

Evaluation of lead–calcium–tin–aluminium grid alloys for valve-regulated lead/acid batteries

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Abstract

Cast lead–calcium alloys have been generally employed in valve-regulated lead/acid (VRLA) batteries since they appeared in the early 1970s. Some minor elements such as aluminium, silver, bismuth and some alkaline earth metals are also added to lead–calcium alloys to improve the alloy properties and the battery performance. A convenient method for the addition of aluminium into the alloy, compared with other methods reported, is presented. On addition to lead–calcium alloys, bismuth can form a Bi–Ca compound according to the de-bismuthizing equation: $3\text{Pb}_2\text{Ca} + 2\text{Bi} \rightarrow \text{Bi}_2\text{Ca}_3 + 9\text{Pb}$. There is a slight solubility of Bi_2Ca_3 in the lead at its melting point (327 °C) with an amount of 0.048 wt.% resident bismuth. It is confirmed that the creep strength and the corrosion resistance is distinctly increased by the addition of silver into the grid alloy, but the associated gassing problem should be considered when such alloys are employed in VRLA batteries. Addition of sodium can refine grain sizes and increase the mechanical properties of the grid alloy, but the corrosion resistance of sodium-contained grids is inferior. A general description of experiments and application of tin, aluminium, bismuth, silver and sodium as additives in lead–calcium alloys is given.

Keywords: Valve-regulated lead/acid batteries; Lead/acid batteries; Grid alloy; Bismuth; Lead; Calcium

1. Introduction

Tracing the development of the lead–calcium alloy system, it is not without surprise that the compositions of the alloys, i.e. the concentration ranges of the minor elements, — even those reported lately [1,2] — show little significant variation since the alloys were introduced forty years ago [3]. Moreover, this is despite the considerable progress that has been achieved, both in theoretical research and commercial production.

Lead–calcium alloys were studied as early as 1859, and the application of the alloys in lead/acid batteries was first reported by Thomas et al. [4] in 1935. In the first applications, the lead–calcium alloys were only used in stand-by power batteries on float service because of the poor charge/discharge performance and comparatively poor cycle life.

Since the 1970s, there has been a growing demand in the battery market for low-maintenance and maintenance-free batteries. The traditional lead–antimony alloys are unsuitable for such types of batteries. This is because, during battery operation, antimony dissolves from the positive grid, deposits on the negative plate and, by virtue of its low hydrogen overpotential, causes excessive gassing. Obvi-

ously, this produces high water loss and demands routine maintenance.

The lead–calcium alloy system, due to its high hydrogen and oxygen overpotentials, has received greater and greater attention. Unfortunately, earlier results showed that the lead–calcium alloy used for grids was unsatisfactory, because the battery capacity declined sharply after deep-discharge cycles. This phenomenon was termed the ‘antimony-free effect’. Such abnormal phenomenon is also observed in positive plates of low-antimony-lead (<3 wt.% Sb) and, thus the term ‘premature capacity loss’ (PCL) has been adopted and now is widely accepted. Detailed investigations and discussions on PCL have been presented recently by Pavlov [5] and Hollenkamp et al. [6].

There has been a series of studies that have involved the improvement of lead–calcium alloy grids by further additions of other elements to the binary alloys. A review on the research and development of lead–calcium alloys was given recently by Bagshaw [7].

Tin is the most common additive in lead–calcium alloys. Tin can improve the mechanical properties and castability of battery grids. The most attractive property of tin is the influence on the positive plates, i.e. suppression of the passivation

of the positive plate. Pavlov and co-workers [8] have made great progress in the investigation of this phenomenon. A review has been compiled recently by Culpin et al. [9]. A tin content of about 0.5 wt.% has been normally used in lead–calcium alloys, but now 1–2 wt.% Sn is preferred for cast grids. Prengaman [2] pointed out that lead–calcium alloys with high tin contents were susceptible to severe penetrating corrosion and, thus, could not be used effectively for thin grids.

