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PHASE RELATIONS IN Bi - RICH PART OF THE Bi-Ga-Ni SYSTEM

D. Živković[a,*], D. Manasijević[a], Lj. Balanović[a], D. Minić[b], V. Ćosović[c], A. Kostov[d], Ž. Živković[a]

[a] University of Belgrade, Technical Faculty, Bor, Serbia
[b] University of Pristina, Faculty of Technical Sciences, Kosovska Mitrovica, Serbia
[c] University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia
[d] Mining and Metallurgy Institute, Bor, Serbia

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Abstract

The results of phase relations investigation in bismuth-rich part of ternary Bi-Ga-Ni system are presented in this paper. Two sections with constant bismuth content equal to 80 and 90 at% were investigated experimentally using DSC and SEM-EDS methods and predicted thermodynamically by CALPHAD method. Calculated phase diagrams showed reasonable agreement with experimental data.

Keywords: *Bi-Ga-Ni system, phase diagram, CALPHAD, DTA, SEM-EDX*

1. Introduction

Gallium alloys are usually used in semiconductor processing, mirror production, for dental amalgams, low temperature solders etc. [1-6].

Some of Ga-Ni-based alloys, such as Ga-Ni-Mn, Ga-Ni-Fe or Ga-Ni-Co, are also well known due to their shape memory effect [7-9]. Also, other alloys in that group of materials, such as Ga-Ni-Me (Me=Pd, Pb, Sb, Sc, Si, Sn, Ta, Te, Ti, V, Zn, Zr), are scientifically described and examined widely [10]. Bi-Ga-Ni system has not been thermodynamically investigated, nor was its phase diagram defined yet. Constitutive binary systems - Bi-Ga [11,12], Ga-Ni [13,14] and Bi-Ni [15,16], were examined and well described in literature from thermodynamic and phase diagram point of view, while the newest thermodynamic assessment of these binaries is given in COSTMP0602 thermodynamic databases [17].

The results of experimental investigation - thermal and structural analysis, and thermodynamic prediction of phase relations in Bi-rich part of the Bi-Ga-Ni system using Calphad technique, are presented in this paper.

2. Experimental

2.1 Samples

The alloys investigated in this paper were prepared by metals - bismuth, gallium and nickel of 99.99% purity. The samples were prepared by melting in an induction furnace under protective atmosphere. The mass loss was less than 1%.

The compositions of used samples are given in Table 1.

Table 1. *Composition of used samples in Bi-Ga-Ni system – sections with 90%Bi (a) and 80%Bi (b)*

a)						
Alloy	xBi	xGa	xNi	mass %Bi	mass %Ga	mass %Ni
E1	0,9	0,07	0,03	86,75	11,81	1,44
E2	0,9	0,04	0,06	90,00	7,00	3,00
E3	0,9	0,02	0,08	92,31	3,59	4,10
b)						
Alloy	xBi	xGa	xNi	mass %Bi	mass %Ga	mass %Ni
E4	0,8	0,16	0,04	72,73	25,45	1,82
E5	0,8	0,1	0,1	78,05	17,07	4,88
E6	0,8	0,04	0,16	84,21	7,37	8,42

2.2 Techniques

Differential scanning calorimetry (DSC) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) were used for the experimental investigations in this paper.

Thermal analysis of chosen samples was performed using DSC method, by TA instruments SDT Q600 thermal analyzer under following

* *Corresponding author: dzivkovic@tf.bor.ac.rs*

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conditions - heating rate of 5 ◦C/min, dynamic argon atmosphere, alumina crucibles, sample masses 25-30mg.

Structural analysis and equilibrium phase chemical compositions were examined by JEOL JSM-6460 scanning electron microscope equipped with Oxford Instruments energy dispersive spectrometer, under following conditions - EDS resolution up to 10 nm, acceleration voltage 0.2-30 kV and magnification up to 300000 x. No etching was applied for microscopic examination. The experimental accuracy of presented results is ±2 at%.

