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Trends in battery alloy demand from a European perspective

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Abstract

This paper discusses the demand in Europe for lead battery alloys by volume and type. The technical implications of the required changes in specification and quality are detailed from a lead-producer's perspective.

Lead consumption

In Europe, a total of 1.7 million tonnes of lead are consumed each year. The market is divided as shown in Fig. 1. A comparison is also given with the corresponding situation in the USA. It can be seen that, in Europe, 50% of the lead consumption is associated with the battery industry. In the USA, 82% from a total of 1.2 million tonnes consumed is used by the battery industry. There are still other major uses of lead in Europe, but batteries dominate and their domination will no doubt increase

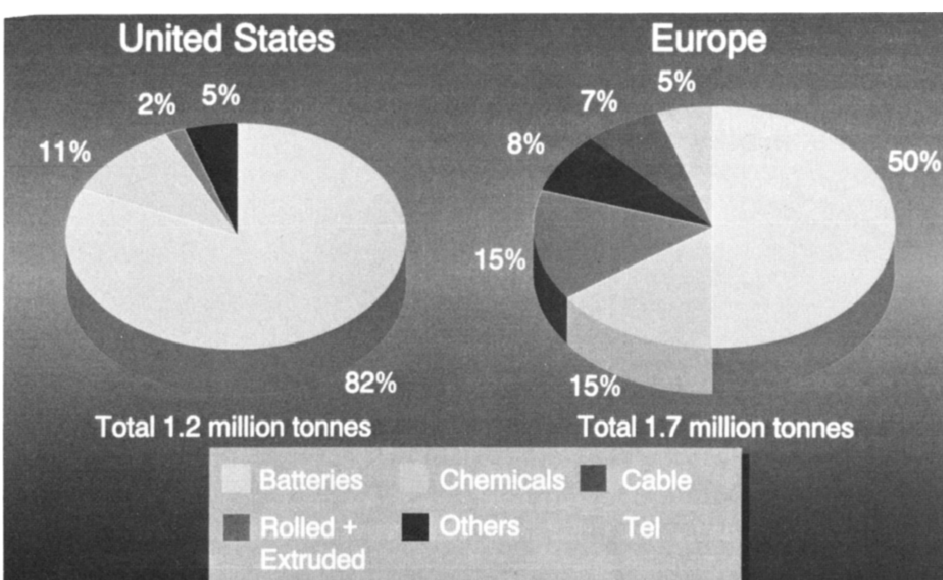

Fig. 1. Lead consumption by industry, 1992.

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in the future. The comparable figure for the Asian market lies somewhere between that of the USA and Europe at about 70%. It should be noted, however, that both the European and US battery markets are considered to be mature, with growth rates in recent years of no more than 1% per annum. Again, as a further comparison, and depending on which set of statistics are chosen, the Asian market growth has been between 3.5 and 5% per annum in recent years.

Figure 2 gives the breakdown of lead consumption by the different battery sectors. Both markets are dominated by automative batteries. The higher share in the USA is a reflection of the larger car population in that country.

Trends in grid-alloy usage

Figure 3 shows the different types of lead alloys required for grid production by the different battery sectors. As far as traction cells are concerned, the deep-discharge performance characteristics of the antimonial–lead battery are still considered to be advantageous. With further research and development, however, this situation may change. Due to the need for reduced maintenance and low gas emission, lead–calcium has almost fully taken over in standby/stationary battery design. The situation in both Europe and the USA are similar for both the traction and standby sectors.

The automotive battery picture is somewhat different. In the USA, since the early 1980s, lead–calcium or hybrid batteries have gradually taken over the market. The penetration of lead–calcium into the European market has been a relatively slow process. In the early days of lead–calcium grids, most European manufacturers showed a distinct preference for antimonial–lead. It has only been in the last three to four years that the trend towards lead–calcium and hybrid batteries has increased. With the improved technology of grid making, either by continuous casting or expanded grid manufacture, and the technical advantages of lead–calcium batteries, the move towards a greater use of such alloy in hybrid or all lead–calcium batteries is certain to continue.

