Journal of Power Sources, *31* (1990) 163 - 168

A NEW LEAD–CALCIUM ALLOY FOR MAINTENANCE-FREE LEAD/ACID BATTERIES

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Introduction

Lead–calcium alloys are widely used for the grids of lead/acid battery plates. New types of low-maintenance or maintenance-free lead/acid batteries are usually composed of lead–calcium negative grids and low-antimony–lead positive grids [1]. Calcium-based alloys are, however, difficult to prepare and cast into electrode grids because the calcium is subject to a 'burning loss' during smelting or casting. Efforts have been made to improve its processibility and mechanical properties by adding other elements [2, 3]. In the authors' laboratory, special protective measures are adopted to maintain the calcium content; tin and aluminium are also added to the alloy. The resulting Pb–Ca–Sn–Al alloy has a very high hydrogen overvoltage and enhanced mechanical properties [4]. For further improvement, a fifth element — sodium — has been introduced into the alloy. The new alloy has very good casting performance, relatively high hydrogen overvoltage, and very good mechanical properties.

Experimental

Lead–calcium master alloy, tin, aluminium and sodium were added to molten lead, in a given ratio and order, at a set temperature and under special protection. The melt was uniformly mixed by stirring and cast into electrode rods (4 mm dia.) and mechanical test specimens.

The mechanical properties of the alloys (*i.e.*, tensile strength, tensile elongation at break, Vickers microhardness) were measured using standard procedures [4].

Morphological observations and energy dispersive X-ray analysis (EDXA) were carried out with a JEOL JXA-840 electron microscope. Before examination, the alloy samples were electrolytically polished in an ethanol solution of $HClO_4$ (ethanol:$HClO_4$ = 5:1).

Cyclic voltammograms were recorded using a cell consisting of a test electrode (alloy rod in Teflon tube), a counter electrode (platinum foil), and

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0378-7753/90/$3.50

a reference electrode (Hg/Hg_2SO_4). The electrolyte was a solution of sulphuric acid (sp. gr. = 1.285). The cell was de-oxygenated by bubbling pure nitrogen for 40 min. In order to obtain a stable cyclic voltammogram, the alloy electrode was anodically polarized at 5 mA cm^{-2} for 15 min and then scanned between −700 and −1300 mV at a rate of 20 mV s^{-1} for about 20 cycles.

Results and discussion

Mechanical properties

Elemental compositions and mechanical properties of the Pb–Ca alloys are listed in Table 1. The data indicate clearly that the addition of sodium affects the tensile strength, hardness and elongation. The tensile elongation increases with sodium content, whereas the tensile strength and hardness exhibit maxima near a sodium content of 0.043 - 0.077 wt.%. Obviously, excessive sodium results in a decrease in both the strength and hardness of the alloys.

Scanning electron microscopy (SEM)

Figure 1 shows electron micrographs of alloys with different sodium contents. It is noticeable that incorporation of the proper amount of sodium (*i.e.*, 0.043 - 0.077 wt.%) results in smaller crystal grains and narrower and more winding inter-crystalline boundaries (*cf.* Fig. 1(b) and (c) with (a)). When the sodium content is above 0.1 wt.%, larger crystal grains and thicker boundaries are observed (Fig. 1(d)). When the sodium content reaches 0.23 wt.%, the crystal grains are very coarse and the boundaries are broad (Fig. 1(e)), features that are found with pure lead [5].

Electron microanalysis

Figure 2 presents an EDXA study of the two-dimensional distribution of sodium in the alloys. It can be seen that the element is uniformly distributed

TABLE 1

Effect of sodium on the mechanical properties of Pb–Ca alloys

Alloy composition (wt.%)				Tensile strength (MPa)	Vickers micro-hardness (MPa)	Tensile elongation (%)
Ca	Sn	Al	Na			
0.10	0.3	0.05	0	25.5	86.2	11.1
0.13	0.3	0.05	0.034	28.7	99.1	15.0
0.14	0.3	0.05	0.043	29.5	107.7	21.7
0.12	0.3	0.05	0.077	29.6	118.6	26.9
0.13	0.3	0.05	0.12	29.3	87.2	28.9
0.09	0.3	0.05	0.23	25.6	84.4	30.0

