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A new lead alloy for automotive batteries operating under high-temperature conditions

L. Albert *, A. Goguelin, E. Jullian

Metaleurop recherche, av Albert Einstein, B.P. 120, 78193 Trappes Cedex, France

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Abstract

The operating conditions of automotive and some industrial batteries are involving increasingly higher temperatures and heavier duty cycles. These place stress on the positive-grid materials which are presently not sufficiently resistant to corrosion and to creep. Conventional lead–calcium–tin–aluminium alloys can usually be optimized by a proper choice of calcium and tin contents for each specific manufacturing technology. With the new requirements of customers and the typical behaviour of these conventional alloys, however, there is no more room for improvement without searching for additional alloying elements. The work reported here shows how the doping of conventional lead–calcium–tin–aluminium alloys with barium improves mechanical properties (tensile strength and creep resistance) and increases corrosion resistance at temperatures between 50 and 75°C. Grid materials prepared by two manufacturing technologies (gravity cast; continuous cast followed by expansion) are investigated. Both the mechanical properties and the corrosion behaviour of the resulting grids are evaluated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alloy; Barium; Calcium; Corrosion; Creep; Lead-acid battery; Overageing; Tin

1. Introduction

New car designs have caused a change in the heat balance under the hood and this has resulted in significant rises in temperature. Accordingly, automotive batteries are suffering from excessive corrosion of the positive grids and, hence, premature failure. In certain applications, industrial standby batteries also experience similar conditions and, therefore, encounter the same life problems.

The work reported here focuses on the general properties of lead–calcium–tin–aluminium alloys and explains why further optimization of the calcium and tin contents cannot be achieved. Rather, it appears that addition of a new alloying element is required. Particular attention is directed towards the outstanding improvements which can be achieved by doping conventional lead–calcium–tin–aluminium alloys with barium.

Since the quality of the grid material depends on both alloy composition and manufacturing technology, an investigation has been made of grids obtained by gravity casting and by continuous casting and expansion.

* Corresponding author. Tel.: +33-1-30-66-28-70; Fax: +33-1-30-66-27-28

2. Experimental

2.1. Grid casting

Samples for laboratory-scale experiments (tensile strength, creep resistance and hardness) were cast as a 3-mm thick slab, by pouring the alloy (at 600°C) into a copper mould (at 25°C). Such conditions are considered to be very close to the high cooling rates (about 40°C s^{-1}) and the solidification rate experienced during industrial gravity casting.

Industrial gravity-cast grids were manufactured on a TBS single mould machine, at a rate of 14 to 17 grids min^{-1} and a grid thickness of 1.15 mm (automotive design). The alloys were held at 550°C before being poured, via a ladle, into a mould maintained at 190°C. The grids were left to cool at room temperature on the caster grid rack.

Industrial continuously cast and expanded grids were produced by means of the Cominco Multi-alloy Caster. The alloy was held at 400°C and the cooling drum at 40°C. The strip was cast at a rate of about 16 m min^{-1} and passed through a rotary expander at a speed of approximately 7 m min^{-1}.

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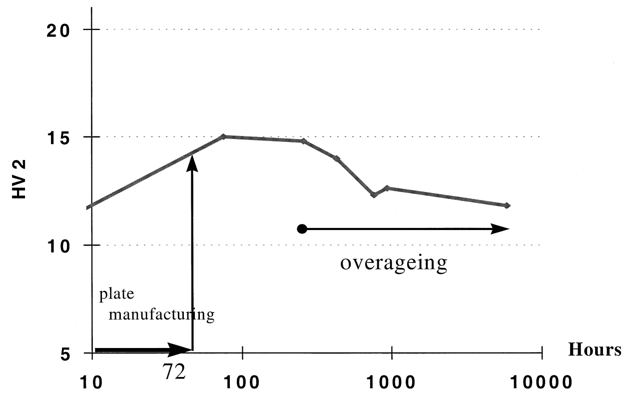


Fig. 1. Hardness of Pb-0.08 wt.% Ca-0.6 wt.% Sn-0.02 wt.% Al vs. time, at 60°C.

2.2. Characterization of bare grids

2.2.1. Mechanical properties

The mechanical properties of grids were evaluated in terms of a creep test, a tensile strength test, and hardness measurements.

The creep test was carried out under a load of 20.7 MPa on standard shaped coupons, and the time to failure was monitored.

