Journal of Mining and Metallurgy 43 B (2) (2007) 141 - 150

Journal of
Mining and
Metallurgy

SUPPLEMENTARY X-RAY STUDIES OF THE Ni-Sn-Bi SYSTEM

G. P. Vassilev*, K.I. Lilova,*** and J.-C. Gachon*****

* University of Plovdiv, "Paisii Hilendarski" Faculty of Chemistry, Plovdiv, Bulgaria,
** University of Sofia "St. Kliment Ohridski", Faculty of Chemistry, Sofia, Bulgaria,
*** LCSM, UMR 7555, University "Henri Poincaré", Faculty of Science, Nancy, France

(Received 12 June; accepted 23 September 2007)

Abstract

Phase equilibria were studied in the system Ni-Sn-Bi. Special attention has been paid to the identification of the reacently found ternary phase. For this purpose samples were synthesized using intimately mixed powders. After annealing and quenching, all alloys were analyzed by scanning electron microscope and by X-ray diffraction. The results give evidences about the existence of a ternary compound with approximate formula Ni_6Sn_2Bi to Ni_7Sn_2Bi. Overlapping of some neighbouring diffraction peaks of this phase with NiBi and Ni_3Sn_LT is the reason for the difficulties related to the X-ray diffraction identification of the ternary phase.

Keywords: phase diagrams, Ni-Sn-Bi, ternary compound, X-ray diffraction, solders

1. Introduction

Environmental concerns are the main reason that the lead-bearing solders are under way to be phased out of use in the near future. In this connection intensive studies of prospective multicomponent lead-free systems, mainly based on tin plus bismuth or zinc, are in progress. Moreover, nickel substrates are massively applied in the electronic devices. In this view, investigations of nickel substrates wetting by molten Sn-Bi solders and the kinetics of the corresponding interfacial reactions were done [1-3]. It was reported that either $NiBi_3$ or Ni_3Sn_4 phases grow from liquid tin-bismuth solders, depending on the concentration. The end-systems Bi-Sn, Ni-Bi and Ni-Sn binary phase diagrams are relatively known [4, 5] but the investigations continue [6, 7, 8].

Corresponding author: gpvassilev@excite.com

DOI:10.2298/JMMB0702141V

Although the knowledge of a phase diagram is of fundamental importance for developing new materials, systematic explorations of the Ni-Sn-Bi alloys were not undertaken until now. To revamp this void, phase equilibria studies of this ternary system were performed recently by Vassilev et al. [9] and a formerly unknown ternary compound with approximate formula Ni_7Sn_2Bi was observed. In this study we report auxiliary X-ray studies of the nickel-rich region of the ternary equilibrium diagram.

2. Experimental

Supplementary samples were synthesized and studied, in order to inquire the phase equilibria related with the formerly unknown Ni-Bi-Sn compound previously reported [9]. For this purpose, five samples with nominal composition 68% Ni, 20% Sn and 12% Bi were annealed in evacuated and sealed quartz tube at 873 K, for two weeks, and quenched in cold water. Powders (325 mesh) of pure metals (Ni (4N), Sn (5N), Bi (4N)) (production of Goodfellow) were used. It happened that during the annealing all pellets (5 mm of diameter and 3 to 4 mm thick) stuck together, thus they were treated as one sample referred further as S1. In order to avoid some side reactions, previously observed in sealed silica tubes, a specimen with the same nominal composition (S2) was prepared and put in an alumina crucible placed into iron container. This container was heated at 873 K in a furnace for two weeks, under flowing argon atmosphere and quenched in cold water. The specimen S2, already annealed at 873 K for two weeks, was annealed for 3 months yet to verify the phase equilibria.

In addition, mechanical alloying method was applied to synthesize the ternary phase. For that purpose, a ribbon (1.5 mm thick) of Ni, Sn and Bi powders (325 mesh) was produced using manual rolling-mill. The composition of the mixture was 68% Ni, 19% Sn and 13% Bi. This way of preparation should provide more homogeneous samples. This specimen, denoted as S3, was annealed at 903 K for 3 months in evacuated and sealed quartz tubes.

