

Research Article

Jolanta Romanowska*

Calorimetric study on Bi-Cu-Sn alloys

<https://doi.org/10.1515/htmp-2019-0052>

Received Dec 05, 2017; accepted Mar 28, 2019

Abstract: The paper presents results of calorimetric investigation of the Bi-Cu-Sn system by means of differential scanning calorimetry (DSC) at the temperature interval 25–1250°C. Values of liquidus, solidus and invariant reactions temperatures, as well as melting enthalpies of the selected alloys were determined. Microstructure investigation of the alloys were performed by the use of a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS).

Keywords: Bi-Cu-Sn alloys, calorimetry, microstructure

1 Introduction

The toxicity of lead containing solders resulted in the EU decision to prohibit the use of lead in electronic products and the use of high-lead containing Pb-Sn solders for high temperature soldering applications. Therefore, intensive studies of prospective multicomponent lead-free systems, mainly based on tin plus bismuth or zinc are in progress. Moreover, copper substrates are commonly applied in the electronic devices. In this view, it is important to understand the interactions between these solders and the substrate which, in turn, implicates the investigations of the phase equilibria in the Bi-Cu-Sn system.

The Sn-Bi are the most promising lead-free solder alloys due to the low melting temperature, good tensile strength, creep resistance and low cost [1, 2]. The eutectic point of Sn-58Bi solder – 139°C [3] is lower than 183°C for the eutectic Pb-Sn solders [4]. Unfortunately, frangibility and poor ductility limits application of these alloys [5].

Interfacial reaction kinetics between molten Sn-58Bi solder and Cu substrates was studied by Li *et al.* [6]. Their investigations revealed that an intermetallic layer formed at the interface between molten Sn-58Bi solder and Cu substrate includes Cu₆Sn₅ and Cu₃Sn intermetallic com-

pounds. The statistical thickness variations of both the Cu₆Sn₅ and Cu₃Sn phases follow the normal distribution, except at the extreme of the cumulative probability curves. This suggests that various mechanisms play their roles relatively independently during the different stages of the interfacial reaction, with the weak interdependence between them affecting only the extrema. Cu₃Sn single crystal consists of high ultimate strength depending on the material directions and strain rate [7], whereas Cu₆Sn₅ fibres cause increment in tensile strength [8]. Thermodynamic properties of liquid Bi-Cu-Sn alloys were determined by calorimetric method by Flandorfer *et al.* [9]. Measurements were carried out using a Calvet type microcalorimeter and a drop calorimetric technique. Partial and integral enthalpies of mixing of liquid ternary alloys at 750°C were determined. The data were fitted on the basis of an extended Redlich-Kister-Muggianu model for substitutional solutions. Tin activities were measured by the electromotive force measurements (e.m.f.) method by Kopyto *et al.* [10] for three cross-sections with constant x_{Bi}/x_{Cu} ratio equal to 1/3, 1/1 and 3/1 and for various tin contents. Bismuth activities in liquid Cu-Sn-Bi alloys were measured by Wnuk and Romanowska at 1100°C by means of the vapour saturation method for $x_{Bi} < 0.15$. The interaction parameters ϵ_{Bi}^{Cu} and ϵ_{Bi}^{Sn} were determined by the least squares method. The experimental values of ϵ_{Bi}^{Cu} and ϵ_{Bi}^{Sn} were compared with values calculated on the basis of the “central atom” theory [11]. Romanowska [12] measured bismuth activities in Bi-Cu-Sn liquid alloys by means of the vapour saturation method at 1100°C, 1150°C and 1200°C. These results were coupled with the data from the literature for binary systems Bi-Cu, Bi-Sn and Cu-Sn in order to obtain a thermodynamic description of the ternary liquid alloys Bi-Cu-Sn, using the geometrical Muggianu approach [13]. Values of Redlich-Kister [14] ternary ${}^0L_{Bi,Cu,Sn}^L$, ${}^1L_{Bi,Cu,Sn}^L$, ${}^2L_{Bi,Cu,Sn}^L$ parameters were estimated on the basis of experimental values. The Muggianu extension of the Redlich - Kister formula with parameters values obtained in this work [12] well describes experimental points.

