

# Co–Sn–Zn liquid phase thermodynamic properties investigation performed by different geometric models and by CALPHAD method

## Raziskava termodinamičnih lastnosti tekoče faze Co–Sn–Zn z različnimi geometričnimi modeli in CALPAD-metodo

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### Abstract

Predictions for the liquid Co–Sn–Zn alloys thermodynamic properties (molar excess Gibbs energy) were presented in this paper. The calculations were performed in the temperature range 1 000–2 000 K. Geometric models were used and the respective calculated molar excess Gibbs energies were compared to Calphad method assessments. The concentration dependences of the liquid phase thermodynamic properties along vertical sections with Sn/Zn ratios of 1 : 5, 1 : 1 and 5 : 1 were estimated. Ternary interaction parameters ( $L^0$ ,  $L^1$  and  $L^2$ ) of the liquid phase were determined using General solution (geometric) models from thermodynamic data of the binary end-systems (Co–Sn, Co–Zn, Sn–Zn).

**Key words:** sgeneral solution model, ternary interaction parameters, ternary systems, Calphad method

### Izvleček

V članku je predstavljena napoved termodinamičnih lastnosti (molske prebitne proste Gibbsove energije) tekočih zlitin Co–Sn–Zn. Izračuni so bili izvedeni v temperaturnem območju 1 000–2 000 K. Uporabljeni so bili geometrijski modeli. Odgovarjajoče izračunane molske prebitne proste Gibbsove energije so bile primerjane z oceno po Calpad-metodi. Termodinamične lastnosti tekoče faze v odvisnosti od koncentracije so bile določene za vertikalne prereze in razmerja Sn/Zn 1 : 5, 1 : 1 ter 5 : 1. Ternarni interakcijski koeficienti ( $L^0$ ,  $L^1$  and  $L^2$ ) so bili določeni z uporabo modela posplošene rešitve iz končnih binarnih sistemov (Co–Sn, Co–Zn, Sn–Zn).

**Ključne besede:** model posplošene rešitve, ternarni interakcijski parametri, ternarni sistem, Calpad-metoda

## Introduction

The Co–Sn–Zn system is interesting as potential materials using in industrial application like alloys applicable as lead free materials<sup>[1]</sup>. These materials are expected to be designed on the basis of systems containing low-melting elements like Sn and Zn. It is well known that the classical lead-tin based alloys represent a serious health and environmental risk. Pb-containing alloys use recently<sup>[2]</sup> but the replacement of the whole variety of Sn–Pb based materials turned out to be a very difficult task<sup>[3]</sup>.

The binary end-systems Co–Sn<sup>[4]</sup> and Co–Zn<sup>[5]</sup> have been intensively studied. They exhibit a large numbers of intermetallic phases. The binary system Sn–Zn represents a simple eutectic phase diagram<sup>[6]</sup>.

This ternary system is included in the thermodynamic database developed by the European concerted action Solders<sup>[6]</sup> and reliable thermodynamic optimization is available. The task of the present study is to apply different ways to assess the thermochemical properties of the ternary melt Co–Sn–Zn.

## Theoretical fundamentals of the assessments

The so-called “geometric models” give the possibility to predict the thermodynamic properties of a ternary phase (in this case – liquid) using the data for the respective binary end systems. In this work, assessments were done using the most common classic geometric models of Kohler<sup>[7]</sup>, Toop<sup>[8]</sup>, and Hillert<sup>[9]</sup> as well as the general solution model (GSM) developed by Chou<sup>[10, 11]</sup>.

Hillert<sup>[9]</sup> classified the geometric models as symmetrical (e.g.<sup>[7]</sup>) and asymmetrical (e.g.<sup>[8, 9]</sup>). Such a universal approach was developed recently by Chou<sup>[10, 11]</sup> and was successfully applied to a variety of cases<sup>[12, 13, 14]</sup>. Nevertheless, a brief description of the techniques used is described below.

The molar excess Gibbs energy ( $\Delta G^E$ , J mol<sup>-1</sup>) of the ternary liquid phase was chosen as parameter which values have to be calculated by various models and compared. This function describes the contribution of the non-ideal

mixing to the thermodynamic properties of a solution phase. The molar excess Gibbs energies values of every binary end-system are necessary as starting points and calculated by means of Thermo-Calc software package<sup>[15]</sup>. The composition dependence of the binary Gibbs molar excess energies ( $\Delta G_{ij}^E$ ) was given by Redlich-Kister formalism<sup>[16]</sup>.

