

LEAD-STRONTIUM ALLOYS FOR BATTERY GRIDS

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(Received August 25, 1977)

Summary

The metallurgical properties of lead-strontium alloys were studied in relation to the properties required for lead-acid battery grids. The castability of all the alloys tested was as good as the corresponding alloys containing calcium. The mechanical properties of binary alloys containing 0.08% strontium or more and of ternary alloys containing 0.04% strontium or more indicated that these alloys could be handled and processed by normal production techniques. The creep and stress corrosion properties of the binary and ternary alloys were not good enough to consider them for use in deep cycled motive power batteries but the addition of up to 0.25% silver to the ternary alloys gave adequate creep and stress corrosion characteristics for this application. Ternary alloys containing 1 - 2% tin suffered from severe intergranular corrosion the effects of which could be overcome to some extent either by grain-refining the alloys with cerium mischmetal or by producing a fine-grained alloy grid by wrought techniques. Alloys which could be considered for battery application were lead-0.1% strontium for standby batteries, lead-0.5% tin-0.1% strontium for automotive batteries and lead-0.5% tin-0.01 - 0.25% silver-0.1% strontium for special motive power batteries if the cost could be afforded. A small addition of aluminium protected all the alloys from loss of alloying constituents in the molten state by oxidation.

Introduction

The electrochemical disadvantages of antimony in increasing the rate of self discharge and hydrogen evolution of lead-acid batteries are well established. Over the years, there has been a reduction in the antimony content of grid alloys both for electrochemical and economic reasons and grid alloys now usually contain 4 - 6% antimony. Alloys containing even lower amounts of

antimony have been used for some time in special applications such as submarine cells where Admiralty "B" alloy [1] containing 3% antimony, 1.5% tin and 0.05% selenium is used for positive grids. In more recent years, alloys containing only 2% antimony, grain refined with selenium [2, 3], have been proposed for automotive battery grids where improved maintenance characteristics are required.

Various antimony-free alloys have also been investigated. However, the only alloy system to be used to any great extent is the lead-calcium series. Binary lead-calcium alloys, normally containing 0.05 - 0.1% calcium, have been used in telephone standby batteries [4 - 6] and small portable batteries [7]. A rolled sheet of lead-1.5% tin-0.06% calcium has been used in lead/perchloric acid batteries for many years but more recently the properties of wrought lead-tin-calcium alloys have been investigated in detail [8, 9] and this alloy system is now being used in both the cast and the wrought forms in grids of maintenance-free automotive batteries.

The properties of lead-barium and lead-tin-barium alloys have also been studied in some detail. A lead-3% tin-0.05% barium alloy [10] was proposed for use as a positive grid but extensive tests have shown that poor results are obtained from cells containing grids of this alloy and other barium-containing alloys.

Strontium lies between calcium and barium in group IIA of the periodic table and the characteristics of lead-strontium alloys are therefore of interest to the battery technologist. There are several references in the literature to lead-strontium alloys. An early reference [11] advocated the use of 10% strontium in bearing alloys and various patents [12 - 16] have included strontium as an auxiliary hardener for lead-calcium alloys used for bearing alloys. There are two references to lead-strontium alloys specifically for storage battery electrodes. Canfield *et al.* [17] proposed an alloy containing 0.2 - 0.6% strontium together with 0.2 - 2% tin, with or without the addition of barium or calcium. Bouton *et al.* [18] proposed a lead alloy containing 0.01 - 0.15% calcium, 0.005 - 0.05% barium and 0.005 - 0.2% strontium. They claimed that the alloy had good strength and freedom from corrosion embrittlement.

Very little systematic work has been carried out on lead-strontium alloys. Hofmann [19] suggested that lead-strontium was very similar to the lead-calcium system and the equilibrium diagram [20] of the lead rich end supports this view, showing a peritectic transformation at a very low strontium content.

In the present work, it was proposed to study the properties of binary lead alloys containing 0.05 - 0.5% strontium and ternary alloys containing 0.05 - 0.35% strontium and 0.05 - 5% tin. Since it was known that silver improved the corrosion resistance of lead-calcium alloys [21], the effect of up to 0.25% silver was also investigated. In addition, the effects of aluminium (for protection against oxidation, as in lead-calcium alloys [22]) and cerium mischmetal (for grain-refining action as in lead-calcium alloys [23]) were thought worthy of study.

