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論 文

Thermodynamic Properties of Liquid Sn-Bi-Sb Alloys

Iwao Katayama, Dragana Živkovič, Dragan Manasijevic, Toshihiro Tanaka,
Zivan Živkovič, and Hiromi Yamashita

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Activity of tin in liquid Sn-Bi-Sb was derived by EMF measurement of galvanic cell with fused salts electrolyte in the temperature range of 700 to 1000 K in the whole composition range. Activity of tin at 900 K shows very small positive deviation from Raoult's law for Sn-Bi alloys and moderately negative deviation for Sn-Sb alloys. Activity of ternary alloys along $Sb_yBi_{(1-y)}$-Sn ($y = 0.25$, 0.50 and 0.75) shows negative deviation and the deviation becomes large with increasing Sb content. Excess free energy of mixing is derived using Darken's method for Gibbs-Duhem equation and the values are compared with those by model calculations based on the three constitutive binary data.

1. INTRODUCTION

Low melting alloys such as tin-lead alloys are widely used as solder materials. Development of the lead-free solders has been tried because of the health concerns and environmental reasons. Thermodynamic properties of these alloy systems are closely related to the surface tension which is one of the important properties in the development of the solders.[1)]

The purpose of this study is to determine the activity of tin in liquid Sn-Bi-Sb alloys and in the two border systems(Sn-Bi and Sn-Sb) as one of the candidates for lead-free solder materials by fused salt EMF method and compare the results derived from the measurements with the model calculations based on the constitutive three binary data.

The Sn-Bi phase diagram is of simple eutectic type and activity of Sn in liquid Sn-Bi alloys was assessed in1996 by Lee *et al.*[2)] Activity of Sn shows slightly positive deviation from Raoult's law and its temperature dependence is also very small. The activities measured by various authors were in accordance with one another. Joensson and Agren[3)] assessed thermodynamic properties of Sn-Sb system. Activity of Sn in liquid Sn-Sb alloys deviates positively from Raoult's law and Vassiliev *et al.*[4)] confirmed the activity values. For these two binary systems references are shown in our previous paper.[5)]

There seem no experimental data on thermodynamic activity of Sn-Bi-Sb liquid alloys.

2. EXPERIMENTAL

As the experimental equipment, experimental procedure and some experimental results are already shown in our previous paper,[5)] only the outline is described here.

The cell with fused salt is represented as follows:

$$(-)\mathrm{Sn(pure)} \mid \mathrm{Sn^{2+}(KCl\text{-}LiCl)} \mid \mathrm{Sn\text{-}alloys}(+) \qquad \text{(I)}$$

Activity of tin (a_{Sn}) in the Sn-alloys is calculated from the EMF (E/mV) of the cell from eq.1.

$$\Delta \overline{G}_{Sn} = RT \ln a_{Sn} = -2EF \qquad (1)$$

where $\Delta \overline{G}_{Sn}$ is partial molar free energies of mixing of tin, R is gas constant, T is temperature and F is Faraday constant. Cell temperature was controlled at desired temperature within ± 1.0 K. Under the argon atmosphere the cell temperature was raised to about 900 K and held at the temperature for equilibration. After the

Table 1 Temperature dependence of EMF of cell: $Sn|Sn^{2+}(LiCl\text{-}KCl)|liq.Sn\text{-}alloys$, and thermodynamic property of the alloys at 900 K.

