Thermochimica Acta 510 (2010) 24–31

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

The determination of the integral enthalpies of mixing of liquid Au–In–Sn alloys and the enthalpy of formation of the $Au_4In_3Sn_3$ compound

A. Watson[a,*], G. Borzone[b], N.Parodi[b], G. Cacciamani[b]

[a] *Institute for Materials Research, School of Process, Environmental and Materials Engineering, The University of Leeds, Leeds, UK*
[b] *Department of Chemistry and Industrial Chemistry, Genoa University, Via Dodecaneso 31, 16146 Genoa, Italy*

ARTICLE INFO

Article history:
Received 8 December 2009
Received in revised form 15 June 2010
Accepted 18 June 2010
Available online 30 June 2010

Keywords:
High temperature calorimetry
Alloy thermochemistry
Enthalpy of formation
Enthalpy of mixing
Lead-free solders

ABSTRACT

With a view to modelling the Au–In–Sn alloy system, the enthalpies of mixing of liquid Au–In–Sn alloys have been measured as a function of Au content by drop calorimetry at 609 °C for constant In:Sn ratios of 1:1, 1:3 and 3:1. For each of the three sections studied, the enthalpies of mixing were exothermic. In addition, the enthalpy of formation of the ternary $Au_4In_3Sn_3$ at 298 K was measured both by direct-reaction calorimetry and by tin-solution calorimetry.

1. Introduction

The drive to remove lead from electronic component manufacture has been on-going for a number of years. Lead is known to be toxic and its accumulation in the human body can result in a number of adverse health effects. This has led to legislation regarding the use of lead in electronics manufacture throughout the world, which in Europe was manifest in the WEEE and RoHS directive that came into force at the end of 2006 [1].

A major issue regarding a switch to lead-free materials is the lack of a single suitable 'drop-in' replacement for the traditional lead–tin solder. This has become the subject of study for two major European COST Actions; COST 531 and COST MP0602, the latter focussing on replacement materials for high-lead solders for high temperature applications. A major research output of both of these COST Actions is a database of thermodynamic parameters that will enable modelling of binary, ternary and higher-order systems to investigate possible solder formulations and their chemical interaction with substrate materials.

The Au–In–Sn system has been investigated as part of this research effort. This system is relevant to the lead-free soldering process, In and Sn being solder alloy components and Au either as a solder component itself or a possible substrate element. In–Sn solders are recommended for soldering to gold because they do not readily leach or dissolve the gold substrate material [2]. The aim of this contribution was to characterize the thermodynamic properties of the Au–In–Sn system as one of the limiting systems important for the understanding of contacts between lead-free In–Sn base alloys and Au containing substrates.

A careful analysis of the available literature data regarding the Au–In–Sn ternary system revealed the need for further experimental investigations of both phase equilibria and thermodynamics in order to be able to produce a reliable modelling of the system. No systematic study of the thermodynamic properties of the system has been undertaken. Isothermal and polythermal phase equilibria were investigated as part of the overall study of the system [3], and the resulting data were combined with the information presented here to give a thermodynamic modelling and assessment of this system [4].

The determination of the enthalpy of formation of the ternary compound has been carried out, primarily by direct-reaction calorimetry but in addition by tin-solution calorimetry to act as confirmation of the result. Enthalpies of mixing of the liquid phase have also been measured and are presented here.

2. Experimental

2.1. Enthalpy of formation

The metals used for enthalpy of formation determinations were indium ingot 99.999 mass %, tin 99.999 mass % and gold 99.99+ mass% nominal purity. Two alloys of selected composition were

---

* Corresponding author.
E-mail address: a.watson@leeds.ac.uk (A. Watson).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.06.018

Table 1
Samples for standard enthalpies of formation of solid Au–In–Sn alloys at 300 K. Samples 1 and 2 produced *via* direct-reaction calorimetry. Samples 3–5 prepared for solution calorimetry.

Alloy number	$-\Delta_f H^\circ$ (kJ/mol $Au_{0.4}In_{0.3}Sn_{0.3}$)	Alloy composition by Microprobe analysis at%			Thermal treatment	Phase analysis	Microprobe analysis at%		
		Au	In	Sn			Au	In	Sn
1	20.6 ± 0.5	45.0	32.0	23.0	Obtained by direct-reaction calorimetry at $T = 380\,^\circ C$	$AuIn_{1-x}Sn_x$	50.5	33.1	16.4
						>90% $Au_4In_3Sn_3$	39.9	30.2	29.9
2	23.0 ± 0.5	43.9	30.0	26.1	Obtained by direct-reaction calorimetry at $T = 375\,^\circ C$	$AuIn_{1-x}Sn_x$	50.0	34.5	15.5
						>90% $Au_4In_3Sn_3$	41.2	29.3	29.5
3		38.7	30.6	30.7	Annealed at 300 °C for 20 days	$Au_4In_3Sn_3$	39.5	28.7	31.8
						very small quantity of $AuIn_{2-x}Sn_x$	33.5	42.4	24.1
4		38.6	30.2	31.2	Annealed at 130 °C for 40 days	$AuIn_{1-x}Sn_x$	49.8	35.7	14.5
						$AuIn_{2-x}Sn_x$	33.3	47.5	19.2
						>80% $Au_4In_3Sn_3$	39.2	30.2	30.6
5		38.2	29.7	32.1	Annealed at 300 °C for 20 days	$AuIn_{1-x}Sn_x$	50.0	35.9	14.1
						$AuIn_{2-x}Sn_x$	33.1	46.6	20.3
						>90%$Au_4In_3Sn_3$	38.9	30.1	31.0

prepared directly in the direct-reaction calorimeter (as described below). In order to determine consistent thermodynamic data, samples on the $Au_4In_3Sn_3$ composition were also prepared in order to obtain uniform and well-homogenized samples to be used for the determination of the enthalpy of formation using solution calorimetry.

