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ABSTRACT

Tests were made on automobile-type batteries, and the results showed that although the corrosion properties of Pb-Ca-Sn alloys were good, the growth characteristics and life were poor in comparison with a standard alloy containing 8% Sb and 0.25% Sn and with an alloy containing 4% Sb, 0.2% Sn, 0.5% As, and 0.25% Ag. Indications were that the oxide corrosion product of lead exerts the surface stress that causes growth (lengthening of grid members), and that the cracking of the lead oxide layer that results from this growth permits increased corrosion. Furthermore, indications were that proper choice of composition produces an alloy structure in which the stresses tend to be perpendicular to the grid, and hence do not cause growth. This alloy structure, however, has a higher corrosion rate. On the basis of the results, an alloy containing 8.5% Sb, 4.5% Sn, and 0.13% Ag was chosen as one which should give the best compromise between the growth properties and the inherent corrosion properties, and which would have the necessary tensile strength. Preliminary testing shows it to be comparable to the better commercial alloys, which means that this course of investigation should be carried further.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

NRL Problem C05-04

Projects NR 475-000. Task NR 475-003, and NS 677-100

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THE EFFECT OF CORROSION AND GROWTH ON THE LIFE OF CYCLING LEAD-ACID CELLS

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INTRODUCTION

One of the major factors leading to loss of capacity and eventual failure in the lead-acid battery is the corrosion of the lead alloy grid that acts as a support for the positive active material and as a conductor of electricity. This condition is aggravated by so-called growth, a phenomenon whereby the grid dimensions actually increase during life, causing the plates to buckle and break and the pellets of active material to become loosened and even dislodged.

Previous work (1, 2, 3) indicated that the growth of positive grids resulted from stress imposed on the grids by the corrosion product formed during life. Consequently, recent work on extending the life of the lead-acid cell has been directed toward developing alloys with improved growth characteristics, as well as alloys with lower corrosion rates — the primary direction of earlier work.

Corrosion rate studies (2, 3) and growth studies (3) indicated that cells having grids made of ternary alloys of Pb-Ca-Sn, which showed relatively good growth and corrosion characteristics under certain conditions, should have longer life than cells utilizing the standard antimonial alloys, 8 to 12% Sb. To test this conclusion, automobile-type batteries were made with grids of the ternary alloys and they were life-tested under a cycling routine against two sets of batteries, one having grids of 8% Sb and the other having grids of a quaternary alloy of Pb-Sb-As-Ag.[†]

The test did not turn out as anticipated; those batteries containing ternary alloys of Pb-Ca-Sn had appreciably shorter lives than those containing the other alloys. While the corrosion properties of the Pb-Ca-Sn alloys were good, their growth characteristics were very poor. This result plainly indicated that the growth theory as previously developed was either wrong or incomplete. Certain information from the test results and additional work led to the belief that the theory was incomplete rather than wrong. To expand the theory and test it further, an alloy was sought which would combine the well-known good growth properties of the antimonial alloys with the corrosion resistance of the tin alloys. A quaternary alloy of Pb-Sb-Sn-Ag was selected as having a desirable combination of properties, and it was incorporated in batteries and tested.

EXPERIMENTAL WORK

Automobile-type batteries having grids of the alloy compositions listed in Table 1 were tested. In the first test four batteries each of Alloys A1 and A2 (Pb-Ca-Sn alloys) and of Alloy B (Pb-Sb-As-Ag[†]) were included. After the batteries were received from the cooperating commercial laboratory, they were immediately given a freshening charge, followed by a few cycles in 1.210 specific gravity acid. Then they were divided into three

*Presently with Electric Auto-Lite Co., Toledo, Ohio.

†All test batteries were supplied by the Electric Storage Battery Co.

‡The small amount of Sn in Alloy B was an impurity.

TABLE 1
Alloy Compositions Used in the
Growth and Corrosion Tests

Alloy Designation	Alloy Composition (weight percent)					
	Sb	Ca	Sn	As	Ag	Pb
A1	--	0.09	4.50	--	--	Rem.
A2	--	0.15	4.50	--	--	Rem.
B	4.0	--	0.20	0.50	0.25	Rem.
C	8.0	--	0.25	--	--	Rem.
D	8.5	--	4.50	--	0.13	Rem.
E	--	--	4.50	--	--	Rem.
F	6.0	--	--	--	--	Rem.

gravity groups as follows: the specific gravity of two batteries of each alloy was allowed to remain at 1.210, the gravity of the third battery was adjusted to 1.275, and that of the remaining battery to 1.310. This was accomplished during the gassing phase of the last preliminary charge.

They were then all connected in series and put on an automatic cycle which consisted of three cycles daily, discharging for 3.9 hours at 13.3 amperes and charging for 4.1 hours at 13.9 amperes. Thus the discharge amounted to 52 ampere-hours or about one-half the rated capacity (100 ampere-hours), while the charge amounted to 57 ampere-hours or about 9% overcharge. This charge procedure was sufficient to put back the charge completely in every cell, but it was not enough to equalize gravity in the cells with grids of Pb-Ca-Sn, Alloys A1 and A2. The cells containing As, Alloy B, did equalize gravity — no doubt because of their higher earlier gassing rates. This cycle maintained the temperature of the cells between 100° and 106°F. Toward the end of their life, it became necessary to put the arsenical-alloy cells on a two-step charge with about 15% overcharge to maintain capacity and to prevent too-violent gassing at the end of charge.

To test capacity, discharges were run every thirty cycles or so at 25 amperes after overnight charges at 5 amperes. At various times during life, cells were pulled and examined and corrosion and growth measured. Corrosion was measured by weight loss after stripping the grids in an alkaline hydrazine solution.

Also part of the first test was a separate test on standard commercial batteries with 8% Sb, Alloy C. Although the cycling routine was the same, from about 25 to 150 cycles their temperature ran around 95°F, so that their overall corrosion rate must have been a little lower and their life slightly prolonged in comparison with the other cells. The 1.310 specific gravity was not used in these cells, nor was corrosion-growth data obtained. Bare-grid tests of 9-1/2% Sb alloy grids were made, however, and provided corrosion-growth data which probably is not much different than that which the 8% Sb alloy would have afforded.

The results of the first test suggested changes in the alloy composition for reasons to be brought out in the subsequent discussion. A second test used actual batteries with grids made up of the improved alloy that was suggested, a Pb-Sb-As-Ag alloy of composition D, Table 1. Nine batteries containing grids of this alloy were cycled in series with three control grids of a commercially used alloy, Pb-Sb-As-Ag, Alloy B. They were divided into the same three gravity groups used in the first test, each group containing

three batteries with the improved alloy and one with the control, and they were cycled and tested in the same manner as described previously. Unfortunately, after the first hundred cycles of operation, both the test batteries and the controls were falling so far below the rated capacity that a modified cycling procedure was necessary. Although the batteries never attained as much as 80% of their rated capacity, even at the beginning, the test was continued in an effort to obtain corrosion and growth data on the two alloys. The rapid decrease in capacity necessitated frequent reduction in the cycling current to keep the discharge within the actual capacities of the cells and to assure that overcharge was not excessive. Every effort was made, however, to insure that both battery types received comparable treatment.

