THERMODYNAMIC INVESTIGATION OF THE Al-Sb-Zn SYSTEM

TERMODINAMSKA RAZISKAVA SISTEMA Al-Sb-Zn

Grega Klančnik, Jožef Medved

University of Ljubljana, Faculty of Natural Science and Engineering, Department of Materials and Metallurgy, Aškerčeva 12,SI-1000 Ljubljana, Slovenia
grega.klancnik@omm.ntf.uni-lj.si

In this paper, thermodynamic calculations for the liquid alloys in the ternary Al-Sb-Zn system are presented. The general solution model (GSM) was used for the thermodynamic prediction of the liquid alloys in ternary Al-Sb-Zn at 1350 K. Oelsen's calorimetric method was used for the determination of the aluminium activity close to the Al-Zn sub-binary system. The Knudsen effusion method with a mass spectrometer (KEMS) was used for a determination of the zinc activity in the solid aluminium-rich corner.

Keywords: Al-Sb-Zn, thermodynamics, general solution model

V prispevku je predstavljen termodinamski izračun za taline v ternarnem sistemu Al-Sb-Zn. Za napoved termodinamskih lastnosti pri 1350 K smo uporabili splošen model raztopin (GSM). Uporabili smo Oelsenovo kalorimetrijo za določitev aktivnosti aluminija v bližini binarnega sistema Al-Zn. Ravno tako smo uporabili Knudsenovo efuzijsko metodo z masnim spektrometrom (KEMS). Tako smo določili aktivnost cinka v aluminijevem kotu.

Ključne besede: Al-Sb-Zn, termodinamika, splošni model raztopin

1 INTRODUCTION

The determination of the thermodynamic properties of the Al-Sb-Zn system is important. In order to investigate lead-free alloys for high temperature soldiers [1] or classical applications [2], three different thermodynamic prediction methods were used: Chou, as the general solution method (GSM); asymmetric Toop; and the symmetric Muggianu method [3]. The experimental results were compared to the mentioned thermodynamic models in the ternary Al-Sb-Zn system, in the section with the molar ratio $w(Zn) : w(Sb) = 9 : 1$ at 1000 K and 1350 K. No ternary interaction parameters were used in these calculations.

2 EXPERIMENTAL

Oelsen's calorimetry was used for the experimental determination of the thermodynamic properties in the ternary liquid system Al-Sb-Zn. Some of the experimental data in the Al-Zn binary system were determined with the Knudsen's effusion method. Mono-atomic zinc and oligomeric antimony are present further in the Al-Sb-Zn ternary system; the Knudsen cell was equipped with a mass spectrometer (KEMS). The measurements were made in the Al-rich corner only, at low temperatures since the volatility of the zinc and antimony was high.

2.1 The Knudsen effusion method

The Al-Zn binary system was investigated by applying Knudsen's effusions method. In the effusion method the vapour pressure P is calculated using the effusion velocity with the equation:

$$P = \sqrt{\frac{2\pi RT}{M}} \cdot \frac{1}{kA} \cdot \frac{G}{\tau} \cdot \left(1 + \frac{kA}{\alpha B}\right) \qquad (1)$$

where A is the geometric area of the effusion orifice, KA is the effective area, K is the Clausing factor, B is the effective vaporization area, M is the molecular weight of the effusing molecule, R is the gas constant, G is the weight of the effused molecule and τ is the time.

If we consider that the product αB is much higher than KA, equation 1 is obtained as:

$$P \cdot kA = \sqrt{\frac{2\pi RT}{M}} \cdot \frac{G}{\tau} \qquad (1.1)$$

And further:

$$\frac{p_i \cdot kA}{p_i^0 \cdot kA} = a_i \qquad (1.2)$$

The measurements for the Al-Zn alloys were made at 833 K in vacuum. The system was evacuated to a pressure of 10^{-3} mbar. About 0.3 g of charge material was placed in the Al_2O_3 crucible. The purities of the metals were 99.99 % for the zinc as well as for the aluminium. To ensure the saturation of the vapour phase, the lid was extra sealed on the Al_2O_3 crucible so the effused molecules could have effused only from a small

orifice. After each experiment a zinc ring appeared on the inside of the crucible as a result of the saturation of the zinc. The measurements for the Al-Zn-Sb ternary system were made in the temperature range 478–566 K to prevent instrumental errors as a result of the large evaporation of zinc and antimony.