3. Thermodynamic calculation of the Bi-Ga-Ni phase equilibria

Thermodynamic assessment of the Bi-Ga binary system was carried out by Girard [12]. The latest thermodynamic assessment of the Bi-Ni binary system was performed by Vassiliev et al [16] and thermodynamic assessment of the Ga-Ni binary system was done by Yuan et al. [14]. Calculated phase diagrams of the Bi-Ga, Bi-Ni and Ga-Ni binary systems are shown in Fig 1.

The phase diagram of the Bi-Ga (Fig.1a) binary system is characterized by the appearance of the liquid miscibility gap. There are no solubility in solid phases.

There are two intermediate phases in the Bi-Ni binary system (Fig.1b). The BiNi phase has very narrow homogeneity range and Bi_3Ni phase is stoichiometric compound.

The phase diagram of the Ga-Ni binary system (Fig.1c) is quite complex. It consists of the liquid solution, fcc-(Ni) solid solution with large solubility of Ga, Ga phase with no solubility of Ni and following

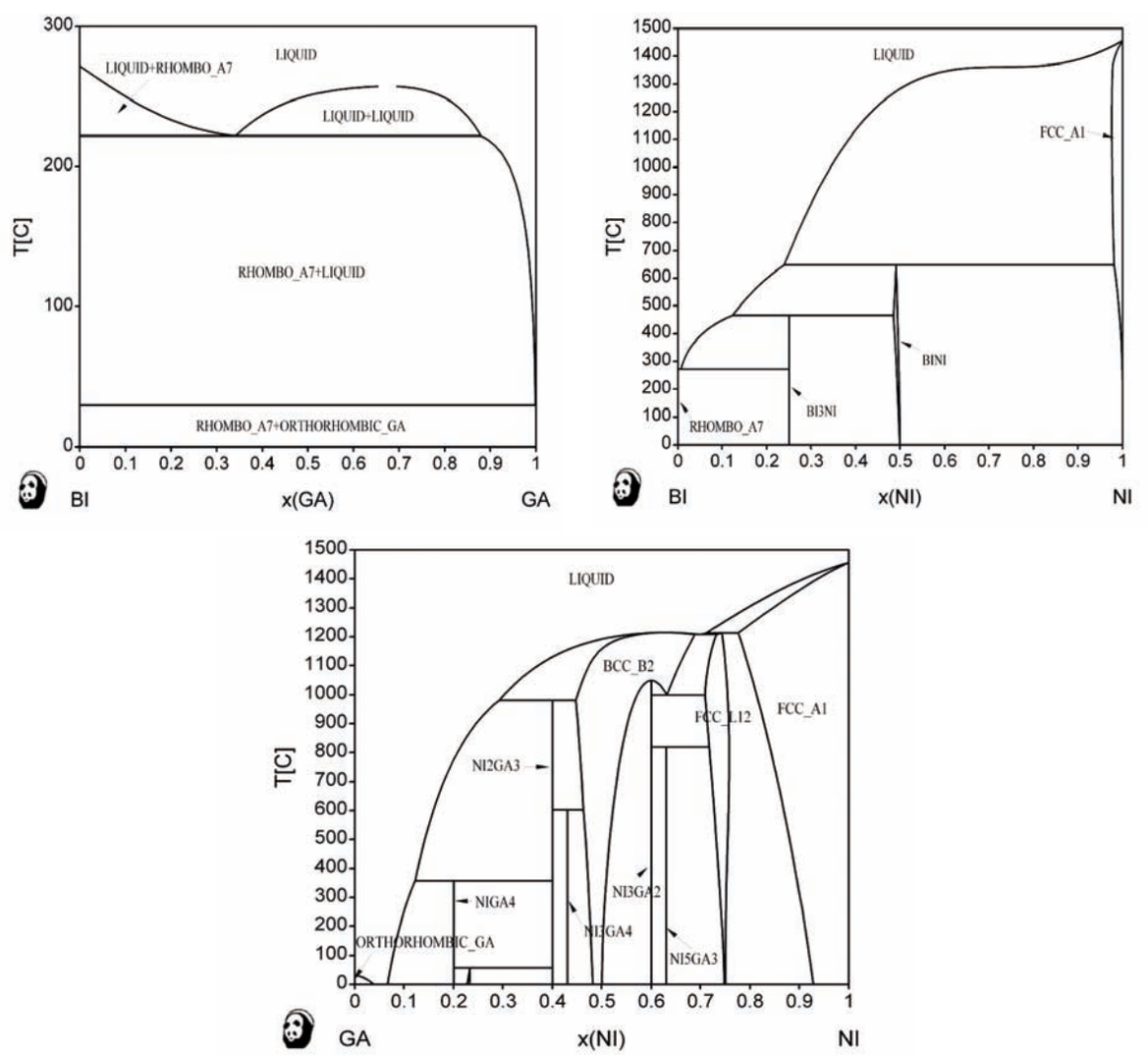

Figure 1. *Calculated phase diagrams of binary systems - Bi-Ga [12], Bi-Ni [16] and Ga-Ni [14]*

Table 2. *Thermodynamic models and parameters used in this work*

Phase and thermodynamic model	Thermodynamic parameters	Ref.
LIQUID (Bi,Ga,Ni)	${}^{0}L^{LIQUID}_{Bi,Ga} = 8401.6 + 0.996135T$	[12]
	${}^{1}L^{LIQUID}_{Bi,Ga} = -560.9 - 2.43423T$	[12]
