Experimental study and thermodynamic calculation of Au-Bi-Sb system phase equilibria

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Abstract. Phase equilibria in the Au–Bi–Sb ternary system have been studied experimentally and calculated by the CALPHAD method. Three calculated isopleths from each element corner with equal molar ratio of the other two elements were compared with the DTA results from this work. Three ternary invariant reactions were noted. Calculated isothermal sections in the temperature range of 200- 400°C were presented. Calculated phase diagram of isothermal section at 300°C was compared with the results of SEM/EDX analysis. Reasonable agreement between calculations and experimental data was observed in all cases.

Introduction

The lead-tin alloy systems have been the most commonly used soldering materials in electronic interconnection and packaging because of their low cost and unique combination of physical, chemical, mechanical properties, manufacturability and reliability. However, because of environmental and health concerns, the intensive search for alternative solder alloys is in progress.

Thermodynamic modelling of phase equilibria in perspective systems represents first necessary step for development of new lead-free soldering materials. For this purpose, in the frame of COST 531 action [1] and SGTE (Scientific Group Thermodata Europe), thermodynamic database based on recent version 4.4 SGTE [2] values of Gibbs energies for a pure element was developed [3]. It contains the data for carefully tested binary phase diagrams, suitable for prediction of phase equilibrium in multicomponent systems.

Knowledge of the phase equilibria in the Au-Bi-Sb ternary system is desirable for the development of lead-free solder alloys. There are only two references concerning phase equilibria of this ternary system. Gather [4] studied an isothermal section of the Au–Bi–Sb ternary system at 493 K. Paul et al. [5] studied diffusion properties of Au2Bi and AuSb2 intermetallics at 230 and 330°C by the diffusion couple method. In this paper, the Au-Bi-Sb ternary system is investigated via experiment and thermodynamic binary-based prediction according to CALPHAD technique [6-8]. Calculated sections were compared with DTA and SEM/EDX results from the present study.

Experimental procedure

All samples were prepared from metals of 99.99 wt.% purity. Weighted amounts of metals were melted and annealed in evacuated and sealed quartz capsules at 300°C for 200 hours. After annealing, samples prepared for DTA measurements were gradually cooled down in order to obtain desired equilibrium at room temperature. Samples prepared for SEM-EDX investigation were quenched into ice water from 300°C.

DTA measurements were carried out with the Derivatograph (MOM Budapest) apparatus with Pt/Pt10%Rh thermocouples under following conditions: argon atmosphere, heating rate 5 K/min and sintered Al_2O_3 as the reference specimen.

The equilibrium compositions in quenched samples were determined using JEOL scanning electron microscope with accelerating voltage 20kV and EDX analyzer.

