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# Thermal analysis and microstructural investigation of Cu-rich alloys in the Cu–Al–Ag system

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## 1. Introduction

Shape memory effect presents the ability of some plastic deformed metals and alloys to establish the original form due to a complete or nearly complete disappearance of deformation during the heating. Special characteristic of these materials is so-called thermoelastic martensitic transformation – shape memory phenomenon manifested in simple or double shape memory effect or superelasticity (pseudoelasticity). Under certain circumstances during martensitic transformation the change of material shape may be reversible, so the material can store two geometric shapes and form both high temperature and low temperature structures [1,2].

Shape memory alloys of the ternary Cu–Al–Ag system, which belong to a wider group of Cu–Al based shape memory materials, have been investigated for a long time. Nevertheless, these alloys still present actual investigation topic for many fields of material science and engineering application due to their different properties.

Although Cu–Al based alloys are convenient materials for application in engineering, bioengineering, medicine, electronics, cosmic technology, etc. [1,3,4], Cu–Al–Ag ternary system has not been investigated completely from thermodynamic and phase

# equilibria point of view, which was the main reason for the

research presented in this paper. According to literature, constitutive binary systems Cu–Al, Cu–Ag and Ag–Al have been explored in details for their thermodynamic, phase equilibria and crystalografic properties. Campbell's dilatometric investigations in 1902 [5] was among first research works related to the Cu–Al system. Since that time, numerous authors studied thermodynamic properties [6–9], phase equilibrium and metallography of the Cu–Al system [10–14]. The other two constituent systems, Cu–Ag and Ag–Al, were the subjects of many researches, too [15–23]. Great contribution to thermodynamic optimizations of these systems is from Witusiewicz with co-workers [24], who revised existing thermodynamic descriptions of the constituent binaries Cu–Al, Cu–Ag and Ag–Al by modeling Gibbs energy using CALPHAD method including their experimental results.

First investigation of the ternary Ag–Al–Cu system was carried out in 1930 by Ueno, who reported some vertical sections based on cooling curves [25,26]. Later, Massalski and Perepezko [27] suggested that phase equilibria from Ref. [26] was to be considered as approximate and proved that all observed phases were structurally analogous to those of the constituent binary systems and no new ternary phases were found [28]. Also, important contribution to the investigation of phase relations and transformations in ternary Cu–Al–Ag system was given by Adorno and da Silva [29–35], who especially studied martensitic transformations in that system.

ABSTRACT

Copper rich region in shape memory Cu–Al–Ag system was experimentally investigated using DTA and calculated using optimized thermodynamic parameters according to CALPHAD method. Overall composition alloys were chosen along three vertical sections with constant copper content of 70, 80 and 90 at%. Experimentally determined solidus and liquidus temperatures were compared with the results of thermodynamic calculation and good mutual agreement was noticed.

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Z.S. Šimšić et al./Journal of Alloys and Compounds 612 (2014) 486-492

Phase	TD database name	Pearson symbol	Space Group	TD model
Liquid	LIQUID	_	_	(Ag, Al, Cu) <sub>1</sub>
(Ag) (Al) (Cu)	FCC_A1	cF4	Fm3m	$(Ag, Al, Cu)_1(Va)_1$
β	BCC_A2	cI2	Im3m	(Ag, Al, Cu, Va) <sub>1</sub> (Va) <sub>3</sub>
ξ	HCP_A3	hP2	P6 <sub>3</sub> /mmc	(Ag, Al, Cu) <sub>1</sub> (Va) <sub>0.5</sub>
μ	CUB_A13	cP20	P4132	(Ag, Al, Cu) <sub>1</sub> (Va) <sub>1</sub>
θ	XZ2_C16	tI12	I4/mcm	$(Ag, Al, Cu)_1(Al)_2$
η	ALCU_ETA	mC20	C2/m	$(Al, Cu)_1(Ag, Cu)_1$
ζ	ALCU_ZETA	-	_	(Al) <sub>9</sub> (Ag, Cu) <sub>11</sub>
3	ALCU_EPS	hP4	P6 <sub>3</sub> /mm	$(Al, Cu)_1(Cu)_1$
δ	ALCU_DEL	-	-	$(Al)_2(Cu)_3$
γD8	GAMMA_D83	cP52	P43m	$(Al)_4(Al, Cu)_1(Ag, Cu)_8$
γ	GAMMA_H	-	-	$(Al)_4(Al, Cu)_1(Ag, Cu)_8$

Table 1	
Considered phases of the Ag-Al-Cu ternary system	, their crystallographic data and thermodynamic models.

