Surface Tension and Density Measurements of Sn-Ag-Sb Liquid Alloys and Phase Diagram Calculations of the Sn-Ag-Sb ternary system

Zbigniew Moser¹, Władysław Gąsior¹, Janusz Pstruś¹, Satoru Ishihara², Xing Jun Liu³, Ikuo Ohnuma³, Ryosuke Kainuma³ and Kiyohito Ishida³

¹*Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 30-059 Krakow, Reymonta Street 25, Poland*

²*R&D Institute of Metals and Composites for Future Industries, Sendai 980-8577, Japan*

³*Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan*

The maximum bubble pressure method has been used to measure the surface tension of pure antimony and the surface tension and density (dilatometric method) of Sn-3.8 at%Ag eutectic base alloys with 0.03, 0.06 and 0.09 molar fraction of antimony at a temperature range from 550 to 1200 K. The linear dependencies of surface tension and density on temperature were observed and they were described by straight-line equations. Moreover, experimental determination of phase diagram and thermodynamic calculations in the Sn-Ag-Sb system were performed and the resulting optimized thermodynamic parameters were used for modeling of the surface tension. In addition, a non-equilibrium solidification process using the Scheil model was simulated and compared with the equilibrium solidification behavior of a Sn-Ag-Sb alloy.

(Received November 6, 2003; Accepted January 26, 2004)

Keywords: lead-free solder, microsoldering, thermodynamics, calphad

1. Introduction

In 1999 a co-operation program on Pb-free soldering materials of Institute of Metallurgy and Materials Science in Poland and Tohoku University in Japan has been initiated. In Poland, experimental studies were focused on physical properties like surface tension, viscosity and density, while in Japan measurements of phase equilibria were performed. The latter, combined with assessed thermodynamic data were used for obtaining the optimized thermodynamic parameters. Optimized thermodynamic parameters are the starting point for verification of existing phase equilibria or for calculation of new phase equilibria and for modeling of physical properties.

Examples of such trends were published jointly in the case of Ag-In¹⁾ and Sn-Ag-In²⁾ liquid alloys. The separate experimental studies³⁾ in Krakow on surface tension and density on binary low melting eutectics and on third additions to binary eutectics have shown that the comparison of the surface tension with the values calculated from optimized thermodynamic parameters is reliable. However, the temperature dependence of the surface tension is always linear, while the modeled results by the Butler's model⁴⁾ are curvilinear. The reason is not yet explained, and in addition in the case of simple eutectic systems like Ag-Bi⁵⁾ even the opposite trend (lowering of the surface tension with temperature) was observed. It was proved that these limitations of the Butler's model are not connected with optimized thermodynamic parameters, but rather in some assumptions in this model.⁵⁾

It should be noted that most of the studies on Pb-free soldering materials is limited to ternary alloys based on tin, but as they do not satisfy physical properties, mechanical properties and wettability when comparing with traditional Pb-Sn⁶⁾ alloys, the nowadays studies are focused on multi-component systems. The most promising candidates to replace Pb-Sn solders are eutectic alloys Sn-Ag⁷⁾ and Sn-Ag-Cu.⁸⁾

While in Ref. 8 it was confirmed that Cu addition increases the surface tension of eutectic Sn-Ag alloy and therefore only small amounts of Cu are considered, in Ref. 9 the main interest was stressed on phase equilibria and on equilibrium and non-equilibrium solidification processes using the Scheil model as well as on the prediction of the melting equilibria when adding various amounts of In and Bi to the ternary eutectic Sn-Ag-Cu. Simulation calculations of quaternary and quinary additions are important for the design of new Pb-free soldering materials including also the sequence of the formation of intermetallic compounds on the Cu substrate. It was noted by Lee *et al.*¹⁰⁾ that the first forming intermetallic compound plays the most important role in the soldering process and the prediction is possible when combining thermodynamics with diffusion.

The main aim of these joint studies is to correlate experimental surface tension with calculations by means of Butler's model using optimized thermodynamic parameters. In parallel, solidification simulation was performed and the change of the terminating temperatures of solidification was analyzed.

2. Experimental Procedure

2.1 Determination of phase equilibria

Ternary Sn-Ag-Sb alloys were prepared using pure tin (99.99%), silver (99.99%) and antimony (99.99%) in evacuated transparent quartz capsules at 1073 K for 3 h. Specimens were equilibrated at 373 K for 40 d and then quenched in iced water. Microstructure examination of each specimen was carried out by optical microscopy. Equilibrium compositions in multiphase specimens were determined by electron probe microanalysis (EPMA). Liquidus temperatures and phase transformation temperatures were also determined by differential scanning calorimetry (DSC), which was carried out in an atmosphere of flowing argon. The samples were heated and cooled at rates of 3 K/min in a sealed copper pan. An empty copper pan with a lid was used

Fig. 1 Experimental arrangements for surface tension measurements by the maximum bubble pressure method.

as a reference. The data are taken from heating curve.

