

## TRENDS IN LEAD/ACID BATTERY ALLOY USE AND METALLURGY

W F GILLIAN

*The Broken Hill Associated Smelters Pty Ltd, 114 William Street, Melbourne, Vic 3000 (Australia)*

### Alloy production

The world production of automotive batteries in the period 1975 - 1984 is presented in Fig 1 [1]. It can be seen that this production has risen from 123 million units in 1975 to 187 million units in 1984. A closer regional analysis of the data reveals some interesting growth patterns. For example, the annual growth rates in the U.S.A and Europe have been 4.5 and 2.6%, respectively, whereas the figure for Japan has been 8.4% and that for Asia a remarkable 11.2%. There are a number of factors that account for this latter dramatic growth rate, but, principally, it has been due to Asia's shift from a nett importer to a nett exporter of batteries. The region now supports export markets in Australia, Canada, the U.S.A., the Middle East and Europe. This export orientation, particularly to the U.S.A. (Fig. 2), is also the prime cause of the technological pressures placed upon Asian lead/acid battery manufacturers.

Examination of the trends in grid alloy use in the U.S.A (Fig. 3) and Australia (Fig. 4) reveals that two main types of alloy system are in common use (i) calcium alloys, (ii) low antimony alloys. In essence, the shift is towards the removal or reduction of antimony from the grid in order to produce low-maintenance and maintenance-free batteries. In the U.S.A. situation, three main construction philosophies have emerged: (i) lead-calcium, (ii)

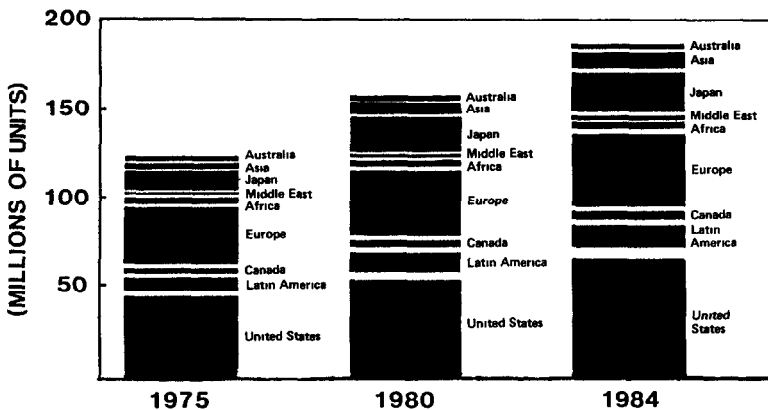


Fig 1 World production of automotive batteries 1975 - 1984 [1]

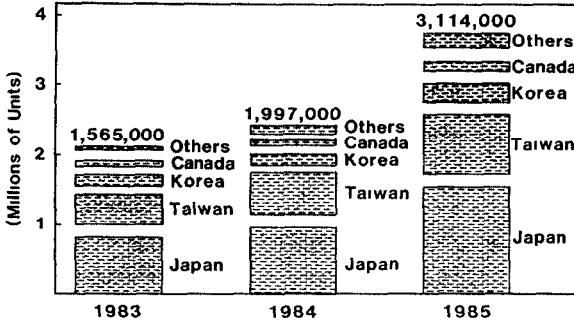


Fig 2 Imports of automotive batteries into the U S A (source U S Department of Commerce)

