Journal of Power Sources, *31* (1990) 169 - 175

EFFECT OF SOME ELEMENTS ON THE PERFORMANCE OF LEAD–ANTIMONY ALLOYS FOR LEAD/ACID BATTERIES

ZHIYUN JIANG,* YUANDUO LU, SHUZHEN ZHAO, WEIQING GU and ZHONGHUA ZHANG

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin 130022 (China)

Introduction

Low-antimony–lead alloy has been generally used as a grid material for lead/acid batteries. In recent times, the antimony level has been reduced from the original value of ~11 wt.% to as low as 1.8 - 2.5 wt.%. In order to compensate for the loss in the mechanical properties and castability that accompany this decrease in antimony content, arsenic and other grain-refining agents are added to the lead-based alloys. A direct consequence of this approach is a remarkable improvement in the overall performance of the lead/acid batteries. Many attempts have been made [1 - 3] to elucidate the role of antimony, arsenic and other grain-refining agents, but a complete understanding has yet to be achieved. Thus, it is essential to gather further knowledge of the characteristics of battery-grid alloys, particularly with regard to the effect of the additives.

This paper reports the results of studies of a series of Pb–Sb alloys containing different additives using metallography, electron-beam microprobe analysis, cyclic voltammetry, corrosive weight-loss, and mechanical measurements. In particular, attention is drawn to the influence of antimony, silver, arsenic, copper and sulphur additives on corrosion resistance, mechanical properties, electrochemical behaviour, and the distribution of antimony-rich inter-crystalline phases in the alloys.

Experimental

An HDV-7 potentiostat and an XFD-8 function generator (both made in China) were used in the electrochemical experiments. The test electrode was constructed from a Pb–Sb alloy rod fixed in a Teflon tube. The apparent surface area of the test electrode was about 0.2 cm^2. The reference electrode was Hg/Hg_2SO_4. Sulphuric acid solution of sp. gr. = 1.28 (25 °C) was used as the electrolyte solution. In order to obtain relatively stable cyclic voltammograms, the test electrode was subjected to preliminary anodic polarization

---

*Author to whom correspondence should be addressed.

0378-7753/90/$3.50

at a constant current of 5 mA cm^{-2} for 15 min. The potential was then scanned between 1.6 V and -1.3 V at 30 mV s^{-1} for 10 cycles and the cyclic voltammogram recorded.

The metallography of the Pb–Sb alloy samples was examined after electropolishing the alloys in an alcoholic solution of perchlorate. The pretreatment of the metallographic analysis of the samples after the corrosion test was different. In that case, the samples were alternately polarized with anodic and cathodic currents for 360 h at 30 °C, and then boiled in a mixed solution of NaOH and sugar to remove surface oxides.

Electron microprobe analysis was conducted with an Hitachi HHS-2x scanning electron microscope. For the mechanical measurements, an LJ-500 pull test machine and a 71 type microsclerometer (both made in China) were used. The other experimental conditions are described elsewhere [4].

Results and discussion

Figure 1 shows metallographs for pure lead and lead alloys. The white regions in Fig. 1(d) - (h) are the α-phase of Pb–Sb alloys and the dark regions represent a mixture of α- and β-phases. The latter was considered to be an antimony-rich inter-crystalline phase. Figure 2 shows the two-dimensional distribution of antimony and arsenic, as determined by the electron microscope. The white regions in Fig. 2(a) - (g) represent the enrichment of antimony in crystal boundaries. These correspond well with the dark regions of the metallographs. For the Pb–11.2wt.%Sb alloy, the crystal boundary no longer exists and the β-phase disperses in a continuous matrix of α-phase.