The Gibbs molar excess energy of a ternary phase ( $\Delta G_{123}^E$ ), consisting of the elements 1, 2 and 3, was given by the expression:

$$\Delta G_{123}^E = x_1 x_2 \Delta G_{12}^E + x_2 x_3 \Delta G_{23}^E + x_3 x_1 \Delta G_{31}^E + \Delta G_{123}^E \quad (1)$$

where  $\Delta G_{123}^E$  is the contribution of the ternary non-ideal mixing. In the simplest case of a regular ternary solution it may be assessed as:

$$\Delta G_{123}^E = x_1 x_2 x_3 L_{123} \quad (2)$$

where  $L_{123}$  is a ternary interaction parameter that might be temperature and concentration dependent.

The most essential equations, associated to the geometrical models<sup>[7, 8, 9]</sup> were used for calculations.

Equation (3) can be used as an introduction of the General solution model (GSM) of Chou<sup>[10, 11]</sup>:

$$\Delta G_{123}^E = x_1 x_2 x_3 f_{123} \quad (3)$$

Here  $f_{123}$  is the ternary interaction coefficient, related to the Redlich-Kister ternary interaction parameters  $L_{ijk}$  ( $f_{123} = x_1 \times L_{123}^0 + x_2 \times L_{123}^1 + x_3 \times L_{123}^2$ ).

$\xi_{ij}$  are “similarity coefficients”, that were defined by the term  $\eta_i$  called “deviation sum of squares. Equation (4) presented model of Chou.

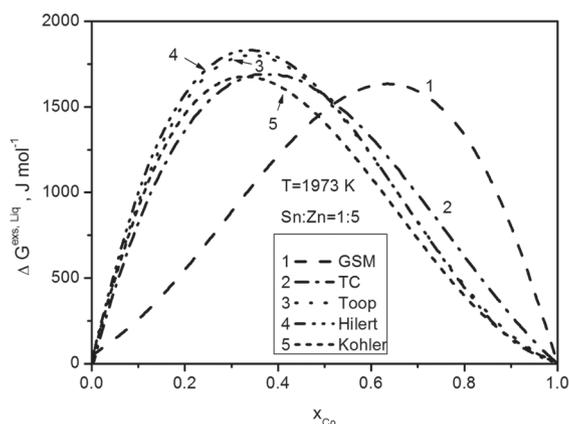
$$f_{123} = (2\xi_{12} - 1)\{L_{12}^2((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + L_{12}^1\} + (2\xi_{23} - 1)\{L_{23}^2((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + L_{23}^1\} + (2\xi_{31} - 1)\{L_{31}^2((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + L_{31}^1\} \quad (4)$$

Basic thermodynamic information on the binary subsystems, needed for the assessment, was taken from<sup>[6]</sup>. The optimized Redlich-Kister parameters of each system are presented in

Table 1. They were used for the calculation of the molar excess Gibbs energies of the binary end-systems liquid phases. In this work: Co is represented as component 1, Sn - component 2 and Zn - component 3.

## Results and discussion

Calculations of the coefficients  $f_{123}$  were done along three sections of the Co–Sn–Zn system with molar Sn : Zn ratios 1 : 5, 1 : 1 and 5 : 1 in the interval 1 000–2 000 K at amount fractions of cobalt equal to 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1. In such a way a large amount of data was obtained and used thereafter to derive the parameters  $L_{ijk}$ . The results for the ternary parameters are shown in Table 2. Comparative reviews of the molar Gibbs excess energies ( $\Delta G^E$ , J mol<sup>-1</sup>) assessed at 1 973 K by using different geometric models (GSM<sup>[10, 11]</sup>, Toop<sup>[8]</sup>, Hilert<sup>[9]</sup> and Kohler<sup>[7]</sup>) and by the Calphad method (binary parameters only)<sup>[6]</sup> are shown in Figures 1–3. Figure 1 shows calcula-

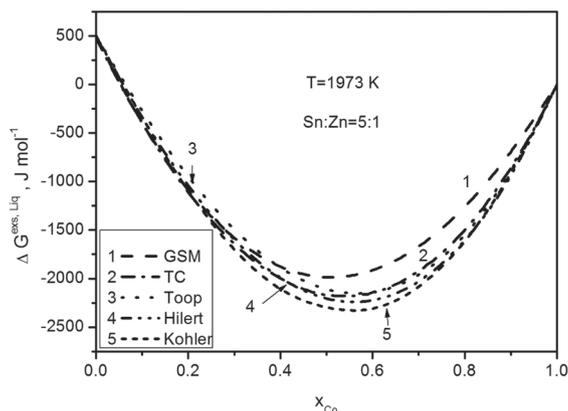


**Figure 1:** Calculated molar Gibbs excess energies ( $\Delta G^E$ /(J mol<sup>-1</sup>)) of the liquid phase, along a section with constant molar Sn/Zn ratio equal to 1 : 5 at 1 973 K.

