

The Pb–Ca–Sn system: Experimental investigations for $x(\text{Ca}) \leq 0.25$ composition and thermodynamic modelling

Y. Cartigny*, J. Ravaux, L. Aranda, J.M. Fiorani, A. Maître, M. Vilasi

Laboratoire de chimie du solide mineral, UMR 7555, Université Henri Poincaré, boulevard des aiguillettes, BP 239, F-54506 Vandoeuvre les Nancy Cedex, France

Received 6 November 2006; received in revised form 5 June 2007; accepted 9 June 2007
Available online 19 July 2007

Abstract

Lead–calcium–tin alloys are extensively used as electrodes in acid batteries. They are synthesised by casting/hardening and subject to microstructural evolution during use. The change from an “aged” metallurgic structure to an “over-aged” structure is associated, in particular, with a deterioration of mechanical properties.

The determination of the Pb–Ca–Sn ternary phase diagram, and in particular the evolution of the limits of solubility of calcium and tin in a lead matrix as a function of the temperature, is essential to appreciate the oversaturation degree after hardening and to optimise the necessary thermal treatment to obtain the stabilisation of the aged state.

Some experimental measurements were carried out (radiocrystallography, differential thermal analyses, microprobe, ...) for the $x(\text{Ca}) \leq 0.25$ composition domain. They have allowed putting in light the inconsistencies between experimental data provided by the literature. Phase boundaries information was used to model the Pb–Ca–Sn system with a CALPHAD approach. Related thermodynamic databank is presented in this paper.

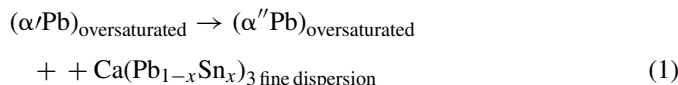
© 2007 Elsevier B.V. All rights reserved.

Keywords: Pb–Ca–Sn alloys; Thermodynamic modelling; Lead acid battery; Phase boundaries

1. Introduction

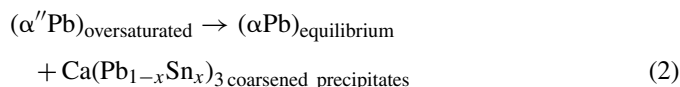
Lead–calcium–tin alloys are usually used as electrode materials in maintenance-free batteries application. Indeed, they have demonstrated very interesting mechanical and electrochemical properties [1].

The industrial synthesis of these alloys is based on the structural hardening process. Quenching of liquid alloy causes oversaturated lead solid solution. This one reaches its aged state by a succession of metallurgical transformation following general Eq. (1), which the nature depends on the Sn/Ca weight ratio [2]:



This latest metallurgical state (“aged” state) is very interesting because of its good efficiency for mechanical and electrochemi-

cal behaviour [1]. An adapted thermal treatment (determined by the TTT diagrams [3]) permits to stabilise it. These properties are altered by the ultimate metallurgical transformation, called over-ageing, which can take place during use and which follows Eq. (2):



So, the knowledge of phase boundaries in the Pb–Ca–Sn ternary system will be crucial for predicting and increasing the mechanical and electrochemical properties of these alloys. In particular, the effect of the tin content on the calcium solubility in lead matrix must be refined in order to optimise the structural hardening step and the thermal treatment stabilizing the aged state.

This present paper consists on experimental investigations of the Pb–Ca–Sn ternary system for $x(\text{Ca}) \leq 0.25$ composition domain followed by a thermodynamic calculation using the CALPHAD (CALculation of PHase Diagram) method.

* Corresponding author. Tel.: +33 2 35 52 29 54; fax: +33 2 35 52 29 59.
E-mail address: yohann.cartigny@univ-rouen.fr (Y. Cartigny).

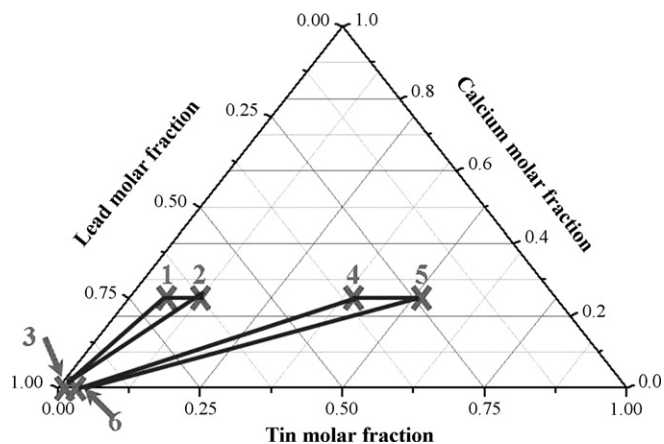


Fig. 1. Experimental isothermal section of the Pb–Ca–Sn system at 393 K characterised by Maître et al. [5] (labels details in Table 1).

2. State of art

Three important works can be cited concerning the experimental phase boundaries investigation in the $x(\text{Ca}) \leq 0.25$ composition domain.

