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The Effect of Sb Addition on Sn-Based Alloys for High-Temperature Lead-Free Solders: an Investigation of the Ag-Sb-Sn System

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Today there is renewed interest in alloys belonging to the Sb-Sn-X (X = Cu, Ag, Bi) ternary systems and their phase equilibria, phase transformations, and thermodynamic properties because of their possible use as high-temperature lead-free solders in the electronics industry. The integral mixing enthalpy of Ag-Sb-Sn liquid alloys has been measured along five different sections ($Ag_{0.25}Sn_{0.75}$, $Ag_{0.50}Sn_{0.50}$, $Sb_{0.30}Sn_{0.70}$, $Sb_{0.50}Sn_{0.50}$, and $Sb_{0.70}Sn_{0.30}$) at 530°C, 600°C, and 630°C, using a high-temperature Calvet calorimeter by dropping pure elements (Ag or Sb) in the binary alloy liquid bath. The ternary extrapolation models of Muggianu and Toop were used to calculate the integral enthalpy of mixing and to compare measured and extrapolated values. Selected ternary alloys have been prepared for thermal investigation by using a differential scanning calorimeter at different heating/cooling rates in order to clarify the temperature of the invariant reactions and the crystallization path.

Key words: Ag-Sb-Sn system, enthalpy of mixing, lead-free solder, calorimetry

INTRODUCTION

In recent years, the electronics industry has been involved in the development of a new generation of solder interconnects to replace Pb-Sn with Pb-free solder alloys. This is due to legal, environmental, and technological factors which call for alternative lead-free soldering materials. Among the huge number of systems proposed, many of the most promising lead-free alloys are tin-based systems.[1] Sn-Ag-Cu system solders are currently being considered to be the choice for replacing 63 wt.%Sn-37 wt.%Pb eutectic alloy, whose melting point is 183°C. However, high-temperature Pb-Sn solder with 90 wt.% to 95 wt.% Pb (melting temperature around 280°C), which are used for flip-chip joints, also need to be replaced, and Ag-Sb-Sn alloys can be one of the promising series of high-temperature lead-free solders. As well as an appropriate melting range, Ag-Sb-Sn alloys also show good thermofatigue resistance.[2] Commercial solders based on the Ag-Sb-Sn system are currently available, e.g., CASTIN (0.8Cu-0.5Sb-2.5Ag-96.2Sn, wt.%) and J-alloy (Sn-25Ag-10Sb, wt.%). Knowledge of the thermodynamic properties of a solder system is important for understanding the soldering process as well as the final reliability of the joints. However, literature data for the Ag-Sb-Sn system are scarce. The aim of the current work is to measure the mixing enthalpy of Ag-Sb-Sn liquid alloys and to clarify the phase relations in the Ag-Sb-Sn system on the basis of some key selected alloy compositions.

LITERATURE REVIEW

Some thermodynamic data are available in the literature for the Ag-Sb-Sn ternary system and its

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constituent binary systems. The thermochemical data concerning the mixing enthalpy of liquid alloys obtained by calorimetric measurements as well as the phase diagram literature data about the ternary system are reviewed here. Some available information on activity is also reported.

Ag-Sb System

Calorimetric measurements were performed by Kawakami,[3] who obtained the Ag-Sb mixing enthalpies at 1050°C in the $0.18 < x_{Sb} < 0.79$ composition range, and by Ehrlich[4] at 975°C for the $0.075 < x_{Sb} < 0.90$ composition range. These results were reported by Hultgren.[5] Castanet[6] carried out experiments for the whole composition range at 677°C, 827°C, and 1027°C and observed a strong temperature dependence of the enthalpy of mixing. Predel and Emam[7] studied calorimetrically the thermodynamic properties of the liquid alloys at 1000°C over the entire composition range. Electromotive force (EMF) measurements were carried out by Vechorv,[8] Nozaki,[9] and Okajima and Sakao[10] at different temperatures, and vapor pressure measurements were carried out by Hino.[11]

Ag-Sn System

Kleppa[12] measured the mixing enthalpy of Ag-Sn alloys in the composition range $0.64 < x_{Sn} < 0.99$ at 450°C using a dissolution calorimeter with a liquid tin bath. Direct reaction calorimetry has been employed by different scientists to measure the mixing enthalpy for the Ag-Sn system: Wittig and Gehring[13] in the composition range $0.072 < x_{Sn} < 0.931$ at 975°C, Castanet[14] in the range $0.05 < x_{Sn} < 0.95$ at 1000°C, and Rakotomavo[15] in the range $0.02 < x_{Sn} < 0.934$ at 1100°C. Recently, Flandorfer[16] carried out calorimetric measurements at five temperatures in the interval of 500°C to 1250°C, mainly in the Sn-rich side, and at 1250°C for the Ag-rich side. The data published up to 1973 have been assessed by Hultgren.[5]

The activity of Ag in liquid alloys has been determined by Yamaji[17] and Okajima[10] by an EMF method. The activity of Sn in liquid Ag-Sn alloys has been extensively measured at different temperatures by Frantik,[18] Yanko,[19] Nozaki,[9] Laurie,[20] Elliot,[21] Chowdhury,[22] Kubaschewski,[23] Yamaji,[17] Okajima,[10] Fahri,[24] Seetharaman,[25] Iwase,[26] and Kameda.[27]

Sb-Sn System

The mixing enthalpy of liquid Sb-Sn alloys has been measured by Kawakami,[3] Witting and Gehring,[28] Yasawa,[29] Sommer,[30] and Azzaoui[31] at various temperatures. Dissolution enthalpy of solid Sb in liquid Sn at 450°C was measured by Kleppa[32] by Sn solution calorimetry. EMF measurement has been carried out and the chemical potential of the liquid phase was determined by Frantik and McDonald,[33] Yanko,[34] Hao,[35] Itho,[36] and Vassiliev.[37,38]

Ag-Sb-Sn System

Gather[39] measured the mixing enthalpy of the Ag-Sb-Sn ternary system along four sections at 951°C and one section at 980°C using a heat flow calorimeter. Onderka[40] performed electrochemical studies of the thermodynamic properties of ternary Ag-Sb-Sn alloys by an EMF method along three cross-sections with a constant Ag/Sb ratio equal to 1/3, 1/1, and 3/1. The Sn compositions were from 10 at.% up to 80 at.% Sn at 10 at.% intervals, and the measurements were carried out in the temperature range from 973 K to 1223 K.

Literature data relating to the invariant reactions detected in the Ag-Sb-Sn system are summarized in Table I, together with the experimental results determined in this work. Table II summarizes the binary invariant reactions relevant to the Ag-Sb-Sn ternary system.

Masson and Kirkpatrick[2] as well as Chen[42] determined the liquidus surface and the invariant reactions of the Ag-Sb-Sn system using differential thermal analysis (DTA) combined with metallographic analysis. Cheng and Lee[43] determined the Ag-Sb-Sn isothermal section at room temperature in the Ag-rich corner by x-ray diffraction (XRD) and metallographic analyses. The isothermal sections at 220°C and 250°C were reported, respectively, by Oberndorff[44] and Chen[42]; Lin[45] investigated the isothermal sections at 400°C and 150°C and Zheng[46] reported the room temperature isothermal section. Oh[47] critically assessed all available experimental data and achieved a satisfactory representation of the literature data. However, no experimental information was available for the invariant reaction for which a temperature value of 329°C, higher than p_6 (321°C), was calculated, and a P-type equilibrium was suggested. Schmid-Fetzer[48] reviewed the literature relating to this system and proposed the solidification diagram, mainly on the basis of the work of Oh. However, he pointed out that the invariant reaction P_1: $L + \beta + \varepsilon \leftrightarrow Sn_3Sb_2$ reported by Oh[47] is not correct, since the composition of Sn_3Sb_2 is not located in the tie-triangle formed by the other three phases. Therefore, Schmid-Fetzer modified the invariant reaction to U-type (U_2: $L + \beta \leftrightarrow \varepsilon + Sn_3Sb_2$). Recently, Chen[42] performed differential scanning calorimetry (DSC) analysis using a scanning rate of 10°C/min and proposed a temperature of 314°C for this reaction. Moreover, in a previous paper,[49] the same authors stated that the Sn_3Sb_2 phase is stable down to room temperature, while during a critical reinvestigation on Sb-Sn performed by us,[50] we proved the decomposition of this phase, in agreement with Predel's version.[51] The more recent assessment of the Ag-Sb-Sn system made by Gierlotka[52] was based on Chen's experimental results,[42,49] and therefore the phase relations should be revised.

EXPERIMENTAL PROCEDURES

The starting materials were Ag (Johnson-Matthey Ltd., 99.99%), Sn (Newmet koch, 99.999%),

Table I. Invariant reactions detected in the Ag-Sb-Sn ternary system

Type of Reaction	Invariant Reaction	Temperature (°C)		Reference
		Experimental	Calculated	
U_1	$L + (Sb) \leftrightarrow \varepsilon + \beta$		375	47
P_1	$L + \beta + \varepsilon \leftrightarrow Sn_3Sb_2$		329	
U_2	$L + Sn_3Sb_2 \leftrightarrow \varepsilon + (Sn)$		232	
U_1	$L + (Sb) \leftrightarrow \varepsilon + \beta$	379		42
U_2	$L + \beta \leftrightarrow \varepsilon + Sn_3Sb_2$	314		
U_3	$L + Sn_3Sb_2 \leftrightarrow \varepsilon + (Sn)$	233		
U_1	$L + (Sb) \leftrightarrow \varepsilon + \beta$	375		This work
U_2	$L + \beta \leftrightarrow \varepsilon + Sn_3Sb_2$	308		
U_3	$L + Sn_3Sb_2 \leftrightarrow \varepsilon + (Sn)$	229		

Table II. Binary invariant reactions relevant to the Ag-Sb-Sn ternary system

Binary System	Type of Reaction	Invariant Reaction	*T* (°C)	Reference
Ag-Sb	p_2	$L + (Ag) \leftrightarrow \zeta$	702.5	41
	p_3	$L + \zeta \leftrightarrow \varepsilon$	558	
	e_1	$L \leftrightarrow \varepsilon + (Sb)$	485	
Ag-Sn	p_1	$L + (Ag) \leftrightarrow \zeta$	724	41
	p_4	$L + \zeta \leftrightarrow \varepsilon$	480	
	e_3	$L \leftrightarrow \varepsilon + (Sn)$	221	
Sb-Sn	p_5	$L + (Sb) \leftrightarrow \beta$	421	50
	p_6	$L + \beta \leftrightarrow Sn_3Sb_2$	321	
	p_7	$L + Sn_3Sb_2 \leftrightarrow (Sn)$	244	
	e_2	$Sn_3Sb_2 \leftrightarrow \beta + (Sn)$	243	

and Sb (Newmet koch, 99.999%). Ag pieces were cleaned with diluted HCl and then heated in a quartz tube under vacuum at 700°C for 30 min to remove impurities from the surface; the surfaces of Sn pieces were mechanically cleaned.

