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PROCEEDINGS

Edited by
Saša Stojadinović
and
Dejan Petrović

November 29th – 30th 2021

Bor, Serbia

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EXPERIMENTAL AND THERMODYNAMIC STUDY OF ISOTHERMAL SECTIONS AT 600 °C AND 400 °C OF TERNARY Bi-Cu-Ge SYSTEM

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Abstract
Experimental and computation thermodynamic is very important for future development of materials and knowledge of phase diagram. Knowlegde of phase diagram without experimental confirmation is not worth a lot. In this study both calculation and experiments were performed for better knowledge of isothermal sections. Calculated phase diagrams were two isothermal sections at 600 °C and 400 °C. Calculations were done by using PANDAT software and thermodynamic data from literadute. Experimental were performed on 12 annealed alloys. Six alloys were prepared per isothermal section. Compositions od alloys and phases presented in microstructures were tested with SEM-EDS while determination of phases in samples were checked with XRD.Results of EDS were compared with calculated isothermal sections and good agreement were reached.

***Keywords**: ternary Bi-Cu-Ge system, SEM-EDS analysis,XRD analysis, isothermal sections.*

1. INTRODUCTION

Germanium is important semiconductor and it is known that by addition of Bi to Ge-based materials their semiconducting properties can be improved [1]. Beside, it germanium based alloys are extensively used in electrical and electronic industry [2]. In this paper ternary Bi-Cu-Ge system is in focus. Cu is chosen as a alloying element due to the key properties of copper such as excellent electrical and heat conductivity, good erosion, corrosion and biofouling resistance, high strength, good machinability, non-magnetic, etc. [3,4]. In this work studied ternary alloys were from isothermal sections at 600 °C and 400 °C. Used experimental techniques included scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) and X-ray powder diffraction (XRD). The experimental results were compared with the calculated phase diagrams of the isothermal sections at 400 C and 600 °C. Reasonable agreement between the calculated phase diagrams and the experimental data was obtained. For studied ternary Bi-Cu-Ge system it was not necessary to introduce new ternary parameters.

2. EXPERIMENTAL

Ternary alloys for experimental tests are prepared from high pure Bi, Cu and Ge (99.999 at. %) elements, produced by Alfa Aesar, Germany. All samples are melted and re-melted five times in an induction furnace, to preserve homogeneity. Such samples are divided in two groups. One group is with 6 samples used for phase equilibriumat 600 °C. Second group of samples are used for phase equilibriumat 400 °C. The average mass of theeachternary alloy sample was about 4 g. Such prepared samples were tested by XRD and SEM-EDS.

Used device for SEM-EDS analysis was JEOL JSM-6460 scanning electron microscope paired with Oxford Instruments X-act energy dispersive X-Ray spectroscope. The used XRD device was Bruker D2 PHASER powder diffractometer equipped with a dynamic scintillation detector and ceramic X-Ray Cu tube (KFL-Cu-2 K). XRD patterns were recorded in a 2θ range from 10 to 75° with a step size of 0.02° and then analyzed using the Topas 4.2 software and ICDD databases PDF2 (2020).

3. RESULTS AND DISCUSSION

3.1.Isothermal section at 600 °C

Six ternary samples annealed at 600 °C for five weeks were tested with SEM-EDS and XRD. Results of tests are presented in Table 1.

Table 1.Combined results of SEM-EDS and XRD analyzes of the selected alloys annealed at 600 °C.

No.	Composition of samples (at.%)	Determined phases		Compositions of phases (at.%)			Lattice parameters (Å)
		EDS	XRD	Bi	Cu	Ge	
1	89.13 Bi 0.86 Cu 10.01 Ge	L (Ge)	- (Ge)	93.52±0.5 0.01±0.3	1.58±0.2 0.19±0.1	4.90±0.1 99.80±0.7	- *a*=*b*=*c*=5.6531
2	36.75 Bi 25.64 Cu 37.61 Ge	L (Ge) η	- (Ge) η	93.88±0.2 0.03±0.3 0.09±0.6	2.29±0.8 0.08±0.3 75.73±0.1	3.83±0.3 99.89±0.4 24.18±0.6	- *a*=*b*=*c*=5.6547 a=5.2902, b=4.2003, c=4.5487
3	38.22 Bi 33.54 Cu 28.24 Ge	L (Ge) η	- (Ge) η	93.18±0.5 0.05±0.5 0.07±0.5	3.28±0.2 0.77±0.5 73.82±0.4	3.54±0.2 99.18±0.1 26.11±0.5	- *a*=*b*=*c*=5.6552 a=5.2892, b=4.2123, c=4.5531
4	36.75 Bi 51.04 Cu 12.21 Ge	L ε ξ	- ε ξ	93.52±0.1 0.55±0.7 0.37±0.2	5.72±0.7 76.47±0.5 83.40±0.2	0.76±0.4 22.98±0.3 16.23±0.1	- a=b=4.1673, c=7.5003 *a*=*b*=2.6022, *c*=4.2352
5	32.15 Bi 63.93 Cu 3.92 Ge	L (Cu)	- (Cu)	91.68±0.4 0.74±0.3	8.27±0.1 93.30±0.2	0.05±0.3 5.96±0.6	- *a*=*b*=*c*=3.6652
6	10.11 Bi 86.34 Cu 3.55 Ge	L (Cu)	- (Cu)	90.95± 0.7 0.56±0.2	8.63±0.5 96.33±0.4	0.42±0.2 3.11±0.1	- *a*=*b*=*c*=3.6611

