On improving the corrosion and growth resistance of positive Pb-acid battery grids by grain boundary engineering

E.M. Lehockey [a,*], D. Limoges [a], G. Palumbo [a], J. Sklarchuk [b], K. Tomantschger [b], A. Vincze [b]

[a] *Ontario Hydro Technologies, 800 Kipling Avenue, Building K.R., Toronto, ON, Canada M8Z 5S4*
[b] *Cominco Product Technology Centre, Sheridan Science Technology Park, Mississauga, Canada*

Abstract

A frequent failure mode of Starting–Lighting–Ignition (SLI) and other lead-acid batteries relates to weight loss and growth of positive electrode grids, arising from intergranular corrosion/cracking and creep. The present investigation examines the impact of increasing the frequency of grain boundaries having low-Σ misorientations ($\Sigma \leq 29$), described by the Coincident Site Lattice (CSL) model. Such grain boundaries are known to be resistant to intergranular degradation phenomena. Electrode microstructures of various PbCaSn alloys processed to contain frequencies of special boundaries in excess of 50% exhibited significant reductions in weight loss and grid growth relative to both cast and rolled grid products. Modifying the crystallographic structure of grain boundaries in Pb alloy battery grids thus provides an opportunity for extending the service life and/or minimizing grid thicknesses (weight) and hence, material costs in battery production. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Starting–lighting–ignition; Grain boundary engineering; Intergranular corrosion

1. Introduction

Positive grid corrosion and growth are among the most important factors governing the reliability and longevity of lead-acid batteries used in Starting-Lighting-Ignition (SLI) applications. As 'under-hood' temperatures of modern vehicles increase due to reductions in engine compartment size, battery weights, etc, and with improved service life performance being demanded by OEMs, the need for improving positive grid resistance, to meet these environmental and operating challenges, is becoming increasingly urgent.

Weight loss and growth of positive battery grids both originate from localized intergranular corrosion and creep along grain boundaries in the microstructure. Intergranular corrosion on the surface of a positive grid is illustrated in Fig. 1. Traditionally, improvements in positive grid corrosion and growth have been achieved by alloying additions (e.g., Ag, Se, As) within the confines of cost and electrical performance (e.g., internal resistivity) [1]. For example, these alloying additions are principally used as grain size refiners that reduce the depth of attack by intergranular corrosion. Likewise, adjusting cooling rates during casting also minimizes grain size with similar beneficial effects on the depth of intergranular attack. While these grain size-refining techniques have been effective in improving corrosion resistance and minimizing weight loss, it has often been at the expense of growth performance. As grain size is reduced, the number of sites (grain boundaries) available for sliding (creep) increases. The present authors and others have previously reported that grain boundaries having certain crystallographic misorientations described by low-Σ values in the Coincident Site Lattice (CSL) Model possess good atomic fit along the interface and exhibit increased resistance to diffusion [2,3], cracking [3], corrosion [4], creep (grain boundary sliding) and cavitation [5,6]. A detailed review of the CSL model and its implications on material properties can be found elsewhere in the literature [7,8]. Unfortunately, the frequency with which
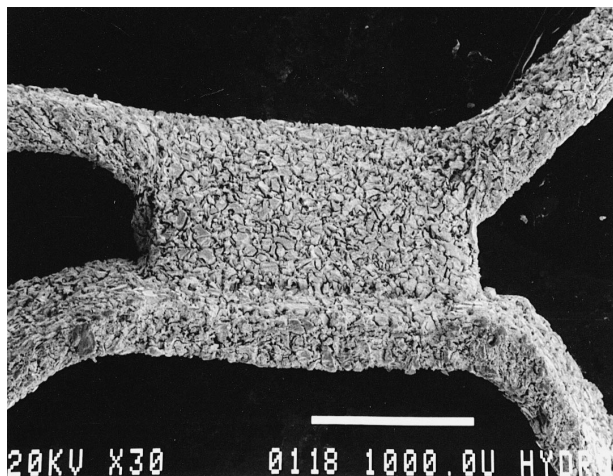
Fig. 1. SEM micrograph illustrating the intergranular nature of corrosion in positive lead-acid battery grids.

these boundaries occur naturally in most engineering materials is relatively low (approx. 12%). The present contribution reports on the effect of processing to increase the frequency of these 'special' grain boundaries in positive grid microstructures, on their corrosion and growth characteristics.

