THERMODYNAMIC PROPERTIES PREDICTION OF Mg-Al-Zn MELTS BASED ON THE ATOM AND MOLECULE COEXISTENCE THEORY

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Abstract

A developed and verified thermodynamic model based on the atom and molecule coexistence theory (AMCT) is employed to predict activities relative to pure liquids in standard state in Mg-Al, Mg-Zn, Al-Zn and Mg-Al-Zn melts through the calculated mass action concentrations of structural units, i.e., N_i. According to AMCT, N_i can be extrapolated and calculated by the chemical equilibrium constant of a structural molecule, i.e., K_i, in the Mg-Al-Zn ternary system and binary subsystems. In this paper, the standard Gibbs free energy function, for reported activities and mixing thermodynamic properties in Mg-Al, Mg-Zn and Al-Zn melts, was regressed and optimized. The results showed that K_i and N_i were deduced by Gibbs free energy function at the studied temperature. The results of calculating thermodynamic properties in the full composition range for liquid Mg-Al-Zn from 880 to 1100 K, as well as Mg-Al from 923 to 1073 K, Mg-Zn from 880 to 973 K and Al-Zn from 1000 to 1073 K, are presented in the paper by coupling with N_i and AMCT. An excellent agreement is noticed between the calculated values of this study and measured thermodynamic data from the references, suggesting that the AMCT can be well applied to describe and predict the activities of the Mg-Al-Zn system and its subsystems.

Keywords: Thermodynamic prediction model; Atom and molecule coexistence theory; Regression and optimization; Mass action concentrations; The Mg-Al-Zn system and its subsystems

1. Introduction

Magnesium, aluminum and zinc alloys have been the promising materials in various fields, including the lightweight metal, functional materials in electronics and protective coatings [1-3]. Since the various applications of Mg-Al-Zn, previous researchers had directed tremendous attention to the Mg-Al-Zn system, especially to the thermodynamic behavior of the molten system. During the investigation of thermodynamic properties in liquid Mg-Al-Zn ternary system including Mg-Al [3-6], Mg-Zn [8-10] and Al-Zn [11-13] subsystems, some thermodynamic models and empirical formulas, listed in Table 1, were established and introduced to describe thermodynamic reaction abilities. Nevertheless, one of the potential problems for thermodynamic models is that the artificial parameters are employed in prediction formulas, triggering controversial results in the prediction models, so that the above mentioned prediction

models may not work well. Moreover, very limited number of studies have been devoted to the thermodynamic properties in Mg-Al-Zn alloys. Even though Živković *et al*. [4] calculated the activities between 900 to 1200 K in the Mg-Al-Zn system by the general solution model, thermodynamic data for comparisons is not sufficient. Liang *et al*. [5] assessed thermodynamics by the crystal structure and cubic symmetry information, but within a limited temperature range in Mg-Al-Zn melts. Therefore, a thermodynamic prediction model without artificial parameters should be employed to investigate thermodynamic properties of Mg-Al-Zn system with more comparisons and wider temperature intervals in the present paper.

A thermodynamic model without artificial parameters, based on the atom and molecule coexistence theory, can be applied to predict the activities through the calculated mass action concentrations in binary solutions and binary melts [14]. The atom and molecule coexistence theory, *i.e.,*
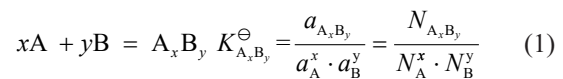
AMCT, has been developed and verified through comparisons between the measured activities relative to pure liquids as standard state and mass action concentrations of structural units, *i.e.*, N_i, indicating that the mass action concentrations can be applied to substitute the measured activities of corresponding elements relative to pure liquids as standard state [15-18]. Therefore, in order to investigate the thermodynamic properties of Mg-Al-Zn in the full composition range more effectively, AMCT can be well applied to discuss the reaction abilities above the liquid temperature.

Considering great practical significance, the current research aims to contribute to the thermodynamic study of Mg-Al-Zn ternary melts and its binary subsystems on the basis of AMCT in the full composition range from 880 K to 1100 K by calculating N_i. Since N_i can be deduced and calculated according to the obtained $K_i^\ominus$ in Mg-Al-Zn ternary melts and binary subsystems, the process of regression and modification for the chemical equilibrium constant and standard molar Gibbs free energy function of structural molecules, *i.e.*, $K_i^\ominus$ and, $\Delta G_i^\ominus$ in Mg-Al, Mg-Zn and Al-Zn binary melts will be presented in the paper. What's more, once $K_i^\ominus$ and $\Delta G_i^\ominus$ were obtained, thermodynamic properties at the given temperature in the full composition range can be extrapolated and calculated through AMCT. In order to test the accuracy of thermodynamic

properties predicted by AMCT, the calculation thermodynamics results are compared with the reference data in the Mg-Al-Zn ternary system and binary subsystems in this paper.

2. Hypotheses

According to the AMCT [15-18], Zhang *et al.* [16, 17] argued that both atoms and their intermetallic compound molecules, *i.e.*, structural characteristics, can coexist in melts. The main points of AMCT [15-18] can be briefly summarized as: 1) Structural units are composed of both atoms and molecules according to phase diagram at elevated temperature; 2) The atoms would participate in chemical equilibrium reactions with intermetallic molecules, such as:

$$x\mathrm{A} + y\mathrm{B} = \mathrm{A}_x\mathrm{B}_y \quad K_{\mathrm{A}_x\mathrm{B}_y}^\ominus = \frac{a_{\mathrm{A}_x\mathrm{B}_y}}{a_\mathrm{A}^x \cdot a_\mathrm{B}^y} = \frac{N_{\mathrm{A}_x\mathrm{B}_y}}{N_\mathrm{A}^x \cdot N_\mathrm{B}^y} \quad (1)$$

where $K_{\mathrm{A}_x\mathrm{B}_y}^\ominus$ presents the chemical equilibrium constant of $\mathrm{A}_x\mathrm{B}_y$; a_i the activity of the given structural unit; N_i the mass action concertation of the structural unit; 3) The chemical reaction above obeys the mass action law; 4) The mass action concentrations can be applied to substitute the measured activities of corresponding elements relative to pure liquids as standard state.

Given assumptions and main points, Zhang *et al.*

Table 1. Models of previous studies on thermodynamic properties in Mg-Al-Zn system

Temperature /K	System	Model description	Ref.
900-1200	Al-Mg-Zn	Živković *et al.* applied the general solution model to calculate the activities and mixing thermodynamics, which needs regular-solution parameters relying on the temperature.	[4]
933	Al-Mg-Zn	Liang *et al.* optimized the selected coefficients with thermodynamic, crystallographic information and sublattice formula to investigate the integral enthalpy and chemical potential.	[5]
883-933	Al-Mg-Zn	Kim *et al.* investigated calorimetric and activities in liquid Al-Mg-Zn by the association model with parameters relying on the binary bordering liquid alloys.	[6]
947-1080	Al-Mg	Tang *et al.* proposed an exponential formulation to replace the liner interaction parameters in Redlich-Kister polynomial, in order to describe excess thermodynamic properties.	[7]
680-923	Mg-Zn	Yuan *et al.* studied the mixing enthalpy data and activity data by means of the substitutional solution model, where thermodynamic parameters had been optimized by the Thermo-Calc software.	[8]
680-1000	Mg-Zn	Ghosh *et al.* modified a set of self-consistent parameters in quasi-chemical model and symmetric Kohler geometric model to predict thermodynamics.	[10]
1000	Al-Zn	Balanović *et al.* calculated the thermodynamic properties based on the Oelsen thermodynamic method, where the concentration fluctuation in the long-wavelength limit parameters were introduced.	[11]
880-1100	Mg-Al-Zn and it's binary subsystems	The thermodynamic properties Mg-Al-Zn and binary subsystems melts are determined by AMCT	This study

