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# Comparison of Prediction of Phase Equilibria in the Ag–In–Sb System at 200°C with Experimental Data

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**Summary.** Binary thermodynamic data, successfully used for phase diagram calculations of binary systems Ag–In, Ag–Sb, and In–Sb, were used for prediction of phase equilibria in ternary Ag–In–Sb system at 200°C. Symmetrical *Redlich–Kister–Muggianu* model for ternary thermodynamic function calculation was proved to be best valid in this ternary system. Predicted equilibria were compared with experimentally (SEM, EDX) determined composition of phases in chosen alloys after long term annealing and with the results of DTA measurements.

**Keywords.** Phase diagrams; Thermodynamics; Ag–In–Sb system.

## Introduction

Silver-based binary and ternary alloys present a wide and important group among numerous lead-free solder materials. The Ag–In–Sb system is one of the possible candidates and therefore this ternary system and its binary subsystems have been a subject of different investigations recently [1–4].

The first step performed in this work included testing and verification of literature data for phase equilibria in 3 binary systems (Ag–In, Ag–Sb, In–Sb). The thermodynamic predictions of phase equilibria in these systems were compared with experimental data. Nevertheless, there is still no complete data to give a full overview on thermodynamic behavior and phase equilibria of mentioned ternary system. Therefore, some new results of thermodynamic investigation and phase equilibria of the Ag–In–Sb system are presented in this contribution.

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## Thermodynamic Modelling

### *Pure Elements*

The pure solid elements at 298.15 K and 1 bar in their stable form 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 [1] was used.

### *The Binary Systems*

The thermodynamic descriptions of binary alloys were taken from literature.

Thermodynamic data for the Ag–In system were published in Ref. [2], for the Ag–Sb system in Ref. [3], and thermodynamic data for the system In–Sb were taken from Ref. [4].

### *Liquid and Solid Solution Phases*

The *Gibbs* energies of liquid, hcp, fcc, and epsilon solid phases are described by the sub-regular solution model with the *Redlich-Kister* polynomial [5] as follows by Eqs. (1)–(3) where ${}^{m}L^{\phi}_{\mathrm{A,B}}$ is the temperature-dependent parameter optimised on the basis of the available thermodynamic and phase diagram data, and A, B are elements of the system.

$$G^{\phi}_{m} = {}^{\circ}G^{\phi}_{\mathrm{A}}x^{\phi}_{\mathrm{A}} + {}^{\circ}G^{\phi}_{\mathrm{B}}x^{\phi}_{\mathrm{B}} + RT(x^{\phi}_{\mathrm{A}}\ln x^{\phi}_{\mathrm{A}} + x^{\phi}_{\mathrm{B}}\ln x^{\phi}_{\mathrm{B}}) + G^{\mathrm{E}}(T, x_{\mathrm{B}}) \tag{1}$$

$$G^{\mathrm{E}}(T, x_{\mathrm{B}}) = x^{\phi}_{\mathrm{A}}x^{\phi}_{\mathrm{B}}L^{\phi}_{\mathrm{A,B}} \tag{2}$$

$$L^{\phi}_{\mathrm{A,B}} = \sum_{m=0}^{n} {}^{m}L^{\phi}_{\mathrm{A,B}}(x_{\mathrm{A}} - x_{\mathrm{B}})^{m} \tag{3}$$

The solid solution phases in all binary systems were treated according to this model.