Preparation

Lead-strontium master alloys were prepared by adding pure strontium metal to pure lead at 450 °C. The melts were heated gently, maintaining, as far as possible, an argon atmosphere in the open crucible. Just above 500 °C, an exothermic reaction occurred which caused a rapid increase in temperature to 650 - 700 °C. The melt was stirred and cast into a slab mould into which argon was fed. The amount of strontium lost through oxidation in these crude conditions varied considerably and was sometimes as high as 50%. The master alloys usually contained 3 - 4% strontium.

Dilute binary lead-strontium alloys were prepared from pure lead and master alloy by adding the latter at 450 - 480 °C. Some difficulty was experienced in loss of strontium by oxidation and the melts had to be cast as quickly as possible after alloying, to reduce this loss. The more complex alloys were prepared in the same way adding tin, silver and cerium misch-metal to the melt before the addition of the master alloy.

The alloys containing a small amount of aluminium were prepared by adding aluminium to the lead melt before the addition of the other alloying elements. Alternatively, aluminium was added to the master alloy in which case no addition was necessary during the final alloying procedure. The alloys containing aluminium could be held at 480 - 500 °C for periods without loss of strontium.

The lead-strontium master alloys were analyzed spectrographically by a solution technique using synthetic standards. The final alloys, containing lower amounts of strontium, were analyzed on the spectrograph using solid pencil electrodes with solid standards which, in turn, were analyzed spectrographically by a solution technique using synthetic standards.

Experimental

Sample bars of the experimental alloys were cast using a melt temperature of 450 °C and a mould temperature of 150 °C followed by air cooling. Hardness tests were carried out on a planed transverse section of 19 mm diameter within 24 hours of casting and after further intervals of time. Two indentations were made on each specimen using a Hounsfield Tensometer with a 5 mm diameter ball and a 25 kg load for 15 seconds.

Tensile tests were also carried out on the Hounsfield Tensometer using specimens of 12.5 mm and 50 mm gauge length. Two bars of each alloy were tested one day after casting and two bars fourteen days after casting.

Creep tests were carried out on specimens of cross-section 12 × 3 mm and gauge length 200 mm, cast from a melt temperature of 450 °C in a mould at 150 °C followed by air cooling. A constant load was used with an initial stress of 1.4 kg/mm². Several specimens of each alloy were tested.

Rapid anodic corrosion tests were carried out on slabs of cross-section 25 × 25 mm and thickness 3 mm, cast under the same conditions. The tests

were for 24 hours at a current density of 155 mA/cm^2 in 1.250 s.g. sulphuric acid. Two specimens of each alloy were tested. The slabs were weighed before and after test (after stripping off the corrosion product by treatment with hot glycerol followed by ammonium acetate solution). Transverse sections were taken through the slabs in order to examine the mode of attack.

Stress corrosion tests were carried out on specimens of 3 mm diameter and gauge length 120 mm, cast under the same conditions. A constant load to give an initial stress of 1.4 kg/mm^2 and a current density of 8.5 mA/cm^2 in 1.250 s.g. sulphuric acid were used. The specimens were tested to fracture, at least two tests being carried out on each alloy.

Specimens of 9 mm diameter cast under the same conditions were polished and etched in a dilute nitric acid–ammonium molybdate solution and their structures were examined under the microscope.

Although no quantitative test for castability was carried out, rough assessments were made from the test pieces cast for other tests. The creep and stress corrosion specimens gave a good indication of the tendency of alloys to have “short runs” or “hot tears”.

Results

Metallography

Photomicrographs of binary lead–strontium alloys are shown in Figs. 1 - 3. Secondary phase was present in alloys containing 0.15% strontium (Fig. 1) and, with increase in strontium content, the network of secondary phase became finer and more easily seen. In alloys containing more than 0.5% strontium, primary Pb_3Sr compound was present which appeared in the form of “stars” (Figs. 2 and 3).