[16, 17] introduced formulas and conclusions of mixing thermodynamic properties presented as follows.

$$\Delta_{mix} G_m = \sum x \cdot \left[\sum_{i=3}^{i} N_i \cdot \Delta G_i^\ominus + RT \sum_{j=1}^{j} N_j \cdot \ln N_j \right] \quad (2)$$

$$\Delta_{mix} H_m = \sum x \cdot \sum_{i=3}^{i} N_i \cdot \Delta H_i^\ominus \quad (3)$$

$$\Delta_{mix} S_m = \sum x \cdot \left[\sum_{i=3}^{i} N_i \cdot \Delta S_i^\ominus - R \sum_{j=1}^{j} N_j \cdot \ln N_j \right] \quad (4)$$

where $\Delta_{mix} G_m$ is the integral molar Gibbs energy of mixing; $\Delta_{mix} H_m$ the integral molar enthalpy of mixing; $\Delta_{mix} S_m$ the integral molar entropy of mixing; $\sum x$ the sum mass action concentration of component elements; T the temperature; R the gas constant; $\Delta G_i^\ominus$, $\Delta H_i^\ominus$ and $\Delta S_i^\ominus$ are the Gibbs energy, enthalpy and entropy of the structural molecule i, respectively.

3. Results and discussion

In order to investigate thermodynamic properties in Mg-Al-Zn melts based on AMCT, the information of structural units in the Mg-Al-Zn ternary system should be deduced by Mg-Al, Mg-Zn and Al-Zn binary subsystems. Zhang et al. [16, 17] have studied activities and mixing thermodynamics in the molten Mg-Al at 1073 K and Al-Zn at 1000 K. However, due to the calculation results built on a given temperature without optimization and the lack of enough measured data for comparison [16-17] for Mg-Al and Al-Zn, it is necessary to investigate and confirm the Mg-Al, Al-Zn system, as well as Mg-Zn melts with more data. The present paper would reassess the Mg-Al, Al-Zn systems and evaluate the Mg-Zn, Mg-Al-Zn by verifying the results, both measured and calculated in the mentioned melts. Hence, combined with reported activities, mixing thermodynamics and chemical reaction isotherm, the results of calculations would be more reliable through regression and modification in the present paper.

3.1 Mg-Al binary system

According to AMCT [15-18], the mass action concentration, i.e., N_i can be calculated, once $K_i^\ominus$ could be obtained. In order to describe N_i at other temperature, all the $K_i^\ominus$ of structural molecules at the same temperature should be known. However, very limited amounts of experimental activities data have been found in the literature for Mg-Al system, so that $K_i^\ominus$ can't be regressed directly based on AMCT [15-18]. Fortunately, Bhatt et al. [19] measured the activity and mixing parameter of liquid Al-Mg alloys by vapor pressure measurements at 1000 K, while Lu,

Tiwari, and Hultgren et al. [20-22] applied EMF method to measure the activities and mixing thermodynamics measurement at 1073 K. Considering the lack of enough measured activities with respect to the wider temperature and concentration ranges in liquid Mg-Al, optimization should be applied to those measured data, so that the function between $\Delta S_i^\in$ and T could be obtained.

According to the previous works of Zhang et al. [16, 17], two kinds of atoms, Mg and Al, as well as three kinds of structural molecules, i.e., Mg_2Al, $Mg_{17}Al_{12}$ and $MgAl_2$, coexisting in the Mg-Al system at 1073 K, are included in the present study. In addition, once the activities and the mixing thermodynamics from literature [19-22] are substituted into Eqs. (6)-(8), the thermodynamic parameters, i.e., $K_i^\ominus$, $\Delta H_i^\ominus$, $\Delta S_i^\ominus$ and $\Delta G_i^\ominus$ summarized as Table 2, could be regressed.

$$1 - \left(x_{Al} + 1 \right) N_{Mg} - \left(1 - x_{Mg} \right) N_{Al} =$$
$$\left(x_{Al} - 2x_{Mg} + 1 \right) K_{Mg_2Al}^\ominus N_{Mg}^2 N_{Al}$$
$$+ \left(12x_{Al} - 17x_{Mg} + 1 \right) K_{Mg_{17}Al_{12}}^\ominus N_{Mg}^{17} N_{Al}^{12} + \quad (5)$$
$$\left(2x_{Al} - x_{Mg} + 1 \right) K_{MgAl_2}^\ominus N_{Mg} N_{Al}^2$$

$$\Delta_{mix} G_m = \sum x \left[\sum_{i=3}^{i} N_i \cdot \Delta G_i^\ominus + RT \sum_{j=1}^{j} N_j \cdot \ln N_j \right]$$
$$= \left(N_{Mg} + N_{Al} \right) \begin{pmatrix} N_{MgAl_2} \Delta G_{MgAl_2}^\ominus \\ + N_{Mg_{17}Al_{12}} \Delta G_{Mg_{17}Al_{12}}^\ominus \\ + N_{Mg_2Al} \Delta G_{Mg_2Al}^\ominus + \\ RT \begin{pmatrix} N_{Mg} \ln N_{Mg} + N_{Al} \ln N_{Al} \\ + N_{MgAl} \ln N_{MgAl} \\ + N_{Mg_{17}Al_{12}} \ln N_{Mg_{17}Al_{12}} \\ + N_{Mg_2Al} \ln N_{Mg_2Al} \end{pmatrix} \end{pmatrix} \quad (6)$$

$$\Delta_{mix} H_m = \sum x \sum_{i=3}^{i} N_i \cdot \Delta H_i^\ominus$$
$$= \left(N_{Mg} + N_{Al} \right) \begin{pmatrix} N_{MgAl_2} \Delta H_{MgAl_2}^\ominus + \\ N_{Mg_{17}Al_{12}} \Delta H_{Mg_{17}Al_{12}}^\ominus \\ + N_{Mg_2Al} \Delta H_{Mg_2Al}^\ominus \end{pmatrix} \quad (7)$$

$$\Delta_{mix} S_m = \sum x \left[\sum_{i=3}^{i} N_i \cdot \Delta S_i^\ominus - R \sum_{j=1}^{j} N_j \cdot \ln N_j \right]$$
$$= \left(N_{Mg} + N_{Al} \right) \begin{pmatrix} N_{MgAl_2} \Delta S_{MgAl_2}^\ominus + N_{Mg_{17}Al_{12}} \Delta S_{Mg_{17}Al_{12}}^\ominus \\ + N_{Mg_2Al} \Delta S_{Mg_2Al}^\ominus \\ -R \begin{pmatrix} N_{Mg} \ln N_{Mg} + N_{Al} \ln N_{Al} \\ + N_{MgAl} \ln N_{MgAl} + N_{Mg_{17}Al_{12}} \ln N_{Mg_{17}Al_{12}} \\ + N_{Mg_2Al} \ln N_{Mg_2Al} \end{pmatrix} \end{pmatrix} \quad (8)$$

$$\Delta G_i^{\ominus} = - RT\ln K_i^{\ominus} = \Delta H_i^{\ominus} - T\Delta S_i^{\ominus} \qquad (9)$$

where Eq. (5) is the regression for primary $K_i^{\ominus}$; Eqs (9) is the chemical reaction isotherm; and j in Eq. (9) represents structural molecules, *i.e.,* Mg_2Al, $Mg_{17}Al_{12}$ and $MgAl_2$, respectively, according to AMCT [16-17].

