FRENCH-UKRAINIAN JOURNAL OF CHEMISTRY (**2017**, VOLUME **05**, ISSUE **02**)

Thermochemical properties of liquid alloys along x_{Cu} / x_{Sb} = 0.2/0.8 section of the ternary Cu-Sb-Ce system

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Keywords: *Copper, Cerium; Antimony; Calorimetry; Enthalpy of mixing*.

The enthalpies of mixing of liquid alloys of the ternary Cu–Sb–Ce system were studied by high-temperature calorimetry along the cross-section x_{Cu} / x_{Sb} = 0.2/0.8. The composition dependence of these values were modelled using four "geometric" models and also the analytical method of Redlich–Kister–Muggianu. A comparison of the experimental data for the cross section x_{Cu} / x_{Sb} = 0.2/0.8 and simulated values of the enthalpies of mixing showed that the most suitable for describing the properties of liquid alloys of ternary Cu–Sb–Ce system is the Toop model.

Introduction

Rare-earth antimonides, especially multicomponent d-metal containing phases, are of great interest due to their special electrophysical properties and peculiarities of their electronic structure. New thermoelectric materials with scutterudite structure that containe 3d transition metals and rare earth metals are widely studied nowadays. The alloys of the Cu–Sb–Ce ternary system belong to this family of materials. The enthalpies of formation of multicomponent alloys in liquid state reflect the essential features of the component interaction and contribute to a better understanding of the behaviour of materials both in liquid and in solid state.

Earlier in [1] the enthalpies of mixing of liquid alloys of the ternary Cu–Sb–Ce system were simulated through the whole Gibbs composition triangle using the Toop "geometric" equation [2]. The following thermochemical properties of liquid boundary binary systems were used for modelling:

- Sb–Ce – [3], high temperature calorimetry at 1600 K ($\Delta_m H^{extr.}$ = –123.0 kJ mol^{-1} at x_{Ce} = 0.55);
- Cu–Sb – [4], the thermodynamic properties of these melts were simulated for the entire composition interval using the ThermoCalc calculations based on the ideal associated solution model taking into account all

experimental information presented in the literature (at 1375 K $\Delta_{\mathrm{m}}H^{\mathrm{extr.}}$ = –5.9 kJ mol^{-1} at x_{Sb} = 0.75);

- Cu–Ce – [5], high temperature calorimetry at 1523 K ($\Delta_{\mathrm{m}}H^{\mathrm{extr.}}$ = –12.3±0.6 kJ mol^{-1} at x_{Ce} = 0.34).

The calculated value of integral enthalpies of mixing for ternary melts demonstrated a monotone increase of exothermic enthalpies of mixing from the copper corner to the Ce–Sb side of the triangle.

In present work we have experimentally determined enthalpies of mixing of liquid ternary alloys along $\mathrm{x_{Cu}} / \mathrm{x_{Sb}}$ = 0.2/0.8 section via isoperibolic high-temperature calorimetry at 1300 K.

Experimental part

The experiments were carried out in a high temperature solution calorimeter in purified helium medium under a pressure of 10^5 Pa at 1300 K. The apparatus and experimental technique were similar to those employed in the previous investigations [3, 6]. The purity of elements used in the experiments was 99.9 % for Ce, 99.95 % for Cu and 99.99 % for Sb. Cerium was mechanically treated and stored in petroleum ether to prevent oxidation; cerium samples were prepared in a glove box filled with purified helium.

The partial heats of mixing of cerium were measured in the process of successive introduction of metal samples taken at 298 K (masses within 0.01–0.03 g) into the calorimetric bath (a liquid metal or an alloy, placed in a zirconia crucible). The initial mass of a metal in the bath was about 2 – 3 g. The variation in the alloy concentration after each dropping was less than 1.5 at. %. Consequently, we can determine the partial molar enthalpies with sufficient accuracy. Temperature measurements were carried out with WRe5/WRe20 thermocouples.

