

Lead alloys: past, present and future

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Abstract

The most critical non-active component in the lead/acid battery is the grid or substrate. A review of the work on grids and grid alloys in the period 1960–1993 has been carried out by the Advanced Lead–Acid Battery Consortium and, in this paper, the results are analyzed in relation to the effort expended on different alloy systems. Lead–antimony alloys and the effects on them of additions of arsenic, tin, and grain-refining elements (selenium, sulfur, copper), together with lead–calcium alloys and the effect on them of tin additions, have received the greatest attention in the past. Proposals are made for future studies. Possible evolutionary developments include the addition of silver and higher amounts of tin to lead–calcium alloys, more detailed investigations of lead–strontium and lead–lithium alloys containing tin and/or silver, and further work on very-low-antimony alloys. More speculative projects are very rapidly cooled alloys, the use of aluminium as grids or spines, plastic/lead-coated copper negative grids, corrosion-resistant coatings of lead compounds on the grids and, finally, a substrate for a bipolar plate that is based on conductive inorganic compounds.

Keywords: Lead; Battery; Alloy; Grid

1. Introduction

The most critical non-active component in a lead/acid battery is the grid. This is used to support the positive and negative active materials, and also to provide a conductive path for the current to and from the plates during charge and discharge. Almost from the time when pasted and tubular plates were invented, it was recognized that the mechanical and electrochemical properties of the respective grids and spines might be improved by using lead alloys rather than the pure lead which had been used in the traditional Planté plates.

As a result of many investigations by battery workers by the end of the first half of the twentieth century, various lead alloys had become established. The main alloying system used in grids was lead–antimony. This was usually based on the eutectic composition of about 11 wt.% antimony as such an alloy was easy to cast into the complex form required for battery grids. By the 1950s, the antimony content employed by some manufacturers was decreasing, and alloys containing 6–9 wt.% antimony were becoming more common. Some battery technologists had also recognized that small amounts of other elements (e.g., arsenic and tin) were

beneficial in the operation of a battery, at least in the case of the positive-grid alloy.

By the 1950s, the phenomenon of antimony poisoning was also well recognized and alternative alloy systems were being tested in batteries. The favourite alternative was a binary lead–calcium alloy. This system had been investigated extensively, notably in the USA, for telephone applications in order to prevent the changes in floating characteristics during the life of a battery that might be caused by antimony poisoning.

Since 1960, a considerable amount of research and development of grid alloys has been carried out. A review of this work has been carried out under the auspices of the Advanced Lead–Acid Battery Consortium (ALABC). This paper gives a short analysis of the results of the review, and summarizes the present position in the use of lead alloys in battery grids. The final part of the paper presents suggestions for future work on grid alloys in order to try to meet the demanding requirements for batteries into the next century.

2. Grid alloy research: 1960–1993

As part of the programme for developing an improved lead/acid battery for modern electric vehicles and to provide a basis for future research in grid alloys, the

ALABC has carried out a review (Project Pb-001) of the information available and published since 1960. This review [1] included all the work in Europe and the USA that could be uncovered by searching various data bases, as well as by examining battery literature and patents and other available information supplied by companies. Each paper or patent was summarized in a single sheet record. The records were coded into alloy types. For investigations involving more than one alloy, a record was included in each alloy category. In all, the search resulted in 1797 records.

From an analysis of the records, it is interesting to note the amount of effort devoted to each alloy category. Table 1 shows a broad analysis by major alloy type. Not surprisingly, the main effort has been in lead–antimony and lead–calcium alloys, with only a small amount of work on other alloys containing barium, strontium or lithium, or on the dilute alloys of the ASTAG (arsenic–tellurium–silver) or ASTATIN (arsenic–tellurium–silver–tin) type.

2.1. Lead–antimony alloys

The research and development into lead–antimony alloys can be further analyzed in relation to additional elements included in the alloys. Table 2 shows an analysis on this basis.

