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Thermodynamics/Calorimetry

Thermodynamics of liquid and undercooled liquid Al–Cu–Ni–Si alloys

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Abstract

The partial and the integral enthalpies of mixing of liquid Al–Cu–Ni–Si alloys have been determined by high temperature isoperibolic calorimetry for four isopleths at 1575±3 K. A least-square regression analysis of the data together with the literature values of the constituent binaries and ternaries results a consistent analytical representation of the enthalpy of mixing of liquid Al–Cu–Ni–Si alloys at 1575 K.

The regular association model describes adequately the thermodynamic properties of the liquid constituent ternaries on the basis of their constituent binaries, respectively, if additional ternary association reactions with the stoichiometries $Al_2Cu_1Ni_1$, $Al_1Cu_3Si_1$, $Al_1Ni_2Si_1$, and $Cu_2Ni_2Si_1$ are assumed. The calculated Gibbs energy for the ternaries demonstrate that there are minima for the Al–Cu–Ni (-42.8 kJ mol^{-1}), Al–Ni–Si (-54.6 kJ mol^{-1}), Al–Cu–Si (-24.4 kJ mol^{-1}) near the ternary compositions $Al_{0.45}Cu_{0.10}Ni_{0.45}$, $Al_{0.20}Ni_{0.55}Si_{0.25}$, and $Al_{0.17}Cu_{0.50}Si_{0.33}$, respectively, whereas the minimum for the liquid Cu–Ni–Si alloys (-52.0 kJ mol^{-1}) corresponds to the binary composition $Ni_{0.58}Si_{0.42}$. The Gibbs energy of liquid quaternary alloys were estimated on the basis of the results from the regular association model for the constituent ternaries using the Kohler scheme in combination with an empirical enthalpy–entropy model. The minimum of the Gibbs energy of mixing of the quaternary alloys is observed at the composition $Al_{0.19}Cu_{0.08}Ni_{0.50}Si_{0.23}$.

Keywords: Al–Cu–Ni–Si; Calorimetry; Enthalpy of mixing; Regular association model; Gibbs energy

1. Introduction

In a series of publications we have reported the enthalpy of mixing of the ternary liquid alloys Al–Cu–Ni [1], Al–Cu–Si [2], Al–Ni–Si [3], and Cu–Ni–Si [4]. The present paper deals with the direct calorimetric measurements of the enthalpy of mixing of liquid quaternary Al–Cu–Ni–Si alloys and the modelling of the thermodynamic properties of these alloys in the liquid and undercooled liquid state. Such data are, at present, not available in the literature, although they are essential for the thermodynamic analysis of the behaviour of these alloys under different conditions as well as for the optimisation of the phase diagram of this quaternary system.

2. Experimental

The partial and the integral enthalpies of mixing of liquid Al–Cu–Ni–Si alloys were measured at

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1575±3 K using a high temperature isoperibolic calorimeter described previously [5]. The experimental set up and the procedures for the determination of the partial and the integral enthalpies of mixing of liquid ternary alloys simultaneously in the same experimental run have previously been described in Refs. [6–8]. The experiments were carried out under pure argon gas at atmospheric pressure. For the measurements the thermocouples were made of Pt-6%Rh/Pt-30%Rh and a thermopile was made of W-5%Re/W-20%Re. The alloy samples were prepared from nickel (STREM Chemicals, purity 99.9%), aluminium (ChemPur Feinchemikalien und Forschungsbedarf GmbH, purity 99.999%), silicon (Johnson Matthey GmbH, purity 99.9999%) and copper (Johnson Matthey GmbH, purity 99.999%). The heat effects were measured by successive dropping of solid samples (pure components) from 298 K through a charging tube into an alumina reaction crucible containing the melt. The masses of these samples were so small that the composition change in the bath did not exceed 1–3 at.%. This allows us to determine directly the partial enthalpy of mixing of all components in the same experimental run. The measurements were performed along four isopleths $Al_{66}Ni_{17}Si_{17}$–Cu, $Al_{33}Ni_{33}Si_{33}$–Cu, $Al_{17}Ni_{17}Si_{66}$–Cu, and $Al_{17}Ni_{66}Si_{17}$–Cu using the method described in Ref. [8].

The partial enthalpy of mixing ($\Delta\overline{H}_i$) of the component i (i=Al, Cu, Ni, Si) starting from the liquid Al–Ni–Si alloys has been calculated from the area F_i under a temperature–time curve using the following relations [7,8] (standard states: Al(l), Cu(l), Ni(l) and Si(l)):

$$\Delta\overline{H}_i(x) = -\Delta H^{\mathrm{T}}_{298,i} + W(x)F_i(x), \quad i = \mathrm{Al},\ \mathrm{Cu}, \tag{1}$$

$$\Delta\overline{H}_i(x) = -\Delta H^{\mathrm{T}}_{298,i} - \Delta H_{\mathrm{fus},i} + W(x)F_i(x), \quad i = \mathrm{Ni},\ \mathrm{Si} \tag{2}$$

where x=x_{Cu} (mole fraction of copper), $\Delta H^{\mathrm{T}}_{298,i}$ and $\Delta H_{\mathrm{fus},i}$ are the heat content and the molar heat of fusion of component i. In Eq. (2) the differences between the unknown heat capacity of the undercooled liquid state and the known heat capacity of the crystalline state are not considered. The composition dependent heat equivalent of the calorimeter $W(x)$ is obtained directly from Eqs. (1) and (2) using the Gibbs–Duhem relation [6]:

$$\mathrm{d}W(x) = -\frac{W(x)}{\Phi_\Sigma(x)}\left[\mathrm{d}\Phi_\Sigma(x) + \frac{\Phi_\Sigma(x) - \Theta}{1-x}\mathrm{d}x\right] \tag{3}$$

$$\Phi_\Sigma(x) = \sum_i x_i F_i(x), \qquad \Theta = F_{\mathrm{Cu}}(x),$$
$$x_{\mathrm{Al}} = (1-y-z)(1-x), \quad x_{\mathrm{Ni}} = y(1-x),$$
$$x_{\mathrm{Si}} = z(1-x), \tag{4}$$

where y and z are the mole fractions of nickel and silicon of the initial $Al_{1-y-z}Ni_ySi_z$ alloy. The initial condition for the numerical solution of the Eq. (3) is

$$W_{x=0} = \frac{(1-y)\Delta H^{\mathrm{T}}_{298,\mathrm{Ni}} + y\Delta H^{\mathrm{T}}_{298,\mathrm{Si}} + \Delta H_{x=0}}{(1-y)F_{\mathrm{Ni}(x=0)} + yF_{\mathrm{Si}}(x=0)} \tag{5}$$

where $\Delta H_{x=0}$ is the integral enthalpy of mixing of the initial $Al_{1-y-z}Ni_ySi_z$ alloys.

For the measurements performed starting from liquid copper, $\Delta\overline{H}_i$ were calculated using the Eqs. (1)–(4) and the initial value of the heat equivalent is given by

$$W_{(x_{\mathrm{Al}}=0,x_{\mathrm{Ni}}=0,x_{\mathrm{Si}}=0)} = \frac{\Delta H^{1575}_{298,\mathrm{Cu}}}{F_{\mathrm{Cu}(x_{\mathrm{Al}}=0,x_{\mathrm{Ni}}=0,x_{\mathrm{Si}}=0)}}, \tag{6}$$

with Θ=$F_{\mathrm{Ni}}(x)$, x=x_{Ni} (mole fraction of nickel), x_{Al}=$x(1-y-z)/y$, x_{Cu}=$1-x/y$, x_{Si}=xz/y.

The values of the heat contents of the components as well as the heats of fusion of nickel and silicon were taken from SGTE data for the pure elements [9].

The integral enthalpy of mixing is calculated from the partial ones using simultaneously the three following methods:

$$\Delta H\left(\sum_k \Delta n_k\right) = \frac{\Delta H_{x=0} n_0 \sum_k \Delta\overline{H}_k \Delta n_k}{n_0 + \sum_k \Delta n_k} \tag{7}$$

$$\Delta H(x) = \sum_i x_i \Delta\overline{H}_i(x) \tag{8}$$

$$\Delta H(x)_{y/(1-y-z)-\mathrm{const},z/(1-y-z)=\mathrm{const},y/z=\mathrm{const}} = (1-x)\left[\Delta H_{x=0} + \int_{x=0}^{x=1} \frac{\Delta\overline{H}_{\mathrm{Cu}}(x)}{(1-x)^2}\mathrm{d}x\right] \tag{9}$$

where n_0 is the mole number of the initial alloy, Δn_k and k are the mole number and the number of the sample successively dropped. This allowed us to

check whether the measured data are consistent with the Gibbs–Duhem equation. To avoid further self-inconsistency of the data, which occurs in the process of a numerical determination of $W(x)$ due to some scattering of the experimental F_i values, an iteration procedure based on the minimisation of the deviations between the results from Eqs. (7)–(9) by the least-squares method was applied, as described previously [8].

3. Results and discussion

The results obtained for the partial and the integral enthalpies of mixing of the liquid quaternary Al–Cu–Ni–Si alloys of four composition cuts are summarised in Tables 1–4. Fig. 1a–d show the experimental partial enthalpies of mixing of the components along the isopleths in combination with literature data of the constituent binaries and of some vertical composition sections of the ternary alloys. The liquid phase is stable at 1573 K along the compositions with $0 \le x_{Cu} \le 1$ for the isopleths $Al_{66}Ni_{17}Si_{17}$–Cu, $Al_{33}Ni_{33}Si_{33}$–Cu, and $Al_{17}Ni_{17}Si_{66}$–Cu, whereas $Al_{17}Ni_{66}Si_{17}$–Cu exhibits a homogenous range of $0.26 \le x_{Cu} \le 1$. In general, the partial functions change regularly with the composition of copper. From Fig. 1d (curves 1 to 3) follows that the limiting partial enthalpy of mixing of copper ($x_{Cu} \to 0$) varies as a function of the composition of the initial liquid Al–Ni–Si alloy with significant positive deviations from additive values.

