A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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EXPERIMENTAL STUDY ON THERMODYNAMICS OF THE Cu-Ni-Sn-Bi LIQUID ALLOYS

BADANIA TERMODYNAMICZNE CIEKŁYCH STOPÓW Cu-Ni-Sn-Bi

The activity of Bi in dilute Cu-Ni-Sn-Bi alloys has been determined by the method of equilibrium saturation with metal vapour at T= 1398, 1448 and 1473 K. As the method of equilibrium saturation is a comparative one, it is necessary to have an appropriate reference mixture. The Cu-Bi alloy was accepted as the reference mixture. The interaction parameters ε_{Bi}^{Bi}, ε_{Bi}^{Ni} and ε_{Bi}^{Sn} were determined by the least squares method.
Keywords: activity, interaction parameter, multicomponent alloys

Aktywność bizmutu w ciekłych rozcieńczonych stopach Cu-Ni-Sn-Bi w temperaturze T=1398, 1448 i 1473K wyznaczono porównawczą metodą równowagowego nasycania, stosując stop Cu-Bi jako roztwór wzorcowy. Parametry oddziaływania ε_{Bi}^{Bi}, ε_{Bi}^{Ni} i ε_{Bi}^{Sn} wyznaczono metodą najmniejszych kwadratów.

1. Introduction

In recent years much effort was put into developing alternative lead-free solder alloys due to the environmental and health concerns on lead usage. Ternary, quaternary and higher order systems containing Sn, Zn, Sb, Bi, Cu and other elements have been examined, but there remain many systems deserving further investigations. Since many of multicomponent systems where promising Pb-free phases are expected to be found contain Bi and Zn, a thorough examination of systems with these elements should be carried out. This paper presents a part of a general examination of Cu-Ni-X-Y (X, Y = Sn, Bi, Zn, Ti) based alloys in relation to development of lead free solders. There is a lot of experimental data for binary, ternary or quaternary Cu-Ni-X-Y alloys [1-15], but there has been no data for the Cu-Ni-Sn-Bi system and this paper shows the results of experimental work on it.

2. Experiments

The analyzed alloys show considerable differences between vapour pressures of their elements. For instance at T=1473K: p^*_{Sn}= 9.4*10^{-3} hPa, p^*_{Ni}= 1.16*10^{-4} hPa, p^*_{Cu}= 3.95*10^{-3} hPa, p^*_{Bi}= 25.80 hPa [16]. As the vapour pressure of Bi is much higher than that of other elements, the activity measurements of Bi were carried out by the comparative method of equilibrium vapour saturation, that is a modified isothermal isopiestic method [4,8,10,11]. Apparatus used in experiments is presented in Figure 1.

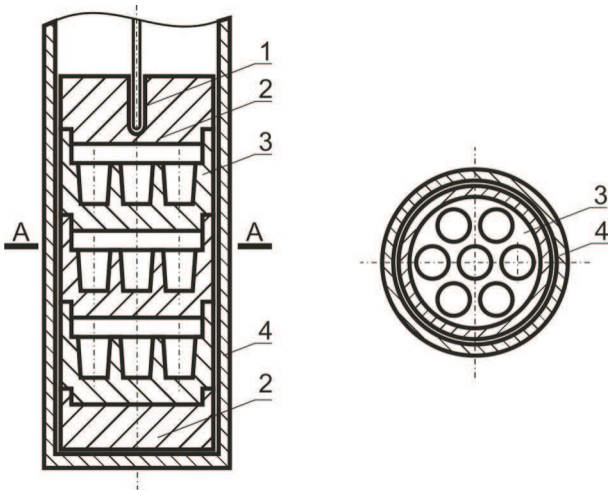

Fig. 1. Apparatus for the equilibrium saturation. (1 – [Ni-(Ni-Cr)] thermocouple and alundum sheath for thermocouple, 2 – graphite blocks, 3 – graphite blocks with grooves for alloys, 4 – chamber)

The Cu-Ni-Sn alloys of different compositions were placed in five grooves of each block and the reference

