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Mechanical and corrosion properties of low antimony lead alloys

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The mechanical properties (tensile strength, hardness, and relative elongation) of lead alloys containing 2–3% Sb, 0·1–0·5% Sn, and 0·1–0·5% As in the as-cast state and after annealing and quenching were determined. It is established that quenching significantly improves the mechanical properties of the alloys. By variation of the tin content and the thermal treatment conditions it is possible to obtain within certain limits the desired mechanical properties. The anodic dissolution c.d. of lead, and lead alloys containing 2·2% Sb, 0·11% As and 0·25% Sn was determined as a function of the potential. It is found that this alloy has a higher rate of anodic dissolution and lower oxygen overvoltage than those of pure lead.

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1. Introduction

The lead grid alloys used currently in the battery industry contain 6–12% Sb. These alloys have a tensile strength from 4·8–5·4 kg mm^{-2}, hardness (H_B) from 12·0–14·0 kg mm^{-2}, and elongation from 14–24%. The good castability of these alloys leads to a high productivity of the casting machines. Antimony, however, has adverse effects on some of the battery characteristics. Thus the oxygen and hydrogen overvoltage of the Sb alloys is lower than that of pure lead. Antimony diminishes the corrosion resistance of the positive grid, and finally the high antimony content in the negative plate leads to the formation of stibine which is toxic [1, 2].

One of the methods to supress the adverse effects of antimony without decreasing its advantageous role is to reduce its content in the alloy down to 2–3%. Low antimony lead alloys have been studied previously [3–7].

The reduction of antimony content leads to a deterioration in the mechanical properties and in the castability of the alloys. This can be partly compensated by the introduction of small amounts of arsenic and tin.

The present paper is part of a systematic study of the mechanical and electrochemical properties of low antimony lead alloys.

2. Experimental

2.1. *Preparation of the alloys*

The antimony-lead alloys were prepared by addition of 99·8% metallic antimony to the lead melt (99·99% Pb) at 480°C. The ternary Pb–Sb–As alloys were prepared by the addition of Pb–2% As alloy to the Pb–Sb alloy. The quaternary Pb–Sb–As–Sn alloys were prepared by addition of tin to the ternary Pb–Sb–As alloy. The exact composition of the alloys was assessed analytically.

2.2. *Determination of the mechanical properties of the alloys*

(1) the tensile strength σ_B and the relative elongation δ were measured on standard specimens 12 mm in diameter on a 500 kg tensile machine 'Amsler'. The elongation rate was 6 and 10 mm min^{-1}. Three specimens of each alloy were tested. The values presented in the graphs are the average ones.

(2) The hardness (H_B) was measured on cast and polished cylinders with a length 20 mm and OD 20 mm with the aid of a Brinnell-Rockwell tester, at a load of 15·62 kg with a 2·5 mm sphere. The loading lasted 30 s.

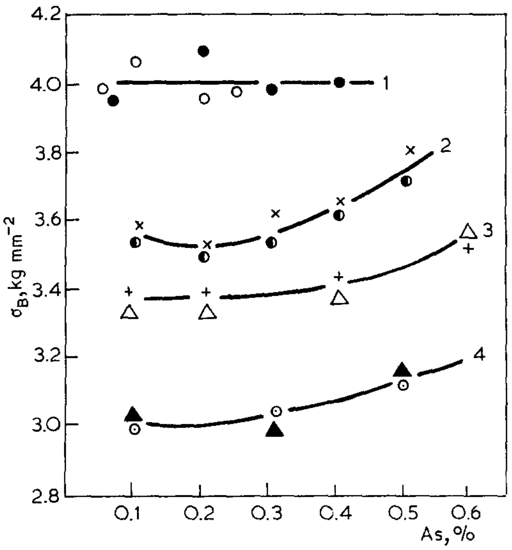

Fig. 1. Effect of arsenic on the tensile strength σ_B at a constant content of Sb and Sn in the alloy. Curve 1: ○, 3% Sb–0·3% Sn–Pb; ●, 3% Sb–0·6% Sn–Pb. Curve 2: ◐, 2·5% Sb–0·1% Sn–Pb; ×, 2·5% Sb–0·25% Sn–Pb. Curve 3: △, 2% Sb–0·1% Sn–Pb; +, 2% Sb–0·25% Sn–Pb. Curve 4: ⊙, 1·5% Sb–0·1% Sn–Pb; ▲, 1·5% Sb–0·25% Sn–Pb.

2.3. *Determination of the stationary corrosion rates*

The stationary corrosion rate determination was carried out by the method [8] reported earlier. The test electrodes with an area of 6·5 cm^2 were polarized anodically in a 7 N H_2SO_4 solution. The polarization was carried out galvanostatically at current densities from 0·1–45 mA cm^{-2}. The stationary corrosion rate of the lead alloys and the oxygen evolution rate were measured as a function of the potential.