In KEMS, the partial pressure is relative to any species at temperature T and is correlated to the ion intensity [4,5]:

$$p_j = \frac{kTI_{jk}^*}{\sigma_j \eta_k \gamma_k} \qquad (2)$$

σ_j – ionization cross-section of species,
K – instrumental constant,
I_{jk}^* – intensity of ion k formed from the molecular species j,
T – absolute temperature inside the Knudsen cell,
η_k – isotope abundance,
γ_k – multiplier efficiency for ion k.

The partial pressure ratio can be determined without knowledge of the values of the equation parameters just by measuring the ion intensity between two species relative to the temperature. In order to conduct the measurement, at least 300 mg of each species in a powdered state is necessary.

2.2 The Oelsen Calorimetry method

The Oelsen Calorimetry used in this paper is based on classic calorimetry as a classic thermodynamic method. Based on equation (3) a tangent construction for a determination of $-Rlna_{x,T}$ was made at 1000 K and 1350 K in the specific section (**Figure 1**) [6].

$$-\frac{G_i^M}{T} = \int_{1/T_0}^{1/T} H_{x,T} \, d\left(\frac{1}{T}\right) = -R \ln a_i \qquad (3)$$

where G_i^M is the partial molar Gibbs energy for the component i. The measurements were made in an interval from T_0 to T. Each measurement gives a measured enthalpy value $H_{x,T}$ for the composition x at temperature T. The activities for the component i were derived using a tangent construction for the determination of $-Rlna_{x,T}$. Apart from the activities values, the activity coefficients and other thermodynamic properties were also determined.

A type-K thermocouple (Ni-NiCr) was used for the temperature measurements. To achieve the best sensitivity possible, relatively thin wires were used. The preparation of samples was made with metals of 99.99 % purity. The melting was made under an argon atmosphere in an Al_2O_3 crucible. The measurements themselves were made in air. After each measurement the crucible with the sample was covered in order to prevent heat losses. The measurements were made with a calorimeter with a determined constant $C_{cal} = 324.9$ J K^{-1}. The Al_2O_3 crucible was taken into account while determining the C_{cal}.

2.3 Calculation of total excess Gibbs energy in the Al-Sb binary system at 1000 K

The calculation of the total excess Gibbs energy for the Al-Sb binary system at 1000 K was made on the basis of the following thermodynamic models: the unary phase model, the disordered solution phase model and the stoichiometric compound phase model.

The term for the unary phase is:

$$^0G_i^\phi(T) = a + bT + cT + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \qquad (4)$$

where the $^0G_i\phi$ is the Gibbs energy for the pure element i with the structure ϕ at 298.15 K. The liquid phase was calculated as a disordered solution phase and it is described with the following relation:

$$G^{\text{Liquid}} = x_i \,^0G_i^{\text{Liquid}} + x_j \,^0G_j^{\text{Liquid}} + \\ + RT(x_i \ln(x_i) + x_j \ln(x_j)) + {}^{ex}G^{\text{Liquid}} \qquad (5)$$

where the excess Gibbs energy of the liquid phase is calculated through the Redlich-Kister polynomial relation, and x_i correspond to the mole fraction of component i:

$$^{xs}G^{\text{Liquid}} = x_i x_j \sum_{n=0}^{m} ({}^nL_{i,j}^{\text{Liquid}}(x_i - x_j)^n) \qquad (6)$$

and

$$^nL_{i,j}^{\text{Liquid}} = a_n + b_n T \qquad (7)$$

Only one stoichiometric phase appears in the Al-Sb binary system, and its Gibbs free energy is described with the following relation:

$$G^\phi = x_i \,^0G_i^{\phi 1} + x_j \,^0G_j^{\phi 2} + \Delta G_f \qquad (8)$$

where $^0G_{i,j}\phi 1,2$ is the Gibbs free energy for the components i and j in standard states. ΔG_f represents the Gibbs free energy of formation and is calculated from the parameters a and b:

$$\Delta G_j = a + bT \qquad (9)$$

2.4 Prediction methods

Chou suggested the so-called general solution thermochemical model. The calculations were made using similarity coefficients determined through excess Gibbs energy data of the constituent binaries. In practise the GSM method gives good agreement with the experimental data. Two geometrical models were also used in this paper: the symmetric Toop and the asymmetric Muggianu model [7,8,9].