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mixture Cu-Bi was placed in the sixth groove. This alloy was the only source of Bi vapour in the system. Pure cooper was placed in the seventh groove. Three blocks with grooves with alloys were placed between two graphite blocks (Fig.1). That assured constant temperature during heating. The apparatus was placed in a tube made of extra-fine, creep resistant steel, which served as a chamber. The air from the chamber was pumped out and argon was let in. The argon pressure (20 hPa for 1398K, 40hPa for 1448K and 50 hPa for 1473K) guaranteed free migration of Bi vapour between alloys. The chamber with grooves with alloys was placed inside an isothermal zone of the resistant furnace and kept at a fixed temperature (1398, 1448 and 1473K) and alloys saturated with the bismuth vapour for a time necessary to attain equilibrium between Bi(g) in all alloys (2h). At the equilibrium state, the activity of Bi was the same in all alloys inside a closed system:

$$a_{Bi(Cu-Bi)} = a_{Bi(Cu-Ni-Sn-Bi)} \tag{1}$$

Equal Bi concentration in both Cu-Bi alloys (grooves sixth and seventh) guaranteed equilibrium attainment.

Than, argon was let into a chamber till the pressure reached 900 hPa. As the chamber was taken out from the furnace, bismuth evaporation was stopped and alloys solidified quickly.

If the alloys' equilibrium compositions and activity coefficient of Bi in the reference Cu-Bi alloy are known, it is possible to calculate the activity coefficient of Bi in the Cu-Ni-Sn-Bi alloy:

$$\gamma_{Bi(Cu-Ni-Sn-Bi)} = x_{Bi(Cu-Bi)} * \gamma_{Bi(Cu-Bi)}/x_{Bi(Cu-Ni-Sn-Bi)} \tag{2}$$

where $x_{Bi(Cu-Bi)}$ and $x_{Bi(Cu-Ni-Sn-Bi)}$ denote the equilibrium mole fraction of Bi in Cu-Bi and Cu-Ni-Sn-Bi respectively, and $\gamma_{Bi(Cu-Bi)}$ and $\gamma_{Bi(Cu-Ni-Sn-Bi)}$ are the corresponding activity coefficients of Bi.

Samples of the reference and the studied alloys of 3.5 g were prepared by melting carefully weighed masses of metals at an argon pressure of 0.1 Pa. The equilibrium compositions of the alloys were determined by the weighing. The accuracy of weighing was $\pm 10^{-4}$g.

The quantities determined experimentally, *i.e.* the argon pressure and the equilibration time were meant to ensure the attainment of equilibrium between Bi(g) in the reference and the studied mixture. It was established that for the temperature 1398, 1448 and 1473 K the time necessary to reach equilibrium was 2 hours and the argon pressure was 20, 40 or 50 hPa.

3. Results

The activity of bismuth in Cu-Ni-Sn-Bi at 1398, 1448 and 1473 K was determined by the equilibrium saturation method. The activity coefficient of bismuth (γ_{Bi})þ in this alloy was calculated from the equation (2). The experimental values of Bi activity coefficient are presented in Tables 1-3.

TABLE 1
Experimental values of bismuth activity coefficient γ_{Bi} at 1398K

Lp	Cu-Ni-Sn-Bi				Cu-Bi	
	x_{Ni}	x_{Sn}	x_{Bi}	γ_{Bi}	x_{Bi}	γ_{Bi}
1	0.0093	0.0674	0.0471	4.0449	0.0787	2.4189
2	0.0189	0.0394	0.0507	3.5279	0.0727	2.4599
3	0.0094	0.0512	0.0523	3.4181	0.0727	2.4599
4	0.0186	0.0554	0.0534	3.4579	0.0756	2.4396
5	0.0281	0.0416	0.0599	3.0793	0.0756	2.4396
6	0.0094	0.0358	0.0616	3.3732	0.0882	2.3568
7	0.0374	0.0194	0.0632	2.8278	0.0727	2.4599
8	0.0279	0.0279	0.0640	2.7917	0.0727	2.4599
9	0.0188	0.0176	0.0659	2.8054	0.0758	2.4386
10	0.0093	0.0192	0.0663	2.7873	0.0758	2.4386
11	0.0372	0.0308	0.0667	2.7650	0.0756	2.4396
12	0.0554	0.0231	0.0701	2.7158	0.0787	2.4189
13	0.0463	0.0230	0.0705	2.6166	0.0756	2.4396
14	0.0092	0.0264	0.0724	2.8712	0.0882	2.3568
15	0.0185	0.0088	0.0726	2.5440	0.0758	2.4386
16	0.0093	0.0091	0.0736	2.5100	0.0758	2.4386
17	0.0461	0.0080	0.0741	2.4118	0.0727	2.4599
18	0.0184	0.0268	0.0751	2.7685	0.0882	2.3568
19	0.0278	0.0067	0.0795	2.3253	0.0758	2.4386
20	0.0552	0.0093	0.0810	2.2779	0.0756	2.4396
21	0.0640	0.0129	0.0812	2.3432	0.0787	2.4189
22	0.0276	0.0178	0.0817	2.5444	0.0882	2.3568
23	0.0364	0.0079	0.0897	2.3168	0.0882	2.3568