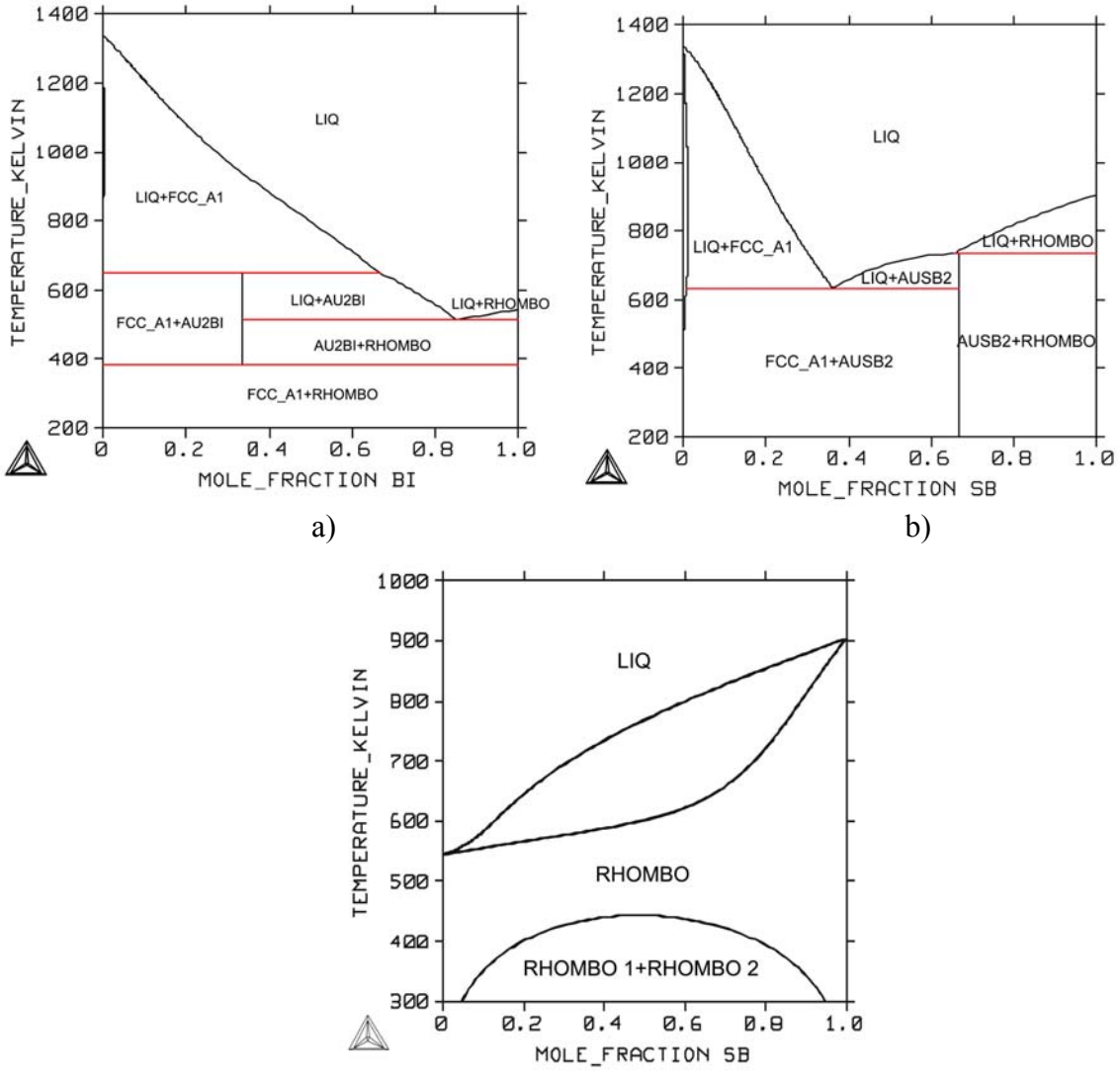
Thermodynamic modeling. The pure solid elements in their stable form at 298.15 K and under the pressure of 1 bar were chosen as the reference state for the systems (SER). The Version 4.4 of the SGTE Unary Database (Scientific Group Thermodata Europe) of phase stabilities for stable and metastable states of pure elements [2] was used.

Thermodynamic data for the Au–Bi system were taken from Ref. [9], for the Bi–Sb system were published in Ref. [10], and thermodynamic data for the system Au–Sb were taken from Ref. [11]. All this data are included in the COST 531 Database for Lead Free Solders [3].

The following phases from constitutive binary subsystems were considered for thermodynamic binary-based prediction: liquid phase, the Au-based fcc solution (denoted as FCC_A1), Sb and Bi rich solid solution (denoted as RHOMBOHEDRAL_A7), intermediate phase from Au-Bi binary systems with very narrow concentration range of existence denoted as Au2Bi and intermediate phase from Au-Sb binary system with very narrow concentration range of existence denoted as AuSb2.

The Gibbs energies of the liquid, fcc and rhombohedral phases are described by a substitution solution model and a Redlich-Kister formalism. Au2Bi and AuSb2 compounds were treated as stoichiometric compounds.

