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THE EFFECT OF AGEING ON THE ANODIC CORROSION OF Pb–Sb ALLOYS

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Summary

Information on the changes that may be expected in the corrosion resistance of battery grids of Pb–4% Sb and Pb–6% Sb alloys as a function of time is provided.

The influence of ageing time (at 20 °C) upon the corrosion weight losses is accounted for by the microstructural changes that take place in the alloys. These changes refer to both the precipitation of fine beta-phase particles in the alpha matrix (post-solidification precipitate) and the spheroidization of the relatively coarse beta-phase particles segregated during solidification. The cooling rate of grids during casting may affect greatly their ageing behaviour.

Introduction

The effects of lead alloy composition and cast structure on the anodic corrosion of lead alloys have been discussed in previous papers [1, 2]. However, since we are concerned with ageable alloys, where certain properties undergo considerable changes upon the passage of time, it is reasonable to think that corrosion may also be affected by the ageing process.

An attempt is made in this paper to reveal the nature and magnitude of the ageing effects on the anodic corrosion of cast grids of Pb–Sb alloys, under conditions which simulate those of lead–acid batteries.

Experimental

The research is confined to two binary alloys containing 4% and 6% Sb, which are representative of the current trends in antimonial lead used for the manufacture of battery grids.

Cooling rates during alloy solidification and in the immediately following stages must logically influence the amount of constituent which remains in solution and can later precipitate on ageing at room temperature. For this reason the corrosion tests have been made on grids slowly-

TABLE 1

Solidification and cooling conditions during the casting of Pb—4% Sb and Pb—6% Sb grids in an anodized aluminium mould.

Cooling condition	Time elapsed from pouring to completion of solidification (s)	Cooling rate of the solidified alloy			
		Average values within the following temperature intervals:			
		251° - 200°C	200° - 150°C	150° - 100°C	100° - 50°C
Fast cooling	8	50 - 53 °C/s	19 - 20 °C/s	6.8 - 7.2 °C/s	1.4 °C/s
Slow cooling	180 - 315	0.081 - 0.094 °C/s	6.0 °C/s*	3.2 °C/s*	1.2 °C/s*

*Slowly cooled grids are withdrawn from the mould at 200 °C and then allowed to air-cool.
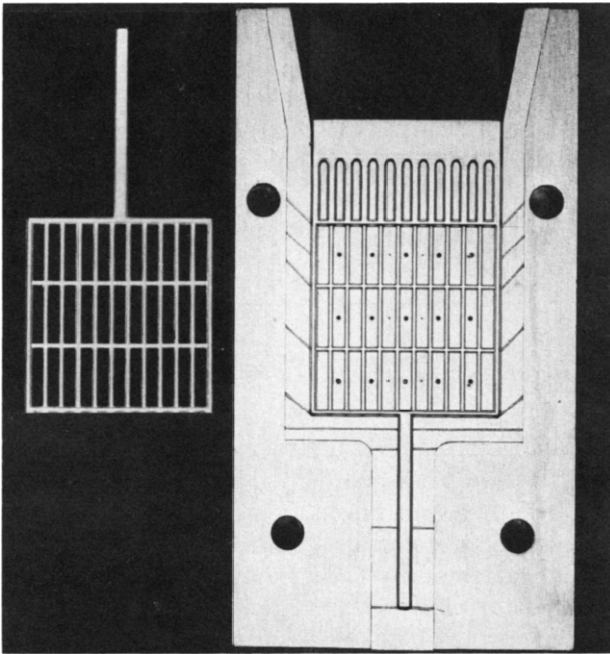

Fig. 1. View of one of the halves of the permanent aluminium mould used for casting the grids. On the left, the experimental grid.

cooled (condition A) and rapidly-cooled (condition B) during casting, considering that the majority of practical cases are to be found between these two extreme conditions.

Under condition A the cast grid was left to cool off inside the air-exposed mould while under condition B the mould with the grid inside was immersed into cold water immediately after pouring. In a few tests the terminals of a thermocouple were provided inside the mould cavity and connected to a graphic recorder. As Table 1 shows, there is a con-

siderable change in cooling rates depending on the experimental procedure adopted.