3. Results and discussion

The ternary compound Ni_6Sn_2Bi was (as previously reported [9]) observed by electron probe microanalyser (EPMA) in the supplementary synthesized specimens: S1 (annealed at 873 K), S2 (annealed at 873 in iron container) and S3 (annealed at 903 K). In these three samples the following phase equilibria were found: S1 - Ni_3Sn+NiBi+Ni_7Sn_2Bi (Fig. 1); S2 - (Ni)+NiBi+Ni_6Sn_2Bi (after two weeks of annealing), NiBi and Ni_6Sn_2Bi (after three months of annealing); S3 - NiBi, Ni_3Sn and Ni_7Sn_2Bi.

Fig. 2 represents X-ray diffractogram (Cu K_α) of the powdered sample S1 (curve 1) compared to experimental patterns of Ni_3Sn_LT [6] (curve 2) and of NiBi [10] (curve 3). The diffractogram was checked up for the presence of other phases (e.g. the most probable was (Ni)). Systems of diffraction peaks belonging to NiBi and Ni_3Sn_LT and another system of 15 peaks that probably are associated with the formerly unknown ternary phase Ni_7Sn_2Bi were found (Table 1).

The diffractograms are noteworthy with overlapping of some neighboring diffraction peaks. Four peaks are single (these at 2θ = 27.2, 29.6, 30.8, 32.0, 43.5 deg), while nine represent multiple diffraction, i.e. double and triple peaks. The overlapping of the peaks is probably due to similar crystal structure parameters of the present phases.

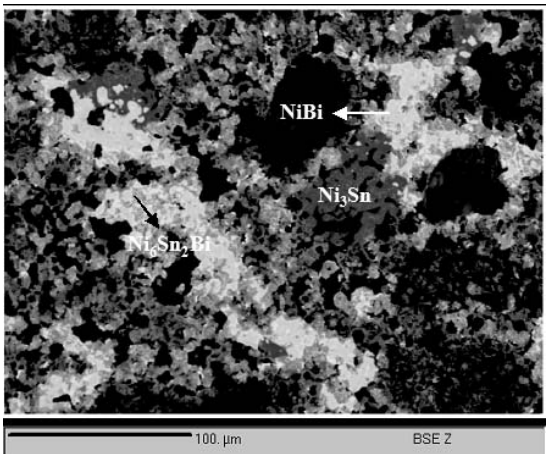

Fig. 1. Micrograph of specimen S1 in back-scattered electrons. The dark phase is of Ni_3Sn; small light phase represents NiBi and the light gray phase - Ni_7Sn_2Bi

For example, according to the literature data [11], NiBi and Ni_3Sn_LT [12] belong to the space group No 194, $P6_3mmc$ with cell parameters: a=4.0700, b= 5.3500, Wyckoff 2a, 2c, Pearson symbol hP4 (NiBi) and a= 5.2960, b= 4.2480, Wyckoff 2a, 6h, Pearson symbol hP8 (Ni_3Sn_LT). Three peaks of both compounds are practically overlapped (33.6-33.8; 42.5-42.6; 44.5-44.8). Other six peaks have a difference between diffraction angles about 0.6-0.7 deg. Thus, it could be admitted that the ternary compound belongs to the same space group with cell parameters similar to those of the compound Ni_3Sn_LT. Examples of overlapping peaks are represented in Fig 3 A&B.

The peak a of curve 3 in Fig. 3A. is related to the phase NiBi. Twin peaks b and d of curve 1 are related to Ni_3Sn_LT and probably to Ni_7Sn_2Bi, respectively. The peak c (curve 2) is related to Ni_3Sn_LT.

In Fig. 4 are represented two X-ray diffractograms (D2 and D3) of the powdered sample S3, superimposed with the experimental patterns of NiBi [10] and Ni_3Sn [6]. The diffractograms were checked up for the presence of other phases. Systems of diffraction peaks belonging to NiBi and Ni_3Sn_LT and two systems of six and eight peaks for D2 and D3, respectively, that probably can be associated with the formerly unknown ternary phase Ni_7Sn_2Bi were found. (Tables 2-4).