A least-square regression analysis of the partial enthalpies of mixing of the Al–Cu–Ni–Si alloys results in the following relationships (in kJ mol^{-1}; $x = x_{Cu}$): isopleth $Al_{66}Ni_{17}Si_{17}$–Cu

$$\Delta\overline{H}_{Al} = (-75.5 \pm 6.5)x + (1-x)^2[(-14.6 \pm 1.4) + (99.2 \pm 8.1)x + (-1097.1 \pm 95.3)x^6] \quad (10)$$

$$\Delta\overline{H}_{Ni} = (11.1 \pm 1.0)x + (1-x)^2[(-148.1 \pm 3.8) + (-244.8 \pm 49.8)x + (-490.1 \pm 111.9)x^2 + (-1538.5 \pm 508.7)x^8] \quad (11)$$

Table 1
Enthalpies of mixing of liquid $Al_{33}Ni_{33}Si_{33}$–Cu alloys measured at 1575±3 K

Added substance (i)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Run 1; Starting amount (mmol): n_{Ni}=17.391; n_{Si}=17.386; n_{Al}=17.392						
Si	1.0005	80.21	0	2.0	0	−47.5
Al	0.8678	27.95	0	−15.9	0	−47.0
Ni	0.9388	−66.51	0	−129.8	0	−48.5
Cu	1.3030	44.57	0.0116	−1.9	0.0232	−47.4
Cu	1.6319	44.77	0.0369	−1.5	0.0507	−46.1
Cu	1.9687	44.37	0.0663	−1.8	0.0819	−44.6
Si	0.8082	77.77	0.0813	0.2	0.0808	−44.0
Al	0.9160	34.38	0.0802	−8.7	0.0796	−43.5
Ni	0.8213	−65.52	0.0791	−129.5	0.0785	−44.6
Cu	2.1496	41.62	0.0939	−4.5	0.1092	−43.3
Cu	2.3511	39.46	0.1249	−6.7	0.1405	−42.0
Cu	2.6485	35.08	0.1569	−11.3	0.1732	−40.8
Si	0.8866	77.29	0.1721	0.7	0.1711	−40.3
Al	0.9345	30.28	0.1699	−12.7	0.1688	−39.9
Ni	0.9303	−60.81	0.1677	−125.2	0.1666	−41.1
Cu	2.2377	37.86	0.1791	−8.2	0.1916	−40.1
Cu	3.0435	39.56	0.2075	−6.1	0.2233	−38.7
Cu	3.0797	38.64	0.2382	−7.0	0.2530	−37.5
Si	1.0254	69.16	0.2514	−7.4	0.2498	−37.2
Al	0.9568	28.48	0.2484	−14.3	0.2469	−36.9
Ni	0.9490	−60.99	0.2455	−126.1	0.2441	−37.9

Table 1 (*Continued*)

Added substance (i)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Cu	3.1552	38.47	0.2579	−7.1	0.2716	−36.8
Cu	3.8209	38.84	0.2870	−6.5	0.3023	−35.4
Cu	3.9184	38.68	0.3168	−6.5	0.3313	−34.3
Si	1.0610	61.80	0.3294	−14.7	0.3276	−34.1
Al	1.1199	25.19	0.3257	−17.7	0.3238	−33.9
Ni	1.0768	−44.98	0.3220	−109.0	0.3202	−34.7
Cu	3.9231	39.76	0.3333	−5.2	0.3464	−33.6
Cu	4.8642	38.43	0.3614	−6.5	0.3763	−32.3
Cu	4.2489	39.95	0.3882	−4.7	0.4002	−31.3
Si	1.3387	57.19	0.3978	−19.3	0.3954	−31.1
Al	1.3165	21.61	0.3931	−21.4	0.3908	−31.0
Ni	1.3682	−40.88	0.3885	−104.9	0.3862	−31.9
Cu	3.8366	39.69	0.3961	−5.0	0.4060	−31.0
Cu	4.0884	40.63	0.4159	−3.8	0.4258	−30.1
Run 2; Starting amount (mmol): n_{Cu}=51.081						
Cu	1.2652	64.56	1	0	1	0
Cu	1.1519	65.03	1	0	1	0
Si	0.6623	0.62	0.9939	−82.7	0.9878	−1.0
Ni	0.6781	86.42	0.9817	7.8	0.9756	−0.9
Al	0.6341	−36.98	0.9700	−74.3	0.9644	−1.7
Cu	1.2180	64.35	0.9648	0.6	0.9652	−1.7
Si	1.2640	−2.28	0.9546	−84.9	0.9441	−3.5
Ni	1.2609	67.37	0.9341	−5.1	0.9240	−3.5
Al	1.2386	−32.60	0.9146	−71.7	0.9051	−4.9
Cu	1.3738	61.59	0.9061	0.1	0.9072	−4.8
Si	2.1505	−4.98	0.8919	−87.1	0.8767	−7.6
Ni	2.1792	47.23	0.8623	−19.2	0.8478	−8.0
Al	2.1175	−28.5	0.8347	−69.6	0.8215	−9.9
Cu	1.2888	60.18	0.8232	1.4	0.8248	−9.7
Si	2.3179	−2.11	0.8115	−84.9	0.7982	−12.1
Ni	2.3547	33.21	0.7856	−29.7	0.7729	−12.7
Al	2.3140	−21.65	0.7612	−64.7	0.7496	−14.2
Cu	1.5375	57.34	0.7520	1.3	0.7545	−13.9
Si	2.7879	12.35	0.7415	−72.3	0.7285	−15.9
Ni	2.7432	19.36	0.7165	−41.2	0.7046	−16.8
Al	2.7998	−16.07	0.6932	−60.4	0.6817	−18.2
Cu	1.1063	50.64	0.6838	−2.6	0.6858	−18.0
Si	2.7985	17.85	0.6752	−66.8	0.6645	−19.5
Ni	2.6989	5.41	0.6549	−54.1	0.6452	−20.5
Al	2.7219	−4.49	0.6361	−49.9	0.6269	−21.3
Cu	1.3644	47.04	0.6295	−4.4	0.6321	−21.1
Si	3.5534	32.26	0.6210	−52.6	0.6098	−22.2
Ni	3.4793	−2.60	0.5996	−61.9	0.5895	−23.5
Al	3.5378	5.34	0.5798	−40.2	0.5701	−24.1
Cu	1.2747	49.20	0.5726	−0.5	0.5751	−23.8
Si	3.2863	44.76	0.5667	−39.1	0.5583	−24.3
Ni	3.3685	−24.88	0.5501	−85.0	0.5420	−26.0
Al	3.2411	8.21	0.5346	−37.1	0.5272	−26.3
Cu	1.5910	45.55	0.5304	−2.8	0.5335	−26.0
Si	1.5025	41.77	0.5302	−40.6	0.5269	−26.2

Table 2
Enthalpies of mixing of liquid $Al_{17}Ni_{17}Si_{66}$–Cu alloys measured at 1575±3 K

Added substance (i)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Run 1; Starting amount (mmol): n_{Ni}=9.2554; n_{Si}=35.9183; n_{Al}=9.3080						
Si	3.1546	86.64	0	−5.1	0	−24.9
Ni	0.7974	−68.12	0	−120.5	0	−26.2
Al	0.8270	39.55	0	−9.9	0	−25.9
Cu	1.0386	43.60	0.0086	−10.2	0.0172	−25.7
Cu	1.7011	40.68	0.0307	−13.1	0.0442	−25.3
Cu	1.7074	41.05	0.0570	−12.8	0.0698	−25.0
Si	3.1688	85.67	0.0682	−7.0	0.0665	−24.1
Ni	0.8008	−69.82	0.0661	−121.2	0.0657	−25.3
Al	0.8492	35.64	0.0653	−13.8	0.0649	−25.1
Cu	2.4313	38.48	0.0809	−14.9	0.0969	−24.8
Cu	2.7460	39.72	0.1138	−13.2	0.1306	−24.4
Cu	3.0718	37.01	0.148	−14.7	0.1654	−24.0
Si	3.5000	83.89	0.1618	−5.2	0.1582	−23.2
Ni	0.9269	−59.68	0.1573	−114.5	0.1564	−24.2
Al	0.8529	32.30	0.1555	−15.6	0.1547	−24.1
Cu	4.0900	33.55	0.1748	−16.8	0.1949	−23.8
Cu	4.1938	36.35	0.2135	−12.2	0.2322	−23.2
Cu	4.7603	34.99	0.2515	−11.4	0.2707	−22.6
Si	3.5569	75.43	0.2658	−2.6	0.2609	−21.9
Ni	0.8860	−61.15	0.2597	−124.2	0.2586	−22.8
Al	0.8752	29.64	0.2575	−14.1	0.2563	−22.7
Cu	5.2450	31.66	0.2747	−13.8	0.2932	−22.3
Cu	5.5629	28.74	0.3109	−15.5	0.3286	−22.0
Cu	5.4779	33.56	0.3443	−8.5	0.3601	−21.3
Si	3.2365	63.13	0.3553	−7.0	0.3504	−20.9
Ni	0.8485	−57.21	0.3492	−128	0.3479	−21.7
Al	0.7899	23.32	0.3468	−17.5	0.3457	−21.7
Cu	5.3158	29.37	0.3594	−13.2	0.3731	−21.3
Cu	5.6668	28.95	0.3865	−13.3	0.3999	−21.0
Cu	5.6636	26.14	0.4122	−16.9	0.4245	−20.8
Si	3.7670	66.37	0.4189	−0.6	0.4132	−20.3
Ni	0.9201	−55.69	0.4118	−128.4	0.4105	−21.0
Al	0.9493	26.16	0.4092	−13.0	0.4078	−20.9
Cu	6.3922	29.13	0.4204	−13.4	0.433	−20.6
Cu	6.9509	27.03	0.4456	−16.9	0.4581	−20.4
Run 2; Starting amount (mmol): n_{Cu}=46.754						
Cu	1.1771	78.34	1	0	1	0
Cu	1.4226	76.89	1	0	1	0
Si	1.1251	3.05	0.9889	−81.2	0.9777	−1.8
Si	1.0646	1.03	0.9676	−82.4	0.9575	−3.5
Ni	0.5657	72.70	0.9523	−10.5	0.9471	−3.5
Al	0.6378	−47.20	0.9414	−77.1	0.9357	−4.4
Cu	1.1645	67.13	0.9364	−4.4	0.9371	−4.4
Si	1.4705	−0.35	0.9246	−83.3	0.9122	−6.5
Si	2.1541	7.47	0.8951	−78.1	0.8780	−9.2
Ni	0.9150	36.51	0.8712	−33.2	0.8643	−9.6
Al	0.9382	−29.08	0.8575	−66.1	0.8506	−10.5
Cu	1.6114	66.45	0.8526	−2.2	0.8546	−10.3
Si	2.1541	17.88	0.8400	−70.5	0.8254	−12.3

