UDK 544.3:669.017.13:669.715'721'5
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 46(5)477(2012)

PREDICTION OF THE THERMODYNAMIC PROPERTIES FOR LIQUID Al-Mg-Zn ALLOYS

NAPOVEDOVANJE TERMODINAMIČNIH LASTNOSTI TEKOČE ZLITINE Al-Mg-Zn

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Prejem rokopisa – received: 2012-02-22; sprejem za objavo – accepted for publication: 2012-03-29

The results of a thermodynamic-property prediction for liquid Al-Mg-Zn alloys using the general solution model are presented in this paper. Calculations were done in nine sections of the system with different molar ratios of Mg:Zn, Zn:Al and Al:Mg in the temperature range of 900–1200 K. Partial and integral molar quantities – including the activities for all three components, the integral molar excess Gibbs energies and the integral molar enthalpies of mixing – were obtained. Some of the calculation results were compared with the experimental data available in the literature, showing a good agreement with it.

Keywords: thermodynamics of alloys, Al-Mg-Zn system, general solution model

V članku so predstavljeni rezultati raziskav termodinamičnih lastnosti tekočih zlitin Al-Mg-Zn, napovedanih z uporabo splošnega modela raztapljanja. Izračuni so bili izvršeni v devetih prerezih sistema z različnimi molarnimi deleži Mg:Zn, Zn:Al in Al:Mg v območju temperatur 900–1200 K. Dobljene so bile parcialne in celotne molarne količine, vključno z aktivnostmi za vse tri komponente, skupni molarni presežek Gibssove energije in skupna molarna entalpija mešanja. Ugotovljeno je dobro ujemanje izračunanih rezultatov z razpoložljivimi eksperimentalnimi podatki iz literature.

Ključne besede: termodinamika zlitin, sistem Al-Mg-Zn, splošni model raztapljanja

1 INTRODUCTION

The so-called ZA alloys – zinc-aluminum-based alloys – have a wide application in different fields of industry[1,2]. The ternary Al-Mg-Zn system belongs to this group of materials, which are of interest as the lead-free solders for die attach[1–4]. Therefore, different properties of this system were investigated in order to define it more completely[5–9].

The thermodynamics and the phase equilibria of the Al-Mg-Zn system have been examined widely[10–20]. Most of the literature data is related to the phase-diagram determination[10–17]. A complete reference compilation concerning the experimental data obtained for the above-mentioned ternary alloys up to 1998 can be found in the work of Liang et al.[19], while the last review is given in an article by Raghavan[15] from 2010.

The liquidus projection of the Al-Mg-Zn system is shown in **Figure 1**, according to Refs. [14] and [17].

Among the numerous researches, there are only a few thermodynamic studies[17–19]. Experimental thermodynamic investigations of the Al-Mg-Zn system in the liquid state were done for the chosen sections at the temperatures of 883 K and 933 K using vapor-pressure measurements[17], EMF[18] and mixing calorimetry[19], while the thermodynamic assessments can be found in[20,21].

Considering the available literature and the lack of a complete thermodynamic data with respect to the wider temperature and concentration ranges, the results of the thermodynamic-property prediction for the liquid Al-Mg-Zn alloys in the temperature interval of 900–1200 K, using the general solution model, are given in this paper as a contribution to a full thermodynamic description of this ternary system.

2 THEORETICAL FUNDAMENTALS

The general solution model for the calculation of the thermodynamic properties of ternary systems based on the known binary thermodynamic data has been provided by Chou[22,23]. It breaks down the boundary between symmetrical and asymmetrical models, and has already been proved in some practical examples[24,25] as the correct and accurate model. This model was developed for multicomponent systems and its basic equations are as follows[22]:

$$\Delta G^E = \sum_{\substack{i,j=1 \\ i\neq j}}^{m} x_i x_j \left[A_{ij}^0 + A_{ij}^1 \cdot \left((x_i - x_j) + \sum_{\substack{k=1 \\ k\neq i,j}}^{m} A_{ij}^1 x_k (2\xi_{i(ij)}^{(k)} - 1) \right) \right] \quad (1)$$