Three samples of about 2–3 g were prepared by melting pieces of the constituent metals in alumina crucibles in an induction furnace under an argon atmosphere. The samples were annealed at 300 °C for 20 days (Table 1, samples 3 and 5) and at 130 °C for 40 days (Table 1, sample 4) in order to reach the equilibrium state, before quenching into cold water.

2.1.1. *Direct-reaction calorimetry*

Calorimetric measurements were performed using a laboratory built high temperature drop calorimeter, a detailed description of which is reported elsewhere [5].

The calorimetric alloys were synthesised directly in the high temperature reaction calorimeter using pressed pellets of the mixed powders weighing about 0.7 g sealed in tantalum crucibles under an argon atmosphere. The samples were dropped from a room temperature thermostat (300 K) into the high temperature calorimeter (see Table 1). The preparation of the calorimetric samples starting from a mixture of fine powders guarantees a fast reaction between different elements avoiding any oxidation, and the use of sealed crucibles prevents any material loss.

Each calorimetric measurement is divided into two runs: a “reaction run” and a “reference run”; an exhaustive description of the procedure is given in [5]. To perform a measurement, after thermal equilibration, the sample is dropped from an over-standing thermostat (at $T = T_0 = 27\,^\circ C$) into the calorimeter. This is referred to as the reaction run. The heat effect is evaluated by a series of calibration runs performed by dropping specimens of known heat content (typically pieces of pure silver weighing 1.0–1.5 g). In the following we report the reaction occurring and the equations used to determine the measured heat.

In the reaction run, the heat effect Q_1 is due to the reaction:

$$x\mathrm{Au}(\mathrm{cr},T_c) + y\mathrm{In}(\mathrm{cr},T_c) + z\mathrm{Sn}(\mathrm{cr},T_c) \rightarrow \mathrm{Au}_x\mathrm{In}_y\mathrm{Sn}_z(\mathrm{cr},T_c) \qquad (1)$$

at T_c working calorimetric temperature, plus the enthalpy increment of Au, In and Sn and of the tantalum crucible.

Therefore, Q_1 for 1 mol of alloy $Au_xIn_ySn_z$ is:

$$\begin{aligned} Q_1 &= x(H_{Tc} - H_{T0})(\mathrm{Au, cr}) + y(H_{Tc} - H_{T0})(\mathrm{In, cr}) \\ &+ z(H_{Tc} - H_{T0})(\mathrm{Sn, cr}) + (m_{cruc}/180.95)(H_{Tc} - H_{T0})(\mathrm{Ta, cruc}) \qquad (2) \\ &+ \Delta_f H(\mathrm{Au}_x\mathrm{In}_y\mathrm{Sn}_z, \mathrm{cr}, T_c) \end{aligned}$$

where m_{cruc} is the mass of the tantalum crucible. In the reference run, the heat effect Q_2, is due to the enthalpy increments of the compound and of the tantalum crucible

$$\begin{aligned} Q_2 &= (H_{Tc} – H_{T0})(\mathrm{Au}_x\mathrm{In}_y\mathrm{Sn}_z, \mathrm{cr}) \\ &\quad + (m_{cruc}/180.95)(H_{Tc} - H_{T0})(\mathrm{Ta, cruc}) \qquad (3) \end{aligned}$$

By taking the difference, $(Q_1 - Q_2)$, the crucible effects cancel out. The result is the $\Delta_f H(Au_xIn_ySn_z, cr, T_c)$, corrected for the difference in the heat contents of metals and compound, that is the $\Delta_f H(Au_xIn_ySn_z, cr, T_0)$ at T_0

$$Q_1 - Q_2 = \Delta_f H(\mathrm{Au}_x\mathrm{In}_y\mathrm{Sn}_z, \mathrm{cr}, T_0)$$

The measurement errors are estimated to be ±0.3–0.5 kJ/mol of atoms in any run. The accuracy of calorimetric measurements is related to the actual processes occurring in the calorimeter, e.g. completeness of the synthesis reaction, attainment of the equilibrium state, presence/absence of side reactions, etc. To this end, the composition of the sample and the related working temperature of the calorimeter were carefully selected on the basis of the information available on the phase diagram, in order to have fast synthesis reactions.

2.1.2. *Tin-solution calorimetry*

Direct-reaction calorimetry is a powerful experimental technique for the determination of heats of formation, but for confirmation purposes, it was decided to measure the same quantity by a different but complementary technique.

The apparatus used for this work was a commercially built Setaram HT1500 high temperature calorimeter. The apparatus, which works on the Calvet principle, has been described in detail elsewhere [6]. The calorimetric cell comprises a reaction crucible which sits in tandem with a reference crucible within the calorimetric detector. The detector is a twin crown of 44 thermocouple junctions; 22 in contact with the reaction crucible and 22 in contact with the reference crucible. The useable volume of the crucible in this instrument is quite small, which limits the amount of material that can be used in the experiment significantly. This is owing to the small bore of the reaction crucible (8 mm) and the configuration of the thermocouple junctions in the thermopile. It has already been shown [6] that the sensitivity of the instrument changes with the amount of material present in the crucible, and for this reason, it is limited to approximately 750 mm^3.

