AGEING BEHAVIOUR OF CAST Pb–Sb BATTERY GRIDS

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Summary

The behaviour of cast Pb–4%Sb and Pb–6%Sb battery grids has been studied by following the changes with time of tensile properties, microhardness, and electrical resistivity in alloys cooled at different rates after casting.

The effects of the different cooling conditions on ageing have been explained by the resulting distribution of antimony in the α portion of the dendrites, which has been measured by an electron microprobe procedure, and compared with theoretical distributions calculated from non-equilibrium cooling conditions. The effects of the different variables on the expected behaviour of the grids are discussed.

Introduction

Ageing of lead–antimony alloys and the influence on the ageing process of several factors such as ageing temperature, alloying elements, quenching conditions, plastic deformation and low-temperature treatments after quenching, has been extensively studied in solution-treated and quenched alloys with antimony contents lower than the solubility limit of 3.5 wt.% Sb. As a result, there is a widely accepted explanation of the precipitation mechanisms which can be found in earlier papers by the authors, and which include a review of the literature [1, 2].

The most important use of lead–antimony alloys is in the manufacture of cast battery grids, and it seems natural to apply the acquired knowledge to practical applications. The main difficulty arises from the fact that, in practice, industrial alloys have higher antimony contents, and, on the other hand, most precipitation studies have been carried out on solution-treated and quenched material.

It thus became clear that the studies had to be completed by research into the ageing processes in more concentrated alloys cast under conditions similar to those found in industrial practice.

However, a compromise has to be made in this approach; the conditions have to be reproducible, and special care has to be taken concerning the in-

fluence on the antimony retained in solid solution, which is responsible for the ageing processes, of such factors as melt and mould temperatures, and cooling rates within the mould and after mould knock-out.

Experimental

The details of the casting procedure have been described in detail by Feliú *et al.* [3] and only a brief summary is included here.

Two alloys — Pb–4 wt.% Sb and Pb–6 wt.% Sb — were prepared from 99.97%Pb and 99.7%Sb. The impurity contents in the lead were Sb < 0.001, As < 0.002 5, Bi < 0.008, Sn < 0.01, Fe < 0.002 4, Ag < 0.004, Zn < 0.000 4, Cu < 0.001 wt.%. The mould was made from aluminium with an anodized inner surface and the grids were 50 × 50 mm with an arm and frame thickness of 1.5 and 2 mm, respectively. The melt temperature was 520 °C and the mould temperature 265 °C to ensure good mould filling.

Two cooling rates were used:

(a) rapid cooling: the mould was water-cooled after pouring the grid;

(b) slow cooling: air cooling of the mould down to 200 °C and subsequent mould knock-out and air cooling of the grid.

The cooling rate was measured in a series of trials prior to the experiments, as described in ref. 3, recording the temperature by means of a thermocouple welded to the interior of the mould.

The grids from which all the experimental specimens were cut were kept in a thermostatted chamber at 20 ± 1 °C.

The specimens for the electrical resistivity measurements consisted of the arms of the grids. The first measurement was carried out ten minutes after pouring the grid, and the value obtained was taken as the as-cast value. This is the correct procedure, since no changes in the electrical resistivity occur immediately. All the values were referred to R_o, and the results are plotted as R/R_o *vs.* time curves, as is usual.

As the size of the grids did not allow hardness tests to be performed, microhardness tests were carried out on polished sections of the grid arms. A special mount, which allowed the test pieces to rest on a lead base, was used. The mount was filled with resin and polished at the same time as the specimen. The load was 20 g and the indentation time 5 s. Every measurement was the mean of six indentations.

Tensile tests are normally carried out on specimens of standard size and shape. In our case, an effort has been made to preserve the original structure of the grid, and the vertical portions of the frames were used as tensile specimens; we have made this unusual approach as we have always considered it to be very important to study the actual condition of the grids. Moreover, it was more important to know the variation of properties with time than their absolute value. To ensure accurate and reproducible location of the specimens in the tensile machine they were mounted in hollow brass cylinders. The cylinders were filled with a molten lead–tin alloy (m.p. 227 °C) and the

ends of the specimens were inserted into the cylinders which were then water cooled.

