Thermodynamic Properties of Liquid Ag-Au-Sn Alloys

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The thermodynamic properties of liquid Ag-Au-Sn alloys were studied with an electromotive force (EMF) method using the eutectic mixture of KCl/LiCl as a liquid electrolyte. Activities of Sn in the liquid alloys were measured at three cross-sections with constant molar ratios of Ag:Au = 2:1, 1:1, and 1:2 with tin in the concentration range between 20 at.% and 90 at.% from the liquidus of the samples up to 1030 K. The integral Gibbs energies at 973 K and the integral enthalpies were calculated by Gibbs–Duhem integration.

Key words: Liquid alloys, Ag-Au-Sn, EMF, thermodynamic properties

INTRODUCTION

The aim of this investigation is to determine thermodynamic properties of materials that could be used as replacements for Pb solders for high-temperature applications. The study of lead-free systems is essential, as lead is harmful to the environment and health. In order to develop these new materials, information on the phase diagrams, the phase equilibria, and the melting behavior are necessary. Other properties such as the melting temperature, the solidification path, and the surface properties also need to be determined. In Pb–Sn solders the effect of fatigue is linked to the lead-rich phase,¹ which tends to embrittle with thermomechanical variation in stress, leading to cracking. It is expected that replacements for lead will result in better mechanical behavior and stability. For high-melting solders there are some materials available such as Ag–Sn, Au–Sn, and Sn–Ag–Cu solders. Many investigations have been done on binary Ag–Sn and Au–Sn systems.^{2–7} Eutectic 80Au–20Sn (wt.%) solders are widely used for high-temperature applications for optoelectronics such as laser diodes and photodiodes because of their good creeping properties and high tensile strength. They are also used in flip-chip technology.⁸ The 80Au–20Sn composition shows a low tendency to create oxide layers, enabling flux-free soldering with the advantage of lack of flux contamination on electronic devices. Tin-rich

eutectic solder is not used in joining technology, as it would result in embrittlement of the solder connection.⁹ Due to its high yield stress, eutectic 80Au–20Sn (wt.%) solder is partially able to compensate thermomechanical stress. A further possibility to minimize tension is to use other flux-free solders with low yield stress such as Ag–Sn. Hence Ag may be added to Au–Sn solders to improve their thermomechanical behavior and reduce cost. Properties such as melting point and electrical conductivity will not be seriously affected, as Ag has good conductivity and its chemical properties are close to those of Au. Earlier works have also considered the Ag–Au–Sn system. Calorimetric measurements have been carried out by Li et al.¹⁰ Some information on thermal analysis was given by Evans and Prince.¹¹ Thermodynamic optimization using the CALPHAD method has been done by Wang et al.¹² An experimental investigation and thermodynamic assessment of phase equilibria in the Ag–Au–Sn system has been carried out by Gao et al.¹³

In this work the thermodynamic properties of the ternary Ag–Au–Sn system were measured at three cross-sections at Ag:Au = 2:1, 1:1, and 1:2 with an EMF method. The concentration of tin was in the range between 20 at.% and 90 at.%.

EXPERIMENTAL PROCEDURES

Ternary alloys were prepared from high-purity metals (tin ingots, purity 99.999%; gold sheet, purity 99.95%; silver shot, purity 99.9%). Tin was a product of Johnson Matthey GmbH, Germany, whereas gold and silver were products of Ögussa,

(Received October 7, 2009; accepted May 11, 2010; published online June 12, 2010)

Austria. To remove impurities from the silver surface, silver shot was heated for 10 min at 1083 K in a carbon crucible under vacuum. The metals were sealed into quartz capsules under vacuum and melted together at 1073 K. After 1 week, the alloys were quenched in ice water.

