A study of the corrosion of negative-plate lead–antimony lugs in lead/acid batteries

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Abstract

Corrosion of the negative-plate lug of a lead/acid battery has been investigated by means of metallographic examination, electron microprobe and chemical analysis, and electrochemical techniques. The results show that both the metallographic texture of the alloy and the distribution of antimony in the alloy play an important role in the corrosion process. Since, for large lugs, the chilling rate after casting varies at different locations, the crystallines in the central part of the lug are more disordered and smaller in size than those in the edge regions. The content of antimony in the surface layer of the central part is higher than that at the edge. Depolarization of oxygen dissolving in the electrolyte causes both the antimony and the lead in the alloy to become corroded. The uneven distribution of antimony and its surface segregation serve to accelerate the corrosion of the central part of the plate lug.

Introduction

Lead–antimony alloys were first proposed for lead/acid battery grids in 1881 by Sellon, cited in ref. 1. Since then, these alloys have been widely used in practice. The normal range of the antimony content is 2.5 to 6 wt.% in most applications. Lead–antimony alloys have good castability, high tensile strength and good cycling characteristics for the positive plate. Furthermore, production costs are low. On the other hand, the corrosion of positive grid and the self-discharge caused by antimony shorten the battery life.

With respect to the problem of corrosion, previous studies [2–5] have concentrated almost exclusively on the examination of the process at the positive grid. By contrast, equivalent investigations of the corrosion of the negative grid have rarely been reported. This is probably because the latter form of corrosion is not usually serious in automotive or small batteries. Prolonged service of large traction or large stationary batteries, however, the negative grids (especially the plate lugs) can become seriously corroded. It is even possible for a hole to develop in the plate lug (Fig. 1), or for the welding seam to split open. In order to extend the service life of such batteries, it is essential to study and understand the processes that are responsible for negative-grid corrosion.

In the work reported here, the metallographic structure and electrochemical properties of different parts on the negative plate lugs have been investigated by means of linear sweep voltammetry, electron probe microscopy, and metallographic techniques. The likely causes of the corrosion of the lugs are discussed.
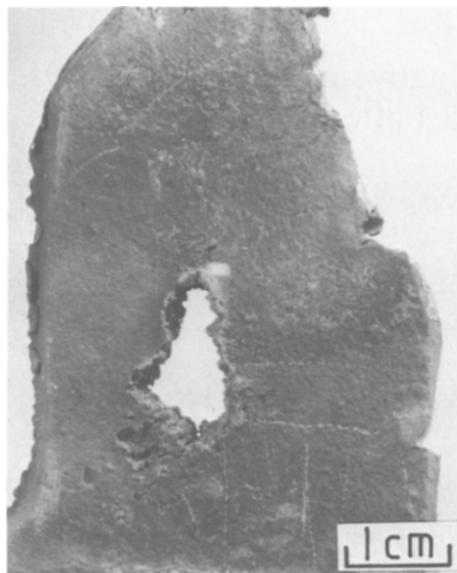
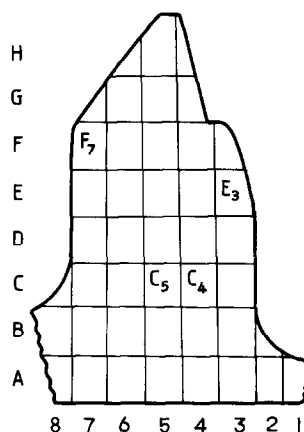Figure 1. Example of corrosion at a negative-plate lug.

Fig. 2. Schematic illustration of sectioning of the negative-plate lug for electrode preparation.

Experimental

Specimen preparation for metallographic examination

Specimens were taken from a negative grid that had not been pasted and used. The plate lug was fabricated from a Pb–7wt.%Sb alloy and had an area of ~35 cm^2 and a thickness of 0.3 cm. It was cut into about 40 sections (see Fig. 2). The latter were used for metallographic studies. The surfaces of the individual sections were polished on various grades of emery paper (up to 600 grit) in the presence of alcohol, and then were exposed to a short (3 min) chemical corrosion in a polishing agent (30% hydrogen peroxide, 30 ml; 98% acetic acid, 10 ml; glycerin, 100 ml). Next, the specimens were mechanically polished on a chamois leather that was impregnated with kerosene. This treatment was continued until the surface of each section took on a bright, mirror-like, appearance. The specimens were then rinsed with redistilled water and etched for 2 min in an alcohol (95 ml) and nitric acid (5 ml) mixture. Finally, the specimens were washed thoroughly with redistilled water. At this stage, the surface was dull-grey in colour. Micrographs were obtained using a metallurgical microscope.