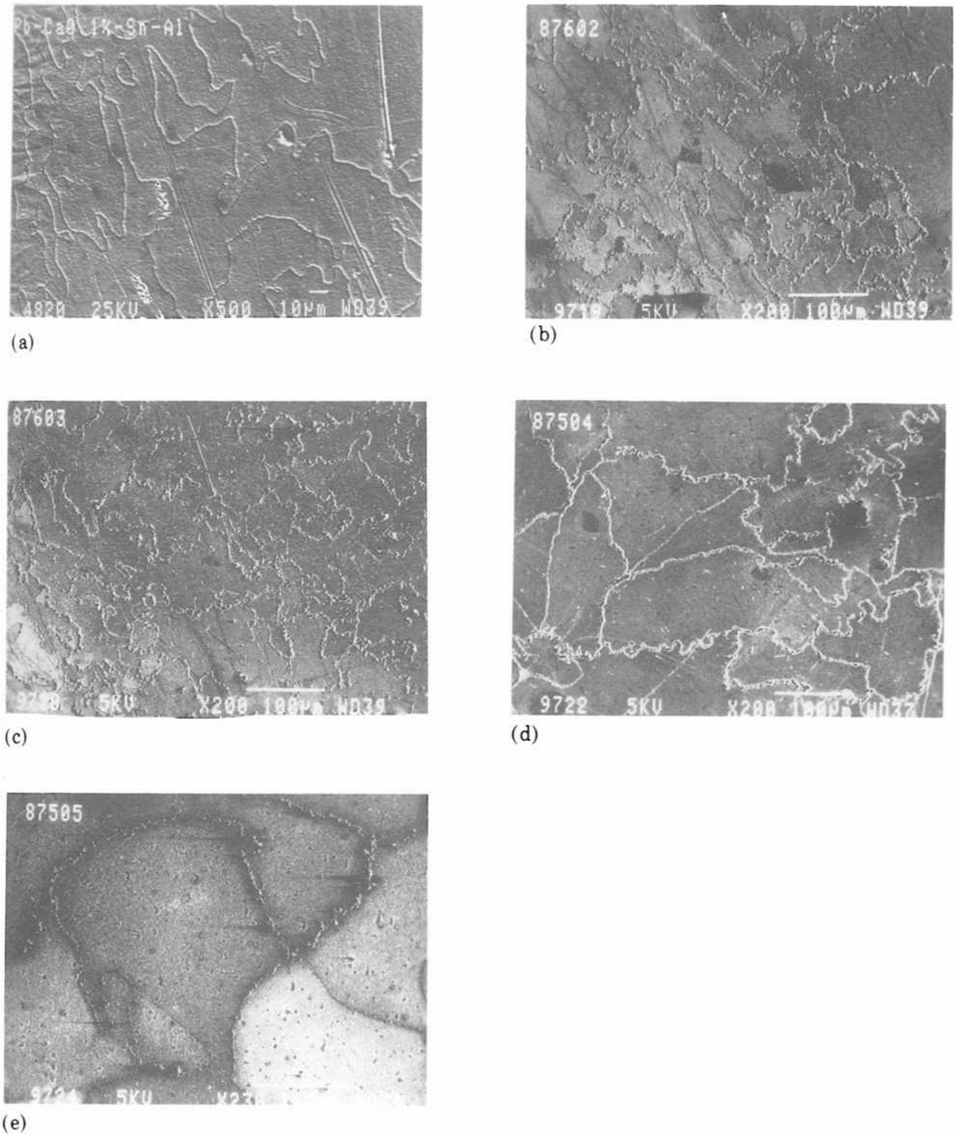

Fig. 1. Electron micrographs of Pb–Ca alloys containing different sodium contents: (a) Pb–0.1wt.%Ca–Sn–Al; (b) Pb–0.14wt.%Ca–Sn–Al–0.043wt.%Na; (c) Pb–0.12wt.%Ca–Sn–Al–0.077wt.%Na; (d) Pb–0.13wt.%Ca–Sn–Al–0.12wt.%Na; (e) Pb–0.09wt.%Ca–Sn–Al–0.23wt.%Na.