### *Stoichiometric Compounds in Ag–In and In–Sb Systems*

The solubility of the compound phases in this system is very narrow and is not clearly determined according to the literature. The $Ag_2In$ and InSb phases are treated as stoichiometric compounds. Then, the *Gibbs* energy of the compound, *e.g.*, $Ag_m In_n$, is generally described as given by Eq. (4) where $\Delta G^{\mathrm{f}}_{\mathrm{Ag}_m\mathrm{In}_n}$ represents the *Gibbs* energy of formation per mol of atoms of the $Ag_m In_n$ compound and is expressed by Eq. (5).

$$G^{\mathrm{Ag}_m\mathrm{In}_n}_{m} = \frac{m}{m+n}{}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ag}} + \frac{n}{m+n}{}^{\circ}G^{\mathrm{fcc}}_{\mathrm{In}} + \Delta G^{\mathrm{f}}_{\mathrm{Ag}_m\mathrm{In}_n} \tag{4}$$

$$\Delta G^{\mathrm{f}}_{\mathrm{Ag}_m\mathrm{In}_n} = \mathrm{A} + \mathrm{B}T \tag{5}$$

## Prediction of Thermodynamic Function in the Ag–In–Sb System

Comparing to available data on the constitutive binaries, there are only two references [6, 7] presented in literature up to now, dealing with thermodynamics of liquid Ag–In–Sb alloys. First one is the work of *Itabashi et al.* [6], who performed EMF (electromotive force) measurements with zirconia solid electrolyte for determination of indium activities in a few sections of the investigated system in temperature range from 970 to 1280 K. The other reference is the work of *Gather et al.* [7], who determined the enthalpies of mixing in liquid state for the Ag–In–Sb system using a heat flow calorimeter. As a contribution to the more complete knowledge of thermodynamic behaviour of this lead-free solder system, the results of binary based thermodynamic properties calculation for liquid Ag–In–Sb alloys are presented and compared with the mentioned experiments in this paper.

The values of integral molar *Gibbs* excess energies, $G_{ij}^{\mathrm{E}}$, for the constitutive binary systems Ag–In, In–Sb, and Sb–Ag taken from *Moser et al.* [2], *Cui et al.* [3], and *Oh et al.* [4], respectively, were used as the starting binary thermodynamic data for the calculation. All these data are included in COST 531 binary database [8].

One of the most important steps in the calculation of thermodynamic properties for ternary systems is to select the most adequate model. In order to investigate which model is the most appropriate for the Ag–In–Sb system, existing literature data [6] for the section from indium corner with a molar ratio of Sb:Ag equal to 1:1 were compared with the results calculated based on binary data [2–4], included in Version 1.1 of the COST 531 Binary Database for Lead Free Solders [8], according to the following calculation methods: general solution model (GSM) [9, 10], *Kohler* [11], *Muggianu* [12], *Toop* [13], and *Hillert* [14]. The calculations of $G^{\mathrm{E}}$ for ternary liquid phase were done using these models. The results for the section with a molar ratio of Sb:Ag equal to 1:1 at 1200 K, compared with literature data [6], are shown in Fig. 1.

Further, the root mean square deviation analysis was applied on $G^{\mathrm{E}}$ data obtained for the mentioned two sections in order to determine accurately the most adequate

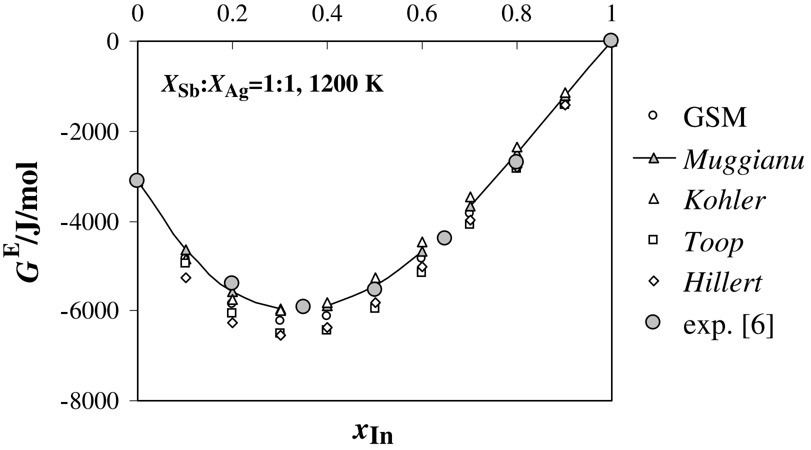

**Fig. 1.** Comparison between calculated (according to various models) and experimental literature data [6] for $G^{\mathrm{E}}$ of liquid Ag–In–Sb alloys in the section with molar ratio Sb:Ag = 1:1