For the ternary Cu–Sb–Ce system partial molar enthalpies of Ce were determined along the section of the concentration triangle with a constant molar fraction ratio $\mathrm{x_{Cu}} / \mathrm{x_{Sb}}$ = 2/8. In this case about six Cu samples of appropriate masses were added to a calorimetric bath containing liquid Sb until the desired component ratio was achieved and then small cerium samples were introduced into the bath to obtain partial molar enthalpies of Ce.

The experimental method is based on the measurement of the temperature change Δ*T* of calorimetric bath plotted as a function of temperature relaxation time (*t*), the heat effects being calculated from the Δ*T* vs. *t* curve by numerical integration.

The resulting heat balance equation for the exothermic effect is:

$$-\mathrm{k}\int \Delta \mathrm{T}(\mathrm{t})\,\mathrm{d}\,\mathrm{t} = \Delta \mathrm{H}^{\mathrm{T}}_{\mathrm{Ce,298}} + \Delta \overline{\mathrm{H}}_{\mathrm{Ce}} \qquad (1)$$

where $\Delta H^{T}_{Ce,298}$ is the enthalpy change for heating of 1 mole of metal dropped into the bath from 298 K to the temperature of liquid bath, computed from the Ref. [7]; $\Delta \overline{H}_{Ce}$ is the unknown partial molar enthalpy of mixing of Ce; k is the molar thermal equivalent of the calorimeter. It was determined in calibrating droppings at the beginning (using the same component as that in the bath) and at the end (using specimens of W, 99.96 % purity) of each experimental series.

The set of the experimental $\Delta \overline{H}_{Ce}$ data points computed from Eq. (1) was treated statistically (in the form of a partial *α*-function defined as $\alpha_{Ce} = \Delta \overline{H}_{Ce}(1 - x_{Ce})^{-2}$) by a least-squares analysis using Forsythe orthogonal polynomials and applying the *F*-test for a correct choice of polynomial degree [8]. Finally, the α_{Ce} function was represented as a polynomial series as follows:

$$\alpha_{Ce} = Q_0 + Q_1 x_{Ce} + Q_2 x_{Ce}^2 + ... + Q_j x_{Ce}^j \qquad (2)$$

where Q_j are the polynomial coefficients, j is the polynomial degree.

For the ternary system the Darken method gives the following expression for the integral enthalpy of mixing:

$$\Delta_m H = (1 - x_{Ce}) \left[\int_{x_{Ce}=0}^{x_{Ce}} \alpha_i dx_i + \Delta_m H_{x_{Ce}=0} \right]_{x_{Cu}/x_{Sb}}$$

(3)

where $\Delta H_{x_{Ce}=0}$ is the integral molar enthalpy of mixing of corresponding binary Cu–Sb liquid alloy (with the above indicated molar fractions ratio x_{Cu} / x_{Sb}).

Results and discussion

The composition dependence of partial mixing enthalpy of cerium of liquid alloys along investigated section is given in **Figure 1**.

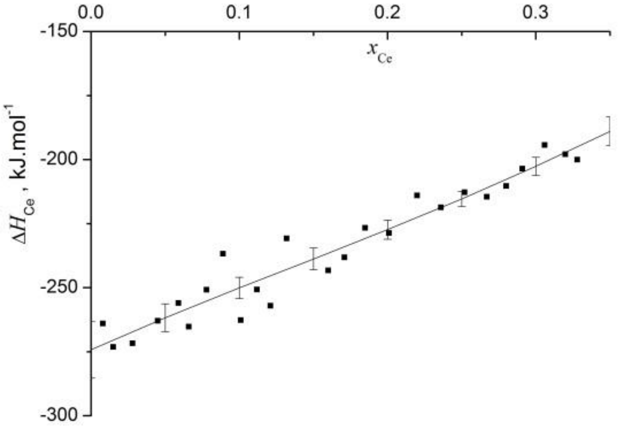

Figure 1. The partial mixing enthalpies of cerium in liquid ternary alloys along x_{Cu} / x_{Sb} = 0.2/0.8 section at 1300 K.

