



## Thermodynamic investigation of the Pb – Sb system

S. Hassam<sup>a,\*</sup>, D. Boa<sup>b</sup>, Y. Fouque<sup>a</sup>, K.P. Kotchi<sup>b</sup>, J. Rogez<sup>a</sup>

<sup>a</sup> Institut Matériaux Microélectronique Nanosciences de Provence (IM2NP), UMR 6242 CNRS, Université Paul Cézanne, Provence et Sud Toulon-Var, Avenue Escadrille Normandie-Niémien, 13397 Marseille Cedex 20, France

<sup>b</sup> Laboratoire de Thermodynamique et de Physico-Chimie du Milieu, Université d'Abobo- Adjamé, UFR – SFA, 02 BP 801 Abidjan 02, Côte d'Ivoire

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### ABSTRACT

The enthalpies of mixing of lead – antimony alloys were determined at 973 K in the range  $0.2 < X_{Sb} < 0.6$  by direct liquid–liquid reaction calorimetry (DLLRC). The results are compared with data of the literature. The mixing enthalpies in the Pb – Sb liquid phase are weakly negative over the entire investigated concentration range with a minimum at  $\Delta_{mix}H_m = -70 \text{ J mol}^{-1}$  at  $X_{Sb} = 0.4$ . In addition, the Pb – Sb phase diagram on the Pb-rich side was revised using differential scanning calorimetry (DSC). The coordinates of the eutectic point have been ensured. An optimization of the binary Pb – Sb system was finally performed. The calculated phase diagram and thermodynamic functions agree well with experimental data.

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### 1. Introduction

The Pb – Sb system is a simple eutectic formed by two solid phases, fcc Pb and rhombohedral Sb, and a liquid phase. The liquidus has been determined by several scientists and their data are in good agreement [1–3]. The solidus and solvus in the Pb-rich region are also well established [4,5]. Experimental data of Pb – Sb system were already critically evaluated by Ashtakala et al. [6]. The calculated phase diagram is in good agreement with the selected experimental data. The calculated eutectic composition and temperature are 17.5 at.% Sb and 524.85 K, respectively. The maximum solubilities of Sb in Pb and of Pb in Sb are respectively 5.8 and 1.9 at.%. Taskinen and Teppo [7] and Lee et al. [8] carried out the thermodynamic modelling and the calculation of the phase diagram using the Calphad method [9]. Based on their own experimental data and the literature, Othani et al. [10] have published another thermodynamic description of the Pb – Sb system.

Thermodynamic activities in liquid alloys have been determined by the e.m.f. method [3,11–16]. These measurements agree well within the experimental uncertainty and are reviewed by Hultgren et al. [17]. The activity values are deviating only slightly from Raoult's law.

The enthalpies of formation of the fcc Pb solid solution were measured by Diller et al. [18] at 525 K by solution calorimetry.

The enthalpy of mixing in liquid phase has been measured calorimetrically by Kawakami at 1073 K [19], Wittig and Gehring at 973 K [20], Yazawa et al. at 945 K [21], Badawi at 950 K [22] and Badawi et al. at 907 K [23]. The results are largely scattered close to zero. The recent calorimetric results of Azzaoui et al. at 892 K [24], disagree with those of Wittig and Gehring [20] and Yazawa et al. [21]. The mixing enthalpies evaluated by Moser et al. [3] diverge notably from the previous authors. In order to attempt to solve these disagreements, new calorimetric measurements have been carried out at 973 K using a liquid–liquid direct reaction device. The binary phase diagram was also reinvestigated in the range  $0.07 \leq X_{Sb} \leq 0.40$  by differential scanning calorimetry. The eutectic composition and temperature were determined. Combining the new results with experimental data available in the literature the binary system has been reoptimized with the Thermo-Calc code [25].