A significant number of investigations covered binary alloys. It was recognized that, whilst a decrease in antimony content in the positive grid below the traditional 6–11 wt.% caused a reduction in antimony poisoning of the negative plate, it also reduced the number of deep cycles that a battery could withstand. Much of the work on lead–antimony alloys was therefore basic research on the effects of antimony on the corrosion product, on the interface between the grid and the active material, and on the morphology of the active material itself.

Table 1
Analysis of grid alloy research and development, 1960–1993, by major alloy types (ALABC Project Pb-001)

Alloy	Effort (%)
Pure lead	3.8
Lead–antimony	35.5
Lead–calcium	30.1
Lead–barium	1.2
Lead–strontium	1.5
Lead–lithium	0.9
Dilute As–Te–Ag–(Sn)	2.1
Other binary systems	6.3
Composite grids	9.6
Other metal grids	2.9
Grid design	4.4
Surveys	1.7

Table 2
Analysis of research and development, 1960–1993, of grid alloys containing antimony (ALABC Project Pb-001)

Alloy	Effort (%)
Lead–antimony	27
Lead–antimony–arsenic	22
Lead–antimony–tin	22
Lead–antimony–silver	3.5
Lead–antimony–selenium	8
Lead–antimony–copper	5
Lead–antimony–sulfur	2.5
Lead–antimony–cadmium	5
Others	5

It was also recognized that low-antimony alloys had inferior properties in relation to castability, mechanical strength and corrosion under battery operating conditions. Much of the research work was therefore devoted to the effects of additional elements to the basic lead–antimony system. The two most widely used elements have been arsenic and tin and this is reflected in the number of records concerned with these elements (Table 2).

Basically, arsenic exerts two major effects on the properties of lead–antimony alloys: (i) it increases the rate of age-hardening which, in practical terms, means decreasing the time that a grid has to be stored after casting before further processing; (ii) it increases the creep resistance which, in turn, increases the durability of the positive plate, especially during deep cycling. One of the first companies to make use of this increased durability was the Electric Storage Battery Company of the USA who added 0.5 wt.% arsenic to its 6 wt.% antimonial alloy used for positive grids, even in automotive applications.

The effect of an addition of tin is to increase the fluidity of molten lead–antimony alloys thereby increasing the castability, and also to increase the cycle life of batteries containing very thin plates. The latter feature was first recognized by the Chloride Electrical Storage Company in the early 1960s when as much as 2.5 wt.% tin was added to a 9 wt.% antimonial alloy for positive grids in a special military battery that was used in cycling service.

Since the 1960s, many fundamental and practical investigations have been carried out on the effects of both arsenic and tin on lead–antimony grid alloys, as shown in Table 2. By comparison, the amount of effort on the effect of silver additions has been very low, despite the fact that by 1960 at least one company – the Electric Storage Battery Company of the USA – was using a small amount of silver in the positive grids of its first-line automotive batteries. Silver increases both the corrosion resistance and the creep resistance of lead–antimony alloys and, therefore, it has a marked influence on the durability of batteries in any application

where the final failure mode is corrosion and disintegration of the positive grid. The disadvantage of silver is its relatively high cost and this no doubt explains both the lack of interest in its use in batteries and the corresponding small amount of effort devoted to it.

In the period 1960–1993, there has been continuous pressure to reduce the amount of antimony in battery grids. This has resulted from both cost-reduction exercises and the need to produce low-maintenance batteries. With reduction in antimony content to below 6 wt.%, there was a need for alloy development to improve the properties. Most of the effort was towards refining the grain size of the low-antimony alloys, both to improve castability and to reduce the effects of intergranular corrosion of the positive grid during actual battery operation. Although selenium had been used as a grain refiner in a lead–3 wt.% antimony alloy in positive grids of submarine batteries in the UK, no other work had been carried out prior to 1960. Since then, the increased amount of effort devoted to grain-refining additions can be seen in Table 2, namely, 8% on selenium, 5% on copper and 2.5% on sulfur. All these elements refine the grain size of low-antimony alloys, but selenium is the most effective and the most widely used.