TABLE 2
Experimental values of bismuth activity coefficient γ_{Bi} at 1448K

Lp	Cu-Ni-Sn-Bi				Cu-Bi	
	x_{Ni}	x_{Sn}	x_{Bi}	γ_{Bi}	x_{Bi}	γ_{Bi}
24	0.0093	0.0672	0.0501	3.5526	0.0782	2.2757
25	0.0189	0.0393	0.0515	3.2657	0.0728	2.3083
26	0.0093	0.0511	0.0541	3.1060	0.0728	2.3083
27	0.0186	0.0553	0.0558	3.1945	0.0784	2.2745
28	0.0374	0.0194	0.0630	2.6659	0.0728	2.3083
29	0.0280	0.0415	0.0630	2.8303	0.0784	2.2745
30	0.0279	0.0279	0.0642	2.6192	0.0728	2.3083
31	0.0094	0.0357	0.0649	3.1072	0.0917	2.1975
32	0.0188	0.0175	0.0670	2.6315	0.0773	2.2808
33	0.0093	0.0191	0.0672	2.6233	0.0773	2.2808
34	0.0555	0.0232	0.0693	2.5671	0.0782	2.2757
35	0.0371	0.0307	0.0695	2.5654	0.0784	2.2745
36	0.0461	0.0229	0.0733	2.4336	0.0784	2.2745
37	0.0461	0.0080	0.0739	2.2750	0.0728	2.3083
38	0.0185	0.0088	0.0741	2.3811	0.0773	2.2808
39	0.0093	0.0091	0.0754	2.3394	0.0773	2.2808
40	0.0092	0.0264	0.0757	2.6629	0.0917	2.1975
41	0.0184	0.0267	0.0780	2.5846	0.0917	2.1975
42	0.0278	0.0067	0.0800	2.2039	0.0773	2.2808
43	0.0641	0.0129	0.0801	2.2207	0.0782	2.2757
44	0.0550	0.0093	0.0835	2.1347	0.0784	2.2745
45	0.0275	0.0177	0.0846	2.3810	0.0917	2.1975
46	0.0363	0.0079	0.0925	2.1780	0.0917	2.1975

TABLE 3
Experimental values of bismuth activity coefficient γ_{Bi} at 1473K

Lp	Cu-Ni-Sn-Bi				Cu-Bi	
	x_{Ni}	x_{Sn}	x_{Bi}	γ_{Bi}	x_{Bi}	γ_{Bi}
47	0.0093	0.0672	0.0500	3.4101	0.0768	2.2170
48	0.0189	0.0394	0.0502	3.1591	0.0704	2.2541
49	0.0093	0.0512	0.0529	3.0013	0.0704	2.2541
50	0.0186	0.0553	0.0564	3.0458	0.0777	2.2120
51	0.0374	0.0433	0.0602	2.8313	0.0768	2.2170
52	0.0375	0.0195	0.0613	2.5903	0.0704	2.2541
53	0.0280	0.0415	0.0628	2.7386	0.0777	2.2120
54	0.0280	0.0279	0.0629	2.5253	0.0704	2.2541
55	0.0094	0.0357	0.0636	3.0147	0.0892	2.1487
56	0.0466	0.0315	0.0636	2.6783	0.0768	2.2170
57	0.0188	0.0176	0.0648	2.5621	0.0745	2.2305
58	0.0093	0.0192	0.0659	2.5221	0.0745	2.2305
59	0.0372	0.0308	0.0687	2.5035	0.0777	2.2120
60	0.0555	0.0232	0.0688	2.4765	0.0768	2.2170
61	0.0463	0.0081	0.0713	2.2276	0.0704	2.2541
62	0.0185	0.0088	0.0716	2.3198	0.0745	2.2305
63	0.0462	0.0229	0.0720	2.3865	0.0777	2.2120
64	0.0094	0.0091	0.0726	2.2890	0.0745	2.2305
65	0.0092	0.0264	0.0745	2.5736	0.0892	2.1487
66	0.0184	0.0268	0.0766	2.5035	0.0892	2.1487
67	0.0279	0.0068	0.0779	2.1317	0.0745	2.2305
68	0.0642	0.0129	0.0792	2.1521	0.0768	2.2170
69	0.0551	0.0093	0.0820	2.0958	0.0777	2.2120
70	0.0275	0.0177	0.0831	2.3077	0.0892	2.1487
71	0.0364	0.0079	0.0903	2.1222	0.0892	2.1487