**Table 1.** The root mean square (RMS) deviation to experimental data for each calculation model

| Model | *Toop* | *Hillert* | *Kohler* | *Muggianu* | GSM |
|---|---|---|---|---|---|
| RMS [J/mol] | 153.33 | 149.64 | 100.66 | 95.28 | 119.12 |

model for liquid Ag–In–Sb alloys among the used ones (Eq. (6)) where RMS means root mean square deviation, $N$ is the number of counting points, $G^{E}_{exp}$ are experimental, literature results [6] for $G^{E}$, and $G^{E}_{calc}$ are calculated values for $G^{E}$.

$$\mathrm{RMS} = 1/N \cdot [\Sigma(G^{E}_{exp} - G^{E}_{calc})^2]^{1/2} \tag{6}$$

The results of such analysis, done for the experimentally investigated sections with a molar ratio Sb:Ag equal to 1:1 and 4:1, are presented in Table 1, pointing out that: a) ternary system Ag–In–Sb could be regarded as a symmetric system and b) *Muggianu* model is the most adequate model for its thermodynamic description.

For that reason, all further calculations of thermodynamic properties of that ternary system should be done using *Muggianu* model.

## Prediction of Phase Equilibria at 200°C in the Ag–In–Sb System

Only binary diagrams are known in the system Ag–In–Sb, the ternary system was not studied experimentally yet. No phase data and no thermodynamic data are available for ternary parameters. Therefore the prediction of ternary phase diagram in this system was calculated only on the base of binary thermodynamic data using *Redlich–Kister–Muggianu* model for ternary thermodynamic functions.

**Table 2.** Results of experimental determination of composition of samples by SEM – EDX analysis

| | Overall experimental composition/at% | Theoretic. predicted phases | Experiment. determined phases | Compositions of phases/at% | | |
|---|---|---|---|---|---|---|
| | | | | Ag/at% | In/at% | Sb/at% |
| 1 | 84.0 ± 0.7 Ag<br>6.5 ± 1.1 In<br>9.5 ± 0.5 Sb | HCP_A3<br>FCC_A1 | HCP_A3 | 84.0 ± 0.7 | 6.5 ± 1.1 | 9.5 ± 0.5 |
| 2 | 64.5 ± 0.9 Ag | Rhombo | Rhombo | 0.5 ± 0.1 | 0.3 ± 0.1 | 99.2 ± 0.1 |
| | 2.2 ± 0.4 In | Epsilon | Epsilon | 76.7 ± 0.3 | 0.9 ± 0.2 | 22.4 ± 0.2 |
| | 33.3 ± 0.7 Sb | HCP_A3 | HCP_A3 | 78.5 ± 0.2 | 3.5 ± 0.4 | 18.0 ± 0.3 |
| 3 | 25.8 ± 1.0 Ag | InSb | InSb | 0.3 ± 0.3 | 50.5 ± 0.4 | 49.2 ± 0.3 |
| | 38.2 ± 0.8 In | HCP_A3 | HCP_A3 | 74.0 ± 1.3 | 14.3 ± 1.7 | 11.7 ± 1.6 |
| | 36.1 ± 0.5 Sb | | | | | |
| 4 | 17.4 ± 1.1 Ag | Rhombo | Rhombo | 0.4 ± 0.1 | 0.7 ± 0.1 | 98.9 ± 0.1 |
| | 20.7 ± 0.9 In | InSb | InSb | 0.1 ± 0.1 | 50.4 ± 0.2 | 49.5 ± 0.1 |
| | 61.9 ± 1.7 Sb | HCP_A3 | HCP_A3 | 77.7 ± 0.6 | 6.6 ± 0.4 | 15.7 ± 0.5 |
| 5 | 35.86 ± 2.92 Ag | $Ag_2In$ | $Ag_2In$ | 67.1 ± 0.5 | 32.9 ± 0.5 | |
| | 49.85 ± 1.84 In | InSb | InSb | 1.6 ± 0.3 | 48.1 ± 0.6 | 50.3 ± 0.5 |
| | 14.3 ± 1.43 Sb | Liquid | Liquid | 3.9 ± 0.9 | 94.5 ± 1.3 | 1.6 ± 1.1 |