One of the major problems in the use of lead–calcium–tin alloys is the control of calcium content. Calcium is very susceptible to oxidation, which is especially severe when the alloy is agitated by stirring, pumping, or is accepting the return of trim scrap from cast grids and reject grids when the temperature at the melt pot is over 450 °C.

To prevent calcium oxidation, the simplest way is to add aluminium to the alloys. Aluminium dissolved in the alloy affords the covering of the molten alloy with a layer of aluminium and aluminium oxide, which prevents access of oxygen to the molten alloy. A level 0.015 wt.% or more of dissolved aluminium is sufficient to prevent calcium oxidation [10].

Since it is difficult to dissolve aluminium in the lead alloy, elaborate methods have been devised. These include: molten salt cover; fused salt electrolysis; inert atmosphere, and floating dross cover. A convenient way involves applying a commercially available Ca–Al master alloy for alloying calcium and aluminium in lead, as proposed by Prengaman [11]. Recently, a new method has been reported by Hibbins et al. [12]. This process uses pure calcium and aluminium in the form of granules; the approach offers some advantages over those proposed previously. In the present study, an alternative Sn–Al master alloy was chosen and was found to be more convenient for preparing lead alloys for grid manufacture, both in the laboratory and in the workshop.

Although the cast lead–calcium grid alloys that are commonly used contain a certain amount of aluminium to protect calcium from oxidation, the influence of aluminium on the electrochemical properties of the grid/active-material and on the battery performance is rarely reported.

High-purity lead (99.99 wt.%) has long been considered necessary for good battery performance. The purity of lead, within the range 99.9 to 99.99 wt.%, differs only in the bismuth content, according to standard *ASTM B29-49*. Because of the chemical similarity of bismuth to lead, the removal of bismuth from lead to a level below 250 ppm is both difficult and expensive. This may be one of reasons why the investigation of the effect of bismuth on the lead/acid battery has been of so much interest for both battery manufacturers and lead suppliers. Bismuth can be added into either the grid alloy or the active material. Although the effect of bismuth, whether harmful or beneficial to grid properties and battery performance, has been studied for a long time, there is considerable conflict over its true effect(s). It is now generally agreed, however, that the presence of a certain amount of bismuth is beneficial rather than deleterious. The optimum level has still

to be determined. Recently, Koop et al. [13] presented a detailed review which has clarified the influence of bismuth on battery performance.

Detrimental effects of bismuth on alloy strength have been reported by Prengaman [14]. In this work, 0.012 wt.% Bi was added to pure lead, lead–calcium and lead–calcium–tin alloys. For the lead–calcium alloy, it was found that bismuth promoted the segregation of Ca-rich and Bi-rich regions. This effect, in turn, accelerated the rate of grain-boundary movement. An enhanced segregation of tin and bismuth was observed in lead–calcium–tin alloys with high ratios of Sn to Ca. It was suggested, however, that the resulting development of high levels of bismuth and tin in localized areas might be advantageous from the point of view of improved battery recovery from deep discharge.

Caldwell et al. [15] investigated the effect of bismuth on the hydrogen-evolution reaction on lead–calcium and lead–calcium–tin alloys. It was reported that low levels of bismuth (<0.018 wt.%) had little influence on the gassing rate; a greater effect was promoted by the calcium and tin constituents.

A report from Maja and Penazzi [16] showed that the presence of bismuth suppressed hydrogen evolution and enhanced oxygen reduction. This result implied that bismuth might improve the performance of the gas recombination in valve-regulated lead/acid (VRLA) batteries.

Cycle-life testing of automotive batteries with lead–calcium–tin grids containing various amounts of bismuth has been reported by Devitt and Myers [17]. In an overcharge life test, based on *SAE J537*, no ill effects due to bismuth were observed. By contrast, in a cycle-life test based on *SAE J240*, battery endurance tended to increase with increasing bismuth content for lead–0.07wt.%Ca–0.7wt.%Sn grids containing 7 to 480 ppm bismuth, i.e. up to 0.048 wt.% Bi).

