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Experimental Investigations by Wet-Chemical Synthesis of Ternary Bi-Cu-X System (X = Sb, Sn, Zn): Part II: Bi-Cu-Sn

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Running title: **Lead Free Solders**

Abstract
Investigation of the Bi-Cu-Sn system by different methods is presented. The experimental results are connected with lead-free solder materials. The Bi is a low melting element and this is reason to include as elements appropriate for investigations of lead free solder materials. The Cu substrate is regularly used in microelectronic industries, but it is also used as a constituent of multi-component lead-free solders.The Sn is element with more good quality and with wide application in lead-free solders. The system are investigate using wet-chemical analyze to determined quantity of Bi and electro gravimetric method to determined quantity of Cu in the mixture of Bi(III), Cu(II) and Sn(II) hydroxides. The mixtures are investigated for nano particles, but only microparticles are determined.

Practical applications
Lead free solders are materials, which will replace the toxic Sn-Pb based alloys. This is a current challenge and requires a thorough study of the new prospective materials properties.

Key words: ternary systems, lead-free solder materials, micro and nano particles

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Introduction

The Bi-Cu-Sn ternary system is system belongs to the groupstudied from the interaction of solder with substrates. Some studies of ternary system fined in literature connected with thermodynamics and phase equilibria investigations.

Interfacial reaction kinetics between molten Sn-Bi solder and Cu substrates was studied (Li et al, 2006). Thermodynamic properties of the liquid Bi-Cu-Sn alloys were determined by calorimetric method (Ipser at al., 2007), tin activities were measured by e.m.f. method (Kopyto et.al.,2009) and Bi activities in liquid Cu-Sn-Bi alloys were determined (Wnuk et al., 2006).

Due to the frequent use of Cu as a substrate material in electronics, it was important to understand the interactions between the solders and the substrates, based on the knowledge of the phase equilibria, thermodynamics and other characteristics of the Bi-Cu-Sn system (Živković et al., 2010). The results of thermodynamic analysis and characterization of Bi-Cu-Sn alloys as advanced lead-free solder materials for high temperature application were presented in this paper. Wet-chemical methods for the synthesis of nano- and micro-sized particles may play an important role in novel lead-free materials as solders (Official Journal of Lead Free Solders, 2003).

To achieve the development of new solders, a detailed knowledge of the reactions between the metallization layer and the soldering materials is important. The use of Bi in microelectronic solders is also prospective. This was especially valid for the lead-free low-temperature solders that were now under development. The typical lead-containing low-temperature solders until now were lead-rich Pb-Sn alloys (90-95 wt % Pb) whose melting temperature was around 578 – 583 K. They show excellent reliability but must be replaced due to environmental concerns (Gandova et al.,2010, Masalski, 1996).

Materials and methods

The co-precipitation of Bi, Cu and Sn were performed in this investigation. The initial solutions were hydroxides of the pertinent elements. It was found that Cu and Bi can be co-precipitated quantitatively, but Sn seen in different place in co-precipitation. The substances obtained in such a way will be analyzed by wet-chemistry analysesfor Bi and electrolysis for Cu elements and used % methods to determined quantity of Sn.

Some preliminary experiments were performed on the co-precipitation of Bi, Cu and Sn. Pure $Bi(NO_3)_3.5H_2O$, $CuSO_4.5H_2O$and $SnCl_2.2H_2O$ were used as starting substances. Weigh quantities of three salts were mixed mechanically and afther that thay presipetated with different quantities NaOH.

Co-precipitations were performed by two series samples. First co-precipitates salts with stoichiometric quantity NaOH and second by NaOH with 20 % more quantity.

Solution of NaOH was added slowly by drops (around 1 hour for each precipitation). The chemical reactions interaction presented below.

$$Bi(NO_3)_3 + 3NaOH \rightarrow Bi(OH)_3 + 3NaNO_3 \quad (1)$$
$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4 \quad (2)$$
$$SnCl_2 + 2NaOH \rightarrow Sn(OH)_2 + 2NaCl \quad (3)$$

The samples preliminary compositions are presented in Table 1.

