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Calorimetric investigations and thermodynamic calculation of Zn–Al–Ga system

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Abstract The results of calorimetric investigations and thermodynamic calculation of Zn–Al–Ga system are presented in this article. The research was carried out experimentally, using Oelsen calorimetry in temperature interval 800–1,000 K, and by thermodynamic calculation, applying general solution model in temperature interval 800–1,600 K. The enthalpy space diagram, the enthalpy isotherm diagram, as well as the values for zinc activities, partial and integral molar Gibbs excess energies have been determined. Comparison of experimentally obtained results and the results calculated by general solution model was done at the temperatures 800, 900, and 1000 K, which indicated a good mutual agreement.

Keywords Alloy thermodynamics · Calorimetry · Thermodynamic predicting methods · Ternary system Zn–Al–Ga

Introduction

Zinc–aluminum alloys—more commonly referred to as ZA and usually alloyed with copper and magnesium, were originally developed for gravity casting. They proven themselves in a wide variety of demanding applications as engineering materials well suited to applications requiring high as-cast strength, hardness, and wear resistance [1].

However, recently, ZA group of materials have been considered for applications as potential lead-free solders [2–5]. Therefore, an interest in investigation of different Zn–Al-based alloys increased recently in this field. One of the systems, interesting from that point of view, is the Zn–Al–Ga system, shown in Fig. 1.

Many researches has been done in order to study that system phase equilibria [6–12], while, thermodynamic investigations are not numerous and not complete [9, 13]. Ansara et al. [6] first established Zn–Al–Ga phase diagram by thermodynamic modeling, but Aragon et al. [7–9] gave significant contribution to its determination, using different experimental techniques. Further, Mathon et al. [10] presented the optimization of mentioned ternary system, while its phase equilibria were revisited by Jardet et al. [11, 12] using advanced experimental methods. Concerning thermodynamic investigations of Zn–Al–Ga system, there are only few data—experimental measurements of mixing enthalpies in the liquid at 717 K by Bourkba [13] and calorimetric measurements on two isobaric invariant reactions done by Aragon et al. [9].

As a contribution to the better knowledge of this system thermodynamics, the results of experimental investigation of selected sections in the Zn–Al–Ga system using Oelsen calorimetry and thermodynamic calculation according to general solution model, are presented in this article.

Experimental

The Oelsen calorimetry method, described in references [14–18], was used for the experimental thermodynamic analysis of the section from zinc corner with a constant molar ratio of Al–Ga = 1:1 in the ternary Al–Ga–Zn system. According to the requirements of the utilized method, the total volume of all samples was constant –0.5 cm^3, and their compositions and masses are given in Table 1.

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Fig. 1 The ternary Zn–Al–Ga system