## Results of Verification of Predicted Phase Equilibria in the Ag–In–Sb System – SEM-EDX Results

The SEM (scanning electron microprobe) with EDX (energy dispersive X-ray) analysis can give us very important information of composition of phases. Reasonable agreement between the experimental data and binary based prediction in In rich part of ternary cross section was found. All results from SEM analysis are shown in Table 2 and Fig. 2.

The agreement between predicted phases and experimentally determined phases of samples 2, 3, 4, and 5 is perfect. Two-phase structure (HCP_A3 and FCC) was predicted in sample 1, but single-phase structure was analysed. The experimental composition of sample 1 is close to the border of single- and two-phase area. Therefore it is possible that the structure of sample 1 falls into the single-phase field.

## DTA Results

DTA (differential thermal analysis) was performed by heating of samples. Temperatures of beginning of phase transitions were read using software, which evaluates results of DTA analysis. Results are drawn in Fig. 3 for the section of In:Sb = 1:1.

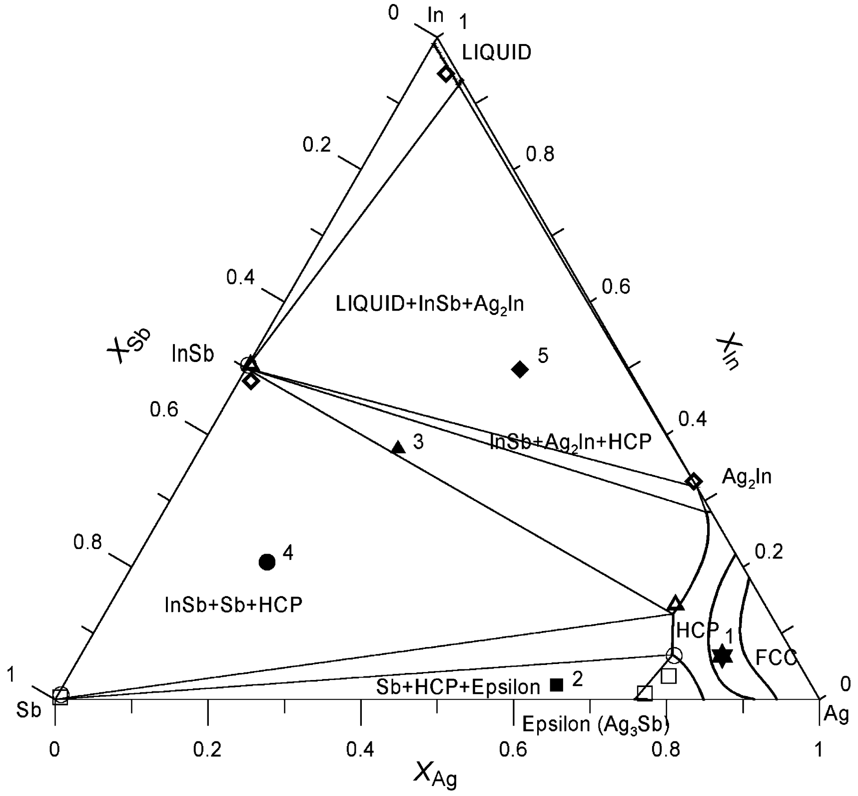

**Fig. 2.** Results of SEM analysis, comparison with prediction at 200°C; full symbols – overall composition, empty symbols – compositions of phases; number of samples – see Table 2

