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Investigation of the Intergranular Corrosion of Lead-Antimony Grid Alloys

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ABSTRACT

Microscopic examination of grid sections that had been in service for periods up to 10 years indicated that the ultimate cause of grid failure was an intergranular type of stress corrosion. While the overall corrosion resistance indicated the possibility of many additional years of service, this intergranular corrosion at isolated points had in many cases completely severed the grid member. It appeared that this corrosion was caused by a combination of stress developed in the corrosion product and microporosity in the casting. Two distinct corrosion mechanisms were observed. One type depended upon fairly acidic conditions, and the corrosion product was a hard film of lead dioxide which appeared to offer some protection to the underlying metal. The other type was generated where acid concentrations were low and was much more destructive. The corrosion product formed in this case varied from black to white and did not protect the underlying metal.

PROBLEM STATUS

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

AUTHORIZATION

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INVESTIGATION OF THE INTERGRANULAR CORROSION OF LEAD-ANTIMONY GRID ALLOYS

INTRODUCTION

The development at NRL of new methods for the microscopic examination of mixtures of inorganic crystals has been applied to the examination of battery plates in the lead-acid storage battery. Preliminary investigation of such plates has led to the observation that plates made by different manufacturers have quite distinct and different microstructures. Since it appears that the microstructure or crystal morphology in battery plates is directly related to battery performance, it has become customary to examine any plate samples that the manufacturers of batteries care to submit. The morphologies of the active materials of the various plates are then compared with the results of experiments conducted at NRL.

Samples are solicited from battery manufacturers with the understanding that results of the examination of the plates may be used in a published report but that the source of such plates will not be divulged. It is also understood that the plate samples furnished will be used only to further fundamental battery research and not as a basis for individual product evaluation.

The methods used in the examination of plate active materials are also well suited for the study of corrosion in the grid. This report discusses the study of such a corrosion problem encountered in the grids of a number of plate samples obtained from one manufacturer. While the present study is concerned with this one group of plates, the corrosion problem does not concern only this manufacturer. It is believed that this is one of the general corrosion processes that cause grid failure and therefore deserves special consideration.

PROCEDURE

The procedure used in the preparation of these samples is similar to that which has been described elsewhere (1), but a number of refirements have been found necessary to produce samples with the detail shown herein. Very briefly the process consists of impregnating the samples with a low-viscosity polyester containing a catalyst. After hardening and curing, the samples are sectioned and mounted. In the preliminary stages they are prepared in the manner of conventional metallographic specimens, but they are finished by a dry polishing process that develops relief by sensitivity to very small differences in phase reflectivity and hardness. Since no etch is employed, soluble constituents are retained and materials of very different chemical composition can be examined in juxtaposition. Details of this refined process will be published later.

GENERAL OBSERVATIONS

Only a small portion of each of the grids was available for examination. The samples received had been cut out of larger plates on the basis of crack detection made from radiographs of the entire plates. The plates were evidently from an industrial type of battery. The individual plates, based on the dimensions of the radiographs, were approximately 6 by 12 inches in size. The samples were estimated to be 1/4 inch thick. Samples

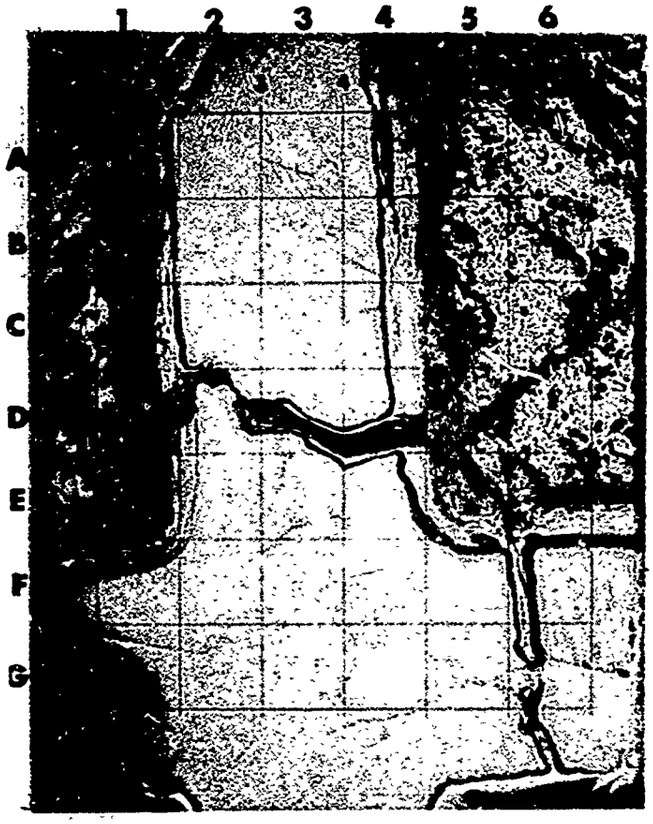

Fig. 1 - A cross section of the junction of two grid members. The photograph shows two major examples of intergranular grid corrosion as found in the 10-year-old battery. A portion of the corrosion layer along the surface of the grid and some of the surrounding active material are also shown. Lines forming the squares are 550 microns apart and the original magnification is 20X.

were obtained from batteries that were 1-1/2, 7, and 10 years old. It is understood that the samples were from batteries that had been on irregular charge-discharge cycles throughout the period of their use.

The samples still retained a large amount of active material at the end of the 10-year period. This was very adherent to the grid and was hard and well retained except at the center of the pellets, where some disintegration appeared to have taken place.

MICROSCOPIC EXAMINATION

Microscopic examination showed that intergranular corrosion was much more extensive than revealed by the radiographs. It was evident that the radiographs could show complete failure as in Fig. 1 but not smaller failures representing much less overall corrosion.

In order to facilitate the identification of certain areas, lines to form squares have been superimposed upon some of the photographs. The line numbers within the first photograph should be disregarded. The numbers and letters in the margin of the picture will be used to designate the area under discussion.