Cyclic voltammograms of lead alloys with different amounts of antimony were compared. It was found that the quantity of electricity associated with the reduction peak of PbO_2 at $\sim$1.1 V was around 310 mC cm^{-2} when the antimony content was below 11.2 wt.%, and markedly decreased if the antimony content was above this amount (Table 1). For example, the reduction peak of PbO_2 for a Pb–20wt.%Sb alloy almost disappears (Fig. 3). Furthermore, the reduction peaks of divalent lead at about -900 mV (Fig. 3) indicate that large amounts of divalent lead exist on the electrode surface. This suggests that the divalent lead remains unoxidized, even at potentials more positive than that for evolution of oxygen. This phenomenon is probably due to the formation of a complex between lead and antimony oxides on the electrode surface, as reported by Tamura [5]. The fact that the interval between the peak potentials for the reduction of divalent lead on Pb–20wt.%Sb and Pb–7wt.%Sb alloys is about 100 mV provides further evidence for the formation of such a complex on the Pb–20wt.%Sb alloy.

It is well known that the cause of the corrosion of Pb–Sb alloys is the selective dissolution of the antimony-rich inter-crystalline phase [6]. As mentioned above, the crystal boundary in lead alloys with low antimony contents, such as Pb–3.5wt.%Sb, has a high concentration of antimony and is called an antimony-rich inter-crystalline phase. In addition, it is difficult to

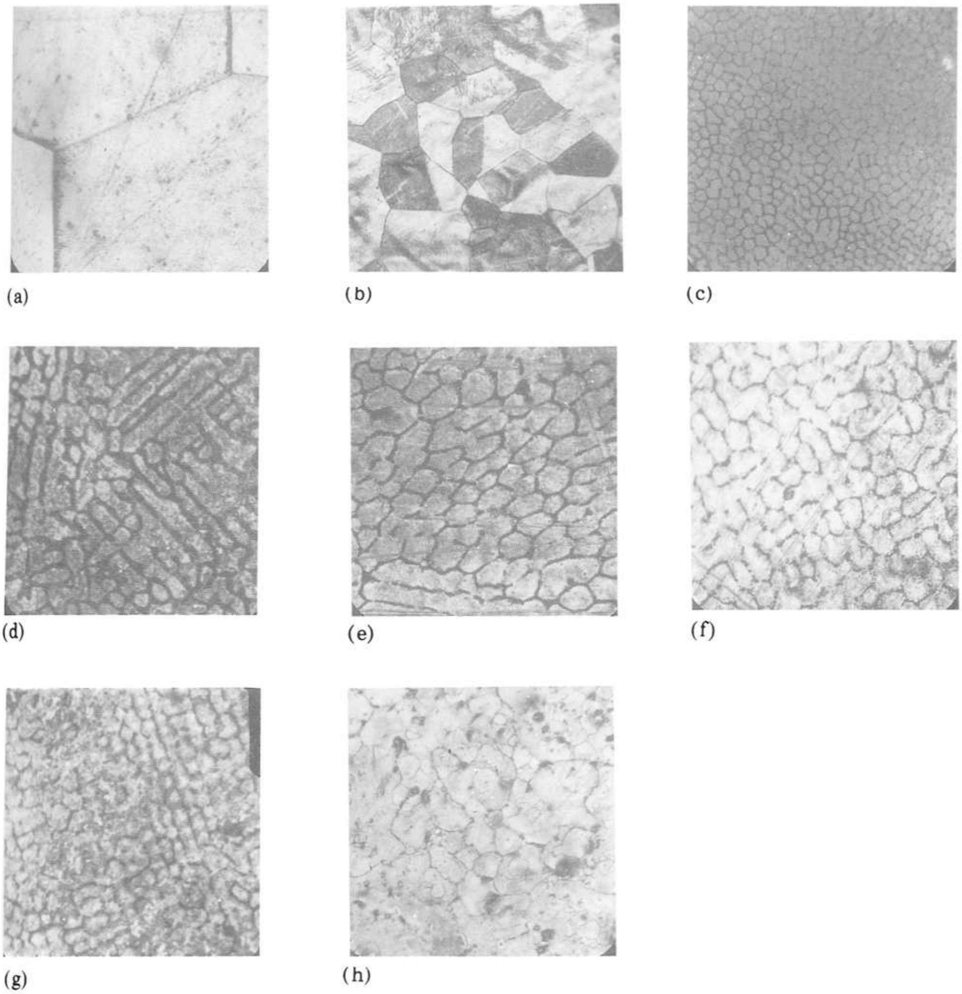

Fig. 1. Metallographs of lead alloys (× 200). (a) Pb; (b) Pb–0.15wt.%As; (c) Pb–0.05wt.%Cu; (d) Pb–7wt.%Sb; (e) Pb–3.5wt.%Sb; (f) Pb–3.5wt.%Sb–0.15wt.%As; (g) Pb–3.5wt.%Sb–0.15wt.%As*; (h) Pb–1.8wt.%Sb–0.18wt.%As*. *Contains grain-refining agents.

