Improved grid alloys for deep-cycling lead–calcium batteries

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Abstract

Lead–calcium standby batteries contain free acid, thick grids of low calcium content, and are discharged infrequently. Valve-regulated lead/acid batteries (VRLAs) are deeply discharged, contain immobilized electrolyte, and contain much thinner grids of lead–calcium–tin alloys. Tin is added to enhance rechargeability from deep discharge and to enhance the mechanical properties of the alloys, particularly creep resistance. Until 1980, lead–calcium–tin alloys suffered from wide variations in grain structure, caused mainly by poor control of the calcium content. The latter is due to calcium oxidation and the inclusion of suspended oxide into the grids. The introduction of aluminium into lead–calcium and lead–calcium–tin–aluminium alloys prevents calcium loss from the melt. Lead–calcium–tin–aluminium alloys can be produced to the desired specification without fear of either calcium loss or poor control of grain structure. Aluminium also serves both as a nucleant to significantly reduce the initial cast grain-structure and as a means to enhance the precipitation of calcium in lead–calcium–tin alloys. Grain-structure control is now possible even in very high tin-content alloys. Lead–calcium–tin alloys with aluminium are not susceptible to penetrating grain boundary corrrosion and will become the favored alloys for deep-cycling VRLAs of the future.

Introduction

Lead–calcium alloys have been used extensively in standby power batteries for over 60 years. These batteries operate in telephone float service and are discharged infrequently. The positive grids consist of very low calcium (0.03 to 0.04 wt.% Ca) alloys with a very large grain size. The large grained, thick grids suffer some penetrating corrosion, but resist growth during the long life of the batteries (up to 30 years). Negative grids are generally produced from 0.070 to 0.09 wt.% calcium alloys. Control of the calcium content is a major problem with calcium alloys. Elaborate methods have been developed to prevent calcium loss, to determine the melt-pot composition, and to add master alloy to replace the calcium lost to oxidation. The major cause of telephone battery failure is production of fine grains that result in growth of the positive plate. Fine-grained castings are caused by improper control of casting conditions and introduction of impurities and casting defects [1, 2].

During the past ten years, a large number of valve-regulated lead/acid batteries (VRLAs) have been introduced for deep-discharge applications. In addition, UPS or standby-power batteries have been constructed from lead–calcium alloys and use either gelled electrolyte or glass-mat separators to

immobilize the electrolyte. Standby-power batteries are cycled more frequently than telecommunications batteries. These deep-discharge batteries generally contain lead–calcium–tin alloy positive grids and lead–calcium negative grids. The tin is added to the positive grid to permit recharge from deep discharge [3]. The major problem with lead–calcium–tin alloys has been the loss of calcium during processing. Low calcium produces very soft grids, changes the mode of calcium precipitation and produces penetrating corrosion [4, 5]. The high calcium oxidation rate causes significant amounts of suspended calcium oxide. Some of the latter is entrained in the grids and thus causes defects. Since UPS and other VRLAs have relatively thin grids compared with telephone batteries, control of the calcium content and reduction of the casting defects is a major concern.

Modern lead–calcium alloys utilize aluminium to prevent calcium loss during processing [6]. A process has been developed to introduce easily the aluminium into lead–calcium alloys [7]. Once alloyed, aluminium provides a protective oxide skin on the surface of the melt pot. This effectively prevents the loss of calcium. Approximately 0.01 to 0.03 wt.% aluminium is required to protect the calcium from oxidation; the actual amount depends upon the rate of metal use and the agitation of the melt pot. Aluminium additions also greatly decrease the amount of calcium oxides suspended in the cast grids and, hence, the number of casting defects. Finally, aluminium eliminates the need to monitor melt-pot composition, reduces dross generation, and permits lead–calcium–tin alloys with high tin contents to be used for positive grids without the fear of potentially severe penetrating corrosion.

