Analytic Approach to Alloys Thermodynamics: Ternary Cu-Ga-Ni system

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In this paper are presented the results of the calculation of thermodynamic properties in liquid state for ternary Cu-Ga-Ni alloys using the newest version of general solution model. Calculation was carried out in temperature interval 1473-2073 K, along 3 cross sections from corner of each metal, with ratios between two other metals 1:3, 1:1 and 3:1. Partial and integral molar thermodynamic properties in liquid phase for the Cu-Ga-Ni ternary system are determined, presented and discussed. Calculated data is compared with data available from literature and good agreement between these two sets of data was observed. Additionally, isothermal section of phase diagram at 298 K is calculated using Thermo-Calc software and presence of eleven different phases is detected. Presented thermodynamic data for the Cu-Ga-Ni alloys could be useful for the further assessment of this system and its phase diagram as well as for completing thermodynamic description of these alloys.

Keywords: *Ternary Cu-Ga-Ni system, Thermodynamics, Calculation, General solution model*

1. Introduction

Thermodynamic properties have always held an important place in the study of metallic systems. In the past, thermodynamic quantities mainly have been studied experimentally, but researchers have sought a way to develop different models that would enable calculation of the thermodynamic properties of studied systems, which would not only significantly lower experimental research expenses, but also speed up the research process. For calculation of thermodynamic properties of multicomponent systems different geometric models have been developed, such as Toop[1], Muggianu[2], general solution model[3-5] etc.

Among available models, general solution model developed by Chou[3,4] has been proved to be most reasonable one in all aspects. This geometric model has been successfully used by different researchers for calculation of thermodynamic properties[6–10], construction and/or evaluation of phase diagrams[11–13], computing physicochemical properties[14–16] and solving technical problems[17–20]. In 2010 Zhang and Chou[5] published new, improved version of general solution model for calculation of thermodynamic properties of liquid mixtures, based on binary Redlich–Kister type parameters and this version has been used to predict thermodynamic properties of metallic systems in liquid phase[21].

Ternary Cu-Ga-Ni system has great technical and theoretical significance because:

- copper, gallium and nickel are elements included in developing different high temperature lead free solder materials[22],
- presence of Cu-Ga-Ni alloy is detected during study of Pb-free joints produced by using a diffusion soldering method[23],

- this type of alloys are used to develop new microelectronic interconnect materials[24] and
- these alloys are basis for forming different multicomponent shape memory alloys like Ni-Cu-Mn-Ga[25,26] and Ni-Mn-Fe-Cu-Ga[27].

Despite all of these facts, there is considerable lack of available data on thermodynamic properties of ternary Cu-Ga-Ni alloys in literature (there is just one recent paper dealing with this topic[28]), although that type of data is essential in further research of phase diagram and understanding of complex processes which occur during bonding and soldering with gallium based materials. Accordingly, the aim of this work is to conduct thermodynamic analysis of ternary Cu-Ga-Ni system using general solution model.

2. Theoretical fundamentals

Among many available methods for calculation thermodynamic properties of ternary system based on information about constitutive binary systems, Chou's general solution model (GSM)[3] has been proved to be most reasonable one in all aspects, overcoming inherent defects of the traditional symmetrical and asymmetrical geometric models. This model breaks down boundaries between symmetrical and asymmetrical systems and generalizes various kinds of situations; also accuracy of calculation has been proven in practical examples[29-32].

Recently, a new, improved version of general solution model based on Redlich-Kister parameters was presented by Zhang and Chou[5]. Since older version of GSM involved a series of integration processes which significantly complicated calculation and considering that a large number of real systems

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can be approximately fit through a Redlich–Kister polynomial, a new formalism, based on the binary Redlich–Kister type parameters, was presented.

Therefore, this new GSM version is utilized for calculating the thermodynamic properties of Cu-Ga-Ni ternary system.

