Mg–Al–Zn–Sn quaternary system is then established based on the Muggianu extrapolation [71].

Figure 10a shows the calculated isothermal section of Mg–Al–Zn–Sn quaternary system at 573.15 K and 10 at.% Sn. Compared with Fig. 3b, the existence of $Mg_2Sn$ was conformed in this isothermal section. Due to the addition of Sn, the number and types of phases in the corresponding regions change. The existence of $Mg_2Sn$ could improve the strength of Mg alloys. Figure 10b shows the calculated vertical section of this quaternary system along $Mg_{0.90}Al_{0.06}Zn_{0.02}Sn_{0.02}$—$Mg_{0.98}$ $Zn_{0.02}$. Taking point A as an example, it can be found that the $(Mg)_{hcp}$, $Mg_{12}Zn_{13}$, and $Mg_2Sn$ are finally solidified structure. It is very obvious that the $Mg_{12}Zn_{13}$ will not appear in the Mg–Al–Sn system. Thus, it can be seen that the addition of 2 at.% Zn has a great influence on phase diagrams of Mg–Al–Sn ternary system. According to Fig. 10, it should be noted the addition of Sn/Zn has a great influence on the Mg–Al–Zn/Mg–Al–Sn ternary system. Hence, the establishment of self-consistent thermodynamic database of the Mg–Al–Zn–Sn quaternary system is of importance.

## Experimental Validation

Kim et al. [72] investigated the microstructures of 5 as-cast Mg–Al–Zn–Sn alloys by means of optical microscope (OM), SEM, and XRD. The corresponding optical micrographs and SEM images were also provided in the original publication [72]. In their work, ingot was fabricated by a squeeze cast. The quaternary alloys were induction melted at 750 °C in a mild steel crucible under protective atmosphere and cast into a permanent mould.

In the present work, the solidified phase fractions of two as-cast samples (Mg–5Al–1Zn–1Sn (wt%) and Mg–5Al–1Zn–5Sn (wt%)) from [72] were counted by using the Image-Pro software based on the SEM images. To validate the reliability of established thermodynamic database of this quaternary system, the Scheil solidification simulations were performed to obtain the solidified phase fractions for the two as-cast alloys. The simulation results were then compared with the experimental data. The Scheil solidification mode, which is based on the assumption of the fast diffusion in the liquid phase but no diffusion in the solid, is much closer to the actual casting conditions, compared with the equilibrium solidification. Based on the current simulation results, the solidification sequences for Mg–5Al–1Zn–1Sn are $L \rightarrow (Mg)_{hcp}$, $L \rightarrow \gamma + (Mg)_{hcp}$, and $L \rightarrow (Mg)_{hcp} + \gamma + Mg_2Sn$,

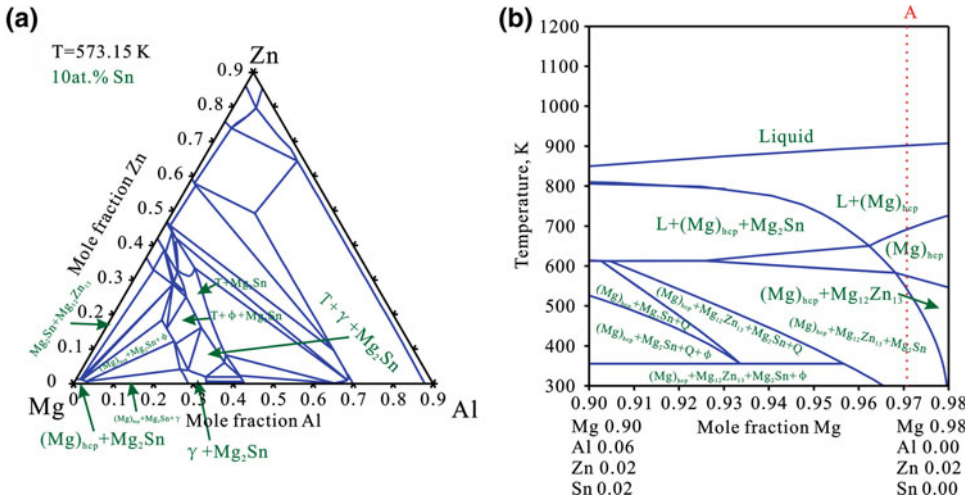


**Fig. 10** **a** Calculated isothermal section of the quaternary Mg–Al–Zn–Sn system at 573.15 K and 10 at.% Sn, **b** Calculated vertical section of the quaternary Mg–Al–Zn–Sn system along $Mg_{0.90}Al_{0.06}Zn_{0.02}Sn_{0.02}$—$Mg_{0.98}Zn_{0.02}$, in the present work

