Available online at www.sciencedirect.com

Thermochimica Acta 412 (2004) 39–45

thermochimica acta

www.elsevier.com/locate/tca

Thermodynamics of liquid aluminium–copper–silicon alloys

D.S. Kanibolotsky [a,b], O.A. Bieloborodova [b], V.A. Stukalo [b], N.V. Kotova [b], V.V. Lisnyak [b,*]

[a] *Biophysical Department, Academician Bogach Institute, 2, Glushkova Avenue, Corpus 12, 03022 Kiev, Ukraine*
[b] *National Taras Shevchenko University, 64, Volodymyrska Street, UA-01033 Kyiv, Ukraine*

Received 14 June 2003; received in revised form 24 June 2003; accepted 29 August 2003

Abstract

In this paper, thermodynamic properties of liquid Al–Cu–Si alloys were studied by electromotive force method with liquid electrolyte at 920–1250 K and by high-temperature isoperibolic calorimetry at 1750 ± 5 K. The integral enthalpy of mixing in ternary Al–Cu–Si melts was estimated by Bonnier model for definition of boundary binary systems contribution to ternary alloys thermodynamics. The satisfactory agreement between experimental and estimated data demonstrates that thermodynamic properties of ternary liquid alloys are mainly defined by thermodynamic behaviour of boundary binary systems. Analysis of concentration and thermal dependencies of thermodynamic functions of mixing in liquid Al–Cu–Si alloys has been performed. It has been established that increasing of temperature results in decreasing of the integral enthalpy of mixing. This fact is probably associated with contribution of silicon clusters into ternary alloys thermodynamics.

Keywords: Thermodynamic properties; Electromotive force method; Calorimetry; Liquid alloys; Al–Cu–Si

1. Introduction

The Al–Cu–Si alloys are widely applied in an industry mainly as light constructional materials. The alloys have excellent technical characteristics, among them low solidification shrinkage, which allows to manufacture casting details of intricate profile in particular for internal-combustion engines [1,2]. The exhaustive knowledge on liquid state thermodynamics of initial melts is necessary for improvement of casting processes. Therefore, this paper presents the results of calorimetric and electrochemical study of liquid Al–Cu–Si alloys.

2. Experimental

2.1. Calorimetry

High-temperature isoperibolic calorimetry (HTICal) was used for study of enthalpies of mixing in ternary Al–Cu–Si liquid alloys. The aluminium partial enthalpies of mixing have been measured for five radial sections with x_{Si}:x_{Cu} ratio are: 0.15:0.85; 0.3:0.7; 0.5:0.5; 0.65:0.35 and 0.85:0.15 for $0.0 \leq x_{Al} \leq 0.6$. The reagents of Alpha (Johnson Matthey) origin: silicon bars (purity, 99.9999%), copper wire (purity, 99.99%) and aluminium wire (purity, 99.999%) were applied. Tungsten wire (purity, 99.96%) of the same origin was used for the calorimeter calibration. Calorimetric measurements technique and data treatment have been comprehensively reported in [3,4]. The experimental temperature was 1750 ± 5 K and the initial component in the crucible was silicon (1–1.6 g).

2.2. Electromotive force (EMF) method with liquid electrolyte

The ternary alloy samples for EMF study were prepared by standard arc-melting technique from the same components, which were used for calorimetric measurements. The reagents of Sigma-Aldrich Chemical Co, namely sodium chloride, aluminium chloride and potassium chloride constituted liquid electrolyte. The stated purity of sodium chloride and potassium chloride was 99.5%. The purity of $AlCl_3$ was higher than 99.95%. EMFs of galvanic cells $Ta\,|\,(-)\ Al_{liq}\,|$ azeotropic solution of $AlCl_3 + KCl + NaCl\,|\,(Al_xCu_ySi_{1-x-y})_{liq}\ (+)\,|\,Ta$ were studied in the temperature range from 920 up to 1250 K.

---

[*] Corresponding authors. Fax: +380-44-2302505.

E-mail addresses: lisnyak@chem.univ.kiev.ua (V.V. Lisnyak), Kanibolotsky@mail.univ.kiev.ua (D.S. Kanibolotsky).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00442-8

The EMF cell construction, routine of electrochemical experimental technique and mathematical processing of the basic experimental data have been described in [4,5]. Thermodynamic properties of liquid ternary alloys were measured for three radial sections of Al–Cu–Si Gibbs–Roseboom triangle, two of which were with constant x_{Si}:x_{Cu} relations (0.15:0.85 and 0.3:0.7 for $0.2 \leq x_{\mathrm{Al}} \leq 0.8$) and one jointed eutectic point in binary A1–Si system with copper angle of concentration triangle (x_{Al}:x_{Si} = 0.879:0.121). Integral excess Gibbs free energies ($\Delta_{\mathrm{mix}}G^{xs}$) and enthalpies ($\Delta_{\mathrm{mix}}H$) of mixing were defined from partial ones by integration of Gibbs–Duhem equation:

$$\Delta_{\mathrm{mix}}\Phi = (1-x_{\mathrm{Al}})\left[\int_{0}^{x_{\mathrm{Al}}/(1-x_{\mathrm{Al}})} \Delta_{\mathrm{mix}}\bar{\Phi}_{\mathrm{Al}} \times \mathrm{d}\left(\frac{x_{\mathrm{Al}}}{1-x_{\mathrm{Al}}}\right) + \Delta_{\mathrm{mix}}\Phi^{0}\right], \qquad (1)$$

where x_{Al} is an aluminium mole fraction, $\Delta_{\mathrm{mix}}\Phi$ is the integral excess thermodynamic function of mixing i.e. $\Delta_{\mathrm{mix}}G^{xs}$ or $\Delta_{\mathrm{mix}}H$; $\Delta_{\mathrm{mix}}\bar{\Phi}_{\mathrm{Al}}$ is the partial thermodynamic function of Al, and $\Delta_{\mathrm{mix}}\Phi^{0}$ is a optimised excess integral thermodynamic function of mixing in initial Cu–Si system [6] (see Table 1, Eqs. (3) and (4)).

2.3. Interpolation of ternary alloys thermodynamic functions of mixing

Two different interpolation methods were used for presentation of ternary alloys thermodynamic functions of mixing.

Method I [10] was grounded on common treatment of experimental data for studied sections and literature data for boundary binary systems, which where presented through ζ-function:

$$\zeta = \frac{\Delta_{\mathrm{mix}}\Phi}{(1-x_{\mathrm{Al}})(1-x_{\mathrm{Si}})(x_{\mathrm{Al}}+x_{\mathrm{Si}})}. \qquad (10)$$

The values of ζ-function were treated by least square regression for polynomials:

$$\begin{aligned}\zeta ={}& Q_{0,0} + Q_{0,1}x_{\mathrm{Al}} + Q_{1,0}x_{\mathrm{Si}} + Q_{0,2}x_{\mathrm{Al}}^{2} \\ &+ Q_{2,0}x_{\mathrm{Si}}^{2} + Q_{1,1}x_{\mathrm{Al}}x_{\mathrm{Si}} + Q_{0,3}x_{\mathrm{Al}}^{3} + Q_{3,0}x_{\mathrm{Al}}^{3} \\ &+ Q_{1,2}x_{\mathrm{Al}}^{2}x_{\mathrm{Si}} + Q_{2,1}x_{\mathrm{Al}}x_{\mathrm{Si}}^{2}. \qquad (11)\end{aligned}$$

This form of the thermodynamic functions of mixing representation allows to norm data in Gibbs–Roseboom triangle vertexes. Method I treats data for boundaries and for the ternary system with the same probability. Besides, the advantage of Method I is simple and convenient form of the data representation for using in thermodynamic calculations.

The calculation of $\Delta_{\mathrm{mix}}G^{xs}$ and $\Delta_{\mathrm{mix}}H$ by Method I were performed on the basis of thermodynamic data for boundaries presented by Eqs. (2)–(9) (shown in Table 1). The $\Delta_{\mathrm{mix}}H$ data for boundary A1–Cu system were taken from [8] at $T = 1590$ K. The approach is pertinent because, as it is shown in [8], $\Delta_{\mathrm{mix}}H$ in liquid A1–Cu alloys depends on temperature run negligibly. Moreover, this temperature is maximal at which reliable thermodynamic data are available for wide range of A1–Cu system. The $\Delta_{\mathrm{mix}}G^{xs}$ for A1–Cu melts was derived by extrapolation of optimised data [8] from 1373 to 1173 K using $\Delta_{\mathrm{mix}}H$ calorimetric data of [9]. The extrapolation was performed in an assumption of overcooled liquid alloys existence.

The interpolation Method II [3,11] consists in statistical treatment of differences between experimental $\Delta_{\mathrm{mix}}H$ data for the sections and calculated through one of geometric models by formula:

$$\begin{aligned}\Delta_{\mathrm{mix}}H_{\mathrm{AlCuSi}} ={}& x_{\mathrm{Al}}x_{\mathrm{Si}}(1-x_{\mathrm{Al}}-x_{\mathrm{Si}}) \\ &\times (Q'_{0,0} + Q'_{0,1}x_{\mathrm{Al}} + Q'_{1,0}x_{\mathrm{Si}} + Q'_{0,2}x_{\mathrm{Al}}^{2} \\ &+ Q'_{2,0}x_{\mathrm{Si}}^{2} + Q'_{1,1}x_{\mathrm{Al}}x_{\mathrm{Si}}). \qquad (12)\end{aligned}$$

The Bonnier geometric model [12] is optimal algorithm for thermodynamic functions representation in the case, when one of boundary binary systems relates to regular or ideal solutions, whereas in two others the strong component interaction is observed between atoms of different sorts. In our case the A1–Si system is characterised by insignificant negative enthalpies of mixing [8] and tending to zero integral

Table 1
Evaluated parameters for the polynomial representation of thermodynamic functions[a] concentration dependences for boundaries of Al–Cu–Si system

