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Journal of Power Sources 116 (2003) 185–192

JOURNAL OF POWER SOURCES

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New lead alloys for high-performance lead–acid batteries

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Received 10 September 2002; accepted 21 November 2002

Abstract

Consumers require lead–acid batteries with a high level of reliability, low cost and improved life, and/or with less weight and good tolerance to high-temperature operation. To reduce the thickness (weight) of the grids, the alloy materials must exhibit higher mechanical properties and improved corrosion resistance. In this study, the performance of negative and positive grids is evaluated in battery tests. The results demonstrate that continuously cast and expanded grids made from barium-doped lead–calcium–tin alloys meet performance requirements. For negative grids, improvement in the mechanical properties can lead to reliable thinner grids. For positive grids, the alloys exhibit improved mechanical properties and greater corrosion resistance. These features provide extremely good creep behaviour during battery operation such that performance under the hot SAE J240 test is superior to that achieved previously with expanded grids.

Keywords: Barium; Calcium; Continuous casting; Lead alloy; Lead–acid battery; Tin

1. Introduction

Consumers require lead–acid batteries with the following properties: low cost, maintenance-free operation, reliability, long life, less weight, good tolerance to high-temperature operation. This is especially true for the original equipment market (OEM) where car manufacturers require high reliability to insure warranties of 3 years or more. These requirements will become increasingly important given the expected changes in global automotive power systems to higher power ranges, such as the switch to 42-V PowerNets. The valve-regulated lead–acid (VRLA) battery appears to be the best compromise between price and performance, but improvements in grid alloys, separator materials, battery design and battery management are still required. The improvements being sought for grid materials are [1]:

- higher mechanical properties to reduce the thickness of the grids;
- improved corrosion behaviour to reduce the thickness of the grids and/or to increase battery life;
- steady properties, i.e. no deterioration with ageing (such as overageing of lead–calcium–tin alloys).

These requirements have been partially met through the use of lead–calcium–tin alloys and continuous grid-manufacturing technologies. For example, maintenance-free batteries have triggered the replacement of lead–antimony alloys by lead–calcium–tin alternatives for both negative and positive grids. In 2000, battery production in Europe showed that lead–calcium–tin alloys accounted for 76 and 47% of the alloys used for negative grids and positive grids, respectively. Better reliability and cost savings through weight reduction have also been achieved by the use of continuous manufacturing technologies which require lead–calcium or lead–calcium–tin alloys. In 2000, for example, 50% of the negative grids manufactured in Europe were processed by continuous processes such as continuous casting and rolling.

It must be kept in mind that the properties of a grid material is defined not only by the combination of the alloy and the associated manufacturing process, but also by the procedure used to characterise the material (the procedure should be standardised). Thus, to meet fully the performance requirements of grids, there are two technical fields of investigation, namely, the alloys themselves and the grid-manufacturing technologies. This paper reports the results obtained for positive and negative grids that use improved alloys and that are processed by means of present continuous technologies.

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doi:10.1016/S0378-7753(02)00705-X

2. Experimental

2.1. Grid manufacturing

Continuously cast and expanded grids were produced by means of the TeckCominco Multi-alloy Caster. The alloy is held at 400 °C and the cooling drum at 40 °C. The strip is cast at a rate which depends on its thickness, i.e. about 19 m min^{-1} for 0.95-mm thick strip for positive grids, and about 21 m min^{-1} for 0.75-mm thick strip for negative grids. The strips then pass through rotary expanders at a speed of about 37 m min^{-1}.

Rolled and expanded grids are produced by means of the Properzi rolling device. A 6.5-mm thick slab is cast on a wheel at 10 m min^{-1} and is then rolled to a thickness of 0.95 mm at a final rate of 66 m min^{-1}. The strips then pass through a rotary expander, again at a speed of about 37 m min^{-1}.

