Effect of bismuth on the corrosion behaviour of lead in sulphuric acid

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Abstract

To determine the maximum tolerable level of bismuth in lead/acid battery grid manufacture, a series of anodic corrosion experiments is carried out under conditions closely simulating those experienced in the positive-plate grid of an operative lead/acid battery. Weight loss is taken as a measure of the corrosive destruction of a series of binary lead–bismuth alloys with bismuth contents up to 2300 ppm. The results reveal the crucial role of both bismuth itself and the metallurgical structure (e.g., grain size) of the alloy. In particular, the alloy composition determines both the mechanism and the kinetics of the corrosion process. Long-term exposure tests show that the resistance to corrosion is significantly reduced at bismuth concentrations above 200 ppm.

Introduction

To date, there has been limited research on the effects of bismuth on lead/acid battery performance (e.g., grid corrosion, cycle life, gassing, etc.). Furthermore, the published data provide conflicting views on whether bismuth is deleterious or, in fact, beneficial to battery performance.

The effects of calcium, tin and bismuth on the initial strength of calcium–lead alloys was studied by Myers *et al.* [1]. Bismuth (up to 1000 ppm) was shown to increase the rate at which calcium–lead alloys age harden. This was brought about by grain refinement. Moreover, bismuth was found to exert no deleterious effects on alloy strength.

Life-cycle tests were carried out by Devitt and Myers [2] on automotive batteries with Pb–Ca–Sn grids containing various amounts of bismuth. The batteries were cycled to failure using two procedures: one designed to cause failure by corrosion, the other to closely model service in an automobile. Bismuth, up to 420 ppm, was found to have no effect on the rates of either gassing or grid corrosion in the batteries. There was no deleterious effect on cycle life with increasing bismuth. In fact, endurance improved as the bismuth content was increased. In an earlier study [3], however, bismuth was seen to promote the corrosion of the lead lattice. More specifically, the

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corrosion resistance of bismuth-containing alloys was found to pass through a minimum at ~3.5 wt.% Bi. Another detailed investigation [4] showed that the presence of bismuth both encourages grid growth and increases the shedding of positive active material.

More recently, Hampson et al. [5] carried out a detailed study of the effect of bismuth on the electrochemical behaviour of lead. Using cyclic voltammetry and potential step techniques, these workers showed that concentrations as low as 0.06 wt.% Bi in lead render the alloy much more susceptible to anodic corrosion than either pure lead or antimonial (5 wt.%) lead alloy. The relationship between bismuth content and depth of corrosion attack was not linear; a maximum stability concentration was observed at ~0.15 wt.% Bi. These workers suggested that if the beneficial properties of bismuth, as reported elsewhere in the literature (i.e., lower self-discharge and gassing rates than antimony and increase cycle life), were combined with the optimum level of the alloy for minimum anodic corrosion, then bismuth could be a suitable replacement for antimony in lead/acid batteries.

From the above, it is obvious that there is still considerable disagreement concerning the influence of bismuth on battery performance, particularly with regard to grid corrosion and the level that can be tolerated in grid alloys. Most of the results published to date have been obtained either from fundamental electrochemical studies on lead alloys in sulphuric acid, or from tests on a small number of lead/acid batteries. In most instances, it is difficult to make direct comparisons between the different investigations as both the experimental conditions (i.e., electrode potentials, acid concentration, exposure time, etc.) and the examined range of bismuth concentrations vary widely.

In the present study, the corrosion of Pb–Bi alloys (Bi content 0 to 2300 ppm) over a range of experimental conditions has been systematically investigated using weight-loss analysis.

Experimental

Potentiostatic anodization experiments were performed on test electrodes immersed in solution at room temperature. A basic three-compartment cell was used containing a 'multiple' working electrode, a pure lead counter electrode, and a Hg/Hg_2SO_4 reference electrode. All potentials are reported with respect to this latter electrode. The cell was interfaced to an AMEL model 551 potentiostat and the potential of the anodic oxidation was regulated at a preset value. The experimental set-up (Fig. 1) was designed to allow the simultaneous oxidation of a maximum of 10 specimens under the same conditions, including exposure time.

