

Thermodynamic Properties of Eutectic Silumins Doped by Transition Metals

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The thermodynamic properties of the liquid silumins $(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Tr}_x$, where $\text{Tr} = \text{Cu}, \text{Fe}, \text{Ni}$ and Ti , have been measured, using the electromotive force method at 1040 K. It has been found that diluted solutions of Fe or Ni in eutectic silumins at Tr molar fractions of $0 < x_{\text{Fe}} \leq 0.035$ and $0 < x_{\text{Ni}} \leq 0.027$ are characterized by positive deviations from ideality for aluminium. However, the deviations become negative at increasing of the Tr concentration. However, molten silumins doped by Ti and Cu show negative deviations from Raoult's law for aluminium at the studied concentrations. Thermodynamic activity of Al in the silumins decreases in the sequence of $\text{Fe} \rightarrow \text{Ni} \rightarrow \text{Cu} \rightarrow \text{Ti}$ for the dopants.

Key words: Silumins; Al–Si–(Cu, Fe, Ni, Ti); Liquid Alloys; Electromotive Force Method; Thermodynamic Activity; Gibbs Energy.

1. Introduction

Transition metals (Tr) are frequently used as dopants in aluminium-silicon commercial alloys (silumins). For the creation of new silumins and for optimisation of technological processes of alloy production it is necessary to know the thermodynamics of the initial liquid alloys at temperatures close to the liquidus. However, no thermodynamic data are available for eutectic silumins doped by transition metals below 1173 K [1]. So, the present contribution is devoted to the determination of the thermodynamic properties of liquid eutectic Al–Si alloys doped with Cu, Fe, Ni and Ti by means of the electromotive force (EMF) method at 1040 K.

2. Experimental

The reagents: silicon bars (purity 99.99% mass), wires of iron (purity 99.95%), titanium, nickel, aluminium and copper (all of 99.99% purity), were supplied by Alfa. The alloys for the EMF study were prepared by standard arc-melting technique. The salts of Sigma-Aldrich, NaCl, KCl and AlCl_3 , were all of 99.95% purity. The elec-

tromotive forces were measured in galvanic cells of type: $(-) \text{Ta} | \text{Al}_{\text{liq}} | \text{AlCl}_3 + \text{KCl} + \text{NaCl}$ (azeotropic solution) $| \{ (\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Tr}_x \}_{\text{liq}} | \text{Ta} (+)$, where $\text{Tr} = \text{Cu}, \text{Fe}, \text{Ni}$ or Ti . The EMF cell and experimental technique have been described in [1, 2]. The EMF values in mV were given by the equation

$$E = A + BT \quad (1)$$

with T in K. It is known, that

$$\Delta_{\text{mix}} \bar{G}_{\text{Al}} = -10^{-3} ZFE = RT \ln a_{\text{Al}}, \quad (2)$$

where $\Delta_{\text{mix}} \bar{G}_{\text{Al}}$ = partial Gibbs free energy of mixing of Al [J mol^{-1}], Z = ion charge, F = Faraday constant [$\text{J mol}^{-1} \text{K}^{-1}$], $E = A + BT$, a_{Al} = Al activity, or alternatively

$$\Delta_{\text{mix}} \bar{G}_{\text{Al}} = \Delta_{\text{mix}} \bar{H}_{\text{Al}} - T \Delta_{\text{mix}} \bar{S}_{\text{Al}}, \quad (3)$$

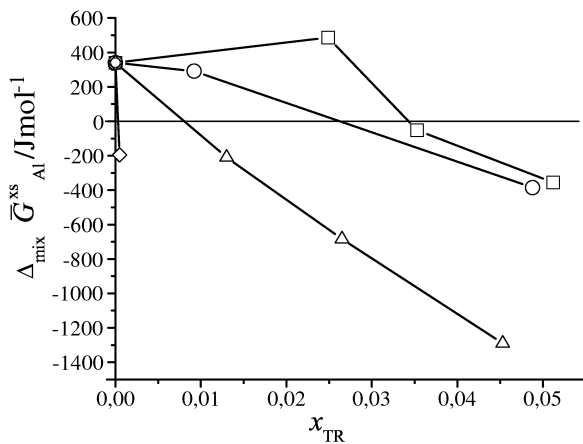
where $\Delta_{\text{mix}} \bar{H}_{\text{Al}}$ = Al partial enthalpy of mixing [J mol^{-1}], $\Delta_{\text{mix}} \bar{S}_{\text{Al}}$ = Al partial entropy of mixing [$\text{J mol}^{-1} \text{K}^{-1}$]. Thus the following equations can be obtained:

$$\Delta_{\text{mix}} \bar{H}_{\text{Al}} = -10^{-3} ZFA, \quad (4)$$

Table 1. EMF of the $\text{Al}_{\text{liq}}|\text{AlCl}_3+\text{KCl}+\text{NaCl}|\{(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Tr}_x\}_{\text{liq}}$ (Tr = Cu, Fe, Ni and Ti) galvanic cells.

$x_{\text{Cu}} = 0.0130, A = 4.64, B = 0.00032$		$x_{\text{Cu}} = 0.0265, A = 6.78, B = 0.00023$		$x_{\text{Cu}} = 0.0453, A = 6.19, B = 0.00337$		$x_{\text{Fe}} = 0.0249, A = 3.03, B = 0.00011$		$x_{\text{Fe}} = 0.0353, A = 0.55, B = 0.00438$		$x_{\text{Fe}} = 0.0512, A = 0.35, B = 0.00606$		$x_{\text{Ni}} = 0.0092, A = 1.00, B = 0.00204$		$x_{\text{Ni}} = 0.0488, A = -2.29, B = 0.00862$		$x_{\text{Ti}} = 0.0005, A = 1.66, B = 0.00277$	
T/K	E/mv	T/K	E/mv	T/K	E/mv	T/K	E/mv	T/K	E/mv	T/K	E/mv	T/K	E/mv	T/K	E/mv	T/K	E/mv
923	4.8	1010	7.1	977	9.2	971	2.7	971	4.5	1001	6.3	913	3.0	1000	6.7	1083	4.4
969	4.9	1091	6.7	998	9.6	986	2.7	983	5.1	1023	6.7	955	2.6	1009	6.1	1046	4.6
1025	5.1	1111	7.3	1013	9.3	998	3.2	986	4.9	1025	6.5	966	3.1	1029	6.4	1006	4.7
1077	5.3	1123	7.3	1018	9.6	1073	2.8	998	4.7	1045	6.9	1001	2.9	1064	6.9	988	4.3
1116	4.6	1145	7.2	1018	10.2	1089	3.0	1018	5.2	1051	6.6	1009	3.3	1068	7.0	967	4.0
1125	5.4	1148	6.7	1097	9.8	1098	2.9	1044	5.4	1071	6.9	1011	3.1	1116	7.4	936	4.5
1211	4.8			1141	10.1	1109	3.0	1098	5.6	1095	6.9	1044	3.2			920	4.2
				1158	10.0	1143	2.8	1109	5.0			1068	3.2			1116	4.6
						1018	3.2					1072	2.9			1128	5.0
												1119	3.4			1170	4.8
																1186	5.2

Tr	x_{Tr}	a_{Al}	γ_{Al}	$\Delta_{\text{mix}}\bar{G}_{\text{Al}}$	$\Delta_{\text{mix}}\bar{G}_{\text{Al}}^{\text{xs}}$ kJ mol ⁻¹	$\Delta_{\text{mix}}\bar{H}_{\text{Al}}$	$\Delta_{\text{mix}}\bar{S}_{\text{Al}}$	$\Delta_{\text{mix}}\bar{S}_{\text{Al}}^{\text{xs}}$ J mol ⁻¹ K ⁻¹
—	0.0	0.914	1.041	—0.78	0.34	—0.65	0.1	—1.0
Cu	0.0130	0.847 ± 0.009	0.976	-1.44 ± 0.09	—0.21	—1.3	0.1	—1.1
	0.0265	0.791 ± 0.016	0.924	-2.03 ± 0.17	—0.68	—2.0	0.1	—1.2
	0.0453	0.723 ± 0.006	0.861	-2.81 ± 0.08	—1.29	—1.8	1.0	—0.5
Fe	0.0249	0.907 ± 0.005	1.058	-0.85 ± 0.05	0.49	—0.9	0.0	—1.3
	0.0353	0.843 ± 0.007	0.994	-1.48 ± 0.08	—0.05	—0.2	1.3	—0.1
	0.0512	0.800 ± 0.004	0.960	-1.92 ± 0.04	—0.36	—0.1	1.8	0.2
Ni	0.0092	0.901 ± 0.005	1.034	-0.90 ± 0.05	0.29	—0.3	0.6	—0.6
	0.0488	0.800 ± 0.008	0.956	-1.93 ± 0.08	—0.39	0.7	2.5	1.0
Ti	0.0005	0.859 ± 0.005	0.978	-1.32 ± 0.05	—0.20	—0.5	0.8	—0.3