Before EMF measurements, the liquidus of the alloys was determined by differential thermal analysis so that the temperature range for EMF measurements could be determined. Thermal analyses were performed on a 404S DTA instrument (Netzsch, Germany), equipped with type S thermocouples (Pt/Pt-10 wt.% Rh). Samples weighing 200 mg to 300 mg were used for the DTA measurements. The DTA instrument was calibrated using high-purity metals Au, Sb, and Sn as standards to establish internal calibration. Evacuated, sealed quartz tubes were used for the measurements to avoid oxidation of the alloys. Two heating and cooling curves were recorded with a heating and cooling rate of 5 K/min. The average values of the melting points obtained from the two heating curves were taken and are given in Table I.

An EMF method with liquid electrolyte was used to determine the activity of tin in the liquid alloys. The electrolyte consisted of the eutectic mixture of

KCl (purity 99.5%) and LiCl (purity 99%) with addition of 0.5 at.% SnCl₂ (purity 98%). Cleaning of the electrolyte and assembly of the EMF cell are described in Ref. 14.

For the EMF measurements, the following cell arrangement was used:

There are several conditions that must be satisfied to achieve accurate EMF measurements. The charge of the electropositive ion Me^{n+} has to be known exactly, and Me^{n+} should be the only charge transfer through the electrolyte and the only reaction on the surface of the electrodes. The electrical conduction through the electrolyte should be purely ionic. No reaction of the electrode and the electrolyte with the apparatus should occur. Concentration changes of the electrodes and the electrolyte during the measurement must be taken into account. During the EMF measurement, no electricity should pass through the cell, which can be achieved by using a voltmeter with an input impedance of more than 10^{10} Ohm. At higher temperatures, for KCl-LiCl at ~ 1123 K, the electrolyte can exhibit some electrical conductivity, so this should be the upper temperature limit for the EMF measurement.

Under reversible conditions the Gibbs free energy change for the reaction is given by

$$\Delta \overline{G}_{\text{Sn}} = -z \cdot F \cdot E = RT \cdot \ln a_{\text{Sn}}, \quad (1)$$

where z is the number of exchanged electrons, F is the Faraday constant (96,485 C/mol), E is the electromotive force in volts, R is the universal gas constant (8.3145 J/K/mol), T is the temperature in Kelvin, and a_{Sn} is the thermodynamic activity of tin in the ternary alloy. As reference electrode, pure tin was used.

Plots of EMF versus temperature were least-square-fitted, and the EMF was expressed by the equation

$$E [\text{mV}] = a [\text{mV}] + b [\text{mV/K}] \cdot T [\text{K}], \quad (2)$$

where a is the ordinate intercept and b is the slope. The results are given in Table II.

Table I. Liquidus temperature of the samples at the three cross-sections Ag:Au = 2:1, 1:1, and 1:2

Ag:Au 2:1 Cross-section		Ag:Au 1:1 Cross-section		Ag:Au 1:2 Cross-section	
x, Sn	Liquidus T [K]	x, Sn	Liquidus T [K]	x, Sn	Liquidus T [K]
0.2	975	0.2	967	0.2	948
0.3	831	0.3	793	0.3	744
0.4	751	0.4	701	0.4	637
0.5	700	0.5	666	0.5	622
0.6	677	0.6	620	0.6	586
0.7	648	0.7	603	0.7	559
0.8	581	0.8	571	0.8	525
0.9	514	0.9	490	0.9	485