**Table 1:** Optimized parameters ( $L_{ij}^0$ ,  $L_{ij}^1$ ,  $L_{ij}^2$ ) for the liquid binary phases of the Co–Sn<sup>[4]</sup>, Co–Zn<sup>[5]</sup> and Sn–Zn<sup>[6]</sup> systems used in the present work;  $T$  – temperature, K

| System, $i$ - $j$ | $L_{ij}^0(T)$ /(J mol <sup>-1</sup> )                    | $L_{ij}^1(T)$ /(J mol <sup>-1</sup> )                  | $L_{ij}^2(T)$ /(J mol <sup>-1</sup> ) |
|-------------------|--|--|---------------------------------------|
| Co–Sn             | $-113\,890 + 568.4038 * T$<br>$-68.169 * T * LN(T)$      | $-56\,193.26 + 283.7657 * T$<br>$-33.6875 * T * LN(T)$ | 0                                     |
| Co–Zn             | $-15\,017 + 12.735 * T$                                  | $+51\,758 - 29.752 * T$                                | 0                                     |
| Sn–Zn             | $+19\,314.64 - 75.89949 * T$<br>$+ 8.751396 * T * LN(T)$ | $-5\,696.28 + 4.20198 * T$                             | $+1\,037.22 + 0.98362 * T$            |

tions for the molar ratio Sn : Zn = 1 : 5. In this figure all curves exhibit positive values for the Gibbs excess energies. These positive deviations can be related to a possible miscibility gap in liquid phase at Co–Zn side in the ternary diagram. In this case, the values assessed by symmetrical models<sup>[7]</sup> were quite similar and were accompanied by the Calphad-type calculated quantities. The same conclusion is valid for the values calculated by both asymmetrical methods<sup>[8, 9]</sup>. The GSM-assessed molar Gibbs excess energies deviate from all others.

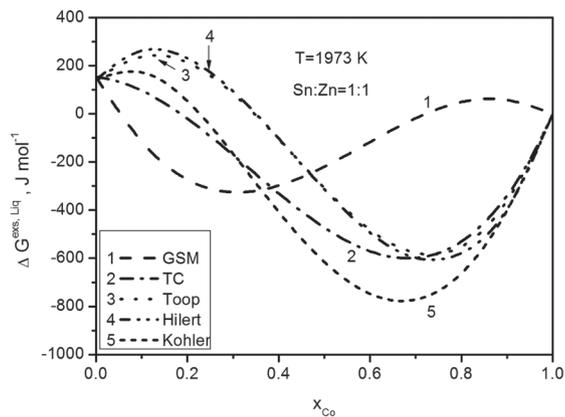


**Figure 2:** Calculated molar Gibbs excess energies ( $\Delta G^E$ , J mol<sup>-1</sup>) of the liquid phase, along a section with constant molar Sn : Zn ratio equal to 5 : 1 at 1 973 K.

Most of the assessments predict (in general) negative  $\Delta G^E$  with a minimum in the composition interval of 0.5–0.55 amount fraction cobalt is shown in Figure 2. The calculations based on the GSM<sup>[10, 11]</sup> deviate from all others predicting a minimum at around 0.4–0.5 amount fractions cobalt.

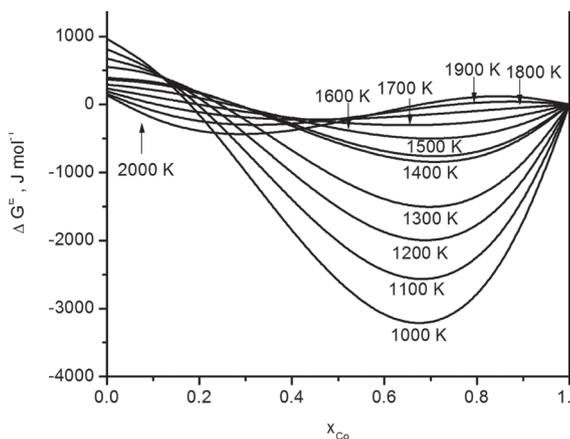
In Figure 3 the molar Gibbs excess energies along the section with Sn:Zn molar ratio equal to 1 : 1 all curves are with sign-changing values. Small negative values, up to around  $-700$  J mol<sup>-1</sup>