The tensile strength test was performed on standard coupons with an Instrom TTDM machine at a rate of 5 mm min^{-1}.

Vickers hardness measurements were conducted by means of a Testwell durometer under a load of 2 kg. Six points of measurement were undertaken and were distributed over the whole planar surface in order to obtain a mean sample hardness.

2.2.2. Corrosion resistance

The corrosion resistance of bare grids was determined under two different conditions, as cited on each graph (Figs. 9 and 12).

All potentials are referred to the mercurous sulfate/mercury reference electrode (Hg/Hg_2SO_4). The corrosion resistance was evaluated by determining the amount of corrosion product and by analyzing the corrosion profile across cross-sections of the grid wires and their associated corrosion layers. The amount of corrosion product was

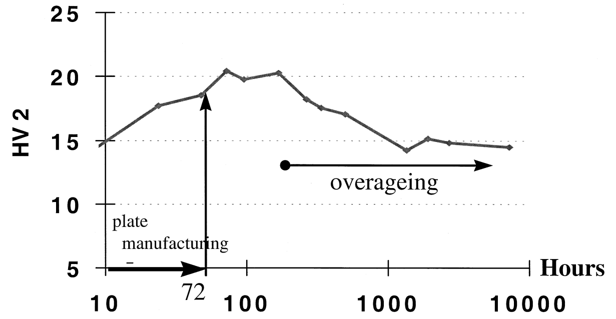


Fig. 2. Hardness of Pb-0.08 wt.% Ca-1.2 wt.% Sn-0.02 wt.% Al vs. time, at 60°C.

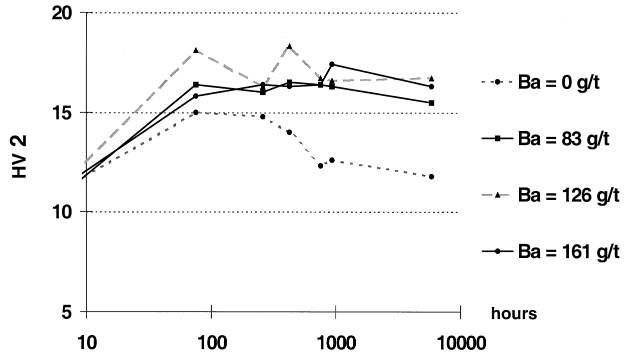


Fig. 3. Hardness of Pb-0.08 wt.% Ca-0.6 wt.% Sn-0.02 wt.% Al vs. time, at 60°C. Barium content as shown.

obtained by comparison of the grid weights before and after removal of the oxidized products by reduction in a CH_3COOH/N_2H_5OH solution [1].

2.2.3. Ageing procedure

To simulate the first stages of battery-plate manufacture (curing, drying and formation) as well as the end-use conditions, slabs or grids were kept for different periods in an oven regulated at 60 ± 3°C. After ageing, the microstructure was characterized by examination of a cross-section which was polished mechanically to 3 μm, etched by a solution composed of one-part H_2O_2 (30%) and three-parts acetic acid, and then exposed by treatment with a solution of acetic acid (250 g l^{-1}) and ammonium molybdate (100 g l^{-1}).

To confirm optical observations of microstructure overageing, measurements of microhardness were performed under a load of 25 g.

3. Results

3.1. Knowledge of conventional lead–calcium–tin–aluminium alloys

To answer the question ''how to improve the conventional Pb–Ca–Sn–Al alloy family?'' it is necessary to know precisely their present properties. The initial prime

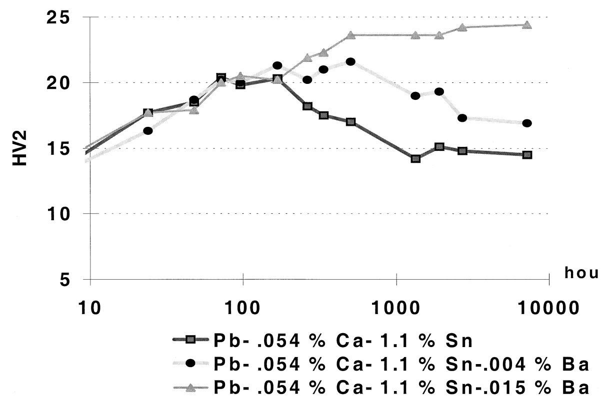


Fig. 4. Grid hardness vs. time, at 60°C.