The phase relations in Cu-rich (Cu  $\ge 90$  wt%) ternary alloys of the Ag–Al–Cu system were metallographically investigated by Pansery and Leoni [36]. They determined the reaction temperatures for the alloys with 90 wt% Cu:  $\beta + \alpha(Cu) \leftrightarrow \alpha(Cu)' + \gamma D8_3$ to 838 K, liquid +  $\alpha(Cu) \leftrightarrow \alpha(Cu)' + \alpha(Ag)$  to 1052 K and liquid  $\leftrightarrow$ liquid' +  $\alpha(Cu) + \beta$  to 1295 K [34].

There are literature references concerning thermodynamic investigations related to this system, but not completed yet [25,37–41]. So, Chang et al. [37] compiled thermodynamic data on different Cu–Al-based ternary systems [41]. Flandorfer and

Hayer [38] experimentally determined partial and integral enthalpy of mixing of molten Cu–Al–Ag alloys at 1146 K. Based on available literature data and their own experimental results, Witusiewicz et al. [24,25,39] performed thermodynamic modeling of mentioned ternary system using CALPHAD method. Recently, Živković et al. [41] calculated thermodynamic properties for ternary Cu–Al–Ag and Cu–Al–Au systems at 1100 K using general solution model.

Considering presented literature review and having in mind that the alloys in Cu-rich part of Cu-Al-Ag phase diagram exhibit

Table 2					
Binary and ternary	thermodynamic	parameters	used in	this	study.

Phase and thermodynamic model	Thermodynamic parameter	Ref.
LIQUID (Ag, Al, Cu) <sub>1</sub>	${}^{0}L_{A\sigma,AI}^{\text{LIQUID}} = -15021.6 - 20.5379T$	[22]
	${}^{1}L_{A\sigma Al}^{\text{LIQUID}} = -20455.6 - 17.2912T$	[22]
	$^{2}L_{A\sigma Al}^{\text{LIQUID}} = -3821 - 17.169T$	[22]
	${}^{3}L_{A\sigma,AI}^{\text{LIQUID}} = 7027.6 - 12.2469T$	[22]
	${}^{4}L_{A\sigma,AI}^{\text{LIQUID}} = 7660.6 - 5.8572T$	[22]
	${}^{0}L_{Ag,Cu}^{IIQUID} = 14462.47 - 1.5159T$	[22]
	${}^{1}L_{Ag,Cu}^{\text{LIQUID}} = -934.13 + 0.3188T$	[22]
	${}^{0}L_{ALCu}^{LIQUID} = -66622 + 8.1T$	[45]
	${}^{1}L_{ALCu}^{LIQUID} = 46800 - 90.8T + 10T \ln T$	[45]
	${}^{2}L_{ALCu}^{LIQUID} = -2812$	[45]
	${}^{0}L_{\text{Ag,AL,Cu}}^{\text{LIQUID}} = -133982$	[23]
	${}^{1}L_{\text{Ag,AL,Cu}}^{\text{LIQUID}} = 30555.6 - 72.096T$	[23]
	${}^{2}L_{\text{Ag,Al,Cu}}^{\text{LIQUD}} = -165118 + 78.691T$	[23]
FCC_A1 (Ag, Al, $Cu$ ) <sub>1</sub> (Va) <sub>1</sub>	${}^{0}L_{Ag,Al:Va}^{FCC-A1} = -7153.7 - 19.5619T$	[22]
	${}^{1}L_{\text{Ag,A}:\text{Va}}^{\text{FCC}-\text{A1}} = -16540.8 - 21.694T$	[22]
	${}^{2}L_{\text{Ag,Al:Va}}^{\text{FCC}-\text{A1}} = 4273.8 - 27.8392T$	[22]
	${}^{3}L_{ m Ag,Al:Va}^{ m FCC\_A1} = -8100.2$	[22]
	${}^{0}L_{Ag,Cu:Va}^{FCC\_A1} = 34816.85 - 8.8758T$	[22]
	${}^{1}L_{\text{Ag,Cu:Va}}^{\text{FCC}\_A1} = -3206.71 - 0.57034T$	[22]
	${}^{0}L_{Al,Cu:Va}^{FCC_A1} = -53520 + 2T$	[45]
	${}^{1}L_{Al,Cu:Va}^{FCC\_A1} = 38590 - 2T$	[45]
	${}^{2}L_{\text{AI,Cu:Va}}^{\text{FCC}-\text{A1}} = 1170$	[45]
	${}^{0}L_{Ag,Al,Cu:Va}^{FCC_A1} = 72814 - 270.009T$	[23]
	${}^{1}L_{\text{Ag,AI,Cu:Va}}^{\text{FCC}-\text{A1}} = -7437.2$	[23]
	${}^{2}L_{Ag,Al,Cu:Va}^{FCC_A1} = -124167.34$	[23]
BCC_A2 (Ag, Al, Cu, Va) $_1$ (Va) $_3$	${}^{0}L_{\text{Ag,Va:Va}}^{\text{BCC}-\text{A2}} = 50000$	[22]
	${}^{0}L_{ m Ag,Al:Va}^{ m BCC\_A2} = -31689.8381 - 8.2147T$	[22]
	${}^{1}L_{Ag,Al:Va}^{BCC\_A2} = -52755.6444$	[22]
	${}^{2}L_{Ag,AI:Va}^{BCC\_A2} = 66460.6673 - 84.6018133T$	[22]
	${}^{0}L_{\text{Ag,Cu:Va}}^{\text{BCC}\_\text{A2}} = 12500$	[22]