2.2 Surface tension and density measurements

The maximum bubble pressure method was used in the surface tension measurements. The method is based on the known capillarity equation:

$$\sigma = \frac{1}{2} r \Delta p \quad (\text{N/m}) \quad (1)$$

describing the relation between the surface tension σ , the radius of the capillary r and the pressure Δp necessary to form and to detach the gas bubble from the end of the capillary. The Δp is, in fact, the pressure difference between the gas pressure and the hydrostatic pressure of the liquid alloy and it is given by the following equation:

$$\Delta p = p_g - p_a \quad (\text{N/m}^2) \quad (2)$$

$$\Delta p = g(\rho_m h_m - \rho_a h_a) \quad (\text{N/m}^2) \quad (3)$$

where; p_g — the gas pressure, p_a — the hydrostatic pressure, g — the acceleration of gravity, ρ_a and ρ_m — the density of the investigated liquid alloy and manometer liquid, h_a — the immersion depth of the capillary and h_m — the height of the manometer liquid. Scheme of the experimental set for measuring of the surface tension is shown in Fig. 1. The surface tension calculated from eq. (1) presents the approximate value, thus, the exact values of surface tensions were calculated using the procedure proposed by Sugden.¹¹⁾

Densities of the (Sn-Ag)_{eu}+Sb liquid alloys were measured by the dilatometric method (shown schematically in Fig. 2) based on the measurement of the height of constant weight of the alloy in the crucible of the diameter D . The density is calculated from the following equation:

$$\rho = \frac{m}{V} \quad (4)$$

$$V = \frac{\pi D^2 H}{4} \quad (5)$$

In eqs. (4) and (5) ρ is the density, m — the weight of alloy, V — the volume of the alloy, D — the crucible diameter and H — the height of the alloy in the crucible. The correction on the thermal expansion of the crucible was made at each

Fig. 2 Experimental scheme for density measurements by the dilatometric method. MMS denotes micrometer screw.

measurement temperature.

The maximum bubble pressure method has been used to measure the surface tension of pure antimony and the surface tension and density (dilatometric method) of Sn-3.8 at% Ag eutectic base alloys with 0.03, 0.06 and 0.09 molar fraction of antimony at a temperature range from 550 to 1250 K.

The (Sn-Ag)_{eu}+Sb alloys were prepared by melting in a graphite crucible an appropriate amount of tin (99.999 at%), silver (99.995 at%) and antimony (99.999 at%) directly before measurements. The protective atmosphere of high purity gas mixture of Ar-20 vol.% H₂ was used in measurements of both surface tension and density.

3. Thermodynamic Models

3.1 Description of Gibbs energy

The Gibbs energy of solution phases, such as liquid, (Ag): fcc, ζ : hcp, β -SbSn: B1, (β Sn): bct and (Sb): rhombohedral phases are described by the subregular solution model as follows:

$$G_m^\varphi = x_{Ag}^\varphi \circ G_{Ag}^\varphi + x_{Sb}^\varphi \circ G_{Sb}^\varphi + x_{Sn}^\varphi \circ G_{Sn}^\varphi + RT(x_{Ag}^\varphi \ln x_{Ag}^\varphi + x_{Sb}^\varphi \ln x_{Sb}^\varphi + x_{Sn}^\varphi \ln x_{Sn}^\varphi) + {}^{ex}G_m^\varphi \quad (6)$$

where $\circ G_i^\varphi$ and x_i^φ are the molar Gibbs energy and the mole fraction of the pure component i in φ phase, respectively. R is the gas constant and T is the absolute temperature. The term ${}^{ex}G_m^\varphi$ consists of the binary excess Gibbs energy described by the Redlich-Kister polynomial and the ternary one, extrapolation from the binary energies by Muggianu formula and ternary interaction as follows;

$${}^{ex}G_m^\varphi = x_{Ag}^\varphi x_{Sb}^\varphi L_{Ag,Sb}^\varphi + x_{Ag}^\varphi x_{Sn}^\varphi L_{Ag,Sn}^\varphi + x_{Sb}^\varphi x_{Sn}^\varphi L_{Sb,Sn}^\varphi + x_{Ag}^\varphi x_{Sb}^\varphi x_{Sn}^\varphi (x_{Ag}^\varphi {}^0 L_{Ag,Sb,Sn}^\varphi + x_{Sb}^\varphi {}^1 L_{Ag,Sb,Sn}^\varphi + x_{Sn}^\varphi {}^2 L_{Ag,Sb,Sn}^\varphi) \quad (7)$$