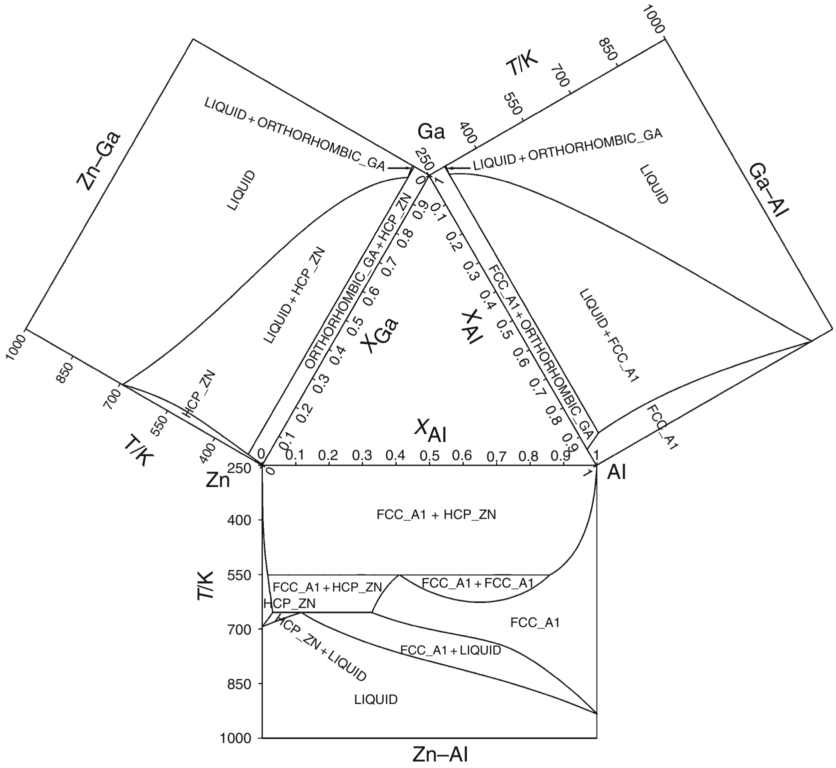

Table 1 Composition and masses of the investigated samples in Zn–AlGa section of Zn–Al–Ga system

Alloy	x_{Al}	x_{Ga}	x_{Zn}	m_{Al}/g	m_{Ga}/g	m_{Zn}/g
A1	0.5	0.5	0	0.6191	1.5998	0
A2	0.4	0.4	0.2	0.5116	1.3220	0.6201
A3	0.3	0.3	0.4	0.3967	1.0252	1.2824
A4	0.2	0.2	0.6	0.2738	0.7075	1.9912
A5	0.1	0.1	0.8	0.1419	0.3667	2.7518
A6	0	0	1	0	0	3.5700

Used metals were of the analytical grade. The water equivalent for the calorimeter was determined by a standard method using dissolved Na_2CO_3 and its value was 4,465 J/K. All experiments were carried out in air atmosphere. The samples were cooled in the furnace to the room temperature. Schematic representation of the used Oelsen calorimeter is given in Fig. 2. The calorimeter is composed of a Dewar flask with water, a stirrer, and a thermometer. It also contains housing from copper sheet into which the iron holder with the sample is added, after being heated in a separate oven to the initial temperature. The temperature of the sample is followed with NiCr–Ni thermocouple during cooling and simultaneously the temperature of the water is measured. The pair of values of a temperature measurement in the sample and in the water leads to a point on heat content curve.

Theoretical fundamentals

There are many methods for calculation of thermodynamic properties of ternary systems based on information about binary systems included in their composition, but general solution model [19, 20] was used for predicting of thermodynamic properties of Al–Ga–Zn system in this work.

The basic theoretical interpretations of mentioned model are given as follows:

$$\Delta G^E = x_1x_2\Delta G_{12}^E + x_2x_3\Delta G_{23}^E + x_1x_3\Delta G_{31}^E + x_1x_2x_3f_{123}\ldots \quad (1)$$

$$\Delta G_{ij}^E = X_iX_j\Big(A_{ij}^0 + A_{ij}^1(X_i - X_j) + A_{ij}^2(X_i + X_j)^2 + \ldots + A_{ij}^n(X_i - X_j)^n\Big)\ldots \quad (2)$$

where A_{ij}^0, A_{ij}^1, A_{ij}^2 are parameters for binary system "*ij*" independent of composition, only relying on temperature, and where X_i and X_j indicate the mole fraction of component "*i*" and "*j*" in "*ij*" binary system. The function f is the ternary interaction coefficient expressed by:

$$\begin{aligned} f_{123} =& (2\xi_{12}-1)\{A_{12}^2((2\xi_{12}-1)x_3+2(x_1-x_2))+A_{12}^1\} \\ &+(2\xi_{23}-1)\{A_{23}^2((2\xi_{23}-1)x_1+2(x_2-x_3))+A_{23}^1\} \\ &+(2\xi_{31}-1)\{A_{31}^2((2\xi_{31}-1)x_2+2(x_3-x_1))+A_{31}^1\}\ldots \end{aligned} \quad (3)$$

which is related to the Redlich–Kister ternary interaction parameter [21], so it can be written in the form:

$$f_{123} = x_1 L^0_{123} + x_2 L^1_{123} + x_3 L^2_{123} \ldots \tag{4}$$

with a temperature dependence taken as

$$L^v_{123} = \mathrm{a}^v + \mathrm{b}^v T (v = 0, 1, 2) \ldots \tag{5}$$

where L^v_{ijk} are the Redlich–Kister parameters for the ternary system "*ijk*" and x_i—mole fraction of the component '*i*'. The coefficients signed as ξ_{ij} in Eq. 3 present the similarity coefficients defined by η_i—called the deviation sum of squares:

$$\xi_{ij} = \eta_i / (\eta_i + \eta_j) \ldots \tag{6}$$

where

$$\begin{aligned} \eta_1 &= \int_{X_i=0}^{X_i=1} \left(\Delta G^E_{12} - \Delta G^E_{13}\right)^2 \mathrm{d}X_1 \\ \eta_2 &= \int_{X_i=0}^{X_i=1} \left(\Delta G^E_{21} - \Delta G^E_{23}\right)^2 \mathrm{d}X_2 \\ \eta_3 &= \int_{X_i=0}^{X_i=1} \left(\Delta G^E_{31} - \Delta G^E_{32}\right)^2 \mathrm{d}X_3 \ldots \end{aligned} \tag{7}$$

and

$$\begin{aligned} X_{1(12)} &= x_1 + x_3 \xi_{12} \\ X_{2(23)} &= x_2 + x_1 \xi_{23} \\ X_{3(31)} &= x_3 + x_2 \xi_{31} \ldots \end{aligned} \tag{8}$$

In all given equations, ΔG^E and $\Delta G^E{}_{ij}$ correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, and x_3 correspond to the mole fraction of components in investigated ternary system.

Results and discussion

Based on the cooling curves obtained by calorimetric measurements, according to the Oelsen procedure [14–16], temperature changes of the calorimeter were determined for all samples in the temperature range up to 1,000 K. According to this data, the enthalpy space diagram and enthalpy isotherm diagram were constructed and presented in Figs. 3 and 4, respectively (it should be noted that in presented diagrams 1 K corresponds to the value of water equivalent).

The basic equation in Oelsen thermodynamic analysis [14–16] is given as:

$$\frac{G^M_i}{T} = \int_{1/T_0}^{1/T} H_{x,T} \mathrm{d}\left(\frac{1}{T}\right) = R \ln a_i \ldots \tag{9}$$

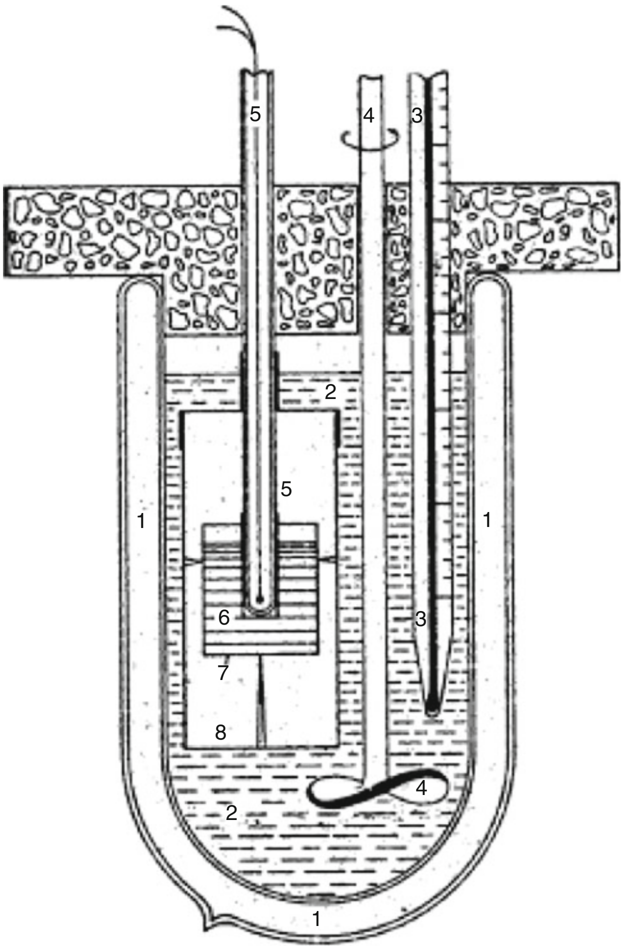

Fig. 2 Oesen calorimeter: *1* Dewar flask, *2* water, *3* Beckman thermometer, *4* stirrer, *5* NiCr–Ni thermocouple, *6* sample, *7* sample holder, *8* copper sheet, *9* thermal insulation