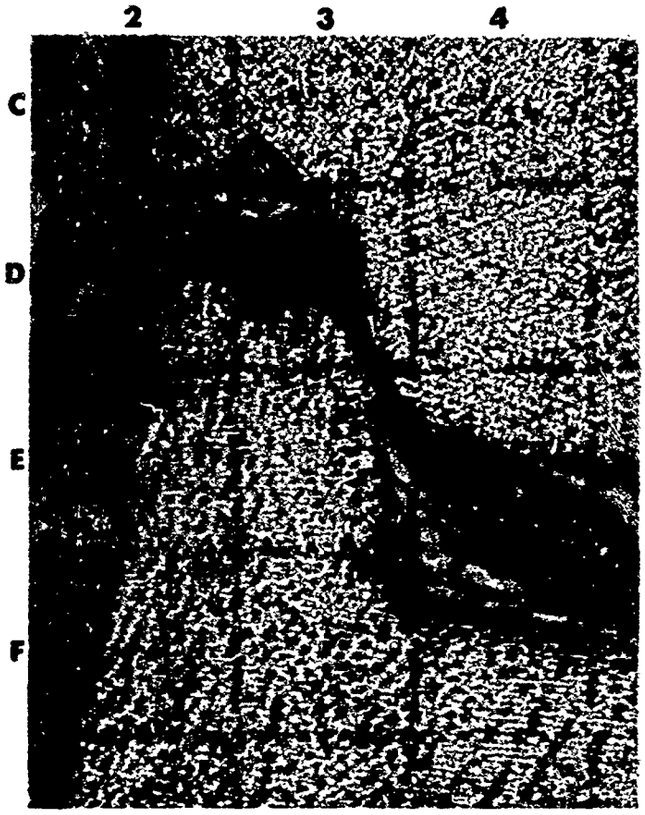

Fig. 2 - A cross section showing an enlargement of D2 of Fig. 1. Note the different microstructure in the grains on each side of the crack, the lateral displacement that occurred during removal of the plate from the cell, and the lack of corrosion product on the metal at the lower edge of the crack in D3 and on the upper edge of the crack in E4. Surface corrosion appears in C2, D2, E2, and F2. Interdendritic corrosion appears near the junction of D3 and E3. Lines forming the squares are 238 microns apart and the original magnification is 100X.

Figure 1 illustrates several features of this intergranular corrosion that should be mentioned. Although not clearly visible at this magnification, all corrosion resulting in cracking proceeded along grain boundaries, often by rather devious paths. This will be illustrated in later photomicrographs. Although intergranular corrosion cracks could initiate at almost any grain boundary intersecting the surface of the grid, the worst cases were always near the junction of two grid members. At the same time only a small portion of all the grain boundaries that intersected the surface, even at such an intersection of two grid members, showed evidence of such a localized attack.

The crack that crosses the grid at D2, D3, and D4 of Fig. 1 has completely severed the grid, and actual separation has occurred, the space between the two sections being filled with the plastic used in the impregnation. The crack itself extends through the grid, the corrosion product at each side of the grid, and into the active material. There have also been lateral and vertical displacements of the two portions of the grid member. It is concluded that the grid sections were displaced after the plate was removed from the cell and dried, and that this caused cracking of the active material. It seems unlikely that the wet active material would exhibit such a clean fracture. Figure 2 is an enlarged view of D2

Fig. 3 - An enlargement of D3 and E3 in Fig. 2. Note the interdendritic corrosion adjoining the crack in areas D3, D4, E3, and E4. Also note the different type of corrosion product in F4 and G4 and the thin layer of still another type of corrosion product adhering to each side of the crack in D3. Lines forming the squares are 60 microns apart and the original magnification is 400X.

in Fig. 1. D2 and D3 of Fig. 2 show corrosion on only one side of the crack, also indicating that the grid segments were displaced after removal of the plate from the cell. Otherwise such an unprotected metal surface would show a definite corrosion layer. A similar condition can be seen in the upper left portion of E4 in Fig. 2.

Investigation of other open cracks involving complete separation of the grid led to the conclusion that all such cracks resulted from stress applied to the weakened grid during or after removal from the cell. It was decided that before removal the grid sections had been joined by the corrosion product in the grain boundary over at least part of the cross section.

Figure 2 shows that the two sections of the grid have been displaced vertically and laterally so that the portion of the crack shown in D3 and E4 has been narrowed somewhat and the areas formerly adjacent are no longer so. This area is shown at somewhat higher magnification in Fig. 3. Casual inspection might suggest that here also there is very little corrosion on either side of the crack. Closer inspection reveals a thin layer of slightly darker material along each side of the crack and parallel bands in D3 and E3 that are longer than the bright particles of antimony in the surrounding metal. Figure 4 represents the same area at

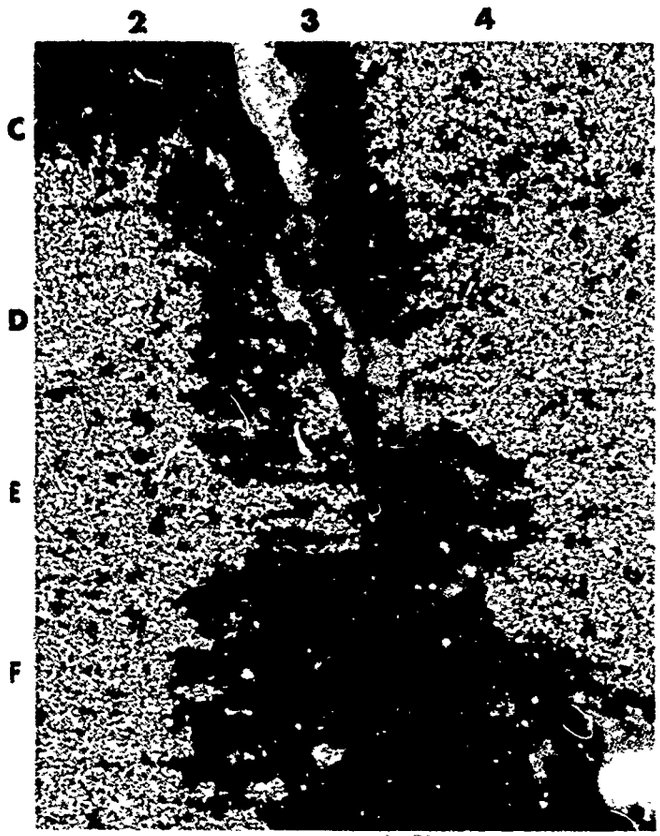

Fig. 4 - Same as Fig. 3 except viewed with polarized light. Lines forming the squares are 60 microns apart and the original magnification is 400X.

the same magnification but illuminated with polarized light. In this picture it can be more clearly seen that extensive lateral corrosion has taken place in a manner that definitely indicates interdendritic corrosion as the dark material in D3, E3, E4, F3, and G3 shows. In addition, comparison of Figs. 3 and 4 reveals that the material along the edge of the crack in F4 and G4 of both photographs differs in appearance from that which occurs in regions of interdendritic corrosion as found in such areas as D3 and E3.