The Gibbs energy of the stoichiometric compound, Sb₂Sn₃ phase, is described as following function;

$$G_{\text{m}}^{\text{Sb}_2\text{Sn}_3} = 0.4^\circ G_{\text{Sb}}^{\text{rho}} + 0.6^\circ G_{\text{Sn}}^{\text{bct}} + \Delta G^f \quad (8)$$

where ΔG^f is the Gibbs energy of formation of the Sb_2Sn_3 phase and $^\circ G_{\text{Sb}}^{\text{rho}}$ and $^\circ G_{\text{Sn}}^{\text{bct}}$ are the molar Gibbs energy of the respective reference states of antimony (rhombohedral) and tin (bct). The orthorhombic ε phases, Ag_3Sb and Ag_3Sn , have mutual solubility, and are modeled as $(\text{Ag}, \text{Sb})_{0.75}(\text{Ag}, \text{Sb}, \text{Sn})_{0.25}$ by a two sublattice formula. The Gibbs energy is described as follows;

$$\begin{aligned} G_{\text{m}}^{\varepsilon} = & y_{\text{Ag}}^{\text{I}} y_{\text{Ag}}^{\text{II}} G_{\text{Ag:Ag}}^{\varepsilon} + y_{\text{Sb}}^{\text{I}} y_{\text{Sb}}^{\text{II}} G_{\text{Sb:Sb}}^{\varepsilon} \\ & + y_{\text{Ag}}^{\text{I}} y_{\text{Sb}}^{\text{II}} G_{\text{Ag:Sb}}^{\varepsilon} + y_{\text{Ag}}^{\text{I}} y_{\text{Sn}}^{\text{II}} G_{\text{Ag:Sn}}^{\varepsilon} \\ & + y_{\text{Sb}}^{\text{I}} y_{\text{Ag}}^{\text{II}} G_{\text{Sb:Ag}}^{\varepsilon} + y_{\text{Sb}}^{\text{I}} y_{\text{Sn}}^{\text{II}} G_{\text{Sb:Sn}}^{\varepsilon} \\ & + 0.75RT(y_{\text{Ag}}^{\text{I}} \ln y_{\text{Ag}}^{\text{I}} + y_{\text{Sb}}^{\text{I}} \ln y_{\text{Sb}}^{\text{I}}) \\ & + 0.25RT(y_{\text{Ag}}^{\text{II}} \ln y_{\text{Ag}}^{\text{II}} + y_{\text{Sb}}^{\text{II}} \ln y_{\text{Sb}}^{\text{II}} \\ & + y_{\text{Sn}}^{\text{II}} \ln y_{\text{Sn}}^{\text{II}}) + {}^{\text{ex}}G_{\text{m}}^{\varepsilon} \end{aligned} \quad (9)$$

where $G_{\text{A:B}}^{\varepsilon}$ is the molar Gibbs energy of the stable or hypothetical $\varepsilon\text{-A}_3\text{B}$ phase and y_{A}^{N} denote the site fraction of element A in the Nth sublattice.

3.2 Modeling of surface tension

In 1932 Butler⁴⁾ considering the equilibrium between a bulk phase and a monolayer at the surface, regarded as an individual phase, derived the relation allowing to calculate the surface tension of the alloys, which for the liquid Sn-Ag-Sb alloys has the following form:

$$\begin{aligned} \sigma &= \sigma_{\text{Ag}} + \frac{RT}{A_{\text{Ag}}} \ln \frac{x_{\text{Ag}}^{\text{S}}}{x_{\text{Ag}}^{\text{B}}} + \frac{1}{A_{\text{Ag}}} ({}^{\text{ex}}\overline{G}_{\text{Ag}}^{\text{S}} - {}^{\text{ex}}\overline{G}_{\text{Ag}}^{\text{B}}) \\ &= \sigma_{\text{Sb}} + \frac{RT}{A_{\text{Sb}}} \ln \frac{x_{\text{Sb}}^{\text{S}}}{x_{\text{Sb}}^{\text{B}}} + \frac{1}{A_{\text{Sb}}} ({}^{\text{ex}}\overline{G}_{\text{Sb}}^{\text{S}} - {}^{\text{ex}}\overline{G}_{\text{Sb}}^{\text{B}}) \\ &= \sigma_{\text{Sn}} + \frac{RT}{A_{\text{Sn}}} \ln \frac{x_{\text{Sn}}^{\text{S}}}{x_{\text{Sn}}^{\text{B}}} + \frac{1}{A_{\text{Sn}}} ({}^{\text{ex}}\overline{G}_{\text{Sn}}^{\text{S}} - {}^{\text{ex}}\overline{G}_{\text{Sn}}^{\text{B}}) \end{aligned} \quad (10)$$

Equation (10) relates the surface tension of the solution with this property of pure metals as well as with the surface area of the metallic monolayer and excess Gibbs energies of the components in the surface and the bulk phases.

