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## THERMAL, STRUCTURAL AND ELECTRICAL PROPERTIES OF SOME Bi-Cu-Ni ALLOYS

### STRUKTURA, WŁAŚCIWOŚCI TERMICZNE I ELEKTRYCZNE WYBRANYCH STOPÓW Bi-Cu-Ni

The Bi-Cu-Ni ternary system belongs to the group of potential Cu-Ni-based advanced lead-free solder materials for high temperature application. In this study microstructure investigation of the slow-cooled Bi-Cu-Ni samples was done using SEM-EDS analysis. The samples compositions were chosen along three cross-sections with molar ratio Cu:Ni=1:3, 1:1 and 3:1. The experimentally obtained phase structure was compared with the results of thermodynamic calculation according to CALPHAD method. Also, new results regarding thermal and electrical properties investigations of these alloys are presented in this paper, based on DSC and electroconductivity measurements.

*Keywords:* Bi-Cu-Ni alloys, lead-free solders, characterization

Trójskładnikowe stopy Bi-Cu-Ni należą do grupy potencjalnych zaawansowanych bezołowiowych materiałów do lutowania w wysokiej temperaturze opartych na stopach Cu-Ni. Analizę mikrostruktury wolno schłodzonych próbek Bi-Cu-Ni wykonano za pomocą technik SEM-EDS. Do badań wybrano próbki charakteryzujące się stałym molowym stosunkiem Cu:Ni=1:3, 1:1 i 3:1. Doświadczalnie otrzymaną strukturę faz porównano z wynikami obliczeń termodynamicznych metodą CALPHAD. Ponadto, nowe wyniki dotyczące badań właściwości cieplnych i elektrycznych stopów zostały przedstawione w tym artykule, na podstawie pomiarów DSC i przewodności elektrycznej.

### 1. Introduction

Among environmental friendly alternatives to Sn-based solders, one of the potential lead-free systems for high temperature application is the Bi-Cu-Ni system, especially in the frame of the study of phenomena occurring at the interface between Pb-free solders and various substrate materials, i.e. Cu, Ni (P), Pd and Au, formed within the interconnect during fabrication and service [1].

Therefore, this system has been examined recently in the frame of COST MP0602 "HISOLD" project [1] and described in recent references [2-4]. Gao et al. [2] investigated phase equilibria of the Bi-Cu-Ni system at 300, 400, and 500°C using metallography and electron probe microanalysis on equilibrated alloys and diffusion couples. Marković et al. [3] performed thermodynamic modeling of the Bi-Cu-Ni system using CALPHAD technique. Lately, the results of experimental thermodynamic investigation of Bi-Cu-Ni liquid alloys by means of vapour saturation method were reported by Romanowska [4], while Wnuk [5] presented experimental results of thermodynamic exploration of quaternary Cu-Ni-Bi-based alloys using the same method.

In this work, the SEM-EDS analysis was performed in order to examine the microstructure of slowly cooled Bi-Cu-Ni

ternary samples. The experimentally obtained results of microstructure investigation were compared with the calculated phase equilibria data at room temperature and good agreement was noticed. Also, thermal and electric properties of investigated samples were determined and the obtained results were discussed with respect to the results of microstructure analysis.

Having in mind the importance of knowledge on the advanced solder Bi-Ni based alloys [6] for the understanding of the processes occurring during soldering and during operation of the soldered devices, the results of these results could be of interest for further investigation of Bi-Cu-Ni ternary alloys.

### 2. Experimental

Selected Bi-Cu-Ni alloys from three sections from bismuth corner with molar ratio Cu:Ni = 1:3, 1:1 and 3:1, which composition and masses given in Table 1, have been experimentally investigated using SEM-EDS, DSC, and electrical conductivity measurements.

The samples were prepared by induction melting of metals with purity higher than 99.99%, under high purity argon atmosphere. The alloy samples were homogenized at 800°C for several hours under argon atmosphere and then slowly cooled

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to room temperature. The total mass losses of the prepared ingots were less than 1 mass%.