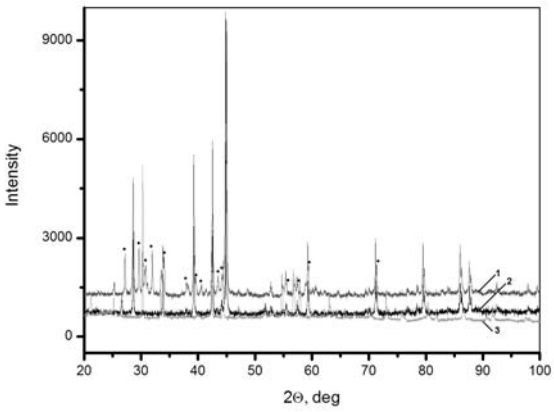

Fig. 2. X-ray diffractograms (Cu K_α) of the powdered sample S1 (curve 1) compared to experimental patterns of Ni_3Sn_LT (curve 2) and NiBi (curve 3). The intensity of the diffraction peaks (counts per second) is plotted along the ordinate, and the diffraction angles (2θ, deg) are plotted along the abscissa. The peaks probably belonging to the ternary compound Ni_7Sn_2Bi are marked by asterisk

Table 1. Diffraction peaks (298 K, Cu $K_{\alpha 1}$) of the specimen S1 (diffractogram D1). No - number of the diffraction peak; 2θ- diffraction angles, deg, d - interlattice distances, nm; Intensity - relative intensity (%) of the diffraction peaks

Intensity %	d nm	2θ deg	Phase
11	0.3510	25.3	NiBi
16	0.3288	27.2	Ni_7Sn_2Bi
30	0.3117	28.6	Ni_3Sn_LT
17	0.3015	29.6	Ni_7Sn_2Bi
17	0.2945	30.3	NiBi
14	0.2900	30.8	Ni_7Sn_2Bi
17	0.2799	32.0	Ni_7Sn_2Bi
13	0.2669	33.6	NiBi
18	0.2649	33.8	Ni_3Sn_LT
16	0.2632	34.1	Ni_7Sn_2Bi
23	0.2370	37.9	Ni_7Sn_2Bi
35	0.2294	39.2	Ni_3Sn_LT
10	0.2273	39.4	Ni_7Sn_2Bi
12	0.2223	40.6	Ni_7Sn_2Bi
38	0.2124	42.5	NiBi
24	0.2120	42.6	Ni_3Sn_LT
12	0.2078	43.5	Ni_7Sn_2Bi
60	0.2051	44.2	Ni_7Sn_2Bi
48	0.2034	44.5	NiBi
100	0.2015	44.8	Ni_3Sn_LT
13	0.2014	45.0	Ni_6Sn_2Bi
11	0.1734	52.8	Ni_3Sn_LT
10	0.1674	54.8	NiBi
13	0.1659	55.4	Ni_3Sn_LT
12	0.1658	55.5	Ni_7Sn_2Bi
11	0.1617	56.9	NiBi
12	0.1606	57.3	Ni_3Sn_LT
18	0.1605	57.4	Ni_7Sn_2Bi
18	0.1559	59.2	Ni_3Sn_LT
19	0.1555	59.4	Ni_7Sn_2Bi
19	0.1324	71.1	Ni_3Sn_LT
16	0.1321	71.3	Ni_7Sn_2Bi
18	0.1205	79.5	Ni_3Sn_LT
18	0.1124	86.5	Ni_3Sn_LT
15	0.1107	88.2	Ni_3Sn_LT