In eq. (10), σ_{Ag} , σ_{Sb} and σ_{Sn} are the surface tensions of pure

silver, antimony and tin in (mN/m), A_i is the molar surface area in a monolayer of pure liquid i ($i=\text{Ag}, \text{Sb}, \text{Sn}$) in (m^2), x_{Ag} , x_{Sb} , x_{Sn} are the mole fractions of Ag, Sb and Sn in the surface and the bulk phase, respectively and ${}^{\text{ex}}\overline{G}_i^{\text{S}}$ and ${}^{\text{ex}}\overline{G}_i^{\text{B}}$ are the partial excess Gibbs energies of the component i in the surface and bulk phase. The molar surface area, A_i is calculated from the equation:

$$A_i = LN^{1/3} V_i^{2/3} \quad (\text{m}^2) \quad (11)$$

In eq. (11), N is Avogadro's number, and V_i is the molar volume of pure liquid i in (m^3), L is usually set to be 1.091 for liquid metals assuming close packed structures.¹²⁾

Finally, the relationship between excess Gibbs energy of component i in bulk and surface phases is assumed to be equal as follows:

$${}^{\text{ex}}\overline{G}_i^{\text{S}} = \beta {}^{\text{ex}}\overline{G}_i^{\text{B}} \quad (\text{J/mol}) \quad (12)$$

β is a parameter corresponding to the ratio of the coordination number Z in the surface phase to that in the bulk phase $Z^{\text{S}}/Z^{\text{B}}$ and is assumed to be equal to 0.83 for liquid.^{13,14)}

4. Results and Discussion

4.1 Determination of phase equilibria

Typical microstructures of Sn-30Ag- x Sb (mass%); (a) $x = 15$, (b) $x = 35$, and (c) $x = 50$ alloys equilibrated at 373 K for 40 d are shown in Fig. 3. In this isothermal section, a two-phase and two three-phase microstructures were obtained. The equilibrium compositions determined by EPMA are listed in Table 1. Transition temperatures in isopleth sections at 8Ag, 30Ag, 10Sn and 15Sb (mass%) were also measured by DSC as listed in Table 2.

Table 1 Equilibrium composition at 373 K in the Sn-Ag-Sb system.

Equilibrium Relation	Composition (mass%)					
	Phase 1		Phase 2		Phase 3	
Phase 1/Phase 2/Phase 3	Ag	Sb	Ag	Sb	Ag	Sb
$\beta\text{-SbSn}/\varepsilon\text{-Ag}_3(\text{Sb}, \text{Sn})/(\beta\text{Sn})$	0.3	41.5	70.0	2.0	1.7	3.6
$\beta\text{-SbSn}/\varepsilon\text{-Ag}_3(\text{Sb}, \text{Sn})/\text{—}$	0.4	50.7	72.3	10.5	—	—
$\beta\text{-SbSn}/\varepsilon\text{-Ag}_3(\text{Sb}, \text{Sn})/(\text{Sb})$	1.3	59.0	71.9	14.5	0.2	90.4

(a) Sn-30Ag-15Sb

(b) Sn-30Ag-35Sb

(c) Sn-30Ag-50Sb (mass%)

Fig. 3 Optical microstructures of (a) Sn-30Ag-15Sb, (b) Sn-30Ag-35Sb and (c) Sn-30Ag-50Sb (mass%) equilibrated at 373 K for 40 d.

Table 2 Transformation temperatures determined by DSC.

Alloy composition (mass%)		Liquidus/K	Other transformation temperature/K
Ag	Sb		
8.0	37.4	652	623, 596, 581, 507
30.0	15.0	710	595, 586, 506
30.0	28.4	704	643, 581, 505
30.0	50.0	734	710, 650