Table 2 (*Continued*)

Added substance (*i*)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Si	2.1256	34.08	0.8120	−59.1	0.7985	−13.8
Ni	1.1433	4.50	0.7917	−55.8	0.7848	−14.6
Al	1.1718	−4.53	0.7780	−48.9	0.7712	−15.2
Cu	1.4462	59.97	0.7736	−3.5	0.7760	−14.9
Si	3.1866	49.78	0.7589	−45.5	0.7418	−16.3
Si	3.4608	72.27	0.7248	−29.1	0.7078	−16.8
Ni	1.6050	−32.51	0.7005	−87.6	0.6931	−18.3
Al	1.7429	20.91	0.6855	−27.4	0.6778	−18.5
Cu	1.5863	48.26	0.6810	−8.0	0.6842	−18.3
Si	2.7202	74.97	0.6730	−20.0	0.6619	−18.4
Si	3.7456	79.16	0.6476	−17.7	0.6334	−18.3
Ni	1.6596	−40.40	0.6275	−99.6	0.6216	−19.9
Al	1.4648	17.08	0.6165	−28.6	0.6115	−20.0
Cu	1.7767	31.27	0.6152	−18.9	0.6190	−20.0
Si	4.0269	80.53	0.6060	−7.4	0.5930	−19.5
Si	4.1195	84.04	0.5808	−6.4	0.5686	−18.9
Ni	2.0923	−51.96	0.5628	−120.3	0.5570	−21.0
Al	2.0878	22.76	0.5514	−19.3	0.5458	−21.0
Cu	1.5044	30.27	0.5491	−15.1	0.5523	−20.9
Si	4.8636	75.04	0.5401	−2.2	0.5280	−20.1
Ni	1.2575	−51.96	0.5250	−124.6	0.5221	−21.2
Al	1.1718	24.89	0.5194	−14.6	0.5167	−21.2

Table 3
Enthalpies of mixing of liquid $Al_{66}Ni_{17}Si_{17}$–Cu alloys measured at 1575±3 K

Added substance (*i*)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Run 1; Starting amount (mmol): n_{Ni}=10.417; n_{Si}=10.414; n_{Al}= 40.495						
Si	0.7228	80.14	0	−3.7	0	−26.7
Ni	0.7173	−93.47	0	−151.8	0	−28.2
Al	2.8369	45.09	0	−0.8	0	−27.0
Cu	1.3911	28.26	0.0104	−21.1	0.0208	−26.9
Cu	1.7027	26.73	0.0329	−22.5	0.0450	−26.7
Cu	1.7688	23.64	0.0570	−25.4	0.0690	−26.7
Si	0.6444	76.73	0.0687	−5.7	0.0684	−26.5
Ni	0.6662	−77.95	0.0681	−137.8	0.0677	−27.6
Al	2.3400	44.14	0.0667	−1.0	0.0656	−26.7
Cu	1.9891	26.71	0.0778	−22.2	0.0900	−26.6
Cu	2.4171	25.94	0.1040	−22.8	0.1180	−26.5
Cu	2.9664	26.43	0.1341	−22.1	0.1501	−26.3
Si	0.7833	79.28	0.1494	−1.6	0.1487	−26.1
Ni	0.7190	−80.28	0.1481	−141.7	0.1474	−27.1
Al	2.9519	41.14	0.1449	−3.2	0.1424	−26.3
Cu	3.5990	26.76	0.1596	−21.6	0.1768	−26.1
Cu	3.7343	26.74	0.1933	−21.4	0.2098	−25.9
Cu	5.1789	25.80	0.2306	−22.1	0.2514	−25.7
Si	0.7655	75.34	0.2504	−3.7	0.2494	−25.5

Table 3 (*Continued*)

Added substance (i)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Ni	0.7463	−68.41	0.2485	−131.2	0.2475	−26.3
Al	2.9482	36.95	0.2440	−6.6	0.2405	−25.7
Cu	5.3678	28.54	0.2593	−19.0	0.2781	−25.4
Cu	5.8100	24.53	0.2965	−23.0	0.3149	−25.3
Cu	5.7313	24.29	0.3313	−23.1	0.3476	−25.2
Si	0.7157	71.22	0.3466	−6.4	0.3456	−25.1
Ni	0.7821	−58.31	0.3445	−122	0.3433	−25.7
Al	2.9444	34.63	0.3393	−8.3	0.3352	−25.3
Cu	6.1971	27.60	0.3510	−19.4	0.3668	−25.0
Cu	6.8580	29.65	0.3826	−16.9	0.3984	−24.6
Cu	6.4725	25.63	0.412	−21.2	0.4255	−24.4
Si	0.7085	65.01	0.4244	−11.8	0.4234	−24.4
Ni	0.7207	−50.11	0.4224	−114.2	0.4213	−24.8
Al	2.6923	30.23	0.4175	−12.4	0.4136	−24.6
Cu	6.9115	27.26	0.4267	−19.3	0.4398	−24.4
Cu	6.5527	23.02	0.4512	−23.8	0.4626	−24.3
Run 2; Starting amount (mmol): n_{Cu}=47.997						
Cu	1.4383	74.15	1	0	1	0
Cu	1.5501	74.00	1	0	1	0
Si	0.8616	0.08	0.9917	−83.0	0.9834	−1.4
Ni	0.8519	99.61	0.9754	12.1	0.9675	−1.2
Al	3.1929	−39.61	0.9398	−73.7	0.9122	−5.3
Cu	1.6555	68.58	0.9135	−0.5	0.9147	−5.2
Si	0.8047	−2.46	0.9084	−84.8	0.9021	−6.3
Ni	0.7514	63.32	0.8964	−11.6	0.8907	−6.3
Al	3.0260	−33.49	0.8690	−70.5	0.8473	−9.5
Cu	1.8066	63.19	0.8494	−2.2	0.8516	−9.3
Si	1.1928	−1.69	0.8438	−84.3	0.8360	−10.6
Ni	1.1757	34.63	0.8286	−31.4	0.8212	−11.0
Al	4.4018	−19.68	0.7956	−61.1	0.7701	−14.1
Cu	1.8837	60.73	0.7730	−1.3	0.7760	−13.8
Si	0.8937	15.61	0.7713	−70.8	0.7666	−14.5
Ni	0.9337	27.00	0.7618	−36.8	0.7570	−14.8
Al	3.5971	−11.25	0.7395	−54.7	0.7221	−16.6
Cu	1.8333	59.89	0.7252	−0.3	0.7284	−16.2
Si	1.2853	29.13	0.7227	−59.3	0.7169	−16.9
Ni	1.2966	11.29	0.7113	−49.4	0.7056	−17.4
Al	4.7727	−2.73	0.6863	−47.8	0.6670	−19.1
Cu	1.6382	52.15	0.6701	−4.7	0.6731	−18.8
Si	1.1643	46.22	0.6688	−43.7	0.6644	−19.1
Ni	1.1143	−2.28	0.6604	−61.3	0.6563	−19.7
Al	4.2350	6.09	0.6417	−40.1	0.6272	−20.6
Cu	1.7200	51.82	0.6305	−3.7	0.6338	−20.3
Si	1.5346	56.34	0.6288	−33.8	0.6239	−20.5
Ni	1.6698	−17.87	0.6187	−75.9	0.6135	−21.4
Al	5.8370	14.90	0.5966	−31.8	0.5798	−22.0
Cu	1.5642	46.10	0.5828	−7.1	0.5859	−21.8
Si	1.7197	65.34	0.5813	−23.6	0.5767	−21.8
Ni	1.7022	−28.52	0.5722	−86.8	0.5678	−22.8
Al	6.4563	23.94	0.5522	−22.8	0.5366	−22.8
Cu	1.7625	35.94	0.5401	−15.4	0.5435	−22.7
Si	1.0646	64.18	0.5411	−22.8	0.5387	−22.7

Table 4
Enthalpies of mixing of liquid $Al_{17}Ni_{66}Si_{17}$–Cu alloys measured at 1575±3 K

Added substance (i)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Run 1; Starting amount (mmol): n_{Cu}=47.131						
Cu	1.5312	67.77	1	0	1	0
Cu	1.5595	68.07	1	0	1	0
Si	0.8047	1.94	0.9921	−81.7	0.9842	−1.3
Ni	1.6647	84.11	0.9687	2.3	0.9531	−1.2
Al	0.7788	−45.06	0.9462	−78.5	0.9393	−2.3
Ni	1.4824	83.96	0.9266	3.0	0.9139	−2.2
Cu	1.5973	66.49	0.9151	−0.1	0.9164	−2.1
Si	0.8688	−29.09	0.9094	−104.6	0.9025	−3.6
Ni	1.6102	75.08	0.8902	−2.8	0.8779	−3.6
Al	0.8863	−48.60	0.8714	−82.0	0.8649	−4.8
Ni	1.7550	68.05	0.8526	−7.1	0.8403	−4.8
Cu	1.4242	65.14	0.8421	0.5	0.8439	−4.7
Si	1.1180	−42.13	0.8365	−115.2	0.8292	−6.7
Ni	1.8674	62.22	0.8175	−10.7	0.8057	−6.8
Al	1.1718	−57.06	0.7987	−89.9	0.7917	−8.2
Ni	2.4382	58.95	0.7779	−11.8	0.7640	−8.3
Cu	1.7137	62.41	0.7668	0.7	0.7697	−8.1
Si	1.5132	−45.52	0.7617	−119.4	0.7537	−10.4
Ni	2.5064	57.32	0.7412	−12.0	0.7287	−10.5
Al	1.4277	−50.81	0.7219	−87.2	0.7151	−11.9
Ni	3.3532	47.41	0.7002	−18.6	0.6852	−12.2
Cu	1.4934	61.89	0.6881	3.5	0.6910	−11.9
Si	1.6307	−54.27	0.6842	−129.1	0.6775	−14.2
Ni	3.2476	56.16	0.6647	−9.7	0.6520	−14.0
Ni	3.0670	57.44	0.6409	−6.6	0.6297	−13.8
Al	1.5761	−58.05	0.6243	−98.3	0.6189	−15.2
Cu	1.6146	58.52	0.6222	3.6	0.6255	−14.9
Si	1.9476	−55.91	0.6191	−133.3	0.6126	−17.3
Ni	3.6752	49.40	0.6012	−13.0	0.5898	−17.2
Al	1.9172	−50.17	0.5841	−92.0	0.5785	−18.6
Ni	3.8269	49.81	0.5679	−11.1	0.5573	−18.3
Cu	1.8475	56.77	0.5611	5.2	0.5650	−17.9
Si	1.5631	−52.42	0.5609	−133	0.5567	−19.6
Ni	4.8032	50.29	0.5449	−9.0	0.5330	−19.1
Al	1.6651	−48.58	0.5291	−93.7	0.5252	−20.2
Run 2; Starting amount (mmol): n_{Ni}=17.822; n_{Si}=4.593; n_{Al}=4.580; n_{Cu}=27.004						
Cu	1.2920	78.65	0.5118	10.1	0.5118	−18.8
Si	0.8296	−80.25	0.5080	−143.7	0.5042	−20.7
Ni	1.6698	60.47	0.4969	−13.6	0.4896	−20.5
Al	0.7751	−69.04	0.4864	−97.5	0.4832	−21.5
Ni	1.5778	48.92	0.4768	−22.1	0.4705	−21.5
Cu	1.4415	80.39	0.4767	11.5	0.4829	−20.7
Si	1.1394	−86.32	0.4785	−148.2	0.4741	−23.0
Ni	2.4314	58.16	0.4653	−14.7	0.4564	−22.7
Al	1.1459	−65.49	0.4525	−95.3	0.4485	−24.0
Ni	2.0429	50.78	0.4418	−19.8	0.4351	−23.9
Cu	1.1677	73.80	0.4399	7.6	0.4446	−23.3
Si	1.2212	−74.17	0.4408	−139.9	0.4369	−25.3
Ni	2.5677	54.41	0.4293	−16.4	0.4216	−25.0