Two types of specimens were tested namely, rods and coupons. The rods were made by machine turning, while the coupons were produced by mechanically rolling the rod-shaped samples. Both specimen types were etched in 10 wt.% nitric acid and polished by very light application of dry
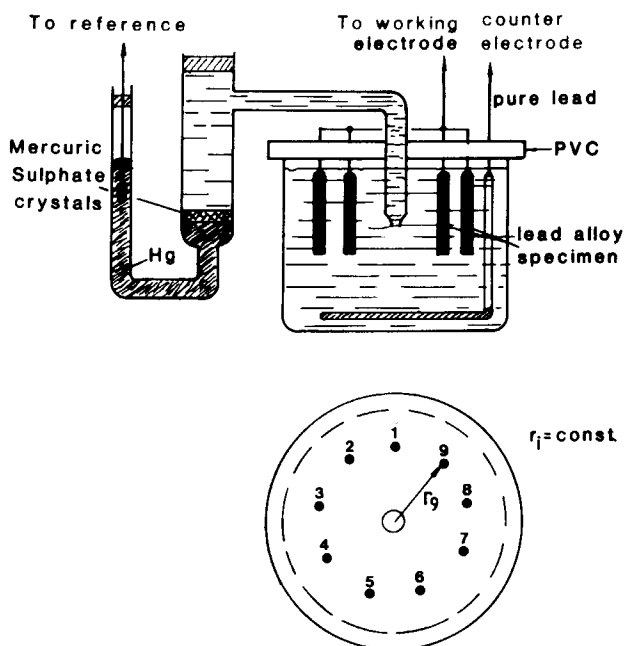
Fig. 1. Potentiostatic corrosion cell.

TABLE 1

Experimental conditions for weight-loss tests

Experiment no.	Potential (V)	H_2SO_4 concentration (M)	Exposure time (h)
I	1.00	5	235
II	1.00	2	480
III	1.00	2	333
IV	1.12	2.2	168
V	1.10	4	212
VI	1.10	4	220

tissue paper. The dimensions and weight of each sample were recorded. After termination of the corrosion experiment, the specimens were washed with water and collectively placed in a hot bath of hydrazine–mannitol for stripping of the corrosion product. Finally, the specimens were dried and the individual weight-losses determined. The latter were calculated in terms of electrode unit area (mm^2) and plotted as a function of bismuth content.

The experimental conditions employed for each set of weight-loss experiments are given in Table 1. The test parameters were selected in order to simulate the operating conditions experienced by the grid of the positive plate in a healthy lead/acid battery during open-circuit stand. A potential of

1.00 V has been shown [6, 7] to correspond to the maximum corrosion rate of lead in H_2SO_4 solution; while the values of 1.10 and 1.12 V reflect, respectively, the potential of a discharged and charged positive plate at open circuit. Correspondingly, the electrolyte concentration is 2 M in a discharged cell and 4 M in a fully-charged cell.

Results and discussion

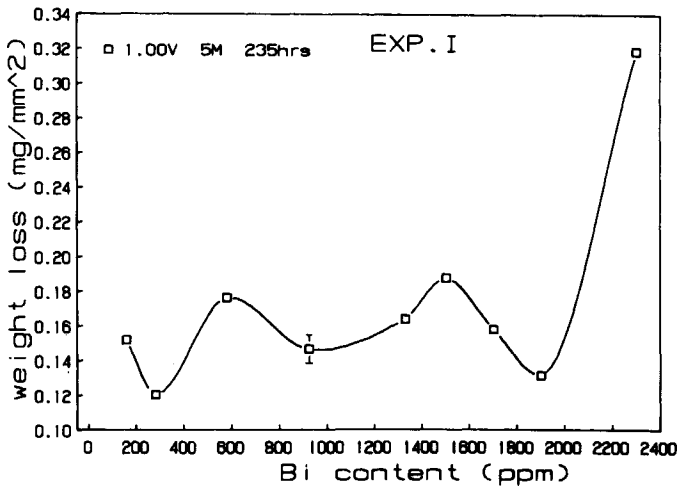Before discussing the results of the corrosion studies shown in Figs. 2–7, and their implications, it is necessary to examine the role of a few