	${}^{2}L^{LIQUID}_{Bi,Ga} = 754.8 - 0.682275T$	[12]
	${}^{3}L^{LIQUID}_{Bi,Ga} = -1162.5$	[12]
	${}^{0}L^{LIQUID}_{Bi,Ni} = -6440 + 13.288T$	[16]
	${}^{1}L^{LIQUID}_{Bi,Ni} = -11315 - 1.457T$	[16]
	${}^{0}L^{LIQUID}_{Ga,Ni} = -122488.59 + 35.72T$	[14]
	${}^{1}L^{LIQUID}_{Ga,Ni} = -29685 + 14T$	[14]
	${}^{2}L^{LIQUID}_{Ga,Ni} = -37051.9 + 22.10T$	[14]
FCC_A1 $(Bi,Ga,Ni)_1(Va)_1$	${}^{0}L^{FCC\_A1}_{Bi,Ni:Va} = 20000 + 12.5T$	[16]
	${}^{0}L^{FCC\_A1}_{Ga,Ni:Va} = -130526 + 40T$	[14]
BCC_B2 $(Ga,Ni)_{0.5}(Ni,Va)_{0.5}$	$G^{BCC\_B2}_{Ga:Ni} = -54030.75 + 16.50T + 0.5G^{BCC\_A2}_{Ga} + 0.5G^{BCC\_A}_{Ni}$	[14]
	$G^{BCC\_B2}_{Ga:Va} = 5000 - 0.5T + 0.5G^{BCC\_A2}_{Ga}$	[14]
	$G^{BCC\_B2}_{Ni:Ni} = G^{BCC\_A2}_{Ni}$	[14]
	$G^{BCC\_B2}_{Ni:Va} = -G^{BCC\_B2}_{Ga:Ni} + G^{BCC\_B2}_{Ni:Ni} + G^{BCC\_B2}_{Ga:Va}$	[14]
	${}^{0}L^{BCC\_B2}_{Ga,Ni:Ni} = -8724 - 2.38T$	[14]
	${}^{0}L^{BCC\_B2}_{Ga,Ni:Ni} = -8724 - 2.38T$	[14]
	${}^{0}L^{BCC\_B2}_{Ga:Ni,Va} = -35016.4 + 20.3T$	[14]
	${}^{0}L^{BCC\_B2}_{Ni:Ni,Va} = -35016.4 + 20.3T$	[14]
BINI $(Bi)_{0.333}(Ni)_{0.333}(Bi, Ni,Va)_{0.333}$	$G^{BiNi}_{Bi:Ni:Bi} = 0 + 0.666G^{SER}_{Bi} + 0.333G^{SER}_{Ni}$	[16]
	$G^{BiNi}_{Bi:Ni:Va} = -3550 + 0.333G^{SER}_{Bi} + 0.333G^{SER}_{Ni}$	[14]
	${}^{0}L^{BiNi}_{Bi:Ni:Bi,Va} = -1647 + 1.434T$	[14]
BI3NI $(Bi)_{0.75}(Ni)_{0.25}$	$G^{Bi_3Ni}_{Bi:Ni} = -5395 + 0.75G^{SER}_{Bi} + 0.25G^{SER}_{Ni}$	[14]
