



A Calorimetric Investigation of the Liquid Bi-Ni Alloys

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Received 26 Apr 2016, Revised 01 Jul 2016, Accepted 05 Jul 2016

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Abstract

The partial and integral enthalpies of mixing of liquid binary Bi-Ni alloys were determined at 1273 and 1573 K. The calorimetric measurements were carried out using two different calorimeters. A Calvet-type twin micro-calorimeter system (HT-1000) was used for $T = 1273$ K with a drop calorimetric technique. For higher temperature $T = 1573$ K a multi High-Temperature micro-calorimeter (MHTC) has been used with a manual drop. The experimental data at 1273 and 1573 K have been compared to each other and to the assessed results available in the literature. Finally, the experimental binary data were evaluated by means of a standard Redlich-Kister polynomial fit.

Keywords: Enthalpy of mixing, partial enthalpy of mixing, liquid alloys, calorimetry, Bi-Ni.

1. Introduction

Lead-tin solders are commonly used in electronic packaging due to their unique combination of chemical, physical, thermal and mechanical properties. However, lead and lead containing substances are among the top chemicals posing a considerable threat to human life and environment [1, 2].

Although it is now widely agreed that there is no drop-in replacement for the standard tin-lead solders that have been used worldwide, a range of possible alternatives has been investigated, all with very high tin contents with different additives, such as Ag, In, Bi, Sb, Cu, Zn, Au etc.

In printed circuit boards (PCB) manufacturing, a solderable surface finish is coated over the Cu traces to maintain solderability over a period of shelf time. Nickel layers, both electrolytic and electroless, are used in several important lead-free finishes, such as the Au/Ni and Pd/Ni, which have the additional advantage of being very flat, making them ideal for fine lead-pitch and area-array surface mount components.

Moreover, it is known that Ni is plated as an under bump metallurgy (UBM) layer on the substrate prior to soldering in modern microelectronic package [3-6]. A knowledge of the thermodynamic properties of the Bi-Ni system is important, as both elements are possible constituents of multicomponents, such as Bi-Ni-Sn. Thus, information on thermochemistry and phase relation of solder forms the base for a systematic alloy design which is desired to avoid complex and time consuming trial and error developing methods. Experimental thermochemical data such as mixing enthalpies are indispensable for the thermodynamic optimization of phase diagrams and the estimation of several physical properties, e.g. surface tension, viscosity and wettability.

In this work, the partial and integral enthalpies of mixing of liquid Bi-Ni alloys were determined at 1273 and 1573 K.

2. Bibliographic survey of Bi-Ni binary system

2.1. Phase diagram data

The phase diagram of the Bi-Ni binary system has been studied by several authors. In 1908, Portevin [7] and Voss [8] have measured the liquidus using thermal analysis. The experimental data on the liquidus are in good agreement with each other. However, a discrepancy of the peritectic temperature of intermetallic compound BiNi has been noted. Shavinski et al. [9] reported that the composition and temperature of the eutectic reaction ($L \leftrightarrow \text{Bi}_3\text{Ni} + \text{rhombohedral (Bi)}$) are 99.47 at.% Bi and 543 K, respectively. Nash [10] pointed out that the peritectic temperature (911 K) reported by Voss [8] is too low compared with the experimental data (927 K) of Portevin [7]. Feschotte and Rosset [11] investigated the Bi-Ni binary system and determined the eutectic and peritectic temperatures in this binary system. Their experimental results reveal that the intermetallic compound BiNi has a narrow homogeneity range and Bi_3Ni is a stoichiometric compound. Recently, Vassilev et al. [12] determined the solidus of fcc (Ni) phase as well as the compositions and temperatures of the invariant reactions by electron microprobe analyses, optical microscopy and differential scanning calorimetry. It was found that the narrow homogeneity region of BiNi is 50-52 at.% Bi and Bi_3Ni is a stoichiometric compound. In 2007, Seo et al. [13], using the diffusion couple method, measured accurately the homogeneity region of BiNi at different temperatures (473-873 K). More recently, a detailed description of the binary Bi-Ni system was given by Wang et al. [14]. All previous experimental data [7-9, 11-13] were taken into account in their optimization [14].