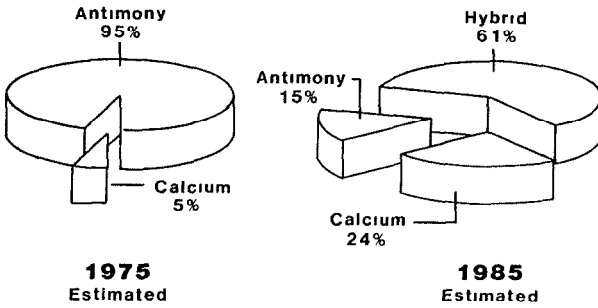


Fig 3 Grid alloy trends for replacement batteries in the U S A

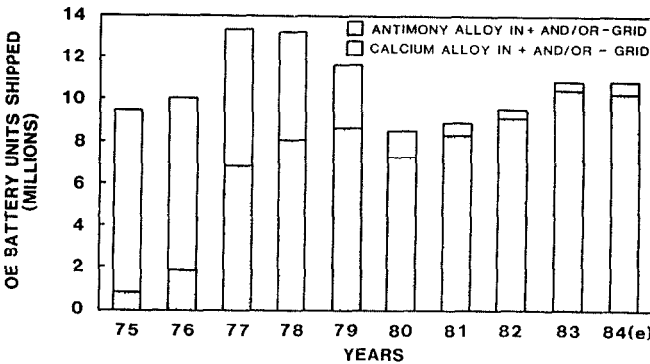


Fig 4 Grid alloy trends for original equipment (OE) batteries in Australia

low-antimony, and (iii) hybrid, *i.e.*, low-antimony positives, calcium negatives. The hybrid system is the most popular and claims to offer a combination of the advantages of the other two alloys.

## Alloy selection

With the availability of different types of alloy, the manufacturer is faced with the problem of alloy selection and how to view this selection with regard to the company's own manufacturing capability. In terms of export markets, the manufacturer is often restricted in choice, but if the target is the domestic market then there is more room to manoeuvre. The correct way to tackle the issue of alloy selection is to consider it to be one of a number of physical design criteria that include number and size of plates, type of separator, volume of electrolyte, etc. With this approach, an appreciation of selection consequences can be visualized, and provision can be made within the manufacturing process to accommodate any changes that may be required. No better example to illustrate this point could be found than the use of the calcium-based alloy system. In this situation, perhaps the easiest step is to decide what alloy to use. The problems, however, often develop from a lack of understanding of the downstream requirements of curing, material handling, alloy contamination, etc., that are essential to realise the benefits of such an alloy system

## Operational problems with alloys

Having made a case for considering alloy selection as an integrated component in the overall manufacturing process, and not merely as a stand-alone or independent technology, attention must now be focused on the effects of such selection on the battery-making operations themselves. In particular, it is necessary to identify limitations or restrictions that a given alloy will impose. These problems, by nature, are not permanent and will change with increased knowledge and/or the application of appropriate technology. Thus, it is important that individual manufacturers place themselves in a position where they can keep up with movements in technology, and then take advantage of opportunities as they arise.

The choice of grid alloy has caused problems in the following battery preparation areas:

*Alloy melting pots.* Pots without adequate temperature control cannot be used for the group of low-antimony alloys which require the addition of grain refiners (nucleants) Such pots are also unsuitable for calcium alloys.

*Grid casting* Hand casting or the use of unregulated moulding technology will prohibit the use of low-antimony and calcium alloys

*Pasting operations* The type of plate-handling equipment will determine the success of pasting with different alloy types. For example, flash-drying ovens that only support the plate by the lugs would be unsuitable for very-low-antimony or calcium alloys, but would be acceptable for high-antimony alloys. On the other hand, employment of a chain belt that will support the plates in a horizontal position, will allow the use of all the new alloy systems

**Curing process** The replacement of antimony from grid alloys by calcium has required more sophisticated curing procedures, *e g* , ovens in which temperature, humidity, etc., can be controlled.

**Formation** Problems occur in the tank formation of plates having low-antimony or calcium alloy grids Both these types of alloy are intrinsically softer than their predecessors and consequently are subject to “bowing” during the formation process, this results in high internal scrap rates Thus, it is better to employ container formation. However, appropriate process technology is required before this technique can be offered to the market.