This paper presents results of calorimetric investigation of the Bi-Cu-Sn system by means of differential scanning calorimetry (DSC) at the temperature interval 25–1250°C, values of liquidus and solidus temperature, the melting enthalpy, temperatures of invariant reactions and

*Corresponding Author: Jolanta Romanowska: Rzeszów University of Technology, Faculty of Mechanical Engineering and Aeronautics, 2, W.Pola street, 35-959 Rzeszow, Poland; Email: jroman@prz.edu.pl

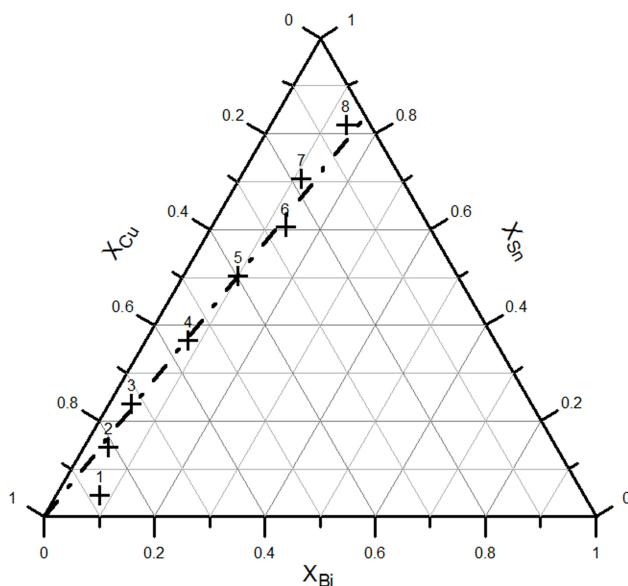


Figure 1: Chemical composition of alloys.

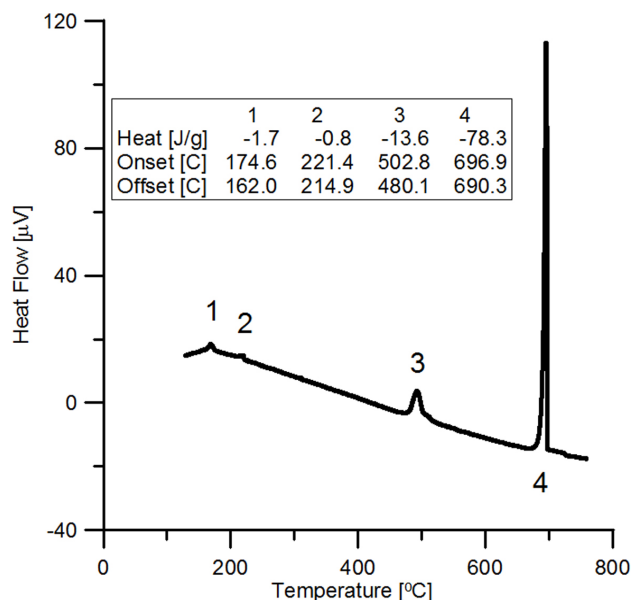


Figure 2: DSC curve of the alloy no 2.

microstructure of the selected alloys. Some microstructure analysis of the alloys was performed using a scanning electron microscope Hitachi S-3400 equipped with an energy dispersive spectroscopy (EDS). The presented research is a contribution to an overall examination of Cu-Ni-X-Y systems ($X, Y = \text{Sn, Bi, Zn, Ti}$) in relation to development of a new lead free solders in the frame of the COST action MP0602.