Table II. Experimentally determined EMF data

Ag:Au 2:1 Cross-section		Ag:Au 1:1 Cross-section		Ag:Au 1:2 Cross-section	
x, Sn	EMF [mV]	x, Sn	EMF [mV]	x, Sn	EMF [mV]
0.2	$79.34 + 0.0602 \times T(\pm 0.05)$	0.2	$107.08 + 0.0552 \times T(\pm 0.49)$	0.2	$126.76 + 0.0436 \times T(\pm 0.49)$
0.3	$16.53 + 0.0685 \times T(\pm 0.68)$	0.3	$17.05 + 0.0837 \times T(\pm 0.74)$	0.3	$41.65 + 0.0760 \times T(\pm 0.59)$
0.4	$-12.74 + 0.0728 \times T(\pm 0.21)$	0.4	$6.68 + 0.0606 \times T(\pm 0.26)$	0.4	$12.78 + 0.0649 \times T(\pm 0.49)$
0.5	$-5.67 + 0.0421 \times T(\pm 0.05)$	0.5	$-2.29 + 0.0509 \times T(\pm 0.04)$	0.5	$7.71 + 0.0429 \times T(\pm 0.81)$
0.6	$-9.95 + 0.0390 \times T(\pm 0.12)$	0.6	$-4.11 + 0.0372 \times T(\pm 0.03)$	0.6	$4.52 + 0.0280 \times T(\pm 0.78)$
0.7	$-7.08 + 0.0253 \times T(\pm 0.29)$	0.7	$0.83 + 0.0171 \times T(\pm 0.1)$	0.7	$-1.11 + 0.0197 \times T(\pm 0.26)$
0.8	$-0.81 + 0.0103 \times T(\pm 0.02)$	0.8	$-0.42 + 0.0113 \times T(\pm 0.05)$	0.8	$0.26 + 0.0071 \times T(\pm 0.56)$
0.9	$-1.25 + 0.0056 \times T(\pm 0.08)$	0.9	$-0.05 + 0.0046 \times T(\pm 0.03)$	0.9	$-1.54 + 0.0041 \times T(\pm 0.04)$

From the temperature dependence of E , the partial molar enthalpy $\Delta\bar{H}_{\text{Sn}}$ and the partial molar entropy $\Delta\bar{S}_{\text{Sn}}$ were derived using the following equations:

$$\Delta\bar{H}_{\text{Sn}} = z \cdot F \left[E - T \left(\frac{\partial E}{\partial T} \right) \right]_{x,p} = -z \cdot a \cdot F, \quad (3)$$

$$\Delta\bar{S}_{\text{Sn}} = z \cdot F \left(\frac{\partial E}{\partial T} \right)_{x,p} = z \cdot b \cdot F. \quad (4)$$

The integral excess Gibbs free energy and the integral enthalpy of mixing were determined by adopting the Gibbs–Duhem equation given by Elliot and Chipman¹⁵ as:

$$\Delta G^{\text{xs}} = (1 - X_{\text{Sn}}) \left[\Delta G_{\text{Sn}=0}^{\text{xs}} + \int_0^{X_{\text{Sn}}} \frac{\Delta \bar{G}_{\text{Sn}}^{\text{xs}}}{(1 - X_{\text{Sn}})^2} dX_{\text{Sn}} \right]_{X_{\text{Ag}}/X_{\text{Au}}}, \quad (5)$$

$$\Delta H = (1 - X_{\text{Sn}}) \left[\Delta H_{\text{Sn}=0} + \int_0^{X_{\text{Sn}}} \frac{\Delta \bar{H}_{\text{Sn}}}{(1 - X_{\text{Sn}})^2} dX_{\text{Sn}} \right]_{X_{\text{Ag}}/X_{\text{Au}}}. \quad (6)$$

$\Delta G_{\text{Sn}=0}^{\text{xs}}$ and $\Delta H_{\text{Sn}=0}$ represent the limiting excess Gibbs energy and enthalpy values of the binary Ag–Au system. X_{Sn} is the substance amount fraction of tin in the alloy.