The dissolution technique involves measuring the heat effect on dissolving samples of the compound and its constituent elements in an appropriate solvent in a series of experiments. Samples are dropped from room temperature (T_1) into the solvent bath (in this case of tin) within the calorimeter, which is held at a higher temperature (T_2).

$$Q_1 = x\mathrm{Au_4In_3Sn_3}(\mathrm{cr},T_1) \rightarrow 4x\mathrm{Au}(\mathrm{sol'n}T_2) + 3x\,\mathrm{In}(\mathrm{sol'n}T_2) + 3x\mathrm{Sn}(\mathrm{sol'n},T_2) \qquad (4)$$

Eq. (4) represents the dissolution and dissociation of the $\mathrm{Au_4In_3Sn_3}$ ternary compound in liquid tin giving a measurable heat effect Q_1. Three complementary experiments involving the dissolution of the pure components lead to:

$$Q_2 = \mathrm{Au}(\mathrm{cr},T_1) \rightarrow \mathrm{Au}(\mathrm{sol'n}T_2) \qquad (5)$$

$$Q_3 = \mathrm{In}(\mathrm{cr},T_1) \rightarrow \mathrm{In}(\mathrm{sol'n}T_2) \qquad (6)$$

$$Q_4 = \mathrm{Sn}(\mathrm{cr},T_1) \rightarrow \mathrm{Sn}(\mathrm{sol'n}T_2) \qquad (7)$$

The reaction defined by Eq. (7) is just the enthalpy increment of tin between the drop temperature and the bath temperature and so this particular step is not performed, the data being taken from standard tables [7].

The enthalpy of formation of the ternary compound is thus given by the sum of the heat effects for the reactions, (4)–(7), namely:

$$4Q_2 + 3Q_3 + 3Q_4 - Q_1/x = \Delta_f H(\mathrm{Au_4In_3Sn_3},\mathrm{cr},T_1) \qquad (8)$$

Eqs. (4)–(6) assume that the dissolution of the solute is to infinite dilution. In order to arrive at such a value experimentally, a series of samples are dissolved sequentially and the heats of dissolution plotted with respect to bath composition and extrapolated back to zero solute content.

The heat effects are recorded as an emf from the thermopile detector of the instrument. The emf curve is then integrated with respect to time to give the heat effect. In order to convert this integration to give the heat effect in Joules it is necessary to calibrate the instrument with material of known heat content, and for this purpose, small pieces of recrystallized alumina are used. At the beginning and the end of each run, a piece of recrystallized alumina is dropped into the solvent bath and the heat effect measured. Using standard data [7] it is then possible to calculate a calibration value that can then be used to determine the heat effects produced on dropping the samples in order to calculate the heats of dissolution.

The calorimeter was prepared by adding approximately 3.5 g of tin (purity as given in the previous section) to the reaction crucible that was then placed inside the calorimeter furnace. The reaction crucible was evacuated and back-filled with high-purity argon four times in order to minimise the oxygen partial pressure inside the calorimeter. The calorimeter furnace was then programmed to 673 K for the dissolution experiment, and once this temperature was achieved, the calorimeter was left for approximately 1 h to allow the system to equilibrate. The experimental run comprised five drops; four dissolution drops and an alumina calibration drop. Each measurement lasted in the region of 30 min, which was sufficient time for the emf output from the thermopile to return to the baseline.

2.2. Enthalpies of mixing

The thermodynamic properties of the liquid phase were determined using the same Setaram HT1500 calorimeter as used in the dissolution experiments. Enthalpies of mixing were determined at ~600 °C along lines of constant In/Sn ratios of 1/3, 1/1 and 3/1. At the beginning of each run, appropriate weighed amounts of In and Sn are placed in the bottom of the reaction crucible of the calorimeter. The crucible is inserted into the calorimeter and evacuated and back-filled with pure argon; a process that is repeated at least four times in order to minimise the oxygen partial pressure within the reaction crucible.

Because the amount of material used in the experiments has to be limited (see above), the size of the solute samples and the number of drops that can be made is relatively small using this apparatus in comparison with others that have been employed (e.g. [8]). The initial size of the solvent bath was in the region of 0.2 g (0.0018 mol) and the solvent samples approximately 0.025 g ($\sim 1.3 \times 10^{-4}$ mol).

Enthalpies of mixing are determined by measuring the heat effects (Q_i) produced on dissolving (in this case) a series of Au samples in the In/Sn solvent bath. For the first mixing drop:

$$Q_1 = x_1\mathrm{Au}(\mathrm{cr},T_1) + \mathrm{In}_y\mathrm{Sn}_z(\mathrm{sol'n},T_2) \rightarrow \mathrm{Au}_{x1}\mathrm{In}_y\mathrm{Sn}_z(\mathrm{sol'n},T_2) \qquad (9)$$

where T_1 and T_2 are the drop and solvent bath temperatures, respectively, and y and z are the moles of In and Sn in the solvent bath. For the second drop:

$$Q_2 = x_2\mathrm{Au}(\mathrm{cr},T_1) + \mathrm{Au}_{x1}\mathrm{In}_y\mathrm{Sn}_z(\mathrm{sol'n},T_2) \rightarrow \mathrm{Au}_{x1+x2}\mathrm{In}_y\mathrm{Sn}_z(\mathrm{sol'n},T_2) \qquad (10)$$

