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Low-antimony lead-alloy expanded grids: preliminary performance data

J. Sklarchuk, M. J. Dewar, E. M. Valeriote and A. M. Vincze
Cominco Product Technology Centre, 2380 Speakman Drive, Sheridan Park, Mississauga, Ont., L5K 1B4 (Canada)

Abstract

Low-antimony lead alloys have been successfully produced by a unique continuous casting process. The alloys contain 1 to 3 wt.% antimony, 0.01 to 0.20 wt.% arsenic and 0.2 to 0.3 wt.% tin. Battery grids fabricated from these alloys are found to have electrochemical properties that are superior to those of conventional gravity-cast, low-antimony, lead-alloy grids. Preliminary results are presented.

Introduction

Continuous plate-production processes based on expanded metal or other technologies have been proven to be very cost effective in the automotive battery industry. The combination of high-speed, reduced material requirement and automated manufacture provides plates of higher quality and lower cost. Continuous plate-production processes are being used for both positive and negative plates. The vast majority of continuous plate production today is, however, limited to the negative plate. One of the main reasons for the current situation is that many manufacturers favour the hybrid battery design using low-antimony (low-Sb), lead-alloy grid positives together with lead–calcium (Pb–Ca) negatives. Unfortunately, continuous processes have suffered technical difficulties in producing low-Sb positive-plate grids that have adequate performance and service life. Excessive corrosion and grid growth have hindered some of the attempts to produce a commercially viable low-Sb, lead-alloy, positive-plate grid.

Over the last three years, Cominco has been developing a new process to produce cost-effectively a low-Sb strip that can be expanded into a positive plate and will exhibit a performance that is equivalent to, or better than, the conventional gravity-cast counterpart. The process for making the strip is now established. Development activity over the last year has focused increasingly on optimization of the alloy- and strip-casting conditions in order to maximize both performance and battery life.

In most of the tests to date, a nominal composition of Pb–1.7wt.%Sb–0.15wt.%As–0.2wt.%Sn has been used for the strip. No grain refiners (such as selenium) are used to cast the alloy. Antimony levels as high as 3 wt.%, and as low a 1 wt.%, have also been cast. Arsenic levels have been varied from 0.01 wt.% to about 0.2 wt.%. The strip is an as-cast product and is porosity free. Depending on the test, it is evaluated either in the form of a coupon or as a rotary-expanded grid.

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Electrochemical testing at Cominco's laboratories and selected battery companies has been in progress for the past year. This paper present details of the test methodology and some of the results obtained at Cominco's Product Technology Centre.

Experimental

Scope of testing

The overall scope of the programme, as shown in Table 1, has covered three basic areas, namely: corrosion testing; cycling tests, and metallurgical, chemical and mechanical analysis. Corrosion testing was one of the initial efforts with the new material, because it was important to determine first that corrosion resistance was either similar to, or better than, incumbent materials. As the results began to confirm satisfactory corrosion resistance, a parallel series of studies was begun to determine grid-growth characteristics. Complementing the electrochemical work, a metallurgical programme investigated physical and grain structure changes in the strip that were caused by changes in alloy and casting conditions. As the casting process improved, the role of grain refiners became less significant, and these additives were eventually eliminated from the alloy. Physically, a low-Sb strip from the Cominco process is a softer material than its Pb–Ca counterparts. The tensile strength of low-Sb strip is typically around 32 MPa (4500 psi), regardless of the Sb level.

Test focus

The left-hand column of Table 2 summarizes the test variables for corrosion testing that constituted the focus of this paper, namely: 50 to 200 mV overpotential (the open-circuit voltage of a positive plate was 1150 mV versus the Hg/Hg_2SO_4 reference electrode), 50 to 70 °C test temperatures, 1 to 3 wt.% Sb levels, with particular attention to the 1.75 to 2 wt.% Sb range, and different casting variables. Proprietary

TABLE 1

Overall scope of testing

Corrosion testing	rotary expanded grids book-mould grids strip coupons
Cycling tests	single plate cells full-size batteries
Strip analysis	composition tensile strength creep resistance grain structure

TABLE 2

Test focus

Test variables	Performance parameter
Overpotential: 50 to 200 mV Temperature: 50 to 70 °C Composition: 1 to 3 wt.% Sb, 0.01 to 0.2 wt.% As Casting variables	Weight loss Grid growth Gassing/anodic current

concerns regarding the new technology restrict disclosure of details regarding casting variables, except to say that the latter can be closely controlled. The right-hand column of Table 2 lists those performance parameters that were measured to determine the effects of the test variables.