x_{Sn}	x_{Sb}	x_{Bi}	$E/mV = a+bT/K$	a_{Sn}	$\Delta\overline{G}_{Sn}^{Ex}$/kJmol^{-1}	ΔG^{Ex}/kJmol^{-1}
Sn-Bi binary system						
0.800		0.200	0.623 + 0.00847T/K±0.38	0.810	0.0899	0.301
0.700		0.300	-1.13 + 0.01537T/K ± 0.32	0.722	0.231	0.379
0.600		0.400	-2.25 + 0.02257T/K +0.52	0.629	0.350	0.410
0.500		0.500	0.086 + 0.02727T/K ± 2.38	0.531	0.453	0.413
0.400		0.600	1.20 + 0.03417T/K ± 0.43	0.439	0.702	0.383
0.300		0.700	-1.68 ~ 0.04947T/K ± 0.32	0.332	0.757	0.324
0.200		0.800	0.873 + 0.06507T/K ~ 0.07	0.226	0.930	0.250
0.100		0.900	0.04 + 0.09167T/K ± 0.44	0.121	1.402	0.139
Sb/Bi=1/3 (Sn-Bi-Sb ternary)						
0.800	0.050	0.150	-0.171 + 0.00977T/K ± 0.30	0.802	0.0201	-0.017
0.700	0.075	0.225	6.47 + 0.00747T/K ± 0.35	0.713	0.143	-0.057
0.600	0.100	0.300	-0.756 + 0.02167T/K ± 0.39	0.594	-0.080	-0.098
0.500	0.125	0.375	1.30 + 0.02947T/K ± 0.48	0.488	-0.176	-0.092
0.400	0.150	0.450	0.422 + 0.03707T/K ± 0.18	0.380	-0.377	-0.058
0.300	0.175	0.525	4.36 + 0.05037T/K ± 0.26	0.278	-0.567	0.010
0.200	0.200	0.600	5.95 + 0.0679 T/K ± 0.33	0.177	-0.901	0.114
0.100	0.225	0.675	8.46 + 0.0948 T/K ± 0.33	0.089	-0.871	0.240
Sb/Bi=1/1(Sn-Bi-Sb ternary)						
0.800	0.100	0.100	0.589 + 0.00937T/K ± 0.41	0.794	-0.0586	-0.305
0.700	0.150	0.150	2.11 + 0.0143 T/K ± 0.26	0.680	-0.222	-0.398
0.600	0.200	0.200	1.74 + 0.02267T/K ± 0.42	0.566	-0.436	-0.427
0.500	0.250	0.250	7.81 + 0.0241 T/K ± 0.24	0.468	-0.497	-0.416
0.400	0.300	0.300	6.91 + 0.03767T/K ± 0.81	0.350	-1.002	-0.356
0.300	0.350	0.350	13.64 + 0.05077T/K ± 0.54	0.217	-2.424	-0.144
0.200	0.400	0.400	8.74 + 0.07217T/K ± 0.63	0.150	-2.171	0.169
0.100	0.450	0.450	13.53 + 0.10087T/K ± 0.83	0.068	-2.887	0.502
Sb/Bi=3/1(Sn-Bi-Sb ternary)						
0.800	0.150	0.050	0.884 + 0.00927T/K ± 0.16	0.790	-0.0926	-0.623
0.700	0.225	0.075	-0.609 + 0.0185 T/K + 0.48	0.662	-0.421	-0.830
0.600	0.300	0.100	2.64 + 0.02357T/K + 0.42	0.541	-0.772	-0.916
0.500	0.375	0.125	6.05 + 0.0305 T/K ± 0.41	0.421	-1.285	-0.896
0.400	0.450	0.150	6.72 + 0.0373T/K ± 0.30	0.354	-0.915	-0.845
0.300	0.525	0.175	12.87 + 0.05287T/K ± 0.20	0.211	-2.641	-0.709
0.100	0.675	0.225	16.73 + 0.10057T/K ± 0.70	0.063	-3.452	-0.008
Sn-Sb binary system						
0.800	0.200		1.84 + 0.00867T/K ± 0.46	0.782	-0.171	-0.948
0.700	0.300		1.09 + 0.01677T/K ± 0.28	0.660	-0.442	-1.283
0.600	0.400		4.84 + 0.02097T/K ± 0.88	0.544	-0.739	-1.521
0.500	0.500		7.44 + 0.03057T/K ± 0.41	0.406	-1.552	-1.630
0.400	0.600		10.73 + 0.04147T/K ± 0.47	0.290	-2.401	-1.570
0.300	0.700		15.92 + 0.05377T/K ±0.59	0.191	-3.380	-1.357
0.200	0.800		19.75 + 0.07077T/K ± 0.52	0.117	-4.038	-1.022
0.100	0.900		15.47 + 0.11027T/K + 0.43	0.052	-4.894	-0.594

