# Cu–Al–Zn System: Calculation of thermodynamic properties in liquid phase

**Lidija Gomidželović[1], Ivan Mihajlović[2], Ana Kostov[1], Dragana Živković[2]**

[1]*Mining and Metallurgy Institute Bor, Bor, Serbia*
[2]*University of Belgrade, Technical Faculty in Bor, Bor, Serbia*

*Abstract*

We present the results of thermodynamic analysis of Cu–Al–Zn ternary system, which belongs to a group of copper-based shape memory materials. A general solution model was used for calculation of thermodynamic properties in the temperature interval from 1373 to 2173 K, in sections from Cu, Al and Zn corner, respectively, with following ratios of 1:3, 1:1 and 3:1. Additionally, based on the obtained results, ternary interaction parameters were determined using Mathematical Modeling System (MLAB).

*Keywords*: Cu–Al–Zn, general solution model, MLAB, ternary interaction parameters.

*Available online at the Journal website: http://www.ache.org.rs/HI/*

SCIENTIFIC PAPER

**UDC 536.7:544.3**

*Hem. Ind.* **67** (1) 157–164 (2013)

doi: 10.2298/HEMIND120306041G

Alloys belonging to ternary Cu–Al–Zn system are interesting to researchers because their field of application is growing. These materials, mostly used like Cu-based shape memory materials [1–4], have also found application in catalysis [5–7], electronics [8] and production of metal matrix composites [9]. Research studies have mainly been focused on different aspects of martensitic transformation [10–16] and shape memory effect [17–20] in Cu–Al–Zn alloys. Corrosion behavior [21], microstructure and mechanical properties of Cu––Al–Zn alloys have also been investigated [22–25]. The phase diagram of Cu–Al–Zn system, due to technical importance, had been investigated in a number of studies and many reviews of experimental data have been conducted. A detailed review of this data was presented by Liang and Chang [26]. However, a serious lack of thermodynamic data on this system is noticeable in the literature. Using the electromotive force method, Sebkova and Kubicek [27] measured activities of Al in Zn-rich liquid alloys at 700, 750, and 800 °C, and their results showed a positive deviation from ideal behavior. Using the isopiestic method, Sugino and Hagiwara [28] measured the activities of Zn in Cu-rich liquid alloys at 1100 and 1150 °C. Their data show positive deviation for Zn in Cu-rich liquid alloys. Van *et al*. [29] determined thermodynamic properties of ternary Al––Cu–Zn alloys containing 25 to 62 at.% Al by electromotive force method, between 420 and 920 °C. From EMF values, activities of Al for three quasi-binary sections ($x_{Cu}/x_{Zn}$ = 7/3, 1, and 3/7) at 850 °C were determined, and negative deviation from ideal behavior, more pronounced at high $x_{Cu}/x_{Zn}$ ratios, was observed. Based on the descriptions of its three constituent binaries and ternary experimental data available in the literature, Liang and Chang [26] developed a thermodynamic description of the Al–Cu–Zn system (Figure 1).

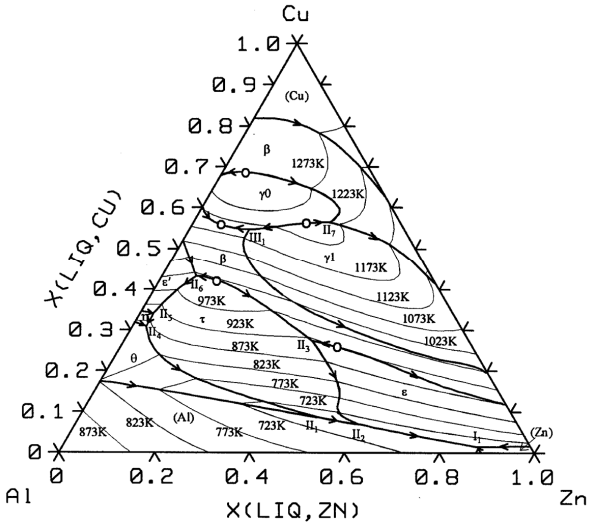


*Figure 1. Calculated liquidus projection [26].*

Within computational phase studies of quaternary Al-Cu-Mg-Zn system, Seifert *et al.* [30] calculated isothermal section at 673 K for Cu-Al-Zn system (Figure 2).

A thermodynamic description of the Cu–Al–Zn in the copper-rich corner was also done by Miettinen [31]. The objective of this work is to complement the knowledge of the thermodynamic properties of Cu–Al––Zn ternary system, due to a noticeable lack of them in the literature.