2.2. Characterization

2.2.1. Mechanical properties

The mechanical properties of the grids were evaluated by conducting tensile tests on the strips. The tests are performed on standard coupons with an Instron 5567 machine at a rate of 25 mm min^{-1}.

2.2.2. Corrosion of bare grids

The corrosion behaviour of bare grids was evaluated under the following conditions: (i) acid of 1.270 relative density at 20 °C; (ii) 75 °C; (iii) 200 mV overpotential (1350 mV versus calomel electrode); (iv) 20 days. The weight loss was determined from a comparison of the grid weights before and after removal of the oxidised products by reduction in a CH_3COOH/N_2H_5OH solution [2]. The corrosion profile on cross-sections of the grids was observed without chemical etching.

2.2.3. Battery corrosion test

The testing procedure was defined as follows [3]:

(i) the electrolyte level was decreased by 1 cm in all cells;
(ii) the battery was charged for 2 weeks at 14.4 V and $I_{max} = 2 \times I_{20}$ A in a water bath set at 60 ± 3 °C;
(iii) the battery was discharged at I_{20} A to 12.5 V;
(iv) rest period of 3 weeks at 60 ± 3 °C;
(v) the battery was charged for 3 weeks at 14.4 V and $2 \times I_{20}$ A at 60 ± 3 °C.

After the test, the battery was dismantled and subjected to the same teardown procedure as that described above for the corrosion testing of bare grids.

2.2.4. Hot SAE J240 test

The test was performed at 75 °C as follows [4]:

(i) discharge: 4 min ± 1 s at 25 ± 0.1 A;
(ii) charge: 14.8 ± 0.03 V for 10 min at a maximum rate of 25 ± 0.1 A;
(iii) steps (i) and (ii) performed for 100 h with a switching delay of not more than 10 s;
(iv) rest at 75 °C for 60–72 h;
(v) rapid discharge at I_{cc} (cold-cranking rate) for a minimum discharge time of 30 s;
(vi) battery placed back on test at step (ii) without a separate recharge.

The test was considered to be complete when the voltage fell below 7.2 V within 30 s of discharge.

2.2.5. 50% Depth-of-discharge cycling test

Cycling tests at 50% depth-of-discharge (50% DoD) were conducted at 40 ± 2 °C as follows [3]:

(i) discharge for 2 h at $5I_{20}$; terminate when battery voltage was less than 10 V;
(ii) charge for 5 h at 16 ± 0.1 V with current limit of $5I_{20}$;
(iii) stages (i) and (ii) performed until termination criterion was reached.

3. Results for negative grids

For the negative grids, the target is to produce thinner grids at very low cost. This can only be achieved by the use of continuous manufacturing processes (i.e. continuous casting or rolling) together with an optimised alloy.

3.1. State-of-the-art grid alloys

To improve conventional grid materials, it is necessary to characterise their properties and limitations. In Europe, the continuous casting of a lead–calcium alloy strip followed by expansion is the most common continuous technology. In this case, the limitation to decreasing the thickness is related to the hardening kinetics and the mechanical properties of the alloy. Both these features are governed by the calcium content. To obtain very stiff grids, it is necessary to specify a calcium content of more than 0.1 wt.%. At this level, however, the hardening kinetics are also increased and elongation becomes too low to enable expansion. With less than 0.1 wt.% Ca, the mechanical properties after hardening are rather weak and determine the smallest achievable thickness that can be handled on grid-manufacturing lines. This limitation can be overcome by the use of Ba-Tech® alloy (a barium-doped lead–calcium alloy produced by Metaleurop) processed in the TeckCominco Multi-alloy caster.

3.2. Improvement in mechanical properties

A typical Ba-Tech® alloy for negative grids contains 0.09 wt.% Ca, 0.012 wt.% Ba, and some Al. The performance of this alloy is compared with that of a conventional lead—0.09 wt.% calcium alloy processed by means of the same continuous casting technology (the ‘reference’ alloy).