equilibrium EMF was measured, the cell temperature was increased or decreased to the new temperature in about 30 min and held constant. EMF of the cell was measured at every ten min.

3. EXPERIMENTAL RESULTS

At each alloy composition of the alloys linear relations between E and T are obtained.[5] The results are shown in **Table 1** with the thermodynamic properties derived by well known eqs.(1), (2) and (3) at 900 K.

$$\Delta\overline{G}_{Sn}^{Ex} = \Delta\overline{G}_{Sn} - \Delta\overline{G}_{Sn}^{ideal} = RT\ln\gamma_{Sn} \quad (2)$$

Table 2 Interaction parameters and its temperature dependence.

parameters/Jmol^{-1}	800 K	900 K	1000 K	$a+bT$/K
A_{SnSb}	−6000	−6000	−6000	−6000
B_{SnSb}	−6500	−6650	−7000	$-4467-2.5T$/K
A_{SbBi}	2700	3700	4700	$-5300+10T$/K
B_{SbBi}	3700	3000	1700	$11800-10T$/K
A_{BiSn}	1250	1350	1450	$450+T$/K
B_{BiSn}	1800	2000	2150	$408+1.75T$/K
W_{Sn}(Sn-Bi-Sb)	−3000	−2730	−3499	$-831-2.495T$/K
W_{Sb}(Sn-Bi-Sb)	−2839	3302	10498	$-56363+66.685T$/K
W_{Bi}(Sn-Bi-Sb)	−3255	−11266	−13820	$38096-52.825T$/K

$$\Delta G^{Ex} = (1-x_i)\left[\int_1^{x_i}\frac{\Delta\overline{G}_i^{Ex}}{(1-x_i)^2}dx_i\right]_{x_j/x_k} - x_j\left[\int_1^{0}\frac{\Delta\overline{G}_i^{Ex}}{(1-x_i)^2}dx_i\right]_{x_k/x_j=0} - x_k\left[\int_1^{0}\frac{\Delta\overline{G}_i^{Ex}}{(1-x_i)^2}dx_i\right]_{x_j/x_k=0} \quad (3)$$

where ΔG^{ideal} is the Gibbs free energy of mixing for ideal solution, γ is activity coefficient ($=a/x$).

For liquid Sn-Sb and Sb-Bi and Bi-Sn alloys, excess free energies of mixing ΔG^{Ex} in this study are presented in the quasi regular solution equations as follows;

$$\Delta G_{i-j}^{Ex} = x_i x_j(A_{i-j}x_i + B_{i-j}x_j) \quad (4)$$

$$\Delta G_i^{Ex} = x_j^2\{2A_{i-j}(1-x_j) - (1-2x_j)B_{i-j}\} \quad (5)$$

$$\Delta G_j^{Ex} = (1-x_j)^2\{A_{i-j}(1-2x_j) + 2B_{i-j}x_j\} \quad (6)$$

where x_j and x_i are mole fraction of component j and i, respectively and A_{i-j} and B_{i-j} are interaction parameters between i−j. They are determined by fitting the excess free energy of mixing, which are obtained from the activity measurement and the data for each binary alloy based on the Gibbs-Duhem relation. For Sb-Bi binary alloys, the extrapolated value of the ternary data to $x_{Sn}=0$ is used. They are shown in **Table 2**.