RESULTS OF TESTS WITH THE Pb-Ca-Sn ALLOYS

In the capacity-life curves for the first test as shown in Fig. 1, the comparatively poor showing of the Pb-Ca-Sn grids, Alloys A1 and A2, is quite evident. Initially (Fig. 2) the corrosion rates of the Pb-Ca-Sn grids are appreciably lower than rates for the arsenical grid, Alloy B. This was expected from the previous work (2, 3). The growth characteristics of the Pb-Ca-Sn grid (Fig. 3) are much worse than those of the 9-1/2% Sb grid. In this regard, the arsenical alloy is better than the straight 9-1/2% Sb alloy.

The short life of the Pb-Ca-Sn alloys evidently is not to be explained on the basis of corrosion rates, because these alloys are inherently more corrosion resistant than the antimonial alloys. This is shown by the early portion of the corrosion curves of Fig. 2 as well as other data (2, 3). The upswing in the corrosion rate toward the end of life is typical of both of the Pb-Ca-Sn alloys investigated in this test and is also true of the 9-1/2% Sb alloy (3). It is unquestionably due to growth; when growth starts, the protective PbO_2 film which is formed by the corrosion process cracks and less protection results. Comparison of Figs. 2 and 3 shows the influence of growth quite clearly, because the upswings in the corrosion curves start approximately at the values of weight loss which correspond to the zero intercepts of the corrosion-growth curves. The increased rate of corrosion of growing grids hastens grid failure and this effect would be expected to be ruinous in grids with poor growth resistance.

Obviously, there is a correlation between growth and life, because the life of these test cells increases as growth resistance increases. Furthermore, just as was shown for the 9-1/2% Sb alloy (3), the first major drop in capacity occurs when growth begins. This is shown in Figs. 4 and 5 where capacity and growth are both plotted against the number of cycles.

The capacity-life curves of the arsenical grids, Alloy B shown in Fig. 5, are very interesting. They all show a minimum in the curve at 75 cycles, shortly after an initial peak in capacity is reached. When one of these cells was pulled at 75 cycles, it was found that the vertical frame members of the positive grids had grown to the extent of 1%. There was no measurable growth in any other members. As the test progressed and the other arsenical cells were examined, it was found that growth in the vertical frame members stopped completely. The initial capacity loss was no doubt due to the loosening of the active material structure and the loss of contact with that part of the grid immediately associated with the vertical frame members. The subsequent capacity recovery occurred because the whole positive plate had not yet reached its maximum capacity when this phenomenal growth occurred. This result is strong evidence for the deleterious effect of growth on capacity as previously proposed (2, 3) and leads to the conclusion that ultimate failure can be associated with general grid growth simply due to loosening of the active material structure and loss of contact with the grid.

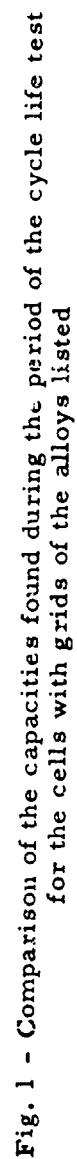


Fig. 1 - Comparison of the capacities found during the period of the cycle life test for the cells with grids of the alloys listed