Lam et al. [18] examined the influence of bismuth on the age-hardening and corrosion behaviour of low-antimony–lead alloy systems. Their results showed that the addition of bismuth had no significant effect on the age-hardening behaviour, general microstructure or grain size of the alloy, but influenced the morphology of the eutectic in the inter-dendritic regions. The corrosion rate of the grid decreased with increase in bismuth content. Moreover, bismuth contents of up to 0.09 wt.% did not affect the self-discharge behaviour of the batteries.

Lead–calcium alloys suffer more severe positive-grid growth in service than lead–antimony alloys. This growth is the result of a combined action that may be attributed to a swelling effect and creep-type deformation. The swelling effect in the grids is due to growth of inter-granular corrosion products during battery service. The tensile strengths of cast lead–calcium and lead–antimony alloys are similar, but the creep strength of cast lead–calcium alloys is much lower than that of their antimony counterparts.

Silver is a promising grid additive. Dasoyan and Aguf [19] pointed out that the addition of silver considerably disperses the structure of lead and lead–antimony alloys and increases

the compactness of the lead dioxide film. The formation of a high-dispersion inter-metallide causes an increase in the corrosion resistance of the alloy. The authors stated that the lead-calcium alloy system does not differ much in corrosion resistance from normal lead-antimony alloys. Silver is required in order to increase the corrosion resistance of lead-calcium alloys.

Some alkali earth metals, e.g. lithium, sodium and potassium, have also been proposed as grain-refining additives. Lead alloys containing lithium have been found to be of no use in commercial batteries, due to the inferior corrosion resistance. The improved mechanical properties of lead alloys containing sodium have been reported [20], but the influence on the corrosion resistance, which is of great concern for such alkali metal additives, has not been reported. The addition of a certain amount of alkali metal ions (such as Na^+ ions) to the electrolyte has proved to be beneficial to the battery performance [21].

The mechanism of the influence of different additives on the corrosion resistance of lead and lead alloys can be quite different. There are, however, some general principles that make it possible to classify the alloy additives. The classification of small additions, according to their effect on the rate of anodic corrosion of lead and lead alloy, can be carried out on the basis of the theory of modification. According to the hypothesis, alloying elements that do not show any influence on the structure of the alloy generally either do not change the rate of anodic corrosion of the alloy or cause intensification of corrosion. As a rule, additives that regulate the process of crystallization and cause marked dispersion of the grain dimension, increase the corrosion resistance of the metal [19].

2. Experimental

2.1. Sample preparation

Pure lead (99.99 wt.%), calcium (99.5 wt.%), tin (99.8 wt.%), aluminium (99.9 wt.%) were purchased as commercial products from PR China.

Table 1
Effects of some elements on the mechanical properties of Pb–Ca–Sn–Al alloys at room temperature

Alloy composition (wt.%)						Vickers micro-hardness	Elongation	Tensile strength
Ca	Sn	Al	Ag	Bi	Na		(%)	(kgf mm^{-2})
0.105	0.548	0.018				14.9	32.1	3.44
0.107	0.540	0.012	0.026			16.4	17.6	4.21
0.102	0.561	0.010	0.053			16.5	17.5	4.50
0.110	0.529	0.012	0.071			17.9	17.2	4.63
0.087	0.530	0.009		0.033		13.4	34.9	3.28
0.082	0.527	0.014		0.059		13.9	30.4	3.41
0.088	0.569	0.018		0.072		14.3	26.2	3.58
0.104	0.460	0.022	0.024	0.032	0.05	16.8	17.4	4.12
0.121	0.470	0.011		0.032	0.05	17.2	16.1	4.24

2.2. Tin–aluminium binary alloy

In order to dissolve aluminium in lead, tin–aluminium binary alloys, with 5 and 10 wt.% Al, were prepared. According to the tin–aluminium phase diagram, the melting points of these two alloys are about 470 and 530 °C, respectively. The resulting alloy was poured into ingots as a master alloy for preparing the cast grid alloy. The total weight loss during the process was about 1 wt.% (both tin and aluminium), and the composition of the master alloys was analysed by measuring the melting point of the binary alloy. A vertical tube furnace with a sealed lip and an automatic temperature controller were used for the alloy preparation.