All these steps were carried out immediately after casting the grid.

It was confirmed that this procedure was satisfactory as, in the tensile tests, all the fractures occurred at the centre of the specimen, and not at the point where the arms crossed. The lateral arms were cut off at a sufficient distance to avoid notch- and deformation effects. From the stress–strain curves the U.T.S., 0.2% proof stress, and elongation values were determined.

Results

The electrical resistivity results are shown in Fig. 1. All points correspond to the mean of at least two specimens. In slowly cooled Pb–4%Sb alloy, slightly different results were found for different groups of specimens, which indicates that the initial antimony distribution was not the same for all of them. As the casting procedure did not differ, it seems reasonable to assume that the antimony distribution is very sensitive to minor variations in the casting or cooling conditions. As expected, all specimens aged appreciably and the rate for slowly cooled specimens was higher than that for rapidly cooled specimens. For the Pb–6%Sb alloy the reverse was the case: slowly cooled specimens aged less and they stabilized at a value of $R/R_o \approx 0.91$, a change which should be considered as small.

Microhardness results are shown in Fig. 2. In slowly cooled Pb–4%Sb specimens there is a maximum value at around 3 000 h followed by a decrease to the value attained at 500 h. Rapidly cooled specimens show a similar trend, with considerably smaller changes and the maximum value for a much shorter period. For the Pb–6%Sb alloy, rapidly cooled specimens always have
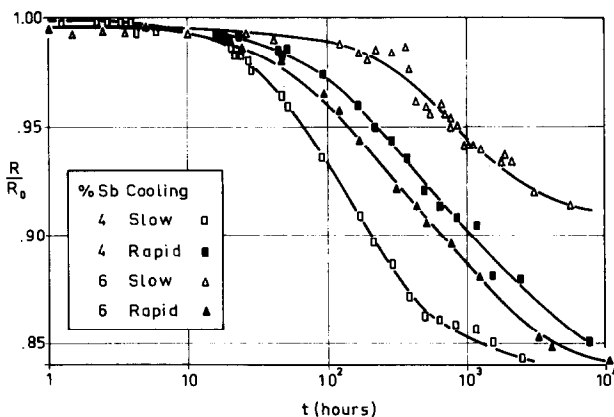

Fig. 1. Variation of electrical resistivity with time at 20 °C for Pb–4%Sb and Pb–6%Sb cast grids after slow and rapid cooling.
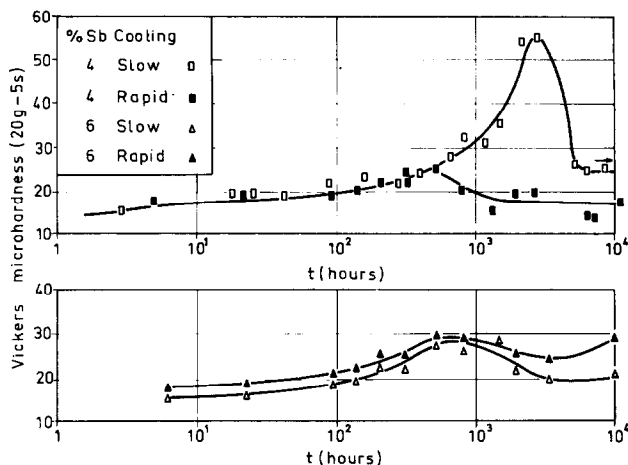
Fig. 2. Variation of microhardness with time at 20 °C for Pb–4%Sb and Pb–6%Sb cast grids after slow and rapid cooling.

higher hardness values than slowly cooled specimens; maximum hardness is found at 900 h. The differences tend to increase after ageing for 10 000 h.