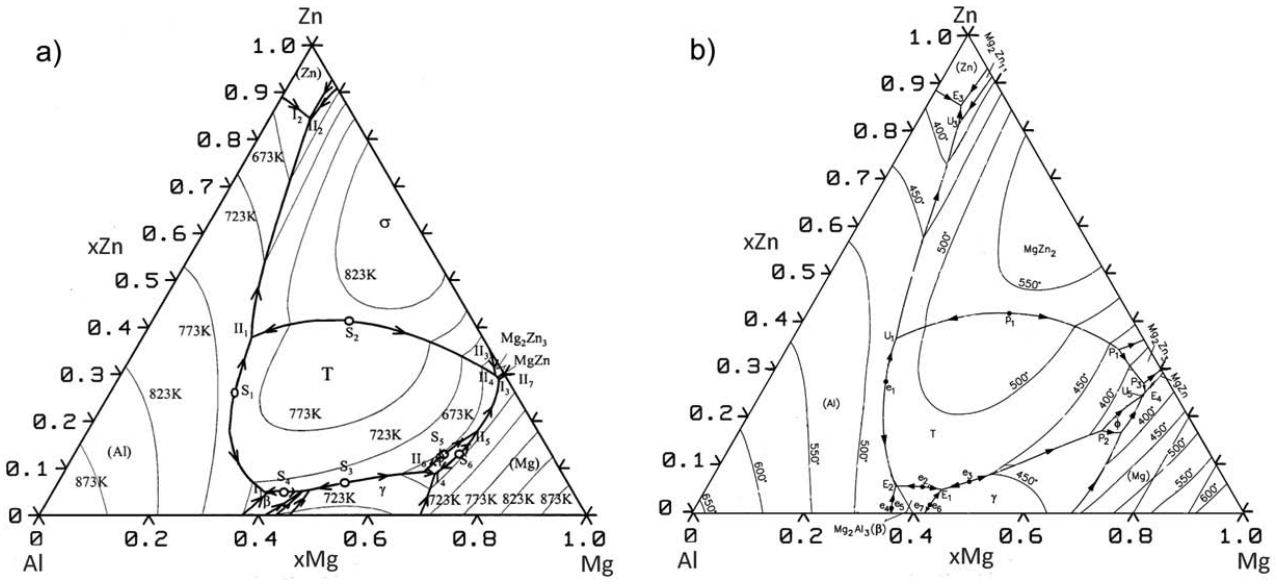

Figure 1: Al-Mg-Zn liquidus projection: a) [17] and b) [14]
Slika 1: Projekcija likvidusa Al-Mg-Zn: a) [17] in b) [14]

where A^{o}_{ij}, A^{1}_{ij}, A^{2}_{ij} are the regular-solution parameters for the binary system *ij* independent of the composition, relying only on the temperature:

$$\Delta G^{E}_{ij} = X_i X_j \left(A^{o}_{ij} + A^{1}_{ij} (X_i - X_j) + A^{2}_{ij} (X_i - X_j)^2 + \ldots + A^{n}_{ij} (X_i - X_j)^2\right) \quad (2)$$

where X_i and X_j indicate the mole fractions of components *i* and *j* in the *ij* binary system, which is expressed as:

$$X_{i(ij)} = x_{i+} \sum_{\substack{k=1 \\ k \neq i,j}}^{m} x_k \xi^{(k)}_{i(ij)} \quad (3)$$

and where the coefficient entered as $\xi^{(k)}_{i(ij)}$ in Eq.(3) presents the similarity coefficient of component *k* to component *i* in the *ij* system, and is defined as:

$$\xi^{(k)}_{i(ij)} = \frac{\eta(ij,ik)}{\eta(ij,ik) + \eta(ji,jk)} \quad (4)$$

where $\eta(ij,ik)$ is the function related to the excess Gibbs free energy of the *ij* and *ik* binaries:

$$\eta(ij,ik) = \int_{x_i=0}^{X_i=1} (\Delta G^{E}_{ij} - \Delta G^{E}_{ik})^2 \, \mathrm{d}X_i \quad (5)$$

In all the equations given, ΔG^{E} and ΔG^{E}_{ij} refer to the integral molar excess free energies for the multicomponent and binary systems, respectively, while x_1, x_2, x_3 refer to the mole fraction of the components in the investigated multicomponent system.