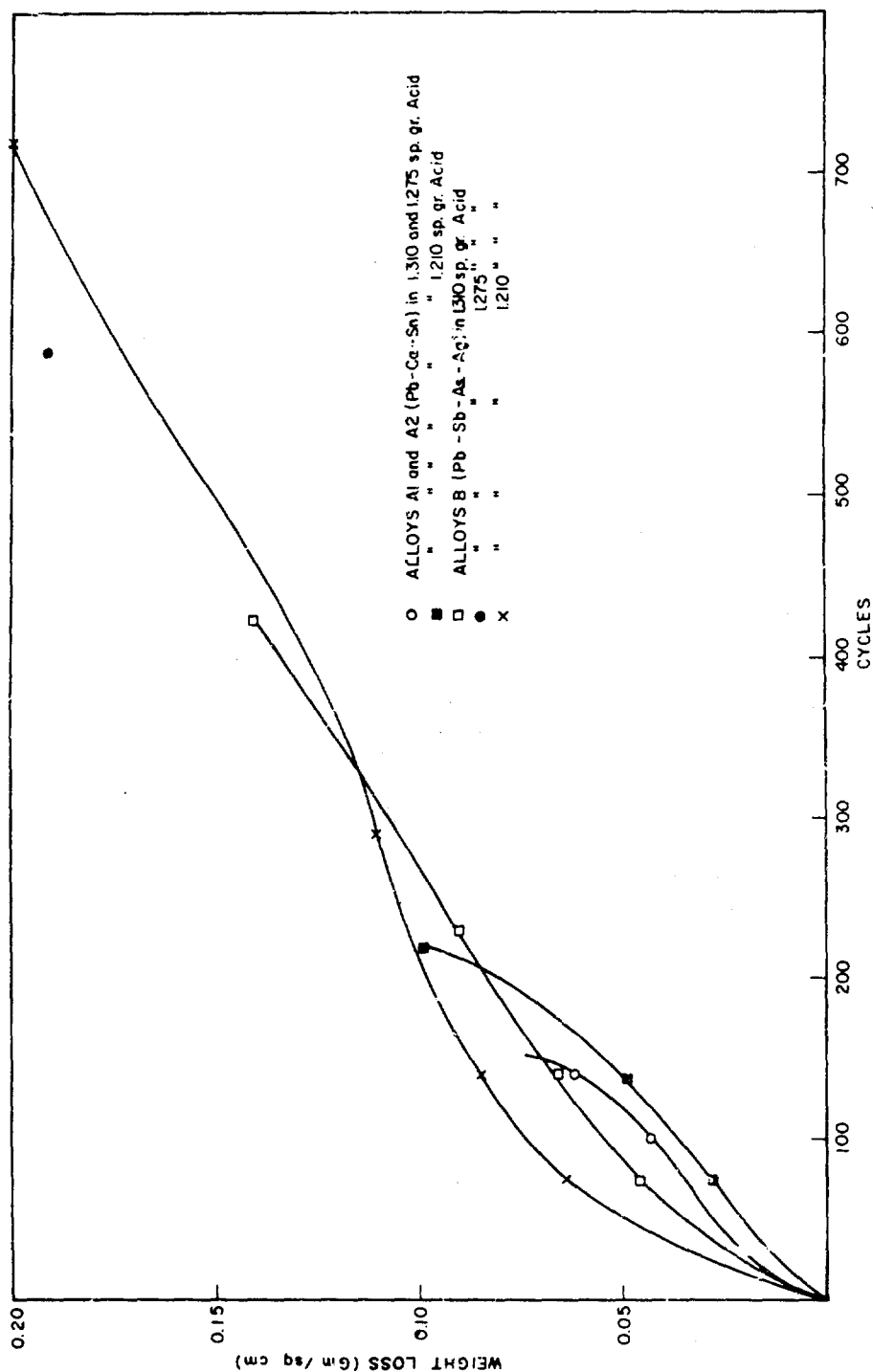


Fig. 2 - Comparison of the weight losses during test for the grid alloys listed

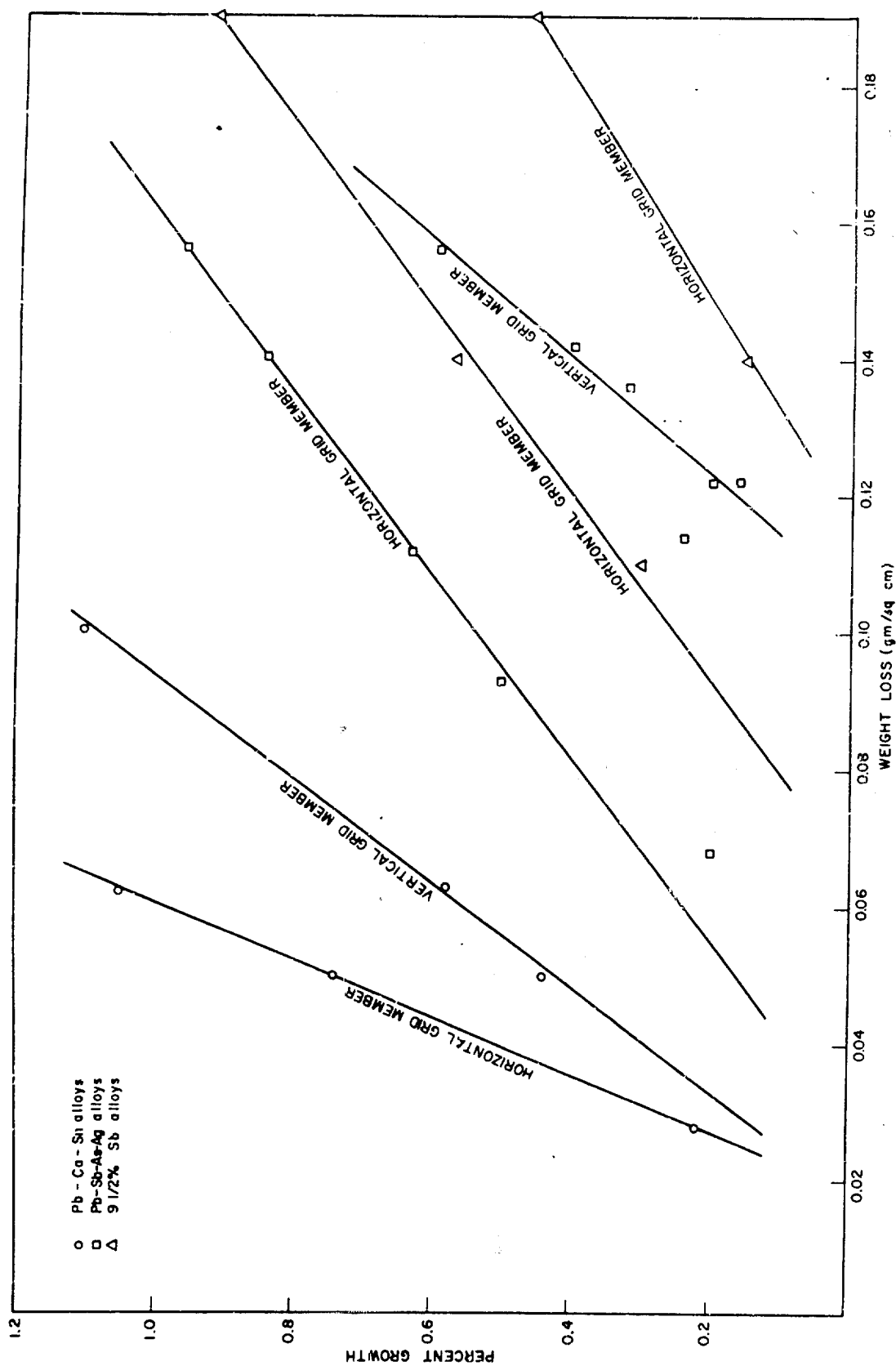


Fig. 3 - Comparison of the weight losses with growth, showing the differences in horizontal and vertical grid members for the same alloy and comparing the alloys listed

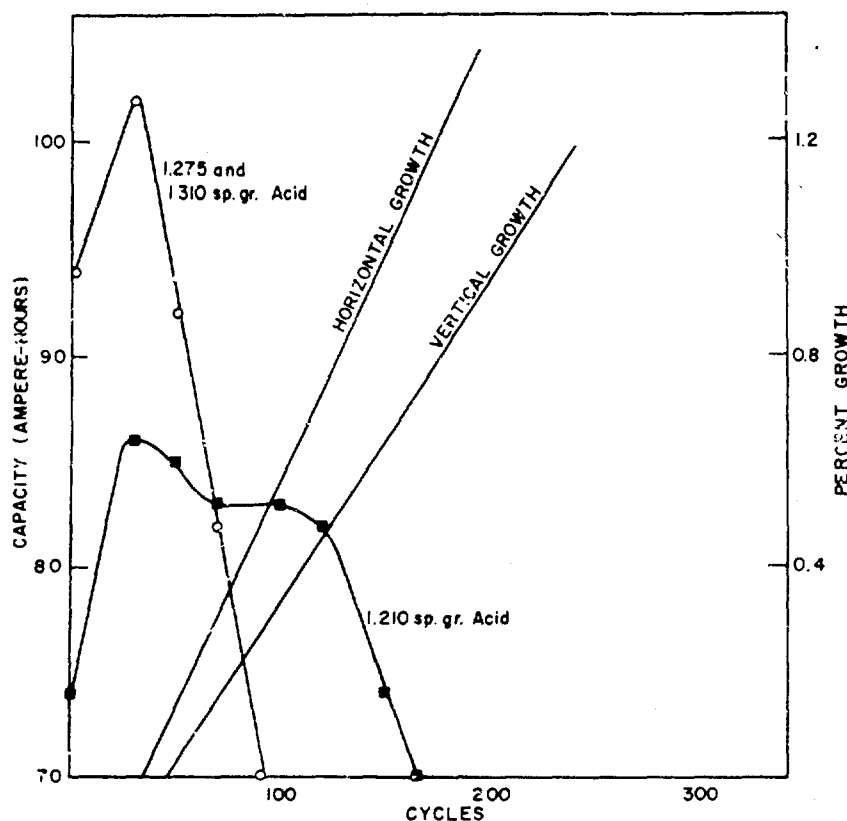


Fig. 4 - The effect of acid specific gravity on the capacity of Pb-Ca-Sn alloys and comparison of growth of the horizontal and vertical grid members during life

It should be observed here that frequently cells fail or appear to fail because of fracture of the grid members, resulting in loss of metallic paths for electron flow and, hence, in increased resistance. This result is only the logical end result of growth and must certainly bring about failure if the process described above has not already done so.*

Lengthening of the grid members beyond the elastic limit is the process of creep and the obvious result of this is that a kind of stress-corrosion cracking becomes possible due to opening up of fissures between grains under stress. Bad castings are generally blamed for cracked grids; however, they are probably only to be regarded as supplementing the fundamental cause of failure, namely, stresses set up by growth.