The cast lead–calcium–tin–aluminium grid alloys were prepared by employing a specially designed container. Dissolution and reaction mainly take place inside the container rather than in the molten-lead pot. The preparation of lead–calcium–tin–aluminium alloys was performed in a workshop at a battery company in PR China.

Some other elements, such as silver, bismuth and sodium were directly added into the molten lead–calcium alloys. Due to their good miscibility with lead, these elements improved the properties of the lead–calcium alloys.

All sample rods (diameter: 10 mm) used in this study were gravity cast manually at 450 °C in a steel mould held at 180 °C. The sample rods were cooled in forced air. All samples were stored for over two weeks before testing in order to avoid age-hardening effects.

2.3. Composition analysis

The results of chemical analyses (inductively coupled plasma spectroscopy (ICP)) on the casting rods and grids are presented in Table 1. Some samples were also analysed by electron probe microanalysis (EPMA) in order to confirm the ICP results.

2.4. Microstructure

The microstructures of cross sections of the cast lead–calcium grid alloys were examined by optical microscopy.

Table 2
Procedure used for grinding and polishing the grid-alloy samples

Equipment autopolisher	Grinding			Polishing		
	1	2	3	1	2	3
Base	SiC-paper	SiC-paper	SiC-paper	DP-mol	DP-nap	OP-chem 0.05 μm
Grain	500	800	1200 ^a	DP-spray 3 μm Red	DP-spray 1 μm Red	OP-S ^b
Lubricant	Paraffin	Paraffin	Paraffin			
Speed (rpm)	300	300	300	150	150	150
Pressure (N)	90	90	90	120	90	60
Times (s)	60	60	60	120	120	120

^a Subsequent etching in solution 1.

^b 90 ml OP-S + 10 ml solution 2, 100 ml distilled H₂O, 139 ml HNO₃. Solution 2: 84 ml glycerine, 8 ml CH₃COOH, 8 ml HNO₃.

Table 3
Stripping solution

Solution chemicals	Amount
Hydrazine dihydrochloride (g)	100
Ammonium acetate (g)	150
Glacial acetic acid (g)	40
H ₂ O (l)	1

The samples were mounted in epoxy resin (Araldite) at room temperature. The mounted samples were ground and polished by an automatic polisher (Struers Abramin, Denmark). Micrographs were taken with a Nikon-optiphot (UFX-II, Japan) system. The procedures used for sample treatment are detailed in Tables 2 and 3.

2.5. Mechanical strength and hardness

Dumb-bell samples (diameter: 5 mm, length/diameter: 4) for elongation and tensile strength measurements were machined from cast sample rods. Tensile strength results were collected on an Instron Mechanical Testing Machine (Model-4302, UK) and an average value obtained from three test samples. Measurements of Vickers hardness were performed on a Micro Hardness Testing Machine (Leco M-400-H1, Japan).

2.6. Grid growth

Tests were performed on two 12 V batteries (fabricated in a workshop) with a nominal capacity of 45 Ah. The grid composition is given in Table 1. One battery (A) was cycled at 100% depth-of-discharge (DOD) until failure; the C/10 rate was used on the first cycle, then the C/5 rate was applied until the capacity declined to 60% of the nominal value. The second battery (B) was stored for 15 months, i.e. left on open stand without charging/discharging and was then tested under 100% DOD at the C/10 rate.

The sample batteries, after test, were disassembled. The growth of the positive grids was measured after the active material had been removed by a 'stripping' solution.

3. Results and discussion

The dissolution of aluminium in the molten lead is very difficult due to the aluminium oxide layer on the surface of aluminium metal and the low solubility of aluminium in molten lead. Aluminium dissolution can be improved, however, by increasing the molten lead temperature up to 600 °C. Unfortunately, such a high temperature is not suitable for practical application.