(continued on next page)

Phase and thermodynamic model	Thermodynamic parameter	Ref.
	${}^{0}L_{AI,Cu:Va}^{BCC-A2} = -73554 + 4T$	[45]
	${}^{1}L_{Al,Cu:Va}^{BCC\_A2} = 51500 - 11.84T$	[45]
	${}^{0}L_{Ag,Al,Cu:Va}^{BCC\_A2} = -9336.6 - 71.008T$	[23]
	${}^{1}L_{\text{Ag.Al.Cu:Va}}^{\text{BCC}\_A2} = -83662.3 + 19.3248T$	[23]
	${}^{2}L_{\text{Ag.ALCu:Va}}^{\text{BCC},A2} = -17673.5 - 19.3249T$	[23]
HCP_A3 (Ag, Al, Cu) <sub>1</sub> (Va) <sub>0.5</sub>	${}^{0}L_{A\sigma,AIVa}^{HCP_{A3}} = 10711.2 - 24.2233T$	[22]
	${}^{1}L_{A\alpha}^{HCP}A3} = -328502.3 + 27.2062T$	[22]
	${}^{2}L_{A\alpha}^{HCP}A3} = 973509.5$	[22]
	${}^{3}L_{A\alpha}^{HCP}A3 = -1386464.7 - 175.7596T$	[22]
	${}^{4}L_{A\alpha}^{HCP}A3 = 881517.7$	[22]
	${}^{0}L^{HCP}_{ACCOVA} = 21000$	[22]
	${}^{0}L^{HCP}A3$ ${}^{0}L^{HCP}A3 = -43225.5769 + 10T$	[22]
	${}^{1}L_{ALCMA}^{HCP}$ = 60000	[22]
	${}^{0}I^{\text{HCP}A3}_{AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA$	[23]
	${}^{1}I_{\text{HCP},A3}^{\text{HCP},A3} = -8366774 + 193822T$	[23]
	${}^{2}I^{\text{HCP}}_{A3}$ , $-199490 \pm 159.98T$	[23]
CUB A13 (Ag. Al. Cu) <sub>1</sub> (Va) <sub>1</sub>	$0_{Ag,Al,Cu:Va} = -155156 + 155.561$ $0_{I}^{CUB}A^{13} = 495359831 = 20.4T$	[22]
	$L_{Ag,AI:Va} = 43333.3631 - 20.41$	[22]
	$L_{Ag,AI:Va} = -307070 - 28.43131$ 2/CUB_A13 - 179694 4 + 110.4507T	[22]
	$L_{Ag,AI:Va} = 178084.4 + 110.43571$ 0/CUB_A13 COSEO	[22]
	$\frac{1}{4g_{cu:Va}} = 05050$	[23]
	$L_{Ag,Al,Cu:Va} = -495000$	[23]
	$L_{Ag,AI,Cu:Va} = -520000$	[23]
X72 C16 (Ag Al Cu) (Al)	$L_{Ag,Al,Cu:Va}^{22} = -495000$	[25]
$\sqrt{22}$ C10 (Ag, Ai, Cu) <sub>1</sub> (Al) <sub>2</sub>	$G_{Ag,AI}^{XZZ} = 873 + 5.7321 + 2GHSERAL + GHSERAG$	[40]
	${}^{6}G_{AL,AI}^{022C10} = 30249 - 14.4397 + 3GHSERAL$	[45]
	$^{0}G_{CU,AI}^{VZZ-CI0} = -47406 + 6.75T + 2GHSERAL + GHSERCU$	[45]
	$L_{Ag,Cu:Al}^{L2ZCIG} = 16306$	[40]
	$U_{AI,Cu:AI}^{L2Z-L16} = 2211$	[45]
ALCU_ETA (AI, CU) <sub>1</sub> (Ag, CU) <sub>1</sub>	${}^{0}G_{ALCO_EIA}^{ALCO_EIA} = 18000 - 8T + GHSERAL + GHSERAG$	[23]
	$^{0}G_{CLAG}^{ALCU_{ETA}} = 75000 + GHSERCU + GHSERAG$	[23]
