

Corrosion Behaviour of Rapidly Solidified Lead-Aluminium Alloys for Battery Grids

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ABSTRACT

Rapidly solidified (RS) Pb-Al alloy in H_2SO_4 solution at room temperature ($30^\circ C$) was found to be more corrosion resistant to that of conventional Pb-Sb alloy. Polarization curves, for RS and as cast Pb-4Al, Pb-5Sb alloys and Pb, indicated that the critical and passive current densities were lowest in Pb-Al alloys. Further, RS alloy showed more corrosion resistant behaviour than all other alloys and metal under investigation. Oxygen evolution reaction potential was not affected by aluminium addition to the lead alloy.

INTRODUCTION

Lead grid alloys used in battery industry generally contain 6-12% antimony. Though the addition of antimony in this range leads to desirable mechanical and casting properties, it makes the alloys less corrosion resistant mostly due to overcharging and self-discharging¹⁻⁴. Under anodic attack of the grid, during overcharge, antimony can also pass into the solution, (in the +5 oxidation state), and be transferred to the negative grid, where it is reduced. The antimony ultimately deposited on the electrode surface and thus lowers the hydrogen evolution potential than lead. This process leads to gas evolution on the negative electrode with subsequent water loss and self-discharging of battery⁵⁻⁷. Attempts have been made either to reduce the level of Sb in the grid or to replace it completely. The most successful ones were, addition of calcium, tin, magnesium and aluminium⁸, which modified the electrochemical properties of the alloys.

The objective of the present work is to explore the effect of Al addition to lead, on the corrosion behaviour of Pb-Al alloys. The paper reports a comparative study on the corrodibility of commercial Pb, Pb-Sb and Pb-Al, as cast as well as RS alloys in sulphuric acid potentiodynamically. The metallographic and mechanical properties are also studied.

EXPERIMENTAL PROCEDURE

RS ribbons of Pb-4Al alloy were produced by melt spinning the cast ingots prepared by mechanical mixing. The ribbons were cut into small pieces and compacted in hydraulic press to produce compacts of 35 mm diameter. Metallographic examinations were carried out on the ribbons as well as on the mechanically mixed and RS, compacted samples. Mechanical properties were determined using Hounsefield Tensometer.

The working electrodes were prepared by cold mounting of 1 sq. cm. of alloys in acid resistant resin. The electrolyte used for polarization study was 10M H₂SO₄ and was prepared from Analar- grade reagent and double distilled water. All measurements were made at room temperature (30 ± 1°C) with respect to the Hg/ Hg. SO₄ reference electrode. The electrical contacts were made through copper rods from the back side of the mold by drilling and making threads into the mold. Before introduction to the electrolyte, the electrode surface was prepared by polishing on 0/0 to 4/0 grades emery papers, cleaned thoroughly on wet tissue paper and finally, rinsed with distilled water. Polarization experiments were performed using an E & G Princeton Applied Research Potentiostat/Galvanostat Model 273A. Two cylindrical graphite electrodes were used as counter electrode.

RESULTS AND DISCUSSION

Metallographic Examination

Figure 1 shows the optical micrographs of Pb-4Al alloys (a) as cast and (b) rapidly solidified ribbon. It may be noted that aluminium has a tendency to solidify in the form of globules due to surface tension in the pool of molten lead (Fig.1a). A single phase morphology is seen in figure 1b, which is due to the dissolution aluminium in the matrix. due to rapid cooling. SEM micro-photograph and EDAX of RS compacted pellet of Pb-4Al alloy reveals the distribution of aluminium particles embedded in lead matrix (Fig. 2).

Mechanical Properties

Tensile testing of Pb-4Al alloy, produced by mechanical mixing route, carried out by tensometer and values are summarized in Table-1. The values for Pb-5Sb are also given for comparative study.

