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Effect of calcium, tin and silver contents in the positive grids of automotive batteries with respect to the grid manufacturing process

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Abstract

A study has been undertaken in order to compare the properties of grids produced by rolling expansion and by gravity casting in some specific test conditions. In both types of grids, the effects of calcium, tin and silver contents have been investigated. After bare grid study, a series of electrical tests has been carried out followed by thorough tear down analysis. The mechanical properties of rolled expanded grids have been found to be improved by an increase of tin content from 0.8% to 1.2%, silver and calcium content having no significant effect. The resistance to corrosion of bare grids at equilibrium potential is strongly dependent on the acid density. At low acid density corresponding to the most severe condition, grid corrosion is limited by a high tin content (1.2%) and by a low calcium content (0.04%). There is no effect of silver. In hard conditions of use such as storage and overcharge at high temperature, battery life is increased with a higher tin content for all technologies, and by a smaller extent by the addition of silver on gravity casted grids. A high tin content improves the battery rechargeability after a deep discharge. In conclusion, the addition of silver has only a poor impact on the behaviour of rolled expanded grids. On gravity casted grids, in the same conditions, the addition of silver associated with a low calcium content has been found to improve the battery life slightly. In high temperature conditions of overcharge and storage, the battery life obtained with rolled expanded grids is higher than that with gravity cast, whatever the alloy.

Keywords: Lead acid battery; Positive grid manufacturing; Lead alloys; Battery life tests

1. Introduction

In SLI batteries, a constant increase in the requirements of customers is observed, such as increased heat under the hood, and increased load raise supplied by the battery. The ability of positive grids to withstand corrosion and deep discharge is a prerequisite to achieve these goals.

An additional requirements is for low maintenance batteries and this has led today to an extensive use of antimony-free alloys for both positive and negative grids.

The influence of calcium, tin and silver content in these alloys has already been widely studied. Some studies reported the effectiveness of tin to prevent the development of a high impedance passivation layer at the grid/active material interface [1–3]. Other studies showed that microstructure and mechanical properties depend on the weight ratio of tin:calcium [4], and on the grid manufacturing process [5–7]; all these parameters having a significant influence on the corrosion behaviour of such grids [8,9]. Silver addition has been found to improve the corrosion behaviour of lead calcium tin alloys [10].

As the properties of the grids depend on alloy composition as well as grid manufacturing process, a study has been undertaken in order to compare the properties of grids produced by rolling expansion and by gravity casting in some specific test conditions. In both types of grids, the effects of calcium, tin and silver contents have been investigated. After bare grid studies, a series of electrical tests have been carried out followed by thorough tear down analysis.

2. Experimental

Positive grids have been produced by the rolling expansion process and by the gravity casting process on standard production lines with different alloy compositions. The same time was used before the expansion for series 1–5.

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Table 1
Positive grid alloy composition according to the grid manufacturing process of the different prototypes

	Rolled expanded metal					Gravity casting		
Series	1	2	3	4	5	6	7	8
Ca (%)	0.08	0.04	0.04	0.04	0.08	0.09	0.09	0.05
Sn (%)	0.8	1.2	1.2	0.8	0.8	1.2	0.6	0.6
Ag (%)	< 0.001	< 0.001	0.03	0.03	0.03	< 0.001	0.03	0.03
Al (%)	0.005/0.015	0.005/0.015	0.005/0.015	0.005/0.015	0.005/0.015	0.005/0.015	0.005/0.015	0.005/0.015

The grid weight was the same for the two different processes. For the negative grid, a standard lead calcium alloy was used.

Electrical tests have been performed on L1 type batteries (50 Ah), assembled in order to have similar initial performances and the same acid to mass ratio for both different processes.

For each component, tin, silver and calcium, two levels of concentrations have been studied. The different series of prototypes tested are presented in Table 1.

3. Mechanical tests on wrought strip and rolled expanded grids

Previous work has presented the influence of grid manufacturing process and alloy composition on mechanical properties [5]. For each alloy composition mechanical tests have been performed on the wrought strip and on the expanded grid.

3.1. On strip

The evolution of mechanical properties of the laminated strip has been studied during storage at room temperature. Indeed, the grid manufacturing process parameters, such as ultimate tensile strength (UTS) and elongation of the strip, specify minimum and maximum allowable values during expansion and handling in good conditions. The samples were submitted to a tensile test with an elongation rate of 1 mm/min, using INSTRON traction equipment, in order to measure the UTS and the elongation after rupture of the strip after different periods of storage at room temperature.

The evolution of UTS as a function of storage time is presented in Fig. 1. Fig. 2 shows the variation of elongation during time.

According to these results, the mechanical properties of the wrought strip are influenced by the alloy composition:

- a high tin level (1.2%) increases long term UTS (> 30 days aging) and decreases elongation;
- silver has no effect on UTS but decreases elongation at low Sn content (0.8%);
- a high calcium level (0.08%) increases only short term UTS and has no effect on elongation.

In a first conclusion, we see that a minimum calcium content is needed in order to obtain a sufficient traction resistance. The modification of the mechanical properties of the strip obtained by an increase of tin concentration