The resulting composition dependence of integral enthalpy of mixing of liquid alloys along investigated section is given in **Figure 2**.

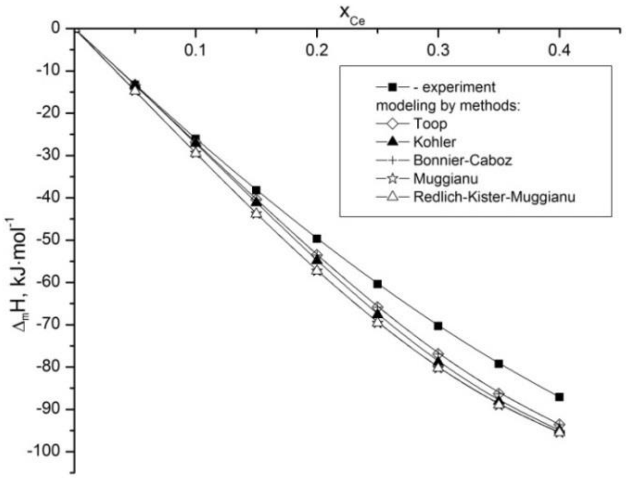

Figure 2. **C**omparison of experimental results of the integral enthalpies of mixing of liquid ternary alloys along $x_{Cu} / x_{Sb} = 0.2/0.8$ section with ones simulated for these alloys according to regular solution models [2, 9-12].

We also calculated the integral enthalpies of mixing of these alloys using four numerical "geometric" methods for regular solutions (Toop [2], Kohler [9], Bonnier-Caboz [10], Muggianu [11]) and the analytical Redlich-Kister-Muggianu method [12]. The last method of calculating of thermodynamic properties of multicomponent systems gives an analytical expression of enthalpies of mixing through the whole Gibbs composition triangle and also makes possible to determine the so called “ternary term” of the interaction of particles in the ternary system.

To perform the $\Delta_m H$ calculations in the ternary system the data on the constituent binary systems were presented in the form of Redlich-Kister polynomials:

$$\Delta_m H_{Ce-Cu} = x_{Ce}\, x_{Cu}(-44.63 + 27.01(x_{Ce} - x_{Cu}) - \\ -17.97(x_{Ce} - x_{Cu})^2 + 7.15(x_{Ce} - x_{Cu})^3 - 0.57(x_{Ce} - x_{Cu})^4)$$
(4)

$$\Delta_m H_{Cu-Sb} = x_{Cu}\, x_{Sb}(-9.48 - 31.05(x_{Cu} - x_{Sb}) - \\ -29.09(x_{Cu} - x_{Sb})^2 + 6.34(x_{Cu} - x_{Sb})^3 + 20.64(x_{Cu} - x_{Sb})^4 + \\ +0.35(x_{Cu} - x_{Sb})^5)$$
(5)

$$\Delta_m H_{Sb-Ce} = x_{Sb}\, x_{Ce}(-492.15 + 48.26(x_{Sb} - x_{Ce}) + \\ +191.63(x_{Sb} - x_{Ce})^2 - 1.26(x_{Sb} - x_{Ce})^3 - 51.66(x_{Sb} - x_{Ce})^4 - \\ -3.10(x_{Sb} - x_{Ce})^5)$$
(6)

The resulting Redlich-Kister-Muggianu equation for the integral enthalpy of mixing in ternary system is as follows:

$$\Delta_m H(x_{Ce}, x_{Ce}, x_{Sb}) = x_{Ce}\, x_{Cu} \sum_{i=0}^{n} {}^{i}L_{Ce-Cu}(x_{Ce} - x_{Cu})^i + \\ + x_{Cu}\, x_{Sb} \sum_{i=0}^{n} {}^{i}L_{Cu-Sb}(x_{Cu} - x_{Sb})^i + x_{Sb}\, x_{Ce} \sum_{i=0}^{n} {}^{i}L_{Sb-Ce}(x_{Sb} - x_{Ce})^i$$
(7),

where ${}^{i}L_{Ce-Cu}, {}^{i}L_{Cu-Sb}, {}^{i}L_{Sb-Ce}$ are the interaction parameters between the elements in the corresponding binary system taken from Eqs. (4) – (6), n is the power of the Redlich–Kister polynomial. This expression does not include ternary term.