The results of the mechanical tests are shown in Fig. 3. In all cases, ageing influences mechanical properties in the same manner. The most important observation from the tensile test results is the decrease in elongation to ≈ 0 for a time of around 1 000 h at which time the U.T.S. and the 0.2% proof stress values coincide. For Pb–4%Sb alloys (Fig. 3(a)), slowly cooled specimens have higher tensile values and lower ductility than rapidly cooled specimens and the U.T.S. values increase after ageing for 1 000 h. For Pb–6%Sb specimens (Fig. 3(b)), the behaviour of slowly and rapidly cooled samples is the opposite, and no further increase in tensile strength is found after 1 000 hours.

Discussion

The results show a difference in behaviour for the two alloys studied which is strongly dependent on cooling conditions after casting.

The variation of properties with time is a consequence of the precipitation of antimony which has been retained in supersaturated solid solution, and it becomes clear that the distribution and concentration of the alloying element are the factors most affected by alloy composition and cooling rate. The β phase is also affected, but previous experience has shown this to be of little importance.

Three factors affect the distribution of antimony within the α phase: (a) solidification conditions; (b) diffusion of antimony during cooling; (c) precipitation of antimony during cooling.
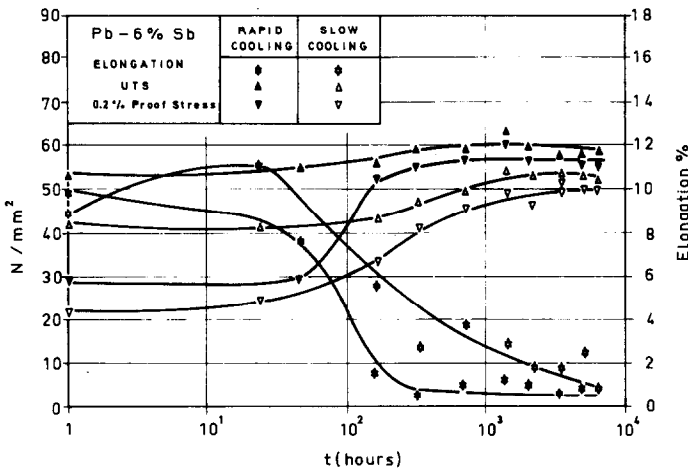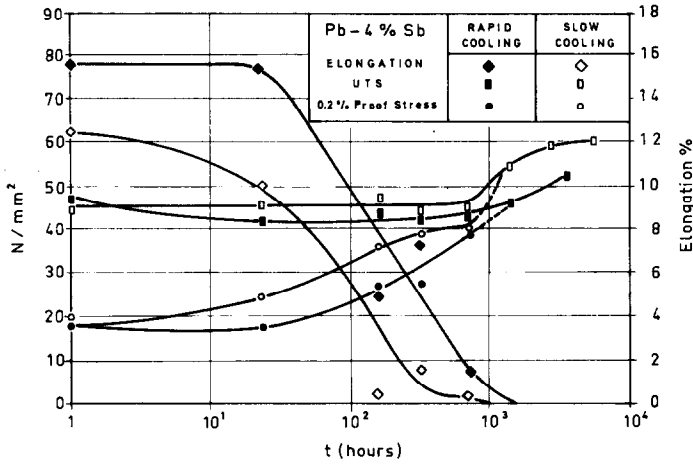
Fig. 3. Variation of elongation, U.T.S. and 0.2% proof stress with time at 20 °C of (a) Pb–4%Sb, (b) Pb–6%Sb cast grids.

With regard to (a), the equilibrium diagram of the lead–antimony system shows when solidification takes place at an infinitely slow rate. For higher cooling rates the probability of diffusion in the solid state will be smaller; this can be considered to be equivalent to withdrawing the already solidified material from the process, and the equilibrium conditions are no longer fulfilled. The non-equilibrium conditions have been treated in detail by Gulliver [4] whose well-known formula will be applied below to obtain the theoretical antimony distribution in the dendrites.