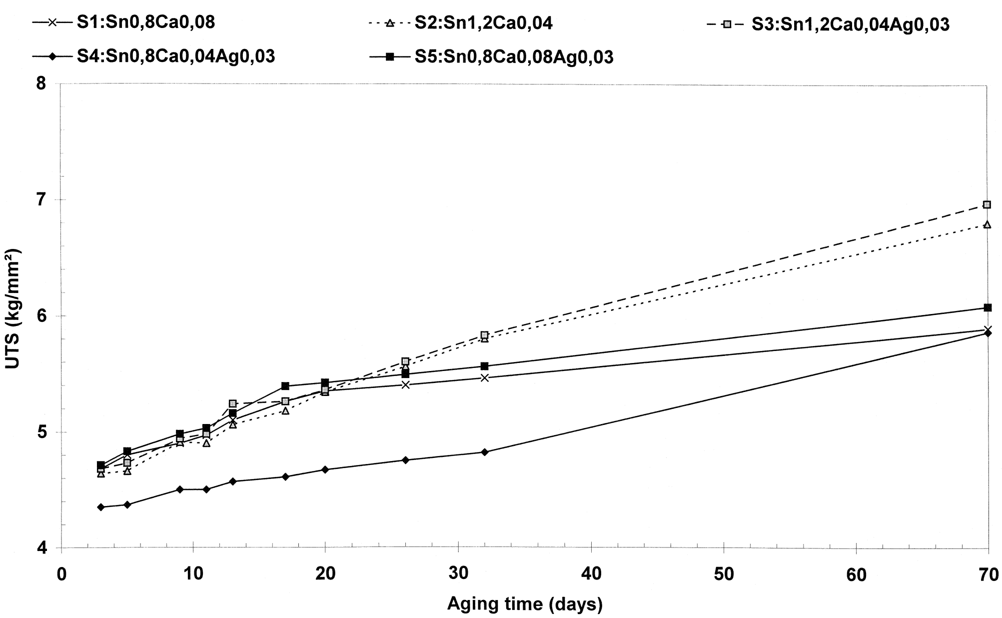

Fig. 1. Mechanical test on wrought strip: UTS vs. aging time at room temperature for different alloy compositions.

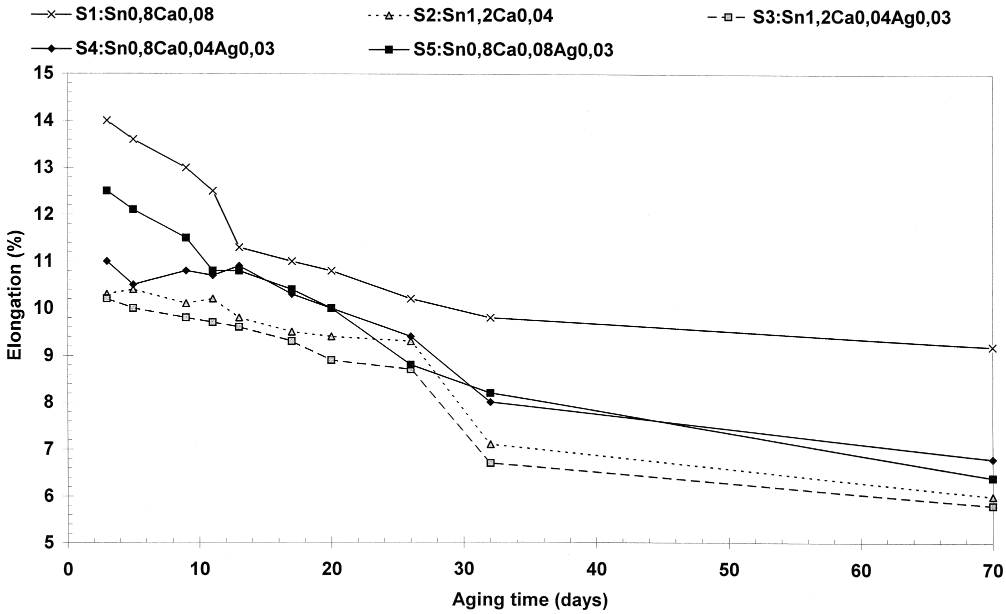

Fig. 2. Mechanical test on wrought strip: elongation vs. aging time at room temperature for different alloy compositions.

will change the expansion process parameters such as the storage time before expansion.

3.2. On grid

3.2.1. Initial properties

The characterization of the mechanical properties of the grid has been carried out in order to evaluate the effect of the modification of the alloy composition on grid stiffness, its ability to resist stress caused by the active material and corrosion layer during charge and discharge of the battery. These properties have been assessed for rolled expanded grids, through a creep test of a piece of grid, three nodes wide, performed after 30 days of storage at room temperature. A low value of elongation measured after 24 h under load indicates that the grids will be able to withstand stress in the battery with a low deformation.

Tests results are presented in Fig. 3:

- when tin content is increased from 0.8 to 1.2%, a strong creep resistance improvement of the grid is obtained;
- silver has no effect at high tin content (1.2%) but improves the creep resistance at low tin content (0.8%);

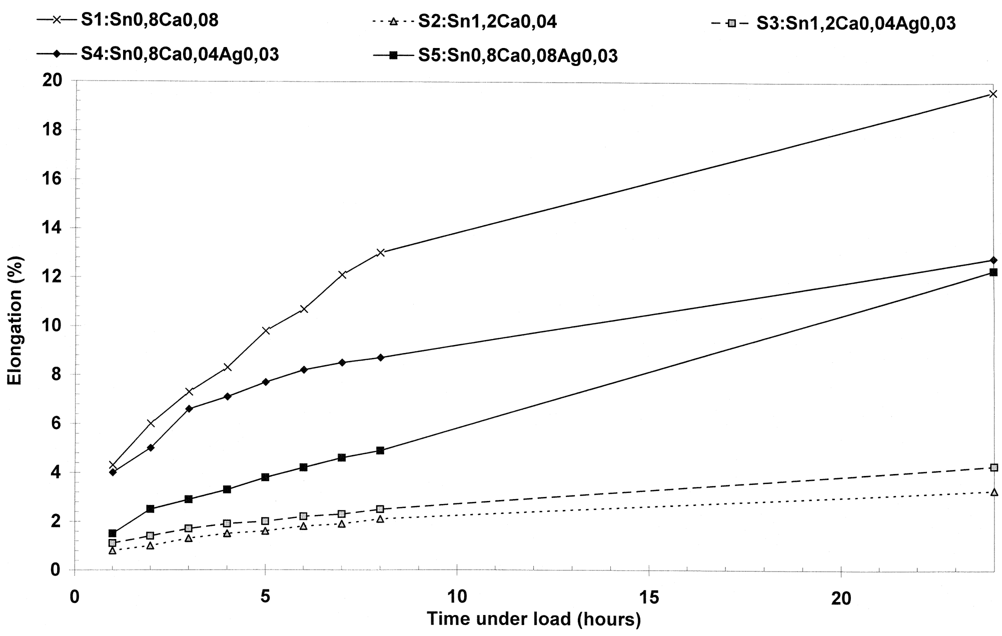

Fig. 3. Creep resistance test on rolled expanded grid: elongation vs. time under load at room temperature for different alloy compositions.