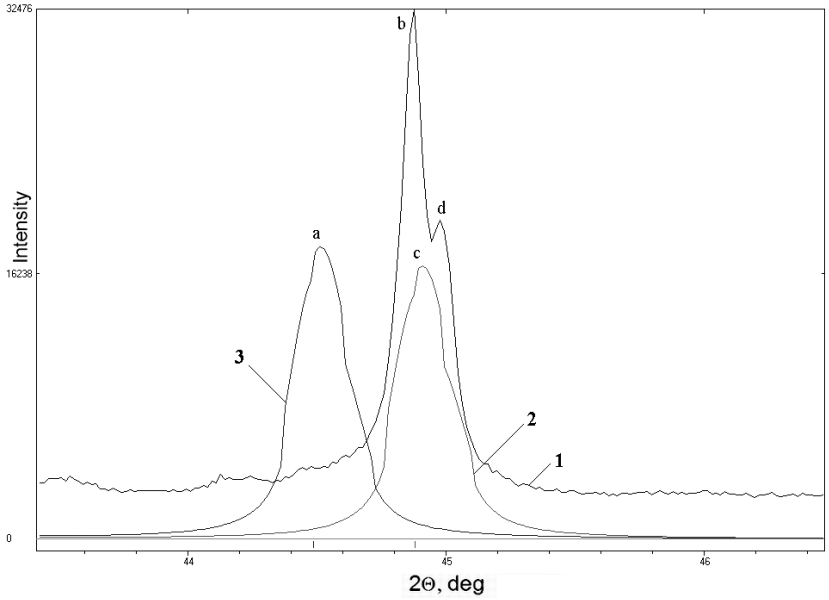

Fig. 3A (from 43.6 to 46,4 deg) and 3B (32.1 to 36.3 deg). Detailed representation of overlapping peaks of NiBi, Ni_3Sn_LT and Ni_7Sn_2Bi. Experimental diffractograms of: specimen S1 (curve 1); and of pure phases Ni_3Sn_LT (curve 2) and NiBi (curve 3)

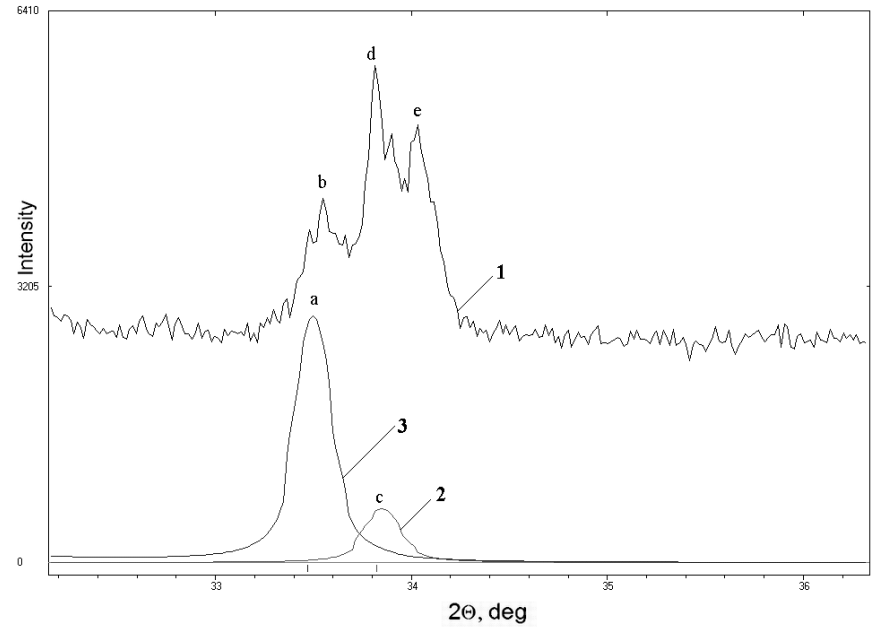

Fig. 3B. Overlapping diffraction peaks (b, d and e) found in experimental diffractograms of specimen S1 (curve 1); a - peak related to pure NiBi (curve 3); b - the respective peak related to NiBi of curve 1; c - peak related to pure Ni_3Sn_LT (curve 2); d - peak related to Ni_3Sn_LT of curve 1; e - hypothetical peak of Ni_7Sn_2Bi