After plate curing, the handling of pasted grids requires a high level of mechanical properties. On the other hand, the expansion of alloy strip requires a rather ductile material. Thus, the expected mechanical properties of the material must meet somewhat contradictory criteria, as follows:

- To expand the strip, the elongation must be high and the ultimate tensile strength (UTS) must be sufficiently high to give the grid adequate stiffness. Furthermore, these mechanical properties must remain rather steady for several weeks at room temperature, which means that ageing kinetics at room temperature should be slow. Accordingly, expansion should be possible even after some weeks of storage.
- For good handling during battery manufacturing and for good battery life, the UTS of the pasted grid (plate) after curing must be at the highest possible value and the creep must be very low. To evaluate the properties of cured materials, the curing step is simulated by heat treatment for 3 days at 72 °C.

The evolution of the mechanical properties of the strips at room temperature is shown in Fig. 1. Barium addition increases the stiffness of the grid, as shown by a UTS which is 35% higher than that of the reference alloy, but the elongation and the YS:UTS ratio remain unchanged (YS: yield strength), i.e. barium-doped strip exhibits a UTS of 42 MPa and an elongation of 17% after 24 h whereas the reference alloy exhibits a UTS of only 30 MPa with the same elongation. For both alloys, there is a small increase in the UTS during the first 2 weeks and then the value remains constant until the fourth week. The gain for barium-doped strip remains at about 35%. The elongation remains constant or even increases a little for both alloys over the same period.

All these results have been confirmed by expansion tests on an industrial scale: the Ba-Tech® materials have been expanded successfully at different ageing times which cover a period between 1 day after casting and 3 weeks storage at room temperature.

The mechanical properties of the ‘cured’ materials are summarised in Fig. 2. The UTS of the barium-doped strip reaches a very high value of 54 MPa, which is 40% higher than that of the reference. Furthermore, it has been demonstrated that barium addition also stabilises the grain structure and thereby gives the material a better reliability [5–7].

Finally, the reliability during casting is higher because of the presence of aluminium in the formulation. The composition of the strip is kept constant during casting because aluminium acts as a protective element against oxidation of the alloy. Therefore, variation in mechanical properties due to variations in the chemical composition of the strip are suppressed.

3.3. Summary

A simple combination of Ba-Tech® alloy for negative grids with a TeckCominco continuous caster enables strips to be cast with constant chemical composition. The formulation is then optimised to produce a stiff strip with sufficient elongation for expansion, which can be performed within a few hours after casting as well as after a few weeks of storage. Afterwards, the cured material exhibits a UTS of 54 MPa, i.e. 40% higher than conventional materials. All these data demonstrate that the manufacture of thinner negative plates is possible. Consequently, the use of this alloy gives a significant reduction in the cost of negative grids.

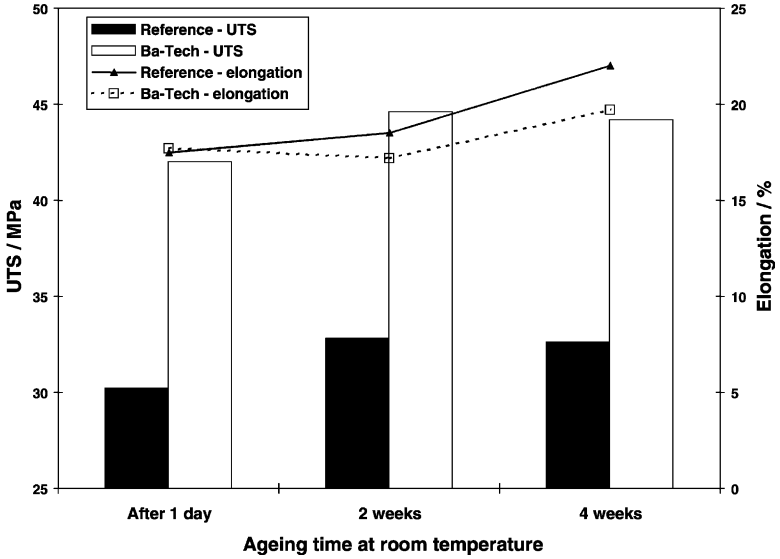

Fig. 1. Evolution of mechanical properties of negative continuous cast strips at room temperature.