For describing the activity coefficient of bismuth (γ_{Bi}) in the reference mixture (Cu-Bi) the equation proposed by Teppo [5] with the following Redlich-Kister [17] parameters was used:

$$\begin{aligned} {}^{0}\mathrm{L}^{\mathrm{L}}_{\mathrm{Bi,Cu}} &= 23844 - 9.84341 * \mathrm{T} \quad [\mathrm{J/mol}] \\ {}^{1}\mathrm{L}^{\mathrm{L}}_{\mathrm{Bi,Cu}} &= -1260.32 - 1.19289 * \mathrm{T} \quad [\mathrm{J/mol}] \end{aligned} \tag{3}$$

As the solutions are dilute ones, they can be described by means of the Wagner equation [18]:

$$\ln\gamma_{Bi} = \ln\gamma^{0}_{Bi} + \varepsilon^{\mathrm{Bi}}_{\mathrm{Bi}}\mathrm{x_{Bi}} + \varepsilon^{\mathrm{Sn}}_{\mathrm{Bi}}\mathrm{x_{Sn}} + \varepsilon^{\mathrm{Ni}}_{\mathrm{Bi}}\mathrm{x_{Ni}} \tag{4}$$

where γ^{∞}_{Bi} is the activity coefficient of Bi in Cu-Ni-Sn-Bi at $x_{Bi} \to 0$, $\varepsilon^{Bi}_{Bi} = (\partial \ln\gamma_{Bi} / \partial x_{Bi})$, $x_{Bi} \to 0$, $x_{Ni} \to 0$, $x_{Sn} \to 0$ is the interaction parameter of Bi in Cu-Ni-Sn-Bi, $\varepsilon^{Sn}_{Bi} = (\partial \ln\gamma_{Bi} / \partial x_{Sn})$ $x_{Bi} \to 0$, $x_{Sn} \to 0$, $x_{Ni} \to 0$ is the interaction parameter of Sn in Cu-Ni-Sn-Bi and $\varepsilon^{Ni}_{Bi} = (\partial \ln\gamma_{Bi} / \partial x_{Ni})$, $x_{Bi} \to 0$, $x_{Ni} \to 0$, $x_{Sn} \to 0$ is the interaction parameter of Ni in Cu-Ni-Sn-Bi.

In the equation (4) values of mole fractions of components and bismuth activity coefficient were determined experimentally, whereas values of $ln\gamma^{0}_{Bi}$, $\varepsilon^{\mathrm{Bi}}_{\mathrm{Bi}}$, $\varepsilon^{\mathrm{Ni}}_{\mathrm{Bi}}$, $\varepsilon^{\mathrm{Sn}}_{\mathrm{Bi}}$ were calculated by means of the least-squares method.

On the basis of the experimental results, the following expressions for the Bi activity coefficients were obtained:

T = 1398K:

$$ln\gamma_{Bi} = 1.34 - 5.61x_{Bi} + 4.76x_{Sn} - 1.58x_{Ni} \tag{5}$$

T = 1448K:

$$ln\gamma_{Bi} = 1.25 - 5.11x_{Bi} + 4.42x_{Sn} - 1.55x_{Ni} \tag{6}$$

T = 1473 K:

$$ln\gamma_{Bi} = 1.20 - 5.13x_{Bi} + 4.49x_{Sn} - 1.25x_{Ni} \tag{7}$$

Values of interaction parameters are presented in Table 4.