4.2 Optimization of phase equilibria

4.2.1 Binary systems

The phase diagram of the Ag-Sb binary system was evaluated by Lee *et al.*,¹⁵⁾ and later, Oh *et al.*¹⁶⁾ made re-evaluation taking into account low temperature equilibria and heats of formation of the solid phases. The thermodynamic assessment of the Ag-Sn binary system has been carried out by Karakaya and Thompson,¹⁷⁾ Chevalier,¹⁸⁾ Kattner and Boettinger,¹⁹⁾ Oh *et al.*¹⁶⁾ and Ohtani *et al.*²⁰⁾ The result of the assessment of Kattner and Boettinger¹⁹⁾ seems to be quite satisfactory except for the lattice stability of the metastable hcp tin phase, ${}^{\circ}G_{\text{Sn}}^{\text{hcp}}$, which causes inconsistency with the hypothetical melting temperature extrapolated from high pressure measurement as pointed out by Ohtani *et al.*²¹⁾ They adopted ${}^{\circ}G_{\text{Sn}}^{\text{hcp}}$ proposed by Karakaya and Thompson¹⁷⁾ to the Kattner's assessment and re-evaluated the interaction parameter of the ζ : hcp phase, $L_{\text{Ag,Sn}}^{\text{hcp}}$.²⁰⁾ Jönsson and Ågren,²²⁾ and Ohtani *et al.*²¹⁾ evaluated the thermodynamic parameter of the Sb-Sn binary system. Both of them yield satisfactory results, however, some lattice stability parameters in the former assessment are different from those in a recent compilation by Dinsdale.²³⁾ In the later assessment, the Gibbs energy of the β -SbSn: B1 ordered phase was formulated by the two-sublattice model and the parameters involving both an ordering and a disordering contributions were evaluated. However, the calculation seemed to be performed under the disordered configuration. Then, the phase diagram cannot be reproduced correctly in the B1 ordered condition with their thermodynamic parameters. In this study, the Gibbs energy of the β -SbSn: B1 phase is described in the sub-regular solution model taking into account the disordering contribution of the evaluated parameters by Ohtani *et al.*²⁰⁾ In the present assessment, thermodynamic parameters were taken from those of the Ag-Sb,¹⁶⁾ Ag-Sn^{17,20)} and Sb-Sn²¹⁾ binary systems. The calculated binary phase diagrams are shown in Fig. 4.

4.2.2 Sn-Ag-Sb ternary system

The enthalpy of mixing in the liquid phase was measured by Gather *et al.*²⁴⁾ Masson and Kirkpatrick measured transition temperatures on some isopleth section by differential thermal analysis (DTA).²⁵⁾ In addition to these experimental results, an isothermal section at 373 K and some isopleth section phase diagrams were considered to optimize the thermodynamic parameters of the Sn-Ag-Sb ternary system. Evaluated and adopted thermodynamic parameters were listed in Table 3. Figure 5 shows a comparison of the experimental and calculated enthalpy of mixing of the liquid phase at 1253 K on some vertical sections ($\text{Sb/Sn} = 4/1, 3/2, 2/3$ and $1/4$ in mole fraction), which shows basic agreement between experiments and calculations. The calculated isothermal section at 373 K is in good agreement with the experimental phase equilibria as shown in Fig. 6. Calculated phase diagrams of the vertical sections in Fig. 7 also show satisfactory agreement with experimental data. Based on the optimized thermodynamic parameters, the liquidus projection and reaction paths were calculated in Fig. 8, in which there are three invariant reactions involving liquid. The result was summarized in Table 4.

According to the comparison between experiment and calculation in the isopleth section on 8 mass%Ag shown in Fig. 7, considerable discrepancies in the thermal arrest temperatures around 508 K at 50–54 mass%Sb measured by Masson *et al.*²⁵⁾ were observed. He mentioned that the tendency for non-equilibrium freezing in the Sn-Ag-Sb system is great, which causes the unexpected thermal arrests at low temperature. Then, the non-equilibrium solidifications are simulated by Scheil model²⁶⁾ to explain this anomaly. Figure 9 shows the calculated results of solidification under equilibrium and non-equilibrium conditions of Sn-8Ag-52Sb (mass%) alloy. In both simulation, solidification starts at 691 K with a primary crystal of (Sb). Under the equilibrium condition, liquid phase disappears at 643 K, which is consistent with the calculated phase diagram shown in Fig. 7. However, tin concentrates into liquid phase with increasing solid phases under the non-equilibrium condition of Scheil model. In consequence, the terminating temperature of solidification falls drastically down to the invariant reaction, Liquid + Sb₂Sn₃ $\rightleftharpoons$ ϵ -Ag₃(Sb,Sn) + (β Sn) at 504.5 K, and further down to the Sn-Ag binary eutectic at

Fig. 4 Calculated Ag-Sb,¹⁶⁾ Ag-Sn^{17,20)} and Sb-Sn²¹⁾ binary phase diagrams.

Table 3 Evaluated and adopted thermodynamic parameters in the Sn-Ag-Sb system.