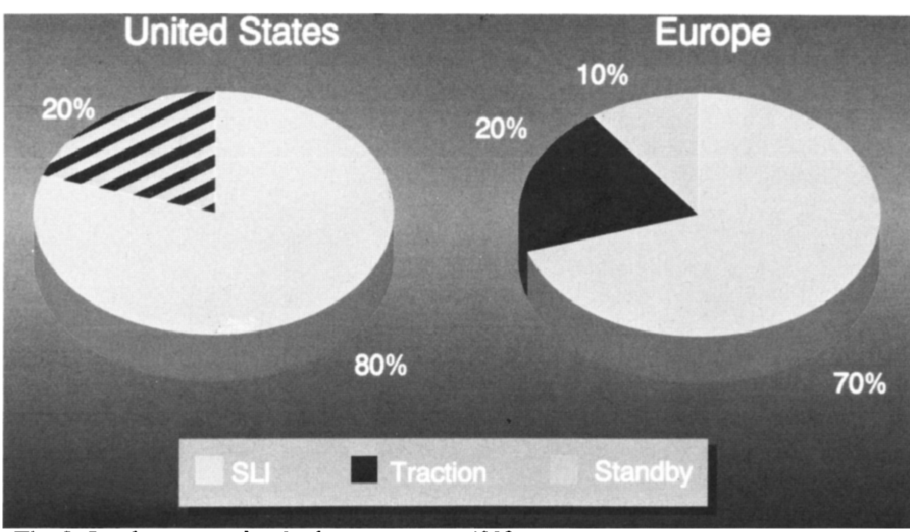

Fig. 2. Lead consumption by battery sector, 1992.

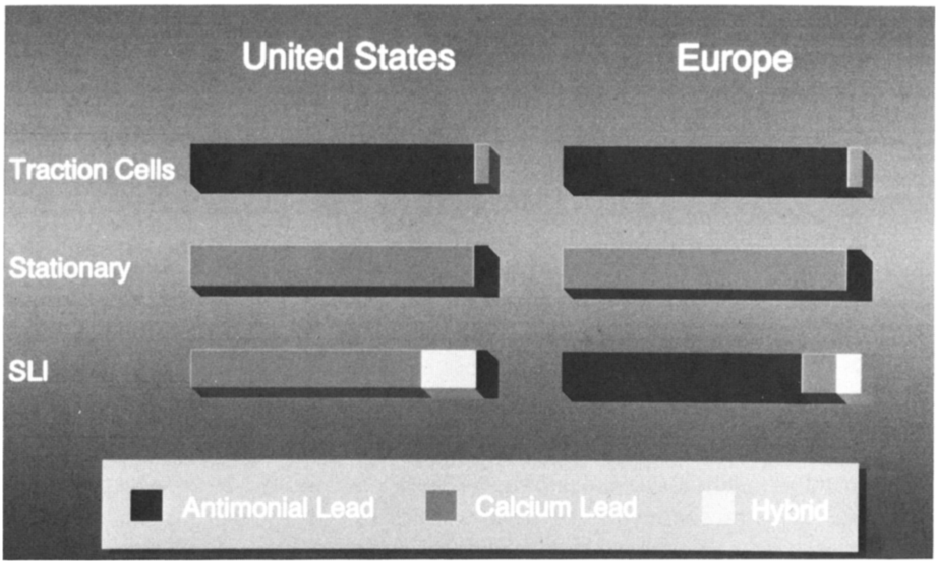

Fig. 3. Grid-alloy requirements, 1992.

Developments in grid-alloy metallurgy

There have been several improvements in grid-alloy metallurgy as battery technology has advanced and the demand for low-maintenance and maintenance-free batteries has increased. In Europe, the gradual transformation from high antimony to low antimony and calcium alloys has required numerous specification changes, increased quality control requirements, and the use of highly accurate and complex analytical techniques. In addition, suppliers of lead alloys have had to improve alloy production procedures to accommodate more complex alloys that must comply with tighter specifications and higher quality requirements.

The secondary refineries of Britannia's Refined Metals Ltd. produce a range of antimonial battery grid alloys. At Northfleet, in the South of England, a new recycling facility was opened in September 1991 to treat lead/acid battery scrap through the use of state-of-the-art technology. The installation of the CX battery breaking and paste desulfurisation system, together with an Isasmelt furnace, conforms with Britannia's aim to be technically advanced and competitive by world standards. The Isasmelt furnace produces soft lead (<0.1 wt.% Sb) and a high antimony slag that is later reduced to produce hard lead (~20 wt.% Sb) [1]. These products are ideal for the production of antimonial battery alloys as they are easily refined, blended and adjusted to the required specification.