During the calculation process, the measured activities of Mg and Al are assumed to be substituted by the mass action concentration, so that Eqs. (5) - (9) are the functions of $K_i^{\ominus}$, $\Delta H_i^{\ominus}$, $\Delta S_i^{\ominus}$ with N_{Mg} and N_{Al}. With the regressing of Eqs. (5) - (9) by the MATLAB software $K_i^{\ominus}$, $\Delta H_i^{\ominus}$, $\Delta S_i^{\ominus}$, as well as $\Delta G_i^{\ominus}$ can be optimized and obtained as it is shown in Table 2. Moreover, the standard molar Gibbs free energy of structural molecules in Mg-Al melts can be expressed as:

$$\Delta G_{Mg_2Al}^{\ominus} = - 54050 + 59.822T \qquad (10)$$

$$\Delta G_{Mg_{17}Al_{12}}^{\ominus} = -177538 + 27.248T \qquad (11)$$

$$\Delta G_{MgAl_2}^{\ominus} = - 22629 + 19.791T \qquad (12)$$

The $K_i^{\ominus}$, at the studied temperature, can be obtained from Eqs. (10) - (12), so that N_i at the same temperature can be calculated based on the AMCT [15-18]. In this paper, in order to describe N_i at more investigated temperature, Eqs. (10) - (12) were extrapolated to calculate $K_i^{\ominus}$ and N_i from 923 to 1073 K. Furthermore, comparisons of calculated quantities by AMCT with the reported activities of Mg or Al and mixing thermodynamic properties [19-22] from 923 to 1073 K are presented in Figure 1.

The results of comparisons between calculated mass action concentrations of Mg(N_{Mg}), Al(N_{Al}) as well as structural molecules N_{MgAl_2}, $N_{Mg_{17}Al_{12}}$, N_{Mg_2Al} by AMCT and measured activities of Mg (a_{Mg}), Al (a_{Al}) relative to pure liquids as standard state in the full composition range of Mg-Al melts are shown in Figure 1(*a*), (*c*) and (*e*) from 923 to 1073 K, respectively. Furthermore, Figure 1(*b*) and (*d*) present the comparison of mixing thermodynamics between calculated and reported of Mg-Al melts at 1000 K and 1073 K, respectively. As can be seen in Figure 1, calculated values have an excellent agreement with the measured data, obviously, indicating the calculated mass action concentration of N_{Mg} and N_{Al}

can be successfully applied to substitute the measured a_{Mg} and a_{Al} in Mg-Al melts in the full composition range from 923 to 1073K.

3.2 Mg-Zn binary system

Based on AMCT [15-18] and Mg-Zn phase diagram, six kinds of structural units, Mg, Zn, $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7 and MgZn, can coexist in molten Mg-Zn system. As the similar regressing process of Mg-Al [16, 17] and Al-Ti [15, 18], the primary regression of $\Delta S_i^{\ominus}$ at four studied temperatures can be obtained with the measured activities of Mg and Zn from the references [8-11, 23] and substituted into Eq. (13). In order to convince researchers, however, the primary $\Delta S_i^{\ominus}$ at four temperatures from Eq. (13) should be optimized with the chemical reaction isotherm, *i.e.*, Eq. (14).

$$1-\left(x_{Al}+1\right)N_{Mg} - \left(1 - x_{Mg}\right)N_{Zn} =$$
$$\left(x_{Al} - 2x_{Mg}+1\right)K_{MgZn_2}^{\ominus}N_{Mg}N_{Zn}^2$$
$$+\left(2x_{Al} - 11x_{Mg}+1\right)K_{Mg_2Zn_{11}}^{\ominus}N_{Mg}^2N_{Zn}^{11} \qquad (13)$$
$$+\left(4x_{Al} - 7x_{Mg}+1\right)K_{Mg_4Zn_7}^{\ominus}N_{Mg}^4N_{Zn}^7 +$$
$$\left(x_{Al} - x_{Mg}+1\right)K_{MgZn}^{\ominus}N_{Mg}N_{Zn}$$

$$\Delta G_i^{\ominus} = - RT\ln K_i^{\ominus} = \Delta H_i^{\ominus} - T\Delta S_i^{\ominus} \qquad (14)$$

where Eq. (13) is the regression for primary $K_i^{\ominus}$, according to AMCT[15-18]; i in Eq. (14) represents structural molecules, *i.e.*, $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7 and MgZn, respectively.

Compared to Section 3.1, there are more activities available in Mg-Zn, enabling $K_i^{\ominus}$ and $\Delta G_i^{\ominus}$ to be modified by the activities without mixing thermodynamics. Therefore, through the primary $K_i^{\ominus}$ and the chemical reaction isotherm, *i.e.*, Eqs. (13) - (14), the standard molar Gibbs free energy of structural molecules of $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7 and MgZn can be described as follows, so that $K_i^{\ominus}$ can be worked out and optimized at studied temperatures.

$$\Delta G_{MgZn_2}^{\ominus} = -170911 + 184.83T \qquad (15)$$

$$\Delta G_{Mg_2Zn_{11}}^{\ominus} = - 29537.93 - 21.0108T \qquad (16)$$

Table 2. *Regressed and optimized results for $K_i^{\ominus}$, $\Delta H_i^{\ominus}$, $\Delta S_i^{\ominus}$ and $\Delta G_i^{\ominus}$*