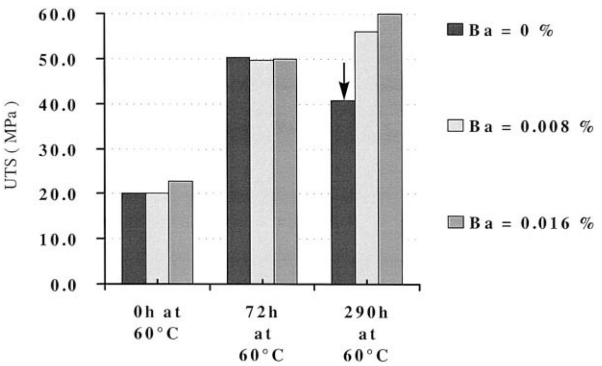


Fig. 5. Tensile strength vs. time of Pb-0.08 wt.% Ca-1.2 wt.% Sn-0.02 wt.% Al, with or without barium.

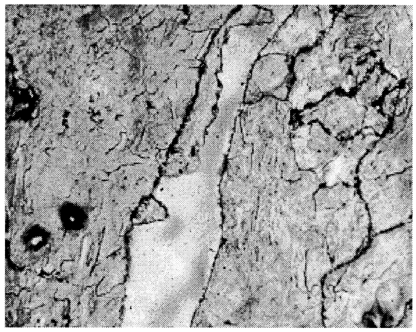
requirement is to examine in detail the age-hardening process. Most publications on these alloys are devoted to studies of their properties at low temperatures, i.e., around 25°C. To enable good handling of grids, manufacturers must establish sufficient strength in the material to sustain the stresses of the first plate-manufacturing stages of pasting and curing. It is well-known [2–4], however, that the natural age-hardening process is thermally activated and, consequently, temperature is the key determinant of the change in physical characteristics with time. The thermal profiles of curing, drying and formation must be taken into account when evaluating the true state of the grid material in formed plates. This information is vital because, at this stage of manufacture, the grid material will exert a strong influence on the eventual life of the battery.

In previous work, the authors have demonstrated that keeping the grid material at 60°C for 72 h provides a good simulation of the thermal profiles during plate curing, drying and formation. By performing such thermal simulation on conventional alloys and then maintaining the grids for a further period at 60°C, to simulate high-temperature battery operating conditions, considerable changes are observed in the microstructure and mechanical properties.

Two examples of age-hardening of gravity-cast slabs are depicted in Figs. 1 and 2. Within the first 72 h (i.e., during simulated plate manufacture), the grid hardens and reaches a value which is not far from the maximum. If the material is then maintained at 60°C, a plateau is reached. After a few hundreds of hours, however, a steady decrease in the mechanical properties occurs, due to microstructure overageing. Increase in tin content (from 0.6 to 1.2 wt.%) does not alter the general behaviour. For a higher tin content, viz., 1.2 wt.%, the plateau is higher, but overageing starts sooner, i.e., after only 200 h, and leads to a sharp drop in hardness and a return to the ‘as-cast’ hardness.

As shown later, higher temperatures not only affect physical properties, but also corrosion resistance and grid growth; the latter two features are linked to the overageing phenomenon.

For a given casting technology, there are only two parameters, namely, the calcium content and the tin content, by which improvements can be made to lead–calcium–tin alloys for positive plates. It has been demonstrated [5] that the Sn:Ca ratio must be maximized to increase the corrosion resistance of gravity-cast grids, but a given lower level of calcium is needed for safe material handling during the battery-manufacturing stages and a high tin content can result in coarser crystallization, penetrating corrosion and a greater tendency towards overage-



Pb- 0.06% Ca- 1.15% Sn - 0.012% Al
overageing > 90%

Fig. 7. Microstructure after ageing for 7200 h at 60°C.

