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Ni–Bi–Zn TERNARY SYSTEM INVESTIGATION USING DIFFUSION COUPLES TECHNIQUE

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Abstract

An investigation of Ni–Bi–Zn system was performed using a diffusion couples technique and the diffusion paths were constructed. For that purpose diffusion couples consisting of solid Ni and liquid Bi–Zn phase were annealed at 450 °C. The phase and chemical compositions of the contact zone were determined by scanning electron microscope. The diffusion layers found in the Ni–Bi–Zn ternary system were Beta1, γ-Ni_5Zn_{21} and liquid. No intermetallic compounds in Bi–Ni binary phase diagram were observed.

Keywords: Solders; Ternary system Ni/Bi–Zn; Ddiffusion couples.

1. Introduction

The main scope of this work is an investigation of the Ni–Bi–Zn ternary system, which a promising candidate for the development of lead-free solders [1], using diffusion couples technique. Nickel is often used for as a substrate in electronic devices and as such is among the components of future solder alloys. Zink and bismuth are prospective lead replacements in the solders composition. The three elements Ni, Bi, and Zn as well as the respective binary phase diagrams were included in the thermodynamic database developed by the European concerted action SOLDERS [2] and reliable thermodynamic optimizations are available. The element Ni is appropriate to including in thermodynamic optimization with other elements. Hu at al. [3] prepared thermodynamic reassessment of the Mn–Ni–Si system using Calphad method including Ni in ternary system with elements as Mn and Si appropriate for high temperature solders. This work presents the first investigation of the solid/liquid Ni–Bi–Zn system using diffusion couples technique and the new data regarding the relevant diffusion paths.

2. Literature review

2.1 Bi–Ni system

The Bi–Ni phase diagram (Fig. 1) is relatively simple. Portevin [4] and Voss [5] constructed the liquidus in the central and Ni-rich side of the system. It should be noted that the data of both authors show an almost horizontal segment of the liquidus at roughly 1650 K from around 12 to 40 at.% Bi. Hägg and Funke [6] studied the structure and stoichiometry of the nickel-bismuth solid compounds (Table 1). Feschotte and Rosset [7] data, obtained by contemporary methods, disagree with the slight change of the liquidus temperature which was expected for the range from around 50 to 75 at.% Bi. They also found that the BiNi-phase homogeneity range is 51±0.3 at.% Bi. More experimental results

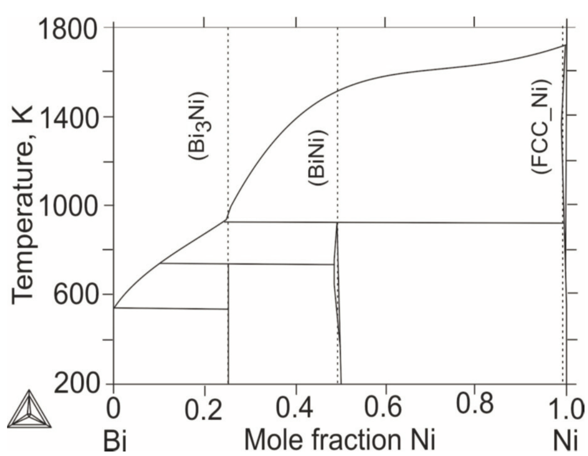

Figure 1. *Bi–Ni phase diagram calculated using the optimization from Vassilev et al. [10]. The dash lines shows phase boundaries between intermetallic compounds according to Table 1.*

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and thermodynamic optimizations of this system were reported recently by Vassilev et al. [8-10]. Seo et al. [11] estimated the thermodynamic parameters of the binary system using a three-sublattice model for the phase BiNi.

2.2 Bi–Zn system

The Bi–Zn phase diagram (Fig. 2) has been extensively studied [12-14] and the first thermodynamic optimization was performed by Malakhov [15]. The system is eutectic type but exhibit a miscibility gap in the liquid phase. Kim and Sunders [16] tried to assess the phase separation region using two interaction parameters only but their approximations were inconsistent. The system was reassessed by Vizdal at al. [2, 17] using the results of Malakhov's work [15] as well as their own experimental data. Lately, Minic at al. [18] reassessed the system in order to optimize the Bi–Sb–Zn phase diagram.

