

X-ray photoelectrospectroscopy study of passive layers formed on lead–tin alloys

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Abstract

Lead–tin alloys were prepared with increasing tin content up to 2.5 wt.% Sn. These alloys were passivated in de-aerated sodium tetraborate solution (pH=9.1) at 0 V versus saturated sulfate electrode. The aim of this X-ray photoelectrospectroscopy (XPS) study was to elucidate the relationship between the alloying tin content and the electronic conductivity of the passive layers. It was found that metallic lead, lead oxide and tin oxide were present in the passive film. XPS did not distinguish SnO from SnO₂ signals, but SnO₂ was assumed to be present for reasons of its thermodynamic stability. The signals of tin, lead and oxygen (main components of the passive films) were depleted in unshifted and shifted signals when the conductivity of the films (evaluated by electrochemical study) became very low. The shifted signals were assumed to have originated from positively charged zones on the surface film due to the low conductivity. The shifting increased when the alloying tin content decreased, that is when the film conductivity decreased. The concentration of tin (as compared with lead) in the passive films was largely increased, up to 44, 28, 14, 13 and 3 wt.%, respectively, for 2.5, 1.5, 1.3, 1 and 0.5 wt.% Sn alloys. Semi-quantitative analysis showed that one of the effects of alloying tin could be the thinning of the passive films, as observed for 2.5 wt.% Sn alloy. The inner layer of the passive films was found to be rich in conducting tin oxide and metallic lead.

Keywords Lead–tin alloys; Passive layers

1. Introduction

With the modern tendency for the industry to produce maintenance-free and valve-regulated batteries, low-antimony or antimony-free lead alloys have been used to minimize loss of water from the electrolyte. However, these new alloys have the disadvantage of developing a passive layer which impedes the electronic conduction through the grid/active material electrode, resulting in loss of cycling capacity, low performance of the positive electrode and low charge acceptance for deep-discharge batteries [1,2]. The passive layer has been identified as tetragonal PbO developed under a lead sulfate layer [3–6] where the pH is increased to a value of 9.3 by selective diffusion of OH⁻ ions. To alleviate the problem of the passivation of the grid, the addition of tin to lead has shown to be a good solution [7–9]. However, the mechanism of the action of tin on the properties of the PbO passive layer is not well known. In a previous work [10], an in situ study of the effect of tin on the passivation of Pb–Sn alloys was carried out. Pb–Sn

alloys were prepared with increasing tin contents up to 2.5 wt.% Sn. These alloys were first passivated in de-aerated sodium tetraborate solution (pH=9.1). Electronic conduction through this passive layer was evaluated by measuring the polarization currents of the ferro-ferricyanide couple which was added to the solution, in the passive range of the alloy electrode. The modification of the electronic conductivity of the passive layer by alloying with tin led to a change in the kinetics of the redox couple reaction. From the kinetic parameters, it was found that no electron transfer was observed on passive lead alloyed with less than 0.8 wt.% Sn. Electronic conductivity of the passive layer, evaluated by the exchange current density of the redox system, increased sharply when the alloying tin content increased from 0.8 to 1.5 wt.%, but reached a plateau for higher tin contents. The steady-state passive current density, which is related to the rate of dissolution of the passive layer, decreased when the alloying tin content increased that is when the electronic conductivity of the passive layer increased.

The relationships between the alloying tin content and the electronic conductivity of the passive layer in a medium of $\text{pH} \approx 9$ has to be explained. Many questions may arise. What is the nature of the passive layer? Which is the oxidation state and the relative concentration of tin and lead in the layer? Is the thickness of the passive layer related to the alloying tin content? Is there a doping effect of PbO or PbO_x by tin [11,12]? Are there Sn^{2+} and Sn^{3+} ions incorporated into the PbO lattice, leading to PbO_x formation [13,14]? Is the dismutation reaction $\text{SnO} + \text{PbO} \rightarrow \text{Pb} + \text{SnO}_2$ possible [15]?

Surface analysis, in particular XPS, could bring out data which may give an answer to the above questions. This is the aim of the present study.

2. Experimental

The preparation of the Pb–Sn alloys (0.5, 0.8, 1, 1.3, 1.5, 2.5 wt.% Sn) are described in a previous paper [10], as well as the electrochemical equipment. The reference electrode used in this study was $\text{Hg}/\text{Hg}_2\text{SO}_4$ /saturated K_2SO_4 , or SSE (saturated sulfate electrode, +642 mV versus NHE). The electrodes were polarized at 0 V versus SSE to develop a passive layer in de-aerated 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ solution ($\text{pH}=9.1$) for 15 to 24 h until a steady-state passive current was attained. After passivation, the samples were rinsed with distilled water, dried, and then transferred to the XPS spectrometer.

