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Challenges from corrosion-resistant grid alloys in lead acid battery manufacturing

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Abstract

During the past several years extremely corrosion-resistant positive grid materials have been developed for lead acid batteries. These alloys consist of a low calcium content, moderate tin content, and additions of silver. Despite the high corrosion resistance these materials present problems in battery manufacturing. The very low calcium contents produce soft grids which harden very slowly and require artificial aging at high temperatures to produce adequate mechanical properties for pasting and subsequent handling. The silver and tin additions yield grids which are very corrosion resistant. The grid, however, must be corroded in the pasting/curing process to permit the paste to adhere to the grids. Battery manufacturers have had to go to great lengths to corrode the grids to provide adequate attachment of the active material. Even with these extraordinary measures it is sometimes difficult to get good paste adhesion to the very corrosion-resistant grids. Grid active material interface problems cause reduced battery life. When lead oxides are used for the paste formulation, the free lead may be corroded preferentially to the grids. For lead antimony and most calcium alloys the grids are corroded preferentially to the free lead giving a good bond between grid and active material even if substantial free lead remains in the cured plate. This paper describes the new corrosion-resistant grid materials, explains the high corrosion resistance, assesses problems of processing corrosion-resistant grids, and suggests modifications of alloy compositions to improve performance.

Keywords: Lead–calcium alloy grids; Microstructures; Paste adhesion; Segregation; Age hardening; Corrosion

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1. Background

During the past 10 years, lead calcium based alloys have replaced lead antimony alloys as the materials of choice for positive grids of both automobile and stationary lead acid batteries. Lead antimony alloys corrode more rapidly than lead–calcium alloys. Antimony is released during the corrosion process and, during recharge, is transferred to the negative plate where it causes unacceptable loss of water, particularly in high heat environments. Lead–calcium alloys do not suffer this severe water loss in service and thus have become the alloy of choice for maintenance-free SLI as well as VRLA batteries.

Lead–calcium alloys have a narrow freezing range and are capable of being processed into both positive and negative grids by a variety of grid manufacturing processes, such as conventional book mold casting, rolling of strip followed by expanding [1], continuous casting of strip followed by expansion [2], continuous grid casting [3], and continuous grid casting followed by rolling [4]. The continuous grid manufacturing processes have been utilized by many battery manufacturers to decrease battery grid weight as well as to reduce grid and pasted plate production costs.

Initially lead calcium alloys generally contained high calcium contents (0.08–0.13% Ca) and relatively low tin contents. Grids produced from these materials hardened rapidly and could be easily handled and processed into plates. Aluminum additions to the alloys dramatically reduced calcium oxide generation during processing and permitted production of grids with much better control of calcium content [5].

In the early 1990s automobile manufacturers modified the exterior of their vehicles to achieve a more aerodynamic shape. This design change caused considerably less air to flow through the engine compartment, dramatically increasing underhood temperatures. At the same time stationary VRLA batteries particularly for telecommunication uses were installed in remote places and exposed to the elements instead of remaining inside climate controlled environments. As a result lead acid batteries were exposed to significantly higher operating temperatures. The higher underhood temperatures and higher operating temperatures led to much more rapid corrosion of the positive grids of these batteries and resulted in more rapid failure of the batteries due to corrosion and growth of the positive grids

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[6]. New lead calcium based alloys were developed to address these problems.

The newer alloys contain much lower calcium than previous alloys. Corrosion of grids has been shown to be related to the calcium content [7]. The newer alloys for SLI batteries also contain silver which further reduces the rate of corrosion and makes the grids more resistant to growth at elevated temperatures [8,9]. The alloys also contain tin contents sufficient to react with all the calcium in the alloy to produce Sn_3Ca, a more stable strengthening precipitate instead of Pb_3Ca [10,11]. These alloys have extremely corrosion-resistant surfaces. Battery grids produced from the alloys are extremely resistant to corrosion at elevated temperatures.

Grids produced from these alloys are not without problems. The conventionally cast grids are extremely difficult to handle because of low mechanical properties. The high corrosion resistance in use also presents problems of producing a good bond between the grid and active material. Continuous production methods such as rolling can produce even more resistant surfaces which may present problems such as active material delamination at elevated temperature.

2. Corrosion-resistant grid alloys

The most effective method to produce highly resistant battery grids is to reduce all impurities and alloying elements and have the grid composition as close as possible to pure lead. Plante cells use pure lead and have extremely long lives. Grid manufacturing processes, however, require more strength than pure lead. This has lead to the use of 0.02–0.05% calcium alloys for corrosion-resistant grids.

Lead–calcium alloys have been shown to require some tin to adequately recover from deep discharge. The minimum tin content has been shown by Giess to be about 0.6% tin [12]. Many of the corrosion-resistant grid alloys contain 0.5–0.7% tin. To produce stable precipitate particles of Sn_3Ca at least 9:1 Sn/Ca ratio is required. Alloys with higher Sn/Ca ratio of at least 12:1 and possibly 15–20:1 are required to force all the calcium to precipitate as Sn_3Ca instead of Pb_3Ca or a mixed Pb_xSn_yCa precipitate. Tin at these levels also has a beneficial effect on the corrosion resistance of the alloy [13].

