JPEDAV (2006) 27:140-144
DOI: 10.1361/154770306X97164
1547-7037/$19.00 ©ASM International

Electromotive Force Study of the Liquid Silver-Bismuth-Tin Alloys

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(Submitted June 25, 2005; in revised form December 5, 2005)

The Ag-Bi-Sn alloy system has been assessed twice, so far, for its potential applications as a lead-free solder material. The first assessment was based on binary data only; the second assessment introduced ternary parameters. It was noted in conclusion that more experimental studies were needed, especially for the liquid phase. The electromotive force (emf) measurement method was used in this study to determine the thermodynamic properties of liquid Ag-Bi-Sn alloys using solid electrolyte galvanic cells as shown below:

Re, Ag-Bi-Sn, SnO_2 | **Y**ttria **S**tabilized **Z**irconia | Ni, NiO, **Pt,**

Re, Sn, SnO_2 | **Y**ttria **S**tabilized **Z**irconia | Ni, NiO, **Pt.**

Alloy compositions for investigation were chosen along three constant Bi-to-Sn ratio lines (1/3, 1, and 3) and with the silver content changing from 10 up to 90 at.%, every 10 at.%, resulting in a total of 27 different alloy samples. The temperature of the measurements varied from 975 to 1400 K. A linear dependence of the emf on temperature was observed for all compositions, and the appropriate line equations were derived. Excess partial Gibbs energies of Sn were then calculated at 1200 K and compared with the results of the calculations of both assessments; Gibbs energy of formation of SnO_2 was determined as well. It was then shown that our new emf data fit better to the binary formalism-based calculations than to the second assessment results.

Keywords activity, electromotive force (emf), experimental study, experimental thermodynamics, metal alloys, ternary system, thermodynamic properties

1. Introduction

The silver (Ag)-bismuth (Bi)-tin (Sn) alloys attract the interest of scientists due to their potential applications as lead-free solders. They have so far been assessed critically twice: Kattner et al.[1] calculated a phase diagram using only binary data, due to the lack of thermodynamic information for the ternary system; and Hassam et al.[2] carried out calorimetric measurements in the liquid Ag-Bi-Sn alloys along three constant X_{Bi}-to-X_{Sn} ratio lines (1/3, 1, and 3, among others), and at two temperatures 783 and 878 K. They observed both positive and negative deviation from ideal behavior, but no temperature dependence on their results.

Ohtani et al.[3] introduced ternary interaction parameters into a thermodynamic description of the system using their own phase diagram data plus those published by Hassam et al.[4] and the calorimetric results of Hassam et al.[2] as well. They then performed phase diagram calculations, and good agreement with the calorimetric data[2] was observed, but in their conclusion Ohtani et al.[3] underlined the necessity of the further investigations of the thermodynamic properties of the liquid phase. The current study is intended to do that.

2. Theoretical Background

Galvanic cells were used with yttria (8%)-stabilized zirconia solid electrolytes and Ni + NiO reference electrode according to the schemes shown below:

Re, Ag-Bi-Sn, SnO_2 | YSZ | Ni, NiO, Pt (Eq I)

Re, Sn, SnO_2 | YSZ | Ni, NiO, Pt (Eq II)

with electrode reactions as follows:
for the alloy electrode

$$\mathrm{Sn} + 2\mathrm{O}^{-2} \rightarrow \mathrm{SnO_2} + 4\mathrm{e} \qquad \text{(Eq 1)}$$

for the reference electrode

$$2\mathrm{NiO} + 4\mathrm{e} \rightarrow 2\mathrm{O}^{-2} + 2\,\mathrm{Ni} \qquad \text{(Eq 2)}$$

resulting in the overall cell reaction

$$\mathrm{Sn} + 2\mathrm{NiO} \rightarrow \mathrm{SnO_2} + 2\mathrm{Ni} \qquad \text{(Eq 3)}$$

The change of the Gibbs energies of reversible cell reactions of the cell (Eq I and II) are related to the measured electromotive forces as follows:

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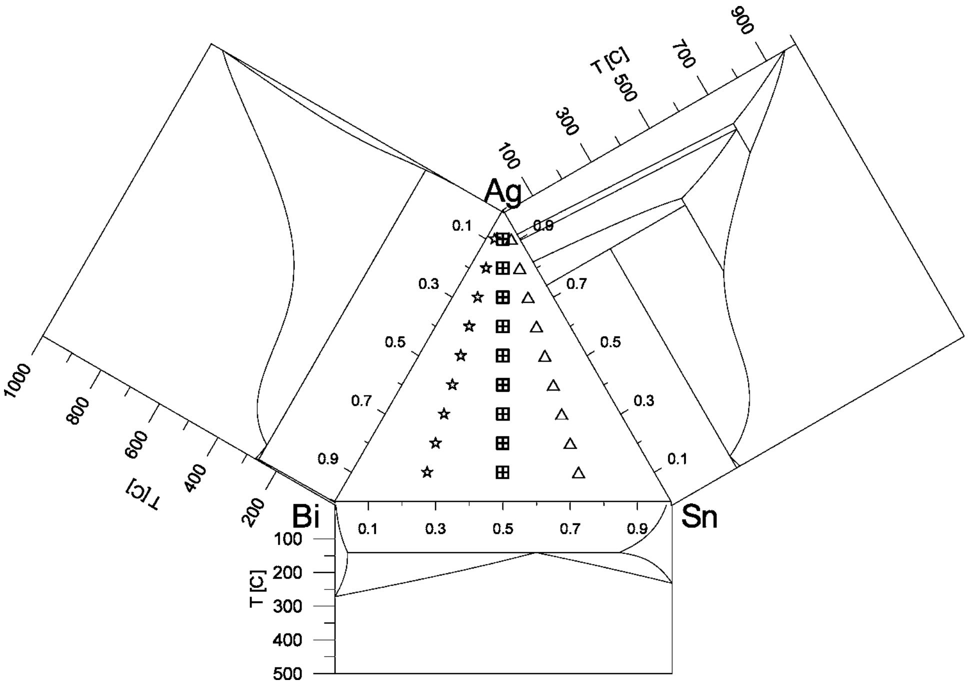

Fig. 1 Alloy compositions of a constant Bi-to-Sn ratio: 3 (stars); 1 (squares); and 1/3 (triangles)

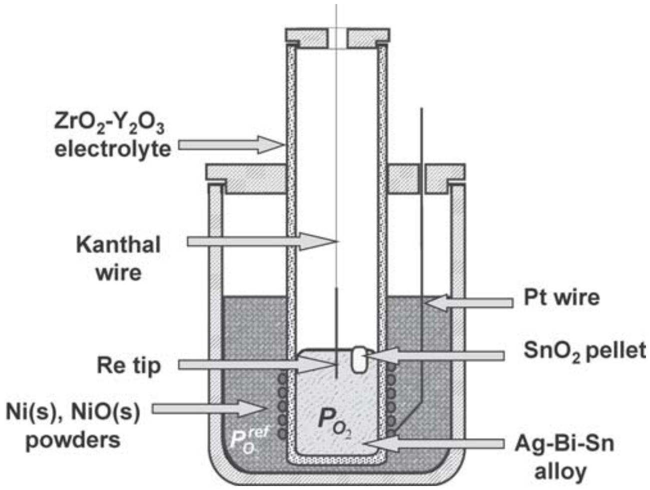

Fig. 2 Cross section through the cell container

$$\Delta G(I) = \Delta G^0_{f(\mathrm{SnO_2})} - 2 \cdot \Delta G^0_{f(\mathrm{NiO})} - RT \ln a_{\mathrm{Sn}} = -4FE \tag{Eq 4}$$

$$\Delta G(II) = \Delta G^0_{f(\mathrm{SnO_2})} - 2 \cdot \Delta G^0_{f(\mathrm{NiO})} = -4FE^0 \tag{Eq 5}$$

where $\Delta G^0_{f(\mathrm{SnO_2})}$,$\Delta G^0_{f(\mathrm{NiO})}$ is the Gibbs energy of formation of tin oxide and nickel oxide, respectively, F is the Faraday constant, R is the gas constant, and E, E^0 is the measured emf.