3 RESULTS AND DISCUSSION

Thermodynamic calculations in the Al-Mg-Zn ternary system were carried out in nine sections along the lines of the following constant molar ratios: Mg : Zn = 1 : 3, 1 : 1, 3 : 1 – the sections from the Al corner; Zn-Al = 1 : 3, 1 : 1, 3 : 1 – the sections from the Mg corner; and Al : Mg = 1 : 3, 1 : 1, 3 : 1 – the sections from the Zn corner. The basic data necessary for the calculation was taken from the literature[20,26,27]. The Redlich-Kister polynomials for the constitutional binaries in the investigated ternary Al-Mg-Zn system are presented in **Table 1**.

Table 1: Redlich-Kister parameters for the liquid phase in the constitutional binaries of the Al-Mg-Zn system
Tabela 1: Redlich-Kisterjevi parametri za staljeno fazo v sestavnih binarnih sistemih iz sistema Al-Mg-Zn

System *ij*	Al-Mg (20)	Mg-Zn (20)	Al-Zn (26)
$A^{o}_{ij}(T)$	–12000+ 8.566**T*	–77729.24+ 680.52266*T –95**T**ln(*T*)+ 40E–3**T*^{2}	10465.55– 3.39259**T*
$A^{1}_{ij}(T)$	1894–3**T*	3674.72+ 0.57139**T*	/
$A^{2}_{ij}(T)$	2000	–1588.15	/

The prediction was done according to the fundamentals of the latest version of the general-solution model[22,23]. Based on the starting data in **Table 1**, similarity coefficients were determined and further calculations were carried out for 81 alloys in all the selected cross sections of the investigated ternary Al-Mg-Zn system in the temperature interval of 900–1 200 K, as shown with Eqs.(1–5). The integral molar enthalpies of mixing were additionally calculated according to following expression:

$$\frac{\mathrm{d}(\Delta G^{E}/T)}{\mathrm{d}T} = -\frac{\Delta H^{M}}{T^2} \quad (6)$$

The results of the thermodynamic predictions, including the values of the ternary integral molar excess Gibbs

