

STUDY OF TEMPERATURE PHASE TRANSFORMATION OF THE TERNARY Bi-Cu-Ge SYSTEM

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Abstract

Decades of scientific work dedicated to the investigation of phase diagrams gave significant benefit to industry and science. After all those years of phase diagram investigation still there is missing information about phase diagram of some ternary systems. One of those systems is Bi-Cu-Ge. It is known importance of Cu-based alloys and Ge-based alloys in electro industry. Since such combination is not tested before this work will provide information about phase diagram of the three vertical sections from ternary Bi-Cu-Ge system. From each vertical sections (Bi-Cu-Ge, Cu-Bi-Ge and Ge-Bi-Cu), 4 alloys were prepared and tested by DTA. Experimentally obtained results were compared with corresponding vertical sections. Experimental temperatures of phase transformation shows close value with calculated one. Temperatures of liquidus curve and primary crystallization were determined.

Keywords: ternary Bi-Cu-Ge system, DTA analysis, vertical sections.

1. INTRODUCTION

In recent period ternary alloys based on Bi-Ge attracted attention. Our group tested ternary systems such as Bi-Ge-Zn, Ga, In, Sn, Ag, Sb [1-3]. On other side copper is recyclable without any loss of quality and can easily make alloys with a lot of elements beside it Cu and Cu-based alloys are wide used in building industry, electronic industry, transportation and many others. So, chosen system Bi-Cu-Ge is important due to the possible application in electronic industry and it is not tested before. In this work studied ternary alloys were from three vertical sections. Used experimental techniques included differential thermal analysis (DTA). The experimental results were compared with the calculated phase diagrams of the selected vertical sections. Reasonable agreement between the calculated phase diagrams and the experimental data was obtained.

2. EXPERIMENTAL

In total 12 ternary alloys were prepared by using high purity Bi, Cu and Ge produced by Alfa Aesar, Germany. Samples were measured in different molar ratio and the total mass of each sample were 4 g. Weighed masses of the samples were melted and re-melted six times under high-purity argon atmosphere. The average weight loss was about 0.5 mass %. Such samples were tested by DTA method with DTG-60H (Shimadzu). Alumina crucibles were used and measurements were performed under flowing argon atmosphere. Samples weighing between 20 and 30 mg were investigated at a heating rate of 5 °C/min.

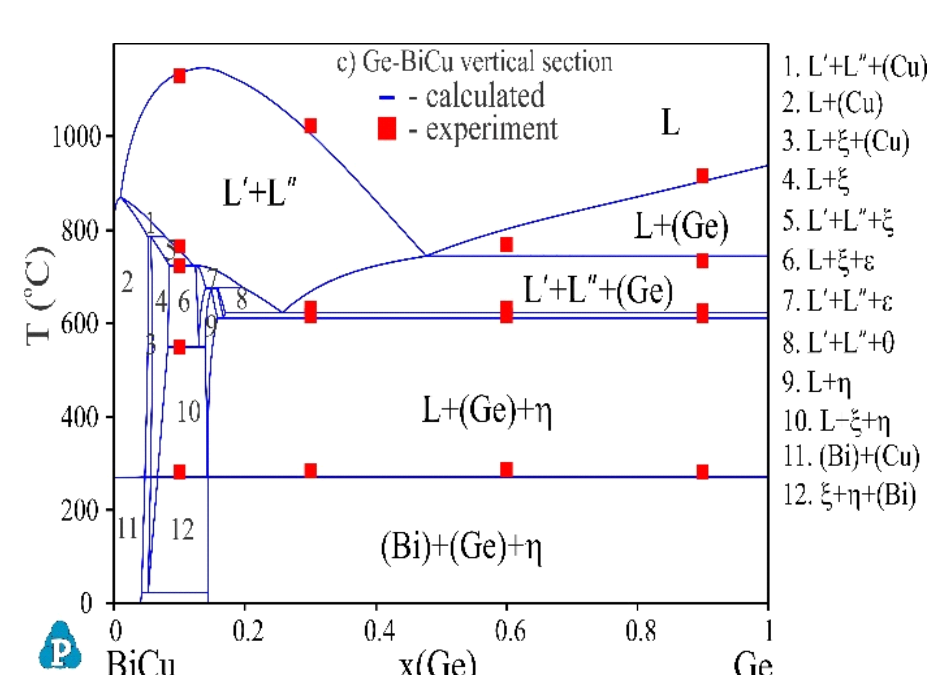


Figure 1. Calculated vertical sections of the ternary Bi-Cu-Ge system compared with DTA experimental results: a) Bi-Cu-Ge, b) Cu-Bi-Ge and c) Ge-Bi-Cu.