Table 2 also shows that 5% of the effort on lead–antimony alloys during 1960–1993 was devoted to ternary lead–antimony–cadmium alloys. This is a very interesting system as pseudo-binary alloys of lead and the compound SbCd exist within it. Such alloys containing 1.5–2.5 wt.% antimony and 1.5–2.5 wt.% cadmium have excellent properties for battery grids and have been used in the USA, even for grids in valve-regulated batteries that employ the principle of oxygen recombination. Extensions to the use of these alloys will no doubt be inhibited by the environmental problems associated with cadmium.

2.2. Lead–calcium alloys

An analysis of the research and development of lead–calcium alloys, in terms of additional elements included in the alloys, is given in Table 3.

Following the original work on binary lead–calcium alloys and their use in batteries for telephones and nuclear submarines in the USA, it is not surprising

Table 3
Analysis of research and development, 1960–1993, of grid alloys containing calcium (ALABC Project Pb-001)

Alloy	Effort (%)
Lead–calcium	32
Lead–calcium–tin	55
Lead–calcium–aluminium	5
Lead–calcium–silver	0.1
Others	7.9

that 32% of all the effort over the period 1960–1993 was devoted to binary alloys. This covers both basic investigations of the alloy system and attempts to use binary alloys in other applications. The development of low-maintenance and maintenance-free batteries and the move towards ‘purer’ systems, with no poisoning of the negative plate, has resulted in the use of binary lead–calcium grids in the negative plates of ‘hybrid’ batteries. Examples are submarine batteries in the UK and automotive batteries, notably in the USA.

The poor metallurgical properties in terms of mechanical strength and creep resistance, causing difficulties, respectively, in handling grids (especially when thin) and growth of positive plates in service, led to investigations of additions of other elements to improve the properties. The recognition that the cycle life of batteries containing lead–calcium grids was very poor (termed both ‘antimony-free effect’ and ‘premature capacity loss’) added urgency to the need for improved alloys by further alloying additions. Table 3 shows that by far the greatest effort was devoted to alloys containing calcium and tin. As a result of this, lead–calcium–tin alloys have become established both in automotive batteries using traditional technology, and in valve-regulated batteries employed in standby applications and small portable devices.

Lead–calcium–tin alloys have much inferior creep properties to the traditional lead–antimony–arsenic alloys but very little work has been carried out to resolve this problem. Nevertheless, the analysis given in Table 3 shows that 0.1% of the effort on lead–calcium alloys between 1960 and 1993 was on additions of silver. This results in improvements in both creep resistance and corrosion resistance and, therefore, will have a dramatic effect on the durability of any battery where the life-limiting determinants are corrosion and disintegration of the positive grid.

The other major problem in the use of lead–calcium alloys is preferential oxidation of calcium in the molten state. This results in a rapid loss of calcium from molten alloys when they are held above 450 °C. Although the problem can be overcome by the use of an inert atmosphere over the molten alloy, the simplest way is by the addition of aluminium to the alloy. Such treatment affords protection of calcium by preferential oxidation and the covering of the molten alloy with a layer of aluminium and aluminium oxide. Work on alloys containing aluminium to protect both lead–calcium and lead–calcium–tin alloys from oxidation amounts to 5% of all the effort during 1960–1993, as shown in Table 3.

2.3. Other alloys

The analysis of all work on alloys in Table 1 reveals that only a small amount of effort has been devoted to systems other than those containing antimony or calcium.

Lead–barium alloys (including alloys that also contain tin or other elements) accounted for 1.2% of the work. In general, they are inferior to lead–calcium alloys: the age-hardening effect of barium is less than that of calcium; lead–barium–tin alloys have a relatively poor castability with the tendency to form hot tears in grid castings; and, finally, the presence of barium in the corrosion product and in the active material at the interface with the grid can result in loss of contact and shedding of active material.

Table 1 shows that lead–strontium alloys have accounted for 1.5% of all the work on grid alloys. In general, lead–strontium and lead–strontium–tin alloys are similar to the corresponding alloys containing calcium, but the properties are somewhat better. Although lead–strontium–tin alloys were used in automotive batteries in the USA for a time, they have found no widespread use. The cost of strontium (until fairly recently) was considerably higher than that of calcium and, obviously, there was little point in making a change for battery applications where lead–calcium alloys were behaving satisfactorily.