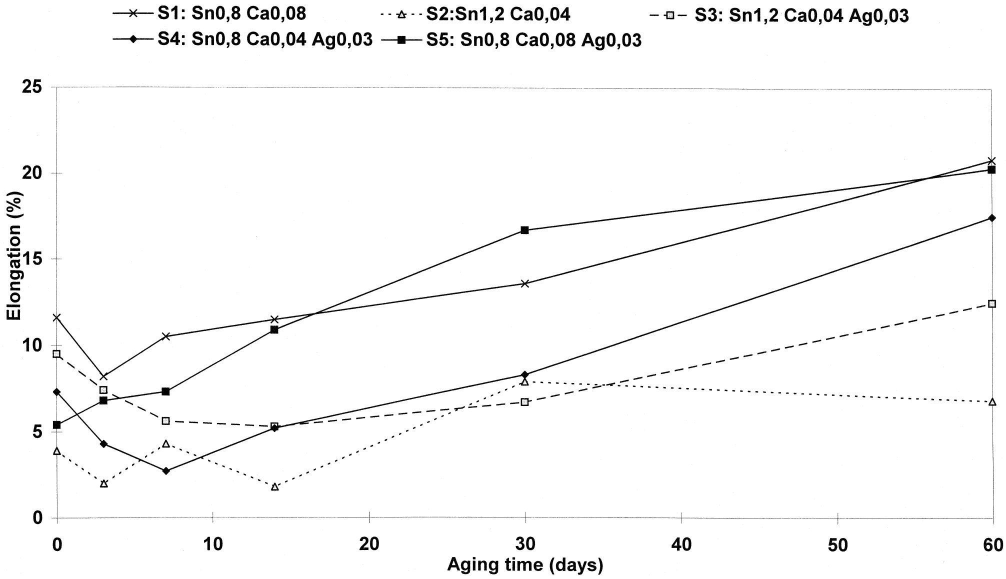

Fig. 4. Creep resistance test on rolled expanded grid after aging: elongation vs. aging time at 75°C for different alloy compositions.

- calcium has no effect on the total elongation after 24 h of test.

3.2.2. After aging

During its service life, the battery is submitted to high temperatures and the mechanical properties of the grid will change. In the first stage, strengthening of the alloy is observed, followed by softening after a longer time. This softening, due to recrystallization and/or overaging has to be limited in order to keep the good initial properties of the grids.

An accelerated recrystallization test has been carried out on rolled expanded grids initially stored during 3 months at room temperature. Grids have been submitted to a temperature of 75°C during 2 months. The mechanical properties and microstructure have been followed by creep test and metallographic observations.

The creep resistance is given by the grid elongation measured after 24 h under load. The evolution of the creep resistance for different periods of storage is presented in Fig. 4.

- A high tin content associated with a low calcium content tends to slow down the recrystallization phenomenon.
- No significant improvement of the mechanical properties is noticed with the addition of silver.

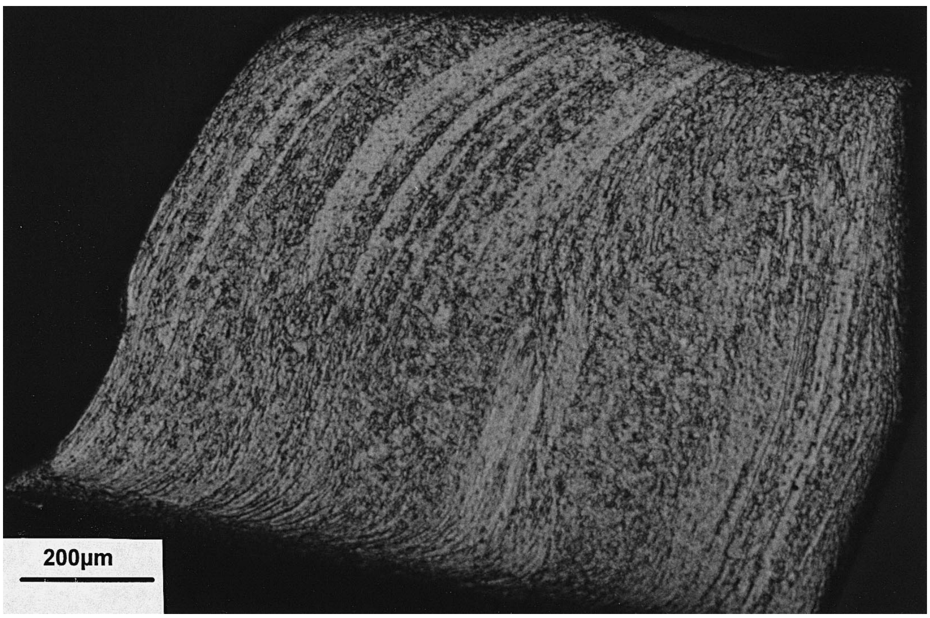

Fig. 5. Recrystallization test at 75°C: metallographic observation of the cross-section of a rib after 30 days of storage at 75°C. Alloy Ca 0.04%, Sn 1.2%.

Table 2
Minimum, maximum and average concentration of silver and tin measured through the cross-section of a grid wire by microprobe analysis (%)

Process	Series	Sn				Ag			
		Microprobe			Nominal	Microprobe			Nominal
		Min	Max	Mean		Min	Max	Mean	
Rolled	1	0.72	1.44	0.99	0.8	0	0.18	0.02	0
Rolled	2	1.01	2.27	1.42	1.2	0	0.14	0.02	0
Rolled	3	1.14	3.57	1.47	1.2	0	6.18	0.16	0.03
Rolled	4	0.63	1.49	0.87	0.8	0	5.12	0.18	0.03
Cast	6	0.78	1.92	1.15	1.2	0	0.13	0.02	0
Cast	8	0.45	2.03	0.78	0.6	0	1.64	0.09	0.03

• Metallographic observations show that the grid microstructure remains constituted by extremely fine grains (see an example in Fig. 5). This very fine structure obtained in rolled expanded grids compared to the grain size of about 50 μm observed on gravity cast grids should not present risks of penetrating corrosion even after storage at very high temperatures.

4. Microprobe analysis

Due to the specific microstructure of grids obtained with the rolling expansion and the gravity casting processes in these various alloy compositions, tin and silver precipitation operates in different ways. This has been confirmed by microprobe analysis carried out on a cross-section of a wire from the centre to the grid wire surface. On rolled expanded grids, the microprobe scanning has been made perpendicularly to the rolling direction, passing through a maximum number of grain boundaries. Samples have been embedded in epoxy resin, mechanically polished and slightly etched to reveal grain boundaries.

