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THERMODYNAMIC PROPERTIES OF LIQUID Al–Si AND Al–Cu ALLOYS

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Abstract

The partial and integral enthalpies of mixing in liquid Al–Si and Al–Cu alloys were determined by high-temperature isoperibolic calorimetry at 1750±5 and 1590±5, respectively. The thermodynamic properties of Al–Si melts were also studied by electromotive force method in temperature range 950–1270 K. The partial and integral excess Gibbs free energies of mixing in liquid Al–Si and Al–Cu alloys were calculated from literature data on thermodynamic activity of aluminium. The comparison of our experimental results with literature data has been performed.

Keywords: Al–Cu, Al–Si, calorimetry, electrochemistry, electromotive force method, liquid alloys, thermodynamics

Introduction

Integral enthalpies of mixing ($\Delta_{\mathrm{mix}}H$) in liquid Al–Si alloys were studied by high-temperature calorimetry in works [1–6]. Comparison of $\Delta_{\mathrm{mix}}H$ data [3] with high-temperature one [1, 2, 4, 5] (Fig. 1) leads to a conclusion about temperature dependence of $\Delta_{\mathrm{mix}}H$ values in this system. This statement is confirmed by data [6], which have been measured at three different temperatures: 1073, 1373 and 1573 K. Though data [6] are rather overstated by absolute value, as detected by comparison with [3], however data [6] testifies that $\Delta_{\mathrm{mix}}H$ is temperature dependent: namely, $\Delta_{\mathrm{mix}}H$ become more negative at melt heating. This fact, probably, is related to structural transformations in the melt and binary clusters formation [7].

The thermodynamic activities of aluminium in liquid Al–Si alloys were determined by electromotive force (emf) method [8, 9], heterogeneous equilibrium method [10] and Knudsen effusion technique [11]. It can be seen from Fig. 2, that the alloys are characterized by negative deviations from Raoult's law.

The data [9–11] are in a good agreement, whereas the thermodynamic activities of [8] show more negative deviations from ideality.

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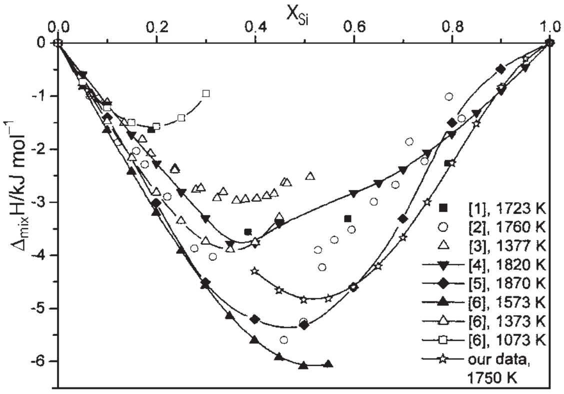