There is a need to produce grid alloys from very low antimony (1.0 to 1.8 wt.% Sb) to high antimony alloys (10 to 12 wt.% Sb). The latter are used in conventional flooded batteries for tubular spines, flat plate grids, straps and terminals. In general, alloys with >5 wt.% Sb are used for industrial and traction batteries, whereas the medium antimony-content alloys (2.5 to 5 wt.%) are used for a range of applications from traction battery grids to positive grids for some automotive batteries and connecting straps. The most popular antimony alloys produced are, however, the low antimony group (1.6 to 2.2 wt.% Sb). This seems to have become the current standard for low-maintenance and maintenance-free automotive battery grids.

The demand for a 'fit and forget' battery has led to the development of the low-antimony grid alloys. During charging of batteries with such grids, the gassing at the negative grid is minimized and hence water loss is significantly reduced. The batteries are built with an excess of electrolyte that is sufficient for the guaranteed life of the battery. It is well known that these low antimony alloys require nucleants to avoid cracking during solidification. Selenium (in concentrations varying from 0.013 to 0.05 wt.%) is the main nucleating agent in the low antimony alloy specifications that are currently produced at Britannia. Sulfur is also added as a nucleant to some alloys, but as the antimony content in the grid is reduced to below 2.0 wt.%, selenium becomes the dominant nucleating agent [2].

In recent years, quality requirements have increased and alloy specifications have become more stringent. For example, in the past, a selenium specification range of 150 or 200 ppm was quite normal, but now some battery companies specify a very tight selenium range of 40 ppm. This has resulted in additional process control and more detailed sampling and analytical procedures.

As expected, with the increasing trend towards low-maintenance or maintenance-free type batteries, the demand for calcium alloys has grown significantly. Clearly, there is a difference of opinion between automotive battery manufacturers on the grid alloy type and composition. At present, there are automotive batteries with: (i) both grids produced from low antimony alloys; (ii) both grids produced from calcium alloys; (iii) the hybrid system of a low antimony alloy positive grid and a calcium alloy negative grid. It is probable that the lead–calcium alloy is already, or will soon become, the dominant alloy for automotive negative grids in Europe, as it is in the USA. The main problem with the use of lead–calcium, or very low antimony positive grids, is the phenomenon of premature capacity loss when the battery is subjected to deep cycling. Tin additions are made to the positive grid alloy to improve its corrosion resistance and to help prevent passivation. For this reason, tin additions up to 1.5 wt.% are specified in some calcium alloys.

New grid casting technology (such as the Wirtz continuous caster) and expanded metal strip technology (such as the Cominco strip caster and expander) are also seen to have an effect on alloy requirements. It is expected that grid production for automotive batteries will become more dependent on these new technologies as productivity and cost both gain importance. It has been reported that the Wirtz continuous caster can produce a double grid width of calcium alloy at 35–45 m per min, and a low antimony alloy at 25–35 m per min [3]. Similarly, the Cominco strip caster operates at 25 m per min and the rotary expander at twice this speed. Each of these machines can probably replace between 8 and 12 conventional book-mould casting machines.

Until now, these new technologies have been limited to negative grid production, but it has recently been reported that the Cominco machine has been installed to produce positive grids for automotive batteries [4]. Trials with a 1 wt.% Sb alloy, grain-refined with selenium, have also been successful on the Wirtz continuous casting machine [5]. Obviously, significant development work is proceeding in this area of grid casting, and there is a need for lead refiners to support their customers with the ability to frequently change alloy specifications and produce small trial alloy batches. In these times of continual development and change, it is vitally important that the alloy supplier is able to demonstrate the necessary flexibility. As an example of this requirement, Britannia currently produces as many as 73 different battery alloys.

The demand for low impurity levels is seen throughout the range of calcium alloys, but particularly for those alloys that are used for valve-regulated lead/acid batteries (VRBs). These batteries are a second generation of lead/acid technology that internally recombine the gases produced during charging. The batteries are sealed, except for a one-way pressure-release valve, and require no maintenance. In addition to VRBs, the batteries are also known as sealed lead/acid (SLA) and recombinant (RE) batteries. The electrolyte is immobilized either by using an absorptive glass mat or by gelling with finely dispersed silica. Oxygen evolved at the positive plate diffuses to the negative plate where it is chemically recombined. The positive and negative grids of VRBs are cast using lead–calcium alloys to reduce hydrogen evolution and impurities must be minimized. Elements that cause gassing during recharge, and that are considered to be problem impurities in VRBs are antimony, arsenic, tellurium, cobalt, nickel, manganese and selenium [6].