The experiments were performed using a high-temperature Calvet-type calorimeter whose details have been described elsewhere.[53] In addition to the previous setup, the Calvet calorimeter was equipped with an automatic sample introducer, which is located in a gas-tight cylinder block and consists of a stepper motor which turns around two discs carrying 15 small crucibles each. Up to 30 samples can therefore be added to the bath in the course of one measurement. The stepper motor was controlled by homemade software (CALMAA) developed in the LabView® environment, which was also used for signal acquisition. The furnace was controlled by an automatic device in order to maintain the temperature of the apparatus constant in a range of ±0.5 K. The error range of the integral mixing enthalpies measured in this work was estimated as ±150 J mol^{-1} (see the "Experimental Results and Discussion" section).

The liquid bath of binary alloy (Ag-Sn or Sb-Sn) was prepared by placing weighed pure metals in a graphite crucible which had been inserted into the calorimetric cell maintained at the selected working temperature; the equilibrium state and a stable baseline were obtained after 6 h. Pieces of the pure metal (Ag or Sb) were dropped into the bath from room temperature. After each series, five pieces of NIST (National Institute of Standards and Technology, Gaithersburg, MD) standard Al_2O_3 were dropped in order to perform calibration. The solvent bath contained around 1.5 g of material, and an interval of 70 min was employed for each drop to ensure complete dissolution. At the beginning of every measurement, the reaction cell as well as the automatic dropping unit were repeatedly flushed with high-purity Ar, and an Ar flow (around 2 L/h) was applied throughout the entire measurement.

The calorimetric experiments were performed along five composition sections of the Ag-Sb-Sn system with a total number of 18 measurements. The starting compositions of the liquid bath were $Ag_{0.25}Sn_{0.75}$, $Ag_{0.50}Sn_{0.50}$, $Sb_{0.30}Sn_{0.70}$, $Sb_{0.50}Sn_{0.50}$, and $Sb_{0.70}Sn_{0.30}$, and the third element was added as the dropped element. The five sections are indicated as sections A–E below. The experiments were performed at three different temperatures: 530°C, 600°C, and 630°C.

The total mass of the samples together with that of the crucibles was checked before and after the measurements; weight loss was found to be negligible.

Table III. Partial and integral enthalpies of mixing of liquid Ag-Sb-Sn alloys at 530°C (reference state: pure liquid components)

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
Section B ($Sb_{0.50}Sn_{0.50}$) first run, i = Ag, starting amount: n_{Sn} = 6.2076 mmol, n_{Sb} = 6.2062 mmol							
0.0000	0.5000	0.0000	–	–	−1423.78	0.0000	–
0.0173	0.4936	0.0128	5.45	34,003	−1284	0.0064	9557
0.0178	0.4872	0.0255	5.30	32,093	−1168	0.0191	7647
0.0193	0.4804	0.0390	5.66	31,638	−1052	0.0323	7192
0.0194	0.4738	0.0522	5.60	31,160	−946	0.0456	6714
0.0196	0.4673	0.0652	5.53	30,458	−850	0.0587	6012
0.0223	0.4602	0.0795	6.58	31,847	−724	0.0724	7401
0.0258	0.4522	0.0956	7.21	30,136	−612	0.0876	5690
0.0261	0.4443	0.1112	7.36	30,404	−498	0.1034	5958
0.0265	0.4366	0.1266	6.54	26,627	−452	0.1189	2181
0.0272	0.4290	0.1418	7.21	28,574	−372	0.1342	4128
0.0273	0.4217	0.1566	7.14	28,196	−301	0.1492	3750
0.0300	0.4138	0.1722	7.71	27,736	−235	0.1644	3291
0.0319	0.4058	0.1882	8.22	27,805	−165	0.1802	3359
0.0323	0.3980	0.2038	8.16	27,263	−108	0.1960	2818
0.0368	0.3895	0.2209	8.93	26,170	−69	0.2123	1724
0.0391	0.3809	0.2382	9.04	24,953	−56	0.2295	507
0.0397	0.3724	0.2550	9.16	24,878	−45	0.2466	433
0.0399	0.3644	0.2712	9.04	24,447	−44	0.2631	1
0.0402	0.3566	0.2868	9.14	24,517	−42	0.2790	72
0.0407	0.3490	0.3019	9.24	24,489	−40	0.2944	43
0.0416	0.3416	0.3168	9.16	23,746	−54	0.3094	−699
0.0427	0.3343	0.3313	9.33	23,566	−71	0.3240	−879
0.0441	0.3271	0.3457	9.24	22,608	−109	0.3385	−1838
0.0441	0.3202	0.3595	9.11	22,286	−153	0.3526	−2160
Section B ($Sb_{0.50}Sn_{0.50}$) second run, i = Ag, starting amount: n_{Sn} = 6.195 mmol, n_{Sb} = 6.196 mmol							
0.0000	0.5000	0.0000	–	–	−1423.78	–	–
0.0355	0.4871	0.0259	10.82	32,889	−1170	0.0129	8388
0.0448	0.4717	0.0567	13.18	31,741	−904	0.0413	7240
0.0466	0.4567	0.0867	13.40	31,017	−668	0.0717	6516
0.0540	0.4404	0.1192	14.84	29,649	−461	0.1030	5148
0.0545	0.4251	0.1497	14.43	28,555	−304	0.1345	4054
0.0561	0.4105	0.1790	14.02	26,949	−209	0.1644	2448
0.0574	0.3965	0.2070	13.91	26,133	−147	0.1930	1632
0.0578	0.3834	0.2333	14.10	26,321	−82	0.2201	1820
0.0584	0.3709	0.2581	13.56	25,051	−61	0.2457	550
0.0587	0.3592	0.2815	13.84	25,436	−30	0.2698	935
0.0593	0.3481	0.3037	13.10	23,824	−50	0.2926	−677
0.0596	0.3377	0.3247	13.02	23,556	−77	0.3142	−945
0.0604	0.3277	0.3447	13.00	23,224	−112	0.3347	−1277
0.0605	0.3182	0.3636	12.91	23,009	−152	0.3541	−1492
0.0607	0.3093	0.3815	12.75	22,665	−199	0.3725	−1836
0.0614	0.3007	0.3985	11.81	20,747	−297	0.3900	−3754
0.0627	0.2925	0.4151	12.56	21,605	−369	0.4068	−2896
0.0628	0.2847	0.4307	11.55	19,831	−484	0.4229	−4670
0.0628	0.2772	0.4455	11.71	20,115	−585	0.4381	−4386
0.0630	0.2702	0.4597	12.48	21,369	−650	0.4526	−3132
0.0637	0.2634	0.4732	11.83	20,025	−746	0.4664	−4476
0.0656	0.2568	0.4865	12.64	20,791	−821	0.4799	−3710
0.0656	0.2504	0.4991	12.05	19,820	−916	0.4928	−4681
0.0656	0.2444	0.5111	11.65	19,161	−1022	0.5051	−5341
0.0680	0.2385	0.5230	12.35	19,589	−1117	0.5171	−4912
Section B ($Sb_{0.5}Sn_{0.5}$) third run, i = Ag, starting amount: n_{Sn} = 6.244 mmol, n_{Sb} = 6.244 mmol							
0.0000	0.5000	0.0000	–	–	−1423.78	–	–
0.0402	0.4855	0.0290	12.11	32,499	−1150	0.0145	8024
0.0422	0.4712	0.0576	12.46	31,854	−898	0.0433	7380
0.0423	0.4576	0.0847	11.95	30,467	−700	0.0712	5992

Table III. Continued

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
0.0426	0.4448	0.1105	11.56	29,265	−546	0.0976	4790
0.0428	0.4325	0.1349	11.63	29,309	−398	0.1227	4834
0.0429	0.4209	0.1581	12.09	30,397	−228	0.1465	5922
0.0444	0.4096	0.1809	11.22	27,258	−147	0.1695	2784
0.0450	0.3987	0.2027	10.93	26,205	−97	0.1918	1731
0.0453	0.3882	0.2235	10.70	25,489	−68	0.2131	1014
0.0454	0.3783	0.2433	10.60	25,195	−48	0.2334	720
0.0491	0.3682	0.2636	11.32	24,860	−36	0.2535	385
0.0520	0.3580	0.2840	11.41	23,674	−57	0.2738	−801
0.0522	0.3483	0.3033	11.80	24,380	−58	0.2936	−95
0.0525	0.3391	0.3217	11.52	23,676	−78	0.3125	−798
0.0527	0.3304	0.3392	11.42	23,377	−104	0.3305	−1098
0.0531	0.3220	0.3560	11.12	22,594	−149	0.3476	−1881
0.0574	0.3134	0.3732	12.13	22,803	−190	0.3646	−1671
0.0577	0.3052	0.3896	11.38	21,268	−269	0.3814	−3207
0.0577	0.2974	0.4052	11.45	21,397	−341	0.3974	−3078
0.0581	0.2900	0.4200	11.22	20,838	−423	0.4126	−3637
0.0593	0.2828	0.4345	11.56	21,033	−498	0.4273	−3442
0.0624	0.2755	0.4489	11.87	20,524	−586	0.4417	−3950
0.0654	0.2684	0.4633	11.87	19,582	−698	0.4561	−4892
0.0668	0.2614	0.4772	12.12	19,568	−808	0.4702	−4907
0.0690	0.2546	0.4908	12.72	19,889	−906	0.4840	−4586
Section C ($Sb_{0.30}Sn_{0.70}$), i = Ag, starting amount: n_{Sn} = 8.875 mmol, n_{Sb} = 3.803 mmol							
0.0000	0.7000	0.0000	–	–	−1199.86	–	–
0.0399	0.6802	0.0284	11.31	30,584	−992	0.0142	6138
0.0406	0.6611	0.0556	11.67	31,002	−780	0.0420	6555
0.0426	0.6422	0.0826	11.77	29,813	−605	0.0691	5367
0.0439	0.6238	0.1088	11.68	28,706	−465	0.0957	4260
0.0445	0.6063	0.1339	11.63	28,203	−346	0.1214	3756
0.0472	0.5887	0.1591	12.17	27,822	−238	0.1465	3375
0.0482	0.5717	0.1833	12.25	27,422	−146	0.1712	2976
0.0503	0.5550	0.2071	12.39	26,574	−80	0.1952	2127
0.0506	0.5392	0.2297	12.21	26,040	−32	0.2184	1593
0.0540	0.5233	0.2524	12.45	24,865	−19	0.2411	418
0.0551	0.5080	0.2743	12.39	24,254	−24	0.2634	−192
0.0554	0.4935	0.2950	11.98	23,335	−55	0.2847	−1112
0.0557	0.4797	0.3147	12.34	23,902	−68	0.3049	−544
0.0573	0.4663	0.3338	11.92	22,446	−122	0.3243	−2000
0.0581	0.4535	0.3522	12.12	22,507	−172	0.3430	−1939
0.0590	0.4412	0.3698	11.98	21,909	−237	0.3610	−2537
0.0590	0.4295	0.3865	11.83	21,636	−305	0.3781	−2811
0.0613	0.4180	0.4029	11.85	20,846	−393	0.3947	−3601
0.0616	0.4070	0.4185	11.95	20,929	−475	0.4107	−3517
0.0638	0.3963	0.4339	11.72	19,822	−584	0.4262	−4625
0.0639	0.3861	0.4485	11.64	19,652	−693	0.4412	−4794
0.0658	0.3761	0.4627	12.26	20,096	−787	0.4556	−4350
0.0659	0.3666	0.4763	11.81	19,331	−897	0.4695	−5116
0.0663	0.3575	0.4893	11.48	18,680	−1017	0.4828	−5767
0.0667	0.3488	0.5017	11.95	19,318	−1117	0.4955	−5128
Section D ($Ag_{0.50}Sn_{0.50}$), i = Sb, starting amount: n_{Ag} = 6.5719 mmol, n_{Sn} = 6.5723 mmol							
0.0000	0.5000	0.0000	–	–	−870.77	–	–
0.0448	0.4864	0.0272	14.52	38,480	−707	0.0140	4999
0.0478	0.4727	0.0547	14.93	37,088	−582	0.0420	3607
0.0485	0.4595	0.0810	15.74	38,535	−422	0.0695	5054
0.0522	0.4461	0.1078	15.97	36,326	−324	0.0966	2844
0.0522	0.4335	0.1330	16.71	37,996	−184	0.1231	4515
0.0525	0.4215	0.1570	16.26	36,766	−86	0.1482	3285
0.0542	0.4098	0.1804	15.62	34,217	−63	0.1723	735
0.0554	0.3985	0.2030	16.44	35,236	−12	0.1956	1755