2.2. Thermodynamic data

Activities of Bi and Ni in liquid phase were investigated by Iwase and Mclean [15] and Vassilev et al. [16]. Iwase and Mclean [15] determined the activities of Ni in liquid phase at 1073 K and 1773 K by electromotive force (EMF) method. Recently, Vassilev et al. [16] measured the activities of Bi in liquid phase at different temperatures (1723 K, 1753 K and 1773 K) using the modified isothermal isopiestic method. On the other hand, the enthalpy of formation of intermetallic compound BiNi was determined by Predel and Ruge [17] using calorimetric technique. Perring et al. [18] measured the heat capacities of BiNi in the temperature range of 310-850 K by differential scanning calorimetry. In the same paper, Vassilev et al. [16] published thermodynamic assessments, using the well known CALPHAD method and reported that positive enthalpy values are expected in the nickel-rich side ($x_{\text{Ni}} > 0.8$) and negative for the alloys at $x_{\text{Bi}} > 0.8$. The experimental data [15-18] were used in the optimization given by Wang et al. [14]. Very recently, Samui et al. [19], using calorimetric technique, have determined enthalpy increments and the enthalpy of decomposition of $\text{Bi}_{0.75}\text{Ni}_{0.25}$ and $\text{Bi}_{0.5}\text{Ni}_{0.5}$ intermetallic compounds. Agarwal et al. [20] have measured the enthalpy of mixing of liquid alloys at different low temperatures (≤ 919 K) within a narrow range of compositions ($0 \leq x_{\text{Ni}} \leq 0.2$).

3. Experimental procedure

The calorimetric measurements were carried out using two different calorimeters. For $T = 1273$ K a Calvet-type twin micro-calorimeter system was used, based on a commercial wire wound resistance furnace (HT-1000, SETARAM, Lyon, France) having two thermopiles with more than 200 thermocouples, equipped with an automatic drop device for up to 30 drops; control and data evaluation was performed with Lab View and HiQ. This system was described in detail by Flandorfer et al. [21]. For higher temperature $T = 1573$ K a commercial Multi High-Temperature micro-calorimeter (MHTC, SETARAM, Lyon, France) was available with one thermopile with 20 thermocouples, a graphite tube resistance furnace, a manual drop device for up to 23 drops; control and data evaluation was performed using the software provided by the company. The measurements were generally performed in graphite crucibles under Ar flow (99.999 vol. %, purification from oxygen, approx. 30 ml/min). At the end of each series the calorimeters were calibrated by five drops of standard $\alpha\text{-Al}_2\text{O}_3$ provided by NIST (National Institute of Standards and Technology, Gaithersburg, MD). The time interval between individual drops was usually 40 minutes and the acquisition interval of the heat flow was 0.5 s. The obtained signals were recorded and integrated. The measured enthalpy (integrated heat flow at constant pressure) is

$$\Delta H_{\text{drop}} = n_i [H_{i(\text{l}), \text{FT}} - H_{i(\text{s}), \text{DT}}] + \Delta H_{\text{reaction}}$$

n_i is the number of moles of the dropped element i , FT = furnace temperature, and DT = drop temperature. $H_{i(l), FT} - H_{i(s), DT}$ was calculated using the polynomials for the thermodynamic data of pure elements in the SGTE data base [22]. For the respective temperatures FT and DT , the averages of the values for each drop of a run was taken because their scattering was low enough and not influence the accuracy of the method. Because of the rather small masses added, the partial enthalpy $\Delta\bar{H}_i$ of the dropped metal i can be considered as:

$$\Delta\bar{H}_i \approx \Delta H_{\text{reaction}} / n_i$$

Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal integration and “chemical errors”, e.g. incomplete reactions or impurities. Considering many calibration measurements done by dropping NIST standard sapphire, the standard deviation can be estimated to be less than $\pm 1\%$ for the HT-1000.

The integral molar enthalpy of mixing, $\Delta_{\text{mix}}H$, was calculated by summing the respective reaction enthalpies $\Delta H_{\text{reaction}}$ and division by the total molar amount of substance.

$$\Delta_{\text{mix}}H = \frac{\sum \Delta H_{\text{reaction}}}{n_j + \sum n_i}$$

n_j stands for the molar amount of substance which was already present in the crucible (starting amount of Bi).

The samples were prepared from Bi pellets (99.999%) and Ni wire (99.98%). The two elements were used without further purification.

All the experimental data of Bi-Ni system can be found in Table 1 and 2. These tables contain information on the exact measurement, starting amounts of Bismuth, added amounts of Nickel, heat effect and the partial and integral enthalpies of mixing of the liquid alloys.