A relatively small mould was used (Fig. 1). It consisted of two aluminium plates of dimensions 170 × 90 × 25 mm, which after having the grid pattern cut on them were anodized in dilute sulphuric acid until an 80 μm thick oxide coating was obtained. The main advantage of this mould is that the permanent coating of Al_2O_3 exhibits constant insulating properties throughout the successive melts. Fig. 1 (left) shows the 1.5 mm thick grid produced by the mould.

Bare (unpasted) grids and pasted grids were subjected to anodic corrosion in sulphuric acid of 1.250 sp. gr. at 20 °C, the pasted ones to reproduce more faithfully the conditions encountered in lead–acid batteries and to obtain additional information on the effect of paste on alloy stability. Paste formulation was 90 g Barton oxide, 14 g red lead, 14 ml distilled water and 10 ml sulphuric acid of 1.380 sp. gr. A current density of 0.84 mA/cm^2 (33 mA for the 39 cm^2 of total surface area of the ensemble of small bars which integrate the grid) was applied for 56 days in the case of the bare grids and for 100 days in the case of the pasted ones (slowness of anodic attack motivates these long periods).

In the pasted grids a small amount of current was used to convert the PbO and Pb of the paste into PbO_2. The current consumed by this process may be estimated at around 4% of the total current applied to the grid during test. At the end of a few hours' testing the grid potential had already attained values corresponding to the PbO_2 electrode.

After completion of the corrosion tests the grids were rinsed in tap water. In the case of pasted grids the major part of the paste adhering to the metal was removed by simple mechanical action. All the grids were finally subjected to a boiling solution of 50 g/l mannitol, 60 g/l sodium hydroxide and 0.62 g/l hydrazine sulphate, which dissolves the PbO_2 without attacking the metal, and then cleaned, dried and weighed.

The samples for internal structure observation were cold mounted in a castable resin, the amount of hardener being regulated so that curing would take place slowly and without an appreciable rise in temperature. They were then ground and mechanically polished and etched with a reagent made up of 10 g of ammonium molybdate, 25 g of citric acid, 1 ml of nitric acid and 100 ml of water.

Ageing conditions

Nearly one-third of the grids were subjected to corrosion testing immediately upon casting and the remainder stored in an isothermal chamber at 20 °C to be tested later on at the end of 4 and 8 months. Thus the study takes into consideration: (a) non-aged grids; (b) 4 months aged grids; (c) 8 months aged grids.