FCC_L12 $(Ni,Ga)_{0.75}(Ga,Ni)_{0.25}(Va)_1$	$G^{FCC\_L12}_{Ga:Ga:Va} = G^{FCC\_A1}_{Ga}$	[14]
	$G^{FCC\_L12}_{Ni:Ni:Va} = G^{SER}_{Ni}$	[14]
	$G^{FCC\_L12}_{Ni:Ga:Va} = -27789 + 1.64T + 0.25G^{SER}_{Ni} + 0.75G^{FCC\_A1}_{Ga}$	[14]
	$G^{FCC\_L12}_{Ga:Ni:Va} = -27789 + 1.64T + 0.75G^{FCC\_A1}_{Ga} + 0.25G^{SER}_{Ni}$	[14]
	${}^{0}L^{FCC\_L12}_{Ga,Ni:Ga:Va} = -55578 + 3.28T$	[14]
	${}^{1}L^{FCC\_L12}_{Ga,Ni:Ga:Va} = 14040 - 8.01T$	[14]
	${}^{0}L^{FCC\_L12}_{Ga,Ni:Ni:Va} = -55578 + 3.28T$	[14]
	${}^{1}L^{FCC\_L12}_{Ga,Ni:Ni:Va} = 14040 - 8.01T$	[14]
	${}^{0}L^{FCC\_L12}_{Ga:Ga,Ni:Va} = 0$	[14]
	${}^{1}L^{FCC\_L12}_{Ga:Ga,Ni:Va} = 4680 - 2.67T$	[14]
	${}^{0}L^{FCC\_L12}_{Ni:Ga,Ni:Va} = 0$	[14]
	${}^{1}L^{FCC\_L12}_{Ni:Ga,Ni:Va} = 4680 - 2.67T$	[14]
NI5GA3 $(Ni)_{0.63}(Ga)_{0.37}$	$G^{Ni_5Ga_3}_{Ni:Ga} = -37622.61 + 5.23T + 0.63G^{SER}_{Ni} + 0.37G^{SER}_{Ga}$	[14]
NI3GA2 $(Ni)_{0.6}(Ga)_{0.4}$	$G^{Ni_3Ga_2}_{Ni:Ga} = -39714.31 + 5.43T + 0.6G^{SER}_{Ni} + 0.4G^{SER}_{Ga}$	[14]
NI3GA4 $(Ni)_{0.43}(Ga)_{0.57}$	$G^{Ni_3Ga_4}_{Ni:Ga} = -47736.8 + 8.87T + 0.43G^{SER}_{Ni} + 0.57G^{SER}_{Ga}$	[14]
NI2GA3 $(Ni)_{0.4}(Ga)_{0.6}$	$G^{Ni_2Ga_3}_{Ni:Ga} = -47379.09T + 8.74T + 0.4G^{SER}_{Ni} + 0.6G^{SER}_{Ga}$	[14]
NIGA4 $(Ni)_{0.2}(Ga)_{0.8}$	$G^{Ni\,Ga_4}_{Ni:Ga} = -24293.51 - 2.74T + 0.2G^{SER}_{Ni} + 0.8G^{SER}_{Ga}$	[14]