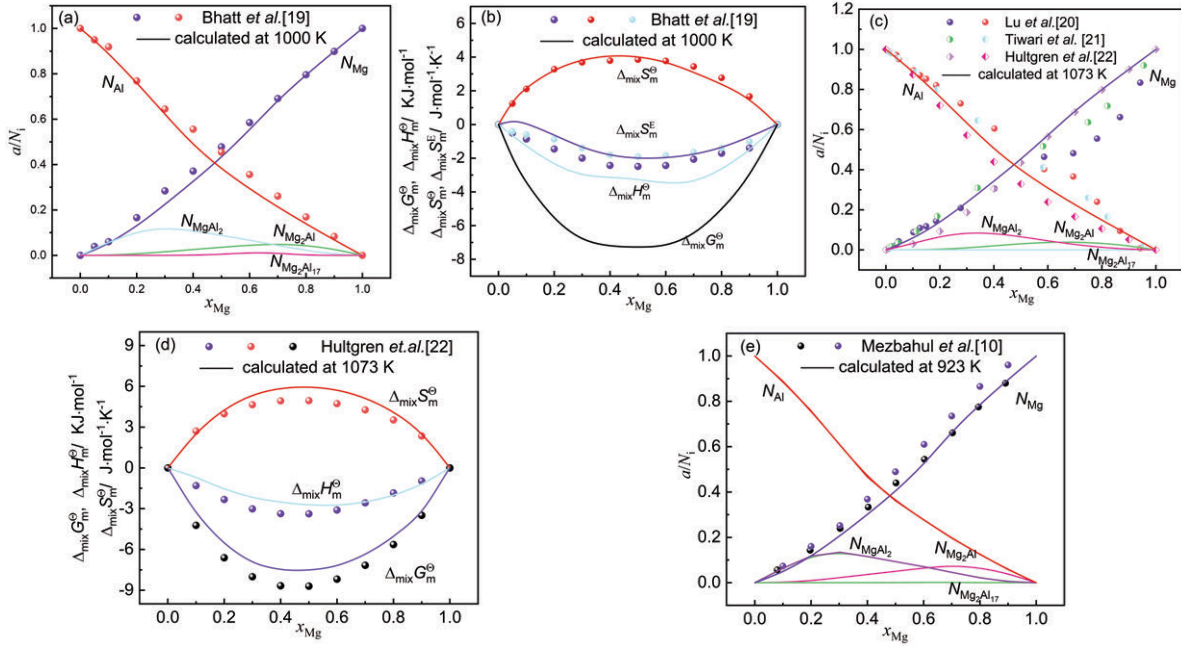| Compound	$\Delta H^{\ominus} / \left(J \cdot mol^{-1}\right)$	$\Delta S^{\ominus} / \left(J \cdot mol^{-1} \cdot K^{-1}\right)$	$\Delta G^{\ominus} / \left(J \cdot mol^{-1}\right)$		$K_i^{\ominus}$	
			1073 K	1000 K	1073 K	1000K
Mg_2Al	-54050	-59.822	-10139	-5,771.981	0.32092	0.49945
$Mg_{17}Al_{12}$	-177538	-27.248	-148301	-150290	16583835	70896627
$MgAl_2$	-22629	-19.791	-1393.59	-2838.33	1,169.079	1,406.904

Figure 1. *Comparison between calculated values and reported data in the full composition range of Mg-Al binary melts from 923 to 1073 K*

$$\Delta G^{\ominus}_{Mg_4Zn_7} = 2277.39 - 75.78T \qquad (17)$$

$$\Delta G^{\ominus}_{MgZn} = -31672.76 + 23.57T \qquad (18)$$

Table 3. *The optimized* $K^{\ominus}_i$ *in Mg-Zn system from 880 to 973 K*

	880 K	923 K	933 K	973 K
$K^{\ominus}_{MgZn_2}$	3.09	1.04	0.82	0.33
$K^{\ominus}_{Mg_2Zn_{11}}$	709.4	587.77	564.02	482.29
$K^{\ominus}_{Mg_4Zn_7}$	6657.3	6754.6	6776.1	6858.4
$K^{\ominus}_{MgZn}$	4.46	3.64	3.48	2.95

Therefore, coupled with AMCT [15-18], the modified equilibrium constants and mass action concentration can be deduced by the extrapolation of Eqs. (15) - (18). The modified $K^{\ominus}_i$ in Mg-Zn system from 880 to 973 K by Eqs. (15) - (18) is listed in Table 3, while the mass action concentrations and comparison activities reported are shown in Figure 2.

Figure 2 shows the comparison between calculated mass action concentration of structural units, such as, N_{Mg}, N_{Zn}, N_{MgZn}, $N_{Mg_2Zn_{11}}$, $N_{Mg_4Zn_7}$, N_{MgZn}, and measured activities of Mg (a_{Mg})or Zn (a_{Zn}) relative to pure liquids as standard state in the full composition range of Mg-Zn melts from 880 to 1073 K, respectively. It is obvious that the calculated mass

action concentrations of N_{Mg} and N_{Zn} nearly equal to the measured a_{Mg} and a_{Zn} in Mg-Zn binary melts in Figure 2(a) to (e), suggesting that thermodynamic properties in the Mg-Zn melts can be predicted and calculated by AMCT at investigated temperature.

3.3 Al-Zn binary system

Balanović *et al*. [11] measured and calculated the activity of Al and Zn at 1000 K, and Wasiur *et al*. [23] summarized the activities of Al-Zn at 1073 K, showing that both Al and Zn have a positive deviation with Raoult's law. Zhang *et al*. [16] argued that this kind of melts can be defined as the heterogeneous system and introduced the calculation process. In addition, Zhang *et al*. [16] had investigated thermodynamic properties of Al-Zn at 1000 K, and argued that there are three structural characteristics, Al, Zn and AlZn, coexisting in Al-Zn melts. Similar as optimization in Section 3.1, through measured data of activities at 1000 K and 1073 K as well as mixing thermodynamics data at 1000 K, this paper has regressed and modified the $\Delta G^{\ominus}_i$ and $K^{\ominus}_i$. Through the liner regression by the MATLAB software, $K^{\ominus}_i$, $\Delta H^{\ominus}_i$ as well as $\Delta S^{\ominus}_i$ can be optimized, with thermodynamic data substituted into Eqs. (2) - (3). with Eqs. (20) - (21).
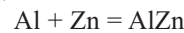
Al + Zn = AlZn

$$K^{\ominus}_{AlZn} = \frac{ab(2 - N_{Al} - N_{Zn})}{(a + b)N_{Al}N_{Zn}} \qquad (19)$$
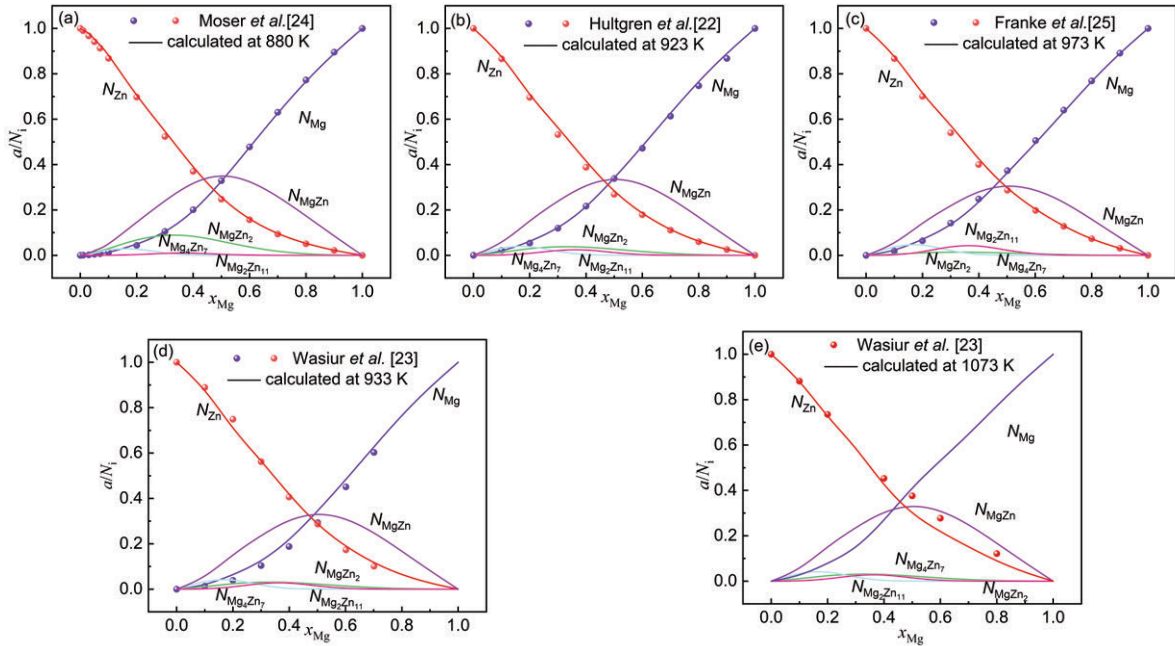
Figure 2. *Comparison of calculated mass action concentration N_i of structural units as $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7 and $MgZn$ in the full composition range of Mg-Zn from 880 to 1073 K, respectively.*

