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Activity of Copper in Liquid Nickel–Copper–Iron Alloys

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Abstract—The activities of copper in liquid nickel–copper–iron alloys at 1600°C were calculated along sections with constant $x_{Ni} : x_{Fe}$ ratios of 3 : 1, 1 : 1, and 1 : 3 (x_i is the mole fraction of a component in an alloy).

The integral molar excess Gibbs energies ΔG^{ex} and enthalpies ΔH of mixing of liquid Ni–Cu–Fe alloys at 1600°C, calculated from experimental data for binary boundary systems, have been reported previously [1, 2]. A number of geometric models and the polynomial Redlich–Kister method have been used in the calculations. Modern techniques for calculation of integral thermodynamic characteristics of liquid ternary metallic systems on the basis of the corresponding properties of binary systems were considered in detail in [3]. As a kind of a calculation reliability criterion in the absence of experimental data for a ternary system can serve the closeness of the results obtained using different geometric models and the analytical technique. For the Ni–Cu–Fe system, calculations of ΔG^{ex} and ΔH by different methods yield reasonably consistent results [1, 2].

The partial molar thermodynamic characteristics of copper in liquid alloys of the system Ni(1)–Co(2)–Fe(3) can be calculated using the known expressions relating the partial and integral parameters in ternary systems [3]. For example, the partial excess Gibbs energy for copper (component 2) along a path with a constant ratio of the other two components ($x_1 : x_3$) is given by

$$\Delta G_2^{ex} = \Delta G^{ex} + (1 - x_2)(\partial \Delta G^{ex}/\partial x_2)_{x_1/x_2}, \qquad (1)$$

where ΔG_2^{ex} is the partial molar excess Gibbs energy for the composition determined by the mole fractions x_1, x_2, and x_3 (or x_2, $x_1 : x_3$), and ΔG^{ex} is the integral molar excess Gibbs energy of the ternary system for the composition under consideration.

Another possibility of estimating the partial molar parameters of copper or any other component of the ternary system is to calculate them from the related

quantities for binary boundary systems. This method is applied to liquid metallic systems rather rarely [4]. At the same time, it follows from the basic equation of the Toop method [3, 4], which is widely used for calculating the thermodynamic characteristics of ternary systems, that

$$\Delta G_2^{ex} = \left[\frac{x_1}{1 - x_2} \Delta G_{2(12)}^{ex} + \frac{x_3}{1 - x_2} \Delta G_{2(23)}^{ex} \right]_{x_2}$$
$$- (1 - x_2)^2 [\Delta G_{13}^{ex}]_{x_1/x_3}, \qquad (2)$$

where $\Delta G_{2(12)}^{ex}$ and $\Delta G_{2(23)}^{ex}$ are the excess partial molar Gibbs energies for component 2 in binary boundary systems 1–2 and 2–3 at a given x_2; and ΔG_{13}^{ex} is the excess integral molar Gibbs energy of the binary boundary system 1–3 at a given ratio $x_1 : x_3$.

The available data on the thermodynamic properties of liquid alloys in the binary boundary systems Ni–Cu, Cu–Fe, and Fe–Ni have been discussed in detail [1, 2]. The input data used in calculations for the system Ni–Cu were based on the results of [5–7], and the ΔG^{ex} and ΔH values recommended by Batalin [8, 9] were adopted for the systems Cu–Fe and Ni–Cu. The dependence of the integral thermodynamic functions on composition was expressed analytically with the use of Redlich–Kister polynomials [1, 2]. The table compares the activities of copper in liquid alloys of the ternary system Ni–Cu–Fe, calculated using Eqs. (1) and (2) for compositions that lie on secants of the concentration triangle with $x_{Ni} : x_{Fe}$ ratios of 3 : 1, 1 : 1, and 1 : 3. The agreement between the results obtained is quite satisfactory. If the only goal of a calculation of the thermodynamic properties of a ternary system from data on binary boundary systems is to obtain the partial molar parameters of a component of

Activity of copper in liquid nickel–copper–iron alloys at 1600°C, calculated using Eqs. (1) and (2)

x_{Cu}	$x_{Ni} : x_{Fe} = 3 : 1$		$x_{Ni} : x_{Fe} = 1 : 1$		$x_{Ni} : x_{Fe} = 1 : 3$	
	(1)	(2)	(1)	(2)	(1)	(2)
0.10	0.35	0.33	0.41	0.41	0.45	0.46
0.20	0.53	0.53	0.61	0.59	0.64	0.62
0.30	0.67	0.64	0.72	0.69	0.74	0.70
0.40	0.74	0.72	0.76	0.75	0.77	0.76
0.50	0.79	0.77	0.80	0.80	0.79	0.80
0.60	0.82	0.81	0.84	0.83	0.83	0.84
0.70	0.85	0.84	0.88	0.86	0.89	0.87
0.80	0.89	0.87	0.91	0.88	0.93	0.89
0.90	0.93	0.92	0.94	0.92	0.94	0.92

the ternary system, then calculation by Eq. (2) seems to be preferable, compared to that by Eq. (1). Figure 1 shows isoactivity lines for copper in Ni–Cu–Fe liquid alloys at 1600°C.