3. Results and discussion

3.1. *Mechanical properties*

Fig. 1 presents the results of the tensile strength measurements of specimens containing 0·1–0.6% As at a constant Sb and Sn content. The data refer to steady state values which are established seven days after casting. As seen from Fig. 1, the tensile strength increases with the increase of Sb. The tensile strength of alloys containing the same amount of antimony and tin grows with the increase of the arsenic content in the upper limits. This is especially emphasized for the alloys with a lower antimony content. The increase in the tin content has no noticeable effect on the tensile strength. Despite the additions of arsenic and tin, the low antimony lead alloys have a lower tensile strength than those of the 6% antimony lead alloy.

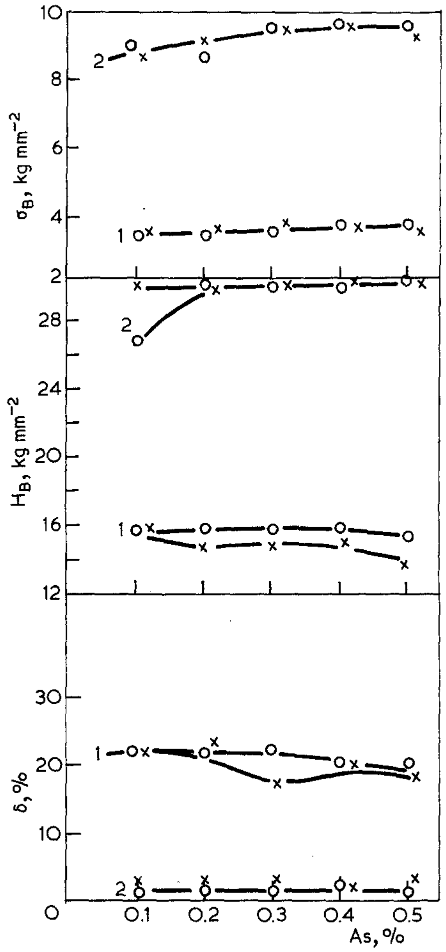

Fig. 2. Dependence of σ_B, H_B and δ on the arsenic content in alloys treated at 200°C for 5 h and water quenched (curves 2) and without thermal treatment (curves 1). ○: 2·5% Sb–0·1% Sn–Pb; ×: 2·5% Sb–0·25% Sn–Pb.

A thermal treatment was introduced to improve the mechanical properties of the alloys. An investigation of thermally treated lead alloys has been carried out previously [3]. The structural diagram of the lead-antimony system shows that alloys containing antimony up to 3% are in the region of the solid solution of antimony in lead and that these alloys can change their mechanical properties through thermal treatment. The specimens were annealed for 3 or 5 h at 200°C, whereupon one part of them was cold water quenched while

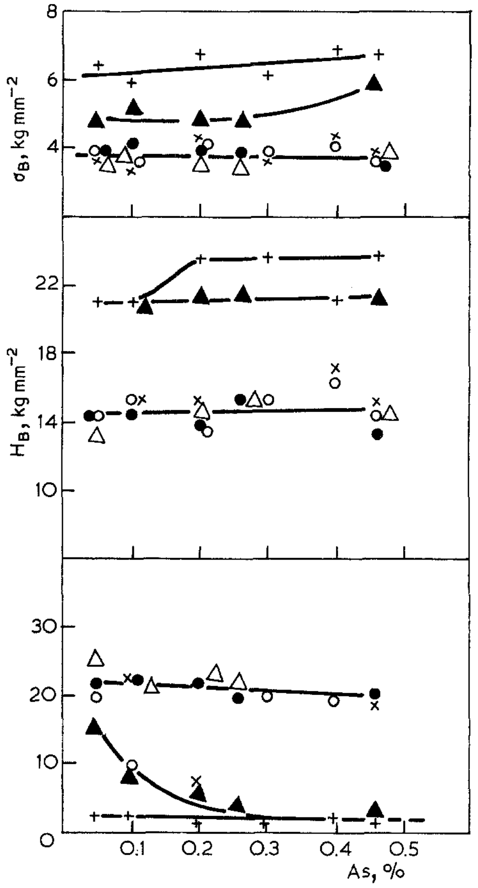

Fig. 3. Dependence of σ_B, H_B and δ on the arsenic content of the following alloys: ○: 3% Sb–0·3% Sn–Pb without thermal treatment; ●: 3% Sb–0·5% Sn–Pb without thermal treatment; ×: 3% Sb–0·3% Sn–Pb 3 h annealed at 200°C and water quenched; △: 3% Sb–0·5% Sn–Pb 3 h annealed at 200°C and water quenched; +: 3% Sb–0·3% Sn–Pb 5 h annealed at 200°C and water quenched; ▲: 3% Sb–0·5% Sn–Pb 5 h annealed at 200°C and water quenched.

another part was cooled at room temperature. The mechanical parameters of the thermally-treated alloy specimens were followed during 25 days. It was established that a steady state condition is attained within 7 days. This steady state values are presented in the following graphs.