Excess free energy of mixing for ternary alloys can be obtained by Kohler's method in which the data of related three binary systems are used. In this study Kohler's treatment is extended by adding the interaction in the ternary system as follows:

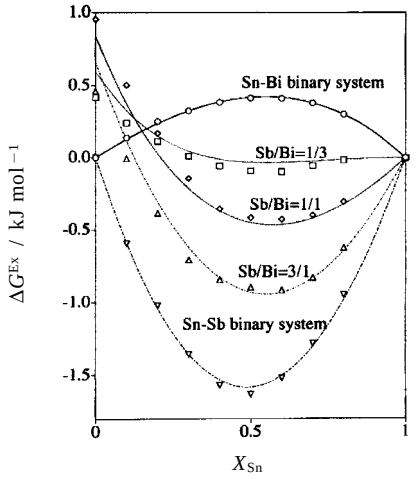

Fig.1 Integral excess Gibbs free energy of mixing in Sn-Bi-Sb alloys at 900 K.

Table 3 Coefficients of Redlich-Kister polynomial form of three binary systems at 900 K.

System *ij*	L^0 ij	L^1 ij	L^2 ij
Sb-Sn[12]	−7233.2	782.6	1840.9
Bi-Sn[13]	1359.4	−241.5	0
Bi-Sb[13]	2284	0	0

$$\Delta G^{Ex} = \frac{x_i x_k}{x_i + x_k}(A_{i-k}x_i + B_{i-k}x_k) + \frac{x_k x_j}{x_k + x_j}(A_{k-j}x_k + B_{k-j}x_j) + \frac{x_j x_i}{x_j + x_i}(A_{j-i}x_j + B_{j-i}x_i) + x_i x_k x_j(w_i x_i + w_k x_k + w_j x_j)$$
where (i,j,k)=(Sn,Bi,Sb) (7)

As excess free energy of mixing of the related three binary systems can be presented by the equation of the quasi-regular solution, eq.(7) presents the values in the ternary system as a function of each composition. Interaction parameters w of the ternary system in eq.(7) is calculated to give the least difference between the experimental values and eq.(7) by Newton method. One of the examples is shown at 900 K in **Fig.1**. In the figure data points correspond to the experimental values obtained in this study as described above and each curve to the calculated value. Interaction parameters are shown in **Table 2**, which can be used for the presentation of the excess free energy of mixing at any composition and temperature in the ternary system.

4. Model calculation from binary systems

There are several traditional models to represent the ternary thermodynamic properties based on three corresponding binary systems, which are classified into two categories according to Hillert:[6] symmetrical model (Kohler,[7] Muggianu[8]) and asymmetrical model (Toop,[9] Hillert[6]). Chou[10] provided a general solution model which breaks down the boundary between symmetrical and asymmetrical models. These models are applied to Ga-Sb-Bi liquid alloys by one of our groups.[11]

At first, we use the literature values of constituent three binary data[12,13] to get the values in ternary alloys by model calculations. For binary systems excess free energy of mixing is calculated in the Redlich-Kister polynomial form (eq.8) by data fitting.

$$\Delta G_M^{Ex} = x_i x_j \sum_{\nu=0}^{n}(x_i - x_j)^{\nu} L_{i,j}^{(\nu)}(T);\ L_{i,j}^{(\nu)}(T) = a_{i,j}^{(\nu)} + b_{i,j}^{(\nu)}T + c_{i,j}^{(\nu)}T^2 \quad (8)$$

The coefficients are shown in **Table 3**. From these data we can get the excess free energy of mixing in the ternary alloys from model calculations. The results at 900 K are shown in **Figs.2(a)-2(c)** for SbaBib-Sn (a:b = 0.25:0.75, 0.50:0.50 and 0.75:0.25) for the model calculations of Chou, Toop and Muggianu. Each model calculation gives little difference in the value of ΔG^{Ex}, but they can reproduce our experimental values only along the line of $Sb_{0.25}Bi_{0.75}$-Sn system.