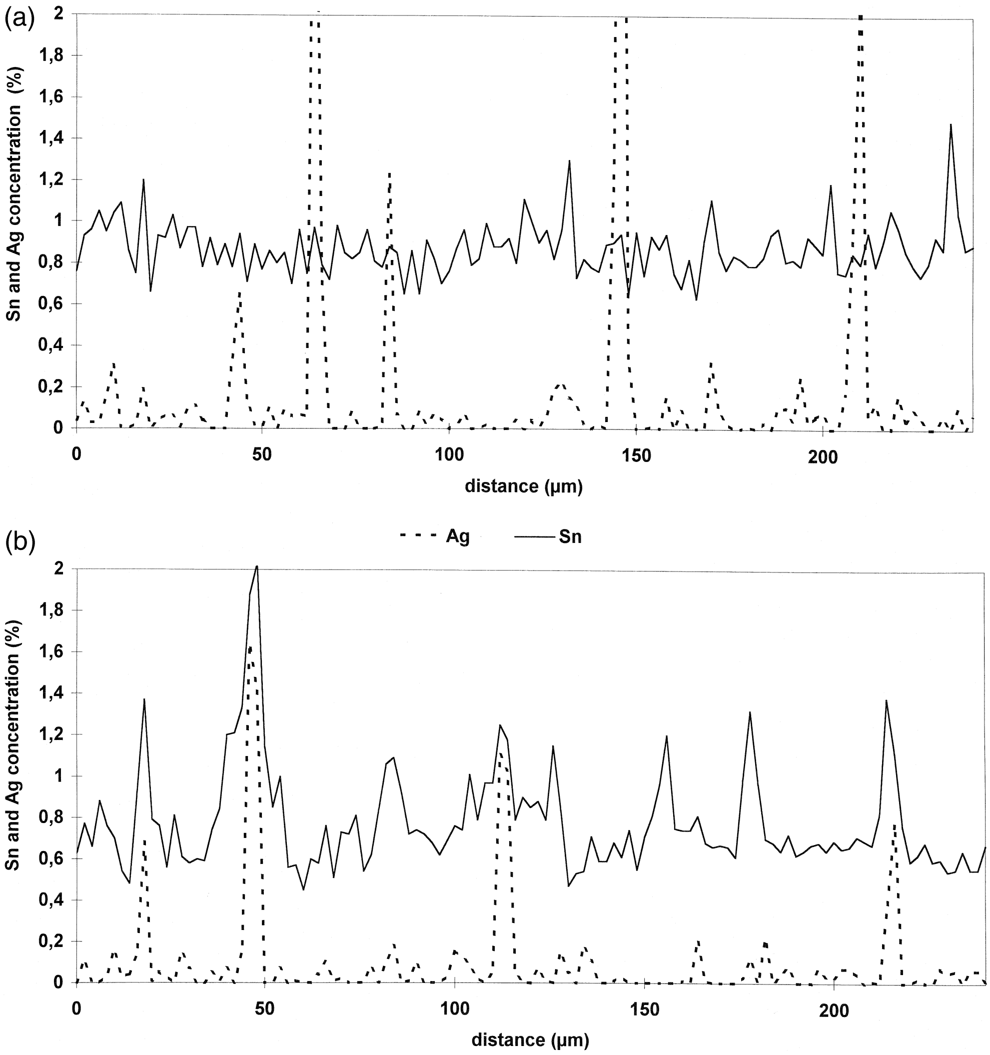

Fig. 6. (a) Microprobe analysis on a rolled expanded grid Ca 0.04%, Sn 0.8%, Ag 0.03%: silver and tin concentration vs. distance from the centre to the edge of the cross-section of a wire. (b) Microprobe analysis on a gravity cast grid Ca 0.05%, Sn 0.6%, Ag 0.03%: silver and tin concentration vs. distance from the centre to the edge of the cross-section of a wire.

The surface of analysis was 2×2 μm^2, scanning over 240 μm with 2 μm step.

Concentration measurements made on the surface of the samples have shown no gradient of calcium concentration for either process.

Concentrations of tin and silver are given in Table 2. Silver average concentration values are below the detection limit of the microprobe analysis (0.18%), and have to be considered as a general background against which silver-rich areas can be identified.

Some examples are shown in Fig. 6a and b.

From these analyses, the following can be seen.

- In rolled expanded grids, tin segregation occurs in the numerous grain boundaries. At a high concentration, this segregation is more pronounced. Coarse silver-rich precipitates can be found dispersed along grain boundaries and not necessarily associated to tin segregation.
- In gravity casted grids, silver and tin precipitates in grain boundaries and cellular sub-boundaries. A strong combination of silver and tin is observed.

This distribution of tin and silver on a limited number of sites with a higher local concentration should lead to a more effective protection against passivation phenomena on gravity cast than on rolled grids.

5. Bare grid corrosion test

Grids have been maintained during 1 month at the $PbO_2/PbSO_4$ equilibrium potential, i.e., 1100 mV against