in curves 2–5 are calculated. Sign-changing positive values are reached to  $300 \text{ J mol}^{-1}$ . Along this section a maximum in the composition interval of 0.6–0.75 amount fractions cobalt are predicted, except by the assessment done using the GSM model (Figure 3, curve 1). The latter is sign-changing as well but deviates symmetrically from each other calculation. The reason for this discrepancy could not be found. These deviations in GSM model is observed in another ternary system - Ni-Bi-Zn<sup>[17]</sup>.



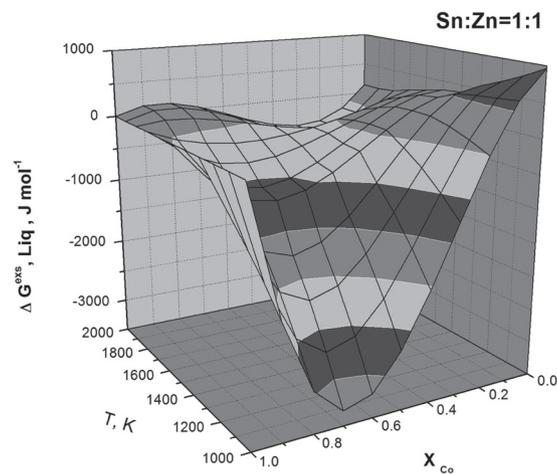
**Figure 3:** Calculated molar Gibbs excess energies ( $\Delta G^E$ ,  $\text{J mol}^{-1}$ ) of the liquid phase, along a section with constant molar Sn : Zn ratio equal to 1 : 1 at 1973 K.

Figure 4 presented molar Gibbs excess energies of the liquid phase in broad temperature range 1 000–2 000 K used GSM model of Chou<sup>[10, 11]</sup>. The calculations exhibit negative Gibbs energies at low temperature. But at temperatures of 1 400 K to 2 000 K Gibbs energies are shown mix of negative and positive values.

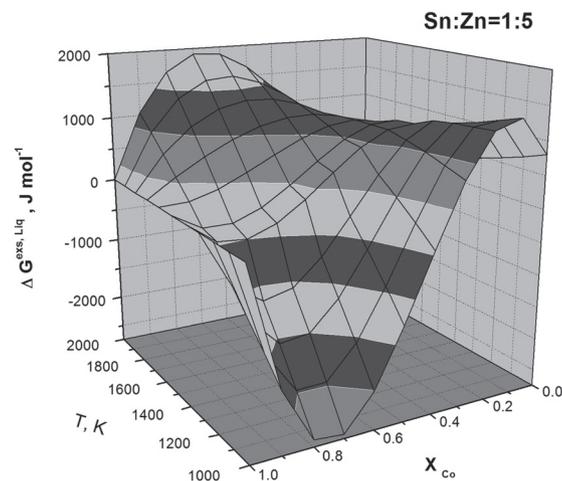


**Figure 4:** Calculated molar Gibbs excess energies ( $\Delta G^E$ ,  $\text{J mol}^{-1}$ ) of the liquid phase in all temperature range according to GSM models.

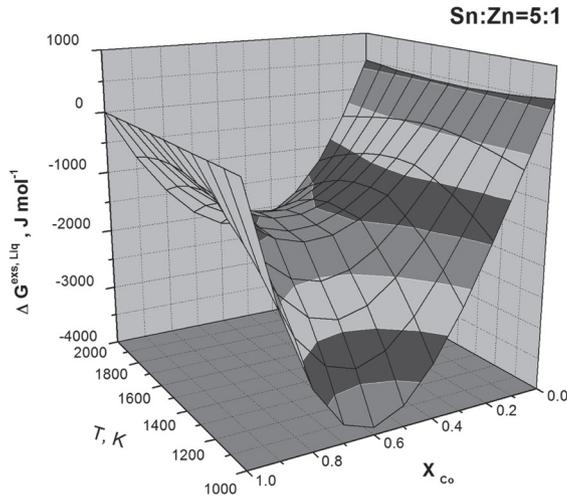
The values of the ternary molar Gibbs excess energies ( $\Delta G^E$ ) in the temperature range 1 000–2 000 K and along sections with Sn : Zn molar ratios equal to 1 : 5, 1 : 1 and 5 : 1, obtained from GSM are shown in Figures 5–7, respectively. These figures give a graphical view of the surfaces calculated at different temperature region (from 1 000 to 2 000 K) constituted by the values of the liquid phase molar Gibbs excess energies and amount fractions Co. Typically, there are maximums (positive  $\Delta G^E$  values) in the Co-rich regions and especially in Co–Zn rich solutions. From another side relatively small negative  $\Delta G^E$  values are predicted for the Co–Sn rich compositions.