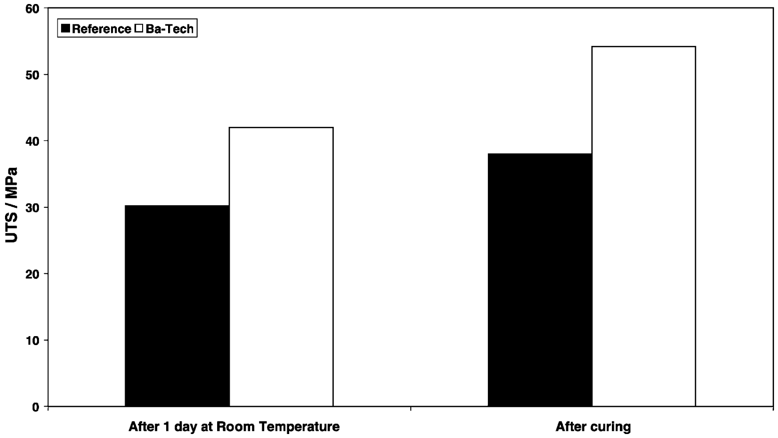

Fig. 2. Evolution of mechanical properties of continuous cast strips after curing (simulated by 72 h at 60 °C).

4. Results for positive grids

For positive grids, the target is to obtain a more reliable and thinner material. This requires improvements in mechanical properties and corrosion behaviour.

4.1. State-of-the-art

Lead–calcium–tin alloys are increasingly replacing lead–antimony alloys for numerous reasons, among which the most important are decrease in water loss and an ability to be used in continuous processes such as continuous casting or rolling. The influence of calcium and tin has been studied extensively. A low calcium content is chosen to improve the corrosion behaviour, and tin is added to counterbalance the corresponding degradation in mechanical properties [8,9].

Recently, it has been considered that the addition of tin alone is not sufficient and that an additional element is required. The latest alloy improvement, which is now in operation, is the addition of silver to a lead–calcium–tin alloy with a low calcium content [9–11]. The efficiency of silver addition, however, has only been demonstrated in book-mould technology [8,12,13] and the mechanical properties immediately after casting are very low [9]. The fact that silver addition is not efficient in continuous grid-manufacturing technologies is a great limitation when production of reliable materials is concerned as it is easy to reach reliability with continuous processes.

Barium is an alternative to silver. The addition of barium to lead–calcium–tin alloys improves both the mechanical properties and the corrosion behaviour, and keeps these properties steady because overageing is prevented [5,6]. While the beneficial impact of barium addition has already been demonstrated for book-mould technology [14], this study focuses on new materials manufactured by two different continuous processes: the TeckCominco Multi-alloy caster and the continuous Properzi rolling machine, both followed by the expansion of the strip with a TeckCominco Rotary expander.

4.2. Materials

The results are given for typical Ba-Tech® materials for positive grids (i.e. 0.06 wt.% Ca, 1.2 wt.% Sn, 0.015 wt.%

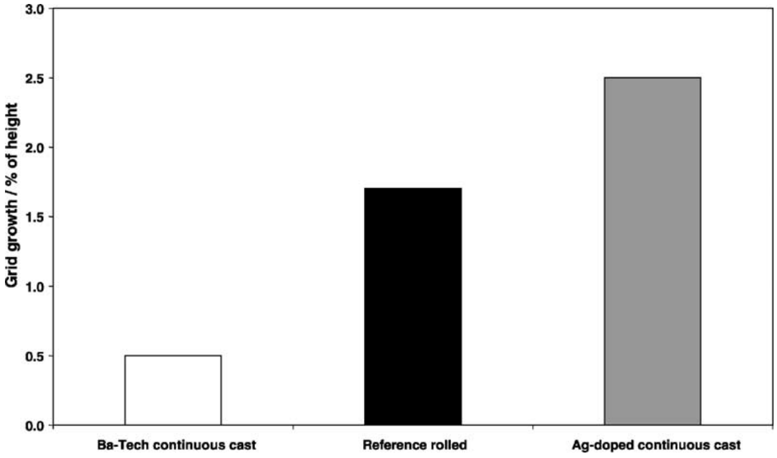

Fig. 3. Grid growth after corrosion tests of bare grids.