Calculated phase diagrams of the constitutive binary systems, based on the thermodynamic dataset used in this study, are shown in Fig. 1.



a) b)

c)

Fig. 1. Optimized binary phase diagrams:
a) Au-Bi binary system; b) Au-Sb binary system; c) Bi-Sb binary system

Results and discussion

Three characteristic isopleths of the Au-Bi-Sb ternary system were experimentally investigated by DTA. The analysis of DTA measurements was performed on DTA curves obtained during the heating of samples.

Mutual comparison between DTA results and calculated phase diagrams is presented in Fig. 2.

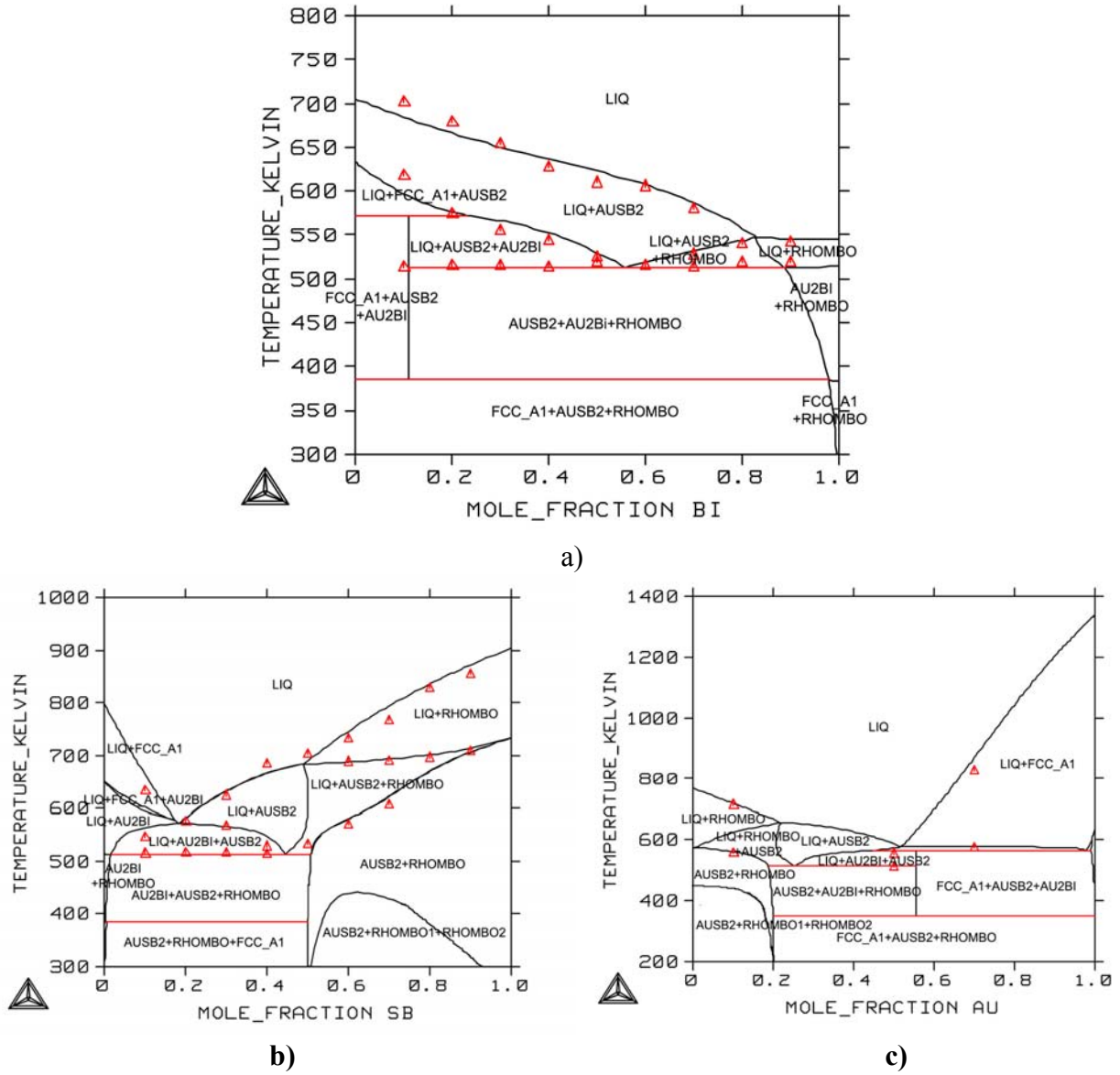


Fig. 2. Calculated isopleths of the Au-Bi-Sb ternary system with DTA results from the present study: a) Au:Sb=1:1, b) Au:Bi=1:1, c) Bi:Sb=1:1

It can be seen that there is a reasonable agreement between DTA results from this work and calculated phase diagrams for all investigated isopleths. Calculated liquidus temperatures are confirmed quite well by DTA measurements.

Calculated vertical section with molar ratio Au:Sb=1:1 includes two primary crystallization areas (Liquid+AUSB2; Liquid+RHOMBO), vertical section with molar ratio Au:Bi=1:1 includes three primary crystallization areas (Liquid+FCC_A1; Liquid+AUSB2; Liquid+RHOMBO), and vertical section with molar ratio Bi:Sb=1:1 also includes three primary crystallization areas (Liquid+FCC_A1; Liquid+AUSB2; Liquid+RHOMBO).