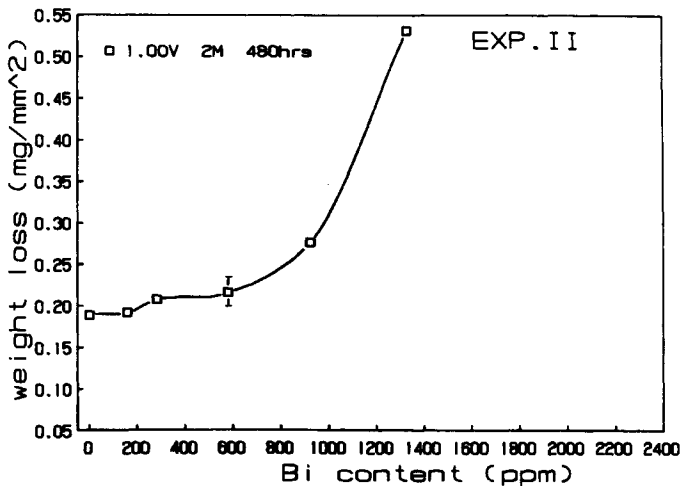Fig. 2. Corrosion experiment I on a rod electrode at 1.00 V, 5 M H_2SO_4 for 235 h exposure.

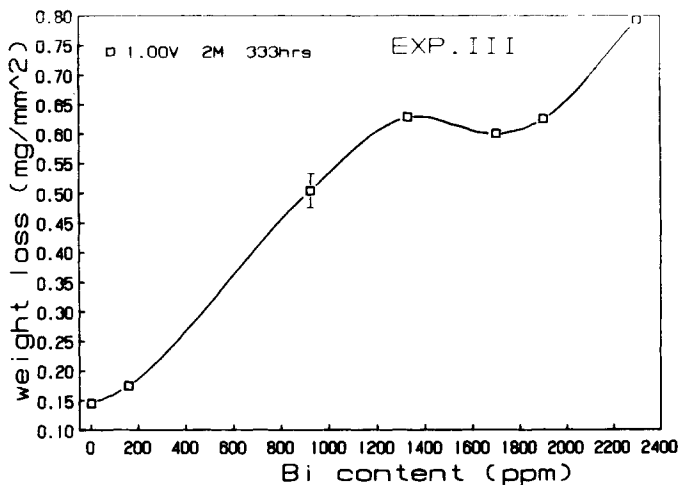Fig. 3. Corrosion experiment II on a rod electrode at 1.00 V, 2 M H_2SO_4 for 480 h exposure.

Fig. 4. Corrosion experiment III on a rod electrode at 1.00 V, 2 M H_2SO_4 for 333 h exposure.
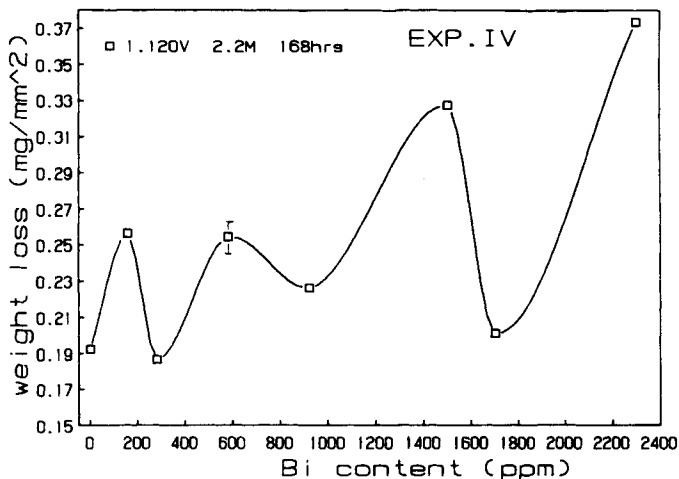

Fig. 5. Corrosion experiment IV on a rod electrode at 1.12 V, 2.2 M H_2SO_4 for 168 h exposure.