The components of the heat effect Q_i are given by:

$$Q_i = x_i(H(\mathrm{Au},\,\mathrm{cr},T_2) - H(\mathrm{Au},\,\mathrm{c},T_1)) + x_i\Delta H(\mathrm{fus},\,\mathrm{Au},T_2) + \Delta H_{\mathrm{r},i} \qquad (11)$$

where $H(\mathrm{Au, cr}, T_2)$–$H(\mathrm{Au, cr}, T_1)$ is the enthalpy increment of Au between T_1 and T_2, $\Delta H(\mathrm{fus, Au}, T_2)$ is the heat of fusion of pure Au at T_2, and $\Delta H_{\mathrm{r},i}$ is the heat effect on mixing Au(l) and the solvent bath at T_2. As the masses of the added samples are relatively small, the partial enthalpy of mixing, h_i, can be derived from:

$$hi \approx \Delta H_{\mathrm{r},i}/x_i \qquad (12)$$

The integral enthalpy of mixing can then be calculated from:

$$\Delta H_{\mathrm{mix}} = \frac{(y+z)\Delta H_{\mathrm{m,B}} \sum_i \Delta H_{\mathrm{r},i}}{y + z + \sum_i x_i} \qquad (13)$$

where y and z are the numbers of moles of In and Sn in the solvent bath, respectively, and $\Delta H_{\mathrm{m,B}}$ is the enthalpy of mixing of the binary alloy forming the solvent bath. The calculated enthalpy of mixing of the ternary liquid is thus referred to the pure liquid metal components.

In the region of 20 mixing drops were made for each system studied, and in order to minimise any shift in calibration owing to the amount of material in the crucible, calibration measurements were made throughout the experimental run. As a preliminary experiment, a reproducibility test of the SETARAM HT1500 was carried out by dropping the alumina calibration pieces into an empty crucible. Five samples were dropped in order to minimise any possible volume effect owing to the configuration of the thermopile. The calibration values determined were within 2% of each other.

3. Results and discussion

3.1. Enthalpy of formation of $\mathrm{Au_4In_3Sn_3}$

The direct-reaction measurements were made at a temperature of around 380 °C. Following the measurement, the alloyed samples were removed from the calorimeter and the composition

Table 2
Measured heats of dissolution of solid Au (at 298 K) in liquid Sn at 675 K. The calculated data are taken from [9] with the reference state of the Au changed from liquid at 675 K to fcc at 298 K to be compatible with the measurement.

Sample				
mass	moles	×(Au)	Heat Effect /J	ΔH/J/mol
0.0177	8.9863E-05	0.002986	−1.16336	−12946
0.0109	5.5339E-05	0.004816	−0.72154	−13038.5
0.0222	1.1271E-04	0.008522	−1.36866	−12143.2
0.0244	1.2388E-04	0.012564	−0.99841	−8059.58
Fitted data			Calculated data for comparison	
4 drops			ΔH (inf):	−11780.4
ΔH (inf) =	−15209.8		Ref: Au(298 K), Sn(675 K)	
Slope =	507190.408			
Std error =	1186.84258			
3 drops				
ΔH (inf):	−13574.7			
Slope:	159061.436			
Std error:	286.753191			
Solvent bath details				
Sn				
mass (g) =	3.5619			
moles =	0.0300			

and state of the samples were examined by means of microscopic analysis (optical and electron probe microanalysis). A Zeiss EVO 40 SEM (Carl Zeiss SMT Ltd., Cambridge, England) operating at 20 kV was used to determine the microstructure. This microscope is equipped with an OXFORD INCA Energy 300 which allowed chemical analysis by energy-dispersive-spectrometry (EDS). It was apparent from the microprobe analysis that there was no indication of reaction between the starting materials and the crucible. Table 1 lists the compositions of the samples following direct reaction in the calorimeter (samples 1 and 2) together with the enthalpy of formation. The enthalpy of formation at 300 K for the $Au_4In_3Sn_3$ determined by direct calorimetry is thus $\Delta_f H^\circ = -21.0 \pm 1.0$ kJ/mol atoms.

Table 1 also shows the compositions of the samples prepared for the dissolution experiments. The annealed samples characterized by SEM analysis showed a uniform distribution of the phases. Analyses were made a several different locations within each of the samples, and it was noted that there was very little variation in composition, suggesting that the equilibrium state had been reached. The presence of primary crystals of $AuIn_{1-x}Sn_x$ in samples 4 and 5 is an indication that the $Au_4Sn_3In_3$ phase melts incongruently as already stated [3]. As the phase constitution of alloy three would seem to contain the highest proportion of the 4:3:3 phase, samples were taken from this alloy for use in the dissolution experiments.

Tables 2 and 3 show the calorimetric results for the dissolution of Au and the 4:3:3 compound in liquid Sn, respectively. The data are presented in the form of the heat effects resulting from dropping the solid sample from room temperature (298 K) into the liquid Sn bath held at 675 K and its subsequent dissolution. Fig. 1 shows the heat values plotted with respect to the bath composition. It can see that the heat effects of the first three drops lie approximately on the same line, with the fourth drop at a less negative value than might be expected. A least squares fit of the first three drops and of all four drops are also shown, together with the assessed value taken from [9], which has been corrected to the same reference state as the measured data. The values of the enthalpy of dissolution to infinite dilution calculated using three and four drops appear to be more negative than the assessed value. There is no obvious reason for this, but it was decided to use that calculated using the least squares fit of the first three drops in the subsequent calculation of the enthalpy of formation of the 4:3:3 compound.