The diffusion of antimony in the already solidified alloy, factor (b), has not been considered. It is clear, however, that for a slower grid cooling

rate, the levelling of the concentration gradient to which the solidification conditions give rise will be more likely.

In respect of factor (c), precipitation of the alloying element during cooling, it should be remembered that higher temperatures favor both the formation and the solution of precipitates. There must be a critical temperature below which the formation of precipitates predominates over their solution; as the temperature decreases further, both effects are not relevant, as precipitation develops during a period which is long compared with the cooling time of the grids. An attempt to evaluate this critical temperature can be made based on the well-known precipitation kinetics of the solution treated and quenched Pb−2%Sb alloy [1].

The precipitation effects are detected shortly after quenching and the maximum hardness is attained after 2 h ageing at 110 °C; the electrical resistivity stabilizes after 200 h. If ageing takes place at other temperatures (80, 50, 20 °C), the maximum hardness is attained after 12, 48 or 1 500 hours, respectively, and the electrical resistivity stabilizes after periods greater than 1 500 h. It must be assumed therefore that the critical temperature lies between 110 and 200 °C; the latter is the solution temperature for that alloy.

When the solidification of the alloy takes place under non-equilibrium conditions, the first solid portions are crystals of low solute concentration; these are surrounded by layers of solid of increasing concentration and the last portion solidifies as eutectic mixture. The grains formed in this way have a dendritic form, and they can be regarded as cylinders made of different layers with the antimony content increasing from the centre to the boundary.

The Gulliver formula allows the concentration of the different layers to be calculated under non-equilibrium solidification conditions if the following assumptions are made:

(a) no diffusion takes place in the solid state; (b) diffusion is complete in the liquid, (c) the equilibrium diagram provides the solidus compositions when cooling takes place through an infinitesimal temperature gradient; (d) the solidus and liquidus lines are straight. Under these conditions, the liquidus composition after the solidification of a portion of the alloy can be deduced from the following expression:

$$\frac{w_L}{w_o} = \left(\frac{x_o}{x_e}\right)^{x_L/(x_L - x_s)}$$

where w_L = mass of remaining liquid; w_o = total mass of the alloy; x_o = alloying element concentration in the original alloy; x_e = percentage of alloying element in the remaining liquid; x_L = percentage of alloying element at the eutectic composition, and x_s = maximum solid solubility of the alloying element.

From this it is possible to calculate the solid phase concentrations. The calculation is carried out by means of a step procedure in which it is assumed that a given percentage of the alloy has already solidified, e.g., 20%, and from this the concentrations of the remaining liquid and solid are calculated. In this way, the non-equilibrium conditions are replaced by five steps, each of

20% transformation. No formal relation exists between the number of steps and the cooling rate, but it is generally assumed that a "few step" procedure is equivalent to rapid cooling and a "many step" procedure approaches slow cooling. Figures 4 and 5 show the results from the application of the Gulliver expression to the alloys studied in the present report when the calculations are carried out in 100, 20, 10 and 5 steps. The plot shows the resulting distribution of concentration *vs.* distance or proportion of solidified mass for an ideal dendrite of radius equal to 10 arbitrary units, and the distribution which corresponds to equilibrium conditions.

In order to compare these theoretical distributions with the actual distribution the following experiment has been carried out by means of the electron microprobe: rapidly cooled and slowly cooled grids of both alloys were prepared metallographically and carbon coated to improve beam stability immediately after casting.

Areas corresponding to dendrites were examined and photographed in the backscattered electron mode. After this, small, square regions with an area of approximately 2 μm^2 were scanned, their location superimposed on the previous image and the intensity of the Sb L_α line compared with that obtained with pure Sb prepared under identical conditions.

