Lead–calcium alloys in the production of lead/acid batteries

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Abstract

In current practice, there is a steady tendency for the increase of production of sealed lead/acid batteries using lead–calcium alloys. The mastering of these alloys is, however, difficult due to debilitating phenomena taking place, the main of which is the instability of alloy composition in the process of grid casting because of calcium oxidation. Thus, production conditions experience certain problems associated with the continuous control of alloy composition, increase of slag formation, the increased consumption of calcium, productivity decrease, increase of rejection and decrease of grid resistance to corrosion. This work examines both lead and lead–calcium alloys, methods for their deformation strengthening, the choice of alloy optimal composition, and procedures for stabilizing calcium during long process periods. A technological scheme is presented for wasteless manufacture of lead–calcium grids of stable composition with control of alloy structure, increased corrosion properties and high productivity.

The composition of the materials used for the current collectors in the plates of lead/acid batteries, and their method of production, greatly influence the performance of the batteries. In particular, the correct choice of the 'grid' materials is important in the manufacture of sealed units. It is recognized that some of the constituents used in traditional types of battery reduce the hydrogen and oxygen overpotential on lead, and thus increase the rate of gas evolution during charging and storage. These materials are therefore unfit for sealed designs. One such example is the lead–antimony alloy containing 4–6 wt.% Sb that is widely used in battery production.

The most acceptable grid alloys for sealed batteries are lead–calcium systems. The latter often contain a minor amount of aluminium (about 0.005 wt.%) that is introduced to prevent the rapid oxidation ('burning down') of calcium during grid preparation and casting. The use of such alloys, however, limits the performance of the positive electrode, especially under deep-discharge conditions. This is due to the formation of a compact oxide–sulphate layer at the grid/active-material interface. This layer is the result of the reduction (discharge) of corrosion products of the lead–calcium grid. Furthermore, the dense structure of this layer prevents its oxidation during subsequent charging processes. The formation of this passivating layer is most marked under deep-discharge service when the polarization is spread evenly on the electrode thickness. As a result, the discharge process proceeds towards the surface of the electrode.

Sometimes, phosphoric acid is added to the electrolyte to depassivate the positive electrode grid. A detailed study of the mechanism of the action of this additive has been performed in the author's laboratories. It has been found that the molecules of H_3PO_4, or phosphate ions ($H_2PO_4^-$), are adsorbed on the surface of the lead dioxide and thereby reduce the effective thickness of the porous layer where the oxide formation processes take place. As a consequence, the interfacial region between the grid and the active mass plays only a small part in the discharge process and is not subject to passivation. This leads to stabilization of the capacity during the cycling process but, in the presence of phosphoric acid, the capacity is 15–20% lower than the nominal value.

Many major battery manufacturers use ternary lead–calcium–tin alloys, containing 0.3 to 0.5 wt.% Sn, in the production of grids for sealed lead/acid batteries. The addition of tin improves the foundry properties; its benefit is particularly noticed when casting thin grids, i.e. less than 1 mm.

Research by Bulgarian and Italian scientists has shown that tin addition influences significantly the anode properties of lead due to the inclusion of tin ions in the crystal lattice of the lead oxides that are formed during the anodic polarization process.

During development of small-sized sealed lead/acid batteries in the U.S.S.R., a closer definition was made of the optimal content of the alloy. In addition, some technological questions that had not been solved in the present literature were solved. In particular, it was necessary to overcome some difficulties connected with the instability of the alloy composition during the foundry process that was due to the high temperatures occurring in the liquefaction and oxidizing processes of calcium. To discover the optimal alloy composition, the mechanical, technological, corrosive and electrochemical properties of the calcium alloys were studied. To enhance the stability of the alloy composition, the influence of different coatings and additions was investigated.

Figure 1 shows the dependence of Pb–Ca alloy hardness on both calcium content and the presence of aluminium and tin additions. A maximum in hardness is found at calcium concentrations between 0.07 and 0.12 wt.%. The absolute value of the alloy hardness increases with time. This behaviour is especially prevalent in the presence of the third component. Besides the hardness, other mechanical properties were studied, such as the limit of rupture strength and the relative lengthening at the point of rupture.

These alloys were subjected to corrosion tests that showed that the samples made of the lead–calcium alloy containing not more than 0.1 wt.% Ca have a lower corrosion rate than those made from lead–antimony. Additions of Al and Sn in the indicated quantities make the samples more resistant to corrosion.