	${}^{0}G_{ALCU}^{ALCU} = -40560 + 3.14T + GHSERAL + GHSERCU$	[45]
	$^{0}G_{Cu,Cu}^{ALCU_{ETA}} = 8034 - 2.51T + 2GHSERCU$	[45]
	${}^{0}L_{ALCU-ETA}^{ALCU-ETA} = -25740 - 20T$	[23]
	${}^{0}L_{AI,Cu:Cu}^{AICU\_ETA} = -25740 - 20T$	[45]
ALCU_ZETA (Al) <sub>9</sub> (Ag, Cu) <sub>11</sub>	${}^{0}G_{Al,Ag}^{ALCU\_ZETA} = 112000 + 9GHSERAL + 11GHSERAG$	[23]
	${}^{0}G_{Al,Cu}^{ALCU\_ZETA} = -420000 + 18T + 9GHSERAL + 11GHSERCU$	[45]
ALCU_EPS (Al, $Cu$ ) <sub>1</sub> ( $Cu$ ) <sub>1</sub>	${}^{0}G_{Al,Cu}^{ALCU\_EPS} = -36976 + 1.2T + GHSERAL + GHSERCU$	[45]
	${}^{0}G_{Cu,Cu}^{ALCU\_EPS} = 8034 - 2.51T + 2GHSERCU$	[45]
	${}^{0}L_{AI,Cu:Cu}^{ALCU\_EPS} = 7600 - 24T$	[45]
	${}^{1}L_{AI,Cu:Cu}^{ALCU\_EPS} = -72000$	[45]
ALCU_DEL $(Al)_2(Cu)_3$	${}^{0}G_{ALCu}^{ALCU\_DEL} = -106700 + 3T + 2GHSERAL + 3GHSERCU$	[45]
GAMMA_D83 (Al) <sub>4</sub> (Al, Cu) <sub>1</sub> (Ag, Cu) <sub>8</sub>	${}^{0}G_{Al:Al:Ag}^{GAMMA\_D83} = -10000 + 5GHSERAL + 8GHSERAG$	[23]
	${}^{0}G_{Al:Cu:Ag}^{GAMMA_D83} = 183000 + 4430T - 766T ln(T) + 0.8T^{2} \\ + 4GHSERAL + GHSERAG + 8GHSERAG$	[23]
	$\begin{array}{l} {}^{0}G_{Al:Al:Cu}^{GAMMA_D83} = -300716 + 3907 - 527\ln\left(T\right) \\ +5GHSERAL + 8GHSERCU \end{array}$	[45]
	${}^{0}G_{Al:Al:Cu}^{GAMMA,D83} = -280501 + 379.6T - 52T ln (T) $ +4GHSERAL + 9GHSERCU	[45]
	${}^{0}L_{Al:Al,Cu:Ag}^{GAMMA\_D83} = 23000 + 6110T - 1061T \ln(T) + 1.115T^{2}$	[23]
	${}^{0}\textit{L}_{Al:Cu:Ag,Cu}^{\text{GAMMA\_D83}} = 23000 + 6110T - 1061T \ln(T) + 1.115T^2$	[23]
GAMMA_H (Al) <sub>4</sub> (Al, Cu) <sub>1</sub> (Ag, Cu) <sub>8</sub>	$^0G_{Al:Al:Ag}^{GAMMA\_H} = -10000 + 5GHSERAL + 8GHSERAG$	[23]
	${}^{0}G_{ALCu:Ag}^{GAMMA,H} = 183000 + 4430T - 766T \ln(T) + 0.8T^{2} + 4GHSERAL + GHSERCU + 8GHSERAG$	[23]
	${}^{0}G_{ALAECu}^{GAMMA,H} = -219258 - 45.5T$ +SCHSERAL + 8GHSERCU	[45]
	${}^{0}G_{ALCUC_{U}}^{GAMMA,H} = -200460 - 58.5T$ +4CHSERAL + 9GHSERCU	[45]
	${}^{0}L_{A1:A1(D1:A2)}^{GAMMA.H} = 23000 + 6110T - 1061T \ln(T) + 1.115T^{2}$	[23]
	${}^{0}L_{ALCU}^{GAMMA_H} = 23000 + 6110T - 1061T \ln(T) + 1.115T^2$	[23]
	${}^{0}\textit{L}_{Al:Cu:Ag,Cu}^{GAMMA\_H} = 23000 + 6110T - 1061T \ln(T) + 1.115T^2$	[2