Test grids

Figure 1 shows the different samples that were tested. These ranged from conventional book-mould grids, to rotary-expanded grids, to both solid and punched coupons. The punched coupons were used to determine growth measurements under extreme test conditions, such as 200 mV and 70 °C. In this type of test, the book-mould and expanded grids frequently had excessive wire breakage, which prevented the acquisition of meaningful growth data, while the solid coupons did not grow sufficiently to obtain reliable measurements.

Test cell

The different test specimens were placed in a test cell that is illustrated in Fig. 2. The cell was circular in design, so that all test electrodes were equi-distant from the counter electrode (which followed the contour of the inner cell wall) and from the centrally located Luggin probe of the reference electrode. Four compartments comprised the cell, each containing five test electrodes. Each compartment could be removed separately at different times to obtain corrosion and growth data as a function of time.

Range of corrosion testing

The ranges of overpotentials and temperatures controlled in the corrosion testing are given in Table 3. The check marks indicate the experimental conditions under which the corrosion testing was performed. Particular attention was given to the 100 mV/50 °C, 50 mV/70 °C and 100 mV/70 °C points because these were considered to be more representative of real-life battery conditions. The other points either represent formation conditions or, in the case of 200 mV/70 °C, extreme laboratory conditions that would never occur simultaneously in a real battery.

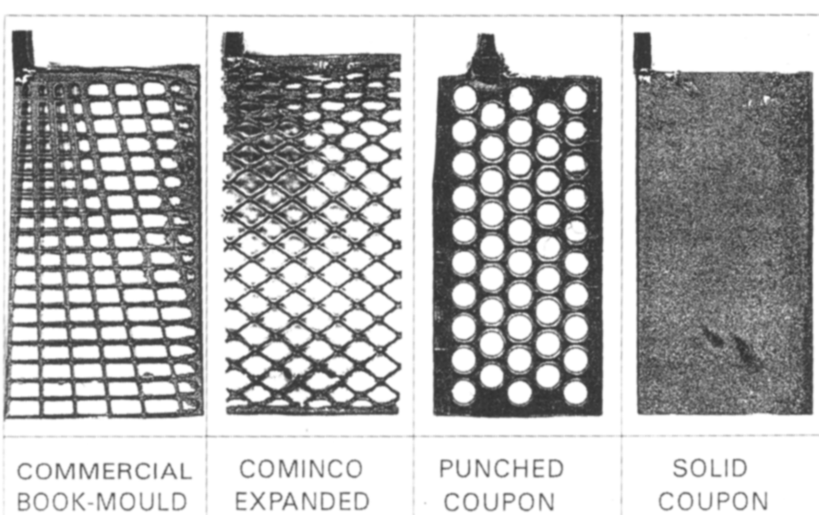

Fig. 1. Designs of low-antimony lead grids and coupons used in corrosion tests.

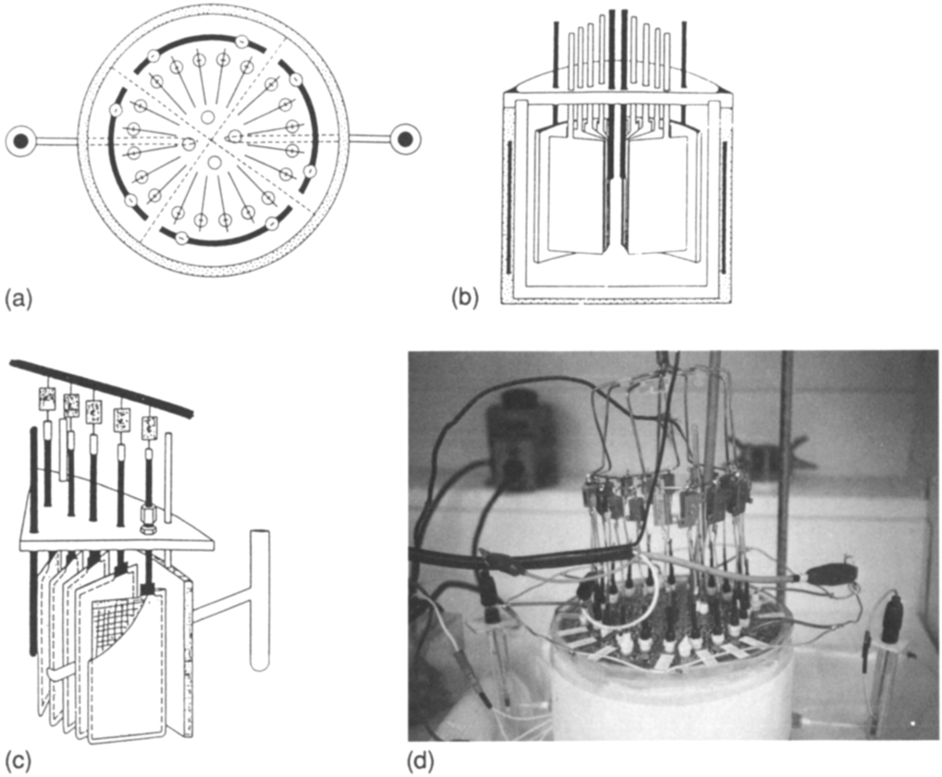

Fig. 2. Corrosion test cell design: (a) top view — 4 segments; (b) vertical section; (c) assembled segment with connections; (d) actual cell.

