Journal of Alloys and Compounds 475 (2009) 102–109

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Study on the structure and property of lead tellurium alloy as the positive grid of lead-acid batteries

W.X. Guo[a], D. Shu[a,*], H.Y. Chen[a], A.J. Li[a], H. Wang[b], G.M. Xiao[b], C.L. Dou[b], S.G. Peng[b], W.W. Wei[b], W. Zhang[b], H.W. Zhou[b], S. Chen[b]

[a] *School of Chemistry and Environment, Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, South China Normal University, Guangzhou, Guangdong 510006, China*

[b] *Zhuzhou Smelter Group Co., Ltd., Zhuzhou Hunan 412004, China*

ARTICLE INFO

Article history:
Received 28 May 2008
Accepted 4 August 2008
Available online 24 September 2008

Keywords:
Lead alloy
Grid alloy
Smelting
Lead-acid batteries

ABSTRACT

A series of novel Pb–Te binary alloys with different contents of tellurium (0.01–1.0 wt.%) were investigated as the positive grid of a lead acid battery. The microstructure of Pb–Te alloys was observed using a polarizing microscope. The morphology of the corrosion layers and corroded surfaces of Pb and Pb–Te alloy electrodes were analyzed by scanning electron microscopy (SEM) following the corrosion test. The electrochemical properties of Pb–Te alloys and Pb–Te–Sn alloy in sulfuric acid solution were investigated by cyclic voltammetry (CV), open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), alternating current voltammetry (ACV), and linear sweeping voltammetry (LSV). The results indicate that the introduction of tellurium results in grain refinement, increased corrosion resistance, and an accelerated oxygen evolution reaction for the Pb–Te binary alloys. The passive films formed on Pb–Te–Sn alloy shows improved performances in comparison to those on Pb–Ca–Sn alloy.

1. Introduction

Nowadays, the major grid material for lead acid batteries is the lead–calcium–tin (Pb–Ca–Sn) alloy. This alloy is especially suitable for the maintenance-free lead-acid battery, because it leads to lower water consumption from the electrolyte. However, an undesirable characteristic is that the Pb–Ca–Sn alloy may suffer deterioration due to severe corrosion at high temperatures [1]. Furthermore, it is easy to form a high impedance passive film composed of Pb(II) oxide between the positive grid and the active materials under deep charge–discharge conditions. As a result, new additives have been sought for introduction to the grid alloys to improve their performance. Rare earths such as Sm and Ce, regarded as effective additives, can inhibit the corrosion of the alloy and decrease the resistance of the anodic Pb(II) oxide film [2,3]. The addition of Ag to a Pb–Ca–Sn alloy can enhance its corrosion resistance, and increase the creep resistance, thereby improving battery durability at high temperatures [4]. It is reported that the addition of tellurium to lead can improve its durability, mechanical strength, and anti-corrosive ability. As an appropriate component for the lead grid alloy, tellurium has been reported by Bashtavelova and Winsel [5], but no further detailed report has been published regarding its modified mechanism under operation condition. The structure and property of Pb–Te binary alloys with various contents of tellurium (0.01–1.0 wt.%) were investigated in detail in this paper. In addition, the characteristics of the passive film formed on the surface of a Pb–Te–Sn alloy in sulfuric solution were investigated.

2. Experimental

2.1. Preparation of the testing alloys

Pb–Te binary alloys with different contents of tellurium were processed by melting the mixtures of pure lead (99.99 wt.%) and pure tellurium (99.99 wt.%) in an electrical furnace under an argon gas atmosphere at 800 K for 15 min, cooling down to room temperature, and served as working electrodes. Pb–Te alloy as the master alloy was mixed with Sn (99.9 wt.%) to form the homogeneous Pb–Te–Sn alloy. Another testing alloy was the traditional Pb–Ca–Sn alloy, which was manufactured by doping the Pb–Ca master alloy with Sn. The sample alloys were cast in a steel mould in two designs: one was a rod with diameter 8.0 mm and length 16 mm, which was used for the electrochemical experiments; the other was a rectangular plate with dimensions 20 mm × 20 mm × 2 mm for use in the corrosion test. The composition of each alloy is listed in Table 1.

2.2. Microstructure

The metallographic samples were prepared from the rod alloys, one end of which was mechanically polished by 1000# and 2000# SiC emery papers. These samples were then chemically polished using a 1:1 (by volume) acetic acid/hydrogen peroxide solution, and etched with a solution containing 9 g of ammonium molybdate, and 15 g of citric acid in 90 g of distilled water. The structure of the alloys was observed using a Nikon LV-UEPT polarizing microscope.

---

* Corresponding author. Tel.: +86 20 39310212; fax: +86 20 39310187.
E-mail address: dshu@scnu.edu.cn (D. Shu).