This area of interdendritic corrosion is shown at still higher magnification in Figs. 5 and 6. Figure 5, taken with vertical illumination, shows that antimony particles are still present in the interdendritic corrosion pockets and that the corrosion product at the edge of the crack is quite different from that within the pockets of dendritic corrosion. Although it cannot be seen from this photograph, the corrosion product at the edge of the crack is also different from that found at the surface of the grid and in portions of the crack open to electrolyte flow. Figure 6 shows this area under polarized light. The photograph imperfectly shows detail that is readily apparent with the benefit of color. It can be seen that the crack is open and filled with plastic. At each side is a layer of light gray-appearing material, whereas the corrosion in the interdendritic pockets is much darker and that at the surface of the grid would appear jet black if visible. This gray-appearing material when seen under polarized light is actually an area of very light yellow mixed with red or almost white material and is composed of individual particles that are usually but not always translucent.

Fig. 5 - A magnified view of D3 and E4 in Fig. 3. Note that the bright antimony particles in the interdendritic corrosion product are still present and that they mark the limit of the light-colored corrosion product in G4. Comparison with Figs. 4 and 5 shows that the darker material contains no antimony particles. Lines forming the squares are 30 microns apart and the original magnification is 800X.

Fig. 6 - Same area as Fig. 5 except viewed with polarized light. Compare with Fig. 5 for the extent of interdendritic corrosion. Note that the material along the surface of the crack and the interdendritic corrosion have different appearances. Lines forming the squares are 30 microns apart and the original magnification is 800X.

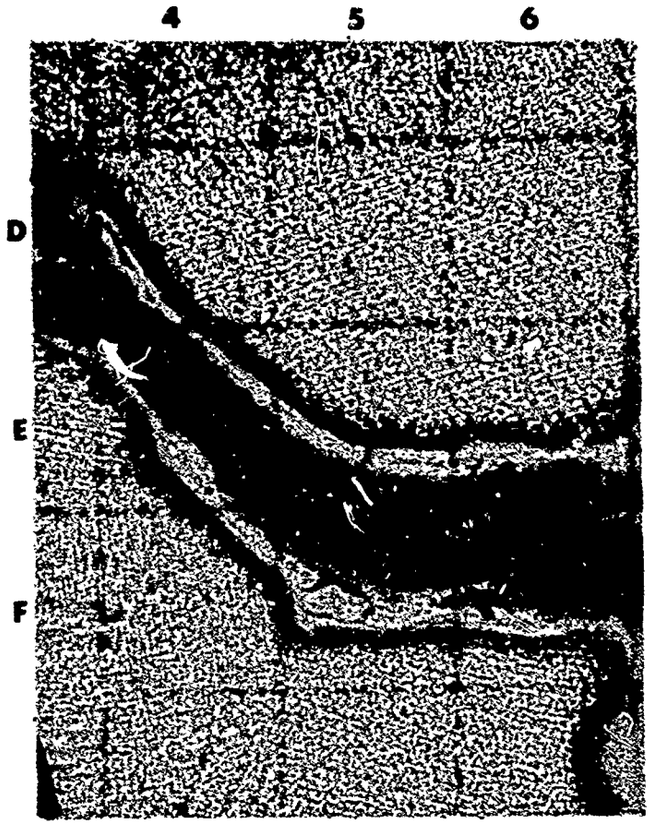

Fig. 7 - Same area as in D3, D4, E3, and E4 of Fig. 1 but at higher magnification. It will be noted that the corrosion here is similar to that at the surface of the grid and that there is no interdendritic corrosion. Lines forming the squares are 238 microns apart and the original magnification is 100X.

From observation of these and other corrosion specimens it was found that the interdendritic type of corrosion with untouched antimony particles and a surface film of sulfate or hydroxide instead of the normal black lead dioxide never occurs near the surface, where there is free access to the acid electrolyte. This will be subsequently illustrated and discussed at greater length, but is mentioned here as evidence that this portion of the boundary between the grains must have been sealed by corrosion product and that the actual break shown could not have taken place during operation.

Figure 7 is an enlargement of the portion of the crack that falls in D4 and partially in D3 of Fig. 1. This portion of the crack shows no penetrating interdendritic corrosion, and the type of corrosion here is similar to that found along the surface of the grid. It is probable that this portion may have actually cracked open during operation.

However, Fig. 8, a somewhat more higher magnified view of the other example of intergranular corrosion at the lower right of Fig. 1, shows that this is not necessarily the case. In this figure the area appears to be entirely filled with corrosion product and there is no indication that the area of intergranular corrosion on the lower side has any internal separation or that the corrosion product is cracked.

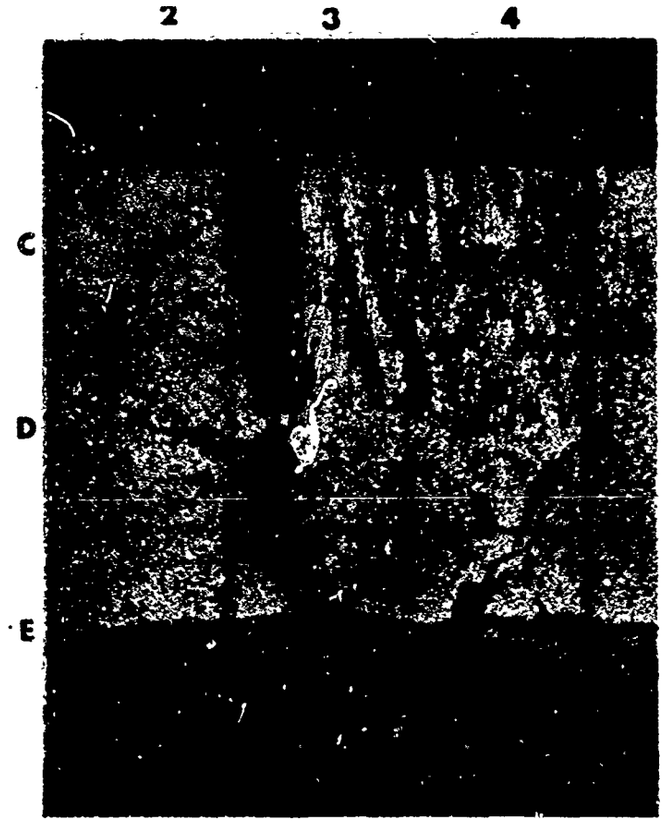

Fig. 8 - A magnified view of F6 and G6 in Fig. 1. The grid has not yet cracked at this point, since the corrosion product at the surface remains intact. Corrosion has proceeded from both sides of the grid along grain boundaries to a near junction at D3, but the long narrow grain in the center does not offer a convenient boundary along which the process can proceed. Lines forming the squares are 476 microns apart and the original magnification is 50X.

Figure 9 shows the portion of the intergranular corrosion that occurs in C3 and D3 of Fig. 8. It can be seen from the surrounding microstructure that the corrosion has definitely followed the grain boundary between the two adjoining grains and has been slowed against the boundary of a grain at right angles to the path of the corrosion. The obstructing grain offers no boundary for extension of the intergranular corrosion except in a direction nearly parallel to the surface. Throughout this study no cracks proceeded very far in a direction nearly parallel to the surface, and this photomicrograph shows no exception.