TABLE 1  
Composition and masses (in g) of investigated Bi-Cu-Ni samples

Section	Sample	Molar content, $x_i$			Mass (in g)		
		$x_{Bi}$	$x_{Cu}$	$x_{Ni}$	$m_{Bi}$	$m_{Cu}$	$m_{Ni}$
Cu:Ni=1:1	A1	0.100	0.450	0.450	1.6518	2.2603	2.0879
	D1	0.400	0.300	0.300	4.1704	0.9511	0.8786
	J1	0.900	0.050	0.050	5.8112	0.0982	0.0907
Cu:Ni=3:1	A2	0.100	0.675	0.225	1.6284	3.3424	1.0292
	C2	0.300	0.525	0.175	3.5378	1.8826	0.5797
	H2	0.800	0.150	0.050	5.5836	0.3184	0.0980
Cu:Ni=1:3	C3	0.300	0.175	0.525	3.5951	0.6377	1.7672
	F3	0.600	0.100	0.300	5.0373	0.2553	0.7075
	J3	0.900	0.025	0.075	5.8148	0.0491	0.1361

The DSC measurements were performed on a SDT Q600 (TA instruments) device. Alumina crucibles were used and measurements were performed under flowing argon atmosphere and heating rate 5°C/min. In order to test reproducibility of the results every measurement was repeated, but no significant temperature deviation was found between the first and repeated series of DSC measurements. The masses of investigated samples were 25-30 mg.

SEM analysis was done using JEOL JSM 6460 apparatus (Oxford Instruments) with energy dispersive spectrometry, EDS of resolution up to 10 nm, acceleration voltage of 0.2-30 kV and magnification up to 300000 x.

Electrical conductivity of investigated samples was measured using the standard procedure using apparatus – SIGMATEST 2.069 (Foerster) eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals, based on complex impedance of the measuring probe with diameter of 8 mm. The measurements were done at room temperature.

The samples were prepared without using of etching agents for structure development.

### 3. Results and discussion

Microstructure examination of alloys in the investigated ternary Bi-Cu-Ni system was done analytically, using CALPHAD method and experimentally, using SEM-EDS. Equilibrium phase diagram of the ternary Bi-Cu-Ni system at room temperature was calculated using optimized thermodynamic parameters published in Ref. [3]. The calculated phase diagram with overall compositions of the experimentally investigated alloys is shown in Fig. 1.

Microstructure investigation of the chosen Bi-Cu-Ni alloys was performed using SEM-EDS analysis, as given in Fig. 2. The elemental compositions of the coexisting phases were determined and the obtained results are given in Table 2. The experimental accuracy of presented results is  $\pm 2$  at.%. According to these results, dark areas in SEM microphotographs are related to (Cu) and (Ni) solid solution phases,

while the areas of light nuances respond to BiNi and Bi<sub>3</sub>Ni compounds, as signed in Fig. 2. Comparison between experimentally determined phase structure from this study and the results of thermodynamic calculation shows mutual qualitative agreement. However, the experimentally determined solubility of Cu in BiNi compound is somewhat higher than calculated one shown in Fig. 1. Also, experimentally obtained solubility of Bi and Ni in (Cu) and Bi and Cu in (Ni) solid solution is higher than calculated, given in Fig. 1. The reason for this difference is probably slow diffusion kinetics for these alloys at room temperature and long time needed to reach equilibrium state.

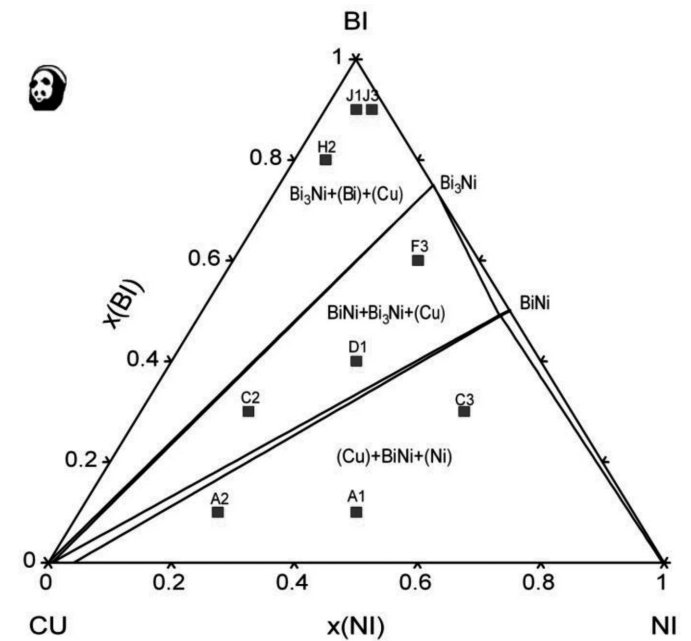


Fig. 1. Calculated phase diagram of the ternary Bi-Cu-Ni system at 25°C with marked overall compositions of the investigated samples