Table 1. Sample compositions (referred to the content of the metals)

N°	At. % Bi	At. % Cu	At. % Sn	System
1	25	45	30	Bi-Cu-Sn
2	20	10	60	Bi-Cu-Sn
3	50	10	40	Bi-Cu-Sn
4	10	70	20	Bi-Cu-Sn
5	30	60	10	Bi-Cu-Sn

The precipitations after preparation were with green-gray colour for all samples. After thatthe next step was filtration using Buhner filter. The synthesised compositions of hydroxides were dried for 24 hours at 105 °C. As a consequence, the chemical compositions of the precipitated hydroxide mixtures might notcorrespond exactly to the chemical compositions of the pertinent elements. This could be explained by a gradual dehydration of the corresponding hydroxides and the formation of CuO (Takaku et al., 2007).

Quantitative analyses of the Bi and Cu content in the precipitates weredone by volumetric and gravimetric methods, respectively. For the determination of Bi dry precipitate mixture were dissolved in concentrated nitric acid. Water was added to adjust the volume to 10 cm^3. The solution was titrated by EDTA (complexon III) using as indicatorxsilenolorange. For different series experiments used different quantities EDTA. For experiment with regular NaOH after titration used around 10 cm^3 EDTA, but for 20 % more NaOH around 9-10 cm^3. Five parallel analyses were performed for each sample. For the determination of copper, samples of the hydroxide mixture were

prepared and analyzed by electrolytic process.Chosen alloy with preliminary determined quantity Cu between 0.05 and 0.1 g dissolve in nitric acid (1:1). After that two electrodes were dept in the same solution. Cathode was preliminary weigh. The time of electrolytic process prolong 45 minutes. When the electrolyzes finished the quantity Cu was determined by weigh cathode after electrolytic process.

Optical digital microscope, like the Bresser Junior USB Hand-held Microscope was used to determined particles size.

Results and discussion

Fig. 1 presented Bi-Cu-Sn phase diagram with chemical compositions on samples according the preliminary composition on hydroxides (Table 1).

Table 2 and Table 3 presented experimental quantitative analyses for determination of Bi with titration samples using EDTA after obtained of hydroxides. In Table 2 were described theoretical and experimental mass of each sample co-precipitated with stoichiometric quantity NaOH. Table 3 described the same values in second series of samples co-precipitated with 20 % more quantity NaOH.

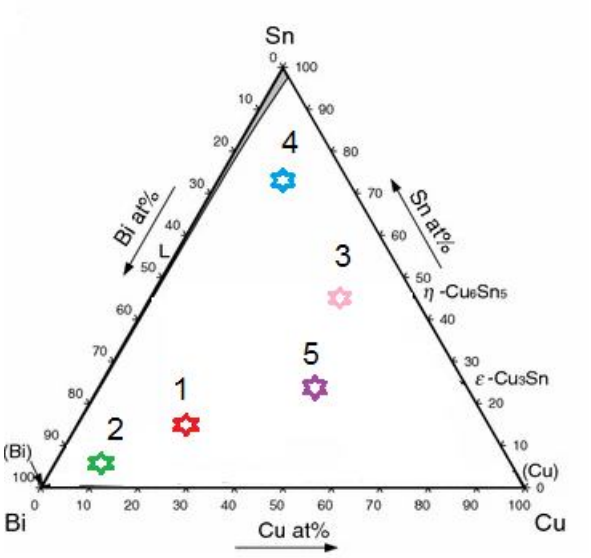

Figure1. Bi-Cu-Sn phase diagram with chemical composition of samples 1-5.

Table 2. Investigation quantity of Bi in system Bi:Cu:Sn with stoichiometric quantity NaOH, by titrating with EDTA.

Sample N^{o}	m(Bi),g theoretical	m(Bi),g after titration	% Bi
1	0.0312	0.0226	72.44
	0.0326	0.0208	63.81
	0.0314	0.0219	69.75
	0.0307	0.0219	71.34
	0.0312	0.0224	71.79
2	0.0316	0.0231	72.89
	0.0306	0.0219	71.76
	0.0314	0.0219	69.92
	0.0311	0.0213	68.53
	0.0317	0.0217	68.59
3	0.0306	0.0226	73.75
	0.0309	0.0222	71.76
	0.0308	0.0209	67.79
	0.0308	0.0207	67.08
	0.0306	0.0196	64.02
4	0.0311	0.0215	69.22
	0.0311	0.0226	72.68
	0.0311	0.0205	65.76
	0.0308	0.0215	69.89
	0.0308	0.0180	58.71
5	0.0309	0.0213	68.97
	0.0311	0.0198	63.68
	0.0308	0.0202	65.69
	0.0315	0.0205	64.92
	0.0306	0.0198	64.72

Table 3.Investigstion quantity of Bi in system Bi:Cu:Sn with NaOH 20 % more, by titrating with EDTA.