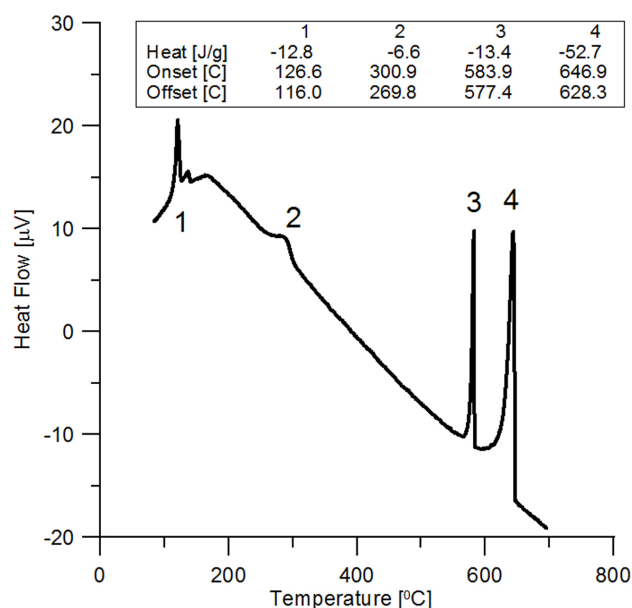


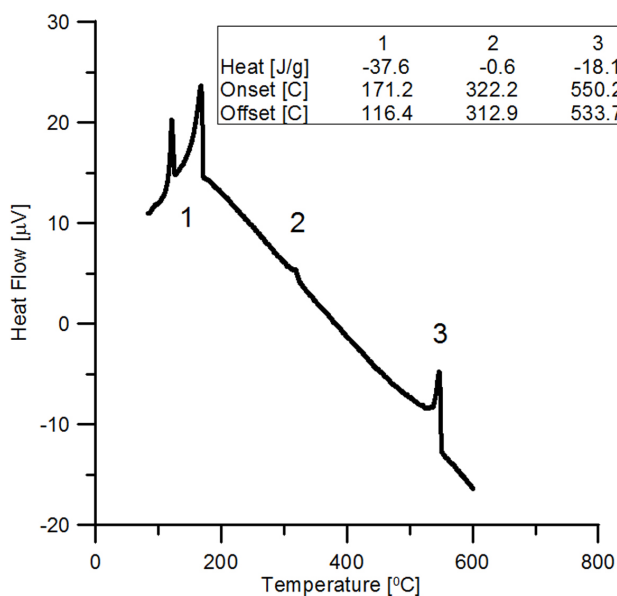
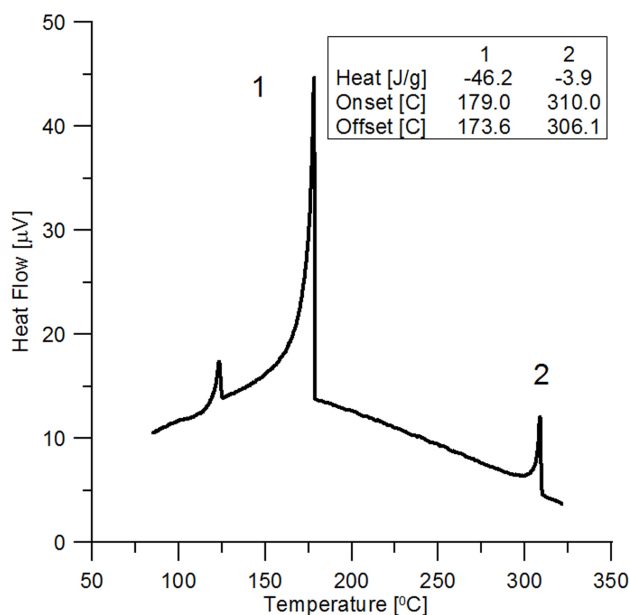
Figure 3: DSC curve of the alloy no 4.

2 Experiments

The investigated alloys were prepared by melting copper and tin of purity 99.999 mass percent in a vacuum furnace and saturating them by vapour bismuth at 1200°C for 2 h under reduced argon pressure [15–17]. Chemical compositions of samples are presented in Figure 1 and Table 1. The compositions of samples were determined by weighing (the accuracy of weighing was 10^{-4} g) and a spectroscopic method by use of the plasma spectrometer ULTIMA 2 HORRIBA JOBIN YWON of accuracy 0.0001 mole fraction. The DSC measurements [18] were carried out using the differential scanning calorimeter [19] Setaram Set Sys Evolution under the following conditions: the argon flow 50ml/min, samples' masses about 50 mg, the temperature interval 25–1250°C. The heating rate was 10°C/min and the cooling rate was 15°C/min. Before realizing the DSC experiments the sensitivity and temperature calibration were performed by measuring the heat of melting and melting temperature of pure indium, tin, bismuth, zinc, aluminum, silver and gold using the same working conditions. Solidus and liquidus temperatures as well as enthalpies of melting were determined by the analysis of thermal effects revealed in DSC curves (see Figures 2–5). Liquidus and solidus temperatures were established as onset and offset temperatures respectively. Temperatures of invariant reactions were established as onset temperatures, whereas thermal effects of phase transitions (ΔH) were determined as the area limited by the DSC curve and the baseline divided by the mass of the sample.

Table 1: Experimental temperatures and heat effects of phase transformations in Bi-Cu-Sn alloys.