Figure 10 shows the portion of intergranular corrosion below that of Fig. 9 and represented by D3 and E3 of Fig. 8. Here also the corrosion is proceeding inward along a grain boundary but has also taken a short incursion along another grain boundary across D3 of Fig. 10. At this magnification it may appear that there is also a grain boundary in the upper left-hand quarter of D4 and that corrosion may be proceeding along it to a junction with the corrosion above.

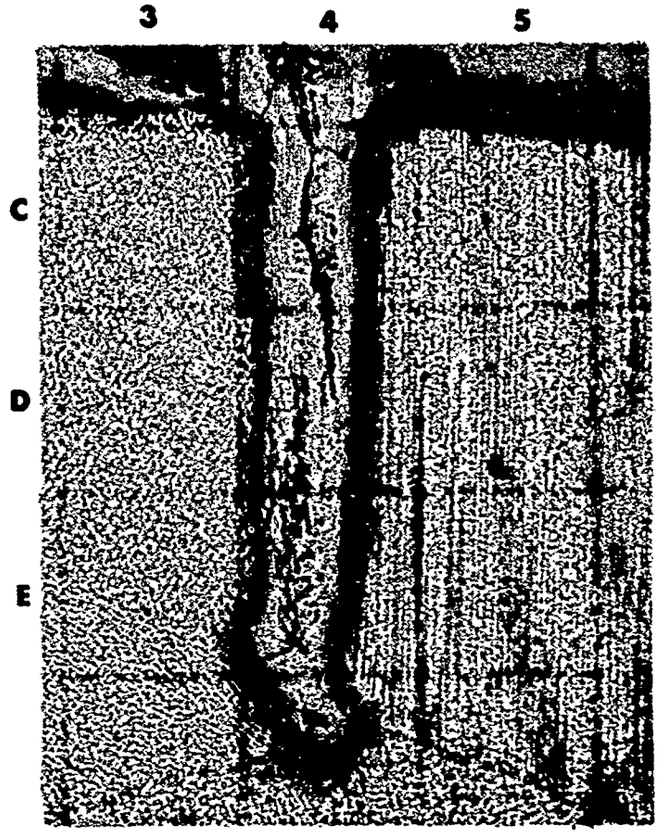

Fig. 9 - The upper portion of the corrosion shown in Fig. 8. The corrosion is intergranular and the grain at the bottom of the photograph has temporarily blocked further extension. Lines forming the squares are 238 microns apart and the original magnification is 100X.

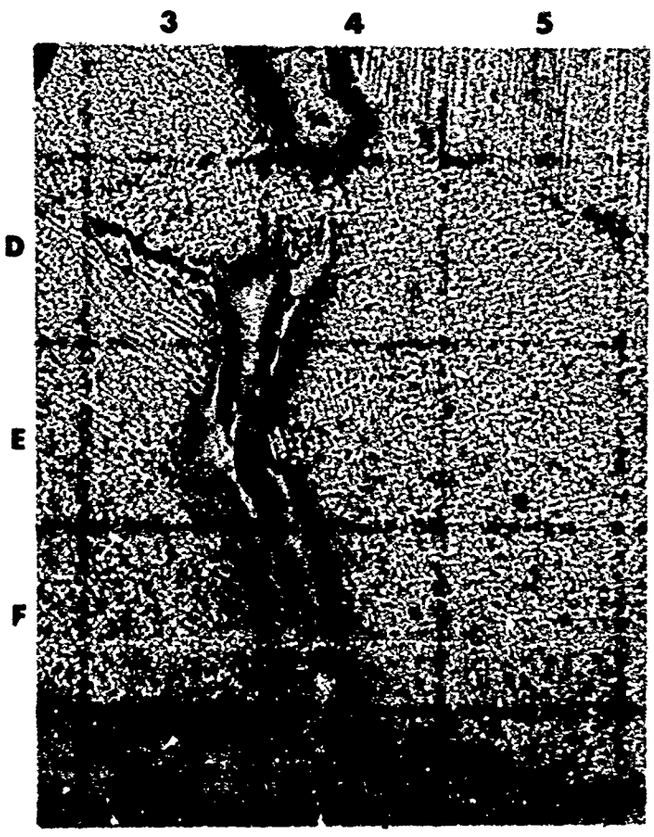

Fig. 10 - The lower portion of the corroded area shown in Fig. 8. Again note the different orientations of the grains bordering the corroded area and the corrosion that has proceeded only a short distance along the grain boundary in D3 that is roughly parallel to the surface. Corrosion has also become interdendritic in several areas. Lines forming the squares are 238 microns apart and the original magnification is 100X.

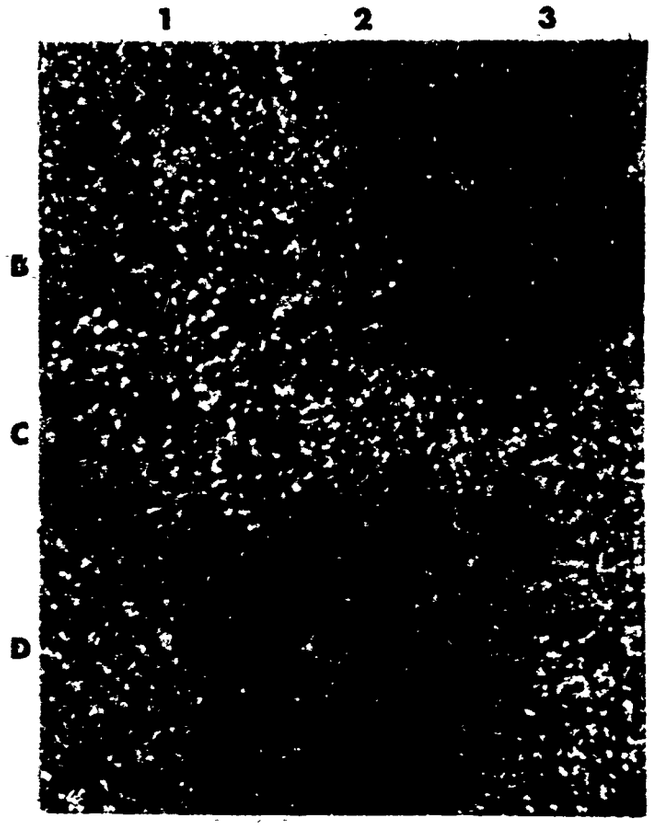

Fig. 11 - A magnified view of D3 and D4 of Fig. 10. Note the interdendritic corrosion that extends from this area and also that the two nearly parallel cracks do not follow interdendritic channels but proceed across them as if directed by stress. Lines forming the squares are 95 microns apart and the original magnification is 250X.