when present at 0.01 and 0.05 wt.%. At contents above 0.1 wt.%, enrichment of sodium in the inter-crystalline boundaries is observed. These results reveal the role of sodium in the alloys. Addition of the correct amount of sodium results in fine crystal grains, and narrow and winding crystalline boundaries. These structural changes are responsible for the observed improvement in

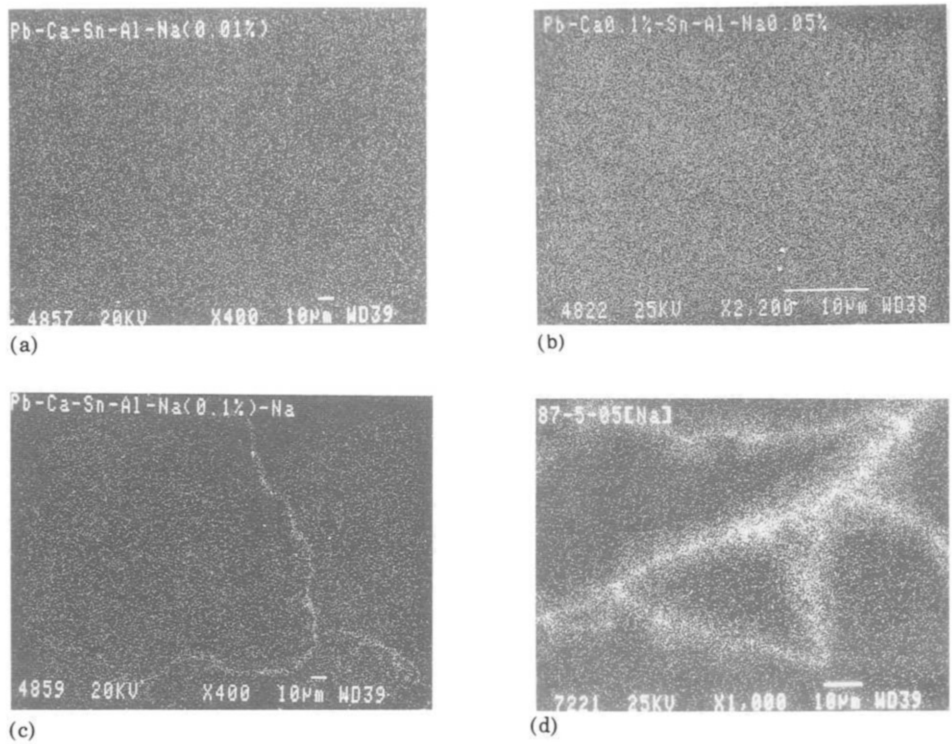

Fig. 2. Sodium Kα images of: (a) Pb–Ca–Sn–Al–0.01wt.%Na; (b) Pb–Ca–Sn–Al–0.05wt.%Na; (c) Pb–Ca–Sn–Al–0.12wt.%Na; (d) Pb–Ca–Sn–Al–0.23wt.%Na.

the mechanical properties, such as tensile strength, hardness and elongation. On the other hand, incorporation of too much sodium results in its enrichment in the crystalline boundaries and coarsening of the crystal grains. Because of the softness and ductility of sodium, the alloy exhibits higher elongation but lower strength and hardness.

Cyclic voltammetry

Cyclic voltammograms of typical lead alloys are presented in Fig. 3. The hydrogen evolution current at −1300 mV is directly related to the hydrogen overvoltage on the test electrode. As shown by the data in Fig. 3, this current is slightly higher for the Pb–Ca–Sn–Al–Na alloy than for the Pb–Ca–Sn–Al alloy, but much lower than those for Pb–Ca and Pb–Sb alloys.

