

PRESENT TRENDS IN LEAD ALLOYS FOR THE MANUFACTURE OF BATTERY GRIDS — A REVIEW*

M. TORRALBA

Centro Nacional de Investigaciones Metalurgias, Ciudad Universitaria, Madrid 3 (Spain)

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Summary

Probable trends in the future requirements for lead acid batteries are briefly reviewed and it is pointed out that the development of maintenance free batteries could have an important place in that future. Such batteries make special requirements on grid materials. Lead-calcium alloys and lead alloys with a low antimony content are favoured for this application. The physical, electrochemical and mechanical properties of these two types of alloy are reviewed together with their respective advantages and disadvantages and the problems that may arise from their use.

Introduction

Lead acid batteries are the oldest and most traditional means for electric power storage. Other types of battery with more desirable technical characteristics, such as a much lower weight/power ratio have been developed in recent decades, but their price is considerably higher. On this account, unless special uses are involved in which price is less significant, lead acid batteries continue to dominate the market.

A passive but very important element of these batteries is the grids which help support the lead oxides which, together with the acid, constitute the active part of the battery. These grids which have been designed to support the active material and to act as electric power conductors have hitherto been made, almost exclusively, from gravity-cast lead-antimony alloys. At present, however, other possibilities are open both with regard to alloys and to the method for the manufacture of the grids; as the users' requirements change, the grid industry is evolving accordingly, but no clear evidence can yet be seen as to the trend that will prevail.

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The sector which exerts a greater demand for batteries is, undoubtedly, the automobile industry. The number of batteries which are produced depends chiefly on the number of vehicle manufactured, the total number of cars on the road, the quality of the batteries and the use being made of the entire number of cars, *i.e.*, on the number of kilometres/vehicle/year travelled.

With reference to the quality of the batteries, the trend is towards a smaller output since as their quality has improved in the past few years, their useful life has increased. It also appears that the installation of alternators in the latest motor cars as well as the use of polypropylene cases contribute to an increase in the duration of the batteries [1]. With regard to the annual output of new vehicles, the tendency in Spain at least is to increase, thus giving rise to a greater production of batteries. It was only in 1974 that there was a decrease in motor car production motivated solely by a reduction in exports. This trend seems likely to continue in spite of the ever rising cost of fuels without any possibility being glimpsed of their becoming cheaper or stable. On the contrary, the general use of the total number of cars on the roads is less, since the petrol/vehicle/year consumption tends to decrease. It would therefore seem that once the domestic motor car market is saturated, the production of batteries will suffer from regression and this might cause investments in R & D to be considered barely profitable. Trends in other more highly developed countries, such as USA, UK or Japan are similar to those previously mentioned even though the saturation of the motor car market was responsible for a more marked reduction in consumption during 1974 and 1975 and for a slower real recovery.

The situation can, however, be considered from a more optimistic viewpoint. On the one hand, industrialized countries are making great efforts to explore and exploit hydrocarbons in areas under their sovereignty, sometimes with considerable success as in the North Sea. In addition, the above-mentioned problems and the new Government regulations on pollution control have brought about intensified research work for producing electrically powered vehicles which would be important users of batteries with different characteristics from the starting and lighting ones being now used. On the other hand, the real solution to current difficulties could be found in a profitable exploitation of other types of energy such as wind, tides, ocean waves and, more particularly, solar energy. These sources of energy are cyclic or irregular in nature so that large-capacity batteries would be required for their adequate use. A similar problem to this is already to be found in hydraulic, thermal and nuclear plants which must operate at a steady rate. With regard to this, an important research project on 100 MWh capacity batteries is now in progress [2].

A rather controversial point which could have considerable significance on the development of battery technology is the so called MF (maintenance-free) battery. This type of battery does not require periodic addition of water and this would seem to be very attractive to car users and has the advantage for the manufacturer that it can be placed in inaccessible points of

the vehicle, thus facilitating design. In spite of all this, the sale of such batteries did not increase much in the USA during 1974 while in Europe they are not currently found in the market. Demand, so it appears, develops slowly due perhaps to the as yet not fully developed technology required for their manufacture.

In any case, modern batteries are required to produce less gassing and less self-discharge which tends to eliminate alloys with high-antimony content as a material for the manufacture of the grids.

These requirements will govern alloys for future use but consideration should also be given to manufacturing methods other than gravity casting, such as die casting or rolling and punching, since the metallographic structures produced by these means have a considerable influence on the properties of the grids.