Fig. 1 Integral enthalpy of mixing in liquid Al–Si alloys

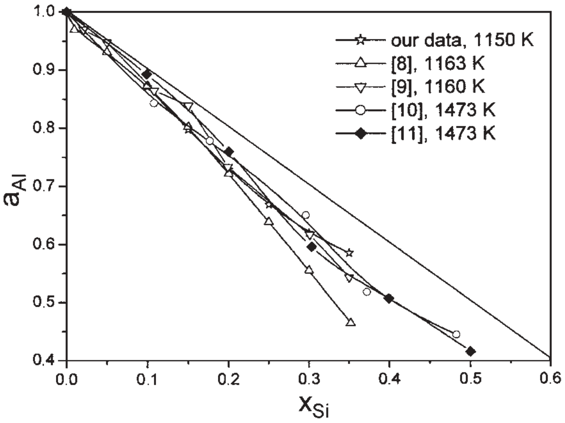

Fig. 2 Thermodynamic activities of aluminium in liquid Al–Si alloys

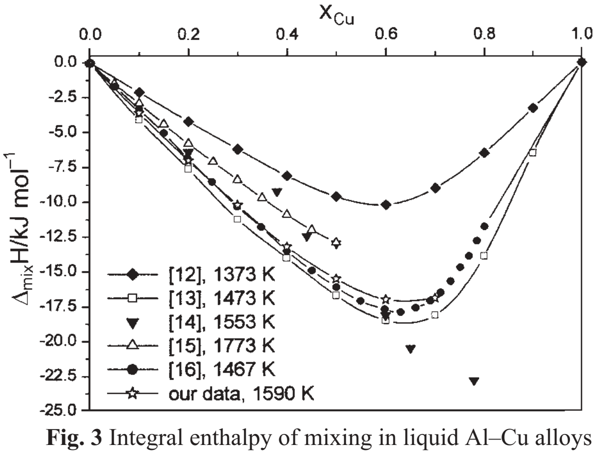

Fig. 3 Integral enthalpy of mixing in liquid Al–Cu alloys

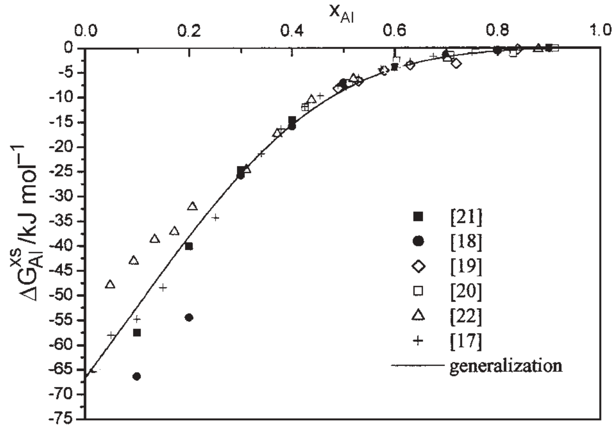

Fig. 4 Partial excess Gibbs free energy of mixing of aluminium in liquid Al–Cu alloys at 1373 K

The thermodynamics of liquid Al–Cu alloys have been studied by high temperature calorimetry [12–16] (Fig. 3), emf [17–19], heterogeneous equilibrium [20], effusion [21], evaporation and condensation [22] methods (Fig. 4).

The $\Delta_{mix}H$ data of [13, 16] are in a good agreement, but data of [12, 15] are less negative then idem (Fig. 3).

The data [17–22] on the thermodynamic activity of aluminium in Al–Cu system are in agreement and show more negative deviations from ideal solutions than activity in Al–Si system. But the copper thermodynamic activities (defined only in [18, 21, 22]) are in disagreement. Therefore, it is of special interest to provide the generalization of aluminium activity data [17–22] and compute copper activity.

As one can see from Figs 1 and 3, numerous data on $\Delta_{mix}H$ in Al–Si and Al–Cu systems are in disparity. That is why presented thermodynamic study of these systems has been conducted by high-temperature isoperibolic calorimetry (HTICal) and emf methods.

Experimental procedures

Both (HTICal and emf) measurements were carried out under purified argon at atmospheric pressure. The alloy samples for emf were prepared by standard arc-melting technique from silicon (purity, 99.99 mass%), aluminium (purity, 99.99 mass%) and copper (purity, 99.95 mass%) reagents of Alpha. The same materials as well as tungsten (Alpha, purity, 99.96 mass%) were used for HTICal experiments. Riedel-de Haën Co. was supplied the salts KCl, NaCl, $AlCl_3$ for liquid electrolyte preparation. The HTICal experiment and emf procedure in general described in [23].

The (–)Al_{Liq} | $AlCl_3$ in KCl+NaCl (azeotropic solution)| $(Al–Si)_{Liq}$ (+) galvanic cells were used for emf experiments at 950–1270 K. In contrast to [23], the alpha function ($\alpha_{Al}=\Delta_{mix}\overline{G}_{Al}^{xs}/(1-x_{Al})^2$) was calculated for the statistical smoothing of experimental $\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$ data. The α_{Al}-function values was treated by least square regression as follows (in kJ mol^{-1}): $\alpha_{\mathrm{Al}}=52.37-93.55x_{\mathrm{Al}}$. The $\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Si}}$ value in liquidus at 1150 K were calculated from Al–Si phase diagram [24] by Wagner equation:

$$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Si}}=\Delta_{\mathrm{m}}S_{\mathrm{Si}}(T_{\mathrm{m}}-T_{\mathrm{l}})-RT\ln x_{\mathrm{Si}} \qquad (1)$$

where $x_{\mathrm{Al}}=0.653$, $\Delta_{\mathrm{m}}S_{\mathrm{Al}}$ is an aluminium entropy of melting, T_{m} is melting temperature of pure silicon, T_{l} is a liquidus temperature (1150 K).