a) Chou model

The correlative term $\eta_{i(ij,jk)}$ is calculated using the deviation square sum rule:

$$\eta_{i(ij,ik)} = \int_{x_i=0}^{x_i=1} (\Delta G_{ij}^{xs} - \Delta G_{ik}^{xs})^2 \, dx_i \qquad (10)$$

Table 1: Thermodynamic parameters of the liquid Al-Sb-Zn system
Tabela 1: Termodinamski parametri taline v sistemu Al-Sb-Zn

System ij	$L_{ij}^0(T)$	$L_{ij}^1(T)$	$L_{ij}^2(T)$	$L_{ij}^3(T)$	$L_{ij}^4(T)$	Ref.
Al – Zn	$10466.6 - 3.39355T$					10
Al – Sb	$-13328 - 5.103T$	$10748 + 0.337T$				11
Sb – Zn	$-11740.942 - 0.1283T$	$-427.582 - 0.8090855T$	$34440.943 - 33.59286T$			12
Sb – Zn	$-43058.4 + 290.880T$ $-37.67392T \ln T$	$-11870.5 + 85.641T$ $-10.30928T \ln T$	$25102.1 - 14.005T$	$-9302.8 + 2.120T$	-9191	13

The similarity coefficients are calculated with the following relation:

$$\xi_{ij} = \eta_{i(ij,ik)} \cdot (\eta_{i(ij,ik)} + \eta_{j(ij,ik)})^{-1} \qquad (11)$$

The ternary system can be expressed as:

$$x_{1(1,2)} = x_1 + x_3 \xi_{12} \qquad (12)$$

$$x_{2(2,3)} = x_2 + x_1 \xi_{23} \qquad (13)$$

$$x_{3(3,1)} = x_3 + x_2 \xi_{31} \qquad (14)$$

The calculation was made on the basis of:

$$\Delta G^{xs} = x_1 x_2 \left\{ (x_1 + \xi_{12} x_3)(x_2 + (1 - \xi_{12}) x_3) \right\}^{-1} \Delta G_{12}^{xs} +$$

$$+ x_2 x_3 \left\{ (x_2 + \xi_{23} x_1)(x_3 + (1 - \xi_{23}) x_1) \right\}^{-1} \Delta G_{23}^{xs} + \qquad (15)$$

$$+ x_1 x_3 \left\{ (x_3 + \xi_{31} x_2)(x_1 + (1 - \xi_{31}) x_2) \right\}^{-1} \Delta G_{31}^{xs}$$

b) Toop model

$$\Delta G^{xs} = \frac{x_2}{1 - x_1} \Delta G_{12(x1)}^{xs} +$$

$$+ \frac{x_3}{1 - x_1} \Delta G_{13(x1)}^{xs} + (x_2 + x_3) \Delta G_{23(\frac{x_2}{x_2 + x_3})}^{xs} \qquad (16)$$

c) Muggianu model

$$\Delta G^{xs} = \frac{4 x_1 x_2}{(1 + x_1 - x_2)(1 + x_2 - x_1)} \Delta G_{12(\frac{1 + x_1 - x_2}{2})}^{xs} +$$

$$+ \frac{4 x_2 x_3}{(1 + x_2 - x_3)(1 + x_3 - x_2)} \Delta G_{23(\frac{1 + x_2 - x_3}{2})}^{xs} + \qquad (17)$$

$$+ \frac{4 x_3 x_1}{(1 + x_3 - x_1)(1 + x_1 - x_3)} \Delta G_{31(\frac{1 + x_3 - x_1}{2})}^{xs}$$

In each case, the partial thermodynamic quantities were calculated from:

$$G_i^{xs} = \Delta G^{xs} + (1 - x_i) \left(\frac{\partial \Delta G^{xs}}{\partial x_i} \right) \qquad (18)$$

The required binary parameters for the Al-Sb-Zn ternary system are presented in **Table 1**. The optimized

Table 2: The optimized parameters for the AlSb phase [11]
Table 2: Optimizirani parametri za fazo AlSb [11]

Phase	a/ (J/mol atom)	b/(J/mol atom K)
AlSb	-40636	15.847

parameters for the stoichiometric Al-Sb phase are given in **Table 2**.

2.5 Liquidus surface construction

The effect of the AlSb phase on the shape of the liquidus surfaces was estimated by using the GSM prediction method from the calculated activities derived from the partial excess Gibbs energy in the ternary system and with projections of the liquidus lines from the sub-binaries, as already discussed before in this paper.