Fig. 2 exemplifies the results of the tensile strength measurements σ_B, the hardness H_B and the relative elongation δ of alloys containing 2·5% Sb, 0·1 or 0·25% Sn, and with an increasing content of As from 0·1 to 0·5%. The plots marked *1* pertain to the as-cast specimens. They do not differ substantially from the values of alloys annealed 5 h at 200°C. The plots marked *2* present the results of the specimens annealed for 5 h at 200°C and quenched in cold water. As seen from Fig. 2, the tensile strength rises approximately two times, the hardness by 25%, while the relative elongation abruptly falls (approximately 10 times) due to the quenching treatment.

Fig. 3 illustrates the results of the measurements of the mechanical properties of the 3·0% Sb lead alloys containing 0·3 or 0·5% tin and 0·1 to 0·5% As. The thermal treatment of these alloys was as follows: one third of the specimens was tested after 3 h annealing at 200°C and water quenching, the second third of the specimens was annealed for 5 h and also quenched, while the rest was tested without any thermal treatment. As seen in Fig. 3, the specimens annealed for 3 h possess the same mechanical properties as the as-cast ones. The specimens quenched after 5 h annealing reveal a higher tensile strength and hardness but also an increased fragility. The increased Sn and Sb content in these specimens brings about a reduction in the improvement of the mechanical properties by thermal treatment. By variations in the tin content and the annealing conditions of the alloys with 3% Sb these processes can be controlled within certain limits in order to attain the desired mechanical properties of the alloys.

3.2. *Determination of the rates of anodic dissolution and oxygen evolution on low antimony lead alloys*

During prolonged polarization in the lead dioxide potential region, two parallel reactions occur on the electrode: first – on the PbO_2/H_2SO_4 (solution) boundary oxygen evolution takes place, and second – on the Pb/PbO_2 boundary the anodic oxidation of the metal (alloy) proceeds. The determination of the rate of these two reactions as a function of the potential was carried out by the method described earlier [8]. The oxidation was performed galvanostatically at various current densities. Fig. 4 presents the steady state anodic dissolution current (i_c) and the steady state oxygen evolution current (i_{O_2}) as a function of the potential. The anode, a lead alloy containing 0·11% As, 0·25% Sn was treated in one of the following modes: (1) no treatment; (2) water quenched after 3 h annealing at 200°C; (3) water quenched after 5 h annealing at 200°C. The same

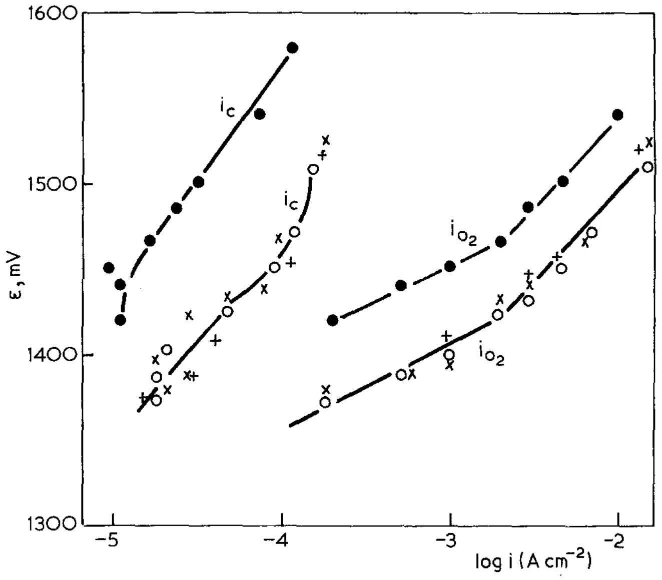

Fig. 4. Steady state anodic dissolution c.d. (i_c) and steady state oxygen evolution c.d. (i_{O_2}) as a function of the oxidation potential of lead (●); lead alloy with 2·2% Sb, 0·11% As, and 0·25% Sn without thermal treatment (○); the same annealed 3 h (×); the same annealed 5 h at 200°C and water quenched (+).

rates were determined with pure lead anodes for comparison. The total c.d. represents the sum of the anodic dissolution c.d. and the oxygen evolution c.d. A comparison of these two current densities as seen from Fig. 4 shows that the anodic dissolution current is only ca. 1–2% of the total c.d.

From Fig. 4 it is obvious that pure lead is more corrosion resistant than the alloy under study. Thus at a total c.d. 1×10^{-3} A cm^{-2} the anodic dissolution c.d. is $1{\cdot}32 \times 10^{-5}$ A cm^{-2} at 1452 mV whereas that of the alloy is $3{\cdot}1 \times 10^{-5}$ A cm^{-2} at 1408 mV.

One can see also in Fig. 4 that the oxygen overvoltage of the alloys is lower than that of pure lead. This is due to the presence of antimony, which strongly affects the oxygen evolution reaction [8]. The thermal treatment of the alloys does not exert any significant influence either on the oxygen evolution or on the anodic dissolution of the alloys.

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