Firstly, Adeva et al. [4] have investigated, by X-ray diffraction, the Pb-rich corner up to 0.2 wt% Ca and 3 wt% Sn. Their method consisted of measuring the lattice parameter of the (αPb) face-centred cubic matrix in function of the tin and calcium composition. These authors claimed that three phases could be present simultaneously, to justify a constant lattice parameter of the lead matrix. The two others phases associated with (αPb) are assimilated by the authors as CaPb_3 and CaSn_3 without any proofs.

Maître et al. [5], by TEM microscopy and EDX measurements, indicated the chemical composition of intermetallic phases in over-aged $\text{PbCa}_{0.08} \text{wt}\% \text{Sn}_{0.6}$ and 2 wt% alloys ($T_{\text{over-ageing}} = 393 \text{ K}$). In a same alloy, they found different composition for the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ components which have L1_2 structure. These results can be expressed as three-phase domains which associate the (αPb) matrix and two specific compositions of the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ isoplethal section. The experimental isotherm section ($T = 393 \text{ K}$) and compositions of phases in triphasic equilibrium are shown in Fig. 1 and Table 1, respectively.

Hertz et al. [6] have investigated by X-ray diffraction the lattice parameter behaviour of the L1_2 structure $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ alloys versus tin composition. These measurements indicate that

Table 1
Composition of phases labelled in Fig. 1 (limits of triphasic domains)

Phase label	Phases composition in atomic percent		
	Pb	Ca	Sn
1	68.25	25	6.76
2	62.25	25	12.75
3	98.919	0.041	1.05
4	35.25	25	39.75
5	23.25	25	51.75
6	96.529	0.041	3.43

there is an extended solid solution between CaPb_3 and CaSn_3 . These results are not consistent with the presence of a three-phase domains determined by Adeva et al. [4] and by Maître et al. [5]. Otherwise, by ATD measurements, Hertz et al. determine the presence of a ternary eutectic equilibrium at 449.15 K for the composition $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ around $x \approx 0.8$. Moreover, this author published a thermodynamic calculation concerning only the lead-rich corner. On the experimental results obtained by Hertz, present authors published a first overall calculation of the Pb–Ca–Sn ternary system, and were presented during the Thermodynamic OF Alloys Conference held in Rome in 2002 [7].

In order to lift the inconsistency between results claimed by different authors, new experimental investigations were carried out. They will permit to determine accurately phases domains for $x(\text{Ca}) \leq 0.25$ in order to improve the thermodynamic description of the system.

3. Experimental procedure

Pb–Ca–Sn alloys were synthesised by using 99.999% lead (Goodfellow), 99.91% tin (Merck) and 99.9% calcium (Ventron) as starting materials. Preparation of Pb–Ca–Sn alloys was carried out in an argon-controlled atmosphere, to avoid calcium losses due to the high reactivity of this element with oxygen. The melting of these alloys was done under argon in a vacuum-controlled atmosphere high frequency furnace. Samples were treated at different temperature to reach equilibrium state and were air-quenched before characterisation.

The identification of phases in equilibrium was carried out by means of electron microprobe examination (with Cameca SX100 apparatus) of metallographical samples. X-ray diffraction (Phillips X'Pert Pro ($\theta - 2\theta$), $20^\circ < 2\theta < 100^\circ$, λ_{Cu}) was carried out to determine the extension of the solid solution $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ (with L1_2 structure) between CaPb_3 and CaSn_3 . Thirteen samples with $x(\text{Ca}) \approx 0.25$ and variable tin composition were synthesised and homogenised at 573 K before air-quenching. The diffraction analyses were done on powder samples in capillary tubes prepared under argon atmosphere with silicon powder as reference. DTA measurements were carried out on these alloys under argon atmosphere on a ATD-TG Setaram 92-type calorimeter (accuracy of the transformation points was $\pm 2 \text{ K}$). Moreover, some diffusion couples were carried out in order to observe the succession of different phases domains in $x(\text{Ca}) \leq 0.25$ composition domain. These ones result from the association of CaPb_3 and CaSn_3 compounds with pure tin and lead, respectively. The diffusion temperature was 438 K under vacuum during 5 and 19 days. Moreover, a series of alloys with $x(\text{Ca}) < 0.25$ composition were synthesised and homogenised in the same way as previously described. Fig. 2 recapitulates the type of investigations in the studied composition domain.

Lastly, the thermodynamic modelling was done using the CALPHAD method with the help of the Parrot module contained in Thermocalc software.

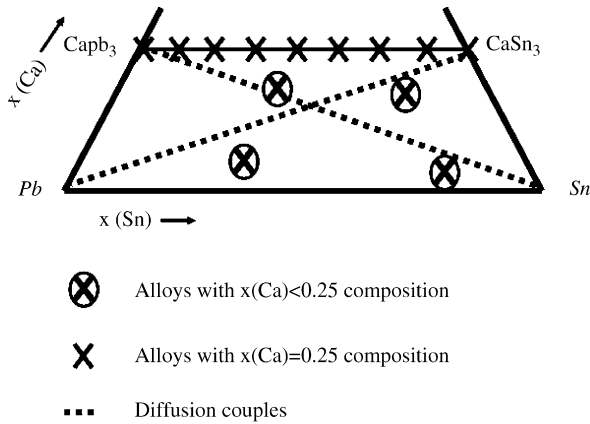


Fig. 2. Type of experimental investigation carried out during the present study.