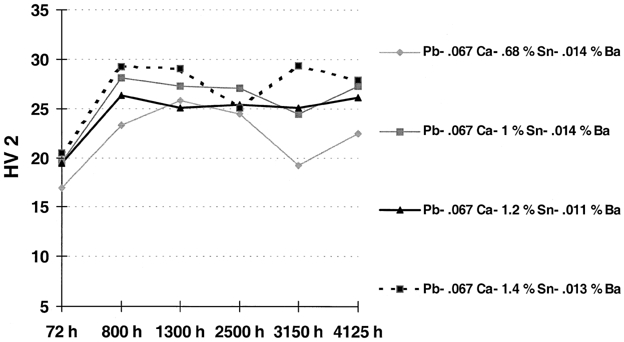
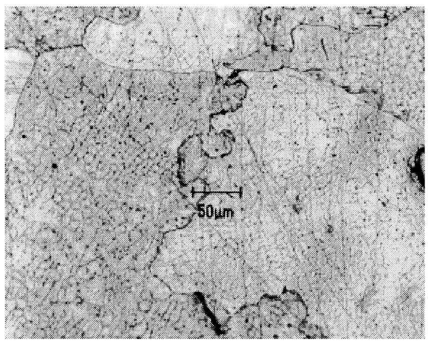


Fig. 6. Grid hardness vs. time, at 60°C, for different tin contents.



Pb- 0.06% Ca- 1.15% Sn - **0.0152% Ba** - 0.012% Al
overageing < 10 %

Fig. 8. Microstructure after ageing for 7200 h at 60°C.

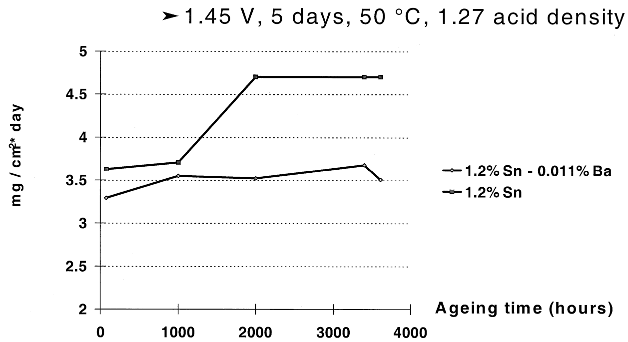


Fig. 9. Weight loss vs. ageing time and barium doping.

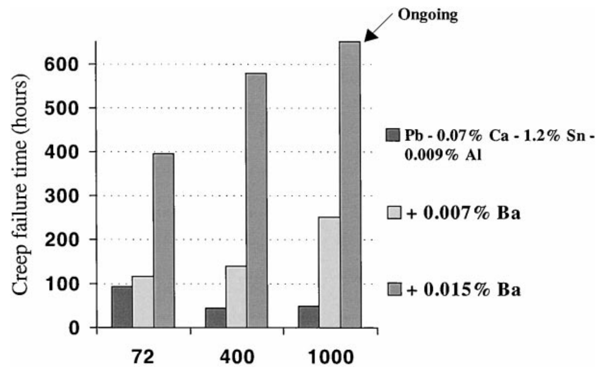


Fig. 11. Creep resistance of expanded grids vs. time, at 60°C, of undoped and doped alloys.

ing. To optimize conventional alloys is therefore really a case of 'trying to square the circle' if a new parameter (or lever) is not available.

3.2. Barium impact on gravity-cast lead–calcium–tin–aluminium alloys

Because grid material is dependent on manufacturing technology, two sets of results will be discussed. The first deals with gravity-cast materials, and the second with continuous cast and expanded grids. Some interesting results for barium-bearing alloys for negative electrode applications will also be considered.

3.2.1. Mechanical properties of gravity-cast materials

The most obvious effects of barium addition, ranging from 0.0083 to 0.0161 wt.%, on lead–calcium–low tin (0.6 wt.%) alloy, cast in 3-mm slabs, is shown in Fig. 3. Barium increases the achievable hardness and stabilizes it at a high level for more than 7000 h at 60°C. Compared with conventional alloy without barium, the gain in hardness is about 4 Vickers units.

Barium is efficient not only for tin at 0.6 wt.%, but also for higher tin contents. As indicated in Fig. 4, at 72 h when the battery would have started its life, the three materials are similar, but after a short period, the barium-free alloy loses its mechanical properties. By contrast, with a sufficient amount of barium (viz., 0.015 wt.%), the material hardness is improved. It does not suffer any further overageing and, accordingly, maintains its elevated performance for more than 7000 h.

Similar trends are observed for the tensile strength, see Fig. 5. After only 290 h, the ultimate tensile strength (UTS) of the barium-free alloy is already reduced by 20%. With barium doping, however, the UTS of the material reaches its maximum value by this time and then stays at 60 MPa, typically a level displayed by rolled material.