Sample no	x_{Bi}	x_{Sn}	Temperature of onset and offset of phase transformation [°C]	Heats of phase transformations [J/g]	Solidus [°C]	Liquidus [°C]	ΔH^M [J/g]
1	0.0788	0.0450	222.3-213.1	-10.19	764.2	902.7	84.0
2	0.0444	0.1445	174.6-162.0	-1.7	696.9	690.3	78.3
			221.4-214.9	-0.8			
			502.8-480.1	-13.6			
3	0.0407	0.2351	222.0-231.2	-0.99	669.3	679.9	90.6
			639.2-628.4	-26.87			
4	0.0771	0.3684	126.6-116.0	-12.8	628.3	646.8	52.6
			300.9-269.8	-6.6			
			583.9-577.4	-13.4			
5	0.0997	0.5036	318.0-307.4	-0.81	578.9	602.5	41.4
6	0.1352	0.6048	171.2-116.4	-37.6	550.2	533.7	18.1
			322.2-312.9	-0.6			
7	0.1134	0.7065	124.0-118.5	-3.36	480.6	489.1	10.1
			178.3-158.6	-33.01			
			330.8-320.2	-1.35			
8	0.1381	0.8182	120.0-124.0	-2.36	306.1	310.0	3.9
			179.0-173.6	-46.8			

**Figure 4:** DSC curve of the alloy no 6.**Figure 5:** DSC curve of the alloy no 8.

3 Results and discussion

Exemplary DSC curves with thermal effects evoked by heating of the alloys are presented in Figures 2-5. Experimental temperatures and heat effects of phase transformations in Bi-Cu-Sn alloys are collected in Table 1 and compared

graphically (Figures 6-8) against values of phase transitions or invariant reactions temperatures of binary alloys constituting the investigated ternary alloy, that is Bi-Cu, Bi-Sn and Cu-Sn alloys [20, 21]. Values of invariant reaction temperatures in ternary alloys were marked with dots (Figures 6-8). The number and chemical composition of

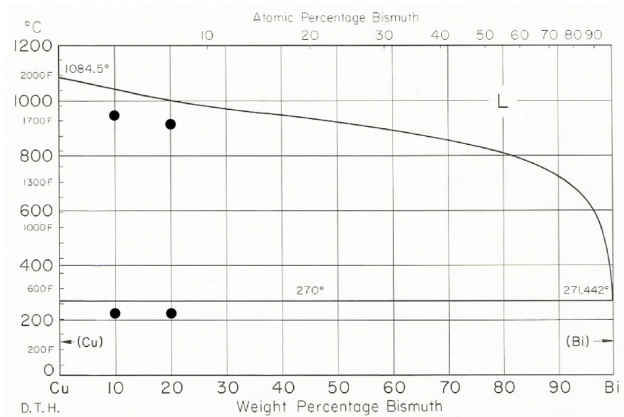


Figure 6: Bi-Cu phase diagram [21] with experimental points (from the left) 1 and 2, Table 1.

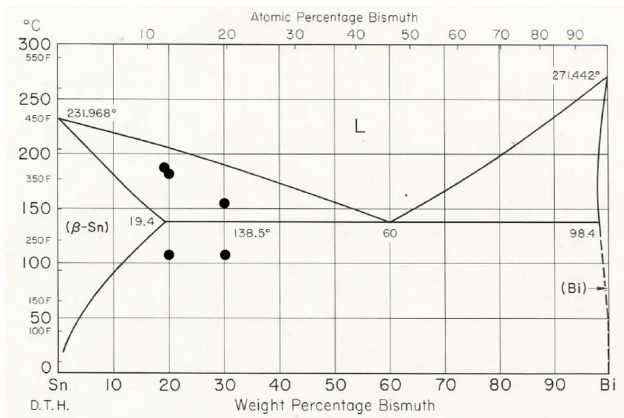


Figure 7: Bi-Sn phase diagram [21] with experimental points (from the left) 7 and 8, Table 1.