It is possible to make a general separation in kind between the two types of failure described. Those alloys which are hard and brittle and do not creep much or elongate much under a tensile test would be more likely to go all the way and fail by fracture. Alloys which yield and elongate to larger extents under tensile or creep would be more likely to fail by the process described first and fracture would not be necessary for failure. Thus it may be concluded that creep studies can be important to the overall problem.

*Other causes of cell failure are loss or "washing" of active materials and shorting. These could be a function of grid growth; however, they must be viewed primarily as a problem in active material retention, for where these are causes of failure, the grids have not been given a true test of their capabilities.

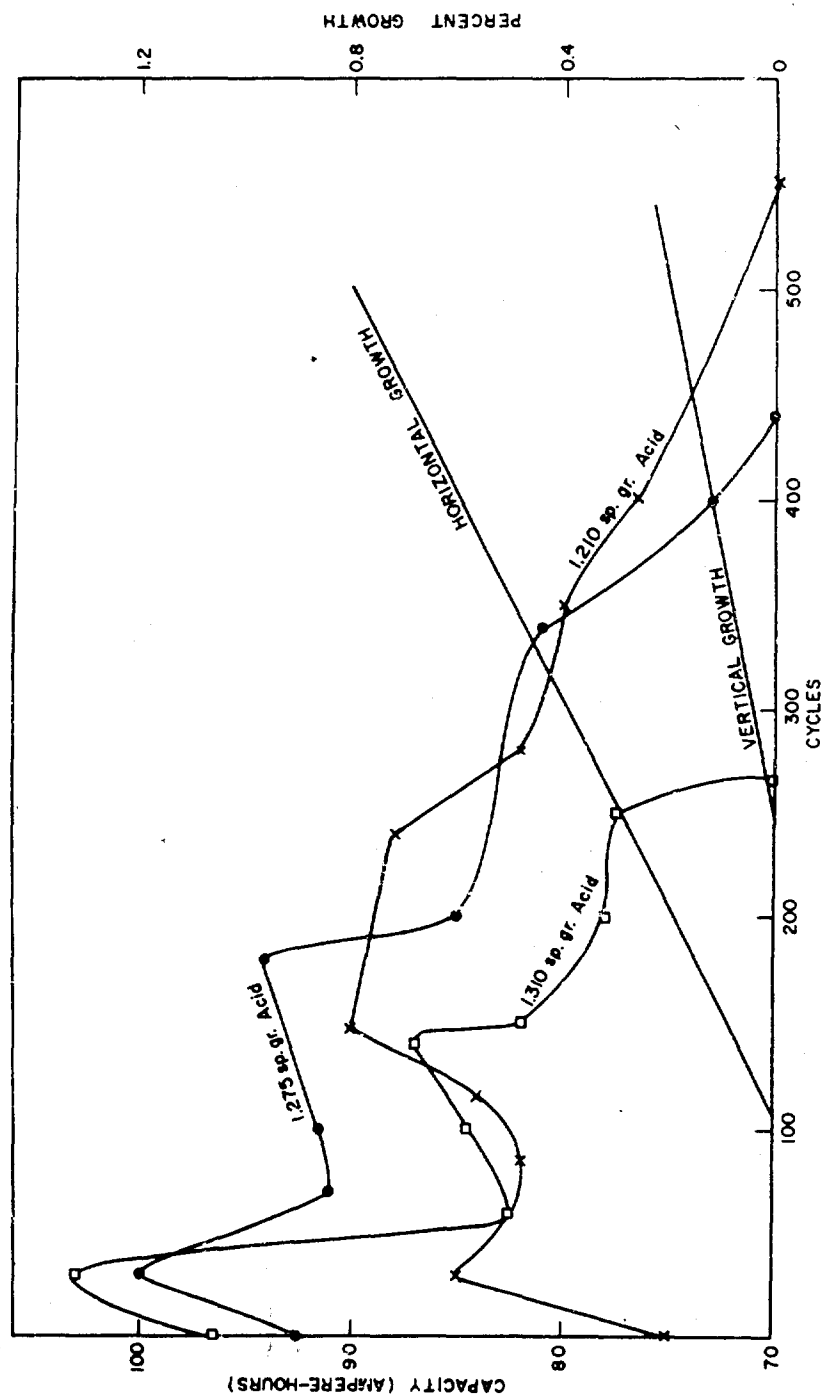


Fig. 5 - The effect of acid specific gravity on the capacity of Pb-Sb-As-Ag alloys and comparison of the growth of the horizontal and vertical grid members during life

At this point it would be well to observe that in no case did the cells of the first test fail because of grid fractures. In fact, the bulk of the active material was actually removed manually with a screwdriver in preparation for stripping the grids for weight-loss determinations and the corroded grids remained intact. In addition, there was almost no active material washing.

When the capacity of one of the high-gravity Pb-Ca-Sn batteries fell to 52 ampere-hours on a 25-ampere discharge, the elements of one cell were pulled and it was observed that almost all the vertical growth had taken place in the bottom half of the plates. This result was to be expected because the vertical members were tapered in cross-sectional area, being heavier at the top. The elements were cut in half horizontally and the bottom half discarded. The top half was given a freshening charge followed by a discharge at 12-1/2 amperes. Its capacity was found to be 40 ampere-hours. In other words, the top half of the cell had not yet failed. This is taken as additional evidence for the effect of growth on capacity.

These results lead again to the proposal that both corrosion rates and growth data should be measured to screen alloys for full-scale testing in batteries (3). It is probably not too much to expect that such data could lead to a prediction of life.

The above discussion doesn't explain why the Pb-Ca-Sn alloys, which looked so good on the basis of the information available from the previous work, failed so miserably in a battery test. Two clues were present to explain this: One was the high initial growth of the vertical frame members in the arsenical alloy batteries; the other was the microscopic examination of the alloys reported in Ref. 3.

Concerning the first clue, microscopic examination of the uncorroded arsenical alloy showed fine, closely packed, star-shaped dendrites of lead metal arranged perpendicular to the surface of the casting, with the small areas between the dendrites consisting of the second-phase — antimony along with other insoluble components. These castings were extremely uniform; all areas gave this appearance.* When the arsenical alloy was corroded, the more soluble (in the electrolyte) antimonial phase corroded out, just as it does in the antimonial alloys (3,4), and left the closely packed, star-shaped dendrites protruding from the surface, like mesas standing on a desert floor. Now, if there should be a difference in growth due to the topography of corrosion and if it is true that the oxide corrosion product of lead exerts a stress on the underlying metal (1,2,3), then in the case of this alloy a large portion of the stress should be exerted in a direction perpendicular to the length of the grid members rather than parallel, and consequently the corrosion would have little tendency to cause growth.