Silver in the range of 0.02–0.05% has been added to further decrease the rate of corrosion. Silver also increases the mechanical properties of the lead calcium alloys and based on its distribution within the grid structure can increase the creep resistance or resistance to growth.

3. Cast lead–calcium–tin–silver alloys: rate of aging

Table 1 shows the rate of age hardening at room temperature of various lead–calcium–tin–(silver) alloys at a relatively low calcium content of about 0.045%. Alloys containing 0 and 0.3% tin age up rapidly. In these materials the calcium is precipitated as rapidly forming Pb_3Ca. The alloys have no tin or insufficient tin to produce Sn_3Ca. As more tin is added (0.5–0.8%), the initial hardness drops because less or no Pb_3Ca is initially produced. Not only is the initial hardness reduced but also the rate of hardening is dramatically slowed. It takes 7 days for alloys containing 0.5% tin or more to reach the same hardness that is reached by the low tin alloys in several hours. The addition of silver to the alloy does not significantly increase the rate of aging or the initial mechanical properties, but ultimately in the aged condition yields higher mechanical properties. A Rockwell hardness value of about 60–70 produces sufficient mechanical properties for adequate handling of grids in pasting operations.

In practice many of the corrosion-resistant grid alloys contain even lower calcium contents than shown in Table 1. These alloys have even slower rates of aging and produce even lower ultimate mechanical properties. The very low and moderate calcium-containing alloys are compared with higher calcium content alloys at various tin contents in Table 2.

Table 1
Rate of aging of Pb–Ca–Sn–(Ag) alloys as a function and aging time at room temperature

Ca (wt.%)	Tin (wt.%)	Hardness Rockwell (*R*)						
		1/2 h	4 h	24 h	48 h	7 Days	14 Days	60 Days
Without silver								
0.046	0	10	52	58	65	68	70	70
0.045	0.3	−2	5	43	55	60	62	70
0.045	0.5	−20	5	0	12	40	48	68
0.044	0.8	−30	−25	−20	1	40	54	80
0.047	1.1	−15	−11	−4	20	50	65	80
With 0.03% silver								
0.045	0	10	52	58	65	68	70	72
0.047	0.3	0	10	42	55	65	68	72
0.045	0.5	−20	−5	7	30	48	70	86
0.042	0.8	−30	−25	−20	0	45	71	86
0.046	1.1	−15	25	45	55	60	80	87

Table 2
Hardness of Pb–Ca–Sn alloys as a function of calcium, tin, and aging time at room temperature

Ca (wt.%)	Tin (wt.%)	Hardness Rockwell (*R*)						
		1/2 h	4 h	24 h	48 h	7 Days	14 Days	60 Days
0.025	0.5	−42	−42	−34	−26	−17	−16	−14
0.025	0.8	−36	−32	−26	−20	−18	−5	31
0.025	1.1	−31	−25	−23	−20	−15	−8	50
0.045	0.5	−20	5	0	12	40	48	68
0.045	0.8	−30	−25	−20	1	40	54	80
0.045	1.1	−15	−11	−4	20	50	65	80
0.065	0.5	48	52	63	66	70	75	84
0.065	0.8	40	43	55	74	80	88	93
0.065	1.1	43	45	60	77	84	90	93

As seen in Table 2, alloys containing very low calcium content (0.025%) and moderate tin contents (0.5–0.8% Sn) do not reach hardness levels sufficient for pasting and processing even after room temperature aging for 60 days. At higher tin contents such as 1.1%, the alloys almost reach sufficient hardness after 60 days of aging at room temperature. These alloys must be heat treated prior to processing to produce adequate hardness. The 0.045% alloys age up faster than the 0.025% alloys but still only the alloy containing 1.1% tin reaches sufficient hardness for processing after storage of 14 days at room temperature. The 0.065% calcium alloys on the other hand reach acceptable levels for processing in 1–2 days, particularly those at the highest tin content shown as 1.1%. Higher tin contents further increase the rate of aging.

4. Segregation of calcium in cast alloys

In lead–calcium alloys a significant segregation of the calcium occurs during solidification. As seen in Fig. 1, the first material to freeze is higher in calcium than the last material to freeze (that in the grain boundaries and subboundaries). If the calcium content of the alloy is 0.04% calcium as shown in Fig. 1, the first material to freeze contains 0.075% calcium while the last material to freeze contains only 0.013% calcium. Table 3 shows the estimated calcium content at the center of the cast dendrites as well as that of the final material to freeze at the subgrain and grain boundaries for various lead–calcium alloys.

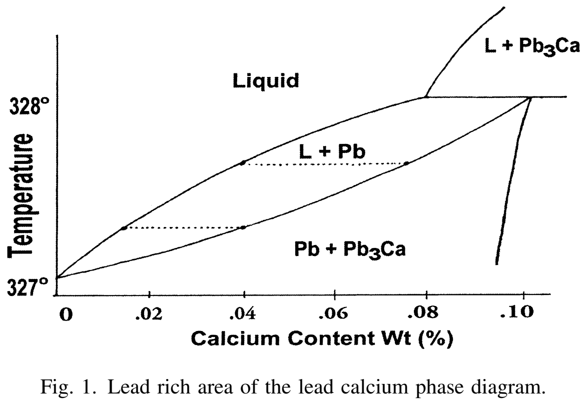

Fig. 1. Lead rich area of the lead calcium phase diagram.

