

Modelling thermodynamic properties of binary Cu–Eu and ternary Al–Cu–Eu melts

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Model calculations of the whole set of thermodynamic properties of liquid alloys for the binary Cu–Eu and ternary Al–Cu–Eu systems have been performed. Authors used the ideal associated solution model (IAS model) for calculation of the entropies and excess Gibbs energies of mixing for these systems. The binaries were given as the Redlich-Kister polynomials. The thermodynamic properties for the ternary system are described using the Redlich-Kister-Muggianu formalism. A comparison of the surfaces of excess Gibbs energy and entropy of mixing for liquid Al–Cu–Eu alloys at 1350 K demonstrates that the ordering related to the formation of rather strong associates in the Al–Eu system significantly affects the concentration dependence of the excess Gibbs energy of mixing in the liquid phase at this temperature.

Introduction

The thermodynamic properties of liquid aluminium alloys with transition and the rare-earth metals are widely studied since the data on thermodynamics of liquid phase are important for the thermodynamic description of phase diagrams of the corresponding systems. Information on phase diagrams is important both for materials science researches and for monitoring and controlling the processes of alloys production. Additives of lanthanides, including europium, to aluminium and its alloys with copper and other transition metals improve their mechanical and electrical as well as give rise to interesting magnetic properties [1–3]. At

the same time, liquid alloys containing europium remain the least studied ones among the lanthanide alloys and require further systematic investigation.

Previously, we have experimentally investigated the enthalpies of mixing of liquid alloys of binary Cu–Eu and ternary Al–Cu–Eu systems at 1300–1450 K [4]; we also have obtained an expression for calculating the enthalpies for the ternary system in the whole concentration range using the Redlich-Kister-Muggianu method and taking into account the term of the specific ternary interaction determined from the experimental data.

However, there is no information on other thermodynamic properties of these systems. Therefore, to obtain complete thermodynamic information, which is necessary for further materials research, we have to assess component activities, Gibbs energies and entropies of mixing of the components of liquid alloys for the constituent Al–Cu (Eu), Cu–Eu binary systems and for the ternary Al–Cu–Eu system in the entire concentration range.

In Ref. [4], the current state of research for each constituent binary system is discussed in detail. Therefore, we briefly present the available thermodynamic data for the binary boundary and for the ternary Al–Cu–Eu systems which are necessary for our further consideration.

For the Al–Cu liquid alloys significant negative values of both the enthalpy of mixing and the Gibbs energy were observed: $\Delta_m H^{\min} = -17.4 \text{ kJ}\cdot\text{mol}^{-1}$ [5] and $\Delta_m G^{\min} = -21.75 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{\text{Al}} = 0.4$ and $T = 1450 \text{ K}$ [6]. The enthalpies of mixing in the liquid Cu–Eu alloys show small exothermic effects ($\Delta_m H^{\min} = -4.1 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{\text{Cu}} = 0.70$ and 1300 K [4]). Information on other thermodynamic functions of melts of this system is currently absent in the literature.

The enthalpies of mixing for the liquid Al–Eu alloys at 1573 K are rather significant exothermic values: $\Delta_m H^{\min} = -23 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{\text{Eu}} = 0.4$ according to the Ref. [7], and the excess mixing entropies ($\Delta_m S^{\text{ex}}$) calculated in [7] by ideal associated solution (IAS) model are

negative, the minimum value of about $-9 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$ is observed at $x_{\text{Eu}} = 0.39$.

The enthalpies of mixing for the liquid Al–Cu–Eu ternary alloys [4] are exothermic with the minimal $\Delta_m H$ value of about $-23.00 \text{ kJ}\cdot\text{mol}^{-1}$ observed in the region of $\text{Al}_{0.6}\text{Eu}_{0.4}$ composition of the binary Al–Eu system.

Phase diagrams of all boundary systems are characterized by a significant number of intermetallic compounds [8] which indicates a significant chemical interaction between components. Regarding the ternary Al–Cu–Eu system, there is no information on ternary compounds and phase equilibria in this system.

Modelling procedure

To obtain the thermodynamic properties of liquid melts of binary Cu–Eu and ternary Al–Cu–Eu systems we have used the Miedema method [9–11], the IAS model [12, 13], the "surrounded" atom (SA) model [14, 15], and the regular solution model with the Redlich-Kister polynomials for binaries and the Redlich-Kister-Muggianu polynomials [16] for the ternary system.