Table-1 Mechanical properties of Pb-4Al and Pb-5Sb alloys

Alloy	UTS (Mpa)	% Elongation (25 mm/GL)	% Reduction in area
Pb-4Al	22	60	95
Pb-5Sb	44.8	Irregular values	94

The mechanical properties of Pb-4Al are comparable with conventional Pb-5Sb alloy. The fractography of tensile tested samples, which is not shown here, indicates the ductile nature of Pb-4Al alloy.

Potentiodynamic Polarization

Prior to polarization experiments, the working electrodes were cathodically pretreated at potential -1.6V for 30 minutes to remove any reducible species present on the surface. The polarization of the electrode was conducted in the potential range of -1.4 to 1.4V to cover passive and oxygen evolution range. Figure 3 shows the polarization curves for as cast and RS compacted Pb-4Al alloys in 10 M H₂SO₄ solution. It is noted from the figure that an activation-passivation reaction phenomenon is involved in both the alloys anode reaction. The extent of activation polarization does not depend on the process of alloy preparation as is seen by the critical current density (I_{crit}) for RS, 2.84 mA/cm² and for as cast alloy, 2.89 mA/cm². Further, passive current density (I_p) for RS as well as cast alloys is 0.05 mA/cm² and 0.22 mA/cm² respectively, which frames an idea that RS alloy is more corrosion resistant to that of as cast one. Transpassive region which is found to attain at about 1V is mainly due to the oxygen evolution reaction and formation of PbO₂ layer from PbSO₄ present on the surface^{2,7}.

The polarization plots for Pb, Pb-5Sb and RS Pb-4Al alloys in 10M H₂SO₄ solution are shown in figure 4. A significant role of rapid solidification was observed towards the passive film formation on the electrode surface. Though the passive region in all the cases is almost same, passive current density for RS compacted electrode was the lowest. The first active-passive transition, which is resulted around -1V, is due to sulphation reaction. In this region (-1.2 to E_c), the current increases due to the dissolution of Pb to Pb²⁺^{7,9} until a critical passivation potential(E_c) is attained where lead sulphate starts precipitating. PbSO₄ forms a passive film on the electrode surface and thus results in a rapid decrease in current density. A close look divides the polarization plots into three different regions. The first one is due to formation and deposition of lead sulphate around -1.1 to -1.0V; second region belongs to the formation of PbO underneath PbSO₄ layer which starts around -0.6V with slight increase in current density and third region is transpassive region at about 1V, where PbSO₄ is oxidized to a polymorphic PbO₂ film^{7,10,11}. Oxygen evolution occurred after the formation of PbO₂ on the surface.

Table-2

Open circuit potential (E_{oc}), critical current density (I_{crit}), passivation current density (I_p), critical passivation potential (E_c) and passivation potential (E_p) for lead and lead alloys in H₂SO₄.

Alloy	- E_{oc} (V)	I_{crit} (mA/cm ²)	- E_c (V)	I_p (mA/cm ²)	- E_p (V)
Pb	1.08	5.06	1.160	0.228	0.718
Pb-5 Sb	1.097	3.68	1.178	0.093	0.709
Pb-4Al	1.094	2.89	1.169	0.216	0.690
Pb-4Al (RS)	1.062	2.84	1.225	0/048	0.962

The electrochemical parameters recorded in H₂SO₄ solution are shown in Table-2. The open circuit potential (E_{oc}), observed in all the cases was quite stable and very close to the reversible potential of PbSO₄ formation. Lower critical (I_{crit}) and Passive (I_p) current densities for Pb-Al alloys indicates that the addition of aluminium provides better corrosion resistant property to the alloys. Further lowering in I_p

value of RS alloy by one order of magnitude to that of as cast one imparts best corrosion resistant property to the RS Pb-Al alloy.

CONCLUSIONS

1. Addition of aluminium, to replace antimony, improves the corrosion resistant behaviour, however, no much improvement is observed on mechanical properties.
2. Rapid solidification route makes the Pb-Al alloy more corrosion resistant further.
3. Oxygen evolution potential was found to be almost same in all the cases shows that the RS Pb-AL alloy can be used as grid material in the battery industry.

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