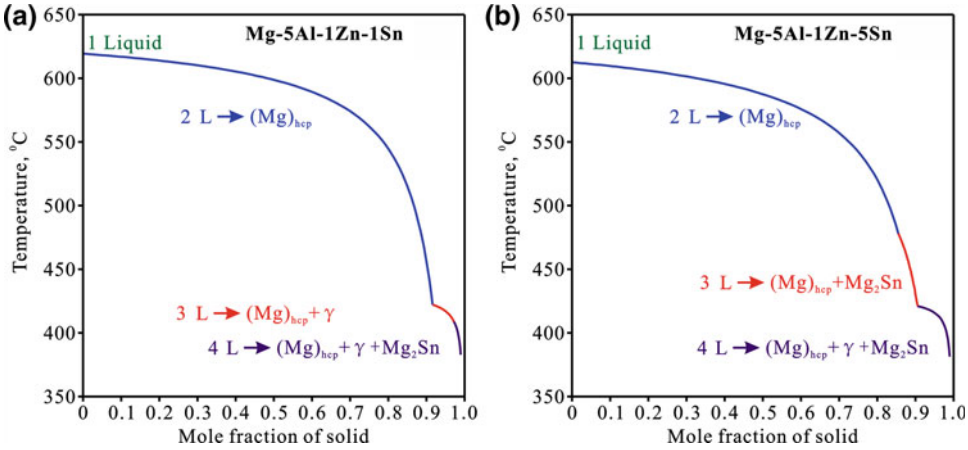


**Fig. 11** Simulated solidification paths of **a** Mg–5Al–1Zn–1Sn (wt %) and **b** Mg–5Al–1Zn–5Sn (wt %) under the Scheil–Gulliver conditions, respectively

while the solidification sequences for Mg–5Al–1Zn–5Sn are $L \rightarrow (Mg)_{hcp}$, $L \rightarrow Mg_2Sn + (Mg)_{hcp}$, and $L \rightarrow (Mg)_{hcp} + \gamma + Mg_2Sn$. The predicted final microstructures of the two alloys contain $Mg_2Sn$, $(Mg)_{hcp}$, and γ phases, which are the consistent as the actual as-cast samples. The simulated solidification paths of the two quaternary alloys are shown in Fig. 11. Moreover, Table 1 shows the contrast results of solidification phase fractions between the calculated results and experimental ones. It should be noted that the experimental values were the average ones determined directly by using the Image-Pro software based on the corresponding SEM images from the original publication [72]. According to Table 1, it should be noted that predicted values for solidified phases are in good agreement with the experimental ones.

## Conclusions

- All thermodynamic descriptions of Mg–Al, Mg–Zn, Mg–Sn, Al–Zn, Al–Sn, and Zn–Sn binary systems were crucially evaluated.
- All thermodynamic descriptions of Mg–Al–Zn, Mg–Al–Sn, Mg–Zn–Sn, and Al–Zn–Sn ternary systems were crucially reviewed.

**Table 1** Solidified phase fractions obtained by Scheil simulation and experimental statistics

| Alloy No. (wt%) | Phase | Calculated results (vol.%) | Experimental statistics (vol.%) |
|---|---|---|---|
| Mg–5Al–1Zn–1Sn | $(Mg)_{hcp}$ | 95.3 | 96.7±0.2 |
| | $Al_{12}Mg_{17}(\gamma)$ + $Mg_2Sn$ | 4.7 | 3.3±0.2 |
| Mg–5Al–1Zn–5Sn | $(Mg)_{hcp}$ | 92.6 | 93.6±0.3 |
| | $Al_{12}Mg_{17}(\gamma)$ + $Mg_2Sn$ | 7.4 | 6.4±0.3 |

- A self-consistent Mg–Al–Zn–Sn quaternary system was established. Moreover, a comparison between the Scheil simulation results and the experimental data showed a very good agreement, indicating that this quaternary thermodynamic database is reliable.

