

Grid alloys for maintenance-free deep-cycling batteries

N. E. Bagshaw

59 Clement Road, Marple Bridge, Stockport, SK6 5AG (U.K.)

Abstract

The basic principles of alloying are outlined and applied to lead alloys for use as grids in cells for maintenance-free deep-cycling applications. Conventional lead-antimony alloys are unsatisfactory from the maintenance-free point of view. Dilute lead-antimony alloys have suitable metallurgical properties but passivation of the grids causes premature failure during cycling. Alloys in which the antimony is tied up as a compound (e.g., SbCd) have good properties and cells containing such alloys can have a satisfactory cycle-life. Experience will show whether antimony poisoning will eventually affect their maintenance-free characteristics. Cells containing antimony-free alloys (e.g., lead-calcium and lead-calcium-tin) have been used successfully in maintenance-free standby cells, but are known to have poor cycling properties. Alternative antimony-free alloys, such as those based on the lead-strontium system have good properties and should be investigated as possible grid alloys for deep-cycling cells.

Introduction

Alloys used for grids in lead/acid batteries have been developed largely on an empirical basis, from experience in their casting and handling in the factory, and from their behaviour and life in service. The traditional alloys were based on the lead-antimony system and have been used since the 1880s as described by Wade [1]. By the 1950s, it had been discovered that a small addition of tin improved the castability and an addition of arsenic improved the service life of deep-cycling batteries. Conventional alloys for traction batteries are still based on this experience and their grid alloys normally contain about 6 wt.% antimony, 0.2 wt.% arsenic and 0.1 wt.% tin.

The disadvantages of antimony in a battery are well known. The positive grid is corroded during overcharge periods and some of the antimony in the corrosion product is subsequently leached out by the electrolyte, is transported to the negative plate and deposited in a finely divided form on the spongy lead active material. Antimony reduces the hydrogen overpotential on lead and results in a greater amount of hydrogen evolution, both on open circuit and on charge. The battery thus requires more frequent topping-up because of the increased amount of water electrolysis.

It is obvious that the traditional lead-antimony alloys cannot be used in low-maintenance or maintenance-free cells unless the water is replenished either by catalytic recombination of hydrogen and oxygen outside the cell

with subsequent return of the water so formed, or by automatic topping-up devices of a mechanical type.

Alternative antimony-free alloys were investigated after the Second World War. The alloys that have received most attention are based on the lead-calcium system. The original work was by Thomas *et al.* [2] in 1947, who reported results of tests of telephone batteries containing grids of lead alloys with 0.065–0.09 wt.% calcium. Ternary lead-tin-calcium alloys were also proposed in the 1950s [3, 4] but considered in more detail in the 1970s [5–8]. Nowadays, lead alloys containing about 0.06 wt.% calcium and 0.5 wt.% tin are used commercially in both low-maintenance automotive batteries and in the new generation of maintenance-free standby batteries where the oxygen cycle is used to prevent the loss of water.

Unfortunately, when cells containing lead-calcium or lead-calcium-tin alloy grids are subjected to charge/discharge cycling with a high depth-of-discharge, premature failures occur. These can take the form of positive grid growth, active material shedding, softening of positive active material, loss of contact between active material and grid, or passivation films between grid and active material. This has given rise to the concept of the 'antimony-free effect' — the view in the battery industry that antimony may be necessary in cells to ensure a long cycling life. Thus, antimony in a cell promotes a good cycling life but militates against maintenance-free characteristics.

The present paper reviews the basic principles of alloying and their application to lead alloys for battery use. It then examines various approaches towards the solution of the problem of a grid alloy that can enable maintenance-free cells to be produced that are capable of deep cycling.

Alloying principles

According to Hume-Rothery's rules [9], if the atomic radii of two elements are different by more than 15%, the solid solubility of one element in the other will be low. Only elements with similar atomic radii will form extensive solid solutions. The radii of various metals taken from Pauling [10, 11] are given in Table 1, where dashed lines are drawn to include the elements whose radii are within 15% of that of lead.