oxidize the divalent lead when the antimony content is high. Thus, it is suggested that the corrosion of the antimony-rich inter-crystalline phase is mainly due to the dissolution of divalent lead.

The effect of antimony content on the corrosive weight-loss, the evolution current of hydrogen, the tensile strength, and the hardness was also studied. The data are listed in Table 1. It can be clearly seen that the corrosive weight-loss increases with increasing antimony content. According to the above analysis of the corrosion mechanism, this tendency is related to an increase in the antimony-rich inter-crystalline phase with increasing antimony content (Fig. 1).

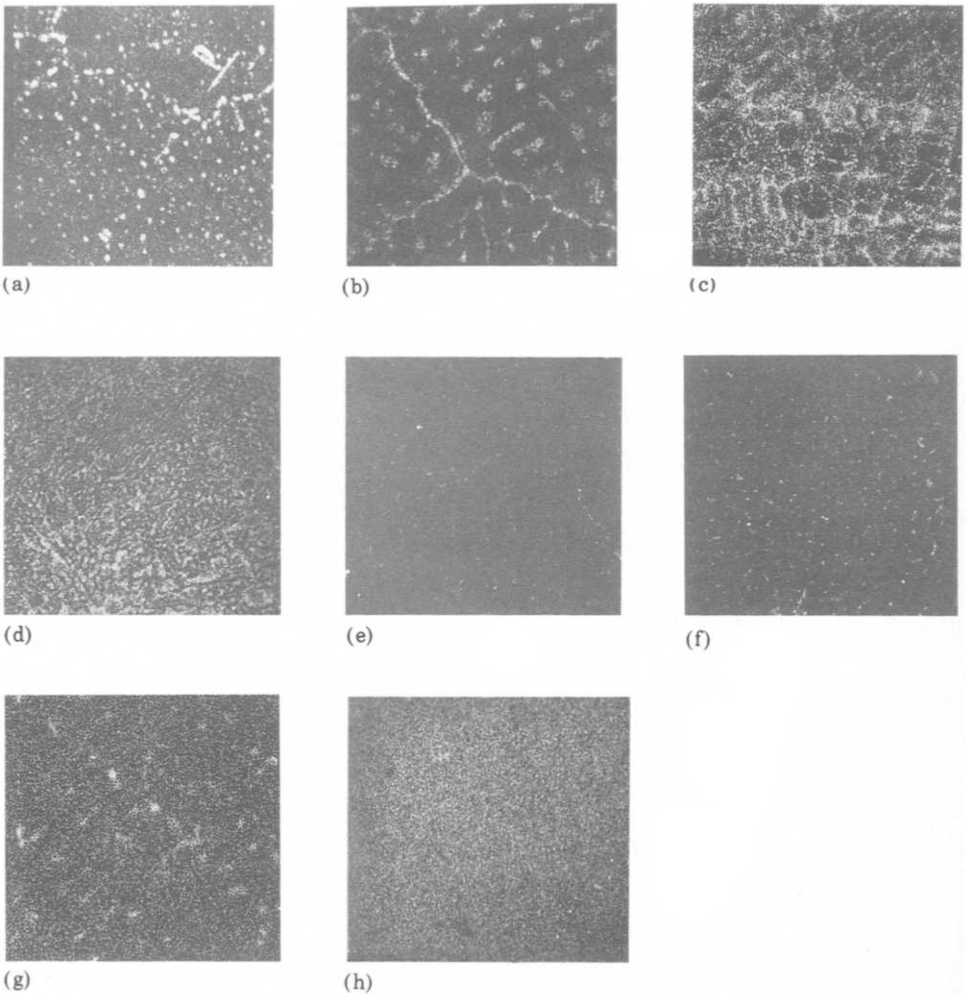

Fig. 2. Electron beam microprobe photographs of distribution of antimony and arsenic (a) - (g) antimony; (h) arsenic. Magnification (g) ×500; remainder ×350. (a) Pb–2wt.%Sb; (b) Pb–3.5wt.%Sb; (c) Pb–7wt.%Sb; (d) Pb–11.2wt.%Sb; (e) Pb–3.5wt.%Sb–0.15wt.%As; (f) Pb–3.5wt.%Sb–0.15wt.%As–0.13wt.%Ag; (g) Pb–1.8wt.%Sb–0.18wt.%As*; (h) Pb–3.5wt.%Sb–0.15wt.%As. *Contains grain-refining agents.