Surface analysis of the passive layers was carried out with a VG Scientific MKII (ESCALAB) apparatus, with the $\text{Mg K}\alpha$ X-ray source ($h\nu=1253.6$ eV). The X-ray power was 300 W. Angle-resolved measurements were made at take-off angle $\theta=90^\circ$. Sputtering of the sample surface was performed with a VG AG21 argon ion gun under an accelerating voltage of 4 KV, a pressure of 10^{-7} millibars and a current density of approximately $75 \mu\text{A}/\text{cm}^2$. The sputtered area was 1 cm^2 and the X-ray beam size was 0.1 cm^2 . All the samples were cleaned by ion sputtering for 3 min before the analysis. Background subtraction (iterative Shirley method), peak synthesis (using Gaussian–Lorentzian curves) and semi-quantitative analysis were carried out with the VG 5000 computing programme. The values of the attenuation lengths of the electrons for the different elements were derived from literature data [16].

3. Results and discussion

3.1. Qualitative analysis of the passive layers

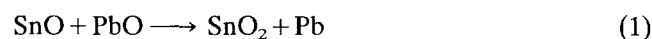
Fig. 1 shows the spectra of Sn level $3d_{5/2}$ and Sn level $3d_{3/2}$ in the passive films of studied Pb–Sn alloys.

Peaks 1 and 2 in Fig. 1(a) and (b) of the 2.5 and 1.5 wt.% Sn alloys concern oxidized tin [17]. The signals of SnO and SnO_2 have been found to be very close [16,18]; it is therefore not possible to know whether SnO or SnO_2 was present in the passive film. The spectra of alloys with lower tin content show two other peaks denoted as 1' and 2' (Fig. 1(c) and (d)). The binding energies corresponding to the tin spectra of alloys are gathered in Table 1. It can be seen that the difference between the two 3d energy levels of oxidized tin (peak 2–peak 1) is 8.5 eV and the difference peak 2'–peak 1' is roughly 8.4 eV. It is then likely that peaks 1' and 2' are shifted from peaks 1 and 2 and are related to oxidized tin signals. The shifting of the binding energy to higher levels may have two origins. The first is the change of the oxidation state or the chemical environment of the element, leading to stronger electronic binding. The second is the decrease in the electrical conductivity of the sample: the emission of electrons following X-ray irradiation will result in the appearance of positive charges on the surface of the sample. If the sample (passive layer in this case) is an insulator or has a very low conductivity, the non-neutralized positive charges will increase the binding energy of electrons in the surface ions and XPS peaks will shift to higher energy levels. The parameters reported in Table 1 show that the shifting of oxidized tin signals 1 and 2 to 1' and 2' attain roughly 5.6 eV (peak 1–peak 1' or peak 2–peak 2') for 1.3 wt.% Sn alloy and 6.6 eV for 1 wt.% Sn alloy. These are quite high values compared with the shift of the binding energy due to the increase of the oxidation state or to the bonding of Sn with a strongly electronegative element, such as in SnF_4 . In fact, it is reported that the shift of the tin signals when oxidized from SnO to SnO_2 is not significant [16,18], and that the shift from SnO to SnF_4 is only 1.2 eV [18]. Therefore, it can be stated that for alloys with less than 1.5 wt.% Sn, the passive layers include positively charged zones because of low electrical conductivity. As the tin content decreases, so does the electrical conductivity of the passive layer [10], and the XPS signals undergo a greater shift (Table 1). The existence of the two types of signals, the shifted and the unshifted, can be explained by the presence of both charged and uncharged zones. When the tin content is higher than 1.5 wt.%, only the uncharged zones are assumed to be present in the passive layer (Fig. 1(a) and (b)). This characteristic should be related to the previous work [10] which showed that these passivated alloys have a high electronic conductivity in a redox solution. On the other hand, the same in situ study showed that the conductivity of the passive layers decreased sharply when the alloying tin decreased from 1.3 to 1 wt.%, to become negligible with 0.5 wt.% Sn. This behaviour is now verified by XPS results which show the shifting of signals, probably

due to the non-conducting property of the corresponding passive layers. For 0.5 wt.% Sn alloy, no signal of oxidized tin was observed. This means that the non-conducting passive films contained no tin oxide, at least in the outer layer.

Fig. 2 shows the signals of oxygen 1s from the passive layers on Pb–Sn alloys. Figure 2(a) corresponds to oxygen in the conducting passive film of 2.5 wt.% Sn alloy, with a peak binding energy of 531.2 eV, a value close to that of oxygen in SnO₂ which is 530.4 eV [17]. Table 2 shows the peak binding energies of oxygen signal from the Pb–Sn alloys and pure lead. With alloys with lower tin contents, this oxygen peak (O) shifted to higher binding energies, the variation of which increased when the tin content decreased: 1.4 eV for 1.5 wt.% Sn, 1.8 eV for 1 wt.% Sn. The oxygen spectra in 2c, and 2d can be deconvoluted into two peaks O and O'. The oxygen peak O' at 538.1 eV is due to PbO_x formed on pure lead. This oxygen peak was assumed to be shifted to higher binding energies under the effect of surface charging on non-conducting lead oxide. On 2.5 and 1.5 wt.% Sn alloys, the oxygen signal came from tin oxide and also from lead oxide. But only one peak was observed at 531.2 and 532.6 eV in the Fig. 2(a) and (b). The proposed explanation was that these oxide films were conducting (as shown by the conductivity study [10]) and the oxygen signal was unshifted. According to Kim et al. [19], the oxygen peak from heat treated PbO_{tetragonal} and PbO_{rhombohedral} was at 528 and 530 eV, respectively (values obtained after shifting correction). These values are far from the 538.1 eV observed for non-conducting lead oxide on pure lead (Table 2). This shifted oxygen signal was explained by the surface charging, in the same manner as for the signal shifting of tin. It is likely that the two peaks O and O' are oxygen signals coming from uncharged and charged regions in the oxide layer (SnO_x and PbO_x) on low tin level alloys (Fig. 2(c) and (d)). The shifts of the peak binding energies (peak O–peak O') are 5.6 and 6.5 eV, respectively, for 1.3 and 1 wt.% Sn alloys.