In this way a map of intensity ratios was made for the different alloys and cooling conditions; from them a plot of isoconcentration lines was drawn. This procedure was not used in the outer part of the dendrite; in fact, in the
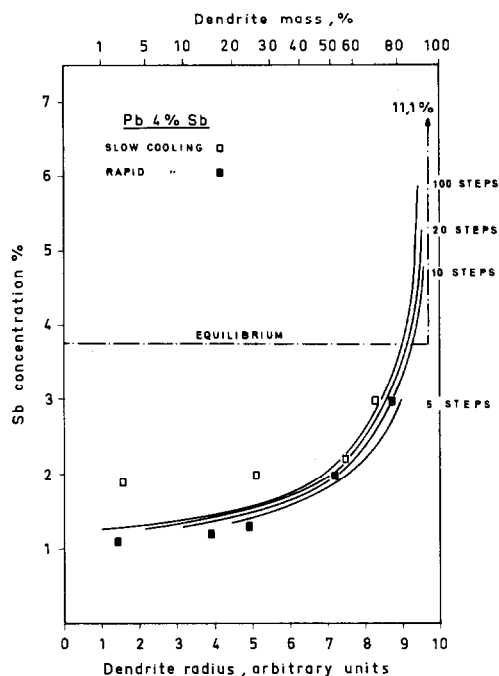

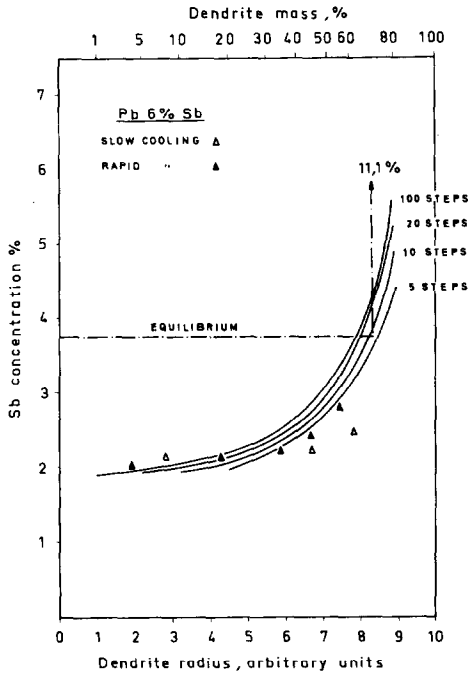Fig. 4. Measured and theoretical distributions of Sb in the dendrites of cast Pb–4%Sb.

Fig. 5. Measured and theoretical distributions of Sb in the dendrites of cast Pb–6%Sb.

eutectic region, the intensity obtained depends heavily on whether the scan has been carried out on mainly α or mainly β material, but this is not relevant to the problem. An example of the procedure is shown in Fig. 6 for a rapidly cooled Pb–6%Sb alloy. The upper part shows the electron image of the dendrite, the superimposed scanned areas, and the intensity ratio values. The lower part shows the isoconcentration lines deduced from it. These data have been plotted in Figs. 4 and 5, for all the alloys and cooling conditions, for comparison with the theoretical values. From Fig. 4 it can be seen that the experimental results agree reasonably well for rapidly cooled specimens, but have higher values for slowly cooled specimens, in the centre of the dendrite. In Fig. 5 the agreement between both values is good for both cooling conditions, and rapidly cooled Pb–6%Sb alloy has higher values than the slowly cooled alloy. With the approximations made, it is reasonable to assume that the actual distribution of the alloying element can be explained by the Gulliver calculation, except for the slowly cooled Pb–4%Sb alloy.

Two main questions, which need explanation, arise from the preceding observations:

(i) Slowly cooled Pb–4%Sb specimens age at a higher rate than rapidly cooled specimens, which implies a higher antimony content in solid solution. This agrees with microprobe results if it is conceded that all the detected antimony is in solid solution.
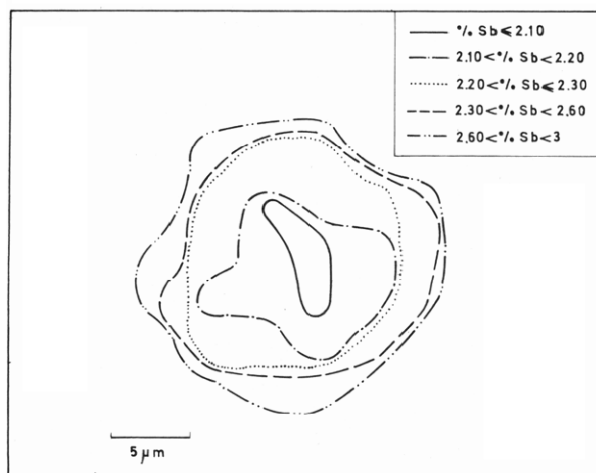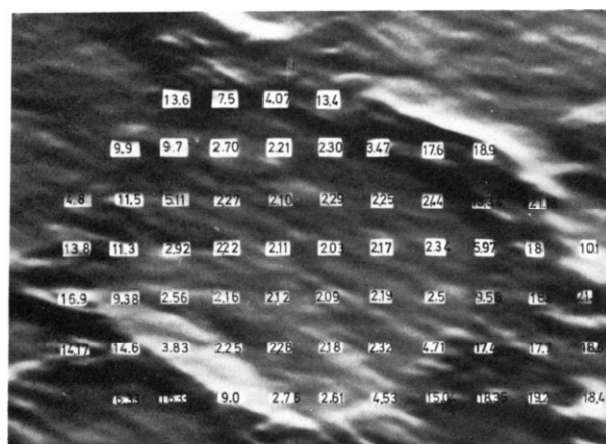
Fig. 6. Example of microprobe determination of Sb distribution and drawing of isoconcentration map. (Intensity ratio values, %).

(ii) Slowly cooled Pb−6%Sb specimens age at a slower rate than rapidly cooled specimens. As no noticeable concentration differences are found in the dendrite centre, we must assume that when the measurements start a fraction of the antimony in the dendrite has already precipitated.

With regard to (i) we must conclude that the higher antimony level detected in the slowly cooled specimens is due to diffusion from the β-rich outer part of the dendrite during cooling of the solidified alloy from 252 °C. The trend in this condition is towards an Sb concentration equal to the 3.5% solubility limit at this temperature; in this case, the cooling time between 252 and 200 °C is 550 s (see ref. 3, Table 1), but for most of this time the alloy temperature will be closer to 200 °C, at which temperature the solubility limit is 2%; this is in agreement with the observed values. After mould knock-out, the temperature drops to 150 °C in 8 s and to 100 °C in 24 s. This time

is too short to allow long range diffusion effects and large concentration differences to occur. Obviously, a fraction of the antimony in solution will precipitate during cooling and will not take part in the room temperature ageing, but even with this assumption, changes during ageing will be more significant than in rapidly cooled samples. In fact, the latter have a concentration after solidification of roughly 1% in the dendrite centre. Subsequent cooling is very fast -100 °C is attained in only ten seconds $-$ and diffusion from the β phase is thus prevented.

For case (ii), it should be noted that during both rapid and slow solidification the concentration in the dendrite centre is close to 2% Sb. Diffusion from the β phase region cannot alter this distribution appreciably, as explained earlier, which is that corresponding to 200 °C. The retained solute, however, precipitates to a larger extent during cooling in slowly cooled specimens, as the time to cool from 200 °C to 100 °C is 24 s, as opposed to 10 s for rapidly cooled specimens.

This explains why slowly cooled specimens age less at room temperature.

A different approach can be used to estimate the amount of antimony retained in the α region of the dendrites: the R/R_o vs. t curves of the cast specimens can be compared with those obtained from solution treated and quenched samples in which all the material is α phase at the start of ageing as supersaturated solid solution. The relevant data are taken from ref. 1, where the materials were of the same quality.