It should be borne in mind that these conditions refer to ageing of grids at the start of the corrosion test. However, as ageing continues throughout the entire duration of the anodic test (56 or 100 days), progressive ageing
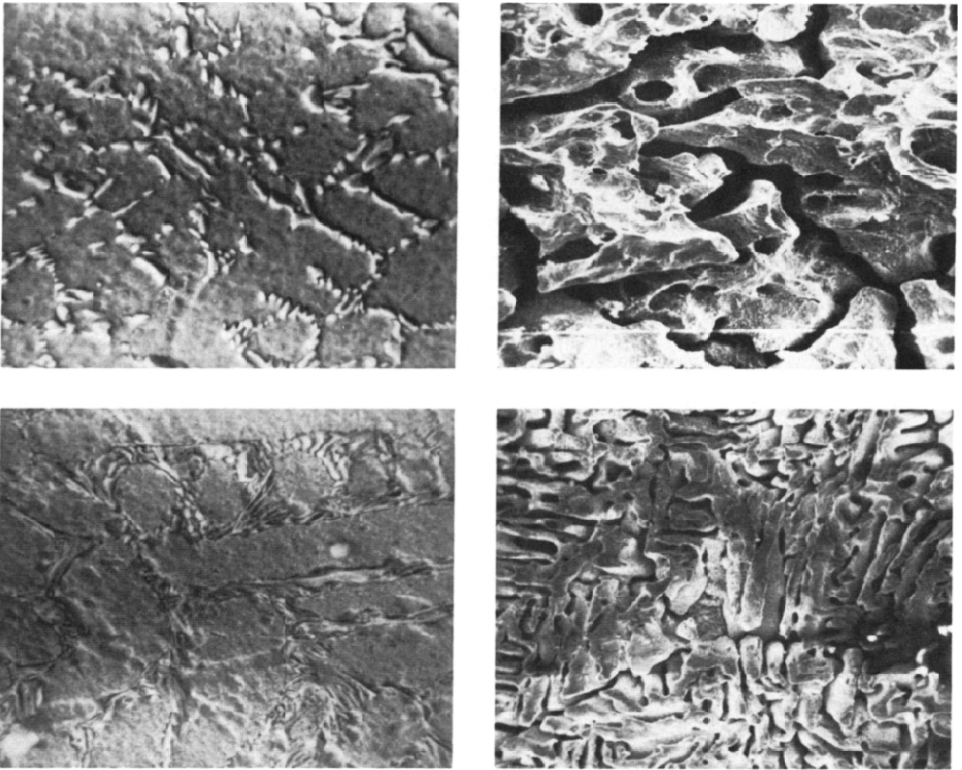
Fig. 2. (left) SEM micrographs of the internal structure of non-aged Pb–6% Sb grids. Typical example of the influcence of casting cooling rate on the structure of the grid. Upper: slowly-cooled; lower: rapidly-cooled. Magnification × 1000.

Fig. 3. (right) SEM micrographs of the external surface of non-aged Pb–4% Sb alloy after being subjected (unpasted) to anodic action. Upper: slowly-cooled; lower: rapidly-cooled. Magnification × 200.

conditions are to be added to those at the beginning. In spite of this, and only to simplify matters, we shall continue to refer in this paper to the corrosion undergone by grids after 0, 4 and 8 months' ageing.

Results

The metallographic structure of cast Pb–4% Sb and Pb–6% Sb alloys changes noticeably with cooling rate as revealed in Fig. 2.

Figure 3 shows the effect of cooling rate on anodic corrosion morphology. Evidently, the alpha-phase dendrites, which the attack leaves in relief, are finer in the grids that have been rapidly cooled during casting.

Figure 4 illustrates the changes produced in the metallographic structure with ageing time. These changes bear relation both to the shape of the
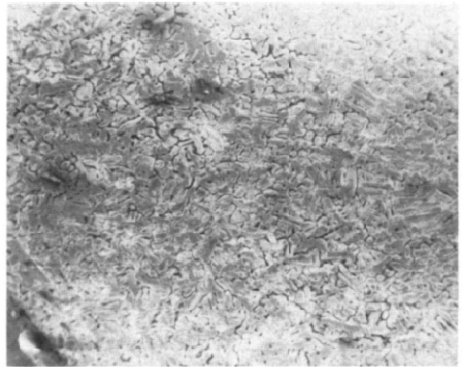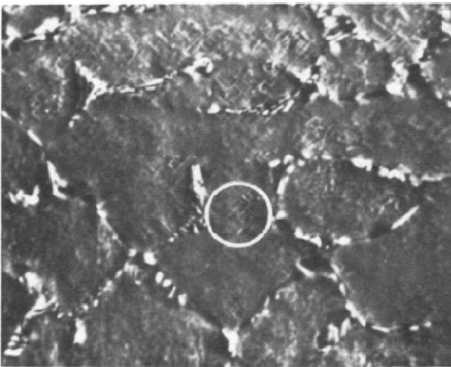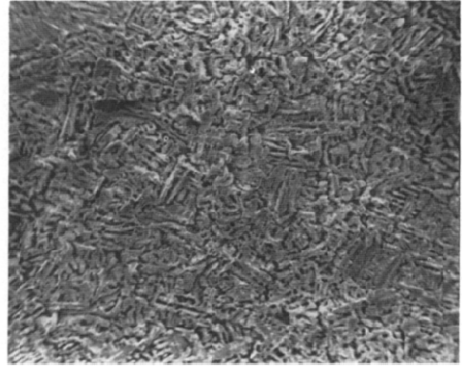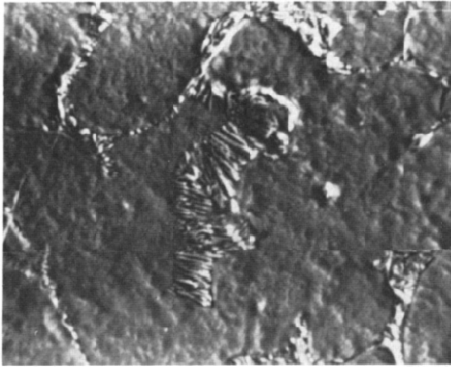
Fig. 4. (left) SEM micrographs showing the influence of ageing on the internal structure of rapidly cooled grids of Pb—4% Sb alloy. Upper: non-aged; lower: 8 months aged. Magnification × 1000.