High-purity, primary, 'four nines' lead, similar to that produced from Mount Isa bullion, is an ideal starting material for the production of calcium alloys for VRB grids. Lead bullion from Mount Isa Mines (Britannia's parent company) has consistently low levels of impurities. The typical impurity levels, after refining at Britannia, are given in Table 1. Valve-regulated batteries currently command a significant share of the standby market and, with further development, it is extremely likely that they will improve their share in both the traction and automotive markets.

The use of aluminium to protect calcium from oxidation during melting and casting is now very common. There has been a trend for some changes in aluminium specified in these alloys, i.e., from a wide range (0.01 to 0.04 wt.%) to tighter ranges at lower levels (e.g., 0.01 to 0.02 wt.% and 0.015 to 0.025 wt.%). It is considered that too much aluminium is detrimental; it results in grid corrosion. By contrast, too little aluminium causes calcium loss. Some of Britannia's customers have requested alloys with aluminium in a specification range of <50 ppm. The use of aluminium to protect calcium in these alloys is not exclusive. Some alloys are produced for VRBs without aluminium. This is because the inclusion of aluminium necessitates a higher temperature for the melt pot, due to the solubility of aluminium in lead. Additionally, there is a potential hazard of explosions that are promoted by finely divided metallic aluminium present in the melting-pot dross.

The gradual change to more complex battery alloys and higher quality requirements has resulted in new processes and alloy-making techniques. Inevitably, this has lead to the need for further investment at lead refineries in both process control and analytical equipment. As an example, Britannia's primary refinery has recently invested in new 300 tonne alloy kettles at a cost of £24 000 each. These kettles are dedicated to the production of particular groups of alloy to avoid cross contamination and,

TABLE 1

Typical impurity levels of Britannia's primary lead refined from MIM bullion

Element (ppm)		Element (ppm)		Element (ppm)		Element (ppm)	
Sn	<1	Bi	15	Ni	<1	Co	<1
Sb	<1	Zn	<1	Te	<1	Mn	<1
Cu	<1	Cd	<1	S	<1	Fe	<1
As	<1	Ag	5	Se	<1		

thereby, guarantee exceptionally low and consistent impurity levels. Additionally, in order to detect impurities to very low limits, a sequential inductively-coupled plasma with a hydride generator has been purchased to add to the spark emission and atomic absorption spectrographic equipment.

High-quality calcium alloys are produced in 60 and 300 tonne alloy kettles with the application of improved process control and alloying techniques. Normally, raw calcium crowns and calcium aluminium master alloy are added to the vortex created by the kettle mixer. Pure calcium, however, is extremely reactive and when a substantial amount is added to a 300 tonne kettle, a calcium recovery of only 70–80% is achieved; the balance is lost by oxidation. A calcium granule injection process is now being used to successfully produce these large alloy batches with a calcium recovery >95%. The 2-mm diameter granules are injected with the aid of an inert transport gas. In less than 30 min, the required calcium content is achieved in a 300 tonne batch. Furthermore, this results in a significant reduction in calcium oxidation and a more cost-effective and cleaner process.

Concluding remarks

At a time when battery technology is changing and alloy development is important, it must be recognized that there is a need for increased customer service (such as the availability of metallographic and analytical facilities), for supporting joint development work with battery companies, and for the facility to produce trial alloys in small quantities.

Although battery grid alloy research is not carried out at Britannia, the company works closely with its customers and fully supports collaborative research projects. Britannia represents MIM as ILZRO members and part-fund several lead research projects. During the last year, the Advanced Lead-Acid Battery Consortium (ALABC) has been established to improve the lead/acid battery so that it can adequately meet the service requirements of the imminent electric-vehicle industry. The ALABC has a four-year, US$ 19 million research programme.

In summary, it is expected that the growth of the battery industry, together with the accompanying changing/increasing technical demands, will present increasing challenges to all those involved with the development of battery alloys.

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