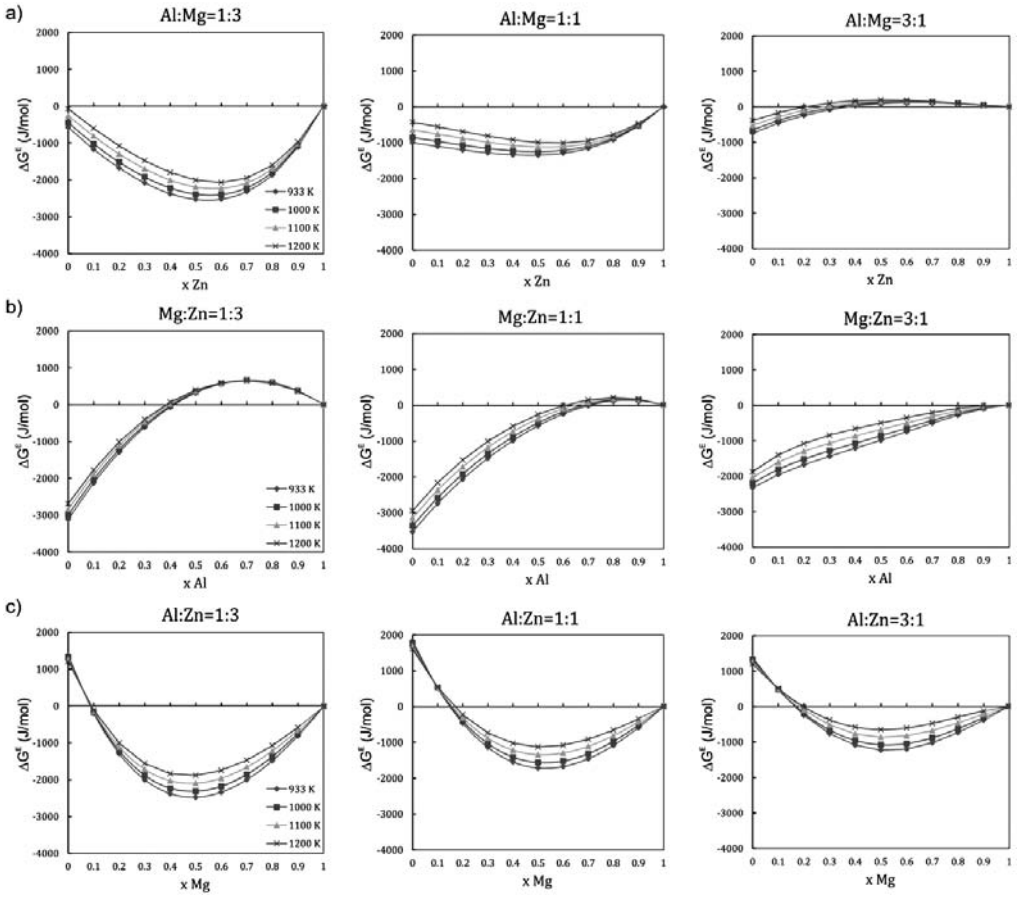

Figure 2: Dependence of the integral molar excess energy on the composition and temperature in the Al-Mg-Zn system: a) sections from the zinc corner; b) sections from the aluminum corner; c) sections from the magnesium corner

Slika 2: Odvisnost skupne molarne presežne energije od sestave in temperature v sistemu Al-Mg-Zn: a) prerez iz cinkovega kota; b) prerez iz aluminijevega kota; c) prerez iz magnezijevega kota

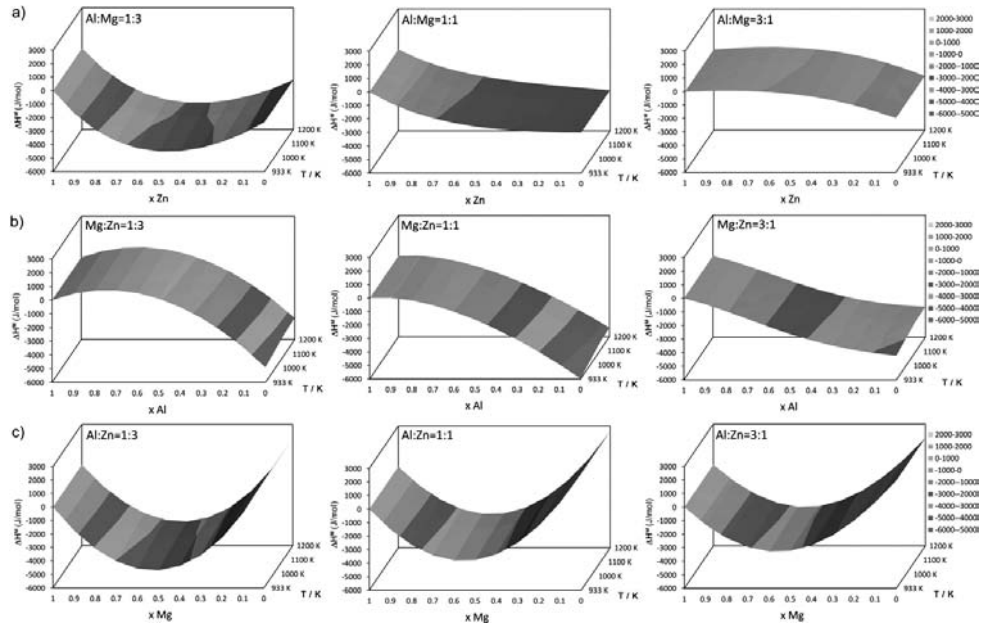

Figure 3: Dependence of the integral molar enthalpies of mixing on the composition and temperature in the Al-Mg-Zn system: a) sections from the zinc corner; b) sections from the aluminum corner; c) sections from the magnesium corner

Slika 3: Odvisnost skupne molarne entalpije mešanja od sestave in temperature v sistemu Al-Mg-Zn: a) prerez iz cinkovega kota; b) prerez iz aluminijevega kota; c) prerez iz magnezijevega kota

