

## Experimental study and modelling of Pb-Bi-Hg system

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**Abstract:** As a first step, an experimental study of the Pb-Bi-Hg system was performed from calorimetric, XRD and EPMA measurements. Results indicated the presence of a ternary intermetallic compound i.e.  $\text{Pb}_{0.549\pm\Delta x}\text{Bi}_{0.307\pm\Delta y}\text{Hg}_{0.144\pm\Delta z}$  with a narrow homogeneity domain. This phase decomposes peritectically above 45°C. In a second step, all the experimental phase diagram data collected during the present study in the ternary system and the thermodynamic quantities (enthalpies of mixing and activities) given in the literature mainly for binary borders were taken into account in a thermodynamic modelling which used the CALPHAD (CALculation PHase Diagram) approach. It appeared that two peritectic invariants exist at 37 and 82°C. Otherwise, the calculation of the isopleth section  $x(\text{Pb})/x(\text{Bi}) = 0.45/0.55$  versus mercury content which is especially interesting for nuclear applications, suggested the rapid decrease of liquidus temperature even with minor mercury additions (inferior to 1 wt.%).

### 1. INTRODUCTION

Accelerator driven system (ADS) are a technical option for transmutation of plutonium, long-lived fission products into short-lived radio-isotopes [1]. In such systems, protons generated by an accelerator impinge on a target in order to produce neutrons by a spallation process. These neutrons are then used for the waste material transmutation. Liquid lead and liquid lead-bismuth eutectic have been chosen as potential spallation target material and cooling agent of the reactor. The long time neutron irradiation effects on Pb-Bi liquid target has been simulated by several authors [2]. The results revealed the formation of mercury, tin or zinc impurities. Concerning Hg, its average content can reach up to one weight percent. Although laboratory simulations are very different from the hybrid reactor conditions, they point out potential risks due to formation of new ternary  $\text{Pb}_x\text{Bi}_y\text{Hg}_z$  intermetallic compounds. Indeed, it can be supposed that these compounds could present a higher melting point than that of the liquid target, and this could induce an accelerated abrasion of the container in T91 alloy.

On this subject, a very recent thermodynamic study [3] of the Pb-Bi-Hg system gave some precious information. In particular, the existence of a ternary intermetallic compound  $\text{Pb}_{0.45}\text{Bi}_{0.35}\text{Hg}_{0.2}$  has been taken into account in the thermodynamic calculation. The authors show that the compound decomposes peritectically above 37°C.

The aim of the present study is to improve the knowledge about this ternary compound composition and crystallographic structure. Indeed, few literature reports [4] underlined this phase existence. Moreover, no precise information is available in the literature about the intermetallic stoichiometry. New results were needed for an accurate thermodynamic description of the Pb-Bi-Hg system. This work will be performed using the CALPHAD method [5].

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Raw materials

The ternary alloys were synthesised from purified liquid mercury (Rhône-Alpes Mercury Society, 99.99%), pure lead (GoodFellow, 99.95%) and pure bismuth (Alfa, 99.9%). After the components were

weighed, the alloys were prepared in a sealed vessel (under vacuum) during a heating up to above lead melting point (i.e. about 400°C). Phase homogeneity was obtained by holding for several hours at this temperature, then the alloys were slowly cooled.

## 2.2. Characterisation of ternary alloys

After cooling, the phases were identified by X-Ray diffraction (Philips X'Pert Pro, Eindhoven, Netherlands), using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), with a back monochromator filtering the fluorescence. The scans were carried out with  $0.02^\circ$  steps, a 16 second recording time for each position, over the range  $25\text{-}110^\circ$  ( $2\text{-}\theta$ ). The  $\text{CuK}\alpha_1$  and  $\text{CuK}\alpha_2$  doublets were easily resolved using an automatic procedure of the Diffract AT program [6]. The X-Ray diffractograms at different temperature were recorded using a TTK 450 temperature cell (Anton Parr) equipped with Capton window foils (temperature limit: 500°C).