**Dry charge process** The two main dry-charge procedures practised in the Asian region — hot dry-press and vacuum ovens — subject the formed plate to considerable heat. Low-antimony and calcium alloys soften under these conditions and therefore become more difficult to process in further stages

**Group burning** Low-antimony and calcium alloys by their nature lend themselves for use in some of the more automated machinery, but will cause problems when subjected to the uncertainty of some of the more manual methods

Undoubtedly, many more problem areas exist, and thereby further emphasize the inter-relation between alloy selection and downstream process

### Low-antimony alloys

Traditionally, antimony alloys with compositions around the eutectic composition of 11.1 wt % have been used for battery alloys The solidification process of these alloys can be described by a model in which nucleation first occurs on cooling the liquid metal and then is followed by crystal

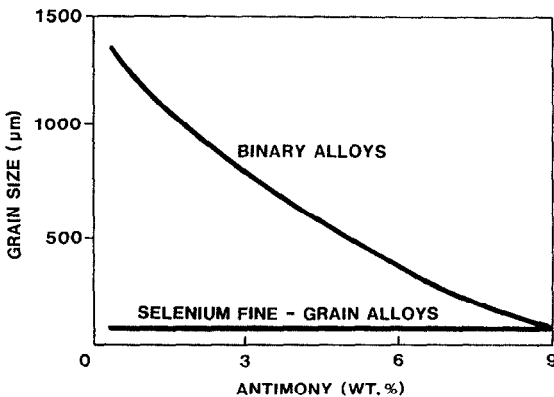


Fig 5 Grain size of lead-antimony alloys as a function of antimony content and the influence of selenium as a grain refiner [3]

growth until the final solidification has taken place. In alloys with lower antimony contents, this process results in the formation of large dendritic grains with preferred orientation (Fig. 5).

The formation of large dendritic grains leads to problems of grain boundary attack, developing into serious intergranular corrosion. As the specific volume of the  $PbO_2$  corrosion layer is 21% greater than that of lead [2], penetration by the corrosion layer along the grain boundaries will induce stress within the lead substrate, accelerating the corrosion front. Further, as this front moves through the structure, attacking the eutectic phase, antimony is selectively leached and enters the electrolyte, to be later deposited on the negative plate during charging. This removal of antimony from the positive plate, and its subsequent transfer to the negative, is responsible for the high gassing rates associated with the traditional antimonial alloys.

With the demand for low-maintenance or maintenance-free designs, one of the first initiatives was to eliminate gassing problems. Unfortunately, the removal of antimony alone is not sufficient, for as the antimony content drops, the individual grain size increases. The latter is accompanied by a reduction in eutectic liquid due to the reduction in antimony. Further, as lead and lead alloys shrink during solidification by approximately 3.5% in volume [3], the resultant larger dendritic grains of a low-antimony alloy produce a resistance to metal feed within the mould cavity. Under these conditions, cracking becomes a major problem. This cracking is serious enough in an alloy with 3 wt.% antimony, but at 2.5 - 1.5 wt.% antimony, or lower, it is critical.

To overcome the cracking problem, the industry has universally adopted the use of "grain refiners" such as copper, selenium, and sulphur. These additives produce a more uniform, fine-grained structure (Fig. 6), which tends to produce a regular, clean casting where grain boundary attack is significantly reduced. Thus, the corrosion layer which develops during curing and formation is homogeneously distributed over the entire grid surface, without producing the disastrous effects that are associated with plate growth.