better shape memory characteristics than other Cu-based alloys [48], the results of experimental determination of phase transition temperatures and structural characteristics for the samples chosen along three vertical sections with constant copper content of 70, 80 and 90 at% are presented in this paper.

#### 2. Experimental

All alloy samples were prepared by induction melting of the starting metals in graphite crucibles under argon atmosphere. Constituent metals were of following purities: Cu – 99.99%, Al – 99.99%, Ag – 99.99%. In order to improve compositional homogeneity, the alloys were melted and cooled repeatedly. The samples masses were 3 g with total metal losses less than 1%.

The phase transformation temperatures of the as-cast alloy samples were determined by DTA method using NETZSCH STA 449F1 Jupiter instrument under following conditions: argon atmosphere, heating rate 10<sup>0</sup>C/min, reference material – alumina.

Scanning electron microscopy was done using SEM TESCAN VEGA TS 5136MM instrument with simultaneously analyzing of the chemical composition by energy dispersive spectrometry (Bruker spectometer) at accelerating voltage of 20 kV. Point analysis by EDS was performed in ten or more points depending of sample, for each phase and average value was calculated.

#### 3. Theoretical basis

Computation of Ag–Al–Cu phase diagram in this paper was done using CALPHAD method [42,43].

CALPHAD method is based on calculation of the Gibbs energy of a phase as a function of its composition, temperature and pressure. Gibbs energy data for all phases appearing in the investigated system should be stored as polynomial functions in the thermodynamic database. When this is fulfilled, calculation of phase equilibria is done using constrained minimization of system's Gibbs energy method [42,43].