The segregation of calcium to the dendrite centers and away from grain boundaries and interdendritic subboundaries has significant effects on the stability and ultimately the corrosion resistance of the alloys as grid materials. As seen in Table 3 the low calcium alloys have very little calcium at the grain boundaries while they have significant calcium at the center of the subgrains. This lack of calcium makes the sub and grain boundaries significantly weaker but more resistant to corrosion than one would expect from the given calcium content.

As the calcium content is raised to levels considered to be low such as 0.050% calcium, the center of the subgrains contains significantly more calcium (0.082% Ca) than the nominal or bulk composition. The grain boundaries at this composition contain about 0.018% calcium. Calcium contents of 0.060% contain 0.090% calcium at the subgrains and 0.025% in the boundaries. This bulk calcium content, while not high, may increase the rate of corrosion of the grain boundaries where high angle misfit occurs. The segregation of calcium away from the low angle subboundaries may reduce the corrosion of these areas.

Raising the calcium content to 0.08% calcium increases the segregation to the subgrain centers to about 0.100% Ca. The calcium content of the subgrain boundaries is increased to about 0.045%. Higher calcium contents such as 0.100% calcium and above dramatically increase the calcium

Table 3
Estimated segregation of calcium at various Pb–Ca alloys between the center of the subgrain and the subgrain boundaries

Bulk calcium content	Center of subgrain	Sub or grain boundary
0.020	0.050	0.005
0.030	0.065	0.010
0.040	0.075	0.013
0.050	0.082	0.018
0.060	0.090	0.025
0.070	0.095	0.035
0.080	0.100	0.045
0.100	0.100[a]	0.080

[a] Plus Pb_3Ca primary particles.

Table 4
Estimated segregation of tin to the subgrain boundaries in Pb 0.4% Ca–Sn alloys

Bulk tin content (wt.%)	Center (wt.%)	Sub or grain boundaries (wt.%)
0.3	0.3	0.4
0.5	0.45	0.8
0.8	0.75	1.5
1.2	1.15	2.6

content of the subgrain boundaries and may produce some primary Pb_3Ca particles.

Calcium contents above about 0.075% calcium have a dramatic increase in the calcium content of the subgrain and grain boundaries. The dramatic increase in the calcium content is associated with more rapid corrosion of grain boundaries. The alloys may undergo structural changes due to grain boundary movement from calcium precipitation due to the high segregation of calcium in the alloys.

5. Tin segregation

Tin segregates in a manner opposite that of calcium in lead–calcium alloys. During solidification some tin is displaced from the solidifying subgrain front to the remaining liquid. Tin is highly segregated to the subboundaries and grain boundaries. Table 4 shows an estimate of the tin segregation to the interdendritic and grain boundaries compared with the bulk tin content of the alloy [14].

Because of the segregation of calcium, tin, and silver, lead–calcium–tin–(silver) alloys may exhibit significantly different mechanical properties, structural stability, and corrosion resistance in different parts of a single grain or in different parts of a casting. Alloys with seemingly minor differences in calcium content or tin content may behave significantly different due to the effects of calcium, tin, and silver segregation.

6. Lead–calcium–tin alloy stability

Many lead–calcium–tin–silver alloy grids, particularly those utilizing lower calcium contents such as 0.03–0.05% calcium have also contained tin at 0.5–0.7%. Table 5 shows how tin and calcium segregation can effect the stability of Pb–Ca–Sn alloys. As seen in Table 5, due to the segregation of calcium in the alloys during solidification, these alloys may not contain sufficient tin to fully precipitate the calcium as Sn_3Ca.

For example, an alloy of 0.040% calcium would require about 0.36% tin at a ratio of 9:1 Sn/Ca to produce the more stable Sn_3Ca. Since higher tin content such as 12:1 shown in Table 5 may be required to force the Sn_3Ca precipitation reaction for completion, a tin content of 0.48 would be required. Due to calcium segregation, however, the centers of the interdendritic regions would require a tin content of 0.68% tin at 9:1 Sn/Ca ratio and 0.90% tin at a 12:1 Sn/Ca ratio. Thus, alloys containing lower calcium contents may require significantly more tin than previously believed required to produce Sn_3Ca and assure good grid stability.

Despite the lower calcium content many of the low calcium corrosion-resistant materials may not be as stable as first believed due to the segregation of calcium during solidification. Thus an alloy of 0.040% calcium may require a tin content of 0.90% or higher and a Sn/Ca ratio of 22:5 or higher to assure stability and complete production of Sn_3Ca rather than the normally calculated 0.5% tin.

Higher bulk tin content not only increases the tin content of the subgrain boundaries and grain but also tend to increases the width of these boundaries. The tin is highly concentrated in areas where the calcium is dramatically reduced, the subgrain and grain boundaries. The tin content at the center of the subgrains is only somewhat reduced where the calcium content is concentrated.