3 RESULTS AND DISCUSSION

3.1 Al-Zn binary system

The alumina crucible used had an inner diameter of 5 mm. The cover was also made from alumina with an orifice in the centre. About 200 mg to 300 mg of charge material was put inside the alumina crucible for each experiment. The zinc vapour was taken as monatomic. The measured thickness of the orifice was 0.23 mm. The effective area *KA* was calculated to be 0.277 mm². The measurements were made at 833 K and the time for each measurement was less than 15 min. More details about the discussed method are available in ref. [14]. A type-S thermocouple was used for the temperature measurement. The measurements were made under a vacuum of 10^{-3} mbar. The change in concentration during the experiment was taken into account. The measurement was made in the solid-liquid equilibrium in the aluminium-rich corner. The results are presented in **Table 3**.

Table 3: Experimental results from the Knudsen effusion method for the Al-Zn binary system at 833 K
Tabela 3: Eksperimentalni podatki, dobljeni s Knudsenovo efuzijsko metodo za sistem Al-Zn pri 833 K

Alloy	P_{KA}/ (bar cm²)	P / bar	x_{Zn}	a_{Zn}	γ_{Zn}	G^{xs}_{Zn}/ (J/mol)
AZ1	$1.815 \cdot 10^{-6}$	$7.9497 \cdot 10^{-4}$	0.051	0.115	2.254	5628
AZ2	$5.226 \cdot 10^{-6}$	$2.2889 \cdot 10^{-3}$	0.199	0.331	1.663	3522
AZ3	$5.052 \cdot 10^{-6}$	$2.2177 \cdot 10^{-3}$	0.237	0.32	1.350	2078
AZ4	$5.803 \cdot 10^{-6}$	$2.5417 \cdot 10^{-3}$	0.305	0.365	1.196	1239
Zn	$1.59 \cdot 10^{-5}$	0.00698	1	1	/	0

3.2 Al-Sb-Zn ternary system

The calculated excess Gibbs energy for different ratios of aluminium, zinc and antimony are presented in **Figure 2**. All the calculations of the thermodynamic properties and the derivations in **Figure 2** were made using the GSM method at 1350 K.

The zinc activities are presented in **Figure 3** according to the three predicting models. All three thermodynamic models predicted negative deviations with respect to Raoult's law at the ratio w(Al) : w(Sb) = 1 : 4. The negativity is no longer present at the ratio 1 : 1 and this becomes more positive by approaching the sub-binary Al-Zn system. No significant differences exist between one and the other predicting methods.

The calculated activities of antimony at 1350 K throughout the entire concentration range show a
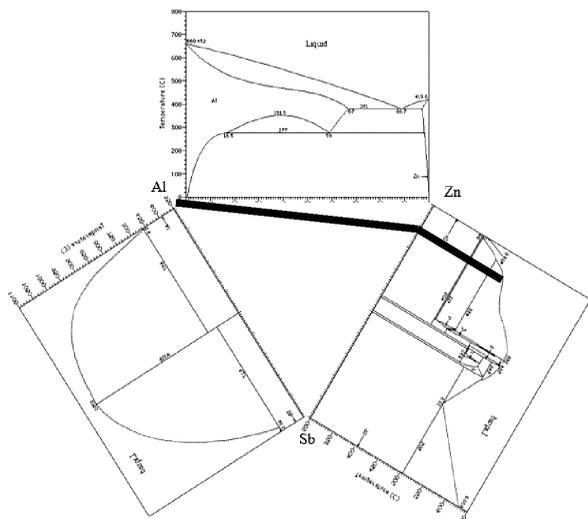

Figure 1: Experimental investigation of the section line with the ratio w(Zn) : w(Sb) = 9 : 1
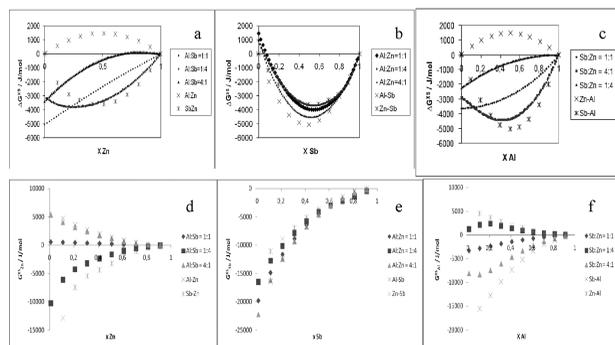**Slika 1:** Eksperimentalna preiskava preseka z razmerjem w(Zn) : w(Sb) = 9 : 1