All phases in the Ag–Al–Cu ternary system considered for thermodynamic calculation of phase equilibria with their crystallographic data and thermodynamic models are presented in Table 1.

Gibbs energies of pure metals Ag, Al and Cu in their stable and metastable phases from SGTE database [44] were used. Optimized thermodynamic parameters from literature, used for calculation of the Ag–Al–Cu phase equilibria in this study, are shown in Table 2.

Fig. 1 shows calculated phase diagrams of binary boundary systems Ag–Al, Ag–Cu and Al–Cu using optimized thermodynamic parameters from Table 2.

#### 4. Results and discussion

Heating and cooling curves obtained by DTA measurements had been analyzed. Every sample was subjected two times to the heating and cooling regime to check the reproducibility of results. Better reproducibility was obtained for heating regime and therefore heating curves were used for determination of phase transition temperatures. Phase transitions temperatures were read using software delivered with the instrument. The total experimental error of the method has been estimated to be  $\pm 2$  °C. The DTA results are presented in Table 3.

The solidus temperatures were taken from the extrapolated onset on heating, while other phase transitions temperatures were taken from the peak maximum temperature [47].

Calculated vertical sections with determined phase transition temperatures from the present DTA measurements are presented in Fig. 2. It can be seen that liquidus temperatures obtained by DTA, are in accordance with calculated values in all cases.

Vertical section with constant copper content of 70 at% presented in Fig. 2(a) shows that there are two areas of primary crystallization – Liquid + (Cu) and Liquidus +  $\beta$ . Predicted liquidus and solidus temperatures are in good agreement with experimentally measured temperatures.



Fig. 1. Calculated phase diagram of binary system: (a) Ag-Al, (b) Ag-Cu, (c) Al-Cu.

Calculated phase diagram of the section with constant copper content of 80 at% (Fig. 2(b)), shows wide region of primary crystallization Liquid + (Cu) and small region of Liquidus +  $\beta$ . Also, an area of copper – based solid solution (Cu) is presented. It can be noticed that experimentally measured solid temperatures are slightly lower compared to the calculated values in the area of (Cu) – copper-based solid solution.

Fig. 2(c) represents vertical section with constant copper content of 90 at%. There is one area of primary crystallization Liquid + (Cu), one high temperature region of copper – based solid

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DTA results for the investigated alloys of the Cu-Al-Ag ternary system.

Sample composition (at%)		Temperature (°C)			
		Solidus (peak onset)	Other phase transitions (peak maximum)	Liquidus (peak maximum)	
Cu = 70%					
Al	Ag				
6	24	777.0	-	932.0	
12	18	769.8	-	927.2	
18	12	775.6	549.7, 554.3	946.8	
<i>Cu</i> = 80%					
4	16	790.0	-	952.0	
8	12	790.9	-	989.8	
12	8	788.6	-	1003.7	
16	4	908.9	788.0, 843.8	1026.1	
<i>Cu</i> = 90%					
2	8	758.3	-	1023.0	
4	6	752.7	-	1040.9	
6	4	971.7	-	1047.5	
8	2	991.8	-	1061.0	
2 4 6 8	8 6 4 2	758.3 752.7 971.7 991.8	- - - -	1023.0 1040.9 1047.5 1061.0	

solution (Cu), and one wide region of two coexisting solution phase: silver – based solid solution (Ag) and copper – based solid solution (Cu): (Ag) + (Cu).

Selected DTA curves recorded during samples heating are presented in Fig. 3.

As can be seen in heating curve for the alloy sample  $Cu_{70}A_{16}A_{24}$  (Fig. 3a), melting of the alloy starts by reaching of the first peak

onset at temperature of 777.0 °C and finishes by reaching the second peak maximum at 932.0 °C. Analogous thermal behavior is presented in Fig. 3b for the heating curve of  $Cu_{80}Al_8Ag_{12}$  alloy sample, where measured solidus and liquidus temperatures are 790.9 °C and 989.8 °C, respectively. In Fig. 3c, DTA heating curve for the alloy sample  $Cu_{90}Al_4Ag_6$  is shown. The temperature of 752.7 °C, which can be associated to solidus transitions (first peak),



Fig. 2. Calculated vertical sections of the Cu-Al-Ag ternary system compared with DTA results from the present study: (a) Cu = 70 at%; (b) Cu = 80 at%; (c) Cu = 90 at%.