It can be seen from Table 1 that although the tensile strength and hardness of the Pb–7wt.%Sb alloy is suitable for the electrode grid of a lead/acid battery, the low hydrogen overvoltage and the unsatisfied corrosion resistance must be improved. If with decrease in the antimony content the crystal boundary becomes narrow (Fig. 1(d) - (e) and Fig. 2(b), (c)), then the corrosion performance can be improved and the hydrogen overvoltage can be raised (Table 1). On the other hand, the temperature range of solidification becomes wide so that when the alloy is cooled rapidly both cracking and

TABLE 1

Effect of antimony content on performance of Pb–Sb alloys[a]

Antimony content (%)	Corrosive weight loss (mg cm^{-2} per day)	Hydrogen evolution current at −1.30 V (mA cm^{-2})	Quantity of electricity (C cm^{-2})	Tensile strength (kg mm^{-2})	Hardness (3 days after casting) (kg mm^{-2})
0	0.88	10.1	303	1.26	6.8
1	0.95	16.5	316		
3.5	1.78	31.5	355	3.4	10.5
7.0	2.23	61.4	309	4.8	13.3
15.0		102	198		
20.0	6.74	133	30		

[a] From cyclic voltammograms.

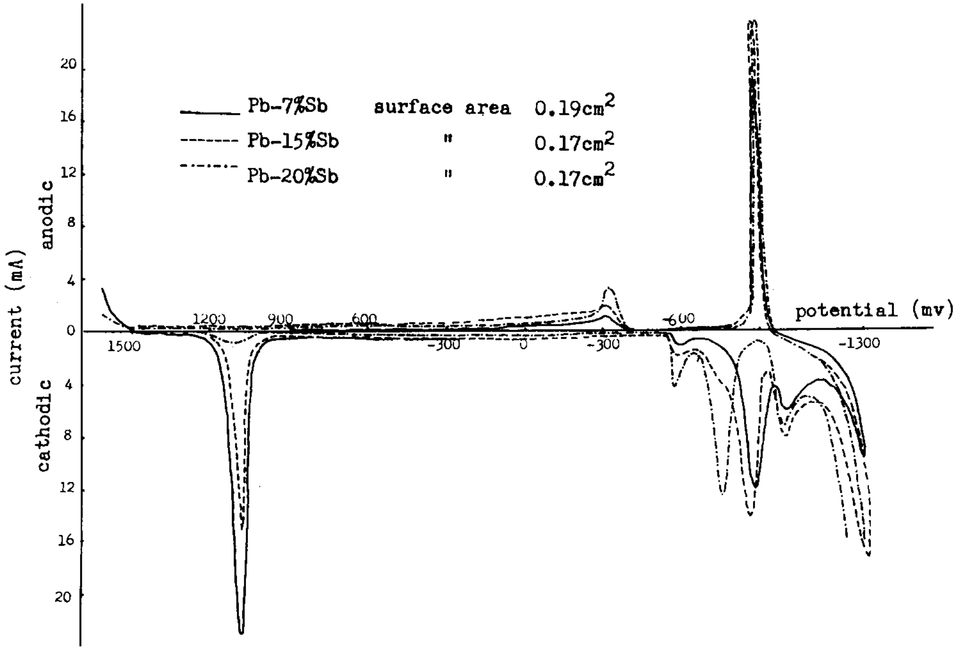

Fig. 3. Cyclic voltammograms for antimonial lead at 25 °C.

porosity development readily occur. The mechanical properties are also not conducive to casting and it is therefore necessary to add other elements to overcome the problems.