intermediate phases - five stoichiometric compounds Ni_5Ga_3, Ni_3Ga_2, Ni_3Ga_4, Ni_2Ga_3, and N_iGa_4 and two ordered phases - the Ni3Ga phase with the cubic L12 crystal structure (FCC_L12 thermodynamic database name) and the NiGa phase with B2-structure (BCC_B2 thermodynamic database name).

Since there are no experimental information about phase equilibria and thermodynamics of investigated ternary Bi-Ga-Ni system in the literature, phase diagram of the Bi-Ga-Ni system was extrapolated using binary formalism of the CALPHAD method [18]. Thermodynamic data for the pure elements were based on the SGTE (Scientific Group Thermodata Europe) values [19]. Binary thermodynamic parameters were taken from the References [12,14,16] and shown in Table 2. Because no data are available on the solubility of Ni and Bi in (Ga) and Ga and Ni in (Bi) solid Bi and Ga were treated as a pure phases in this study.

4. Results and Discussion

The results of thermal analysis, done by DSC, are presented in Table 3. Characteristic DCS curve for the sample E4 is shown in Fig.2 as an example. Sample's solidus temperature was determined as onset temperature of the first peak on heating. Liquidus and other phase transformations temperatures were determined as maximum peak temperature on heating.

Mutual comparison between DSC results and thermodynamic prediction is shown in Fig 3.

The solidus temperature of the samples E2, E3, E5 and E6 is practically constant at 267 °C (average value). This temperature is close to the predicted temperature of ternary eutectic reaction LIQUID -> BCC_B2 + RHOMBO_A7 + Bi3NI at 269.7 °C.

The solidus temperature of the samples E1 and E4 (227 °C average value) is considerably lower than corresponding temperature of the predicted liquid transition reaction LIQUID + NI2GA3 -> RHOMBO_A7 + NIGA4 at 253.3 °C. So, as can be notice, experimentally determined liquidus temperatures of the investigated samples are generally lower than corresponding predicted values.

Table 3. *The results of DSC measurements*

Alloy composition, at%	Temperatures of phase transformations, °C		
	Solidus	Other phase transformations	Liquidus
E1: Bi-90; Ga-7;Ni-3	228	/	896
E2: Bi-90; Ga-4;Ni-6	267	/	905
E3: Bi-90; Ga-2;Ni-8	268	/	875
E4: Bi-80; Ga-16;Ni-4	226	913	995
E5: Bi-80; Ga-10 ; Ni-10	267	/	1064
E6: Bi-80; Ga-4 ; Ni-16	267	/	1006

4.1 Structural analysis

Microstructure investigation of the chosen Bi-Ga-Ni alloys was performed using SEM-EDS analysis, as given in Fig. 4. The elemental compositions of the coexisting phases were determined and the obtained results are given in Table 4.

As can be seen from SEM microphotographs (Fig.3), for the samples E1 and E4 dark phase is

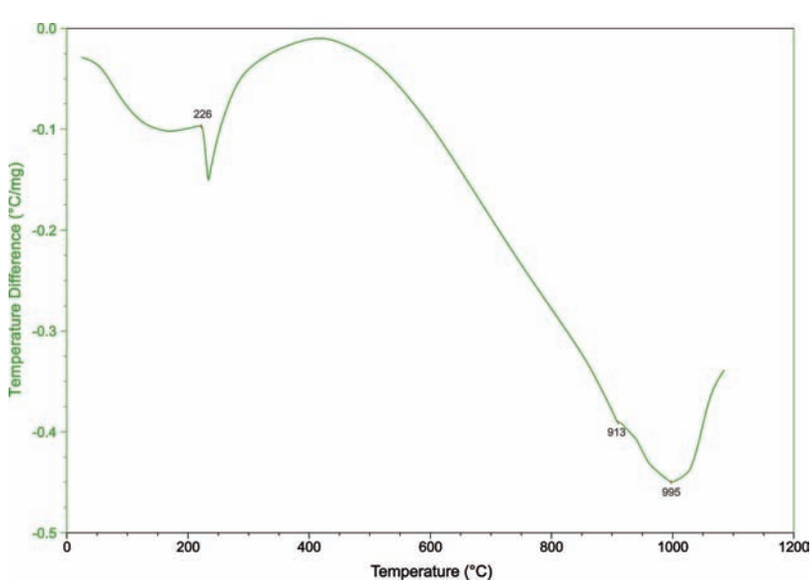

Figure 2. *DSC heating curve for the sample E4 (Bi-80; Ga-16; Ni-4) with determined phase transformation temperatures*