Industrial gravity-casting tests were performed in order to confirm the above interesting findings. With a tin content ranging from 0.7 to 1.4 wt.%, 1.2-mm thick grids for automotive applications were produced without any changes in the casting conditions, compared with those used for routine alloys. The hardness was monitored for up to more than 4000 h (see Fig. 6). For all the barium-doped alloys, the hardness remains constant at a value between 18 and 27 Vickers units. This finding confirms the results obtained in laboratory-scale tests. By comparison, barium-free alloys with the same compositions exhibit hardnesses in the region of 15 to 20 Vickers units.

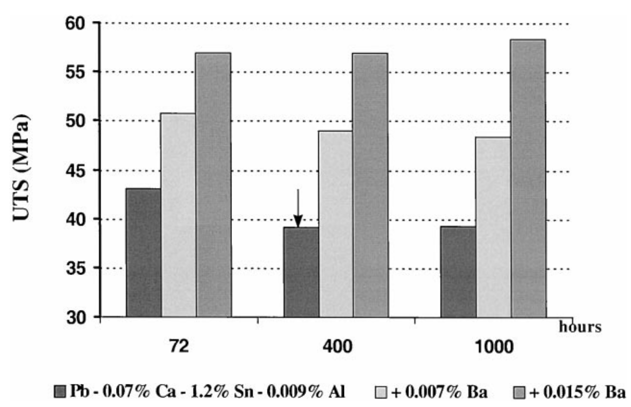


Fig. 10. Ultimate tensile strength (UTS) of expanded grids vs. time at 60°C, with or without barium doping.

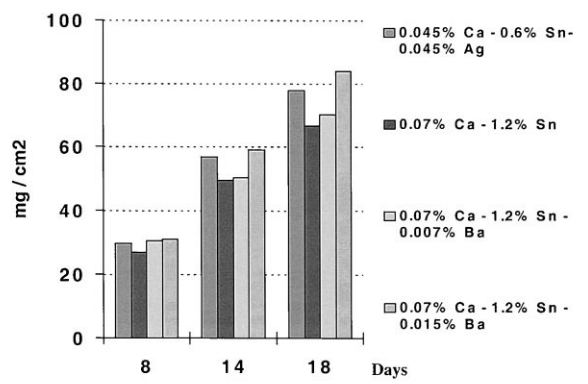


Fig. 12. Weight loss of expanded grids, corroded at 75°C, with 200 mV overvoltage, 1.27 rel. dens. acid.

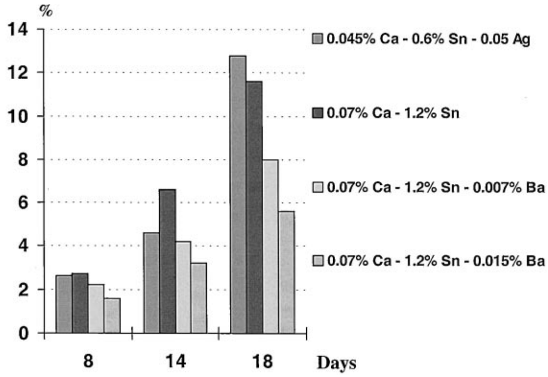


Fig. 13. Grid growth of expanded grids vs. corrosion time, at 75°C, 200 mV overvoltage and 1.27 rel. dens. acid.

3.2.2. Microstructure ageing of gravity-cast grids, kept at 60°C

The difference in mechanical properties after a long ageing time is directly connected to the microstructure. Without barium, the alloy microstructure is 90% transformed by overageing, see Fig. 7. Only one grain in the cross-section has remained stable. Microhardness measurements on this section show that the overaged region reports 13 Vickers units, while good grains exhibit 20 units.

By contrast, a barium-bearing alloy retains its casting microstructure (cell boundaries are visible), even after 7000 h at 60°C. Only a few grain boundaries are slightly influenced by some precipitation, and overageing is very limited and localized (Fig. 8).

3.2.3. Corrosion of gravity-cast grids vs. ageing time

Restricting overageing is not only important for mechanical stability, it also increases the corrosion resistance of grids.

