

## Metallurgy of recycled lead for recombinant batteries

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### Abstract

Recombinant and stationary lead/acid batteries generally use lead–calcium–tin alloys for grids, lead–tin alloys for strap and top lead, and high purity lead for oxide. In many cases, primary lead has been specified for these materials in recombinant batteries because both recycled lead and recycled lead alloys were not thought to be of sufficient purity. With improvements in analytical instruments, it is now possible to determine impurity elements at much lower levels. Because problem elements can be analyzed, refining procedures have now been developed to remove gas-producing impurity elements from recycled lead to levels as low as, or lower than, those in primary lead. These new refinery practices and analytical tests have increased the purity of refined recycled lead, and have permitted the use of recycled lead in recombinant and stand-by batteries. Some elements, deemed to be impurities that must be removed, may in fact be beneficial in alloys for recombinant batteries. This paper examines the purity requirements of lead and lead alloys for recombinant and stand-by batteries, indicates the problem elements, and shows the effects of beneficial elements.

### Introduction

Specifications for high purity lead vary widely around the world. The normal requirement is for 99.99 wt.% lead, i.e., a total impurity content of 0.01 wt.% is permitted. Table 1 shows the typical purity specifications for high purity lead alloys from around the world.

In many cases, these specifications reflect the producers' ability to refine high purity lead. More often, however, the specified levels reflect the ability of analytical instruments to analyze low levels of impurities. Despite wide differences in impurity levels permitted in these lead alloys, the 99.99 wt.% material normally specifies a bismuth maximum of 0.005 wt.%. The USA does not have a specification for 99.99 wt.% pure lead, due to a permitted bismuth content of 0.050 wt.% in high purity lead.

The 99.99 wt.% lead has been specified throughout the world as the material for oxide manufacture, as well as for lead–calcium alloys. Despite limited certification requirements for many elements, the 99.99 wt.% lead has been specified because the procedure used to refine the lead to this purity is believed to remove other, not listed, impurities. In general, recycled lead has not been used throughout much of the world because it contains bismuth at levels exceeding the 0.005 wt.% maximum. Only in the USA, where the high purity lead specification permits the presence of up to 0.050 wt.% bismuth, are battery company specifications written to permit refined recycled lead to be used for battery-grade oxide and lead–calcium alloys. In this material, specification for individual problem elements is more important than overall purity.

TABLE 1

Typical high purity lead specifications from various countries

Element	Impurity content maximum (wt.%)				
	Australia	Canada	Germany	UK	USA
Lead	99.99	99.99	99.99	99.99	99.94
Antimony	0.001	0.0015–0.02	0.001	0.002	0.002
Arsenic	0.001		0.001	traces	
Tin	0.001		0.001	traces	
Bismuth	0.005	0.005	0.005	0.005	0.050
Silver	0.001	0.0015	0.001	0.002	0.0015
Iron	0.001	0.002	0.001	0.003	0.002
Copper	0.001	0.0015	0.001	0.003	0.0015
Cadmium	0.001	NS	NS	traces	NS
Nickel	0.001	NS	NS	0.001	NS
Cobalt	0.001	NS	NS	0.001	NS
Sulfur	0.001	NS	NS	NS	NS
Zinc	0.001	NS	0.001	0.002	0.001
Total impurities	0.01	0.01	NS	NS	NS

NS = no specification.

TABLE 2

Problem elements (gassing) and permitted levels in the battery electrolyte [1]

Element	Maximum level (ppm)
Tellurium	0.1
Antimony	1.0
Arsenic	1.0
Cobalt	1.0
Nickel	1.0
Manganese	3.0
Iron	160.0
Selenium <sup>a</sup>	0.5

<sup>a</sup>Not specified by Pierson *et al.* [1], but accepted permissible value.

In particular, bismuth, the major reason for recycled lead not meeting the 99.99 wt.% purity requirement, is not considered a problem element.

### Acceptable impurity levels for sealed batteries

Pierson *et al.* [1] defined the acceptable levels of impurities in lead for battery grade oxide or lead-calcium grid alloys. They specified various elements that are considered problem impurities in the generation of gas during recharging of maintenance-free batteries. The same elements are disadvantageous in recombinant batteries. The major problem elements are shown in Table 2, along with the suggested respective maximum concentration that is allowable in the electrolyte.

Also of concern are molybdenum, vanadium and chromium, but not at the same levels as the above elements.

If all the impurity in the oxide is considered leachable, the elements shown in Table 2 represent the acceptable levels of each of these impurities in refined lead for sealed batteries.