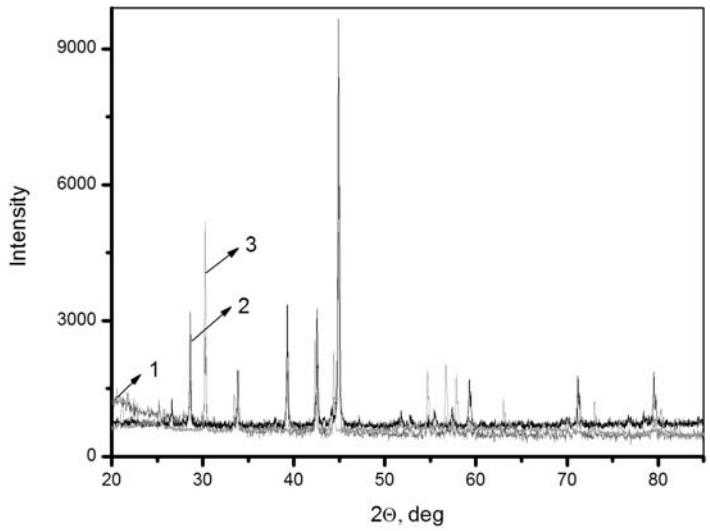

Fig. 4. X-ray diffractograms (D1 and D2) of the powdered sample S3 (curve 1) compared to experimental patterns of Ni_3Sn_LT (curve 2) and NiBi (curve 3). The intensity of the diffraction peaks (counts per second) is plotted along the ordinate, and the diffraction angles (2θ, deg) are plotted along the abscissa

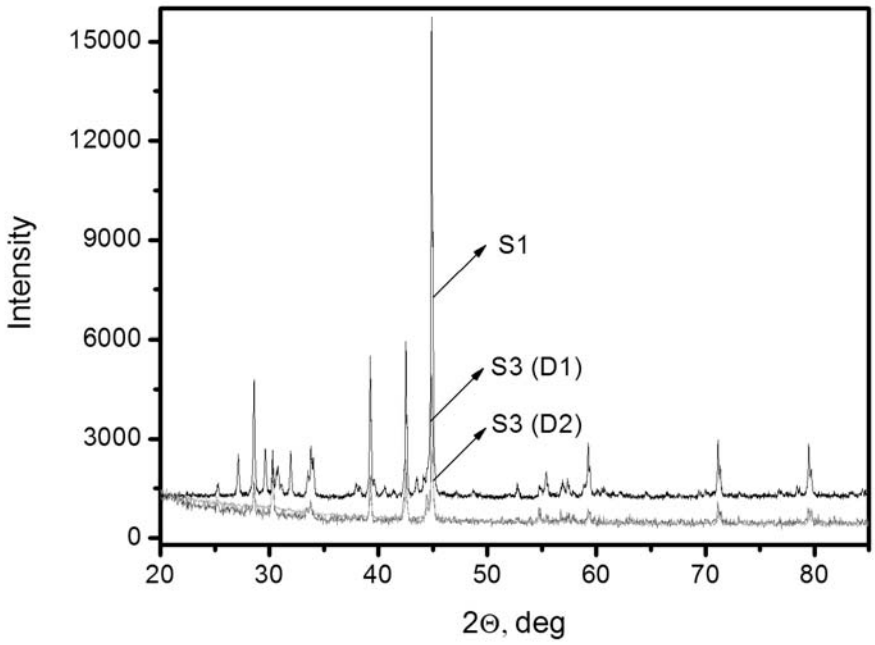

Fig. 5. X-ray diffractograms of specimens S1 and S3 (D1 and D2). The intensity of the diffraction peaks (counts per second) is plotted along the ordinate, and the diffraction angles (2θ, deg) are plotted along the abscissa

Table 2. Diffraction peaks (298 K, Cu $K_{\alpha 1}$) of the specimen S3 (diffractogram D2). No - number of the diffraction peak; 2θ- diffraction angles, deg, d - interlattice distances, nm; Intensity - relative intensity (%) of the diffraction peaks