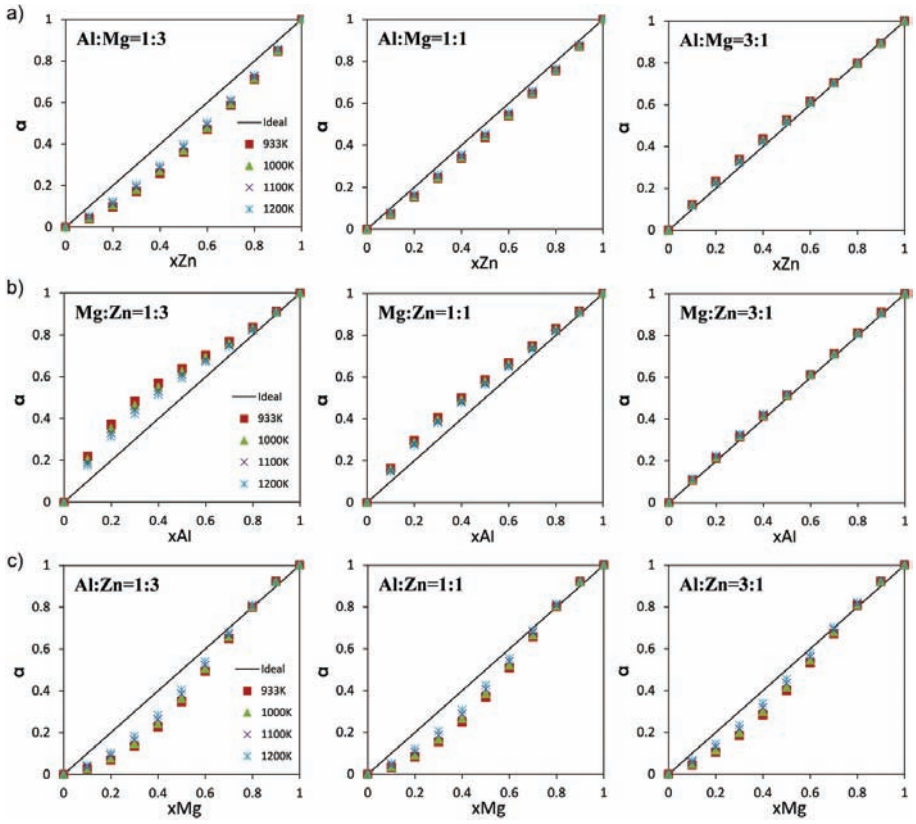

Figure 4: Activity dependence on the composition and temperature in the investigated Al-Mg-Zn system: a) sections from the zinc corner; b) sections from the aluminum corner; c) sections from the magnesium corner

Slika 4: Odvisnost aktivnosti od sestave in temperature v preiskovanem sistemu Al-Mg-Zn: a) prerez iz cinkovega kota; b) prerez iz aluminijevega kota; c) prerez iz magnezijevega kota

energy, the ternary molar enthalpy of mixing and the activities of all three components in the liquid phase, were calculated for all the investigated sections at the investigated temperatures, and presented in **Table 2** and **Figures 2** to **4**, respectively. The calculated activity values for all three components were used for the construction of the iso-activity diagrams at 1000K and shown in **Figure 5**.

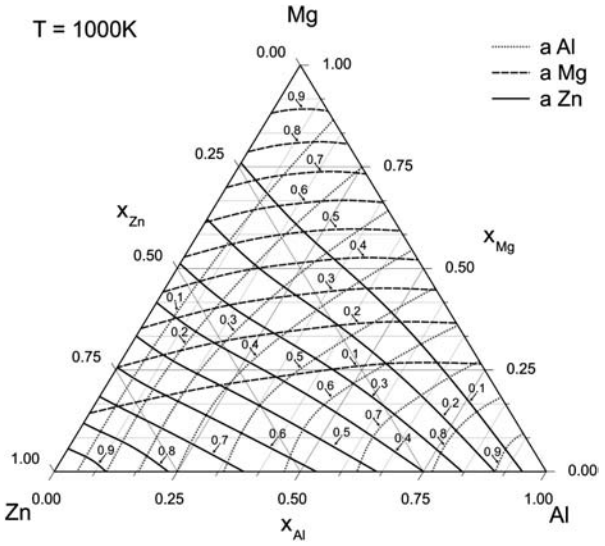

Figure 5: Iso-activity diagrams for the constitutive elements in the ternary Al-Mg-Zn system at 1000 K

Slika 5: Diagram izoaktivnosti za sestavne elemente v ternarnem sistemu Al-Mg-Zn pri 1000 K

Negative values of the integral molar excess Gibbs energies were obtained for most of the concentration range at all the investigated temperatures (**Figure 2**). The most negative value of about –3.5 kJ/mol was present in the section from the aluminum corner with a molar ratio of Mg : Zn = 1 : 1 for the low aluminum concentrations, while the highest positive values of about 0.2 kJ/mol were noticed for the higher contents of zinc and aluminum in sections Mg : Zn = 1 : 1 and Al : Mg = 3 : 1. In the case of the integral molar enthalpies of mixing, the minimum value of -5kJ/mol was noticed for the low aluminum contents in the section Mg : Zn = 1 : 1, while the maximum value of about +3 kJ/mol was obtained for the low magnesium contents in section Al : Zn = 1 : 1.

