CALCIUM PRODUCTS FOR BATTERY GRID PRODUCTION: A SUPPLIER'S PERSPECTIVE

J. T. NAWRACAY

Pfizer Inc., P.O. Box 5848, Wallingford, CT 06492 (U.S.A.)

Introduction

Because calcium is not a well-known metal, an overview is given here of the metal and its uses, especially since many of the effects of calcium experienced in other applications, particularly metals applications, are relevant to the phenomena observed in the treatment of lead with calcium. In this respect, the paper describes the revolutionary impact of calcium on the U.S. battery market, the development of special calcium products that have accelerated the growth of the new battery technology and, finally, the advantage of the special CAL-GRID products for introducing calcium and aluminium into lead.

Calcium plays an important role in the quest for energy-efficient technologies. Since the mid-1970s, the metal has come into widespread use in the production of: ultra-clean, high strength steels; high energy density magnets for electromotive applications; and the lead/acid 'maintenance-free' battery.

While many of the benefits of calcium in metallurgical applications have been known for over 50 years, three factors have been important in its recent development. These are:

(i) efficient use of energy resources;

(ii) development of effective calcium addition technology;

(iii) realization of the cost benefits of calcium in production and in marketable products.

The demand for energy efficiency, which arose from the oil crisis of the 1970s, revolutionized materials' technology. The design objectives for today's higher gas-mileage automobiles required: high-strength, lightweight steels; lightweight electric motors; and down-sized SLI (starting, lighting, and ignition) batteries. Downsizing of the SLI battery for gas mileage consideration has been accompanied by increased performance demands. The smaller four-cylinder engines are more difficult to crank, thus increasing electrical demands, while the growing use of microcomputers for control and other electronics in the car has increased the need for a battery with a greater reserve capacity.

0378-7753/88/$3.50

The development of calcium grid alloys addressed these areas. An ancillary benefit of the calcium SLI battery was a reduction in water loss. Since the battery did not need frequent water additions and could be sealed, the possibility of a longer performance life was offered to the consumer. This became a central theme in marketing the battery; it led to the concept of a 'maintenance-free' (MF) battery. The technical advantages of the MF battery were translated into a major market opportunity by battery manufacturers in the U.S.A.: extensive promotion resulted in rapid acceptance. Calcium MF batteries for automobiles now comprise over 90% of the total U.S. market.

Calcium in SLI batteries

In 1975, calcium MF batteries accounted for approximately 10% of the total U.S. automotive battery market. Sales have grown rapidly and in 1986 have amounted to an estimated 68 million batteries, almost 94% of the market. The use of the lead–calcium alloy in both the positive and the negative grids is essentially exclusive in the original equipment battery market and is about 20% of the replacement battery market.

Coupled with the development of the all-calcium battery has been the important evolution of the hybrid battery. The hybrid battery incorporates a calcium–lead negative grid and an antimony–lead positive grid to obtain the advantages of both alloys. It retains the electrical, corrosion, and maintenance-free aspects of calcium–lead and adds the deep discharge/charge characteristics of the antimony–lead grid. The hybrid battery is an important factor in today's market and accounts for approximately 75% of the replacement battery business.

Calcium additions

Calcium was first used in refining lead and steel because of its benefits as a scavenger. With lead, calcium is used for the removal of bismuth. With steel, its purpose is desulfurization and deoxidation. The metallurgical benefits of calcium combined with the enhanced electrical properties of the calcium grid alloys created a demand for new calcium products. There was also a need for improved methods of adding calcium to molten metal. In the mid-1970s, Pfizer introduced battery-grade calcium with form and chemistry designed for the production of grid alloys.

While the introduction of battery-grade calcium addressed the needs of the industry for improved chemistry and compatability with addition methods then in use, a basic problem remained unresolved. The relatively high melting point of calcium, *viz.* 835 °C, presented a serious challenge to the grid-alloy produced. The higher temperature involved in alloying calcium with lead meant increased energy consumption and lower refractory life. In addition, it was not uncommon for the grid producer to experience calcium losses of over 60% with accompanying heavy drossing.

Basket plunging and vortex plunging are the most common methods of calcium addition. The calcium, often with other alloying additions such as aluminium or tin, was placed in a wire-mesh basket and submerged in the melt. In an attempt to enhance calcium recovery and prevent drossing, other addition methods were attempted such as the vortex addition. Another problem was the continued loss of calcium during further refining. Calcium continued to come out of the melt and oxidize on the surface. Calcium–lead master alloys containing about 1% calcium had to be added to maintain calcium at the appropriate level. Constant monitoring of the melt was required to assure final grid alloy specifications.

CAL-GRID development and advantages

A major breakthrough in the production of calcium–aluminium grid alloys was achieved with the introduction of the alloy CAL-GRID I and, more recently, calcium–aluminium briquettes — CAL-GRID II.

The calcium–aluminium binary phase diagram shows a eutectic at 65 at.% Ca. The melting point of this eutectic is 540 °C, almost 300 degrees lower than the melting point of pure calcium and over 100 °C below that of aluminium. This offered the obvious advantage of a lower melting point and the lower addition temperatures needed to improve the process. Extensive research was conducted on the metallurgy of compositions surrounding this eutectic; a carefully controlled and selected composition was found to have unexpected advantages in both grid production and in the properties of the alloy itself. Before examining these advantages, a brief background on the properties is considered helpful.