Intensity %	d nm	2θ deg	Phase
6	0.3525	25.2	NiBi
25	0.3118	28.6	Ni_3Sn_LT
18	0.3025	29.5	Ni_7Sn_2Bi
53	0.2943	30.3	NiBi
19	0.2675	33.5	NiBi
23	0.2650	33.8	Ni_3Sn_LT
17	0.2631	34.1	Ni_7Sn_2Bi
38	0.2338	38.5	Ni_3Sn_LT
14	0.2280	39.5	Ni_7Sn_2Bi
48	0.2131	42.5	NiBi
23	0.2120	42.6	Ni_3Sn_LT
27	0.2034	44.5	NiBi
74	0.2050	44.7	Ni_7Sn_2Bi
100	0.2015	44.8	Ni_3Sn_LT
10	0.1734	52.8	Ni_3Sn_LT
19	0.1674	54.8	NiBi
16	0.1659	55.4	Ni_3Sn_LT
15	0.1657	55.5	Ni_6Sn_2Bi
18	0.1617	56.9	NiBi
17	0.1606	57.3	Ni_3Sn_LT
18	0.1559	59.2	Ni_3Sn_LT
22	0.1324	71.1	Ni_3Sn_LT
17	0.1321	71.4	Ni_7Sn_2Bi
19	0.1205	79.5	Ni_3Sn_LT
20	0.1124	86.5	Ni_3Sn_LT
16	0.1107	88.2	Ni_3Sn_LT

4. Conclusion

The phase equilibria in the system Ni-Sn-Bi have been studied. The results give evidences about the existence of a ternary compound with approximate formula Ni_6Sn_2Bi to Ni_7Sn_2Bi. Overlapping of some neighbouring diffraction peaks of this phase with NiBi and Ni_3Sn_LT is, probably, the reason for the difficulties related to the X-ray diffraction identification of the ternary phase.

Acknowledgment

This work is related to the European COST action MP0602 (HISOLD).

Table 3. Diffraction peaks (298 K, Cu $K_{\alpha 1}$) of the specimen S3 (diffractogram D3). No - number of the diffraction peak; 2θ- diffraction angles, deg, d - interlattice distances, nm; Intensity - relative intensity (%) of the diffraction peaks

Intensity %	d nm	2θ deg	Phase
5	0.3525	25.3	NiBi
20	0.3189	28.6	Ni_3Sn_LT
43	0.2945	30.3	NiBi
40	0.2942	30.4	Ni_7Sn_2Bi
11	0.2669	33.6	NiBi
12	0.2649	33.8	Ni_3Sn_LT
13	0.2647	33.9	Ni_7Sn_2Bi
37	0.2294	39.2	Ni_3Sn_LT
15	0.2283	39.4	Ni_7Sn_2Bi
30	0.2132	42.3	NiBi
50	0.2124	42.5	Ni_3Sn_LT
51	0.2121	42.6	Ni_7Sn_2Bi
48	0.2034	44.5	NiBi
100	0.2015	44.8	Ni_3Sn_LT
17	0.1727	53.0	Ni_3Sn_LT
19	0.1675	54.8	NiBi
16	0.1659	55.4	Ni_3Sn_LT
13	0.1652	55.6	Ni_7Sn_2Bi
16	0.1621	56.8	NiBi
14	0.1605	57.3	Ni_3Sn_LT
16	0.1603	57.4	Ni_7Sn_2Bi
18	0.1557	59.3	Ni_3Sn_LT
14	0.1551	59.5	Ni_7Sn_2Bi
19	0.1324	71.1	Ni_3Sn_LT
17	0.1321	71.3	Ni_7Sn_2Bi
20	0.1205	79.5	Ni_3Sn_LT

Table 4. Comparison between diffraction peaks of Ni_7Sn_2Bi (T) in S1 (diffractogram D1) and S3 (diffractograms D2 and D3)