The spectra of lead (levels 4f_{7/2} and 4f_{5/2}) are shown in Fig. 3. Oxidized lead (Pb_{ox}) and metallic lead (Pb) were found in the passive layers on the 2.5 and 1.5 wt.% Sn alloys (Fig. 3(a) and (b)). The previous electrochemical study [10] showed that these passive layers exhibited good electronic conductivity. The metallic lead signal may come from the metal underneath the thin passive layer. Another hypothesis was proposed, a dismutation reaction between tin and lead oxides in the passive layer:



It has been shown that the effect of tin in Pb–Sn alloys was to decrease the thickness of the passive layer [20, 21]. In this case, the first assumption may be acceptable.

But the second hypothesis cannot be ruled out. The atomic ratio of metallic lead to oxidized lead was evaluated by measuring the area under each related peak after deconvolution. This ratio was found to be 15%. The passive film on pure lead did not show any signal of metallic lead (Fig. 3(f)). The reason for this absence of metallic lead can be the great thickness of the lead oxide film or the lack of tin and dismutation reaction. Table 3 gathers the peak binding energies of lead signals from the Pb–Sn alloys and pure lead [22]. For weakly conducting passive layers (Fig. 3(c) and (d)) on 1.3 and 1 wt.% Sn alloys, the complicated spectra may be deconvoluted into peaks of metallic lead (Pb) and oxidized lead (Pb_{ox}) in uncharged zones, and shifted lead (Pb') and lead oxide (Pb'_{ox}) signals in charged zones. The metallic lead signal disappears for 1 and 0.5 wt.% Sn alloys and pure lead. On 0.5 wt.% Sn alloy as on pure lead, only the shifted signals were observed. This should be related to the non-conducting behaviour of the corresponding passive films. The difference in binding energies of lead signals, Pb'_{ox} (150.7 eV on pure lead) and Pb_{ox} (143.7 eV on 2.5 wt.% Sn) that is 7 eV, is much higher than the change in binding energies of different lead oxides, as can be seen in Table 4.

The lead oxide could be described as PbO according to many evidences:

(i) thermodynamic stability of PbO in the potential and pH regions considered in this study (Pourbaix diagram [23]);

(ii) analyses of lead oxide formed in sodium tetraborate solution (pH ≈ 9) by photocurrent excitation spectroscopy, coulombmetric measurements, showing the formation of PbO [24–28], and

(iii) lead signal from conducting lead oxide is at the same level of lead signal from PbO_{tetragonal} obtained after shifting correction [22] (Table 3).

3.2. Depth profiles of the passive layers

Sputtering of the passive alloy surface was carried out in order to verify that charged and uncharged zones were also present in the depth of the passive layers. Fig. 4 shows the signal of tin after 13 and 30 min of sputtering. For conducting passive layers (2.5 and 1.5 wt.% Sn alloys), the signal of tin oxide appeared almost unchanged, indicating that the whole layer was conducting. For weakly conducting alloys (1.3 and 1 wt.% Sn) signals 1' and 2', from charged zones, decreased in intensity when the sputtering time increased. This feature means that the inner layer of the passive film is more conducting than the outer layer. It is possible that the inner layer of the passive film contains less non-conducting compound, namely PbO, or, in other words, is richer in conducting tin oxide.