$$\Delta_{mix}G_m = (N_{Zn} + N_{Al}) \cdot$$

$$\begin{pmatrix} K_{AlZn}^{\ominus} N_{Zn} N_{Al} \Delta G_{AlZn}^{\ominus} + \\ RT \begin{pmatrix} N_{Al}\ln N_{Al} + \\ N_{Zn}\ln N_{Zn} + \\ K_{AlZn}^{\ominus} N_{Zn} N_{Al} \ln\left(K_{AlZn}^{\ominus} N_{Zn} N_{Al}\right) \end{pmatrix} \end{pmatrix} \quad (20)$$

$$\Delta_{mix}H_m = (N_{Zn} + N_{Al}) K_{AlZn}^{\ominus} N_{Zn} N_{Al} \Delta H_{AlZn}^{\ominus} \quad (21)$$

$$\Delta_{mix}S_m = (N_{Zn} + N_{Al}) \cdot$$

$$\begin{pmatrix} K_{AlZn}^{\ominus} N_{Zn} N_{Al} \Delta S_{AlZn}^{\ominus} - \\ R \begin{pmatrix} N_{Al}\ln N_{Al} + \\ N_{Zn}\ln N_{Zn} + \\ K_{AlZn}^{\ominus} N_{Zn} N_{Al} \ln\left(K_{AlZn}^{\ominus} N_{Zn} N_{Al}\right) \end{pmatrix} \end{pmatrix} \quad (22)$$

Where Eq. (19) is the regression for primary $K_i^{\ominus}$, according to AMCT[16]; and a and b are the molar fraction of component elements Al and Zn, respectively.

On the basis of $\Delta G_i^{\ominus} = \Delta H_i^{\ominus} - T\Delta S_i^{\ominus}$, the standard Gibbs free energy function of structural molecules in Al-Zn melts can be expressed as:

$$\Delta G_{AlZn}^{\ominus} = 18363.642 - 12.685T \quad (23)$$

Therefore, according to $K_i^{\ominus}$ obtained by Eq. (23), the thermodynamic properties of Al-Zn at 1000 K and 1073 K can be calculated. The results of calculating

mass action concentration in the full composition range of Al-Zn binary melts at different temperature are presented in Figure 3.

Figure 3 (a) and (c) show the comparisons between calculated mass action concentration of Al(N_{Al}), Zn(N_{Zn}) as well as N_{AlZn} and measured activities of Al, Zn (a_{Mg}, a_{Al}) relative to pure liquids as standard state in the full composition range of Al-Zn melts from 1000 to 1073 K, respectively. Figure 3(b) shows the comparison between calculated and reported of mixing thermodynamics. As can be seen in Figure 3, calculated values have an excellent agreement with the measured data, obviously, indicating the calculated mass action concentration of N_{Zn} and N_{Al} can be successfully applied to represent the measured a_{Mg} and a_{Al} in Al-Zn binary melts in the full composition range at a temperature from 1000 K to 1073 K.

3.4 Prediction in Mg-Al-Zn ternary system

Comparisons of calculated thermodynamic properties illustrated excellent consistency with the reported experimental data of Mg-Al, Mg-Zn, Al-Zn in Figures 1-3, respectively, suggesting the revised $K_i^{\ominus}$ and Gibbs free energy function worked well. In addition, the standard Gibbs free energy functions are assumed to never change at above liquid temperature, so that $K_i^{\ominus}$ at other investigated temperatures can be calculated with Eqs. (10) - (12), (15) - (18), and (23). Furthermore, the mass action concentration of component elements can be carried out by the
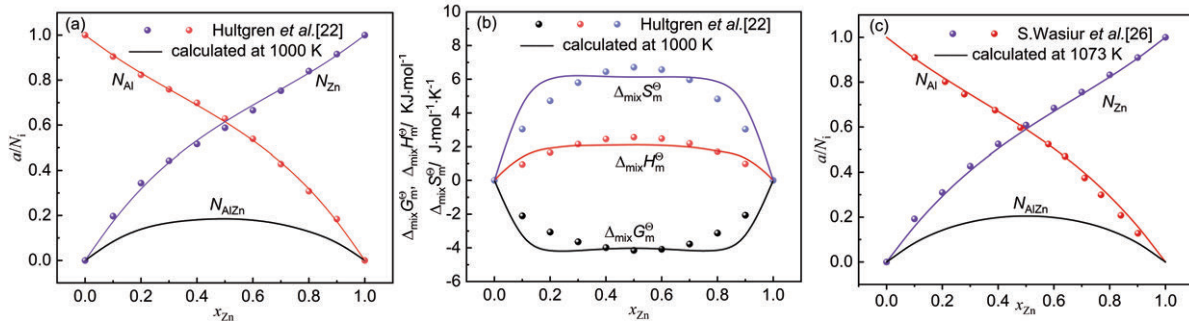
Figure 3. *Comparison of calculated values and reported data in the full composition range of Al-Zn binary melts at different temperature.*

deduced $K_i^\ominus$ at the studied temperature.

The prediction of thermodynamic properties of Mg-Al-Zn melts are carried out on the basis of AMCT with more comparison data in the present paper. Build on the AMCT and the assumptions by Zhang et al. [16] that the homogeneous system together with the heterogeneous system could be subject to the heterogeneous system, suggesting that the Mg-Al-Zn ternary system would be subject to the Al-Zn calculated process. Hence, according to AMCT [16] and aforementioned results in Mg-Al, Mg-Zn, Al-Zn systems, the structural units in Mg-Al-Zn heterogeneous system are composed of three kinds of atoms, Mg, Al and Zn, as well as eight kinds of molecules, $MgAl_2$, $Mg_{17}Al_{12}$, Mg_2Al, $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7, $MgZn$ and $AlZn$, including Mg, $MgAl_2$, $Mg_{17}Al_{12}$, Mg_2Al, $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7, $MgZn$ melts, Al, $MgAl_2$, $Mg_{17}Al_{12}$, Mg_2Al, and $AlZn$ melts, as well as Zn, $MgZn_2$, Mg_2Zn_{11}, Mg_4Zn_7, $MgZn$, $AlZn$ melts. Thermodynamic model can be expressed as:

$$a = x_{Mg} + x_{Mg_2Al} + x_{Mg_{17}Al_{12}} + x_{MgAl_2} + \tag{24}$$
$$x_{MgZn_2} + x_{Mg_2Zn_{11}} + x_{Mg_4Zn_7} + x_{MgZn}$$

$$b = x_{Al} + x_{Mg_2Al} + x_{Mg_{17}Al_{12}} + x_{MgAl_2} + x_{AlZn} \tag{25}$$

$$c = x_{Zn} + x_{MgZn_2} + x_{Mg_2Zn_{11}} + x_{Mg_4Zn_7} + x_{MgZn} + x_{AlZn} \tag{26}$$