Thermodynamic function	Temperature (K)	ζ-Function (kJ mol^{-1})		Reference
$\Delta_{\mathrm{mix}}H$ (Cu–Si)	1281–1910	$-\dfrac{69\,600}{T\,(\mathrm{K})}x_{\mathrm{Cu}}^{2} - 16.2 + 97.7x_{\mathrm{Cu}} - 1094x_{\mathrm{Cu}}^{2} + 3514x_{\mathrm{Cu}}^{3} + 4748x_{\mathrm{Cu}}^{4} + 2216x_{\mathrm{Cu}}^{5}$	(2)	[7]
$\Delta_{\mathrm{mix}}G^{xs}$ (Cu–Si)	1173	$-94.26 + 189.77x_{\mathrm{Si}} - 103.18x_{\mathrm{Si}}^{2}$	(3)	[6]
$\Delta_{\mathrm{mix}}H$ (Cu–Si)	1173	$-144.08 + 436.54x_{\mathrm{Si}} - 445.60x_{\mathrm{Si}}^{2}$	(4)	[6]
$\Delta_{\mathrm{mix}}H$ (Al–Cu)	1590	$-37.72 - 18.45x_{\mathrm{Cu}} - 60.67x_{\mathrm{Cu}}^{2}$	(5)	[8]
$\Delta_{\mathrm{mix}}H$ (Al–Cu)	1463	$-34.2 + 26.2x_{\mathrm{Cu}} - 776x_{\mathrm{Cu}}^{2} + 3190x_{\mathrm{Cu}}^{3} - 6340x_{\mathrm{Cu}}^{4} + 5500x_{\mathrm{Cu}}^{5} - 1600x_{\mathrm{Cu}}^{6}$	(6)	[9]
$\Delta_{\mathrm{mix}}G^{xs}$ (Al–Cu)	1373	$-66.75 - 0.48x_{\mathrm{Al}} + 78.32x_{\mathrm{Al}}^{2} - 47.76x_{\mathrm{Al}}^{3}$	(7)	[8]
$\Delta_{\mathrm{mix}}H$ (Al–Si)	1750	$-2.85 - 72.01x_{\mathrm{Al}} + 78.17x_{\mathrm{Al}}^{2}$	(8)	[8]
$\Delta_{\mathrm{mix}}G^{xs}$ (Al–Si)	1150	$\dfrac{-22.15}{x_{\mathrm{Al}}} + 52.37 - 46.8x_{\mathrm{Al}}$	(9)	[8]

[a] Standard components state used for equations is liquid or overcooled liquid.

excess entropies of mixing [13]. Whereas, in liquid A1–Cu [8] and Cu–Si [7] alloys the significant negative enthalpies of mixing are observed.

Method II represents data for boundaries exactly and leads to less smoothed data for ternary systems. However, Method II represents thermodynamic functions through too complicated equations. Moreover, it is inapplicable in the case when data for boundary systems are incomplete, for example, due to high-temperature liquidus surface run. Thus this method is unusable for calculation of $\Delta_{\mathrm{mix}}G^{xs}$ at 1173 K in Al–Cu–Si system.

3. Results

The examples of primary HTICal and EMF data are plotted in Fig. 1a and b. The expressions for the concentration dependencies of $\Delta_{\mathrm{mix}}H$ and $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Al}}$ along five sections studied by HTICal are listed below (in kJ mol^{-1}):

- For the $\mathrm{Si}_{0.15}\mathrm{Cu}_{0.85}$–Al section:

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Al}} = (1-x_{\mathrm{Al}})^2(-45.64+3.93x_{\mathrm{Al}} + 216.28x_{\mathrm{Al}}^2 - 380.08x_{\mathrm{Al}}^3), \qquad (13)$$

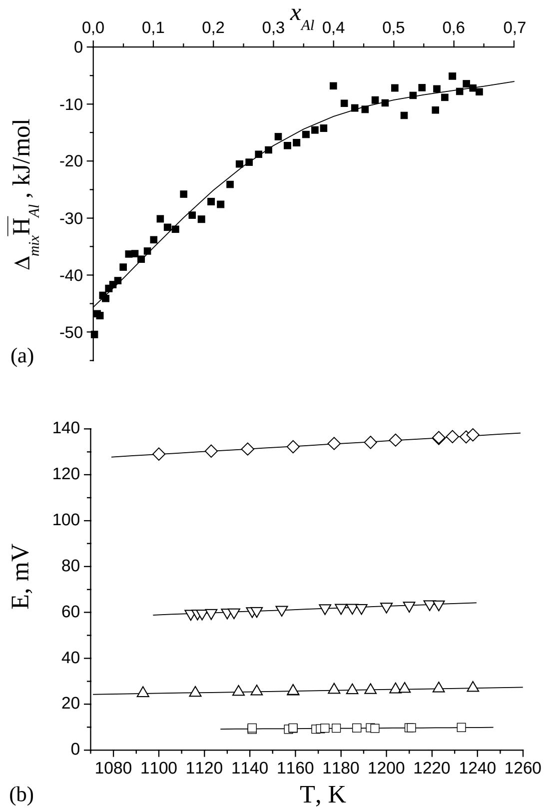

Fig. 1. The initial experimental data for section x_{Si}:x_{Cu}: 0.85:0.15: (a) calorimetric $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Al}}$ values, solid squares are experimental points, line is fitted data; (b) EMF temperature dependence: (◇) $x_{\mathrm{Al}} = 0.2$, (▽) $x_{\mathrm{Al}} = 0.4$, (△) $x_{\mathrm{Al}} = 0.6$, (□) $x_{\mathrm{Al}} = 0.8$, lines are fitted data.