4. Results of experimental investigation

4.1. X-ray diffraction

The cubic-lattice parameters of the L_{12} structure components ($\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$) were determined by XRD analyses and are significant to the crystallographic situation encountered at 573 K (homogenisation temperature). It can be noticed that a loss of calcium is always observed during the synthesis process. For this reason, one or two phases (lead or tin solid solution) are simultaneously present in XRD patterns with the main L_{12} phase (Fig. 3). Fig. 4 shows the variation of $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ lattice parameters versus tin composition. On this representation, three domains can be observed: two rectilinear variations (noticed 1 and 3) and a third one (noticed 2). This latest is not well defined with inconsistent L_{12} phase parameters in a narrow range of composition.

The parameter behaviour in the domains 1 and 3 can be fitted by two rectilinear curves with the following Eqs. (3) and (4),

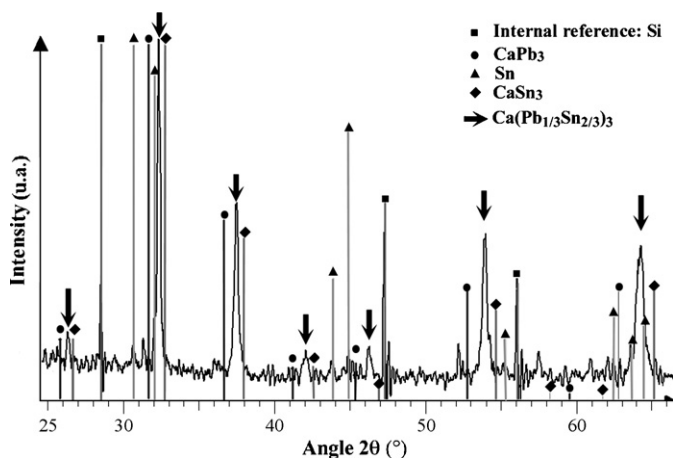


Fig. 3. Typical XRPD pattern recorded on alloys with general composition $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ (L_{12} structure) and compared to theoretical diffractograms of Sn, CaSn_3 (i.e. $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$, $x=1$), CaPb_3 (i.e. $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$, $x=0$) and the internal reference Si. The presented pattern was obtained on alloy synthesised for $x=2/3$ (domain 3 in Fig. 4).

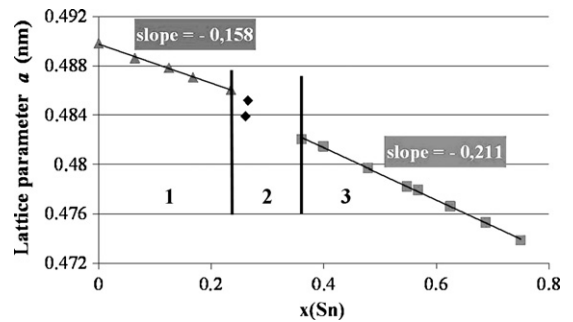


Fig. 4. Lattice parameter behaviour of the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ compounds (L_{12} structure) vs. tin composition after thermal treatment at 573 K and air quenching.

respectively:

$$a \text{ (nm)} = -0.1583x + 0.48976 \quad (R^2 = 0.9976) \quad (3)$$

$$a \text{ (nm)} = -0.2110x + 0.48979 \quad (R^2 = 0.9989) \quad (4)$$

In each domain, the lattice behaviour is in accordance with a Vegard's law. However, the difference observed between the slope of these two rectilinear domains clearly indicates that the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ solid solution was not extended from CaPb_3 up to CaSn_3 contrarily to conclusions made by Hertz et al. [6]. So, at 573 K, two solid solutions must be considered: one issued from CaPb_3 and extended up to nearly $\text{Ca}(\text{Pb}_{0.68}\text{Sn}_{0.32})_3$ composition and a second one issued from CaSn_3 and extended up to nearly $\text{Ca}(\text{Pb}_{0.53}\text{Sn}_{0.47})_3$ composition. Limits of extensions of these domains were not clearly defined and cannot be considered as quantitative information.

4.2. DTA measurements

DTA measurements were carried out on the alloys characterised by X-ray diffraction. Associated thermograms (Fig. 5) present two different transformations: invariant reaction and liquidus point. Only invariant reaction temperature is quantitative

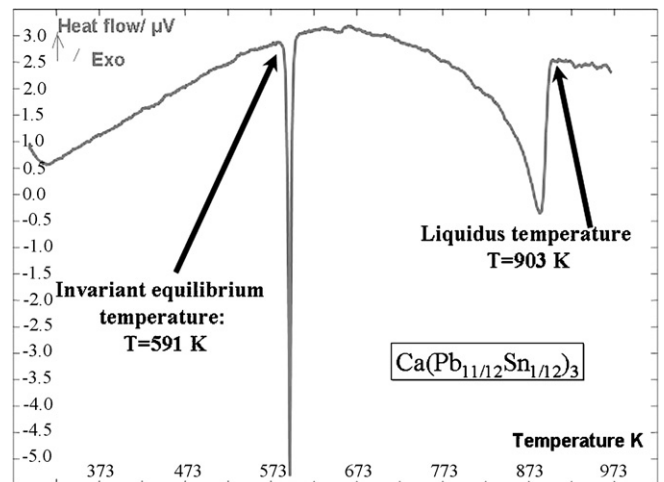


Fig. 5. Thermogram obtained on the $\text{Ca}(\text{Pb}_{11/12}\text{Sn}_{11/12})_3$ compounds (scanning temperature 5 K min^{-1}).