In order to explain the dependence of the mechanical and corrosive properties of the alloys on the calcium content, the micro-structure of experimental samples with different calcium contents was studied. When the calcium value is equal to 0.065 wt.%, the alloy has a large crystalline
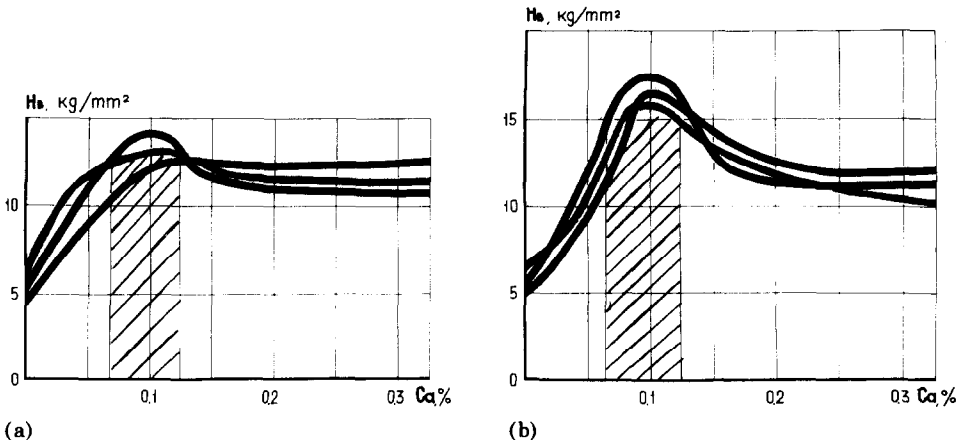
Fig. 1. Dependence of Pb–Ca alloy hardness on Ca content and presence of Al and Sn additions: (a) on the day of casting; (b) 3 days after casting.

structure with distinct grain boundaries. With increasing calcium content, the crystal size of the structure becomes smaller and the grain boundaries are broken. This suggests the presence of inclusions of a second phase comprising a Pb_3Ca inter-metallic compound. The latter is clearly visible in the form of dark star-like formations when the calcium content is 0.25 wt.%.

The change in the structure is associated with a corresponding change in the properties of the alloy. For calcium contents up to 0.10 wt.%, the hardness increases due to both a modification in the alloy structure and a dispersive distribution of sub-microscopic formations of the second phase. Further increase in calcium concentration results in the development of large regions of the second phase. The latter no longer serve as a dispersive hardening factor and the alloy hardness decreases. On the basis of these results, and considering the requirements for batter grids, the optimum grid alloy composition for small-sized, sealed batteries was taken to be: Pb + 0.07–0.10 wt.% Ca + 0.003–0.02 wt.% Al + 0.1 wt.% Sn.

The stability of the alloy composition at elevated temperature is shown in Fig. 2. The surface of the molten metal was protected by a layer of charcoal; Al_2O_3 and Al. Alloys containing 0.10–0.15 wt.% Ca were exposed to a temperature of 500–550 °C and regularly sampled for analysis. The data show that when protection with charcoal and with a layer of Al_2O_3 is applied, the calcium content in the alloy decreases rapidly so that within 1.5 to 2 h it is below the specified level.

The introduction of aluminium to the alloy melt reduces considerably the burning rate of calcium. For instance, with 0.05 wt.% Al, the calcium content can be maintained within the required concentration range for one week. These results are of practical interest and demonstate the possibility of improving the stability of the alloy composition during the foundry process. Nevertheless, in common practice with battery grids casting, where extracted scrap and foundry wastes are returned to the melting pot, the continuity of
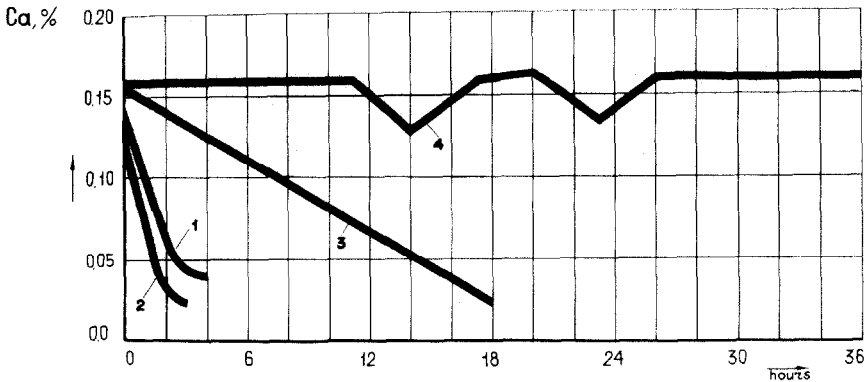
Fig. 2. The action of Al dope on Pb–Ca alloy composition stability at a temperature of 500–550 °C: (1) charcoal protection; (2) Al₂O₃ layer protection; (3) 0.005 wt.% Al added; (4) 0.05 wt.% Al added.