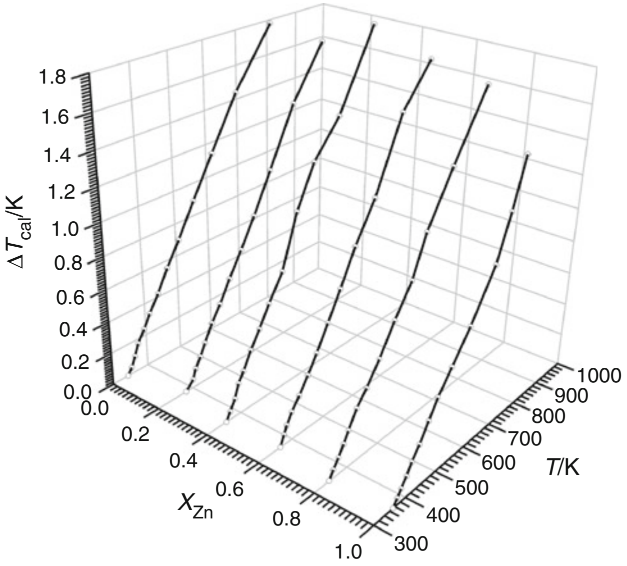

Fig. 3 Enthalpy space diagram

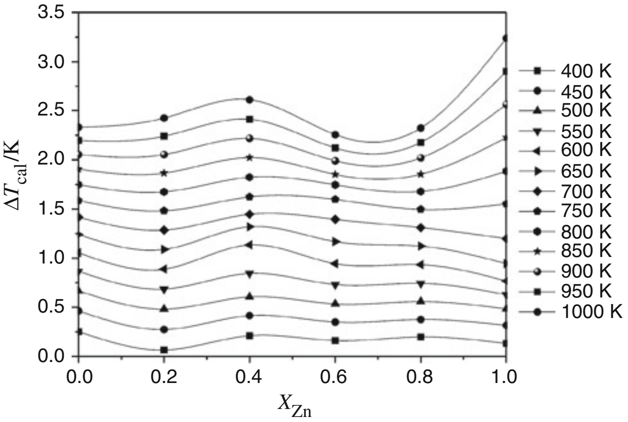

Fig. 4 The enthalpy isotherm diagram for the temperature interval up to 1,000 K

where G_i^M is the partial molar Gibbs energy for component 'i', T_0 the starting temperature, T the final temperature, $H_{x,T}$ the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R the gas constant and a_i is the activity of the component 'i'. Further calculation in the thermodynamic analysis was done based on Eq. 1 and the results of the graphic planimetry [14–16], which enabled the determination of Zn activities, activity coefficients, and partial molar quantities at 800, 900, and 1,000 K. The results are given in Table 2.

Positive deviation from ideal behavior for zinc activities can be noticed in whole concentration area. Also, negative values for partial molar Gibbs energies of mixing in the range from −1.4 to −10.5 kJ mol^{-1} and positive values of partial molar excess Gibbs energies in the range up to 3 kJ mol^{-1}, were obtained for the chosen alloys.

In order to confirm the fact of demixing tendencies for zinc in investigated Zn–AlGa section, the energetics of mixing in liquid alloys has been analyzed through the study of concentration fluctuation in the long-wavelength limit, $S_{cc}(0)$, connected with the microscopic information on liquid alloys [22]. The presence of chemical order is indicated by $S_{cc}(0) < S_{cc}(0,\text{id})$, while on the contrary, if $S_{cc}(0) > S_{cc}(0,\text{id})$, the segregation and demixing in liquid alloys takes place. Using the experimental values for zinc activity presented in this work, $S_{cc}(0)$ at 800, 900, and 1000 K was calculated using following equation:

$$S_{cc}(0) = (1 - x_{Zn}) \cdots a_{Zn}/(\partial a_{Zn}/\partial x_{Zn}) \ldots \qquad (10)$$

and mixing behavior of liquid alloys in the Zn–AlGa section of the Zn–Al–Ga system can be deduced from the deviation of $S_{cc}(0)$ from $S_{cc}(0,\text{id})$, as shown in Fig. 5.