Specimen preparation for electron microprobe examination

A negative-plate lug was cut up in the same manner as described above. One section of each specimen taken at different locations was mechanically polished on various grades of emery paper (up to 600 grit). A very smooth section was obtained by polishing with soft, clean pieces of paper.

Preparation of working electrode

A corroded lug, shown in Fig. 1, was cut into many sections in the same way as that illustrated in Fig. 2. Each section was mounted within epoxy resin. The bottom

of each specimen was cut at an inclined plane of 45°. Before each experiment, the electrode was mechanically polished on various grades of emery paper (up to 600 grit) in the presence of alcohol. This was followed by a thorough washing with redistilled water. The oxide was removed from the electrode surface by polishing with soft, clean pieces of paper. The resulting working electrode was immersed in the cell electrolyte and then galvanostatically polarized for 1 min at 1 mA cathodic current. This procedure eliminated the remainder of the oxide from the electrode surface.

Electrolytic cell and equipment

Electrochemical experiments were conducted using a conventional, three-electrode system. Two platinum counter electrodes (1 cm × 1 cm) were used in a four-compartment glass cell. The compartments were separated by fritted glass discs [6]. The potential of the working electrode was measured against a Hg/Hg_2SO_4 reference electrode that was housed in a compartment that, in turn, was connected to the working-electrode compartment via a Luggin capillary. All potentials were reported with respect to this reference electrode. In all experiments, the test electrode was placed about 1 mm away from the tip of the Luggin capillary in order to minimize the IR drop. The electrolyte was 1.285 sp. gr. (25 °C) H_2SO_4 solution and was prepared from analytical reagent (AR) grade H_2SO_4 and redistilled water at 25 °C. The same electrolyte was used for both the cell and the Hg/Hg_2SO_4 reference electrode. In order to eliminate traces of oxygen, pure nitrogen (passed through activated copper at ~300 °C) was bubbled through the electrolyte. Experiments were performed at a temperature of 25 °C.

Linear potential-sweep experiments were performed with a potentiostat (HDV-7) in conjunction with a function generator (DCD-1). The voltammograms were recorded on an X–Y recorder (LZ3-204) [6]. The compositions at different microregions of the section were analysed by an electron probe X-ray microanalyser (JCXA-733). Micrographs of the metallographic structure were obtained with a metallurgical microscope. In order to determine the distribution of antimony in the surface layer at different parts of the lug, slices of about 0.1 mm in thickness were excised from these regions. The antimony content was chemically analysed using the malachite green extraction method.

Results and discussion

Metallographic structure of Pb–Sb alloy

Examination revealed that the surface of the central region of the lug taken from the new grid is greyer than that at the edges. This is due to a difference in the metallographic structure. For example, photographs (Figs. 3 and 4) show that the edge region (E_3, Fig. 2) has a more defined metallographic structure than the middle region (C_5, Fig. 2). At the edge (Fig. 3), the lead-rich solid solution (black part) presents a complete dendritic structure that is surrounded by a eutectic phase (white part) that consists of lead-rich and antimony-rich solid solutions. The central region (Fig. 4), where corrosion occurs preferentially during battery operation, exhibits a preponderance of irregular antimony-rich solid solution. In the eutectic between the dendritic lead-rich crystals, the white antimony-rich phase consists of many small crystals. These do not connect well with each other and, consequently, the structure is looser and its tensile strength is lower.

The difference between the metallographic structures of regions E_3 and C_5 is clearly due to a difference in the casting conditions. In the latter process, the temperature
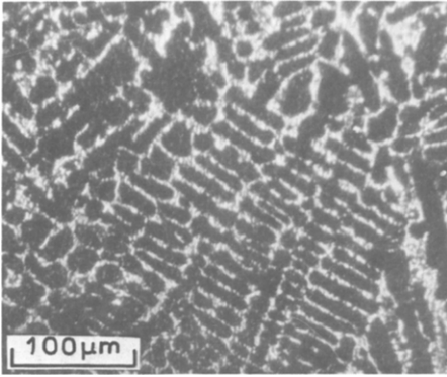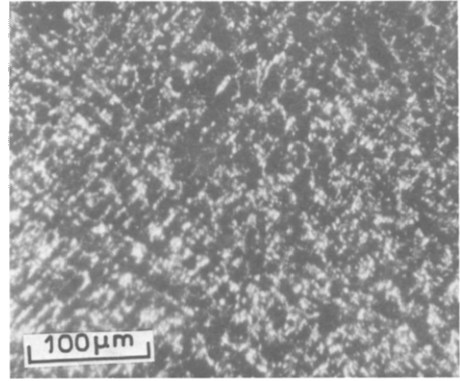
Fig. 3. Metallograph of edge region (E₃) of lug.