Since tin-aluminium binary alloys have a wide range of miscibility [22] and correspondingly low melting points, it should be possible for aluminium to be alloyed in the molten lead via a tin-aluminium master alloy at lower temperatures. It is also possible to control the tin:aluminium ratio in the tin-aluminium master alloy, so that the aluminium content in the lead alloys can be adjusted as required. The main function of aluminium in the lead-calcium system is to protect calcium from oxidation. A dissolved aluminium level of over 0.015 wt.% is recommended.

Fig. 1(a)–(h) shows metallographs of the cast lead-calcium-tin-aluminium alloy and alloys with different additives. All these samples were prepared in the authors' laboratory. The grain size, composition segregation and precipitation distribution are sensitive to the alloy composition, and are also influenced by the casting condition. Sample rods were cast in a 10 mm thick metal mould and cooled in forced air. All tests on these samples were performed after a two-week storage period in order to avoid age-hardening effects.

The microstructures of the samples show that: (i) the higher the calcium content, the finer the grain size; (ii) increase in bismuth content in the lead-calcium alloy does not refine the grain size; (iii) silver additions refine the grains, and (iv) silver or sodium addition produces a much finer grain size.

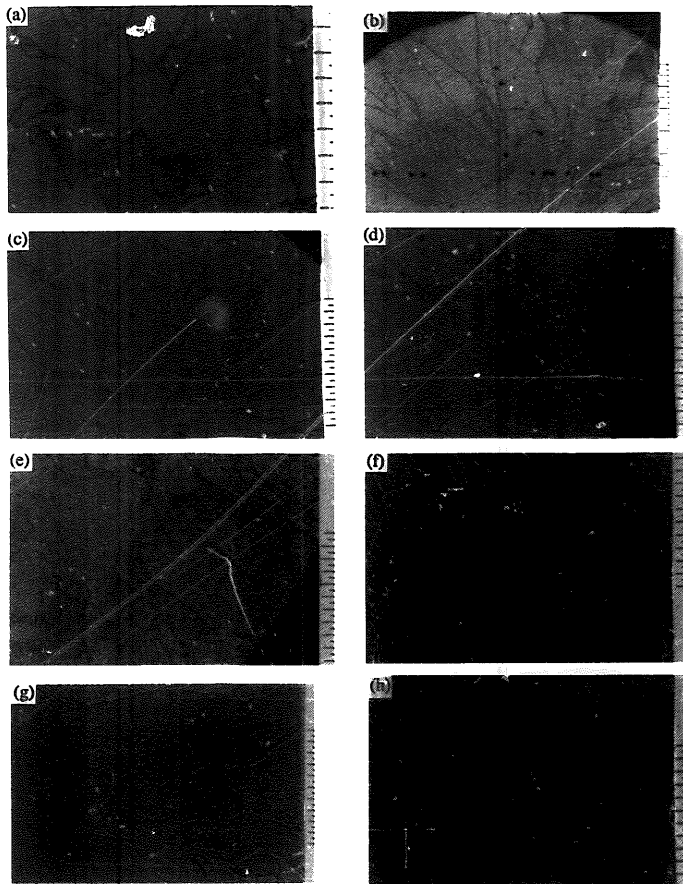


Fig. 1. Microstructure of: (a) Pb-0.105Ca-0.548Sn-0.018Al; (b) Pb-0.107Ca-0.540Sn-0.012Al-0.026Ag; (c) Pb-0.102Ca-0.561Sn-0.012Al-0.053Ag; (d) Pb-0.110Ca-0.529Sn-0.012Al-0.071Ag; (e) Pb-0.087Ca-0.53Sn-0.009Al-0.033Bi; (f) Pb-0.082Ca-0.527Sn-0.014Al-0.059Bi; (g) Pb-0.088Ca-0.56Sn-0.018Al-0.072Bi; (h) Pb-0.104Ca-0.460Sn-0.0226Al-0.024Ag-0.032Bi-0.05Na. Note, dark cross marks in (b) and (d) are from the microhardness test. The ruler attached on the right of each micrograph gives divisions of 0.1 mm.