Table 3 The Redlich–Kister parameters for constitutive binary systems

System *ij*	$L_{ij}^{o}(T)$	$L_{ij}^{1}(T)$	$L_{ij}^{2}(T)$
Al–Zn [23]	10465.55 − 3.39259*T	0	0
Al–Ga [24]	2613.3 − 2.94533*T	692.4 − 0.09271*T	319.5
Ga–Zn [25]	3662.8 + 27.28629*T − 4.2*T*ln$T$	−464.2	0

Table 2 The results of the Oelsen quantitative thermodynamic analysis at investigated temperatures of 800, 900, and 1,000 K (energies in J/mol)

T/K	800 K				900 K				1,000 K			
x_{Zn}	a_{Zn}	γ_{Zn}	G_{Zn}^{M}	G_{Zn}^{E}	a_{Zn}	γ_{Zn}	G_{Zn}^{M}	G_{Zn}^{E}	a_{Zn}	γ_{Zn}	G_{Zn}^{M}	G_{Zn}^{E}
0	0	–	–	–	0	–	–	–	0	–	–	–
0.2	0.320	1.580	−7,680	3,025	0.300	1.500	−9,000	3043	0.280	1.410	−1,0500	2,882
0.4	0.520	1.290	−4,400	1,695	0.490	1.210	−5,400	1457	0.480	1.200	−6,100	1,518
0.6	0.670	1.120	−2,640	758	0.650	1.080	−3,240	583	0.640	1.070	−3,700	547
0.8	0.810	1.010	−1,440	44	0.810	1.010	−1,620	50	0.810	1.010	−1,800	55
1	1	–	–	–	1	–	–	–	1	–	–	–

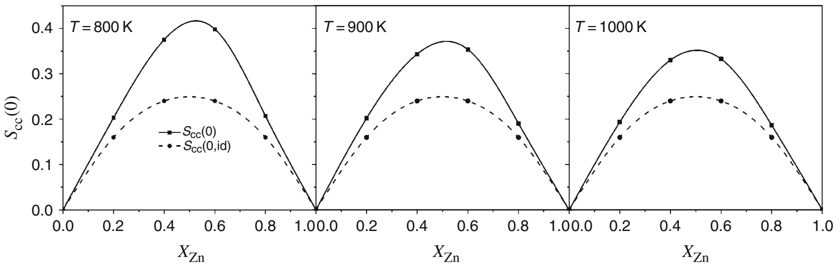

Fig. 5 The concentration fluctuation in the long-wavelength limit, $S_{cc}(0)$ for the liquid alloys in Zn–AlGa section of Zn–Al–Ga system at investigated temperatures

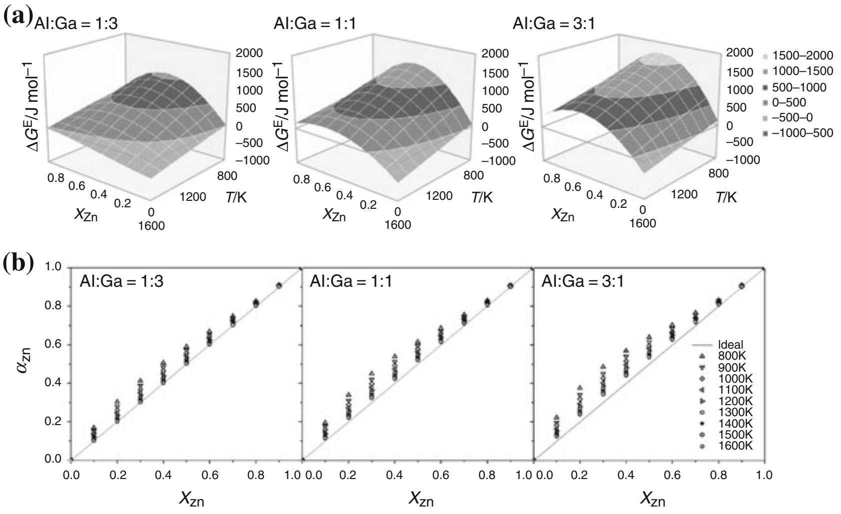

Fig. 6 The results of thermodynamic calculation according to GSM model in temperature range 800–1,600 K. **a** integral molar excess Gibbs energies and **b** zinc activities

The calculated values of $S_{cc}(0)$ are greater than $S_{cc}(0,\text{id})$ for whole concentration interval at all investigating temperatures, indicating to segregation and demixing tendencies in liquid alloys typical for positive deviation from ideal behavior.