Table III. Continued

m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	$\Delta_{mix}\bar{H}$ x_i	$\Delta_{mix}\bar{H}$ (J/mol)
0.0554	0.3878	0.2244	16.05	34,392	13	0.2180	911
0.0569	0.3774	0.2452	16.50	34,426	39	0.2394	944
0.0570	0.3675	0.2650	15.84	32,980	24	0.2599	−501
0.0612	0.3575	0.2851	18.16	35,221	72	0.2801	1740
0.0630	0.3477	0.3046	18.08	34,074	87	0.3001	592
0.0632	0.3384	0.3232	17.34	32,568	59	0.3194	−913
0.0638	0.3295	0.3410	18.12	33,708	64	0.3377	226
0.0643	0.3210	0.3580	19.04	35,150	106	0.3553	1669
0.0645	0.3129	0.3742	19.32	35,549	156	0.3720	2068
0.0654	0.3051	0.3898	18.53	33,643	156	0.3880	162
0.0654	0.2977	0.4046	18.68	33,904	163	0.4033	423
0.0656	0.2906	0.4188	18.89	34,178	176	0.4179	696
0.0663	0.2838	0.4325	19.63	35,147	211	0.4319	1665
0.0666	0.2772	0.4456	18.92	33,726	212	0.4453	245
0.0672	0.2709	0.4582	19.93	35,212	247	0.4582	1731
0.0692	0.2647	0.4706	19.71	33,817	249	0.4707	336
0.0700	0.2587	0.4826	20.23	34,301	262	0.4829	820
Section E ($Ag_{0.25}Sn_{0.75}$), i = Sb, starting amount: n_{Ag} = 3.2011 mmol, n_{Sn} = 9.5982 mmol							
0.0000	0.7500	0.0000	–	–	577.38	–	–
0.0403	0.7310	0.0252	10.27	30,253	479.7	0.0129	−3203
0.0432	0.7118	0.0509	11.35	31,193	405.79	0.0390	−2263
0.0440	0.6932	0.0756	11.82	31,882	352.89	0.0648	−1574
0.0452	0.6751	0.0998	11.92	31,296	285.75	0.0897	−2161
0.0456	0.6578	0.1229	12.59	32,765	260.11	0.1138	−691
0.0458	0.6412	0.1449	12.09	31,330	198.82	0.1369	−2126
0.0464	0.6253	0.1661	11.54	29,530	94.23	0.1589	−3926
0.0481	0.6096	0.1871	12.75	31,457	40.61	0.1803	−1999
0.0496	0.5942	0.2076	12.82	30,687	−31.68	0.2014	−2769
0.0511	0.5792	0.2276	13.30	30,903	−96.81	0.2219	−2554
0.0546	0.5639	0.2480	14.55	31,642	−142.92	0.2424	−1814
0.0586	0.5484	0.2687	15.83	32,063	−177.95	0.2632	−1393
0.0591	0.5336	0.2884	16.73	33,602	−169.06	0.2837	146
0.0601	0.5194	0.3074	16.19	31,981	−204.55	0.3032	−1475
0.0609	0.5057	0.3257	16.68	32,507	−224.5	0.3220	−949
0.0615	0.4926	0.3432	16.20	31,272	−276.14	0.3401	−2184
0.0624	0.4799	0.3600	16.54	31,464	−320.82	0.3574	−1992
0.0643	0.4676	0.3765	17.31	31,957	−351.62	0.3741	−1499
0.0645	0.4558	0.3921	17.37	31,968	−380.66	0.3903	−1488
0.0653	0.4445	0.4072	17.61	32,017	−407.35	0.4058	−1439
0.0664	0.4336	0.4218	18.82	33,644	−392.48	0.4207	188
0.0682	0.4229	0.4361	18.55	32,297	−411.67	0.4352	−1159
0.0657	0.4130	0.4492	17.43	31,485	−448.4	0.4489	−1971
0.0691	0.4032	0.4623	20.02	34,393	−414.93	0.4620	937
0.0696	0.3937	0.4749	18.71	31,918	−441.62	0.4749	−1538

Q_i, heat effect from the drop; Q_{mi}, molar heat effect from the drop element; $\Delta_{mix}H_m$, integral mixing enthalpy of the liquid alloy; $\Delta_{mix}\bar{H}$, partial mixing enthalpy of the drop element.

Thermodynamic equilibrium of the samples was checked by using scanning electron microscopy (SEM) and chemical analysis by energy-dispersive x-ray spectroscopy (EDS) to verify the complete dissolution of the metallic pieces in the bath. A Leica Digital Microscope and a Zeiss EVO 40 SEM (Carl Zeiss SMT Ltd., Cambridge) operating at 20 kV and equipped with electron probe microanalysis (EPMA, INCA 300) were employed.

Several DSC measurements were performed on key-composition alloys synthesized by induction melting to determine the temperatures of the invariant reactions. DSC measurements were performed using a Setaram DSC 111 using closed quartz crucibles. All samples were heated and cooled in two different cycles from 20°C up to and over the melting temperature with a scanning rate of 1°C/min, followed by a second run at 0.3°C/min.

Table IV. Partial and integral enthalpies of mixing of liquid Ag-Sb-Sn alloys at 600°C (reference state: pure liquid components)

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
Section A ($Sb_{0.7}Sn_{0.3}$), i = Ag, starting amount: n_{Sn} = 3.6737 mmol, n_{Sb} = 8.5717 mmol							
0.0000	0.3000	0.0000	–	–	−1068.38	–	–
0.0419	0.2908	0.0307	13.02	33,524	−816	0.0154	7133
0.0419	0.2821	0.0597	13.55	34,889	−538	0.0452	8497
0.0430	0.2737	0.0876	12.98	32,568	−338	0.0736	6177
0.0434	0.2658	0.1141	12.7	31,571	−178	0.1009	5179
0.0448	0.2580	0.1400	12.89	31,042	−37	0.1271	4651
0.0449	0.2507	0.1644	12.53	30,100	70	0.1522	3709
0.0455	0.2437	0.1878	12.28	29,102	144	0.1761	2711
0.0461	0.2370	0.2102	12.41	29,032	213	0.1990	2641
0.0465	0.2305	0.2315	12.11	28,091	253	0.2209	1700
0.0468	0.2244	0.2519	12.18	28,068	291	0.2417	1677
0.0497	0.2183	0.2724	12.57	27,274	308	0.2622	883
0.0508	0.2123	0.2922	12.37	26,275	296	0.2823	−116
0.0534	0.2064	0.3119	12.91	26,080	279	0.3020	−312
0.0536	0.2008	0.3306	12.93	26,026	262	0.3212	−365
0.0541	0.1955	0.3484	12.12	24,160	196	0.3395	−2231
0.0554	0.1903	0.3658	12.44	24,215	133	0.3571	−2177
0.0592	0.1850	0.3833	12.98	23,644	53	0.3745	−2747
0.0601	0.1800	0.4001	13.17	23,639	−23	0.3917	−2753
0.0607	0.1751	0.4162	13.02	23,132	−110	0.4082	−3260
0.0631	0.1704	0.4321	13.4	22,915	−201	0.4242	−3476
0.0638	0.1658	0.4472	13.37	22,609	−297	0.4397	−3782
0.0648	0.1615	0.4618	13.51	22,483	−392	0.4545	−3908
0.0667	0.1572	0.4761	13.77	22,277	−490	0.4689	−4114
0.0688	0.1530	0.4900	14.03	21,992	−594	0.4830	−4400
0.0692	0.1490	0.5033	13.74	21,423	−708	0.4966	−4968
Section B ($Sb_{0.5}Sn_{0.5}$) first run, i = Ag, starting amount: n_{Sn} = 6.2103 mmol, n_{Sb} = 6.2109 mmol							
0.0000	0.5000	0.0000	–	–	−1423.78	–	–
0.0454	0.4836	0.0328	14.73	34,991	−1093	0.0164	8610.22
0.0478	0.4675	0.0650	15	33,860	−805	0.0489	7479.33
0.0494	0.4519	0.0962	14.97	32,698	−566	0.0806	6317.26
0.0503	0.4371	0.1259	14.62	31,343	−383	0.1110	4962.3
0.0504	0.4232	0.1537	14.23	30,461	−240	0.1398	4080.27
0.0506	0.4101	0.1799	13.99	29,821	−124	0.1668	3440.28
0.0522	0.3974	0.2053	14.39	29,737	−15	0.1926	3356.22
0.0523	0.3854	0.2292	13.38	27,589	23	0.2172	1208.25
0.0526	0.3741	0.2518	14.68	30,101	133	0.2405	3720.95
0.0535	0.3633	0.2735	13.54	27,290	157	0.2627	909.54
0.0550	0.3527	0.2946	13.82	27,103	174	0.2841	722.87
0.0558	0.3427	0.3147	13.27	25,644	149	0.3046	−736.51
0.0560	0.3331	0.3338	12.96	24,957	107	0.3242	−1423.23
0.0567	0.3240	0.3521	13.04	24,802	61	0.3429	−1578.7
0.0573	0.3153	0.3695	13.64	25,680	42	0.3608	−700.28
0.0582	0.3069	0.3863	13.24	24,537	−7	0.3779	−1842.95
0.0586	0.2988	0.4024	12.92	23,783	−74	0.3944	−2597.43
0.0587	0.2912	0.4176	13.9	25,545	−93	0.4100	−835.61
0.0597	0.2838	0.4324	13.08	23,628	−159	0.4250	−2752.57
0.0605	0.2767	0.4465	12.1	21,575	−274	0.4394	−4805.28
0.0607	0.2700	0.4601	12.95	23,005	−349	0.4533	−3375.72
0.0627	0.2633	0.4734	12.99	22,351	−439	0.4667	−4029.04
0.0629	0.2570	0.4861	12.74	21,848	−537	0.4797	−4532.53
0.0644	0.2508	0.4985	12.81	21,454	−642	0.4923	−4926.6
0.0656	0.2448	0.5105	13.07	21,499	−743	0.5045	−4881.81
Section B ($Sb_{0.5}Sn_{0.5}$) second run, i = Ag, starting amount: n_{Sn} = 6.1798 mmol, n_{Sb} = 6.1823 mmol							
0.0000	0.5000	0.0000	–	–	−1423.78	–	–
0.0406	0.4851	0.0295	12.75	33,883	−1162	0.0148	7429
0.0427	0.4705	0.0588	13.09	33,074	−928	0.0442	6620