experimental factors of a more implicit nature. Earlier studies [8] demonstrated an association between the extent of anodic oxidation and the basic grain structure of the metal, at least for short-term exposures. Primary crystallization during casting of an alloy may produce a certain microstructure but the latter can alter through an intrinsic mechanism. This is because both lead and its alloys possess the ability to recrystallize at room temperature, with the tendency to form a larger grained and more stable structure. Since the rate of this transient phase of recrystallization is influenced by temperature, it will be referred to hereafter as 'thermal treatment'. Although the process can be accelerated from a few weeks at room temperature to a few hours at around 100 °C [9], the final grain formation can be considered to be an
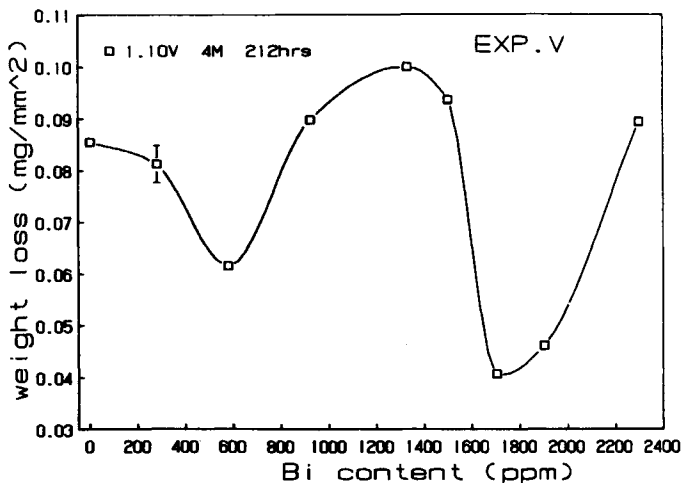
Fig. 6. Corrosion experiment V on a coupon electrode at 1.10 V, 4 M H_2SO_4 for 212 h exposure.
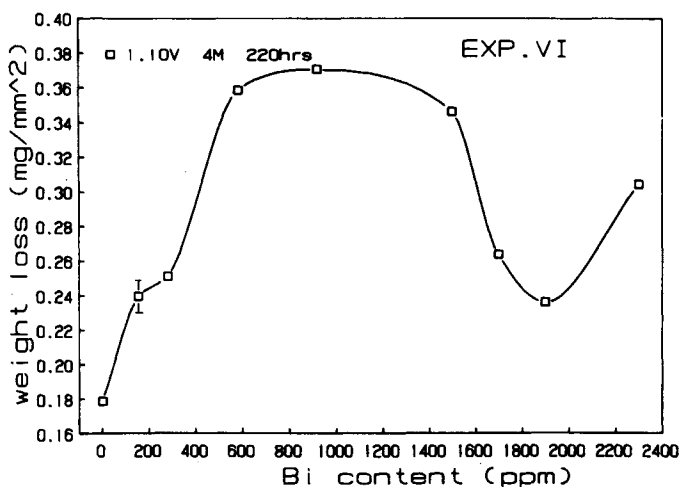

Fig. 7. Corrosion experiment VI on a rod electrode at 1.10 V, 4 M H_2SO_4 for 220 h exposure.

inherent property of each alloy specimen that is dependent mainly upon the bismuth concentration. Thus, in this work, all samples were subjected to sufficient ageing conditions (i.e., shelved for a few months at room temperature) before preparation as corrosion specimens.

The grain microstructure was estimated on a cross-sectional grain-count basis. The variation in grain size for the rod-type alloy series is shown in Fig. 8. Of course, in the case of coupon-type specimens produced from rolled rod samples, mechanical deformation initially causes elongation of the primary grain structure in the direction of rolling. This results in a heavily stressed structure that is prone to a spontaneous release of internal (free)
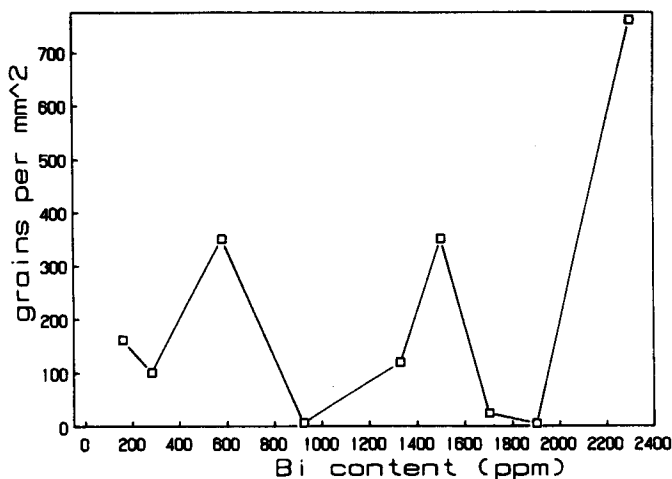
Fig. 8. Grain-size analysis of lead–bismuth alloys.

energy through recrystallization. With coupons, therefore, it is appropriate to distinguish between 'as-rolled' and 'thermally treated' specimens due to the degree of recrystallization that has been allowed to take place from the stressed and partially elongated state to the totally relieved state.