Sample N^o	m(Bi), g theoretical	m(Bi), g after titration	% Bi
6	0.0297	0.0189	63.78
	0.0302	0.0198	65.57
	0.0306	0.0194	63.31
	0.0307	0.0203	65.87
	0.0309	0.0202	65.48
7	0.0308	0.0195	63.60
	0.0306	0.0200	65.43
	0.0306	0.0208	68.24
	0.0309	0.0202	65.48
	0.0306	0.0189	61.90
8	0.0306	0.0195	64.02
	0.0297	0.0185	62.33
	0.0306	0.0193	63.31
	0.0306	0.0198	64.72
	0.0304	0.0191	63.02
9	0.0306	0.0215	70.34
	0.0309	0.0217	70.36
	0.0306	0.0198	64.72
	0.0309	0.0206	66.88
	0.0315	0.0204	64.92
10	0.0296	0.0185	62.54
	0.0306	0.0185	60.50
	0.0306	0.0185	60.50
	0.0315	0.0189	60.13
	0.0307	0.0181	58.90

The experimental results obtained after investigation of quantity Bi in system shows that the Bi was loose from hydroxides mixtures. And in two serious of experiments seen the same results. The more investigations of system were necessary and aim was to found way to determined probably three elements separate and after that prepared mixture of hydroxides. As was mentioned before the Cu content in the samples was analyzed after electrolyzes. The results show that Cu loses around 10-15 % compared with theoretical calculations.

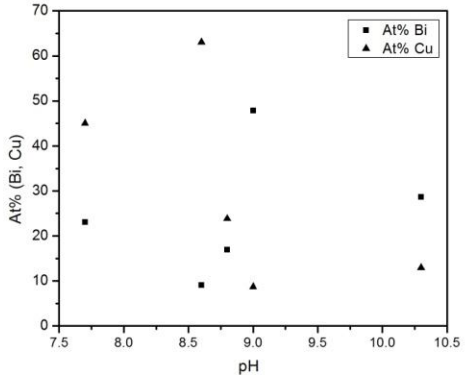

Figure2. Experimental pH of the solutions after filtration versus chemical compositions of Samples 1-5. Figure exhibited precipitated hydroxides with stoichiometric quantity NaOH.

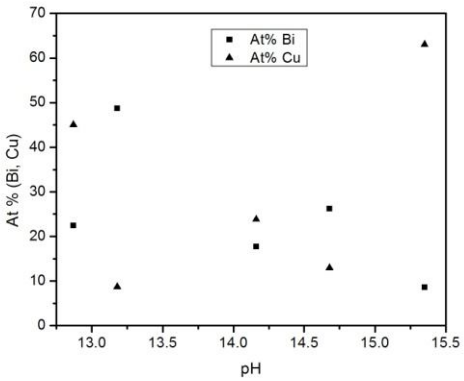

Figure3. Experimental pH of the solutions after filtration versus chemical compositions of Samples 1-5. Figure exhibited precipitated hydroxides with NaOH 20 % more.

The determinations performed for two series samples. First for samples with stoichiometric quantity NaOH and second for sampleswith 20 % more quantity NaOH. Experiments show that samples synthesizes with 20 % more quantity NaOH loose the same % Cucompared with preliminary calculation for element content in the samples. These results probably connected with influence of two elements each other.

Experimental data of the pH value of the aqueous solutions after precipitation of samples with different quantities of NaOH were shown in Figs. 2 and 3. The figures show the Bi and Cu in at. % calculated and compared the quantity Bi and Cu after experimental titration. The experiments exhibited differences between quantity of Bi, before and after preparation of hydroxides. This wasprobably connected with lose some quantity in hydroxides mixture.

Conclusion

On the basis of phase diagram studies, Bi-Cu-Sn lead-free solders were investigated. The experimental results obtained in this work shows that prepared mixtures of hydroxides exhibit influence in each element to other. Particle size of alloys determined as micro sizes, but reduction with hydrogen was necessary to use for determined pure metal particles.

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