With six samples four different phase regions are detected. In microstructure of sample 1, L and (Ge) phase are detected. Samples 2 and 3 detected same three phases L, (Ge) and intermetallic compound η. Sample 4 detected three phases L, ε and ξ. Samples 5 and 6 detected same two phases L and (Cu).

Experimental results given in Table 1 are compared with calculated isothermal section at 600 °C. Calculated phase diagram is performed by using Pandat software and thermodynamic dataset compiled. Calculated isothermal section with EDS results given in Table 1 are presented on Figure 1.

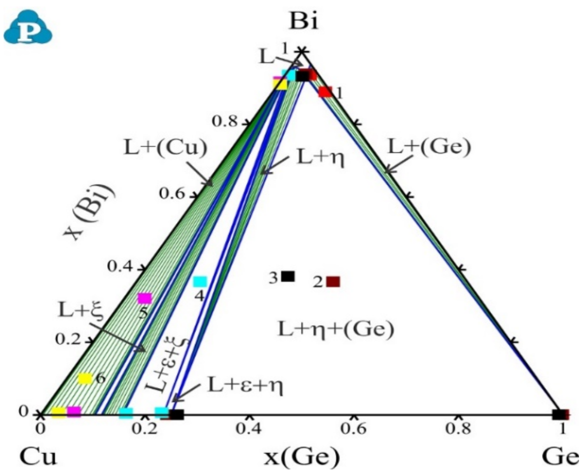

Figure 1. Calculated Bi-Cu-Ge isothermal section at 600 °C compared with EDS results given in Table 1.

On calculated isothermal section ten phase regions are visible. One region is L single phase region oriented to the Bi side, five are two-phase regions L+(Ge), L+η, L+ε, L+ξ and L+(Cu), four are three-phase regions L+η+(Ge), L+ε+η, L+ε+ξ and L+ξ+(Cu). From those ten calculated phase region four are experimentally confirmed with six samples.By comparison it is clear that experimental determined composition of phases is close with experimental composition of phases. As conclusion experiments can well follow calculated isothermal section at 600 °C.

3.2.Isothermal section at 400 °C

Six ternary samples marked with numbers from 7 to 12 are used for testing phaseequilibria at 400 °C. Samples were annealed at 400 °C for five weeks and tested with SEM-EDS and XRD. Results of tests are given in Table 2.

Table 2.Combined results of SEM-EDS and XRD analyzes of the selected alloys annealed at 400 °C.

No.	Composition of samples (at.%)	Determined phases		Compositions of phases (at.%)			Lattice parameters (Å)
		EDS	XRD	Bi	Cu	Ge	
7	47.04 Bi	L	-	99.18±0.1	0.81±0.1	0.01±0.4	-
	11.38 Cu	(Ge)	(Ge)	0.20±0.5	1.62±0.4	98.18±0.5	*a*=*b*=*c*=5.6579
	41.58 Ge	η	η	0.34±0.4	73.53±0.3	26.13±0.1	*a*=5.2911, *b*=4.2087, *c*=4.5541
8	22.54 Bi	L	-	99.82±0.3	0.15±0.4	0.03±0.2	-
	32.81 Cu	(Ge)	(Ge)	0.01±0.7	1.91±0.5	98.08±0.6	*a*=*b*=*c*=5.6558
	44.65 Ge	η	η	0.03±0.4	75.79±0.7	24.18±0.7	*a*=5.2972, *b*=4.2152, *c*=4.5598
9	36.93 Bi	L	-	99.01±0.2	0.68±0.1	0.31±0.6	-
	40.21 Cu	(Ge)	(Ge)	0.12±0.5	1.05±0.3	98.83±0.4	*a*=*b*=*c*=5.6560
	22.86 Ge	η	η	0.54±0.6	72.92±0.7	26.54±0.4	*a*=5.2978, *b*=4.2155, *c*=4.5613
10	30.69 Bi	L	-	98.18±0.1	1.50±0.2	0.32±0.3	-
	55.70 Cu	η	η	0.13±0.3	75.72±0.6	24.15±0.2	*a*=5.2968, *b*=4.2052, *c*=4.5573
	13.61 Ge	ξ	ξ	0.92±0.7	85.41±0.8	13.67±0.1	*a*=*b*=2.6125, *c*=4.2392
11	32.32 Bi	L	-	98.01±0.1	1.81±0.1	0.18±0.5	-
	65.18 Cu	(Cu)	(Cu)	0.15±0.2	94.23±0.2	5.62±0.7	*a*=*b*=*c*=3.6631
	2.50 Ge						
12	63.31 Bi	L	-	98.81±0.5	0.67±0.5	0.52±0.2	-
	35.22 Cu	(Cu)	(Cu)	0.37±0.1	98.20±0.2	1.43±0.3	*a*=*b*=*c*=3.6598
	1.47 Ge						