4. Results and discussion

4.1. Experimental results

In a first step, the partial and the integral enthalpies of mixing of the binary Bi-Ni system were measured at 1273 K. Small pieces (18-30 mg) of pure Ni was dropped into molten Bi (about 1g). It should be noted that on attempts to drop Bi into Ni were not successful because parts of the Bi pieces stuck at the end of the inner glass tube above the crucible without mixing with Ni. Obviously, the Bi pieces start to melt immediately by touching the inner glass tube due to its high vapor pressure.

Figure 1 shows the experimental data of the integral molar enthalpy of mixing for Bi-Ni system at 1273 K. The measured enthalpies of mixing are exothermic. As can be seen, at 1273 K, the kink in the composition dependence of the experimental data at about 36 at% Ni indicates the precipitation of the (Ni) phase. This results is in good agreement with the liquidus point at 1273 K as shown in the Massalski version of the phase diagram (39 at.% Ni) [23].

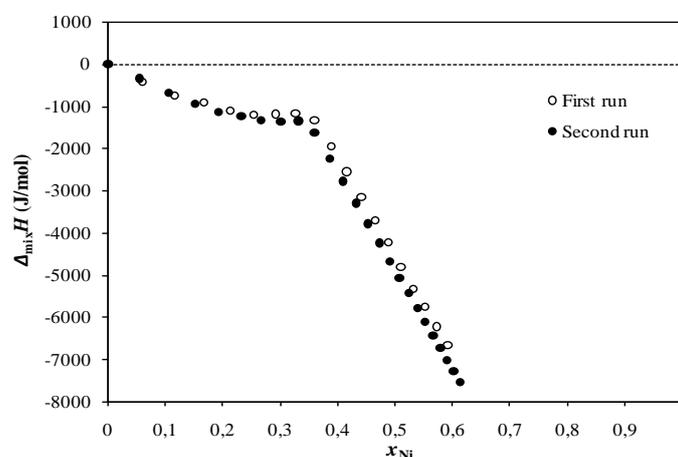


Figure 1: Integral molar enthalpies of mixing at 1273 K in liquid Bi-Ni alloys. Standard states: pure liquid metals.

Table 1: Partial and integral molar enthalpies of mixing in the binary liquid Bi-Ni alloys at 1273 K; reference states: pure liquid metals.

Mole dropped <i>n</i> (Ni) (mmol)	Heat effect (J)	Partial enthalpy		Integral enthalpy	
		x_{Ni}^*	$\Delta\bar{H}_{Ni}$ (J.mol ⁻¹)	x_{Ni}	$\Delta_{mix}H$ (J.mol ⁻¹)
starting amount : n(Bi) = 4.8417 mmol (first run)					
0.0000	—	—	—	0.0000	0
0.3119	12580	0.0303	-7041	0.0605	-426
0.3264	13553	0.0885	-5848	0.1165	-749
0.3330	14480	0.1419	-3886	0.1671	-929
0.3385	14580	0.1900	-4308	0.2129	-1115
0.3468	15359	0.2339	-3086	0.2549	-1220
0.3474	16169	0.2738	-833	0.2927	-1200
0.3510	16326	0.3100	-856	0.3272	-1184
0.3660	15764	0.3435	-4302	0.3598	-1334
0.3671	11955	0.3746	-14804	0.3894	-1958
0.3674	11718	0.4029	-15478	0.4165	-2557
0.3776	11733	0.4292	-16305	0.4419	-3155
0.3933	12225	0.4540	-16292	0.4661	-3725
0.3936	12259	0.4772	-16230	0.4883	-4245
0.4328	12875	0.4995	-17629	0.5107	-4831
0.4660	14573	0.5217	-16098	0.5327	-5337
0.4818	15521	0.5431	-15162	0.5534	-5774
0.4894	15103	0.5631	-16513	0.5727	-6238
0.5428	17015	0.5825	-16027	0.5923	-6685
starting amount : n(Bi) = 5.7774 mmol (second run)					
0.0000	—	—	—	0.0000	0
0.3376	13833	0.0276	-6403	0.0552	-354
0.3445	14033	0.0804	-6638	0.1056	-689
0.3498	14575	0.1286	-5713	0.1516	-947
0.3542	15081	0.1725	-4794	0.1935	-1137
0.3600	15755	0.2128	-3606	0.2321	-1255
0.3658	16195	0.2499	-3101	0.2677	-1341
0.3773	17101	0.2844	-2047	0.3011	-1373
0.3806	17656	0.3165	-983	0.3319	-1356
0.3835	15152	0.3461	-7862	0.3602	-1632
0.3844	11824	0.3733	-16613	0.3864	-2244
0.3849	12070	0.3984	-16012	0.4105	-2784
0.3876	11891	0.4217	-16698	0.4329	-3314
0.3880	11944	0.4433	-16593	0.4537	-3801
0.3896	11972	0.4634	-16645	0.4731	-4257
0.3933	12106	0.4822	-16594	0.4914	-4685
0.3937	12157	0.4999	-16491	0.5084	-5080
0.3946	12220	0.5164	-16405	0.5244	-5448
0.3946	12191	0.5318	-16484	0.5393	-5795
0.3950	12185	0.5464	-16528	0.5534	-6123
0.3960	12018	0.5600	-17028	0.5667	-6447
0.3992	12216	0.5730	-16773	0.5793	-6747
0.4010	12303	0.5852	-16692	0.5912	-7029
0.4012	12334	0.5968	-16632	0.6025	-7294
0.4072	12546	0.6079	-16566	0.6133	-7547