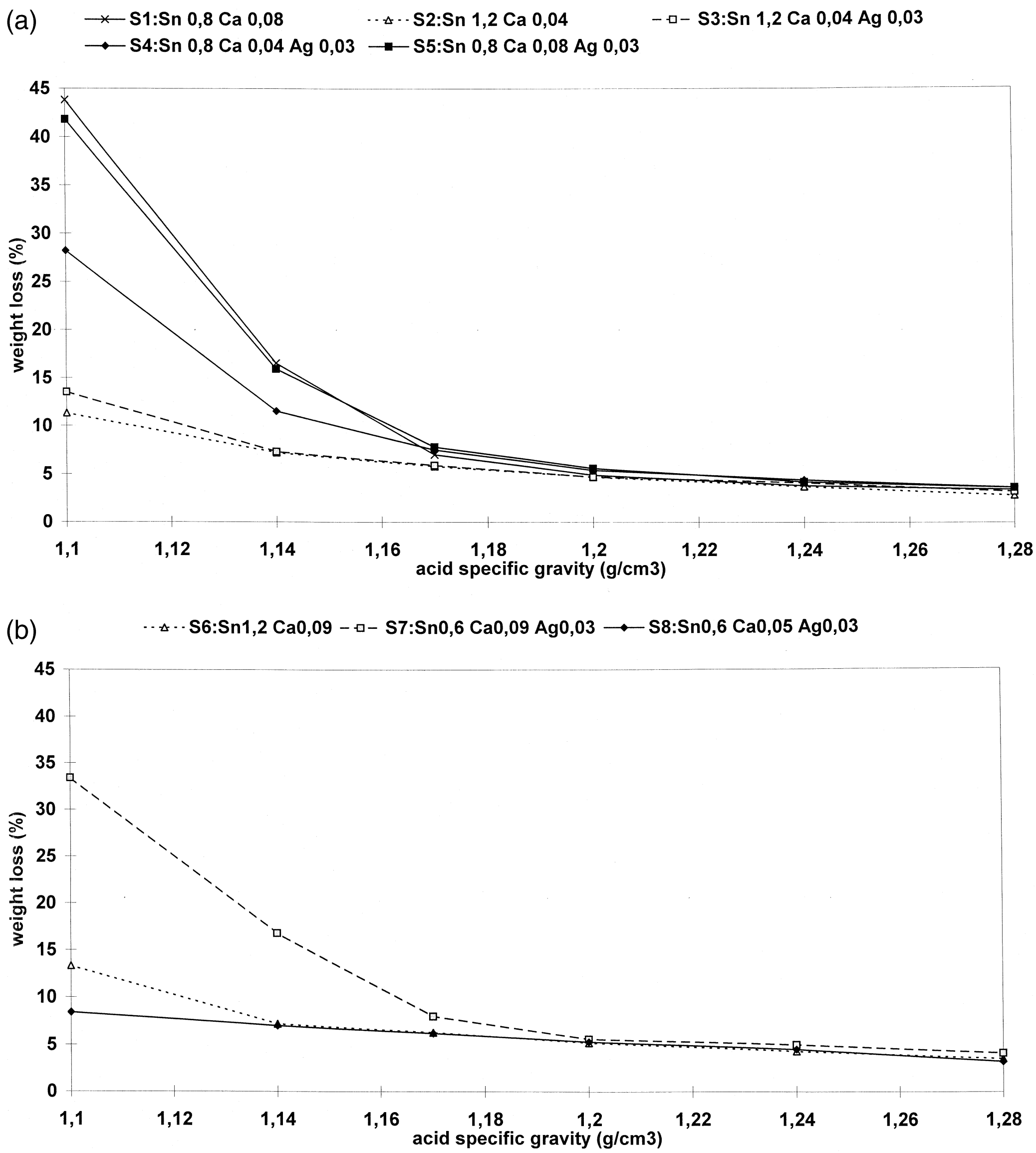

Fig. 7. (a) Corrosion test at the PbO2/PbSO4 equilibrium potential at room temperature on rolled expanded grids: grid weight loss in various acid densities for different alloy compositions. (b) Corrosion test at the $PbO_2/PbSO_4$ equilibrium potential at room temperature on gravity casted grids: grid weight loss in various acid densities for different alloy compositions.

a mercury mercurous sulfate reference electrode, in various acid densities. This test simulates grid corrosion during battery storage, in charged condition (high acid density) and in discharged condition (low acid density). Corrosion is then assessed by grid weight loss measurement after chemical etching and by observation of the corrosion layer with optical microscopy.

From Fig. 7a and b, showing the evolution of grid weight loss as a function of acid density for the different alloy compositions in rolling expansion and gravity casting, the following can be seen.

- In high acid density, alloy composition does not affect the grid weight loss, which remains very low.
- In low acid density, the weight loss is more important, and clearly depends on alloy composition: (a) for rolled expanded grids, corrosion is limited by a high tin content, and to a smaller extent, by a low calcium level; silver has no effect; (b) for gravity cast grids, corrosion is limited by a low calcium content and by a high tin level. A high tin level, up to 1.2%, is more efficient than the addition of silver with a low tin content.
- For all alloys, at all acid densities, corrosion has been found homogeneous, with no evidence of intergranular corrosion.

6. Tests on batteries

The test procedures intend to evaluate the effect of the different alloys and processes on the main operating modes of the battery during its service life that are obviously affected by grid composition and structure.

The initial performances of the batteries, i.e., 20-h rate capacity and cold cranking ability, have been found to be similar for all the different types.

6.1. Open circuit storage

Batteries have been stored in open circuit at 50°C and opened after 8, 16 and 24 weeks of storage for analysis.

When it was possible, positive grid weight loss has been measured in order to determine the corrosion rate of the grid (see Fig. 8).

Grid growth was given by the variation of grid height measured on the opposite side of the lug, which is the most critical side of the plate (see Fig. 9a and b).

6.1.1. Tests results on rolled expanded grids

- Fig. 8 shows that after 24 weeks of storage, the corrosion rate of the positive grid is only slightly dependent on the alloy composition. The corrosion layer has been found to be homogeneous.
- Positive grid growth is reduced when tin content is increased as shown in Fig. 9a.
- The addition of silver reduces the positive grid growth when tin content is low, but this effect declines with time. The same effect is noticed with a high calcium level.
- Self-discharge rate is not influenced by the alloy composition.

6.1.2. Tests results on gravity cast grids

- After the first weeks of storage, the positive grid was already so brittle that grid weight loss could not be