Fig. 5. (right) SEM micrographs showing the influence of ageing on the morphology of the anodic attack in the case of rapidly cooled grids of Pb—6% Sb alloy, tested unpasted. Upper: non-aged; lower: 4 months aged. Magnification × 75.

interdendritic particles of eutectic beta phase and to the precipitation of elongated fine particles of post-eutectic beta phase within the alpha-phase matrix. Although with some difficulty, such particles can be seen in the photomicrograph for 8 months' ageing (*e.g.* within the circle drawn in it). They are the result of an over-ageing phenomenon, which has been verified by microhardness and electrical resistance measurements [3]. As can be seen from Fig. 5, the interdendritic attack appears to be more marked in the non-aged grids than in the aged ones.

Figure 6 shows the effect of paste on the anodic corrosion of Pb—Sb alloy grids. A more uniform attack of the pasted grids is observed as compared with those tested in the bare condition; it is as if the Pb-rich matrix maintained its integrity better under the paste covering.

Figures 7 and 8 summarize the experimental results on anodic corrosion for the two alloys and the various experimental conditions considered. The
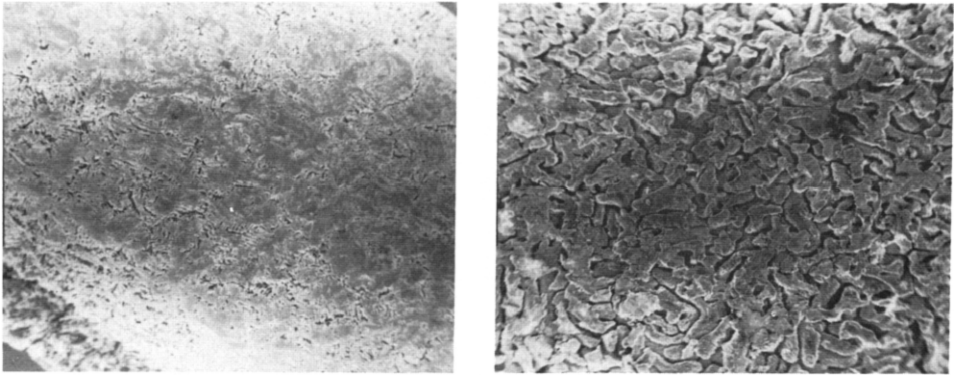
Fig. 6. SEM micrographs showing the influence of "paste" on the morphology of the anodic attack in the case of non-aged grids of Pb—6% Sb alloy. Right: tested unpasted; left: tested in pasted condition. Magnification × 75.
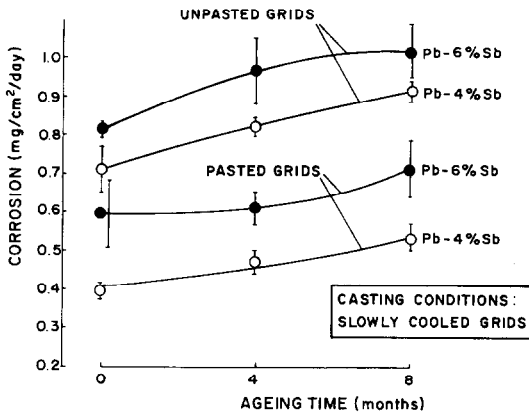