A micrograph of an interior wire member (along the horizontal direction) of the positive grid from battery A, after failure is shown in Fig. 2. The grid growth of the two failed batteries was calculated as the percentage of horizontal increase. Two plates were chosen from battery A and from battery B. The width of the normal grid is 150.0 ± 0.5 mm.

The maximum grid width in battery A was 161.0 ± 0.5 mm. Thus, the maximum grid growth rate = $(161.0 - 150.0) / 150.0) 100\% = 7.3\%$.

The maximum grid width in battery B was 153.5 ± 0.5 mm. Thus, the maximum grid growth rate = $(153.0 - 150.0) / 150.0) 100\% = 2.3\%$.

The outlook of the positive grids from the two failed batteries are given in Fig. 3. Battery B had been left on open circuit for about 15 months and the failure was due to 'sulfation'. The grid from battery B shows no apparent grid growth. Battery A was tested under 100% DOD cycles; the failure was due to severe positive-grid corrosion and growth.

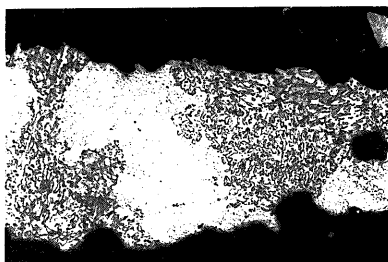


Fig. 2. Microstructure of the positive grid (Pb–0.121Ca–0.47Sn–0.030Al–0.032Bi–0.05Na) from battery A after failure, magnification $\times 10$.

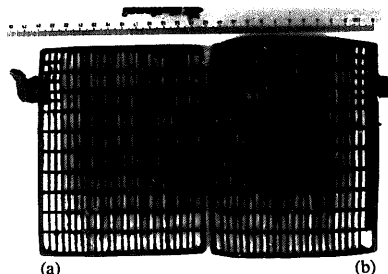


Fig. 3. Outlook size of two positive grids from (a) battery B and (b) battery A after failure.

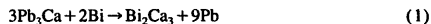
As shown above, the growth rates for battery B and A were 2.3 and 7.3%, respectively.

The low corrosion resistance and low creep strength of the grids were attributed to the extremely fine grains of the grid alloy. Such a fine grain structure was due to the excessive calcium content in the alloy, which was caused by the poorly controlled calcium content during grid manufacturing and the addition of sodium to the alloy. It has been reported [21] that the addition of sodium refines the grains, improves mechanical properties (such as hardness and tensile strength), and enhances casting performance. On the other hand, no information about the creep strength and the corrosion resistance has been reported. The mechanism of grain refining by the addition of sodium can be altered significantly by the addition of silver. Silver, due to its high melting point (961.9 °C), can form nuclei for the formation of finer cast grains and can distribute uniformly in the alloy. Sodium, which has a very low melting point (97.8 °C), does not form such nuclei but can dissolve in the molten lead. The lattice parameter of lead is decreased when sodium is incorporated in the solid lead; thus, a refined grain structure is obtained. The dissolved sodium is prone to segregate at the grain boundaries. The enrichment of such a soft and ductile element at the grain boundaries can enhance the grain movement under stress and give a lower creep strength. Further experimentation showed

that sodium is able to precipitate from the grids into the solution due to its high chemical activity. This can increase the grid corrosion rate and accelerate grid growth during battery service. Of course, the grid behaviour of the sample battery depends on multiple parameters, but the extremely fine grain-size was one of the main causes for the grid growth and the poor corrosion resistance. Thus, before confident beneficial effect(s) on the corrosion property and creep strength are confirmed, sodium is not recommended as an alloying additive in the cast lead–calcium alloy system.