The formalism applied in our work can be briefly presented in such a way: i) calculation of enthalpies of mixing of Cu–Eu melts using the SA model; ii) calculation of formation enthalpies of the binary intermetallic compounds of the Cu–Eu system using the Miedema model, iii) determination of component activities, Gibbs energies and entropies of mixing of these liquid alloys using the IAS model; and, finally, iv)

modelling the Gibbs energies and excess entropies of mixing in the Al–Cu–Eu melts at 1350 K in the whole concentration interval using the Redlich-Kister-Muggianu method.

Miedema method. The formula for calculating the enthalpies of formation of ordered alloys by this method can be presented according to [11] as follows (Eq. 1):

$$(\Delta H_{AB})_{\text{order}} = \Delta H_{AB} \times \left[1 + 8 \left(\frac{\Delta H_{AB}}{f_B^A \left\{ x_A V_A^3 [1 + \mu_A x_B (\Phi_A - \Phi_B)] + x_B V_B^3 [1 + \mu_B x_A (\Phi_B - \Phi_A)] \right\}} \right)^2 \right]$$

where x_A , x_B are the mole fractions of the components A and B; f_B^A reflects the degree to which an atomic cell A is in contact with dissimilar atomic cell B on average; ΔH_{AB} is the mixing enthalpy; V is mole volumes of atoms A and B; Φ is the electron negativity of atoms A and B; μ is an empirical parameter evaluated and reported by Miedema [10].

IAS Model. This model explains the negative deviations from the ideal behaviour of the thermodynamic properties of melts by a noticeable interaction of components and, as a result, the formation of associates from unlike atoms. The A–B liquid alloy is considered as a mixture of monomers A_1 , B_1 and associates $A_i B_j$, which they form. The concentrations of associates and monomers are related by the equilibrium constant of the formation of the corresponding associate. According to MIAS, the activities of the components are considered to be equal to the concentrations of monomers. The

parameters of the IAS model are the number and composition of the associates and the enthalpies and entropies of their formation. At the beginning of the simulation, the set of the associate compositions is determined as well as the initial values of the enthalpies of their formation. As a rule, one can choose the set of the associates taking into account the phase diagram of the corresponding system and general trends of concentration dependences of thermodynamic properties.

Using the formalism of the IAS model, one can obtain a system of nonlinear equations, where the unknown parameters are the enthalpies and entropies of associates formation, as well as molar fractions of associates and monomers. These parameters are retrieved using an iterative interpolation procedure of the experimental data. The numerical criterion of the reliability of the description is the minimal value of the sum of the squares of the discrepancies between the model and experimental values of ΔH calculated according to Eq. (2) [12, 13]:

$$\Delta H = \frac{\sum_{n=1}^N \Delta H_n x_n}{1 + \sum_{n=1}^N (i_n + j_n - 1) x_n}$$

where ΔH is the enthalpy of formation of n -th associate; x_n is molar fraction (activity) of n -th associate.

As a result, upon completion of the iterative procedure, one obtains the values of enthalpies and entropies of formation of associates (which are considered practically

independent of temperature), as well as the activities of melt components and the associates at a given temperature. MIAS is a convenient tool for approximating the thermodynamic properties of melts, extrapolating them to an unexplored region of compositions, and reasonably predicting the full set of thermodynamic mixing functions, especially when experimental data are limited or absent.

The model of the "surrounded atom" (SA). According to [14, 15], the final formula for the calculation the enthalpies of mixing of metal alloys by this method can be given as (Eq. 3):

$$\Delta H = - \frac{x\alpha \sum_1^Z C_Z^j j(2Z-j) \exp\left(j\lambda + j(2Z-j)\left[\frac{\alpha}{RT} - 1.5\sigma\right]\right)}{\sum_0^Z C_Z^j \exp\left(j\lambda + j(2Z-j)\left[\frac{\alpha}{RT} - 1.5\sigma\right]\right)} - \frac{(1-x)\beta \sum_1^Z C_Z^i i(2Z-i) \exp\left(i\lambda + i(2Z-i)\left[\frac{\beta}{RT} - 1.5\pi\right]\right)}{\sum_1^Z C_Z^i \exp\left(-i\lambda + i(2Z-i)\left[\frac{\beta}{RT} - 1.5\sigma\right]\right)}$$

where x is molar fraction of A component; C_Z^j , C_Z^i are the numbers of combinations of j from Z or of i from Z , correspondingly; Z is the number of the nearest neighbours; α , β , π , σ are parameters calculated from the experimental values of partial enthalpies and excess entropies of mixing of melts at infinite dilution; λ is Lagrange factor; T is absolute temperature in K; R is universal gas constant, J·(mol·K)⁻¹.