Basic thermodynamic data on the constituent binary subsystems Zn–Al, Al–Ga, and Ga–Zn, needed for calculation of thermodynamic properties in the investigated Zn–Al–Ga system, were taken from the references [23–25]. Characteristic Redlich–Kister parameters for constitutive binary systems are presented in Table 3.

According to Eqs. 3 and 4, and based on starting data given in Table 3, integral molar Gibbs excess energies have been calculated for three sections in the Zn–Al–Ga system—from zinc corner with molar ratio of Al:Ga = 1:3, 1:1, and 3:1, in wide temperature interval from 800 to 1,600 K. The partial thermodynamic quantities for zinc were derived using well-known expressions:

$$G_i^E = \Delta G^E + (1 - x_i)\left(\partial \Delta G^E / \partial x_i\right) = RT \ln \gamma_i \ldots \tag{11}$$

and

$$a_i = x_i \gamma_i \ldots \tag{12}$$

Obtained results—integral molar Gibbs excess energies and zinc activities, calculated according to GSM calculation method in three chosen sections from Zn corner for investigated temperature range, are shown in Fig. 6, while analytical expressions of obtained polynomial dependencies for $\Delta G^E = f(x_{\text{Zn}})$are given in Table 4.

The values of calculated integral molar excess energies in three chosen sections from Zn corner in Zn–Al–Ga system are in the range from −0.3 to 1.7 kJ mol^{-1}, decreasing from lower up to higher temperatures. In the

Table 4 Analytical expressions of obtained polynomial dependencies for $\Delta G^E = f(x_{\text{Zn}})$ obtained by GSM for three investigated sections from Zn corner in the range 800–1,600 K

Section	T/K	$\Delta G^{\text{E}} = f(x_{\text{Zn}})$
Al:Ga = 1:3	800	$y = -515.0x^3 - 3563x^2 + 4070x + 4.801$
	900	$y = -508.7x^3 - 3154x^2 + 3709x - 49.57$
	1,000	$y = -501.7x^3 - 2712x^2 + 3314x - 103.9$
	1,100	$y = -495.0x^3 - 2237x^2 + 2887x - 158.3$
	1,200	$y = -489.4x^3 - 1732x^2 + 2431x - 212.7$
	1,300	$y = -485.6x^3 - 1198x^2 + 1946x - 267.1$
	1,400	$y = -483.9x^3 - 634.2x^2 + 1435x - 321.4$
	1,500	$y = -484.3x^3 - 42.76x^2 + 898.3x - 375.8$
	1,600	$y = -486.6x^3 + 574.7x^2 + 337.5x - 430.2$
Al:Ga = 1:1	800	$y = -183.0x^3 - 5212x^2 + 5329x + 64.06$
	900	$y = -170.5x^3 - 4880x^2 + 5059x - 9.59$
	1,000	$y = -170.5x^3 - 4880x^2 + 5059x - 9.59$
	1,100	$y = -142.6x^3 - 4156x^2 + 4454x - 156.9$
	1,200	$y = -130.1x^3 - 3762x^2 + 4120x - 230.5$
	1,300	$y = -130.1x^3 - 3762x^2 + 4120x - 230.5$
	1,400	$y = -114.0x^3 - 2904x^2 + 3393x - 377.8$
	1,500	$y = -111.8x^3 - 2439x^2 + 3000x - 451.5$
	1,600	$y = -113.6x^3 - 1951x^2 + 2587x - 525.1$
Al:Ga = 3:1	800	$y = -57.63x^3 - 6452.x^2 + 6389.x + 121.1$
	900	$y = -45.03x^3 - 6149x^2 + 6128x + 65.01$
	1,000	$y = -31.00x^3 - 5836x^2 + 5858x + 8.914$
	1,100	$y = -16.81x^3 - 5514x^2 + 5577x - 47.18$
	1,200	$y = -3.728x^3 - 5179x^2 + 5286x - 103.2$
	1,300	$y = 7.116x^3 - 4832x^2 + 4984x - 159.3$
	1,400	$y = 14.78x^3 - 4470x^2 + 4670x - 215.4$
	1,500	$y = 18.61x^3 - 4093x^2 + 4345x - 271.5$
	1,600	$y = 18.19x^3 - 3699x^2 + 4008x - 327.6$