the aluminium-saturated metal is not always guaranteed. This results in calcium oxidation and changes in alloy composition that, in turn, necessitate permanent control of the alloy composition during grid processing, increases slag formation and calcium consumption, reduces productivity and increases rejects, and influences the corrosion resistance of the grids. Thus, effort has been devoted to developing advanced-technology equipment to achieve high-quality grid castings with a stable alloy composition.

Following the above-mentioned detailed study of the problems associated with the development and manufacture in the U.S.S.R. of sealed, small-sized lead/acid batteries for domestic electronic circuitry, a new environmentally-safe and wasteless technology for the continuous manufacturing of battery plates was designed and tested. This process is shown schematically in Fig. 3 and includes equipment for continuous grid casting, as well as for continuous pasting, enveloping, cutting and drying of battery plates.

The method for manufacturing continuous alloy strip (Fig. 4) involves the use of a rotating drum in a 'crystallizer' with a fixed filling device that contacts with the drum (Fig. 4). The strip is formed by solidification of the melt in the grooves of the rolling drum when molten metal is continuously fed into the slot of the filling device in quantities greatly exceeding the quantity required for the grid formation at the set casting rate. The surplus melt from the filling device is returned to the distributing furnace. The continuous casting installation has twin electric furnaces: in the first, the metal is melted, while in the second (distributing) furnace the melt is fed into the crystallizer.

The controlled supply of lead–calcium alloy from the melting furnace to the distributing unit, and from the latter to the crystallizer and back to the furnace, is carried out by means of magneto-hydrodynamic pumps (MHD) designed in the U.S.S.R. The operation of the pumps is based on the principle
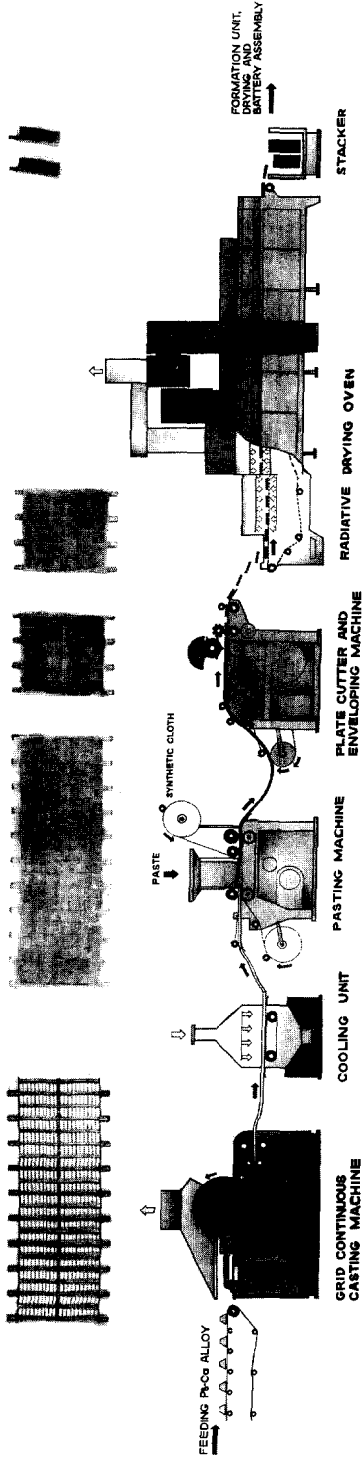
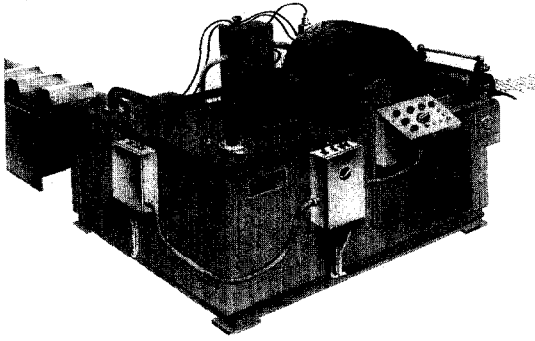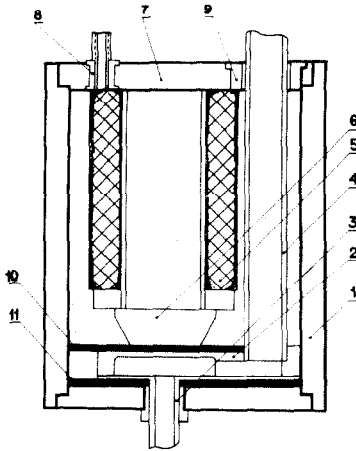Fig. 3. Istochnic continuous casting and plate making system for sealed batteries.