Figure 2: Excess Gibbs energy and partial excess Gibbs free energy of the liquid phase at 1350 K relative to: (a) zinc, (b) antimony and (c) aluminium. Partial excess Gibbs free energy relative to: (d) zinc, (e) antimony and (f) aluminium
Slika 2: Prebitne Gibbsove energije in posamezne Gibbsove proste energije tekoče faze pri 1350 K glede na: (a) cink, (b) antimony in (c) aluminij. Posamezne prebitne Gibbsove energije glede na: (d) cink, (e) antimon in (f) aluminij.
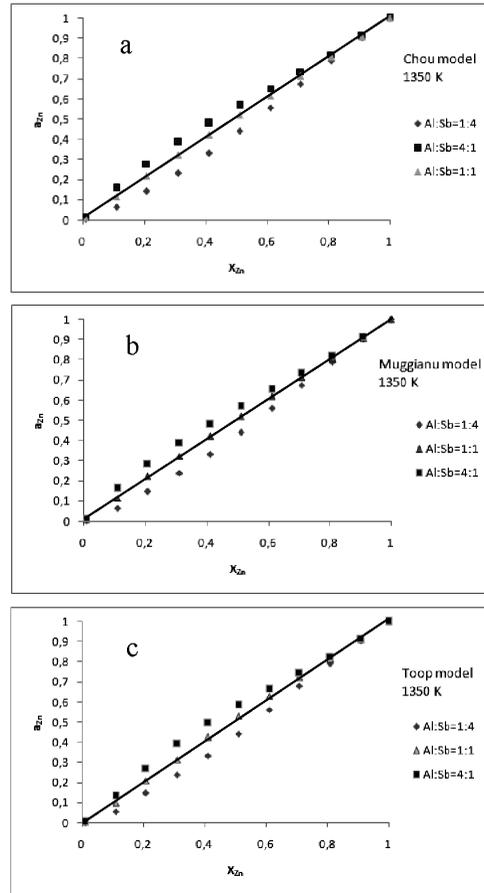

Figure 3: Zinc activities according to: (a) Chou, (b) Muggianu and (c) Toop model at 1350 K
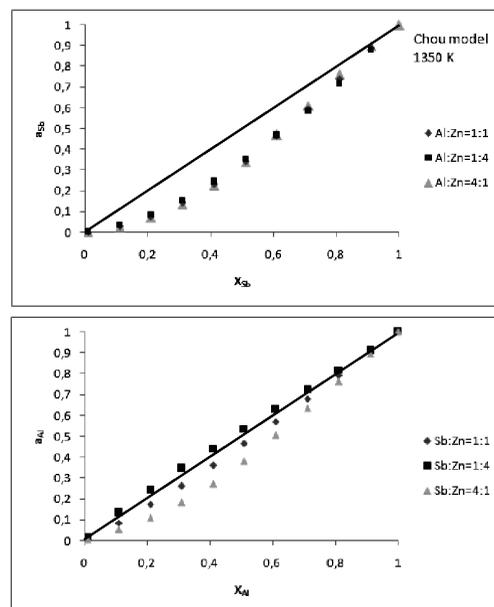**Slika 3:** Aktivnost cinka po: (a) Chou, (b) Muggianu in (c) Toop modelu za 1350 K

Figure 4: (a) Antimony and (b) aluminium activities according to Chou model at 1350 K
Slika 4: Aktivnost (a) antimona in (b) aluminija po modelu Chou za 1350 K
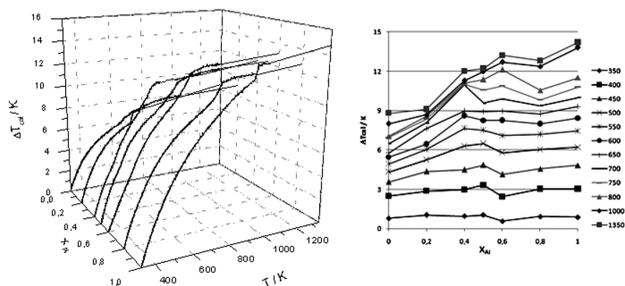
Figure 5: Enthalpy space diagram (a) and enthalpy isotherm diagram (b) for $w(Sb) : w(Zn) = 1 : 9$ section inside the Al-Sb-Zn ternary system
Slika 5: Entalpijski prostorski diagram (a) in entalpijski izotermni diagram (b) v sistemu Al-Sb-Zn z razmerjem $w(Sb) : w(Zn) = 1 : 9$