because it does not depend on the proportion of each phase contrarily to liquidus points. For alloys with composition near CaPb_3 ($\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ with $0.0642 < x < 0.2658$), the detected invariant reaction temperature is nearly 589 K (± 2 K) (Fig. 5). It can be noticed that this transformation was not identified previously in literature. For $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ which contain more tin ($0.5752 < x < 0.6875$), the invariant temperature ($T_{\text{inv}} = 453$ K) reaction seems to be similar than those identified by Hertz in this domain ($T_{\text{inv}} = 449$ K). This ternary eutectic takes place between a particular composition of the isopleth composition ($x(\text{Ca}) = 0.25$), lead solid solution and tin solid solution.

So, these DTA measurements show the presence of new ternary invariant reactions and confirm the existent one.

4.3. Metallographic analyses

Some metallographic investigations were carried out on alloys with $x(\text{Ca}) < 0.25$ composition as well as on diffusion couples. These analyses clearly indicate the presence of three ternary equilibrium; their typical microstructures are shown in Fig. 6. A first three-phase domain associates $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$, αPb and βSn lead and tin solid solution, respectively. The nature as well as the characteristics of this three-phase domain was also determined by previous studies, notably by Hertz et al. [6]. The two others three-phase domains associate two specific composition of the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ isopleth section and the αPb lead solid solution. Chemical compositions of each phase in equilibrium are reported in Table 2.

The nature and the composition of the three-phase domain seem to be similar to those obtained by Maître et al. [5] at 393 K (Fig. 1).

Table 2

Composition of phases belonging to the isopleth section $x(\text{Ca}) = 25\%$ in triphasic equilibrium with lead or/and tin solid solutions (as labelled in Fig. 6)

Domain label	Phase label	Phases composition in atomic percent		
		Pb	Ca	Sn
A	1	72	25	3
	2	61.3	25	13.7
B	3	34.4	25	40.6
	4	26.3	25	48.7
C	5	68.3	25	68.3

4.4. Consistencies between experimental information

The lattice parameter behaviour of the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ are not in accordance with the presence of an extended solid solution between CaPb_3 and CaSn_3 claimed by Hertz et al. These present crystallographic studies for $x(\text{Ca}) = 0.25$ alloys carried out at 573 K allows us to consider the presence of two distinct phases with an L1_2 structure (Fig. 4). It implicates the presence of only one three-phase domain associating two particular composition of the $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ isopleth section at this temperature (limits of the two distinct solid solution). In order to be consistent with the metallographic studies provided by this work and by Maître et al., we must consider that the L1_2 solid solution issued from CaSn_3 present a miscibility gap when the temperature decrease from 573 to 438 K. Thus, overall experimental information is consistent between them and can be used to improve the ternary phase description. Experimental phase boundaries for $x(\text{Ca}) \leq 0.25$ composition described as below

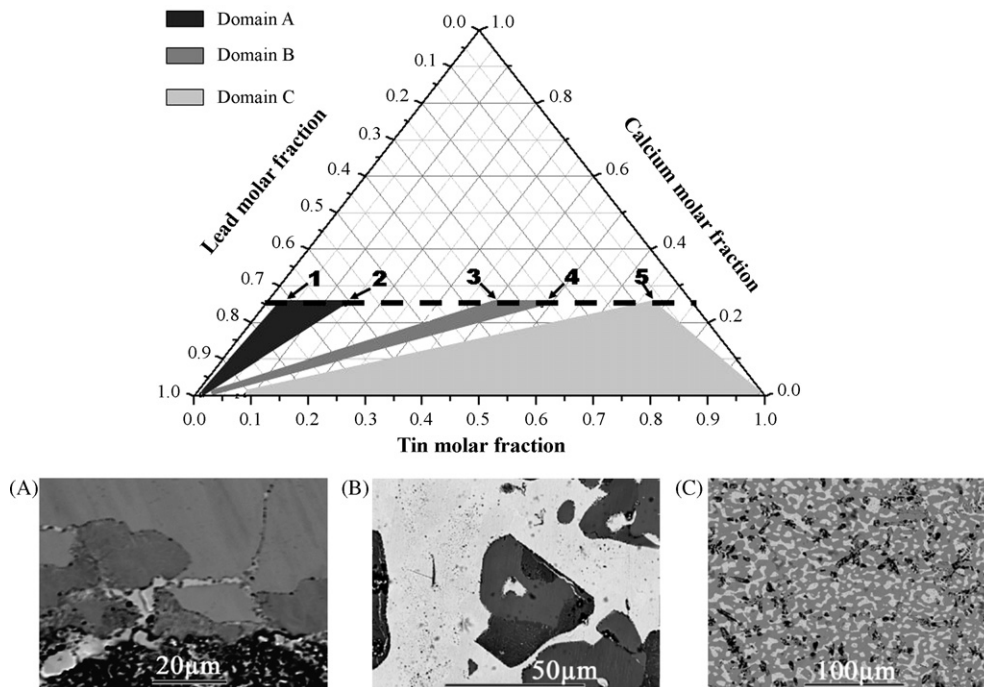


Fig. 6. Typical microstructures at 438 K of the three-phase domains for $x(\text{Ca}) < 0.25$.