The crystallographic structure of the ternary intermetallic phase was determined with the Fulprof software [7] from the  $2\theta$  intensities. The lattice parameters were then refined with the U-Fit program [8] with a  $0.0005 \text{ \AA}$  precision on each parameter.

Chemical compositions were determined by electron microprobe (Cameca SX50): WDX (Wavelength Dispersive X-ray) analysis were done with an electron beam of 20 kV and 20 nA. Bi-L $\alpha$ , Pb-L $\alpha$ , Hg-M $\alpha$  X-ray emission lines were used.

The phase boundaries and the invariant equilibria in the ternary system were identified using a microcalorimeter (Sceres) during the second heating ( $1^\circ\text{C}/\text{min}$ ) of the specimens. Transformation reproductibilities were checked during two or three heating cycles.

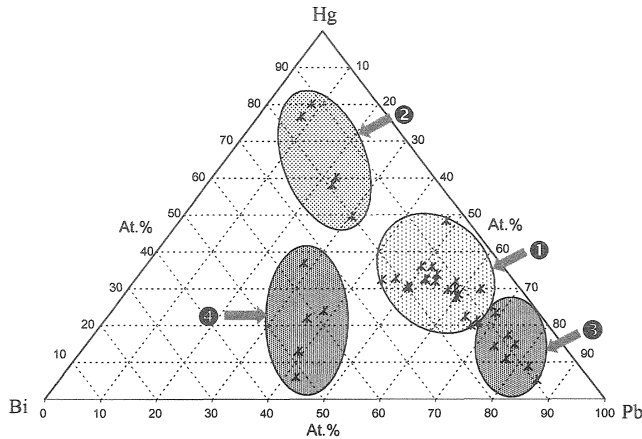
## 3. RESULTS AND DISCUSSION

### 3.1 Experimental investigation of the ternary Pb-Bi-Hg system

Several mixtures of pure lead, mercury and bismuth were prepared in order to study the Pb-Bi-Hg phase diagram at room temperature. WDX and XRD analyses were performed on slowly cooled samples. These specimen compositions are reported in the isothermal section of the phase diagram (Fig.1). They were chosen in order:

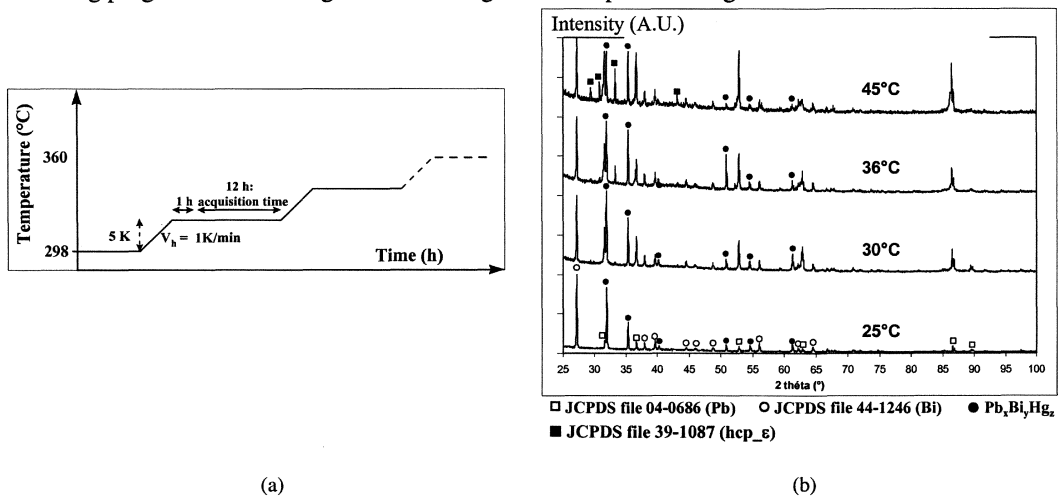
- to precise the chemical composition of the ternary intermetallic compound (zone ❶);
- to evaluate the liquid phase range in the mercury rich corner (zone ❷);
- to determine the phase boundary of the lead solid solution ( $\alpha\text{Pb}$ ) in the lead-rich corner (zone ❸);
- to identify the main ternary invariant equilibria (zone ❹).