x^* Average value before and after each drop.

Table 2: Partial and integral molar enthalpies of mixing in the binary liquid Bi-Ni alloys at 1573 K; reference states: pure liquid metals.

Mole dropped n (Ni) (mmol)	Heat effect (J)	Partial enthalpy		Integral enthalpy	
		x_{Ni}^*	$\Delta\bar{H}_{Ni}$ (J.mol ⁻¹)	x_{Ni}	$\Delta_{mix}H$ (J.mol ⁻¹)
starting amount : n(Bi) = 10.1716 mmol (first run)					
0.0000	—	—	—	0.0000	0
0.5228	26485	0.02444	-7447	0.0489	-364
0.5347	26188	0.07153	-8152	0.0942	-735
0.5608	27155	0.11572	-8706	0.1373	-914
0.5655	27155	0.15700	-9109	0.1767	-1280
0.5849	31023	0.19535	-4094	0.2140	-1398
0.6158	34959	0.23181	-357	0.2497	-1342
0.6312	32819	0.26636	-5134	0.2830	-1502
0.6531	36587	0.29882	-1113	0.3146	-1476
0.6921	38987	0.32987	-797	0.3451	-1436
0.7664	45733	0.36054	2539	0.3759	-1480
0.7821	39101	0.39022	-7134	0.4045	-1501
0.7838	44193	0.41757	-747	0.4306	-1459
0.7883	43880	0.44267	-1465	0.4547	-1451
0.8035	44184	0.46596	-2142	0.4772	-1471
starting amount : n(Bi) = 10.8039 mmol (second run)					
0.0000	—	—	—	0.0000	0
0.5179	22752	0.0229	-5511	0.0457	-252
0.5785	23838	0.0690	-8237	0.0921	-640
0.5912	25335	0.1136	-6589	0.1351	-922
0.5917	26442	0.1547	-4752	0.1742	-1095
0.5963	27546	0.1922	-3243	0.2102	-1189
0.6210	28034	0.2273	-4294	0.2445	-1324
0.6353	30088	0.2606	-2082	0.2766	-1356
0.6375	29472	0.2915	-3206	0.3063	-1432
0.6739	33538	0.3206	323	0.3350	-1359
0.6758	34874	0.3483	2160	0.3616	-1388
0.7072	30664	0.3744	-6079	0.3872	-1413
0.7124	31776	0.3991	-4838	0.4110	-1546
0.7202	35730	0.4221	174	0.4332	-1481
0.7286	36185	0.4437	225	0.4541	-1418
0.7354	35497	0.4639	-1170	0.4737	-1410

x^* Average value before and after each drop.

Figure 2 illustrates the partial molar enthalpy of Ni ($\Delta\bar{H}_{Ni}$). The kink observed in the curve $\Delta_{mix}H = f(x_{Ni})$ (Fig. 1) is in accordance with a sudden drop of the partial values at about the same concentration (36 at.% Ni) caused by primary crystallization of the (Ni) phase. The rather constant partial values after the occurrence of the solid phase are around -17000 J/mol (Fig. 2) which is very close to the enthalpy of melting of pure Ni at 1273 K. In order to cover a more larger liquid composition range and to check a possible temperature dependence, the calorimetric measurements have been done at 1573 K where pure Ni was dropped into about 2 g of molten Bi. Figure 3 shows the integral enthalpy of mixing in the liquid Bi-Ni system at 1573 K together with the results

obtained at 1273 K. As can be seen, the binary alloys are in liquid phase at 1573 K in the all composition range ($0 \leq x_{Ni} \leq 0.55$) with the same minimum as that observed for 1273 K. The fact that enthalpy has the same minimum for both temperatures could mean that no significant temperature dependence of $\Delta_{mix} H$ in the Bi-Ni system.