Table IV. Continued

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
0.0441	0.4563	0.0872	12.85	31,443	−749	0.0730	4988
0.0442	0.4429	0.1140	12.63	30,824	−599	0.1006	4369
0.0444	0.4302	0.1394	12.36	30,021	−479	0.1267	3566
0.0448	0.4181	0.1636	12.27	29,554	−379	0.1515	3099
0.0476	0.4060	0.1878	12.37	28,034	−322	0.1757	1579
0.0489	0.3943	0.2113	13.05	28,792	−245	0.1996	2337
0.0500	0.3829	0.2340	13.32	28,736	−173	0.2226	2281
0.0515	0.3719	0.2560	13.57	28,429	−111	0.2450	1974
0.0519	0.3615	0.2769	13.42	27,899	−67	0.2665	1444
0.0535	0.3513	0.2973	13	26,213	−72	0.2871	−241
0.0536	0.3416	0.3166	12.83	25,820	−88	0.3070	−635
0.0538	0.3325	0.3350	12.63	25,318	−116	0.3258	−1137
0.0563	0.3234	0.3531	13.33	25,535	−138	0.3440	−919
0.0564	0.3148	0.3703	12.55	23,994	−200	0.3617	−2461
0.0567	0.3066	0.3868	12.65	24,060	−257	0.3786	−2395
0.0567	0.2988	0.4023	12.62	24,004	−313	0.3946	−2451
0.0571	0.2913	0.4173	12.52	23,660	−374	0.4098	−2794
0.0599	0.2839	0.4321	12.81	23,067	−451	0.4247	−3388
0.0616	0.2766	0.4466	12.78	22,378	−544	0.4394	−4077
0.0625	0.2696	0.4606	13.3	22,957	−619	0.4536	−3498
0.0625	0.2630	0.4739	12.96	22,367	−704	0.4673	−4088
0.0630	0.2566	0.4867	12.87	22,043	−794	0.4803	−4412
0.0699	0.2499	0.5001	14.13	21,801	−895	0.4934	−4654
Section C ($Sb_{0.3}Sn_{0.7}$), i = Ag, starting amount: n_{Sn} = 8.6522 mmol, n_{Sb} = 3.7076 mmol							
0.0000	0.7000	0.0000	–	–	−1199.86	–	–
0.0419	0.6787	0.0305	12.88	33,152	−957	0.0152	6780
0.0438	0.6577	0.0604	13.11	32,291	−744	0.0454	5920
0.0441	0.6379	0.0887	12.12	29,639	−624	0.0746	3267
0.0446	0.6190	0.1157	12.26	29,658	−508	0.1022	3286
0.0449	0.6011	0.1413	12.32	29,597	−400	0.1285	3226
0.0450	0.5842	0.1654	12.63	30,272	−279	0.1533	3900
0.0454	0.5681	0.1885	11.91	28,301	−218	0.1770	1929
0.0464	0.5525	0.2108	12.23	28,435	−155	0.1996	2063
0.0481	0.5372	0.2326	12.76	28,615	−89	0.2217	2243
0.0512	0.5218	0.2546	13.14	27,692	−48	0.2436	1321
0.0514	0.5072	0.2754	12.2	25,599	−69	0.2650	−773
0.0519	0.4933	0.2953	12.6	26,184	−72	0.2854	−188
0.0601	0.4781	0.3170	13.74	24,656	−123	0.3062	−1716
0.0601	0.4638	0.3374	14.2	25,490	−145	0.3272	−882
0.0604	0.4503	0.3567	13.59	24,270	−202	0.3471	−2102
0.0615	0.4373	0.3753	13.83	24,251	−258	0.3660	−2121
0.0615	0.4251	0.3928	12.06	21,147	−397	0.3840	−5225
0.0618	0.4135	0.4094	13.6	23,737	−458	0.4011	−2635
0.0629	0.4022	0.4254	13.1	22,472	−551	0.4174	−3899
0.0649	0.3913	0.4410	13.47	22,391	−645	0.4332	−3981
0.0651	0.3809	0.4559	13.84	22,930	−719	0.4485	−3441
0.0658	0.3709	0.4701	13.41	21,991	−815	0.4630	−4381
0.0668	0.3613	0.4838	13.18	21,289	−925	0.4770	−5083
0.0680	0.3521	0.4971	13.24	20,998	−1039	0.4904	−5374
0.0694	0.3431	0.5099	13.3	20,667	−1158	0.5035	−5705
Section D ($Ag_{0.5}Sn_{0.5}$), i = Sb, starting amount: n_{Ag} = 6.6702 mmol, n_{Sn} = 6.6709 mmol							
0.0000	0.5000	0.0000	–	–	−877.42	–	–
0.0405	0.4879	0.0243	13.75	41,333	−714	0.0122	5827
0.0436	0.4754	0.0492	13.92	38,881	−610	0.0368	3375
0.0441	0.4634	0.0732	14.09	38,907	−509	0.0612	3401
0.0449	0.4519	0.0963	14.06	38,123	−431	0.0847	2617
0.0449	0.4409	0.1183	14.21	38,540	−346	0.1073	3034
0.0451	0.4303	0.1394	13.97	37,707	−286	0.1289	2202
0.0476	0.4197	0.1606	14.22	36,362	−257	0.1500	856

Table IV. Continued

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
0.0487	0.4094	0.1812	15.24	38,112	−187	0.1709	2606
0.0488	0.3996	0.2008	14.75	36,801	−152	0.1910	1295
0.0491	0.3902	0.2197	14.33	35,545	−147	0.2103	40
0.0492	0.3812	0.2377	15.36	38,011	−86	0.2287	2506
0.0534	0.3718	0.2563	15.93	36,321	−64	0.2470	816
0.0543	0.3628	0.2744	15.56	34,888	−77	0.2654	−618
0.0555	0.3540	0.2919	17.51	38,404	−5	0.2832	2898
0.0573	0.3454	0.3092	17.6	37,390	41	0.3006	1885
0.0575	0.3372	0.3257	17.2	36,409	61	0.3174	904
0.0576	0.3293	0.3414	17.65	37,309	102	0.3336	1803
0.0582	0.3217	0.3566	17.87	37,389	143	0.3490	1884
0.0593	0.3143	0.3714	18.13	37,231	180	0.3640	1726
0.0632	0.3068	0.3864	19.16	36,905	209	0.3789	1399
0.0670	0.2992	0.4015	20.78	37,764	259	0.3940	2259
0.0682	0.2919	0.4162	21.11	37,690	306	0.4089	2185
0.0684	0.2849	0.4302	21.09	37,534	348	0.4232	2029
0.0687	0.2782	0.4436	20.79	36,836	371	0.4369	1330
0.0687	0.2718	0.4564	20.77	36,813	392	0.4500	1308
Section E ($Ag_{0.25}Sn_{0.75}$), i = Sb, starting amount: n_{Ag} = 3.2382 mmol, n_{Sn} = 9.0943 mmol							
0.0000	0.7500	0.0000	–	–	528.78	–	–
0.0352	0.7336	0.0218	10.12	34,145	484	0.0112	−1488
0.0381	0.7167	0.0444	10.85	33,793	429	0.0339	−1840
0.0409	0.6994	0.0675	11.47	33,305	360	0.0573	−2327
0.0415	0.6826	0.0899	11.35	32,467	274	0.0805	−3165
0.0484	0.6641	0.1146	13.49	33,089	196	0.1046	−2544
0.0486	0.6464	0.1381	13.6	33,211	125	0.1292	−2422
0.0506	0.6290	0.1613	14.14	33,173	54	0.1530	−2460
0.0521	0.6121	0.1839	14.73	33,566	−5	0.1762	−2067
0.0547	0.5952	0.2064	15.28	33,168	−74	0.1991	−2464
0.0549	0.5792	0.2277	15.48	33,479	−131	0.2214	−2153
0.0554	0.5639	0.2481	15.87	34,016	−171	0.2425	−1617
0.0570	0.5490	0.2680	16.13	33,585	−221	0.2629	−2048
0.0596	0.5342	0.2877	16.25	32,374	−305	0.2830	−3259
0.0626	0.5195	0.3073	18.05	34,235	−335	0.3028	−1397
0.0634	0.5054	0.3261	18.51	34,659	−353	0.3222	−973
0.0635	0.4921	0.3439	18.46	34,516	−373	0.3406	−1117
0.0636	0.4794	0.3608	18.63	34,779	−386	0.3581	−853
0.0642	0.4672	0.3770	18.38	33,990	−418	0.3748	−1642
0.0676	0.4551	0.3932	19.62	34,457	−438	0.3911	−1176
0.0685	0.4434	0.4088	19.96	34,593	−454	0.4071	−1040
0.0693	0.4322	0.4238	20.1	34,427	−473	0.4224	−1206
0.0698	0.4214	0.4381	20.56	34,963	−478	0.4371	−670
0.0722	0.4109	0.4522	20.79	34,181	−503	0.4514	−1452
0.0739	0.4006	0.4659	20.31	32,626	−566	0.4653	−3006

Q_i, heat effect from the drop; Q_{mi}, molar heat effect from the drop element; $\Delta_{mix}H_m$, integral mixing enthalpy of the liquid alloy; $\Delta_{mix}\bar{H}$, partial mixing enthalpy of the drop element.

After DSC measurement, microstructural analysis was carried out using light optical microscopy (LOM), SEM, and chemical analysis performed using EDS.

Mixing Enthalpy Determination

During each drop (ith) of element A in the liquid bath, a certain amount of heat Q_i is exchanged in the measuring cell:

$$Q_i = Q_{i1} + Q_{i2} = n_i \Delta H_1 + \Delta_{mix} H_i,$$

where n_i refers to the mole number of the ith drop and ΔH_1 is given by $H(A, T_c, l) - H(A, T_r, s)$, corresponding to the enthalpy change of 1 mole of A from the solid state at the drop temperature T_r to the liquid state at the calorimetric temperature T_c expressed in Kelvin. The enthalpies of these two states were calculated by applying polynomials from

Table V. Partial and integral enthalpies of mixing of liquid Ag-Sb-Sn alloys at 630°C (reference state: pure liquid components)