Table 4 (*Continued*)

Added substance (i)	Added amount, Δn_i (mmol)	Area, $F_i \times 10^{-6}$ (mV s mol^{-1})	Partial enthalpy		Integral enthalpy	
			Mole fraction (x_{Cu})	$\Delta\overline{H}_i$ (kJ mol^{-1})	Mole fraction (x_{Cu})	ΔH (kJ mol^{-1})
Al	1.3424	−60.74	0.4178	−92.8	0.414	−26.2
Ni	2.2372	50.85	0.4080	−18.5	0.402	−26.0
Cu	1.4116	75.86	0.4074	10.8	0.4128	−25.4
Si	2.7523	−69.33	0.4058	−136.9	0.3987	−29.1
Ni	5.3484	48.66	0.3864	−18.7	0.3741	−28.5
Al	2.6589	−50.92	0.3685	−86.8	0.3629	−30.2
Ni	5.2377	44.60	0.3528	−20.2	0.3427	−29.7
Cu	1.5564	70.78	0.3481	11.6	0.3534	−29.0
Si	2.7594	−69.55	0.3485	−141.2	0.3435	−32.1
Ni	5.2769	49.95	0.3348	−14.2	0.3261	−31.2
Ni	2.6070	−50.01	0.3221	−89.2	0.3181	−32.7
Al	5.3825	45.51	0.3104	−16.2	0.3028	−31.9
Cu	1.5186	62.06	0.3075	8.4	0.3121	−31.3
Si	3.2507	−68.61	0.3078	−144.5	0.3034	−34.5
Ni	6.5923	46.66	0.2953	−13.5	0.2872	−33.4
Al	3.1002	−47.8	0.2837	−90.6	0.2801	−34.8
Ni	6.0675	38.28	0.2737	−20.1	0.2673	−34.1
Cu	1.3659	60.88	0.2711	12.0	0.2748	−33.6
Si	2.8484	−64.91	0.2719	−146.3	0.2691	−36.0
Ni	6.2549	43.06	0.2632	−13.9	0.2573	−35.0
Al	2.8851	−49.89	0.2547	−96.2	0.2522	−36.2
Cu[a]	1.2385	62.16	0.2553	13.1	0.2585	−35.8

[a]Liquid+solid equilibrium.

$$\Delta\overline{H}_{Si} = (-75.4 \pm 5.8)x + (1-x) \times [(-5.8 \pm 2.4) + (110.5 \pm 9.1)x + (-552.4 \pm 42.2)x^6] \quad (12)$$

$$\Delta\overline{H}_{Cu} = (1-x)^2[(-20.1 \pm 1.5) + (-85.9 \pm 9.0)x + (253.6 \pm 91.3)x^5] \quad (13)$$

isopleth $Al_{33}Ni_{33}Si_{33}$–Cu

$$\Delta\overline{H}_{Al} = (-75.5 \pm 6.5)x + (1-x)^2[(36.5 \pm 11.9) + (252.2 \pm 34.5)x^2 + (-1347.7 \pm 104.2)x^6] \quad (14)$$

$$\Delta\overline{H}_{Ni} = (11.1 \pm 1.0)x + (1-x)^2[(-129.6 \pm 4.7) + (-279.2 \pm 58.1)x + (-344.1 \pm 137.0)x^2 + (-2470.0 \pm 640.1)x^8] \quad (15)$$

$$\Delta\overline{H}_{Si} = (-75.4 \pm 5.8)x + (1-x)[(94.1 \pm 19.4)x + (-113.8 \pm 45.7)x^2 + (-380.5 \pm 70.2)x^6] \quad (16)$$

$$\Delta\overline{H}_{Cu} = (1-x)^2[(-2.0 \pm 1.0) + (-40.6 \pm 6.2)x + (163.1 \pm 62.0)x^5] \quad (17)$$

isopleth $Al_{17}Ni_{17}Si_{66}$–Cu

$$\Delta\overline{H}_{Al} = (-75.5 \pm 6.5)x + (1-x)^2[(-9.9 \pm 1.8) + (910.3 \pm 54.5)x^3 + (-1977.8 \pm 366.1)x^8] \quad (18)$$

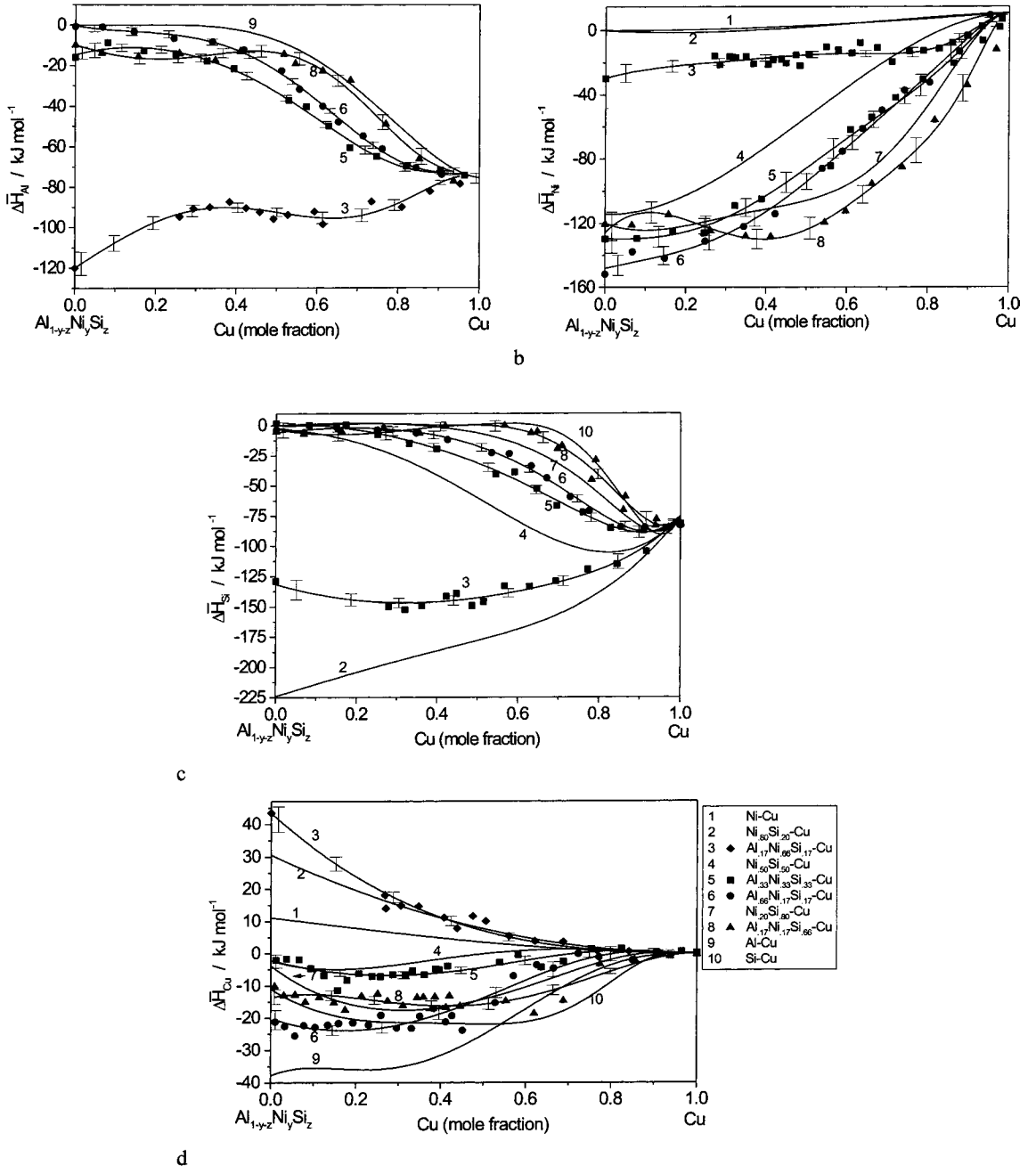

Fig. 1. (a–d) Partial enthalpy of mixing of aluminum (a) nickel (b), silicon (c), and copper (d) of quaternary liquid and undercooled liquid Al–Cu–Ni–Si alloys at 1575±3 K (standard states: Al(l), Cu(l) Ni(l), and Si(l)): points are experimental data; solid lines result from Eqs. (10)–(25); vertical bars are confidence bands at a tolerance of 5%.

$$\Delta\overline{H}_{Ni} = (11.1 \pm 1.1)x + (1-x)^2[(-125.7 \pm 4.1) + (-1543.2 \pm 56.2)x^2 + (-7381.0 \pm 1005.0)x^{10}] \quad (19)$$

$$\Delta\overline{H}_{Si} = (-75.4 \pm 5.8)x + (1-x)[(-2.9 \pm 3.1) + (320.6 \pm 20.0)x^2 + (-825.6 \pm 90.8)x^9] \quad (20)$$

$$\Delta\overline{H}_{Cu} = (1-x)^2[(-13.7 \pm 1.1) + (-194.3 \pm 15.4)x^2] \quad (21)$$

isopleth $Al_{17}Ni_{66}Si_{17}$–Cu

$$\Delta\overline{H}_{Al} = (-75.5 \pm 6.5)x + (1-x)^2[(-119.9 \pm 2.8) + (-31.3 \pm 13.8)x + (-1332.0 \pm 88.2)x^4] \quad (22)$$

$$\Delta\overline{H}_{Ni} = (11.1 \pm 1.1)x + (1-x)^2[(-29.6 \pm 3.0) + (-177.5 \pm 25.0)x^2 + (-2258.6 \pm 260.0)x^8] \quad (23)$$

$$\Delta\overline{H}_{Si} = (-75.4 \pm 5.8)x + (1-x)[(-131.8 \pm 4.4) + (-151.8 \pm 12.9)x + (-169.0 \pm 58.8)x^6] \quad (24)$$

$$\Delta\overline{H}_{Cu} = (1-x)^2[(43.5 \pm 2.0) + (-31 \pm 7.2)x] \quad (25)$$

The regression analysis shows that the experimental data in the copper rich range cannot be described adequately without taking into account the higher order terms given above.