Aluminium additions have a second function. Because aluminium solubility in lead decreases as the lead temperature decreases, metallic aluminium particles can nucleate in the melt prior to solidification of the lead–calcium alloys. Aluminium particles can act as nucleants to produce fine grains. The structure of cast lead–calcium alloys normally consists of large columnar grains [8]. Aluminium-containing alloys have a smaller initial cast grain size. Thus, the final transformed grain size of the casting is more uniform. This paper discusses the grain structures attainable in lead–calcium–(tin)–aluminium alloys and compares these structures with those of conventional alloys.

Experimental

Lead–calcium and lead–calcium–(tin)–aluminium alloys were melted at a temperature of 480 °C. The alloys were cast into a steel mould that was heated to a temperature of about 230 °C. The mould thickness was 6.4 mm. The samples were water quenched to simulate the cooling conditions of battery grids. The cast samples were aged for 30 days to assure completion of any precipitation reactions. The entire cross section of the cast sample was examined. Samples were ground, polished, and etched to reveal the grain structure. Samples of positive battery grids containing high tin contents with/without aluminium were obtained from failed batteries.
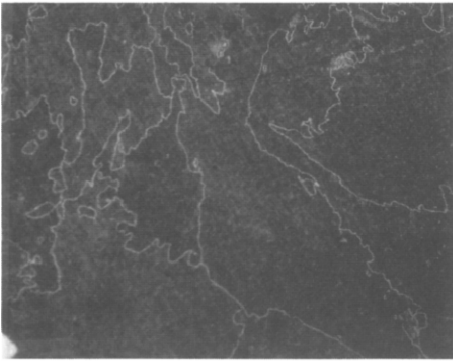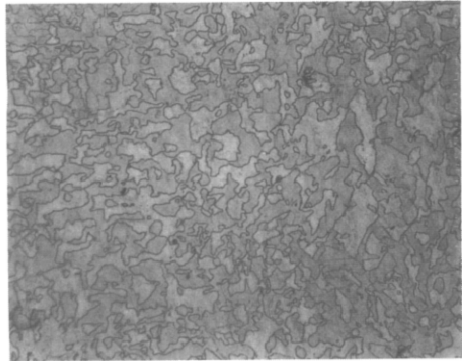
Fig. 1. Pb–0.04wt.%Ca alloy. Magnification 50×.

Fig. 2. Pb–0.09wt.%Ca alloy. Magnification 50×.

Results

Lead–calcium alloys

Lead–calcium alloys exhibit serrated grain boundaries that result from the precipitation of the calcium from solution behind moving grain boundaries [9, 10]. At low calcium contents similar to those used in telephone standby-power batteries, the grain structure is very large and consists of oriented grains with serrated grain boundaries. The structure of a lead–calcium alloy containing 0.04 wt.% calcium is shown in Fig. 1. Higher calcium contents produce better mechanical properties. Negative grids do not generally suffer corrosion and, therefore, utilize higher calcium contents. The grain structure of a binary alloy containing 0.91 wt.% calcium is given in Fig. 2. The structure consists of uniform fine grains with serrated edges forming a continuous interlocking network. The structure is related to the orientation of the original cast grain. Lead–calcium alloys with calcium contents above 0.12 wt.% usually contain small amounts of Pb_3Ca primary particles in the structure.

Lead–calcium–aluminium alloys

The grain structure of lead–calcium–aluminium alloys is significantly different to that of lead–calcium alloys. Figure 3 presents the grain structure of a lead–0.05wt.% calcium alloy containing about 0.02 wt.% aluminium. (Note, in this study, all the alloys contained between 0.018 and 0.022 wt.% aluminium.) The alloy has a finer grain structure than normal lead–calcium alloys of this composition. In addition, the grain boundaries do not exhibit the classical serrations: they are much smoother and do not seem to follow the orientation of the original cast grain which cannot be detected in the material.

The structure of an alloy containing 0.095 wt.% calcium and 0.021 wt.% aluminium is shown in Fig. 4. The grain size is finer than that of the previous
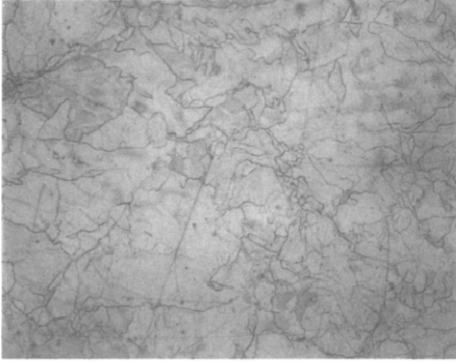
Fig. 3. Pb–0.05wt.%Ca–0.02wt.%Al alloy. Magnification 50×.