We shall now study the current status of grid technology by analyzing possible solutions and trends which could perhaps be applied in the very near future.

Grid alloys

The conditions required for an alloy to be satisfactory for the manufacture of grids are basically as follows: (a) good mechanical properties; (b) good corrosion resistance; (c) electrochemical "cleanliness" (low antimony); (d) good adherence between the grids and the active material; (e) good castability and good weldability; (f) good electrical conductivity; (g) low, stable price.

In addition, with maintenance-free batteries in view, it is necessary that the grid material should not produce gassing, should not get hot during charge or discharge and should not cause self-discharge problems.

Until a few years ago, the materials used for battery grids were almost exclusively lead-antimony alloys. The reason behind this was that antimony confers good mechanical properties and good castability on the lead. The improvement in the mechanical properties is due to two things, at least for antimony contents above 3.5%. The grid hardens because of the formation of eutectic during solidification in the case of contents higher than 3.5%. Also the alpha phase contains antimony in solid solution which undergoes precipitation or age hardening with time. Years ago, the antimony content used to be 11%, close to the eutectic composition, but later, this content has been lowered to about 4 or 5%, which is frequently found today. This decrease in the antimony content was in part due to economic reasons, since the price of antimony has known continual fluctuations which have meant a considerable price increase, but there are important technical reasons. Although antimony improves castability, mechanical properties and paste adherence, it also suffers from the drawback of reducing the grid's electrical conductivity, which in turn reduces the battery output. In addition, the antimony is responsible for self-discharge because it diffuses from the positive

plate and is deposited on the negative plate, causing a reduction of the hydrogen overpotential on the latter, all of which leads to release of hydrogen during battery charge and on open circuit stand. Antimony also causes the electrochemical reactions of charge and discharge to take place with increased released heat, which leads to some water evaporation which precludes the possible use in maintenance-free batteries of lead-antimony alloys.

In order to avoid or reduce these problems, or at least some of them, various possibilities have been studied, such as the substitution of classical grids by plastic supports for the active material. However, the most acceptable trends have been towards the reduction of the antimony content, with or without the addition of other elements, or the substitution of this metallic component by some other suitable ones. Heubner and Petter [3] indicate that for reasons of price and availability, the new metallic compound can only be an alkaline or alkaline-earth element. They also point out that potassium should be excluded due to its low solubility in lead, that beryllium is poisonous, that sodium gives rise to corrosion and that other elements, such as lithium, cause very rapid ageing and embrittlement. At the end of the list it turns out that only calcium seems to have the required properties for antimony substitution. In practice, it appears that all authors agree on this, since the only grids to which ample attention has been given, on which experiments have been conducted, and which have been marketed are those made from Pb-Ca alloys.

Tests have been carried out on Pb-Ba grids, however, which have similar characteristics to those manufactured in Pb-Ca alloys but can be advantageous as negative plates as a permanent source of barium sulphate, which acts as paste expander, and as positive plates owing to the lower solubility of barium compared with calcium [4].

Pb-Ca alloys

Pb-Ca alloys with some tin added to improve their castability, are the main competitors of Pb-Sb alloys in the manufacture of grids for storage batteries. Their use in storage batteries goes back several years in specific applications where low maintenance costs are important. This is due to the fact that such batteries produce less gas and have a lower self-discharge rate than those made from Pb-Sb alloys. Such is the case of storage battery systems designed for the supply of signalling networks such as railway safety systems, emergency lighting systems for hospitals, hotels, etc. In addition, these static batteries are free from vibration which could lead to loosening of paste, since it would appear that the main fault with such an alloy is the poor adherence between the active material and the grid. However, a great effort has recently been made towards the study of the metallurgy of Pb-Ca alloys, and this has already resulted in their use in a certain percentage of starter batteries in motor cars, particularly in the USA.

Pb-Ca alloys belong to the age, or precipitation-hardenable, group of alloys *i.e.*, the solubility of calcium in lead decreases with temperature.