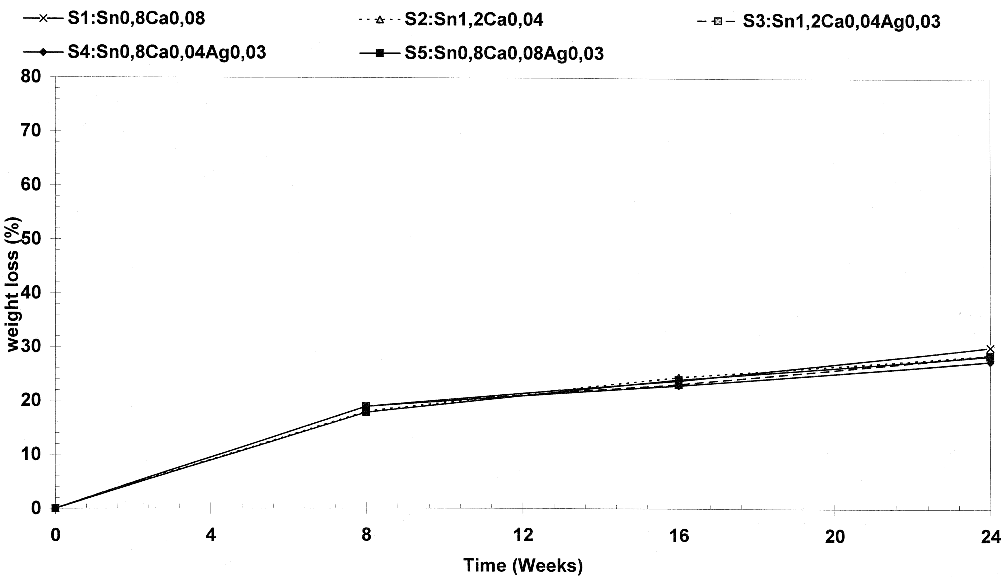

Fig. 8. Corrosion rate of rolled expanded grids during self-discharge test: positive grid weight loss vs. storage time for different alloy compositions.

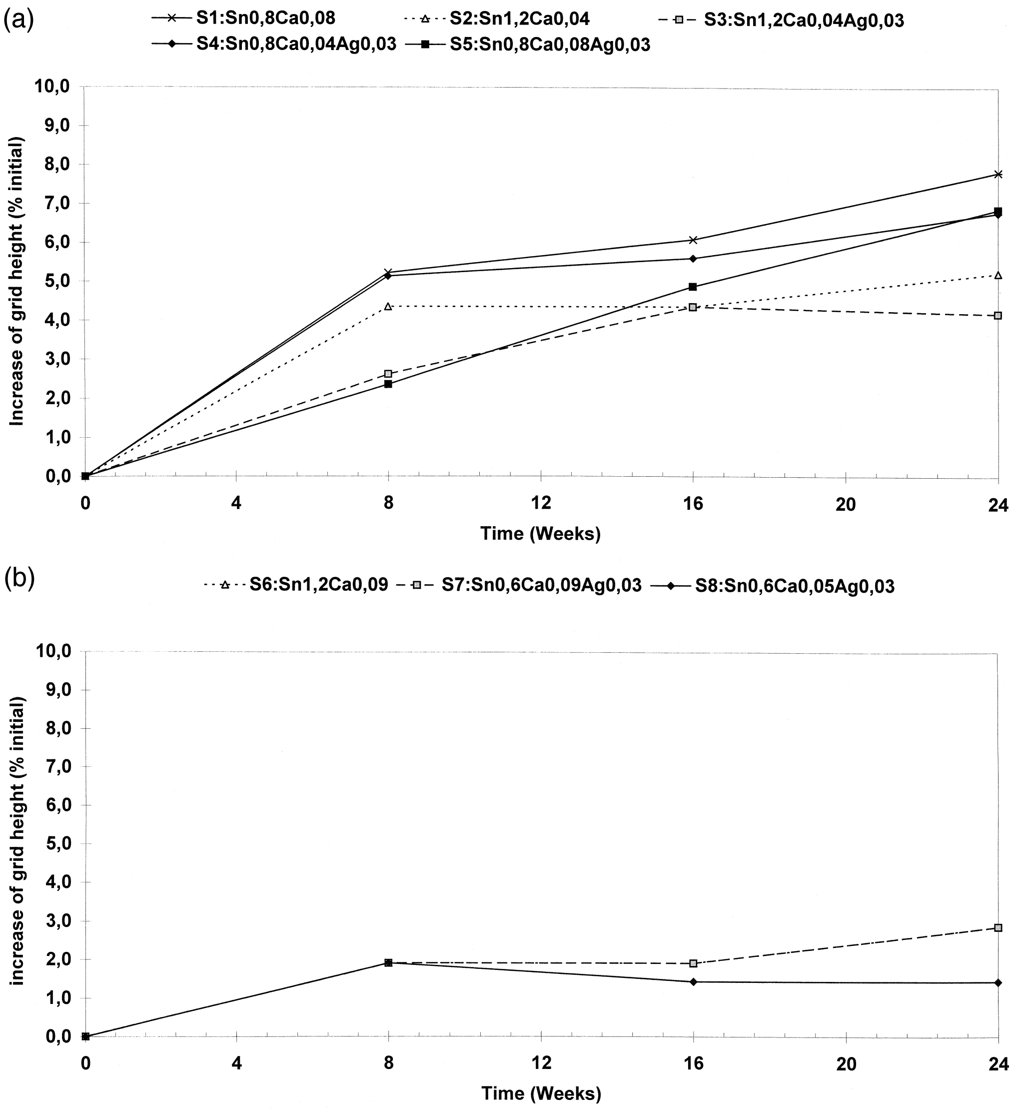

Fig. 9. (a) Grid growth of rolled expanded grids during self-discharge test: increase of positive grid height as a percentage of the initial height vs. storage time for different alloy compositions. (b) Grid growth of gravity cast grids during self-discharge test: increase of positive grid height as a percentage of the initial height vs. storage time for different alloy compositions.

measured. The corrosion layer shows the beginning of penetrating corrosion.

- Positive grid growth is negligible as shown in Fig. 9b, due to the presence of side borders on the grid.
- Self-discharge rate is not influenced by the alloy composition.

6.2. *Overcharge / storage test*

The batteries were submitted to successive schedules:

- 1 week of open circuit storage at constant temperature of 60°C;
- 1 week of overcharge at constant voltage 14 V and constant temperature 60°C;
- a cold cranking test at −18°C then recharge at 14.8 V, 24 h, $I_{max} = Cn/2$, 25°C.

During the whole test, the electrolyte level was maintained.

Parameters followed were:

- overcharge current at the end of the overcharge period;
- weight loss during the overcharge period;
- 10-s voltage during the cold cranking test;
- time to 7.2 V during the cold cranking test.

End of test was reached when at the cold cranking test, time to 7.2 V was less than 30 s. The evolution of time to 7.2 V is presented in Fig. 10a for rolled expanded grids and Fig. 10b for gravity casted grids.