Different deviations from Raoult law were detected considering three constituent metals in the Al-Mg-Zn system. Aluminum shows a positive deviation in the whole composition range of the investigated ternary system, moving towards almost an ideal behavior in the case of the section with a molar ratio of Mg : Zn = 3 : 1. On the other hand, magnesium shows a uniform negative deviation for all the examined sections of the system,

Table 2: Characteristic dependencies of the integral molar excess energies and the integral molar enthalpies of mixing on the composition of the ternary Al-Mg-Zn alloys expressed as ΔG^E (J/mol) = $Ax^2 + Bx + C$ and ΔH^M (J/mol) = $Dx^2 + Ex + F$ at the investigated temperatures

Tabela 2: Značilna odvisnost skupne presežne molarne energije in skupne molarne entalpije mešanja od sestave ternarne Al-Mg-Zn zlitine, izražena kot ΔG^E (J/mol) = $Ax^2 + Bx + C$ in ΔH^M (J/mol) = $Dx^2 + Ex + F$ pri preiskovanih temperaturah

933K

Section	A	B	C	D	E	F
Mg:Zn=1:3	–7444.08	10598.36	–3114.3	–10228	15172	–4917
Mg:Zn=1:1	–4584.48	8210.277	–3522.5	–5510.5	11645	–6040.4
Mg:Zn=3:1	–564.357	2931.14	–2279.32	2085.3	2368.8	–4300.3
Al:Zn=1:3	13523.87	–14194.9	1171.436	22679	–24340	1791.2
Al:Zn=1:1	11246.21	–12525.6	1697.977	20338	–22847	2566.1
Al:Zn=3:1	8269.261	–9230.4	1314.962	16806	–22847	2028.8
Al:Mg=1:3	8058.779	–8123.02	–463.269	13330	–11380	–2168.7
Al:Mg=1:1	2852.942	–2223.04	–930.149	4233.1	–1474.4	–2892.2
Al:Mg=3:1	–2062.89	2678.725	–717.506	–3290	5185.5	–1942.2

1000K

Section	A	B	C	D	E	F
Mg:Zn=1:3	–7301.1	10323.32	–2990.65	–10006	14727	–4694.9
Mg:Zn=1:1	–4608.32	8045.501	–3351	–5214.3	11053	–5744.2
Mg:Zn=3:1	–844.82	3049.588	–2143.19	2307.4	1924.6	–4078.2
Al:Zn=1:3	12810.45	–13429.3	1126.216	21791	–23452	1791.2
Al:Zn=1:1	10540.78	–11745.5	1636.327	19746	–22255	2566.1
Al:Zn=3:1	7633.816	–8521.86	1264.693	16510	–18548	2028.8
Al:Mg=1:3	7728.575	–7927.42	–334.914	12441	–10492	–2168.7
Al:Mg=1:1	2754.998	–2275.25	–785.379	3640.8	–882.13	–2892.2
Al:Mg=3:1	–1990.84	2513.915	–628.224	–3586.1	5481.6	–1942.2

1100K

Section	A	B	C	D	E	F
Mg:Zn=1:3	–7124.355	9967.950	–2827.029	–9799.6	14315	–4488.7
Mg:Zn=1:1	–4692.6	7872.956	–3122.95	–4939.3	10503	–5469.2
Mg:Zn=3:1	–1299.82	3281.329	–1960.96	2513.6	1512.1	–3872
Al:Zn=1:3	11814.41	–12358.4	1059.365	20966	–22627	1791.2
Al:Zn=1:1	9524.121	–10620.6	1544.861	19196	–21705	2566.1
Al:Zn=3:1	6700.34	–7480.99	1189.845	16235	–18273	2028.8
Al:Mg=1:3	7304.49	–7707.24	–142.743	11616	–9666.6	–2168.7
Al:Mg=1:1	2644.862	–2392.36	–568.803	3090.8	–332.13	–2892.2
Al:Mg=3:1	–1868.6	2251.542	–494.81	–3861.1	5756.6	–1942.2