Subtracting Eq 5 from Eq 4, one obtains:

$$RT \ln a_{\mathrm{Sn}} = 4F(E - E^0) \tag{Eq 6}$$

and Sn activity may be calculated directly from emf values by means of Eq 6.

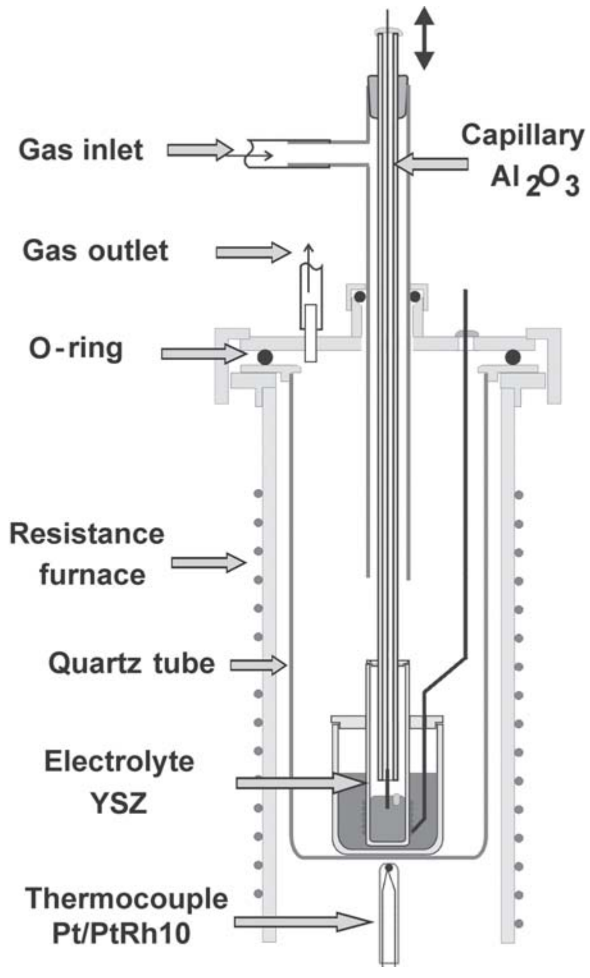

Fig. 3 The scheme of the cell assembly

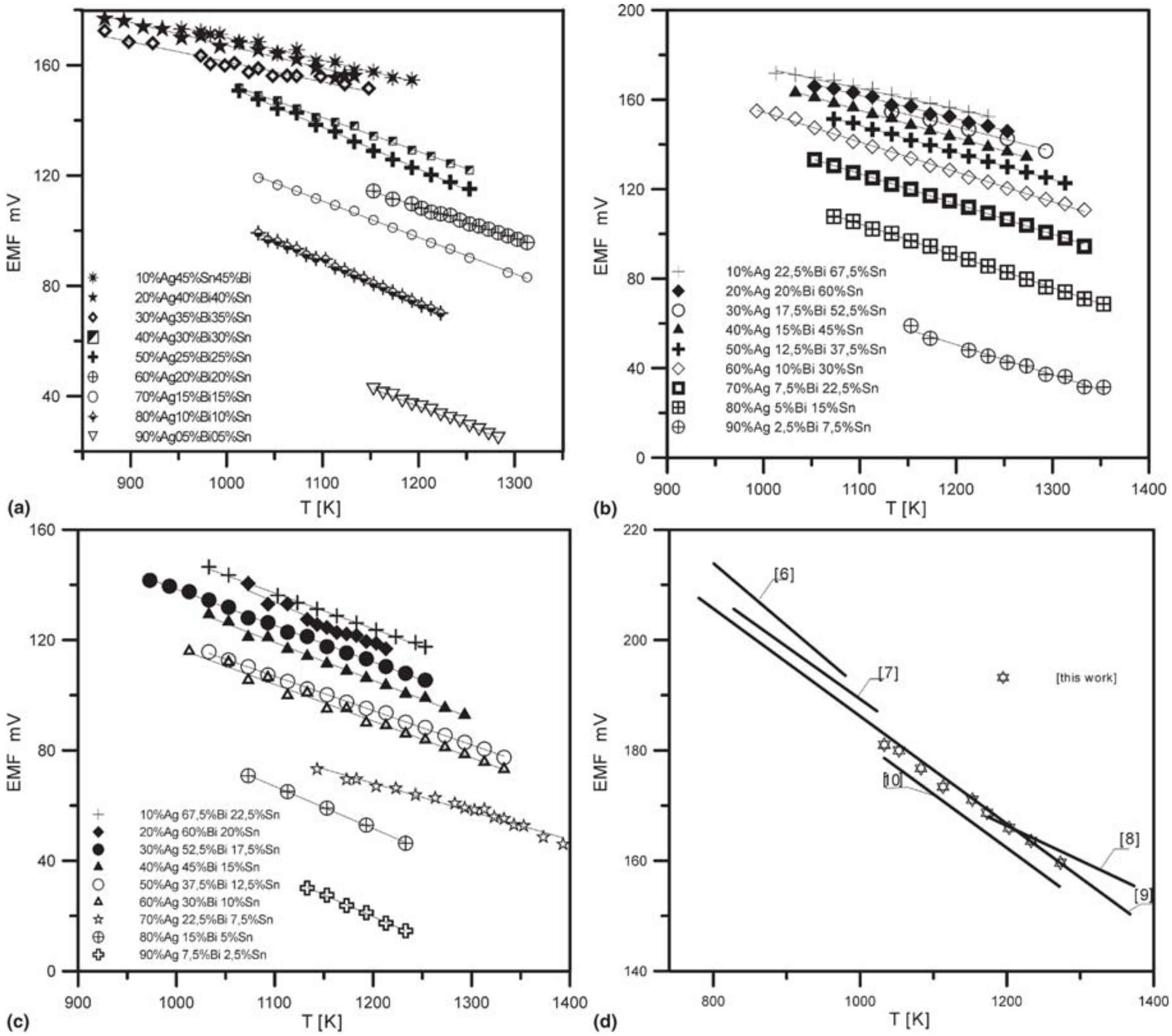

Fig. 4 Plots of emf vs *T* for the cross-sections X_{Bi}/X_{Sn}: (a) 1; (b) 1/3; (c) 3. (d) The emf of the cell (Eq II) compared with the existing literature data[6–10]

Table 1 Straight line coefficients of the emf vs *T* plots for the cells (Eq I) and (Eq II)

	$E = a(\pm\Delta a) + b(\pm\Delta b)\,T$, mV					
	$X_{Bi}/X_{Sn} = 1$		$X_{Bi}/X_{Sn} = 1/3$		$X_{Bi}/X_{Sn} = 3$	
X_{Ag}	$a(\pm\Delta a)$	$b(\pm\Delta b)$	$a(\pm\Delta a)$	$b(\pm\Delta b)$	$a(\pm\Delta a)$	$b(\pm\Delta b)$
0.1	251.1 (±3.1)	−0.0812 (±0.0030)	266.2 (±5.3)	−0.0921 (±0.0047)	279.3 (±2.1)	−0.1294 (±0.0018)