Tests results are given in Table 3. This table shows the following.

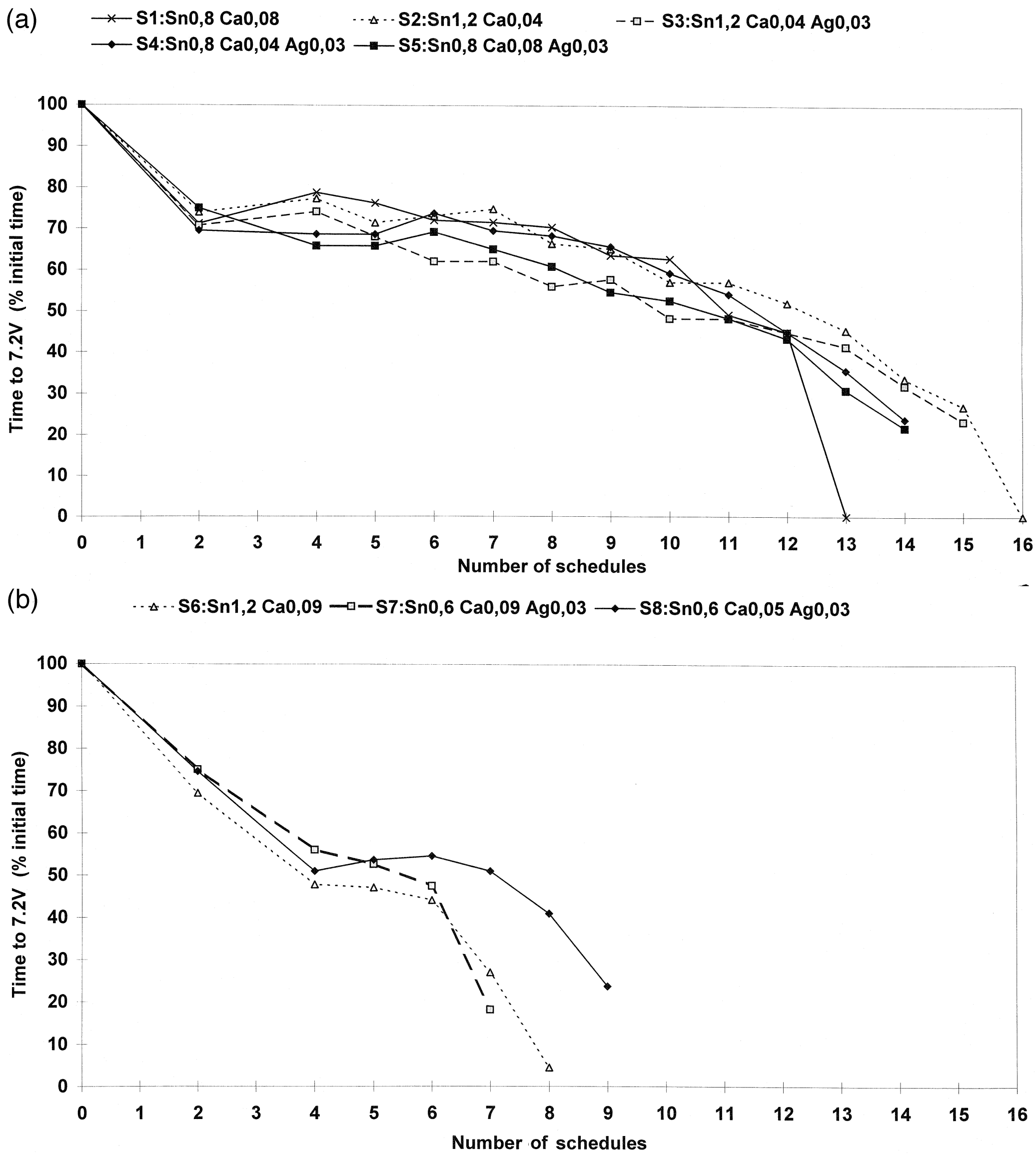

Fig. 10. (a) Overcharge/storage test on rolled expanded grids: time to 7.2 V on cold cranking test vs. number of schedules for different alloy composition. (b) Overcharge/storage test on gravity cast grids: time to 7.2 V on cold cranking test vs. number of schedules for different alloy compositions.

- With rolled grids, the combination of high tin and low calcium contents gives the highest life test; silver addition at low tin content does not lead to a significant improvement of the life test.
- With gravity cast grids, a high tin level up to 1.2% gives better results than the addition of silver with low tin. But the reduction of calcium level has the most significant effect on the improvement of life.

Table 3
Life of batteries in overcharge and storage conditions at 60°C, 14 V for different alloy compositions and processes for the positive grid

	Rolled expanded metal					Gravity casting		
Prototype series	1	2	3	4	5	6	7	8
Ca (%)	0.08	0.04	0.04	0.04	0.08	0.09	0.09	0.05
Sn (%)	0.8	1.2	1.2	0.8	0.8	1.2	0.6	0.6
Ag (%)	< 0.001	< 0.001	0.03	0.03	0.03	< 0.001	0.03	0.03
Number of schedules	13	16	15	14	14	8	7	9
Total time (h) overcharge + storage	4368	5376	5040	4704	4704	2688	2352	3024
Primary failure mode	positive grid growth					positive grid corrosion (weight loss)		

· The total number of schedules reached with rolled expanded grids is around double that with gravity cast grids.

· The primary failure mode can be correlated to the metallographic structure and to the mechanical properties of the grid.

6.3. Deep discharge test

Batteries have been submitted to a 20-h rate discharge and then, without being recharged, connected to a 10-Ω resistance during 2 weeks. This complete discharge was followed by an open circuit storage period of 4 weeks at 50°C. Then, the batteries have been recharged at 14.8 V with a maximum current of 50 A, during 48 h at 25°C.

Parameters followed in order to evaluate the rechargeability of the battery are:
· charging current vs. time;
· residual capacity at the end of the recharge;
· cold cranking performances.

Test results are given by the charging current curves shown in Fig. 11a and b.