TABLE 3

Range of corrosion tests

Overpotential (mV)	Temperature		
	50 °C	60 °C	70 °C
50			✓
100	✓		✓
150		✓	
200	✓		✓

Results

Corrosion results

The results of a corrosion test at 70 °C and 100 mV overpotential are shown in Fig. 3. CBM refers to a conventional book-mould (gravity-cast) grid. CC1 refers to strip made under a particular casting condition and then expanded into a grid, while CC2 is the same alloy as CC1 but the strip was fabricated using a different casting

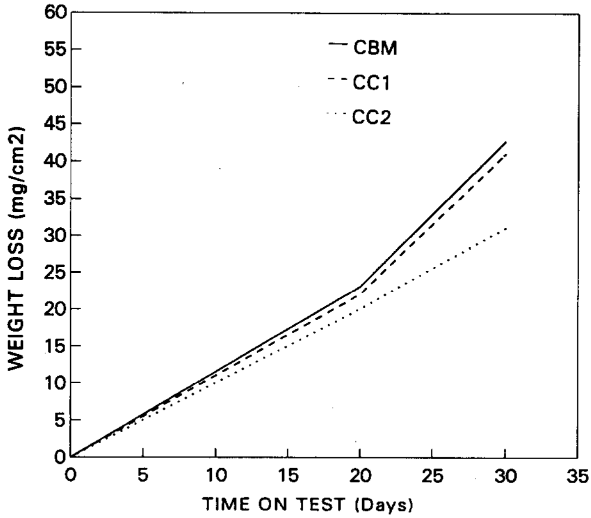

Fig. 3. Weight losses of low-antimony (2 wt.% Sb) lead-alloy bare grids; corrosion tested at 70 °C and 100 mV overpotential.

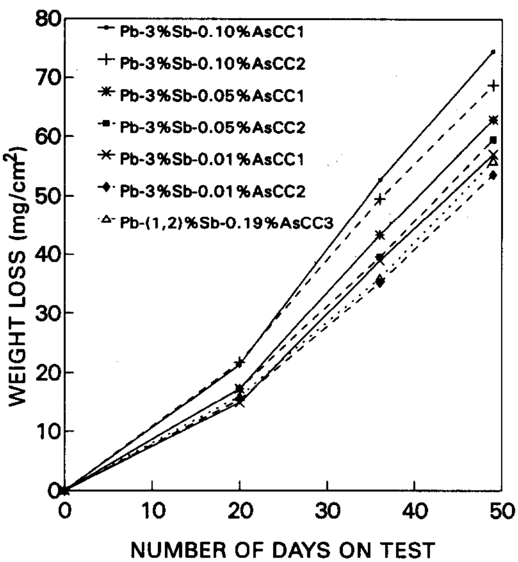

Fig. 4. Weight losses of low-antimony alloys as a function of antimony and arsenic contents, as well as casting conditions tested at 60 °C and 1500 mV overpotential.

condition. The weight losses of different Cominco grid specimens, denoted by casting conditions 1 and 2, are less than those for a commercial book-mould grid. The grid fabricated by casting condition 2, exhibits a 25 to 30% decrease in weight loss, when compared with the book-mould grid, after approximately 30 days in test.

Figure 4 represents weight losses of a Pb–3wt.%Sb alloy with varying arsenic levels, and for two casting conditions, in comparison with 1 to 2 wt.% Sb alloys with a constant (0.19 wt.%) arsenic level. The higher antimony-containing alloy had a similar corrosion resistance to alloys with lower (1 to 2 wt.%) antimony levels, provided that the arsenic levels of the higher-antimony alloy were reduced sufficiently. When other variables were held constant, the weight losses of the Pb–3wt.%Sb alloys increased with arsenic content.