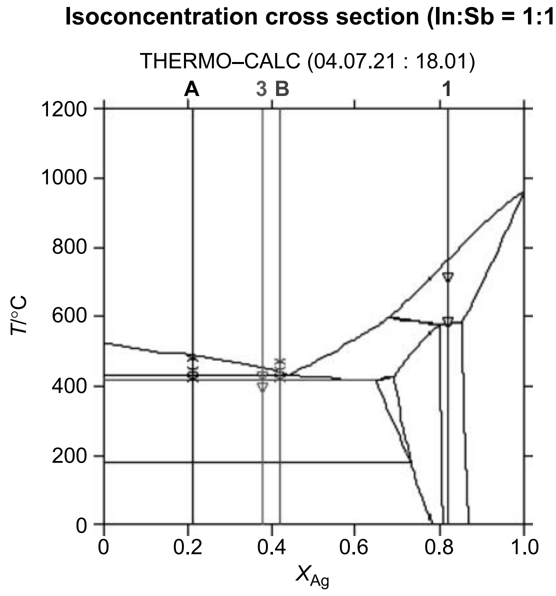

**Fig. 3.** Results from DTA analysis of samples 1 and 3 (set 1 of experiments) and samples A and B (set 2 of experiments) marked into isoconcentration cross section in ratio In:Sb = 1:1

## Discussion of Comparison of Experimental Phase Equilibrium Data with Thermodynamic Binary Based Prediction

The time of annealing plays an important role in reaching thermodynamic equilibrium and when it was taken into account (samples 2 and 4 – 10 weeks of annealing), the reasonable agreement with thermodynamic prediction was reached. Differential thermal analysis curves well confirmed the predicted lines on polythermal section for the ratio In:Sb = 1:1. Melting point is a little overestimated in measurements carried in air (heating rate 10°C/min) and underestimated during measurements in argon (heating rate 5°C/min). The reason for this may be probably the different heating rate. Also, predicted phase equilibria, calculated using symmetrical *Redlich–Kister–Muggianu* model, agree reasonably with experimental determination. In spite of quite good agreement of predicted phase diagram with experiments, more thermodynamic and phase equilibrium data at various temperatures are needed for introduction of ternary interaction parameter of HCP and liquid phases and for detailed assessment.

## Experimental

The purpose of experimental part of study is to analyse phase equilibria on the basis of DTA, metallography, and SEM analysis.

Alloys of Ag–In–Sb were prepared from pure metals (99.999%) by melting of weighted amounts of silver, indium, and antimony in the arc furnace under argon atmosphere. Homogeneity of samples were examined by metallography and SEM analysis. Homogenous samples were annealed in evacuated glass capsule at 200°C for time chosen according to homological temperature and then quenched into cold water. Samples 1, 3, 5 were annealed at 200°C for 48 h and the rest, samples 2 and 4, were annealed for 10 weeks according to homological temperature.

The equilibrium compositions of samples were determined using scanning electron microscope (JEOL JSM-6460) with accelerating voltage 20 kV using EDAX analyser.

Liquidus temperatures and phase transformation temperatures were also determined by DTA experiments. Two sets of experiments for differential thermal analysis were prepared. First set of experiments (samples 1 to 5, Table 2) were carried out in an atmosphere of flowing argon. These samples were heated at a rate of 5°C/min using sintered $Al_2O_3$ as the reference specimen. Weights of samples 1–5 were approximately 1 g.

Second set of experiments (samples A to F) were carried out in an atmosphere of flowing air. These samples were heated at a rate of 10°C/min using sintered $Al_2O_3$ as the reference specimen. DTA of samples A–F were measured by Derivatograph MOM (Budapest). Weights of samples A–F were approximately 2 g, while their compositions were (in at%): A – 21.5% Ag, 39.25% In, 39.25% Sb; B – 42.2% Ag, 28.9% In, 28.9% Sb; C – 30% Ag, 49% In, 21% Sb; D – 50% Ag, 35% In, 15% Sb; E – 30% Ag, 63% In, 7% Sb; F – 50% Ag, 45% In, 5% Sb.

## Acknowledgements

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