Vertical section from bismuth corner crosses three invariant planes. The horizontal lines at the calculated temperatures of 382, 514 and 572 K mark their encountering with the studied section.

The invariant reaction occurring at 572 K corresponds to the transitory peritectic reaction:

LIQ+FCC_A1↔AUSB2+AU2BI

The invariant reaction, calculated at the temperature of 241°C (514 K), appears in all three investigated isopleths and it is experimentally identified by the results of DTA measurements from this study (table 2). This reaction represents ternary eutectic reaction:

LIQ↔ AUSB2+AU2BI+RHOMBO

The temperature of this reaction is equal to the calculated temperature of the eutectic reaction of the Au-Bi constitutive binary system [4].

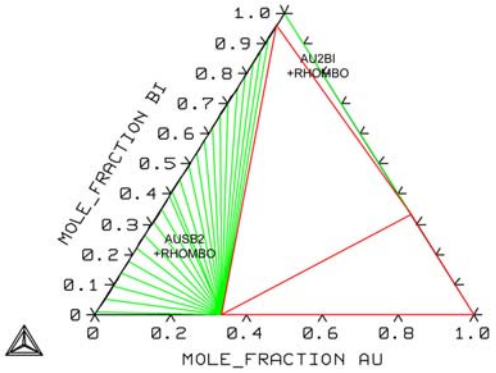
Calculated invariant reaction at 382 K represents decomposition of Au2Bi intermediate phase. Below this temperature Au2Bi phase is not thermodynamically stable. This reaction was not experimentally identified probably because of its very slow rate and long time needed for equilibrium to be reached [4].

Invariant planes at 382 and 514 K also cross vertical sections from antimony and gold corner.

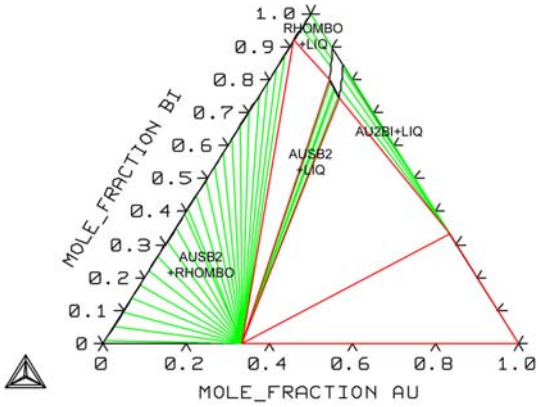
Calculated isothermal sections of the Au-Bi-Sb ternary system in the temperature interval 200-400°C are shown in Fig. 3.