## THEORETICAL FUNDAMENTALS

There are many methods for the calculation of thermodynamic properties of ternary systems based on

Correspondence: L. Gomidželović, Moše Pijade 76a/604, 19210 Bor, Serbia.
E-mail: lgomidzelovic@yahoo.com
Paper received: 4 March, 2012
Paper accepted: 23 April, 2012

information about constitutive binary systems. Chou's general solution model (GSM) [32] has been proven to be the most reasonable one in all aspects among available geometrical models. This model breaks down boundaries between symmetrical and asymmetrical systems and generalizes various kinds of situations, but also completely excludes any human interference in the calculation process. Precision of this model has already been proved theoretically and the accuracy of calculation has also been shown in some practical examples [33]. Therefore, this model is utilized for calculating the thermodynamic properties of Cu–Al–Zn ternary system. The basic equations of the general solution model are given as follows:

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

$$\Delta G^{E}_{ij} = X_i X_j (A^{0}_{ij} + A^{1}_{ij}(X_i - X_j) + A^{2}_{ij}(X_i + X_j)^2 + \\ + \ldots + A^{n}_{ij}(X_i - X_j)^n) \quad (2)$$

$$f_{123} = (2\xi_{12} - 1)\{A^{2}_{12}((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A^{1}_{12}\} + \\ + (2\xi_{23} - 1)\{A^{2}_{23}((2\xi_{23} - 1)x_1 \\ + 2(x_2 - x_3)) + A^{1}_{23}\} + (2\xi_{31} - 1)\{A^{2}_{31}((2\xi_{31} - 1)x_2 + \\ + 2(x_3 - x_1)) + A^{1}_{31}\} \quad (3)$$

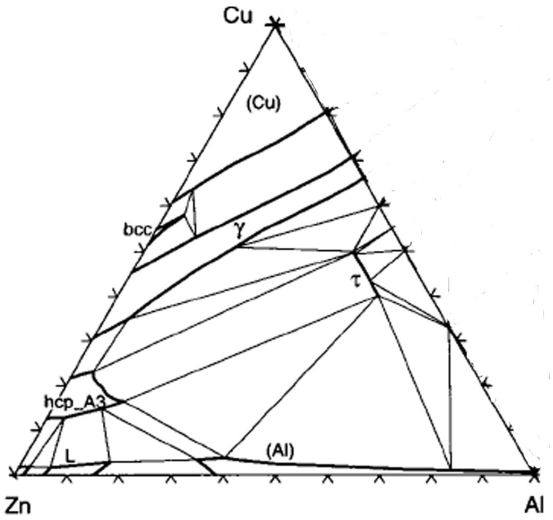


*Figure 2. Calculated isothermal section at 673 K [27].*

The ternary interaction coefficient, $f_{123}$, is related to the Redlich–Kister ternary interaction parameter [32], so it can be written in the form:

$$f_{123} = x_1{}^{0}L_{123} + x_2{}^{1}L_{123} + x_3{}^{2}L_{123} \quad (4)$$

with a temperature dependence taken as:

$${}^{v}L_{123} = a^{v} + b^{v}T, (v = 0,1,2,\ldots) \quad (5)$$

where ${}^{v}L_{ijk}$ are the Redlich-Kister parameters for the ternary system *ijk*; and $x_i$ is the mole fraction of component *i*.

In all given equations, $\Delta G^{E}$ and $\Delta G^{E}_{ij}$ correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while $x_1$, $x_2$ and $x_3$ correspond to the mole fraction of components in investigated ternary system.

Basic thermodynamic data on the constituent binary subsystems Al–Cu, Cu–Zn and Al–Zn, needed for calculation of thermodynamic properties in the investigated Cu–Al–Zn system, were taken from references [34–36].

## RESULTS AND DISCUSSION

For the purpose of further calculation, basic thermodynamic information on the constitutive subsystems in the Cu–Al–Zn system was taken from references [34––35], and presented in the form of Redlich–Kister parameters in Table 1.

Ternary Cu–Al–Zn system has been investigated in 9 sections (Figure 3). Sections were taken from Cu, Al and Zn corner, respectively, with ratios 1:3, 1:1 and 3:1, and with molar content of 0-0.9 for the third component.

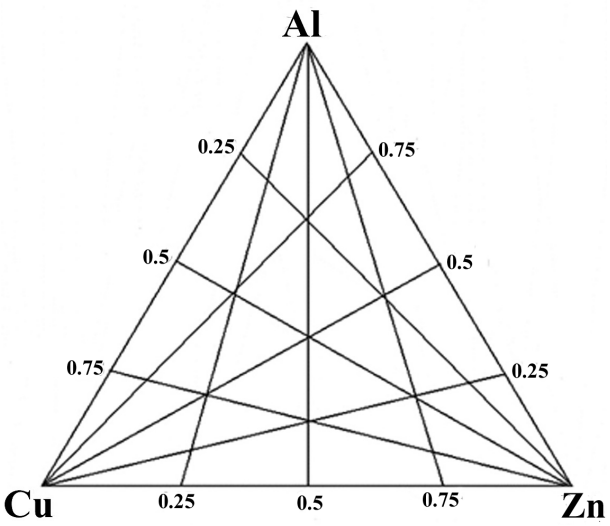


*Figure 3. Schematic diagram of the investigated concentration regions in ternary system Cu–Al–Zn.*