are the starting point of the thermodynamic modelling attained thanks to the CALPHAD method.

5. Principles of thermodynamic modelling

5.1. Pure elements

Following the S.G.T.E. formalism, the Gibbs energy of pure elements i with the structure ϕ is referred to the enthalpy of its standard state element reference (SER) at 298.15 K and is noted:

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

5.2. Primary solid solution

The solid face-centred cubic (FCC)_{A1}(Pb), and (FCC)_{A1}(Ca), body-centred cubic (BCC)_{A5}(Ca), body-centred tetragonal (BCT)_{A2}(Sn) phases are described by a random substitutional model. The excess part of the Gibbs energy in the ternary system is represented using the Redlich–Kister–Muggianu description:

$${}^{\text{ex}}G^\phi = \sum_i \sum_{j>i} x_i x_j \sum_{v=0}^v L_{i,j}^\phi (x_i - x_j)^v + {}^0L_{i,j,k}^\phi x_i x_j x_k \quad (6)$$

Here, the binary interaction parameters ${}^vL_{i,j}^\phi$ are described with linear temperature dependence:

$${}^vL_{i,j}^\phi = a_v + b_v T \quad (7)$$

Ternary interaction ${}^0L_{i,j,k}^\phi$ was not necessary in our calculation to fit experimental values.

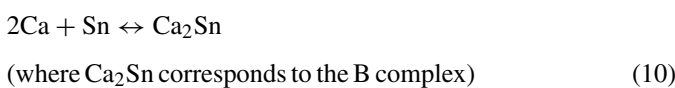
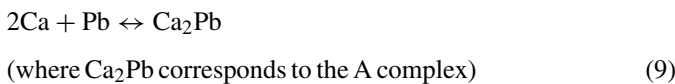
5.3. Liquid phase

In the calcium–lead and calcium–tin systems, the binary liquid phase has been described using the association model [8–10] because of the linear variation of integral enthalpy of mixing versus composition in liquid [11]. In this case, the Gibbs energy of the ternary liquid is given for one mole of formula units and is expressed as the sum of four contributions:

$$G^{\text{liq}} = {}^{\text{ref}}G + {}^{\text{form}}G + {}^{\text{id}}G^{\text{liq}} + {}^{\text{ex}}G^{\text{liq}} \quad (8)$$

where the different contributions are the reference part (${}^{\text{ref}}G$), formation of the associated complex part (${}^{\text{form}}G$), an ideal part (${}^{\text{id}}G^{\text{liq}}$) and excess part (${}^{\text{ex}}G^{\text{liq}}$).

The association model is based on the hypothesis that two complexes A and B, issued from the binary borders Ca–Pb and Ca–Sn, respectively, are formed in the ternary liquid phase following Eqs. (9) and (10):



where Ca, Pb and Sn are pure elements initially present in the mix. Thus, the different parts of the Gibbs energy can be described by Eq. (11)–(13):

$${}^{\text{ref}}G = \{x_{\text{Ca}}[{}^0G_{\text{Ca}}^{\text{Liq}} - H_{\text{Ca}}^{\text{SER}}] + x_{\text{Sn}}[{}^0G_{\text{Sn}}^{\text{Liq}} - H_{\text{Sn}}^{\text{SER}}] + x_{\text{Pb}}[{}^0G_{\text{Pb}}^{\text{Liq}} - H_{\text{Pb}}^{\text{SER}}]\}(y_{\text{Ca}} + 3y_{\text{A}} + y_{\text{Pb}} + 3y_{\text{B}} + y_{\text{Sn}}) \quad (11)$$

$${}^{\text{form}}G = y_{\text{A}} {}^0\Delta G^{\text{A}} + y_{\text{B}} {}^0\Delta G^{\text{B}} \quad (12)$$

$${}^{\text{id}}G = RT \sum_{i=\text{Ca}}^{\text{B}} y_i \ln y_i \quad (13)$$

where R is the perfect gas constant, T the temperature; A, B the two associated species in the liquid, y_{Ca} , y_{Pb} , y_{Sn} , y_{A} and y_{B} the site fraction of each liquid species after association reaction (9) and (10) and normalised to $y_{\text{Ca}} + y_{\text{Pb}} + y_{\text{Sn}} + y_{\text{A}} + y_{\text{B}} = 1$. x_{Ca} , x_{Sn} and x_{Pb} are the initial mole fraction introduced in the solution, without considering the associated species, normalised to $x_{\text{Ca}} + x_{\text{Sn}} + x_{\text{Pb}} = 1$. ${}^0\Delta G^{\text{A}}$ and ${}^0\Delta G^{\text{B}}$ are enthalpies of formation of associated species A and B.