As an example, Fig. 2 shows the composition dependence of the integral enthalpy of mixing of the liquid quaternary alloys along isopleth $Al_{66}Ni_{17}Si_{17}$–Cu obtained from different evaluation methods. Solid and open points represent the values calculated by means of Eqs. (7) and (8), respectively. The solid line is ΔH calculated on the basis of the partial enthalpy of copper given by Eq. (13) using Darken's relationship, i.e. Eq. (9). The good agreement between the results of these three methods of calculations confirms their consistence with the Gibbs–Duhem equation.

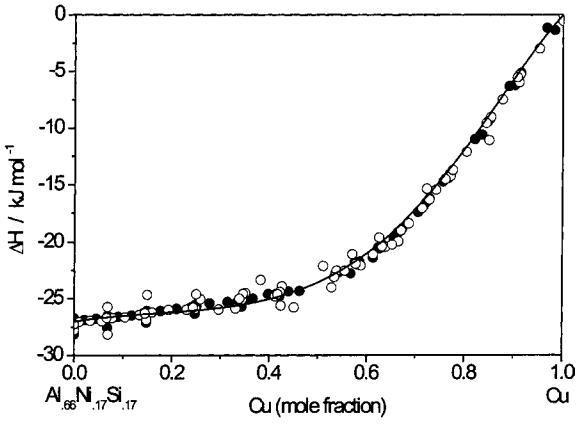

Fig. 2. Integral enthalpy of mixing of liquid quaternary alloy along isopleth $Al_{0.66}Ni_{0.17}Si_{0.17}$ at 1575±3 K (standard states: Al(l), Cu(l), Ni(l), and Si(l)): solid points, open points and line result from Eqs. (7)–(9), respectively.

The experimental values and analytical descriptions of the enthalpies of mixing of liquid alloys of the four constituent ternary systems, i.e. Al–Cu–Ni, Al–Cu–Si, Al–Ni–Si, and Cu–Ni–Si have been presented in our previous works [1–4]. It should be noted, that in these papers the analytical descriptions of the results were performed on the basis of Colinet's right hand interpolation algorithm for the integral properties of a ternary solution from constituent binaries [10]. For the analytical representation of the thermodynamic properties of the solutions in a quaternary system we ought to use right and left hand Colinet geometries simultaneously which leads to an inconsistency of the functions. For this reason it is better to use the interpolation scheme given by Kohler [11]. Therefore, the experimental data from [1–4] and those obtained in the present work for the quaternary alloys were analytically described by means of a least-squares procedure according to Eq. (26).

$$\Delta H = \alpha_{Al-Cu}x_{Al}x_{Cu} + \alpha_{Al-Ni}x_{Al}x_{Ni} + \alpha_{Al-Si}x_{Al}x_{Si} + \alpha_{Cu-Ni}x_{Cu}x_{Ni} + \alpha_{Cu-Si}x_{Cu}x_{Si} + \alpha_{Ni-Si}x_{Ni}x_{Si} + \alpha_{Al-Cu-Ni}x_{Al}x_{Cu}x_{Ni} + \alpha_{Al-Cu-Si}x_{Al}x_{Cu}x_{Si} + \alpha_{Al-Ni-Si}x_{Al}x_{Ni}x_{Si} + \alpha_{Cu-Ni-Si}x_{Cu}x_{Ni}x_{Si} + \alpha_{Al-Cu-Ni-Si}x_{Al}x_{Cu}x_{Ni}x_{Si} \quad (26)$$

where $\alpha_{i-j}=f(x_i/(x_i+x_j))$ or $\alpha_{i-j}=f(x_j/(x_i+x_j))$. In Eq. (26) the first six terms on the right hand side incorporate the interpolation algorithm by Kohler [11] for the integral enthalpy of mixing of a quaternary solution from the constituent binaries. The terms from 7 to 9 and the last one describe the additional ternary and quaternary interactions. For the α functions, the following relationships were found (in kJ mol^{-1}; standard states of Al(l), Cu(l), Ni(l), and Si (l)):

$$\alpha_{\mathrm{Al-Cu}} = (-75.6 \pm 6.5) + (-63.8 \pm 8.8)x + (232.0 \pm 33.0)x^2 + (-131.1 \pm 28.0)x^3, \quad x = \frac{x_{\mathrm{Al}}}{x_{\mathrm{Al}} + x_{\mathrm{Cu}}}, \quad 1357 \le T \le 1575\,\mathrm{K} \quad (27)$$

$$\alpha_{\mathrm{Al-Ni}} = (-202.1 \pm 7.1) + (-218.2 \pm 12.4)x + (316.8 \pm 27.2)x^3 + (-60.1 \pm 15.5)x^7 + [(0.0375 \pm 0.0039) + (-0.0367 \pm 0.0124)x^4]T, \quad x = \frac{x_{\mathrm{Al}}}{x_{\mathrm{Al}} + x_{\mathrm{Ni}}}, \quad 1073 \le T \le 1923\,\mathrm{K} \quad (28)$$

$$\alpha_{\mathrm{Al-Si}} = (-13.8 \pm 0.4) + (5.9 \pm 1.4)x^2, \quad x = \frac{x_{\mathrm{Si}}}{x_{\mathrm{Al}} + x_{\mathrm{Si}}}, \quad 1373 \le T \le 1820\,\mathrm{K} \quad (29)$$

$$\alpha_{\mathrm{Cu-Ni}} = (11.1 \pm 0.6) + (1.1 \pm 0.1)x, \quad x = \frac{x_{\mathrm{Ni}}}{x_{\mathrm{Cu}} + x_{\mathrm{Ni}}}, \quad 1467 \le T \le 1739\,\mathrm{K} \quad (30)$$

$$\alpha_{\mathrm{Cu-Si}} = (-6.96 \pm 0.41)\frac{10^4}{T}x^2 + (-16.2 \pm 2.2) + (97.7 \pm 37.1)x + (-1094 \pm 207)x^2 + (3514 \pm 489)x^3 + (-4748 \pm 515)x^4 + (2216 \pm 199)x^5, \quad x = \frac{x_{\mathrm{Cu}}}{x_{\mathrm{Cu}} + x_{\mathrm{Si}}}, \quad 1281 \le T \le 1900\,\mathrm{K} \quad (31)$$

$$\alpha_{\mathrm{Ni-Si}} = [(-3.713 \pm 0.023) + (-213.8 \pm 18.5)x^2 + (1114.0 \pm 126.4)x^3 + (-2075.3 \pm 310.9)x^4 + (1683.0 \pm 326.0)x^5 + (-504.2 \pm 123.1)x^6] \times \frac{10^5}{T} + (9236.6 \pm 1076.1)x^2 + (-51095.1 \pm 7364.7)x^3 + (100220.1 \pm 18127.4)x^4 + (-84975.8 \pm 18998.1)x^5 + (26496.8 \pm 7178.9)x^6, \quad x = \frac{x_{\mathrm{Si}}}{x_{\mathrm{Ni}} + x_{\mathrm{Si}}}, \quad 1575 \le T \le 1900\,\mathrm{K} \quad (32)$$

$$\alpha_{\mathrm{Al-Cu-Ni}} = (-579.7 \pm 36.8)x_{\mathrm{Al}} + (-111.3 \pm 41.4)x_{\mathrm{Cu}} + (151.0 \pm 36.5)x_{\mathrm{Ni}}, \quad 1467 \le T \le 1700\,\mathrm{K} \quad (33)$$

$$\alpha_{\mathrm{Al-Cu-Si}} = (868.4 \pm 30.0)x_{\mathrm{Al}} + (414.8 \pm 31.3)x_{\mathrm{Si}} + (-885.8 \pm 42.5)x_{\mathrm{Al}}^2 + (-404.4 \pm 48.7)x_{\mathrm{Si}}^2 + (-1570.4 \pm 52.4)x_{\mathrm{Al}}x_{\mathrm{Si}}, \quad T = 1575\,\mathrm{K} \quad (34)$$

$$\alpha_{\mathrm{Al-Ni-Si}} = (-371.7 \pm 15.0) + (450.1 \pm 17.9)x_{\mathrm{Al}} + (2182.0 \pm 62.2)x_{\mathrm{Ni}} + (-2673.3 \pm 72.2)x_{\mathrm{Ni}}^2 + (-72132.0 \pm 1873.0)x_{\mathrm{Al}}^2x_{\mathrm{Ni}}^4, \quad T = 1575\,\mathrm{K} \quad (35)$$

$$\alpha_{\mathrm{Cu-Ni-Si}} = (-1195.4 \pm 43.2)x_{\mathrm{Si}} + (1530.2 \pm 66.2)x_{\mathrm{Si}}^2 + (646.7 \pm 39.0)x_{\mathrm{Ni}}^2 + (-969.9 \pm 129.0)x_{\mathrm{Ni}}x_{\mathrm{Si}}, \quad T = 1575\,\mathrm{K} \quad (36)$$

$$\alpha_{\mathrm{Al-Cu-Ni-Si}} = (2222.5 \pm 141.3)x_{\mathrm{Al}} + (-2025.9 \pm 135.0)x_{\mathrm{Ni}} + (-12229.7 \pm 3272.7)x_{\mathrm{Al}}x_{\mathrm{Ni}}x_{\mathrm{Si}}, \quad T = 1575\,\mathrm{K} \quad (37)$$

With view to a direct use of the thermodynamic properties Eqs. (10)–(37) adequately describe the experimental results. The contribution of the last term of Eq. (26), which describes the additional quaternary interactions, for the composition sections with the ratios $x_{\mathrm{Ni}}/x_{\mathrm{Si}}$=1/4, $x_{\mathrm{Ni}}/x_{\mathrm{Si}}$=1/1, and $x_{\mathrm{Ni}}/x_{\mathrm{Si}}$=4/1 is shown in Fig. 3. This contribution is positive in aluminium rich alloys and is negative in Ni and Si rich alloys. Its absolute value does not exceed 2 kJ mol^{-1}. This proves the existence of rather weak quaternary interactions.