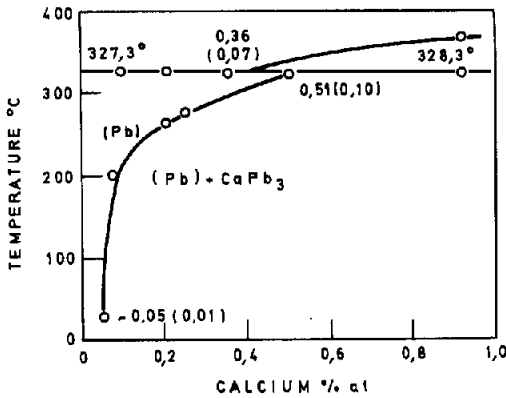


Fig. 1. Phase diagram for lead-calcium [5]

Figure 1 shows the equilibrium diagram for Pb-Ca [5]. From it, one can see that when an alloy with less than 0.07 wt.% Ca solidifies, this amount or an important fraction of it will remain in a supersaturated solid solution, depending on the solidification conditions. With time, however, the alloy tends to find its equilibrium state which is reached by the precipitation of very fine Pb₃Ca particles that distort the lead matrix lattice and provoke its hardening. It is also possible to achieve solid solutions with up to 0.10 wt.% Ca by solidification but the solidification conditions are very critical and cooling will have to be carried out very rapidly when crossing the "liquidus + Pb₃Ca" zone, as calcium would otherwise separate from the lead.

According to Rose and Young [6] in an interesting paper presented to the 5th International Lead Conference held in November 1974, the addition of tin to calcium upgrades its mechanical properties, in a fully aged state, as well as the electrochemical characteristics. The phase diagram for Pb-Ca-Sn, and to a much lesser extent the precipitation mechanisms by which hardening of these alloys takes place, are not very well known; it appears, however, that hardening is partly due to a rapid precipitation of Pb-Ca, and partly to slow, but much more important, precipitation of a hardly known Sn_xCa phase. Both precipitations are important since the mechanical properties required in a grid should be obtained, at least in part, in the shortest possible time from the moment grids are cast, since these should have a certain mechanical strength to withstand, without bending, the mechanical pasting operation, regardless of the service strength required.

In all of these alloys, cooling rate usually has a considerable influence on the properties later obtained by ageing, due in part to the difference in the starting structure of the material, and partly because cooling rate affects the number of retained vacancies which govern the diffusion mechanisms and in turn the precipitation of solute. Rose and Young [6] reporting on a paper by Turowski [7], indicate that cooling rate does not exert any influence on tensile strength and creep of Pb-Ca alloys with contents under 0.06 wt.% calcium. This appears to agree reasonably well with the results obtained by Feliú *et al.* [8] for 0.03 and 0.05 wt.% Ca. On the contrary, for calcium contents

ranging from 0.06 to 0.10%, a rapid water-quench considerably improves the mechanical properties of fully aged alloys. Thus, for an alloy with 0.010%Ca, quenched in water, a tensile strength value of about 5.5 kgf/mm² can be obtained, this being similar to the values for the Pb-4%Sb [8] alloy. When any amount of tin up to a maximum of 1.0% is added to these alloys, there is an improvement in mechanical properties both under tensile and creep conditions and it appears that the optimum conditions are obtained with air cooled alloys containing 0.06 to 0.10%Ca, although the influence of cooling rate seems to be much smaller on ternary alloys than on binary alloys. These authors also state that calcium is a grain refiner while tin has the opposite effect.

Zeman [9], working with grids cast in an industrial type machine and paying attention to the properties attained immediately after casting and on long term, finds that grids with 0.5% Sn harden much more, and at a much higher rate, than those not containing tin or with 0.10%, so that this alloy is advantageous for grid processing. This effect is probably due to the precipitation of Pb₃Ca, which is very fast *versus* that of Sn_xCa and which can be inhibited by the presence of an excess amount of tin.

It would therefore appear that from the viewpoint of mechanical strength a compromise must be reached in alloy composition in order to reconcile good performance during the storage battery life with suitable grid properties for plant processing.

With regard to corrosion resistance, it seems that Pb-Ca-Sn alloys perform better than lead-antimony ones, although the difference is not great and depends on the conditions. In addition, when anodic corrosion tests are carried out, it has been found that the corrosion resistance and the remaining properties of Pb-Sb alloys become modified with time [8]. This makes it very difficult to establish a valid comparison between both types of alloys.

The presence of Pb₃Ca precipitates, however, favours an important reduction in the grain size of Pb-Ca alloys and consequently an increase in preferential intergranular corrosion [10].

From the electrochemical point of view, Pb-Ca alloys have both advantages and disadvantages. From the one aspect, the grids show a tendency towards passivation, owing to the formation during the discharge of a non-conducting corrosion product. This implies the necessity of a higher voltage for recharge which in turn can render useless the equipment normally used for that purpose. This drawback can be overcome by means of tin additions [11].