Next, we use our experimental data for Bi-Sn and Sb-Sn systems and the same data for Bi-Sb system as shown in **Table 4**. Then, we get the results shown in **Figs.3(a)-3(c)**. Only Chou's model calculation is shown. In this case The discrepancy in the values between model calculation and experiment becomes bigger in $Sb_{0.25}Bi_{0.75}$-Sn system, but in the other two systems model calculations can reproduce the experimental data with little uncertainty limits.

5. CONCLUSION

Activities of tin in liquid Sn-Bi, Sn-Sn and Sn-Bi-Sb alloys were derived by emf measurement of galvanic cell with fused salts electrolyte in the temperature range of 700 to 1000 K in the whole composition range. Activity of tin at 900 K shows very small positive deviation

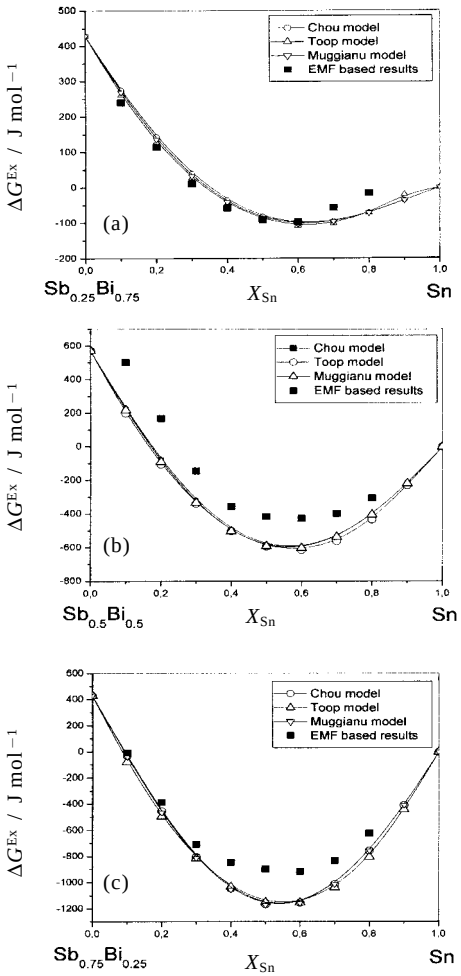

Fig.2 Model calculation of excess free energy of mixing in the ternary alloys at 900 K by using reference data. (a) $Sb_{0.25}Bi_{0.75}$-Sn. (b) $Sb_{0.50}Bi_{0.50}$-Sn. (c) $Sb_{0.75}Bi_{0.25}$-S.

from Raoult's law for Sn-Bi alloys and moderately negative deviation for Sn-Sb alloys. Activity of ternary alloys with the composition ratios of Sb/Bi＝1/3, 1/1 and 3/1 shows negative deviation and the deviation becomes larger with Sb content. Excess free energy of mixing is derived using Darken's method for Gibbs-Duhem equation and interaction parameters in the ternary alloys are obtained.

The experimental values in the excess free energy of mixing were compared with the model calculations based on the constituent three binary data at 900 K.

Table 4 Coefficients of Redlich-Kister polynomial form (this work at 900 K).

System *ij*	L^0 ij	L^1 ij	L^2 ij	L^3 ij
Sn-Sb	−6454.1	235.1809	753.1759	757.3503
Sn-Bi	1647.773	−305.011	184.4522	56.97726
Sb-Bi[13]	2284	0	0	0