· As already shown in previous studies, the improvement of battery rechargeability—shown by a higher maximum current at a shorter time, and a higher capacity

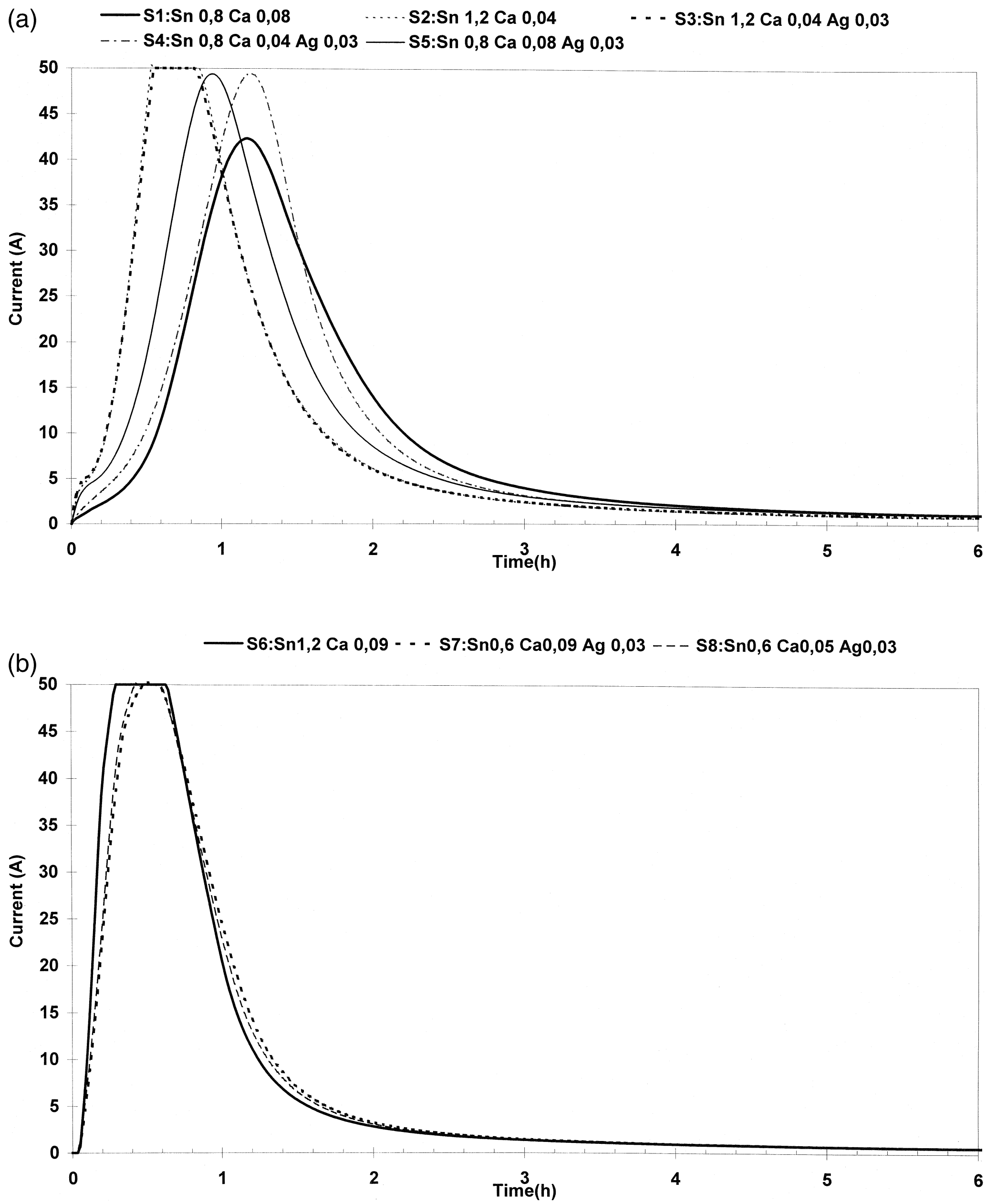

Fig. 11. (a) Deep discharge test on rolled expanded grids: evolution of the charging current vs. time for different alloy compositions. (b) Deep discharge test on gravity cast grids: evolution of the charging current vs. time for different alloy compositions.

absorbed during charging—when tin content is increased from 0.8% to 1.2%, has been confirmed. The high tin effect seems more important with the rolling process than with the gravity cast one, maybe due partially to the different segregation mode of tin in the two processes.

- Silver addition at a low tin content has no significant effect on the rechargeability of rolled expanded grids.
- At low tin level, the battery rechargeability is better in the gravity casting process than in the rolled one. This different behaviour between the rechargeability of rolled expanded and gravity cast grids may also be partially correlated to the different segregation mode of tin in these two cases.

7. Conclusions

The influence of tin, silver and calcium content has been investigated with rolled expanded and gravity cast grids, in order to compare their effect on the mechanical properties of the grids and on battery performance.

- The mechanical properties of rolled expanded grids, mainly characterized by UTS and elongation, have been found to be improved by an increase of tin content from 0.8% to 1.2%. Silver and calcium content have no significant effect.
- The resistance to corrosion of bare grids at equilibrium potential is strongly dependent on the acid density. At low acid density, corresponding to the most severe condition, grid corrosion is limited by a high tin content and by a low calcium content (0.04%). There is no effect of silver.
- This improvement, reached by a higher tin content, leads to a longer battery life in hard conditions of use, such as storage and overcharge at high temperature, and to a better rechargeability of the battery after a deep discharge.
- In these test conditions, it has been noticed that the addition of silver has only a poor impact on the behaviour of rolled expanded grids; on gravity casted grids, in the same conditions, the addition of silver associated with a low calcium content slightly improves the battery life.
- In high temperature conditions of overcharge and storage, the battery life obtained with rolled expanded grids is higher than that with gravity cast, whatever the alloy.
- The choice for each grid manufacturing process must take into account of course the optimization of product performance in accordance with the technical requirements, but also the processability of such alloys. For instance, a certain calcium content is needed in order to have a sufficient traction resistance for the expansion, but a minimum content is preferable in order to improve corrosion resistance of the grid.
- In the most severe battery operating conditions, such as overcharge and storage at high temperature or deep discharge, the best behaviour has been obtained with rolled expanded metal technology. From the conclusions mentioned above concerning the mechanical properties of the alloys and the electrical tests results on batteries, and taking into account the process parameter restraints, the alloy Sn 1.2% Ca 0.08% is a good compromise.

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