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## References

1. Kang YB, Aliravci C, Spencer PJ (2009) Thermodynamic and volumetric databases and software for magnesium alloys. JOM 61 (5):75–82.
2. Imandoust A, Barrett CD, Al-Samman (2017) A review on the effect of rare-earth elements on texture evolution during processing of magnesium alloys. J. Mater. Sci. 52(1):1–29.
3. Lyu S, Li G, Hu T (2018) A new cast Mg-Y-Sm-Zn-Zr alloy with high hardness. Mater. Lett. 217:79–82.
4. Zhang Y, Yang L, Dai J (2014) Effect of Ca and Sr on the compressive creep behavior of Mg-4Al-RE based magnesium alloys. Mater. Design 63:439–445.
5. Shi R, Luo AA (2018) Applications of CALPHAD modeling and databases in advanced lightweight metallic materials. Calphad 62:1–17.
6. Pan H, Ren Y, Fu H (2016) Recent developments in rare-earth free wrought magnesium alloys having high strength: A review. J. Alloys Compd. 663:321–331.
7. Park SH, Jung JG, Kim YM (2015) A new high-strength extruded Mg-8Al-4Sn-2Zn alloy. Mater. Lett. 139:35–38.
8. Liu C, Chen H, He C (2016) Effects of Zn additions on the microstructure and hardness of Mg-9Al-6Sn alloy. Mater. Charact. 113:214–221.
9. Saboungi ML, Hsu CC (1977) Computation of isothermal sections of the Al-H-Mg system. Calphad 1(3):237–251.
10. Saunders N (1990) A review and thermodynamic assessment of the Al-Mg and Mg-Li systems. Calphad 14(1):61–70.
11. Murray JL (1982) The Al-Mg (aluminum-magnesium) system. J. Phase Equilib. 3(1):60.
12. Zuo Y, Chang YA (1993) Thermodynamic calculation of the Al-Mg phase diagram. Calphad 17(2):161–174.
13. Goel NC, Cahoon JR, Mikkelsen B (1989) An experimental technique for the rapid determination of binary phase diagrams: the Al-Mg system. Metall. Trans. A 20(2):197–203.
14. Chartrand P, Pelton AD (1994) 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 Equilib. 15 (6):591–605.
15. Liang P, Tarfa T, Robinson JA (1998) Experimental investigation and thermodynamic calculation of the Al-Mg-Zn system. Thermochim. Acta 314(1–2):87-110.
16. Su HL, Harmelin M, Donnadieu P (1997) Experimental investigation of the Mg-Al phase diagram from 47 to 63 at.% Al. J. Alloys Compd. 247(1–2):57-65.
17. Clark JB, Zabdyr L, Moser Z (1988) Phase diagrams of binary magnesium alloys. ASM International, Materials Park, OH, 353–364.
18. Chadwick RJ (1928) The constitution of the alloys of magnesium and zinc. J. I. Met. 449:285–299.
19. Hume-Rothery W, Rounsefell ED (1929) The system magnesium-zinc. J. I. Met. 41:119–138.
20. Park JJ, Wyman LL (1957) Phase relationship in Mg alloys. WADC Technical Report 57–504:Astia Document No. AD142110.
21. Higashi I, Shiotani N, Uda M (1981) The crystal structure of $Mg_{51}Zn_{20}$. J. Solid State Chem. 36(2):225–233.