1200K

Section	A	B	C	D	E	F
Mg:Zn=1:3	–6979.237	9651.942	–2674.257	–9743.3	14202	–4432.4
Mg:Zn=1:1	–4817.76	7751.966	–2909.49	–4864.3	10353	–5394.2
Mg:Zn=3:1	–1784.52	3551.037	–1789.76	2569.9	1399.6	–3815.7
Al:Zn=1:3	10843.84	–11317.1	993.472	20741	–22402	1791.2
Al:Zn=1:1	8512.729	–9505.34	1454.325	19046	–21555	2566.1
Al:Zn=3:1	5765.485	–6441.27	1115.435	16160	–18198	2028.8
Al:Mg=1:3	6905.864	–7515.85	50.01534	11391	–9441.6	–2168.7
Al:Mg=1:1	2538.665	–2517.19	–351.668	2940.8	–182.13	–2892.2
Al:Mg=3:1	–1749.7	1990.177	–361.146	–3936.1	5831.6	–1942.2

while zinc behaves differently – showing a slightly positive deviation for section Al : Mg = 3 : 1 and negative deviations in the other two sections.

The temperature influence on the calculated thermodynamic properties was not significant in the investigated interval 933–1200 K.

The described tendencies indicate a prevalent existence of the mutual mixing tendencies between the constitutive components in the Al-Mg-Zn system at the investigated temperatures, where magnesium and zinc exhibit a more significant mixing tendency than aluminum.

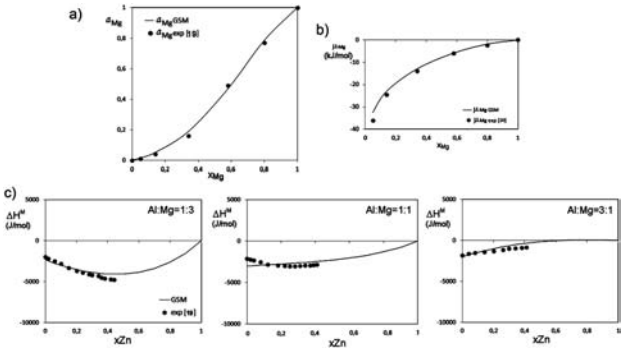

Figure 6: Comparison of calculated and reference-literature experimental values[19,20]

Slika 6: Primerjava izračunanih podatkov z literaturnimi eksperimentalnimi vrednostmi[19,20]

The calculated thermodynamic quantities were compared with the available literature data at the temperature of 933 K [19,20] in order to test the accuracy of the applied prediction model. These comparisons are shown in **Figure 6** for different examples – the magnesium activity (**Figure 6a**), the magnesium chemical potential (b) and the integral molar enthalpies of mixing for the three sections from the zinc corner (c). As can be seen, a good agreement was noticed between the results of this work and the reference experimental data[19,20].

4 CONCLUSION

The calculation of the thermodynamic properties in the ternary Al-Mg-Zn system was done by applying the general solution model. On the basis of the thermodynamic parameters from the constituent binary subsystems, the integral molar excess Gibbs energies and the integral molar enthalpies of mixing were calculated for the whole system, in nine sections from different corners, in the temperature range of 900–1 200 K. The obtained data showed a mostly negative deviation from Raoult law, indicating predominantly mutual mixing tendencies in the investigation system.

We found that: (i) experimental investigation and thermodynamic-property determination at the selected temperatures are rather difficult to perform due to the evaporation of zinc and oxidation of magnesium in the case of the investigated Al-Mg-Zn alloys; (ii) there is a good agreement between the available experimental data and the data calculated in this paper; and (iii) due to the incomplete thermodynamic data relating to the investigated system recorded in the reference literature, the predicted results from this paper can be taken as relevant thermodynamic data relating to the examined multicomponent ZA-based system. This can be done because the accuracy of the model, used in different cases, had already been proven as cited in literature[24,25] and it is important to continuously examine the Al-Mg-Zn alloys[28] and other Al-based ternary alloys[29,30].

Acknowledgment

The results of this paper were obtained in the frame of Project OI 172037 financed by the Ministry of Science and Technological Development, the Republic of Serbia, and a bilateral scientific and technological cooperation project between the Republic of Serbia and the People's Republic of China (2011–2012).

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