The SEM (scanning electron microscope) with EDX (energy dispersive X-ray) analyzer was used for determination of composition of coexisting phases at 300°C. One quenched sample with predicted three-phase structure and one sample with predicted two-phase structure were analyzed.

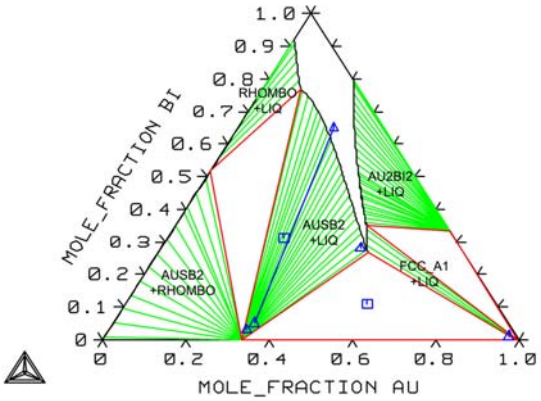
Comparison of calculated phase diagram of the Au-Bi-Sb ternary system at 300°C with experimental results from this work is shown in Fig. 3c.



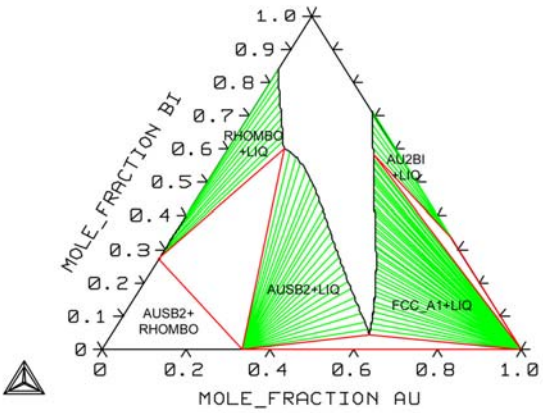
a) 200°C



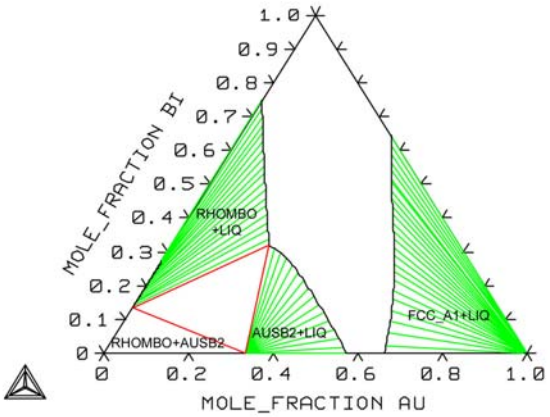
b) 250°C



c) 300°C



d) 350°C



e) 400°C

Fig. 3. Calculated isothermal sections of the Au-Bi-Sb ternary in the temperature interval 200-400°C with the EDX results (square-overall composition; triangle-composition of phase)

From the course of the liquidus temperatures in the calculated isothermal sections it can be estimated that the composition of the liquid in the ternary eutectic reaction is approx: 78 at.% Bi, 5 at.% Sb, and 17 at.% Au.

Conclusion

Phase equilibria in the ternary system Au-Bi-Sb were investigated experimentally, using DTA and SEM/EDX. From the calculated phase diagrams of three isopleths, three invariant reactions have been identified at 382, 514 and 572 K, respectively. The latest two were also registered by the results of DTA measurements.

Three characteristic isopleths and isothermal sections in the temperature range 200-400 oC were calculated using optimized thermodynamic parameters for the constitutive binary systems from the literature. Calculated phase diagram at 300°C was compared with experimental results. Good agreement was noticed.

Acknowledgement

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