Calcium is a highly reactive metal. While not as violently reactive as sodium, under normal atmospheric conditions it does tend to hydrate rapidly. Unless properly stored and handled, calcium will revert to lime within a matter of days. Aluminium, on the other hand, forms a stable and tenacious oxide. Several high-calcium alloys near the eutectic retain the properties of calcium. The surfaces of the alloys are hydrated, sometimes preferentially. These compositions react with water to produce hydrogen gas and calcium hydroxide. The selected composition, CAL-GRID I, is quite stable with respect to moisture. Samples have been left exposed for months with no indication of hydroxide formation. While stable in this sense, the alloy remains pyrophoric under heavy impact. This has not been a problem in normal use, but causes difficulties in shipping overseas.

CAL-GRID I, being a pyrophoric material, is regulated by the international shipping concerns to only 15 kg per container, per drum, which must then be put in a wooden box. Obviously, this packaging greatly increases the cubic size and weight of a shipment of CAL-GRID I on the high seas and therefore results in very costly shipping rates. CAL-GRID II can be packaged in drums containing approximately 113 kg and shipped under the same regulations as those for pure calcium, thus reducing transport costs.

CAL-GRID II is a briquette product, a mixture of calcium and aluminium, currently made in the ratio 73%:27%. However, variations of this ratio can be readily produced and are being considered by some of the major lead producers as battery companies are contemplating different levels of calcium and aluminium for their grids. CAL-GRID II has been reported to be more effective than CAL-GRID I in the sense that addition times are reduced tremendously. Changing the calcium:aluminium ratio does not disturb the eutectic since the briquettes are not an alloy but simply a pressed mixture of the two metals. The calcium in the lead acts as a heat generator and melts the aluminium so that different ratios of the components do not appear to affect the ability of the aluminium to go into solution at bath temperatures ranging between 470 °C and 540 °C. This product is being widely used in the U.S.A. and is also being exported. Continuing research, in close cooperation with lead producers and battery manufacturers, verified the expected advantages of CAL-GRID II and disclosed the following additional benefits.

(i) The alloy has improved significantly the retention of calcium: recoveries have risen from a typical level of 50% with pure calcium to better than 90% with the CAL-GRID alloy. Subsequently, this has been found to be true for CAL-GRID II as well. The expected lower addition temperatures have resulted in lower energy costs, increased refractory life, and extended life of capital equipment.

(ii) The stability of calcium in the melt has been enhanced. Studies of the calcium content of the melt during holding periods have shown that calcium losses are reduced from a typical 20% to less than 5%. The need for constant monitoring of calcium levels and master alloy additions has been lessened. Further, there has been a decrease in the refining time.

(iii) Battery grids produced from CAL-GRID have exhibited better structure and strength. Ageing studies (1 - 35 days) have demonstrated a 15% increase in both yield strength and tensile strength compared with grids containing calcium only. Advantages have also been noted when CAL-GRID is used in tin-containing alloys. The rôle of aluminium appears to be that of a grain refiner. Calcium may also contribute to the improved mechanical properties. CAL-GRID has been reported to have a beneficial effect on fluidity which results in better mould fill and enables the production of lighter gauge grids. The problems of quality control have been reduced.

(iv) Penetrating corrosion of grids is reduced with CAL-GRID. This appears to be a grain boundary effect. Weight-loss corrosion with CAL-GRID is similar to, or slightly higher than, corrosion of grids with calcium only; weight-loss corrosion is significantly lower than that experienced with the antimonial alloys.

Future directions

The need for high energy density SLI batteries will continue. The trend is for grids with decreasing plate thickness and a continuing overall reduction in battery weight. Plate thickness has decreased from a typical 1.9 mm in the early 1970s to 1.3 mm or less in 1986. This, combined with the reduction in the number of grids, has reduced battery grid weights from a typical 4.95 kg to an approximately 3.4 kg level. The weight of the battery is further decreased by the use of less paste. Lead contained in a typical calcium-containing battery is 7.7 kg.

Battery-grid production methods will continue to evolve. Today's conventional techniques involve both cast and expanded grid technologies. Casting technology is used to produce both grid types for the calcium–lead battery. In the case of the hybrid, calcium/antimony–lead battery, the positive antimony grid is cast while the calcium negative grid is either cast or expanded. New developments in continuous casting of grids augur well for the future. The continuous casting technology holds the promise of lower overall production costs and higher efficiencies.

Continuing research in addition methods and the calcium products themselves holds promise. CAL-GRID addresses today's needs of the lead alloy producer and battery manufacturer. Research on the electrochemistry of calcium (*e.g.*, the use of calcium as a replacement for lithium in high energy density batteries) can be expected to result in a better understanding of calcium's electrical characteristics. The development of this product, through close cooperation with the lead and battery industries, has created market and cost opportunities for the producer and a better-quality product for the consumer.