Experiments I to VI have all been conducted on the same fully annealed set of rod specimens with the grain structures shown in Fig. 8. Under the corrosion conditions of experiment I, the extent of corrosion appears to fluctuate almost in unison with the corresponding grain size (cf., Figs. 2 and 8). There are no indications that the corrosion rate depends on the bismuth content *per se*. Similar behaviour was observed under the conditions of experiment IV (Fig. 5). Despite the shift towards a milder potential [7] and lower exposure, weight loss has been on a slightly larger scale, possibly due to the more aggressive electrolyte concentration [6]. The observed corrosion faithfully follows the grain size pattern of Fig. 8. A weight loss of the same order was found with experiment VI (Fig. 7), in which the experimental parameters were fixed at values between those used in experiments I and IV. The data for experiment VI presented in Fig. 7 are less reliable than those in Figs. 2 and 5 because of random errors introduced through the lack of a wax shield on the stems of the rod specimens. Nevertheless, the results of experiment VI present further evidence to support the notion of a non-monotonic relationship between corrosion rate and alloy bismuth content, under the specific range of test conditions chosen in this study.

The viability of the present technique in assessing the corrosion within this narrow window of bismuth concentration was verified through estimation of the order of magnitude of the fixed (or systematic) error associated with each process during the experiment and through computation of the uncertainty in the weight loss. The extent of this uncertainty is indicated by the error bars shown in Figs. 2 to 7.

In summary, the findings from experiments I, IV and VI show, for short-term exposure levels, that the grain structure and the corrosion rate are inter-dependent. Moreover, the relationship between alloy weight loss and grain size is unequivocally inverse, i.e., large grains deter the destructive loss of the metal base during anodization in the short term (~ 200 h exposure).

With longer exposure times, e.g., 333 h in experiment III (Fig. 4), the grain size factor ceases to dominate the weight-loss trend. Rather, the corrosion appears to escalate far more steeply with bismuth content, in a convincingly monotonic fashion. Hints of a grain size effect are still evident (around 1700–1900 ppm Bi) but corrosion appears generally aggravated by the bismuth content. The same situation holds at an even longer exposure of 480 h (experiment II, Fig. 3) where the corrosion rate rises sharply above the 920 ppm Bi level.

Generalizing over the entire series of experiments on the corrosion behaviour of these alloys, it can be asserted that the mode and overall rate of corrosion are the product of a combined effect of both grain structure and bismuth content. The relative significance of the latter two parameters varies with time for exposures of up to 480 h. This exposure period may cover a transient phase in the corrosion mechanism or mode of attack, before a steady-state corrosion process is established.

A possible explanation for this behaviour can be given through the following process scheme: alloys corrode by an inter-dendritic mechanism rather than uniformly [10]. This mode of corrosion is definitely enhanced by the richer distribution of bismuth around the boundary lengths (caused by microsegregation in cast binary alloys [11–13]) because of the less adherent product film from the corrosion of the boundary phase. The number of intergranular regions exposed on the alloy surface decreases with increase in grain size and, consequently, the corrosion rate will be reduced. In the short-term, therefore, grain size controls the extent of corrosion in an inverse relationship. Prolonged exposure, however, results in a mechanism whereby the corrosion front, while progressing along grain boundaries, results in the engulfing of the larger grains and isolation of metallic lead from the base structure. Weight loss is thus boosted to much higher levels, as more material is removed with the corrosion product layer. Metallographic samples that were prepared from alloy specimens with three different bismuth levels (0, 1500, 2300 ppm) and exposed to long-term corrosive conditions (1.1 V, 4 M H_2SO_4, 7 weeks) yielded corrosion profiles that well substantiate the assumption of the above mechanistic scheme, as confirmed by the micrographs show in Fig. 9.