### Recycled lead for batteries

Based on the above information about gassing levels, RSR and US battery manufacturers have developed specifications for recycled lead that reflect accurately the true impurity content of the lead required for sealed batteries, regardless of the source of the metal. The RSR specification for pure lead is given in Table 3.

It can be seen that the specified maximum and typical values for recycled pure lead are, in general, well below the levels specified for 99.99 wt.% lead. Only silver in some specifications and bismuth in all specifications remain outside the 99.99 wt.% levels. The gas-causing elements, however, are closely controlled, and thus this lead is acceptable for sealed batteries despite the fact that it originates from recycled batteries.

### Analysis of low levels of impurities

The refineries of lead recyclers use the same refining techniques as the primary lead smelters. When impurity levels are specified at 10–50 ppm, wet chemical or spark

TABLE 3

Specification and typical values for RSR recycled pure lead

Element	RSR specification (ppm)	Typical value (ppm)
Antimony	0.8	0.4
Arsenic	0.5	<0.1
Bismuth	250.0	120
Cadmium	5.0	<0.1
Chromium	5.0	<0.4
Cobalt	1.0	<0.4
Copper	10	3
Iron	5	<0.4
Manganese	0.5	<0.1
Molybdenum	1.0	<0.2
Nickel	1.0	<0.2
Silver	35	12
Selenium	0.5	<0.1
Tellurium	0.2	<0.1
Tin	10	<1
Vanadium	1.0	<0.5
Zinc	5.0	<1
Sulfur	5.0	<1

spectrographic methods are sufficiently accurate to assure purity for the few elements tested. New methods use atomic absorption spectrophotometry (AAS), inductively coupled plasma (ICP), or direct current plasma (DCP) to analyze impurities at very low levels. Of particular importance is the analysis of antimony, arsenic, selenium, and tellurium. At levels less than 1 ppm, these elements must be analyzed using even more complex equipment. Fox [2] has described the determination of selenium and tellurium in lead via an AAS-graphite furnace or AAS hydride generation. The same technique can be used to analyze antimony and arsenic at low levels of less than 1 ppm.

### **Effect of bismuth**

The major element of concern in recycled lead is bismuth. The concentration varies between 100 and 300 ppm; the value depends on the source of the scrap. There has been a great deal of controversy over the effects of bismuth in oxide. Hoffmann [3] claims that there is no effect up to 0.050 wt.% in lead/acid batteries. Recent work by Miyazaki and Sumida [4] has reported a 20% increase in battery performance when the batteries contain 0.016 wt.% bismuth in the oxide compared with the same oxide material with only 0.0004 wt.% bismuth. Bismuth was more effective when alloyed with the lead prior to production of the battery oxide than when added to the oxide.

Pavlov [5] has indicated that bismuth accelerates the formation of the structure of the positive active material and exerts a catalytic effect on the development of bridges between the individual particles during recharge. Similar catalytic effects of bismuth-doped  $PbO_2$  on the oxidation of a variety of substances has been reported by Yeo and Johnson [6], La Course *et al.* [7], Nielsen *et al.* [8], Yeo *et al.* [9], and Chang and Johnson [10]. Corresponding phenomena have also been reported for antimony and arsenic. This recent evidence indicates that refined, recycled lead that contains bismuth may have beneficial properties, both as an additive to active material as well as the base lead for lead-calcium-(tin) alloys.

### **Effects of bismuth on lead-calcium-(tin) alloys**

The presence of bismuth in lead-calcium alloys has been reported to be deleterious many years ago by Haring and Thomas [11] and more recently by ILZRO [12]. By contrast, other researchers have found [13] no interaction between bismuth and calcium. Davey [14] reported that there is no reaction between calcium and bismuth below 0.034 wt.% bismuth. Thus, recycled lead containing 100–300 ppm bismuth should form no Ca-Bi intermetallic compounds and should be suitable for the production of lead-calcium-(tin) alloys.

Hampson *et al.* [15] found that small additions of bismuth to pure lead increased the corrosion rate although an area of stability was observed. Caldwell and Sokolov [16] found an increase in early hardening with bismuth in lead-calcium-tin alloys, but the effect was less on lead-calcium alloys. Caldwell *et al.* [17] indicated reduced gassing rates on lead-calcium-tin alloys that contained bismuth, while Devitt and Myers [18] reported beneficial effects on the cycling behavior of cells that used lead-calcium-tin alloy grids with various amounts of bismuth. Bourden *et al.* [19] claimed that bismuth increased the rate of the discontinuous reaction in lead-calcium alloys, while no significant effects were seen with lead-calcium-tin alloys. Aluminum refined the grains,

whereas silver increased the rate of continuous precipitation in lead–calcium–tin alloys. Prengaman [20] also demonstrated the control of the grain size of lead–calcium–(tin) alloys with aluminum.