7. Segregation in cast lead–calcium alloys

Fig. 2 shows the segregation due to solidification of a cast lead–calcium–tin–silver alloy. Fig. 3 shows how the grains and subgrains of a grid grow into the liquid alloy from the cold surface of a mold or roll.

Higher calcium contents such as 0.070%, require about 1.1% tin or more to assure complete reaction with the calcium to form Sn_3Ca. At higher calcium contents, the segregation effects are not as severe as those at lower calcium contents. Calcium contents above 0.080% calcium

Table 5
Tin contents required for alloy stability as a function of segregation

Bulk calcium content (wt.%)	Calcium content at center (wt.%)	Tin content required at center @ 9:1 (wt.%)	Tin content required at center @ 12:1 (wt.%)	Tin required in bulk alloy @ 12:1 (wt.%)
0.020	0.050	0.45	0.60	0.25
0.030	0.065	0.59	0.78	0.36
0.040	0.075	0.68	0.90	0.48
0.050	0.082	0.74	0.98	0.60
0.060	0.090	0.81	1.08	0.72
0.070	0.095	0.86	1.14	0.84
0.080	0.100	0.90	1.20	0.96

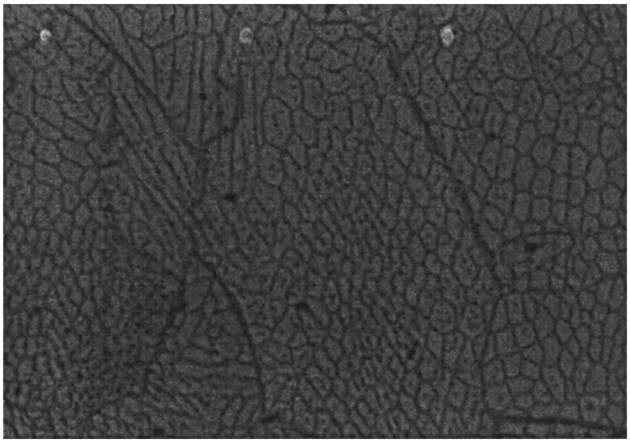

Fig. 2. Segregation of lead–calcium alloys producing low calcium content interdendritic subgrain boundaries (magnification 160×).

contain some calcium as Pb_3Ca intermetallic particles which are not converted to Sn_3Ca regardless of tin content. Fig. 4 shows the structure of an alloy thought to be stable but has become unstable due to calcium segregation and inadequate tin.

8. Silver segregation in cast lead–calcium–tin alloys

Silver segregates to the subgrain and grain boundaries in a manner similar to that of the tin. Grids cast from alloys containing higher tin and silver contents may form a low melting point final freezing liquid which can cause cracking during casting [15]. The slower the rate of solidification of the alloy, the higher is the amount of segregation of silver to the interdendritic subboundaries and grain boundaries. The increased silver in these areas along with the tin is responsible for much of the corrosion resistance seen in low calcium alloys containing tin and silver. Fig. 5 shows how the silver is segregated in lead–calcium–tin–silver alloys.

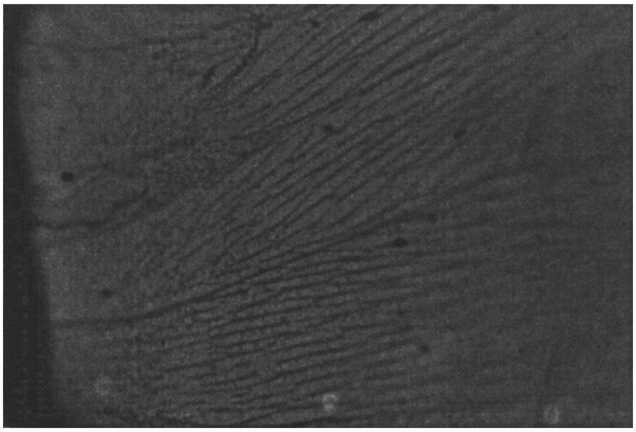

Fig. 3. Growth of grains from the surface of the grid mold. Grains show segregation (magnification 160×).

Fig. 4. Cellular precipitation of Pb–Ca–Sn–Ag alloy with inadequate try to fully react with calcium segregated to the subgrain centers (magnification 160×).

Fouache et al. [14] have indicated that at silver content of 0.030% segregation of silver, interdendritic subgrains and grain boundaries can reach levels between 1.6 and 6.2%. Much lower levels also segregate significantly.

9. Cast low calcium alloys

In lead–calcium alloys containing less than about 0.05% calcium, there is very low calcium at the grain boundaries or interdendritic subgrain boundaries. The calcium is concentrated in the centers of the interdendritic subgrain regions. Tin and silver are more highly concentrated at the interdendritic and grain boundaries. The concentration of tin and silver makes these areas more resistant to corrosion than the same alloys without the segregation. Fig. 5 shows how the subgrains are not corroded while the bulk lead surface has darkened. Because these areas are deficient in calcium, they