Table 2. Thermodynamic properties of liquid $(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Tr}_x$ (Tr = Cu, Fe, Ni and Ti) alloys at 1040 K.Fig. 1. Partial excess Gibbs free energy of aluminium for $(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Tr}_x$ silumins vs. transition element mole fraction at 1040 K. Squares: Al–Si–Fe, circles: Al–Si–Ni, triangles: Al–Si–Cu and rhombs: Al–Si–Ti.

$$\Delta_{\text{mix}}\bar{S}_{\text{Al}} = 10^{-3}ZFB, \quad (5)$$

The integral excess Gibbs free energy and entropy of mixing were calculated by the respective equa-

tions

$$\Delta_{\text{mix}}\bar{G}_{\text{Al}}^{\text{xs}} = \Delta_{\text{mix}}\bar{G}_{\text{Al}} - RT \ln x_{\text{Al}}, \quad (6)$$

$$\Delta_{\text{mix}}\bar{S}_{\text{Al}}^{\text{xs}} = \Delta_{\text{mix}}\bar{S}_{\text{Al}} + R \ln x_{\text{Al}}. \quad (7)$$

3. Results and Discussion

EMF measurements of the alloys are presented in Table 1, and the thermodynamic properties of liquid silumins are listed in Table 2. The Gibbs energy and thermodynamic activity of initial $\text{Al}_{0.879}\text{Si}_{0.121}$ alloy were taken from EMF data of [2] extrapolated to 1040 K. The enthalpy of mixing for the alloy was taken from a calorimetric study of the Al–Si system [3], whereas the entropy was calculated from the EMF Gibbs energy of [2] and the calorimetric enthalpy of mixing [3].

As it can be seen from Fig. 1, the $(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Fe}_x$ melts at iron molar fraction $x_{\text{Fe}} < 0.035$ are characterized by positive deviations from Raoultian for aluminium, whereas at higher iron concentration these deviations change the sign. This fact can be explained as follows: according to our calorimetric study of the Al–Fe–Si system [4], the Fe–Si inter-

action prevails the weak Al–Si interaction at low Fe content. As a result, the Al atoms are freed and, consequently, $\Delta_{\text{mix}} \bar{G}_{\text{Al}}^{\text{xs}}$ becomes positive. The interaction between Al and Fe is intensified and the deviations from Raoultian for aluminium become negative with increasing Fe content. The phenomenon occurs also in $(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Ni}_x$ alloys, but to a less degree. The amplified interaction between Si and Fe or Ni atoms can be explained by the influence of FeSi and NiSi silicides, which are structurally similar and melt congruently at 1683 and at 1265 K, respectively [5]. In such a way the strong interaction between heterogeneous atoms remains at the transition into the liquid phase. Because FeSi monosilicide has a higher melting point and wider primary crystallization field in the

ternary system [6, 7], FeSi effects have a stronger influence on the thermodynamic properties of liquid Al–Si–Fe alloys than those of NiSi on the thermodynamics of Al–Si–Ni melts.

In contrast to Ni and Fe doped silumins, the $(\text{Al}_{0.879}\text{Si}_{0.121})_{1-x}\text{Cu}_x$ alloys are characterized by negative deviations from ideality for the studied aluminium concentrations, which can be explained by strong Al–Cu interaction, associated with possible influence of $\theta(\text{Al}_2\text{Cu})$, $\eta(\text{AlCu})$ and $\varepsilon_2(\text{Al}_3\text{Cu}_4)$ phases [8]. The maximal negative deviations from Raoult's law are observed for $\text{Al}_{0.8786}\text{Si}_{0.1209}\text{Ti}_{0.0005}$ melt, which composition is near the primary crystallization surface of the τ_1 -phase ($\text{Al}_5\text{Si}_{12}\text{Ti}_7$) [9].

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