However, a magnified view of this area (Fig. 11) does not indicate the existence of such a boundary, and the fact that corrosion is proceeding toward the upper corroded area along several parallel channels argues against there being one in this area. There is rather extensive interdendritic-type corrosion at the ends of both cracks. Its true extent can be more clearly seen in Fig. 12, which shows the same area as it appears in polarized light. In this cross section it would seem that interdendritic corrosion from the two sides of the obstructing grain may have already merged.

The rather large cracks in the intergranular corrosion of Fig. 10 are somewhat puzzling. Since the corrosion product occupies more volume than the alloy, one would suppose that this space would be completely filled and that the corrosion product would be exerting considerable stress on the surrounding areas. Since no cracks appear in the lower portion nearer to the surface of the grid it is supposed that this portion is exerting pressure that causes the inner portion to crack before it has corroded to the same extent. Notice for example that a quite large crack occurs at the lower right of D3 of Fig. 10, as if the leverage of the corrosion product in F4 might be literally prying out the grain to the left of F4.

Fig. 12 - Same area as shown in Fig. 11 but illuminated with polarized light. Note the extensive interdendritic corrosion and the two large cracks in the lower corrosion product. Lines forming the squares are 95 microns apart and the original magnification is 250X.

The above examples represent extensive intergranular corrosion, and although they may not represent true cracks they will appear so in the radiographs because of the different densities of the material in the corroded area. While the above examples in the 10-year-old specimen were visible in the radiographs, there were many smaller areas of intergranular corrosion that were not.

Figure 13 shows a case where corrosion along each side of the wedge-shaped grain at the surface has caused sufficient internal stress so that an actual crack has formed, farther from the surface. The crack does not extend to the surface along either side of the wedge-shaped grain. Also, corrosion has occurred along both sides of the open crack and there seems to be no positive way of telling whether this happened before or after the crack itself developed. There were also cases in which internal cracking at the grain boundary occurred without evidence of corrosion having preceded it in the area. It appears that the internal stress produced by the corrosion in a portion of the grain boundary forms a wedge that is sufficiently strong to pry apart the boundary ahead of its advance. See for example Fig. 14, which shows such a crack that formed ahead of the corrosion or, in other words, developed in the alloy at a point farther than the corrosion had penetrated. This crack was free of corrosion and showed clean separation along the grain boundary. Its terminus, not visible in the photograph, was at the boundary of a third grain which evidently better resisted the internal stress.

Fig. 13 - An example of interior stress. The wedge-shaped grain to the left of center has developed intergranular corrosion on each side. The increased volume due to corrosion product has resulted in stress cracking at an interior grain boundary (right of center). Original magnification is 100X.

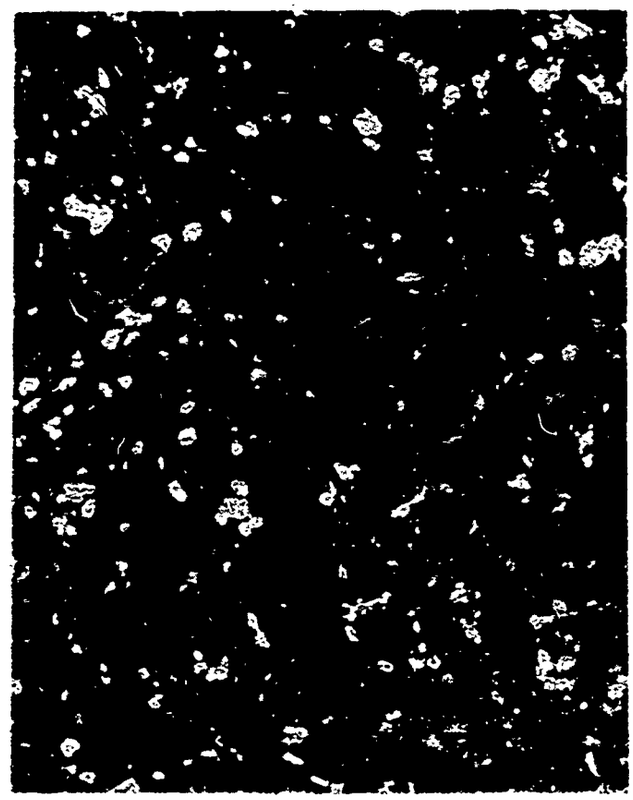

Fig. 14 - An example of interior stress cracking at a grain boundary. No corrosion is present. Lines forming the squares are 30 microns apart and the original magnification is 800X.

Fig. 15 - An example of interior stress cracking at an interdendritic boundary. Here corrosion is present as uniform gray material interspersed with bright antimony particles. The remaining portions of the primary lead dendrites appear as darker, two-toned areas without the bright antimony particles. Microcracks appear along the sides of the areas of primary dendrites. Lines forming the squares are 15 microns apart and the original magnification is 1500X.

It seemed that, if this grain boundary corrosion were able to open up grain boundaries, similar corrosion in the interdendritic spaces of the grain might open up similar cracks. Examination at the highest real magnification of which the microscope was capable indicated that such interdendritic cracks were forming (Fig. 15). At this magnification interpretation becomes difficult because slight changes in elevation between two areas can imitate actual cracks. However, oblique illumination from various angles failed to change the position or appearance of the tiny lines, so it is concluded that they actually represent cracks that may allow the entrance of electrolyte. The existence of such cracks helps to explain the rather catastrophic intergranular corrosion that occurs in such areas.

It should not be assumed from the foregoing that all cases of intergranular corrosion were accompanied by cracking. At the stage at which examination took place there were many examples of intergranular corrosion where no cracking had occurred ahead of the corrosion product. This is shown by Fig. 16, which at fairly high magnification shows no evidence of any crack ahead of the corrosion product or any type of boundary

Fig. 16 - View of a terminus of intergranular corrosion. There is no evidence of any grain boundary defect above the existing corrosion. Note that this corrosion is of the type that leaves the antimony particles undisturbed. Lines forming the squares are 30 microns apart and the original magnification is 800X.

defect. Corrosion had not proceeded very far from the surface, however, and this was generally true where no crack was observed. Based on the limited number of deep cracks available for examination, it can be generally said that whenever the intergranular corrosion had proceeded to a depth exceeding one grain a crack began to open along the grain boundaries ahead of it.

It appears that cracking is propagated by the corrosion product that is formed in the boundary and between dendritic arms. The stresses set up in a sufficient length of intergranular corrosion tend to open up the grain boundary and allow additional corrosion to take place.