*Table 1. Redlich–Kister parameters for constitutive binary systems*

| System *ij* | $L^{o}_{ij}$ / K | $L^{1}_{ij}$ / K | $L^{2}_{ij}$ / K | $L^{3}_{ij}$ / K |
|---|---|---|---|---|
| Al–Cu [34] | –67094+8.555*T* | 32148–7.118*T* | 5915–5.889*T* | –8175+6.049*T* |
| Cu–Zn [35] | –40695.54+12.65269*T* | 4402.72–6.55425*T* | 7818.1–3.25416*T* | 0 |
| Al–Zn [36] | 10465.55–3.39259*T* | 0 | 0 | 0 |

Partial thermodynamic quantities of copper, aluminum, and zinc are calculated according to the equations:

$$G_i^{\mathrm{E}} = G^{\mathrm{E}} + \left(1 - x_i\right)\left(\partial G^{\mathrm{E}} / \partial x_i\right) = RT \ln \gamma_i \quad (6)$$

and

$$a_i = x_i \gamma_i \quad (7)$$

The calculated integral molar Gibbs excess energies, $\Delta G^{\mathrm{E}}$, and activities of the investigated system Cu–Al–Zn, along selected sections and at given temperatures, are presented in Figures 4–6. All thermodynamic properties calculated in this work are related to the liquid phase.

Calculation of thermodynamic properties for ternary system Cu-Al-Zn was performed using the general