On the other hand, according to Gordy [12], elements forming solid solution in one another must have values of electronegativity that are similar. Electronegativity is represented by the symbol x and its unit is the square root of electron volts per bond. Values for various elements are given in Table 2, where dashed lines are drawn to include those elements whose electronegativity is within 0.4 units of that of lead. Within this band, elements are more likely to form compounds with lead. What the data do not show is the possibility of the compounds themselves forming solid solutions in lead.

The information in Tables 1 and 2 indicates that elements which should form extensive solid solutions in lead are thallium, bismuth, indium and tin.

TABLE 1

Atomic radii of elements

Element	Radius (CN12)
Cu	1.276
Zn	1.379
As	1.39
Se	1.40
Al	1.429
Ag	1.442

Cd	1.543
Li	1.549
Hg	1.570
Sb	1.59
Mg	1.598
Te	1.60
Sn	1.620
In	1.660
Bi	1.70
Tl	1.712
Pb	1.746
Na	1.896
Ca	1.970

Sr	2.148
Ba	2.215

This is indeed the case but binary alloys of lead with these elements are unlikely to be suitable for battery grids because the lack of lattice distortion, when these elements are inserted into lead, results in low mechanical properties. On the other hand, the data indicate that elements such as selenium, tellurium, calcium, strontium, lithium and sodium are likely to form compounds with lead. Any compound so formed that will not enter the lead lattice will obviously not form alloys. However, if any compounds are capable of forming some solid solution with lead, these systems should be investigated further. Elements that are unlikely to form compounds, as indicated by Table 2, but are close to the 15% difference in atomic radius in Table 1, are likely to form an alloying system with lead that has good mechanical properties. This is because of a distortion of the lead lattice by the substituting atoms and also a precipitation hardening that takes place during ageing at room temperature. Examples of such elements are cadmium, antimony, magnesium and silver, and alloys with good mechanical properties are indeed formed between lead and these elements.

Lead-antimony alloys are, of course, the established alloys for battery grids. Lead-magnesium alloys have poor resistance for anodic corrosion in sulphuric acid and can be ruled out for battery applications. Lead-cadmium

TABLE 2

Electronegativity of elements

Element	Electronegativity (x)
Se	2.4
Cu	2.2
Te	2.1
As	2.0

Ag	1.9
Sb	1.8
Bi	1.8
Sn	1.7
Al	1.5
Pb	1.5
In	1.4
Tl	1.3
Mg	1.2
Zn	1.2
Cd	1.1

Hg	1.0
Ca	1.0
Sr	1.0
Li	0.95
Na	0.9
Ba	0.9

alloys, quite apart from environmental considerations, are susceptible to hot-tearing and cannot be used for cast grids. Lead-silver alloys (containing 1 or 4.6 wt.% silver) have been shown to have satisfactory properties for deep-cycling [13] but are too expensive for commercial use. There are therefore no straightforward binary systems that can be used to replace lead-antimony alloys and so lead alloys with elements that form compounds and have some solubility in lead, or more complex ternary (and even quaternary) alloys have to be considered.

The following are four major requirements in the alloying of lead for grids in lead/acid cells for deep-cycling applications.

1. Some lattice deformation by solid solution or precipitation within the lead grains. This results in hardness and mechanical strength.

2. Some precipitation in the grain boundaries. This is to lock dislocations and give a higher resistance to creep (since deformation during creep takes place within the grain boundaries). Such factors result in resistance to growth of positive plates in service. Thus, distortion and shorting of plates is prevented and loss of contact between grid and active material by mechanical reasons is also prevented.

3. No precipitates within the grain or in the grain boundaries which have widely different electrochemical properties from lead. Their absence

prevents excessive corrosion and any preferential corrosion at grain boundaries that could eventuate in catastrophic failure.

4. No corrosion product that is capable of forming a passivating film during discharge. This prevents loss of contact between active material and grid by electrochemical means that could result in a poor cycle-life.