Note: R-squared value for fitting process was $R^2 = 1$ in all cases

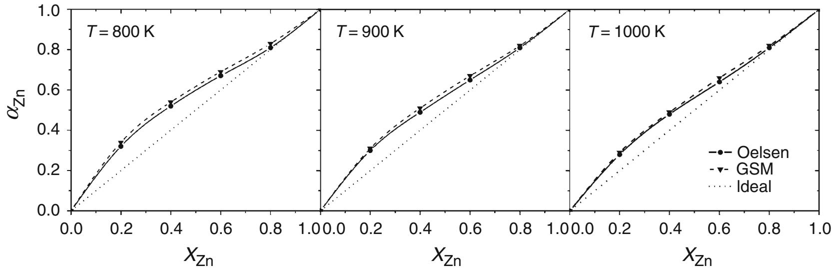

Fig. 7 Comparison of zinc activities obtained experimentally by Oelsen method and calculated according to GSM model at temperature of 800, 900, and 1000 K

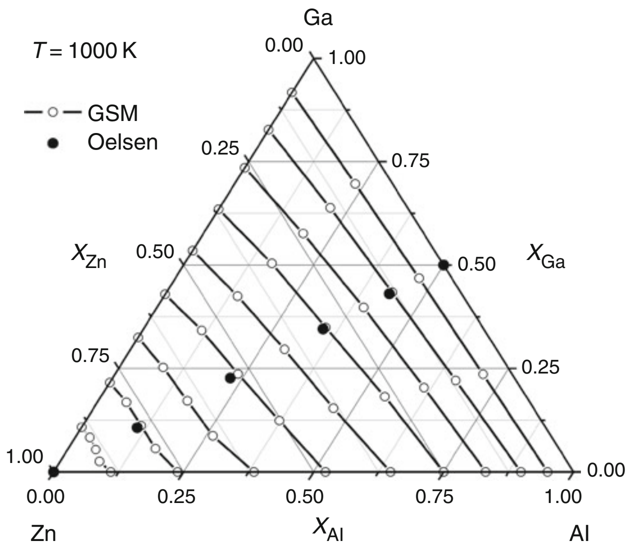

Fig. 8 Zn-isoactivity diagram with compared experimental and calculated results at 1,000 K

greatest part of investigated composition and temperature range, described values are positive, while negative sign is noted only above 1,300 K in a composition interval with $x\text{Zn} < 0.3$. Calculated zinc activities show positive deviation of Raoult law in whole concentration range and for all temperatures, approaching nearer to the line of ideal state as temperature is increasing.

The comparison between the experimentally obtained and calculated results has been done at the temperatures of 800, 900, and 1,000 K, as presented in Fig. 7, while comparison in the form of Zn-isoactivity diagram at 1,000 K is given in Fig. 8.

Satisfying agreement between experimental thermodynamic data on zinc activities, obtained by Oelsen calorimetry and calculated by GSM model, can be noticed, which indicates to the accuracy of applied thermodynamic calculation in the case of mentioned system. Such combination of experimental work and calculation was already found to give good results in thermodynamics of alloys [26–28] and other scientific fields as well [29].

Conclusions

Comparative thermodynamic analysis of AlGa–Zn system was done experimentally by Oelsen calorimetry and using thermodynamic calculation according to general solution model. The results of the comparative analysis for obtained thermodynamic parameters showed positive deviation from Raoult's law in the whole concentration range and fair agreement between experiments and calculation. Finally, the presented thermodynamic data for the Al–Ga–Zn alloys, compensating a lack of experimental thermodynamic information for these alloys, could be useful for further interpretation of the phenomena occurring in mentioned Zn–Al-based multicomponent lead-free system.

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