### 2. Experimental procedures

#### 2.1. Enthalpy of mixing by high-temperature calorimetry

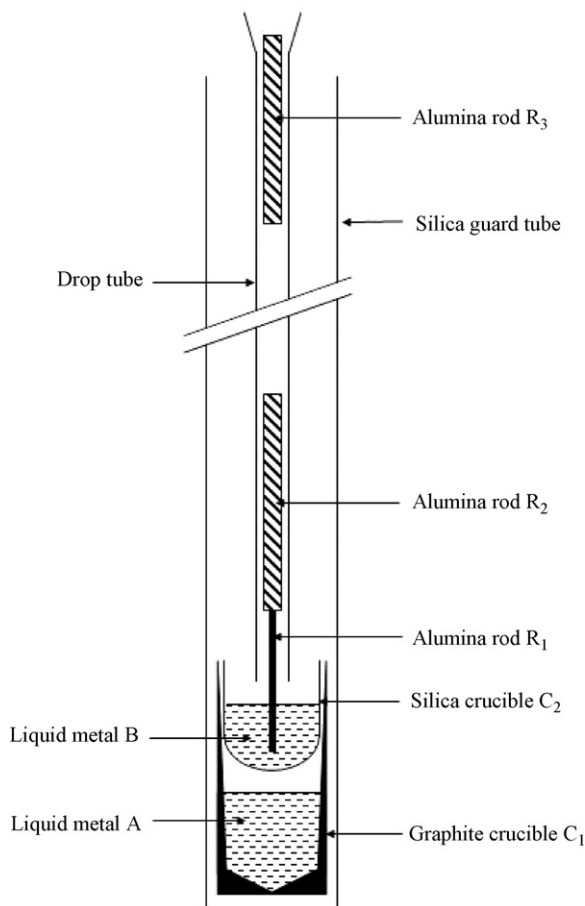
The enthalpies of mixing of the Pb – Sb liquid alloys were determined at 973 K using a Tian-Calvet high-temperature microcalorimeter described elsewhere [26–28]. The purities of elements purchased from Alfa Aesar GmbH & Co. KG are respectively Pb(5N) and Sb(6N). All experiments were performed in high-purity argon (impurities < 5.5 vpm).

\* Corresponding author.

E-mail address: [j.rogez@univ-cezanne.fr](mailto:j.rogez@univ-cezanne.fr) (S. Hassam).

**Table 1**  
Experimental integral enthalpy of mixing in Pb – Sb liquid at 973 K.

$X_{Sb}$	$\Delta_{mix}H_m$ (J mol <sup>-1</sup> )
0.2030	-51.5
0.2175	-42.9
0.2983	-64.0
0.4500	-68.9
0.5950	-51.2
0.5950	-51.1

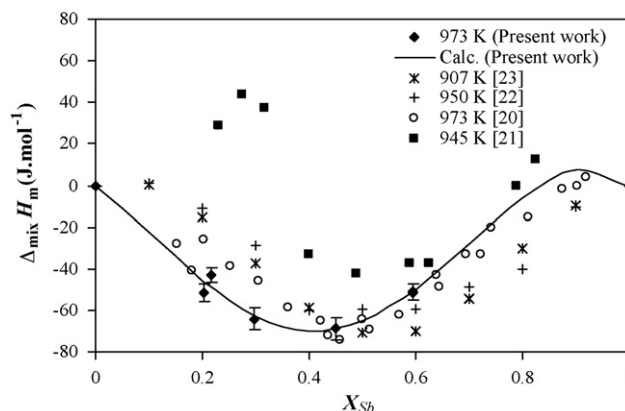


**Fig. 1.** Cross section of the direct liquid-liquid reaction device.

Most of calorimetric investigations use Direct Drop Reaction method [29] where a solid metal at room temperature  $T_0$  is dropped into a liquid one placed inside the calorimetric cell at experimental temperature  $T_C$ . In that method the heat of mixing at  $T_C$  is obtained by subtracting from the global measured heat effect first, the  $T_0$  to  $T_C$  heat content and second, the heat of fusion of the solute metal. These quantities represent generally a too large part to the measured effect and mask the tiny “mixing effect”, typically less than 1 kJ/mol. Therefore, the Direct Drop Reaction method is not suitable.