The basic equation of general solution model for ternary system is:

$$\Delta G^E = x_1 x_2 \sum_{i=0}^{n} L_{12}^i (x_1 - x_2 + (2\xi_{12} - 1)x_3)^i +$$

$$x_2 x_3 \sum_{i=0}^{n} L_{23}^i (x_2 - x_3 + (2\xi_{23} - 1)x_1)^i +$$

$$x_3 x_1 \sum_{i=0}^{n} L_{31}^i (x_3 - x_1 + (2\xi_{31} - 1)x_2)^i \quad (1)$$

where L_{ij}^v are the Redlich-Kister parameters for the binary system ij, independent from composition and only relying on temperature; ΔG^E is integral molar excess Gibbs energy for ternary system and x_i is mole fraction of the component i.

Similarity coefficient ξ is defined as:

$$\xi_{12} = \eta_I / (\eta_I + \eta_{II})$$
$$\xi_{23} = \eta_{II} / (\eta_{II} + \eta_{III}) \quad (2)$$
$$\xi_{31} = \eta_{III} / (\eta_I + \eta_{II})$$

And the deviation sum of squares can be calculated using:

$$\eta_I = \sum_{i=0}^{n} \frac{1}{2(2i+1)(2i+3)(2i+5)} (L_{12}^i - L_{13}^i)^2 +$$

$$\sum_{j=0}^{n} \sum_{k>j}^{n} \frac{1}{(j+k+1)(j+k+3)(j+k+5)} (L_{12}^j - L_{13}^j)(L_{12}^k - L_{13}^k)$$

$$\eta_{II} = \sum_{i=0}^{n} \frac{1}{2(2i+1)(2i+3)(2i+5)} (L_{21}^i - L_{23}^i)^2 +$$

$$\sum_{j=0}^{n} \sum_{k>j}^{n} \frac{1}{(j+k+1)(j+k+3)(j+k+5)} (L_{21}^j - L_{23}^j)(L_{21}^k - L_{23}^k) \quad (3)$$

$$\eta_{III} = \sum_{i=0}^{n} \frac{1}{2(2i+1)(2i+3)(2i+5)} (L_{31}^i - L_{32}^i)^2 +$$

$$\sum_{j=0}^{n} \sum_{k>j}^{n} \frac{1}{(j+k+1)(j+k+3)(j+k+5)} (L_{31}^j - L_{32}^j)(L_{31}^k - L_{32}^k)$$

where for all L_{ij} parameters is valid relation $L_{ij}^k = (-1)^k L_{ji}^k$.

In all equations as given, L_{ij}^x ($x=i, j$ or k) are the Redlich-Kister parameters for the binary system ij, independent from composition and only relying on temperature; ΔG^E is integral molar excess Gibbs energy for ternary system and x_i is mole fraction of the component i. Number n is equal to maximum number of components in system (in this case n=3) and coefficients i, j and k are always numbers between zero and n.

Partial thermodynamic quantities are calculated according to the equations:

$$G_i^E = G^E + (1 - x_i)(\partial G^E / \partial x_i) = RT \ln \gamma_i \quad (4)$$

and

$$a_i = x_i \gamma_i \quad (5)$$

In above mentioned equations G_i^E is partial molar excess Gibbs energy of component i, a_i is activity of component i, γ_i is activity coefficient of component i, T is temperature, R is gas constant (value 8.314 JK^{-1}mol^{-1}), G^E is Gibbs energy for whole system, dependent on composition.

3. Results and discussion

Basic thermodynamic data on the constituent binary subsystems Cu-Ga, Ga-Ni and Cu-Ni, needed for calculation of thermodynamic properties in the investigated Cu-Ga-Ni system, were taken from available literature data[33-35], and presented in the form of Redlich-Kister parameters in Table 1.

Thermodynamic properties of ternary Cu-Ga-Ni system has been investigated in 9 sections (Figure 1), taken from Cu, Ga and Ni corner, respectively, with ratios 1:3 and 3:1, and with molar content of 0-0.9 for the third component.

The calculated integral molar Gibbs excess energies (ΔG^E) and activities of the investigated system Cu-Ga-Ni, along selected sections and at given temperatures, are presented in Figures 2 - 4. All thermodynamic properties calculated in this work are related to the liquid phase.