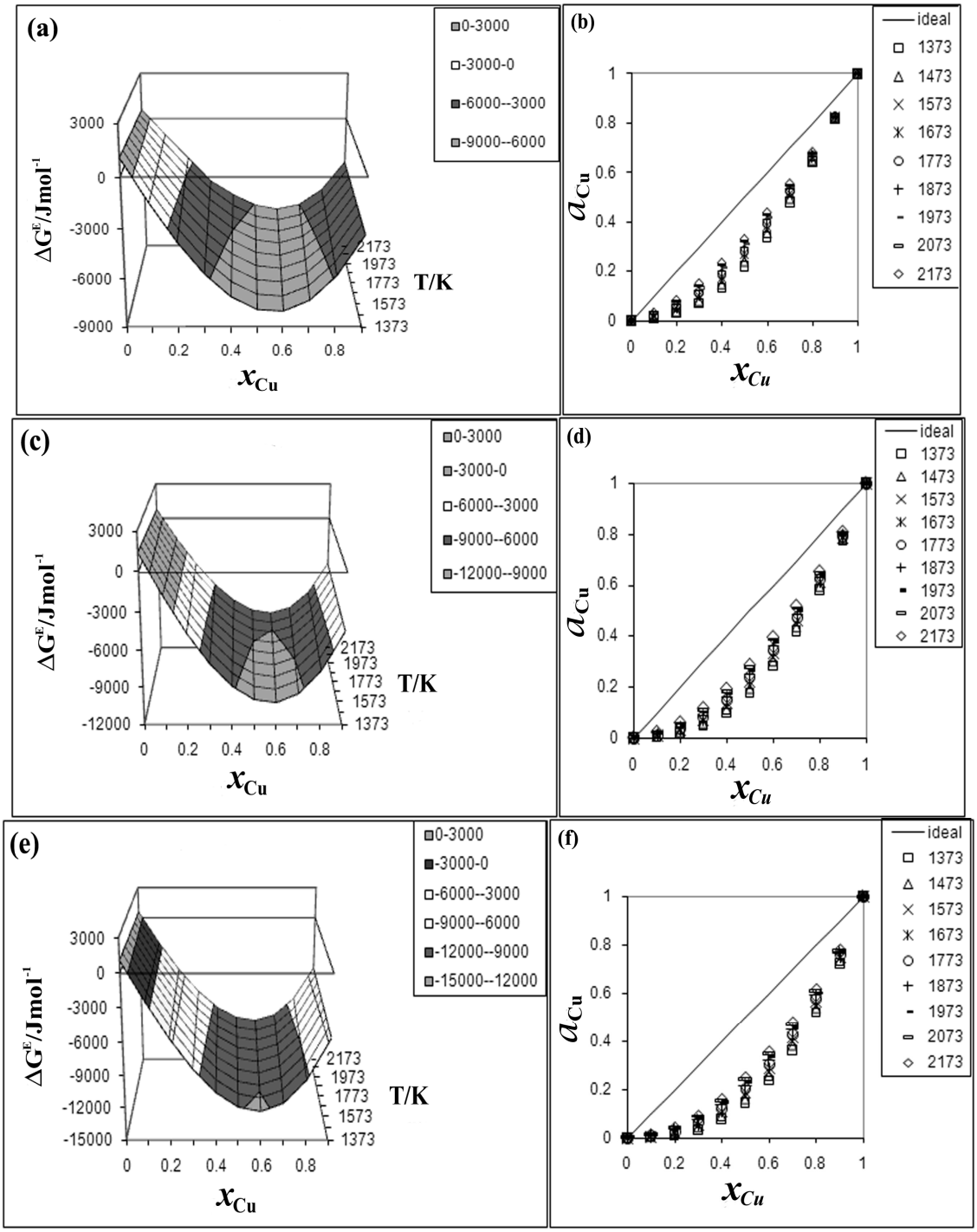


*Figure 4. Results of thermodynamic calculation according to GSM in temperature range 1373–2173 K for cross-sections from copper corner: a) $\Delta G^{E}$ for section Al:Zn = 1:3; b) copper activity for section Al:Zn = 1:3; c) $\Delta G^{E}$ for section Al:Zn = 1:1; d) copper activity for section Al:Zn = 1:1; e) $\Delta G^{E}$ for section Al:Zn = 3:1; f) copper activity for section Al:Zn = 3:1.*