22. Agarwal R, Fries SG, Lukas HL (1992) Assessment of the Mg-Zn System. Z. Metallkd. 83(4):216–223.
23. Wasiur-Rahman S, Medraj M (2009) Critical assessment and thermodynamic modeling of the binary Mg-Zn, Ca-Zn and ternary Mg-Ca-Zn systems. Intermetallics 17(10):847–864.
24. Massalski E, Ohio TB (1990) Metals A. S. M. Binary Alloy Phase Diagrams Park.
25. Ghosh P, Mezbahul-Islam MD, Medraj M (2012) Critical assessment and thermodynamic modeling of Mg-Zn, Mg-Sn, Sn-Zn and Mg-Sn-Zn systems. Calphad 36:28–43.
26. Morishita M, Koyama K, Shikata S (2004) Standard gibbs energy of formation of $Mg_{48}Zn_{52}$ determined by solution calorimetry and measurement of heat capacity from near absolute zero kelvin. Metall. Mater. Trans. B 35(5):891–895.
27. Morishita M, Yamamoto H, Shikada S (2006) Thermodynamics of the formation of magnesium-zinc intermetallic compounds in the temperature range from absolute zero to high temperature. Acta Mater. 54(11):3151–3159.
28. Morishita M, Koyama K, Shikada S (2005) Calorimetric study of $Mg_2Zn_3$. Z. Metallkd. 96(1):32–37.
29. Morishita M, Koyama K (2003) Calorimetric study of $MgZn_2$ and $Mg_2Zn_{11}$. Z. Metallkd. 94(9):967–971.
30. Meng FG, Wang J, Liu LB (2010) Thermodynamic modeling of the Mg-Sn-Zn ternary system. J. Alloy. Compd. 508(2):570–581.
31. Liang P, Seifert HJ, Lukas HL (1998) Thermodynamic modelling of the Cu-Mg-Zn ternary system. Calphad 22(4):527–544.
32. Qi HY, Huang GX, Bo H (2012) Experimental investigation and thermodynamic assessment of the Mg-Zn-Gd system focused on Mg-rich corner. J. Mater. Sci. 47(3):1319–1330.
33. Nayeb-Hashemi AA, Clark JB (1984) The Mg-Sn (Magnesium-Tin) system. Bull. Alloy Phase Diagrams 5(5):466–476.
34. Fries SG, Lukas HL (1993) Optimisation of the Mg-Sn system. J. Chim. Phys. 90:181–187.
35. Jung IH, Kang DH, Park WJ (2007) Thermodynamic modeling of the Mg-Si-Sn system. Calphad 31(2):192–200.
36. Jung IH, Kim J (2010) Thermodynamic modeling of the Mg-Ge-Si, Mg-Ge-Sn, Mg-Pb-Si and Mg-Pb-Sn systems. J. Alloys Compd. 494(1–2):137-147.
37. Kang YB, Pelton AD (2010) Modeling short-range ordering in liquids: the Mg-Al-Sn system. Calphad 34(2):180–188.
38. Morishita M, Koyama K (2005) Standard entropy of formation of $SnMg_2$ at 298 K. J. Alloys Compd. 398(1–2):12-15.
39. Hultgren R, Desai PD, Hawkins DT (1973) Selected Values of the Thermodynamic. Properties of Binary Alloys, American Society for Metals, Metals Park, Ohio.
40. Murray JL (1983) The Al-Zn (aluminum-zinc) system. Bull. Alloy Phase Diagrams 4(1):55–73.
41. Mey SA, Effenberg G (1986) A thermodynamic evaluation of the aluminum-zinc system Z. Metallkd. 77(7):449–453.
42. Mey SA (1993) Re-evaluation of the aluminum-zinc system Z. Metallkd. 84(7):451–455.

