

LEAD ALLOYS INTO THE 1990s

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Introduction

When considering the development of alloys for battery grids it is important to consider:

- (i) the influence of original equipment and replacement markets on the technology choices in world battery manufacturing;
- (ii) the relationship of alloy choice which is dictated by down-stream manufacturing processes.

Another important factor within this framework is the incredible market growth of gas-recombination battery (RE) technology and its consequences on alloy choice. In fact, the title of this paper — *Lead Alloys into the 1990s* — lays down a challenge. This challenge is for manufacturers to position themselves to take full advantage of the many and major changes that are now occurring in the metals and battery industries. In assessing these changes, it is worthwhile to consider the route by which alloy developments have entered the industry.

The automotive battery sector has been the 'test bed' for most of the alloy changes that have occurred or are occurring. That is to say, the battery industry has been very much 'pulled' into change by the automotive industry. Automotive engineers have placed many demands on battery design; these include:

- high cranking performance at low temperature
- reduced weight requirements, but with increased power and energy density
- pressure to remove the battery from the engine compartment, due to higher under-bonnet temperatures and reduced space
- a desirability to 'seal' the battery and render it maintenance free.

Furthermore, due to the fiercely competitive nature of the automotive industry and its dynamic response to technology and materials changes, workers in the battery and battery-supply industries will be pushed to their own innovative limits to maintain the strong position of the lead/acid battery system in this ever-changing environment. In a recent address to a group of automotive engineers, J. Rivard of the Ford Motor Company estimated that by the year 2000 the total electrical power consumption of a vehicle will rise from its present 1 kW to 5 kW. At the same time, the cycle time for the new vehicle development will be reduced by half. Already, the notion of the 'world

car' is becoming a reality with the current global associations between American, Japanese, and European car manufacturers, *e.g.*, Ford/Mazda, Rover/Honda. Such activity will hasten the pace of technological change throughout the world and will compel manufacturers—whether in Asia, Europe or Africa—to meet the necessary design criteria demanded by international consortia.

Lead-antimony alloys

The response to the changing situation in the automotive industry has been marked by a high degree of co-operation between material suppliers and battery manufacturers, particularly in the development of new alloys exhibiting the improved performance characteristics of:

- reduced water loss
- lower electrical resistance
- easier castability and better handling performance
- increased corrosion resistance
- lower cost.

The industry embarked on a systems approach to the development of new alloys. First, it was established that the reduction of antimony was of paramount importance in the development of a new, maintenance-free battery system. Two basic philosophies emerged for alloy design: (i) the complete removal of antimony from the grid, *e.g.*, calcium alloys; (ii) a lowering of the antimony content, using grain refiners such as selenium, sulphur, and copper to compensate metallurgically for the reduced antimony content.

Traditional antimonial alloys, despite their hard, fine-grain structures, were associated with high gassing rates. To lower these gassing rates, it was essential to reduce the level of antimony in the grid alloy. As antimony is reduced, however, large dendritic grain structures are formed. These structures are prone to grain-boundary attack that results in deep intergranular corrosion. This is explained both by the reduced number of nucleating sites in low-antimony alloys and by a reduced availability of eutectic liquid to feed the solidification front. To overcome the problem associated with low-antimony content, the industry has adopted the use of grain refiners such as selenium, sulphur, and copper. These nucleants produce a more uniform, fine-grained structure that tends to produce a regular, clean casting where grain-boundary attack is significantly reduced.

Grain refiners have been used individually, or in combination, and achieve their effect by coming out of solution prior to the solidification of lead. The solid intermetallic forms of the grain refiners act as nuclei for the crystallization of primary-solid-solution material. Further, the solidification of these alloys does not proceed from the mould wall, as with alloys of higher antimony content, but occurs preferentially on the minute particles suspended in the liquid. At the final stages of solidification, instead of dendritic tearing there occurs both grain rotation and a more effective consumption of

the remaining eutectic liquid. Ideally, this nucleation process should continue as the temperature decreases so as to maximize the advantage of this grain-control mechanism and to overcome the problem of a wider freezing range common to low-antimony alloys. Therefore, a combination of grain refiners should be used, particularly in the very-low-antimony alloys. Selenium, which forms the intermetallic compound lead selenide, has an overall advantage as a grain refiner when compared with sulphur; this is due to its higher solubility in lead and its tendency to be more stable on remelting. Selenium is usually used in conjunction with sulphur and copper in the very-low-antimony alloys, *i.e.*, less than 1 wt.%.

Despite the excellent performance of the above alloys, there are a number of considerations that need addressing. Higher temperatures are required to maintain the grain-refining level. Metal temperatures should be kept between 460 and 500 °C: not only is this applicable to molten metal in the bath, but also to that residing in feedlines, ladles, etc. Small variations in temperature will cause significant losses of nucleants and will, in turn, result in grid failure.

It has also been suggested that as the antimony content is reduced to levels of 1.5 wt.% and below, passivation problems, similar to those found with calcium alloys, may be experienced. It is claimed that this problem can be ameliorated by the addition of tin. High tin levels, however, also influence the nucleating process and can cause casting difficulties. It has been recommended, therefore, that tin levels of 0.3 - 0.4 wt.% be maintained in such alloys.