On the other hand, these grids have better electrical conductivity than those made from Pb-Sb alloys, which causes an improvement in the general performance of the battery and particularly in the so-called "cold cranking rating" which is the current a battery can supply during 30 s at -17.8 °C (0 °F) with a voltage not lower than 1.2 V per cell [10], although the last advantage can be important only at very high discharge rates.

Another interesting aspect of Pb-Ca alloys is that they can be rolled without recrystallization being produced which would impair the mechanical

properties. The structure thus obtained is very fine and keeps for an indefinite time at room temperature.

A very rigid control of the chemical composition of the alloy and production parameters must, however, be kept since any slight variations can deeply alter the properties of the product. Some very good and inexpensive battery grids can be manufactured with these rolled materials by various methods, among which is punching following by deep drawing of sheet, whereby the latter is expanded and gives rise to a product of a similar appearance to wire netting that can be cut to grid dimensions, the amount of trim produced being very small.

Adherence between lead-calcium-(tin) alloys and the active material or paste is not, it appears, very good but concrete information is lacking.

Another very interesting aspect if these alloys are to replace the classical Pb-Sb ones, is the purity required in the lead to produce them. The bibliography available does not provide much information on the matter but it appears that the purity required is higher than that now being used. Should this be correct, the alloys would considerably increase in price thereby reducing their competitiveness. This lack of information is mainly due to the fact that Pb-Ca grids were at first developed by primary lead producers. In the last few years, however, some secondary lead producers have also tested grids manufactured with this type of lead, and claim that it is an adequate material and even that minor Bi contents can accelerate age-hardening [1].

In spite of the difficulties that the processing of lead-calcium-(tin) alloys might present and the drawbacks they may have, it is clear that they have a great future and are already available in the market to form the grids in the cells of many types of commercial storage batteries of various forms and sizes, such as starter batteries for motor cars.

Pb-Sb alloys

As previously mentioned, grids manufactured in Pb-Sb alloys have the several drawbacks of price, self-discharge and release of gases. These can all be mitigated by reducing the amount of antimony in the alloys, but in that case there is the risk of desirable properties, such as mechanical strength, being lost in part. It appears this can be avoided by adding small amounts of other alloying elements or by means of special heat treatments. Consequently, Pb-Sb alloys with small antimony content may be the successors of the present ones containing over 4%Sb, competing with lead-calcium-(tin) alloys. As a matter of fact, this type of battery is already being marketed.

Pb-Sb alloys, like Pb-Ca ones, belong to the ageable type as can be seen from the phase diagram given in Fig. 2 [13]. Little information is available as yet on how these alloys age when working with grids cast industrially but, on the other hand, it is known that a solution-treated and water-quenched, Pb-2%Sb alloy attains a hardness of the order of 16 kgf/mm² after fifty days at room temperature, without addition of any other alloying element [14].

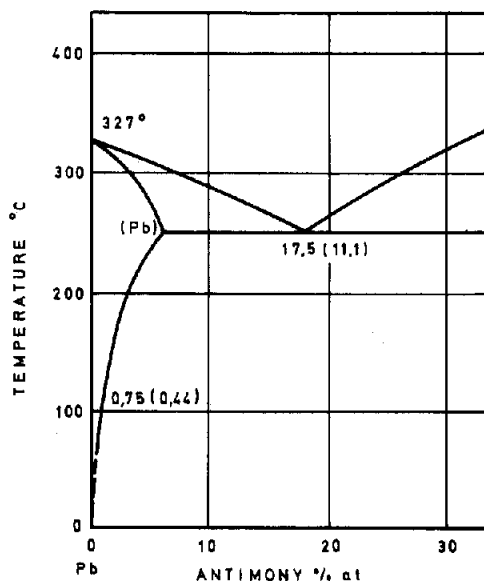


Fig. 2. Phase diagram for lead-antimony [13].

This hardness seems to be sufficient for the grid during pasting and service but fifty days of aging is clearly excessive. A requirement for higher hardness is not a technical obstacle and can be overcome since, if the grid is given a treatment which consists in keeping it for one day at -10°C followed by one day at room temperature, a hardness of 17 kgf/mm^2 can be attained [15].

These low temperature treatments can be combined in very different forms. Even working, not at the optimum temperature of -10°C , but quenching at temperatures slightly over 0°C , which presents less technical problems, still leads to considerable acceleration of hardening.