2.3 Ni–Zn system

The Ni–Zn phase diagram (Fig. 3) was studied by Vassilev et al. [19, 20]. Four intermediate phases are found in that system: β, β1, γ, and δ. The β phase is a high-temperature phase - stable between 675°C and 1040°C. The β_1 phase is a low-temperature phase while the γ phase is a γ-brass type with homogeneity range from 74-85 at.% Zn. The δ phase is formed at 88.9 at.% Zn and 489°C through a peritectic reaction and has a very narrow homogeneity range.

2.4 Ni–Bi–Zn system

Few studies of the ternary Ni–Bi–Zn system are reported [21, 22]. An isothermal section of the Ni–Bi–Zn ternary system at 450°C was determined experimentally using the equilibrated alloys approach [21]. It was found that the liquid phase was in equilibrium with all phases of the Ni–Zn binary system except the (Ni). Experimental results also indicated that the third element, Zn or Bi, is almost insoluble in the Ni–Bi and Ni–Zn intermetallic compounds. Xu et al. [22] investigated isothermal sections at 600 ^{0}C and 750 ^{0}C stem. The electromigration effect on the Zn/Ni and Bi/Ni interfacial reactions was studied by Chen using reaction couple techniques [23]. Three phases, β_1-NiZn, γ-Ni_5Zn_{21}, and δ-$NiZn_8$ formed in the Zn/Ni couples reacted at 150°C and 200°C between 4 h and 360 h, and the reaction layers grew thicker with longer reaction time. Only $NiBi_3$ phase was found in the Bi/Ni couples reacted at 150, 170, 185 and 200°C. However, the growth rate of the $NiBi_3$ phase was enhanced in the Bi/Ni couples reacted at 150° C and 170° C using 300 A/cm^2 electric current. A mathematical model was proposed to describe the electromigration effect on the crystal growth of the intermetallic compounds. The physical parameters in the models were determined by optimization based on experimental measurements, and the results indicated that the values of the apparent effective charge of Bi and Ni decreased sharply with the temperature increase.

Table 1 shows the pure elements and the binary phases with their concentration in the three binary systems.

The phase diagrams of the binary systems within the ternary Ni–Bi–Zn system are shown on Figs. 1–3.

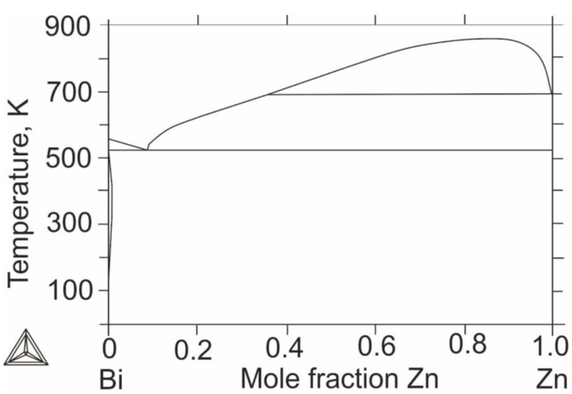

***Figure** 2. Bi–Zn phase diagram calculated using the parameters from Malakhov [15].*

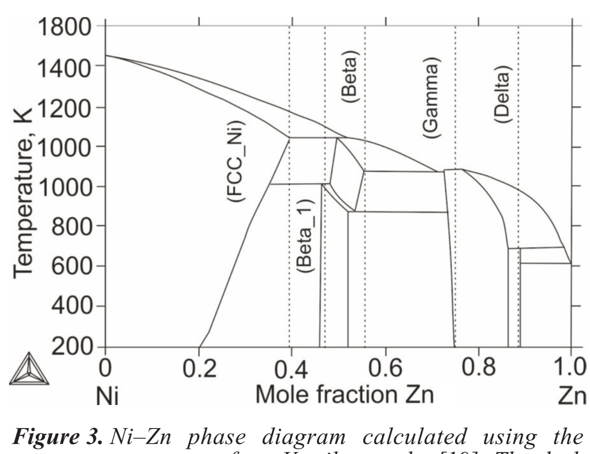

***Figure 3.** Ni–Zn phase diagram calculated using the parameters from Vassilev et al. [19]. The dash lines shows phase boundaries between the intermetallic compounds according to Table 1.*