For all of the compositions near the Pb-Hg border (i.e. in zone ❶), a new phase is observed: an intermetallic phase containing approximately 55 wt.% Pb, 31 wt.% Hg and 14 wt.% Bi.



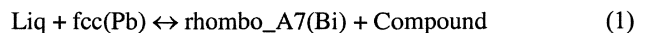
**Figure 1:** Isothermal section of the Pb-Bi-Hg phase diagram at room temperature.

Moreover, in order to confirm its existence and to ascertain its stability domain versus temperature, some X-ray diffraction patterns at different temperatures have been recorded, from 25 to 45°C, following the heating program shown in Fig. 2a. Diffractograms are reported in Fig.2b.



**Figure 1:** Temperature program (a) and X-ray patterns for a 55 wt.% Pb-31 wt.% Hg-14 wt.% Bi sample (b).

These results show that the ternary compound decomposes above about 45°C. This result is not too far from the first modelling of Pb-Bi-Hg [3] which gives the equilibrium (1) at about 37°C:



It appears that this new intermetallic compound would admit a narrow substoichiometric domain around the composition 55 wt.% Pb, 31 wt.% Hg and 14 wt.% Bi. This homogeneity range was determined by coupling EPMA, XRD experiments which led to the following results:

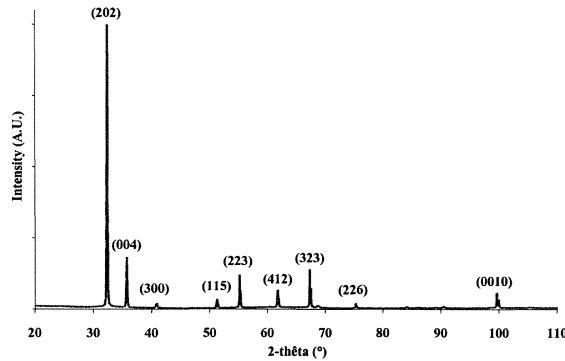
$$- 0.5145 < x(\text{Pb}) < 0.5338 \quad (2)$$

$$- 0.1265 < x(\text{Bi}) < 0.1553 \quad (3)$$

$$- 0.3233 < x(\text{Hg}) < 0.3590 \quad (4)$$

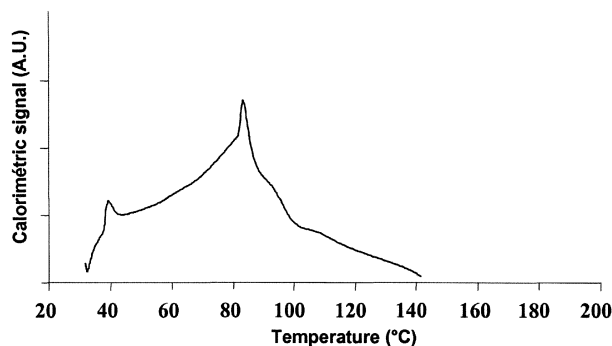
It can be noticed that the chemical composition proposed by Malyutin et al. [4] without accurate experimental data, i.e.  $\text{Pb}_{0.45}\text{Bi}_{0.35}\text{Hg}_{0.2}$ , is not included in this domain. From the X-ray pattern of the pure

ternary intermetallic phase (Fig. 3), it is possible to determine its crystallographic structure with Fulprof Software [7]. This intermetallic compound seems to adopt a tetragonal symmetry. The lattice parameters were refined with the help of U-fit software [8] in the case of a primitive Bravais lattice:  $a = b = 7.665 \pm 0.006 \text{ \AA}$ ,  $c = 10.084 \pm 0.002 \text{ \AA}$ .



**Figure 3:** XRD pattern of the  $\text{Pb}_{0.549}\text{Bi}_{0.307}\text{Hg}_{0.144}$  alloy obtained at the room temperature.