Where a, b and c in Eqs. (24) - (26) are the molar fraction of component elements Mg, Al and Zn, respectively. What's more, the mass action concentration of component elements, N_i, based on Eqs. (24) - (26) and AMCT [16] can be expressed with Eqs. (27) - (29).

$$1 = N_{Mg} + \left(\begin{matrix} N_{Mg_2Al} + N_{Mg_{17}Al_{12}} + N_{MgAl_2} + N_{MgZn_2} + \\ N_{Mg_2Zn_{11}} + N_{Mg_4Zn_7} + N_{MgZn} \end{matrix} \right) / a$$

$$= N_{Mg} + \left(\begin{matrix} K_{Mg_2Al}^\ominus N_{Mg}^2 N_{Al} + K_{Mg_{17}Al_{12}}^\ominus N_{Mg}^{17} N_{Al}^{12} + \\ K_{MgAl_2}^\ominus N_{Mg} N_{Al}^2 + K_{MgZn_2}^\ominus N_{Mg} N_{Zn}^2 \\ + K_{Mg_2Zn_{11}}^\ominus N_{Mg}^2 N_{Zn}^{11} + K_{Mg_4Zn_7}^\ominus N_{Mg}^4 N_{Zn}^7 + \\ K_{MgZn}^\ominus N_{Mg} N_{Zn} \end{matrix} \right) / a \tag{27}$$

$$1 = N_{Al} + \left(N_{Mg_2Al} + N_{Mg_{17}Al_{12}} + N_{MgAl_2} + N_{AlZn} \right) / b$$

$$= N_{Al} + \left(\begin{matrix} K_{Mg_2Al}^\ominus N_{Mg}^2 N_{Al} + K_{Mg_{17}Al_{12}}^\ominus N_{Mg}^{17} N_{Al}^{12} + \\ K_{MgAl_2}^\ominus N_{Mg} N_{Al}^2 + K_{AlZn}^\ominus \cdot N_{Al} \cdot N_{Zn} \end{matrix} \right) / b \tag{28}$$

$$1 = N_{Zn} + \left(\begin{matrix} N_{MgZn_2} + N_{Mg_2Zn_{11}} + N_{Mg_4Zn_7} \\ + N_{MgZn} + N_{AlZn} \end{matrix} \right) / c$$

$$= N_{Zn} + \left(\begin{matrix} K_{MgZn_2}^\ominus N_{Mg} N_{Zn}^2 + K_{Mg_2Zn_{11}}^\ominus N_{Mg}^2 N_{Zn}^{11} + \\ K_{Mg_4Zn_7}^\ominus N_{Mg}^4 N_{Zn}^7 + K_{MgZn}^\ominus N_{Mg} N_{Zn} + \\ K_{AlZn}^\ominus N_{Al} N_{Zn} \end{matrix} \right) / c \tag{29}$$

According to Eqs. (27) - (29) and the $K_i^\ominus$ obtained from Eqs. (10) - (12), (15) - (18), and (23), mass action concentrations of components, i.e., N_{Al}, N_{Mg}, N_{Zn}, can be calculated at the studied temperature in Mg-Al-Zn system from 880 to 1100 K. In order to describe the thermodynamic properties of Mg-Al-Zn system at details, thermodynamic calculation would be carried out in two sections: 1) the results of thermodynamic calculations in the Mg-Al-Zn melts determined for nine sections with the constant molar ratios of two components at different temperature are given in the following figures, i.e., as Figure 4, the Al corner sections, Mg :Zn=1:3, 1:1 ,3:1; as Figure 5, the Mg corner sections, Al : Zn: =1:3, 1:1 ,3:1 as well Figure 6, the Zn corner sections, Al :Mg =1:3, 1:1 ,3:1; 2) the iso-activity diagrams at studied temperatures are introduced for Mg, Al and Zn component elements shown in Figure 7.

Thermodynamic properties of Mg-Al-Zn melts in the full composition range from 880 K to 1100 K are investigated in the paper by them with N_i. The N_i obtained in Section 3.1-3.4 has a good agreement with the reported activities data from literature. Therefore, the mass action concentrations of structural units based on the AMCT can well represent and describe the activities relative to pure liquids as standard state in Mg-Al, Mg-Zn and Al-Zn binary melts as well as the Mg-Al-Zn ternary melts.

The activities in Mg-Al-Zn has been shown above, therefore, according to AMCT, the mixing Gibbs free energy can be predicted and calculated by Eqs. (30) - (31).
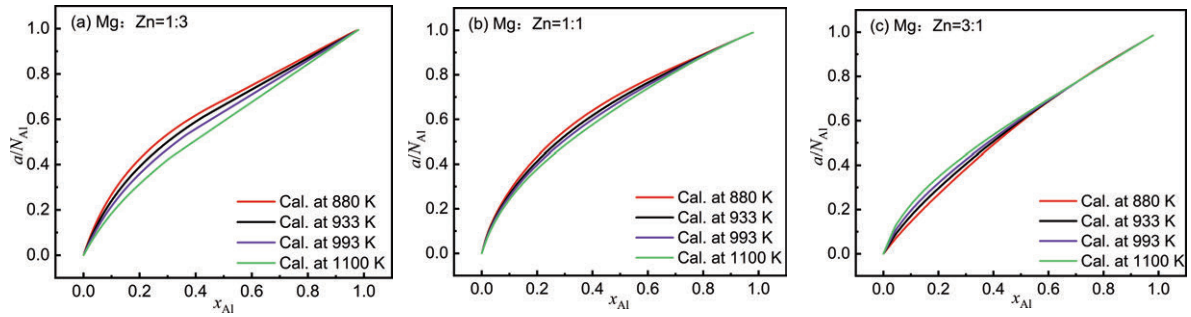
Figure 4. *Mass action concentration dependence on the composition and temperature in the studied Mg-Al-Zn system from the Al corner sections, Mg:Zn=1:3, 1:1, 3:1.*
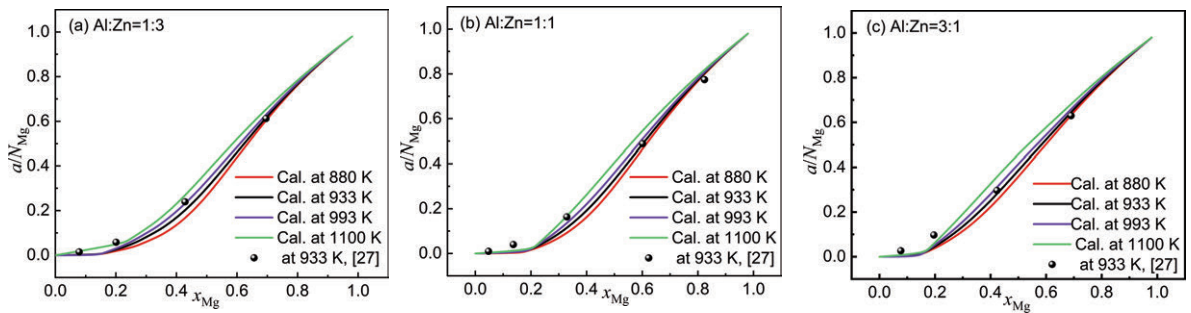