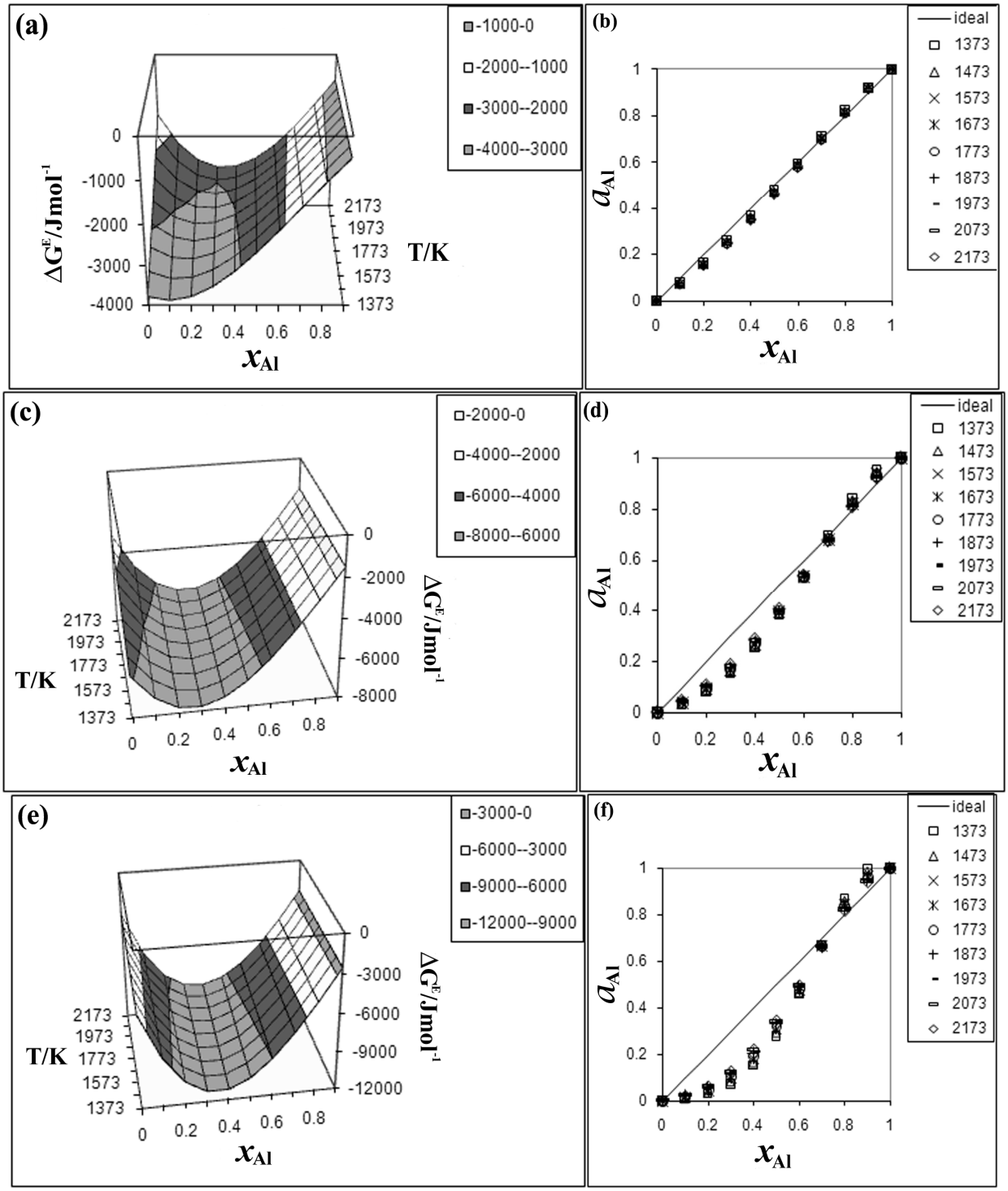


*Figure 5. Results of thermodynamic calculation according to GSM in temperature range 1373–2173 K for cross-sections from aluminum corner: a) $\Delta G^E$ for section Cu:Zn = 1:3; b) aluminum activity for section Cu:Zn = 1:3; c) $\Delta G^E$ for section Cu:Zn = 1:1; d) aluminum activity for section Cu:Zn = 1:1; e) $\Delta G^E$ for section Cu:Zn = 3:1; f) aluminum activity for section Cu:Zn = 3:1.*

solution model. The values for excess integral Gibbs energy of investigated sections from the corner of aluminum and zinc were negative, with minimum values up to –15 kJ/mol, while for the investigated section from the corner of copper Gibbs energy was between 3 and –15 kJ/mol. Also, it was noticed that the value of copper activities show pronounced negative deviation from Rault's law for all investigated sections.

For aluminum activity, variable character of deviation from Rault's law is characteristic for all investigated sections, deviation is negative up to $x_{Al}$ = 0.8, and