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.08.011

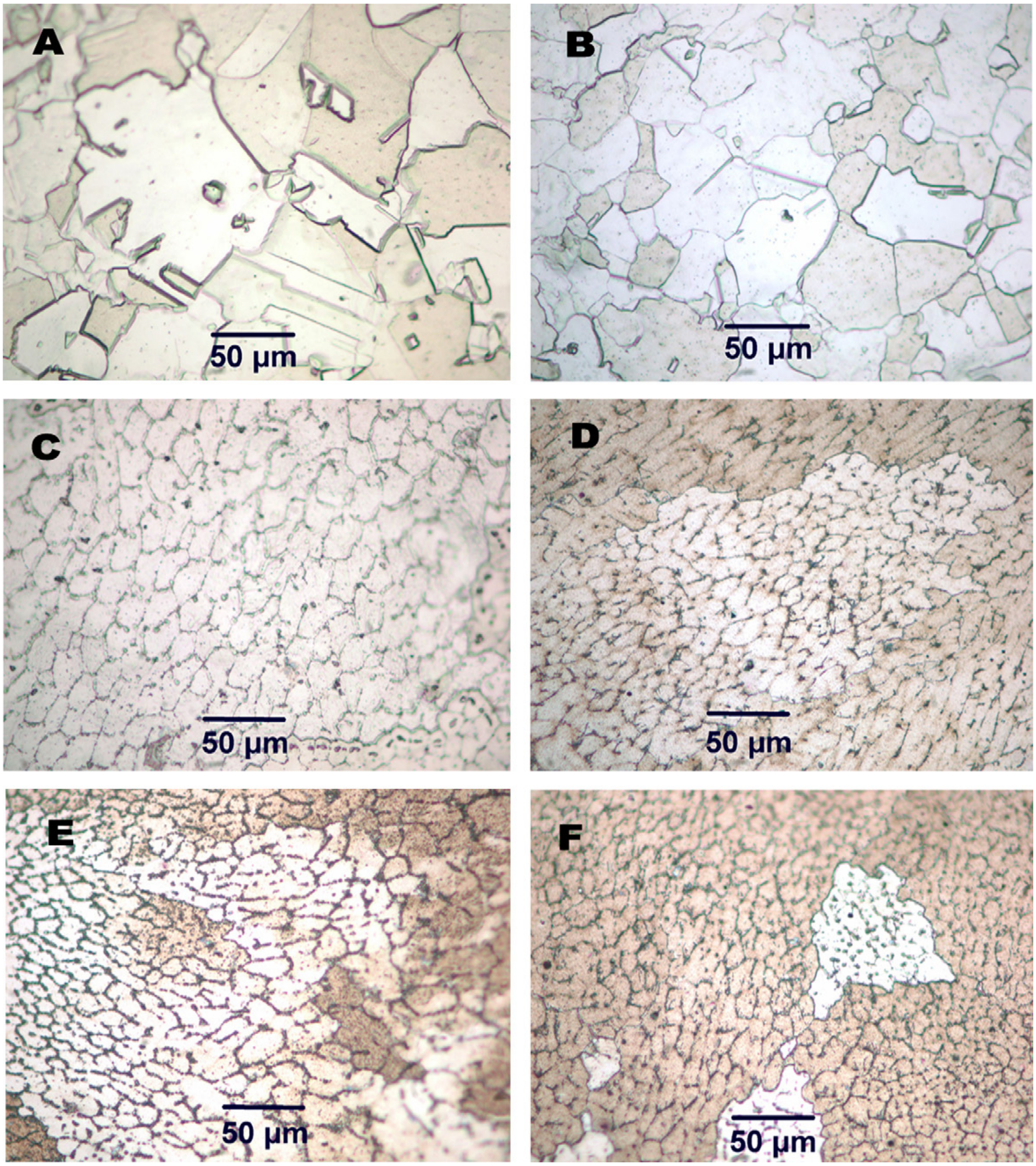

Fig. 1. Micrographs of Pb and Pb–Te alloys with different Te contents. (A) Pb; (B) Pb–0.01 wt.%Te; (C) Pb–0.03 wt.%Te; (D) Pb–0.1 wt.%Te; (E) Pb–0.3 wt.%Te; (F) Pb–1.0 wt.%Te.

2.3. *Electrochemical experiments*

A three-electrode configuration was used for the electrochemical experiments. The working electrode was a rod of lead alloy sealed in epoxy resin except for the working surface, which was one end of the rod; the other end was welded with a copper wire to connect the instrument. The counter electrode was a platinum plate (0.5 cm^2). The reference electrode was a Hg/Hg_2SO_4 electrode: all potentials reported in this paper were referred to this electrode. The electrolyte was 1.28 g cm^{-3} H_2SO_4 solution prepared from H_2SO_4 and double-distilled water. Before each test, the working electrodes were mechanically polished by 1000# and 2000# SiC emery papers, then washed with double-distilled water, and a cathodic potential of −1.2 V was applied for 10 min in order to eliminate the oxide formed during pretreatment. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), alternating current voltammetry (ACV), and linear sweeping voltammetry (LSV) measurement were performed using a PGSTAT30 (Autolab, Eco Echemie B.V. Company).

Table 1
Composition of the testing alloys

Alloys	Contents of the additives (wt.%)		
	Te	Ca	Sn
1# Pb	–	–	–
2# Pb–Te	0.01	–	–
3# Pb–Te	0.03	–	–
4# Pb–Te	0.10	–	–
5# Pb–Te	0.30	–	–
6# Pb–Te	1.00	–	–
7# Pb–Te–Sn	0.03	–	0.90
8# Pb–Ca–Sn	–	0.08	0.90

2.4. *Corrosion test*

Corrosion test was conducted in five cells in series connection. Each cell was assembled with two positive plate electrodes and two negative plate electrodes. The negative electrodes were pure lead plates, and the positive electrodes were Pb–Te plates. The corrosion test was carried out with a constant current of 10 mA cm^{-2} at a constant temperature of 60 °C for 20 days. The corrosion layer of one corroded elec-