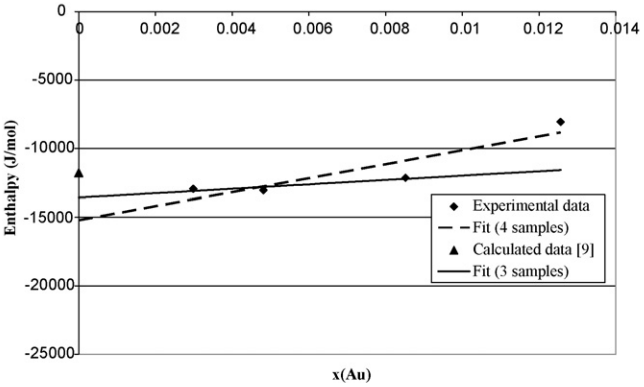

Fig. 1. Variation of the enthalpy of dissolution of Au in liquid Sn at 675 K (Ref: Au(fcc, 298 K), Sn(liquid, 675 K)).

Table 3
Calculation of the enthalpy of formation of the $Au_4In_3Sn_3$ compound. The Heat effects listed refer to the dissolution of solid at 298 K in liquid Sn at 675 K and are given with standard error. The value given for In comes from the enthalpy of solution at infinite dilution given by Kleppa [10] with an appropriate correction for the change of reference state in order to correspond to the Au measurement. The value for Sn (enthalpy increment) comes from the SGTE Unary database, v4.4 [7].

	Heat effect (ΔH J/mol)	Standard error	Cumulative error	$H_{675}-H_{298}$ (J/mol)	ΔH_{fus} (J/mol)	ΔH_{sol} (J/mol)	
Au	−13,575	286.75	114.70	9870.97	12,552	−35997	(Measured Table 2)
In	13,316	13.26	3.98	13,903		−587	[10]
Sn	17,858			17,858			[7]
Compound	27,660	265.86	265.86				
$\Delta_f H$	−23,738	J/mol atoms	384.54				
	−23.74	kJ/mol atoms	0.38				

Table 4
Heat effects and integral enthalpies of mixing at 882.6 K along the section In:Sn 1:3 (ref: Au(l), $In_{0.25}Sn_{0.75}$(l)).

			Alloy composition (molar fraction)					Heat effect (Q_n /J)			Integral ΔH mix (J/mol)		
Sample	Mass/g	Moles ($\times 10^{-3}$)	Sn	In	Au	Total moles ($\times 10^{-3}$)	Calibration value (J/mV s)	Cal1	Cal2	Mean	Cal1	Cal2	Mean
Al_2O_3 (1)	0.0084	0.0824					0.009629						
Au (1)	0.0333	0.1690	0.6833	0.2280	0.0887	1.9061		−5.84	−6.21	−6.03	−3063.8	−3258.3	−3161.1
Au (2)	0.0272	0.1381	0.6372	0.2126	0.1502	2.0442		−4.78	−5.09	−4.94	−5197.5	−5529.4	−5363.5
Au (3)	0.0380	0.1929	0.5822	0.1943	0.2235	2.2370		−6.72	−7.16	−6.94	−7753.8	−8255.0	−8004.4
Au (4)	0.0286	0.1452	0.5467	0.1824	0.2708	2.3822		−4.38	−4.49	−4.43	−9121.2	−9634.9	−9378.0
Au (5)	0.0324	0.1645	0.5114	0.1707	0.3179	2.5467		−4.85	−4.93	−4.89	−10437.9	−10949.0	−10693.5
Al_2O_3 (2)	0.0049	0.0481					0.012917						
Al_2O_3 (3)	0.0084	0.0824					0.008399						
Au (6)	0.0401	0.2036	0.4736	0.1580	0.3684	2.7502		−5.22	−5.17	−5.20	−11563.2	−12019.9	−11791.6
Au (7)	0.0312	0.1584	0.4478	0.1494	0.4028	2.9086		−4.06	−4.03	−4.05	−12330.6	−12750.3	−12540.4
Au (8)	0.0277	0.1406	0.4272	0.1425	0.4303	3.0492		−3.36	−3.31	−3.34	−12864.9	−13247.6	−13056.3
Au (9)	0.0257	0.1305	0.4096	0.1367	0.4537	3.1797		−3.22	−3.16	−3.19	−13350.8	−13697.0	−13523.9
Au (10)	0.0246	0.1249	0.3941	0.1315	0.4743	3.3046		−2.37	−2.26	−2.31	−13562.5	−13864.3	−13713.4
Au (11)	0.0327	0.1660	0.3753	0.1252	0.4995	3.4705		−2.94	−2.79	−2.87	−13762.0	−14004.3	−13883.1
Al_2O_3 (4)	0.0049	0.0481					0.009160						
Al_2O_3 (5)	0.0049	0.0481					0.008990						
Au (12)	0.0317	0.1609	0.3587	0.1197	0.5216	3.6315		−2.70	−2.81	−2.76	−13896.6	−14157.1	−14026.9
Au (13)	0.0241	0.1223	0.3470	0.1158	0.5372	3.7538		−2.01	−2.09	−2.05	−13979.1	−14253.1	−14116.1
Au (14)	0.0230	0.1168	0.3365	0.1123	0.5512	3.8705		−1.28	−1.39	−1.33	−13887.0	−14182.7	−14034.8
Au (15)	0.0244	0.1239	0.3261	0.1088	0.5651	3.9944		−1.53	−1.64	−1.59	−13839.1	−14153.9	−13996.5
Au (16)	0.0240	0.1218	0.3164	0.1056	0.5780	4.1162		−1.71	−1.81	−1.76	−13845.4	−14175.7	−14010.6
Al_2O_3 (6)	0.0084	0.0824					0.008471						

Bath starting composition: 0.0499 g In, 0.1546 g Sn = 1.3025E−3 mol Sn; 4.346E−04 mol In.