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
Section A ($Sb_{0.7}Sn_{0.3}$) first run, i = Ag, starting amount: n_{Sn} = 3.7882 mmol, n_{Sb} = 8.8517 mmol							
0.0000	0.3000	0.0000	–	–	−1068.38	–	–
0.0358	0.2920	0.0256	12.32	37,116	−799	0.0128	9479
0.0369	0.2845	0.0506	12.21	35,684	−571	0.0381	8047
0.0406	0.2767	0.0767	13.1	34,806	−358	0.0637	7169
0.0425	0.2690	0.1026	13.38	33,961	−172	0.0896	6325
0.0429	0.2616	0.1272	13.4	33,703	0	0.1149	6066
0.0458	0.2541	0.1521	13.69	32,232	131	0.1396	4595
0.0466	0.2470	0.1759	13.66	31,609	239	0.1640	3972
0.0466	0.2402	0.1985	13.83	32,002	352	0.1872	4365
0.0483	0.2336	0.2206	13.39	29,911	405	0.2096	2274
0.0488	0.2272	0.2418	13.5	29,841	454	0.2312	2204
0.0494	0.2212	0.2621	13.74	29,995	505	0.2519	2358
0.0528	0.2150	0.2826	13.18	26,916	471	0.2723	−721
0.0553	0.2089	0.3029	14.56	28,404	479	0.2927	767
0.0572	0.2030	0.3227	14.43	27,215	453	0.3128	−422
0.0586	0.1973	0.3418	14.04	25,841	390	0.3322	−1796
0.0587	0.1918	0.3600	14.66	26,931	360	0.3509	−705
0.0587	0.1867	0.3771	14.03	25,790	300	0.3685	−1847
0.0596	0.1817	0.3936	14.63	26,478	262	0.3854	−1159
0.0597	0.1770	0.4093	13.54	24,466	173	0.4015	−3171
0.0611	0.1725	0.4245	14.24	25,143	104	0.4169	−2494
0.0615	0.1681	0.4391	13.79	24,188	14	0.4318	−3448
0.0616	0.1639	0.4530	13.31	23,307	−93	0.4460	−4330
0.0630	0.1599	0.4665	14.2	24,316	−173	0.4597	−3321
0.0661	0.1559	0.4799	14.48	23,622	−269	0.4732	−4015
0.0716	0.1517	0.4937	15.59	23,484	−373	0.4868	−4153
Section A ($Sb_{0.7}Sn_{0.3}$) second run, i = Ag, starting amount: n_{Sn} = 3.6568 mmol, n_{Sb} = 8.5322 mmol							
0.0000	0.3000	0.0000	–	–	−1068.38	–	–
0.0358	0.2921	0.0265	11.9	35,853	−823	0.0133	8197
0.0361	0.2845	0.0518	11.97	35,768	−590	0.0392	8112
0.0368	0.2771	0.0764	11.82	34,659	−394	0.0641	7003
0.0373	0.2700	0.0999	12.09	34,968	−197	0.0882	7312
0.0373	0.2633	0.1224	11.4	32,964	−60	0.1111	5308
0.0381	0.2568	0.1441	11.59	32,824	70	0.1332	5168
0.0398	0.2503	0.1657	12.15	32,936	201	0.1549	5280
0.0456	0.2432	0.1892	13.89	32,851	342	0.1775	5195
0.0482	0.2362	0.2126	13.92	31,156	433	0.2009	3500
0.0482	0.2296	0.2347	13.63	30,504	500	0.2236	2848
0.0485	0.2233	0.2557	13.47	29,966	550	0.2452	2310
0.0486	0.2173	0.2756	12.73	28,247	551	0.2657	591
0.0498	0.2115	0.2950	12.57	27,236	525	0.2853	−420
0.0509	0.2059	0.3137	13.28	28,143	524	0.3043	487
0.0601	0.1996	0.3346	14.86	26,677	479	0.3241	−979
0.0611	0.1936	0.3545	15.44	27,267	453	0.3446	−389
0.0619	0.1879	0.3736	14.89	25,952	389	0.3641	−1704
0.0635	0.1824	0.3920	15.56	26,433	342	0.3828	−1223
0.0663	0.1770	0.4101	15.5	25,218	259	0.4010	−2438
0.0687	0.1717	0.4277	16.28	25,566	189	0.4189	−2090
0.0692	0.1667	0.4444	15.41	24,021	77	0.4361	−3635
0.0693	0.1619	0.4602	16.22	25,251	6	0.4523	−2405
0.0699	0.1574	0.4753	15.11	23,322	−115	0.4678	−4334
0.0717	0.1530	0.4899	16.13	24,260	−206	0.4826	−3396
0.0734	0.1488	0.5040	15.96	23,455	−317	0.4970	−4201
Section B ($Sb_{0.5}Sn_{0.5}$), i = Ag, starting amount: n_{Sn} = 6.2017 mmol, n_{Sb} = 6.2021 mmol							
0.0000	0.5000	0.0000	–	–	−1423.78	–	–
0.0353	0.4871	0.0257	11.46	35,012	−1194	0.0129	7497
0.0373	0.4743	0.0515	11.97	34,628	−975	0.0386	7112

Table V. Continued

						$\Delta_{mix}\bar{H}$	
m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	x_i	(J/mol)
0.0379	0.4618	0.0763	12.02	34,214	−774	0.0639	6698
0.0407	0.4492	0.1015	12.4	32,873	−606	0.0889	5358
0.0422	0.4368	0.1263	12.5	31,942	−468	0.1139	4427
0.0423	0.4251	0.1498	12.56	32,017	−334	0.1380	4502
0.0423	0.4140	0.1720	12.24	31,224	−228	0.1609	3708
0.0435	0.4031	0.1937	12.54	31,106	−128	0.1829	3590
0.0444	0.3926	0.2147	12.52	30,428	−49	0.2042	2912
0.0493	0.3816	0.2368	13.65	29,867	18	0.2258	2351
0.0501	0.3710	0.2580	12.88	27,728	24	0.2474	212
0.0511	0.3608	0.2785	13.47	28,436	49	0.2683	920
0.0517	0.3510	0.2980	13.21	27,554	48	0.2883	38
0.0522	0.3416	0.3168	13.15	27,174	38	0.3074	−341
0.0546	0.3323	0.3353	13.82	27,298	31	0.3260	−218
0.0555	0.3234	0.3531	13.57	26,373	−1	0.3442	−1143
0.0558	0.3149	0.3701	13.67	26,430	−29	0.3616	−1085
0.0598	0.3063	0.3874	13.88	25,046	−96	0.3787	−2470
0.0602	0.2981	0.4038	13.73	24,609	−171	0.3956	−2907
0.0606	0.2903	0.4195	13.7	24,392	−249	0.4116	−3124
0.0617	0.2827	0.4346	13.97	24,429	−323	0.4270	−3087
0.0630	0.2754	0.4493	13.78	23,601	−416	0.4419	−3915
0.0639	0.2683	0.4634	14.27	24,094	−493	0.4563	−3422
0.0709	0.2609	0.4782	15.59	23,724	−584	0.4708	−3792
0.0718	0.2538	0.4924	15.38	23,103	−689	0.4853	−4413
Section C ($Sb_{0.3}Sn_{0.7}$), i = Ag, starting amount: n_{Sn} = 8.7920 mmol, n_{Sb} = 3.7684 mmol							
0.0000	0.7000	0.0000	–	–	−1199.86	–	–
0.0382	0.6808	0.0274	11.95	33,738	−998	0.0137	6153
0.0387	0.6624	0.0537	11.97	33,359	−815	0.0406	5774
0.0410	0.6439	0.0801	12.25	32,229	−663	0.0669	4644
0.0431	0.6256	0.1062	12.68	31,738	−526	0.0931	4153
0.0436	0.6081	0.1312	12.52	30,970	−417	0.1187	3385
0.0440	0.5915	0.1550	12.41	30,429	−327	0.1431	2844
0.0454	0.5752	0.1783	12.54	29,783	−258	0.1667	2198
0.0464	0.5594	0.2008	12.66	29,433	−200	0.1895	1848
0.0486	0.5438	0.2231	12.73	28,255	−176	0.2119	670
0.0496	0.5288	0.2446	13	28,269	−152	0.2338	684
0.0503	0.5144	0.2652	12.51	26,828	−169	0.2549	−757
0.0510	0.5005	0.2849	12.79	27,044	−179	0.2751	−541
0.0556	0.4863	0.3053	13.54	26,272	−211	0.2951	−1313
0.0583	0.4721	0.3255	14.21	26,286	−243	0.3154	−1299
0.0613	0.4582	0.3455	14.53	25,572	−295	0.3355	−2012
0.0620	0.4448	0.3645	14.59	25,380	−351	0.3550	−2205
0.0623	0.4322	0.3825	14.16	24,516	−428	0.3735	−3069
0.0625	0.4202	0.3996	14.25	24,601	−499	0.3911	−2983
0.0646	0.4085	0.4163	14.64	24,446	−572	0.4080	−3139
0.0648	0.3974	0.4322	14.06	23,413	−670	0.4243	−4172
0.0665	0.3867	0.4476	14.57	23,626	−759	0.4399	−3959
0.0686	0.3762	0.4626	14.79	23,249	−856	0.4551	−4336
0.0713	0.3658	0.4774	15.15	22,923	−961	0.4700	−4661
0.0728	0.3558	0.4917	15.51	22,980	−1060	0.4845	−4605
Section D ($Ag_{0.5}Sn_{0.5}$), i = Sb, starting amount: n_{Ag} = 6.4764 mmol, n_{Sn} = 6.4771 mmol							
0.0000	0.5000	0.0000	0	–	−879.91	–	–
0.0402	0.4876	0.0249	13.18	39,912	−771	0.0124	3501
0.0409	0.4756	0.0489	13.56	40,358	−655	0.0369	3947
0.0427	0.4636	0.0728	14.07	40,108	−545	0.0608	3697
0.0430	0.4522	0.0956	13.85	39,210	−463	0.0842	2799
0.0434	0.4412	0.1176	13.64	38,251	−407	0.1066	1840
0.0452	0.4303	0.1394	14.34	38,614	−343	0.1285	2203
0.0474	0.4195	0.1611	15.49	39,790	−249	0.1502	3379
0.0475	0.4091	0.1817	15.08	38,651	−187	0.1714	2240