The resulting integral $\Delta_m H$ values obtained for these alloys according to four "geometric" regular solution models [9-11] and Redlich–Kister–Muggianu method [12], are also given in **Figure 2** for comparison with experimental results.

It can be seen that the Redlich-Kister-Muggianu method without calculating the ternary term gives the very similar results to those of other "geometric" models. At the same time the results of the experiment are more endothermic than those of regular solution calculations. It is an evident indication that specific positive "ternary contribution" into the values of the enthalpies of mixing exists in this system. But it is difficult to make reasonable estimates of this contribution through the whole composition triangle basing on the data of a single section. Further experimental studies of the ternary Cu–Sb–Ce alloys are necessary in order to make reliable estimates of "ternary" contribution in this system.

From **Figure 2** we can confirm our earlier conclusion made in [1] that the Toop method is the most suitable for describing the concentration dependence of enthalpies of mixing in the ternary Cu–Sb–Ce system.

Figure 3 demonstrates isolines of enthalpies of mixing obtained by Toop modelling for the entire Gibbs triangle and experimentally obtained $\Delta_m H$ values for an individual cross x_{Cu} / x_{Sb} = 0.2/0.8 section.

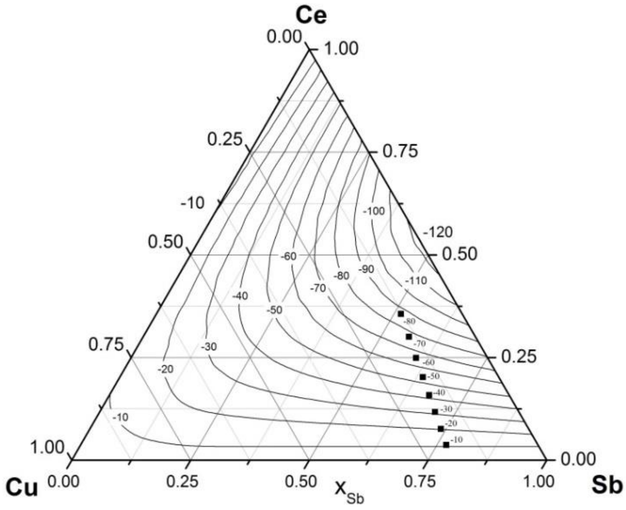

Figure 3. The integral enthalpies of mixing in ternary Cu–Sb–Ce alloys: solid lines – modelling in Ref. [1] by Toop equation and black squares – experimental values.

The existence of the positive ternary contribution to the interaction of the components observed in studied system is in good agreement with previously made conclusion about significant reduction of component interaction of Sb with Ce due to the copper additions to the Ce–Sb alloys. As it was mentioned earlier, Sb–Ce interaction provides the main contribution to the energy of ternary alloy formation. Although the certain positive contribution of ternary interaction is observed the region of maximum interaction of the components in the liquid state in this system fully corresponds to a concentration range of existence of ternary compounds in the solid state, which indicates the same character of components interaction in the liquid and solid state in studied system.

Conclusions

The enthalpies of mixing of liquid alloys of the ternary Cu–Sb–Ce system were studied by high-temperature calorimetry along the cross-section x_{Cu} / x_{Sb} = 0.2/0.8. The composition dependences of these values were modelled using four "geometric" models and also the analytical method of Redlich-Kister-Muggianu. A comparison of the experimental data for the cross section x_{Cu} / x_{Sb} = 0.2/0.8 and simulated values of the enthalpies of mixing showed that the most suitable for describing the properties of liquid alloys of ternary Cu–Sb–Ce system is the Toop model.

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