For the integration of the excess Gibbs free energy in the ternary system, ΔG^{xs} values of the Ag–Au system were taken from Hultgren et al.¹⁶ and calculated to the temperature used for the measurements by combining the enthalpy ΔH with the excess entropy term $T \cdot \Delta S^{\text{xs}}$, assuming that ΔH and ΔS^{xs} are constant. The same procedure was carried out to determine the values for the Gibbs free energy of the Ag–Au system by combining the enthalpy ΔH with the entropy term $T \cdot \Delta S$. The interaction parameters for the Gibbs free energy and the Gibbs free excess energy were then calculated by using a Redlich–Kister fit. The interaction parameters for the enthalpy were calculated from the experimental data determined by Fitzner et al.¹⁷

The excess Gibbs free energies for the systems Ag–Sn and Au–Sn were calculated from the EMF of the measurements of Kameda which covered the temperature range of 686 K to 983 K for the Ag–Sn system¹⁸ and the temperature range of 944 K to 1256 K for the Au–Sn system.¹⁹ The interaction parameters for the Gibbs free energy and the Gibbs free excess energy were calculated by using a Redlich–Kister fit. For the calculation of the interaction parameters for the enthalpy for the Au–Sn

system the data from Hultgren et al.¹⁶ were taken, and for the Ag–Sn system the interaction parameters were determined from the work of Flandorfer et al.²⁰

For the integration of the enthalpy of mixing for the ternary system the limiting enthalpy values were calculated from the experimental data of the calorimetric measurements of the Ag–Au system obtained by Fitzner et al.¹⁷

RESULTS AND DISCUSSION

Our investigation started from the binary Ag–Au system by adding Sn. The activity of Sn was measured along three cross-sections. The T versus EMF curves at each composition exhibited straight lines, expressed by Eq. 2. From the EMF data, the activity of tin, the partial Gibbs free energy, and the partial molar enthalpies and entropies were calculated and are given in Table III. The integrated thermodynamic quantities are listed in Table IV.

The activities of Sn in the ternary Ag–Au–Sn system and in the Ag–Sn¹⁰ and Au–Sn system¹¹ at 973 K are shown in Fig. 1. In the Ag–Sn system, the activities show a negative deviation from Raoult's law up to ~37 at.% Sn, after which it becomes positive. At the Ag:Au 2:1 cross-section, the activity of Sn is less than in the Ag–Sn system. It was observed that the value for the activity at 50% Sn is

Table III. Activities and partial thermodynamic properties of the Ag:Au = 2:1, 1:1, and 1:2 cross-sections at 973 K

x, Sn	a	$\Delta\bar{G} [\text{J/mol}]$	$\Delta\bar{H} [\text{J/mol}]$	$\Delta\bar{S} [\text{J/mol K}]$
Ag:Au 2:1 cross-section				
0.2	0.041	−26,607	−15,310	11.61
0.3	0.1394	−15,949	−3190	13.22
0.4	0.2512	−11,188	2458	14.05
0.5	0.4308	−6804	1094	8.12
0.6	0.5098	−5455	1921	7.53
0.7	0.6593	−3265	1367	4.88
0.8	0.804	−1766	156	1.99
0.9	0.9026	−832	241	1.08
Ag:Au 1:1 cross-section				
0.2	0.0217	−30,993	−20,664	10.65
0.3	0.0922	−19,288	−3290	16.15
0.4	0.2097	−12,639	−1289	11.69
0.5	0.3242	−9114	442	9.82
0.6	0.4655	−6190	794	7.18
0.7	0.6546	−3429	−160	3.3
0.8	0.777	−2042	80	2.18
0.9	0.8991	−861	9	0.89
Ag:Au 1:2 cross-section				
0.2	0.0177	−32,649	−24,461	8.41
0.3	0.0631	−22,367	−8037	14.67
0.4	0.1636	−14,662	−2466	12.52
0.5	0.3068	−9569	−1488	8.28
0.6	0.4654	−6187	−872	5.4
0.7	0.6452	−3543	214	3.8
0.8	0.8283	−1523	−51	1.37
0.9	0.9435	−471	297	0.79