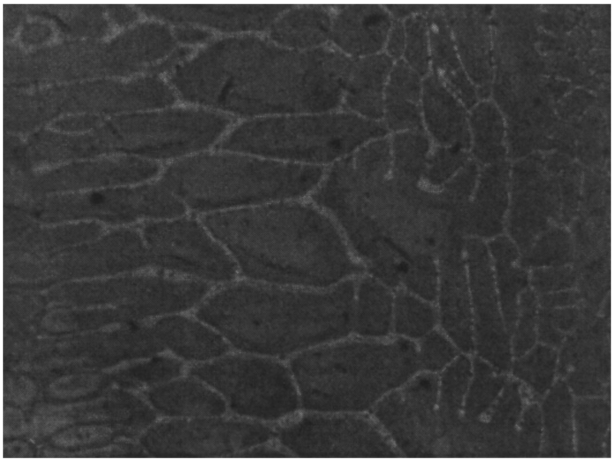

Fig. 5. Segregation of silver to the tin-rich interdendritic subgrain boundaries: subboundaries outlined as white; dark dots in subgrain boundaries show silver segregation (magnification 320×).

are also significantly weaker than similar boundary areas containing more calcium and strengthen at a slower rate. Thus, in cast lead–calcium–tin alloys grids are susceptible to deformation between the more rigid grains. Under stress localized bending or working of grain boundaries may occur during handling of the grids. Silver segregated to the grain boundary areas and interdendritic regions will locally increase the resistance to creep but offers little resistance to localized deformation until strengthening by Sn_3Ca precipitation occurs.

The extremely low calcium concentration and segregation of high tin and silver to the interdendritic subboundaries and grain boundaries make these areas particularly resistant to corrosion. The resistance to corrosion not only occurs when the grids are in service (even at elevated temperatures) but also occurs during pasting and curing. At this time a bond between the grid and active material must be produced. If a good bond is not achieved between the grid and active material during curing, the plate will perform poorly, particularly, in recovery from discharge, recharge, and elevated temperature performance.

10. Heat treatment of low cast calcium grids

Lead–calcium–tin–silver alloy grids containing moderate tin contents (0.6–0.8%) and calcium contents lower than 0.05% must be heat-treated to increase the rate of hardening of the grids. During the heat treatment, the calcium reacts with the tin contained in the interdendritic zones to form Sn_3Ca. During the elevated temperature aging the calcium in the matrix can react with the tin. In addition, the calcium in the boundary areas reacts with the high tin contents present there. The Sn_3Ca strengthens these areas, greatly increasing the resistance to bending and deformation.

Because calcium ions are relatively immobile at room temperature, the low calcium–tin–silver alloys would take months to reach acceptable mechanical properties for handling without heat treatment. This is particularly true for alloys with calcium contents at or below 0.040% calcium as seen in Table 2.

11. Corrosion resistance

The mechanism of this corrosion resistance is believed to be due to the unique structures which occur in Pb–Ca–Sn–Ag alloys during solidification. The tin and silver are segregated to the interdendritic and grain boundaries in the same manner. This results in the formation of very small corrosion-resistant cells on the surface of the lead alloy as seen in Fig. 6. Rapid cooling of the material decreases the size of the interdendritic tin and silver cell spacing [16]. Because of the control of the calcium and tin contents, these cells are not destroyed by grain boundary movement caused by cellular precipitation in higher calcium and lower tin alloys.

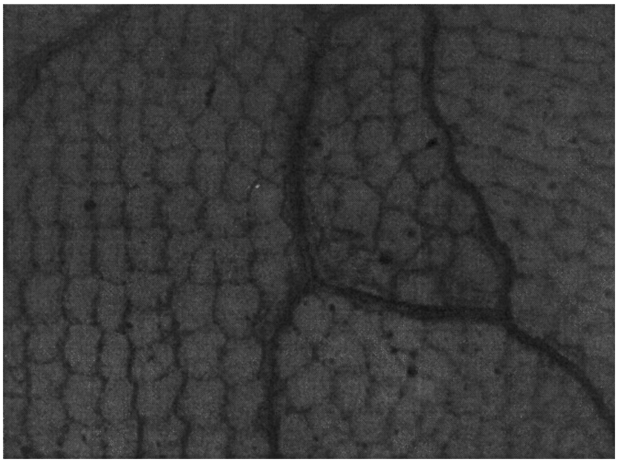

Fig. 6. Formation of segregation cells on the surface of a battery grid via the segregation of tin and silver to the subgrain boundaries (magnification 500×).

12. Paste adhesion to cast low calcium–tin–silver grids

Grids which are produced from conventional cast, continuous cast, or continuous cast-expanded processes all contain significant segregation of calcium, tin, and silver. At low calcium contents, the grain boundaries and subgrain interdendritic boundaries may be more corrosion resistant to the paste than the centers of the interdendritic regions. These center areas contain higher calcium content while the grain and subboundaries contain much lower contents than the bulk alloy.

In grids produced from lead–antimony alloys and higher calcium alloys with low tin content, the grain boundaries in these alloys are more susceptible to corrosion during curing than the underlying lead surface. In lead–antimony alloys, the antimony increases the rate of oxidation of the lead, both at the grain boundary as well as the surface. Segregation of antimony to the interdendritic regions dopes these regions with antimony and makes these areas more susceptible to corrosion by the water and oxygen in the paste. Not only is the rate of attack by the paste increased in lead–antimony alloys but the interdendritic segregation of antimony also produces local areas which accelerate attachment of the active material.