Fig. 4. Metallograph of central region (C₅) of lug.

at the lug edge falls more rapidly than that at the centre as the mould is chilled. According to the phase diagram for lead–antimony binary alloy, dendritic lead-rich crystals are formed first during the fast-chilled processes of the edge (E₃), and then the liquid among the dendritic crystals is solidified as the eutectic. Thus, a complete and homogeneous metallographic structure is obtained in the edge region, and the alloy with this structure has high tensile strength and is evenly corroded during battery operation. In the centre of a large lug, however, the lead-rich dendritic crystals are formed more slowly because of the slow-chilled rate. As a result of these processes, the concentration of antimony in the liquid phase varies from a low level at the edge to a high level in the central region of the lug. Therefore, more antimony-rich phases appear in the central region. Furthermore, when all the liquid is solidified, the temperature in the centre of the large lug falls more slowly than that at the edge. This causes more antimony to diffuse out of the lead-rich phases in the lug centre and the antimony becomes concentrated in the intercrystalline region. Thus, serious macrosegregation occurs at the central region, C₅. Moreover, because the edge of the lug is solidified earlier during the casting of a large grid, the alloy shrinkage is different at different parts of the lug. As a result, greater internal stress exists in the central parts; it is even possible for shrinkage cracks to appear. Hence, this alloy with an uneven structure is more susceptible to corrosion during the battery operation.

Chemical analysis

For alloys other than fast-chilled types, a higher content of antimony appears on the surface than is expected from the bulk alloy composition. Thus, in the centre of the lug, the inverse segregation, i.e., decreased concentration of the solute towards the centre of the casting with an abnormally high concentration at or near the surface, appears more likely. In order to verify an inverse segregation phenomenon for the lug, surface layers about 0.1 mm thick were removed from different parts and then analysed chemically. The experimental data showed that the antimony content in the surface layers at the centre (specimen C₅) and the edge (specimen E₃) of the plate lug was 7.6 wt.% and 6.8 wt.%, respectively. This observation indicates that a higher antimony concentration occurs in the surface of the central region because of the slow-chilled rate at this location. Thus, central parts of the lug have poor corrosion resistance.

Linear sweep voltammetry

A specimen of the negative-plate lug that had been corroded to give a hole was sectioned into many small parts. A central part near the corrosive hole was labelled as electrode M_2 (position C_4 in Fig. 2) and an edge part far away from the corrosive hole as electrode M_1 (position F_7 in Fig. 2). The linear sweep voltammograms for the two electrodes are shown in Fig. 5. In the positive-going sweep, peak A is due to the formation of $PbSO_4$. The latter is reduced in the reverse sweep and defined as peak D. Peaks B and C are due to the formation and reduction of antimony oxide, respectively. For the initial scan, the oxidation peaks of lead and antimony on electrode M_2 are larger than those on electrode M_1. Comparison of the charges associated with these two peaks reveals that the ratio of the oxidation charge of the antimony to the formation charge of the lead sulfate is 1.62 and 0.62 on electrodes M_2 and M_1, respectively. Furthermore, the extent of antimony oxidation on electrode M_2 is much greater than that on electrode M_1. From the content of antimony in the alloy and the charges of peaks A and B, an estimation can be made of the corrosive depth of both lead and antimony on the two electrodes during the first cycle. Calculation revealed that the corrosive depth of antimony is about five and ten times greater than that for lead on electrodes M_1 and M_2, respectively. Nevertheless, there is little difference between the antimony contents of the two electrodes. It is suggested that this phenomenon is caused by the different structure and texture at the different parts of the lug. The structure/texture of electrode M_2, i.e., near the corrosive hole, is looser than that of electrode M_1. This feature renders lead and antimony in the centre of the lug more prone to corrosion. Furthermore, the appreciable segregation of antimony can also accelerate the oxidization and dissolution of antimony. Although the electrode potential of the negative plate in a lead/acid battery is much more negative than that of the antimony/antimony oxide electrode, the oxygen produced on the positive plate during the charge process can diffuse through the electrolyte to the surface of the negative plate and thus depolarize the antimony/antimony oxide electrode. As a consequence,
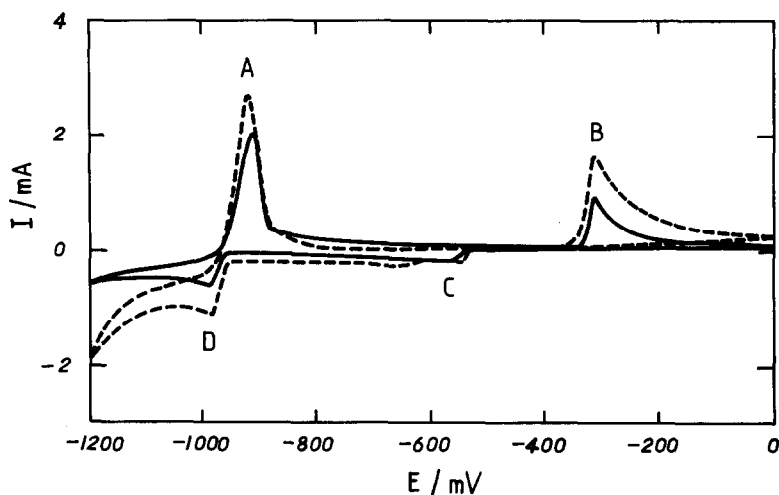