When the cells are maintenance-free, however, there is a further requirement that no antimony (or any other element which poisons the negative plate) should be leached out of the grids. This is to avoid the possibility of reduction in hydrogen overpotential on the negative plate.

In order to meet these requirements, there are three possible approaches to the alloying problem:

1. to reduce the antimony content to a level where the degree of antimony poisoning of the negative plate is insignificant;
2. to 'tie up' the antimony by using ternary alloy systems where the antimony is present only as a compound with another element;
3. to remove the antimony altogether by using an alternative alloy system.

Dilute lead-antimony alloys

Alloys containing 2-3 wt.% antimony have been used for several years in automotive, submarine and standby batteries of conventional flat-plate design containing free electrolyte. Nevertheless, even at this relatively low level, antimony is leached out of the positive grid and some antimony poisoning of the negative plate occurs. Such alloys cannot be used, therefore, in maintenance-free cells based on the oxygen cycle (so-called 'recombination' cells).

If the antimony content of the alloy is reduced to 1 wt.% or less, there is no eutectic in the grain boundaries and all the antimony is present either in solid solution or as a sub-microscopic precipitate formed during ageing. In these circumstances, the amount of antimony that can be leached out of the positive grid during anodic corrosion is minimized and the degree of antimony poisoning may be insignificant. Maintenance-free standby cells using a dilute alloy of this type are manufactured [14] although it is too early to know the effects of long-term service.

It is usual to overcome casting difficulties in dilute alloys by the addition of a small amount of selenium. The electronegativity of selenium is quite different from that of lead and, as predicted from Table 2, a compound is formed between the two elements with a composition of PbSe. During cooling, this compound precipitates in the molten alloy in a finely-divided form and acts as nuclei for the crystallizing lead-antimony grains to give a fine-grain alloy and better castability.

The mechanical strength of a lead-1wt.% antimony alloy is only 1.8 kg mm^{-2} but this is sufficient for modern machinery and processing. Because there is little or no precipitation in the grain boundaries, however,

the binary alloy has a poor creep strength. The addition of 0.2 wt.% arsenic (which precipitates in the grain boundaries either as arsenic or as an arsenic-antimony solid solution) strengthens the grain boundary and imparts good creep resistance, and thus inhibits grid growth during battery service.

The corrosion product formed on dilute lead-antimony alloy gives cause for concern. Work carried out for ILZRO by Fuchida *et al.* [13] showed that the main constituent of the corrosion film on a lead-1wt.% antimony alloy was α -PbO₂, whereas alloys containing more than 2 wt.% antimony had corrosion products with a high proportion of β -PbO₂. Furthermore, the lead sulphate film formed on discharge of the α -PbO₂ was two-dimensional and completely covered the surface, causing passivation and difficulties in recharge. The barrier layer resulted in a poor cycle-life from cells containing grids of lead-1wt.% antimony alloy. The deep-discharge performance of cells containing dilute lead-antimony alloys is therefore questionable.

Lead-antimony-cadmium alloys

An alternative approach to reducing the likelihood of antimony poisoning in cells is to use grid alloys in which the antimony is present as a compound. Antimony and cadmium form an inter-metallic compound, SbCd. The ternary equilibrium phase diagram for the lead-antimony-cadmium system has been given by Hofmann [15]. By taking the vertical section joining the lead corner of this diagram to the compound SbCd on the side of the diagram joining antimony and cadmium, a pseudo-binary eutectic system is obtained. This is shown in Fig. 1. The pseudo-binary eutectic composition is 8.7 wt.% SbCd (corresponding to 4.5 wt.% antimony and 4.2 wt.% cadmium) and its melting point is 275 °C, compared with the melting points of lead and SbCd compound of 327 and 456 °C, respectively.

The use of lead-antimony-cadmium alloys containing approximately equal amounts of the two alloying additions was first proposed by Couch [16]. The system was examined in more detail in 1968 when alloys containing up to 5 wt.% each of antimony and cadmium, and also quaternary alloys containing up to 0.1 wt.% silver, were investigated [17]. Further results were reported in 1979 by Willhite *et al.* [18].

