

CASTING TECHNOLOGY FOR LEAD-CALCIUM GRIDS

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Trends in grid design

In the U.S.A., automotive lead/acid batteries using lead-calcium grids have dominated both the original equipment (OE) and the replacement markets in recent years. Over 90% of OE batteries are all-calcium, that is, both the positive and negative grids are constructed from calcium. This figure has increased from only 10% in 1975. A similar dramatic increase in the shift towards calcium grids has also occurred in the replacement sector. In 1975, less than 5% of replacement batteries used a calcium grid, today the share is 85% with 24% being all-calcium and 61% being a hybrid design (*i.e.*, lead-antimony positive, lead-calcium negative).

Casting lead-calcium grids

Calcium alloys used in automotive lead/acid batteries consist of a corroding grade of lead, about 0.08 wt % calcium, from 0.25 to 1.0 wt % tin, and perhaps some aluminum. From a casting standpoint, there are three major differences when comparing a calcium alloy with an antimony alloy containing between 2.75 and 5 wt.% antimony. These differences are (i) hardness after casting; (ii) oxidation rates at high temperatures, (iii) melting and solidification temperatures.

First, consider the problem of hardness after casting. The major differences between these two alloys is the hardness, or stiffness, of the grid immediately after ejection from the mould. The calcium alloy is much softer than antimony alloys at this stage and therefore it requires more careful handling by the casting machine and by the operator when removing and stacking the trimmed grids.

The second major difference is the respective rates of oxidation of the two types of alloy. The calcium alloy oxidizes, or drosses, more rapidly than antimony alloy. This makes calcium alloys more sensitive to agitation caused by lead pumps, the loading of pigs or scrap lead into the pot, or excessive lead temperatures.

The third difficulty lies in the melting and solidification temperatures. A common 4.5 wt.% lead-antimony alloy is fully liquid at approximately 296 °C. When cooled down, it will start to solidify at 296 °C but does not become fully solid until it is cooled to about 252 °C. In the casting operation, this alloy must be poured into the mould and kept above 296 °C until the cast is complete. It must then be cooled about 26 °C before the grid

can be ejected from the mould. By comparison, the calcium alloy is liquid at 327 °C. When cooled, it is solid at about 324 °C depending on the exact alloy composition. In the casting operation, this alloy must be poured into the mould and kept above 327 °C until the cast is complete, then cooled about 3 °C for the grid to solidify before being ejected from the mould. Thus, in a given example, the calcium alloy is liquid at approximately 25 °C higher than the antimony alloy and solidifies at a temperature that is approximately 54 °C higher. Therefore, to cast this alloy, it must be poured at a higher temperature and the mould temperature must be higher to prevent solidification before the cast is complete. In other words, calcium alloy runs hotter, it drosses more rapidly, and it is softer and more difficult to handle.

In more specific terms, differences in the operating temperatures of the two types of alloy are as follows:

(i) *Lead pot* Calcium is run slightly hotter (up to 10 °C) than 4.5 wt % antimony. Low antimony is even hotter at 454 °C, and calcium–aluminum runs at 482 °C or above.

(ii) *Feedlines* These are operated at about 10 °C hotter for low antimony, calcium, and calcium–aluminum than for 4.5 wt % antimony.

(iii) *Ladle* Temperatures for calcium alloy are about 10 °C higher than for 4.5 wt % antimony. 2.75 wt % antimony and calcium–aluminum are in the same temperature range as calcium.

(iv) *Grid mould* Again, temperatures need to be higher. The mould gate operates around 150 °C on antimony and about 200 °C on calcium. Both low antimony and calcium–aluminum run slightly hotter than 4.5 wt % antimony.

(v) *Lower mould* The temperature for 4.5 wt % antimony is 170 °C while calcium must be processed at 204 °C. Again, calcium–aluminum and low antimony run slightly hotter (at 193 °C) than 4.5 wt % antimony.

(vi) *Upper mould* Temperature controls are not required on any of the alloys other than calcium. The upper-mould temperature for calcium is 204 °C, *i.e.*, the same as for the lower mould.