A possible explanation for the initial growth of the vertical frame members is this: During the pasting process, the pasting machine cold-worked the surface of the vertical frame members and in the process flowed or laid over the perpendicular dendrites, smearing the surface with the lead phase. In the subsequent corrosion, a considerable parallel component of stress would be applied, with resultant growth. The growth stopped when this surface layer was corroded through, and normal corrosion (for this alloy), largely in the perpendicular direction, began.

On the other hand, microscopic examination of pure lead and of lead-tin alloys (3) had shown a uniform, smooth corrosion penetration over the surface, presumably because there is no soluble second phase present to be eaten out selectively. In these alloys the

*Its appearance may be contrasted with that of the straight antimonial alloys where the lead dendrites of the various grains are oriented in all directions with respect to the surface: some perpendicular, some parallel, and others at various angles.

full effect of the stress due to the corrosion product should be felt. Remembering then that the previous growth data (3) had been obtained with cold-rolled strips of the alloys, it seems quite possible that this is the explanation for the poor showing of the Pb-Ca-Sn alloys on the battery test. That is, in obtaining the previous data (3) in the cold-rolled antimonial alloys, the dendritic structure favorable to growth resistance was probably smeared over, with a resulting smooth corrosion topography. Growth resistance would then be largely dependent on tensile strength and almost to no extent dependent on corrosion topography.

If this explanation is true, it means that in the design of a grid alloy for longer life, both corrosion rate and growth rate (and topography) must be considered. The two factors are in conflict, because the alloy structure which results in a favorable topography for growth resistance inherently leads to a higher corrosion rate while, on the other hand, the lower corrosion rate associated with smooth corrosion automatically results in poor growth resistance. It is a question of obtaining an optimum combination of the two opposing effects. This analysis should apply in particular to thin grids, namely, to automobile-type battery grids. At low grid thickness the growth properties should be relatively more important, but as grid thickness increases the corrosion rate factor should become increasingly more important, because the increased thickness gives more time for the alloy to corrode at the low rate characteristic of cells on float (3, 5).

DEVELOPMENT OF THE IMPROVED GRID ALLOY OF Pb-Sb-Sn-Ag

In order to test the effect of corrosion topography, two preliminary experiments were performed. In the first, cold-rolled thin strips of a 4-1/2% Sn alloy were corroded. One pair of strips was scored crosswise with a razor on both sides with the scoring marks as closely spaced as possible. One pair was left smooth. At the end of the corrosion period, growth and corrosion were measured and it was found that the scored samples had grown 20% less in spite of having lost 2-1/2 times more metal than the unscored samples and of having the tensile strength reduced by the scoring process.

In the second experiment, cast strips of several alloys were corroded against cold-rolled strips of the same thickness of the same alloys. The strips were 1 cm wide and 0.1 cm thick. The cold-rolled samples had been reduced approximately 50%. Two "smooth corroding" alloys, one with 4-1/2% Sn and the other with 4-1/2% Sn and 0.15% Ca (Alloys E and A2 in Table 1), and two "rough corroding" alloys, one with 6% Sb and the other with 4% Sb, 0.2% Sn, 0.5% As, and 0.25% Ag (Alloys F and B), were used.

The growth data are shown in Fig. 6. It will be observed that the Sn alloys show little difference between the cast and cold-rolled specimens, whereas the antimonial alloys show considerable difference, the cast strips of the latter having much better growth resistance than the rolled strips. These data are interpreted to mean that corrosion topography does play a very important part in growth, which would indicate that the explanations offered for the poor test results with the Pb-Ca-Sn alloys and the growth of the vertical frame members are essentially correct.

With this background it was considered possible that a combination of Sn and Sb in an alloy might result in an advantageous compromise between the corrosion rate and growth resistance factors to produce a longer life grid. Reference to a handbook (6) showed that an alloy of about 5% Sn and 8 to 10% Sb had very good tensile strength, up to 13,000 lb/sq in. Castings for tensile strength measurements showed that as Sn concentration increased, the alloy approached a maximum tensile strength near 5% Sn. Microscopic examination of this alloy showed a microstructure very similar to the 8% Sb alloy, so that good growth characteristics should result. Automobile-type grid castings were made of an 8-1/2% Sb, 4-1/2% Sn alloy, and bare-grid corrosion tests showed superior growth