It appears that all the published corrosion data deal with the behaviour of 'freshly' cast materials. These data are appropriate for low-temperature working conditions, but not for treatment at 60°C, as shown in Fig. 9. Several sets of grids were aged for different periods at 60°C and then submitted to a corrosion test at end-of-charge conditions at 50°C. The weight losses of bare grids are similar for both alloys as long as overageing has not fully affected the grids. After 1000 h of ageing, however, conventional alloy is overaged and the corrosion rate is increased by more than 25%. On the other hand, barium-doped alloy exhibits steady corrosion behaviour throughout battery life.

From ongoing tests on battery prototypes, no adverse effects on electrical characteristics have been observed to date in cycling tests at 50°C. Tear-down analyses at the end of tests will determine if barium, released from corrosion products, moves to the positive active mass and modifies it in some way.

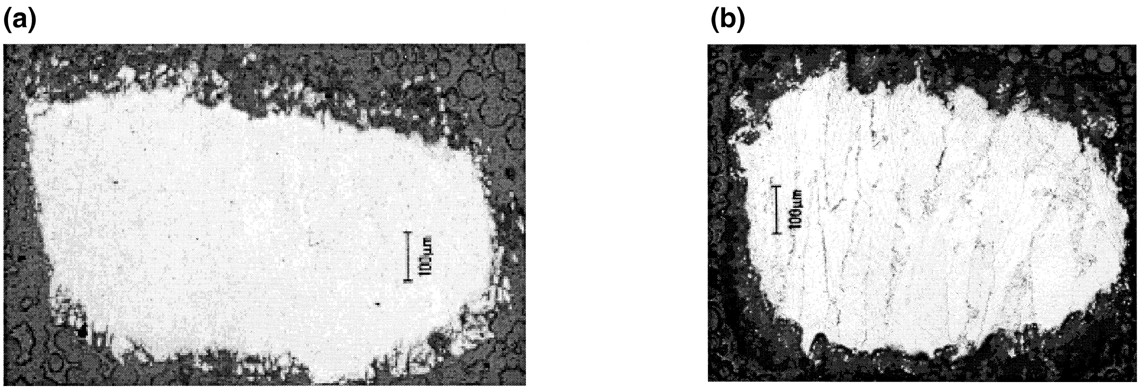
3.3. Barium impact on continuously cast and expanded materials

3.3.1. Mechanical properties

Examination of the tensile properties of continuously cast strips (Fig. 10) reveals that barium addition to Pb-0.07 wt.% Ca-1.2 wt.% Sn-0.009 wt.% Al improves markedly the mechanical properties. After only 400 h, barium-free alloy is affected by overageing and loses 5 MPa. If sufficient barium is added, the UTS is close to 60 MPa, i.e., the level of performance given by rolled sheet. Again, barium blocks any overageing phenomenon.

It has to be emphasized that as ageing kinetics are rather slow at room temperature, barium-containing and barium-free alloys behave similarly. They retain adequate ductility to be expanded without any problems after one week of storage time.

The impact of barium on creep resistance is even more outstanding. There is a six-fold gain in the time to reach failure when the optimum addition of barium is made (see Fig. 11).



Pb - 0.07 % Ca - 1.2 % Sn - 0.08 % Al - 0.017 % **Ba**

Fig. 14. Corrosion mode after 18 days, at 75°C, 200 mV overvoltage: (a) cross-section after reduction of corroded products; (b) cross-section etched to reveal microstructure.

3.3.2. Corrosion behaviour of mesh materials

As far as the corrosion of mesh materials is concerned, three main features must be considered, namely: weight loss, corrosion mode and grid growth.

3.3.2.1. Weight loss of bare electrodes. Undoped, barium-doped and silver-doped mesh grids were submitted to corrosion tests at 75°C (Fig. 12). Barium addition increases slightly the corrosion rate compared with barium-free alloy. This is because barium diminishes the grain width and, accordingly, increases the number of grain boundaries. Barium-doped and silver-doped materials exhibit the same behaviour.

3.3.2.2. Grid growth vs. corrosion time at 75°C. The various alloys display a marked difference in grid growth. While silver-doped and conventional alloys suffer a 12% growth in area, barium doping of the tin-rich alloy reduces this growth by a factor of two after 18 days of corrosion under very severe conditions (Fig. 13). As far as is known, this is the first time that a continuously cast and expanded material could compete successfully with rolled and expanded mesh.