Resistivity vs. time curves usually have a stability period, sometimes called the incubation time, a more or less steep decrease later, and finally a stabilization period, after which the precipitation of the element in solution stops. It is generally accepted that the total variation of resistivity during the ageing period can be taken as a measure of the amount of solute in solid solution at the start of the process. The value, $t_{50\%}$, is usually taken as an indicator of the development of the process. This is the time for the resistivity to attain 50% of the total variation. With the data of ref. 1, a plot can be made of $t_{50\%}$ vs. antimony content for 1,2 and 3% Sb alloys (Fig. 7). If the $t_{50\%}$ values found in the present study are used in Fig. 7, the estimation in Table 1 can be made for the retained Sb in solid solution (uncorrected values).

The results agree reasonably well with those previously mentioned. The low equivalent values for the Pb–6%Sb specimens as compared with the slowly cooled Pb–4%Sb specimens, should, however, be noted. It must be remembered that the proportion of the specimen involved in the process is considerably smaller in the case of the Pb–6%Sb than in the Pb–4%Sb specimens. In fact, if we consider the equilibrium diagram, the proportion of α phase for cooling under an equilibrium condition is 59.7% for Pb–6%Sb and 77.5% for Pb–4%Sb alloys. This is not a close estimate, but if we allow that for non-equilibrium cooling a similar proportion holds, the corresponding corrected values are as shown in Table 1 and the differences found are more reasonable. Metallographic examination [3] in fact shows a larger proportion of eutectic regions in Pb–6%Sb under all cooling conditions. Other differ-
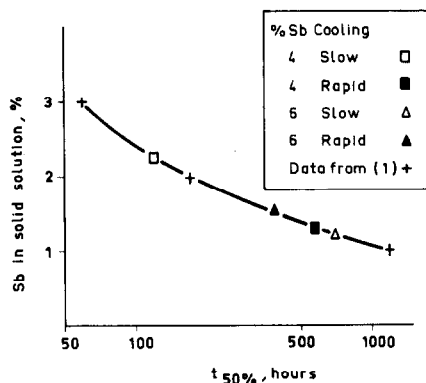
Fig. 7. Plot of $t_{50\%}$ resistivity values *vs.* Sb concentration of 1,2, and 3% Sb alloys and equivalent values for cast Pb–4%Sb and Pb–6%Sb alloys.

ences can be attributed to minor precipitation effects within the eutectic region, experimental errors, approximations made, and differences in the thermal capacity of the alloys which act on the solidification conditions.

Microhardness results are not easily compared with other results in the literature, as the measurements are normally carried out by means of Brinell hardness measurements; in Fig. 2 it can be seen, however, that maximum microhardness values increase with the amount of antimony which can precipitate. The values are very high, however, as compared with those found in ref. 2. This cannot be attributed solely to the different test used, but also to the hardening effect of the β phase.

Tensile results show an increase in U.T.S. from 40 to 60 N/mm^2 and embrittlement of the material. It should be noted that overaged specimens, which are relatively soft so far as hardness is concerned, do not show a decrease in tensile properties, while elongation values decrease to 0. This effect has been reported earlier [6] for other Pb–Sb alloys and is attributed to the difference in strength between the matrix precipitated with β particles and the depleted regions near grain boundaries where discontinuous precipitation occurs; it can, then, be assumed that a similar phenomenon takes place in these alloys.

TABLE 1

Alloy (wt.% Sb)	Cooling	$t_{50\%}$ (h)	Equivalent %Sb in s.s.	
			uncorrected	corrected
4	rapid	576	1.3	1.7
4	slow	120	2.2	2.8
6	rapid	360	1.55	2.6
6	slow	696	1.2	2.0

Conclusions

The most important conclusion which can be drawn from the foregoing is that the antimony contents of the alloys used for the manufacture of cast battery grids are by no means the most important variable as regards the mechanical strength of the grids. Casting and cooling conditions have been shown to be more important, as they are determinant factors concerning the amount and distribution of the antimony retained in solid solution.

In respect of ageing phenomena, the only negative effect on the properties of grids is loss of ductility with time. Hardness increases with time, and even if the grids are softened on overageing, the values are always higher than those of the as-cast grids. Tensile strength does not increase appreciably, although 0.2% proof stress increases up to twice the original value.

Acknowledgements

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