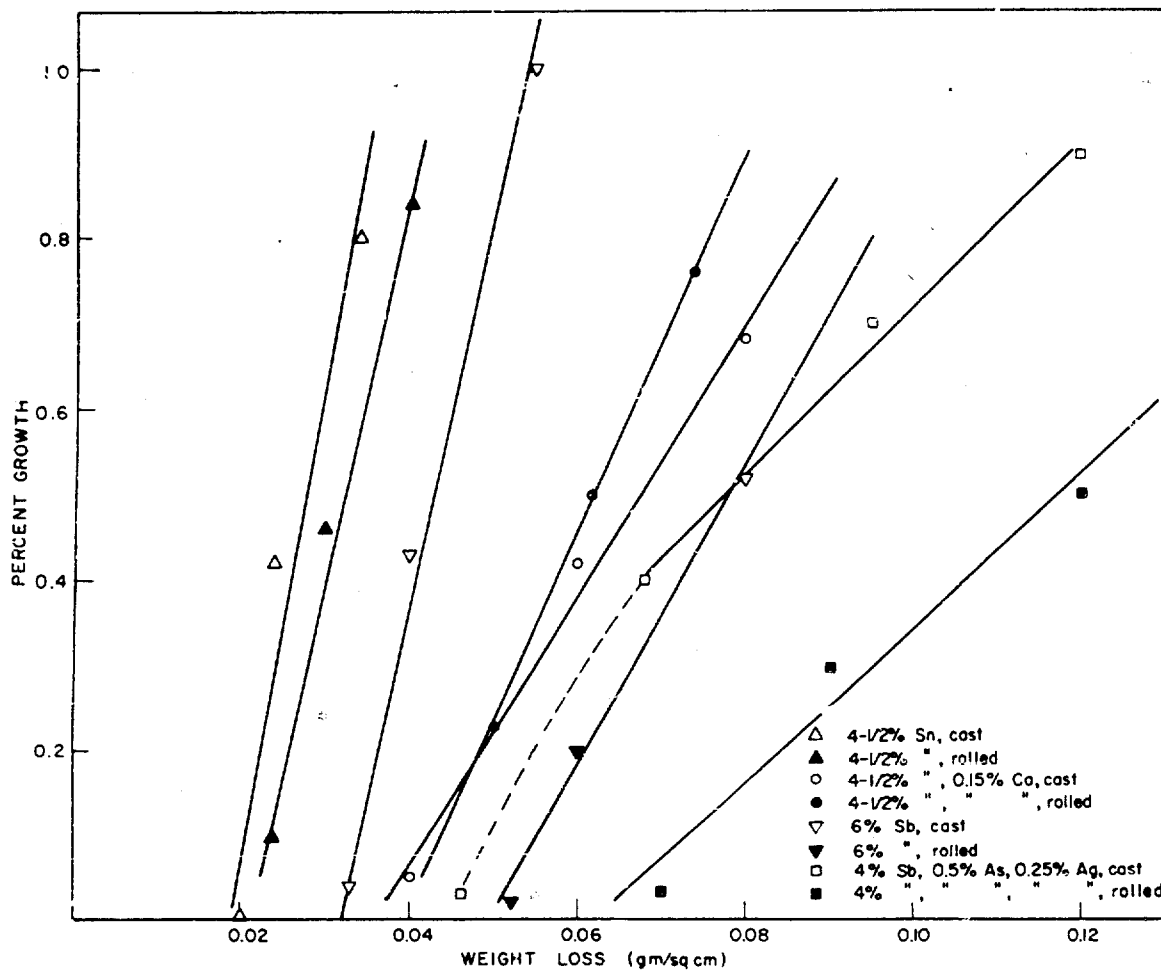


Fig. 6 - Comparison of growth and weight loss figures for the alloys listed, showing the differences in the same alloy produced by changing from as-cast to cold-rolled material

resistance of this alloy in comparison with the others. In fact, these grids did not begin to grow in either direction at a weight loss of 0.14 gm/cm^2 , which may be compared with an onset-of-growth figure of approximately 0.10 gm/cm^2 for the arsenical alloy and approximately 0.08 gm/cm^2 for the 9-1/2% Sb alloy. Corrosion rate measurements showed weight-loss curves lying between those for the arsenical alloy and the Pb-Ca-Sn alloys. Therefore, the combination of increased growth resistance and lower corrosion rate (in comparison with the arsenical alloy) should result in a battery with a life on the cycling test longer than that of the arsenical alloy, the best so far tested. On the cycle test, at a grid thickness of 0.08 in., rough estimates indicated double life or more.

The addition of 0.1% Ag to this alloy improves the microstructure, making it very similar in appearance to the arsenical alloy. Furthermore, the addition of 0.1% Ag raised the tensile strength to 17,800 lb/sq in. While no other preliminary work was done with this Ag-containing alloy, it was considered that the addition of 0.1% Ag should not increase the corrosion rate, and in view of the improved microstructure and tensile strength, it was selected for battery tests. Automobile-type batteries containing this alloy were made and life-tested with the arsenical alloy as a control.

RESULTS OF TESTS WITH THE Pb-Sb-Sn-Ag ALLOY

The capacity-life curves for the Pb-Sb-Sn-Ag grids, Alloy D, are shown as compared with the Pb-Sb-As-Ag, Alloy B, in Fig. 7. The rapid loss of capacity in both test alloy and control made the results of this test somewhat inconclusive. Unlike the first group of batteries, in which the active material was hard and brittle and showed almost no shedding, the active material in this group of batteries was found to be soft and subject to very rapid shedding and washing.

A similar set of batteries cycled by the manufacturer showed the same condition as described above, and this condition was definitely not caused by the grid alloy used. The manufacturer attributed the poor capacity of these plates to the method of manufacture. Investigation revealed that these grids were not cast in the mold currently being used in production but in an old mold which produced somewhat thicker and heavier grids. To avoid trouble in assembly, the grids were pasted with a minimum of overpasting to keep the plate thickness within specified limits and the active material weight was therefore below standard; it can also be assumed that the paste was not compacted to the extent practiced in production.

Whatever the cause, the active material was definitely substandard, and this, rather than grid alloy failure, was the factor that determined cell life. The cells had a low initial capacity, and there was no increase in capacity during the first few cycles except in the case of the Pb-Sb-Sn-Ag alloy in 1.310 and 1.275 specific gravity acid.

Examination of the active material of the positive plate revealed that it had a rather unusual light reddish-brown color instead of the dark brown usually observed. This paste also washed freely from the positive plates during charge so that sediment buildup was very rapid and exposure of the grid bars occurred after only a very few cycles.

Considering the time and effort expended in preparing these batteries for test, it was decided to continue the test although the batteries, even from the beginning, were operating in a range of capacity below that ordinarily considered as signifying complete failure in such tests.

The results of capacity vs life tests as shown in Fig. 7, for the reasons mentioned above, have very little actual significance other than to show the similar behavior of the two alloys. The increase of capacity at 188 cycles of operation is somewhat startling. This increase took place after the cells had been standing on open circuit for one week in a fully charged condition. An attempt to reproduce this by similar treatment after 290 cycles produced no noticeable gain in capacity.

Neither alloy series exhibited any measurable growth (increase in overall grid dimensions). Growth evidently had occurred, however, because the small horizontal grid members were buckled in both types of grids. Apparently the soft active material offered no support for the small horizontal grid members and as growth took place they buckled to relieve the strain rather than exerting force parallel to the plane of the grid. Thus, though growth took place, the overall grid dimensions remained unchanged. A visual comparison of the degree of distortion in the two grids of different alloy showed no marked difference, the Pb-Sb-Sn-Ag grids being very slightly less distorted in every case, indicating that growth had been slightly less.

Weight-loss figures (Fig. 8) indicate that in 1.210 specific gravity acid the Pb-Sb-Sn-Ag grid, Alloy D, corrodes less while in 1.275 and 1.310 specific gravity acid it corrodes more than the Pb-Sb-As-Ag grid, Alloy B. Thus, in the specific gravity range usually employed, the Pb-Sb-Sn-Ag alloy would probably corrode at about the same rate or perhaps slightly less than the Pb-Sb-As-Ag alloy.