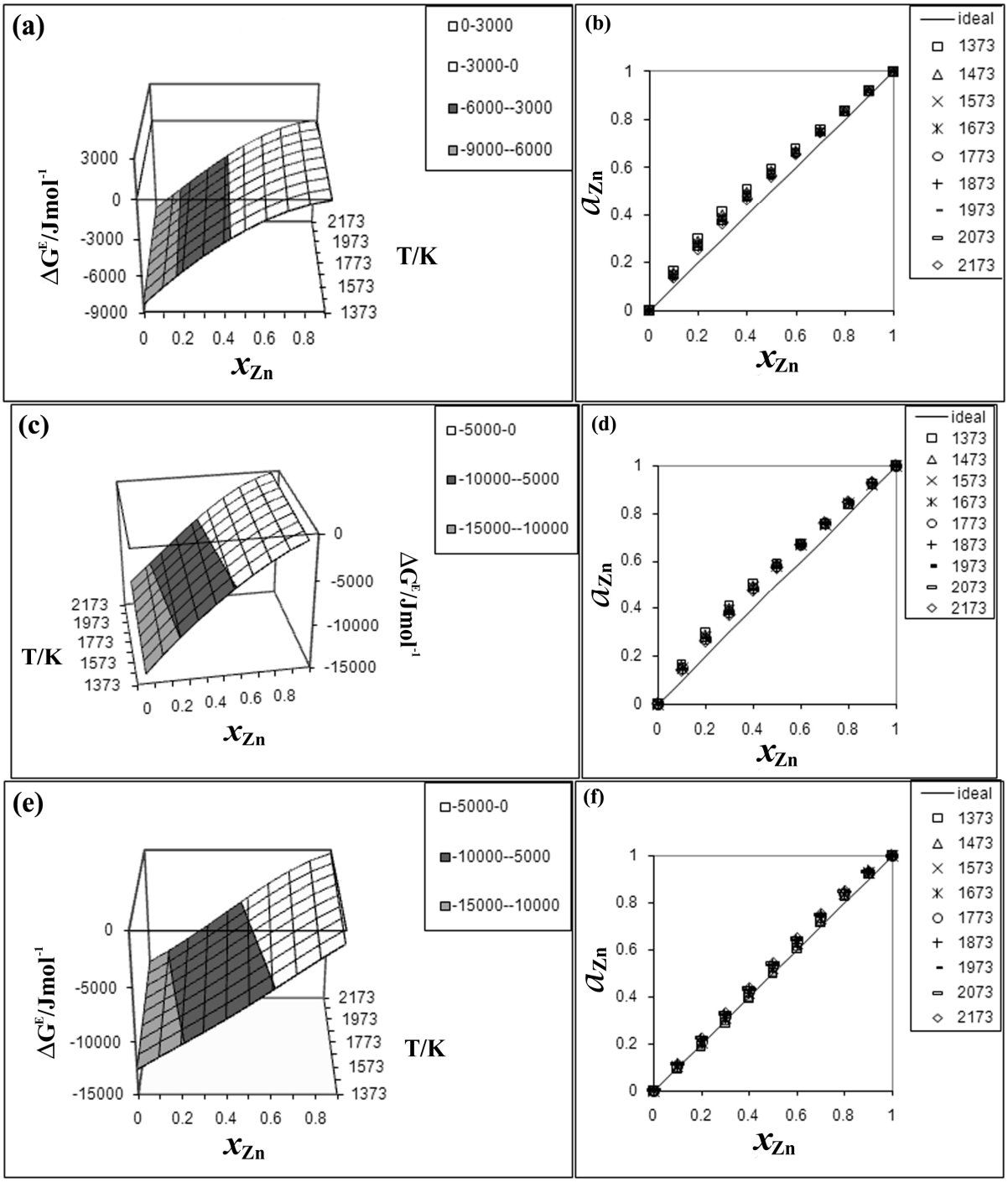


*Figure 6. Results of thermodynamic calculation according to GSM in temperature range 1373–2173 K for cross-sections from zinc corner: a) $\Delta G^E$ for section Cu:Al = 1:3; b) zinc activity for section Cu:Al = 1:3; c) $\Delta G^E$ for section Cu:Al = 1:1; d) zinc activity for section Cu:Al = 1:1; e) $\Delta G^E$ for section Cu:Al = 3:1; f) zinc activity for section Cul:Al = 3:1.*

for section Cu:Zn = 1:3 values of aluminum activities are near to ideal solution.

Zinc activity shows a positive deviation from the Rault's law for all three investigated sections, but it can be noticed that with increase of copper contents in alloy, this derivation is decreasing, and for section Cu:Al = = 3:1 zinc activities are near ideal conditions. From this it can be concluded that zinc content increase in the alloy reduces the miscibility of alloy components.

Additionally, aluminum activity values at $T$ = 1123 K were calculated and compared with available literature data [29] (Figure 7). Data obtained analytically and experimentally show good agreement.

Ternary interaction coefficients $f_{123}$ were calculated using Eq. (3), in the temperature range 1373–2173 K,

and the obtained values were then used to determine the of ternary interaction parameters $L^{v}_{ijk}$, according to Eqs. (4) and (5). The process of fitting was performed using the MLAB program [37] and the results are presented in Table 2.

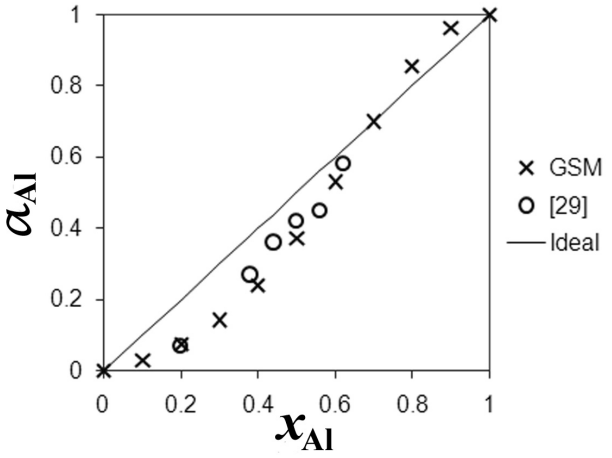


*Figure 7. Dependence of aluminum activities from composition (at T = 1123 K, for section Cu:Zn = 1:1), calculated according to GSM and compared with literature data [29].*

Although the common way to obtain the ternary interaction parameters is the optimization based on the experimental data from literature, it could be also done using the estimation method, without applying experimental data [38,39].

## CONCLUSION

Calculation of thermodynamic properties of the Cu–Al–Zn system has been done using the general solution model. Redlich-Kister ternary interaction parameters were obtained for investigated system in the temperature interval from 1373 to 2173 K. Presented thermodynamic data for the Cu–Al–Zn 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.

**Acknowledgement**

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic Serbia for financial support to the projects No.: 172037and 34005.

## REFERENCES

[1] A. Milosavljević, A. Kostov, R. Todorović, Smart materials: shape memory alloys, Bakar **36** (2011) 39–44 (in Serbian).

[2] L. Janke, C. Czaderski, M. Motavalli, J. Ruth, Applications of shape memory alloys in civil engineering structures - Overview, limits and new ideas, Mater. Struct. **38** (2005) 578–592.

[3] Z.G. Wei, R. Sandström, S. Miyazaki, Shape-memory materials and hybrid composites for smart systems Part I, J. Mater. Sci. **33** (1998) 3743–3762.

[4] W.M. Huang, Z. Ding, C.C. Wang, J. Wei, Y. Zhao, H. Purnawali, Shape memory materials, Mater. Today **13** (2010) 54–61.

[5] J. Li, W. Zhang, L. Gao, P. Gu, K. Sha, H. Wan, Methanol synthesis on Cu–Zn–Al and Cu–Zn–Al–Mn catalysts, Appl. Catal., A **165** (1997) 411–417.

[6] F. Huber, H. Meland, M. Rønning, H. Venvik, A. Holmen, Comparison of Cu–Ce–Zr and Cu–Zn–Al mixed oxide catalysts for water-gas shift, Top. Catal. **45** (2007) 101––104.