2. Experimental

Coupons $(5 \times 10 \times [0.05–0.09]$ cm) of various Pb alloys having compositions listed in Table 1 were strip-cast. Alloy compositions were selected to represent a range of alloys used in commercial SLI applications. A portion of the cast samples of each alloy were Grain Boundary Engineered (GBE™) using a proprietary, low-cost, metallurgical treatment to elevate the frequency of 'special' CSL grain boundaries in the microstructure. A second sample set was given a conventional rolling treatment using a 50% reduction in thickness. Cast, rolled, and GBE™-processed battery grids measuring 5×10 cm, and having a capacity of approximately 2.5 to 3 Ah, were formed using a rotary expander consistent with current grid production practices. The Grain Boundary Character Distribution (GBCD) in the conventional and GBE™ materials was characterized using a JEOL 840 SEM equipped with Orientation Imaging Microscopy (OIM). Misorientations between adjacent grains are calculated from changes in the electron backscatter pattern (EBSP) as the incident electron beam 'steps' in discrete intervals across the raster area. A complete description of the OIM technique is available in the literature [9].

Differences in corrosion (weight loss) and growth performance between cast, rolled, and GBE™ materials were evaluated using standard static polarization and cycling tests [10–12]. All grid electrodes were weighed to the nearest milligram and immersed in a corrosion cell con-

taining a solution of 1.27 s.g. H_2SO_4 at 70°C/75°C. All grids were polarized at a 200 mV over-potential (1.35 V vs. Hg/Hg_2SO_4 Reference Electrode) for periods of up to 20 days. In separate tests, grids were also pasted, formed and assembled into individual battery cells. Positive grids were cycled between 0.8 V ($PbSO_4$) and 1.4 V (PbO_2) with respect to the reference electrode at a rate of two cycles/day for 35 days. Test grids were removed periodically from each experiment, cleaned in a 'stripping' solution consisting of 100 g NaOH, 10 g Hydrazine dihydrochloride, and 20 g Mannitol in 1 l of water and subsequently re-weighed to establish mass loss. The effect of grain boundary structure on minimizing changes in overall area growth was determined by digitally scanning the grids and comparing their *geometric* areas before and after corrosion testing.

3. Results and discussion

Orientation images showing the effect of Grain Boundary Engineering on the distribution of special and general grain boundaries in the microstructure of a PbCaSn alloy (Table 1) are shown in Fig. 2a. Processing increases the frequency of special CSL grain boundaries (delineated by dark lines) from 12% in conventional (rolled or cast) material to values in excess of 65%. As indicated in Fig. 2b, increases of similar magnitude in the frequency of 'special' grain boundaries are readily achieved in a wide range of commercially significant PbCaSn and PbSb alloys. In many alloys, such as the PbCaSnAg and 'Hi' Sn materials, 'special' boundary fractions as high as 70% can be reproducibly obtained by suitable processing.

Grid weight loss and growth as a function of time under polarization are compared in Fig. 3a and b, respectively, for cast, rolled, and GBE™ PbCaSnAg alloys. Consistent with present trends in battery production, rolled grids show marginally better performance than cast material with regard to growth. However, weight loss performance is somewhat poorer than the cast material. As shown in Fig. 3a and b, processing to elevate the special grain boundary fraction reduces accumulated weight loss and growth after 20 days by approximately 16 and 75%, respectively, relative to both rolled and cast products. Reductions in corro-