Lattice stability/J·mol ⁻¹				
	Ag	Sb	Sn	
Liquid	SGTE ²³⁾	SGTE ²³⁾	SGTE ²³⁾	
(Ag): fcc	SGTE ²³⁾	SGTE ²³⁾	SGTE ²³⁾	
ζ: hcp	SGTE ²³⁾	SGTE ²³⁾	+2400 − 3.1 <i>T</i> + ° <i>G</i> _{Sn} ^{bct17,21)}	
β-SbSn	+8000 + ° <i>G</i> _{Ag} ^{fcc*}	+8800 + ° <i>G</i> _{Sb} ^{rho21)}	+11910 + ° <i>G</i> _{Sn} ^{bct21)}	
(βSn): bct	+4184.1 + ° <i>G</i> _{Ag} ^{fcc17)}	SGTE ²³⁾	SGTE ²³⁾	
(Sb): rhombohedral	—	SGTE ²³⁾	SGTE ²³⁾	
ε-(Ag,Sb) ₃ (Ag,Sb,Sn)	+4750 − 0.5 <i>T</i> + ° <i>G</i> _{Ag} ^{fcc16)}	+20000 − 10 <i>T</i> + ° <i>G</i> _{Sb} ^{rho16)}	—	
(αSn): diamond	—	—	SGTE ²³⁾	
Thermodynamic parameter/J·mol ⁻¹				
	Ag-Sb ¹⁶⁾	Ag-Sn ^{17,20)}	Sb-Sn ²¹⁾	Ag-Sb-Sn*
Liquid: (Ag,Sb,Sn)				
⁰ <i>L</i>	−821.8 − 9.6561 <i>T</i>	−4902.5 − 4.30532 <i>T</i>	−5695.14 − 1.709 <i>T</i>	+97781.06 − 80 <i>T</i> *
¹ <i>L</i>	−19309.0 + 4.4239 <i>T</i>	−16474 + 3.12507 <i>T</i>	+782.595	−15902.99*
² <i>L</i>	−10381.2	−7298.6	+1840.91	+12222.87*
(Ag): (Ag,Sb,Sn)				
⁰ <i>L</i>	−22937.9 + 54.18535 <i>T</i>	+9998.4 + 6.28658 <i>T</i>	—	—
¹ <i>L</i>	−530.7 − 58.38697 <i>T</i>	−44740.4	—	—
ζ: (Ag,Sb,Sn)				
⁰ <i>L</i>	−23050.3 + 38.36772 <i>T</i>	+5590 + 3.56 <i>T</i>	—	—
¹ <i>L</i>	−5357.5 − 45.06379 <i>T</i>	−42400	—	—
β-SbSn: (Ag,Sb,Sn)				
⁰ <i>L</i>	—	—	−59610 + 25.867*	—
(βSn): (Ag,Sb,Sn)				
⁰ <i>L</i>	+5 <i>T</i>	+19096.3	+25400 − 36.23 <i>T</i>	—
¹ <i>L</i>	—	—	−10400 + 36.23 <i>T</i>	—
(Sb): (Sb,Sn)				
⁰ <i>L</i>	—	—	−5760 + 11.834 <i>T</i>	—
Sb ₂ (Ag,Sn) ₃				
<i>G</i> _m ^{Sb₂X₃} − 0.4° <i>G</i> _{Sb} ^{rho} −0.6° <i>G</i> _X ^{SER}	Sb ₂ Ag ₃ : +3800*	—	Sb ₂ Sn ₃ : −1738 −3.484 <i>T</i>	—
ε-(Ag,Sb) ₃ (Ag,Sb,Sn)				
<i>G</i> _m ^{ε-X₃Y} − 0.75° <i>G</i> _X ^{SER} −0.25° <i>G</i> _Y ^{SER}	Ag ₃ Sb: −338.5 −4.5184 <i>T</i> Sb ₃ Ag: +23223.9	Ag ₃ Sn: −2876.9 −3.57565 <i>T</i>	Sb ₃ Sn: +10000*	—
⁰ <i>L</i>	Ag ₃ (Ag,Sb): −4873.3 (Ag,Sb) ₃ Sb: +5932.3	—	—	Ag ₃ (Sb,Sn): −3500.0*

* -Evaluated value in the present work.

494 K. This must be the reason of the low arrest temperatures detected by Masson *et al.*²⁵⁾

4.3 Determination of density and surface tension

The temperature dependencies of the surface tension and the density are listed in Tables 5 and 6 and the respective linear equations were determined using the least squares method. The variance analyze²⁷⁾ was used for calculation of errors of surface tension and density. Temperature dependence of the surface tension of pure antimony is plotted in Fig. 10. Results of this study are close to Refs. 28 and 29 and do not exceed 10 mN/m and the agreement is contained in the experimental errors of the maximum bubble pressure method. Larger differences of about 20 mN/m are noted in comparison with Ref. 30.

Figure 11 represents the temperature dependence of the

surface tension of the investigated ternary alloys in comparison with the data of binary eutectic Sn-Ag from Ref. 6. It is easily seen that the addition of antimony decreases the surface tension. The same tendency is observed for the isotherm of the surface tension plotted in Fig. 12 at the temperatures 523 and 1173 K. In Fig. 12 solid lines are calculated from eq. (10), using Butler's model with present thermodynamic parameters. The agreement with calculated data is contained within the experimental errors of the maximum bubble pressure method.