Fig. 4. Grid continuous casting machine.

1 - CASE
2 - OPERATING CELL
3 - INLET PIPE
4 - OUTLET PIPE
5 - SOLENOID

6 - STEEL MAGNETIC CORE
7 - COVER
8,9 - SLEEVE
10,11 - INSALTING PAD

Fig. 5. Scheme of MHD pump.

of interaction between the current run through the molten metal and an external magnetic field. As a result of such interaction, the melt contained in the working cell becomes rotated and is ejected into the output pipe under the action of centrifugal force (Fig. 5).

Before starting, the MHD pumps should be placed in the electric furnace containing the melt so that the latter fills the working cell. This must be achieved in such a fashion that the alloy amount, its supply to the filling device, and return to the furnace are all performed from very deep inside the melt without disturbing the continuity of the protective, aluminium-saturated metal film. This will ensure good stability of the lead–calcium alloy. Such process conditions are achieved with equipment discussed here and provide a high-quality, continuously cast, alloy strip. To meet the required

hardness properties, the strip is cooled, rolled into a coil, and stored for only a short period before feeding into the paster (Fig. 6).

Pasting of the continuous alloy strip requires the use of a special chemical/mechanical-resistant cloth with a low electrical resistance. Such a synthetic cloth prevents cracking and loss of paste, reduces environmental hazards, and suppresses the shedding of positive active material in batteries using free electrolyte.

After coming from the paster, the strip is fed into a cutting device (Fig. 7) for separation into individual plates. The latter are continuously fed into a drying oven that uses radiant heat (Fig. 8).

After drying, the plates are directed to the formation section. This process is carried out either in the battery container or in a tank, according to the type of battery.
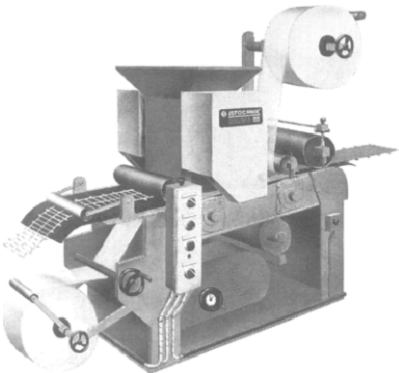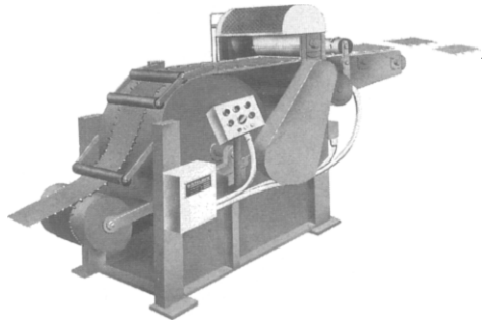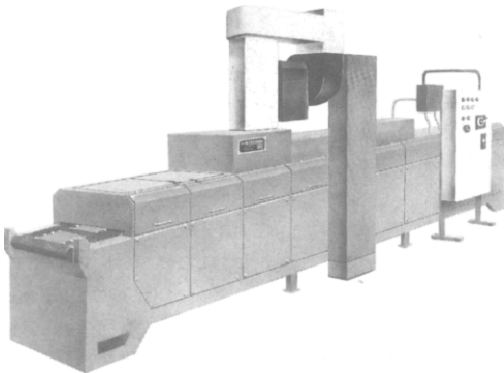

Fig. 6. Pasting machine.

Fig. 7. Plate cutter and enveloping machine.

Fig. 8. Radiative drying oven.