negative deviation from Raoult's law (**Figure 4a**). The difference of the activity values at different ratios is relatively small. The calculated aluminium activities are also negative, but already positive at the concentration ratio $w(Sb) : w(Zn) = 1 : 4$ because of the influence of the positive excess Gibbs energy of the Al-Zn sub-binary system (**Figure 4b**).

The Oelsen calorimetric method was used for a determination of the activity of aluminium in the Al-Sb-Zn ternary system. The enthalpy space diagram and the corresponding enthalpy isotherm diagram are presented in **Figure 5**.

A positive integral mixing enthalpy is expected from the enthalpy isotherm diagram. However, a negative integral mixing enthalpy is present near the Zn-Sb binary system at higher temperatures as a result of a possible presence of an intermetallic compound. In this case the presence of the stoichiometric AlSb phase is expected.

A good agreement was achieved when comparing the calculated and the experimentally determined data (**Figure 6**). In both cases the activities of the aluminium are positive at both temperatures 1000 K and 1350 K. The data are presented in **Tables 4 and 5**.

Table 4: Results of Oelsen's thermodynamic analysis at 1350 K for $w(Zn) : w(Sb) = 9 : 1$
Tabela 4: Rezultati Oelsenove termodinamske analize pri 1350 K za $w(Zn) : w(Sb) = 9 : 1$

x_{Al}	a_{Al}	γ_{Al}	G_{Al}^{xs}/(J/mol)	G_{Al}^{M}/(J/mol)
0	/	/	/	/
0.2	0.246	1.23	2323	−15741
0.4	0.464	1.16	1666	−8619
0.5	0.561	1.12	1272	−6488
0.6	0.651	1.09	967	−4818
0.8	0.810	1.01	112	−2365
1	1	1	0	0

The calculation and the experimental determination of the concentration fluctuations in the long wavelength Scc(0) is an important tool for studying the segregation and/or presence of the chemical order. The calculation was made on the basis of the relation:
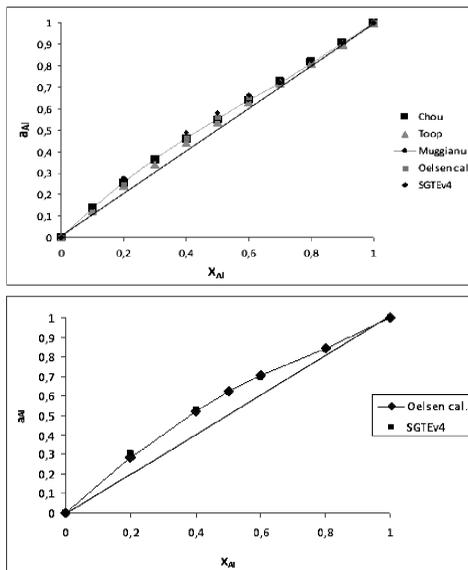

Figure 6: Activities obtained at: (a) 1350 K and (b) 1000 K for $w(Zn) : w(Sb) = 9 : 1$
Slika 6: Določene aktivnosti za: (a) 1350 K in (b) 1000 K za $w(Zn) : w(Sb) = 9 : 1$

Table 5: Results of Oelsen's thermodynamic analysis at 1000 K for $w(Zn) : w(Sb) = 9 : 1$
Tabela 5: Rezultati Oelsenove termodinamske analize pri 1000 K za $w(Zn) : w(Sb) = 9 : 1$

x_{Al}	a_{Al}	γ_{Al}	G_{Al}^{xs}/(J/mol)	G_{Al}^{M}/(J/mol)
0	/	/	/	/
0.2	0.285	1.43	2974	−10437
0.4	0.521	1.30	2181	−5421
0.5	0.62	1.24	1786	−3974
0.6	0.707	1.18	1376	−2883
0.8	0.842	1.05	406	−1430
1	1	1	0	0