The integral excess Gibbs free energy of mixing near liquidus was computed using measured $\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$ values at $x_{\mathrm{Al}}=0.659$ and calculated $\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Si}}$ at $x_{\mathrm{Al}}=0.653$. The determined $\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$ value (–2.74 kJ mol^{-1}) were related to the average molar ratio $x_{\mathrm{Al}}=0.656$. The $\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$ values in whole studied concentration range were calculated by Darken's method:

$$\Delta_{\mathrm{mix}}G^{\mathrm{xs}}=(1-x_{\mathrm{Al}})\left(\int_{0.656}^{x_{\mathrm{Al}}}\alpha_{\mathrm{Al}}\mathrm{d}x_{\mathrm{Al}}+C\right) \qquad (2)$$

where constant C is equal to –2.74 kJ mol^{-1}.

Partial and integral excess entropies of mixing in liquid Al–Si melts were computed using enthalpies of mixing determined in [6] at 1073 K.

The combined calculation method for determination of $\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$ from literature data on thermodynamic activity of aluminium is described below. The partial excess Gibbs free energies of mixing of aluminium were calculated from activity values (Fig. 4). Then appropriate α_{Al} function set was found from $\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$.

The α_{Al} function was proceeded via least square regression for polynomial model:

$$\alpha_{\mathrm{Al}}=Q_0+Q_1x_{\mathrm{Al}}+Q_2x^2_{\mathrm{Al}}+\ldots+Q_{\mathrm{j}}x^{\mathrm{j}}_{\mathrm{Al}} \qquad (3)$$

where Q_{j} are coefficients. The Fisher's exact test was used for polynomial degree definition.

The integral excess Gibbs free energies of mixing were calculated by Darken's method. After Darken's integration the Eq. (3) should be as follows:

$$\Delta_{\mathrm{mix}}G^{\mathrm{xs}}=x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(Q_0+1/2Q_1x_{\mathrm{Al}}+1/3Q_2x^2_{\mathrm{Al}}+\ldots+(j+1)^{-1}Q_{\mathrm{j}}x^{\mathrm{j}}_{\mathrm{Al}}) \qquad (4)$$

The $\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$ for Al–Cu system have been computed for two temperatures: 1373 and 1473 K. In the case of calculation at 1373 K, the initial aluminium activities were taken from [17–22]. While, the initial data for calculation at 1473 K were taken from [20, 21] because the activity values of aluminium for this temperature are given only in these works. The calculation for Al–Si liquid alloys was conducted for 1473 K, and the initial α_{Al} values using in treatment were from [10, 11].

Table 1 Partial and integral enthalpies of mixing in liquid Al–Si and Al–Cu alloys, kJ mol^{-1}

Al–Si at 1750 K				Al–Cu at 1590 K			
x_{Al}	$-\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Al}}\pm2\sigma$	$\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Si}}\pm2\sigma$	$-\Delta_{\mathrm{mix}}H\pm2\sigma$	x_{Cu}	$-\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Cu}}\pm2\sigma$	$-\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Al}}\pm2\sigma$	$-\Delta_{\mathrm{mix}}H\pm2\sigma$
0.0	2.9±0.4	0	0	0.0	38±11	0	0
0.1	12.1±1.7	0.41±0.02	0.8±0.1	0.1	35.0±5.4	0.13±0.07	3.6±0.6
0.2	14.3±1.5	0.7±0.1	2.3±0.3	0.2	33.5±3.2	0.4±0.2	7.0±0.8
0.3	12.2±1.3	0.0±0.2	3.7±0.4	0.3	31.9±2.6	0.9±0.5	10.2±1.1
0.4	8.3±0.9	–2.2±0.4	4.6±0.5	0.4	29.4±1.9	2.3±0.8	13.2±1.3
0.5	4.1±0.7	–5.6±0.7	4.9±0.6	0.5	25.4±1.1	5.6±1.1	15.5±1.1
0.6	0.8±0.8	–9.6±1.8	4.3±0.7	0.6	20.1±0.7	12.3±1.6	17.0±1.1
0.7	–	–	–	0.7	13.8±0.8	24.2±4.1	16.9±1.8