Table 1
Nominal compositions of selected alloys used in this study

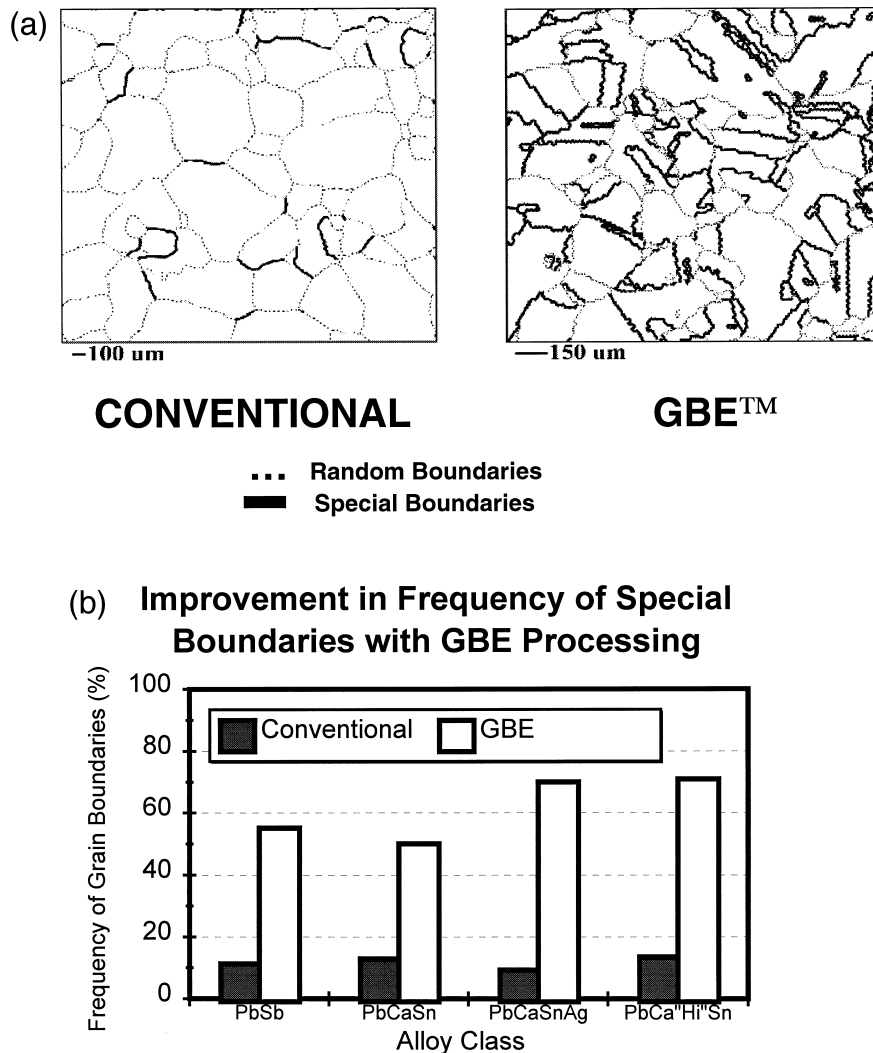| Alloy designation	Composition				
	Pb	Sb	Ca	Sn	Ag
PbCaSnAg	bal	–	0.03	0.7	0.06
PbCaSn	bal	–	0.06	1.0	–
'Hi' Sn	bal	–	0.06	1.7	–
PbSb	bal	1.7	–	–	–

Fig. 2. (a) Schematic OIM images comparing the distribution of special boundaries in the cast and GBE™ PbCaSn alloy. (b) Increases in the special boundary frequency achievable among various commercially significant positive grid alloys (Table 1) by Grain Boundary Engineering.

sion and growth rates of this magnitude suggest the potential for reducing present grid thicknesses or extending operating life by 30–75%. This is consistent with results previously reported by the present authors wherein growth rates in GBE grids were similar to conventional grids having twice the nominal thickness [13,14].

Reductions in the *rates* of (a) weight loss and (b) grid growth under static corrosion and cycling conditions accrued by enhancing the frequency of low-Σ CSL boundaries in the three PbCaSn alloys are summarized in the bar graphs of Fig. 4. Percentages shown reflect reductions in the rate of growth/weight loss between the conventional (cast) and GBE™-processed material. Microstructures in which high fractions of the grain boundaries present are crystallographically 'special', exhibited reductions in weight loss of 16 to 46%. Weight loss accumulated in certain cycled PbCaSn alloys was similar to that normally found in PbSb systems [13,14]. Special boundaries appeared to be more effective in reducing weight loss under

cycling compared with static polarization conditions. This reflects predominance for 'general' attack under static corrosion conditions, which remains largely unaffected by local grain boundary structure. In contrast, cycling tends to favor localized, intergranular attack driven by oxide volume changes associated with excursions across the $PbO_2/PbSO_4$ potential during charge/discharge [15,16]. The presence of 'special' low-CSL boundaries had a greater impact on grid growth than weight loss. Growth rates decreased by 29 to 72% as special boundary fractions exceeded 50%, approaching growth rates normally associated with PbSb alloys. In general, the results in Fig. 4 demonstrate that significant improvements can be made in the corrosion and growth performance of a wide range of commercial battery grid alloys. In addition, the magnitude of improvement in corrosion and growth often exceeded differences in performance among the different conventionally processed alloy compositions, suggesting that grain boundary structure control may be equally important, or

perhaps more important, than alloy selection in extending battery life.