In alloys containing up to 0.1% strontium, the addition of 0.5 - 1% tin accentuated the grain boundaries. Increasing the tin content to 3% resulted in the appearance of a secondary phase network within the grains. In alloys containing 0.15% strontium or more, this effect was less marked since

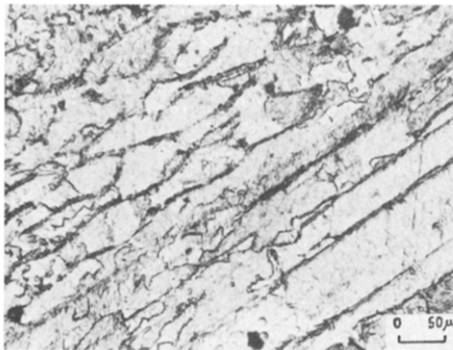


Fig. 1. Lead–0.16% strontium alloy.

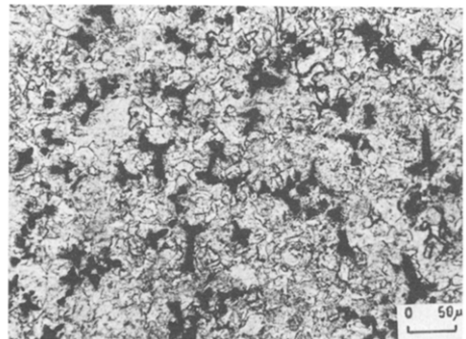


Fig. 2. Lead–0.5% strontium alloy.

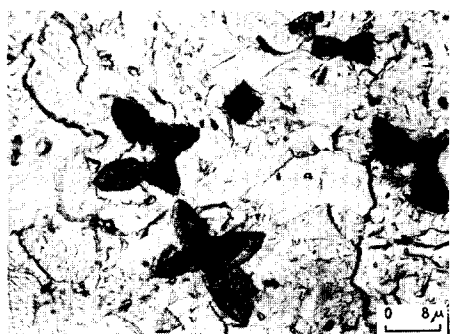


Fig. 3. Lead-0.5% strontium alloy.

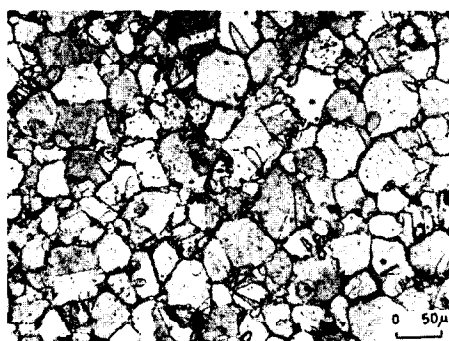


Fig. 4. Lead-0.5% tin-0.1% strontium with additions of aluminium and cerium mischmetal.

secondary phase was already present in the structure. The addition of silver to the alloys resulted in a considerable amount of secondary phase within the grains.

Aluminium additions had little effect on the structure of any of the alloys. However, cerium mischmetal caused grain refinement in all the alloys to which it was added (Fig. 4).

Mechanical properties

The hardness values of lead-strontium alloys and also the effects of small additions of aluminium, cerium mischmetal and silver on the hardness of the alloys are shown in Table 1. The hardness after 1 day increased with increase in strontium content, levelling out at about 0.3% strontium. The maximum hardness of the alloys, however, levelled out at 0.1 - 0.15% strontium. The main age-hardening occurred in the first two weeks but the maximum was not reached until five weeks after casting. No softening was detected with longer ageing times.

The addition of 0.05% aluminium had little effect on the hardness of lead-strontium alloys. However, additions of both aluminium and 0.05% cerium mischmetal resulted in a lower hardness figure. Silver additions had no effect on the hardness of lead-strontium alloys.

The hardness values of lead-tin-strontium alloys are given in Table 2. The hardness increased with increase in strontium content and the maximum hardness again appeared to be levelling out at 0.15% strontium. Tin increased the maximum hardness and with alloys containing 0.1% strontium or less, the hardness increased with increase in tin content up to 3%. The main age-hardening occurred in the first two weeks but the maximum hardness was not reached until five weeks after casting. The alloys containing 0.5 - 1% tin tended to soften slightly (by about 2 BHN units) with further increase in ageing time.