From figure 1, can be notice good agreement with calculation and experimental results. Figure 1a) presents calculated vertical section Bi-Cu-Ge compared with experimental result of for samples 1-4. From calculation it is clear that first detected temperature of all samples is related to the same transformation which is related to the ternary eutectic reaction $L \rightarrow (Ge)+(Bi)$. According to the calculation reaction appears at 271.07 °C, while experimental temperature is in range of 269.09 to the 279.47 °C, which are close to calculated value. Second detected temperatures on samples 1, 2 and 3 is related to the $\theta \rightarrow L+(Ge)+\eta$ calculated at 611.64 °C while experiment are 610.19 to the 613.53 °C which are close to each other. This transformation did not confirm on sample 4 while according to the calculation it should be. Third detected temperatures on samples is related to the $L \rightarrow L'+(Ge)+\theta$ with calculated temperature at 623.05 °C. Experiment determined temperatures are 622.34, 629.30, 634.16 and 636.21 °C which are slightly higher than calculated one. On sample Bi_{0.13}Cu_{0.39}Ge_{0.48} is also determined temperature of transformation $L'+L'' \rightarrow L'+L''+(Ge)$ at 701.30 °C. Last temperature on all samples is liquidus temperature and all experimental temperatures agree well with calculated. Tested samples from vertical section Cu-Bi-Ge are marked with numbers 5, 6, 7 and 8. On each sample four temperatures were detected. By comparing DTA results and calculated vertical section Figure 1b), it can be noticed that all four temperatures detected with samples 5 and 7 corresponds to the same phase transformation on each sample. First temperatures are related to the ternary eutectic reaction $L \rightarrow (Ge)+(Bi)+\eta$ calculated at 271.07 °C. Experimentally detected temperature of this reaction are 278.10, 279.14 and 277.33 °C which are close to calculated one. Second detected temperatures are 613.80, 614.87 and 612.70 °C which are related to the ternary peritectic transformation $\theta \rightarrow L+(Ge)+\eta$ calculated at 611.64 °C. Third temperature on samples 6 and 7 are 627.10, 633.78 and 629.23 °C respectively. This temperatures are related to the $L \rightarrow L'+(Ge)$ phase transformation calculated temperature at 623.05 °C. Last temperatures on those samples are liquidus temperature. Sample 8, from same vertical section as samples 5 to 7, detected different phase transformations than samples 5 to 7. First temperature is related to the transformation $L+\eta \rightarrow \xi+(Bi)$, second to the $L+\epsilon \rightarrow L'+\xi$, third to the $L'+L'' \rightarrow L'+L''+(Ge)$ and last one to the liquidus temperature. Four samples from vertical section Ge-Bi-Cu are tested and marked with numbers 9 to 12. Sample 9 detected five phase transformations. First one is related to the $L+\eta \rightarrow \xi+(Bi)$ reaction calculated at 270.46 °C while experimental one is at 278.31 °C, next temperature is detected at 548.90 °C and it is corresponding to the $L+\epsilon \rightarrow \xi+\eta$ reaction with calculated temperature at 549.31 °C. Third temperature detected with sample 9 is at 723.90 °C while calculated is at 723.67 °C, this