Three different phase regions are detected by six tested samples. In microstructure of samples 7, 8 and 9 three phases were detected. Detected phases are L, (Ge) and intermetallic compound η. Sample 10 detected three phases L, ηand ξ. Samples 11 and 12 detected same two phases L and (Cu). EDS results shows that L phase detected in all samples is rich with bismuth and can dissolve small amount of other two elements. Solid solution (Ge), detected in samples 7, 8 and 9 is rich with germanium with 98.08, 98.18 and 98.83 at. % and the rest is bismuth and copper.Intermetallic compound η is line compound with composition 75 at. % Cu and 25 at. % Ge, in our study detected η phase has variation in composition. Composition of η phase detected on samples annealed at 400 °C hasslightly different composition and it is in range from 72.92 to 75.79 at. % of Cu and 24.15 to 26.54 at. % Ge rest is a small amount of bismuth. According to the literature ξ phase have composition of Cu from 83.5 to the 90.2 at. % and rest is germanium, which is in range with composition of this phase detected in sample 10, 85.41 at. % of Cu.On samples 11 and 12 (Cu) solid solution is detected with composition of 94.23 to the 98.20 at. % of Cu which is in range with literature composition 88.3-100 at.% Cu.

Experimental results given in Table 2 are compared with calculated isothermal section at 400 °C. Calculated isothermal section with EDS results given in Table 2 are presented on Figure 2.

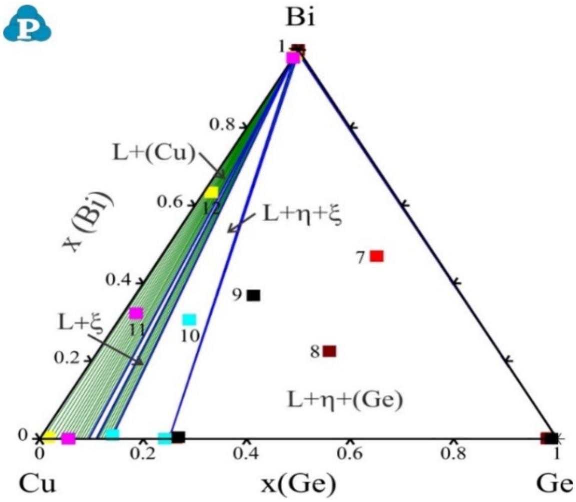

Figure 7. Calculated Bi-Cu-Ge isothermal section at 400 °C compared with EDS results given in Table 3.

On calculated isothermal section six phase regions are visible. Three are two-phase regions L+η, L+ξ and L+(Cu) and three are three-phase regions L+η+(Ge), L+η+ξandL+ξ+(Cu). From those six calculated phase region three are experimentally confirmed with six samples. Confirmed phase regions are L+η+(Ge) with samples 7, 8 and 9, L+η+ξ with sample 10 and L+(Cu) with sample 11 and 12. By comparison it is clear that experimental determined composition of phases is close with experimental composition of phases. As conclusion experiments can well follow calculated isothermal section at 400 °C.

4. CONCLUSION

The ternary Bi-Cu-Ge system was experimentally and analytically tested. Twelve samples were prepared and test by using SEM-EDS and XRD. Analytical by using Calphad approach two isothermal sections at 600 °C and 400 °C were calculated.The isothermal section at 600 °C was investigated with 6 ternary alloys and four different phase regions were detected. The isothermal section at 400 °C was investigated with 6 ternary alloys and three different phase regions were detected. In those samples ternary compounds and large solubility in intermetallic compound and solid solutions were not detected. In general, it can be concluded that phase equilibria of ternary Bi-Cu-Ge system presented in this paper is confirmed by experiments. Experiment agrees well with calculated phase diagrams and there is no necessity to introduce new ternary parameters for description of ternary Bi-Cu-Ge system.

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