In traditional cast lead–calcium–tin alloys containing high calcium contents and low tin contents used for SLI grids, the original cast in segregation is destroyed by moving grain boundaries which deposit Pb_3Ca particles in the matrix behind the boundaries. The discontinuous precipitation process destroys the subgrain boundaries and creates significantly more grain boundary area. As the boundaries move they may also accumulate CaO and other oxide particles.

These particles can make the grain boundaries even more reactive due to a concentration of calcium oxides at the grain boundaries. Concentration of calcium in the grain boundaries makes the grain boundary–areas more alkaline when contacted by the water in the paste. The higher number of grain boundaries, lack of alloy segregation, and oxides at the grain boundaries can make the lead grid surface susceptible to rapid attack by the water in the paste. The calcium in the grain boundaries may also contribute to a higher localized pH in that region. Higher pH increases the solubility of Pb^{2+} ions and enhances the attachment of the 3BS or 4BS crystals created during curing to the grid surface.

In low calcium alloys containing tin and silver, the interior of the subgrains contain the highest calcium content. There are no, however, any grain boundaries in these regions to promote localized attack and attachment of the paste. Precipitation of Sn_3Ca does not require moving grain boundaries and, thus, grain boundary surface area remains as the original cast grain structure. In the areas of the interdendritic regions and grain boundaries, higher tin and silver contents due to segregation during solidification reduce the rate of lead oxidation of these areas during curing, particularly at high tin contents. As some of the lead on the surface is oxidized, it may be subsequently be reduced back to metallic lead by reaction with high concentrations of tin. The most likely areas for active material attachment, the sub and grain boundaries are the most resistant due to the segregation of tin and silver to these areas. Tin affects the oxidation of the grid surface by the following reactions:

$$2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2$$

$$Pb(OH)_2 + Sn \rightarrow Pb + SnO + H_2O$$

$$Pb(OH)_2 + SnO \rightarrow Pb + SnO_2 + H_2O$$

$$2Pb(OH)_2 + Sn \rightarrow SnO_2 + 2H_2O + 2Pb$$

Tin in the interdendritic and grain boundaries can dramatically reduce the rate of oxidation of the lead at the grid surface by reducing the $Pb(OH)_2$ gel-like corrosion product back to lead and creating SnO_2. As seen in Fig. 7, high tin contents can significantly reduce the reactivity of a lead surface.

The high segregation of tin to the interdendritic areas as well as the reaction of calcium with tin to form Sn_3Ca instead of Pb_3Ca further reduce the reactivity of the interdendritic regions. Because the tin takes twice the amount of oxygen to form an oxide layer as lead, areas of high tin content are much more difficult to oxidize and bond to the basic sulfate crystals formed in the curing process. Despite the higher calcium segregation to the subgrains, there are no boundaries to aid attachment. The very areas where the active material normally first oxidizes the lead surface and adheres (the sub and grain boundaries) are the areas most resistant to oxidation.

The low calcium–tin–silver alloys are the first grid alloys which have a lower rate of oxidation during curing than the free-lead particles in the paste. Not only does the tin reduce the rate of oxidation, but the high silver content of these alloys also reduces the rate of oxidation in the subgrain and grain boundary areas.

13. Rolled alloys

Rolled lead–calcium–tin alloys which are expanded into battery grids have difficulties similar to that of the cast grids in making the active material adhere to the grid surface. In the rolling process, the grains are bent from the vertical and elongated in the horizontal or rolling direction as seen in Fig. 8. Expansion of that material into grids produces grid wires with grain structure oriented along the length of the

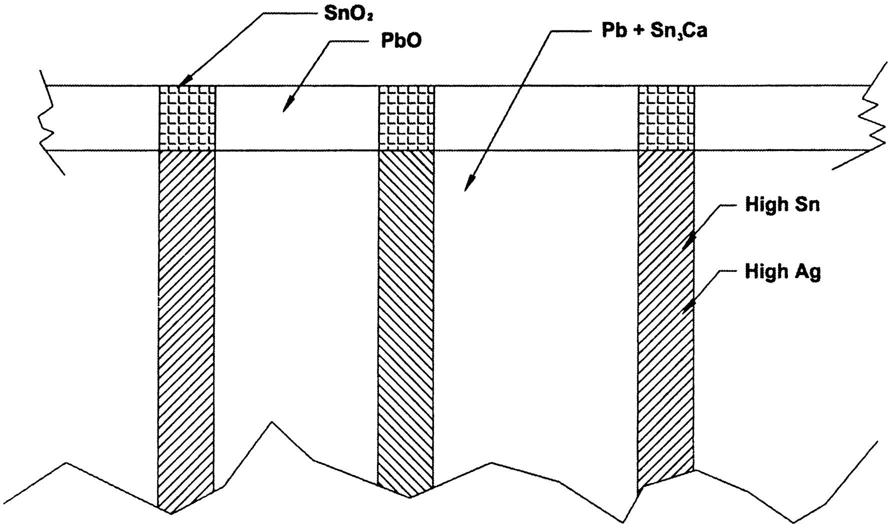

Fig. 7. Corrosion of Pb–Ca–Sn–Ag cast surface during curing.