Fig. 4 illustrates the variations of the integral enthalpy of mixing of the liquid and undercooled liquid quaternary alloys with the ratios of the mole fractions of nickel and silicon, calculated according to the relationships given above. With increasing $x_{\mathrm{Ni}}/x_{\mathrm{Si}}$ ratio the ΔH-values decrease. The minimum

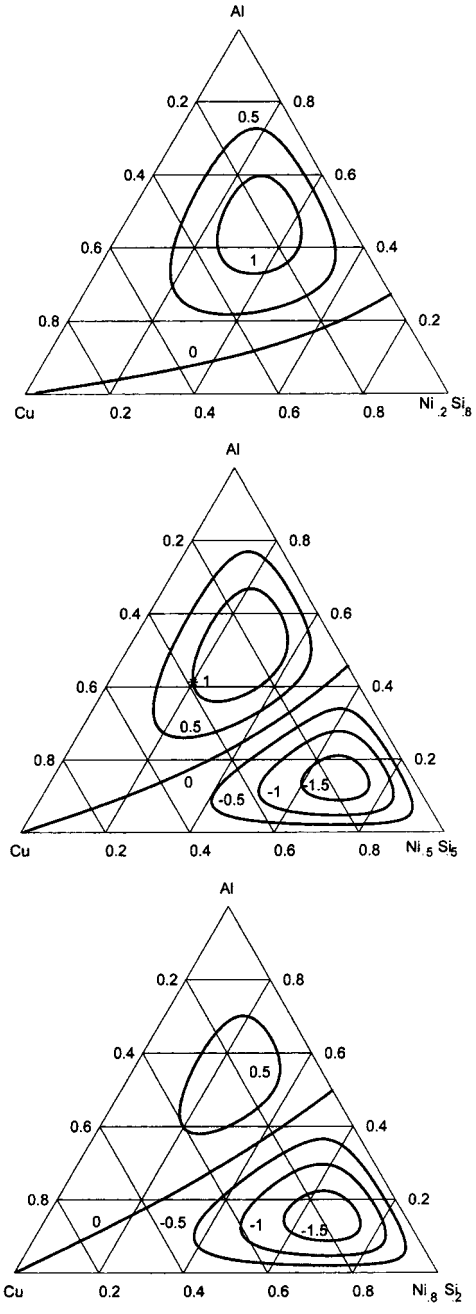

Fig. 3. Variation of the contribution of the last term of Eq. (26) describing the additional quaternary interactions of the integral enthalpy of mixing, with the ratio of mole fractions of Ni and Si of liquid and undercooled liquid Al–Cu–Ni–Si alloys (in kJ mol^{-1}; T=1575±3 K).

corresponds to the composition of the ternary intermetallic compound Ni_2AlSi.

4. Modelling of the thermodynamic properties of liquid Al–Cu–Ni–Si alloys

The integral enthalpy of mixing of liquid Al–Cu–Ni–Si alloys exhibits highly negative values and a strongly asymmetric dependence on composition with a sharp minimum near the ternary composition Ni_2AlSi which is most probably due to a chemical short range order (CSRO). The regular association model given by Sommer [12] is capable to describe the relation between CSRO and thermodynamic properties. For the enthalpy and entropy of mixing of liquid alloys with k components the following relationships result [12,13]:

$$\Delta H = \left(\frac{1}{2} \sum_{k=1}^{k'} \sum_{l=1}^{k'} C_{k,l}^{\mathrm{reg}} \frac{n'_k n'_l}{\sum_{i=1}^{k'} n'_i} + \sum_{i=1}^{k'} n'_i \Delta H_i^0 \right) \times \left(\sum_{j=1}^{k} n_j \right)^{-1} \tag{38}$$

and

$$\Delta S = \left(\sum_{i=1}^{k'} - R n'_i \ln z_i + n'_i \Delta S_i^0 \right) \left(\sum_{j=1}^{k} n_j \right)^{-1}, \tag{39}$$

where k is the number of components, n the number of moles of the components, k' the number of species (monomer, associate), n'_i the number of moles and z_i the mole fraction of the species. $C_{k,l}^{\mathrm{reg}}$ represents an interaction parameter between the species k and l ($C_{k,k}^{\mathrm{reg}}$=0). Interactions between different associates are not taken into account. ΔH_i^0 and ΔS_i^0 are the enthalpy and entropy of formation of the associates. It was assumed that they are temperature dependent. For a temperature T, if ΔH_i^0 and ΔS_i^0 are fixed at T_0, the following relationships can be used [12]

$$\Delta H_i^0(T) = \Delta H_i^0(T_0) + A(T - T_0) + \frac{B}{2}(T^2 - T_0^2) + \frac{C}{3}(T^3 - T_0^3), \tag{40}$$

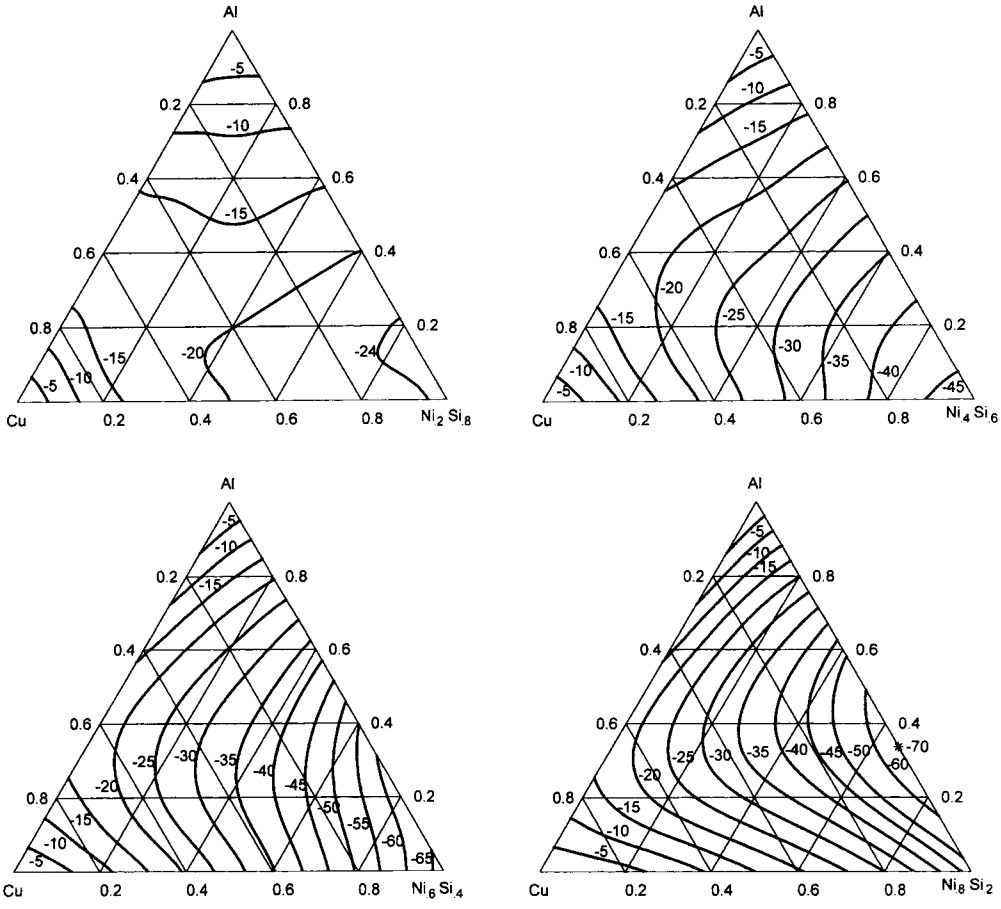

Fig. 4. Variation of the integral enthalpy of mixing of liquid and undercooled liquid Al–Cu–Ni–Si alloys at 1575±3 K with the ratio of mole fractions of Ni and Si (in kJ mol^{-1}; standard states: Al(l), Cu(l), Ni(l) and Si(l)).

$$\Delta S_i^0(T) = \Delta S_i^0(T_0) + A \ln\left(\frac{T}{T_0}\right) + B(T - T_0) + \frac{C}{2}(T^2 - T_0^2). \quad (41)$$

The equilibrium values of n_i' are determined by the law of mass action [12,13]:

$$\exp\left[-\frac{(\Delta H_i^0 - T\Delta S_i^0)}{RT}\right] = z_i \gamma_i' \left(\prod_{j=1}^{k} (z_j y_j')^{e_{i,j}}\right)^{-1}. \quad (42)$$

γ' is the activity coefficient of the species k' and $e_{i,j}$ the stoichiometric factor of the component j in the associate i. The parameters $\Delta H_i^0(T_0)$, $\Delta S_i^0(T_0)$, A, B, C, and the interaction parameters $C_{k,l}^{\mathrm{reg}}$ are determined by fitting the experimental $\Delta H(T)$ and activity data by solving Eqs. (38), (39) and (42) iteratively.