TABLE 1
Hardness of lead-strontium alloys

Composition (wt.%)				Hardness (BHN)	
Strontium	Aluminium	Cerium mischmetal	Silver	After 1 day	Maximum
0.021				5.9	7.8
0.082				10.9	15.3
0.17				11.7	15.5
0.36				12.5	15.5
0.56				14.3	16.6
0.036	0.05			9.1	10.0
0.094	0.05			9.7	13.0
0.25	0.05			14.1	15.5
0.08	0.05	0.05		7.8	12.4
0.25	0.05	0.05		12.2	13.4
0.30	0.05	0.05		11.3	13.8
0.05			0.25	9.3	11.5
0.12			0.25	11.5	15.0

TABLE 2
Hardness of lead-tin-strontium alloys

Composition (wt.%)				Hardness (BHN)	
Strontium	Tin	Aluminium	Cerium mischmetal	After 1 day	Maximum
0.04	0.5			6.4	12.2
0.06	0.5			12.9	16.5
0.11	0.5			19.0	21.3
0.08	0.5	0.05		9.5	16.6
0.19	0.5	0.05		12.6	18.1
0.13	0.5	0.05	0.05	8.5	14.2
0.21	0.5	0.05	0.05	10.7	13.2
0.028	1.0			8.9	15.0
0.063	1.0			17.5	19.3
0.10	1.0			18.8	21.0
0.033	2.0			15.9	16.6
0.049	2.0			18.4	18.8
0.012	3.0			8.4	10.0
0.027	3.0			12.9	15.0
0.055	3.0			18.2	20.0
0.14	3.0			22.2	22.2
0.04	3.0	0.05		13.2	16.6
0.09	3.0	0.05		15.8	18.2
0.13	3.0	0.05	0.05	11.5	13.0
0.18	3.0	0.05	0.05	12.7	14.1
0.02	5.0			11.5	13.5
0.09	5.0			15.0	19.0
0.21	5.0			19.9	21.5

The addition of aluminium tended to decrease the hardness of the lead-tin-strontium alloys but there was a significant decrease in the hardness when both aluminium and cerium mischmetal were added to the alloys.

Lead-tin-strontium alloys with additions of 0.1 and 0.25% silver were also tested. The additions had little effect on the hardness values of the alloys. The results of tensile tests on some of the alloys are given in Table 3. As expected, the tensile strength changed with composition in a similar manner to the hardness except that the addition of silver to lead-tin-strontium alloys resulted in a slight increase in tensile strength. In general, the elongation decreased with increase in tensile strength. The high elongation figure for the binary lead-0.27% strontium alloy was due to "necking" of the specimens during the tests.

TABLE 3
Mechanical properties of lead-strontium alloys

Composition (wt.%)			Ageing time (days)	Mechanical properties		
Strontium	Tin	Silver		Tensile strength (kg/mm ²)	Yield point (kg/mm ²)	Elongation (%)
0.06			1	2.21	1.26	35
			14	2.68	1.89	30
0.27			1	3.31	2.37	57
			14	3.71	2.52	35
0.39			1	4.10	3.47	17
			14	4.89	3.63	24
0.87			1	4.66	3.55	16
			14	5.05	3.95	18
0.06	0.5		1	3.08	2.37	26
			14	4.50	2.37	16
0.3	0.5		1	4.73	3.79	24
			14	5.37	4.10	24
0.05	3.0		1	3.63	2.52	31
			14	4.26	3.16	26
0.42	3.0		1	4.10	2.84	24
			14	4.58	3.31	19
0.08	0.5	0.25	1	2.68	1.50	19
			14	5.21	4.10	21
0.31	0.5	0.27	1	5.37	4.10	17
			14	5.52	3.95	15
0.07	2.7	0.27	1	3.63	2.05	23
			14	4.89	3.47	33
0.5	2.7	0.30	1	4.73	3.31	24
			14	5.37	3.31	25

The results of creep tests are given in Table 4. Since reproducibility was not good, ranges of results are given. In the case of the binary alloys, there was an increase in creep life with increase in strontium content. High strains, due to "necking" were observed in the case of the lead-0.3% strontium alloy. Tin

TABLE 4
Creep resistance of lead-strontium alloys

Composition (wt.%)			Time to fracture (h)	Strain at fracture (%)
Strontium	Tin	Silver		
0.1			60 - 105	0.20 - 0.24
0.2			105 - 180	0.39 - 0.78
0.3			142 - 188	25
0.5			1175 - 2291	3.0 - 3.4
0.20	0.5		530 - 600	0.13 - 0.14
0.10	1.0		725 - 912	0.07 - 0.20
0.12	2.0		1892 - 13,560	0.16 - 0.85
0.11	3.0		8928 - 14,304	0.38 - 0.42
0.08	0.5	0.16	0.07% strain after 17,500 hours	
0.1	0.5	0.27	0.04% strain after 17,500 hours	

increased the creep life still further. However, silver had a very marked effect on the creep strength. For example, a lead-0.5% tin-0.16% silver-0.08% strontium alloy showed a strain of only 0.7% after 2 years and none of the alloys containing silver had failed after four years.