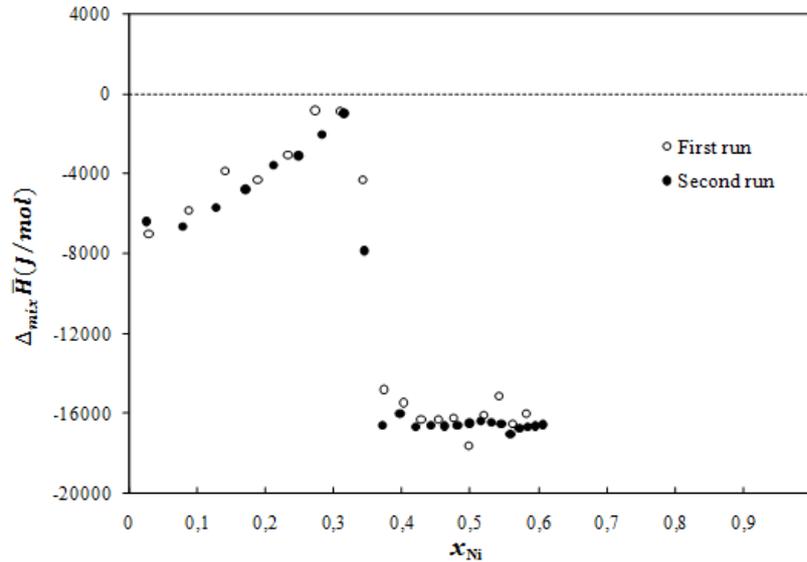


Figure 2: Partial molar enthalpies of mixing at 1273 K in liquid Bi-Ni alloys. Standard states: pure liquid metals.

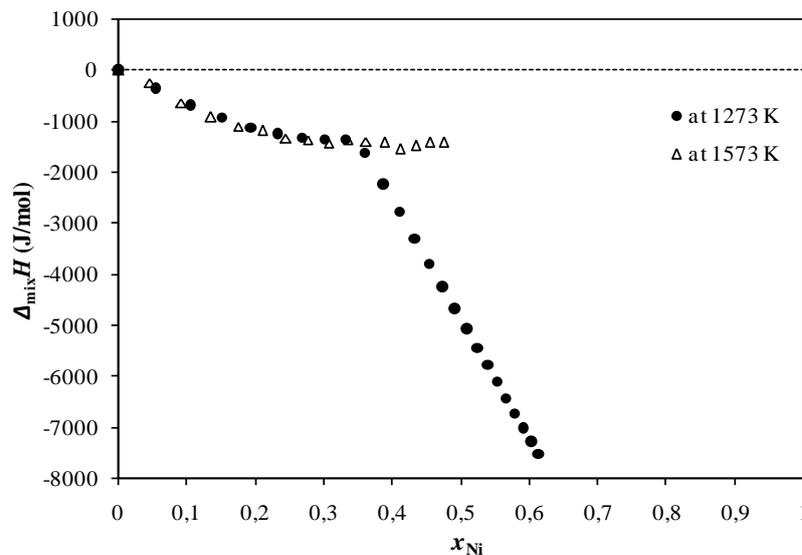


Figure 3: Integral molar enthalpies of mixing at 1273 and 1573 K in liquid Bi-Ni alloys. Standard states: pure liquid metals.

Additionally, graphical comparisons of the enthalpies of mixing of liquid alloys, calculated with coefficients optimized by various authors [13, 14, 16] and measured by Agarwal et al. [20] (Table 3) are plotted in Figure 4. Surprisingly, Seo et al [13] have reported endothermic enthalpy of mixing values in the entire range of compositions. Indeed, Vassilev et al. [16], in their optimization, have showed an exothermic values of $\Delta_{mix} H$ for $0 \leq x_{Ni} \leq 0.8$ with a minimum of ≈ -2300 J/mol at $x_{Ni} = 0.3$ and a positive values in the Ni-rich side ($0.8 \leq x_{Ni} \leq 1$) with a maximum of about 240 J/mol at $x_{Ni} = 0.9$. Wang et al [14] have optimized the enthalpy of mixing and showed a large endothermicity range ($0.23 \leq x_{Ni} \leq 1$) and a narrow exothermicity range ($0 \leq x_{Ni} \leq 0.23$). The experimental values reported by Agarwal et al [20] are more exothermic than our results. The calculated results [13,14] are very different from our results, probably due to their parameters used in their calculations.