With regards to the other solution, *i.e.* the addition of small amounts of other elements and the reduction in antimony content, a considerable experience already exists both at the laboratory and industrial levels. For example, grids of an alloy of lead-3% antimony-1.5% tin-0.05% selenium have been in British naval use for over 20 years with satisfactory results [12, 16, 17], and British Rail have also been experimenting, for seven years with batteries containing 3% antimony [18]. The tests were carried out on two alloys with compositions of Pb-3%Sb-0.5%As-0.1%Ag and Pb-3%Sb-1.3%Sn-0.05%Se compared to a classical one with 8%Sb and to grids manufactured from dispersion-strengthened lead. The batteries manufactured from these alloys were used for the supply of lighting systems and for diesel engine starters. These batteries were kept in service for five years at the end of which they were subjected to various capacity and self-discharge tests, being later opened and examined for corrosion rate verification. The results were so promising, in particular with the Pb-3%Sb-1.3%Sn-0.05%Se, that the latter has recently been adopted as a normal alloy, in spite of the fact that the metals added

are expensive and that the batteries turn out to be about 10% more expensive than those formerly used.

It also appears that there is a commercial firm selling starter batteries, which require very little maintenance, containing about 2% Sb in the grids.

Borchers *et al.* [19] have studied the properties of grids cast with an industrial-type machine, using alloys with antimony contents ranging from 3.5 to 1.6% and various tin, selenium and arsenic additions. The studies were centred on mechanical properties, particularly hardness, and they were thus able to follow both long-term (service) and short-term (plant processing) ageing. With this purpose in mind not only was the influence of the alloying elements studied but also the cooling rate and, in some cases, the effect of a heat treatment. Among the indicated alloying elements arsenic seems to be the most important. Thus, the Pb-3.5%Sb-0.02%Se-0.02%Sn alloy aged at room temperature, takes about 26 hours to attain a Brinell hardness of 11 kgf/mm², and at the end of three weeks the value has only reached 11.5. If 0.05% As is added to this alloy, a hardness value of 11 kgf/mm² will be obtained in just two hours, while after three weeks, it will have a hardness of 19 kgf/mm². Under these conditions the grid may be pasted after ageing for one day and its mechanical strength during service will be sufficient. The authors also verified that cooling rate and heat treatments exert a considerable influence. Thus, the Pb-1.6%Sb-0.05%As-0.02%Sn alloy which if quenched by water spraying has an initial hardness of 9 kgf/mm² (suitable for processing) will, when subjected to a 5 min solution heat treatment at 275 °C and forthwith water-quenched, have the same initial hardness but will reach a hardness value 16 in less than a day.

Berndt and Nijhawan [20] comparing several low-antimony alloys with a high-antimony one have found that the floating current does not change in Pb-2%Sb batteries after several years service, whereas 7%Sb batteries in the same conditions show a much higher current consumption. They also found that selenium additions favour the presence of finer grain size, avoid fragility and improve castability, as had been previously pointed out by Waterhouse and Willows [17].

Conclusions

It appears that the lead-acid storage battery will for many years continue to be the most widely used. However, the manufacture of the grids may undergo considerable modifications, including production by methods other than casting. What is clearly evident is that a world-wide trend exists to eliminate wholly or in part the antimony currently used since this element presents technical and economic problems. There are two possible solutions: (a) the use of Pb-Ca alloys; (b) the use of low-antimony Pb-Sb alloys.

Both solutions seem feasible. The first has electrochemical advantages but presents difficulties in production since calcium tends to react with oxygen in the atmosphere; thus controlled atmosphere crucibles should be

used and this makes it necessary to replace or modify the current grid production machines. In addition, it appears that the adherence of paste to these grids is not good. The second solution does not overcome the problems of the present day grids although it does considerably reduce their importance. It has, however, the advantage that no modifications to the present equipment are required.

It is unlikely that both trends will exist simultaneously in one country or in a group of countries geographically close, since a most important source of lead for batteries comes from old batteries themselves and if these are of different materials serious problems would arise in recovery. The presence of calcium does not appear to pose any problem since this element oxidizes and disappears upon scrap melting. Scrap refining to a suitable degree of purity for the preparation of the alloys could, however, represent a problem. On the other hand, if Pb-Ca batteries are to be prepared and Pb-Sb scrap is available, the refining of this scrap would give rise to an antimony stock hard to dispose of. Modern plants for scrap recovery are almost automatic with a very high output capacity and this makes it very difficult to adapt them for the simultaneous or alternative use of two different types of alloys. The current attitude of manufacturers seems to indicate there is a resolute trend in the USA towards the Pb-Ca grids, while in Europe Pb-Sb grids with a low antimony content are more in demand.

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