Calculation of thermodynamic properties for ternary system Cu-Ga-Ni was performed using the general solution model. Excess integral Gibbs energy values for investigated sections from nickel corner are negative, with minimum values up to -14 kJ/mol, for gallium corner those values are between 4 kJ/mol and -14 kJ/mol, while for the investigated section from the corner of copper Gibbs energy is within 0 kJ/mol to -18 kJ/mol.

For cross section Ga:Ni=1:3 copper activity shows positive deviation from Rault's law which with increase of copper content in alloy slowly decreases and for $x_{Cu} > 0.6$ coincides with the ideal state line. Other investigated cross sections from copper corner shows variable character of deviation from Rault's law, in section Ga:Ni=1:1 copper activity has positive deviation up to $x_{Cu} = 0.4$, and for Ga:Ni=3:1 border copper content at which deviation changing from positive to negative occurs is $x_{Cu} = 0.2$.

For gallium activity is characteristic pronounced negative deviation from Rault's law for all investigated sections, but for alloys with high gallium content ($x_{Ga} > 0.9$) deviation coincides with the line of ideal state and even becomes slightly positive.

Nickel activity shows a negative deviation from the Rault's law for Cu:Ga=1:3 and Cu:Ga=1:1 sections, up to $x_{Ni} > 0.8$, while for section Cu:Ga=3:1 nickel activities positively derivate from ideal state line.

Because of notable absence of experimental data related to thermodynamics of this system in literature, data obtained by calculation are compared with data obtained using Redlich-Kister-Muggianu (RKM) model[28] (Figure 5). Compared values show very good agreement.

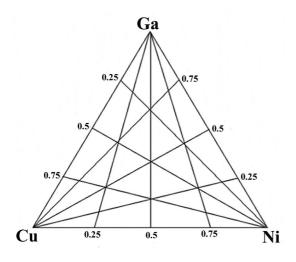| System ij	L^o_{ij} (T)	L^1_{ij} (T)	L^2_{ij} (T)
Cu-Ga [33]	-58110.5+154.5439*T-18.3753*T*lnT	-33884.7+1.9151*T	-11256.9
Ga-Ni [34]	-122488.59+35.72*T	-29685+14*T	-30751.9+22.1*T
Cu-Ni [35]	12048.61+1.29893*T	-1861.61+0.94201*T	0

Figure 1: Schematic diagram of the investigated concentration regions in ternary Cu-Ga-Ni system.

Additionally, isothermal section of ternary Cu-Ga-Ni phase diagram at 298K (Figure 6) is calculated using Thermo-Calc software[36,37] developed by Thermo-Calc Software AB, based on CALPHAD[38,39] approach to calculation of phase diagrams. Thermo-Calc is a powerful and flexible software package based upon a powerful Gibbs Energy Minimizer and developed for performing various kinds of thermodynamic and phase diagram calculations. Calculations are based on thermodynamic data which is supplied in a database SSOL5. Wide selections of high-quality databases for various purposes that include many different materials are available and data included in databases is provided by experts through critical assessment and systematic evaluation of experimental and theoretical data, following the well-established CALPHAD technique.

Eleven different phases can be identified in isothermal section of ternary Cu-Ga-Ni system (Figure 6) and five of
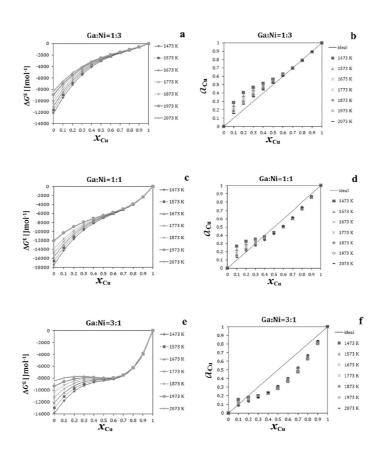