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(-11.41-45.64x_{\mathrm{Al}}+1.97x_{\mathrm{Al}}^2 + 72.09x_{\mathrm{Al}}^3 - 95.02x_{\mathrm{Al}}^4). \qquad (14)$$

- For the $\mathrm{Si}_{0.3}\mathrm{Cu}_{0.7}$–Al section:

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Al}} = (1-x_{\mathrm{Al}})^2(-30.32+18.49x_{\mathrm{Al}}), \qquad (15)$$

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(-13.78-30.32x_{\mathrm{Al}}+9.24x_{\mathrm{Al}}^2). \qquad (16)$$

- For the $\mathrm{Si}_{0.5}\mathrm{Cu}_{0.5}$–Al section:

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Al}} = (1-x_{\mathrm{Al}})^2(-23.55+68.13x_{\mathrm{Al}} - 422.99x_{\mathrm{Al}}^2 + 622.47x_{\mathrm{Al}}^3), \qquad (17)$$

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(-9.76-23.55x_{\mathrm{Al}}+34.07x_{\mathrm{Al}}^2 - 141.0x_{\mathrm{Al}}^3 + 155.62x_{\mathrm{Al}}^4). \qquad (18)$$

- For the $\mathrm{Si}_{0.65}\mathrm{Cu}_{0.35}$–Al section:

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Al}} = (1-x_{\mathrm{Al}})^2(-20.84+38.72x_{\mathrm{Al}}-539.3x_{\mathrm{Al}}^2 + 1816.87x_{\mathrm{Al}}^3 - 1793.13x_{\mathrm{Al}}^4), \qquad (19)$$

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(-6.79-20.84x_{\mathrm{Al}}+19.36x_{\mathrm{Al}}^2 - 179.77x_{\mathrm{Al}}^3 + 454.22x_{\mathrm{Al}}^4 - 358.63x_{\mathrm{Al}}^5). \qquad (20)$$

- For the $\mathrm{Si}_{0.85}\mathrm{Cu}_{0.15}$–Al section:

$$\Delta_{\mathrm{mix}}\bar{H} = (1-x_{\mathrm{Al}})^2(-13.99+25.62x_{\mathrm{Al}}-94.5x_{\mathrm{Al}}^2), \qquad (21)$$

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(-2.22-13.99x_{\mathrm{Al}} - 12.81x_{\mathrm{Al}}^2 - 31.5x_{\mathrm{Al}}^3). \qquad (22)$$

The partial enthalpies of mixing of aluminium for the sections with confidence intervals are listed in Table 2. Corresponding to interpolation Method I, the $\Delta_{\mathrm{mix}}H$ in ternary system is given by the equation (in kJ mol^{-1}):

$$\Delta_{\mathrm{mix}}H = (1-x_{\mathrm{Al}})(1-x_{\mathrm{Si}})(x_{\mathrm{Si}}+x_{\mathrm{Al}}) \times(-105.55+92.5x_{\mathrm{Al}}+155.68x_{\mathrm{Si}} - 20.23x_{\mathrm{Al}}^2 - 60.16x_{\mathrm{Si}}^2 - 64.82x_{\mathrm{Al}}x_{\mathrm{Si}}). \qquad (23)$$

The $\Delta_{\mathrm{mix}}H$ concentration dependence in liquid Al–Cu–Si alloys derived from experimental data using Method II is

Table 2
The partial enthalpy of mixing (kJ mol^{-1}) of aluminium in liquid Al–Cu–Si alloys at 1750 K

x_{Al}	x_{Si}:x_{Cu}				
	0.15:0.85	0.3:0.7	0.5:0.5	0.65:0.35	0.85:0.15
0.0	−45.6 ± 4.3	−30.3 ± 2.8	−23.6 ± 6.0	−20.8 ± 3.7	−14.0 ± 2.4
0.1	−35.2 ± 2.0	−23.1 ± 1.8	−16.5 ± 2.5	−16.8 ± 2.0	−10.0 ± 0.9
0.2	−25.1 ± 1.8	−17.0 ± 1.1	−14.0 ± 2.1	−14.7 ± 1.4	−8.1 ± 0.9
0.3	−17.3 ± 1.2	−12.1 ± 0.8	−11.9 ± 1.5	−11.4 ± 1.1	−7.3 ± 0.7
0.4	−12.2 ± 1.0	−8.3 ± 0.7	−8.7 ± 1.3	−7.7 ± 0.8	−6.8 ± 0.5
0.5	−9.3 ± 0.7	−5.3 ± 0.6	−4.3 ± 0.9	−5.3 ± 0.6	−6.2 ± 0.5
0.6	−7.6 ± 0.5	−3.1 ± 0.5	−0.5 ± 1.1	−5.1 ± 0.5	−5.2 ± 0.7