**Figure 5:** Ternary molar Gibbs excess energies calculated along the selected sections and at the retained temperatures.

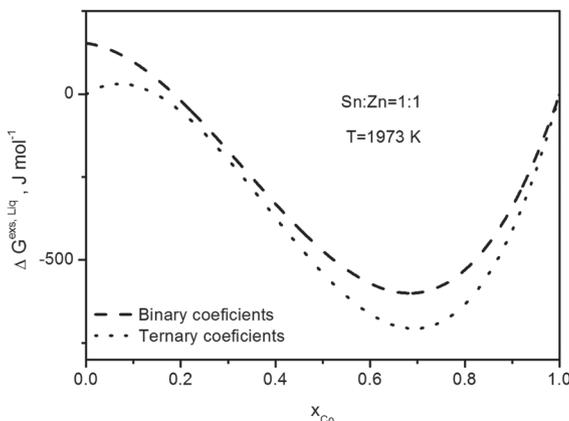


**Figure 6:** Ternary molar Gibbs excess energies calculated along the selected sections and at the retained temperatures.

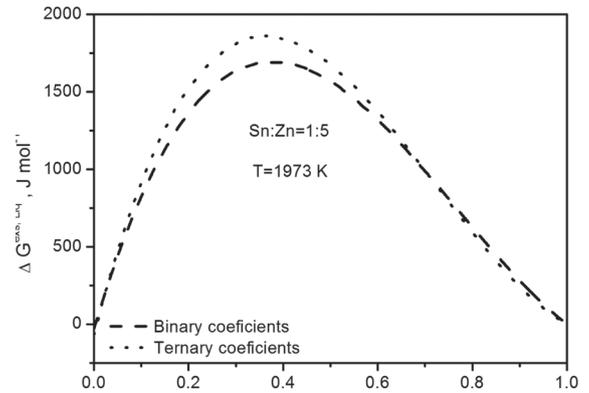


**Figure 7:** Ternary molar Gibbs excess energies calculated along the selected sections and at the retained temperatures.

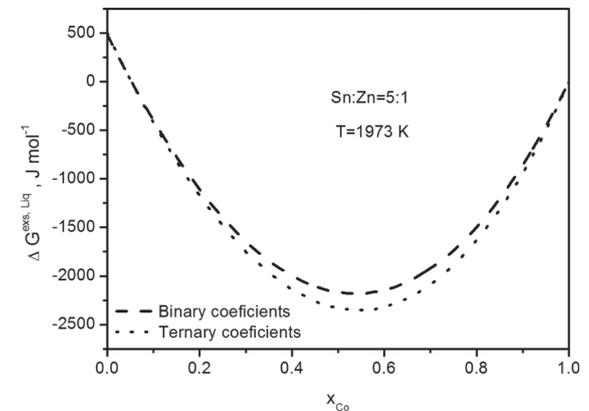
Figures 8–10 presented comparative review between molar Gibbs excess energies of the liquid phase calculated at 1973 K with binary coefficients of liquid phase<sup>[4–6]</sup> and with ternary coefficients obtained in this work. At calculations with molar ratios Sn : Zn equal to 1 : 1 and 5 : 1 observed that Gibbs energy calculated with ternary coefficients is more negative than calculated with binary parameters only. At Sn : Zn ratio equal to 1 : 5 appeared positive values of molar Gibbs excess energy with binary and ternary parameters. This is probably connected with miscibility gap in Co-Zn corner in the ternary phase diagram.



**Figure 8:** Comparative analysis between Gibbs free energy of the liquid phase, along a section with constant molar Sn : Zn ratio equal to 1 : 1.



**Figure 9:** Comparative analysis between Gibbs free energy of the liquid phase, along a section with constant molar Sn : Zn ratio equal to 1 : 5.



**Figure 10:** Comparative analysis between Gibbs free energy of the liquid phase, along a section with constant molar Sn : Zn ratio equal to 5 : 1.