Table IV. Calculated integral thermodynamic quantities at the Ag:Au = 2:1, 1:1, and 1:2 cross-sections at 973 K

x, Sn	ΔG [J/mol]	ΔG^{xs} [J/mol]	ΔH [J/mol]
Ag:Au 2:1 cross-section			
0	-6849	-1700	-3862
0.2	-13,205	-5038	-8526
0.3	-14,101	-5570	-8787
0.4	-13,990	-5456	-7711
0.5	-13,111	-4928	-6411
0.6	-11,708	-4204	-5158
0.7	-9827	-3340	-3886
0.8	-7337	-2259	-2584
0.9	-4259	-1114	-1276
Ag:Au 1:1 cross-section			
0	-7408	-1800	-4323
0.2	-14,876	-6050	-9840
0.3	-16,082	-7200	-10,193
0.4	-16,013	-7204	-8959
0.5	-15,128	-6717	-7528
0.6	-13,599	-5911	-5988
0.7	-11,341	-4717	-4408
0.8	-8434	-3264	-2870
0.9	-4856	-1665	-1420
Ag:Au 1:2 cross-section			
0	-6672	-1520	-3766
0.2	-15,008	-6840	-11,606
0.3	-16,507	-8002	-12,032
0.4	-16,735	-8201	-11,181
0.5	-15,916	-7733	-9697
0.6	-14,265	-6761	-7942
0.7	-11,859	-5373	-5987
0.8	-8662	-3584	-3930
0.9	-4711	-1566	-1887

Fig. 1. Activity curves of Sn for the three cross-sections Ag:Au = 2:1, 1:1, and 1:2 at 973 K, for the binary Ag-Sn at 973 K¹⁸ and Au-Sn at 973 K¹⁹. **Fig. 2. Integral excess Gibbs free energy for the Ag:Au 2:1, 1:1, and 1:2 cross-sections at 973 K and for the binary Ag-Sn at 973 K¹⁸ and Au-Sn at 973 K¹⁹.**

more positive than expected. The sample of Ag:Au 2:1 and 50 at.% Sn was measured twice but gave nearly identical results. We have no explanation for the more positive value of the activity of Sn at this composition. At the Ag:Au 1:1 cross-section, the negative deviation from Raoult's law increases. This is also observed for the activities at the Ag:Au 1:2 cross-section from 20 at.% to 70 at.% Sn. However, at 80 at.% and 90 at.% Sn, positive deviation from Raoult's law was observed.

The excess Gibbs free energy values become more negative from the Ag-rich side (Ag:Au 2:1) to the Au-rich side (Ag:Au 1:2). This agrees with the results for the binaries Ag-Sn and Au-Sn taken from Kameda.^{18,19} The curves are shown in Fig. 2. The trend for the Gibbs energy curves is the same (Fig. 3). It has been observed that the minimum ΔG and ΔG^{xs} is shifted to higher tin content from the Ag-rich to the Au-rich side.

The integrated enthalpies of mixing are shown in Fig. 4, compared with data from Li¹⁰ obtained by calorimetric measurements. The raw data of the calorimetric measurements were used to calculate via Redlich-Kister-Muggianu polynomials the enthalpy values for the cross-sections that were measured with the EMF method. The minimum ΔH is also shifted to higher tin content from the Ag-rich to the Au-rich side. As shown in Fig. 4, the ΔH values determined with the EMF method are in good agreement with the data obtained by calorimetric measurements.

Fig. 3. Integral Gibbs free energy curves ΔG (kJ/mol) for the Ag:Au 2:1, 1:1, and 1:2 cross-sections at 973 K.

Fig. 4. Integral enthalpy of mixing for the Ag:Au 2:1, 1:1, and 1:2 cross-sections at 973 K.

The iso-excess Gibbs free energy curves of the ternary system are plotted in Fig. 5, where the minimum is located at ~56 at.% Au and 44 at.% Sn. For the Gibbs free energy the minimum is also located at ~56 at.% Au and 44 at.% Sn. The iso-Gibbs free energy curves are plotted in Fig. 6. The plotted iso-enthalpy curves are shown in Fig. 7. All

Fig. 5. Iso-excess Gibbs free energy curves ΔG^{xs} (kJ/mol) at 973 K for the ternary Ag-Au-Sn system.