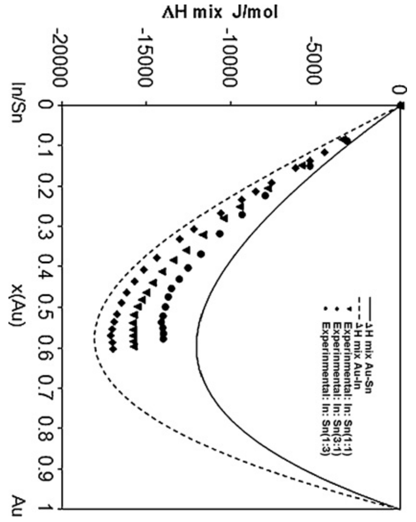

Fig. 2. Experimental integral enthalpies of mixing of ternary Au–In–Sn liquid alloys plotted with respect to Au content at In:Sn ratios of 1:1, 3:1 and 1:3. Included are assessed enthalpies of mixing of binary Au–In and Au–Sn alloys at 882.6 K, taken from the COST 531 thermodynamic database [2007Kro]. Reference states are Au(liquid) and In:Sn (liquid alloy).

A series of experiments were also conducted for the dissolution of In in liquid Sn, but the results were poor in that they showed little consistency with each other. This may be due to some degree melting of the In sample (its melting point being below the temperature of the solvent bath) taking place before it comes into the contact with the Sn bath leading to a large scatter in the resulting heat effects measured. For the purposes of this work, the enthalpy of dissolution of In in liquid Sn was taken from [10]. The uncertainty in the measurement was calculated from the weighted sum of the standard errors for the Au and In drops, however, the resulting uncertainly value would seem to be optimistic. Nevertheless, the enthalpy of formation determined by tin-solution calorimetry is in good agreement with the value from the direct reaction work, given above, even if the latter value is probably the more reliable of the two.

The measured heat effect on dissolving solid Au from 298 K into liquid Sn at 675 K has been resolved into its component parts and given in Table 3. It's interesting to note the big difference between the enthalpy of dissolution of the Au and that for In given in [10]. This has been discussed in [9] in relation to the enthalpy of dissolution of other noble metals in tin, such as Cu and Ag, Au being much more electronegative than the other two metals and exhibiting a more negative enthalpy of dissolution.

3.2. Enthalpies of mixing of Au–In–Sn liquid alloys

Tables 4–6 show the resulting heat effects of successive drops of Au into In/Sn baths with ratios 1:3, 1:1 and 3:1, respectively. It has already been stated that it was necessary to drop calibration pieces throughout each run. As each run could last for a number of days it was decided to calibrate at the beginning and end of each session; a number of sessions making a run. The calibrations are shown in the tables as Al_2O_3(*). The heat effects were then calculated using three calibrations values; using the calibration drop determined from the first calibration drop for the session (Cal1), using the calibration determined from the calibration drop at the end of the session (Cal2) and thirdly, using a mean of the two calibration values. The integral enthalpies of mixing at 882.6 K were then derived using Eq. (13) and are listed in the respective tables. The mean values of the enthalpies of mixing are plotted in Fig. 2 together with the assessed enthalpies of mixing for the liquid phase for the Au–In and Au–Sn binary systems, taken from the COST 531 thermodynamic database [11]. It can be seen that the ternary enthalpies of mixing lie comfortably between the enthalpy of mixing curves of the two Au containing binaries indicating that only a modest ternary interac-

Table 5

Heat effects and integral enthalpies of mixing at 882.6 K along the section In:Sn 1:1 (ref: Au(l), $In_{0.5}Sn_{0.5}$(l)).