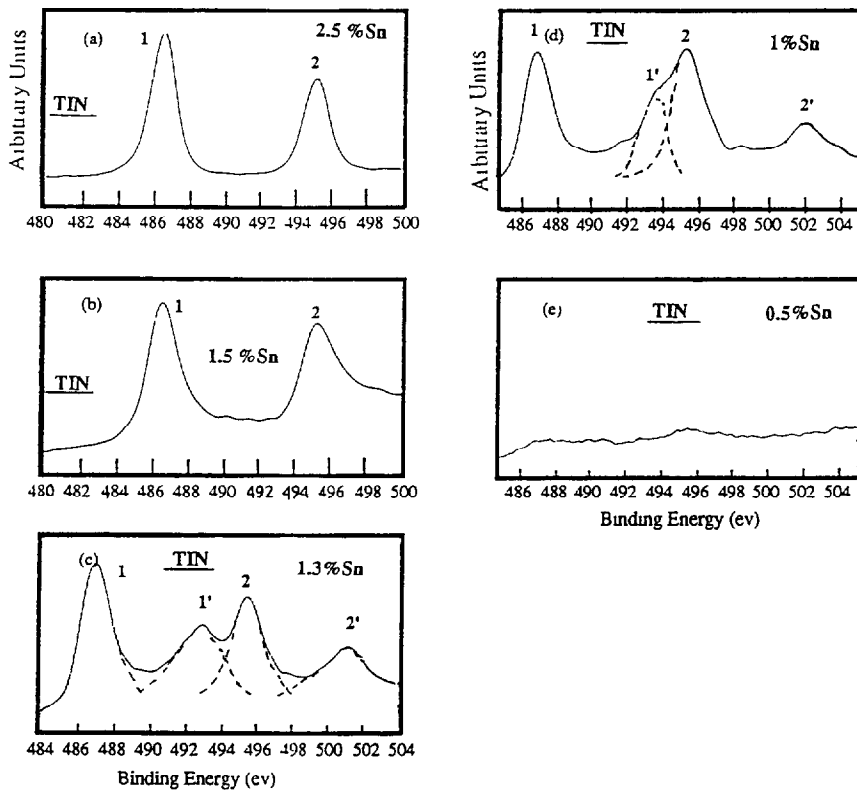


Fig. 1. Spectra of tin ($3d_{5/2}$ (2) and $3d_{3/2}$ (1)) in the passive films on lead-tin alloys after 3 min sputtering.

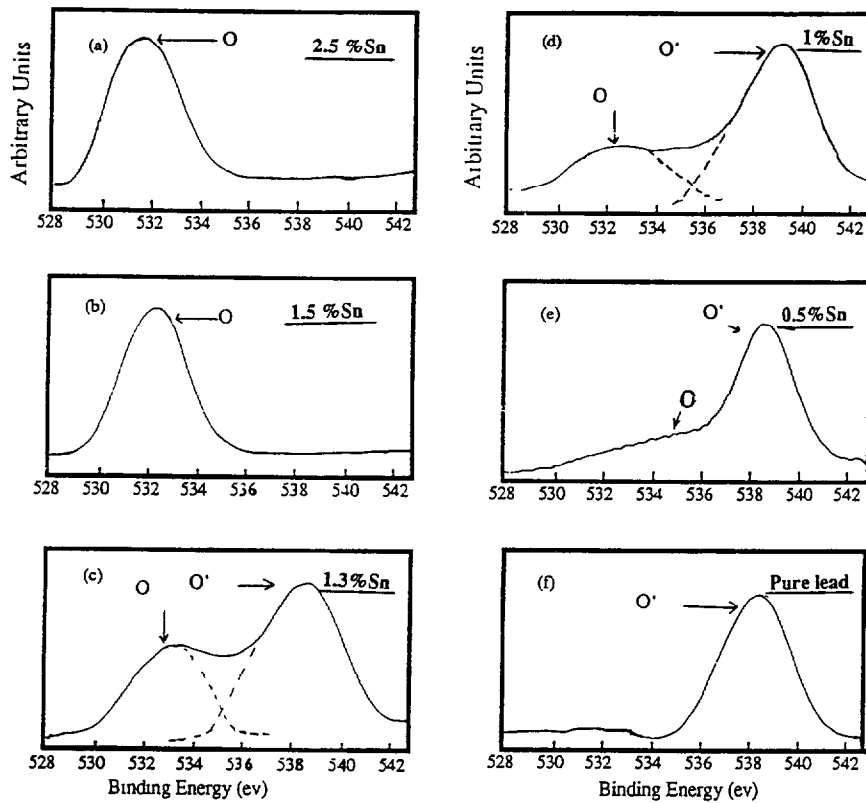


Fig 2 Spectra of oxygen 1s in the passive films on lead-tin alloys and on pure lead after 3 min sputtering