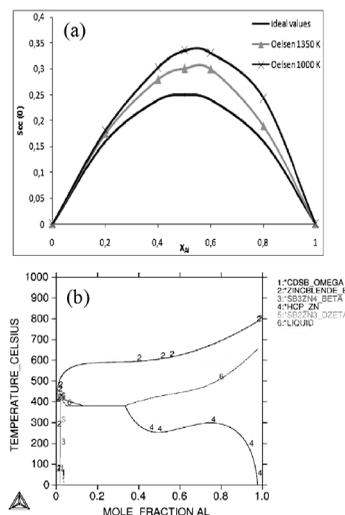**Figure 7:** (a) Concentration fluctuations in the long wavelength Scc(0) at 1000 K and 1350 K for Al-ZnSb section and (b) the corresponding isopleths diagram
Slika 7: (a) Koncentracijska fluktuacija v dolgem redu dosega Scc(0) pri 1000 K in 1350 K za prerez Al-ZnSb in (b) pripadajoč izopletni diagram
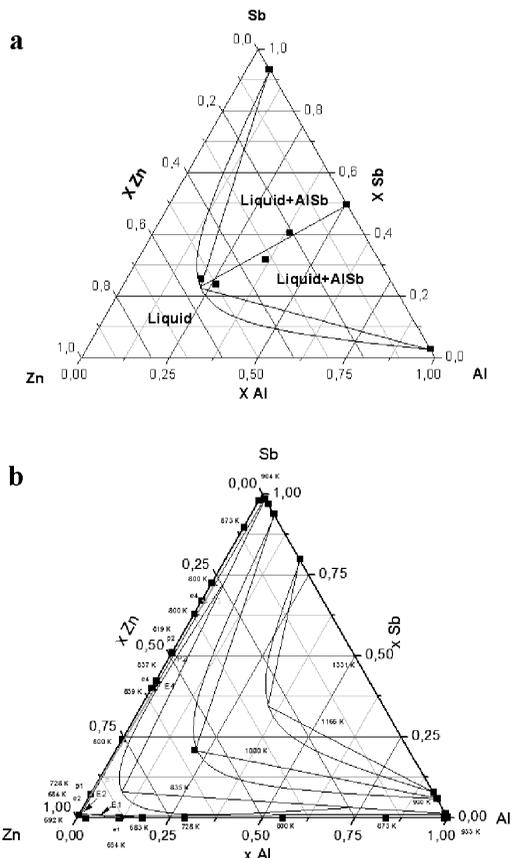
a

b

Figure 8: Thermodynamic prediction of the extension of two phase regions inside the ternary system at 1000 K using the GSM and projections of the sub-binaries with calculations.
Slika 8: Termodinamska napoved raztezanja dvofaznega območja v ternarnem sistemu pri 1000 K z uporabo GSM in binarnih projekcij

$$Scc(0) = \frac{(1-x_{Al})a_{Al}}{\partial a_{Al}/\partial x_{Al}} \qquad (19)$$

The results of Scc(0) at 1000 K and 1350 K are presented in **Figure 7** and show a positive deviation from the ideal curve. This can be related to the presence of the miscibility gap in the solid and is also confirmed with the calculation of the isopleth phase diagram (**Figure**

7b). A tendency for decreasing the deviation from ideal values with an increasing temperature was also determined. It is worth mentioning that the calculated and experimentally determined Scc(0) are higher than the ideal in the zinc-rich corner at temperatures of 923 K in the Sb-Zn binary system, where the starting point of our measurements is located [15]. Nevertheless, the calculation was made using only aluminium activities.

The calculation in **Figure 8** shows that two phase region extend through the Zn-rich corner. No invariant reactions are expected at 1000 K inside the ternary Al-Sb-Zn system. From the literature we know that the liquid region is pushed to the Zn-rich corner in the sub-binary Al-Zn and Sb-Zn systems [16].

The thermodynamic calculation using the SGTEv4 database predicts six invariant reactions in this system given in **Table 7**. The denotations for all the inter-metallics in the Al-Sb-Zn system are given in **Table 8**.