The growth of low-antimony alloys has been supported by the significant change to low-maintenance and hybrid maintenance-free construction philosophies in all the major markets of the world. This trend is continuing with a number of major companies electing to replace calcium-alloy batteries with all-low-antimony designs.

Lead-calcium alloys

In attempts to meet battery requirements in new-generation vehicles, the lead-calcium system was considered to offer much promise. Early alloys used a calcium composition in the range 0.08 - 0.11 wt.%, with the addition of tin. Some companies employed high tin levels (0.5 - 0.7 wt.%) while others preferred lower levels (0.3 - 0.4 wt.%). Although tin was initially added to both positive and negative alloys, today it tends to be restricted to positive grids. The latter are conventionally cast, or are fabricated from rolled calcium sheet or cast calcium rolls produced by the direct method.

Unfortunately, the early alloys were not entirely free from problems. As calcium is very reactive, it produces large quantities of oxide dross and intermetallic compounds that cause losses in productivity and quality. Serious corrosion problems developed in many early calcium batteries; this brought about some hesitation on the part of manufacturers. To overcome

these limitations, calcium alloys with the addition of aluminium were introduced. The mechanism by which the aluminium assists would appear to be similar to the action of tin, namely, an Al-rich oxide skin is formed and, while it remains intact, air is excluded from the melt and calcium loss is inhibited. Some movement in the level of aluminium has occurred since its first introduction at levels of 0.03 - 0.05 wt.%. At these levels, drossing problems were experienced due to the formation of aluminium-rich intermetallics caused by aluminium coming out of solution when the melt temperature inadvertently fell to low temperatures. Current levels of around 0.015 - 0.025 wt.% appear to have overcome this problem.

Novel applications of alloys in the battery industry

Two significant new approaches to improved battery performance via the use of novel conductivity paths have been developed in recent years.

Copper-stretch-metal (CSM) technology

The CSM technology is used only for negative electrodes. It consists of taking a copper sheet or coil and passing it through a standard metal-expanding machine. Once an expanded copper sheet has been produced, the following processing steps are required:

- (i) the expanded metal is electroplated: first, with a lead-tin alloy that may also contain selenium; second, with a pure-lead coating;
- (ii) the grid length is trimmed to required size;
- (iii) a plastic bottom bar is injection-moulded to the bottom of the grid;
- (iv) a lead-alloy top bar is automatically cast onto the grids; this renders the grids available for 'normal' battery processing.

The main advantage of CSM lies in the ability to reduce the battery or cell total impedance. Impedance refers to the totality of all the cell resistances. These include polarization effects, electrolyte resistance, and the sum of the grid resistances. As such, CSM batteries are able to give much improved short-term discharge and re-charge characteristics. These advantages have allowed the batteries to find a wide range of applications, *e.g.*, traction, load-levelling, and submarine duties.

Lead-coated wire (Electrosource) technology

This process is simply an extension of the conventional extrusion process. The Electrosource Company has developed a computer-controlled extruder capable of coating a wide variety of small-diameter core materials with lead.

The smallest pure-lead extruded wire has a 0.015 in. dia., over a 0.008 in. fibre-glass yarn. The largest diameter wire extruded is a 0.250 in. pure-lead sheath over a bundle of 12 lead-coated copper wires. Wire production rates of 400 ft min⁻¹ have been achieved with 0.025 in. dia. pure lead over 0.013 in. dia. fibreglass. At this rate, production of one 6 in. × 6 in. grid every 7.2 s

would be achieved. Using the existing control computer, 10 heads per station could be simultaneously operated, thus bringing the rate down to 0.72 s per grid.

The process has been successful on pure lead, calcium alloys, and low-antimony alloys. The resultant battery performance results have been impressive. Using this process, a battery designer can specify core and coating on the basis of its essential electrochemical characteristics. In particular, the extruded pure-lead surface is dense, almost amorphous in appearance, and has a high resistance to cycling corrosion.

Sealed lead/acid batteries

Sealed lead/acid batteries have been one of the most significant developments over recent years. In these batteries, oxygen evolved during charge is recombined at the negative electrode. The battery design incorporates a pressure-relief valve for safety purposes under abuse conditions. By virtue of this design, such batteries are more correctly known as valve-regulated, sealed batteries. In these designs, oxygen is allowed to diffuse to the negative electrode where it will react quickly with the lead and produce water. As long as the charging current is below a critical value, dependent upon the rate at which oxygen is consumed, hydrogen will not be evolved and the cell will never lose water.

These new, sealed designs have provided significant improvements in performance, such as:

- high gas-recombination efficiencies and very low water loss, giving a sealed, unspillable and safer product
- lower internal resistance with consequent benefits in power output, particularly at high rates and low temperatures
- higher energy densities per unit volume and weight
- better charge acceptance, particularly under cold conditions
- improved vibration and shock resistance
- no acid stratification during service, resulting in stable top-of-charge voltages, improved charge efficiency, and elimination of the need for equalization charges.

Nevertheless, these performance improvements are dependent on increasingly tighter specifications for pure lead used in oxide manufacture. Emphasis is placed on metals that contribute significantly to gassing (*i.e.*, manganese, cobalt, nickel, tellurium, antimony, and arsenic) as opposed to those elements that do not cause appreciable gassing (*e.g.*, bismuth, tin, silver). Such requirements will impose severe limitations on the use of secondary metals in this particular market niche.