Results and discussion

Results of calorimetric study of liquid Al–Si, Al–Cu alloys can be presented in the form of following equations:

$$\Delta_{\mathrm{mix}} H_{(\mathrm{Al–Si})} = x_{\mathrm{Al}}(1-x_{\mathrm{Al}})(-2.85-72.01x_{\mathrm{Al}}+78.17x_{\mathrm{Al}}^2) \tag{5}$$

$$\Delta_{\mathrm{mix}} H_{(\mathrm{Al–Cu})} = x_{\mathrm{Cu}}(1-x_{\mathrm{Cu}})(-37.72-18.45x_{\mathrm{Cu}}-60.67x_{\mathrm{Cu}}^2) \tag{6}$$

The partial and integral enthalpies of mixing in liquid binary systems with estimated intervals are listed in Table 1.

Presented data on $\Delta_{\mathrm{mix}}H$ for Al–Si system are in accordance with [5] as one can see from Fig. 1. Consequently, the $\Delta_{\mathrm{mix}}H$ data measured at 1723 and 1820 K in works [1, 4] are understated by absolute value. The determined integral enthalpies of mixing for liquid Al–Cu alloys are almost coincide with [16]. Therefore, data [12, 15] must be taken as understated.

In contradiction to binary Al–Si system, the liquid Al–Cu alloys are characterized by more negative $\Delta_{\mathrm{mix}}H$ values and the function extremum is displaced into area of copper enriched alloys. This fact is explained by intermediate compound $\mathrm{Cu_3Al}$ existence, which congruently melts at 1322 K [24]. The strong interaction between

Table 2 Results of electrochemical study of Al–Si system at 1150 K

x_{Si}	$-\Delta_{\mathrm{mix}}\overline{G}_{\mathrm{Al}}$	$-\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$	α_{Al}	γ_{Al}
	kJ mol^{-1}			
0.096	1.15	0.18	0.887	0.981
0.116	1.74	0.56	0.834	0.943
0.145	2.07	0.57	0.805	0.942
0.194	3.04	0.97	0.728	0.904
0.243	3.83	1.17	0.670	0.885
0.292	4.47	1.17	0.627	0.885
0.341	4.77	0.78	0.607	0.922

Table 3 The thermodynamic properties of components in liquid Al–Si alloys at 1150 K

x_{Al}	α_{Al}	α_{Si}	$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$	$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Si}}$	$\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$	$\Delta_{\mathrm{mix}}\overline{S}^{\mathrm{xs}}_{\mathrm{Al}}$	$\Delta_{\mathrm{mix}}\overline{S}^{\mathrm{xs}}_{\mathrm{Si}}$	$\Delta_{\mathrm{mix}}S^{\mathrm{xs}}$
			kJ mol^{-1}			J mol^{-1} K^{-1}		
0.65	0.584	0.189	–1.03	–5.91	–2.74	–	–	–
0.7	0.619	0.166	–1.18	–5.65	–2.52	–3.16	11.96	1.37
0.75	0.668	0.135	–1.11	–5.86	–2.30	–1.57	7.79	0.77
0.8	0.728	0.100	–0.9	–6.60	–2.04	–0.70	4.78	0.41
0.85	0.797	0.065	–0.61	–7.93	–1.71	–0.30	2.90	0.19
0.9	0.871	0.035	–0.31	–10.04	–1.29	–0.14	2.17	0.06

Table 4 The thermodynamic properties of liquid Al–Cu and Al–Si alloys, determined by common treatment of the literary data, in kJ mol^{-1}