**Table 2**  
Experimental results of DSC measurements.

Alloy composition		$m_t$ (mg)	$M$ (g mol <sup>-1</sup> )	$T_{eutectic}$ (K)	$T_{liquidus}$ (K)	$\Delta H_{eut}$ (J mol <sup>-1</sup> )
$X_{Pb}$	$X_{Sb}$					
0.930	0.070	607.27	201.22	525.3	571.4	1403
0.900	0.100	727.26	198.70	525.3	558.5	2700
0.850	0.150	675.66	194.38	525.4	536.9	5123
0.800	0.200	776.47	190.11	525.3	558.7	5766
0.700	0.300	616.33	181.57	525.3	635.2	5056
0.600	0.400	688.04	173.02	525.3	673.2	4413



**Fig. 2.** Integral molar enthalpies of mixing of Pb – Sb liquid. Comparison with literature.

Indeed, in the case of Pb – Sb binary system the liquid-liquid mixing enthalpies present a near to zero value. In order to improve the final accuracy of measurements and at most ensure the sign of interaction, we have carried out direct liquid-liquid reaction (DLLR) method which consists in dropping the liquid metal B previously stabilized at the experimental  $T_C$  temperature into the liquid metal A considered as the solvent and maintained also at the same temperature. This method has already been used in various setups [30–33].

The high-temperature liquid-liquid mixing device is described in Fig. 1. The  $C_1$  graphite crucible holds 2–8 g of antimony liquid metal; a  $C_2$  silica crucible containing about 10 g of lead liquid metal is positioned just above the  $C_1$  crucible. The  $C_2$  crucible is so manufactured that the bottom is made thin enough to be broken with a single weak knock given by the falling down alumina rod  $R_3$  and transmitted by both the alumina rods  $R_1$  and  $R_2$ . The  $R_3$  rod initially at ambient temperature moves on a few centimeters in the higher part of the guard tube far from the isothermal thermopile zone. Only the thin  $R_1$  rod moves in a reproducible manner in the measurement area of the thermopile and induces a part of the heat effect to be measured in the blank experiment. Liquid lead is then released and mixes with liquid antimony forming rapidly a homogeneous phase. Indeed at 973 K, added to the high temperature natural convection, the mixing phenomenon is greatly helped by density difference between lead (10.205 g/cm<sup>3</sup>) and antimony (6.448 g/cm<sup>3</sup>).

At 973 K the vapour pressure of Sb is about  $10^{-4}$  atm [17]. The mass loss in antimony do not exceed 0.1% during the experiment.

The measured heat effect corresponds to the liquid-liquid mixing enthalpy at the calorimeter temperature added to the break off heat effect which represents about 10 J. In order to evaluate correctly the mixing part of the measured enthalpy, for each run, blank experiments were achieved. It consists in mixing liquid Pb in  $C_2$  crucible into liquid Pb in  $C_1$  crucible, with the same thermal conditions as the previous Pb – Sb mixing experiment.

The calorimeter is calibrated by additions of  $\alpha$  alumina pieces purchased from N.I.S.T [34] in the empty graphite crucible.

The relation used to calculate the molar mixing enthalpies is

$$\Delta_{mix}H_m \text{ (J mol}^{-1}\text{)} = \left( KS_2 - KS_1 \frac{n_{Pb}(Sb)}{n_{Pb}(Pb)} \right) \frac{1}{n_t} \quad (1)$$

$K$  represents the calibration constant,  $S_2$  is the area of thermogram corresponding to the dropping of liquid lead into liquid antimony,  $S_1$  is the area of thermogram corresponding to the dropping of liquid lead into liquid lead,  $n_{Pb}(Sb)$  is the number of moles of lead used in the Pb – Sb mixing,  $n_{Pb}(Pb)$  is the number of moles of lead used in the Pb – Pb mixing, and  $n_t$  is the total number of moles of alloy.

Taking into account principally the reproducibility of the blank effect, the uncertainty in the final value of the enthalpy of mixing shown in Table 1, is estimated to be  $\pm 8\%$ .

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