Table 3
Thermodynamic properties of aluminum in ternary Al–Cu–Si alloys determined by EMF

x_{Al} (x_{Cu})	a_{Al}	γ_{Al}	$\Delta_{mix}\bar{G}_{Al}$ (kJ mol^{-1})	$\Delta_{mix}\bar{G}^{xs}_{Al}$ (kJ mol^{-1})	$\Delta_{mix}\bar{H}_{Al}$ (kJ mol^{-1})	$\Delta_{mix}\bar{S}_{Al}$ (J mol^{-1} K^{-1})	$\Delta_{mix}\bar{S}^{xs}_{Al}$ (J mol^{-1} K^{-1})
x_{Si}:x_{Cu} = 0.15:0.85 (T = 1173 K)							
0.2	0.01921 ± 0.0001	0.0960	−38.55 ± 0.04	−22.85	−18.8 ± 1.1	16.8 ± 0.9	3.4
0.4	0.1602 ± 0.0004	0.4005	−17.86 ± 0.02	−8.92	−5.1 ± 0.7	10.9 ± 0.6	3.3
0.6	0.463 ± 0.001	0.771	−7.51 ± 0.02	−2.53	−2.0 ± 0.6	4.7 ± 0.5	0.4
0.8	0.756 ± 0.002	0.945	−2.73 ± 0.03	−0.56	−0.6 ± 1.4	1.8 ± 0.2	−0.1
x_{Si}:x_{Cu} = 0.3:0.7 (T = 1173 K)							
0.2	0.0470 ± 0.0002	0.2352	−29.81 ± 0.03	−14.12	−12.0 ± 0.9	15.2 ± 0.8	1.8
0.4	0.1727 ± 0.0007	0.4318	−17.13 ± 0.03	−8.19	−5.3 ± 0.9	10.1 ± 0.8	2.4
0.6	0.500 ± 0.001	0.834	−6.75 ± 0.02	−1.77	−2.0 ± 0.6	4.1 ± 0.5	−0.2
0.8	0.764 ± 0.003	0.955	−2.62 ± 0.04	−0.45	−0.6 ± 1.7	1.7 ± 1.5	−0.1
x_{Si}:x_{Cu} = 0.879:0.121 (T = 1073 K)							
0.0130[a]	0.851 ± 0.009	0.981	−1.44 ± 0.09	−0.18	−1.3 ± 1.1	0.1 ± 1.0	−1.1
0.0265[a]	0.796 ± 0.011	0.930	−2.03 ± 0.12	−0.64	−2.0 ± 2.4	0.1 ± 2.2	−1.2
0.0453[a]	0.728 ± 0.006	0.867	−2.84 ± 0.08	−1.27	−1.8 ± 1.2	1.0 ± 1.2	−0.5

[a] These values are for x_{Cu}.

presented by following expressions (in kJ mol^{-1}):

$$\Delta_{mix}H = \frac{x_{Al}}{x_{Al}+x_{Si}}\Delta_{mix}H_{Al\text{–}Cu}(x_{Cu}) + \frac{x_{Si}}{x_{Al}+x_{Si}} \times \Delta_{mix}H_{Cu\text{–}Si}(x_{Cu}) + (x_{Al}+x_{Si})\Delta_{mix}H_{Al\text{–}Si} \times \left(\frac{x_{Al}}{x_{Al}+x_{Si}}\right) + \Delta_{mix}H_{AlCuSi}, \quad (24)$$

$$\Delta_{mix}H_{Al\text{–}Si} = \frac{x_{Al}}{x_{Al}+x_{Si}}\left(1-\frac{x_{Al}}{x_{Al}+x_{Si}}\right) \times \left[-2.85 - 72.01\frac{x_{Al}}{x_{Al}+x_{Si}} + 78.17\left(\frac{x_{Al}}{x_{Al}+x_{Si}}\right)^2\right], \quad (25)$$

$$\Delta_{mix}H_{AlCuSi} = x_{Al}x_{Si}(1-x_{Al}-x_{Si}) \times (304.21 - 1022x_{Al} - 1019x_{Si} + 359x_{Al}^2 + 676x_{Si}^2 + 2352x_{Al}x_{Si}). \quad (26)$$

The $\Delta_{mix}H_{Cu\text{–}Si}(x_{Cu})$ and $\Delta_{mix}H_{Al\text{–}Cu}(x_{Cu})$ have been derived from Eqs. (2) and (5), respectively (shown in Table 1).