The excess Gibbs energy is expressed by the Redlich–Kister–Muggianu description:

$${}^{\text{ex}}G^{\text{Liq}} = \sum_i \sum_{j>i} x_i x_j \sum_{v=0}^v L_{i,j}^{\text{Liq}} (x_i - x_j)^v + {}^0L_{i,j,k}^{\text{Liq}} x_i x_j x_k \quad (14)$$

where i, j and k are three possible species among the five existing in ternary liquid and ${}^0L_{i,j}^{\text{Liq}}$ describes interaction between two species of the mix and are defined like Eq. (7). Among the 10 interactions generated between species, Table 3 shows those used in the calculation. The excess ternary interaction parameter ${}^0L_{i,j,k}^{\text{Liq}}$ was omitted in the modelling because it was not necessary to fit experimental values in our case.

5.4. Intermetallic compounds

The Gibbs energy of overall binary intermetallic compounds, A_pB_q , considered as stoichiometric, is expressed by the following equation referring to the pure elements in their SER state:

$$G^{\text{A}_p\text{B}_q} = \frac{p}{p+q} [{}^0G_{\text{A}}^{\text{SER}} - H_{\text{A}}^{\text{SER}}(298.15)] + \frac{q}{p+q} [{}^0G_{\text{B}}^{\text{SER}} - H_{\text{B}}^{\text{SER}}(298.15)] + \Delta G^{\text{A}_p\text{B}_q} \quad (15)$$

with $\Delta G^{\text{A}_p\text{B}_q} = a + bT$ representing the formation Gibbs energy of the compound referenced to the standard state of pure elements.

5.5. Line compounds

No ternary phase is present in the Pb–Ca–Sn system. Moreover, binary compounds CaPb_3 and CaSn_3 are extended in the ternary system. So, the sub-lattice model was used to describe

Table 3
Binary interactions used for the ternary liquid calculation (notched boxes)

	Pb	Ca	Sn	Ca ₂ Pb	Ca ₂ Sn
Pb					
Ca					
Sn					
Ca ₂ Pb					
Ca ₂ Sn					

these phases. For CaPb₃ and CaSn₃, calcium content is constant and the substitution of lead and tin on the first sub-lattice is described as following:

$$\phi = (\text{Pb}_{y_{\text{Pb}}} \text{Sn}_{y_{\text{Sn}}})_3 \text{Ca} \quad (16)$$

where y_{Pb} and y_{Sn} represent the molar fraction of lead and tin on the first sub-lattice.

The Gibbs energy of the phase ϕ is described as the sum of the three following contributions expressed as:

$$\text{ref } G^\phi = y_{\text{Pb}} G^{\text{CaPb}_3} + y_{\text{Sn}} G^{\text{CaSn}_3} \quad (17)$$

$$\text{id } G^\phi = 3RT(y_{\text{Pb}} \ln y_{\text{Pb}} + y_{\text{Sn}} \ln y_{\text{Sn}}) \quad (18)$$

$$\text{ex } G^\phi = y_{\text{Pb}} y_{\text{Sn}} \sum_{\nu=0}^{\nu} L_{\text{Pb,Sn}}^\phi (y_{\text{Pb}} - y_{\text{Sn}})^\nu \quad (19)$$

where G^{CaPb_3} and G^{CaSn_3} are the free enthalpies of formation of CaPb₃ and CaSn₃ compounds.

6. Optimisation

Binary interaction parameters, optimised during previous studies and related to the Pb–Sn [12], Ca–Pb [9] and Ca–Sn [10] binary borders, were integrated in the ternary databank. Optimised parameters related to the ternary system are shown in Table 4.

Table 4
Optimised set of parameters related to the ternary Pb–Ca–Sn system

Phase	Parameter	Value (J (mol of atoms) ⁻¹)
Liquid	$L_{\text{Ca}_2\text{Pb}_1, \text{Sn}}^{0, \text{L}}$	-99720.62
	$L_{\text{Ca}_2\text{Sn}_1, \text{Pb}}^{0, \text{L}}$	-7853.96
CaPb ₃	$G_{\text{Ca:Pb}}^{0, \text{CaPb}_3}$	0.25 GHSERCA + 0.75 GHSERPb - 32407.5 + 0.8453T
	$G_{\text{Ca:Sn}}^{0, \text{CaPb}_3}$	0.25 GHSERCA + 0.75 GHSERSn + 1404401.57 - 166.5748T
	$G_{\text{Ca:Pb, Sn}}^{0, \text{CaPb}_3}$	-2364288.51 + 526.5265T
	$G_{\text{Ca:Pb, Sn}}^{1, \text{CaPb}_3}$	926445.99 - 366.6736T
	$G_{\text{Ca:Sn}}^{2, \text{CaPb}_3}$	-7926.74642 + 5.1728T
CaSn ₃	$G_{\text{Ca:Pb}}^{0, \text{CaSn}_3}$	0.25 GHSERCA + 0.75 GHSERSn - 37722.5 + 0.1.2394T
	$G_{\text{Ca:Sn}}^{0, \text{CaSn}_3}$	0.25 GHSERCA + 0.75 GHSERPb - 31409.5948 + 0.8477T
	$G_{\text{Ca:Sn, Pb}}^{0, \text{CaSn}_3}$	-8564.8544 + 15.1933T
	$G_{\text{Ca:Sn, Pb}}^{1, \text{CaSn}_3}$	-8217.7861 + 5.6663T
	$G_{\text{Ca:Sn, Pb}}^{2, \text{CaSn}_3}$	-7926.74642 + 5.1728T