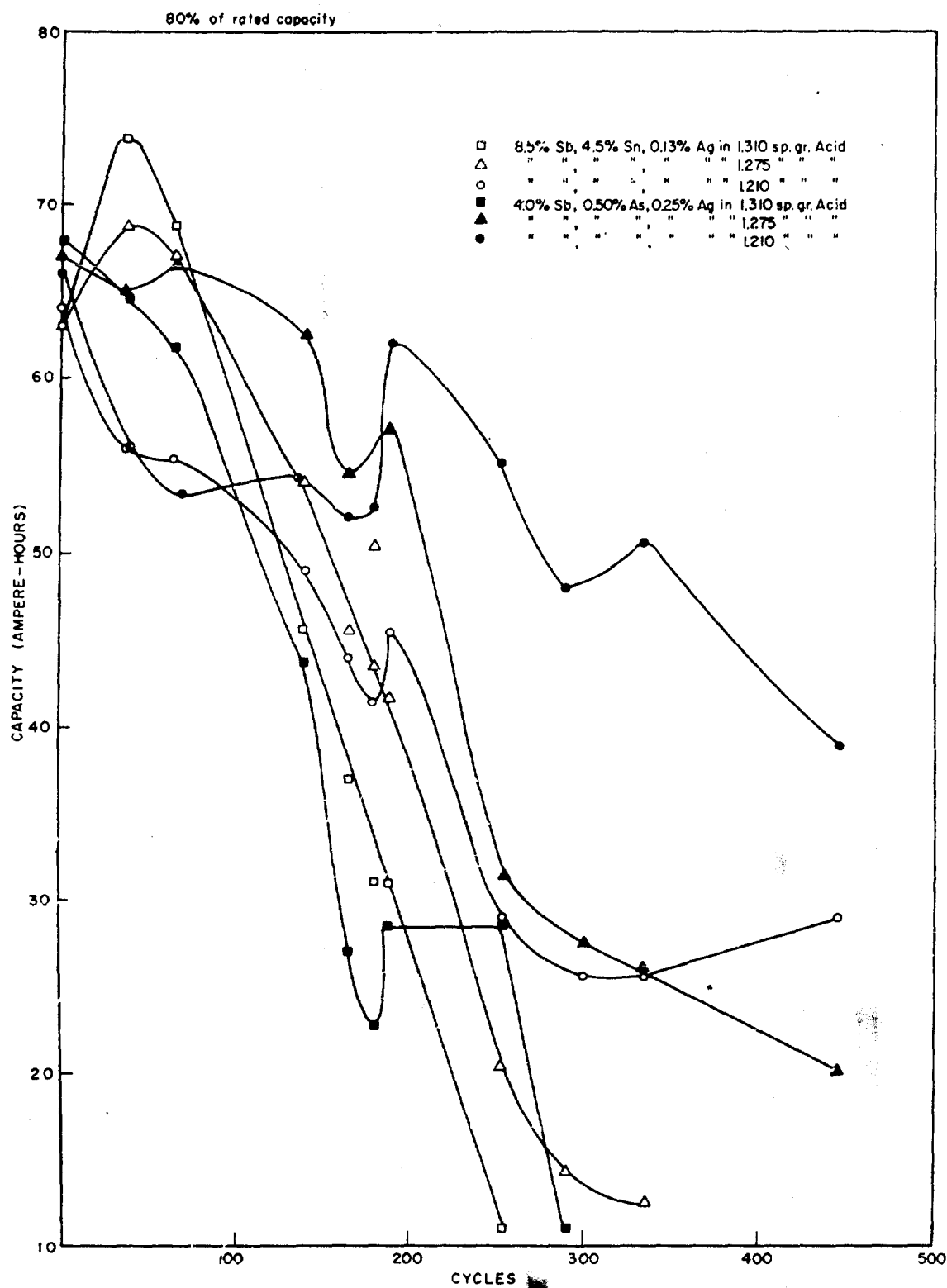


Fig. 7 - Comparison of capacities obtained during the cycling of cells with grids of the composition listed

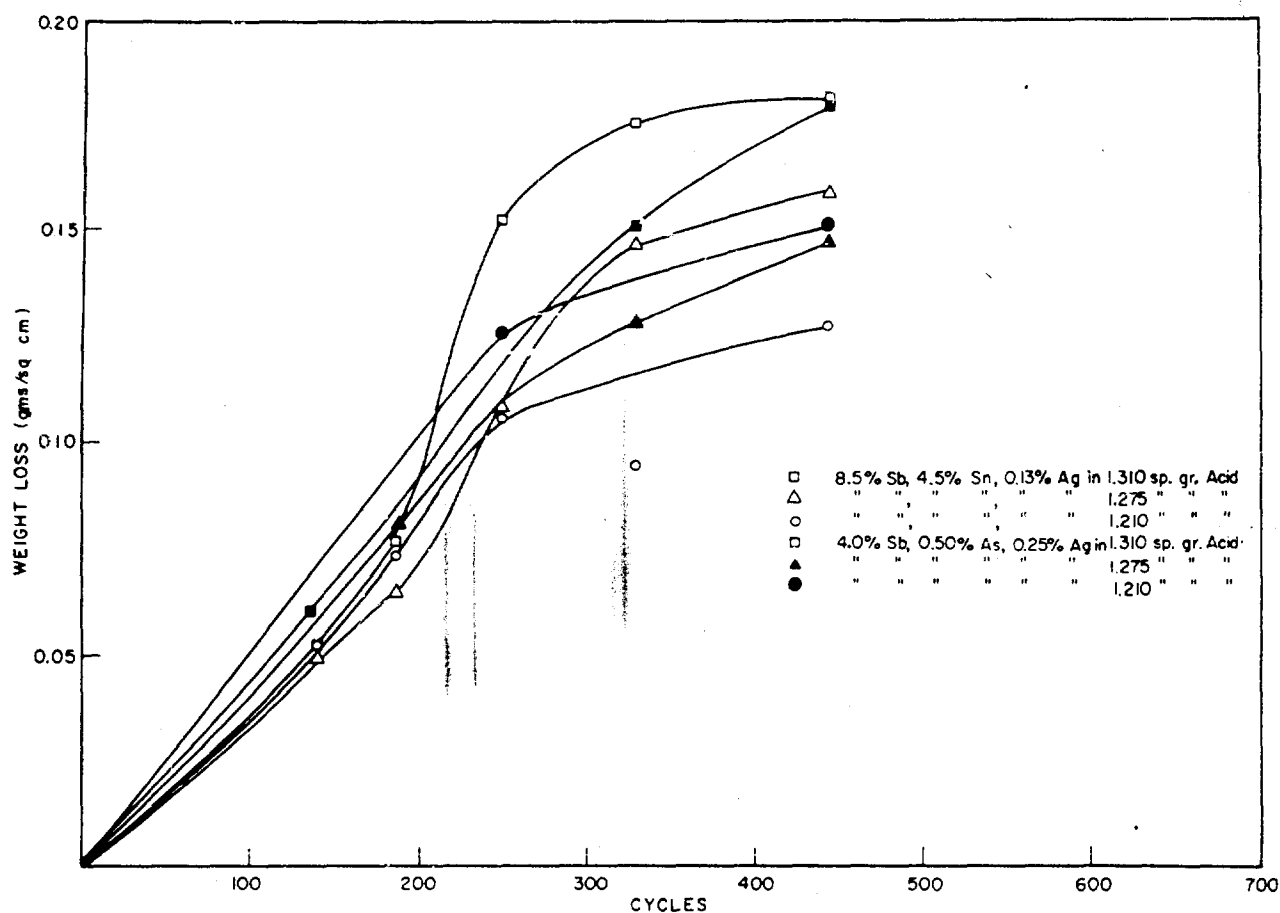


Fig. 8 - Comparison of weight losses during the cycling of grids of the compositions listed

Microscopic examination of the corrosion pattern for the two alloys indicated that the Pb-Sb-Sn-Ag gave a slightly more penetrating type of corrosion than did the Pb-Sb-As-Ag. There was also a difference in the corrosion product that was indicative of the corrosion mechanism. In the Pb-Sb-Sn-Ag alloy the corrosion product after a considerable number of cycles remained dense and unbroken, but as corrosion proceeded this corrosion product began to strip off, maintaining a fairly uniform thickness of that unbroken part next to the metal (Fig. 9). The Pb-Sb-As-Ag alloy on the other hand formed a corrosion product that developed numerous cracks at an early stage and these cracks appeared to penetrate to the metal surface, but having thus relieved stress this corrosion product showed no tendency to peel and merely got thicker as corrosion proceeded (Fig. 10). This may explain why the capacity was slightly better for cells containing the Pb-Sb-As-Ag alloy, because with the very soft paste that these plates contained, peeling of the stressed corrosion product in the Pb-Sb-Sn-Ag may have tended to dislodge active material from the plates.