The thermodynamic activities, activity coefficients and partial for aluminium thermodynamic functions of mixing determined by EMF are listed in Table 3. Integral excess Gibbs free energy of mixing in all studied concentration range can be presented via Method I for 1173 K (in kJ mol^{-1}):

$$\Delta_{mix}G^{xs} = (1-x_{Al})(1-x_{Si})(x_{Si}+x_{Al}) \times (-70.26 + 17.09x_{Al} + 62.01x_{Si} + 25.64x_{Al}^2 + 43.61x_{Si}^2 + 76.85x_{Al}x_{Si}). \quad (27)$$

4. Discussion

The integral enthalpies of mixing presented using Method I by Eq. (23) and II by Eq. (24) and simulated by the Bonnier model are in satisfactory agreement for the most part of Gibbs–Roseboom triangle (Fig. 2a). The $\Delta_{mix}H$ isolines of Method I correspond better to geometric model, then isolines of Method II. The isolines of Method II are in better agreement with those simulated by Bonnier model only for extrapolation area at $x_{Al} > 0.6$. The satisfactory agreement

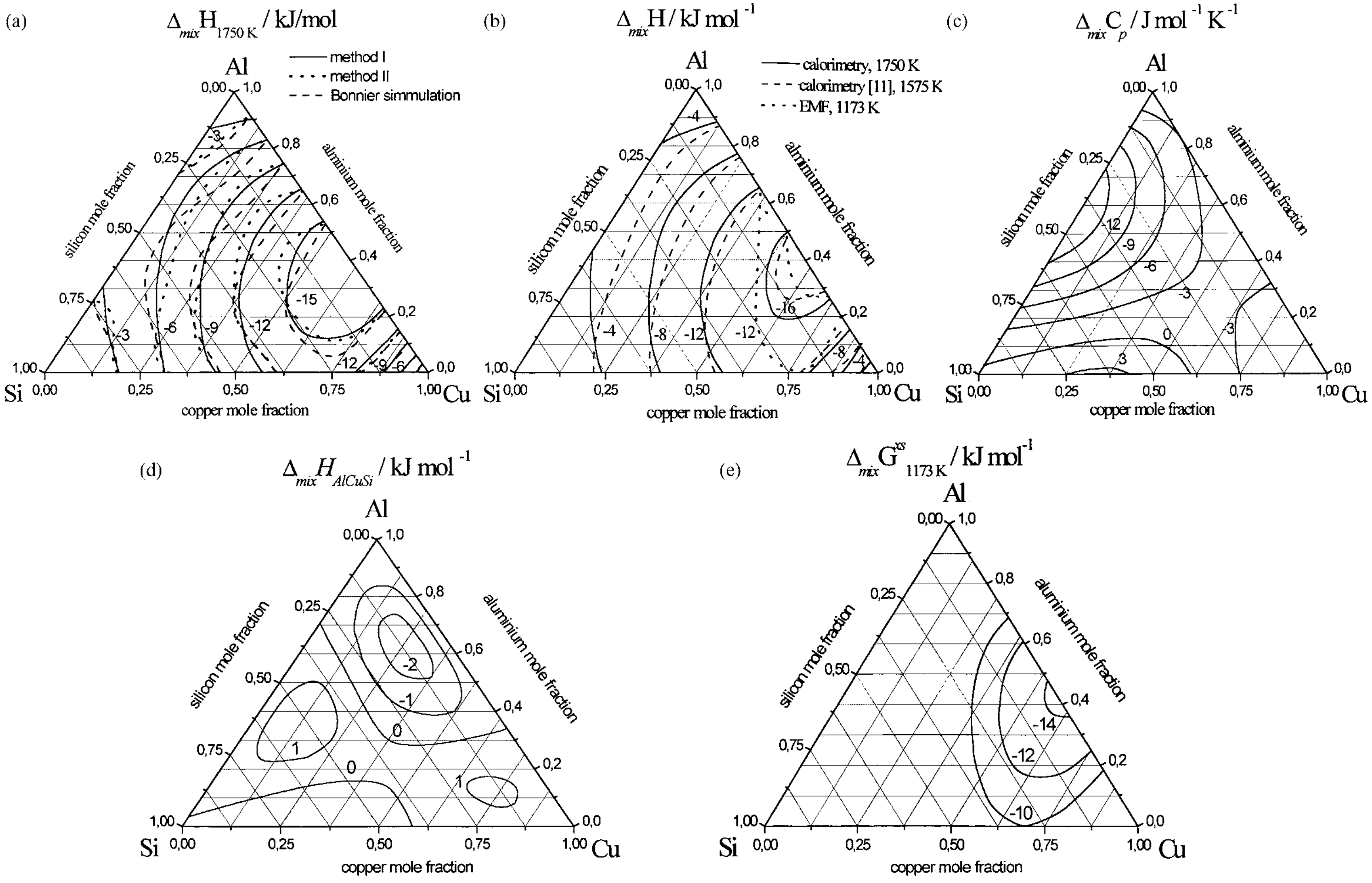

Fig. 2. Projection of thermodynamic functions of mixing isolines on the Gibbs–Roseboom triangle for Al–Cu–Si system: (a) experimental and estimated $\Delta_{\text{mix}}H$, (b) $\Delta_{\text{mix}}H$ at different temperatures, (c) $\Delta_{\text{mix}}C_p$, (d) $\Delta_{\text{mix}}H_{\text{AlCuSi}}$ and (e) $\Delta_{\text{mix}}G^{xs}$.

between experimental and estimated integral enthalpies of mixing testify, that thermodynamic behaviour of ternary liquid alloys are predominantly defined by thermodynamic properties of binary boundary systems.