No	Intensity %	d nm	2θ deg	Specimen/Diffractogram	Note
1	16	0.3288	27.2	S1/D1	Single peak (T)
2	17	0.3015	29.6	S1/D1	Single peak (T)
3	18	0.3025	29.5	S3/D2	Single peak (T)
4	14	0.2900	30.8	S1/D1	Double peak (T, NiBi)
5	40	0.2942	30.4	S3/D3	Double peak (T, NiBi)
6	17	0.2799	32.0	S1/D1	Single peak (T)
7	17	0.2631	34.1	S3/D2	Triple peak (NiBi, Ni_3Sn_LT,T)
8	16	0.2632	34.1	S1/D1	Triple peak (NiBi, Ni_3Sn_LT,T)
9	13	0.2647	33.9	S3/D3	Triple peak (NiBi, Ni_3Sn_LT,T)
10	23	0.2370	37.9	S1/D1	Single peak (T)
11	10	0.2273	39.4	S1/D1	Double peak (Ni_3Sn_LT,T)
12	14	0.2280	39.5	S3/D2	Double peak (Ni_3Sn_LT,T)
13	15	0.2283	39.4	S3/D3	Double peak (Ni_3Sn_LT,T)
14	12	0.2223	40.6	S1/D1	Single peak (T)
15	51	0.2121	42.6	S3/D3	Highest relative intensity; Triple peak (NiBi, Ni_3Sn_LT,T)
16	12	0.2078	43.5	S1/D1	Single peak (T)
17	74	0.2050	44.7	S3/D2	Highest relative intensity; Double peak (Ni_3Sn_LT,T)
18	60	0.2051	45.0	S1/D1	Highest relative intensity; Double peak (Ni_3Sn_LT,T)
19	13	0.2014	44.2	S1/D1	Single peak (T)
20	13	0.1652	55.6	S3/D3	Single peak (T)
21	15	0.1657	55.5	S3/D2	Single peak (T)
22	12	0.1658	55.5	S1/D1	Triple peak (NiBi, Ni_3Sn_LT)
23	16	0.1603	57.4	S3/D3	Double peak (Ni_3Sn_LT,T)
24	18	0.1605	57.4	S1/D1	Double peak (Ni_3Sn_LT,T)
25	14	0.1551	59.5	S3/D3	Double peak (Ni_3Sn_LT,T)
26	19	0.1555	59.4	S1/D1	Double peak (Ni_3Sn_LT,T)
27	16	0.1321	71.3	S1/D1	Double peak (Ni_3Sn_LT,T)
28	17	0.1321	71.4	S3/D2	Double peak (Ni_3Sn_LT,T)
29	17	0.1321	71.3	S3/D3	Double peak (Ni_3Sn_LT,T)

References

1. S.K. Kang, R.S. Rai, S. Purushothaman, *J. Electron. Mater.* 25 (1996) 1113.

2. W. H. Tao, C. Chen, C. E. Ho, W. T. Chen, C. R. Kao, *Chem. Mater.* 13 (2001) 1051.

3. J.-I. Lee, S.-W. Chen, H.-Y. Chang, C-M. Chen, *J. Electron. Mater.* 32 (2003) 117.

4. T. Massalski, Binary Alloy Phase Diagrams, CD-ROM, Ohio, USA, *ASM International,* 1996.

5. D. Malakhov, X. J. Liu, I. Ohnuma, R. Kainuma, H. Ohtani, K. Ishida, *Mat. Trans.,* 43 (2002) 1879.

6. G.P. Vassilev, K.I. Lilova, J.C. Gachon, *Therm. Acta,* 447 (1) (2006) 106-108.

7. G.P. Vassilev, K.I. Lilova, J.C. Gachon, Calorimetric studies of the Ni-Sn system, In: Proceedings of VIIIth Int. Workshop of Assoc. Phase Diagram and Thermod. Committee, Košice, Slovakia, 19 November 2005, Ed. W. Zakulski, ISBN 83-921845-5-6, Published by: Ins. Met. and Mat. Sc., Polish Academy of Sciences, Krakow, Poland, p. 27-34.

8. C. Schmetterer, H. Flandorfer, K. W. Richter, U. Saeed, M. Kauffman, P. Roussel, H. Ipser, *Intermetallics*, 15 (7) (2007) 869.

9. G. P. Vassilev, K.I. Lilova, J.-C. Gachon, Phase diagram investigations of the Ni-Sn-Bi system, submitted to *JALCOM.*

10. G.P. Vassilev, K.I. Lilova, *Cryst. Res. Technol.* 42 (2007) 237.

11. G. Hagg, G. Funke, Z. Phys. Chem. B 6, 272 (1929) *(in German)*

12. Lyubimtsev A., A. Baranov , A. Fischer , L. Kloo , B. Popovkin, The structure and bonding of Ni3Sn, *Journal of Alloys and Compounds,* 340 (2002) 167-172