Fig. 6. Iso-Gibbs free energy curves ΔG (kJ/mol) at 973 K for the ternary Ag-Au-Sn system.

iso-curves shown herein were calculated using Redlich-Kister-Muggianu polynomials.

CONCLUSIONS

The thermodynamic properties of the liquid ternary Ag-Au-Sn alloys were measured and compared with previous data obtained from calorimetric investigations. From the results of the EMF measurements the change of the thermodynamic properties of the binary Ag-Au system with the addition of Sn is described. The minimum of ΔG , ΔG^{xs} , and ΔH is shifted to higher tin content from the Ag-rich to the Au-rich side.

Fig. 7. Iso-enthalpy curves ΔH (kJ/mol) at 973 K for the ternary Ag-Au-Sn system.

We hope that our data will serve as an input for the estimation of some thermodynamic properties of higher-order systems. Furthermore, they will help to support the calculation of the ternary phase diagram.

ACKNOWLEDGEMENT

Financial support by the Austrian Science Foundation (FWF) under Grant Nos. P19461-N19 and P20488-N19 is gratefully acknowledged.

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REFERENCES

1. J. Hwang, *Solder Materials*, In: *SMT*, vol. 14 (2000).
2. D.G. Ivey, *Micron* 29, 281 (1998).
3. Y.T. Lai and C.Y. Liu, *J. Electron. Mater.* 35, 353 (2006).
4. T. Takenaka, S. Kano, M. Kajihara, N. Kurokawa, and K. Sakamoto, *Mater. Trans.* 46, 1825 (2005).
5. M.T. Sheen, C.M. Chang, H.C. Teng, J.H. Kuang, K.C. Hsieh, and W.H. Cheng, *J. Electron. Mater.* 31, 895 (2002).
6. J.Y. Tsai, C.W. Chang, Y.C. Shieh, Y.C. Hu, and C.R. Kao, *J. Electron. Mater.* 34, 182 (2005).
7. J.H. Park, J.H. Lee, Y.H. Lee, and Y.S. Kim, *J. Electron. Mater.* 31, 1175 (2002).
8. J. Kloeser, F. Bechthold, and H. Reichl, *IEEE CPMT*, 19A, (1996).
9. W. Scheel, *Optische Aufbau- und Verbindungstechnik in der elektronischen Baugruppenfertigung* (Templin: Verlag Markus A. Detert, 2002).
10. Z. Li, M. Dallegri, and S. Knott, *J. Alloy. Compd.* 453, 442 (2008).
11. D.S. Evans and A. Prince, *Met. Sci.* 8, 286 (1974).
12. J. Wang, H.S. Liu, L.B. Liu, and Z.P. Jin, *CALPHAD* 31, 545 (2007).
13. F. Gao, C.P. Wang, Y.Y. Li, X.J. Liu, Y. Takaku, I. Ohnuma, and K. Ishida, *J. Electron. Mater.* 38, 2096 (2009).
14. A. Mikula, *Metall. Trans. B22*, 601 (1992).
15. J.F. Elliot and J. Chipman, *J. Am. Chem. Soc.* 73, 2682 (1951).
16. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (Metals Park, Ohio: ASM, 1973).
17. K. Fitzner, Q. Guo, J. Wang, and O.J. Kleppa, *J. Alloy. Compd.* 291, 190 (1999).
18. K. Kameda, *J. Jpn. I. Met.*, 28, 542 (1987).
19. K. Kameda, S. Sakairi, and Y. Yoshida, *J. Jpn. Inst. Met.* 41, 950 (1977).
20. H. Flandorfer, C. Luef, and U. Saeed, *J. Non-Cryst. Solids* 354, 2953 (2008).