Calorimetric experiments permitted determining the temperatures of invariant equilibria and of the liquidus. For example, the DSC thermogram obtained for  $\text{Pb}_{0.39}\text{Bi}_{0.48}\text{Hg}_{0.13}$  (Fig. 4) reveals the presence of two invariants at 37 and 82°C and the liquidus temperature ( $\approx 100^\circ\text{C}$ ).



**Figure 4:** DSC thermogram obtained with a heating rate of  $1^\circ\text{C}/\text{min}$  for  $\text{Pb}_{0.39}\text{Bi}_{0.48}\text{Hg}_{0.13}$ .

### 3.2 Thermodynamic modelling of the ternary system

The thermodynamic optimisation of the Pb-Bi-Hg phase diagram was performed with Thermocalc software [9] using the Parrot module. The different formalism used are exposed in the following part.

#### 3.2.1 Thermodynamic models

The Gibbs energy of each of the pure elements  $i$  with the structure  $\phi$ , referred to the enthalpy of its standard state SER at 298.15 K, is described as a function of temperature by the following equation:

$${}^0G_i^{\phi(T)} - H_i^{\text{SER}} = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (5)$$

where SER stands for Standard Element Reference. This quantity is denoted GHSE*R* <sub>$i$</sub>  when the structure  $\phi$  corresponds to the standard state SER. Values of the coefficients  $a$  to  $h$  are taken from the SGTE database [10].

The liquid, Fcc(Pb), Rhombo\_A7(Bi), Rhombo\_A10(Hg) and hcp\_ε(Pb,Bi) solution phases are described by a substitution model and their molar Gibbs energies are expressed by:

$$G^\phi = \sum_i x_i {}^0G_i^\phi + RT \sum_i x_i \ln x_i + {}^{\text{ex}}G^\phi \quad (6)$$

where the index  $\phi$  denotes the appropriate phase and  $x_i$  represents the molar fraction of component  $i$ . The first term represents the contribution of the pure components of the phase, the second term the ideal Gibbs energy of mixing and the third term the excess Gibbs energy which is represented by a Redlich-Kister polynomial:

$${}^{\text{ex}}G^\phi = x_i x_j \sum_{v=0}^{\nu} L_{i,j}^\phi (x_i - x_j)^v \quad (7)$$

where the binary interaction parameter  ${}^{\nu}L_{i,j}^\phi$  is described as a function of temperature by the following equation:

$${}^{\nu}L_{i,j}^\phi = a_\nu + b_\nu T + c_\nu T \ln T \quad (8)$$

For a ternary solution, such as the liquid and the primary solutions Rhombo\_A7(Bi), Rhombo\_A10(Hg), Fcc(Pb)), the excess Gibbs energy is expressed by:

$${}^{\text{ex}}G^\phi = \sum_i \sum_{j>i} x_i x_j \sum_{v=0}^{\nu} L_{i,j}^\phi (x_i - x_j)^v + L_{i,j,k}^\phi x_i x_j x_k \quad (9)$$

where  $L_{i,j,k}^\phi$  is an excess ternary interaction parameter which is considered to be linearly dependent on temperature. In this study, only the ternary parameter for the liquid phase has been evaluated. Although some works [11-12] mentioned a range of homogeneity for  $\text{HgPb}_2$ , up to 10 at. % at room temperature, it is treated here as a stoichiometric compound.

Since no information is available about the atomic distribution and to reduce the number of adjustable parameters, the ternary intermetallic phase will be introduced in the calculation as a stoichiometric compound with the median composition  $\text{Pb}_{0.549}\text{Bi}_{0.307}\text{Hg}_{0.144}$ . Its Gibbs energy, referred to the pure elements in their standard (SER) state, can be expressed by the following equation:

$$G^{\text{Bi}_4\text{Hg}_6\text{Pb}_c} = \frac{a}{a+b+c} {}^0G_{\text{Bi}}^{\text{Rhombo\_A7}} + \frac{b}{a+b+c} {}^0G_{\text{Hg}}^{\text{Rhombo\_A10}} + \frac{c}{a+b+c} {}^0G_{\text{Pb}}^{\text{Fcc}} + \Delta G_f^{\text{Bi}_4\text{Hg}_6\text{Pb}_c} \quad (10)$$

with  $\Delta G_f = A + BT$  being the Gibbs energy of formation of the compound per mol of atoms.