Table 1. *Description of the binary phases relevant to the Ni–Bi–Zn system*

Phase	Binary system	Composition at. %	Pearson Symbol	Space group	Prototype	Literature
(Bi)	Bi–Zn	»100 at.% Bi	hR2	$R\bar{3}m$	aAs	[24]
η-Zn	Bi–Zn	»100 at.% Zn	hP2	$P6_3mmc$	Mg	[24]
(Ni)	Ni–Bi	» 0 ат % Bi	cF4	$Fm\bar{3}m$	Cu	[24]
NiBi	Ni–Bi	47-51 at. % Bi	hP_4	$P6_3/mmc$	NiAs	[25]
$NiBi_3$	Ni–Bi	75 at. % Bi	oP16	Pnma	$CaLiSi_2$	[25]
(Bi)	Ni–Bi	»100 at. % Bi	hR2	$R\bar{3}m$	αAs	[24]
(Ni)	Ni–Zn	0 » 39at. % Zn	cF4	$Fm\bar{3}m$	Cu	[25]
β (NiZn)	Ni–Zn	47.5 » 58.5 at. % Zn	cP2	$Fm\bar{3}m$	CsCl	[24]
β1(NiZn)	Ni–Zn	45.5 » 52 at. % Zn	tP2	P4/mmm	AuCu	[24]
$\gamma(Ni_5Zn_{21})$	Ni–Zn	70 » 85 at. % Zn	cI52	$I\bar{4}3m$	Cu_5Zn_8	[25]
$\delta(NiZn_8)$	Ni–Zn	89 at.% Zn	mC28	C2/m	$CoZn_{13}$	[25]

3. Experimental

Several experimental procedures were used for the samples preparation. Each solid part consisted of cubic solid Ni while the respective liquid part contained preliminary synthesized Bi–Zn alloys with certain Bi:Zn ratios (Table 2). Pellets of Bi and granules of Zn were used for the synthesis. Three different compositions, corresponding to different Bi/Zn ratios, from the Bi–Zn melts were chosen. A resistance furnace with electronic regulator and temperature controller PXR was used. The Bi–Zn alloys were prepared first and used as the liquid phase part of the diffusion couples. The bismuth granules and the zinc pellets were cut in small pieces. The samples were placed in evacuated and sealed borosilicate tubes, annealing at 450^0 C for 3 days, quenched in cold water, and cut. Evacuated and sealed borosilicate glass tubes, containing the already reacted Bi–Zn alloys (around 10 g) and nickel were annealed in the same resistance furnace. A solid/liquid (Ni)/(Bi+Zn) diffusion couples were formed as a solid (Ni), liquid (Bi+Zn) type. The annealing of the diffusion couples was performed at 450^0 C for 8 days and at 450^0 C for 14 days. After the annealing the ampoules were quenched in cold water. After that the samples were analyzed by scanning electron microscope (SEM). The chemical composition of selected spots was measured by energy-dispersive spectroscopy (EDS) analysis. The results of the analysis are shown in Table 3.

Table 2. *Thermal treatment of the diffusion couples in the system Ni–Bi–Zn. Time – duration of the annealing in days; Ratio – atomic ratio between bismuth and zinc content of the liquid phase;* t, ^{0}C – annealing temperature.

No	Time, d	Ratio (Bi:Zn)	t, ^{0}C
1	8	1:09	450
2	8	9:01	450
3	8	1:03	450
4	8	3:01	450
5	14	1:09	450
6	14	9:01	450

4. Results and Discussion

Three phases except (Ni) were observed (Table 3).

Selected micrographs obtained by SEM are shown in Figs. 4-7. Two liquid phases were found after the annealing depending on the chemical composition. It should be added that the liquid phase of samples with L-Bi is more rich in Bi (0.889 to 0.964 mole fractions Bi) and shows a smooth liquid structure while the samples with L-Zn are more rich in Zn (0.936 to 0.979 mole fractions Zn) and show rough liquid structure. It can be concluded that those particular samples followed different crystallization paths.

Figs 4, 5 shows the micrographs of samples 1 and 2 (Table 2). Three phases are observed – Beta1, Gamma and Liquid (Fig. 4). The intermetallic compounds belong to the system Ni–Zn. No intermetallic compounds from the system Bi–Ni were observed. Similarly, according to Fig. 5 the sample is rich in Bi but no Bi–Ni intermetallics are found.

Figs. 6 and 7 present two samples heated for a longer time (Table 2). No binary Bi–Ni phases were observed. Fig. 6 depicts the liquid part of the sample 5. In Fig. 7 small crystals belonging to γ-Ni_5Zn_{21} phase situated in Bi-rich liquid phase can be seen.