Table 7: Predicted invariant reactions in the Al-Sb-Zn ternary system from the SGTEv4 database
Tabela 7: Napovedane invariantne reakcije v ternarnem sistemu Al-Sb-Zn s podatkovno bazo SGTEv4

E1	559.1 °C	$L \rightarrow \beta\text{-}Sb_2Zn_3 + \gamma\text{-}Sb_3Zn_4 + AlSb$
U1	538.44 °C	$L + \gamma\text{-}Sb_3Zn_4 \rightarrow SbZn + AlSb$
E2	509.29 °C	$L \rightarrow SbZn + (Sb) + AlSb$
P1	446.71 °C	$L + \beta\text{-}Sb_2Zn_3 + AlSb \rightarrow \alpha\text{-}Sb_2Zn_3$
E3	409.6 °C	$L \rightarrow (Zn) + \alpha\text{-}Sb_2Zn_3 + AlSb$
E4	380.7 °C	$L \rightarrow (Al)^* + (Zn) + AlSb$

* (Al) or β-Al phase. β-Al phase decomposes at lower temperature to α-Al + (Zn)

Table 8: Phase Information
Tabela 8: Podatki o fazi

Phase Name**	Stoichiometric formula *	Phase name**	Stoichiometric formula *
Sb₂Zn₃_T	$\beta\text{-}Sb_2Zn_3$	CdSb_OME	SbZn
Sb₂Zn₃_D	$\alpha\text{-}Sb_2Zn_3$	Zincblend	AlSb
Sb₃Zn₄_G	$\gamma\text{-}Sb_3Zn_4$	Rhombone	(Sb)
FCC_A1	(Al)	HCP_Zn	(Zn)

*denotations of stoichiometric formula are taken by Okamoto [19]

Table 6: Experimental results from the KEMS method for 0.77Al0.13Sb0.1Zn from 478 K to 566 K
Tabela 6: Eksperimentalni rezultati, dobljeni z metodo KEMS za 0.77Al0.13Sb0.1Zn v območju 478–566 K

T/K	$1/T$	$I+(Zn)$	$p(Zn)$ /Pa	$p(Zn\ pure)$/ Pa	K	a (Zn)	γ_{Zn}	G^{xs}_{Zn}/(J/mol)
478	0.002092	780	5.67E-04	0.000855594	1.52E-09	6.63E-01	6.63	7519
461	0.002169	300	2.13E-04	0.000256755	1.54E-09	8.29E-01	8.29	8106
494	0.002024	1800	1.34E-03	0.002462639	1.51E-09	5.44E-01	5.44	6955
503	0.001988	3450	2.60E-03	0.004333383	1.50E-09	5.99E-01	5.99	7489
505	0.00198	4050	3.06E-03	0.004899798	1.50E-09	6.24E-01	6.24	7688
509	0.001965	4870	3.70E-03	0.006246299	1.49E-09	5.92E-01	5.92	7524
515	0.001942	6400	4.89E-03	0.008927265	1.49E-09	5.48E-01	5.48	7286
534	0.001873	17420	1.36E-02	0.026233813	1.47E-09	5.20E-01	5.20	7318
542	0.001845	22200	1.75E-02	0.040378946	1.46E-09	4.34E-01	4.34	6619
557	0.001795	46400	3.73E-02	0.087665647	1.44E-09	4.25E-01	4.25	6705
intbl566	0.001767	78600	6.38E-02	0.136857484	1.43E-09	4.66E-01	4.66	7244

*K – Instrumental constant, I – Intensity of zinc

The presented model, using the GSM for the prediction of the extension of AlSb + L two-phase region inside the ternary system also predicts six invariant reactions (**Figure 8**). The calculation of the invariant ternary reaction E1 was made on the assumption that the eutectic reaction (L → γ-Sb$_3$Zn$_4$ + β-Sb$_2$Zn$_3$) appears at higher temperatures in the Zn-Sb binary system [17,18,19]. A peritectic reaction was also obtained (L + β-Sb$_2$Zn$_3$ → γ-Sb$_3$Zn$_4$) by other authors [20,21,22].

4 CONCLUSIONS

The results from the Oelsen Calorimetry show a good agreement with the results from the Chou, Toop and Muggianu models. A positive deviation from the Raoults' law was determined by the obtained activity of aluminium in the Al-Sb0.1Zn0.9 section (**Table 6**). A positive deviation of the zinc activity was also confirmed in the aluminium-rich corner with the sample 0.77Al0.13Sb0.1Zn in an extended temperature range. Using the SGTEv4 we were able to predict the nature of various heterogeneous equilibria in the Al-Sb-Zn system. These thermodynamic data are being published for the first time, to the best of our knowledge.

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