Fig. 7. Corrosion rates of slowly cooled grids of Pb—4% Sb and Pb—6% Sb alloys after being aged for various periods of time at 20 °C.
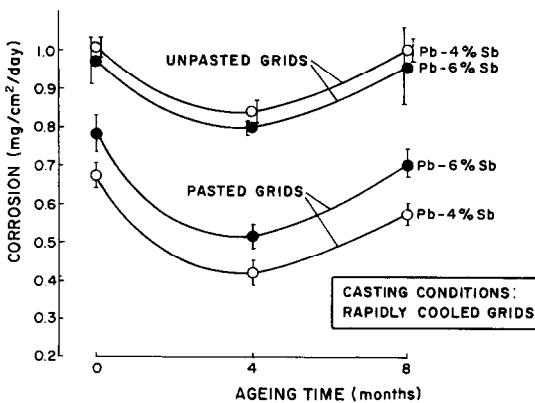

Fig. 8. Corrosion rates of rapidly-cooled grids of Pb—4% Sb and Pb—6% Sb alloys after being aged for various periods of time at 20 °C.

tests have been carried out in sextuplicate. The variation limits for a 95% level of confidence are indicated at each point. Oddly, the scatter is considerably less for the 4% Sb than for the 6% Sb alloy. As can be seen, ageing promotes an increase in corrosion susceptibility of the slowly cooled grids. In the case of the rapidly cooled ones, the corrosion rate at the end of 8 months is comparable to that of the grids tested immediately after casting but 20 - 35% higher than that measured after 4 months' ageing; that is, the corrosion rate passes through a minimum at an intermediate ageing.

After 4 months' ageing the rapidly cooled grids are somewhat less attacked during the anodic test than the slowly cooled ones, whereas their behaviour just after casting is the opposite. For longer ageing times the type of cooling undergone by the grid during casting seems to lose significance insofar as corrosion losses are concerned.

As Figs. 7 and 8 show, the anodic corrosion rate of pasted grids decreases considerably with regard to that of unpasted (bare) grids. The ageing effect on corrosion is more marked comparatively with the pasted grids than with the grids directly exposed to the electrolyte (Figs. 7 and 8).

Discussion

Structure of Pb–Sb alloys and mode of attack

When the temperature of the liquid hypoeutectic Pb–4% Sb and Pb–6% Sb alloys is lowered to the liquidus line, solidification begins, and the first solid to form is the alpha (Pb-rich) phase. Primary solidification progresses dendritically. Once the eutectic temperature is reached the beta (Sb-rich) phase starts then to solidify; at this moment the alpha- and beta-phases solidify simultaneously filling the remaining spaces between the primary dendrites. In the grids cast under rapid cooling conditions the eutectic structure consists of alpha- and beta-lamellae. In the slowly cooled grids the eutectic beta phase particles acquire relatively spheroidal shapes between the thick alpha-phase dendritic branches.

Mao *et al.* [4] have shown that the acicular shape of the eutectic beta phase present in the as-cast Pb–4.5% Sb alloy changes towards globular forms during ageing at room temperature. A similar behaviour has been observed in this research with the Pb–4% Sb and Pb–6% alloys cast under rapid cooling conditions; the eutectic structure becomes disarranged with time giving rise to a discontinuous distribution of partially globulized particles along the interdendritic boundaries. This structure is similar to a certain extent to that of the slowly cooled alloy.