We have applied this model for the description of the partial and integral enthalpies of mixing of the constituent ternary alloys on the basis of the appropriate parameters for their constituent binaries (Table 5). The results of the description of the enthalpy of the ternaries are shown in Fig. 5 in comparison with experimental data approximated by Eqs. (26)–(37). The ternary model parameters used additionally are listed in Table 6. Obviously, the description by the model results in a good agreement with the experimental values for all constituent ternary systems. Maximal deviations between values compared do not exceed 0.5, 2, 2, and 3 kJ mol^{-1} for the Al–Cu–Si, Al–Cu–Ni, Cu–Ni–Si, and Al–Ni–Si systems,

Table 5
Regular association model parameters of the constituent binaries of the liquid Al–Cu–Ni–Si alloys (in kJ mol^{-1}, T_0=1575 K)

System	Al–Cu	Al–Ni	Al–Si	Cu–Ni	Cu–Si	Ni–Si
Associate	Al_1Cu_3	Al_1Ni_1	Al_1Si_1	–	Cu_3Si_1	Ni_2Si_1
$\Delta H^0_{A_iB_j}$ (1575 K)	−82.1	−128.1	23.4	–	−83.0	−233.4
$\Delta S^0_{A_iB_j}$ (1575 K)	−0.0361 K^{-1}	−0.0337 K^{-1}	−0.0207 K^{-1}	–	−0.0296 K^{-1}	−0.0652 K^{-1}
$C^{reg}_{A,B}$	−43.4	−59.3	−10.1	13.2	−18.2	−124.3
C^{reg}_{A,A_iB_j}	−79.7	−25.2	−50.3	–	−11.0	−21.0
C^{reg}_{B,A_iB_j}	−20.1	−36.9	−40.3	–	−16.2	−84.7
A	–	2.61×10^{-2}	–	–	−0.38	−5.36
B	–	1.30×10^{-5}	–	–	0.56×10^{-3}	6.66×10^{-3}
C	–	-2.04×10^{-8}	–	–	-0.21×10^{-6}	-2.02×10^{-6}
Data used for fitting/reference	[5]	[14–21]	[22–27]	[5]	[33–38]	[2,28–32]

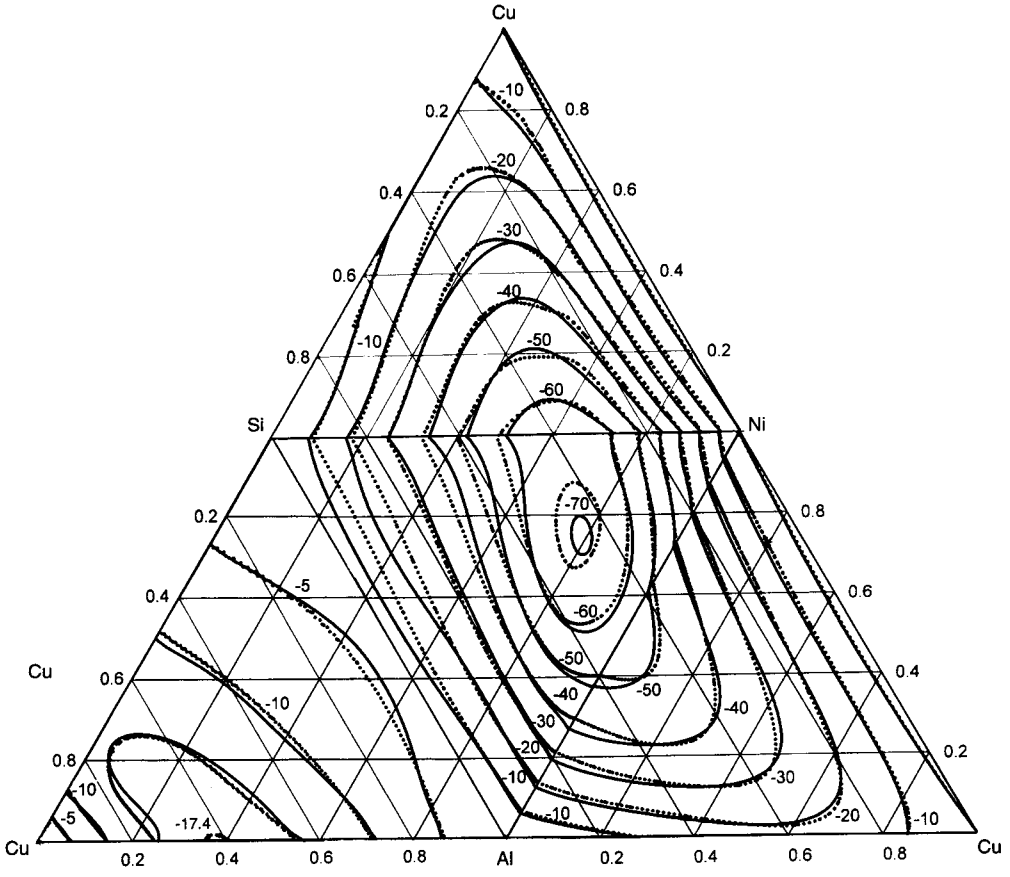

Fig. 5. Comparison between the experimental values of the integral enthalpy of mixing of the constituent ternaries approximated by Eq. (26) (solid lines) and calculated values using the regular association model (dotted lines) (in kJ mol^{-1}; T=1575 K; standard states: Al(l), Cu(l), Ni(l), and Si(l)).

Table 6
Regular association model parameters, which describe the assumed ternary association reactions (in kJ mol^{-1}; T=1575°K)

System	Al–Cu–Ni	Al–Cu–Si	Al–Ni–Si	Cu–Ni–Si
$\Delta H^0_{A_iB_jC_k}$ (1575 K)	$Al_2Cu_1Ni_1$	$Al_1Cu_3Si_1$	$Al_1Si_1Ni_2$	$Cu_2Ni_2Si_1$
$\Delta S^0_{A_iB_jC_k}$ (1575 K)	−194.33	−124.5	−322.0	−148.2
$C^{reg}_{A_iA_iB_jC_k}$	-3.99×10^{-2} K^{-1}	-4.19×10^{-2} K^{-1}	-7.35×10^{-2} K^{-1}	1.91×10^{-2} K^{-1}
$C^{reg}_{A_iA_jB_jC_k}$	−29.14	5.2	−29.7	17.0
$C^{reg}_{B_iA_jB_jC_k}$	−7.02	−57.1	0	−29.1
$C^{reg}_{C_iA_jB_jC_k}$	−73.41	−13.2	−76.5	46.0

respectively, which is within the confidence bands of the experimental data. Such a good correspondence enables a reasonable estimation of the entropy and the Gibbs energy of mixing of the constituent ternary alloys. The latter function is illustrated in Fig. 6 as the projections of the isosections on the Gibbs composition triangles. Obviously, the minima of the integral Gibbs energy of mixing for the Al–Cu–Ni (−42.8 kJ mol^{-1}), Al–Ni–Si (−54.6 kJ mol^{-1}), Al–Cu–Si (−24.4 kJ mol^{-1}) are observed near the ternary compositions $Al_{0.45}Cu_{0.10}Ni_{0.45}$, $Al_{0.25}Ni_{0.50}Si_{0.25}$, and $Al_{0.17}Cu_{0.50}Si_{0.33}$, respectively. The minimum for the liquid Cu–Ni–Si alloys (−52.0 kJ mol^{-1}) corresponds to the binary composition $Ni_{0.58}Si_{0.42}$.

Using the model parameters determined from the basic binary and ternary systems given in Tables 5 and

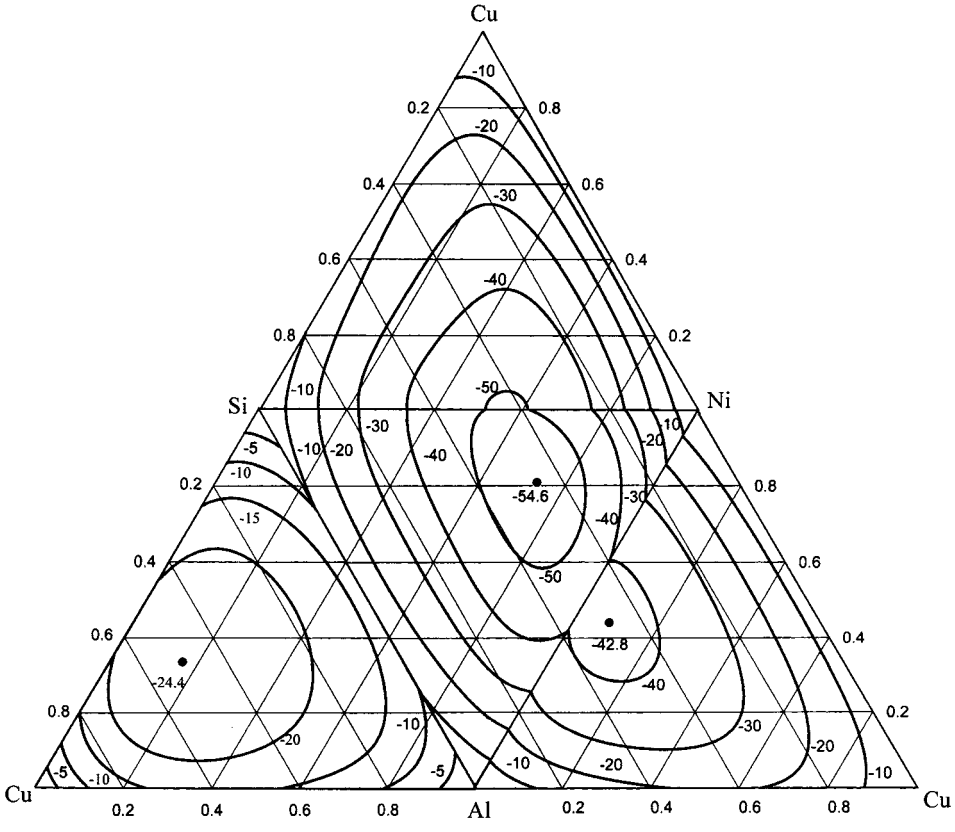

Fig. 6. Calculated Gibbs energy of mixing of liquid and undercooled liquid constituent ternary alloys of the quaternary Al–Cu–Ni–Si system using the association model (in kJ mol^{-1}; T=1575 K; standard states: Al(l), Cu(l), Ni(l), and Si(l)).