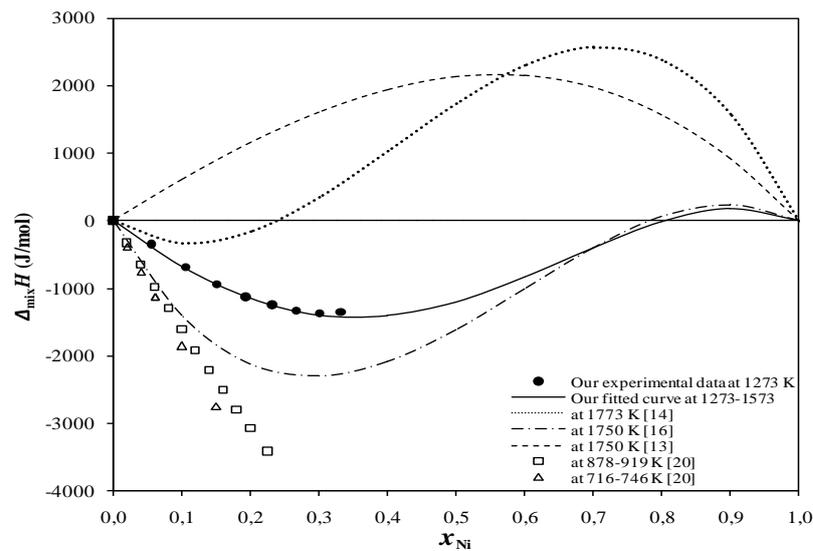


Figure 4: Comparison of experimental and calculated enthalpies of mixing values in the liquid Bi-Ni system.

4.2. Binary modeling

The experimental data for binary liquid Bi-Ni alloys at 1273 and 1573 K were fitted by a least squares using the well known Redlich-Kister polynomial as proposed by Ansara and Dupin [24] for substitutional solutions:

$$\Delta H_{\text{mix}} = \sum_i \sum_{j>i} \left[x_i x_j \sum_v L_{ij}^{(v)} (x_i - x_j)^v \right]$$

With i and j equal to 1 or 2 for the two elements under consideration in alphabetical order (Bi and Ni). $L_{ij}^{(v)}$ ($v = 0, 1, 2, \dots$) are the interaction parameters of the constituent binaries (see table 3). As it was impossible to measure the integral enthalpies of mixing in the rich-Ni region (due to the difficulty to add Bi into Ni) and taking into account the results reported par Vassilev et al. [16]: $\Delta_{\text{mix}}H = 0$ at $x_{\text{Ni}}=0.8$, the fitted curve, with three interaction parameters $L^{(0)}$, $L^{(1)}$ and $L^{(2)}$ shows an exothermic values up to 80 at.% Ni with a minimum of -1350 J/mol at 36 at.% Ni. A slightly endothermic maximum of about 200 J/mol at around 90 at.% Ni.

Table 3: Binary interaction parameters.

System	$^{(v)}L$			References	Temperature (K)
	$^{(0)}L$	$^{(1)}L$	$^{(2)}L$		
Bi-Ni	8542	-2140	0	[13]	1750
	-6438	-11315	0	[16]	1750
	6944	-13225	0	[14]	1773
	-27700	8780	0	[20]	716-746
	-23270	6650	0	[20]	878-919
	-4792	-5916	3135	This work	1273-1573

Conclusion

The partial and integral enthalpies of mixing of liquid binary Bi-Ni alloys have been measured at 1273 and 1573 K. The experimental data have been compared to each other and to the assessed results available in the literature. The results showed that no significant temperature dependence of enthalpy in the studied system. Finally, the experimental binary data were evaluated by means of a standard Redlich-Kister polynomial fit.

Acknowledgements- The authors would like to thank Prof. H. Flandorfer and Prof. H. Ipser who allowed us to realize the calorimetric measurements in the laboratory of Inorganic Chemistry (material chemistry group) at Vienna University.

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