3.3.2.3. Corrosion mode. Analysis of a cross-section of barium-doped alloy after 18 days of corrosion showed that about 28% of the weight was eaten away (see Fig. 14). The picture on the left was obtained after having removed the corroded products by reduction. This procedure is the only way to reveal the real corrosion mode. It is seen that the corrosion has proceeded evenly over the whole surface of the grid, with no sign of penetrating corrosion.

To reveal the microstructure and confirm that no over-ageing had occurred, another cross-section preparation was made, with use of an etching agent which corrodes artificially the grid contour. No detectable change of the microstructure was detected.

3.4. Barium impact on cast grids for negative electrodes

Up to now, rather high calcium contents (0.13 wt.%) have been used for alloys intended for negative grid manufacture. If a hardness of 13 Vickers units is reached just after gravity casting, it remains steady afterwards. Use of a lower calcium content requires storage for several days before the grids can be handled. Industrial casting tests demonstrate that barium speeds up the hardening process of low-calcium–lead alloys.

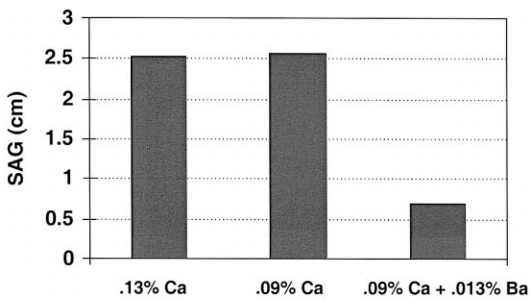


Fig. 15. Sag of gravity-cast grids after 20 h at 25°C.

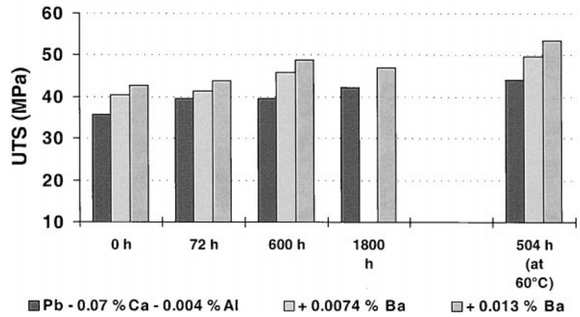


Fig. 16. Ultimate tensile strength (UTS) of continuously cast strips vs. ageing time at different temperatures.

In Fig. 15, double gravity-cast grids of different alloy composition are compared by measuring the sag at the end of the doubled grids, free to bend at one-half of the total length. After 20 h, this sag is reduced by a factor of five in the case of the barium-containing alloy. The barium-doped grid emits a metallic noise!

The same behaviour was observed for continuously cast strips (see Fig. 16). Directly after leaving the cooling drum of the Cominco Multi Alloy Caster, the strip bending is already smaller. The stiffness of barium-bearing alloys is improved immediately after casting—it attains the level reached by a barium-free alloy after at least 72 h of storage. This stiffness continues to increase with time and stays at a high value, even at 60°C.

Barium addition to lead–low calcium alloy is thus very efficient in accelerating the hardening process for both gravity-cast and continuously cast grids. It also improves the level of stiffness and maintains this level for a long time.

It is considered that all these properties shorten storage time, save metal inventory and decrease the scrap from deformed plates throughout the plate-manufacturing process. For those manufacturers who use thicker grids, barium-bearing alloy would permit the casting of grids with a thinner gauge and with the same mechanical properties.

4. Conclusions

In summary, the following conclusions can be drawn from the above observations.

(1) Conventional Pb–Ca–Sn–Al alloys suffer disadvantages such as limited scope for improvement by working only on calcium and tin contents and unsteady properties due to the overageing phenomenon.

(2) Metaleurop has patented a family of barium-bearing alloys that presents a set of outstanding and potentially very useful properties.

(3) Optimized barium doping provides the following benefits.

- stops the overageing of conventional Pb–Ca–Sn alloys
- maintains the mechanical properties at higher and steady levels
- decreases the grid area growth and promotes even corrosion
- improves the corrosion resistance of gravity-cast grids when the whole life of the material is considered

All these results are very encouraging, but they must be confirmed through tests in actual batteries before it can be stated with certainty that the new alloy technology provides a real technical breakthrough for the battery industry. Such testing campaigns are in progress and the authors hope, in the near future, to present further results which demonstrate that barium-doped lead–calcium–tin alloy is a success story for the battery industry.

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