The method by which intergranular corrosion begins is perhaps better illustrated in the 7-year-old specimen. Examination of this grid revealed many areas such as that shown in Fig. 17. This corrosion is taking place along the line of junction of B2 and C2 with B3 and C3. Here there is no evidence of a crack either in the metal or in the corrosion product. The corrosion product formed along the grain boundary between the two adjacent grains evidently differs from that formed along the surface of the grid. Examination of the termination point of the corrosion in such an attacked grain boundary did not reveal any visible crack, and the grain boundary here appears no different from those that were not attacked (Fig. 16).

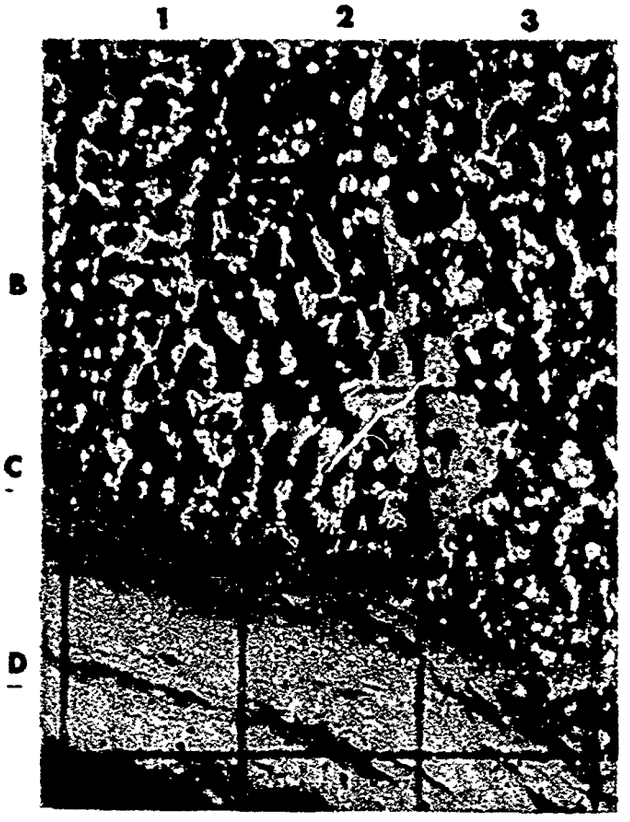

Fig. 17 - Typical beginning of grain boundary corrosion in a 7-year-old battery. The surface layer of corrosion is thick and dense. Lines forming the squares are 60 microns apart and the original magnification is 400X.

One feature of grain boundary corrosion that was invariably noticed was the presence of unattacked antimony particles in the corrosion product. This was always the case in areas of interdendritic corrosion, where penetration was deep and at times present as an inner layer under a thick and protective corrosion product at the grid surface. This is taken to indicate that acid concentration must be very low in such areas. This phenomenon is illustrated more clearly in Fig. 18, which shows the relationship between dendritic structure, segregated antimony particles, and the corrosion product.

Figure 17 also shows that an elementary type of interdendritic corrosion takes place all along the grid surface underneath the corrosion layer and that here too there is a narrow zone where corrosion and antimony particles coexist.

Figure 19 shows another example of grain boundary corrosion in which the penetration and the interdendritic penetration along the boundary are much deeper than in Fig. 17, although there is still no visible cracking. There is also evidence of interdendritic corrosion along the surface of the grid beneath the layer of corrosion product. However, although interdendritic alignment along the metal surface above the crack is the same as at the intergranular boundary, nowhere along the metal surface is there any such penetrating type of attack as that which occurs in the vicinity of the grain boundary. This can also be seen in Fig. 20, a view of the same area by polarized light. Near the surface

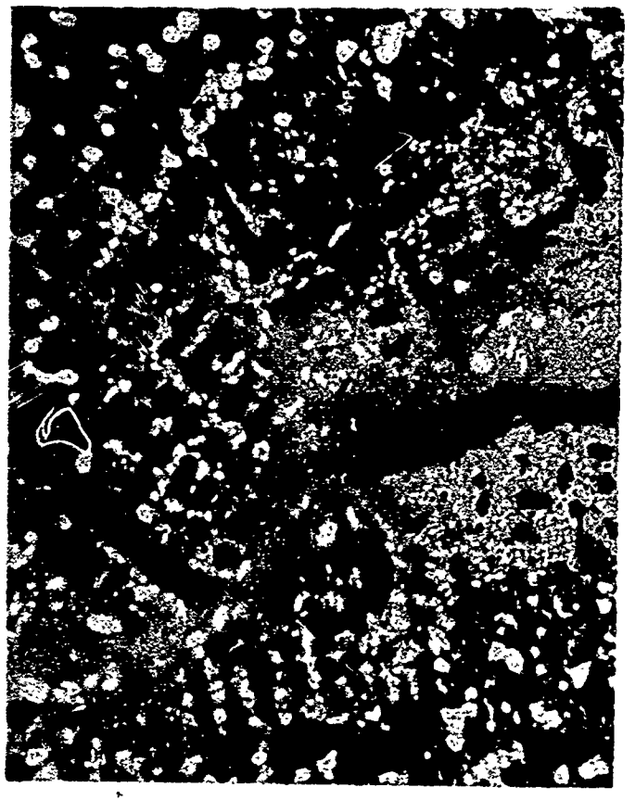

Fig. 18 - Typical interdendritic corrosion, proceeding nearly at right angles to the grain boundary that crosses the photograph near the center. The particles of undissolved antimony remain undisturbed where they were precipitated during freezing. Note the crack that has developed here a considerable distance within the metal. Original magnification is 800X.

Fig. 19 - Example of an unusually extensive intergranular corrosion in the 7-year-old battery. Even with extensive interdendritic corrosion and consequent increase in volume in this area there has been no actual cracking. The interdendritic corrosion extends much farther between the primary dendrites adjacent to the grain boundary than at the metal surface, although the dendritic branches are all part of the same grain. Original magnification is 250X.