Fig. 5. First cyclic voltammogram for Pb–Sb alloy: (——) electrode M_1, surface area 0.21 cm^2, and (– – –) electrode M_2, surface area 0.24 cm^2. Initial sweep potential: −1200 mV; sweep rate: 4 mV s^{-1}.
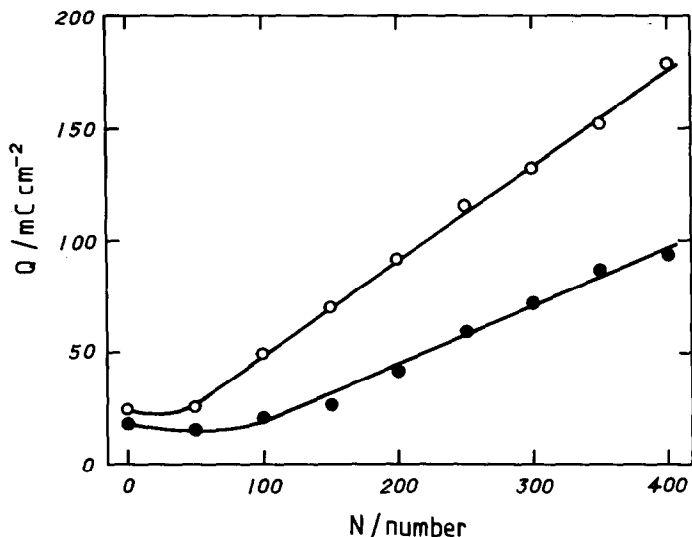
Fig. 6. Relationship between formation charge of $PbSO_4$ (Q) and cyclic number (N). Cycles for (●) electrodes M_1 and (○) M_2 were conducted over the potential range -1500 and -700 mV at 16 mV s^{-1}.

antimony in the alloy can be dissolved into the electrolyte and, therefore, corrosion proceeds more readily at the central part of the negative-plate lug.

The charge associated with $PbSO_4$ formation during linear sweep voltammetry is displayed in Fig. 6 as a function of cycle number. The degree of corrosion of the two electrodes (i.e., the charge due to $PbSO_4$ formation) is directly proportional to the number of the potentiodynamic cycles. The amount of corrosion increases more rapidly for electrode M_2; the slopes of the curves are 0.43 and 0.28 mC cm^{-2} per cycle for electrodes M_2 and M_1, respectively. The increase in corrosion with each cycle is probably due to the further oxidation of the metallic lead beneath the passivation layer of lead sulfate. It is calculated that the penetration of corrosion during each cycle is 1.1×10^{-7} and 6.9×10^{-8} cm for electrodes M_2 and M_1, respectively. Thus, the alloy on the surface of the plate lug is also oxidized and reduced and the corrosive film becomes thicker and thicker during the charge/discharge service of the battery. Because the corrosive depth at the central part extends more rapidly than that at the edge part and there is a volume expansion accompanying the oxidation of lead to lead sulfate, a hole likely occurs in the central region of a large plate lug.