Another factor revealed by microscopic examination was a noticeable difference in the nature of the corrosion product next to the metal surface. Although the outer shell of the corrosion product was apparently the same for the two alloys, there was always a thin layer of a yellow corrosion product next to the metal surface in the case of the Pb-Sb-As-Ag alloy (Fig. 10) which was completely absent in the case of the other alloy (Fig. 9).

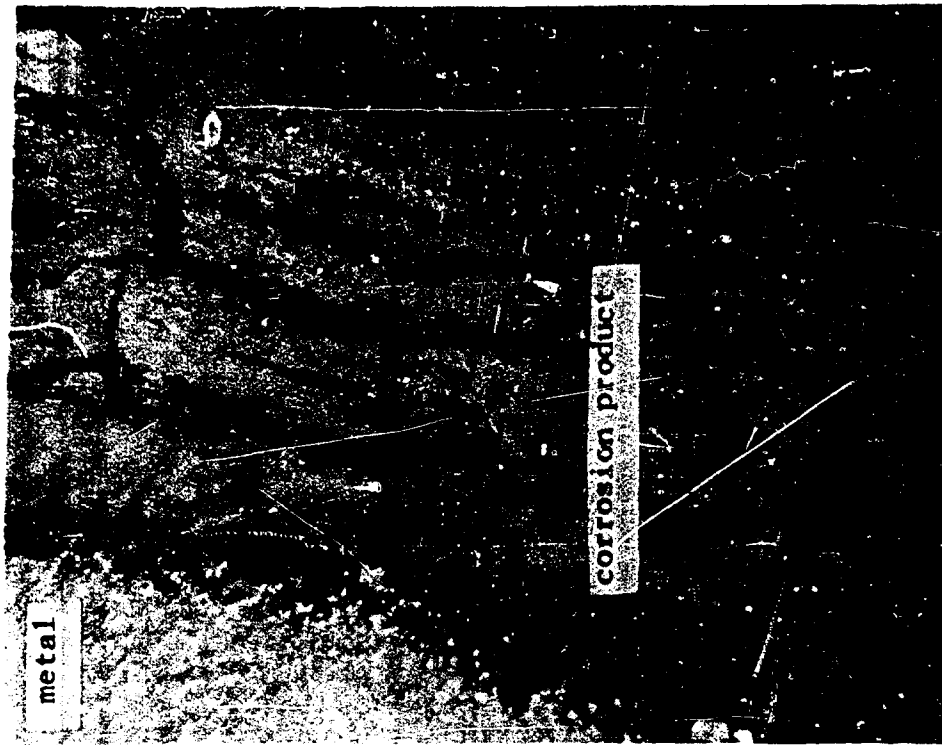


Fig. 10 - The type of grid corrosion product obtained from the Pb-Sb-As-Ag alloy, showing the very thick but considerably broken up corrosion product X300



Fig. 9 - The type of grid corrosion product obtained from the Pb-Sb-Sn-Ag alloy, showing a dense and unbroken but rather thin part next to the surface but with the outer portion completely broken up X300

CONCLUSIONS

1. Corrosion of grid alloys is hastened by the growth of the as yet uncorroded metal that still remains. When growth starts, the protective PbO_2 film which is formed by the corrosion process cracks and less protection results.
2. Both corrosion rates and growth data should be measured in screening alloys for full-scale testing in batteries. Such data, properly taken and evaluated, could probably lead to a prediction of life.
3. There appears to be a difference in growth due to the topography of corrosion. The oxide corrosion product of lead appears to exert a stress on the underlying metal and if a large portion of this stress can be directed in a direction perpendicular rather than parallel to the length of the grid members, the corrosion will have little tendency to cause growth.
4. The alloy structure may be designed so as to produce a corrosion with stresses directed perpendicular to the length of the grid members, but this leads to conflict because the alloy structure which results in a favorable topography for growth resistance inherently leads to a higher corrosion rate; on the other hand, the lower corrosion rate associated with smooth corrosion automatically results in poor growth resistance. It becomes a question of obtaining an optimum combination of the two opposing effects.
5. The Pb-Sb-Sn-Ag alloy herein reported offers one solution for combining these two opposing effects.
6. The fact that this first alloy selected on the basis of these considerations should rival one of the better commercially available alloys indicates that this course of investigation should be carried further.

REFERENCES

1. Thomas, U. B., Forster, F. T., and Haring, E. E., Trans. Electrochem. Soc. 92:322 (1947)
2. Lander, J. J., J. Electrochem. Soc. 98:220 (1951)
3. Lander, J. J., and Burbank, J. B., "Positive-Grid Corrosion in the Lead-Acid Cell: Corrosion Rates of Tin Alloys and the Effect of Acid Concentration on Corrosion," NRL Report 4078, November 7, 1952; see also Lander, J. J., "Effect of Corrosion and Growth on the Life of Positive Grids in the Lead-Acid Cell," J. Electrochem. Soc. 99:467 (1952)
4. Burbank, J. B., and Simon, A. C., "The Relation of the Anodic Corrosion of Lead and Lead-Antimony Alloys to Microstructure," J. Electrochem. Soc. 100:11 (1953)
5. Lander, J. J., "Further Studies on the Anodization of Lead in Sulfuric Acid Solution," NRL Report 4475, January 31, 1955
6. "Metals Handbook," Cleveland: American Society for Metals, 1939 edition, p. 1550

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-- 3 - ENTRY CLASSIFICATION: UNCLASSIFIED
-- 5 - CORPORATE AUTHOR: NAVAL RESEARCH LAB WASHINGTON D C
-- 6 - UNCLASSIFIED TITLE: THE EFFECT OF CORROSION AND GROWTH ON THE
-- LIFE OF CYCLING LEAD-ACID CELLS.
-- 8 - TITLE CLASSIFICATION: UNCLASSIFIED
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--11 - REPORT DATE: 19 MAR 1958
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--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--23 - DESCRIPTORS: *STORAGE BATTERIES, CORROSION, LIFE EXPECTANCY
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