The original Redlich-Kister-Muggianu equation that describes corresponding thermodynamic properties ($\Delta\Phi$) of ternary systems is taken from [16] as follows (Eq. 4):

$$\Delta\Phi = x_{Al}x_{Cu} \sum_{i=0}^n {}^iL_{Al-Cu} (x_{Al} - x_{Cu})^i + x_{Cu}x_{Eu} \sum_{i=0}^n {}^iL_{Cu-Eu} (x_{Cu} - x_{Eu})^i + x_{Al}x_{Eu} \sum_{i=0}^n {}^iL_{Al-Eu} (x_{Al} - x_{Eu})^i + x_{Al}x_{Cu}x_{Eu} (x_{Al} {}^0L_{Al-Cu-Eu} + x_{Cu} {}^1L_{Al-Cu-Eu} + x_{Eu} {}^2L_{Al-Cu-Eu})$$

where ${}^iL_{Al-Cu}$, ${}^iL_{Cu-Eu}$ and ${}^iL_{Al-Eu}$ are the coefficients of the Redlich–Kister polynomial for the constituent binary systems, n is the power of this polynomial, ${}^0L_{Al-Cu-Eu}$, ${}^1L_{Al-Cu-Eu}$ and ${}^2L_{Al-Cu-Eu}$ are the ternary interaction parameters.

Results and discussion

As mentioned above, the results of the experimental study of the enthalpies of mixing of liquid Cu–Eu alloys were presented in Ref. [4]. The enthalpies of mixing in the Cu–Eu liquid alloys exhibit exothermic effects, being not very large in magnitude [4]. In [14, 15] it was shown that the concentration dependences of the thermodynamic functions of systems characterized by minor deviations from the ideal behaviour can be described by the «surrounded» atom model with a sufficient degree of accuracy. However, an attempt to describe the concentration dependence of the integral enthalpy of mixing of liquid Cu–Eu alloys by the simple SA model did not yield the satisfactory result. Therefore, taking into account the significant difference in atomic sizes of copper and europium atoms, we have performed the SA modelling replacing the molar fraction of the component by the atomic surface area fraction.

Such an approach was successfully applied previously by authors [17] for simple regular solution model. Atomic surface area fractions of the components were computed using data from [11].

Figure 1 demonstrates the calculated and experimental values of the integral enthalpy of mixing of Cu–Eu melts at 1350 K.

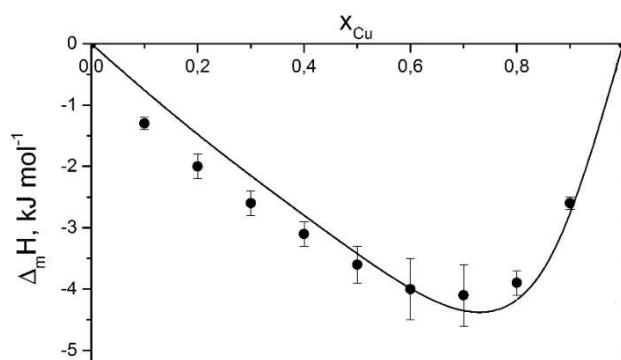


Figure 1. Enthalpies of mixing in the liquid Cu–Eu alloys at 1350 K: experimental data points (●) [4] and calculated curves (SA) (solid line).

Despite the fact that the minimum of the calculated curve of the integral enthalpy of mixing obtained by SA model ($\Delta_m H^{\min} = -4.49$ kJ·mol⁻¹ at $x_{Cu} = 0.75$) is somewhat shifted compared to the experiment, the satisfactory agreement between the experimental and calculated $\Delta_m H$ values is observed (with an average relative error of modelling of about 6%).

Although such a modification of the SA model has successfully described the concentration dependence of the enthalpy of mixing, some doubts remain about the results of the similar modelling of the entropy and,

consequently, the Gibbs energy of the Cu–Eu alloys.