### Structural aspects of bismuth in lead and alloys

The effect of bismuth on the grain structure of pure lead, lead–calcium and lead–calcium–tin alloys has been determined on cast samples using the following procedure. Primary lead containing about 0.0003 wt.% bismuth and RSR-recycled pure lead containing 0.012 wt.% bismuth were used as the base lead to produce lead–calcium and lead–calcium–tin alloys. Pure lead, lead–0.07wt.% calcium, lead–0.85wt.% calcium–0.3wt.% tin, and lead–0.08wt.% calcium–1.2wt.% tin alloys were cast into steel molds heated to 100 °C. Each alloy contained 0.006 wt.% aluminum. This was sufficient to prevent calcium loss, but low enough to avoid influencing the metal structures. In each case, the metal was heated to 450 °C and then cast into 6 mm thick molds. The castings were quenched to room temperature. The resulting samples were sectioned, mounted, ground, polished and etched within 1 h of casting. The grain structure was evaluated.

### Pure lead

Figure 1 shows the grain structure of the low-bismuth, pure-lead sample that has very low levels of impurities. The structure consists of large, oriented, columnar grains that grow from the mold surfaces to the center of the casting.

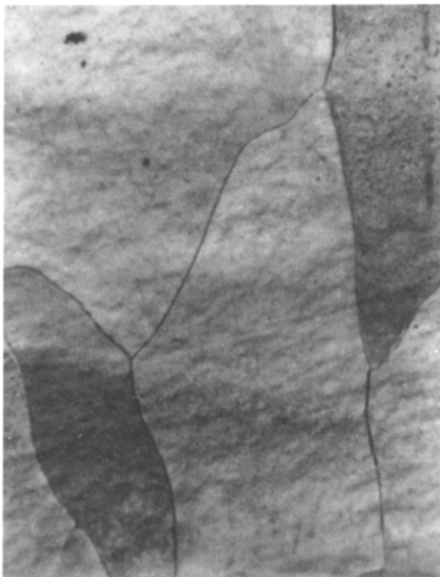


Fig. 1. Grain structure of low-bismuth, pure lead ( $\times 160$ ).

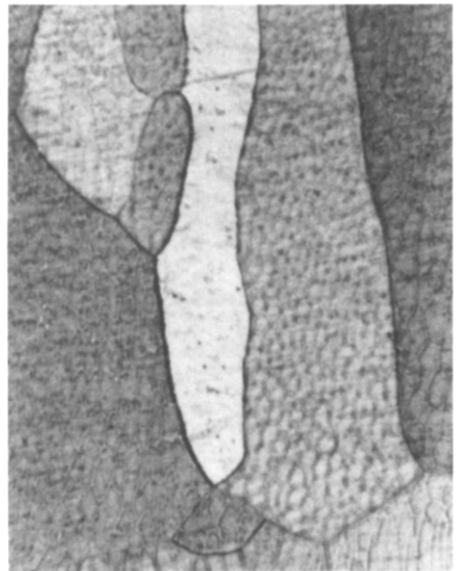


Fig. 2. Grain structure of recycled pure lead containing bismuth ( $\times 160$ ).

Figure 2 shows the grain structure of RSR pure lead that contains equally low levels of impurities, except for the presence of 0.0120 wt.% bismuth. The metal shows the same large, oriented, columnar grains as the low-bismuth lead. In addition, however, the grains exhibit the presence of a cored structure in which bismuth has segregated to the interdendritic boundaries. Thus, despite having a composition far from the bismuth–lead eutectic region, there is sufficient segregation of the bismuth to produce a cored structure. The latter is believed to account for the effects of bismuth on lead–calcium alloys.

### Lead–calcium alloys

The initial, as-cast, grain structure of a lead–0.07wt.% calcium alloy produced from low-bismuth pure lead is given in Fig. 3. There is a small amount of coring as the calcium segregates from the lead during solidification in the reverse segregation reaction. The segregation of calcium is not well defined, but is evident to a much greater extent than in pure lead without calcium.

Figure 4 shows the initial, as-cast, grain structure of a lead–0.07wt.% calcium alloy produced from recycled pure lead that contains 0.012 wt.% bismuth. This material displays well-defined cell boundaries within the cast grains. The enhanced segregation of the bismuth-rich regions that surround the calcium-rich interior of the cells may be due to the fact that the slightly lower melting point of the bismuth-rich regions provides sharper definition of the cell regions.