0.2	250.4 (±3.8)	−0.0833 (±0.0038)	276.4 (±3.5)	−0.1041 (±0.0030)	304.9 (±11.2)	−0.1556 (±0.0097)
0.3	233.7 (±4.7)	−0.0725 (±0.0046)	278.7 (±6.3)	−0.1090 (±0.0052)	270.5 (±1.7)	−0.1320 (±0.0015)
0.4	276.8 (±2.0)	−0.1234 (±0.0017)	288.8 (±1.2)	−0.1214 (±0.0011)	270.3 (±3.0)	−0.1374 (±0.0026)
0.5	304.2 (±2.4)	−0.1515 (±0.0021)	280.7 (±0.7)	−0.1203 (±0.0006)	243.6 (±1.2)	−0.1243 (±0.0010)
0.6	245.7 (±1.9)	−0.1142 (±0.0016)	287.9 (±1.8)	−0.1335 (±0.0015)	250.0 (±4.1)	−0.1328 (±0.0035)
0.7	255.7 (±1.4)	−0.1318 (±0.0012)	275.4 (±1.4)	−0.1350 (±0.0012)	191.2 (±5.1)	−0.1025 (±0.0040)
0.8	255.8 (±1.5)	−0.1516 (±0.0014)	261.2 (±1.3)	−0.1425 (±0.0011)	235.0 (±2.6)	−0.1528 (±0.0022)
0.9	198.3 (±2.5)	−0.1350 (±0.0021)	211.3 (±6.9)	−0.1340 (±0.0055)	213.5 (±6.6)	−0.1615 (±0.0055)
	$E^0 = a^0(\pm\Delta a^0) + b^0(\pm\Delta b^0)\,T$, mV					
0	$a^0(\pm\Delta a^0)$ 273.6 (±2.0)				$b^0(\pm\Delta b^0)$ −0.0895 (±0.0017)	