Therefore, we have decided to perform further calculations and to find thermodynamic activities of the components, Gibbs energies and entropies of mixing of liquid Cu–Eu alloys according to the IAS model. According to the phase diagram data in [18] and [19], four intermetallic compounds exist in this system, namely Cu₅Eu, Cu₂Eu, CuEu, CuEu₂. The composition of these intermetallics gives a general idea of which compositions of associates should be taken into account when considering liquid alloys of this system. As noted earlier, enthalpies of formation of the corresponding associates are required as initial input. Because of the complete lack of the information on the thermodynamics of Cu–Eu alloys excluding that in Ref. [4], as a starting point of our IAS model calculations we used the values of the enthalpies of formation of the intermetallic compounds estimated by the Miedema method. We used both calculations according to Eq. (1) from Ref. [11], as well as the data obtained with the Entall Miedema Calculator [20]. The results are given in **Table 1** to compare these two methods. One can see that the results are in a good agreement, so we used the computational formalism given in [11] in subsequent calculations.

Table 1. Standart enthalpies of formation of intermetallic compounds in Cu–Eu system, $\text{kJ} \cdot (\text{mol} \cdot \text{atom})^{-1}$

Compound	$\Delta_f H$ calculated by	
	Entall Miedema Calculator [20]	Eq. (1), [11]
Cu ₅ Eu	-8.79	-9.37
Cu ₂ Eu	-14.48	-13.53
CuEu	-13.76	-13.88
CuEu ₂	-9.45	-11.35

Taking into account the Cu–Eu phase diagram, as well as the concentration dependence of the enthalpy of mixing for liquid Cu–Eu alloys [4] and using general approaches of the IAS model, we considered several possible sets of associates that can determine thermodynamic properties of liquid Cu–Eu alloys. The best agreement between the experimental and simulated values of the enthalpies of mixing was achieved for the following set of associates: Cu₃Eu and CuEu. The values of the enthalpies and entropies of formation ($\Delta_f S$) of Cu₃Eu and CuEu associates obtained as a result of the IAS calculations are given in **Table 2**.

Table 2. Enthalpies and entropies of formation of the associates in the liquid Cu–Eu alloys

Associate	$\Delta_f H$, $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f S$, $\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$
CuEu	-37.3	-29.6
Cu ₃ Eu	-41.2	-19.5

The concentration dependences of the activities of the pure components (a_i) and corresponding associates ($a_{\text{Cu}_x\text{Eu}_{1-x}}$) of the melts of the studied system calculated by MIAS are shown in **Figure 2**.

Figure 3 shows the comparison of the values of the integral enthalpy of mixing of the Cu–Eu melts at 1350 K calculated by MIAS with the experiment.

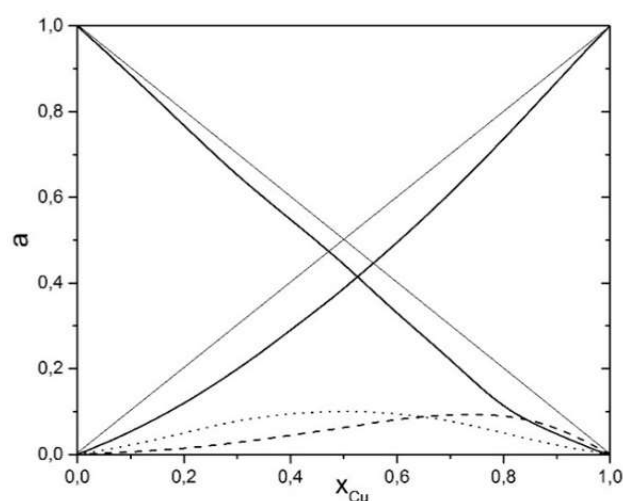


Figure 2. Concentrations of the structural units of an associated Cu–Eu solution, $T = 1350 \text{ K}$: --- a_i ; ---- $a_{\text{Cu}_3\text{Eu}}$; a_{CuEu} .

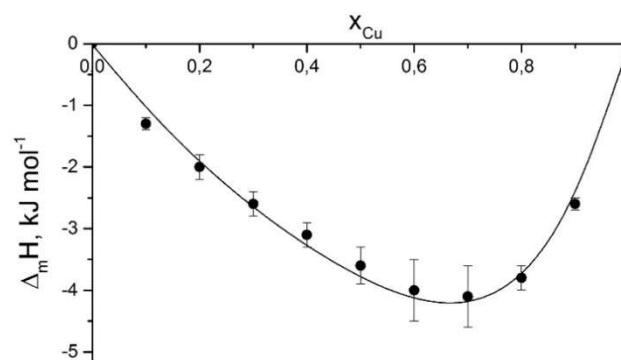


Figure 3. Enthalpies of mixing in the liquid Cu–Eu alloys at 1350 K: experimental data points (●) [4] and calculated curve by MIAS (solid line).