	Al–Cu, 1373 K [17–22]					Al–Cu, 1473 K [20, 21]					Al–Si, 1473 K [10, 11]				
x_{Al}	$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$	$\Delta_{mix}\overline{G}^{\mathrm{xs}}_{\mathrm{Cu}}$	$\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$	α_{Al}	α_{Cu}	$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$	$\Delta_{mix}\overline{G}^{\mathrm{xs}}_{\mathrm{Cu}}$	$\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$	α_{Al}	α_{Cu}	$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Al}}$	$\Delta_{\mathrm{mix}}\overline{G}^{\mathrm{xs}}_{\mathrm{Si}}$	$\Delta_{\mathrm{mix}}G^{\mathrm{xs}}$	α_{Al}	α_{Cu}
	kJ mol^{-1}					kJ mol^{-1}					kJ mol^{-1}				
0	–66.75	0	0	0	1	–80.01	0	0	0	1					
0.1	–52.40	–0.79	–5.95	0.001	0.840	–55.97	–1.23	–6.70	0.010	0.904					
0.2	–37.81	–3.37	–10.26	0.007	0.595	–37.70	–4.43	–11.08	0.046	0.697					
0.3	–25.01	–7.62	–12.84	0.034	0.359	–24.23	–8.87	–13.48	0.138	0.485	–6.59	–1.21	–2.82	0.175	0.6
0.4	–15.04	–12.96	–13.79	0.107	0.193	–14.65	–13.98	–14.25	0.302	0.319	–4.84	–2.15	–3.23	0.269	0.5
0.5	–8.10	–18.58	–13.34	0.246	0.098	–8.17	–19.25	–13.71	0.513	0.208	–3.36	–3.36	–3.36	0.380	0.3
0.6	–3.84	–23.74	–11.80	0.429	0.050	–4.06	–24.24	–12.13	0.7186	0.138	–2.15	–4.84	–3.23	0.503	0.2
0.7	–1.60	–27.83	–9.47	0.608	0.026	–1.69	–28.59	–9.76	0.871	0.097	–1.21	–6.59	–2.82	0.634	0.1
0.8	–0.60	–30.75	–6.63	0.759	0.014	–0.52	–32.02	–6.82	0.959	0.073	–0.54	–8.61	–2.15	0.766	0.0
0.9	–0.17	–33.17	–3.47	0.887	0.005	–0.08	–34.38	–3.51	0.994	0.060	–0.13	–10.89	–1.21	0.890	0.0

atoms of different types is remained at transition into the liquid, resulting in binary clusters formation [25]. However, the Al–Si system phase diagram is simple eutectic type [24] and characterized by low interatomic interaction.

The initial non-smoothed electrochemical experimental data on Al–Si system are listed in Table 2.

The thermodynamic properties of liquid Al–Si alloys (emf, 1150 K) are listed in Table 3.

As it can be seen from Table 3, the negative integral excess Gibbs free energies of mixing and positive $\Delta_{mix}S^{xs}$ values are observed in binary Al–Si system. The positive $\Delta_{mix}S^{xs}$ values can be explained by non-configurative contributions. The experimentally measured thermodynamic activities of aluminium correspond well to data of [9–11], as one can see in Fig. 3.

The results of common treatment of literature data on aluminium thermodynamic activity are listed in Table. 4.

The integral excess Gibbs free energy of mixing can be written as follows (in kJ mol^{-1}):

$$\Delta_{mix}G^{xs}=x_{Al}(1-x_{Al})(-13.45) \text{ (system Al–Si, 1473 K)} \quad (7)$$

$$\Delta_{mix}G^{xs}= x_{Al}(1-x_{Al})(-66.75-0.48x_{Al}++78.32x_{Al}^{2}-47.76x_{Al}^{3}) \text{(system Al–Cu, 1373 K)} \quad (8)$$

$$\Delta_{mix}G^{xs}= x_{Al}(1-x_{Al})(-80.01+56.35x_{Al}-12.02x_{Al}^{2}) \text{(system Al–Cu, 1473 K)} \quad (9)$$

It has been observed from Table 4, that the partial and integral excess Gibbs free energies of mixing in Al–Cu system are negative. The aluminium partial excess Gibbs free energy of mixing at infinite dilution changes from –66.8 up to –80.0 kJ mol^{-1} at melt heating from 1373 up to 1473 K. The $\Delta_{mix}G^{xs}$ function reach an extremum at x_{Al}=0.4. The partial and integral excess Gibbs free energy of mixing in Al–Si system are negative too. The extreme $\Delta_{mix}G^{xs}$ value is equal to –3.36 kJ mol^{-1} at equimolar composition.

Conclusions

The calorimetric study of liquid Al–Cu and Al–Si alloys demonstrates negative integral enthalpies of mixing, which are greater by absolute value for Al–Cu system. This thermodynamic behavior is associated with binary clusters influence. The positive values of integral excess entropy of mixing in liquid Al–Si alloys determined by emf can be related to the non-configurative contributions. The experimental data determined by HTICal and emf show a good agreement with literature. The generalization of literature data on aluminum thermodynamic activity has allowed to comprehensively describing thermodynamic properties of these alloys.

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