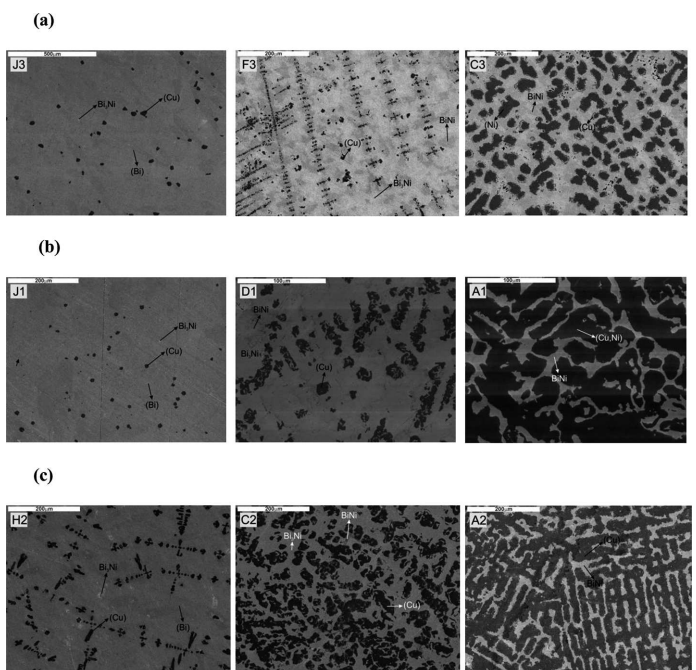


Fig. 2. SEM microphotographs of chosen samples in investigated sections with molar ratio Cu:Ni equal to 1:3 (a), 1:1 (b) and 3:1 (c)



(LIQUID  $\leftrightarrow$  FCC\_A1 + BI<sub>3</sub>NI + RHOMBO\_A7) – ternary eutectic at 269°C and (LIQUID + BINI  $\leftrightarrow$  FCC\_A1 + BI<sub>3</sub>NI) – quasi-peritectic at 430°C were confirmed.

The results of electrical conductivity measurements are presented in Table 4, where the values obtained for three series and determined average values are given. As can be seen, with increase of bismuth content the decrease in electrical conductivity is noticeable for all samples in three investigated sections, which is in accordance with the electrical conductivity of pure bismuth ( $\approx$  0,867 MS/m [7,8]). Such dependence is a consequence of higher amounts of intermetallic compounds and bismuth in the structure of samples that reduce their electrical conductivity.

TABLE 4

The results of electrical conductivity measurements of investigated samples

Sample	Electrical conductivity (MS/m)			
	I series	II series	III series	Average value
A1	1.678	1.675	1.681	1.678
D1	1.173	1.172	1.173	1.173
J1	0.907	0.904	0.902	0.904
A2	2.826	2.824	2.830	2.827
C2	1.523	1.520	1.522	1.522
H2	1.005	1.006	1.006	1.006
C3	1.193	1.198	1.202	1.198
F3	0.958	0.959	0.959	0.959
J3	0.888	0.890	0.889	0.889

#### 4. Conclusion

The Bi-Cu-Ni alloys from three sections from bismuth corner with molar ratio Cu:Ni = 1:3, 1:1 and 3:1 have been

characterized using different experimental methods, such as DSC, SEM-EDS and electrical conductivity measurements. By thermal analysis, characteristic phase transition temperatures and liquidus temperatures were determined. All existing phases in this ternary system were confirmed by structural analysis. Dark phase in all investigated samples is related to Cu-Ni-based FCC\_A1 phase, while light phase is related to Bi-Ni-based compounds BiNi and Bi<sub>3</sub>Ni. Electrical conductivity decreases with bismuth concentration increase in all investigated alloys.

Obtained results present a contribution to more complete knowledge of thermal, structural and electrical properties of Bi-Cu-Ni alloys as a new potential lead-free solder material for high temperature application.

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