TABLE 4

Values of interaction parameters

T [K]	$\ln\gamma^{0}_{Bi}$	ε^{Bi}_{Bi}	ε^{Sn}_{Bi}	ε^{Ni}_{Bi}
1398	1.34	-5.61	4.76	-1.58
1448	1.25	-5.11	4.42	-1.55
1473	1.20	-5.13	4.49	-1.25

The comparision between the calculated and experimental Bi activity coefficients for some fixed Ni concentrations at 1398K is presented in Figs. 2-5.

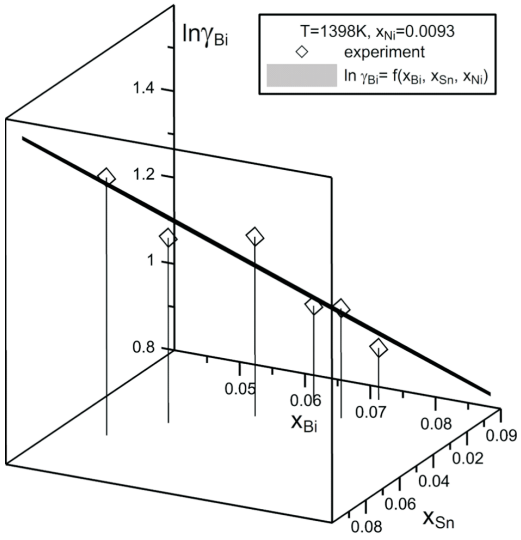

Fig. 2. Experimental and calculated values of γ_{Bi} for x_{Ni}=0.0093

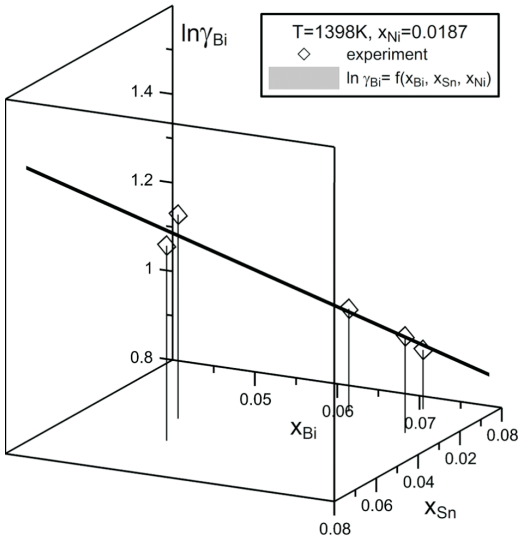

Fig. 3. Experimental and calculated values of γ_{Bi} for x_{Ni}=0.0187

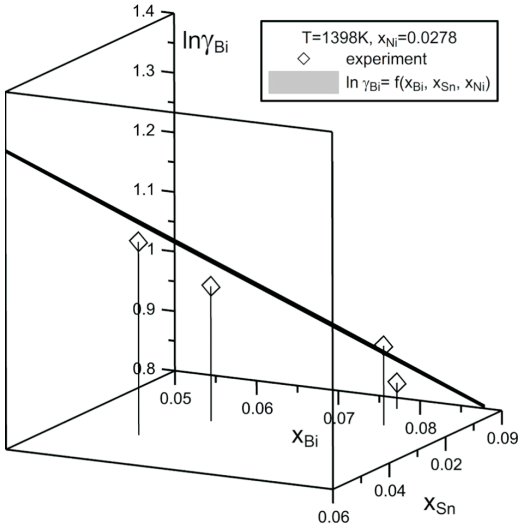

Fig. 4. Experimental and calculated values of γ_{Bi} for x_{Ni}=0.0278

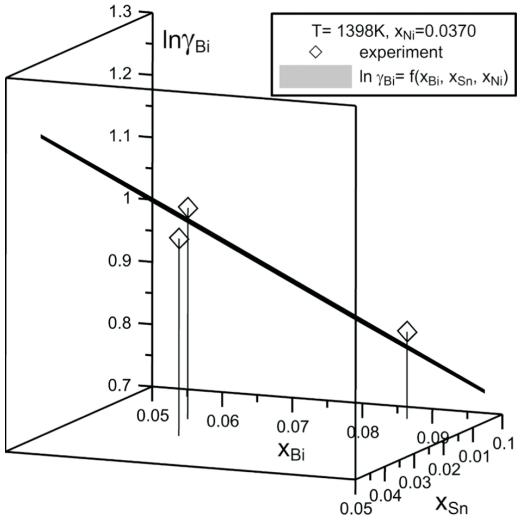

Fig. 5. Experimental and calculated values of γ_{Bi} for x_{Ni}=0.0370

The temperature dependence of interaction parameters is presented in equations (8-11) and Figure 6.