ternary alloys is presented in Table 1. From the left : Figure 6 - alloys no. 1 and 2; Figure 7 - alloys no. 7 and 8; Figure 8 – alloys no. 3, 4, 5, 6 and 8. Lines in these figures refer to binary alloys [21]. Upper points in Figure 6 represent transition from one-phase region (liquid phase) to two-phase region (liquid + (Cu)), whereas lower points indicate transition from two phase region (liquid + (Cu) to another two phase region ((Cu) + (Bi)). In Figure 7 upper points represent transition from one phase region (liquid phase) to two phase region (liquid + (β -Sn)), whereas lower points indicate transition from two phase region (liquid + (β -Sn) to another two-phase region ((β -Sn) + (Bi)). In Figure 8 upper points represent transition from one phase region (liquid phase) to two phase region (liquid + (Cu₃Sn) – 2 right points, or from 2 phase region (liquid + γ) to (liquid + (Cu₃Sn)). Points in the middle indicate transition from two phase region (liquid + (Cu₃Sn) to other two phase regions: ((Cu₃Sn) + (Cu₆Sn₅) – left points) and ((Cu₆Sn₅) + liquid – right points). Whereas lower points

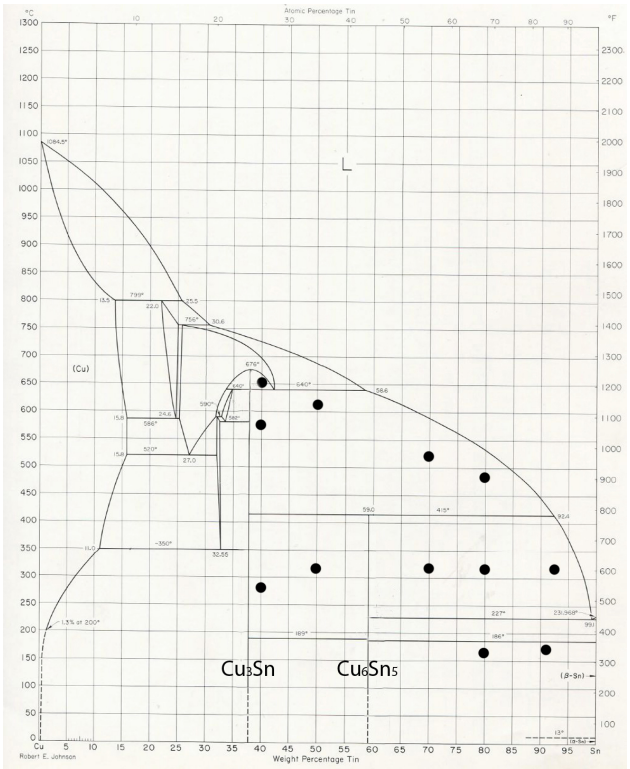


Figure 8: Cu-Sn phase diagram [21] with experimental points (from the left) 3,4,5,6,8 Table 1.

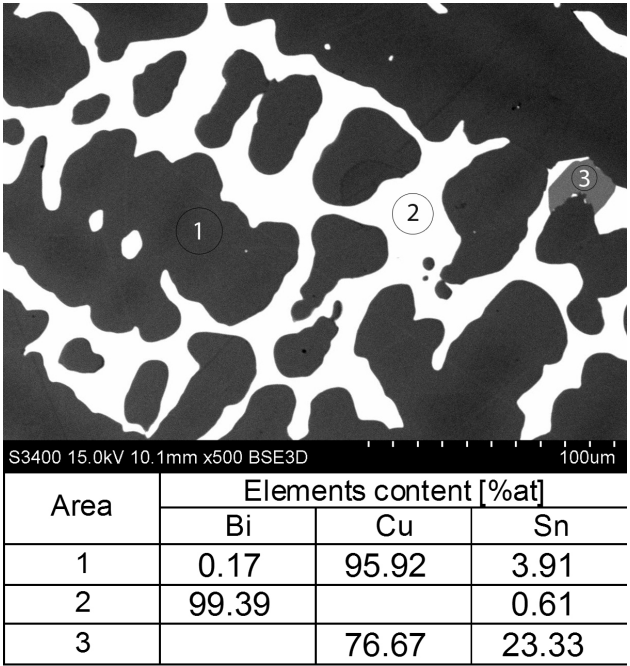


Figure 9: Microstructure of the alloy no. 1.

are the evidence of transition from ((Cu₆Sn₅) + liquid) to (Cu₆Sn₅) + Sn. Values of the enthalpy of melting ΔH^M are higher for alloys of higher Cu concentration, and smaller