Table 5
Phases in equilibrium on the isoplethal section $x(\text{Ca})=0.24999$ drawn in Fig. 7

Phase domain	Phases in equilibrium
1	Liquid
2	Liquid + CaPb ₃
3	Liquid + CaPb ₃ + CaSn ₃
4	Liquid + CaSn ₃
5	CaPb ₃ + α Pb
6	CaPb ₃ + CaSn ₃ + α Pb
7	CaSn ₃ + α Pb
8	CaSn ₃ #1 + CaSn ₃ #2 + α Pb
9	CaSn ₃ + β Sn
10	α Pb + β Sn + CaSn ₃

In the liquid phase, the nature of binary interaction parameters used in the optimisation are listed in Table 2. It must be noticed that ternary interaction parameter was not necessary to restore experimental available information. Moreover, there is no ternary compound in this system.

The modelling can be used to draw isoplethal section at $x(\text{Ca})=0.2499$ (Fig. 7 and Table 5) which shows the good restoration of overall experimental data. New phase domains as well as the invariant reactions provided by the different authors are consistent.

The demixion of the Ca(Pb_{1-x}Sn_x)₃ L1₂ phase, suggested by our experimental investigations, is well restored by the calculation too and appears from 467 K to lower temperature. It can be noticed that the critical demixion temperature was cal-

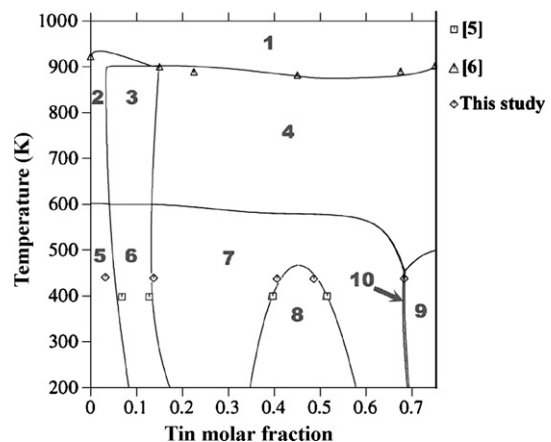


Fig. 7. Calculated isoplethal section at $x(\text{Ca})=0.2499$ in comparison with experimental data.

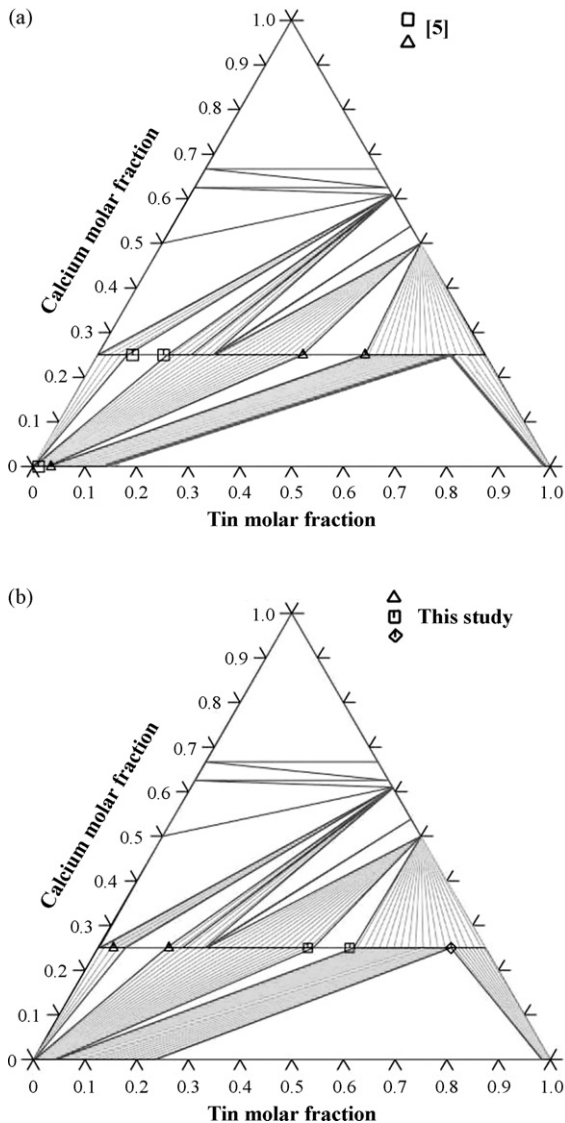


Fig. 8. Calculated isothermal section at 393 K (a) and 438 K (b) in comparison with experimental data.

culated without experimental information and must be certainly refined.