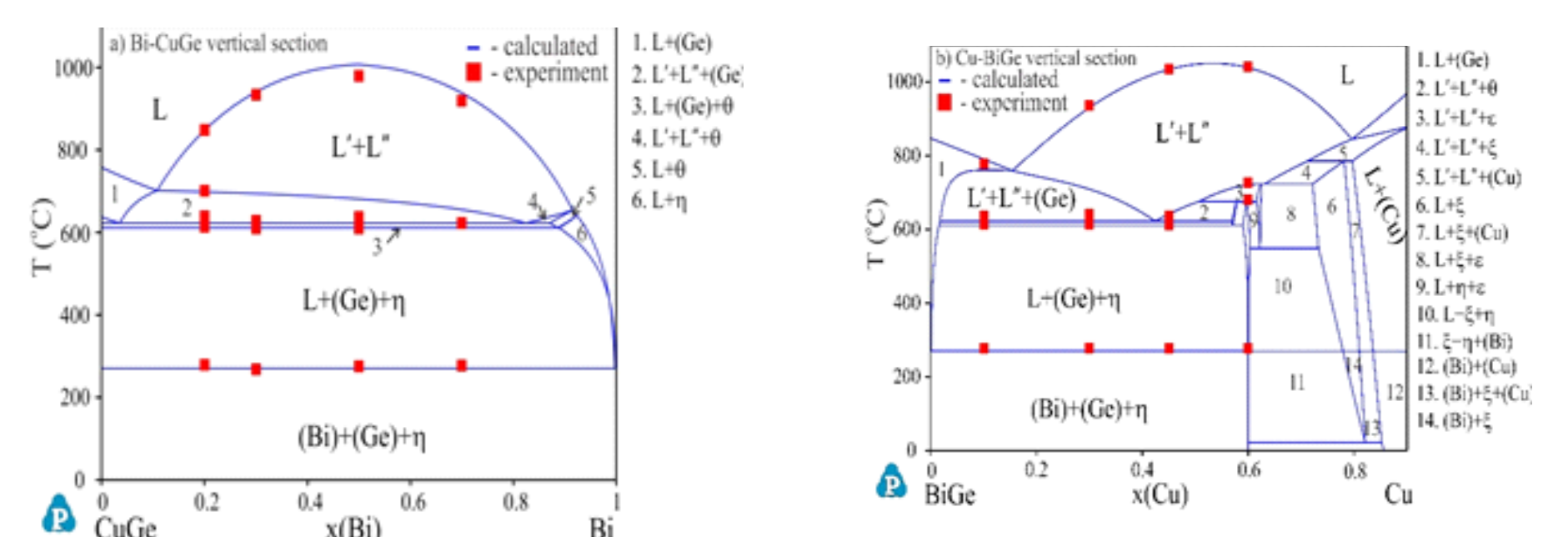
1. RESULTS AND DISCUSSION

Twelve ternary samples were selected for DTA tests. The samples were placed in alumina crucibles and characteristic temperatures were recorded under protective flowing Ar atmosphere. Weights of the analyzed alloy samples were between 30 and 40 mg and a reference material was an empty alumina crucible. Determination of phase transition temperatures was carried out according to recommendations from the literature [4,5]. The liquidus and temperatures of monovariant phase transitions were determined from peak maxima while the solidus temperature and the temperatures of invariant reactions were determined from onset temperatures of the corresponding peaks. Such determined temperatures from DTA heating curves from 12 samples are summarized in Table 1.

Table 1. Phase transition temperatures of the studied alloys from the ternary Bi-Cu-Ge system determined by DTA at pressure p = 0.1 MPa.