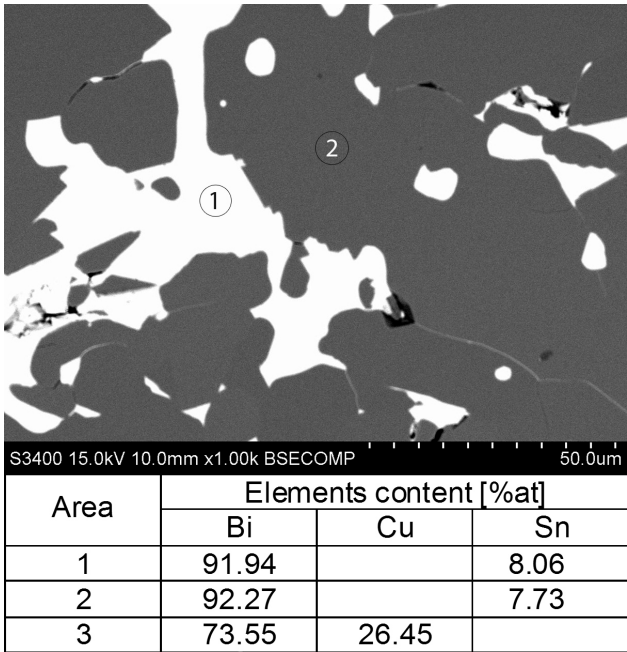


Figure 10: Microstructure of the alloy no. 3.

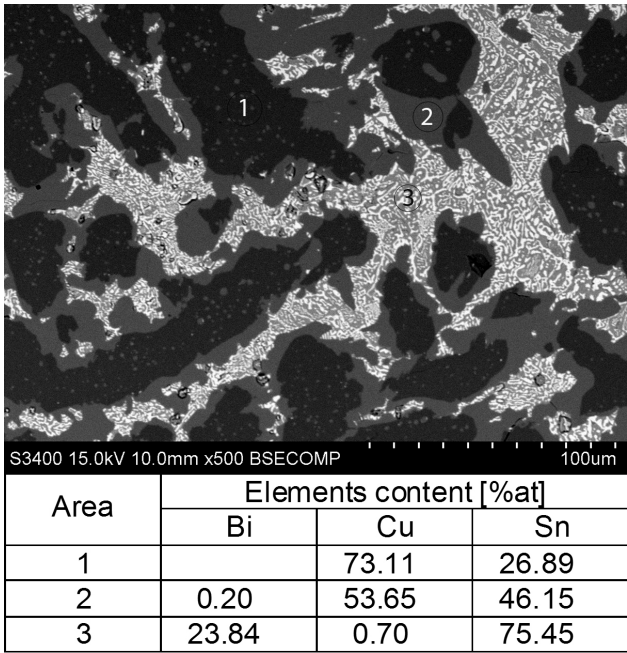


Figure 11: Microstructure of the alloy no. 4.

for alloys of smaller Cu concentration, but for all alloys are significantly smaller than for pure components ($\Delta H_{Cu}^M = 208$ J/g, $\Delta H_{Sn}^M = 60$ J/g, $\Delta H_{Bi}^M = 54$ J/g [21]). For an alloy no. 2, containing more than 80% at Cu, enthalpy of melting and temperatures of liquidus and solidus are significantly smaller than for pure Cu. For alloys of high Sn concentration, for instance alloy no. 8, containing more than 80% at Sn liquidus and solidus temperatures are higher

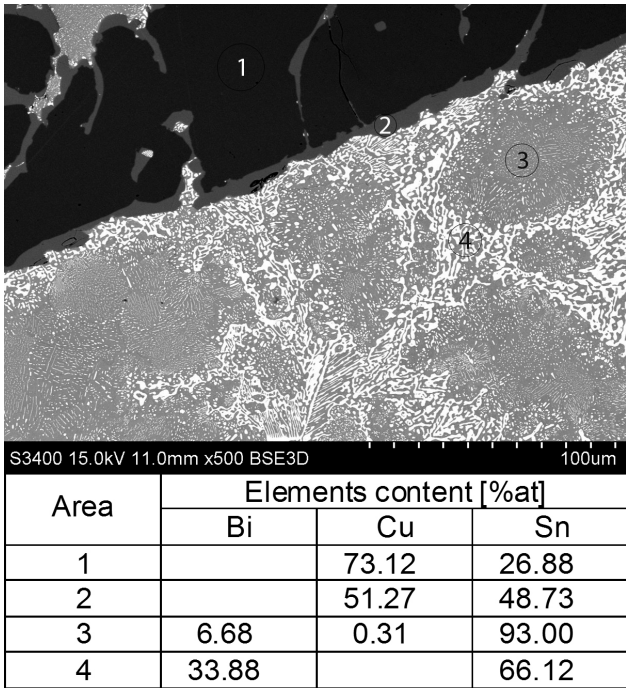


Figure 12: Microstructure of the alloy no. 6.