As one can see there is a good agreement between the experimental and MIAS values (within the measurement uncertainty limits, with an average relative error of modelling of about 2 %) which indicates a suitable choice of the set of associates as well as the validity of the assumption about the existence of proposed associates in Cu–Eu melts.

The obtained MIAS values of the activities of the components of the Cu–Eu liquid alloys were used to calculate the excess Gibbs energies of mixing of this system. The concentration dependence $\Delta_m G_{\text{Eu-Cu}}^{\text{ex}}$ at 1350 K is presented in the form of the following Redlich-Kister polynomial (Eq. 5):

$$\Delta_m G_{\text{Cu-Eu}}^{\text{ex}} = x_{\text{Cu}} x_{\text{Eu}} (-11.1 - 6.5(x_{\text{Cu}} - x_{\text{Eu}}) - 8.3(x_{\text{Cu}} - x_{\text{Eu}})^2 - 6.1(x_{\text{Cu}} - x_{\text{Eu}})^3 - 0.96(x_{\text{Cu}} - x_{\text{Eu}})^4 + 8.2(x_{\text{Cu}} - x_{\text{Eu}})^5)$$

The concentration dependence of the excess Gibbs energy of mixing in the Cu–Eu melts is asymmetric with respect to the equiatomic composition. The minimum $\Delta_m G_{\text{Eu-Cu}}^{\text{ex}}$ is equal to ($-3.23 \text{ kJ}\cdot\text{mol}^{-1}$) and observed at $x_{\text{Cu}} = 0.7$.

As to the ternary Al–Cu–Eu system studied in [4], it is now possible to obtain complete thermodynamic dataset, in particular the values of the excess Gibbs energy of mixing for the ternary liquid alloys, using the values obtained in this work for the binary Cu–Eu system and the values from literature for the constituent binary Al–Cu and Al–Eu systems.

The parameters describing the excess Gibbs energies of mixing for boundary binary systems in the form of a set of coefficients of Redlich-Kister polynomials are given in **Table 3**. For the Al–Cu system, the data from Ref. [6] calculated at 1350 K are presented. The interaction parameters for the Al–Eu system at the same temperature we calculated according to the data in [7].

The interaction parameters shown in **Table 3** were used in the subsequent modelling of the thermodynamic properties of liquid Al–Cu–Eu alloys.

Table 3. The binary interaction parameters for the excess Gibbs energy $\Delta_m G^{\text{ex}}$ in liquid alloys of the Al–Cu, Cu–Eu and Al–Eu systems at 1350 K, $\text{kJ}\cdot\text{mol}^{-1}$

System	Interaction parameters
Al–Cu	${}^0L_{\text{Al-Cu}} = -55.3$
	${}^1L_{\text{Al-Cu}} = 22.4$
	${}^2L_{\text{Al-Cu}} = -2.2$
	${}^3L_{\text{Al-Cu}} = 0.13$
Cu–Eu	${}^0L_{\text{Cu-Eu}} = -11.1$
	${}^1L_{\text{Cu-Eu}} = -6.5$
	${}^2L_{\text{Cu-Eu}} = -8.3$
	${}^3L_{\text{Cu-Eu}} = -6.1$
	${}^4L_{\text{Cu-Eu}} = -0.96$
	${}^5L_{\text{Cu-Eu}} = 8.2$
Al–Eu	${}^0L_{\text{Al-Eu}} = -44.1$
	${}^1L_{\text{Al-Eu}} = -21.0$
	${}^2L_{\text{Al-Eu}} = -14.4$

	${}^3L_{\text{Al-Eu}} = 5.3$
	${}^4L_{\text{Al-Eu}} = 25.36$

Thus, the integral Gibbs energy of mixing of Al–Cu–Eu melts can be calculated as follows (Eq. 6):

$$\Delta_m G = RT \sum_i x_i \ln x_i + \Delta_m G_{\text{Al-Cu-Eu}}^{\text{ex}}$$

where x_i is the mole fraction of component i ($i = \text{Al, Cu and Eu}$). The first term represents the ideal mixing term of the Gibbs energy while the last term is the excess Gibbs energy which one can obtain from the three constituent binaries using Redlich–Kister polynomials and the Muggianu extrapolation method.

Gibbs energy of mixing isolines for the liquid Al–Cu–Eu alloys at 1350 K are given in **Figure 4** in the whole concentration triangle.