Note: Single standard deviations in parentheses

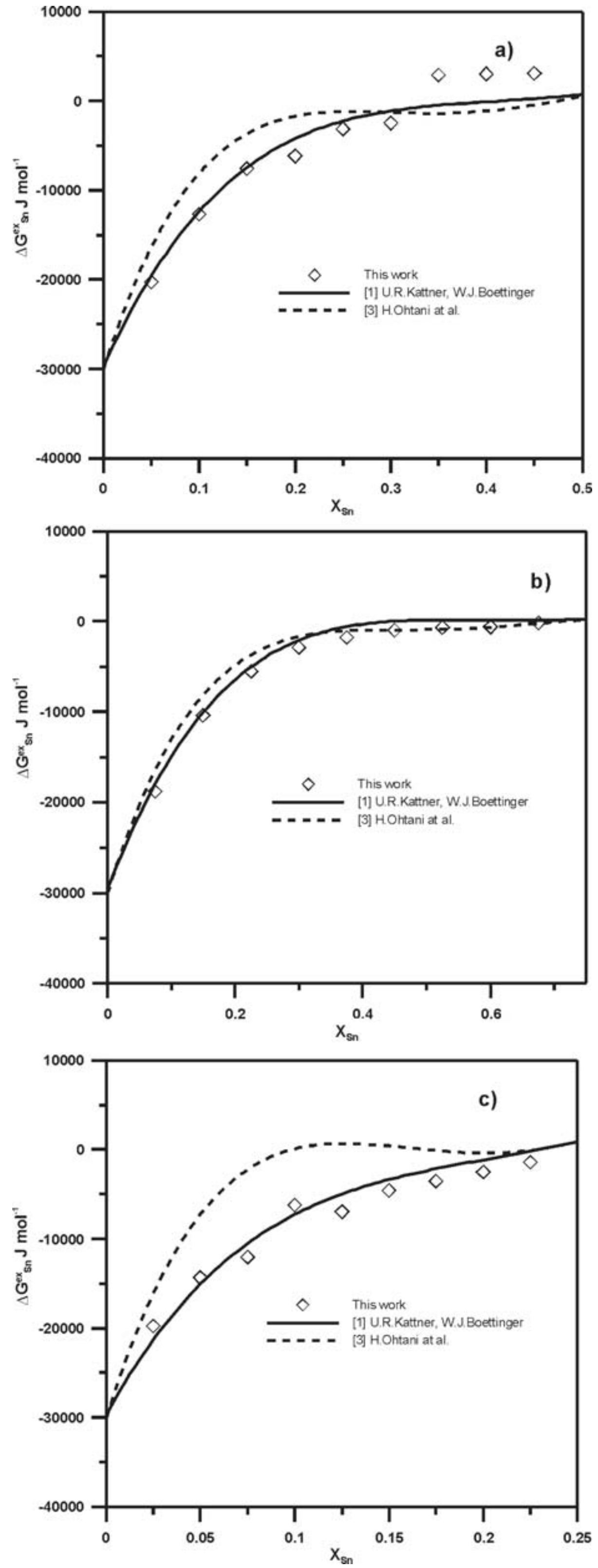

Fig. 5 Comparison of values of ΔG^{ex}_{Sn} derived from emf data with the results of the assessment calculations of Eq 1 and 3 for the cross sections $X_{Bi}/X_{Sn} = 1$, 1/3, and 3 on the plots of (a), (b), and (c), respectively

3. Experimental Details

The emf values were measured at temperatures ranging from 975 to 1400 K, and the compositions of alloys were chosen in such a way as to keep the X_{Bi}-to-X_{Sn} ratio constant along three cross sections equal to 3, 1, and 1/3 with Ag content varying from 0.1 to 0.9 mol fraction at 0.1 increments; sample compositions are schematically shown in Fig. 1.