The degree of antimony poisoning from cells containing positive grids of the pseudo-binary alloys can be assessed from the results of charge-retention tests. One such test, at 40 °C [17], showed that cells containing pseudo-binary alloy positive grids were 100% better than cells containing lead-3wt.% antimony grids. Another indication of the purity of the system is the use by one manufacturer of pseudo-binary alloy grids in maintenance-free standby cells employing the oxygen cycle.

The lead-SbCd system has some very useful properties. An alloy containing 3.9 wt.% SbCd (2 wt.% antimony and 1.9 wt.% cadmium) has a tensile strength of 4.8 kg mm⁻² and its creep strain is only 0.15% after 2 years at a

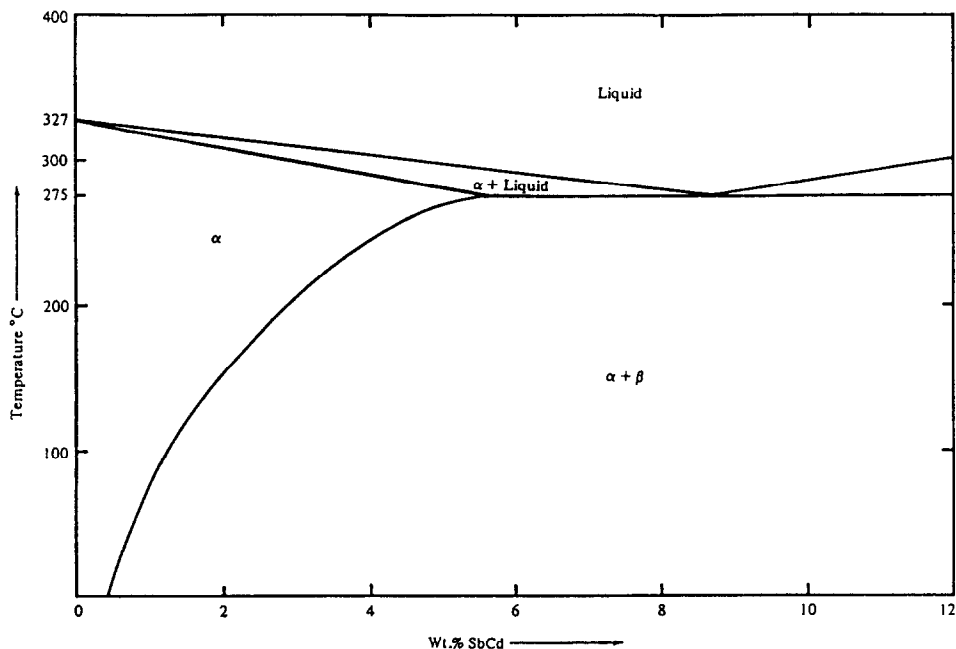


Fig. 1. Equilibrium diagram for the pseudo-binary Pb-SbCd system.

load of 1.4 kg mm^{-2} . These figures are comparable with those for standard lead-6wt.% antimony-0.2wt.% arsenic alloys used in deep-cycling traction batteries and indicate good resistance to plate growth. The pseudo-binary alloys with an addition of silver have even better creep properties.

The actual rate of corrosion of the lead-3.9wt.%SbCd alloy, (as measured from anodic weight-loss experiments) is about 70% of that for standard lead-6wt.% antimony alloys. Furthermore, the structures of the corrosion products from the two alloys were very similar in appearance. They are not compact and would not be expected to form passivating layers on discharge.

Actual cycling tests have been carried out on relatively small flat-plate cells containing 13 plates ($14.5 \times 12.5 \text{ cm}$) with relatively thin grids (positive grid thickness 1.7 mm), using a 4 h discharge (5-h rate) and an 8 h recharge. Cells containing the lead-3.9wt.%SbCd alloy completed 225 cycles before the capacity dropped to 80% of the nominal. Cells containing the standard traction alloy also completed 225 cycles before failure. It would appear, therefore, that alloys of the pseudo-binary lead-SbCd system are suitable for cycling.