			Alloy composition					Heat effect (Q_n /J)			Integral ΔH mix (J/mol)		
Sample	Mass	Moles ($\times 10^{-3}$)	Sn	In	Au	Total moles ($\times 10^{-3}$)	Calibration value (J/mV s)	Cal1	Cal2	Mean	Cal1	Cal2	Mean
In	0.1057	0.9206					0.042641						
Au (1)	0.0330	0.1675	0.4559	0.4604	0.0838	1.9996		−6.95	−6.78	−6.86	−3475.0	−3391.1	−3433.1
Au (2)	0.0297	0.1508	0.4239	0.4281	0.1480	2.1504		−5.73	−5.61	−5.67	−5893.7	−5763.9	−5828.8
Au (3)	0.0301	0.1528	0.3958	0.3997	0.2045	2.3032		−5.55	−5.46	−5.50	−7912.2	−7750.2	−7831.2
Al_2O_3 (1)	0.0204	0.2001					0.039444						
Al_2O_3 (2)	0.0205	0.2011					0.037123						
Au (4)	0.0277	0.1406	0.3730	0.3767	0.2503	2.4438		−5.18	−5.13	−5.15	−9575.3	−9402.4	−9488.8
Au (5)	0.0190	0.0964	0.3588	0.3624	0.2788	2.5403		−3.38	−3.35	−3.36	−10540.6	−10363.8	−10452.2
Au (6)	0.0301	0.1528	0.3385	0.3418	0.3197	2.6930		−4.87	−4.85	−4.86	−11752.3	−11576.9	−11664.6
Au (7)	0.0318	0.1614	0.3193	0.3225	0.3582	2.8545		−4.67	−4.66	−4.67	−12723.0	−12555.7	−12639.4
Au (8)	0.0223	0.1132	0.3072	0.3102	0.3826	2.9677		−3.67	−3.69	−3.68	−13474.8	−13318.7	−13396.7
Au (9)	0.0282	0.1431	0.2930	0.2959	0.4110	3.1108		−4.15	−3.81	−3.98	−14189.9	−13930.3	−14060.1
Al_2O_3 (3)	0.0265	0.2599					0.035627						
Al_2O_3 (4)	0.0049	0.0481					0.010355						
Au (10)	0.0302	0.1533	0.2793	0.2820	0.4387	3.2641		−4.15	−3.81	−3.98	−14795.9	−14443.0	−14619.4
Au (11)	0.0289	0.1467	0.2673	0.2699	0.4628	3.4108		−3.79	−3.05	−3.42	−15270.2	−14716.1	−14993.1
Au (12)	0.0232	0.1178	0.2583	0.2609	0.4808	3.5286		−3.03	−2.40	−2.72	−15618.3	−14906.0	−15262.2
Au (13)	0.0236	0.1198	0.2498	0.2523	0.4978	3.6484		−3.07	−2.42	−2.74	−15946.8	−15078.5	−15512.7
Au (14)	0.0304	0.1543	0.2397	0.2421	0.5182	3.8027		−3.82	−2.69	−3.25	−16304.5	−15173.5	−15739.0
Al_2O_3 (5)	0.0084	0.0824					0.032991						
Al_2O_3 (6)	0.0083	0.0814					0.033244						
Au (15)	0.0328	0.1665	0.2297	0.2319	0.5384	3.9692		−2.93	−2.77	−2.85	−16359.5	−15236.0	−15797.8
Au (16)	0.0292	0.1482	0.2214	0.2236	0.5550	4.1174		−2.35	−2.18	−2.26	−16340.2	−15217.2	−15778.7
Au (17)	0.0280	0.1421	0.2140	0.2161	0.5699	4.2595		−2.33	−2.18	−2.25	−16342.0	−15221.1	−15781.5
Au (18)	0.0285	0.1447	0.2070	0.2090	0.5840	4.4042		−2.30	−2.14	−2.22	−16327.0	−15206.6	−15766.8
Au (19)	0.0273	0.1386	0.2007	0.2026	0.5967	4.5428		−2.16	−2.00	−2.08	−16304.2	−15183.4	−15743.8
Au (20)	0.0226	0.1147	0.1957	0.1977	0.6066	4.6575		−1.97	−1.85	−1.91	−16324.9	−15207.3	−15766.1
Al_2O_3 (7)	0.0051	0.0500					0.036249						

Bath starting composition: 0.1057 g In, 0.1082 g Sn = 9.115E−4 mol Sn; 9.206E−04 mol In. For this run, the first calibration piece was In.

Table 6

Heat effects and integral enthalpies of mixing at 882.6 K along the section In:Sn 3:1 (ref: Au(l), $In_{0.75}Sn_{0.25}$(l)).

