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Research on thin grid materials of lead-acid batteries

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Abstract: A detailed investigation on Pb-Ca-Sn alloys was made in order to choose suitable grid alloys materials for thin plate lead-acid batteries. The electrochemical performances of alloys were investigated by electrochemical corrosion experiment, scanning electron microscope (SEM), and cyclic voltammetry (CV) test. The results indicate that Pb-Ca-Sn-Bi-Cu alloys can be used to make the grids used for thin grid lead-acid batteries, the content of bismuth has primary effects on the corrosion resistance of grid alloys, the composition of alloys plays an important role on batteries performance, and appropriate scale of elements can be choosed to obtain optimal electrochemical performance. The lead-acid batteries using this kind of grid show good performance by cycle life test.

Key words: lead-acid batteries; grid; alloys; corrosion

1. Introduction

During the past 10 years, lead calcium based alloys have replaced lead antimony alloys as the materials of choice for positive grids of lead-acid batteries. To make high power thin grids has become an active research area, including thin grids used in spirally wound lead-acid batteries. Thin plate is the key technique to make this kind of batteries. Thin plate decides that batteries have good performances. To make thin grid is the previous job to produce thin plate. The thin grid should be prepared to 0.2 – 0.5 mm in thick. It is reported that grid has been prepared to be about 0.05 – 0.08 mm in thickness[1]. For this kind of grids it should be made sure that they should have good corrosion-resistance, and then its electrochemical performance should satisfy the demand of batteries. Rolling method is also used to prepare this kind of grids. How to choose suitable grid materials is the key factor.

Grids based Pb-Ca-Sn alloys have been used widely as a kind of good performance grid materials [2-4]. In this article, the electrochemical performance of Pb-Ca-Sn alloys was investigated. Bismuth and copper as the additive also were used. Grid performance test for different alloys was made, which indicates that they were different obviously.

2. Experimental

2.1. Composition of alloys

Alloy A: Pb-0.075%Ca-1.2%Sn; Alloy B: Pb-0.075% Ca-1.2%-Sn-1.5x% Bi-1.0y%Cu; Alloy C: Pb-0.05%Ca-0.9%Sn-1.5x%Bi-1.0y%Cu; Alloy D: Pb-0.05%Ca-0.9%Sn-1.0x%Bi-0.75y%Cu (x, y: molar ratio coefficients of the additive elements, $0.01 < x < 0.08$, $0.1 < y < 0.8$).

2.2. Corrosion experimental

Alloys should be casted according to the composition. Corrosion experimental samples is Φ 5.75 mm, longer than 35 mm. Samples should be polished to be velvet, and weighed

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exactly. Large area of pure lead was used as negative plate, and electrolyte is 1.28 $g \cdot cm^{-3}$ sulfuric acid solution. Samples were immerged in electrolyte solution about 35 mm with the current density for 8.13 $mA \cdot cm^{-2}$. Afterwards, corrosion samples were taken out, and then boiled in sugar-alkali solution (160 g NaOH + 20 g sucrose + 1000 ml distilled water). Removing corrosion product on the surface, and cleanout, drying, weigh up. Corrosion-resistant performance can be investigated by calculating the mass difference before corrosion experimental and after.

2.3. Metallography experimental

Samples should be incised into small pieces. Although some polishing was done automatically, it was found that the best results were achieved by hand. First a file was used to rub alloys pieces, and then polished by metallography sand paper for 600, 800, 1200, 2000 grit. Then immerge into corrosion solution (70% acetic acid + 30% H_2O_2: for volume) for about several seconds. After that, metallography samples was examined using an S-4700 SEM made by HITACHI company in Japan.

2.4. CV test

All the samples were prepared like those used in corrosion experimental. All the sides of samples were stabilized by encapsulation in resin, rotundity surface was polished by metallography sand paper. Electrolyte was 1.28 $g \cdot cm^{-3}$ sulfuric acid, reference electrode was Hg/Hg_2SO_4 (electrolyte is 1.28 $g \cdot cm^{-3}$ H_2SO_4), Large area of pure lead was used as the counter electrode. CV test was examined using CHI630 electrochemical analysis apparatus made in SHANGHAI CHENNENG of China. The range of scan was 1.0 – 1.6 V with 1 $mV \cdot s^{-1}$ as a scan rate.

2.5. Preparation of grids and battery

Alloy ingot was casted according to the composition. Alloys was rolled to lead foil with the thickness of 0.2 mm, then cut it out to anticipant shape, and made holes symmetrically, therefore grid was prepared. After the procedure of paste mixing, assemblage, curing, drying, formation, lead-acid batteries of thin plate were produced[5]. The thickness of the plate is about 0.8 mm.

2.6. Test of cell performance

In this step, BTS-5V/10A high precision cell test system was used. The apparatus was made by NEWARE company in SHENZHEN of China. High-rate discharge test was examined by Arbin Instruments (5 V/200 A) made in USA.

3. Results and discussion

3.1. Comparative of corrosion resistance performance

Table 1 is the results of corrosion experimental, which shows that the result is different with different composition of alloys. Pb-Ca-Sn based alloys with Bi and Cu adding is more corrosion-resistant than Pb-Ca-Sn alloy itself. This conclusion will be proved in metallography experimental. The corrosion resistance decreases for the four alloys in the order of D > A > C > B.

Table 1. Results of corrosion experiments

Number of alloys	A	B	C	D
Corrosion rate/ ($mg \cdot A^{-1} \cdot h^{-1}$)	21.74	25.28	21.90	14.68

3.2. Analysis of metallography experimental

The results of SEM test for this four alloys are illustrated by Fig. 1. In Figs. 1(a) and (d), the crystal particle is symmetrical without presence of secondary phase. But there is some acerate material in Figs. 1(b) and (c), and square-typed material exists in Fig. 1(c). Due to the presence of the secondary phase, the corrosion resistance of the alloys will be decreased, so alloy B and C can be easily corroded in electrolyte.

In this experimental, EDS was used in order to determine the composition of the second-