Table V. Continued

m_i (g)	x_{Sn}	x_i	Q_i (J)	Q_{mi} (J/mol)	$\Delta_{mix}H_m$ (J/mol)	$\Delta_{mix}\bar{H}$ x_i	$\Delta_{mix}\bar{H}$ (J/mol)
0.0477	0.3993	0.2015	14.83	37,845	−148	0.1916	1434
0.0497	0.3895	0.2211	15.11	37,015	−130	0.2113	604
0.0498	0.3801	0.2398	15.22	37,203	−108	0.2305	792
0.0509	0.3710	0.2580	15.85	37,918	−69	0.2489	1507
0.0521	0.3621	0.2758	15.96	37,293	−46	0.2669	883
0.0528	0.3536	0.2929	16.18	37,304	−24	0.2843	893
0.0540	0.3452	0.3096	17.6	39,674	54	0.3013	3263
0.0542	0.3372	0.3256	16.87	37,903	87	0.3176	1492
0.0570	0.3292	0.3417	17.32	37,002	99	0.3336	591
0.0611	0.3210	0.3580	19.13	38,113	139	0.3499	1702
0.0611	0.3132	0.3736	18.98	37,813	170	0.3658	1402
0.0646	0.3054	0.3893	20.29	38,248	211	0.3815	1837
0.0648	0.2979	0.4042	20.42	38,369	254	0.3968	1958
0.0662	0.2906	0.4188	20.53	37,749	280	0.4115	1338
0.0681	0.2835	0.4330	21.01	37,564	302	0.4259	1153
0.0692	0.2766	0.4468	21.51	37,848	329	0.4399	1437
0.0700	0.2700	0.4600	21.47	37,344	344	0.4534	933
Section E ($Ag_{0.25}Sn_{0.75}$), i = Sb, starting amount: n_{Ag} = 3.3226 mmol, n_{Sn} = 9.9680 mmol							
0.0000	0.7500	0.0000	0	–	505.51	–	–
0.0347	0.7343	0.0210	9.82	33,610	428	0.0108	−3090
0.0396	0.7171	0.0439	11.48	34,399	363	0.0332	−2300
0.0397	0.7006	0.0658	11.19	33,453	278	0.0562	−3247
0.0399	0.6849	0.0868	11.36	33,799	205	0.0781	−2900
0.0404	0.6696	0.1072	11.58	34,015	139	0.0993	−2684
0.0408	0.6549	0.1269	11.75	34,175	79	0.1197	−2525
0.0427	0.6401	0.1465	12.31	34,219	20	0.1397	−2480
0.0427	0.6260	0.1653	12.05	33,494	−52	0.1593	−3205
0.0437	0.6122	0.1837	12.36	33,574	−122	0.1782	−3126
0.0442	0.5989	0.2015	12.68	34,060	−178	0.1966	−2639
0.0469	0.5853	0.2196	13.24	33,524	−247	0.2148	−3176
0.0475	0.5722	0.2371	13.6	33,991	−303	0.2328	−2708
0.0486	0.5594	0.2542	14.36	35,084	−333	0.2503	−1615
0.0491	0.5470	0.2707	14.29	34,561	−374	0.2673	−2139
0.0493	0.5351	0.2865	14.21	34,219	−420	0.2837	−2480
0.0501	0.5235	0.3019	14.43	34,197	−466	0.2995	−2503
0.0515	0.5122	0.3171	15.09	34,789	−498	0.3150	−1911
0.0521	0.5012	0.3318	15.14	34,485	−536	0.3300	−2214
0.0524	0.4905	0.3460	15.45	34,991	−561	0.3446	−1708
0.0562	0.4796	0.3605	16.86	35,606	−573	0.3590	−1093
0.0586	0.4688	0.3750	17.36	35,159	−595	0.3736	−1541
0.0634	0.4576	0.3899	18.96	35,502	−610	0.3884	−1197
0.0634	0.4469	0.4041	18.49	34,626	−644	0.4031	−2073
0.0725	0.4353	0.4196	21.7	35,532	−658	0.4180	−1167

Q_i, heat effect from the drop; Q_{mi}, molar heat effect from the drop element; $\Delta_{mix}H_m$, integral mixing enthalpy of the liquid alloy; $\Delta_{mix}\bar{H}$, partial mixing enthalpy of the drop element.

Ref. 54. $\Delta_{mix}H_i$ refers to the contribution of the ith drop to the integral enthalpy of mixing.

All the enthalpies are considered in the standard state, but the superscript "°" is omitted, for clarity, in the text.

After i drops, the total contribution to the mixing enthalpy due to dropping A into the original bath is

$$\sum_{j=1}^{i}\Delta_{mix}H_j = \sum_{j=1}^{i}(Q_j - n_j\Delta H_l).$$

Considering n_0 moles of pure B bath, after i drops of A, we obtain the integral mixing enthalpy

$$\Delta_{mix}H = \sum_{j=1}^{i}\Delta_{mix}H_j.$$

For a measurement performed starting with n_0 moles of the bath formed by a binary liquid alloy, the excess mixing enthalpy of the binary bath $\Delta_{mix}H_0 = n_0{\cdot}\Delta_{mix}H_m$ must be taken into account.

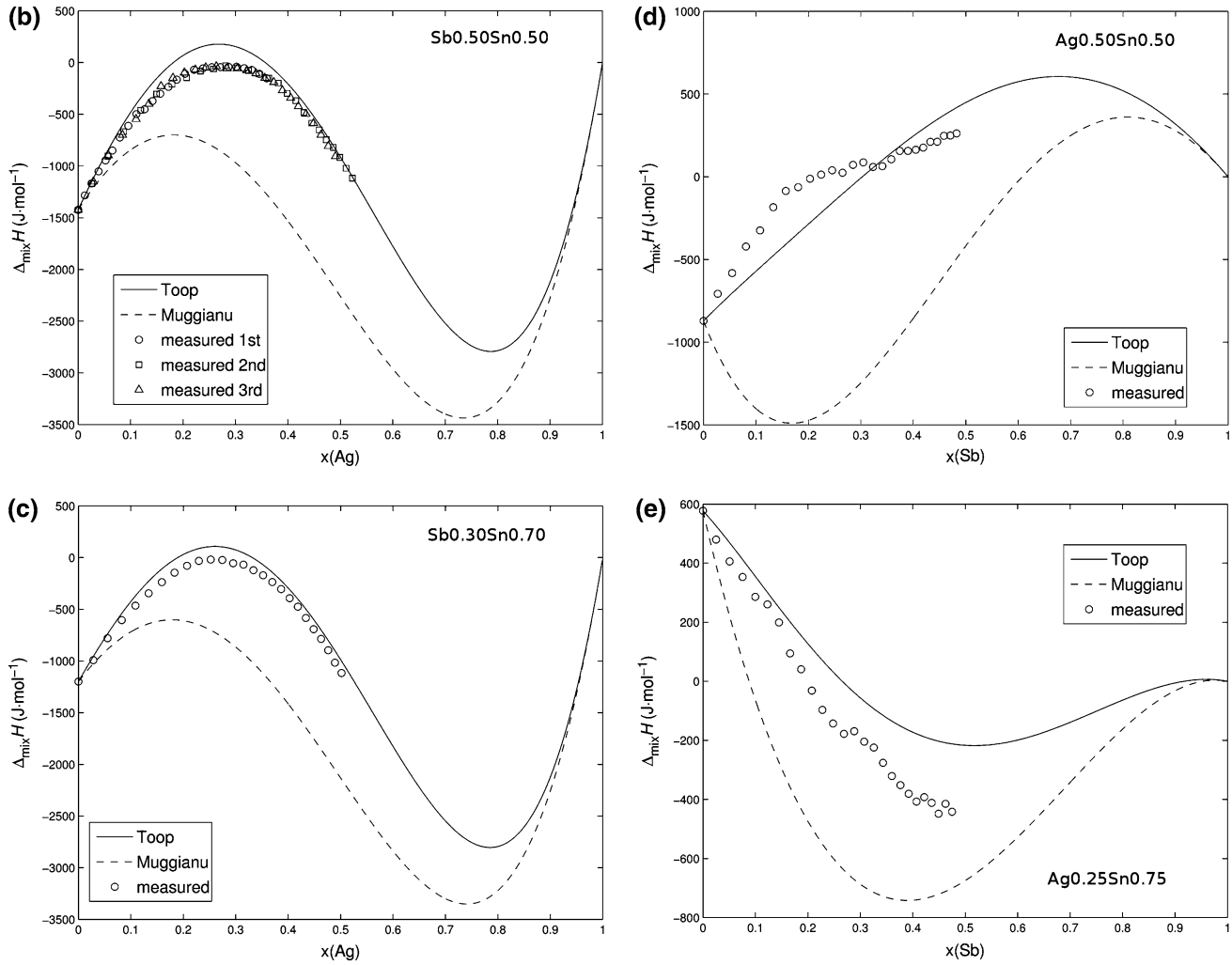

Fig. 1. Integral molar enthalpies of mixing of liquid Ag-Sb-Sn alloys at 530°C. The experimental values are presented together with those calculated by Toop and Muggianu methods. Reference state: pure liquid components. The letters refer to the measured sections (also indicated inside each figure): B: Sb0.5Sn0.5; C: Sb0.3Sn0.7; D: Ag0.50Sn0.50; E: Ag0.25Sn0.75.

Therefore, after i drops, the total mixing enthalpy of the liquid alloy is

$$\Delta_{\mathrm{mix}}H = \Delta_{\mathrm{mix}}H_0 + \sum_{j=1}^{i} \Delta_{\mathrm{mix}}H_j.$$

For all the measurements, the molar mixing enthalpy can therefore be expressed as follows:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \frac{\Delta_{\mathrm{mix}}H}{\sum_{j=0}^{i} n_j}.$$

In case n_i is very small, $n_i \ll m$, where m is the number of moles of the alloy $A_xB_yC_z$; the reaction of mixing and thus the heat effect can be related only to n_i moles of solid metal A added without a significant change in the global composition, and the partial mixing enthalpy can be derived directly as

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{m}} = \frac{\Delta_{\mathrm{mix}}H_i}{n_i}.$$

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results along with the experimental conditions, which include the starting amount of the bath, the experimental temperature, and the mass of each drop, are reported in Tables III–V. The integral enthalpy refers to the alloy concentration after each drop, while the averaged composition before and after each drop was considered for the partial enthalpy. The excess mixing enthalpy values for the binary bath alloys were taken from the COST MP0602 database.[55] In all, six measurements were performed along section B (pure Ag dropped into a $Sb_{0.5}Sn_{0.5}$ liquid bath). For all three temperatures studied, the integral mixing enthalpies became positive as the Ag concentration increased, and the trend showed a maximum at around 30 at.% Ag. The values obtained from different runs for the same temperature and composition are close to each other, with a