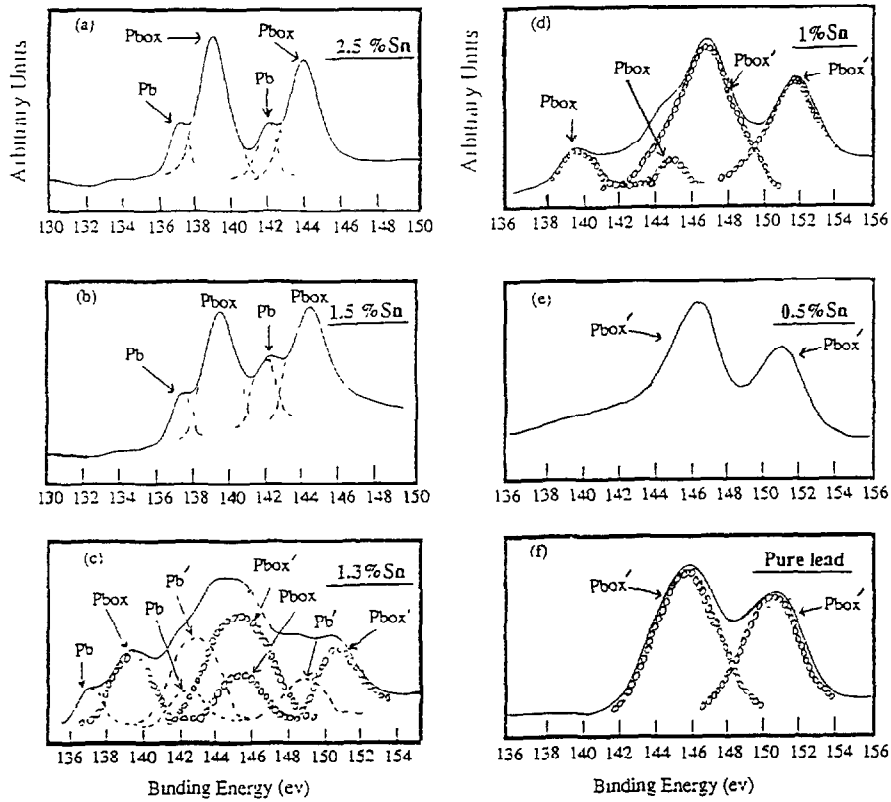


Fig 3. Spectra of lead ($4f_{7/2}$, $4f_{5/2}$) in the passive films on lead-tin alloys and on pure lead after 3 min sputtering.

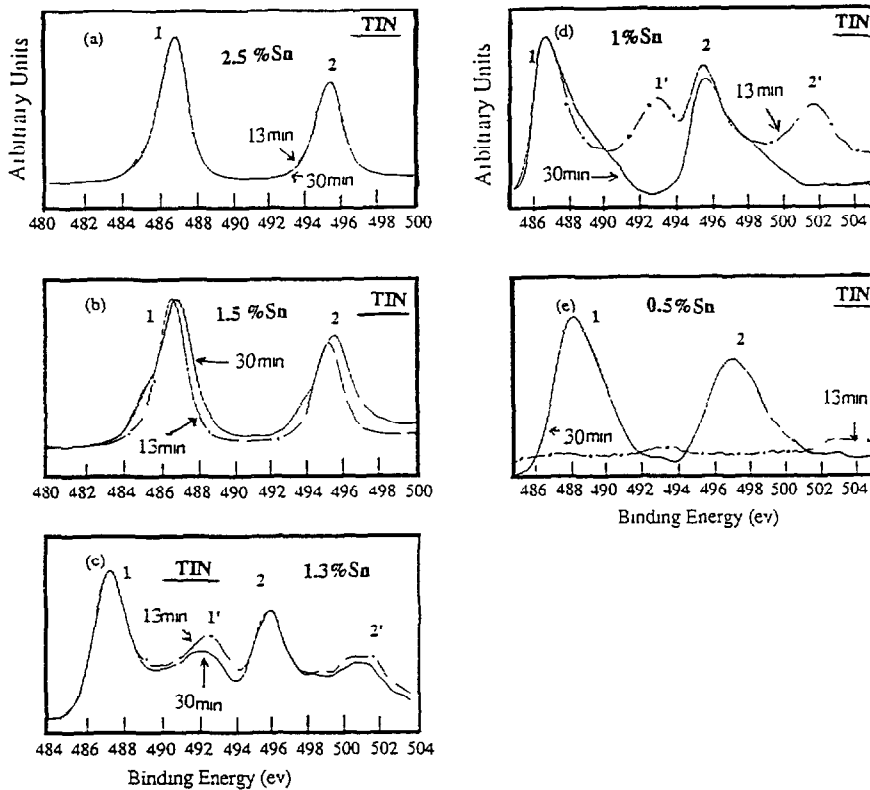


Fig 4. Spectra of tin ($(3d_{5/2})$ (2) and $3d_{3/2}$ (1)) in the passive films on lead-tin alloys, after 13 and 30 min sputtering.