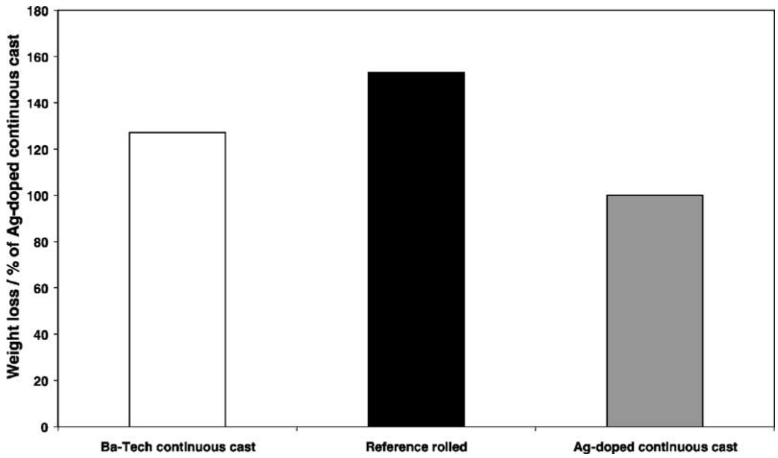

Fig. 4. Weight loss after corrosion tests of bare grids.

Ba, and Al) and a thickness of 0.95 mm. These materials are compared with either a conventional lead, 0.08 wt.% calcium, 1.4 wt.% tin alloy processed with rolled technology ('rolled reference') or a conventional continuous cast lead, 0.04 wt.% calcium, 0.75 wt.% tin alloy doped with 0.02 wt.% silver.

4.3. Strips and bare grids

Immediately after casting, the continuous Ba-Tech® strip exhibits a UTS of 39 MPa, whereas the silver-doped, continuous cast strip has a UTS of 22 MPa. Barium-doped continuous cast and cured material exhibits a UTS of 60 MPa after 72 h at 60 °C, which is close to the UTS of rolled materials, versus 67 MPa for both reference and barium-doped alloys. Furthermore, the material properties are more steady because barium addition also stabilises the grain structure so that the overageing phenomenon is blocked [5–7].

Corrosion tests performed on bare grids (see Section 2.2.2) have demonstrated that the Ba-Tech® continuous cast material exhibits: (i) grid growth which is three times lower than the rolled reference (see Fig. 3); (ii) weight loss which is 25% lower than the rolled reference (see Fig. 4).

4.4. Battery corrosion test

Typical Ba-Tech® material for positive grids (e.g. 0.06 wt.% Ca, 1.2 wt.% Sn, 0.015 wt.% Ba, and Al) and a thickness of 0.95 mm have been subjected to the test procedure outlined in Section 2.2.3. The corrosion profiles for Ba-Tech® continuous cast grids, Ba-Tech® rolled grids and the rolled reference grid are presented in Fig. 5. The corrosion profiles are very similar, with a dense and homogeneous corrosion layer without penetrating cracks. The grid growth after the test is shown in Fig. 6. It appears that barium addition also influences the creep properties as the grid growth is reduced by 25% for both barium-doped materials compared with the reference alloy—the height increase is only 2.5 mm.