***Table 3.** Results of the microscope analysis of the Ni/Bi–Zn diffusion couples. No – specimen's number; X_{ij} – constituent's mole fraction obtained in selected spots; phases – identified phases; Remarks – supplementary notes.*

Nº	Spectrum Nº	X_{Ni}	X_{Bi}	X_{Zn}	Phases	Remarks
1	1	0.991	0.001	0.008	Fcc-Ni	Dark layer
	2	0.488	0.001	0.511	Beta 1	White grey layer
	3	0.136	0.008	0.856	γ - Ni_5Zn_{21}	Dark grey layer
	4	0.163	0.001	0.836	γ - Ni_5Zn_{21}	Dark grey layer
	5	0.168	0.001	0.831	γ - Ni_5Zn_{21}	Dark grey layer
	6	0.039	0.025	0.936	L-Zn	White grey matrix
2	1	0.982	0.009	0.009	Fcc-Ni	Dark layer
	2	0.103	0.014	0.883	γ - Ni_5Zn_{21}	Dark grey particle
	3	0.01	0.952	0.038	L-Bi	White matrix
3	1	0.988	0.003	0.009	Fcc-Ni	Dark layer
	2	0.146	0.019	0.835	γ - Ni_5Zn_{21}	Dark grey layer
	3	0.122	0.01	0.868	γ - Ni_5Zn_{21}	Dark grey layer
	4	0.486	0.003	0.511	Beta 1	White grey layer
	5	0.494	0.01	0.496	Beta 1	White grey layer
	6	0.01	0.038	0.952	L-Zn	White grey matrix
4	1	0.986	0.014	0	Fcc-Ni	Dark layer
	2	0.13	0.015	0.855	γ - Ni_5Zn_{21}	Dark grey particle
	3	0.012	0.964	0.024	L-Bi	White matrix
5	1	0.974	0.007	0.019	Fcc-Ni	Dark layer
	2	0.019	0.01	0.971	L-Zn	White grey matrix
	3	0.01	0.011	0.979	L-Zn	White grey matrix
	4	0.072	0.927	0.001	L-Bi	White matrix
	5	0.111	0.025	0.864	γ-Ni_5Zn_{21}	Dark grey particle
	6	0.108	0.017	0.875	γ-Ni_5Zn_{21}	Dark grey particle
6	1	0.941	0.033	0.026	Fcc-Ni	Dark layer
	2	0.029	0.946	0.025	L-Bi	White matrix
	3	0.032	0.027	0.941	γ-Ni_5Zn_{21}	Dark grey particle
	4	0.044	0.04	0.916	γ-Ni_5Zn_{21}	Dark grey particle
	5	0.046	0.889	0.065	L-Bi	White matrix
	6	0.124	0.025	0.851	γ-Ni_5Zn_{21}	Dark grey particle
	7	0.118	0.017	0.865	γ-Ni_5Zn_{21}	Dark grey particle

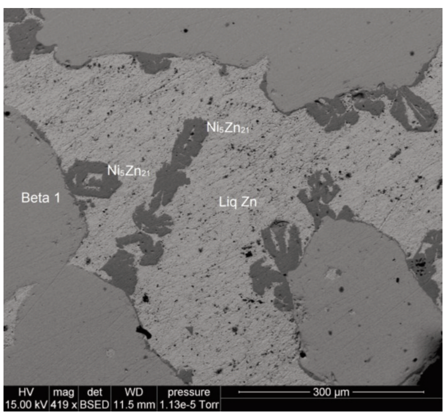

***Figure 4.** Micrograph of sample № 1 (Table 2) in back scattered electrons. The phases grown at 450° C for 8 days between pure solid Ni and liquid phase with Bi/Zn ratio of 1/9 are shown.*

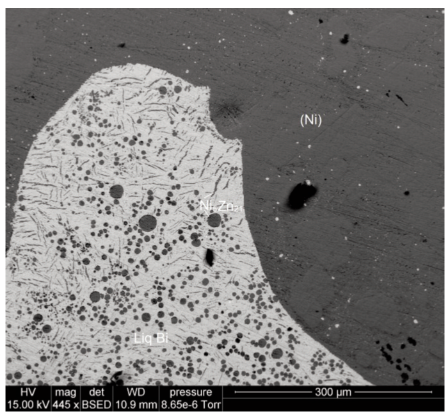

***Figure 5.** Micrograph of sample № 2 (Table 2) in back scattered electrons. The phases grown at 450 °C for 8 days between pure solid nickel and liquid phase with Bi/Zn ratio of 9/1 were shown.*