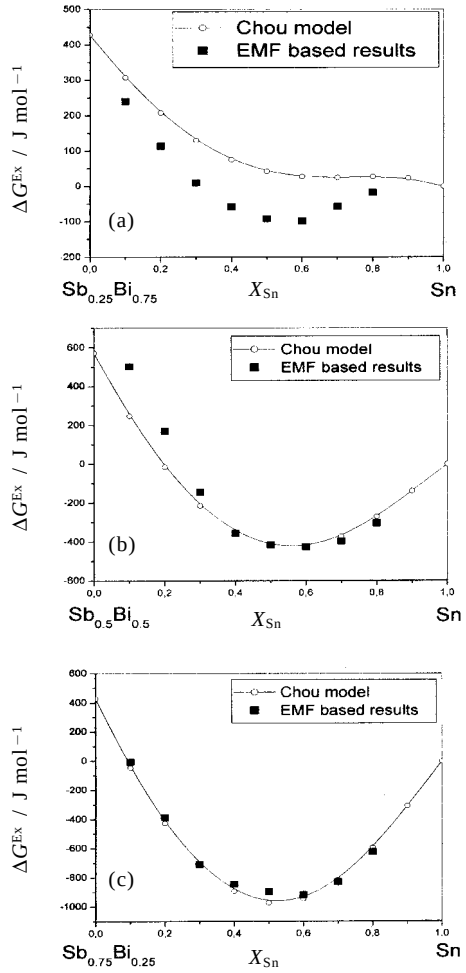

Fig.3 Model caluculation of the excess free energy of mixing in the ternary alloys at 900 K by using present data. (a) $Sb_{0.25}Bi_{0.75}$-Sn. (b) $Sb_{0.50}Bi_{0.50}$-Sn. (c) $Sb_{0.75}Bi_{0.25}$-Sn.

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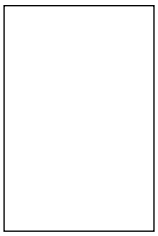
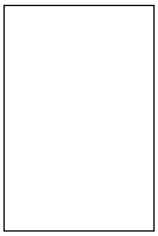
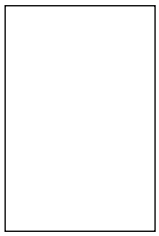


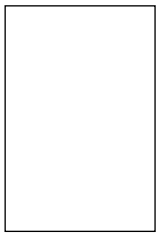
Iwao Katayama
Graduate School of Eng., Osaka Univ., TEL. 06-6879-7460, FAX. 06-6879-7522, e-mail: katayama@mat. eng. osaka-u.ac.jp
研究テーマ：材料熱力学，セラミックセンサー
趣味：卓球



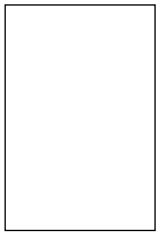
Dragana Živkovič
Technical Faculty Bor, Univ. of Belgrade, TEL.&FAX. +381-30 424 547, e-mail: dzivkovic@tf.bor.ac.yu
研究テーマ：Thermodynamics
趣味：Choir singing



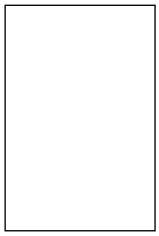
Dragan Manasijevic
Technical Faculty Bor, Univ. of Belgrade, TEL.&FAX. +381-30 424 547, e-mail: dmanasijevic@tf.bor.ac.yu
研究テーマ：Tehrmodynamics
趣味：Painting, Basketball



Toshihiro Tanaka
Graduate School of Eng., Osaka Univ., TEL. 06-6879-7504, FAX. 06-6879-7505, e-mail: tanaka@mat.eng.osaka-u.ac.jp
研究テーマ：材料熱力学，高温物性学，界面制御工学
趣味：キャンプ



Zivan Živkovič
Technical Faculty Bor, Univ. of Belgrade, TEL.&FAX. +381-30 424 547, e-mail: jmm@eunet.yu
研究テーマ：Metallurgy of non-ferrous metals
趣味：Wine making



Hiromi Yamashita
Graduate School of Eng., Osaka Univ., TEL. 06-6879-7457, FAX. 06-6879-7457, e-mail: yamashita@mat.eng.osaka-u.ac.jp
研究テーマ：触媒材料科学
趣味：旅行，スポーツ