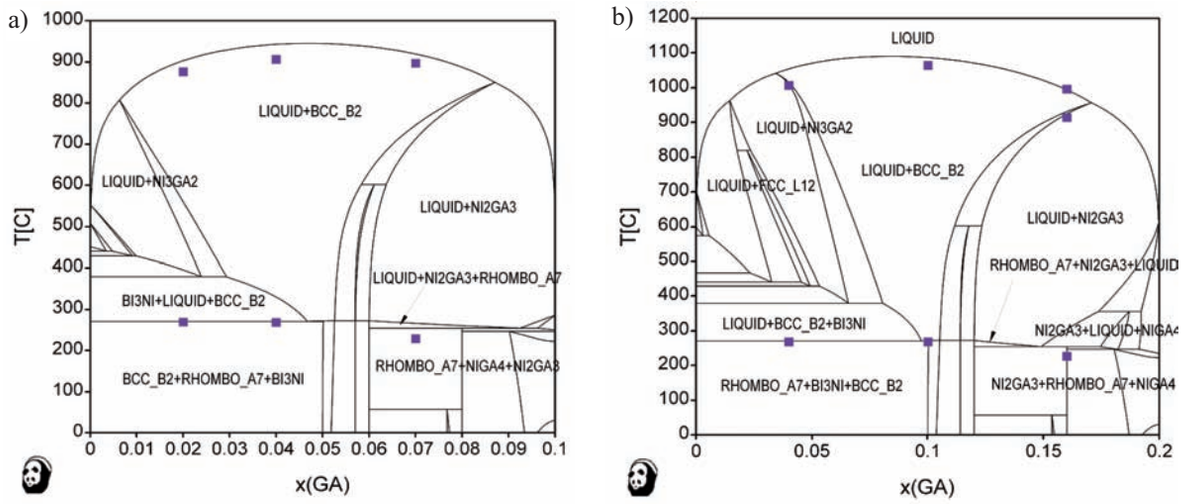

Figure 3. *Predicted vertical sections - (a) 90 at.% Bi and (b) 80 at.% Bi - with DTA results from this work*