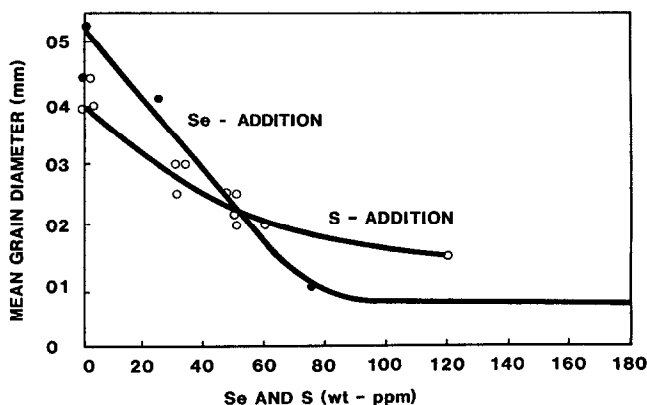


Fig 6 Effect of grain refiners on the grain size of lead-antimony alloys

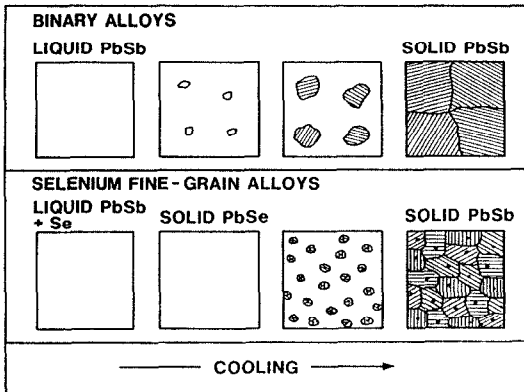


Fig 7 Schematic representation of the solidification process of binary and selenium grain-refined hypo-eutectic lead-antimony alloys [3]

Grain refiners have been used individually or in combination, and achieve their effect by coming out of solution prior to the solidification of lead (Fig 7). Their solid inter-metallic forms act as nuclei for the crystallization of primary-solid-solution material. Further, the solidification of these alloys does not proceed from the mould wall as with alloys with higher antimony contents, but occurs preferentially on the minute particles suspended in the liquid. At the final stages of solidification, instead of dendritic tearing there occur both grain rotations [4] and a more effective consumption of the remaining eutectic liquid. Ideally, this nucleation process should continue as the temperature decreases so as to maximize the advantage of this grain-control mechanism and to overcome the problem of a wider freezing range common to low-antimony alloys. Therefore, a combination of grain refiners should be used, particularly in the very-low-antimony alloys. Selenium, which forms the inter-metallic compound lead selenide, has an overall advantage as a grain refiner when compared with sulphur, due to its higher solubility in lead and its tendency to be more stable on remelting. Selenium is usually used in conjunction with sulphur and copper in the very low antimony alloys, *i.e.*, less than 1 wt %.

Low-antimony alloys perform quite well in battery applications, no major changes are required in grid-casting technology as is the case with calcium alloys. In addition, the use of antimony-based alloys allows improved depth-of-discharge through enhanced bonding chemistry at the grid/paste interface. The new alloys also give improved fluidity and corrosion resistance when compared with high-antimony alloys, and in terms of conductivity are equivalent to the calcium-based alloys (Fig. 8) [5]. However, problems will develop if these new, low-antimony alloys are not maintained at the correct temperature in the melting pot, *i.e.*, 460 - 500 °C. If the temperature falls below these levels, the additives will come out of solution and be lost within the melting-pot dross. This, in turn, places considerable pressure on the manufacturer to have some compositional control over the casting operations.

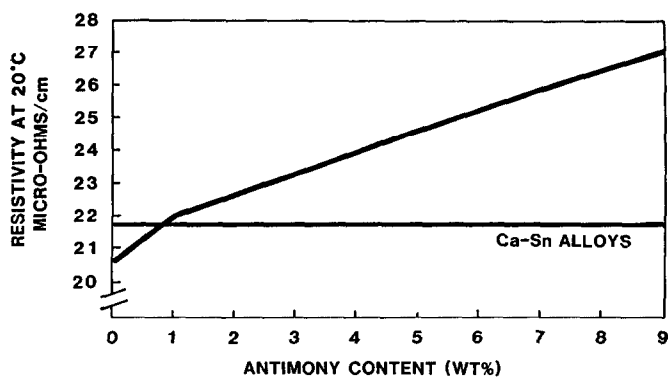


Fig 8 Resistivity of lead alloys as a function of antimony content [5]