On the proceeding two figures are represented densities. Figure 13 shows temperature dependence of the density and similarly as for the surface tension addition of antimony decreases density in comparison with density data for binary eutectic Sn-Ag.⁶⁾ In Fig. 14 the experimental isotherms at two temperatures of 523 and 1073 K are fitted by curvilinear

Fig. 5 Comparison between measured and calculated enthalpy of mixing of the liquid phase.

Fig. 6 Calculated phase diagram of isothermal section at 373 K compared with present experimental data.

Fig. 7 Calculated phase diagrams of isopleth sections at (a) 8 mass% Ag, (b) 30 mass% Ag, (c) 15 mass% Sb, and (d) 10 mass% Sn compared with present experimental data and Masson *et al.*²⁵⁾

Table 4 Calculated invariant reactions in the Sn-Ag-Sb system.

Invariant reaction	Symbol in Fig. 8	Temperature/K	Liquid composition (mass%)
Liquid + (Sb) $\rightleftharpoons$ ε + β	PE1	661.2	Sn-14.6Ag-46.1Sb
Liquid + β $\rightleftharpoons$ ε + Sb ₂ Sn ₃	PE2	584.3	Sn-6.5Ag-18.9Sb
Liquid + Sb ₂ Sn ₃ $\rightleftharpoons$ ε + (β Sn)	PE3	504.5	Sn-3.4Ag-6.2Sb

Fig. 8 Calculated liquidus projection diagram in the Sn-Ag-Sb system. The continuous thin lines denote the liquidus at individual temperatures.

dependence using the following two equations:

$$\text{at } 525 \text{ K; } \rho = 7051.9 - 2075.7x_{\text{Sb}} \quad (\text{kg/m}^3) \quad (13)$$

while

$$\text{at } 1073 \text{ K; } \rho = 6722.5 - 3618.7x_{\text{Sb}} + 20024x_{\text{Sb}}^2 \quad (\text{kg/m}^3) \quad (14)$$

5. Conclusion

The phase equilibria of the Sn-Ag-Sb ternary system, including an isothermal section at 373 K as well as four isopleth sections were determined by EPMA and DSC, respectively.

Thermodynamic assessment of the Sn-Ag-Sb system was carried out based on the experimental data. The thermodynamic parameters for describing the Gibbs energy were optimized, resulting in good agreement between calculated and experimental values of phase equilibria and thermodynamic properties.

The surface tension and the density of the (Sn-3.8at%Ag)_{eu} + Sb liquid alloys were measured using the maximum bubble-pressure method and the diametric method, respectively. The linear dependencies of surface tension and density on temperature were observed. Additionally, the surface tension was calculated based on the Butler's model and like in other previously investigated systems, the curvilinear dependence on temperature has been observed.

Fig. 9 Solidification simulation under equilibrium condition and Scheil model.²⁶⁾

Table 5 Temperature dependencies of the surface tension of (Sn-Ag)_{eu}+Sb alloys together with the errors calculated for A and B parameters and the surface tension calculated at 523 K.

x_{Sb}	$\gamma = A + BT$ /mN·m ⁻¹	γ (523 K) /mN·m ⁻¹	Err (A) /mN·m ⁻¹	Err (B) /mN·m ⁻¹ ·K ⁻¹
0.00	$= 586.4 - 0.0904T$	539.1 ± 12.5	± 15.6	± 0.0179
0.03	$= 559.8 - 0.0704T$	523.0 ± 6.7	± 6.7	± 0.0078
0.06	$= 545.9 - 0.0614T$	513.8 ± 7.0	± 6.6	± 0.0075
0.09	$= 538.0 - 0.0578T$	507.7 ± 11.9	± 12.9	± 0.0136
1.00*	$= 419.0 - 0.0561T_m$	368.3 ± 3.9	± 10.7	± 0.0100

* - γ of Sb calculated at melting temperature (904 K)

Table 6 Temperature dependencies of the density of (Sn-Ag)_{eu}+Sb alloys together with the errors calculated for A and B parameters and the density calculated at 873 K.

x_{Sb}	$\rho = A + BT$ /kg·m ⁻³	ρ (873 K) /kg·m ⁻³	Err (A) /kg·m ⁻³	Err (B) /kg·m ⁻³ ·K ⁻¹
0.00	$= 7364.5 - 0.599T$	6842 ± 27	± 40	± 0.047
0.03	$= 7316.5 - 0.637T$	6760 ± 58	± 122	± 0.159
0.06	$= 7288.0 - 0.663T$	6709 ± 75	± 123	± 0.156
0.09	$= 7141.8 - 0.543T$	6668 ± 75	± 120	± 0.127

Fig. 10 Surface tension of antimony in comparison with the data from Refs. 28–30.

Fig. 11 Temperature dependencies of the surface tension of (Sn-Ag)_{eu}+Sb liquid alloys. Symbols are referred to experimental data and the solid lines are calculated from equations in Table 5.