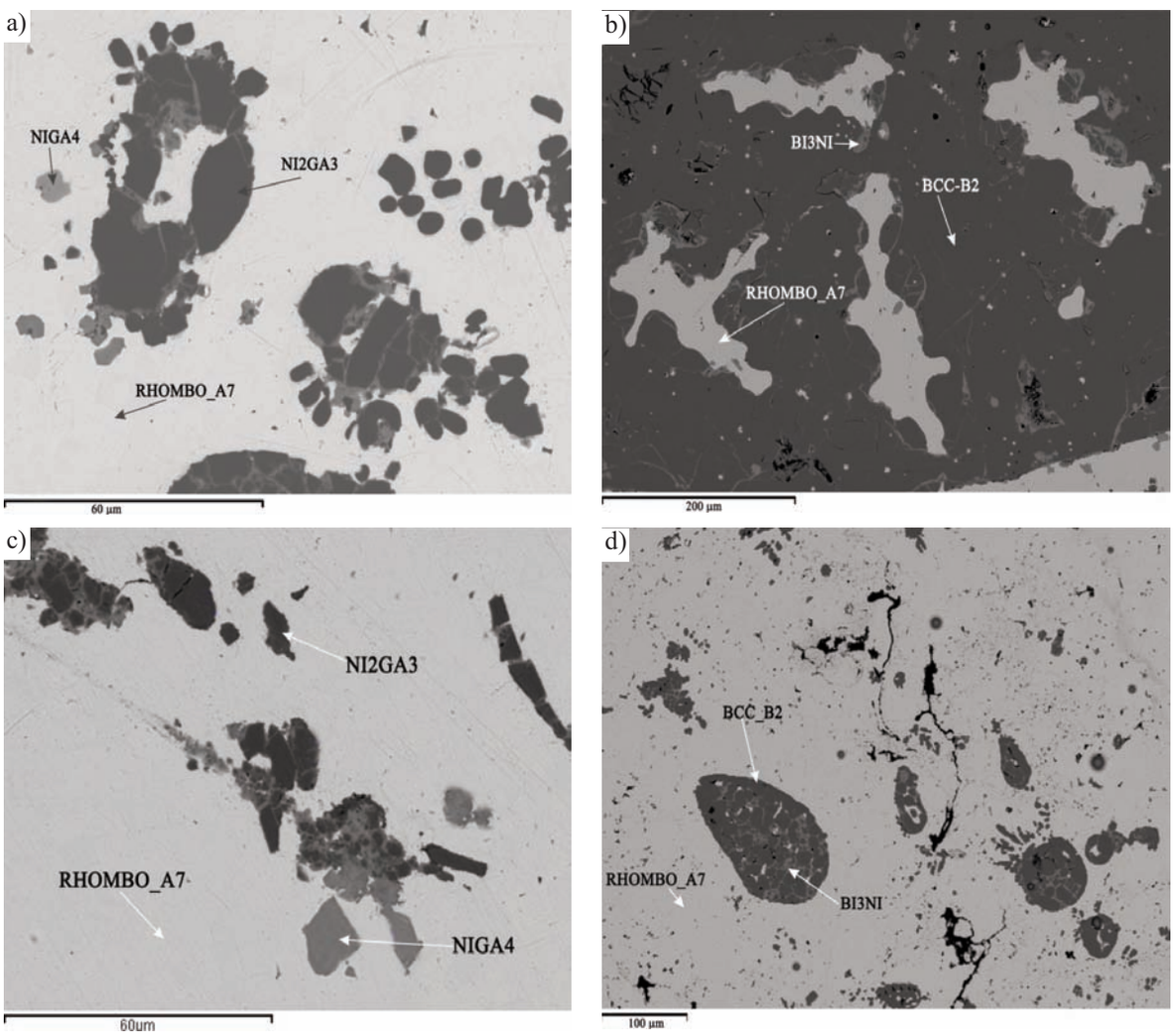

Figure 4. *Characteristic SEM microphotographs for the samples - section with 90%Bi: E1 (a), E3 (b), and section with 80%Bi: E4 (c) and E5 (d) (Note: in Fig3b black areas presents pores)*

related to Ni2Ga3 intermetallic compound, gray phase corresponds to NiGa4 intermetallic compound, while light phase represents (Bi)-based solid solution (RHOMBO_A7). On the other hand, microstructures of the samples E4 and E5 consists of (Bi,Ga)-based solid solution (BCC_B2) – dark phase, Bi3Ni intermetallic compound – grey phase and (Bi)-based solid solution (RHOMBO_A7) - light phase.

According to the results of comparison between predicted and experimentally obtained phase equilibria for investigated samples, it could be seen that qualitative mutual agreement exists. However, some of the phases determined-Bi3Ni and NiGa4 include solubility of third component, which was not expected regarding to the thermodynamic prediction.

5. Conclusions

Phase relations in the Bi-rich part of the Bi-Ga-Ni system were investigated using thermodynamic prediction according to CALPHAD approach and experimentally, using SEM-EDX and DSC methods. Two vertical sections, with 90 at.% Bi and 80 at.% Bi were calculated and compared with experimental results from this work. Characteristic phase transformation temperatures of selected samples with the compositions along two investigated vertical sections were determined using DSC. Two invariant effects, at 267 °C and 227 °C, were observed on DSC heating curves. First thermal signal at 267 °C is in good agreement with predicted ternary eutectic reaction at 269.7 °C. Experimentally determined liquidus temperatures are considerably lower than predicted ones. The results of microstructure analysis confirmed the presence of the predicted phase structure at room temperature.

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Table 4. *Comparison between predicted (CALPHAD) and experimentally determined (EDX) phases for investigated sections*

Sample	Predicted phases	Experimentally determined phases (EDX)	at% Ni	at% Ga	at% Bi
E1	RHOMBO_A7	RHOMBO_A7	0	0.99	99.01
	NI2GA3	NI2GA3	38.53	61.48	0
	NIGA4	NIGA4	7.05	84.53	8.43
E3	RHOMBO_A7	RHOMBO_A7	0.75	0	99.25
	BCC_B2	BCC_B2	55.48	44.52	0
	BI3NI	BI3NI	16.845	12.085	71.07
E4	RHOMBO_A7	RHOMBO_A7	0	0	100
	NIGA4	NIGA4	13.92	85.12	0.96
	NI2GA3	NI2GA3	38.04	61.69	0.28
E6	RHOMBO_A7	RHOMBO_A7	0.25	0	99.75
	NI2GA3	NI2GA3	38.26	61.74	0
	BCC_B2	BCC_B2	55.38	44.62	0

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