4. Summary

Collectively, the evidence presented above clearly demonstrates the importance of controlling grain boundary structure to improve the corrosion and growth resistance of positive grids used in SLI and other lead-acid batteries. Reductions in corrosion and growth of the magnitude demonstrated above directly translate into both cost and performance benefits in terms of enhanced energy density and/or material cost savings. Reductions in corrosion and growth of 20 and 75%, respectively, accrued from altering the grain boundary structure can be expected to provide a two- to four-fold longer service/cycle life, or alternatively, facilitate commensurate reductions in present grid thicknesses. The potential for improved cycle life and energy density may also play an important role in Electric

(a)
Weight Loss Performance
Pb 0.029Ca 0.73Sn 0.062Ag

Temperature = 75C
1.27 s.g. H_2SO_4
200 mV Overpotential
Thickness= 0.9mm (0.035")

◆ Cast ■ Rolled △ GBE

(b)
Area Growth Performance
Pb 0.029Ca 0.73Sn 0.062 Ag

Temperature = 75C
1.27 s.g. H_2SO_4
200 mV Overpotential
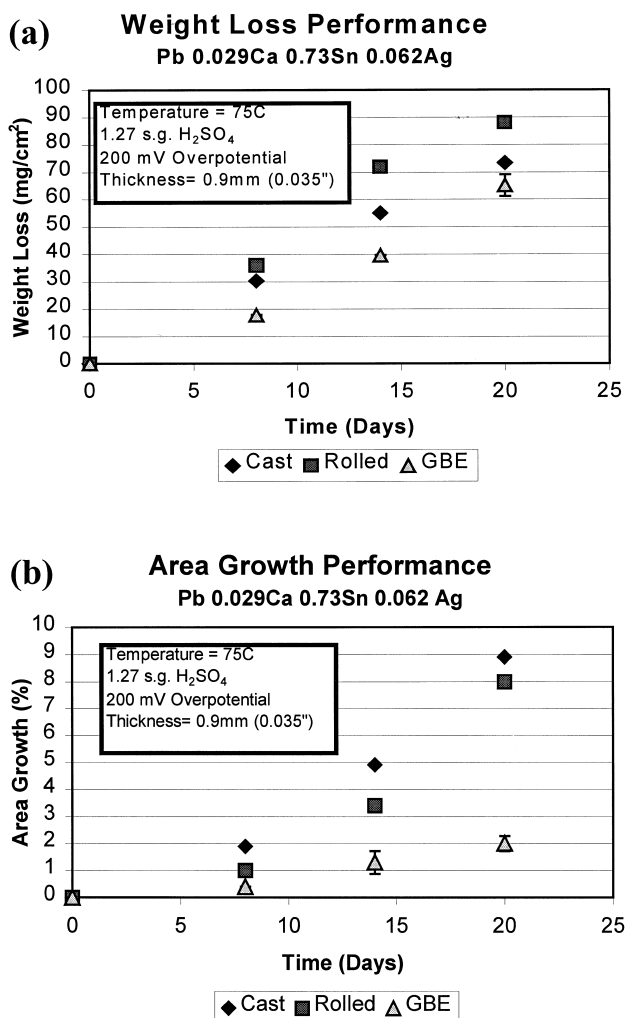Thickness= 0.9mm (0.035")

