

Lead–calcium alloy development: quality improvement

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Abstract

In the 1980s, most of the European lead producers and battery manufacturers had an interest in the lead–calcium alloys developed in the North American market. Fifteen years later, the alloy is used in most of the automotive and industrial batteries produced in Europe. During this development period, the composition of lead–calcium alloy has been improved. Physical metallurgy and electrochemistry research carried out by the lead industry has established the composition of the lead–calcium for negative grids. Metaleurop, as a lead producer, initiated in 1975 the production of lead–calcium alloys for sealed lead/acid batteries and was quickly convinced of the necessity to improve the performance of the alloy by further fundamental research (in 1980) and supporting customers' efforts. The parameters involved in the production battery plates are well specified. The composition of the alloy is dependent on the equipment used to cast the alloy. Improving the hardness by increasing the calcium content over 0.10 wt.% may not be the solution when melting and cooling conditions should also be adapted. The addition of aluminium to prevent calcium oxidation is efficient, its level being linked to the remelting and casting conditions. © 1997 Elsevier Science S.A.

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1. Introduction

Lead–calcium alloys offer an effective alternative to the use of antimony in lead alloys for lead/acid battery grids. As a consequence, water consumption is lowered and maintenance-free batteries can be designed. In the 1970s, lead producers and battery manufacturers in the North American market had an interest in continuous grid-production processes and maintenance-free batteries [1]. Accordingly, a new technology was developed for converting lead–calcium–tin strip into grids through a continuous expansion process. The properties of the alloys were also improved to allow grids to be cast with traditional procedures.

At that time, the European market used Pb–3wt.%Sb alloys; alloys with reduced antimony content (1.8 wt.%) to reduce water consumption were also under investigation. The development of Pb–Ca alloys was initiated in Europe in 1975. The first industrial production started in 1980 with the installation of a Delco Remy plant in France. At the same time, Magneti Marelli introduced the expanded grid [2].

During this developmental period, the knowledge of the

Pb–Ca alloy system was improved both by fundamental studies performed in cooperation with the University of Nancy [3–7] and in collaboration with customers, and through the investigations of various authors involved with Pb-alloy research [8–11]. These cooperations led mainly to advances in the hardening mechanism in Pb–Ca alloys with respect to the calcium content. An improved understanding of the performance of the alloys enhanced their use. The main advancement was the adaptation of the alloy formulation to suit the casting equipment.

2. Lead–calcium alloys for negative grids

2.1. The effect of calcium content on performance

2.1.1. Fluidity

The binary Pb–Ca diagram displays a peritectic reaction in the range 0.06 to 0.08 wt.% Ca. When the calcium content is higher, an intermetallic compound Pb_3Ca precipitates in large, square-shaped blocks. This diagram shows that there is no real gain to be made in fluidity by increasing the calcium content above 0.1 wt.%. Indeed, experience shows that it is easier to cast Pb–Ca grids with a calcium content of 0.010 wt.%.

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Table 1
Pb–Ca hardness as a function of calcium content after 5 min and 48 h of air cooling

Ca wt. %	HV (5 min)	HV (48 h)
0.07	11	12
0.08	11	13
0.10	12	15
0.11	11	11
0.14	11	11

2.1.2. Hardening

When the alloy was developed, most users tended to increase the calcium content to prevent calcium losses and also to improve the hardening. At that time, there was a confusing situation with a large number of alloy compositions with or without tin. The hardening process of cast alloys was not clearly explained in the literature. In the 80s, however, a few researchers [3,4] described the hardening of lead by calcium. A discontinuous reaction takes place in oversaturated cast Pb–Ca alloys. A two-fold hardening in two separate stages is observed. The hardness increases from 11 HV and reaches 15 HV. The microstructure has a characteristic ‘puzzle’ aspect and precipitation of intermetallics is not observed. Oversaturation, favourable to the hardening process, is obtained with a calcium content of 0.10 wt.% and air-cooled material. Increase in calcium content does not increase the hardening process, see Table 1.

When adding tin, a continuous structural hardening is observed with a bulk precipitation of a finely dispersed phase. With this precipitation the hardness increases from 6 to 16 HV. The as-cast product has a lower hardness than the aged product [5–7].