			Alloy composition					Heat effect (Q_n/J)			Integral ΔH mix (J/mol)		
Sample	Mass	Moles ($\times 10^{-3}$)	Sn	In	Au	Total moles ($\times 10^{-3}$)	Calibration value (J/mV s)	Cal1	Cal2	Mean	Cal1	Cal2	Mean
Al_2O_3 (1)	0.0030	0.0294					0.009233						
Au (1)	0.0303	0.1538	0.2334	0.6815	0.0851	1.8083		−5.70	−5.85	−5.78	−3152.9	−3235.3	−3194.1
Au (2)	0.0123	0.0624	0.2256	0.6588	0.1156	1.8707		−2.55	−2.63	−2.59	−4408.8	−4534.1	−4471.4
Au (3)	0.0089	0.0452	0.2203	0.6432	0.1364	1.9159		−1.83	−1.89	−1.86	−5261.3	−5415.4	−5338.3
Au (4)	0.0080	0.0406	0.2157	0.6299	0.1544	1.9565		−1.84	−1.91	−1.88	−6091.8	−6281.2	−6186.5
Au (5)	0.0176	0.0893	0.2063	0.6024	0.1913	2.0458		−3.43	−3.53	−3.48	−7500.5	−7730.0	−7615.2
Au (6)	0.0111	0.0563	0.2008	0.5862	0.2130	2.1022		−2.35	−2.43	−2.39	−8415.0	−8677.5	−8546.2
Au (7)	0.0110	0.0558	0.1956	0.5711	0.2333	2.1580		−2.23	−2.30	−2.27	−9231.2	−9520.1	−9375.6
Al_2O_3 (2)	0.0026	0.0255					0.010232						
Al_2O_3 (3)	0.0029	0.0284					0.010239						
Au (8)	0.0195	0.0990	0.1870	0.5460	0.2670	2.2570		−3.72	−3.68	−3.70	−10475.8	−10733.6	−10604.7
Au (9)	0.0249	0.1264	0.1771	0.5171	0.3058	2.3834		−5.11	−5.04	−5.08	−12065.3	−12280.5	−12172.9
Au (10)	0.0173	0.0878	0.1708	0.4987	0.3305	2.4712		−3.16	−3.13	−3.14	−12914.9	−13110.2	−13012.6
Au (11)	0.0364	0.1848	0.1589	0.4640	0.3771	2.6560		−6.02	−5.98	−6.00	−14282.3	−14450.4	−14366.4
Au (12)	0.0259	0.1315	0.1514	0.4421	0.4065	2.7875		−4.04	−4.02	−4.03	−15057.5	−15212.2	−15134.9
Au (13)	0.0283	0.1437	0.1440	0.4205	0.4356	2.9311		−3.78	−3.79	−3.79	−15609.9	−15760.9	−15685.4
Au (14)	0.0294	0.1492	0.1370	0.4001	0.4629	3.0803		−3.77	−3.79	−3.78	−16078.9	−16228.7	−16153.8
Al_2O_3 (4)	0.0038	0.0373					0.009786						
Al_2O_3 (5)	0.0048	0.0471					0.009089						
Au (15)	0.0300	0.1523	0.1306	0.3812	0.4882	3.2326		−3.42	−3.50	−3.46	−16378.5	−16547.3	−16462.9
Au (16)	0.0376	0.1909	0.1233	0.3600	0.5167	3.4235		−3.99	−4.12	−4.05	−16630.1	−16828.9	−16729.5
Au (17)	0.0269	0.1365	0.1186	0.3462	0.5353	3.5600		−2.81	−2.91	−2.86	−16781.4	−17000.8	−16891.1
Au (18)	0.0292	0.1482	0.1138	0.3323	0.5538	3.7083		−2.87	−3.00	−2.93	−16884.3	−17129.1	−17006.7
Au (19)	0.0268	0.1360	0.1098	0.3206	0.5696	3.8443		−2.59	−2.71	−2.65	−16959.7	−17227.4	−17093.6
Au (20)	0.0316	0.1604	0.1054	0.3077	0.5869	4.0047		−2.22	−2.45	−2.33	−16835.2	−17147.9	−16991.6
Au (21)	0.0317	0.1609	0.1013	0.2958	0.6028	4.1656		−2.52	−2.71	−2.61	−16789.0	−17136.7	−16962.8
Al_2O_3 (6)	0.0083	0.0814					0.008202						

Bath starting composition: 0.1514 g In, 0.0501 g Sn = 4.221E−4 mol Sn; 1.2324E−03 mol In.

tion parameter is required to successfully model the ternary liquid phase [4]. It is not meant to imply in this figure that the enthalpies of mixing of the binary In–Sn system are zero, but only to illustrate that the effect of dissolving Au in liquid In–Sn alloys lies in between the 'limiting' curves representing the dissolution of Au into pure In and pure Sn liquids. It should also be stressed that the reference states for the ternary data plotted in Fig. 2 are pure Au(l) and the respective In–Sn liquid alloys.

4. Conclusions

Two different calorimetric techniques have been used successfully to investigate the thermodynamic properties of the Au–In–Sn ternary system, namely the enthalpy of formation of the 4:3:3 ternary compound and the ternary enthalpies of mixing of the liquid phase. These data have been used in a *Calphad* modelling of the system that has been published elsewhere.

Acknowledgements

This work has been carried out in the framework of COST Action 531 "Lead-Free Solder Materials" and COST MP0602 "HISOLD" supported by COST-ESF, which is acknowledged with thanks. The work was part funded through UK EPSRC Platform Grant (GR/R95798) "Metallurgy at the Interface".

References

[1] Official Journal of the European Union, p. L 37/19–L 37/23, 13.2.2003.
[2] C.F. Coombs, Printed Circuits Handbook, 5th edn., McGraw-Hill, New York, 2001.
[3] G. Borzone, N. Parodi, G. Cacciamani, A. Watson, Phase equilibria in the Au–In–Sn ternary system, CALPHAD 33 (1) (2009) 17–22.
[4] G. Cacciamani, G. Borzone, A. Watson, Thermodynamic modelling and assessment of the Au–In–Sn system, CALPHAD 33 (1) (2009) 100–108.
[5] G. Cacciamani, G. Borzone, R. Ferro, On a simple high temperature direct reaction calorimeter, J. Alloys Compd. 220 (1995) 106–110.
[6] A. Watson, F.H. Hayes, Enthalpies of formation of solid Ni–Cr & Ni–V alloys by direct reaction calorimetry, J. Alloys Compd. 220 (1995) 94–100.
[7] A.T. Dinsdale, SGTE data for pure elements", CALPHAD 15 (4) (1991) 317–425 (n.b. version 4.4 of the database was used in this work).
[8] C Luef, A. Paul, H. Flandorfer, A. Kodentsov, H. Ipser, Enthalpies of mixing of metallic systems relevant for lead-free soldering: Ag–Pd and Ag–Pd–Sn, J. Alloys Compd. 391 (2005) 67–76.
[9] A. Yassin, R. Castanet, Enthalpies of dissolution of elements in liquid tin I. Copper, silver and gold and rare earth metals, J. Alloys Compd. 307 (191–198) (2000).
[10] O.J. Kleppa, A calorimetric investigation of some binary and ternary liquid alloys rich in tin, J. Phys. Chem. 60 (7) (1956) 842–846.
[11] A. Kroupa, A.T. Dinsdale, A. Watson, J. Vrestal, J. Vizdal, A. Zemanova, The COST 531 lead-free solders thermodynamic database, JOM 59 (7) (2007) 20–25.