Analysis further reveals that 0.9% of all effort on grid alloys was devoted to lead alloys containing lithium (Table 1). The mechanical properties of such alloys are better than those of corresponding alloys containing calcium, but the corrosion resistance is inferior. Lead–lithium alloy grids have found no use in commercial batteries.

Dilute alloys containing small amounts of arsenic, tellurium and silver (ASTAG), and later also containing tin (ASTATIN), have also received some attention; they account for 2.1% of all effort on grid alloys (Table 1). These alloys were first developed specifically for use in submarine cells, to eliminate the deleterious effects of antimony. They have also found some use in stationary batteries in Sweden and Italy.

The category of composite grids, shown in Table 1 to have occupied 9.6% of the effort, covers many different types. Various attempts have been made to strengthen lead by non-conventional alloying techniques. For example, dispersion-strengthened lead (a fine dispersion of lead oxide in lead with components manufactured by powder metallurgical techniques) received a high degree of attention during the 1960s and 1970s. The material was shown to have satisfactory mechanical and corrosion properties. Interest subsequently waned, however, because of the difficulties in joining the material without losing its properties. Fibre-reinforced lead (a lead matrix reinforced by a dispersion of non-metallic fibres) has also been investigated but, so far, has found no use in commercial batteries. Attempts have also been made to reduce the weight of batteries by using lead–plastic composite grids or plates. These have taken the form of a plastic grid support with a conductive lead insert, lead-coated plastic grids, lead-impregnated

plastic fibre mats, and plastic supports to thin, low-strength lead conductive grid configurations. To date, composite materials have not found extensive application in commercial batteries, although plastic grids containing lead inserts have been used in some military batteries.

Other metals have also been proposed as an alternative to lead alloys for grids and the data in Table 1 show that 2.9% of all the effort on grid alloys was devoted to this approach in the period 1960–1993. When the metal grids are further protected (by lead or by thin films of precious metals), they can of course also be considered as composite grids. The main success in this area has been the use of copper (coated with lead) in large negative plates. The increased conductivity of such plates results in an increase in the performance of a battery, particularly at high discharge rates. Copper negative grids have been used for many years in tall submarine cells produced in Germany and, more recently, have also been used in large traction cells.

3. The way forward

Since the Second World War, enormous strides have been made in the technology of lead/acid batteries. In the case of battery grids, low-antimony and antimony-free alloys have been developed to suit modern needs in both conventional and valve-regulated batteries. More sophisticated manufacturing equipment has been developed, so both cast and wrought grids can be produced at high rates and to precise dimensions.

Looking to the future, there is still work to be done. If lead/acid batteries are to play their proper part in future low-emission or emission-free road vehicles, the energy density must be significantly increased and maintenance-free units capable of over one thousand deep discharges must be developed. This may involve thinner and lighter grids with consequential higher corrosion and growth resistance. Grid alloys are required that can be employed in recombination cells without giving rise to premature capacity loss. Some of the possible evolutionary and revolutionary developments to meet these requirements are suggested below.

3.1. Evolutionary developments

Some of the evolutionary developments are given in Table 4. One of the major problems in batteries containing low-antimony or antimony-free grids is premature loss of capacity on cycling. There is much evidence to suggest that tin in the positive grid is beneficial in this respect. Lead–calcium alloys, in common use for batteries developed for non-cycling applications, contain about 0.5 wt.% tin, but higher tin contents should be examined for cycling duties. Cast grids containing 1–2 wt.% tin are prone, however, to severe intergranular corrosion and, consequently, higher