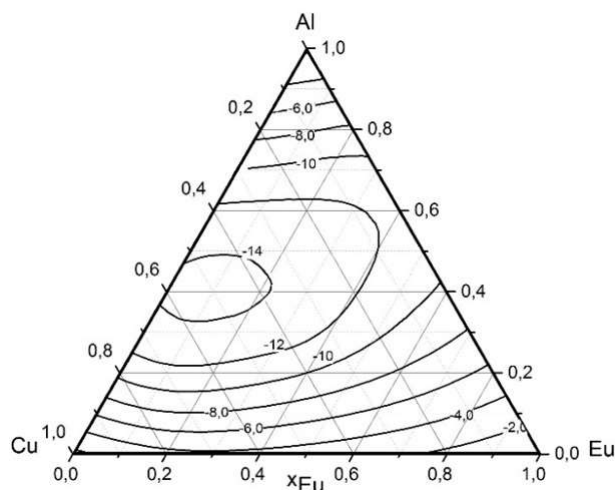


Figure 4. The excess Gibbs energy isolines in the ternary Al–Cu–Eu liquid phase at 1350 K calculated using the Redlich–Kister–Muggianu formula, $\text{kJ}\cdot\text{mol}^{-1}$

Since there are no data on the experimental determination of the Gibbs energy of mixing for the Al–Cu–Eu system, the

parameter of the specific ternary interaction cannot yet be established.

We have also calculated the values of the excess entropy of mixing of ternary melts of the Al–Cu–Eu system at 1350 K (**Figure 5**).

Obtained values of the excess entropies of mixing together with previously obtained enthalpies of mixing in the ternary Al–Cu–Eu system [4] give the possibility to assess Gibbs energies of mixing and activities of the components of liquid ternary alloys at different temperatures assuming slight temperature dependence of $\Delta_m H$ and $\Delta_m S^{\text{ex}}$ values.

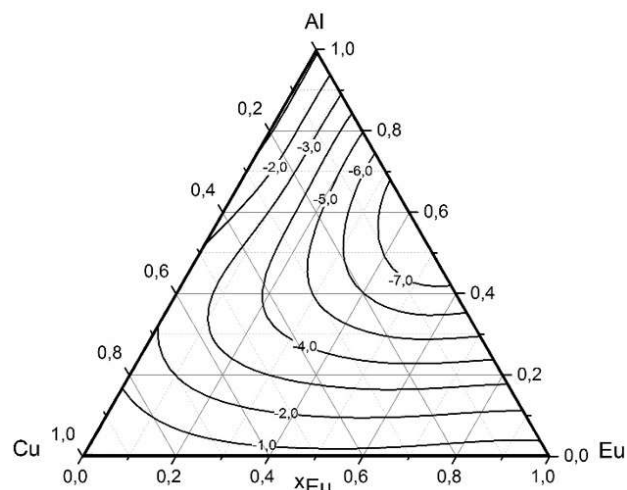


Figure 5. The excess entropy isolines in the ternary Al–Cu–Eu liquid alloys at 1350 K, $\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$

A comparison of the topology of the isolines of excess thermodynamic functions of mixing at 1350 K allows concluding that decrease in entropy connected with strong associates formation in the binary Al–Eu system has a significant effect on the concentration dependence of the excess Gibbs energy and the shape of mixing curves at this temperature.

Conclusions

For the first time, the complete set of thermodynamic functions of mixing for the Cu–Eu binary system has been simulated using the ideal associated solution model. The tendency towards the formation of associates is demonstrated, and the thermodynamic parameters of the formation of the corresponding associates are determined. The results of thermodynamic modelling of the enthalpies of mixing are in good agreement with the experimentally obtained values.

Using the thermodynamic parameters obtained in this work for the Gibbs energies of mixing of liquid Cu–Eu alloys, literature data on the Gibbs energies of the Al–Cu and Al–Eu binary systems, and the experimental values of the enthalpies of mixing obtained for this ternary system in our previous work, the full set of thermodynamic functions of mixing of the liquid phase for the Al–Cu–Eu ternary system has been simulated by the Redlich-Kister-Mugianu method.

It should be noted that in the absence of experimental information on the activities of the components in this system, taking into account the fact that their experimental determination is a laborious and expensive study, the results of the performed thermodynamic modelling can be used for further thermodynamic assessments of the Al–Cu–Eu ternary system and can be integrated into thermodynamic databases for multicomponent aluminium alloys in such

software packages as, for example, Thermo-Calc.

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