Fig. 4. Pb–0.095wt.%Ca–0.021wt.%Al alloy. Magnification 50×.

alloy (Fig. 3) and the structure is considerably different to that of an alloy with the same calcium content but not containing aluminium (Fig. 2). The structure is more 'blocky', the grains are more regular, and the serrations of the grain boundaries are much less pronounced or non-existent. There is no evidence that the grains follow the pattern of an initial cast grain morphology. On the other hand, there is some indication of grain boundary movement. The final grain structure is larger than that formed in the absence of aluminium.

Figure 5 gives the grain structure of an alloy containing 0.15 wt.% calcium and 0.023 wt.% aluminium. The grain size is virtually identical to that of the 0.09 wt.% calcium alloy (Fig. 4) but contains some large primary Pb_3Ca particles. In general, the latter are larger than those found in alloys without aluminium, and may have formed on aluminium particles that were already present in the system.

Lead–calcium–tin–aluminium alloys

Aluminium changes significantly the grain structure of lead–calcium–tin alloys. Tin additions to lead–calcium alloys increase markedly the mechanical properties. At any calcium content, higher tin contents not only increase both the yield and the ultimate tensile strength, but also increase the creep strength by as much as 2 to 3 orders of magnitude [11]. Aluminium also increases the mechanical properties of lead–calcium–tin alloys by assuring that all the calcium in the alloy is present as the dissolved metallic form and not as suspended oxide.

Figure 6 presents the grain structure of an alloy containing 0.06 wt.% calcium and 0.6 wt.% tin without aluminium. The structure consists of large oriented grains with tin segregated to the inter-dendritic boundaries. Such structures are extremely stable and do not decompose readily into finer grains without the application of additional energy, such as mechanical working. Nevertheless the large grain structures are subject to penetrating corrosion.
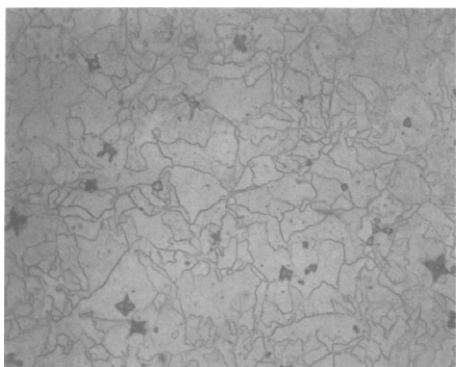
Fig. 5. Pb–0.15wt.%Ca–0.022wt.%Al alloy. Magnification 50 ×.
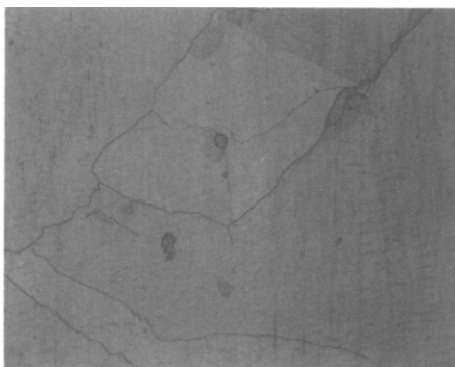
Fig. 6. Pb–0.06wt.%Ca–0.6wt.%Sn alloy. Magnification 25 ×.

The grain structure of an alloy containing 0.058 wt.% calcium, 0.60 wt.% tin and 0.018 wt.% aluminium is given in Fig. 7. The grain size is relatively fine compared with that of the alloy in Fig. 6. There is some evidence of slightly serrated grain boundaries. This suggests cellular precipitation and grain boundary movement. This alloy is used for positive grids in long life (10 years or more) VRLAs for UPS systems. Most alloys for such systems contain higher calcium contents for more rapid ageing.