Fig. 3. DTA heating curves for some investigated samples: (a),  $Cu_{70}Al_6Ag_{24}$  (b)  $Cu_{80}Al_8Ag_{12},$  (c)  $Cu_{90}Al_4Ag_6,$  (in at%).



Fig. 4. Calculated isothermal section of ternary Cu–Al–Ag system at 25  $^{\circ}$ C with signed nominal compositions of investigated samples.



Fig. 5. SEM micrographs of as-cast al1loy samples: (a)  $Cu_{70}Al_{12}Ag_{18}$ , (b)  $Cu_{80}Al_{12}-Ag_{8}$ , and (c)  $Cu_{90}Al_4Ag_6$  (in at%).

was taken from the extrapolated onset on heating, while liquidus temperature, 1040.9 °C, is represented by the maximum of the second peak and associated with the end of the (Cu)-solution phase melting. It can be noticed from DTA measurements, that all investigated alloy samples are melted in wide temperature region (about 150°), with presented good agreement between experimental and calculated phase transition temperatures.

The isothermal section of ternary Cu–Al–Ag system at room temperature, calculated using CALPHAD method and optimized thermodynamic parameters from Table 2, with overall compositions of investigated alloys samples, is shown in Fig. 4.

Microstructure of alloys samples is investigated using scanning electron microscopy with energy dispersive X-ray spectroscopy. SEM micrographs of selected samples with marked phases, determined using SEM-EDS, are presented in Fig. 5.

According to SEM micrographs (Fig. 5) representing the microstructure of the as-cast alloys from the Cu-rich region of the Cu–Al–Ag system ( $Cu_{70}Al_{12}Ag_{18}$ ,  $Cu_{80}Al_{12}Ag_8$  and  $Cu_{90}Al_4Ag_6$ ), two phases are visible – predominant dark phase, corresponding to copper-based solid solution, (Cu), and bright-grey phase corresponding to silver- based solid solution (Ag).

Average compositions of the dark and bright-grey phases for the samples given in Fig. 5 are respectively: Fig. 5a) 84.9Cu–10Al–5.1Ag and 13Cu–2.5Al–84.5Ag, Fig. 5b) 85.6Cu–9.7Al–4.7Ag and 20Cu–2.5Al–77.5Ag, and Fig. 5c) 93Cu–2Al–5Ag and 17.4Cu–2.6Al–80Ag. Small amount of aluminum presented in investigated alloys is dispersed uniformly in the microstructure, as can be seen in presented Fig. 5a–c.

Considering previously described SEM-EDS results, it can be noticed that similar microstructure was obtained for all other investigated samples in the sections with 70%, 80% and 90 at%Cu. There is a qualitative agreement between experimental and calculated results. Only in the case of three samples  $Cu_{80}Al_{16}Ag_4$ ,  $Cu_{70}$ .  $Al_{18}Ag_{12}$  and  $Cu_{70}Al_{24}Ag_6$ , obtained results for the  $\gamma$ D8-phase wasn't clearly identified, although expected by calculation (Fig. 4). The reason for such disagreement may be the fast cooling of the samples, so it was not possible to reach equilibria state at low temperatures.

## 5. Conclusions

Copper – rich region of the ternary Cu–Al–Ag system was explored in the present study. Phase diagram of this system has been investigated using thermodynamic prediction according to CALPHAD method and experimentally by DTA. Phase transition temperatures of the selected as-cast alloy samples along three vertical sections were determined using DTA when a reasonable agreement between calculated and experimentally obtained transition temperatures was achieved. Similar microstructure was obtained by SEM-EDS for all investigated samples, showing the presence of two solid solutions based on copper and silver, with qualitative agreement between experimental and calculated results.

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