Further feedback on the mechanisms of the alloy corrosion is obtained from experiment V (Fig. 6) which employed rolled coupon specimens and constitutes a short-term test under similar conditions. The corresponding graph (Fig. 6) depicts a similar fluctuation with grain size, and resembles the mechanism of the short-term experiments I, IV and VI on rod specimens. The average weight loss in experiment V is, however around 25% of the levels recorded for the rod specimens under identical conditions. The lower
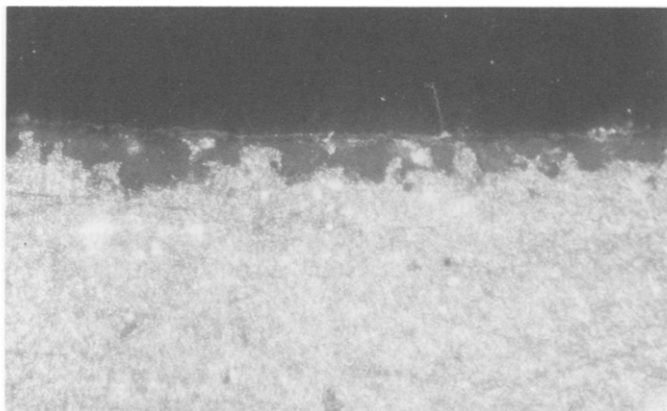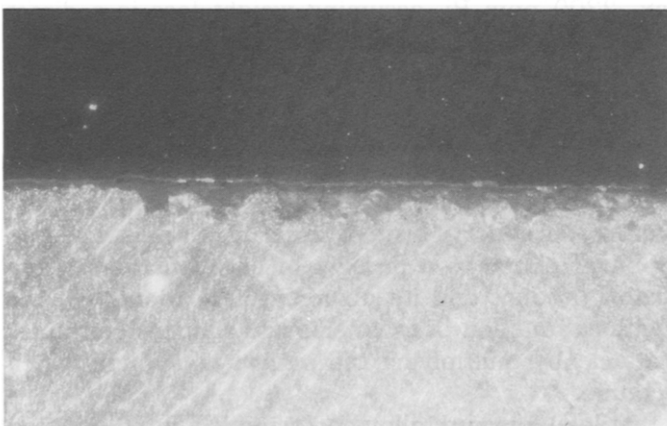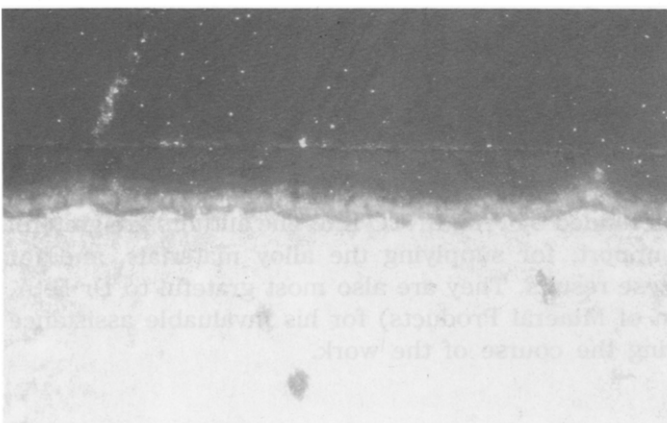
Fig. 9. Comparison of corrosion profiles on lead and two lead–bismuth alloys: (a) pure lead, (b) 1500 ppm Bi, (c) 2300 ppm Bi (×23).

weight-loss levels for the rolled coupon specimens are thought to be due to increased passivity of the planar surface films, compared with the rod curvature where product growth occurs radially and results in mechanical incoherence of the passivating corrosion surface layer.

An additional important finding is that the recrystallized grain structure depends on the primary structure in such a way that the grain-size proportions of the primary cast structure are virtually retained, in the examined bismuth range. This conclusion is based on a comparison of grain-size analyses on the cast and rolled alloy series, and does not claim to be conclusive.

Conclusions

From the results of the present study, it can be concluded that for a given potential, corrosive environment, and exposure time the corrosion of Pb–Bi binary alloys (max. 2300 ppm Bi, assuming weight loss is a direct measure of the extent of anodic attack) is predominately governed by three distinguishable physical parameters: (i) bismuth content; (ii) grain size; (iii) boundary length.

The bismuth content of the alloy proportionally influences the rate of penetration of the corrosion front, either along the grain boundary or within the grain itself, or both. As regards the resistance or passivity of these alloys to anodic conditions, therefore, the effect of bismuth appears to be detrimental. Grain size has justifiably been related to a process of encapsulation of the alloy mass by the corrosion product and its obvious implications. On the other hand, boundary length (a function of grain size and shape) determines the extent of corrosive attack, by multiplying the pathways through which corrosion may take its course.

With the realization that lead–bismuth alloy corrosion is a multi-facetted problem and that comprehensive elucidation of its mechanism is difficult, it is suggested that for a given bismuth level in the alloy, the optimization of the performance of these alloys as grid positives for the lead/acid battery lies in a compromise between grain size and boundary length.

Acknowledgements

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