Equation (2) makes it possible to estimate, on the basis of data for binary boundary systems, the limiting activity coefficient for copper in Ni–Fe liquid alloys. At $x_2 = 0$ ($x_{Cu} = 0$), Eq. (2) takes the form

$$(\Delta G_2^{ex})^\infty = x_1[\Delta G_{2(12)}^{ex}]^\infty + x_3[\Delta G_{2(23)}^{ex}]^\infty - [\Delta G_{13}^{ex}]_{x_1/x_3}. \quad (3)$$

In turn, knowledge of the limiting excess Gibbs energy for component 2 enables calculation of the activity coefficient for this component at infinite dilution by considering liquid alloys 1–3 of various compositions as solvents:

$$(\Delta G_2^{ex})^\infty = RT \ln \gamma_{2(13)}^\infty. \quad (4)$$

The quantities $\Delta G_{2(12)}^{ex}$ and $\Delta G_{2(23)}^{ex}$, related to binary systems 1–2 and 2–3, can be calculated using the Redlich–Kister polynomial, which describes the concentration dependence of the integral excess Gibbs energy in these systems. For example, the following dependences were obtained for the Ni–Cu system (ΔG^{ex} is in kJ mol^{-1}, 1873 K):

$$\Delta G^{ex} = x_{Ni}(1 - x_{Ni})[18.8829 - 3.5732(2x_{Ni} - 1)$$

$$- 0.3147(2x_{Ni} - 1)^2],$$

and for the Cu–Fe system

$$\Delta G^{ex} = x_{Cu}(1 - x_{Cu})[29.5990 + 0.2475(2x_{Cu} - 1)$$

$$+ 6.8151(2x_{Cu} - 1)^2].$$

As already reported [1], equations of this kind describe experimental data with high precision.

Now, a polynomial relation for the binary system 1–2 is considered in the general form:

$$\Delta G^{ex} = x_1(1 - x_1)[b_1 + c(2x_1 - 1) + d(2x_1 - 1)^2]. \quad (5)$$

For the binary system 1–2, Eq. (1) takes the form

$$\Delta G_1^{ex} = \Delta G^{ex} + (1 - x_1)(\partial \Delta G^{ex}/\partial x_1)_{P,T}, \quad (6)$$

$$\Delta G_2^{ex} = \Delta G^{ex} - x_1(\partial \Delta G^{ex}/\partial x_1)_{P,T}. \quad (7)$$

Differentiation of Eq. (5) and substitution of the appropriate values into Eqs. (6) and (7) yields

$$\Delta G_1^{ex} = (1 - x_1)^2[b + c(4x_1 - 1) + d(12x_1^2 - 8x_1 + 1)], \quad (8)$$

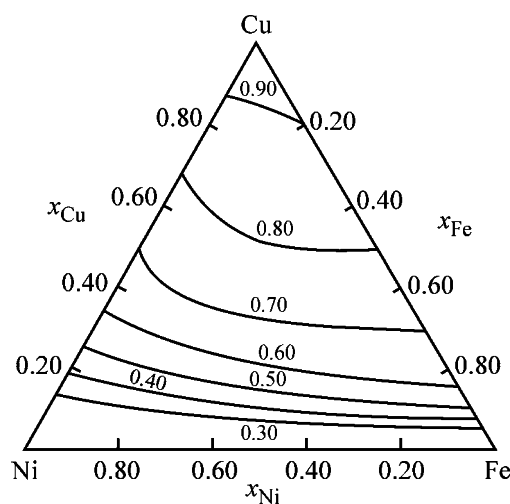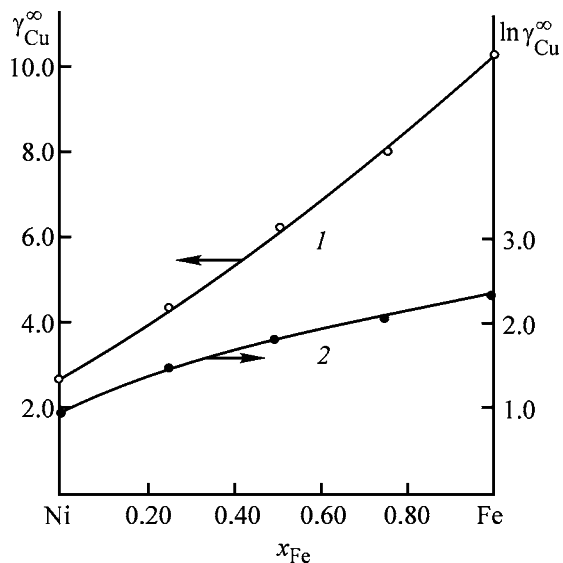Fig. 1. Isoactivity lines for copper in liquid Ni–Cu–Fe alloys at 1873 K.