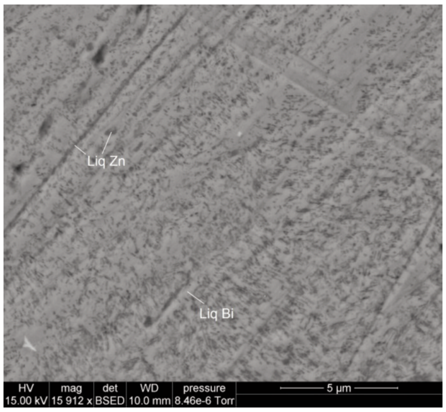

Figure 6. *Micrograph of the liquid phase part of sample № 5 (Table 2) in back scattered electrons. The darker areas are Zn–rich while the lighter are Bi–rich.*

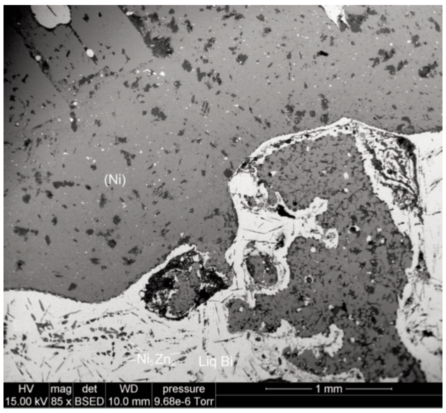

***Figure** 7. Micrograph of sample № 6 (Table 2) in back scattered electrons. The phases grown at 450 °C between pure solid nickel and a liquid phase with Bi/Zn ratio of 9/1 were shown.*

The calculated isothermal section of Ni–Bi–Zn system at 450^{o}C using the experimental results of Liu et al. [21] is presented on Fig. 8. Calculations were representative from data of Dinsdale at al. [2]. Only the binary parameters from the three binary systems were used for the calculations. All phases characteristic for the isothermal section at that temperature are presented, including the Bi–Ni and Ni–Zn intermetallics. According to the experimental results in this work, some intermetallic phases were not found. Liu et al. [21] annealed the alloys at 1100^{o}C for 30 hours, quenched in cold water and after that prepared new samples for 30 days at 450^{o} C. The difference in the experimental results between [21] and this work can be explained with the small enthalpies of formation of the Bi–Ni intermetallic compounds compared with strong, negative enthalpies of formation of the binary Ni–Zn phases [6, 14]. Additionally, the synthesis conditions were different.

The experimental results for samples 1-4 (Table 2) combined with the calculated phase diagram at the same temperature (450^{o}C) [21] were used to construct the diffusion paths in the ternary Ni–Bi–Zn system. Two diffusion paths pass along γ-Ni_5Zn_{21} phase and two along Beta1 and γ-Ni_5Zn_{21}. The diffusion paths presented into phase diagram (Fig. 8) were in agreement with the experimental results obtained in this work.

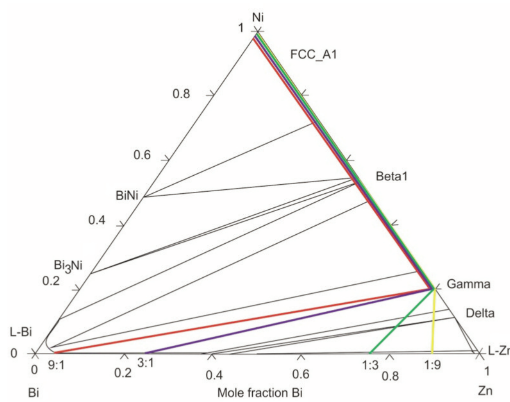

Figure 8. *Diffusion paths in the ternary system Ni–Bi–Zn connected with samples 1–4 (Table 2) heating at 450^{o} C (8d).*

5. Conclusion

Ternary diffusion couples Ni/Bi–Zn were prepared and investigated by scanning electron microscope. Experimental data about the diffusion paths were obtained.

In the Ni–Bi–Zn system diffusion paths pass through Ni–Zn compounds that can be explained by the large values of the Gibbs energies of formation of Ni–Zn compounds or by nucleation difficulties for the Bi–Ni phases.

Acknowledgments

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