For a 0.09wt.% calcium–0.60wt.% tin–0.02wt.% aluminium alloy, the grain structure (Fig. 8) contains the more normal serrated grain boundaries seen in lead–calcium alloys that do not contain aluminium. The serrated boundaries are believed to be due to the orientation of the tin segregation in the original cast grains. The black spots in the structure of Figs. 7 and 8 are pits caused by the corrosion of the aluminium particles during etching.

The grain structure of an alloy containing 0.12 wt.% calcium, 0.80 wt.% tin and 0.021 wt.% aluminium is shown in Fig. 9. The alloy was not etched
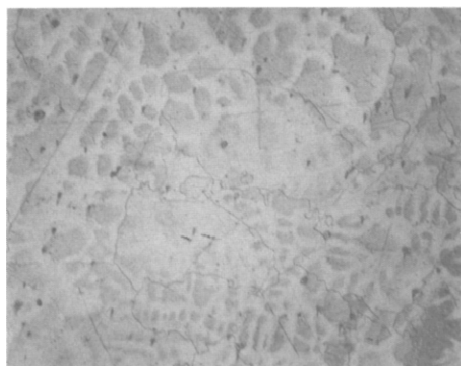

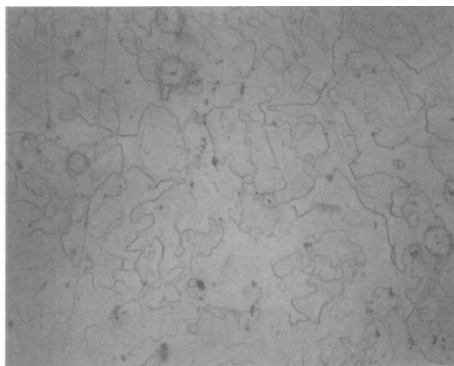Fig. 7. Pb–0.058wt.%Ca–0.6wt.%Sn–0.018wt.%Al alloy. Magnification 50 ×.

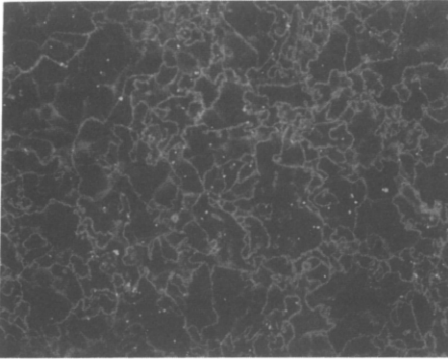Fig. 8. Pb–0.090wt.%Ca–0.6wt.%Sn–0.02wt.%Al alloy. Magnification 50 ×.

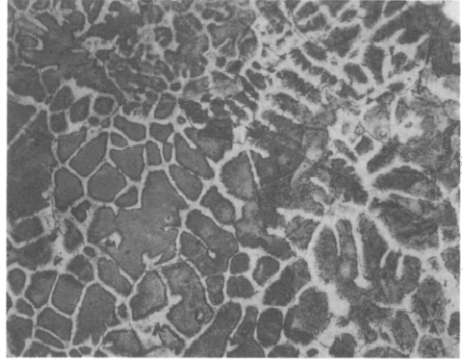Fig. 9. Pb–0.12wt.%Ca–0.84wt.%Sn–0.021wt.%Al alloy. Magnification 50×.

Fig. 10. Pb–0.072wt.%Ca–1.38wt.%Sn–0.02wt.%Al alloy. Magnification 50×.

but allowed to oxidize to show the aluminium particles (white) and the grain boundaries. The aluminium particles appear to be close to the center of the grains. This suggests that the calcium precipitation reaction may begin from the boundary of the aluminium particle in the centre of the original cast grain.

Figure 10 presents the grain structure of a lead–0.072wt.% calcium–1.38wt.% tin–0.02wt.% aluminium alloy. Note the extensive segregation of tin to the inter-dendritic boundaries. The grain size is about twice as large as that seen in Fig. 7 for an alloy with a similar calcium content. This level of tin in a conventional alloy without aluminium would produce extremely large grains. There has been extensive grain boundary movement throughout the sample, but this is difficult to see in Fig. 10. The extensive tin segregation in the cast alloy produces areas with tin contents of an order of magnitude greater than those in the surrounding alloy. Segregation in the very high tin alloys is not completely eliminated by the grain boundary movement of the calcium precipitation reaction. Thus tin is made more available to the active material at the grid/active-material interface.