Figure 5. *Measured activities and mass action concentration dependence on the composition and temperature in the studied Mg-Al-Zn system from the Mg corner sections, Al:Zn=1:3, 1:1, 3:1.*
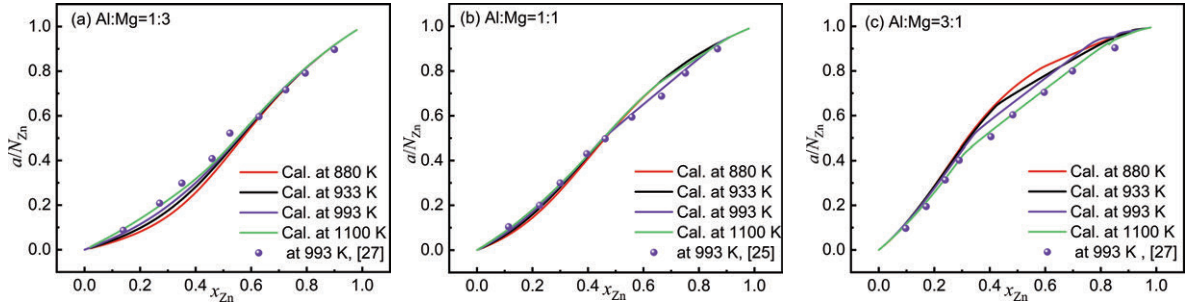

Figure 6. *Measured activities and mass action concentration dependence on the composition and temperature in the studied Mg-Al-Zn system from the Zn corner sections, Al:Mg=1:3, 1:1, 3:1.*
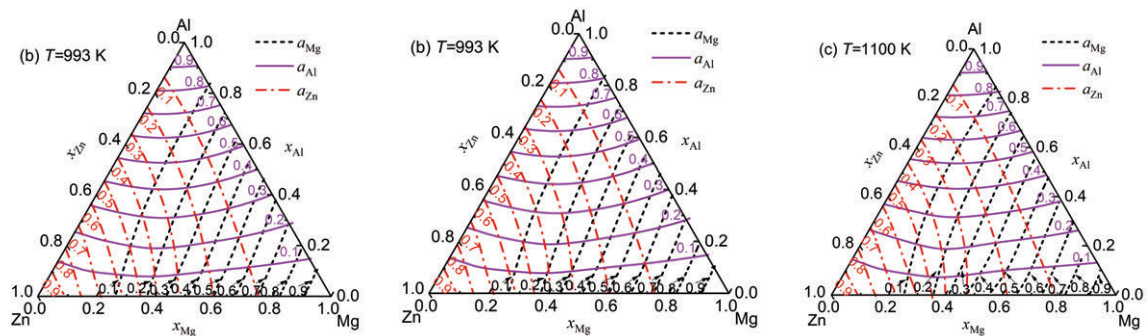

Figure 7. *Iso-activities diagrams for constitutive elements in the ternary Mg-Al-Zn system from 933 to 1100 K, respectively.*

$$\Delta G_i^{\ominus} = RT \ln N_i \tag{30}$$

$$\Delta_{mix} G_m = \sum x \cdot \left[\sum_{i=3}^{i} N_i \cdot \Delta G_i^{\ominus} + RT \sum_{j=1}^{j} N_j \cdot \ln N_j \right]$$

$$= RT \cdot \left(N_{Mg} + N_{Zn} + N_{Al} \right) \cdot$$

$$\begin{bmatrix}
N_{Mg} \cdot \ln N_{Mg} + N_{Zn} \cdot \ln N_{Zn} + \\
N_{Al} \cdot \ln N_{Al} + N_{Mg_2Al} \cdot \ln N_{Mg_2Al} \\
+ N_{Mg_{17}Al_{12}} \cdot \ln N_{Mg_{17}Al_{12}} + \\
N_{MgAl_2} \cdot \ln N_{MgAl_2} + N_{MgZn_2} \cdot \ln N_{MgZn_2} \\
+ N_{Mg_2Zn_{11}} \cdot \ln N_{Mg_2Zn_{11}} + N_{Mg_4Zn_7} \cdot \ln N_{Mg_4Zn_7} \\
+ N_{MgZn} \cdot \ln N_{MgZn} + N_{AlZn} \cdot \ln N_{AlZn}
\end{bmatrix} \tag{31}$$

The mixing Gibbs free energy was calculated same as for Figures 4~6, *i.e.* keeping the constant molar ratios of two components at different temperature. The results were presented as Figure 8, Figure 9, and Figure 10.

The standard molar mixing Gibbs free energy of Mg-Al-Zn melts change of composition from 880 K to 1100 K was further deduced. With the aid of AMCT, the thermodynamic properties of Mg-Al-Zn can be calculated and predicted well.

4. Conclusion

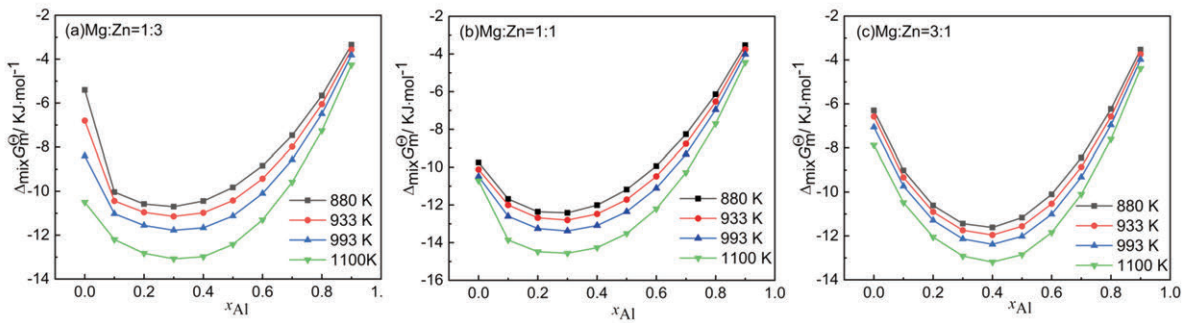According to the current research results on the alloy melt structure, it is generally believed that there