Fig. 12 Surface tension isotherms calculated at 523 and 1073 K. Symbols represent the values calculated from equations in Table 5. Continuous lines show the values calculated from Butler's model.⁴⁾

Fig. 13 Temperature dependencies of density of (Sn-Ag)_{eu}+Sb liquid alloys. Symbols are referred to experimental data and the values calculated from equations in Table 6 show the continuous lines.

Fig. 14 Isotherms of the density of (Sn-Ag)_{eu}+Sb liquid alloys at 523 and 1073 K. Symbols referred to the experimental data and continuous lines show the values calculated at 523 and 1073 K from eqs. (13) and (14).

REFERENCES

- 1) Z. Moser, W. Gasior, J. Pstrus, W. Zakulski, I. Ohnuma, X. J. Liu, Y. Inohana and K. Ishida: *J. Electronic Mater.* **30** (2001) 1120–1128.
- 2) X. J. Liu, Y. Inohana, I. Ohnuma, R. Kainuma, K. Ishida, Z. Moser, W. Gasior and J. Pstrus: *J. Electronic Mater.* **31** (2002) 1139–1151.
- 3) Z. Moser, W. Gasior and J. Pstrus: *Inzynieria Materialowa* **2** (2002) 65–68.
- 4) J. A. V. Butler: *Proc. R. Soc. London Ser. A* **135** (1932) 348–375.
- 5) W. Gasior, Z. Moser, J. Pstrus, B. Krzyzak and K. Fitzner: *J. Phase Equilib.* **2** (2003) 21–39.
- 6) W. Gasior, Z. Moser and J. Pstrus: *J. Phase Equilib.* **22** (2001) 20–25.
- 7) Z. Moser, W. Gasior and J. Pstrus: *J. Phase Equilib.* **22** (2001) 254–258.
- 8) Z. Moser, W. Gasior, J. Pstrus and S. Ksiezarek: *J. Electronic Mater.* **31** (2002) 1225–1229.
- 9) I. Ohnuma, M. Miyashita, K. Anzai, X. J. Liu, H. Ohtani and K. Ishida: *J. Electron Mater.* **29** (2000) 1137–1144.
- 10) B. J. Lee and H. M. Lee: *Design and Reliability of Solders and Solder Interconnections*, eds. R. K. Mahidhara, D. R. Frear, S. M. L. Sastry, K. L. Murty, P. K. Liaw and W. Winterbottom, (The Minerals, Metals and

- Materials Society, 1997).
- 11) S. Sugden: J. Chem. Soc. **124** (1924) 858–868.
 - 12) T. Tanaka and T. Iida: Steel Res. **65** (1994) 21–28.
 - 13) T. Tanaka, K. Hack, T. Iida and S. Hara: Z. Metallk. **87** (1996) 380–389.
 - 14) T. Tanaka, K. Hack and S. Hara: MRS Bull. **24** (1999) 45–50.
 - 15) B.-Z. Lee, C.-S. Oh and D. N. Lee: J. Alloy. Compd. **215** (1994) 293–301.
 - 16) C.-S. Oh, J.-H. Shim, B.-J. Lee and D. N. Lee: J. Alloy. and Compd. **238** (1996) 155–166.
 - 17) I. Karakaya and W. T. Thompson: Bull. Alloy Phase Diagram **8** (1987) 340–347.
 - 18) P.-Y. Chevalier: Thermochim. Acta **136** (1988) 45–54.
 - 19) U. R. Kattner and W. J. Boettinger: J. Electronic Mater. **23** (1994) 603–610.
 - 20) H. Ohtani, I. Satoh, M. Miyashita and K. Ishida: Mater. Trans. **42** (2001) 722–731.
 - 21) H. Ohtani, K. Okuda and K. Ishida: J. Phase Equilib. **16** (1995) 416–429.
 - 22) B. Jönsson and J. Ågren: Mater. Sci. Technol. **2** (1986) 913–916.
 - 23) A. T. Dinsdale: CALPHAD **15** (1991) 317–425.
 - 24) B. Gather, P. Schröter and R. Blachnik: Z. Metallk. **78** (1987) 280–285.
 - 25) D. B. Masson and B. K. Kirkpatrick: J. Electronic Mater. **15** (1986) 349–353.
 - 26) E. Scheil: Z. Metallk. **34** (1942) 70–72.
 - 27) W. Volk: *Applied Statistics for Engineers, 2nd Edition*, (McGraw-Hill Book Comp., 1969).
 - 28) I. Lauerma and F. Sauerwald: Z. Metallk. **55** (1964) 605–612.
 - 29) V. Somol and M. Beranek: Sb. Vysk. Sk. Chem.-Technol. Praxe Anorg. Chem. Technol. **B30** (1984) 199–205.
 - 30) V. B. Lazarev: Russ. J. Phys. Chem. **38** (1964) 325–330.