Corrosion of high tin alloys

Lead–calcium alloys containing high tin contents, such as those described in the previous section, were believed to be susceptible to severe penetrating corrosion and, thus, could not be used effectively for thin grids. The large grain size common to lead–calcium–tin alloys contributes to the penetrating corrosion by presenting only a few grain boundaries as active corrosion sites. In addition, precipitation reactions stalled at grain boundaries present more reactive areas for corrosion.

A typical corrosion profile in a lead–0.07wt.% calcium–0.6wt.% tin alloy battery grid is given in Fig. 11. There is extensive penetrating corrosion into the grid. The grid, however, contains extensive amounts of oxidic material at the grain boundary. In the bottom of the photograph there is a large
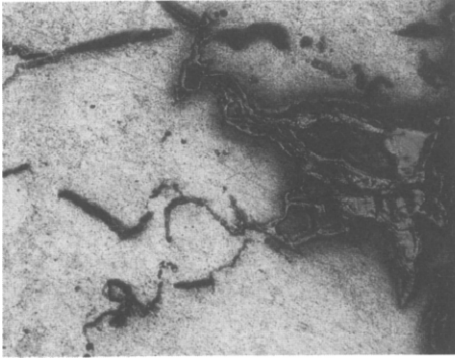
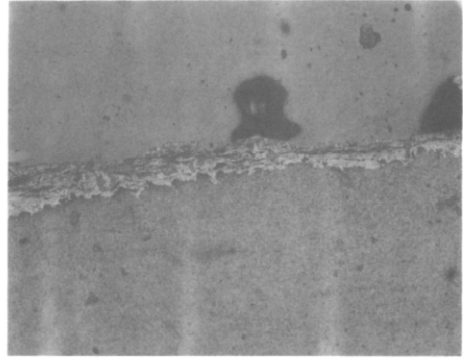Fig. 11. Corrosion profile of battery grid from failed battery: Pb–0.07wt.%Ca–0.6wt.%Sn alloy. Magnification 150 ×.

Fig. 12. Corrosion profile of battery grid from failed battery: Pb–0.09wt.%Ca–0.6wt.%Sn–0.015wt.%Al alloy. Magnification 150 ×.

amount of oxide at the grain boundary that has not yet been reached by the corrosion front. The grid also exhibits porosity at the grain boundaries; this can accelerate corrosion.

Figure 12 shows the corrosion profile of a battery grid using 0.09wt.% calcium–0.6wt.% tin–0.02wt.% aluminium (Fig. 8). There is no evidence of penetrating corrosion despite the relatively large grain size. Equally, there is also no indication of porosity or entrained oxidic material that might lead to penetrating corrosion. After 12 months service, this battery grid had suffered only minor corrosion of the grids.

Discussion

Aluminium additions to lead–calcium and lead–calcium–tin alloys significantly alter the grain structures of the alloys. Lead–calcium–aluminium alloys have more 'blocky' grain structures than similar alloys without aluminium. This is believed to be due to a nucleating effect of the aluminium (to produce an initially finer cast grain structure) and decreased calcium segregation.

Aluminium additions to lead–calcium–tin alloys produce different grain structures than those seen in binary alloys. The aluminium produces a significantly finer initial cast grain size. In addition, the aluminium facilitates the calcium precipitation reaction by providing sites for the initiation of grain boundary movement. After 30 days the original cast structure is almost completely transformed. The final grain size appears to be determined by the calcium content rather than by the tin/calcium ratio, as is the case for alloys without aluminium. The uniform, relatively fine, grain size — even at high tin contents and calcium contents about 0.09 to 0.11 wt.% — permits the

use of additional tin in these alloys with accompanying benefits in electro-chemical and mechanical properties. The controlled grain structure also prevents the occurrence of penetrating corrosion.

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