43. Chen SL, Chang YA (1993) A thermodynamic analysis of the Al-Zn system and phase diagram calculation. Calphad 17(2):113–124.
44. Mathon M, Jardet K, Aragon E (2000) Al-Ga-Zn system: reassessments of the three binary systems and discussion on possible estimations and on optimisation of the ternary system. Calphad 24(3):253–284.
45. Luo Q, Li Q, Zhang JY (2013) Experimental investigation and thermodynamic optimization of the Al-Zn-Ti system in the Al-rich corner. Intermetallics 33:73–80.
46. Liang SM, Schmid-Fetzer R (2016) Thermodynamic assessment of the Al-Cu-Zn system, Part III: Al-Cu-Zn ternary system. Calphad 52:21–37.
47. Hayes FH (1991) User aspects of phase diagrams: proceedings of the International Conference, held at the Joint Research Centre, Petten, The Netherlands, 25–27th June, 1990. Woodhead Pub Ltd.
48. Ansara I, Dinsdale AT, Rand MH (1998) COST 507, thermochemical database for light metal alloys, in: European Communities, vol. 2, Belgium.
49. Flandorfer H, Rechchach M, Elmahfoudi A (2011) Enthalpies of mixing of liquid systems for lead free soldering: Al-Cu-Sn system. J. Chem. Thermodyn. 43(11):1612–1622.
50. Cheng T, Tang Y, Zhang L (2019) Update of thermodynamic descriptions of the binary Al-Sn and ternary Mg-Al-Sn systems. Calphad 64:354–363.
51. Lee BJ (1996) Thermodynamic assessments of the Sn-Zn and In-Zn binary systems. Calphad 20(4):471–480.
52. Ohtani H, Miyashita M, Ishida K (1999) Thermodynamic study of the Sn-Ag-Zn system. J. Jpn. I. Met. 63:685–694.
53. Yang C, Chen F, Gierlotka W (2008) Thermodynamic properties and phase equilibria of Sn-Bi-Zn ternary alloys. Mater. Chem. Phys. 112(1):94–103.
54. Chen SL (1994): Ph.D. Thesis, University of Wisconsin–Madison, Madison, WI.
55. Kattner UR, Boettinger WJ (1992) Thermodynamic calculation of the ternary Ti-Al-Nb system. Mat. Sci. Eng. A-Struct. 152(1–2):9-17.
56. Chen SL, Zuo Y, Liang H (1997) A thermodynamic description for the ternary Al-Mg-Cu system. Metall. Mater. Trans. A 28(2):435–446.
57. Liang H, Chen SL, Chang YA (1997) A thermodynamic description of the Al-Mg-Zn system. Metall. Mater. Trans. A 28 (9):1725–1734.
58. Doernberg E, Kozlov A, Schmid-Fetzer R (2007) Experimental investigation and thermodynamic calculation of Mg-Al-Sn phase equilibria and solidification microstructures. J. Phase Equilib. Diff. 28(6):523–535.
59. Bamberger M (2006) Phase formation in Mg-Sn-Zn alloys-thermodynamic calculations versus experimental verification. J. Mater. Sci. 41(10):2821–2829.
60. Jung IH, Park WJ, Ahn S (2006) Thermodynamic modeling of the Mg-Sn-Zn-Al system and its application to mg alloy design. Magnesium Technology 2006:457–461.
61. Lin KL, Wen LH, Liu TP (1998) The microstructures of the Sn-Zn-Al solder alloys. J. Electron. Mater. 27(3):97–105.
62. Sidorov V, Drápala J, Uporov S (2011) Some physical properties of Al-Sn-Zn melts. EPJ Web of Conferences. EDP Sciences 15:01022.
63. Smetana B, Zlá S, Kroupa A (2012) Phase transition temperatures of Sn-Zn-Al system and their comparison with calculated phase diagrams. J. Therm. Anal. Calorim. 110(1):369–378.
64. Drápala J, Kostiuková G, Smetana B (2015) Thermodynamic and experimental study of tin-zinc-aluminum ternary system. Adv. Sci., Eng. Med. 7(4):291–295.
65. Knott S, Mikula A (2002) Thermodynamic properties of liquid Al-Sn-Zn alloys: A possible new lead-free solder material. Mater. Trans. 43(8):1868–1872.
66. Knott S, Flandorfer H, Mikula A (2005) Calorimetric investigations of the two ternary systems Al-Sn-Zn and Ag-Sn-Zn. Z. Metallkd. 96(1):38–44.
67. Cheng T, Zhang LJ (2019) Thermodynamic re-assessment of the Al-Sn-Zn ternary system. J. Min. Metall. Sect. B-Metall. 55 (3):439–449.
68. Dinsdale AT (1991) SGTE data for pure elements. Calphad 15 (4):317–425.
69. Ansara I, Burton B, Chen Q (2000) Models for composition dependence. Calphad 24(1):19–40.
70. Hao D, Hu B, Zhang K (2014) The quaternary Al-Fe-Ni-Si phase equilibria in Al-rich corner: experimental measurement and thermodynamic modeling. J. Mater. Sci. 49(3):1157–1169.
71. Muggianu YM, Gambino M, Bros JP (1975) Enthalpies of formation of liquid alloys. J. Chim. Phys. 72(1):83–88.
72. Kim BH, Jeon JJ, Park KC (2008) Microstructural characterisation and mechanical properties of Mg-xSn-5Al-1Zn alloys. Int. J. Cast Metals Res. 21(1–4):186-192.