Solid solutions between CaPb_3 and CaSn_3 are claimed in the calculation as two different phases with the same structure. However, it appears more realistic to describe these phases as one with a narrow miscibility gap at 573 K (Fig. 4) and a second one, which appears with the temperature decrease (Fig. 6). Present authors attempt to calculate the phase diagram with considering $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)$ solid solution as one phase but the calculation of the related Gibbs energy was not possible with Thermocalc software which showed its calculation limits. So, the consideration of two distinct phases with the same structure was chosen as the best description of the solid solution between CaPb_3 and CaSn_3 .

Isothermal sections presented in Fig. 8 confirm the good accordance between calculated and experimental phase domain at 393 and 438 K.

For the manufacturing of lead alloys (like $\text{PbCa}_{0.08\text{wt}\%}\text{Sn}_{0.6-2\text{wt}\%}$, in battery industry), the calculated ternary phase

boundaries are primordial because they enable to define the single-phase domain required to the re-homogenisation process. Moreover, the knowledge of the tin solubility in lead–calcium solid solution is crucial to develop any alloy compositions for acid battery applications. In particular, the tin content in αPb after ageing process increases the corrosion resistance in sulfuric acid of these ternary alloys [1]. Otherwise, it must be noticed that the Ca solubility in αPb drops drastically with the temperature decrease: the calcium solubility is 300 times less at 300 K than at 573 K. According to this present calculation, the calcium solubility in the αPb matrix strongly decreases with the increase of Sn content: for example, after an introduction of 1 wt% of tin, the calcium solubility is divided by 2 at 573 K and by 300 at 300 K. Simultaneously, when increasing the Sn content, $\alpha\text{Pb} + \text{L1}_2$ tie-line crosses very rapidly the L1_2 solid line from the CaPb_3 border to near the CaSn_3 border (Fig. 8). This latter result confirms the experimental information provided by literature [5]. Indeed, the tin content of the hardened precipitates $\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$ of L1_2 -type increases during the over-ageing process as it is predicted by the tie-line evolution on the isothermal section drawn at 300 K.

7. Conclusions

The knowledge of phase boundaries in the Pb–Ca–Sn ternary system is primordial to adapt thermal treatments in order to reach their optimal properties in battery applications.

Experimental investigations carried out during this study in a $x(\text{Ca}) \leq 0.25$ composition domain provide two important results;

- the solid solution between CaPb_3 and CaSn_3 ($\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$) seems to be non-extended at 573 K,
- the presence of three three-phase domain for $x(\text{Ca}) \leq 0.25$ at lower temperature ($T \leq 438$ K) is confirmed and refined.

The calculation restore overall experimental information on the ternary system. However, further investigations must be carried out to confirm the phases repartition in Pb–Ca–Sn system. In particular the critical demixion temperature of the L1_2 phase ($\text{Ca}(\text{Pb}_{1-x}\text{Sn}_x)_3$) must be refined.

The present thermodynamic modelling restore overall experimental information related to the ternary system and furnishes a precise description of the Pb–Ca–Sn system in function of composition and temperature. Moreover, the industrial process applied on the lead–calcium–tin alloys for battery applications find some justifications in this calculated phase diagram. So, this thermodynamic calculation can be used to improve the alloy composition and the thermal treatment applied to lead acid batteries electrodes in order to stabilise the aged state.

References

- [1] G. Bourguignon, Thesis (3rd cycle), University of Nancy I, France, 2003.
- [2] L. Bouriden, J.P. Hilger, J. Hertz, J. Power Sources 33 (1991) 27–50.
- [3] A. Maître, G. Bourguignon, J.M. Fiorani, J. Ghanbaja, J. Steinmetz, Mater. Sci. Eng. A 358 (2003) 233–242.
- [4] P. Adeva, G. Caruana, M. Aballe, M. Torralba, Mater. Sci. Eng. A 54 (1982) 229–236.

- [5] A. Maitre, G. Bourguignon, J.M. Fiorani, J. Steinmetz, J. Ghanbaja, P. Lailler, *Mater. Sci. Eng. A* 340 (2003) 103–113.
- [6] J. Hertz, C. Fornasieri, J.P. Hilger, M. Notin, *J. Power Sources* 46 (1993) 299–310.
- [7] Y. Cartigny, J.M. Fiorani, A. Maître, M. Vilasi, *Intermetallics* 11 (2003) 1205–1210.
- [8] F. Sommer, *Z. Metallkd.* 73 (1982) 72–76.
- [9] Y. Cartigny, J.M. Fiorani, A. Maître, M. Vilasi, *Thermochim. Acta* 414 (2003) 197–202.
- [10] Y. Cartigny, J.M. Fiorani, A. Maître, M. Vilasi, *Z. Metallkd.* 96 (2005) 1308–1313.
- [11] L. Bouriden, Thesis (3rd cycle), University of Nancy I, France, 1984.
- [12] H. Ohtani, K. Okuda, K. Ishida, *J. Phase Equilib.* 16 (1995) 317.