Fig. 2. (*1*) Limiting activity coefficient of copper, γ_{Cu}^{∞}, and (*2*) its logarithm vs. the composition x_{Fe} of the liquid Ni–Fe alloy at 1873 K.

$$\Delta G_2^{ex} = x_1^2[b + c(4x_1 - 3) + d(12x_1^2 - 16x_1 + 5)]. \quad (9)$$

At $x_1 \to 0$ or $x_1 \to 1$ ($x_2 \to 0$), accordingly,

$$(\Delta G_1^{ex})^{\infty} = b - c + d, \quad (10)$$

$$(\Delta G_2^{ex})^{\infty} = b + c + d. \quad (11)$$

In the boundary system Ni–Cu, copper is component 2 and Eqs. (9) and (11) are to be used for calculating ΔG_{Cu}^{ex} and $(\Delta G_{Cu}^{ex})^{\infty}$. At the same time, copper is component 1 in the boundary system Cu–Fe, and similar calculations require that Eqs. (8) and (10) should be used.

Thus,

$$[\Delta G_{Cu(Ni)}^{ex}]^{\infty} = 18.8829 - 3.5732 - 0.3147$$

$$= 14.995 \text{ kJ mol}^{-1},$$

$$\ln \gamma_{Cu(Ni)}^{\infty} = 0.963, \quad \gamma_{Cu(Ni)}^{\infty} = 2.619.$$

$$[\Delta G_{Cu(Fe)}^{ex}]^{\infty} = 29.5990 - 0.2475 + 6.8151$$

$$= 36.167 \text{ kJ mol}^{-1},$$

$$\ln \gamma_{Cu(Fe)}^{\infty} = 2.323, \quad \gamma_{Cu(Fe)}^{\infty} = 10.201.$$

The limiting values of the activity coefficients of copper in liquid alloys with nickel or iron are reasonably consistent with published experimental data [1].

For the iron–nickel system, the dependence of ΔG^{ex} on the alloy composition at 1873 K is described by the equation

$$\Delta G^{ex} = x_{Fe}(1 - x_{Fe})[-11.0909 + 6.1995(2x_{Fe} - 1)$$

$$- 0.9194(2x_{Fe} - 1)^2].$$

Data on ΔG^{ex} for the system Fe–Ni at $x_{Ni} : x_{Fe}$ of 3 : 1, 1 : 1, and 1 : 3 are required for substitution into Eq. (5). In other words, it is necessary to know ΔG^{ex} at $x_{Ni} = 0.75$, 0.50, and 0.25:

x_{Ni}	0.75	0.50	0.25
x_{Fe}	0.25	0.50	0.75
$\Delta G_{Ni–Fe}^{ex}$, kJ mol^{-1}	–2.704	–2.770	–1.541

As a result, the following values of the limiting thermodynamic functions are obtained for copper in liquid Ni–Fe alloys of various compositions at a temperature of 1873 K:

x_{Ni}	0.75	0.50	0.25
$[\Delta G_{Cu}^{ex}]^{\infty}$, kJ mol^{-1}	22.992	28.351	32.414
$\ln \gamma_{Cu}^{\infty}$	1.476	1.821	2.082
γ_{Cu}^{∞}	4.378	6.176	8.016

Figure 2 shows that the dependence of $\ln \gamma_{Cu}^{\infty}$ and γ_{Cu}^{∞} on the composition of the liquid Ni–Fe alloys is very close to a linear dependence.

CONCLUSIONS

(1) Calculation of the activity of copper in liquid nickel–copper–iron alloys at 1600°C by two different methods yields consistent results.

(2) Estimates of the limiting values of the activity coefficients of copper in liquid Cu–Ni, Cu–Fe, and Cu–(Ni–Fe) alloys are presented. The dependence of γ_{Cu}^{∞} on the composition of the Ni–Fe alloy is nearly linear.

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