### 3.2.2 Results of the thermodynamic modelling of PbBiHg

The modelling of Pb-Bi-Hg is mainly based on the accurate thermodynamic description of the binary borders Pb-Bi, Bi-Hg and Pb-Hg. This work has been already performed in previously [3], taking into account all the available thermodynamic and phase diagram information. The binary interaction parameters so obtained have been used for the present modelling. For the ternary system, the present phase diagram data (intermetallic composition, invariant characteristics,...) were taken into account. Several isotherm sections of Pb-Bi-Hg obtained during this new work are reported in Fig. 5.

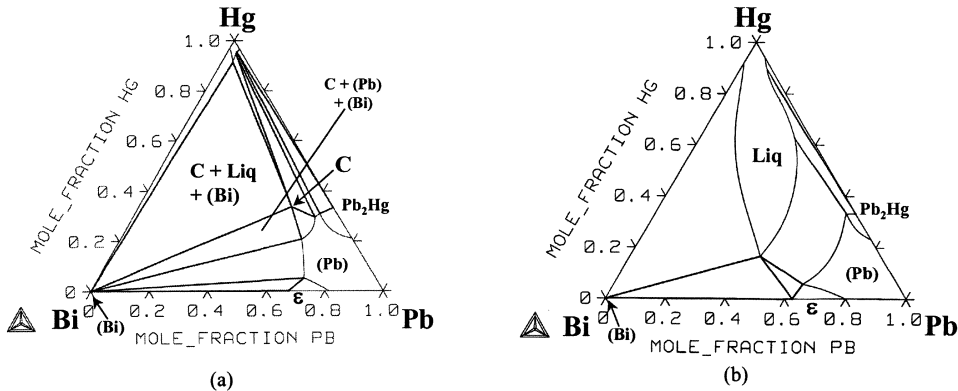
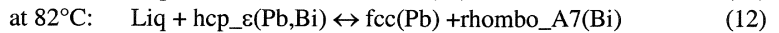
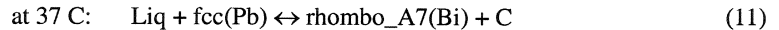
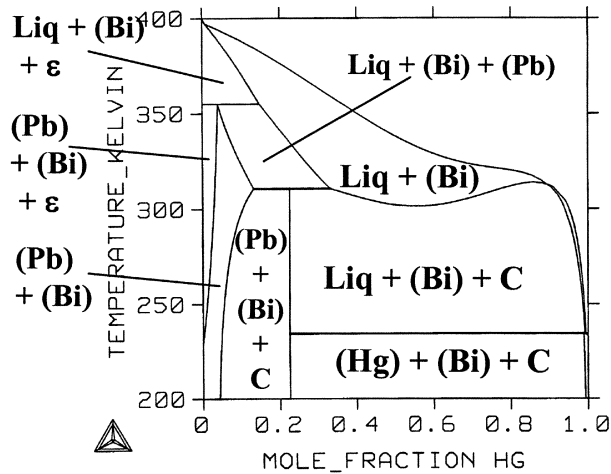


Figure 5: Isothermal sections at 37°C (a) and 82°C (b) of the modelled Pb-Bi-Hg phase diagram.

These isothermal sections confirms the existence of two invariants following:



The isopleth section obtained for  $x(\text{Pb})/x(\text{Bi})=0.45/0.55$  is very interesting for predicting the eutectic Pb-Bi liquid target behaviour in ADS nuclear reactors. In particular, it can be noticed that the higher the Hg content, the lower the liquidus temperature.



**Figure 5:** Isopleth section for  $x(\text{Pb})/x(\text{Bi})=0.45/0.55$  as a function of the mercury molar fraction.

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