Corrosion properties

The results of the anode weight loss of binary lead-strontium alloys and the effects of additions of aluminium, cerium mischmetal and silver on the weight loss are shown in Table 5.

TABLE 5
Corrosion resistance of lead-strontium alloys

Composition (wt.%)				Weight loss (g)	Mode of attack
Strontium	Aluminium	Cerium mischmetal	Silver		
0.05				1.8	General, slight intergranular
0.2				1.8	Interdendritic
0.4				1.8	Interdendritic
0.6				1.9	Interdendritic
0.05	0.05			1.9	General, slight intergranular
0.1	0.05			1.8	General, slight intergranular
0.25	0.05			1.8	Interdendritic
0.11	0.05	0.05		1.8	Intergranular
0.38	0.05	0.05		2.2	Intergranular
0.09			0.28	0.6	Interdendritic
0.15			0.29	0.6	Interdendritic
0.35			0.27	0.7	Interdendritic

In the case of the binary alloys, the strontium content within the limits 0.05 to 0.6% had little effect on the weight loss, and the addition of aluminium had little effect on either the weight loss or the mode of attack. The addition of cerium mischmetal, which grain-refined the alloys, caused the mode of attack to change to intergranular penetration, resulting in a higher weight loss in the case of the alloy containing 0.38% strontium, because of whole grains falling out. The addition of silver led to a marked decrease in weight loss.

The results of the anode weight loss of lead-tin-strontium alloys, together with the effects of aluminium, cerium mischmetal and silver additions are shown in Table 6. With increase in tin content there was first a decrease in weight loss, with a minimum in the region 1.5 - 2.0% tin, followed by an increase which became more rapid above 3% tin. The decrease in weight loss corresponded to a concentration of the attack at the grain boundaries, with severe intergranular attack at 1% tin. With the higher tin concentrations, the mode of attack changed to interdendritic. The addition of aluminium and cerium mischmetal had little effect, although there was a tendency for alloys with such additions to show an increase in weight loss.

TABLE 6
Corrosion resistance of lead-tin-strontium alloys

Composition (wt.%)					Weight loss (g)	Mode of attack
Strontium	Tin	Aluminium	Cerium mischmetal	Silver		
0.06	0.5				1.4	Intergranular
0.14	0.5				1.3	Intergranular
0.2	0.5				1.3	Intergranular
0.08	0.5	0.05			1.3	Intergranular
0.1	0.5	0.05			1.4	Intergranular
0.25	0.5	0.05			1.5	Intergranular
0.05	0.5	0.05	0.05		1.3	Intergranular
0.14	0.5	0.05	0.05		1.5	Intergranular
0.02	1.0				0.8	Severe intergranular
0.14	1.0				0.8	Severe intergranular
0.07	1.0	0.05			1.0	Severe intergranular
0.15	1.0	0.05			1.0	Severe intergranular
0.01	3.0				1.2	Interdendritic
0.06	3.0				0.9	Interdendritic
0.24	3.0				0.9	Interdendritic
0.05	2.7	0.05	0.05		1.0	Intergranular
0.10	2.7	0.05	0.05		1.4	Intergranular
0.17	2.5	0.05	0.05		1.4	Intergranular
0.04	5.0				5.5	Intergranular
0.09	5.0				4.3	Intergranular
0.04	0.5			0.12	0.9	Interdendritic
0.06	0.5			0.27	0.5	Interdendritic
0.09	3.2			0.13	0.48	Interdendritic
0.1	3.0			0.28	0.37	Interdendritic

The addition of 0.1% silver caused a marked reduction in the weight loss and with increasing silver content, to about 0.25%, the weight loss was even smaller

The results of stress corrosion tests on some of the alloys are given in Table 7, where ranges are given when poor reproducibility was obtained. An increase in strontium content led to an increase in stress corrosion life. In general, the alloys containing 3% tin were no better than those containing 0.4% tin. Intermediate tin contents also gave poor results and sections through the specimens after test showed that severe intergranular penetration had taken place, leading eventually to fracture (see Fig. 5). The addition of silver resulted in a marked increase in stress corrosion life.