Lead-SbCd grids can thus be used in maintenance-free deep-cycling batteries but the cost, availability, and environmental pressures associated with the use of cadmium are distinct disadvantages for the system.

Antimony-free alloys

Lead-calcium and lead-calcium-tin alloys are now widely used in the grids of automotive, standby and nuclear submarine batteries. In particular, they are used in maintenance-free cells employing the oxygen cycle.

As expected from the relative positions of lead and calcium in Table 2, a compound is formed between the two elements. This has a composition of Pb_3Ca and a melting point of about $660^\circ C$. The phase diagram [19] shows a peritectic transformation between lead and Pb_3Ca at $328.3^\circ C$, i.e., just above the melting point of lead. The compound Pb_3Ca has an f.c.c. structure with calcium ions at the cube corners and lead ions at the face centres [20]. The lattice parameter of 0.4901 nm is about 1% smaller than that for lead and coherent precipitation occurs. In the rapid cooling conditions of grid casting, solid solutions containing up to at least 0.1 wt.% calcium can be obtained and, after cooling, they age harden with precipitation within the grains. Although this gives sufficient mechanical strength, the creep strength of binary lead-calcium alloys is very low because of the ease with which movement within the grain boundaries can occur. Positive plates in deep-cycling batteries therefore suffer from excessive growth.

The addition of tin somewhat improves the properties. Tin forms a compound with calcium of composition Sn_3Ca . This is analogous to Pb_3Ca , and is isomorphous with it. The solid solubility in the ternary lead-calcium-tin system corresponds to 0.31 wt.% tin and 0.06 wt.% calcium at $25^\circ C$, or 0.69 wt.% tin and 0.18 wt.% calcium at $300^\circ C$. Thus, it is an age-hardening system and commercial alloys in general use, containing about 0.06 wt.% calcium and 0.5 wt.% tin have good mechanical properties. Since the grain boundaries of even the ternary alloys are still relatively weak, the creep resistance is low and the alloys are not suitable for grids in deep cycling cells.

The addition of 0.1 wt.% silver causes a marked increase in creep resistance and a lead-0.06wt.% calcium-0.5wt.% tin-0.1wt.% silver alloy has a creep strength at least equivalent to the conventional lead-antimony-arsenic alloys used in deep cycling batteries. Cycling tests on thin plate cells using a 4 h/8 h schedule gave a life of 177 cycles with the lead-calcium-tin-silver grids, compared with 225 cycles for traditional alloy grids. Thus, maintenance-free deep-cycling cells can be produced with the quaternary alloy.

If the addition of silver is too costly, alternative alloy systems have to be examined. One possibility is alloys based on the lead-strontium system. The latter is somewhat similar to the lead-calcium system, as would be expected from their positions in Tables 1 and 2. The compound Pb_3Sr , with a melting point of $676^\circ C$, shows a peritectic transformation with lead, just above the melting point of lead. The properties of lead-strontium alloys were examined in detail in 1977 [21] and further laboratory studies were reported in 1979 [22].

It was concluded that both binary lead-strontium and ternary lead-strontium-tin alloys had better mechanical and creep properties than the

analogous alloys containing calcium. The creep strength is still somewhat low compared with traditional grid alloys used in cycling batteries. Thus, positive-plate growth could be a problem. In discussion, however, Weinlein *et al.* [22] reported good deep-discharge cycle-life in preliminary cycle testing. With the present need for maintenance-free deep-cycling grids, a lead-0.1wt.% strontium-0.5wt.% tin alloy is certainly worthy of consideration. As in the case of alloys containing calcium, a small addition of silver (0.1%) has a marked effect on creep properties and grids of a quaternary lead-strontium-tin-silver alloy have growth-resistance properties at least as good as those of conventional traction alloys. Since the original work on strontium alloys was carried out, there have been significant potential reductions in the production costs of strontium and further investigations of the application of lead-strontium alloys to cycling applications would be of value.

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