Electron probe experiments

Scanning electron micrographs were obtained for different parts of each specimen section. Figures 7 and 8 show micrographs for the edge of specimens C_5 and E_3, respectively (i.e., rectangular part in Fig. 9), together with the corresponding electron microprobe scanning curves for antimony and lead. The data in Fig. 7 show that the structure of the plate lug surface layer to a depth of about 0.1 mm is different from that of the internal region. In this layer, the crystals are very small in size, and the content of antimony is greater while the content of lead is lower than that in the interior of the alloy. Moreover, the electron microprobe scanning curve shows that the distribution of antimony is irregular while that of lead is uniform. Specimen E_3,
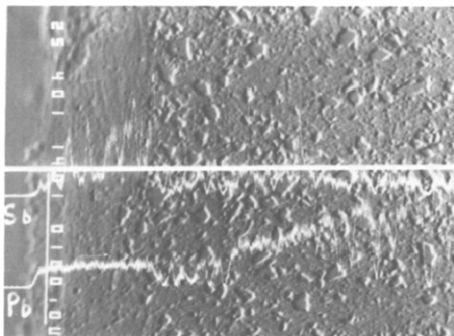
Fig. 7. Electron micrograph of C₅ and electron microprobe scanning curves for Sb and Pb.
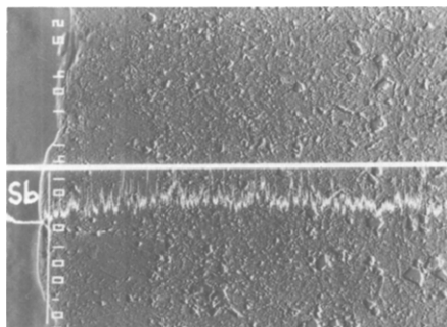
Fig. 8. Electron micrograph of E₃ and electron microprobe scanning curve for Sb.
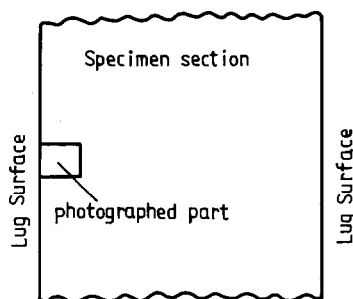

Fig. 9. Schematic illustration of region examined by electron microprobe experiments.

the edge part of the lug does not exhibit this behaviour. This is because the different chilled rates at different parts of the mould have caused marked segregation of antimony in the centre of the lug. This inverse segregation of antimony makes the content of antimony in the surface layer higher than that expected from the bulk alloy composition. The antimony-rich phases in the surface layer are composed of many small crystals. The resulting structure exhibits great disorder and this is in agreement with the information presented in Fig. 4. Consequently, the corrosion resistance of the central part of the lug is lowered.

Conclusions

Effects of casting conditions on alloy properties

The metallographic structure and texture of an alloy, together with the distribution of antimony, depend strongly on the casting conditions of the grid such as grid shape, temperature of the mould and alloy liquid, chilled rates at different parts of the mould, etc. In the production of a large grid, the structure of the plate lug is uneven because the chilled rates vary at different parts of the lug. After the plate lug is solidified, the temperature at the centre falls slowly, the internal stress increases, and the appreciable segregation of antimony appears. As a consequence, the content of antimony in the surface layer of the central region is higher than at the edges of the lug. At

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the same time, the antimony-rich solid solution in the central region of the lug is made up of many small antimony-rich phases. The interconnection of these phases is disordered. The lead-rich solid solution loses its dendritic structure and the tensile strength decreases. Overall, metallographic structure and texture in the central region become looser and more disordered. These characteristics lower the corrosion resistance of the alloy.

Mechanism of negative-plate lug corrosion

Since the chilled rate in the middle of the lug is slow during production of the grid, both segregation of antimony and a loose metallographic structure/texture occur. As a result, electrochemical activation in the central region is higher than at the edges of the lug. During operation of large batteries, especially during overcharge, oxygen evolved at the positive plate can diffuse through the electrolyte to the surface of the negative-plate lug and oxidize antimony as well as lead. If a large amount of electrolyte is consumed and the plate lug emerges from the electrolyte, the same processes will take place. The resulting antimony oxide dissolves in the electrolyte while lead oxide reacts with the sulfuric acid in the electrolyte to produce lead sulfate. Consequently, a porous film is formed on the surface of the central region of the lug and the corrosion depth extends rapidly. This corrosive film can be reduced and oxidized during charge and discharge of the battery, respectively. Because great changes take place in volume during the oxidation of lead to lead sulfate, large internal stresses are created in the surface layer that covers the central part of the lug. Thus, cracks are readily formed in the anodic film. Sulfuric acid solution permeates these cracks and oxidizes the underlying base alloy. This process accelerates the rate of corrosion at the centre of the negative-plate lug and, eventually, a hole may appear after prolonged service of the battery.

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