TABLE 7

Stress corrosion resistance of lead–strontium and lead–tin–strontium alloys

Composition (wt.%)			Stress corrosion life (h)
Strontium	Tin	Silver	
0.26			200
0.6			900
0.14	0.4		450
0.31	0.4		1200 - 2000
0.5	0.4		2300
0.05	2.9		550
0.18	3.0		650
0.4	3.5		1000
0.07	0.5	0.27	5000 (still on test)
0.1	0.47	0.30	5000 (still on test)
0.15	0.45	0.30	5000 (still on test)

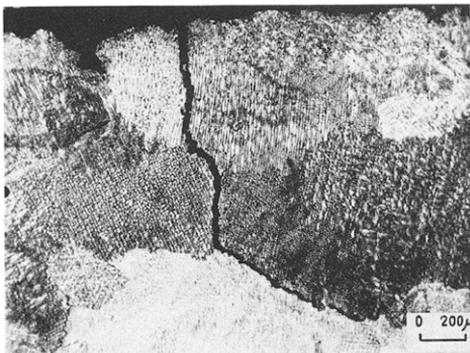


Fig. 5. Intergranular crack in lead–1.5% tin–0.15% strontium alloy.

Discussion

The basic metallurgical requirements for an alloy for use as positive grids in a lead-acid battery are: (1) good castability to enable grids to be cast at economic rates (assuming cast grids and not wrought grids are being used); (2) sufficient mechanical strength to be handled during processing without distortion or fracture; (3) sufficient creep strength to prevent undue growth of the positive plate during service; and (4) good anodic corrosion resistance (under stressed conditions) to prevent excessive corrosion or disintegration in service. The first two properties only are required for an alloy used as a negative grid.

The lead-antimony alloys used traditionally in the battery industry have excellent casting properties and difficulties are usually experienced when low-antimony or antimony-free alloys are used. The castability of the lead-strontium alloys was assessed from the test specimens. Sound castings could be produced from all the alloys tested. However, difficulties were experienced with the binary alloys containing higher amounts of strontium. Some of the castings of alloys containing tin were prone to hot tears and the variability in the results of creep and stress corrosion tests may well be explained to some extent by the presence of hot tears. However, the castability of lead-strontium and lead-tin-strontium alloys is as good as the corresponding alloys containing calcium and, on this basis, it should be possible to cast battery grids in the alloys at reasonably economic rates.

The hardness and tensile strength of a grid alloy give an indication of the ability of the grid to be handled and processed during manufacture. Typical hardness values of lead-antimony alloys are 15 - 20 BHN and when an alloy has a hardness of less than 12 - 13 BHN difficulties begin to be encountered and scrap rates increase. The hardness of all the experimental alloys was mainly a function of the strontium content. With increase in strontium content, more of the harder secondary phase appears. In addition the alloys also harden on ageing, presumably because of submicroscopic precipitation from the supersaturated solid solution. In the case of alloys containing tin, the compound Sn_3Sr may be present in addition to the compound Pb_3Sr .

The addition of cerium mischmetal to the alloys causes a decrease in hardness. This is unexpected as fine-grained alloys, in general, have higher mechanical properties than coarse grained alloys at temperatures below their recrystallization temperatures (since, under these conditions, the grain boundaries have a higher strength than the grains themselves). It may be that cerium mischmetal causes a change in solubility of tin or strontium in lead or that it suppresses the formation of some of the compounds which cause hardening.

The results show that binary alloys containing 0.08% strontium or more and ternary lead-tin-strontium alloys containing 0.04% strontium or more should have sufficient strength for handling during production. In the case of the grain-refined alloys containing aluminium and cerium mischmetal, the

strontium content may have to be increased to ensure good handling properties. It is interesting to note that the mechanical properties of lead-strontium and lead-tin-strontium alloys are somewhat better than those of the corresponding alloys containing calcium and the lead-strontium alloys should therefore be easier to handle in production conditions.