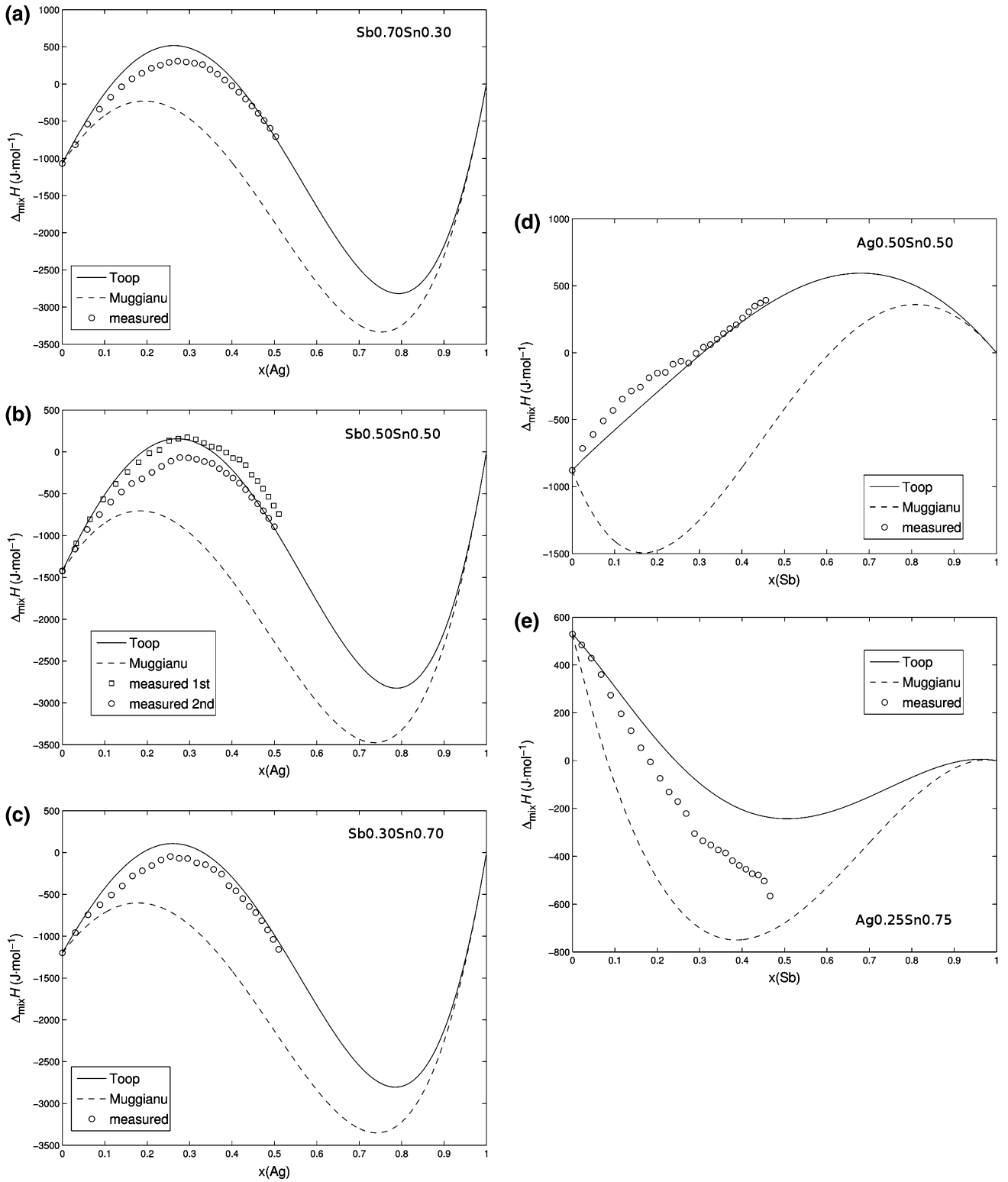

Fig. 2. Integral molar enthalpies of mixing of liquid Ag-Sb-Sn alloys at 600°C. The experimental values are presented together with those calculated by Toop and Muggianu methods. Reference state: pure liquid components. The letters refer to the measured sections (also indicated inside each figure): A: Sb0.7Sn0.3; B: Sb0.5Sn0.5; C: Sb0.3Sn0.7; D: Ag0.50Sn0.50; E: Ag0.25Sn0.75.

maximum difference of about 250 J/mol. The three measurements performed at 530°C show almost the same values, and very good reproducibility can be observed.

Muggianu[56] and Toop[57] extrapolation models were used to calculate the enthalpy of mixing for the Ag-Sb-Sn ternary system from those of the constituent binary systems in order to compare the measured and

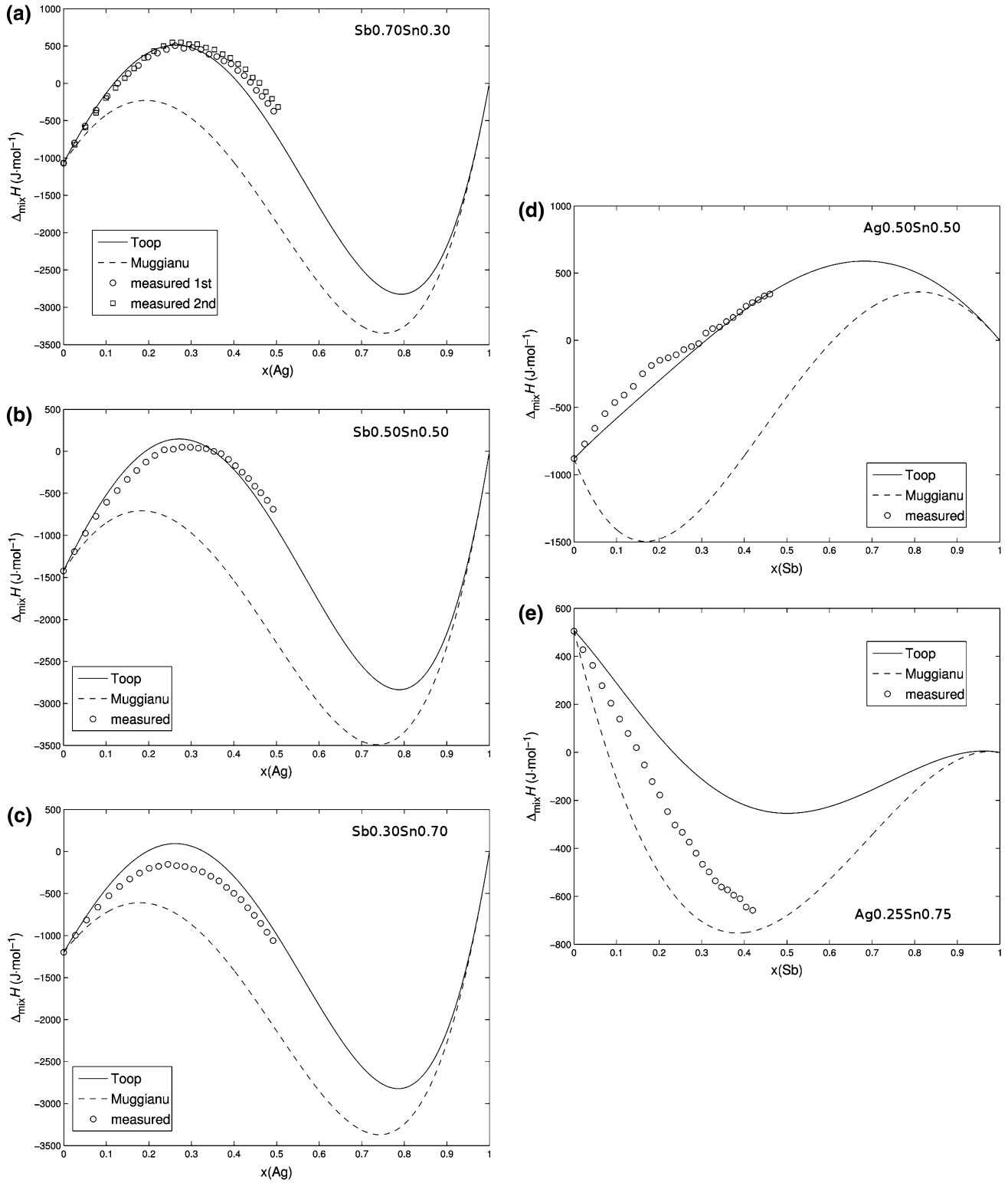

Fig. 3. Integral molar enthalpies of mixing of liquid Ag-Sb-Sn alloys at 630°C. The experimental values are presented together with those calculated by Toop and Muggianu methods. Reference state: pure liquid components. The letters refer to the measured sections (also indicated inside each figure): A: Sb0.7Sn0.3; B: Sb0.5Sn0.5; C: Sb0.3Sn0.7; D: Ag0.50Sn0.50; E: Ag0.25Sn0.75.

predicted values. With the Toop model, Ag was chosen as element A, which is treated differently from the other two elements on the basis that the mixing enthalpy curve Sb-Sn is symmetric, showing a regular solution behavior, and the curves of Ag-Sb and Ag-Sn show a similar S-shape trend. From the

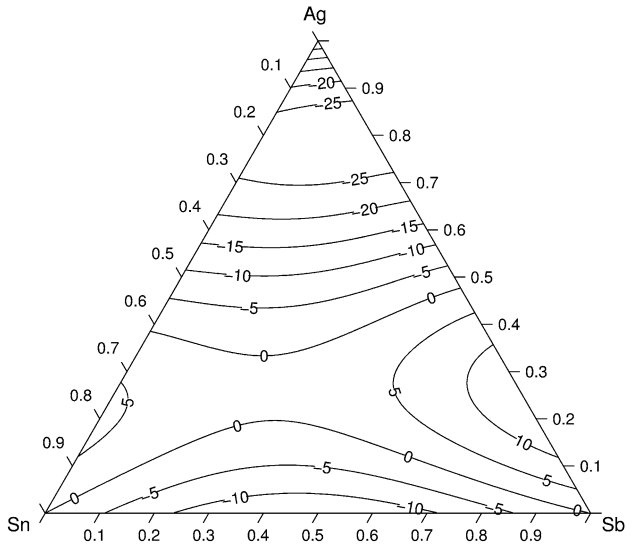

Fig. 4. Isoenthalpy curves (100 J/mol) of the ternary Ag-Sb-Sn alloys at 550°C, obtained using the Toop model (standard states: pure liquid metals).

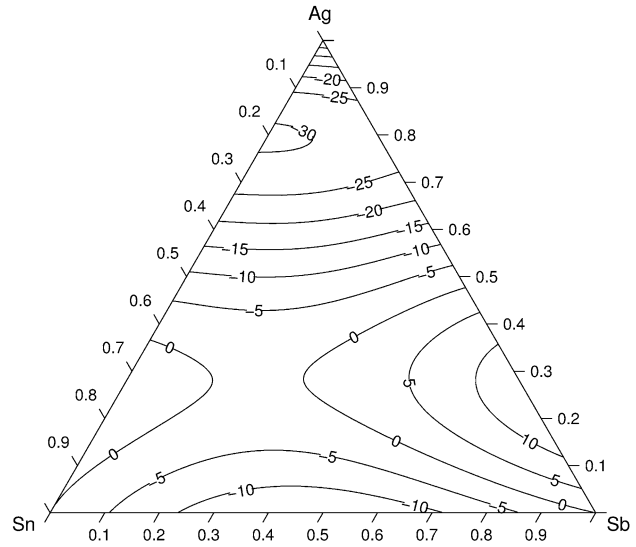

Fig. 5. Isoenthalpy curves (100 J/mol) of the ternary Ag-Sb-Sn alloys at 950°C, obtained using the Toop model (standard states: pure liquid metals).

literature data available for these two binary systems, we may observe a maximum point at the Ag-poor side, indicating a demixing tendency of the liquid alloys and a minimum point in the Ag-rich region which implies a potential compound formation behavior near these compositions, which is consistent with the binary phase diagrams.

The calculated results compared with the experimental measurements along different sections at 530°C, 600°C, and 630°C are shown in Figs. 1–3, respectively.

For sections A ($Sb_{0.7}Sn_{0.3}$), B ($Sb_{0.5}Sn_{0.5}$), and C ($Sb_{0.3}Sn_{0.7}$) in which Ag is the dropped element (Figs. 1c, 2c, 3c, 1b, 2b, 3b, 2a, and 3a), both models predict a similar S-shape trend, and the values calculated with the Toop model are much closer to the experimental values. Generally, the values calculated with the Toop model are always higher than the measured ones, and the difference between the extrapolated and measured values is small, with a maximum difference of about 200 J/mol. Thus no ternary interaction parameters are necessary in order to fit the experimental values.

Considering the measurements made when Sb pieces are dropped in Ag-Sn binary bath (section D, $Ag_{0.50}Sn_{0.50}$ and section E, $Ag_{0.25}Sn_{0.75}$, see Figs. 1d, 2d, 3d, 1e, 2e, and 3e) the two models show different predictions. Concerning section D, the Toop model as well as the measured data indicate increasing mixing enthalpy values with increasing Sb content. The curve calculated using the Toop model shows a single maximum value around 70 at.% Sb content (for which no experimental data are available), while the integral mixing enthalpy extrapolated using the Muggianu model shows an S-shape trend. Using this model, the mixing enthalpy becomes negative with increasing Sb, reaching a minimum value around 18 at.% Sb, which does not fit with the experimental results. Experimentally, we observed a peculiar systematic trend of the mixing enthalpy for all the investigated temperatures, which cannot be reasonably explained. In the composition range from 0 at.% to 30 at.% Sb we observe an irregular trend with a kink around 30 at.% Sb. Beyond this point, for T = 600°C and 630°C good agreement between the experimental and the calculated values obtained with the Toop Model may be observed. Concerning the experimental results obtained for section E, we observed a rapid decrease in the mixing enthalpy values with increasing Sb content. Moreover, we may observe a kink and a slope change at around 30 at.% Sb, which becomes more regular when the temperature changes from 530°C to 600°C and 630°C. The experimental trend lies between the two curves calculated using the Toop and Muggianu models. This experimental behavior could be explained by the possible existence of a liquid miscibility gap which extends up to compositions around 30 at.% Sb. This hypothesis is under evaluation by using CALPHAD modeling.