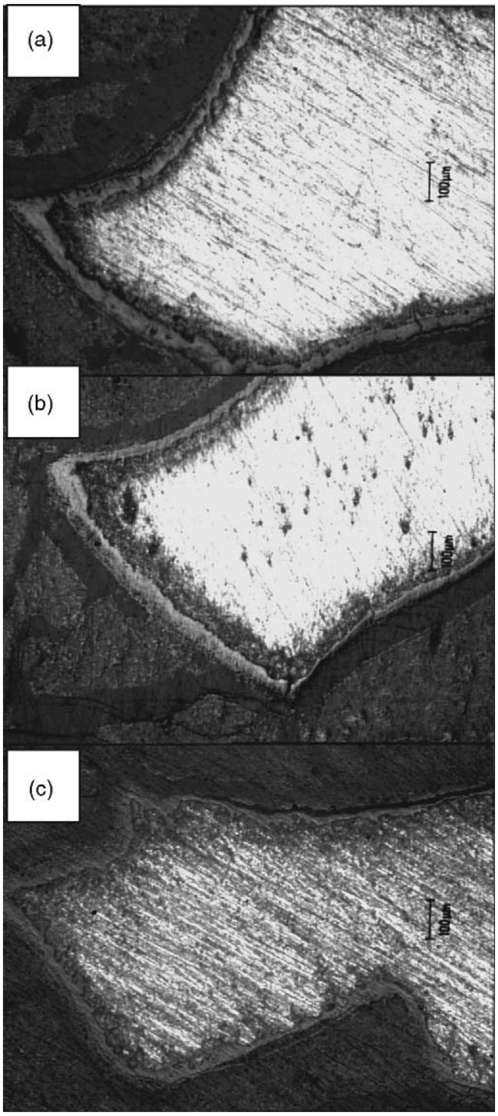

Fig. 5. Corrosion profile after battery corrosion test for: (a) rolled reference; (b) rolled Ba-Tech®; (c) continuous cast Ba-Tech®.

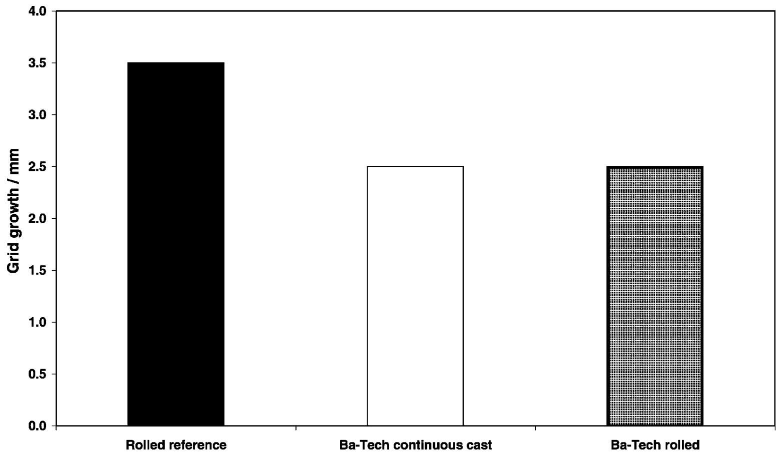

Fig. 6. Grid growth after corrosion test in battery.

The weight loss is higher for materials manufactured by the rolled technology (Fig. 7), i.e. the value for the continuous cast Ba-Tech® material is 12% less than that for the rolled materials.

4.5. Hot SAE J240 test

This test is conducted at 75 °C and has been performed on only the continuous cast Ba-Tech® grids and the rolled reference. The test procedure is summarised in Section 2.2.4. The use of continuous cast, Ba-Tech® positive grids increases the cycle-life, namely, 3861 cycles compared with around 2200 cycles for the reference alloy (Fig. 8). To our knowledge, this is the first time that batteries with expanded positive grids have reached such a high number of cycles (in the range of the test requirements for this type of battery). It has to be noted that this improvement is reached although the failure mode in each case is shrinkage of the negative active-mass and is not directly related to the positive grid. Furthermore, the corrosion profile after test completion is different: the corrosion layer on the continuous cast Ba-Tech® grids is homogenous and dense, without cracking or delamination (see Fig. 9), while some delamination occurs with the rolled reference grid.