[7] J.P. Breen, J.R.H. Ross, Methanol reforming for fuel-cell applications: development of zirconia-containing Cu––Zn–Al catalysts, Catal. Today **51** (1999) 521–533.

*Table 2. Ternary interaction parameters, $L^{v}_{ijk}$ for Cu–Al–Zn system, obtained using the MLAB program*

| System *ijk* | $L^{o}_{ijk}$ / K | $L^{1}_{ijk}$ / K | $L^{2}_{ijk}$ / K |
|---|---|---|---|
| Cu–Al–Zn | 33222.4905–12.8938291*T* | 33003.2723–17.5403409*T* | 29898.6835–15.1789113*T* |

[8] N. Kang, H.S. Na, S.J. Kim, C.Y. Kang, Alloy design of Zn–Al–Cu solder for ultra-high temperatures, J. Alloys Compd. **467** (2009) 246–250.

[9] E. Martinez-Flores, J. Negrete, G. Torres Villasenor, Structure and properties of Zn–Al–Cu alloy reinforced with alumina particles, Mater. Des. **24** (2003) 281–286.

[10] A. Tolley, A. Condo, Application of the large angle convergent beam electron diffraction technique to the characterisation of martensitic phases in Cu–Zn–Al alloys, Mater. Sci. Eng. A **273–275** (1999) 347–351.

[11] M. Stipcich, R. Romero, The effect of post-quench aging on stabilization of martensite in Cu–Zn–Al and Cu–Zn––Al–Ti–B shape memory alloys, Mater. Sci. Eng. A **273––275** (1999) 581–585.

[12] X.M. Zhang, U.M. Liu, J. Fernandez, J.M. Guilemany, Effect of small g-precipitates on the two-way shape memory effect in Cu–Zn–Al alloys, Mater. Des. **21** (2000) 557–559.

[13] J.X. Zhang, Y.F. Zheng, Y.C. Luo, L.C. Zhao, Substructure and boundary structure of deformed 18R martensite in a Cu–Zn–Al alloy, Acta mater. **47** (1999) 3497–3506.

[14] H. Xu, S. Tan, Calorimetric investigation of a Cu–Zn–Al alloy with two way shape memory, Scr. Metall. Mater. **33** (1995) 749–754.

[15] J.L. Pelegrina, R. Romero, Calorimetry in Cu–Zn–Al alloys under different structural and microstructural conditions, Mater. Sci. Eng., A **282** (2000) 16–22.

[16] A. Cuniberti, R. Romero, Differential scanning calorimetry study of deformed Cu–Zn–Al martensite, Scr. Mater. **51** (2004) 315–320.

[17] S. Longauer, P. Makroczy, G. Janak, M. Longauerova, Shape memory effect in a Cu–Zn–Al alloy with dual phase α/β microstructure, Mater. Sci. Eng., A **273**–**275** (1999) 415–419.

[18] J. Cederstrom, V. Kolomytsev, A. Kozlov, P. Titov, G. Zatulskii, S. Kondratjuk, Evolution of the shape memory parameters during multiple transformation cycles under load in Cu–Zn–Al alloys, Mater. Sci. Eng., A **273**–**275** (1999) 804–808.

[19] J. Pons, M. Masse, R. Portier, Thermomechanical cycling and two-way memory effect induced in Cu–Zn–Al, Mater. Sci. Eng., A **273**–**275** (1999) 610–615.

[20] E. Cingolani, M. Ahlers, On the origin of the two way shape memory effect in Cu–Zn–Al single crystals, Mater. Sci. Eng., A **273**–**275** (1999) 595–599.

[21] M.M. Ahmed, Corrosion behaviour of Zn–Al–Cu alloy in HCl solution and its inhibition, Portugaliae Electrochim. Acta **24** (2006) 1–22.

[22] G. Lojena, I. Anžel, A.C. Kneissl, A. Križman, E. Unterweger, B. Kosec, M. Bizjak, Microstructure of rapid solidified Cu–Al–Ni shape memory alloy ribbons, Proc. 13th Int. Scientific Conf. on Achievements in Mechanical and Materials Engineering, Gliwice-Wisla, Poland, 2005, pp. 399–402.

[23] T. Savaskan, M.S. Turhal, Relationships between cooling rate, copper content and mechanical properties of monotectoid based Zn–Al–Cu alloys, Mater. Charact. **51** (2003) 259–270.

[24] S.R. Casolco, G. Dominguez, D. Sandoval, J.E. Garay, Processing and mechanical behavior of Zn–Al–Cu porous alloys, Mater. Sci. Eng., A **471** (2007) 28–33.

[25] H. Pal, S.K. Pradhan, M. De, Microstructure and mechanical property of α-Al–Zn–Cu alloys aged at room temperature, Mater. Trans. JIM **36** (1995) 490–495.