The enhanced segregation of calcium may increase supersaturation and may be responsible for the enhanced grain boundary movement reported in the first cellular

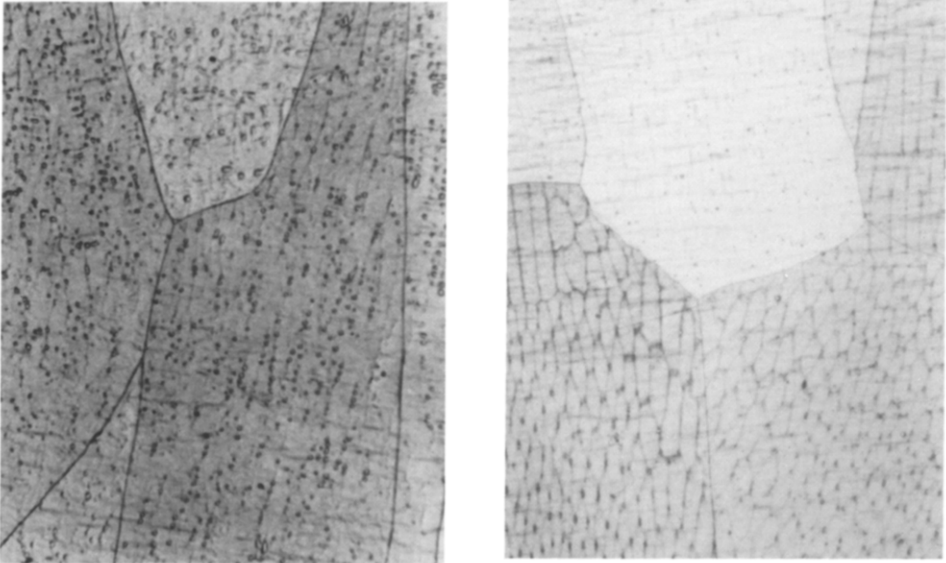


Fig. 3. Grain structure of lead–0.07wt.% calcium alloy with low-bismuth lead ( $\times 160$ ).

Fig. 4. Grain structure of 0.07 wt.% calcium alloy from recycled pure lead, 0.012 wt.% bismuth ( $\times 160$ ).

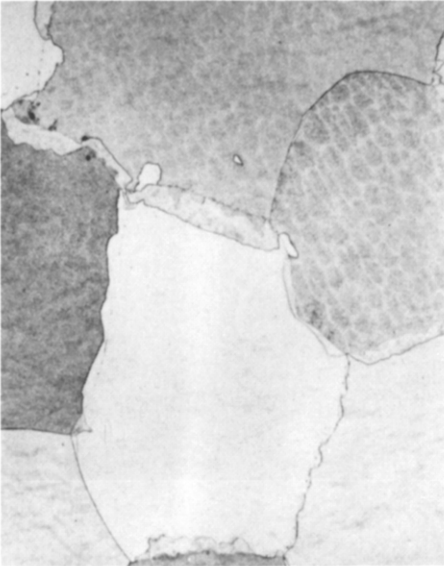


Fig. 5. Grain structure of lead–0.07wt.% calcium, low-bismuth alloy, aged for 5 h ( $\times 160$ ).

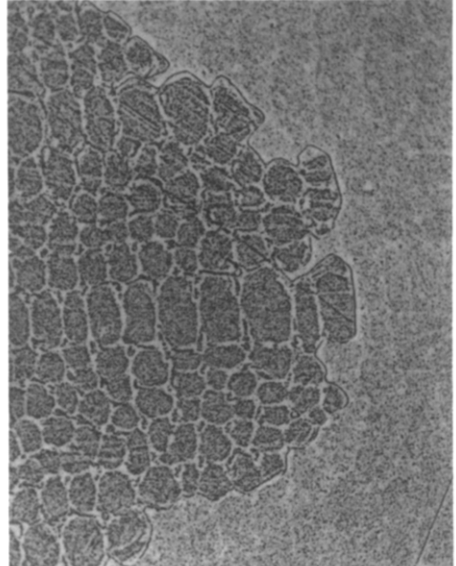


Fig. 6. Grain structure of lead–0.07wt.% calcium alloy from recycled pure lead, 0.12 wt.% bismuth, aged for 5 h ( $\times 500$ ).

transformation in lead–calcium alloys that has been reported by Bouriden *et al.* [19].

Figure 5 shows the grain structure of a low-bismuth lead–0.07wt.% calcium alloy 5 h after casting. The grain-boundary movement is sluggish and moves into the entire width of the grain. The enhanced calcium content in the mildly segregated material does not appear to promote a nonuniform movement of the grain boundaries.