Table 4
Future evolutionary development of grid alloys

Increasing tin content in lead–calcium alloys
Addition of silver to lead–calcium alloys
Lead–strontium alloys
Lead–lithium alloys
Very-low antimony alloys

tin levels will be required. Lead–calcium–tin alloys containing 3 wt.% tin have an acceptable corrosion rate that is similar to that of binary lead–calcium alloys. Nevertheless, as the tin content is further increased, the corrosion rate also increases and may become unacceptable. An alternative approach to the problem is to use tin levels in the ‘danger zone’ of 1–2 wt.%, but to produce a fine-grained alloy in order to overcome the catastrophic effect of intergranular corrosion in coarse-grained grids. Lead–tin–calcium alloys can be grain-refined, for example, by the addition of small amounts of rare-earth elements. A finer grain is also obtained, of course, in grids produced by wrought manufacturing techniques.

Another major problem in batteries containing lead–calcium–tin grids is the growth of the positive plate during deep discharging. This causes loss of contact between the grid and active material and, indeed, this mechanical effect may well be a contributory cause to capacity loss. In metallurgical terms, the growth resistance of grids can be improved by increasing the creep resistance of the alloy. An addition of silver dramatically improves the creep properties of lead–calcium–tin alloys and additions of 0.01 up to 0.25 wt.% should be investigated. The addition of silver has a further advantage as it significantly increases the corrosion resistance of lead alloys and may make it possible to use thinner grids. A recent US patent [2] covers alloys containing 0.025–0.06 wt.% calcium, 0.3–0.7 wt.% tin with an addition of 0.015–0.045 wt.% silver. Even such a low content of silver increases the creep and corrosion resistance and these alloys are claimed to have enhanced immunity to positive grid corrosion in automotive batteries, even when exposed to high under-the-hood service temperatures. For the more arduous conditions of deep-cycling batteries, higher contents of silver will no doubt be required. The cost of silver is high but it should be remembered that, in the field of electric vehicles (EVs), the competition is from other forms of more exotic and more expensive batteries, and it is necessary to explore every avenue to improve lead/acid batteries for traction applications.

Alternatives to alloys based on lead–calcium should also be examined. The substitution of strontium for calcium is a strong possibility as previous work has indicated that lead–strontium alloys have somewhat better metallurgical properties than comparable

lead–calcium alloys. There is little point in changing to strontium for the applications (essentially floating, with relatively little cycling) where lead–calcium alloys are being used but, for the more arduous deep-cycling batteries required for EVs, lead–strontium alloys with additions of tin and silver may give a much longer life.

The alloys that give rise to problems of passivation at the grid/active material interface (one cause of premature capacity loss on cycling) contain alloying elements that have sulfates with low solubility. Lead alloys containing constituents that form sulfates with a higher solubility may be better in this respect. Lead–lithium alloys, for example, may be worth a further examination. Their corrosion resistance is somewhat lower than that of lead–calcium alloys, but this could be counteracted by the addition of a small amount of silver.

Finally, very dilute lead–antimony alloys (containing less than 1 wt.% antimony) warrant more investigation. At this level, the antimony should all be in solid solution and there is a possibility that there will be no poisoning of the negative plate. Additions of arsenic and/or silver to improve creep and corrosion resistance, as well as the addition of a grain refiner such as selenium, will be necessary. The addition of tin (possibly up to 3 wt.%) may be required to combat premature capacity loss.

3.2. Long-term research

A more revolutionary approach to grid and plate development should also be considered, to take lead/acid batteries into the next century. Some of the possible avenues of worthwhile research are given in Table 5.

One of the newer techniques used in the production of alloy components is very rapid cooling. The alloys are cooled so rapidly that the normal precipitation processes do not have time to take place. Elements that are soluble in one another in the liquid state, but normally insoluble in the solid state, can therefore be made to form ‘alloys’ that consist essentially of an intimate mixture of the elements involved. This opens up a new range of lead alloys. The phase equilibrium diagrams of lead alloy systems will have to be examined to choose those which lend themselves to this technique. The best alloy candidates are those with a wide region of miscibility in the molten state at normal casting temperatures, but are ‘immiscible’ in the solid state. Some elements have only a narrow range of miscibility