[26] H. Liang, Y.A. Chang, A Thermodynamic description for the Al–Cu–Zn system, J. Phase Equilib. **19** (1998) 25–37.

[27] J. Sebkova, L. Kubicek, Thermodynamic Properties of a Liquid Zinc -Aluminum-Copper Alloy, Kovové Mater. **23** (1985) 3–7.

[28] S. Sugino, H. Hagiwara, Activity of zinc in molten copper and copper-gold alloys, J. Jpn. Inst. Metals **50** (1986) 1068–1074.

[29] T.D. Van, L. Segers R. Winand, Determination of thermodynamic properties of ternary Al–Cu–Zn alloys by electromotive force method, J. Electrochem. Soc. **14** (1994) 927–933.

[30] H.J. Seifert, P. Liang, H.L. Lukas, F. Aldinger, S.G. Fries, M.G. Hamerlin, F. Faudot, T. Jantzen, Computational phase studies in commercial aluminium and magnesium alloys, Mater. Sci. Tech-London **16** (2000) 1429–1433.

[31] J. Miettinen, Thermodynamic description of the Cu-Al-Zn and Cu-Sn-Zn systems in the copper-rich corner, Calphad **26** (2002) 119–139.

[32] K.C. Chou, A General solution model for predicting ternary thermodynamic properties, Calphad **19** (1995) 315–325.

[33] K.C. Chou, W.C. Li, F. Li, M. He, Formalism of new ternary model expressed in terms of binary regular-solution type parameters, Calphad **20** (1996) 395–406.

[34] V.T. Witusiewicz, U. Hecht, S.G. Fries, S. Rex, The Ag–Al––Cu system: Part I: Reassessment of the constituent binaries on the basis of new experimental data, J. Alloys Compd. **385** (2004) 133–143.

[35] G.W. Dinsdale, A. Kroupa, J. Vizdal, J. Vrestal, A. Watson, A. Zemanova, COST 531 Database for Lead-free Solders, Ver. 2.0, 2006, Unpublished Research.

[36] S. Mey, Re-evaluation of the Al-Zn system, Z. Metallkde. **84** (1993) 451–455.

[37] MLAB Mathematical Modeling System, www.civilized.com (accessed on Feb, 2013).

[38] D. Živković, D. Manasijević, I. Mihajlović, Ž. Živković, Calculation of the thermodynamic properties of liquid Ag–In–Sb alloys, J. Serb. Chem. Soc. **71** (2006) 203–211.

[39] L. Gomidželović, D. Živković, I. Mihajlović, V. Trujić, Predicting of thermodynamic properties of ternary Au–In––Sb system, Arch. Metall. Mater. **51** (2006) 355–363.

## IZVOD

### Cu–Al–Zn SISTEM: PRORAČUN TERMODINAMIČKIH OSOBINA U TEČNOM STANJU

Lidija Gomidželović[1], Ivan Mihajlović[2], Ana Kostov[1], Dragana Živković[2]

[1]*Institut za rudarstvo i metalurgiju Bor, Bor, Srbija*
[2]*Univerzitet u Beogradu, Tehnički fakultet u Boru, Bor, Srbija*

(Naučni rad)

U radu su predstavljeni rezultati termodinamičke analize ternarnog Cu–Al–Zn sistema, koji pripada grupi materijala na bazi bakra sposobnih da pamte oblik. Opšti model rastvora je iskorišćen za proračun termodinamičkih veličina u presecima iz ugla bakra, aluminijuma i cinka sa molskim odnosom druge dve komponente jednakim 1:3, 1:1 i 3:1 u temperaturnom intervalu od 1373 do 2173 K. Vrednosti integralne dopunske Gibsove energije za preseke iz ugla aluminijuma i cinka su negativne sa minimalnim vrednostima do –15 kJ/mol, dok se kod preseka iz ugla bakra Gibsova energija nalazi u granicama od 3 do –15 kJ/mol. Takođe, primećeno je da vrednosti aktivnosti bakra pokazuju izraženo negativno odstupanje od Rault-ovog zakona za sve ispitivane preseke, dok aktivnost aluminijuma negativno odstupa od Rault-ovog zakona do $x_{Al}$ = 0,8, nakon čega vrednosti prelaze u područje pozitivnog odstupanja. Aktivnost cinka pokazuje pozitivno odstupanje od Rault-ovog zakona za sve ispitivane preseke, ali sa porastom sadržaja bakra odstupanje se smanjuje na osnovu čega se može zaključiti da porast sadržaja cinka u leguri negativno utiče na mešljivost. Takođe, na osnovu dobijenih rezultata, pomoću programa MLAB izračunati su ternarni interakcioni parametri.

*Ključne reči*: Cu–Al–Zn • Opšti model rastvora • MLAB • Ternarni interakcioni parametri