$$\ln\gamma^0_{Bi} = -0.00119T + 3.9370 \quad (8)$$

$$\varepsilon^{\mathrm{Bi}}_{\mathrm{Bi}} = 0.0069T - 15.2376 \quad (9)$$

$$\varepsilon^{\mathrm{Sn}}_{\mathrm{Bi}} = -0.0041T + 10.3976 \quad (10)$$

$$\varepsilon^{\mathrm{Ni}}_{\mathrm{Bi}} = 0.0039T - 7.0130 \quad (11)$$

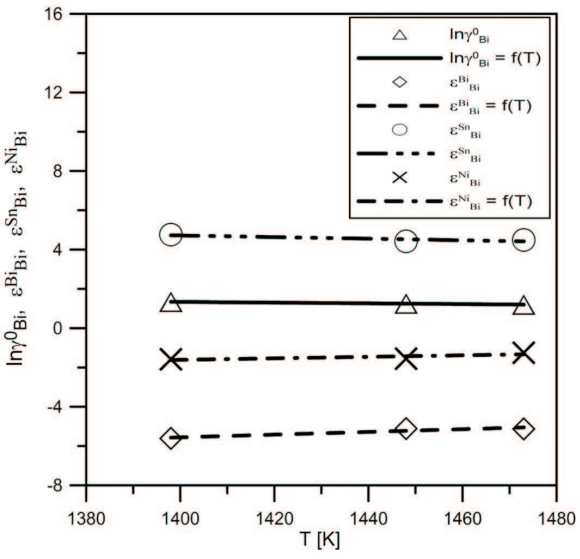

Fig. 6. The influence of temperature on the interaction parameters

We can see from Table 4, Fig. 6 and the equations (8-11) that the values of interaction parameters do not change significantly with the temperature.

As the value of $\varepsilon^{\mathrm{Ni}}_{\mathrm{Bi}}$ is close to 1 (1.58, 1.55, 1.25), the nickel influence on Bi activity is smaller than the influence of other components ($\varepsilon^{\mathrm{Bi}}_{\mathrm{Bi}}$ <-5 and $\varepsilon^{\mathrm{Sn}}_{\mathrm{Bi}}$ >4).

When there is accepted x_{Ni}=0 in Eq. (6), the results obtained are in good agreement with results for the ternary Cu-Sn-Bi alloys obtained on the basis of Eq.(12) [8], see Fig. 7.

$$ln\gamma_{Bi} = 1.156 - 3.240x_{Bi} + 5.383x_{Sn} \quad (12)$$

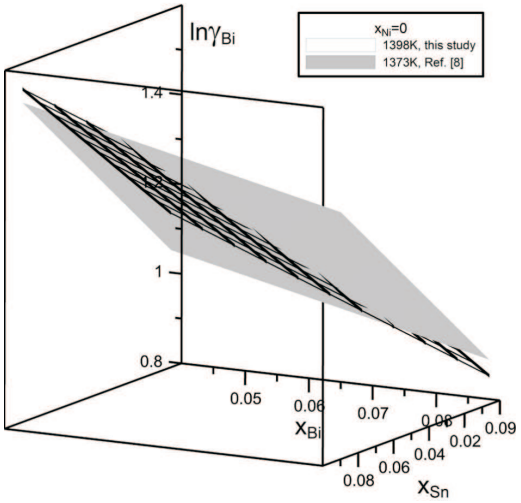

Fig. 7. Calculated bismuth activity coefficient γ_{Bi} in Cu-Sn-Bi and Cu-Ni-Sn-Bi for x_{Ni}=0

4. Conclusions

Using the vapour saturation method, the Bi activities in Cu-Ni-Sn-Bi alloys at the temperature 1398, 1448 and 1473K were measured and interaction parameters were calculated. Theses results, combined with other measurements carried on within the frame of the COST action MP0602 “Advanced Solder Materials for High Temperature Application –HISOLD”, a group project “Design, Process and Control in a Multiscale domain of Cu-Ni-X-Y (X, Y = Sn, Bi, Zn) Based Alloys” allow to construct thermodynamic database that may be useful for the computer modelling of the system and to determine compositions suitable for practical applications as soldering materials.

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