Conclusions

(i) Incorporation of sodium in Pb–Ca–Sn–Al alloys can improve both tensile elongation and casting performance. Tensile strength and Vickers

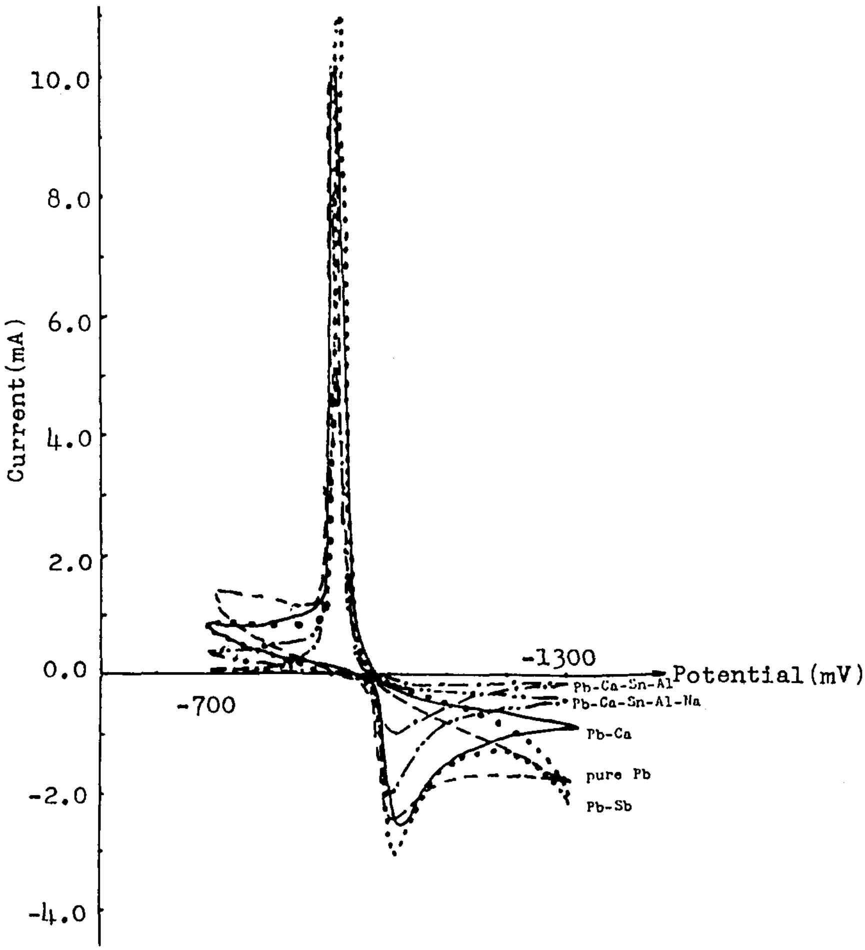

Fig. 3. Cyclic voltammograms of lead-based alloys. Electrode area: 0.26 cm^2 for Pb–0.09wt.%Ca–Sn–Al; 0.15 cm^2 for Pb–0.09wt.%Ca–Sn–Al–0.23wt.%Na; 0.13 cm^2 for Pb–0.18wt.%Ca; 0.23 cm^2 for pure Pb; 0.16 cm^2 for Pb–1.8wt.%Sb.

hardness both increase for sodium contents below 0.1 wt.%, but both decrease above this concentration.

(ii) Hydrogen overvoltage on the Pb–Ca–Sn–Al–Na alloy is slightly lower than that on the Pb–Ca–Sn–Al alloy, but much higher than that on the Pb–Ca or the Pb–Sb alloy. Thus, the most important characteristic of the Pb–Ca–Sn–Al alloy, namely, very high hydrogen overvoltage, is maintained in the sodium-containing system.

(iii) The improvement in the mechanical properties and casting performance of the sodium-containing alloy is attributed to the uniform distribution of sodium, fine crystal grains, and narrow and winding inter-crystalline boundaries. Enrichment of sodium in the latter leads to deterioration of the alloy.

(iv) Sodium is an effective modifier of the Pb–Ca–Sn–Al alloy. Its optimum content is 0.01 - 0.07 wt.%.

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