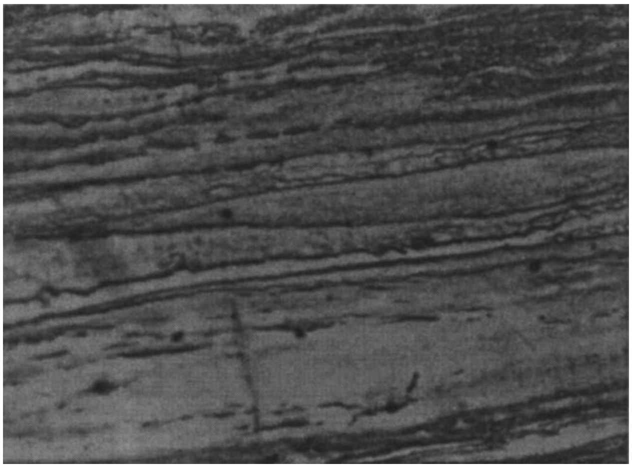

Fig. 8. Rolled lead–calcium–tin alloy strip shows the elongation of the segregated tin-rich subgrains in the rolling direction (magnification 160×).

grid wires. The grid surfaces are subject to corrosion along the oriented surfaces [17].

Despite a structure which looks significantly different, the nature of the rolled material is similar to the original cast material. The cast in segregation of calcium and tin are retained to a large extent in the rolled structure. The elongated directional grain boundaries of the wrought metal are basically the original tin-rich subboundaries elongated in the rolling direction. The tin layers are spread out over the material surface in large areas in the rolling direction. Rolled alloys generally contain more tin than the low calcium, highly corrosion resistant, high temperature resistant, cast lead–calcium–tin–silver alloys. The grain boundaries, however, contain relatively low calcium due to segregation as seen in Table 3 and a much higher tin content. These boundaries present the same corrosion-resistant material where the segregated tin-rich material reaches the surface to the active material although in a different form.

14. Cominco drum cast materials

Continuously cast strip produced from calcium–tin–silver alloys of <0.05% calcium have the same overall structure as the conventional cast alloys. The alloys contain finer grains and very fine interdendritic spacing. Fig. 9 shows the grain structure of the material through the thickness of the cast strip. It consists of an oriented dendritic structure with tin and silver segregated to the subboundaries. The subboundaries are more distinct than in conventional cast alloys or wrought materials.

The top and bottom surfaces of the material contain fine grains with finely segregated subgrains even more oriented and segregated than conventional cast materials as seen in Fig. 10. Despite the appearance of the surface, corrosion of the grid surface is difficult due to the uniform segregation of the tin and silver. The same structure can be seen on the surfaces of conventional cast grids but have a much coarse appearance.

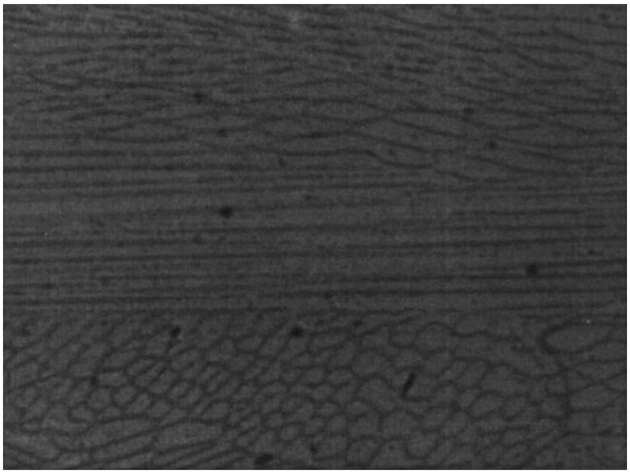

Fig. 9. Cross section of a Cominco continuous cast Pb–Ca–Sn–Ag strip. Note the long crystals growing through the strip (magnification 160×).

15. Oxidation of corrosion-resistant surfaces

The corrosion-resistant surface of conventional cast, rolled-expanded, and Cominco drum cast-expanded material present problems in paste attachment during curing. Companies have gone to great lengths to corrode the corrosion-resistant surfaces to permit the attachment of the active material. These have included using the 4BS steaming chambers to perform a combination heat treatment/surface oxidation step to increase the mechanical properties and, at the same time, produce a surface oxide layer from high temperature steam.

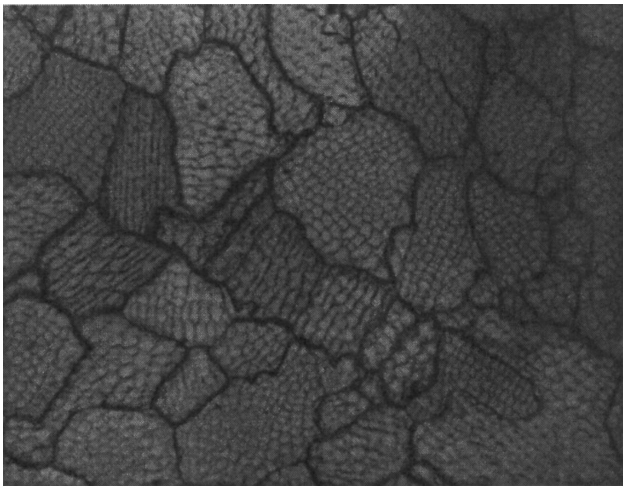

Fig. 10. Surface of a drum cast Pb–Ca–Sn–Ag alloy showing large numbers of fine segregated cells at the surface of the strip (magnification 160×).