The schematic cross section of the cell container is shown on Fig. 2, and Fig. 3 presents the scheme of the cell assembly.

The emf readings were taken for both heating and cooling cycles with measurement made after the equilibrium at each selected temperature was reached; equilibrium was indicated by the attainment of a constant emf value, a detailed description of data reading and acquisition is given elsewhere.[5] The appropriate amounts of pure metals (at least 99.99% pure) were melted directly in the cell during the first heating cycle to prepare samples of the alloys.

In Fig. 2, it can be seen that an electrolyte tube with an alloy sample and a mixture of reference electrode powders were housed in an alumina crucible that was covered by an alumina cap. The cell was located in a gas-tight quartz tube in such a way as to place the cell container within a constant temperature zone of the vertical resistance furnace. The inert atmosphere was maintained inside the cell by passing a 5 mL/min argon flow of quality 5.0 that had been additionally deoxidized using a copper column. The temperature was controlled by a Pt-PtRh10 thermocouple located at the bottom of the quartz tube, and connected to an Omega CN 4800 (Stamford, CT) temperature controller. The emf was measured using a Keithley (Cleveland, OH) 2000 multimeter linked to a data-acquisition system. Each single heating-cooling cycle lasted two to three days, and good reproducibility during both heating and cooling emf readings was observed every time.

4. Results

All emf readings were corrected for the thermoelectric power created by the kanthal-platinum joint. Values of the emf of the cell (Eq I) were plotted on the respective graphs in Fig. 4(a) to (c), and emf values of the cell (Eq II) were compared with the available data from the literature[6-10] on the graph in Fig. 4(d). As can be seen, plots may be approximated by straight lines for all alloy compositions, and the appropriate line coefficients are listed in Table 1, with single standard deviations in parentheses.

The values of the excess partial Gibbs energy of Sn, $\Delta\overline{G}^{ex}_{Sn}$, were then derived directly from emf data by means of the relation:

$$\Delta\overline{G}^{E}_{Sn} = 4F((a - a^0) + (b - b^0) \cdot T) - RT \ln x_{Sn} \qquad \text{(Eq 7)}$$

at the arbitrary temperature of 1200 K, and they were compared with the results of assessment calculations from Ref 1 and Ref 3, which can be seen in the graphs in Fig. 5.

5. Conclusions

Good agreement of our $\Delta G^0_{f(\mathrm{SnO_2})}$ measured values with the available data from the literature (Fig. 4d) is the proof of the proper working of our cells. This, in combination with the good reproducibility of emf readings made both on heating and cooling makes our results reliable.

Comparison of our $\Delta\overline{G}^{\mathrm{ex}}_{\mathrm{Sn}}$ values with those calculated from previous assessments shows that our results fit much better to the data from the study by Kattner et al.[1] than to those of Ohtani et al.[3] Moreover, the positive deviations observed in Fig. 5(a) for the lowest Ag content seem to correspond to those observed by Hassam et al.[2] in their calorimetric results (Fig. 7a in the original article). On the other hand, the heat of formation of the liquid calculated by Ohtani et al.[3] (Fig. 3 in the original article) agrees well with the calorimetric results of Hassam et al.,[2] and the phase diagram calculations of Ohtani et al.[3] also agree with the experimental points of Hassam et al.[4] (Fig. 2, 7, and 8 in the original article).

These contradictions indicate a need for a new assessment of the ternary Ag-Bi-Sn system and for phase diagram calculations to be undertaken.

Acknowledgments

The present study has been carried out within the frame of COST 531 Action ("Lead-free Solder Materials") as a part of Group Project 1. Financial support from the Polish State Committee for Scientific Research under grant No. 62/E-88/SPB/COST/T-08/DZ 459/2003-2006 is gratefully acknowledged.

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