6 and supposing that no quaternary association reaction occurs, the integral enthalpy of mixing was calculated for liquid Al–Cu–Ni–Si alloys. Unfortunately, the Ni rich quaternary alloys show big differences between calculated and experimental values (up to 8 kJ mol^{-1}) due to existence of the quaternary association reactions. As the available programs do not yet allow to take into account these interactions, the excess integral Gibbs energy of liquid quaternary alloys was estimated on the basis of results from the regular association model for the constituent binaries and ternaries using the Kohler scheme. The enthalpy of mixing of Al–Cu–Ni–Si alloys, obtained with the same interpolation scheme, describes the experimental results with a maximal deviation of 1.5 kJ mol^{-1} (see Fig. 3). Finally, for the Gibbs energy the following relationships were found (in kJ mol^{-1}; T=1575 K; standard states of Al(l), Cu(l), Ni(l) and Si (l)):

$$\begin{aligned}\Delta G = {} & \beta_{\mathrm{Al-Cu}} x_{\mathrm{Al}} x_{\mathrm{Cu}} + \beta_{\mathrm{Al-Ni}} x_{\mathrm{Al}} x_{\mathrm{Ni}} + \beta_{\mathrm{Al-Si}} x_{\mathrm{Al}} x_{\mathrm{Si}} \\ & + \beta_{\mathrm{Cu-Ni}} x_{\mathrm{Cu}} x_{\mathrm{Ni}} + \beta_{\mathrm{Cu-Si}} x_{\mathrm{Cu}} x_{\mathrm{Si}} \\ & + \beta_{\mathrm{Ni-Si}} x_{\mathrm{Ni}} x_{\mathrm{Si}} + \beta_{\mathrm{Al-Cu-Ni}} x_{\mathrm{Al}} x_{\mathrm{Cu}} x_{\mathrm{Ni}} \\ & + \beta_{\mathrm{Al-Cu-Si}} x_{\mathrm{Al}} x_{\mathrm{Cu}} x_{\mathrm{Si}} + \beta_{\mathrm{Al-Ni-Si}} x_{\mathrm{Al}} x_{\mathrm{Ni}} x_{\mathrm{Si}} \\ & + \beta_{\mathrm{Cu-Ni-Si}} x_{\mathrm{Cu}} x_{\mathrm{Ni}} x_{\mathrm{Si}} \\ & + \beta_{\mathrm{Al-Cu-Ni-Si}} x_{\mathrm{Al}} x_{\mathrm{Cu}} x_{\mathrm{Ni}} x_{\mathrm{Si}} \\ & + RT(x_{\mathrm{Al}} \ln x_{\mathrm{Al}} + x_{\mathrm{Cu}} \ln x_{\mathrm{Cu}} + x_{\mathrm{Ni}} \ln x_{\mathrm{Ni}} \\ & + x_{\mathrm{Si}} \ln x_{\mathrm{Si}}) \end{aligned} \tag{43}$$

$$\beta_{\mathrm{Al-Cu}} = -33.8 - 28.0x + 5.7x^2, \quad x = \frac{x_{\mathrm{Cu}}}{x_{\mathrm{Al}} + x_{\mathrm{Cu}}}, \tag{44}$$

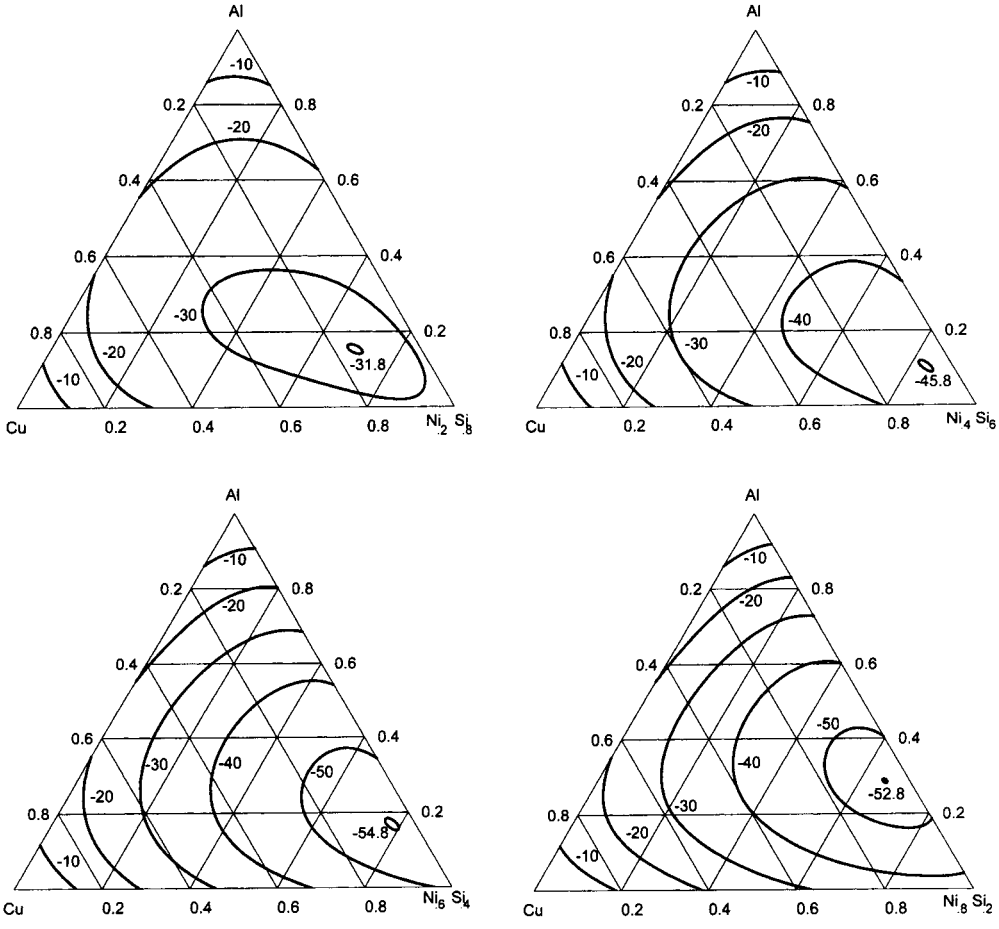

Fig. 7. Variations of the calculated Gibbs energy of mixing of liquid and undercooled liquid quaternary Al–Cu–Ni–Si alloys with the ratio of the mole fractions of Ni and Si (in kJ mol^{-1}; T=1575 K; standard states: Al(l), Cu(l), Ni(l), and Si(l)).

$$\beta_{\mathrm{Al-Ni}} = -91.7 - 135.4x + 117.8x^2, \quad x = \frac{x_{\mathrm{Ni}}}{x_{\mathrm{Al}} + x_{\mathrm{Ni}}}, \tag{45}$$

$$\beta_{\mathrm{Al-Si}} = -13.5 + 0.9x, \quad x = \frac{x_{\mathrm{Si}}}{x_{\mathrm{Al}} + x_{\mathrm{Si}}}, \tag{46}$$

$$\beta_{\mathrm{Cu-Ni}} = 13.6 - 0.9x, \quad x = \frac{x_{\mathrm{Ni}}}{x_{\mathrm{Cu}} + x_{\mathrm{Ni}}}, \tag{47}$$

$$\beta_{\mathrm{Cu-Si}} = -59.6 + 89.9x - 49.7x^2, \quad x = \frac{x_{\mathrm{Si}}}{x_{\mathrm{Cu}} + x_{\mathrm{Si}}}, \tag{48}$$

$$\beta_{\mathrm{Ni-Si}} = -183.5 + 88.1x^2, \quad x = \frac{x_{\mathrm{Si}}}{x_{\mathrm{Ni}} + x_{\mathrm{Si}}}, \tag{49}$$

$$\beta_{\mathrm{Al-Cu-Ni}} = -50.4x_{\mathrm{Ni}} - 291.7x_{\mathrm{Al}} - 165.0x_{\mathrm{Cu}} + 667.3x_{\mathrm{Ni}}x_{\mathrm{Cu}}, \tag{50}$$

$$\beta_{\mathrm{Al-Cu-Si}} = -108.5 + 479.9x_{\mathrm{Cu}} + 291.1x_{\mathrm{Si}} - 448.2x_{\mathrm{Cu}}^2 - 287.9x_{\mathrm{Si}}^2 - 242.9x_{\mathrm{Cu}}x_{\mathrm{Si}} \tag{51}$$

$$\beta_{\mathrm{Al-Ni-Si}} = -758.2 + 1711.1x_{\mathrm{Al}} + 2349.9x_{\mathrm{Si}} - 910.7x_{\mathrm{Al}}^2 - 1653.5x_{\mathrm{Si}}^2 - 2201.5x_{\mathrm{Al}}x_{\mathrm{Si}} \tag{52}$$

$$\beta_{\mathrm{Cu-Ni-Si}} = -412.1 + 84.5x_{\mathrm{Cu}} + 1008.3x_{\mathrm{Si}} - 131.3x_{\mathrm{Cu}}^2 - 845.6x_{\mathrm{Si}}^2 + 249.8x_{\mathrm{Cu}}x_{\mathrm{Si}}, \tag{53}$$

The term of Eq. (43) that describes the quaternary interactions ($\beta_{\mathrm{Al-Cu-Ni-Si}}$) was estimated using an empirical model proposed earlier [39]. This model was successfully applied to liquid binary [38,39], ternary Al–Cu–Zr, Ni–Cu–Zr, Al–Ni–Zr [8,40,41], and quaternary Al–Cu–Ni–Zr alloys [41]. In our case the relationship for $\beta_{\mathrm{Al-Cu-Ni-Si}}$ may be written as [41]:

$$\beta_{\mathrm{Al-Cu-Ni-Si}} = \alpha_{\mathrm{Al-Cu-Ni-Si}}\left(1 - 2\frac{\hat{T}_{\mathrm{m}}}{\hat{T}_{\mathrm{b}}^2}T\right) - RT\left(2\frac{\hat{T}_{\mathrm{m}}}{\hat{T}_{\mathrm{b}}}\right)^{5/2} \tag{54}$$

where $\hat{T}_{\mathrm{m}} = \sum_{i=1}^{n} T_{\mathrm{m},i}/n$; $\hat{T}_{\mathrm{b}} = \sum_{i=1}^{n} T_{\mathrm{b},i}/n$, $T_{\mathrm{m},i}$ and $T_{\mathrm{b},i}$ are the melting and boiling temperatures of the component i (i=Al, Cu, Ni, Si) of the quaternary alloy, n is the number of components of the alloy and $\alpha_{\mathrm{Al-Cu-Ni-Si}}$ is given by Eq. (37). The resulting Gibbs energy at 1575 K is shown in Fig. 7. These results indicate that the minimum of the Gibbs energy of mixing of the quaternary alloys ($-55.0\ \mathrm{kJ\ mol^{-1}}$) shows up at the composition $Al_{0.19}Cu_{0.08}Ni_{0.50}Si_{0.23}$.

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