Silver has been confirmed as an effective additive for increasing both the corrosion resistance and the creep strength, and is presently employed in battery manufacture. The negative effect of silver is the high cost and gassing problems. Effects on self-discharge are still uncertain.

The influence of bismuth on battery performance has been debated for a long time. Overall, the evidence supports the beneficial effects of bismuth on battery performance. Recent results from Lam et al. [18] have strengthened this view point. It should be noted, however, that particular care should be taken to investigate the influence of bismuth on the cast lead–calcium alloy system. During the process of refining lead, i.e. de-bismuthizing of lead, calcium is generally used to remove the bismuth from the lead according to the reaction [23]:



Bismuth contained in lead is therefore first tied up with calcium when the latter is added to the molten lead. There is a slight solubility of the compound Bi_2Ca_3 in the lead at its melting point (327 °C), at 0.048 wt.% Bi content. Only after all the bismuth has been combined with calcium, can lead react to form Pb_3Ca . The equilibrium Bi–Pb diagram shows no compounds, while the main compound in the Bi–Ca series is Bi_2Ca_3 [22]. It has also been proposed to use combinations of calcium with alkali metals during the process of refining lead. These metals reduce the solubility of Bi_2Ca_3 in the lead. Bismuth forms compounds with these metals, which rise to the surface and are removed as dross.

In view of the above situation, higher bismuth contents would lead to the formation of bismuth compounds with calcium in cast lead–calcium–bismuth alloys. Due to the low solubility, the excess Bi_2Ca_3 compound should rise to the surface as dross, rather than dissolve in the molten alloy. This is probably why such different results were observed on the microstructure of lead–calcium–bismuth alloys.

In our experiments, we found that more dross appeared on the surface of the molten lead–calcium alloy after bismuth addition with stirring. If the dross was removed, both the calcium and bismuth contents were lower than expected. Unfortunately, we have not confirmed the existence of the bismuth compound in the alloy, but reaction (1) from the de-bismuthizing process should be applicable. Although the solubility of the bismuth compound at a given temperature in the molten lead alloy has not been further proven (as reported:

0.048 wt.% Bi), a higher bismuth content in the lead–calcium alloy system could be obtained by rapid-cooling.

The mechanical properties of the lead–calcium–tin–aluminium alloys were improved by the addition of silver and bismuth. The data are given in Table 1. The values shown were obtained from the average of three samples. Corrosion properties of the alloys, such as normal corrosion test, accelerated corrosion test, and the effects of the alloys on the electrochemical properties, are under consideration.

4. Conclusions

Lead–calcium alloys are now widely used in the grids of VRLA batteries. Although lead–calcium alloys with different compositions are commercially available, some battery manufacturers prefer to make their own alloys. This study has provided an alloy preparation procedure that is particularly suitable for small-to-middle size battery manufacturers. The effects of some additives, such as silver, bismuth and sodium, on the alloys have been discussed.

The following conclusions can be drawn:

- Aluminium can be alloyed in the molten lead via a tin–aluminium master alloy. A level of aluminium of over 0.015 wt.% is sufficient for preventing calcium loss during grid manufacture.
 - Silver can increase both creep strength and corrosion resistance, but the optimum content has still to be determined.
 - Bismuth has been reported to have beneficial effects on battery performance, most of the evidence reported shows that bismuth contents used in lead alloys are around 0.05 wt.%. A higher bismuth content in cast lead–calcium alloy is prone to form the Bi_2Ca_2 compound. The addition of alkali metals can reduce the solubility of the Bi–Ca compound in lead due to the de-bismuthizing reaction. Higher contents of bismuth in lead–calcium alloys could be obtained by the rapid-cooling technique. In order to confirm this, further investigations are required.
 - Addition of sodium refines the grain size and improves the tensile strength and hardness of lead–calcium alloys, but sodium-containing grids display a poor creep strength and unsatisfactory corrosion resistance.
- From the point of view of battery manufacture, attention should be directed more towards how to control precisely the required element contents during the grid-casting process, than towards the choice of alloy.

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