4.6. 50% Depth-of-discharge DoD cycling test

Due to the excellent corrosion properties of the barium-doped materials, the conditions of plate manufacturing must be optimised to generate a good bonding between the positive active-material and the grid. Depending on the battery-manufacturing process, the number of cycles reached in a 50% DoD cycling test can vary from 20 to more than 120.

4.7. Summary

The above results show that the use of Ba-Tech® alloy for positive grids can enhance battery performance: the mechanical properties are enhanced, even after manufacturing, and the corrosion behaviour is also improved. The combination of these properties gives extremely good creep behaviour in the battery. This is a key issue for expanded materials. These improvements are obtained by manufacturing the grids by

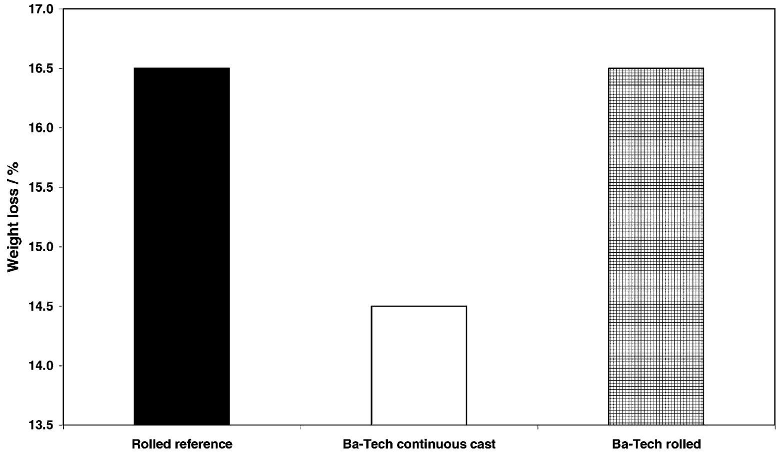

Fig. 7. Weight loss after corrosion test in battery.