Other methods are to increase the aggressiveness of the paste via the addition of persulfates, increasing the alkalinity of the paste through the addition of more water to the paste mix, or pretreatment of the grids with alkaline materials to produce an initial surface oxide layer. The curing time is increased to assure that virtually all the free lead is consumed in the curing cycle and the remaining water and oxygen can react with the grid surfaces.

For the first time positive grids are more corrosion resistant under curing conditions than the free lead in the past mixture. Despite the calcium content of these alloys, the tin and silver content as well as segregation of these alloying elements during solidification reduce the rate of attack of the paste. The free lead in the paste mixture must be reduced to very low values before the grids become attacked. Residual free-lead contents of about 5% may be indicative of inadequate bonding of the active material to the grid. Even low free-lead contents in the cured plates do not assure a good bond. Often the free lead is reduced in the latter stages of curing by drying of the plates. This evaporates the water at exactly the time in which it is needed for oxidation of the grid surface.

16. Behavior of low calcium–tin–silver alloys in high temperature service

Low calcium–tin–silver–lead alloys have shown to have very low rates of corrosion at elevated temperatures, particularly in the hot J240 test. In general, the failure mode of the batteries at elevated temperature has not only been positive grid corrosion, but also delamination of the active material from the grid. The corrosion of the grid in most cases is uniform with little evidence of penetrating corrosion despite exposed grain boundaries.

17. Improved positive grid materials

I believe that the grids typical of the low calcium–tin–silver-type alloys are too corrosion resistant. The low calcium content assures that virtually no calcium or very little is present at the grain and subboundaries. The moderate tin content and high silver alloy content segregate to the grain and interdendritic subgrain boundaries, thus dramatically reducing the rate of corrosion, but also reducing the ability to bond the paste to the grid surface. Uniform corrosion without some penetration may make the alloys prone to paste shedding or delamination of the active material without grain boundary corrosion to attach the active material in these locations. The active material will crack parallel to the surface rather than perpendicular to the surface and delaminate. The low calcium corrosion-resistant alloys are also very weak despite corrosion creep resistance and may deform and structurally change during processing. Rolled material is particularly vulnerable to the delamination due to the orientation of the grains and lack of attachment for the corrosion product.

For the grids to become more friendly to processing, the calcium content must be increased. Calcium contents of about 0.06–0.07% calcium significantly increase the rate of aging of the grids. A grid containing 0.040% calcium may take 60 days at room temperature to reach sufficient mechanical properties for pasting and require heat treatment. Grids produced from alloys containing 0.065% calcium age up much more rapidly and require 1–2 days aging at room temperature to reach sufficient mechanical properties for processing, as seen in Table 2.

The overall corrosion rate of the alloy can be reduced by the addition of higher amounts of tin. Lead–calcium alloys with 0.06–0.07% Ca require tin contents of 1–1.2% or more to produce stable structures. The high tin containing alloys have overall rates of corrosion similar to lower calcium content materials with lower tin contents (0.5–0.6%). The tin must be sufficiently high to assure that the higher calcium content in the center of the subgrains is fully reacted to form Sn_3Ca, as seen in Table 5.

The higher calcium content alloys also assure that a small amount of calcium remains in the interdendritic sub and grain boundaries. This calcium significantly increases the mechanical properties of these boundary areas and makes the materials much easier to handle. With the tin segregation to the subgrains, there is always sufficient tin to react with the calcium in these areas to form Sn_3Ca.

A lower silver content is required to assure reduced potential for cracking during casting and processing of higher tin content alloys. With higher tin contents, the high silver content is not required to produce extra mechanical properties and creep resistance which is required with low calcium alloys. The grain and subboundaries are much stronger and more creep resistant than in lower calcium/lower tin alloys.

Because the alloy contains a higher calcium content, the surface of the grid in contact with the wet paste maintains a higher pH level than lower calcium alloys. Despite higher tin contents, the higher calcium content of the grain and subboundaries as well as the lower silver content also enables the paste to adhere to the boundaries for enhanced adhesion.

The slightly higher rates of corrosion of the grain and subboundaries in service permits the active material to better adhere to the grid. By more localized penetration of the areas of the sub and grain boundaries, some cracking of the corrosion layer perpendicular to the grid surface occurs, improving paste adhesion.

18. Conclusions

1. Segregation of calcium, tin, and silver in Pb–Ca–Sn–(Ag) alloys is responsible for the enhanced corrosion resistance of these alloys.

2. Higher tin contents are required in Pb–Ca–Sn alloys to assure material stability due to segregation of calcium in the alloy castings.
3. The segregation seen in cast alloys is maintained in normal rolled alloys but in a different orientation.
4. The low calcium, high tin, silver alloys are so corrosion resistant that it is difficult to attack active material during pasting and curing.
5. Higher calcium contents may be required to increase the rate of corrosion of the alloys for improved grid processing and battery performance.

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