### Lead-calcium alloys

Of the four systems currently available, namely, the lead-calcium, lead-calcium-tin, lead-calcium-aluminium and lead-calcium-tin-aluminium, the last two are perhaps becoming the most important. The reason for this lies in the oxidation inhibiting effect of aluminium on calcium. It was established very early in the development of calcium-based alloys that the optimum composition lies within the range 0.08 - 0.11 wt.%. At compositions below 0.08 wt.%, the grid material exhibits very poor mechanical strength, and at levels above 0.11 wt % little additional benefit is gained. However, it was some time before the optimum calcium range was within the ability of most battery manufacturers to control.

Early alloys also contained tin in the range 0.5 - 0.7 wt.%, but as this produced a somewhat expensive alloy the tin content of more recent alloys has been reduced to around 0.3 - 0.4 wt.%. The latter tin content range is nearly always specified for positive grids only. The addition of tin to the positive grid is designed to improve the chemistry of the grid/active material interface. In the absence of tin, the positive grid suffers from passivation effects caused by the formation at the grid/active-material interface of a layer of lead sulphate or calcium sulphate. This layer restricts the ability of the plates to recover from deep discharge and thus shortens the life of the battery. In the presence of tin, however, this process is retarded.

Although calcium alloys offered the promise of industry growth and the development of new markets, the new technology was fraught with many problems. Calcium metal was easily oxidized, forming an oxide dross which was suspended throughout the molten metal. These oxide/dross inclusions were responsible for (a) reduced grid-caster productivity, through increased stoppages resulting from drossed-up lead lines, and (b) an increase in product rejection, brought about by a variety of moulding defects. Serious corrosion problems developed in positive plates made from early alloys, e.g., Fig 9 [6]. The mechanism involved in these failures has been defined for

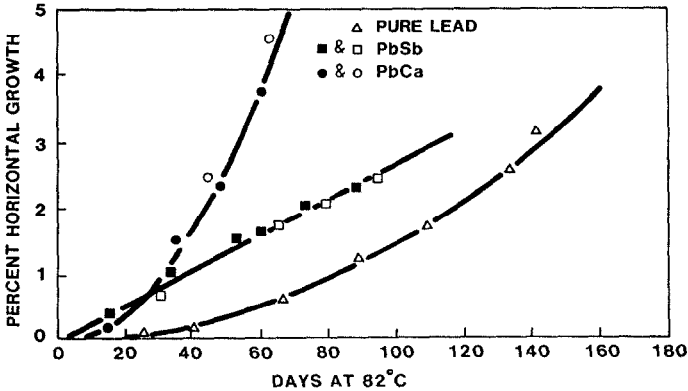


Fig 9 Growth of positive grids in lead/acid batteries [6]

two corrosion routes. In the case of calcium-tin alloys when the calcium levels are high, there is a risk of precipitating a tin/calcium inter-metallic compound ( $\text{Sn}_3\text{Ca}$ ) at the grain boundaries, giving rise to serious stress-induced intergranular corrosion. The second route involves either the formation of calcium oxide inclusions within, or on, the cast grid surface, or the capture and entrapment of air by these same oxide particles within the grid. In either case, the result is deep corrosion penetration at the grain boundaries. With large grain structures, *i.e.*, low calcium levels, this problem of corrosion can be of great concern, particularly at elevated temperatures (over  $60^\circ\text{C}$ ). This should be of particular importance in the South East Asian environment, both for passive battery storage and for under-bonnet applications. It has been reported that the most likely situation for corrosion development occurs while the finished battery sits in a fully charged state at these higher temperatures. In addition, these alloys were prone to 'cold shorts' and problems of joining other metals to the grid, *e.g.*, inter-cell connections. Most of these problems now seem to be avoided with the introduction of aluminium into the alloy.