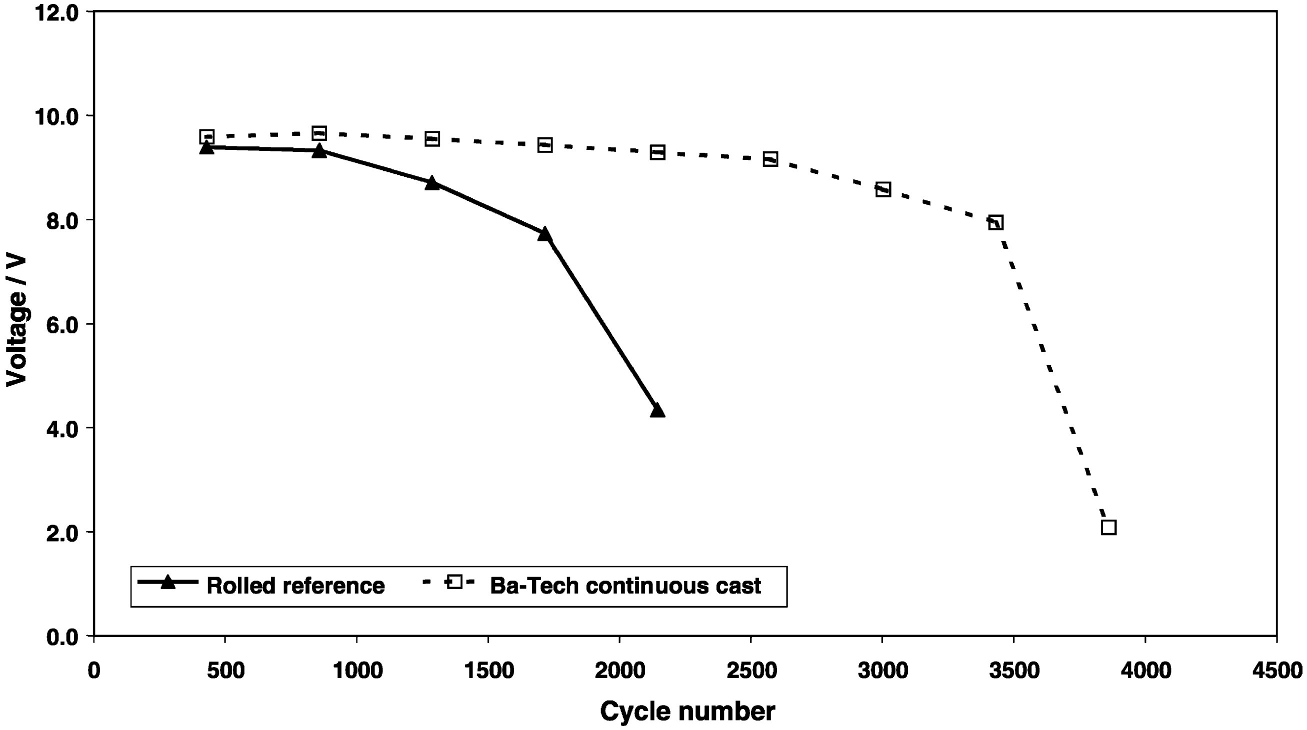

Fig. 8. Hot SAE J240 cycle-life test.

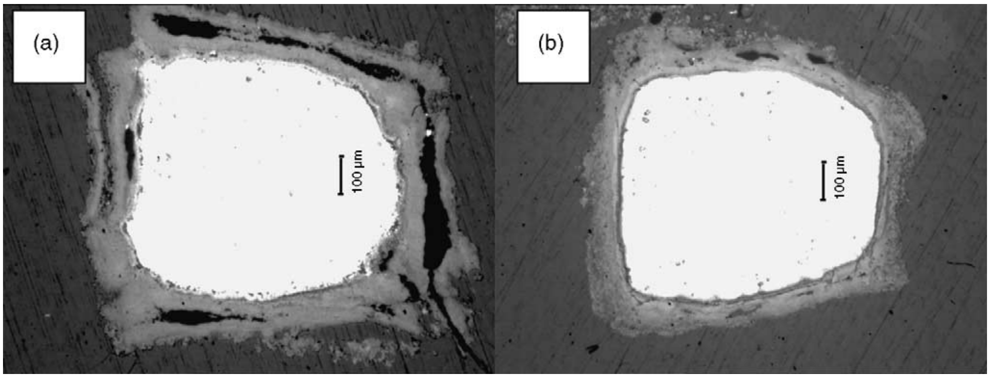

Fig. 9. Corrosion profile after hot SAE J240 test for: (a) rolled reference (1700 cycles); (b) continuous cast Ba-Tech® (3000 cycles).

means of the continuous technologies presently used in plants and which guarantee a high level of reliability for the grid material.

5. Conclusions

For negative grids, it is found that the use of Ba-Tech® alloy combined with continuous casting technology is a very powerful way to decrease the thickness of negative grids to a value well below that possible with a conventional lead–calcium alloy. This opens the way to lighter grid structures.

For positive grids, the Ba-Tech® alloy can be processed by rolling or continuous casting technology, both of which are presently used in battery plants. These materials exhibit an outstanding low rate of grid growth (even at 75 °C), high-mechanical properties, and an homogeneous corrosion profile. Furthermore, for continuous cast materials, the weight loss is lower than for rolled materials and cycle-life in the hot SAE J240 test is improved to levels never reached before with expanded grids.

The first batteries containing Ba-Tech® materials are already on the market and car manufacturers have found them to be satisfactory.

Acknowledgements

The authors are grateful to their partners from the battery industry for fruitful discussions, for the manufacturing of samples, and for battery testing. Special thanks are due to the TeckCominco Product Technology Centre and to DELPHI Energy and Engine Management Systems R&D Centre.

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