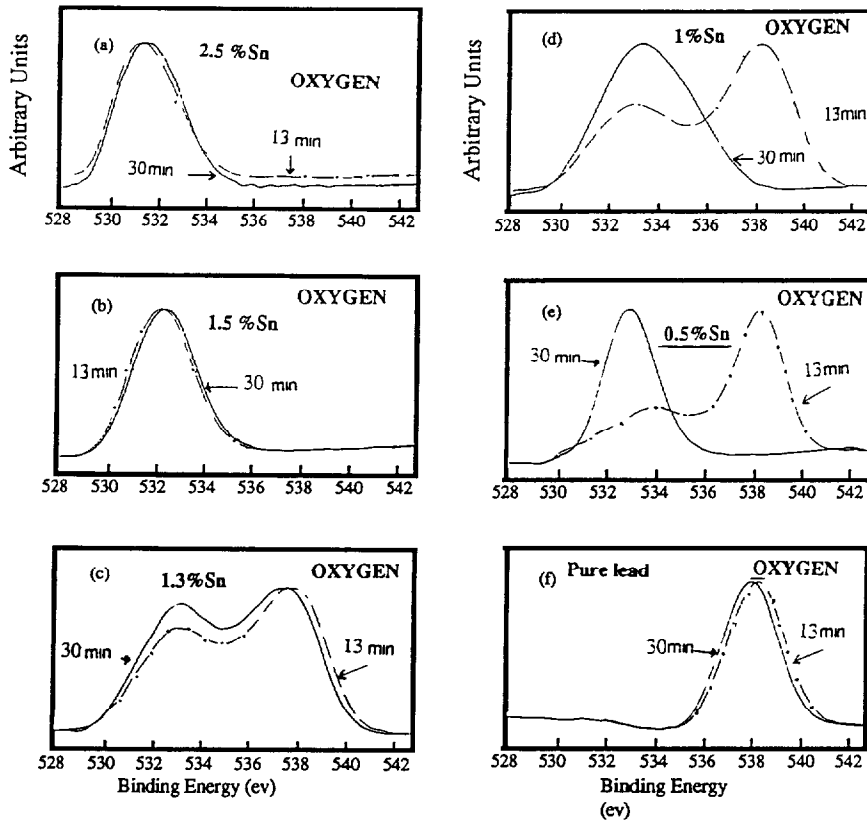


Fig 5. Spectra of oxygen 1s in the passive films on lead-tin alloys and on pure lead after 13 and 30 min sputtering

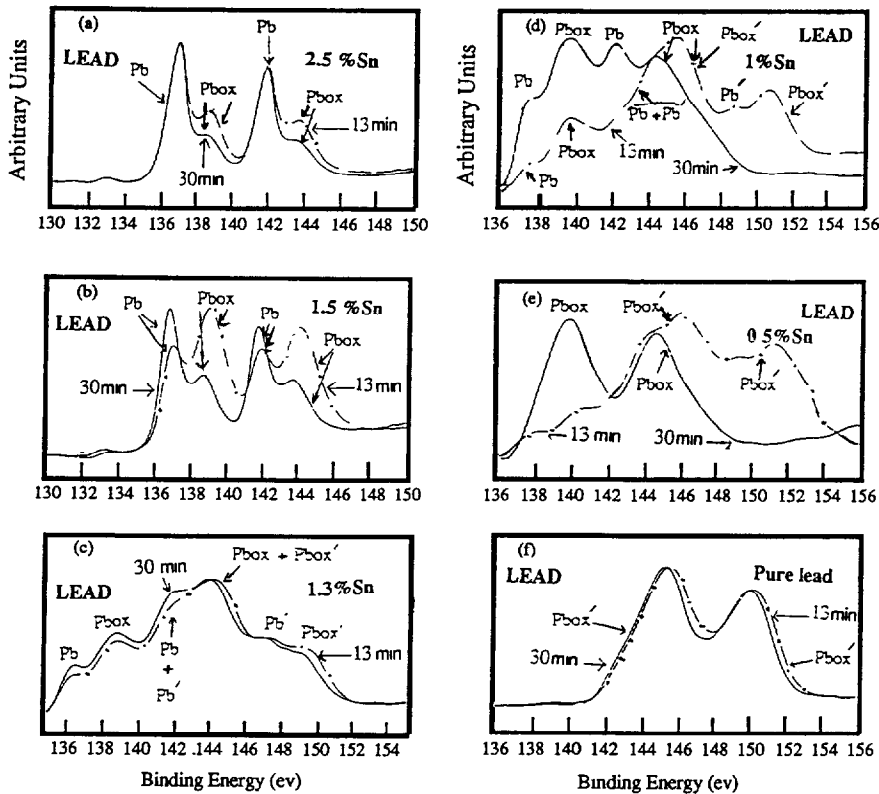


Fig 6 Spectra of lead (4f_{7/2}, 4f_{5/2}) in the passive films on lead-tin alloys and on pure lead after 13 and 30 min sputtering.

Table 1
Peak binding energies of various signals of tin in passivated lead–tin alloys

Alloys	Binding energy (eV)					
	Sn _(ox) 3d _{3/2} (peak 2)	Sn _(ox) 3d _{5/2} (peak 1)	peak 2'	peak 1'	peak 2 – peak 1	peak 2' – peak 1'
2.5 wt.% Sn	495.0	486.5			8.5	
1.5 wt.% Sn	495.2	486.7			8.5	
1.3 wt.% Sn	495.6	487.1	501.1	492.7	8.5	8.4
1 wt.% Sn	495.6	487.1	502.1	493.7	8.5	8.4
0.5 wt.% Sn						
Tin oxide ^a	494.9	486.4			8.5	

^aRef. [17].