Number	Composition (at. %)		Identified phase transition temperature in °C		
	Nominal	EDS	Ternary eutectic reaction	Ternary transition reaction	Liquidus
Vertical section Bi-Cu-Ge					
1	Bi ₂₀ Cu ₄₀ Ge ₄₀	Bi _{20.15} Cu _{39.18} Ge _{40.67}	279.47	613.53/636.21/701.3	849.09
2	Bi ₁₀ Cu ₃₅ Ge ₅₅	Bi _{10.11} Cu _{35.48} Ge _{54.41}	269.09	610.34/629.30	933.10
3	Bi ₆₀ Cu ₂₅ Ge ₁₅	Bi _{60.81} Cu _{25.13} Ge _{14.06}	275.24	610.19/634.16	979.54
4	Bi ₇₀ Cu ₁₅ Ge ₁₅	Bi _{70.05} Cu _{14.81} Ge _{15.17}	278.22	622.34	918.92
Vertical section Cu-Bi-Ge					
5	Bi ₄₅ Cu ₁₀ Ge ₄₅	Bi _{45.08} Cu _{10.87} Ge _{44.05}	278.10	613.80/627.10	778.90
6	Bi ₃₅ Cu ₃₀ Ge ₃₅	Bi _{35.55} Cu _{29.61} Ge _{34.87}	279.14	614.87/633.78	938.19
7	Bi ₁₇ Cu ₄₅ Ge _{37.5}	Bi _{17.45} Cu _{44.87} Ge _{37.70}	277.33	612.70/629.23	1035.74
8	Bi ₂₀ Cu ₆₀ Ge ₂₀	Bi _{19.73} Cu _{61.12} Ge _{19.15}	277.02	681.20/727.20	1041.80
Vertical section Ge-Bi-Cu					
9	Bi ₄₅ Cu ₄₅ Ge ₁₀	Bi _{45.08} Cu _{44.87} Ge _{10.05}	278.31	548.90/723.90/765.61	1128.92
10	Bi ₃₅ Cu ₃₅ Ge ₃₀	Bi _{34.98} Cu _{35.09} Ge _{29.93}	279.11	615.19/631.20	1024.90
11	Bi ₂₀ Cu ₂₀ Ge ₆₀	Bi _{19.33} Cu _{20.87} Ge _{59.78}	280.10	615.70/631.67	768.62
12	Bi ₃ Cu ₃ Ge ₉₀	Bi _{4.35} Cu _{4.91} Ge _{90.74}	277.78	615.30/628.10/733.10	915.90

From recorded DTA results in Table 1, it is visible that on three samples five peaks are detected on eight samples four peaks and on sample Bi₇₀Cu₁₅Ge₁₅ three peaks. It can be noticed that first detected peak of each sample have similar value of temperature and it can be assumed that detected temperatures are related to the same transformation. Last detected temperature on all samples is liquidus temperature while peaks in-between are ternary transition reaction. Experimental temperatures from Table 1 are compared with calculated vertical sections. Calculated vertical sections are Bi-Cu-Ge, Cu-Bi-Ge and Ge-Bi-Cu respectively presented on Figure 1.



temperature corresponds to the reaction $L' \rightarrow L'+\xi+\epsilon$. Next temperature detected at related to the solidification of ξ phase while end temperature is liquidus. Such detected temperatures of same transformations. First three samples is related to the ternary eutectic reaction $L \rightarrow (Ge)+(Bi)+\eta$ calculated at 271.07 °C while experimental are 279.11, 278.10 and 277.33 °C. Second temperature is related to the reaction $\theta \rightarrow L+(Ge)+\eta$ calculated at 611.64 °C experimental are 615.19 and 610.34 °C. Third detected temperatures on samples are 631.64, 631.67 and 623.05 °C which are related to the $L \rightarrow L'+(Ge)+\theta$ with calculated temperature at 623.05 °C. Temperatures are liquid. Sample 11 detected five temperatures. First three one are related to $L \rightarrow (Ge)+(Bi)+\eta$ calculated at 271.07 °C, $\theta \rightarrow L+(Ge)+\eta$ calculated at 611.64 °C, $L \rightarrow L'+(Ge)+\theta$ calculated at 623.05 °C reactions, experimentally detected at 277.78, 615.70, 628.10 °C, respectively. Fourth temperature is at 733.10 °C related to the transformation into $L'+L''+(Ge)$ while last one is liquidus temperature.

As general conclusion after comparison of experimental temperatures and calculated sections good agreement with temperatures is reached in most cases.

1. CONCLUSION

The ternary Bi-Cu-Ge system was experimentally tested. Twelve ternary samples were prepared and tested by using DTA. Three vertical sections were calculated from each corner Bi, Cu and Ge. Each vertical section was tested with four samples by DTA. DTA test shows that phase transformation which were in good agreement with calculated temperatures. It can be concluded that phase equilibria of ternary Bi-Cu-Ge system presented in this paper confirmed by experiments.

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