The low solubility of $PbSO_4$ and the fact that during anodic passivation the sulphate is transformed into PbO_2, even more insoluble, account for the very slow anodic attack of lead in sulphuric acid. Conversely, the high solubility of the antimony corrosion products and the absence of passivation favour the attack of this metal. According to a recent study [5, 6], where composite specimens made up of Sb lamellae embedded in a Pb matrix

were tested, anodic action at 0.84 mA/cm^2 dissolves the Sb at a rate of 2.8 μm/day while the Pb is dissolved at a rate of only 0.22 μm/day. In other words, the beta phase (practically pure Sb) within the structure of the Pb–Sb alloys can be attacked some 13 times more quickly than the alpha (practically pure Pb) phase which makes up the matrix.

Therefore, the beta phase particles supply routes for a fast penetration of the localized attack into the alloy structure. Logically this effect will be much more severe when the beta phase has a lamellar morphology and forms an almost continuous network than when this phase is distributed in an eminently discontinuous form. This fact has already been pointed out by Mao *et al.* [4, 7] in attempting to explain the higher corrosion resistance of certain Pb alloys.

The selective attack along the beta phase may cause undermining of the Pb-rich primary crystals. Figures 3 and 9 clearly illustrate this phenomenon, showing how the preferential attack on certain regions leaves parts of the matrix practically detached. Other papers [2, 5] have pointed out the important role which material disintegration may play on corrosion weight losses.
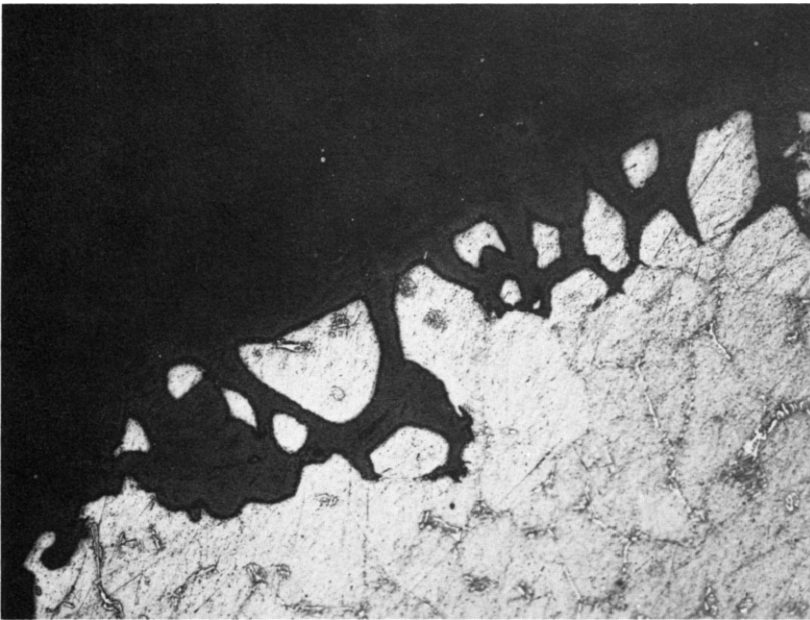

Fig. 9. The preferential attack along the beta phase detaches alpha phase particles (which are retained in their position only by the anodic oxide). Optical microscope photograph of cross-section of Pb–4% Sb grid after being subjected to anodic action. × 200.

Effect of ageing on weight losses

According to the foregoing the total weight loss (ΔP) produced during the corrosion test period must result from the joint action of: ΔP_A = weight loss due to anodic attack of the lead-rich matrix (which may exhibit even-

tually fine post-eutectic beta-phase particles precipitated during ageing); ΔP_B = weight loss due to anodic attack of the eutectic beta phase; ΔP_D = weight loss due to breakdown of practically unattacked portions of lead-rich matrix; so that:

$$\Delta P = \Delta P_A + \Delta P_B + \Delta P_D$$

Consequently, the resulting effect will depend on the individual influence of ageing on each of the terms ΔP_A, ΔP_B and ΔP_D.

Ageing tends to decompose the supersaturated (unstable) solid solution formed upon solidification and cooling. From the corrosion standpoint, it seems reasonable that precipitation of fine (post-eutectic) beta phase particles in the Pb-rich matrix should have some kind of influence on its stability.