The comparison of isoenthalpy lines determined at present study (EMF, 1173 K and HTICal, 1750 K) with literature calorimetric data [11] at 1575 K shows that heats of mixing become more exothermal at temperature increasing (Fig. 2b). It should be noticed that calorimetric data of Stolz for Al–Cu system [9] were used for isoenthalpy lines plotting at 1173 K.

The magnitude of heat capacity change at ternary alloy formation ($\Delta_{\text{mix}}C_p$) can be estimated using temperature dependence of $\Delta_{\text{mix}}H$:

$$\Delta_{\text{mix}}C_p = \frac{d\Delta_{\text{mix}}H}{dT} \approx \frac{\Delta\Delta_{\text{mix}}H}{\Delta T}. \tag{28}$$

For this propose the initial data of [11] were treated by Method I and following expression was derived (in kJ mol^{-1}):

$$\begin{aligned}\Delta_{\text{mix}}H &= (1 - x_{\text{Al}})(1 - x_{\text{Si}})(x_{\text{Si}} + x_{\text{Al}})\\ &\quad \times (-95.36 + 58.08x_{\text{Al}} + 120.38x_{\text{Si}}\\ &\quad + 11.83x_{\text{Al}}^2 - 36.25x_{\text{Si}}^2 + 17.87x_{\text{Al}}x_{\text{Si}}).\end{aligned} \tag{29}$$

The substitution of Eqs. (23) and (29) into Eq. (28) results in the following expression (in J mol^{-1} K^{-1}):

$$\begin{aligned}\Delta_{\text{mix}}C_p &= (1 - x_{\text{Al}})(1 - x_{\text{Si}})(x_{\text{Si}} + x_{\text{Al}})(-58.22 - 197x_{\text{Al}}\\ &\quad + 202x_{\text{Si}} - 183x_{\text{Al}}^2 - 137x_{\text{Si}}^2 - 473x_{\text{Al}}x_{\text{Si}}).\end{aligned} \tag{30}$$

The integral enthalpies of mixing have been extrapolated on 1173 K under the formula (28) using Eqs. (23) and (30). The extrapolation results have been compared with experimental integral enthalpies of mixing determined by EMF (Table 4). The agreement between extrapolated and experimental $\Delta_{\text{mix}}H$ values testifies that $\Delta_{\text{mix}}C_p$ is practically temperature-independent.

As one can see from Fig. 2c, the heat capacity change at alloy formation possesses negative values in practically all concentration range excluding concentration area nearby binary Cu–Si system. The absolute value of $\Delta_{\text{mix}}C_p$ increase, at changing of ternary alloy composition from Cu-corner of Gibbs–Roseboom triangle to Al–Si system. Therefore, temperature dependence of $\Delta_{\text{mix}}H$ increases at copper concentration decreasing.

Table 4
The integral enthalpy of mixing in liquid Al–Cu–Si alloys at 1173 K

x_{Si}:x_{Cu}	x_{Al}	Experimental data (kJ mol^{-1})	Extrapolation (kJ mol^{-1})
0.15:0.85	0.2	−14.2	−14.1
	0.4	−13.6	−14.8
	0.6	−10.3	−10.9
	0.8	−5.8	−4.5
0.3:0.7	0.2	−12.0	−13.9
	0.4	−11.2	−12.6
	0.6	−8.7	−8.6
	0.8	−5.0	−3.5

It is known that $\Delta_{\text{mix}}H$ in liquid Al–Si alloys become more negative at temperature increasing. This thermodynamic behaviour is associated with silicon clusters existence [14]. At melt heating these clusters are destructed, which amplifies the interaction between aluminium and silicon [8].

The same phenomenon is observed for Al–Cu–Si alloys. The atypical $\Delta_{\text{mix}}H$ temperature dependence intensifies for the ternary alloys compositions, which tend to boundary A1–Si system (Fig. 2b, $\Delta_{\text{mix}}C_p$ is increasing with decreasing of copper content). So, the atypical $\Delta_{\text{mix}}H$ temperature dependence in Al–Cu–Si system can be explained by Si–Si and A1–Si bonds redistribution.

This conclusion also is confirmed by differences between experimental and simulated by geometric model $\Delta_{\text{mix}}H$ values, i.e. $\Delta_{\text{mix}}H_{\text{AlCuSi}}$. Corresponding to earlier study [11], $\Delta_{\text{mix}}H_{\text{AlCuSi}}$ at 1575 K is positive and reaches numerical values up to 3.5 kJ mol^{-1}, which manifests the preferable interaction of same type atoms (i.e. silicon clusters formation). Thus, in accordance with present study (Fig. 2d), the $\Delta_{\text{mix}}H_{\text{AlCuSi}}$ at 1750 K reach a maximal positive value of 1.7 kJ mol^{-1} at $x_{\text{Al}} = 0.36$ and $x_{\text{Si}} = 0.52$. Therefore, the silicon clusters concentration at 1750 K is lower then at 1575 K. The microareas of silicon atoms at 1750 K may exist at concentration range nearby Al–Si boundary system, where $\Delta_{\text{mix}}H_{\text{AlCuSi}} > 0$ ($0.2 < x_{\text{Al}} < 0.55$ and $0.35 < x_{\text{Si}} < 0.7$). Moreover, $\Delta_{\text{mix}}H_{\text{AlCuSi}}$ at 1750 K possess also negative values up to −2.5 kJ mol^{-1} at $x_{\text{Al}} = 0.62$ and $x_{\text{Si}} = 0.12$. It can testify that interaction between different type of atoms at the area limited by isoline −1 kJ mol^{-1} ($x_{\text{Al}} > 0.4$ and $x_{\text{Si}} < 0.25$) prevails over interaction between same type of atoms.