Calcium-grid caster

Beginning at the lead pot, the lead pump should be a low rpm design. Gas shielding around the shaft reduces drossing, however, this must be supplied with gas at all times. Not doing so can be extremely dangerous with calcium–aluminum alloys. The lead pump may require special self-cleaning bushings, depending on the calcium alloy. Feedlines must be of the dead-head type with good insulation and heat controls. Lead dispensing valves should be gas shielded to prevent any oxidation taking place in the valve. The pouring ladle should be electrically heated automatically to maintain the proper lead temperature. The ladle also requires gas shielding to prevent dross build up. The amount of gas burning off is then very small and is

contained in the ladle vent hood. By grinding the front face of the ladle, a wiper can be included. Dripping from the ladle into the mould is a definite problem with calcium alloys and causes reduced production. Wirtz have developed a ladle wiper to wipe the lead from the ladle lip after each pour and thereby eliminate down times.

Once the grid is cast, the machine's handling system must ensure that grid distortion does not occur. Ejection of the grid from the mould must be very precise. More ejector pins are required and mould design becomes more important. Since the alloy solidifies at 324 °C, the grids can be very hot when ejected from the mould. It is desirable to cool the pallet entry plate and the trim die to remove heat quickly from the grid. In spite of these high temperatures, hot cracks are never a problem. Grids are either solid or liquid when ejected from the mould.

Other grid handling features have been developed by Wirtz for use with calcium alloys. One is the die-entry gate support assembly. Since calcium alloy is very soft and flimsy after casting, it tends to sag when entering the trim die due to the heavy gate on each grid. This sag produces a mis-trim (a scrapped plate). The gate support assembly has a bar which supports each grid gate until the trim die engages the grid. It then moves away to allow the trim scrap to pass by it.

Another Wirtz feature is the die-entry roller assembly. The flimsy calcium feet easily bend if allowed to free fall into position in the trim die. Again, this binding causes mis-trims and scrap grids. The die-entry rollers support the grid and gently transport it to the trim die allowing it to fall only a short distance, thereby eliminating the problem.

Trimming and stacking of the trimmed grid can be accomplished by conventional means, but the grid is still very soft. The trim die must be more precise to trim clean. The grid stacker is more critical and must handle the grid more gently in order to prevent distortion. Die-exit rollers have been added to eliminate any distortion caused by the free fall of the grids to the stacker. Exit rollers now support the grid and gently transfer it to the stacker rails.

The ability to handle the soft grid actually controls the casting speed. With the proper handling features, casting rates are equal to, or greater than, those achieved with low antimony alloys. Typically, calcium casters are operated at around 18 shots per minute, with some exceeding 20.

Grid moulds need to be designed differently when the alloy is calcium. Calcium-grid moulds require more heat controls, more cooling capability, increased venting, different insulation allowances, and improved ejection. Grids need to be designed with more emphasis on lead flow and turbulence caused by lead. Tapers, radii, and mould finish are all important features which must be considered by the mould maker. At higher mould temperatures, it is necessary to add heat by some means (e.g., electric heaters) and also to control the temperature of the mould cooling fluid. Corking grid moulds for calcium alloys is different from that with antimony alloys. Calcium alloys require a tighter, more durable cork that can withstand the

higher lead temperatures and ejection of the soft calcium grid. Antimony-grid moulds are cut with cork allowances of 0.15 mm in the wires and 0.04 mm in the frames and on the surface. By comparison, calcium grid moulds are cut with the same amount of cork allowance in the wires but with a greater amount on the surface and in the frames. Grid moulds designed for calcium alloy can be run with low antimony alloys at a slightly slower speed. However, antimony moulds do not function well on calcium alloys.

Present status

State-of-the-art Wirtz casting machines can cast thin, lightweight grids from calcium or calcium-aluminum or 1 wt % antimony-lead alloys at speeds of up to 65 m per minute. They produce grid material with thickness variations of less than ± 0.02 mm and weight variations of less than ± 1 g.

A steel-belt pasting machine has proven its ability to paste both stiff and soft paste on grid material as thin as 0.7 mm at speeds of 65 m per minute. Tolerance control of the pasted plates is within ± 2 g on weight and ± 0.05 mm on thickness. These tolerance controls are achieved by precision machine design and without the use of expensive computer control.

A high-speed rotary cutter is capable of cutting pasted strip into individual plates at speeds of up to 65 m per minute at close tolerances.

At the present time, two continuous casting lines are being moved from engineering facilities to production plants. One of these systems will make calcium-alloy negative plates. The other system will make positive and negative plates from 1 wt % antimony alloy.