In a series of complementary tests an attempt has been made to verify experimentally the effect of ageing on the corrosion of specimens of Pb–2% Sb alloy (composition comparable to that of the Pb-rich matrix) in a fully solubilized condition and two different ageing states. After 37 days of anodic action at 1.7 mA/cm^2 the following corrosion weight losses have been measured: (a) supersaturated solid solution (1 hour at 240 °C and water quenching) — 40.1 mg/cm^2; (b) same as condition (a) and ageing at 50 °C for 1 day — 44.1 mg/cm^2; (c) same as condition (a) and ageing at 50 °C for 3 days — 46.4 mg/cm^2, revealing a tendency towards an increase in corrosion susceptibility with ageing of the supersaturated Pb-rich phase.

Apart from the precipitation of minute post-eutectic particles, ageing can cause, as previously mentioned, a change towards rounder shapes of the relatively large particles of eutectic beta phase. Although this phenomenon should not affect the specific rate of selective attack on the beta phase itself, it will modify certainly the possibilities for undermining and detachment of portions of Pb-rich matrix.

Therefore, following the above remarks, it seems likely that with ageing time ΔP_A increases due to the post-eutectic precipitation, ΔP_B remains practically constant, and ΔP_D, in the event of a change, decreases as a result of the spheroidization of the eutectic beta phase.

Under these assumptions, it is now possible to attempt an interpretation of the experimental curves of Figs. 7 and 8, which show the effect on corrosion of the time elapsed from the casting of the grid until the initiation of the corrosion test. If ageing time has a greater influence on ΔP_A (which tends to increase) than on ΔP_D (which tends to decrease), the total weight loss (ΔP), or the resulting average corrosion rate, will logically tend to increase. On the contrary, if the effect of ΔP_D exceeds that of ΔP_A, the total weight loss, or the average corrosion rate, will decrease with ageing time. Apparently, this latter circumstance is met with in the grids that underwent rapid cooling during casting, although only during the first four months of ageing (Fig. 8).

In the slowly cooled grids ΔP_D will hardly depend on grid ageing, since the morphology of the interdendritic·Sb-rich phase particles, which show from the beginning round shapes, remains practically unchanged. In conse-

quence, of the three terms ΔP_A, ΔP_B and ΔP_D, which all together establish the total weight loss, the first ΔP_A will increase while the other two will not change with ageing time, so that ΔP will also increase, as seen in Fig. 7.

This theory is, of course, preliminary and needs to be developed further as the results of new investigations become available in order to provide a full explanation of all the experimental facts.

Effect of alloy concentration and paste coating

Although it is not the main aim of the present report, a brief mention will be made of the influence of Sb concentration and paste coating on grid corrosion since its significance is obvious if we just glance over Figs. 7 and 8.

As a general rule, the grids with a higher Sb concentration have been the more attacked. This was to be expected since the volume of second and anodically much more reactive phase is also greater. The only exception are the rapidly cooled bare grids, where the Pb–4% Sb alloy appears to corrode slightly more than the Pb–6% Sb, although the differences are not significant: overlapping of limits of error in Fig. 8.

Pasting, on the other hand, reduces the attack. This protective effect of the paste is logical if we bear in mind that, apart from interposing a barrier between lead and electrolyte, the paste acting itself as an anode displaces anodic reaction from the metal surface towards the external surface of paste. Since oxygen becomes liberated far away from the metal surface, the possibilities for a direct reaction between oxygen and lead decrease a great deal.

Conclusions

Ageing time affects the anodic stability of the 4% and 6% antimony–lead alloys tested so that the corrosion rate during the first four months can undergo variations of up to 20 - 35%.

The cooling rate during casting of grids also significantly affects the anodic weight losses. Nevertheless, at the end of 8 months the differences due to this variable almost disappear.

It is suggested that the effect of ageing time on corrosion rate may be a consequence of the combined effect of ageing time on: (a) the anodic attack on the lead-rich matrix, and (b) the possibilities for undermining and detachment of parts of the matrix due to preferential dissolution of the second phase.

Acknowledgements

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