A concern with *all* calcium alloys, however, including those with aluminium, is their mechanism of hardening. Their hardness is not induced by the precipitation of nuclei and growth around grain refiners, as described earlier, but by an internal mechanism involving grain boundary migrations, which are much more complex in nature. Initially, all calcium alloy structures possess large 'as cast' grains. On solidification, the grain boundaries begin to migrate at a rate that is dependent on the calcium content. This movement is optimum at levels of between 0.09 and 0.11 wt % calcium, and produces a fine-grain structure. When the grain boundaries have moved throughout the metal, ageing has been completed. It would appear that as an individual boundary moves, it redissolves any calcium phase material in its path, re-precipitating it in its wake. As the rate of precipitation is dependent on calcium concentration, low concentrations of less than 0.09 wt % calcium produce larger movements of the boundary and result in a less coherent or



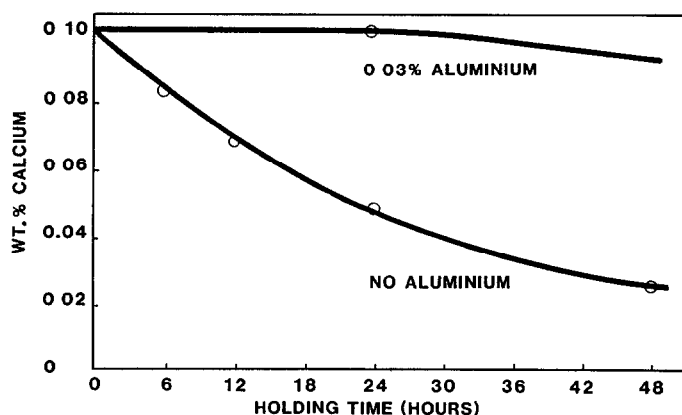


Fig 10 Effect of aluminum addition on the rate of oxidation of calcium [6].

regular structure. It is therefore of critical importance to maintain control of the calcium levels within the material.

Prior to the use of aluminium-containing alloys, the industry relied on its mechanical ingenuity to overcome the problem of calcium losses. This unfortunately gave dubious results. With the addition of aluminium to the alloy, calcium oxidation losses have been almost eliminated (Fig 10). Aluminium concentrations as low as 0.015 wt.% are considered sufficient to ensure maintenance of calcium levels in both the pot and the grid. However, under conditions of normal grid casting, where trim scrap, etc. is being fed back into the melting pot, levels should be increased to around 0.03 wt.% to ensure no dilution losses, etc. The mechanism by which the aluminium assists in this process would appear similar to the action of tin, namely, a metal (aluminium)-rich oxide skin is formed, and while it remains intact air is excluded from the melt and calcium loss is thus inhibited. To maintain this

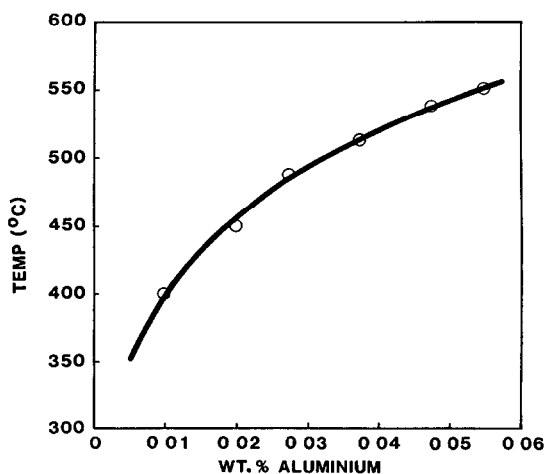


Fig 11 Solubility of aluminum in lead [6]

position, it would be necessary to keep sufficient aluminium in the melt to form a new protective layer whenever the melt is disturbed. One possible disadvantage of the aluminium/calcium alloy system is the need to maintain the melting-pot temperature at around 500 °C (Fig 11) in order to keep the aluminium in solution.

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