Table 5
Long-term research for grids and plate supports

Very rapidly cooled alloys
Lead-alloy-coated aluminium spines
Plastic/copper negative grids
Corrosion resistant coatings
Stable conductive substrates for bipolar plates

in the liquid state, e.g., lead and aluminium, but even in this case, if a molten lead–aluminium alloy were rapidly cooled from a sufficiently high temperature, it is possible (at least in theory) to obtain a solid alloy that contains an intimate mixture of lead and aluminium. If super-alloys with much improved properties (tensile strength, creep strength, corrosion resistance, conductivity) could be obtained by rapid-cooling techniques, methods of grid fabrication and also methods of joining would have to be devised. The latter could be a particular problem as any melting could cause a loss in properties.

The use of other metals as supports in battery plates should also be considered. Lead-coated copper grids are already used in the negative plates of large cycling cells to improve conductivity. Copper cannot be used in positive grids without very thick layers of protective lead, because of the dangers of copper contamination. Aluminium, however, has the double advantage of good conductivity and low weight. Any pin holes in a lead protective coating would allow acid ingress, but it is probable that this would simply result in anodization of the small area of aluminium uncovered, with the formation of aluminium oxide that would prevent further attack. The lead or lead alloy coating on the aluminium positive grid has to be sufficiently thick to cope with the corrosion during the life of the battery. It is also extremely important to have an intimate contact between the aluminium and the lead coating with no layer of aluminium oxide between them. Simple sheathing of aluminium rods or wire, as already proposed, is not good enough as this leaves in place any oxide on the surface of the aluminium. Possible methods for ensuring intimate contact are co-extrusion or co-drawing of lead-coated aluminium rod or wire, or special electrochemical plating methods that would need researching. If satisfactory lead-coated aluminium could be produced, it would have considerable benefits; for example, in the spines of tubular positive plates in batteries for EVs.

Methods of reducing the weight of the negative plate should be examined. The use of a plastic grid with a lead insert has shown some promise although it has been applied to only a limited extent in practical batteries. One of the limitations is the loss of conductivity in the overall plate. But if a plastic/lead-coated copper grid combination was used and the grid was designed by computer to give the most efficient conductivity, a viable lightweight negative plate could be obtained and, thus, would raise the energy density of the battery.

An alternative way of improving the energy density of traction batteries at discharge rates required for EVs is the use of thinner plates, but this results in a shorter cycle life due to corrosion of the positive grid. Methods of coating the positive grid to reduce corrosion should therefore be examined. For example, a coating of barium

metaplumbate has been proposed [3]. The coating can be produced by applying a barium-containing layer to the grid with subsequent chemical reaction to obtain the desired barium metaplumbate. It has been claimed that such a coating can increase corrosion resistance and improve the adhesion of the active material. The use of a barium compound on the positive grids of batteries for EV applications may not be wise, in view of the deleterious effect of barium on the positive active material during cycling, but other similar compounds should be examined.

Finally, the problems with the design of bipolar lead/acid batteries need to be solved. Such a construction gives both a lighter weight and improved efficiency in the use of the active material and results in a significant increase in energy density, which will be required for EV batteries in the future. The first task is to devise a thin substrate that is stable at both positive and negative potentials. If a lead alloy is used, it will need extremely high corrosion resistance to withstand the conditions on the positive side. Titanium cannot be used because it is unstable at negative-plate potentials. Graphite is unstable at positive-plate potentials. One of the possible solutions is to use inorganic compounds that are conductive; for example, the so-called Magneli phases in the titanium–oxygen system [4]. These exhibit some conductivity (similar to that of graphite) and are claimed to be stable in sulfuric acid at both positive and negative potentials. A search for alternative inorganic compounds with electrical conductivity should also be made. One of the problems is that components made with this type of material (by compacting and sintering) are brittle and may not have sufficient resistance to shock and vibration. An alternative approach to making a substrate is to load a plastic material with the conducting oxides in powder form and, thereby, produce a flexible conducting plastic. The problems in making a bipolar lead/acid battery for cycling applications are enormous, but the rewards for success (both technically and commercially) are great.

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