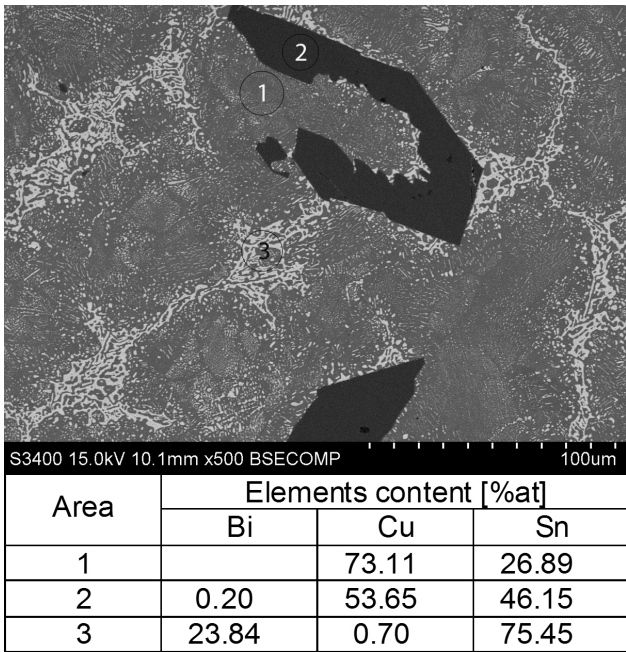


Figure 13: Microstructure of the alloy no. 8.

than for pure tin ($T^M = 232^\circ\text{C}$), but the enthalpy of melting is very small (only 3.9 J/g). For alloy no. 1 ($x_{Bi} = 0.078$, $x_{Sn} = 0.045$) the reported liquidus temperature (902°C) is lower than liquidus temperature of the binary Cu-Sn (Figure 8) and Bi-Cu alloys of similar compositions (Figure 6). The microstructure and phase analysis of alloy no. 1 and

3 (Figure 9, 10) revealed the existence of the Bi-Cu eutectic ($x_{Bi} = 0.993x$, $x_{Cu} = 0.006$). In binary Bi-Cu alloy this eutectic reaction takes place at 270°C, whereas in the investigated ternary alloys (no. 1-3) the reaction temperatures was 222°C (Table 1). It seems that tin decreased the liquidus and eutectic temperatures in the investigated alloys. Moreover, there is a strong evidence of an invariant reaction in ternary alloys of $0.36 < x_{Sn} < 0.82$ at the 120°C (alloys 4–8, Table 1). The microstructure analysis performed by the energy-dispersive spectrometer (EDS) (Figure 11, 12, 13) revealed the existence of the phase of the following composition: $x_{Sn}=0.75$, $x_{Bi}=0.23$ (alloy no. 4), $x_{Sn}=0.66$, $x_{Bi}=0.34$ (alloy no. 6) and $x_{Sn}=0.69$, $x_{Bi}=0.31$ (alloy no. 8) that corresponds to the eutectic composition of the binary Bi-Sn alloy ($x_{Sn}=0.611$ [19]). It may be regarded as an evidence of the eutectic reaction taking place at 120°C, that is lower than in binary Bi-Sn alloy (138.5°C, see Figure 7). It looks like copper decreased the temperature of the eutectic transformation in Bi-Sn alloys. Although bismuth content in the investigated alloys is low ($x_{Bi} < 0.14$), it significantly influences the temperatures of invariant reactions taking place in binary Cu-Sn alloys. Phases of the following compositions: $x_{Cu} = 0.51$, $x_{Sn} = 0.49$ (alloy no. 6, Figure 12) and $x_{Cu} = 0.54$, $x_{Sn} = 0.46$ (alloy no. 8, Figure 13) correspond to the Cu_5Sn_6 phase. This phase is formed in Cu-Sn at 186°C, but in the investigated alloys, invariant temperatures were reported at 179°C, (alloy no. 7, 8), and 171.1°C and for alloy no. 6 (two peaks for Bi-Sn and Cu-Sn eutectics are between 115.9°C and 171.1°C) (Figure 4, 5; Table 1). Cu_3Sn in binary Cu-Sn is formed at 640°C, but in Bi-Cu-Sn at lower temperatures (from 639.2°C to 583.9°C), alloys no. 3, 4, Figure 8, 10. Bismuth decreased the temperature of invariant reactions, so intermetallic phases are formed in lower temperatures; the bigger the bismuth content, the lower the reaction temperature.