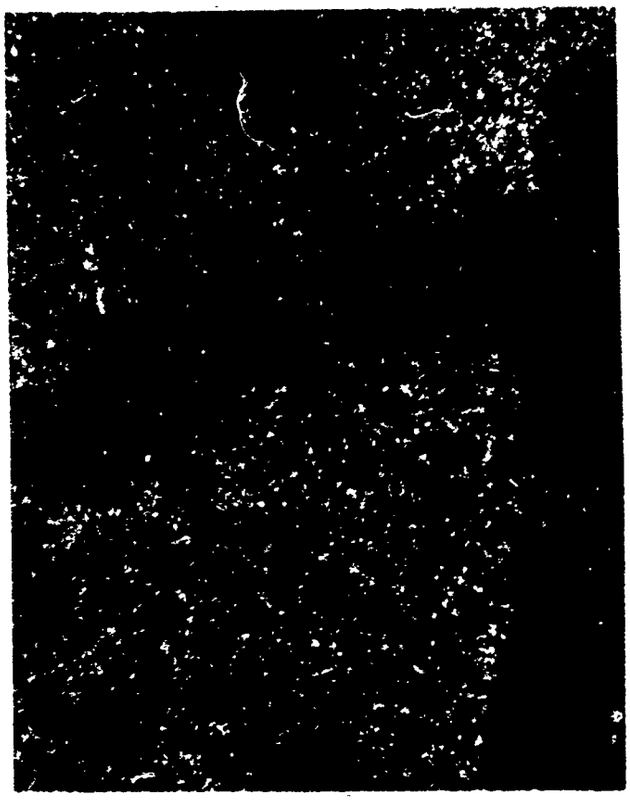

Fig. 20 - A view in polarized light of the same area as Fig. 19. The extensive nature of the interdendritic corrosion can be clearly seen. The darker line bisecting the interdendritic corrosion marks the position of the grain boundary with its included intergranular corrosion. Original magnification is 250X.

the corroded area appears to widen out somewhat, which may indicate that grain boundary separation may have already begun although is not yet visible as a crack.

DISCUSSION

There is no doubt that the type of corrosion described is occurring at grain boundaries. The problem is explaining why it begins there rather than at other points.

First there is the possibility that the grain boundaries are the source of a more easily corroded impurity or that microporosity may occur there during metal freezing. It is also possible that stress is being set up in the alloy and this is causing stress corrosion at grain boundaries. This stress could be the result of stresses set up in the corrosion layer at the surface of the grid if the corrosion product were sufficiently adherent to the grid. On the other hand it might be the result of stresses set up in the active material if its particles were sufficiently cohesive.

Any of these possibilities could be a factor in the present case. The alloy evidently had a fairly high antimony content and therefore segregation and shrinkage would be very probable. However, the portions of the castings available for examination appeared to be in remarkably good condition, and there was no evidence of dross inclusions or

microporosity. Moreover, the tendency for this corrosion to take place mostly along grains with their boundaries aligned nearly perpendicular to the surface and avoid boundaries more nearly parallel to the surface indicates some type of stress mechanism.

The condition of the corrosion product along the surface of the grid was unusually good when the length of service is considered. Not only was the total cross section of corrosion surprisingly small, but the corrosion product formed a layer that was very little cracked or broken and it showed no tendency to crack away from the surface of the grid. This may have been due in part to the hard, adherent, and very dense active material.

It seemed that if the active material were causing the stress the corrosion product should also crack at the site of any cracks in the metal, whereas if the corrosion product were responsible only the metal should crack. If the metal, corrosion product, and active material all crack as a unit, then stress must either be externally applied or occur in the metal itself.

Structure of the Metal in Relation to Microporosity

The size and configuration of the grains in the alloy were uniform and they appeared to have no tendency to form columnar grains. From the subgrain structure it was evident that the dendritic growth forming the skeleton of the grain consisted of many parallel arms or filaments that were remarkably straight. This type of growth indicated a considerable degree of initial supercooling and tended to form relatively pure primary dendrites (the dark structure) with a high concentration of impurity (in this case antimony or a solid solution of antimony) distributed along the length of the primary lead dendrites. These parallel bands of precipitated antimony (the bright particles) outline the primary dendritic structure in the grain and indicate the different orientations of adjacent grains.

Figures 3, 14, 16, and 17 illustrate the relative widths of the primary dendrites (dark gray portions) in relation to the zone of impurity or eutectic (the area containing the bright shiny particles) and show that these precipitated particles are confined to a relatively narrow strip between considerably wider adjacent primary dendritic branches. It is cautioned that these photomicrographs are cross sections and it should be borne in mind that the primary dendrite branches are really parallel, nearly cylindrical bodies and are completely surrounded by a thin shell of the zone containing the bright particles of antimony. If a narrow zone of precipitated particles is left between adjacent dendritic arms of the primary growth, then a similar strip should be left between the advancing arms of dendrites growing from different nuclei or, in other words, at the grain boundary. Generally this was true and a line of such particles was distributed along the grain boundary.

The nature of the primary dendritic structure reveals that considerable supercooling took place before the nucleation of lead crystals began. Hence, once nucleated they grew rapidly with a pronounced dendritic structure until supercooling was relieved. The remaining material was rich in antimony and contained any other impurities as well and was undoubtedly the last to freeze. In other words, at some stage during the total freezing interval this antimony-rich material formed a still-molten layer between the already-solid primary dendritic branches of individual crystals and in the space where individual crystals contacted one another (the grain boundary). But this remaining liquid is confined in the spaces between the already-solid primary crystals and when it finally freezes it must undergo a volume reduction in passing from liquid to solid.

It is a well-known phenomenon that when lead alloys freeze in very thin layers the primary dendritic structure is starkly revealed because of shrinkage in the last portion

to freeze. It is evident that a considerable volume change has occurred, and if this were maintained at the same proportion in thicker sections, there would be very deep cavities at the surface. The fact that this is usually not the case indicates that there must be a great deal of microporosity in the interior of the casting.

If the remaining liquid, which is primarily of eutectic composition, freezes almost simultaneously throughout the system, then microporosity will exist everywhere in this layer. It seems more likely, however, that there will be inequalities in the temperature at various points and that portions of the eutectic will begin to freeze while other parts are still molten. In this case the still-molten portions will tend to feed toward the solidifying portion and the voids will be located at intermediate points.

It could be that freezing of the last portion begins at or near the center of the existing grains, in which case the porous portion would be at the grain boundary and in that part of the dendritic channels in the grains that was next to the grain boundaries. There is some evidence to support this, since it has been noted that interdendritic corrosion that occurs in the material between the primary dendrites of the grain (Fig. 18) proceeds into the grain for a uniform distance from the grain boundary and then appears to stop, even when the crack between grains has proceeded much farther into the interior. This uniform width of the corrosion product along the boundary of any two adjacent grains might be attributed to microporosity caused by withdrawal of low-melting-point material from the grain boundary and from a distance within the channels of the grain consistent with the volume change involved. On the other hand it might result from the protective action of a definite thickness of corrosion product. However, while the thickness was uniform along the boundary of any two adjacent grains it varied at other adjointing grains, indicating that the first assumption might be more correct. This is further supported by the fact that the most probable area for crack formation appears to be very near the point at which large and small grid members cross or at the intersection of horizontal and vertical grid members. At this point the larger mass of metal might well result in slower cooling, with consequent greater metal withdrawal into the interior of the grains and away from grain boundaries.