Table 2
Peak binding energies of oxygen signal from passivated lead–tin alloys and pure lead

Level	Alloys					
	2.5 wt.% Sn	1.5 wt.% Sn	1.3 wt.% Sn	1 wt.% Sn	0.5 wt.% Sn	Pure Pb
O 1s (eV)	531.2	532.6	533	533		
O' 1s (eV)			538.6	539.5	538.1	538.1

Table 3
Peak binding energies of various lead signals from passivated lead–tin alloys and pure lead

Alloys	Binding energy (eV)							
	Pb _{ox} 4f _{5/2}	Pb _{met} 4f _{5/2}	Pb _{ox} 4f _{7/2}	Pb _{met} 4f _{7/2}	Pb' _{ox} 4f _{5/2}	Pb' _{met} 4f _{5/2}	Pb' _{ox} 4f _{7/2}	Pb' _{met} 4f _{7/2}
2.5 wt.% Sn	143.7	141.8	138.9	137.0				
1.5 wt.% Sn	143.8	141.9	139.0	137.1				
1.3 wt.% Sn	144.6	142.6	139.7	137.7	149.4	147.3	144.6	142.6
1 wt.% Sn	144.5		139.7		151.7		146.8	
0.5 wt.% Sn					150.8		145.9	
Pure Pb					150.7		145.8	
PbO ^{a,b}	143.5		138.6					

^aMeasurements referenced to hydrocarbon-contaminant C 1s line, assuming a value of 285.0 eV.

^bRef. [21].

Table 4
Peak binding energies of different lead oxides

Compounds	Oxygen signal (1s) (eV) ^a	Lead signal (4f _{5/2}) (eV) ^b	Lead signal (4f _{7/2}) (eV) ^c
PbO _{tetragonal}	528	143.5	138.6
Pb ₃ O ₄	530	142.9	138.2
PbO ₂	528	142.6	137.8

^aRef. [19].

^bRef. [22].

^cRef. [21].

The same change of oxygen 1s signals can be observed in Fig. 5. The inner oxide layer on 2.5 and 1.5 wt.% Sn alloys was conducting so that just the level of oxygen was the same after 30 min as after 13 min sputtering (Fig. 5(a) and (b)). The peak of oxygen in charged zones of the weakly conducting passive films

on 1.3, 1 and 0.5 wt.% Sn alloys (Fig. 5(c), (d) and (e)) decreased and then disappeared after 30 min of sputtering for 1 and 0.5 wt.% Sn alloys. It can be assumed again that conducting tin oxide gathered in the inner layer while non-conducting lead oxide was predominant in the outer layer of the passive film.

When tin was absent, only the peak of oxygen in the entirely non-conducting PbO layer was observed (Fig. 5(f)).

Lead signals after sputtering are presented in Fig. 6. It is possible to get oxide reduction by argon sputtering, but in our study, the reduction of lead oxide (PbO) was not observed for pure lead (Fig. 6(f)) even after 30 min sputtering. For conducting passive films (Fig. 6(a) and (b)), when the sputtering time increased, the area under the peaks of metallic lead increased, while that under the peaks of oxidized lead decreased. Here again, two assumptions can be made:

(i) as the film thickness decreased, the signal of metallic lead from the lead alloy underneath increased in intensity, and

(ii) the dismutation reaction between SnO and PbO could be more greater at the alloy/oxide interface where the primarily formed SnO reacted with PbO to give SnO₂ and Pb. Part of this lead could be oxidized again into PbO, but some might remain in the metallic state.

From the passive film of 1.3 wt.% Sn alloy (Fig. 6(c)), the complicated signals of lead, deconvoluted into unshifted signals of Pb4f_{5/2,7/2}, Pb_{ox}4f_{5/2,7/2} in uncharged zones and shifted signals in charged zones, moved very slightly to lower binding energy levels, as the sputtering time increased. So, the passive film can be considered as a mixture of conducting tin oxide, probably a small quantity of metallic lead, and non-conducting lead oxide. The inner part of the passive film was very slightly more conducting, conceivably due to a higher tin oxide content. With weakly conducting passive films (1 wt.% Sn alloy, Fig. 6(d)), the sputtering depth profile shows a large increase of lead (Pb) and oxidized lead (Pb_{ox}) in uncharged zones, while Pb_{ox} and Pb' in charged zones disappeared in the inner part of the film, where the predominant tin oxide increased the conductivity. For 0.5 wt.% Sn alloy, the passive film of which was found to be non-conducting by the previous electrochemical study [10], the outer part of the film was thought to be composed essentially of non-conducting lead oxide, and the inner part was more conducting, due to the enrichment of tin oxide. Finally, the passive film on pure lead gave only shifted signals of lead oxide, owing to its non-conducting character.