◆ Cast ■ Rolled △ GBE

Fig. 3. Effect of GBE™ processing on the variation in (a) weight loss and (b) grid growth with polarization time in the PbCaSnAg alloy.
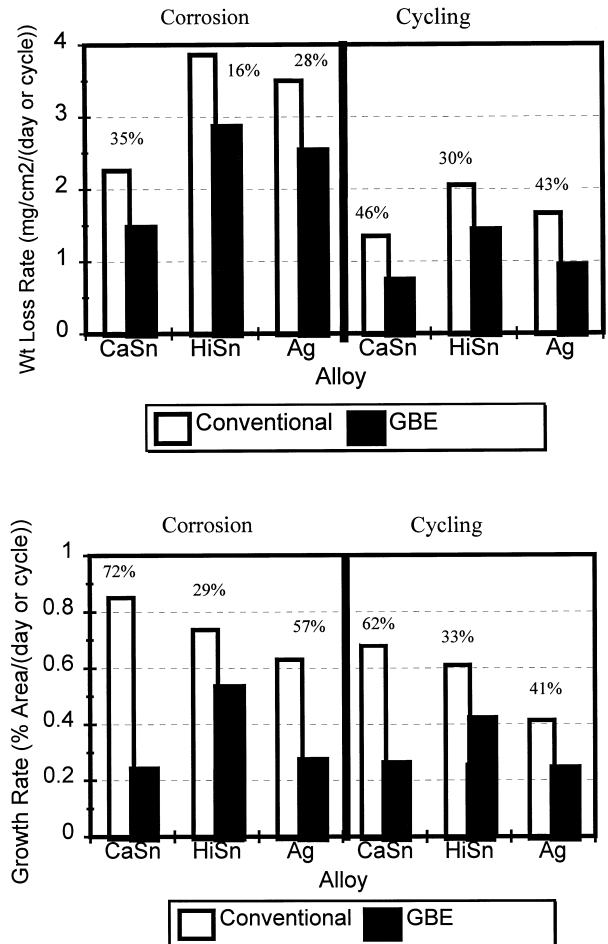
Fig. 4. Effect in increasing the frequency of special boundaries on grid resistance to weight loss and geometric area growth among the three PbCaSn alloys considered. Grid thicknesses are 0.59 mm (0.023″). [Test Conditions: 200 mV over-potential, 1.27 s.g. H_2SO_4 at 70°C. Note: Units of weight/growth for static and cycling tests are normalized against days and cycles, respectively].

Vehicle (EV) applications if lead-acid systems are to compete with emerging technologies that are currently more expensive and not as reliable (eg. NiMH, Zinc–Air) [16,17].

References

[1] A.J. Salkind, G. Mayer, Lead-acid batteries, in: H.B. Crawford et al. (Eds.), Handbook of Batteries and Fuel Cells, McGraw-Hill, New York, ISBN 0-07-037874, 1983, pp. 14–15.
[2] C.W. Haynes, R. Smoluchowski, Acta Met. 3 (1995) 130.
[3] G. Palumbo, U. Erb, K.T. Aust, Materials Science and Engineering A 185 (1994) 93.
[4] P. Lin, G. Palumbo, U. Erb, K.T. Aust, Scr. Met. 33 (1995) 1387.
[5] T. Watanabe, Res. Mechanica 11 (1984) 47.
[6] H. Kokawa, T. Watanabe, S. Karashima, Phil. Mag. A 44 (1981) 1239.
[7] G. Palumbo et al., Special properties of grain boundaries, in: D. Wolf, S. Yip (Eds.), Materials Interfaces, Chapman & Hall, 1992, p. 190.

[8] K.T. Aust, U. Erb, G. Palumbo, Interfacial structures and properties, Mechanical Properties and Deformation Behaviour of Materials Having Ultra-fine Microstructures, 1993, p. 107.

[9] B. Adams, S.I. Wright, K. Kunze, Metallurgical Transactions A 24A (1993) 819.

[10] E.M. Valeriote, J. Sklarchuk, M.S. Ho, Proceedings of the symposium on advances in lead-acid batteries, Electrochem. Soc. 84–14 (1984) 224–240.

[11] E.M. Valeriote, J. Electrochem. Soc. 128 (7) (1981) 1423.

[12] J. Sklarchuk, M.J. Dewar, E.M. Valeriote, A.M. Vincze, Journal of Power Sources 42 (1993) 47.

[13] E.M. Lehockey, G. Palumbo, P. Lin, A.M. Brennenstuhl, Metallurgical Transactions 29A (1998) 387.

[14] E.M. Lehockey, G. Palumbo, P. Lin, in: W.A.T. Clark et al. (Eds.), Proceedings of the D.A. Smith Symposium on Boundaries and Interfaces in Materials, TMS, September 14–18, 1997, Indianapolis IN.

[15] J.J. Lander, J. Electrochem. Soc. 98 (1968) 220.

[16] H. Bode, Lead acid batteries, Wiley-Interscience, New York, 1977, pp. 322–346.

[17] M.J. Riezenman, The search for better batteries, IEEE Spectrum, May, 1995.