Arsenic can play an important role in improving certain properties of Pb–Sb alloys. Addition of 0.15 wt.% As can refine the lead crystal grains (Fig. 1(a), (b), (e), (f)), narrow the antimony-rich phase (Fig. 2(b), (e)), and increase the hardness of the alloys (Table 2). Arsenic itself is well distributed in the alloys (Fig. 2(h)). Lead–3.5wt.%Sb–0.15%As alloy is, however, still difficult to cast.

The addition of a small amount of silver to Pb–Sb alloys can reduce the corrosive weight-loss (Table 2) and produce a good distribution of antimony in the alloys (Fig. 2(f)). The results of metallographic analysis of the Pb–Sb alloy samples after the corrosion tests indicate that the phenomenon of inter-crystalline corrosion is not present. This finding is consistent with the corrosion mechanism involving the selective dissolution of the crystal boundary.

Figure 1(g) shows a metallograph of Pb–3.5wt.%Sb–0.15wt.%As alloy with small amounts of copper, tin and sulphur. The crystal grains in this alloy are finer and more spherical than those in the alloy without these additives. These differences may be responsible for the improvement in both the mechanical properties and the castability of the alloy with the additives.

Although the fluidity of Pb–2.75wt.%Sb or Pb–1.8wt.%Sb alloys is inferior to that of a Pb–3.5wt.%Sb alloy, and thus cracking and porosity often occur during casting, experimental results demonstrated that after adding small amounts of grain-refining agents (such as copper, tin, and sulphur) and selecting the proper processing conditions, satisfactory castability, tensile strength and hardness for Pb–2.75wt.%Sb and Pb–1.8wt.%Sb alloys can be obtained (Table 2). The antimony-rich inter-crystalline phase in Pb–1.8wt.%Sb is obviously narrow, the antimony is well distributed in the alloy, and the corrosive weight loss is less than that for the Pb–3.5wt.%Sb alloy.

Tests with lead/acid batteries showed that Pb–1.8wt.%Sb and Pb–2.75wt.%Sb alloys when combined with a proper amount of grain-refining agents are suitable materials for the positive grids of maintenance-free and deep-cycling lead/acid batteries.

TABLE 2

Effects of some elements on performance of low-antimony lead alloys

Alloy composition (%)					Corrosive weight loss (mg cm^{-2} per day)	Tensile strength (kg mm^{-2})	Hardness (3 days after casting) (kg mm^{-2})
Sb	As	Ag	Sn	Al			
3.5					1.78	3.4	10.8
3.5	0.15				1.96	3.5	13.1
3.5[a]	0.15				1.78	4.3	12.1
3.5	0.15	0.05	0.02		1.10	4.4	11.9
3.5	0.15	0.05	0.02	0.05	1.34	4.8	13.4
3.5	0.15	0.10	0.02	0.05	0.88	4.7	12.6
2.75[a]	0.15				1.63	3.5	12.9
1.8[a]	0.18				1.36 - 1.46	3.7	12.5

[a]Containing grain-refining agents.

References

1 N. A. Hampson and S. Kelly, *J. Appl. Electrochem.*, *10* (1980) 597.
2 E. Hameenoja and N. A. Hampson, *J. Appl. Electrochem.*, *14* (1984) 449.
3 A. Boggio, M. Maja and N. Perazzi, *J. Power Sources*, *9* (1983) 221.
4 Zhiyun Jiang and Suxian Xu, *Acta Chim. Sin.*, *44* (1986) 647.
5 F. Arifuku, H. Yoneyama and H. Tamura, *J. Appl. Electrochem.*, *11* (1981) 357.
6 G. W. Mao and P. Rao, *Br. Corros. J.*, *6* (1971) 122.