Adding calcium to over 0.10 wt.% is sometimes required in order to improve the rigidity of grids when they are extracted from the mold. The intermetallics formed during solidification have an effect on the matrix rigidity. A calcium content above 0.10 wt.% in the ingot will favour an increase in the dross when remelting the alloy. The intermetallic compound formed during the solidification of the ingot does not remelt easily and has a tendency to float and generate dross. Moreover, if the remelting is operated slowly, the liquid will dissolve the soluble calcium content at the peritectic temperature, i.e., 0.08 wt.%. A high calcium content, when resmelting conditions are inefficient, will provide a calcium content of only 0.08 wt.% in the liquid together with the generation of dross, even with aluminium addition.

2.2. Calcium protection by aluminium addition

Aluminium addition to Pb–Ca alloys has been described by Prengamann [9]. The optimum aluminium content is directly dependent on the casting equipment. When pumps on furnaces and mould feeding systems are not well

adapted to calcium alloys, the aluminium consumption is significant. The aluminium consumed through oxidation by the alloy and the grids is over 150 g per tonne. If the residual content in the grids is lower than 50 g per tonne, calcium oxidation will commence. Progressively, the calcium content decreases and the alloy performance changes with increase in the dross.

When using a Pb–Sb alloy, the total amount of dross is low. Compared with the metal input, the dross output is lower than 5% and frequently 3%. When a Pb–Ca alloy is being made, the dross ratio often reaches 10%. Drosses are generated by many factors and before examining the effect of each of these, it is important to describe the method used for measuring the dross content of ingots.

2.3. Dross test

During remelting alloys with calcium contents greater than 0.12 wt.%, care must be taken with the melting rate. As described above, the intermetallic compound Pb_3Ca segregates in the upper part of the ingot and corresponds to the end of the solidification.

According to the type of heating device, intermetallics will redissolve in the molten pool or will settle towards the dross on top of the bath. On average, 30 min (maximum) is needed to remelt the ingot in the casting machine kettle. Accordingly, specific equipment has been designed that is able to melt ingots within 30 min and to reach 450 °C. Performing the same test over 90 min increases the drossing rate of the ingot by 45%.

Another key point is the skimming procedure. The authors use a steel spoon with 3 mm holes. The operator’s skill influences greatly the amount of lead that can be entrapped. From one operator to another, drossing rates can vary by 100%.

Due to the inherent inaccuracy of the method, a large number of tests (between 5 and 7) should be carried out in order to reach a good evaluation of the mean value with a low standard deviation. As the day-to-day observed values are very low, i.e., below 1%, the need for a more accurate estimation of the true value could be a waste of time and money.

Table 2
Dross ratio under optimized and non-optimized conditions (ratio in % = output dross/input alloy)

Conditions	Optimized	Non-optimized
Ingot quality	1	2
Remelting conditions	1	3
Pumping	0	2
Spray turbulence	1	2
Head remelting	2	4
Humidity on heads		1
% Total	5	14

2.4. Origin of drosses in casting operations

In an ingot, the dross content is less than 1%, and when casting conditions are not well optimized it may be over 2%, see Table 2. After remelting the ingots, metal has to be transferred to the mould. Pumping equipment may oxidize the liquid metal and generate 2% dross. Liquid-spray turbulence, when feeding the mould, will form oxide layers. These will induce weaknesses in the grid frame. When grid heads are remelted, the oxide will generate an extra 2% dross compared with the normal level of 2%.

Cooling of the grid by water does not improve the hardening of the binary Pb–Ca alloy; it oxidizes the head and, when remelting, increases the dross ratio by 1%. A normal remelting of heads generates 2% in the dross ratio. When the casting machine is on test and does not operate efficiently, grids are often remelted in the furnace. Under these conditions, the dross ratio will be over 4%. Aluminium may reduce the formation of drosses. The initial content has to be sufficiently high to protect the calcium in oxidizing conditions. With optimized equipment, the aluminium consumed to protect the metal is less than 50 g per tonne.

In total, the difference between the dross ratio in an optimized and a non-optimized plant is over 8%. It is considered to be difficult to obtain a ratio of less than 5%, but there is scope to reduce the ratio when it is above 10%.

3. Conclusions

Progress in the research of the physical metallurgy of Pb–Ca alloys has resulted in considerable development of the product. The lead producer is now able to recommend an alloy specification for negative grids in line with the casting equipment. To minimize costs when using this alloy, attention must be paid to the dross ratio. When operating conditions are optimized this ratio may be reduced by a factor of two.

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