Figure 6 demonstrates the nature by which the grain boundaries first move into the areas of bismuth segregation in the 0.07 wt.% calcium alloy that contains bismuth and has been aged for 5 h after casting. The grain boundaries move into the central part of the cell that has the higher calcium content. It would appear that bismuth encourages grain-boundary movement. The moving boundaries remove some, but not all, of the cast-in segregation as they travel through the structure.

### Lead–calcium–tin alloys

In lead–calcium–tin alloys with tin–calcium ratios of about 3:1, the initial cast grains consist of large, oriented crystals with extensive segregation of tin. Figure 7 shows the as-cast, grain structure of a lead–0.085wt.% calcium–0.3wt.% tin alloy that contains bismuth. The regions of both tin and bismuth segregation accelerate the grain-boundary movement in many areas. All the movement occurs initially in the interdendritic region rather than in the calcium-rich cell centers. The bismuth segregation appears to accelerate the hardening of the low-tin alloy more than that of the binary alloy.

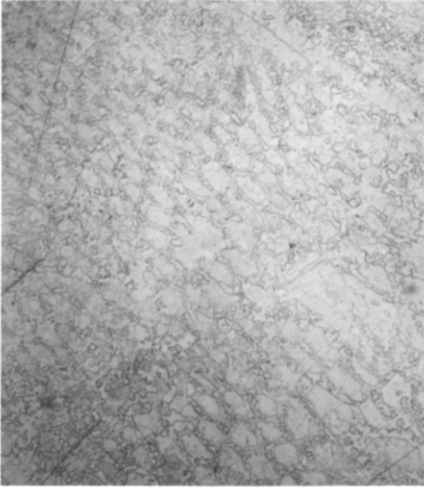


Fig. 7. Grain structure of lead-0.085wt.% calcium-0.3wt.% tin alloy from recycled pure lead with 0.012 wt.% bismuth ( $\times 320$ ).

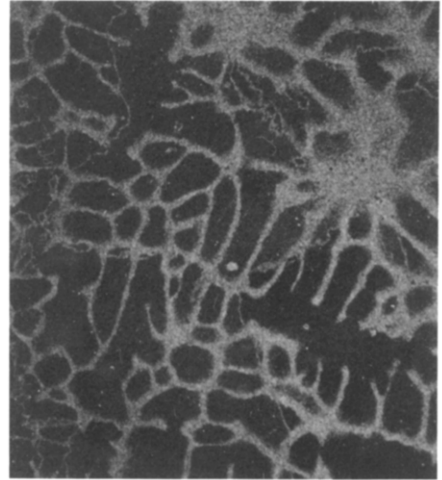


Fig. 8. Grain structure of 0.08wt.% calcium-1.2wt.% tin alloy from recycled pure lead, 0.012 wt.% bismuth ( $\times 320$ ).

At higher tin contents, (i.e., greater than 9:1), where precipitation of  $Pb_3Ca$  does not predominate, bismuth additions merely enhance the segregation of tin to the interdendritic boundaries. Figure 8 demonstrates the enhanced segregation of bismuth and tin in a lead-0.08wt.% calcium-1.2wt.% tin alloy (tin-calcium ratio 15:1) with 0.012 wt.% bismuth. The enhanced segregation may permit better use of the tin and bismuth to assist the recovery of lead/acid batteries from deep discharge. Analysis of the tin and bismuth in the interdendritic areas has revealed that the tin and bismuth contents are as high as 6 wt.% and 0.05 wt.%, respectively, despite much lower values in the bulk alloy. The bismuth and tin concentrate in the interdendritic areas. At high tin-calcium ratios, the calcium precipitation is converted from cellular precipitation to continuous precipitation. Silver in the recycled lead alloy (12 ppm) is slightly higher than that in the low-bismuth, primary lead sample (7 ppm). Bouriden *et al.* [19] have indicated that silver enhances continuous precipitation. Continuous precipitation retains both the cast-in segregation and the areas of higher tin and bismuth content; both these features can, in turn, affect battery performance.

## Conclusions

1. The high bismuth content of refined recycled lead leads to enhanced segregation in lead-calcium and lead-calcium-tin alloys.
2. The enhanced segregation in lead-calcium and in lead-calcium-tin alloys with low tin-calcium ratios increases the rate of grain boundary movement in cellular precipitation.
3. With bismuth-containing lead-calcium alloys, the grain boundary movement seems to be initiated at the interdendritic segregation areas, rather than primarily at the grain boundaries.



4. With lead–calcium–tin alloys that have high tin–calcium ratios, the enhanced segregation of tin and bismuth (that results in high levels of these elements in localized areas) may be beneficial in terms of improved battery performance under deep-discharge conditions.

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