Figure 8. Mixing Gibbs free energy calculated dependence on the composition and temperature in the studied Mg-Al-Zn system from the Al corner sections, Mg:Zn=1:3, 1:1, 3:1.
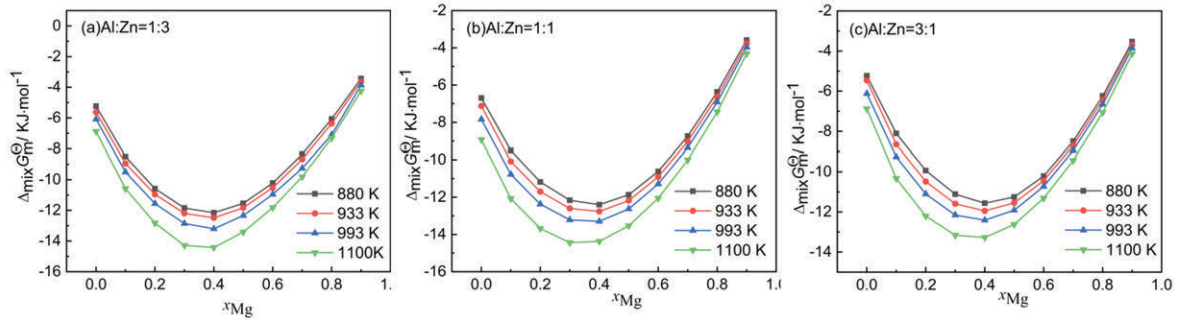
Figure 9. Mixing Gibbs free energy calculated dependence on the composition and temperature in the studied Mg-Al-Zn system from the Mg corner sections, Al:Zn=1:3, 1:1, 3:1.
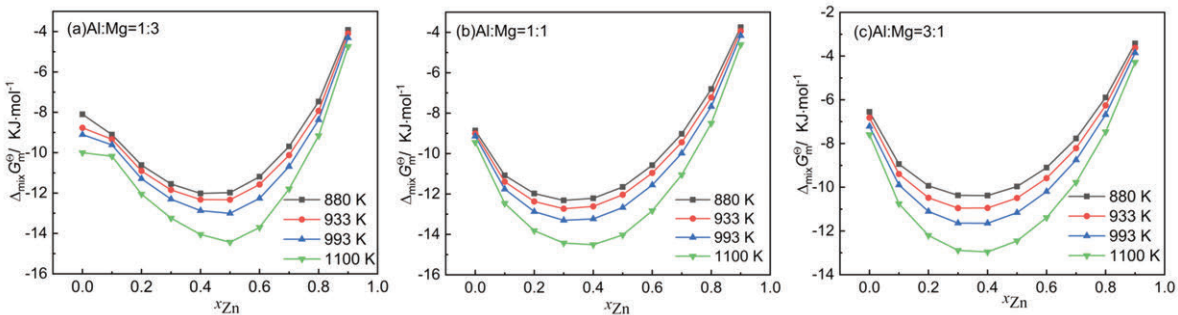
Figure 10. Mixing Gibbs free energy calculated dependence on the composition and temperature in the studied Mg-Al-Zn system from the Zn corner sections, Al;Mg=1:3, 1:1, 3:1

are short-range and medium-range ordered structures in the alloy melt [28], with various intermetallic compounds existing in the form of clusters or associates. Based on the above, Zhang *et al.* [17, 18] proposed the atom and molecule coexistence theory (AMCT) and the hypothesis. Therefore, the prediction of thermodynamic properties of Mg-Al-Zn melts has been carried out based on the AMCT. Critical evaluations and optimizations of the constituent subsystems Mg-Al, Mg-Zn and Al-Zn have been present.

1) The chemical reaction equilibrium constant and standard molar Gibbs free energy function of structural molecules, *i.e.*, $K_i^{\ominus}$ and $\Delta G_i^{\ominus}$, are regressed and optimized in Mg-Al melts with the activities and mixing thermodynamics at 1000 K and 1073 K, due to the lack of enough activities data. Moreover, the standard molar Gibbs free energy of structural molecules in Mg-Al melts can be expressed as:

$$\Delta G_{Mg_2Al}^{\ominus} = -54050 + 59.822T;$$

$$\Delta G_{Mg_{17}Al_{12}}^{\ominus} = -177538 + 27.248T;$$

$$\Delta G_{MgAl_2}^{\ominus} = -22629 + 19.791T;$$

2) The $K_i^{\ominus}$ in Mg-Zn binary system is regressed with sufficient activities data from 880 to 973 K. Therefore, coupling with chemical reaction isotherm and primary regressed $K_i^{\ominus}$, the standard molar Gibbs free energy of structural molecules in Mg-Zn melts can be deduced as:

$$\Delta G_{MgZn_2}^{\ominus} = -170911 + 184.83T;$$

$$\Delta G_{Mg_2Zn_{11}}^{\ominus} = -29537.93 - 21.0108T;$$

$$\Delta G_{Mg_4Zn_7}^{\ominus} = 2277.39 - 75.78T;$$

$$\Delta G_{MgZn}^{\ominus} = -31672.76 + 23.57T.$$

3) With measured data of activities at 1000 K and 1073 K as well as mixing thermodynamics data at 1000 K, $K_i^{\ominus}$ and $\Delta G_i^{\ominus}$ in Al-Zn have been regressed and optimized in this paper. What's more, the standard Gibbs free energy function of structural molecules in Al-Zn melts can be given as: $\Delta G_{AlZn}^{\ominus} = 18363.642 - 12.685T$.

4) Mass action concentrations of components, *i.e.*, N_{Al}, N_{Mg}, N_{Zn}, can be calculated at studied temperatures in Mg-Al-Zn system from 880 to 1100 K, through AMCT and the obtained standard Gibbs free energy functions in subsystems. Once $K_i^{\ominus}$ and $\Delta G_i^{\ominus}$ were obtained, thermodynamic properties at given temperature in the full composition range can be extrapolated and calculated with AMCT.

Thermodynamic calculations at studied temperatures are carried out in two sections: calculation of N_i determined for nine sections with the constant molar ratios of two components, *i.e.*, the Al corner sections, Mg:Zn=1:3, 1:1, 3:1; the Mg corner sections, Zn:Al=1:3, 1:1 ,3:1 and the Zn corner sections, Al:Mg =1:3, 1:1, 3:1, respectively, as well as the iso-activity diagrams.

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PREDVIĐANJE TERMODINAMIČKIH OSOBINA Mg-Al-Zn RASTOPA NA OSNOVU TEORIJE O KOEGZISTENCIJI ATOMA I MOLEKULA

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Apstrakt

Termodinamički model koji je razvijen i verifikovan na osnovu teorije o koegzistenciji atoma i molekula (AMCT) je primenjen za predviđanje aktivnosti u odnosu na čiste tečne metale kao standardno stanje u Mg-Al, Mg-Zn, Al-Zn i Mg-Al-Zn rastopima putem izračunavanja koncentracija mase strukturnih jedinica, tj. Ni. Prema ovoj teoriji, Ni može da se proceni i izračuna uz pomoć konstante hemijske ravnoteže za strukturni molekul, tj. Ki, u Mg-Al-Zn ternarnom sistemu i binarnom podsistemu. U ovom radu je funkcija Gibsove energije za dobijene aktivnosti i termodinamičke veličine mešanja Mg-Al, Mg-Zn i Al-Zn rastopa podvrgnuta postupku regresije i optimizacije. Rezultati su pokazali da su vrednosti za Ki i Ni dobijene pomoću funkcije Gibsove energije na ispitivanim temperaturama. Rezulati izračunavanja termodinamičkih osobina u celom opsegu sastava za tečni Mg-Al-Zn rastop na temeperaturama od 880 do 1100 K, kao i za Mg-Al rastop na temperaturama od 923 do 1073 K, Mg-Zn između 880 i 973 K i Al-Zn rastop između 1000 i 1073 K, predstavljeni su u ovom radu, zajedno sa Ni i teorijom koegzistencije atoma i molekula. Primećeno je odlično slaganje između izračunatih vrednosti dobijenih tokom ovog istraživanja i termodinamičkih podataka iz literature. Rezulatati ukazuju da teorija o koegzistenciji atoma i molekula može biti primenjena za opisivanje i predviđanje aktivnosti kod Mg-Al-Zn sistema i njegovih podsistema.

Ključne reči: Termodinamički model za predviđanje; Teorija koegzistencije atoma i molekula; Regresija i optimizacija; Koncentracija mase; Mg-Al-Zn sistem i njegovi podsistemi.