Figure 2: Results of thermodynamic calculation according to GSM in temperature range of 1473-2073K for cross-sections from copper corner: a) integral molar excess Gibbs energy (ΔG^E) and b) copper activity for cross section Ga:Ni=1:3; c) ΔG^E and d) copper activity for cross section Ga:Ni=1:1; e) ΔG^E and f) copper activity for cross section Ga:Ni=3:1.
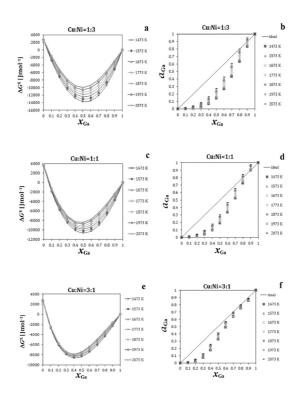
Figure 3: Results of thermodynamic calculation according to GSM in temperature range of 1473-2073K for cross-sections from gallium corner: a) integral molar excess Gibbs energy (ΔG^E) and b) gallium activity for cross section Cu:Ni=1:3; c) ΔG^E and d) gallium activity for cross section Cu:Ni=1:1; e) ΔG^E and f) gallium activity for cross section Cu:Ni=3:1.
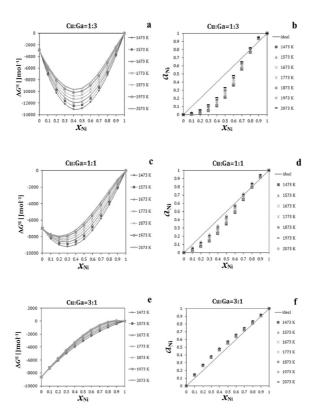

Figure 4: Results of thermodynamic calculation according to GSM in temperature range of 1473-2073K for cross-sections from nickel corner: a) integral molar excess Gibbs energy (ΔG^E) and b) nickel activity for cross section Cu:Ga=1:3; c) ΔG^E and d) nickel activity for cross section Cu:Ga=1:1; e) ΔG^E and f) nickel activity for cross section Cu:Ga=3:1.
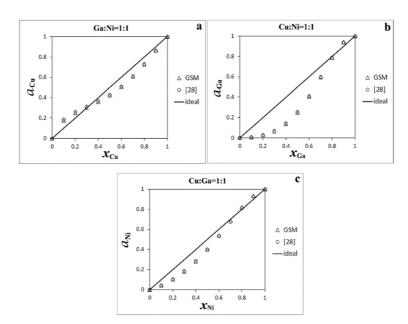
Figure 5: Dependence of copper (a), gallium (b) and nickel (c) activities from composition at 1773 K, predicted according to GSM, compared with literature data[28].
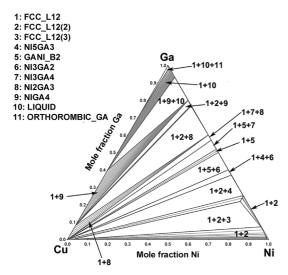

Figure 6: Calculated isothermal section of ternary Cu-Ga-Ni phase diagram at 298K (obtained using Thermocalc 3.0).

them are intermetallic compounds present in phase diagram of binary Ga-Ni binary system[40]. Phase 1 is consisted from nickel with some gallium and copper (due to mutual solubility), phase 2 from copper with little amount of nickel, and phase 3 is pure gallium. It is not surprising to detect liquid phase at room temperature, considering that melting temperature of gallium is just 29.78 °C (302.93 K)[41].

4. Conclusion

Calculation of thermodynamic properties of the Cu-Ga-Ni system has been conducted using general solution model, in temperature interval from 1473 to 2073 K.

Based on this, excess molar Gibbs energies and activity of all components were calculated. Calculated excess integral Gibbs energy for investigated sections is mostly negative, with values in range from 4 kJ/mol to -18 kJ/mol. Activity of nickel and gallium shows negative deviation from Rault's law for all investigated sections, but for alloys with high content of nickel or gallium, deviation becomes slightly positive. Deviation of copper activity values from Rault's law depends from share of two other metals, and for alloy which contain same amount of nickel and gallium (Ga:Ni=1:1) copper activity negatively deviates from ideal conditions after $x_{Cu} = 0.4$.

Isothermal section of ternary Cu-Ga-Ni phase diagram at 298K is calculated using Thermo-Calc software, based on thermodynamic data which is supplied in a database SSOL5 and presence of eleven different phases is detected.

Presented thermodynamic data for the Cu-Ga-Ni alloys could be useful for the further assessment of this system and its phase diagram as well as for completing thermodynamic description of these alloys.

5. Acknowledgement

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