The possibility of impurities as a cause of this corrosion should also not be overlooked. Although there was no evidence of solid phase impurities it is always possible that very small amounts could have a pronounced effect on the corrosion rate. As a result of the rapid growth of primary dendrites, a zone refinement effect is created that tends to concentrate all impurities at the primary dendritic or grain boundaries. There is also the possibility that precipitation of antimony from the supersaturated solid solution might result in internal stresses or minimal cracks.

Consideration of the Possibility of Stress Corrosion

Examination of the available number of pronounced and incipient cracks led to the observation that all grain boundary corrosion in this metal proceeded at nearly right angles to the metal surface. Cracks or corrosion that proceeded in other directions were never observed to have made much progress. While it might be argued that this was the result of preferential shrinkage or microporosity it seems more logical to attribute it to stress operating parallel to the surface of the metal.

As mentioned previously, stresses generated within the active material would cause rupture at both the grain boundary and surface corrosion product. For this reason a very detailed study was made of the few cracks that showed such ruptures. Figure 1 shows one of these cracks. From the fact that bare, uncorroded metal was always visible at one or more points along such cracks, it was concluded that cracks that extended through the corrosion product and into the active material had been extended during or after removal from the cell and that cracking was only observed where corrosion had proceeded

entirely through the grid member with consequent loss of support. It was therefore decided that this corrosion cracking was not a result of stress applied by the active material.

Distinguishing between stress generated within the metal and that generated in the corrosion layer at the surface of the grid was not so easy. Examination of the various available samples indicated that the type of corrosion under discussion had not begun at 1-1/2-year service but was far advanced after 7 years.

With no intermediate samples it is difficult to estimate when this intergranular corrosion would begin to be a problem. Judging from the appearance of the present samples it possibly could appear in the relatively short-lived automobile battery but would probably not be a major cause of failure. In any battery with more than 5 years of service life it could be considered a very important factor. This estimate would no doubt be invalid for other alloy compositions or for grids with different size grains.

Study of the 7-year-old battery indicated a large number of sites where intergranular corrosion was beginning (Fig. 17). A few such sites were characterized by much deeper penetration but no actual crack (Fig. 19). As has been mentioned, this type of grain boundary penetration was characteristically accompanied by small unattacked antimony particles (Fig. 18). The corrosion product also differed in appearance from the surface layer of corrosion (Figs. 3 and 4). In the usual anodic corrosion process antimony vanishes from the surface layer of metal with great rapidity and continues to vanish from each succeeding corroded layer as the corrosion product becomes thicker. In this way a very thick corrosion layer that is dense black when viewed by polarized light and contains no antimony particles can be built up. It has been observed, however, that when the corrosion layer is unusually thick or contains very few cracks a point is reached where corrosion and antimony particles exist together and a very mild interdendritic attack occurs all along the metal surface. In this region antimony particles will be found surrounded by areas of corrosion. As judged by the difference in relief level, this is also a softer material than the outer layers of corrosion.

A similar type of corrosion in which antimony particles are not attacked proceeds inward from the surface of slowly dried but unformed plates. Here the attack is strictly chemical and results from the alkaline nature of the paste (Fig. 21). It will be noted that the individual bright antimony particles are left in their original positions, unattacked by the alkali. However, Fig. 22 (illuminated with polarized light) indicates that the corrosion product is translucent and certainly not an oxide, and its appearance in both photographs differs greatly from the product of the intergranular corrosion under discussion. It is believed that this case also indicates a reduced acidity and that under this circumstance and anodic attack the process becomes very selective for grain boundary and interdendritic attack of the lead solid solution and less destructive to the antimony particles.

In addition, the surface corrosion product becomes even more firmly attached to the metal surface by a mild type of interdendritic corrosion occurring all along the surface. This along with the internal expansion of the surface corrosion layer caused by the ever-increasing volume as lead is converted to lead dioxide will also increase the strain at grain boundaries and help initiate a selective attack.

Once this attack is initiated, the tendency for it to become catastrophic at deep-seated locations tends to produce an additional wedge effect. This effect continues to supply stress internally and aids that being applied by the surface layer of corrosion.

It is also very likely that this entire process occurring at the grain boundary and adjoining interdendritic sites is abetted by the microporosity that undoubtedly must be present in these areas as the result of shrinkage during freezing.

Fig. 21 - An example of the corrosion found on the surface of grids in unformed positive plates. Here the antimony particles are left undisturbed even at the surface, so that a line of antimony particles outlines the original surface as well as the dendritic boundaries. When formation begins these antimony particles will disappear and the corroded portion will be converted to PbO_2. Original magnification is 1600X.

Fig. 22 - Same area as Fig. 21 but illuminated by polarized light. In this case the corrosion product is translucent. Note the odd striated structure of the corrosion product here and in Fig. 21. Original magnification is 1600X.

If the internal stress becomes great enough, it causes cracking of the surface layer of corrosion and may even exert sufficient stress to crack the active material. Electrolyte of higher acidity flowing into this open channel soon converts the interdendritic area of corrosion originally present into a continuous, antimony-free corrosion product of the same type as found on the surface (Fig. 7).

SUMMARY

In summary it can be said that this type of corrosion is intergranular or grain boundary. It does not seem to be produced by growth or expansion of the active material and does not start from visible cracks. It appears first as a definite, specialized type of corrosion at grain boundaries that may be the result of interdendritic shrinkage and microporosity and that is doubtless aggravated by tension set up within the surface corrosion layer. Once initiated, its growth is abetted by the internal stresses set up in the grain boundary by the increasing volume of corrosion product within the boundary.

The only apparent means of avoiding this type of problem would be to add some process of cold work and subsequent annealing to the alloy so that recrystallization and grain boundary migration would occur. Admittedly, this does not seem to be an economically feasible solution. Possibly a casting process involving considerable grain refinement would be helpful, since the fairly large grains in these castings offered an almost straight boundary path across the grid member in many cases.

A final word concerning the active material might be added. As said previously, this material was very dense and hard and from its appearance and performance the author was inclined to think it might contain the reticulate structure that has been the subject of previous reports of this series (2,3). Microscopic examination failed to reveal any such structure, however. X-ray analysis at NRL conducted by Mrs. Jeanne Burbank disclosed that α-PbO_2 was present but not in large quantity. In intermittent charge-discharge operation this active material showed excellent retention. It would be extremely interesting to determine its behavior under float conditions.

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The author would like to acknowledge the source of the samples used in this investigation, but circumstances do not permit this. Instead, the spirit of cooperation and willingness to exchange information that the author has met throughout the battery industry must be acknowledged. It is hoped that this increasing cooperation within the industry will help fortify it against the evermore urgent demands of a rapidly advancing technology.

This report is dedicated to those individuals who furnished the samples used in this investigation with the hope that it will aid them somewhat in the solution of their problems.

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13 ABSTRACT

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