



# The determination of the integral enthalpies of mixing of liquid Au–In–Sn alloys and the enthalpy of formation of the Au<sub>4</sub>In<sub>3</sub>Sn<sub>3</sub> compound

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## 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<sub>4</sub>In<sub>3</sub>Sn<sub>3</sub> at 298 K was measured both by direct-reaction calorimetry and by tin-solution calorimetry.

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## 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

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**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 $\text{Au}_{0.4}\text{In}_{0.3}\text{Sn}_{0.3}$ )	Alloy composition by Microprobe analysis at%			Thermal treatment	Phase analysis	Microprobe analysis at%		
		Au	In	Sn			Au	In	Sn
1	$20.6 \pm 0.5$	45.0	32.0	23.0	Obtained by direct-reaction calorimetry at $T = 380^\circ\text{C}$	$\text{AuIn}_{1-x}\text{Sn}_x$	50.5	33.1	16.4
2	$23.0 \pm 0.5$	43.9	30.0	26.1	Obtained by direct-reaction calorimetry at $T = 375^\circ\text{C}$	$>90\% \text{Au}_4\text{In}_3\text{Sn}_3$ $\text{AuIn}_{1-x}\text{Sn}_x$	39.9 50.0	30.2 34.5	29.9 15.5
3		38.7	30.6	30.7	Annealed at $300^\circ\text{C}$ for 20 days	$>90\% \text{Au}_4\text{In}_3\text{Sn}_3$ $\text{Au}_4\text{In}_3\text{Sn}_3$ very small quantity of $\text{AuIn}_{2-x}\text{Sn}_x$	41.2 39.5 33.5	29.3 28.7 42.4	29.5 31.8 24.1
4		38.6	30.2	31.2	Annealed at $130^\circ\text{C}$ for 40 days	$\text{AuIn}_{1-x}\text{Sn}_x$ $\text{AuIn}_{2-x}\text{Sn}_x$ $>80\% \text{Au}_4\text{In}_3\text{Sn}_3$	49.8 33.3 39.2	35.7 47.5 30.2	14.5 19.2 30.6
5		38.2	29.7	32.1	Annealed at $300^\circ\text{C}$ for 20 days	$\text{AuIn}_{1-x}\text{Sn}_x$ $\text{AuIn}_{2-x}\text{Sn}_x$ $>90\% \text{Au}_4\text{In}_3\text{Sn}_3$	50.0 33.1 38.9	35.9 46.6 30.1	14.1 20.3 31.0

prepared directly in the direct-reaction calorimeter (as described below). In order to determine consistent thermodynamic data, samples on the  $\text{Au}_4\text{In}_3\text{Sn}_3$  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  $300^\circ\text{C}$  for 20 days (Table 1, samples 3 and 5) and at  $130^\circ\text{C}$  for 40 days (Table 1, sample 4) in order to reach the equilibrium state, before quenching into cold water.

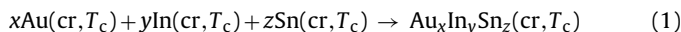
### 2.1.1. Direct-reaction calorimetry

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  $T = T_0 = 27^\circ\text{C}$ ) 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:



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  $\text{Au}_x\text{In}_y\text{Sn}_z$  is:

$$Q_1 = x(H_{T_c} - H_{T_0})(\text{Au}, \text{cr}) + y(H_{T_c} - H_{T_0})(\text{In}, \text{cr}) + z(H_{T_c} - H_{T_0})(\text{Sn}, \text{cr}) + (m_{\text{cruc}}/180.95)(H_{T_c} - H_{T_0})(\text{Ta}, \text{cruc}) + \Delta_f H(\text{Au}_x\text{In}_y\text{Sn}_z, \text{cr}, T_c) \quad (2)$$

where  $m_{\text{cruc}}$  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

$$Q_2 = (H_{T_c} - H_{T_0})(\text{Au}_x\text{In}_y\text{Sn}_z, \text{cr}) + (m_{\text{cruc}}/180.95)(H_{T_c} - H_{T_0})(\text{Ta}, \text{cruc}) \quad (3)$$

By taking the difference,  $(Q_1 - Q_2)$ , the crucible effects cancel out. The result is the  $\Delta_f H(\text{Au}_x\text{In}_y\text{Sn}_z, \text{cr}, T_c)$ , corrected for the difference in the heat contents of metals and compound, that is the  $\Delta_f H(\text{Au}_x\text{In}_y\text{Sn}_z, \text{cr}, T_0)$  at  $T_0$

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

The measurement errors are estimated to be  $\pm 0.3$ – $0.5$  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

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