Gassing

The results of anodic current measurements are given in Fig. 5. Again, the conditions were 70 °C and 100 mV overpotential which simulated more extreme, but possible, real field conditions. The test shows that both types of low-Sb strip grids drew less current than the conventional book-mould grid, and that the grids made by casting condition 2 drew 20 to 25% less current than the book-mould grid after approximately 30 days on test. Since, under these conditions, the current near the end of test is largely due to oxygen evolution, it is concluded that gassing from the CC2-type grids was also less. The commercial potential exists, therefore, to make a hybrid battery with improved maintenance-free characteristics with this material.

Grid growth

The investigations into grid-growth phenomena are still underway and, therefore, firm conclusions have not yet been reached. The following presents the observations to date:

(i) Largely because of design differences, expanded and book-mould grids exhibit different growth behaviour with respect to geometrical and quantitative aspects as well as the potential harmful effects on a battery. Therefore, it is difficult to predict their respective effects on battery life by simply comparing height, width, or area growth measurements.

(ii) Different casting conditions used in fabricating Cominco low-Sb strip can affect grid growth. For example, in some 200 mV/70 °C overpotential tests, significant growth dependence on casting conditions was observed. These test conditions, however, are

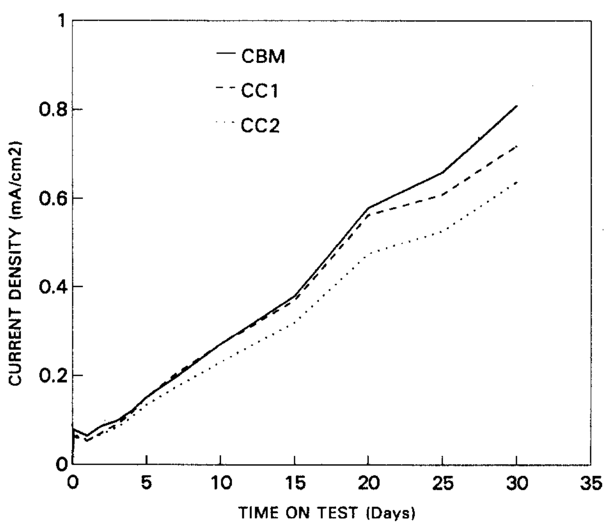

Fig. 5. Corrosion and gassing currents with Pb–2wt.%Sb bare grids; corrosion tested at 70 °C and 100 mV overpotential.

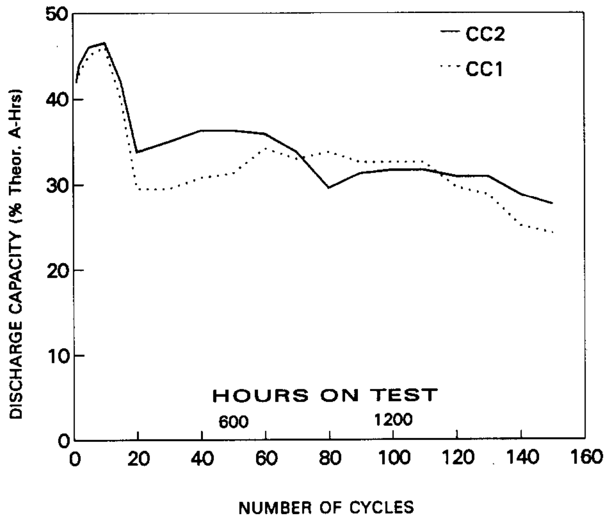

Fig. 6. Cycle test of prototype batteries with positive plates containing low-antimony lead alloys; negative grids: lead–calcium.

very severe and are not considered predictive of field conditions. In the 100 mV/ 50 °C tests, different strip-casting conditions caused relatively small differences in grid growth.

(iii) High-temperature cycling tests were carried out on batteries to assess the effect of casting conditions on both grid growth and battery life. Cominco fabricated full-size test batteries using rotary-expanded low-Sb positive-plate grids and expanded Pb–Ca negative grids. The batteries were submitted to a severe cycling test that is commercially used to determine battery life for conventionally-constructed hybrid batteries. If a battery survives 1000 h, it is considered to have adequate commercial life. Figure 6 shows the results of this test, carried out at 70 °C with two 100% depth-discharges per day and a 15 V limit during charge.

The capacity–time curves are shown for batteries fabricated under two different strip-casting conditions. There was only a small difference in their performance and both batteries easily exceeded the 1000 h requirement. These and some related results indicated that growth of grids need not be a major life-limiting factor for batteries, made from Cominco's low-Sb strip.

Concluding remarks

This paper has described some preliminary test results for a new, low-Sb lead alloy, grid material. The alloy has commercial potential for use in a continuous process to make lead/acid battery positive plates. Further work is required for unequivocal confirmation of the data and to gain a broader perspective of performance under different service conditions. Further optimization of alloy and casting conditions may also enhance certain beneficial properties of the material.