From three boundary binary systems, the greatest interaction between atoms of the different type is observed in liquid Al–Cu alloys ($\Delta_{\text{mix}}H$ reaches extremum of −17.1 kJ mol^{-1} at $x_{\text{Cu}} = 0.65$). The phase diagram of Al–Cu system includes congruently melting binary compound Cu_3Al [15]. The strong interaction between copper and aluminium retains in the melt, which leads to formation of Cu_3Al binary clusters in liquid [8]. The less negative deviation from Raoultian is peculiar to boundary Cu–Si system, $\Delta_{\text{mix}}H^{\text{min}} = -14.0$ kJ mol^{-1} at $x_{\text{Si}} = 0.25$. This composition corresponds to stoichiometry of congruently melting intermediate η-phase [15] and Cu_3Si clusters existing in liquid alloys [16]. The least absolute values of integral thermodynamic functions of mixing are observed for boundary A1–Si system ($\Delta_{\text{mix}}H^{\text{min}} = -4.9$ kJ mol^{-1} at $x_{\text{Si}} = 0.5$). This system is characterised by state diagram of simple eutectic type and weak interaction between aluminium and silicon atoms in the liquid phase.

According to the thermodynamic behaviour of boundary binary systems, the negative $\Delta_{\mathrm{mix}}H$ and $\Delta_{\mathrm{mix}}G^{xs}$ values in ternary alloys increase at composition shift from Al–Si system to copper corner of concentration triangle (Fig. 2a and e), which evidences the components interaction increasing. The greatest interaction in ternary system is observed along Cu_3Si–Cu_3Al_2 section confirmed by maximal negative $\Delta_{\mathrm{mix}}H$ and $\Delta_{\mathrm{mix}}G^{xs}$ values.

5. Conclusion

The increasing of $\Delta_{\mathrm{mix}}H$ absolute values has been observed at heating of A1–Cu–Si liquid alloys. The tendency amplifies at lowering of copper content. The temperature dependence of integral enthalpy of mixing is caused by destruction of silicon clusters at heating, which leads to amplification of interaction between aluminium and silicon.

The concentration dependences of thermodynamic functions of mixing testify that thermodynamic behaviour of Al–Cu–Si liquid alloys is predominantly determined by component interaction in boundary Al–Cu system and in some less extent by the interaction in Cu–Si system.

References

[1] T. Kobayashi, T. Ito, Q. Yao, N. Fatahalla, Mater. Sci. Technol. 15 (1999) 1037.
[2] S. Shivkumar, L. Wang, C. Keller, Z. Metallkd. 85 (1994) 394.
[3] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, Thermochim. Acta., in press.
[4] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, J. Therm. Anal. Calorim. 71 (2003) 583.
[5] T.D. Van, L. Segers, R. Winand, J. Electrochem. Soc. 141 (1994) 927.
[6] E.A. Bieloborodova, T.N. Zinevitch, A.I. Gab, D.V. Prutskov, G.N. Bondarenko, Casting Processes 2 (1994) 55.
[7] V. Witusiewicz, I. Arpshofen, H.-J. Seifert, F. Sommer, F. Aldinger, Z. Metallkd. 91 (2000) 128.
[8] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, J. Therm. Anal. Calorim. 70 (2002) 975.
[9] U.K. Stolz, I. Arpshofen, F. Sommer, B. Predel, J. Phase Equilib. 14 (1993) 473.
[10] A.M. Turchanin, I.V. Nikolaenko, Rasplavy 5 (1993) 60.
[11] V.T. Witusiewicz, I. Arpshofen, H.-J. Seifert, F. Aldinger, J. Alloys Comp. 297 (2000) 176.
[12] E. Bonnier, R. Caboz, C. R. Acad. Sci. (Paris) 250 (1960) 527.
[13] S.C. Schaefer, N.A. Gokcen, High Temp. Sci. 11 (1979) 31.
[14] W.M. Wang, X.F. Bian, H.R. Wang, Z. Wang, L. Zhang, Z.G. Liu, J.-M. Liu, J. Mater. Res. 16 (2001) 3592.
[15] B. Massalski, Binary Alloy Phase Diagrams, vols. 1 and 2, American Society for Metals, Metals Park, OH, 1990, p. 2224.
[16] O. Akinlade, B.C. Anunsionwu, L.A. Hussain, Z. Metallkd. 89 (1998) 27.