It is difficult to state a minimum permissible figure for creep resistance for battery grid alloys since this depends on the size and thickness of grid and on the application for the battery. On the laboratory test, traditional lead-antimony-arsenic alloys give a strain of 0.4 - 0.8% after two years. Batteries containing positive grids of these alloys give a satisfactory service life even on a deep cycling duty. It is questionable whether the lead-strontium or lead-tin-strontium alloys could be used as positive grids in batteries required for this type of service as they would suffer from excessive growth. However, the growth-resistance of the lead-tin-silver-strontium alloys would be good and, from this point of view, the quaternary alloys could be considered for use.

A binary lead-calcium alloy has been used for many years in telephone batteries in the U.S.A. Although the alloy is satisfactory for this application when grid production is carefully controlled, there have been many cases [21, 22] where premature failure has occurred by positive grid growth. This normally occurs when casting conditions are such that a finer grained alloy is produced. It is well-known that higher creep rates (and therefore grid growth rates) occur with fine-grained alloys since under long-term stress conditions grain boundaries are weaker than the grains themselves. Binary lead-strontium alloys have somewhat better creep characteristics than binary lead-calcium alloys and would therefore be expected to behave reasonably well as relatively thick grids in batteries under floating conditions.

The anode weight loss of lead-antimony alloys on laboratory tests is 1.7 - 1.8 g. The values for the weight loss of all the binary lead-strontium alloys are at a satisfactory level. The corrosion resistance of lead-strontium alloys containing up to 3% tin, as measured by the weight loss, is good but alloys containing 1 - 2% tin suffer from severe intergranular corrosion which would result in premature failure in service of positive grids of these alloys by disintegration. This effect could be ameliorated by grain-refining the alloys with cerium mischmetal. Alloys containing 5% tin have high anode weight losses and should not be considered as grid alloys. The addition of silver to all the alloys reduces the anode weight loss to a very low level and a lead-0.5% tin-0.25% silver-0.1% strontium should exhibit excellent corrosion resistance when used as a positive grid alloy.

Positive grids in a battery are subjected to anodic corrosion and, at the same time, are stressed by the corrosion product as it is formed. The results from laboratory stress corrosion tests are therefore often a very good indication of how a positive grid alloy will behave in a battery. Traditional lead-antimony-arsenic alloys have a stress corrosion life of 2000 - 2400 hours whereas "B" alloy (lead-3% antimony-1.5% tin-0.5% selenium) has a life of about 1000 hours. The lead-strontium and lead-tin-strontium alloys gave

better results than the corresponding alloys containing calcium but are not as good as the lead-antimony-arsenic alloys. Some of the alloys are worthy of consideration, for example, as automotive battery grids. The alloys containing 1-2% tin, however, give premature failure and the type of failure is illustrated by Fig. 5 where the combination of corrosion and stress has resulted in deep penetration along the grain boundary. This can be overcome to some extent by grain-refining the alloy with cerium mischmetal or by producing a fine-grained alloy grid by wrought techniques since lead-strontium and lead-tin-strontium alloys, like their lead-calcium counterparts, are readily worked and can be rolled or extruded. The lead-tin-silver-strontium alloys give excellent results on the stress corrosion test and, from this point of view, could be considered for grids in batteries for any application.

Although some of the experimental alloys containing strontium have satisfactory metallurgical properties, battery tests will have to be carried out to ensure their total suitability in practice. Batteries containing lead-calcium grids have been shown to suffer from premature loss of capacity on cycling. This has been attributed to changes in the morphology of the lead dioxide active material [23] or to the growth of a barrier layer of lead sulphate on the positive grid [24 - 26]. It has been suggested [27] that some antimony may be necessary to promote a structure of active material which will remain strong whilst giving a good capacity. It is therefore probable that batteries containing lead-strontium alloys will suffer from the same disadvantage.

Bearing this in mind, it may be worth investigating the use of a lead-0.1% strontium alloy in standby batteries as a replacement for lead-0.06% calcium alloy, a lead-0.5% tin-0.1% strontium in maintenance-free automotive batteries, and a lead-0.5% tin-0.1 - 0.25% silver-0.1% strontium in deep-cycling batteries where the cost of the silver-containing alloy can be afforded. It should, however, be remembered that the present cost of strontium is three times greater than that of calcium. However, there is no doubt that a consideration of the metallurgical properties required for a lead-acid battery grid leads to the conclusion that lead alloys containing strontium may be of interest to the battery industry.

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