The isoenthalpy curves of liquid Ag-Sb-Sn alloys calculated at 550°C and 950°C using the Toop model are shown in Figs. 4 and 5. The general shape of the isoenthalpy lines are the same for the two temperatures, with a saddle point in the central part of the Gibbs triangle. At 950°C, the extrapolated values agree quite well with the experimental results obtained by Gather et al.[39] across the whole composition range. When the temperature changes from 550°C to 950°C, the enthalpy values near the saddle point change from positive to negative, in agreement with the results of Ref. 39.

The DSC analysis data obtained for the Ag-Sb-Sn samples with key selected compositions are

Table VI. Ag-Sb-Sn alloys: experimental DSC results and SEM/EDS global composition

Sample	SEM/EDS Composition			Temperature Detected on Heating (°C)		Temperature Detected on Cooling (°C)		Effects
	x_{Ag}	x_{Sb}	x_{Sn}	1st Run (1°C/min)	2nd Run (0.3°C/min)	1st Run (1°C/min)	2nd Run (0.3°C/min)	
1DSC	0.46	0.40	0.14	375	375	374	375	U_1
				440	439	433	434	Valley
				464	466	448	453	Liquidus
2DSC	0.27	0.37	0.36	229	228	228	228	U_3
				305	305			U_2
				373	374	375	374	U_1
				392	391	388	375	Valley
				434	432	397	386	Liquidus
3DSC	0.30	0.22	0.48	231	231	230	230	U_3
				308	308	300	306	U_2
				346	346	339	328	Valley
				440	442	389	408	Liquidus
4DSC	0.23	0.58	0.19	375	375	375	375	U_1
				428	428	389	395	Valley
				468	459	451	451	Liquidus
5DSC	0.17	0.29	0.54	231	231	230	229	U_3
				309	309	309	309	U_2
				325	323	313	315	Valley
				390	385	370	365	Liquidus
6DSC	0.16	0.37	0.48	228	230	228	229	U_3
				306	306	300	300	U_2
				367	366	348	346	Valley
				393	388	349	349	Liquidus

summarized in Table VI together with the compositions of the alloys obtained by SEM/EDS analysis after DSC measurements. All samples were processed twice: the first heating/cooling was performed at 1°C/min rate and the second at 0.3°/min. The temperature values obtained at different rates (1°C/min and 0.3°C/min) are reported in Table VI. Figure 6 shows the DSC curve of sample 6DSC (Table VI), while Fig. 7 displays a micrograph of sample 4DSC showing large primary crystals of $(Sb)_{ss}$ surrounded by ε phase and by a mixture of ε and β phases. Three ternary invariant reactions have been identified, and good reproducibility of the transformation temperatures obtained may be observed in Table I. The temperatures assigned in this work are in very good agreement with the literature data. The temperature observed for the U_2 invariant reaction ($L + \beta \leftrightarrow \varepsilon + Sn_3Sb_2$, 308°C) is lower than the p_6 invariant reaction temperature,[38,50,51] confirming the U-type invariant equilibrium, in agreement with Refs. 42 and 48.

According to the literature data and our measurements, a reaction scheme for the Ag-Sb-Sn system is proposed in Fig. 8. This scheme is divided by a dashed line: the upper part is in good agreement with the reaction scheme reported by Ref. 48. The part below the dashed line is proposed in order to complete the Scheil diagram. Taking into account that Sn_3Sb_2 is not stable at room temperature,[50,51] one more invariant reaction must be taken into account, connecting e_2, U_2 and U_3, and an E-type reaction, $Sn_3Sb_2 \leftrightarrow \varepsilon + \beta + (Sn)$, is here proposed.

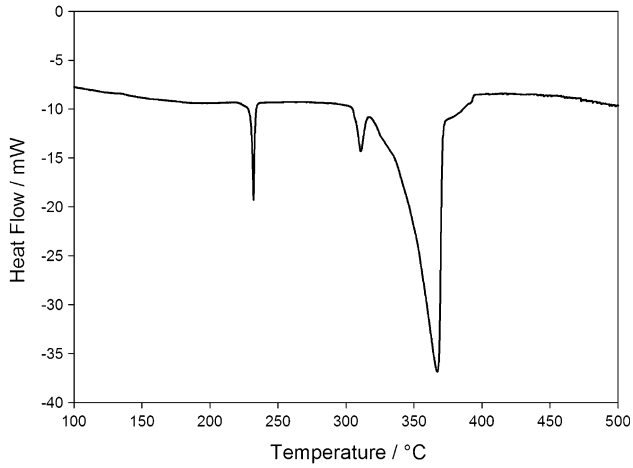

Fig. 6. DSC curve on heating (1°/min) of sample 6DSC, see Table VI.

CONCLUSIONS

A set of mixing enthalpy measurements at 530°C, 600°C, and 630°C obtained by using a high-temperature Calvet-type calorimeter is presented for the Ag-Sb-Sn ternary system. The ternary liquid alloys have been investigated along five different

sections: $Ag_{0.25}Sn_{0.75}$, $Ag_{0.50}Sn_{0.50}$, $Sb_{0.30}Sn_{0.70}$, $Sb_{0.50}Sn_{0.50}$, and $Sb_{0.70}Sn_{0.30}$. No significant temperature dependence of the mixing enthalpy could be observed in the temperature range considered.

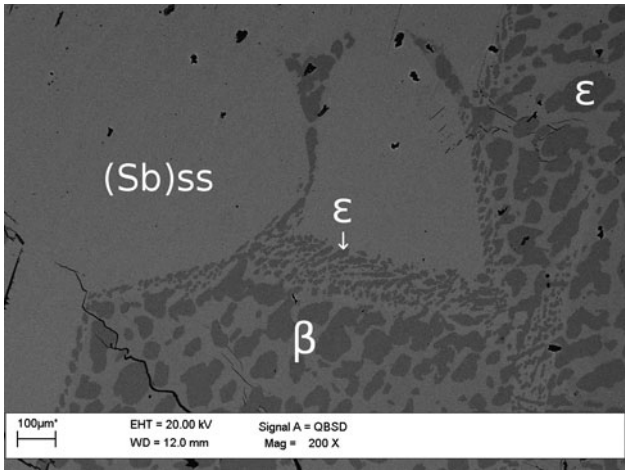

Fig. 7. SEM image (BSE mode) of sample 4DSC (see Table VI). Large primary crystals of $(Sb)_{ss}$ are surrounded by ε phase and by a mixture of ε and β phases.

The experimental data were compared with those calculated from the extrapolation methods, and generally the Toop model gives a suitable representation of the enthalpy of mixing for the liquid ternary system. Unusual behavior was observed experimentally for the addition of pure Sb to the $Sn_{0.75}Ag_{0.25}$ liquid bath, giving an indication of the possible existence of a liquid miscibility gap in the ternary system. Comparing the values of the enthalpy of mixing reported in the literature for the Ag-Sn binary system, we may observe the effect due to the Sb addition following the composition of the Ag-Sn metallic bath. The mixing enthalpy of the $Ag_{0.50}Sn_{0.50}$ alloy becomes less negative when Sb is added, while for the $Ag_{0.25}Sn_{0.75}$ liquid bath, we notice an incremental exothermicity. We should expect that this will affect the thermophysical properties, such as surface tension and wettability, and the reaction products produced at the interface during the soldering process.

DSC measurements have also been performed on samples having selected key compositions in order to identify and confirm the invariant ternary reactions present in the ternary system. No ternary intermetallic compounds were observed in the

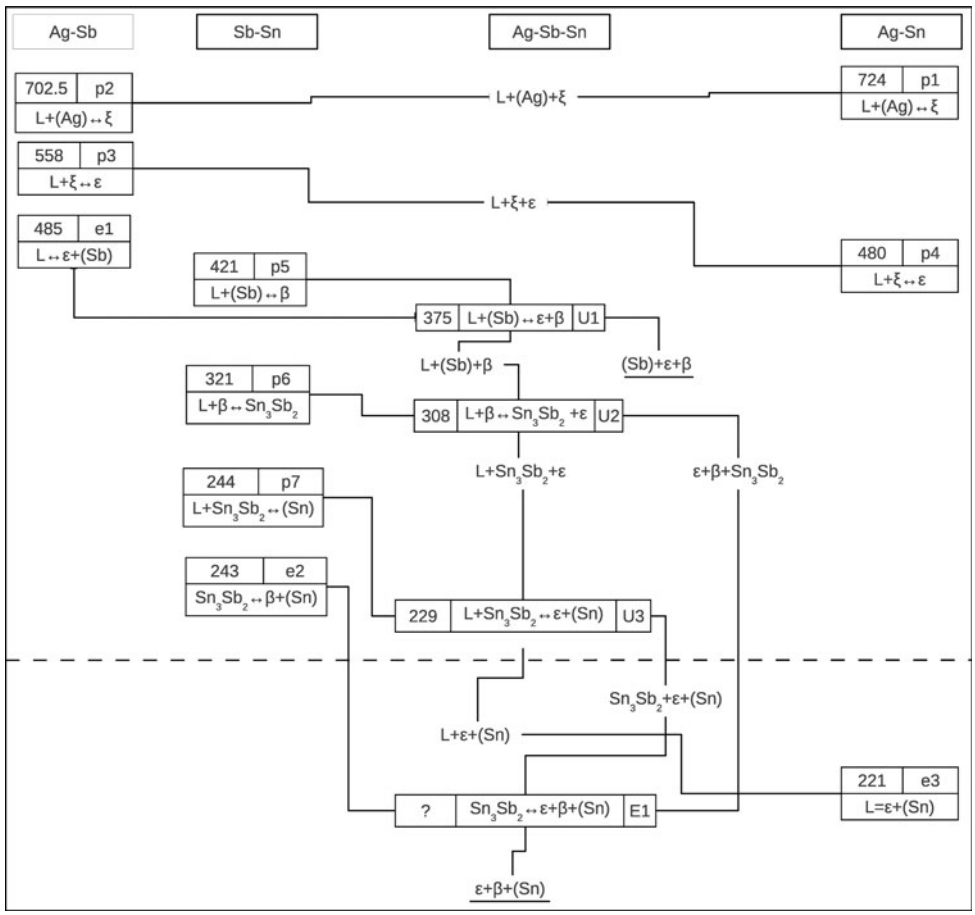

Fig. 8. Ag-Sb-Sn reaction scheme (Scheil diagram). The reported temperatures (°C) of the Ag-Sb-Sn ternary invariant reactions have been obtained during this work. The part below the dashed line is proposed to complete the reaction scheme.

Ag-Sb-Sn ternary system, in agreement with the literature information.

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