4 Conclusions

The calorimetric study has shown that small bismuth addition to Cu-Sn alloys does not influence the liquidus temperature, but enthalpies of melting of the investigated alloys are significantly smaller than for pure elements. Microstructure and chemical composition analysis of the phases revealed the same phases as in binary alloys, that is Cu_3Sn , Cu_5Sn_6 intermetallic phases and Bi-Cu and Bi-Sn eutectics, but they are formed at lower temperatures. Addition of the third element always decreased the temperature of invariant reaction or phase formation even copper, the melting point of which is higher than other elements

(1083°C), decreased the temperature of eutectic reaction in Bi-Sn alloys. Heat effects, enthalpies of melting and liquidus and solidus temperatures determined in this study will be used in thermodynamic description of the Bi-Cu-Sn system according to the CALPHAD method in the frame of the COST Action MP0602.

Acknowledgement: This work was supported by the Polish Ministry of Science and Higher Education (Project no. N N507 44 3834). This work was conducted in the frame of the European action COST MP0602 “Advanced Solder Materials for High Temperature Application (HISOLD)”, project “Design, process and control in a multiscale domain of Cu-Ni-X-Y (X, Y = Sn, Bi, Zn, Ti) based alloys”.

References

- [1] F. Yang, L. Zhang, Z. Liu, S. Zhong, J. Ma, L. Bao, *Advances in Materials Science and Engineering*, (2016) article ID 9265195
- [2] Y. Goch, A. Haseb, M. Sabri, *Electrochimica Acta*, 90 (2013) 265
- [3] M.H. Roh, J.P. Jung, W. Kim, *Microelectronic Reliability* 54 (2014) 265
- [4] M. Kitajima, T. Shono, *Microelectronic Reliability*, 45 (2005) 1208
- [5] X. Chen, F. Xue, J. Zhou, Y. Yao, *Journal of Alloys and Compounds*, 633 (2015) 377
- [6] Li, S.H. Mannan, M.P. Clode, D.C. Whalley, D.A. Hutt, *Acta Materialia*, 55 (2006) 2907
- [7] H.C. Heng, F.C. Yu, W.H. Chen, *Journal of Materials Science*, 47 (2012) 3103
- [8] X. Hu, K. Li, Z. Min, *Journal of Alloys and Compounds*, 566 (2013) 239
- [9] H. Flandorfer, A. Sabbar, C. Luef, M. Rechchach, H. Ipser, *Thermochimica Acta*, 472 (2008) 1.
- [10] M. Kopyto, G. Garzeł, L.A. Zabdyr, *J. of Mining and Metallurgy*, 45 B (2009) 95
- [11] G. Wnuk, J. Romanowska, *Arch. Metall. Mater.*, 51 (2006) 503
- [12] J. Romanowska, *Arch. Metall. Mater.* 56 (2011) 87
- [13] Y.M. Muggianu, M. Gambino, J.P. Bros, *J. Cnim. Phys.*, 72 (1975) 83
- [14] O. Redlich, T. Kister, *Ind. Enging. Chem.*, 40 (1948) 345
- [15] B. Onderka, T. Pomianek, J. Romanowska, G. Wnuk, J. Wypartowicz, *Arch. Metall. Mater.*, 49 (2004) 143
- [16] G. Wnuk, J. Romanowska, T. Pomianek, *J. Chem. Thermodyn.* 35 (2003) 711
- [17] J. Midura, T. Pomianek, *J. Chem. Thermodyn.* 26 (1994) 507
- [18] W. Zielenkiewicz, *Calorimetry*, Institute of Physical Chemistry of the Polish Academy of Sciences (2008)
- [19] A. Concustell, M. Zielińska, A. Revesz, L.K. Varga, S. Surniach, M.D. Baro, *Intermetallics* 12 (2004) 1063
- [20] Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, J. Vizdal, *Atlas of Phase Diagrams for Lead-Free Solders*, COST office 2008
- [21] *Metals Handbook*, AMS Handbook Committee, Metals Park Ohio, 1973.