## Conclusion

Some thermodynamic properties of the Co-Sn-Zn liquid phase were predicted using the general solution model developed by Chou and have been compared with different geometrical models. The general solution model has a middle place between symmetrical and asymmetrical models and gives possibilities for estimating thermodynamic properties and calculating phase diagrams for ternary systems.

Ternary interaction parameters ( $L^0$ ,  $L^1$  and  $L^2$ ) of the liquid phase have been determined using the General solution model from thermodynamic data of the binary end-systems (Co-Sn, Co-Zn, Sn-Zn). The values of ternary parameters are:  $L^0 = +2384.018 - 0.7073 * T$ ;  $L^1 = +1879.167 - 0.0547 * T$ ;  $L^2 = +1622.753 - 0.065 * T$ . The comparative analyses were performed between

Gibbs free energy of the liquid phase with ternary parameters obtained in this work and with binary parameters of each binary system. Good agreement was found indicating that such an approach was possible in systems where no experimental data were available.

## References

- [1] Chen, S. W., Wang, C. H., Lin, S. K. (2007): Phase diagrams of Pb-free solders and their related materials systems. *J. Mater. Electron.*, 18, pp. 19–37.
- [2] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (2003), *Official Journal of the European Union*, L37, pp. 19–24. Available on: <<http://europa.eu.int/eurlex/>>.
- [3] Ipser, H., Mikula, A. (2001): Memorandum of Understanding for the Implementation of a European Concerted Research Action Designated as COST 531 “Lead-free solder materials”, University of Vienna. Available on: <<http://www.univie.ac.at/cost531>>.
- [4] Vassilev, G. P., Lilova, K. I. (2006): Contribution to the thermodynamics of the Co-Sn system. *Archives of metallurgy and materials*, 51, pp. 365–375.
- [5] Vassilev, G. P., Jiang, M. (2004): Thermodynamic Optimization of the Co-Zn System. *Journal of Phase Equilibria and Diffusion*, 25, pp. 259–268.
- [6] Dinsdale, A., Watson, A., Kroupa, A., Vrestal, J., Zemanova, A., Vizdal, J. (2008): Atlas of Phase Diagrams for the Lead-Free Soldering, COST 531 (Lead-free Solders), Printed in the Czech Republic, Vol. 1.
- [7] Kohler, F. (1960): Zur Berechnung der thermodynamischen Daten eines ternären Systems aus den zugehörigen binären Systemen. *Monatshefte für Chemie*, 91, pp. 738–740.
- [8] Toop, G. W. (1965): Predicting ternary activities using binary data. *Trans. Metal Societe.*, 233, pp. 850–854.
- [9] Hilert, M. (1980): Empirical Methods of predicting and representing thermodynamics properties of ternary solution phases. *Calphad*, 4, pp. 1–12.
- [10] Chou, K. C. (1995): A general solution model for predicting ternary thermodynamics properties. *Calphad*, 19, pp. 315–325.
- [11] Chou, K. C., Li, W. C., Li, F., He, M. (1997): Formalism of new ternary model expressed in terms of binary regular-solution type parameters. *Calphad*, 20, pp. 395–406.
- [12] Živković, D., Katayama, I., Yamashita, H., Manasijević, D., Živković, Ž. (2006): Investigation of the thermodynamic model and ternary interaction parameter influence for Sn-Ag-Bi liquid alloys. *RMZ - Materials and Geoenvironment*, 53, pp. 155–161.
- [13] Marjanović, S., Manasijević, D., Živković, D., Gusković, D., Minić, D. (2009): Calculation of thermodynamic properties for ternary Ag-Cu-Sn system. *RMZ - Materials and Geoenvironment*, 56, pp. 30–37.
- [14] Živković, D., Manasijević, D., Mihajlović, I., Živković, Ž. (2006): Calculation of the thermodynamic properties of liquid Ag-In-Sb alloys. *Serb. Chem. Soc.*, 71, pp. 203–211.
- [15] Andersson, J. O., Helander, T., Höglund, L., Shi, P., Sundman, B. (2002): Thermo-Calc & DICTRA, Computational Tools For Materials Science. *Calphad*, 26, pp. 273–312.
- [16] Redlich, O., Kister, A. (1948): Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Industrial Engineering Chemistry*, 40, pp. 345–348.
- [17] Gandova, V., Vassilev, G. (2013): Comparative analyses of thermodynamic properties assessments, performed by geometric models: application to the Ni-Bi-Zn system. *J. Min. Metall. Sect. B-Metall.*, 49, pp. 347–352.