3.3. Quantitative analysis of the passive films

Semi-quantitative analysis of passive layers was made by the XPS equipment used in this study. The computer programme comprises an iterative calculation method based on a χ^2 criterion which allows quantification of elements according to experimental intensities. The results of the XPS analysis of alloys before electrochemical passivation are reported in Table 5. It can be seen that the obtained weight percentages are higher than those defined by the alloy preparation, but the

Table 5

Comparison of analytical results of tin contents in lead-tin alloys by weight percentage and XPS analysis

Alloys composition (wt % Sn)	Tin content				
	2.5	1.5	1.3	1	0.5
XPS analysis (wt % Sn)	3.1	2.1	2	1.9	1

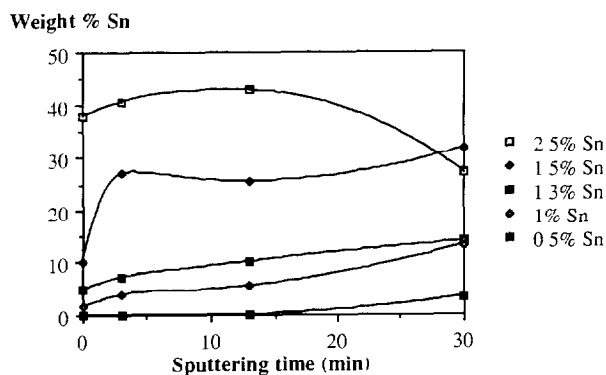


Fig. 7. Depth profile of tin in the passive layers of lead-tin alloys

uncertainty is less than 1 wt.%, and the sense of the variation of the alloy composition follows that of more accurate percentages by weighing.

Semi-quantitative analysis of the passive films followed each sputtering time which varied from 3 to 30 min. Longer sputtering was not carried out owing to possible disturbances which could increase the uncertainty of the results (e.g., increase of surface temperature, change in the nature of the bonds). The results are reported in Fig. 7. The concentration of tin, calculated as wt.%, changed sharply during the first 3 min of sputtering. It is assumed that the contamination layer was removed after this first ion scraping. For conducting passive films on 2.5 and 1.5 wt.% Sn alloys, it is noted that the concentration of tin was largely increased by an average of 42 and 27%, respectively. Enrichment of tin in the passive layer was also observed for low and non-conducting alloys. For 1.3 and 1 wt.% Sn alloys, the tin content continuously increased up to 15 wt.% in the inner layer corresponding to 30 min sputtering. It was nearly 3 wt.% in the inner layer of non-conducting 0.5 wt.% Sn alloy.

The reason for a fast decrease of tin content in the passive film of 2.5 wt.% Sn alloy (from 42 to 27 wt.% between 13 and 30 min sputtering time) may come from the thinness of the passive layer under the effect of tin [20,21] and the increase of the metallic lead signal intensity. To explain the particular enrichment of tin in the passive film, it is necessary to consider the solubility of the species involved in the process of the film formation. As the film was formed by the polarization of Pb-Sn alloys at 0 V versus SSE in alkaline solution (pH = 9.1), Pb was oxidized to Pb(OH)₂

in the first step [10]. However, the solubility of this hydroxide is 155 mg/l of cold water [29]. Meanwhile, tin was oxidized probably to SnO, then oxidized again into SnO₂, the only thermodynamically stable compound of tin in these pH and potential conditions. SnO₂ is sparingly soluble [29]. Therefore, in the passive layer, there was first a selective dissolution of lead as soluble lead hydroxide, and later, sparingly soluble PbO was formed. Part of the PbO might react with transitory SnO to give Pb and SnO₂. By this dismutation reaction, the PbO layer became thinner and the enrichment of tin, as SnO₂, became higher, when enough alloying tin was present, such as in 2.5 and 1.5 wt.% Sn alloys.

The conductivity of the passive layers, as evaluated by the previous in situ study [10], can now be related to the particularly high content of conducting SnO₂. In non-conducting passive layers (0.5 wt.% Sn alloy), the concentration of Sn in the inner layer was found to be 3 wt.% (Fig. 7). One of the proposed mechanism of the action of tin on the electrical property of PbO has been the doping of PbO by tin [11–14]. However, doping usually requires only small amounts of dopant. This study shows that the increase in the conductivity of the passive layer demands a concentration of tin higher than 10 wt.%.

4. Conclusions

This XPS study of the passive film developed on Pb–Sn alloys in 0.1 M Na₂B₄O₇ at 0 V versus SSE has led to the following conclusions:

1. The signals of tin, lead and oxygen (main components of the passive films) were depleted in unshifted and shifted signals when the conductivity of the films (evaluated by electrochemical study) became very low.

2. The shifted signals were assumed to have originated from positively charged zones on the surface film due to the low conductivity. The shifting increased when the alloying tin content decreased, that is, when the film conductivity decreased.

3. The concentration of tin (as compared with lead) in the passive films was largely increased, up to 44, 28, 14, 13 and 3 wt.%, respectively, for 2.5, 1.5, 1.3, 1 and 0.5 wt.% Sn alloys.

4. Semi-quantitative analysis showed that one of the effects of alloying tin could be the thinning of the passive films, as observed for 2.5 wt.% Sn alloy. The inner layer of the passive films was found to be rich in conducting tin oxide and metallic lead.

5. XPS did not distinguish SnO from SnO₂ signals, but SnO₂ was assumed to be present in the passive films, for reasons of its thermodynamic stability.

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