

Lead alloys for maintenance-free and sealed lead/acid batteries

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Abstract

The preparation of low-antimony and lead–calcium multi-element alloys for battery grids are studied. The effects of various minor constituents (tin, aluminium, copper, selenium, cerium, thallium, sulfur, etc.) on the performance and methods for preparing copper–antimony, arsenic–antimony and calcium–aluminium master alloys are described in detail. The reaction mechanism of tin in the alloys and the casting conditions of the alloys are examined.

Introduction

A major research objective for the lead/acid battery is to maximize the working area of the active materials. The thinner the plates, and the greater the number of plates, the larger is the area. Thinner plates require thinner grids made from lead alloys with more sophisticated physical and chemical properties. In recent years, with the rapid development of the automobile and electronic industries, higher performances have been demanded from lead/acid batteries. Many developed countries began to study lead alloys in the early of 1970s. Nowadays, lead/acid batteries are low-maintenance, maintenance-free or sealed. Although the Chinese lead/acid battery industry has been developed considerably, a large proportion of the products is still at a low technological level. The main problem lies with the lead alloys used for the grids. This paper reviews studies [1, 2] of low-antimony and lead–calcium multi-element alloys.

Effects of minor elements on alloy properties

The basic requirements for lead alloys are: good mechanical characteristics, i.e., adequate hardness and strength and little mechanical and heat distortion; good corrosion-resistance, i.e., light intercrystalline corrosion and low corrosion rate; good casting characteristics; good weldability; little pollution; low cost.

To satisfy these requirements, various alloys have been studied. Today, only three types of alloy are widely used, namely:

- (i) high-antimony alloy, 4–11 wt.% Sb, with traces of arsenium, tin, selenium, etc.;
- (ii) low-antimony alloy, 0.8–3 wt.% Sb, with some arsenium, tin, selenium, copper, sulfur, etc.;
- (iii) Pb–Ca–Sn–Al multi-element alloy.

Effect of copper, selenium and sulfur on grain diameter of lead–antimony alloys

For lead–antimony alloys, with decrease of antimony, highly directional dendrites are easily formed when the alloy solidifies. Coarse crystal grains cause heat cracking

and brittle rupture. In order to avoid such problems, many manufacturers add arsenium, tin, copper, selenium, sulfur, cerium, thallium, etc., to the alloys. These elements influence the grain size, as shown in Figs. 1 and 2 [3-5].

In Fig. 1, curve A indicates the effects of copper on the average diameter of the grains. When 200, 400 or 600 g t⁻¹ of copper is added, the grain diameter is ~200, ~135, ~85 μm, respectively. The quantity of copper should be within 400-800 g t⁻¹.

Curve B shows the effects of copper and 100 g t⁻¹ rare earth metal (50 wt.% Ce and 45 wt.% Th) on the average diameter of the grains. If more than 200 g t⁻¹ Cu is added, there is a reduced effect on the diameter.

Curve C displays the effects of copper and 50 g t⁻¹ sulfur on the diameter. Adding rare earth metals to low-antimony alloys may also increase the overcharging resistance and the cycle life of batteries.

The data in Fig. 2 show that selenium plays a more important role than sulfur in reducing the size of the grains. Thus, these elements are often used together. Because the solubility of selenium in lead is higher than that of sulfur, an increase in the concentration of sulfur may improve the nucleation. Chinese battery manufacturers use a low-antimony alloy that contains 400-800 g t⁻¹ copper and 40-70 g t⁻¹ sulfur. Kirov [5] proved that copper also has an influence on the overall corrosion rate of lead and lead-antimony alloys. A lead-copper eutectic alloy containing 0.06 wt.% Cu exhibits minimum corrosion rate and maximum castability and hardness.

Special role of tin in lead alloys

In low-antimony alloys, tin is often used as an alloying element. It serves to improve the casting properties, strength and age-hardening process. In addition, tin plays a special role in enhancing the chemical properties of the interface between the grid and the active material and reducing passivation. When the positive plate is made of pure lead or low-antimony non-tin lead alloy, the plates are often passivated during low-current polarization or during storage under open-circuit conditions. The passivation is due to the formation of a continuous corrosion layer of α-PbO with high resistance. It has been found that tin facilitates the process of oxidation of PbO to PbO_n (1 < n < 2) and lowers the potential at which this reaction commences. This is explained [6] with a model for the oxidation of PbO to PbO_n that is based on the semiconducting properties of PbO, see Fig. 3.

Nijihawan *et al.* [7] have shown that, on adding tin to low-antimony alloys, the cycle life of batteries rises steeply. The batteries had a 5 Ah rated capacity and employed

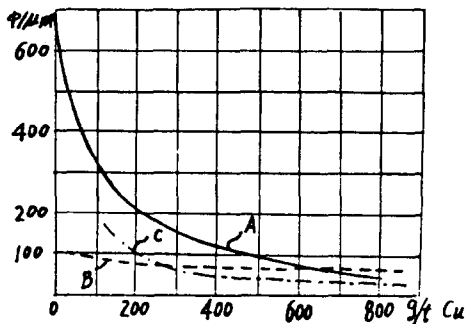


Fig. 1. Effect of copper and rare earth metals on grain size.

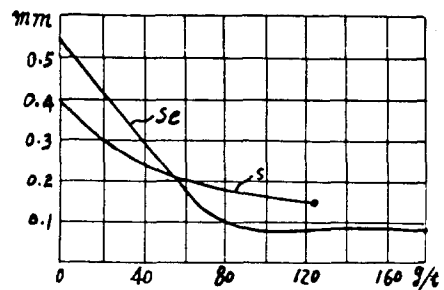


Fig. 2. Effect of selenium and sulfur on grain size.

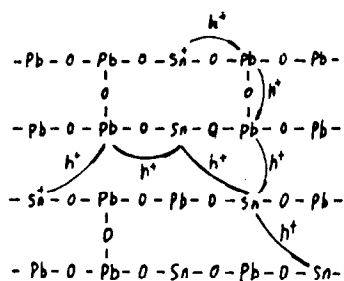


Fig. 3. Two-dimensional scheme of a PbO crystal lattice containing Sn^{2+} and Sn^{3+} ions.

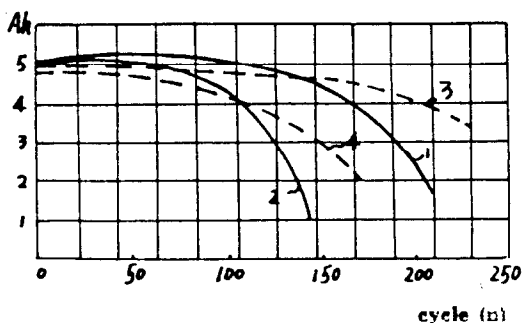


Fig. 4. Effect of tin addition on battery cycle life.

TABLE 1

Grid alloy composition and test conditions (refer Fig. 4)

Curve	Alloy composition (wt.%)				Discharge current (A)	Final voltage (V)
	Sb	As	Se	Sn		
1	1.6	0.05	0.02	0.2	0.25	1.7
2	1.6	0.05	0.02		0.25	1.7
3	2.5	0.05	0.02	0.5	1.0	1.7
4	2.5	0.05	0.02	0.01	1.0	1.7

grids made from low-antimony alloys, Table 1. From the data given in Fig. 4, it can be seen that the cycle life of batteries using a low-antimony alloy containing 0.2 wt.% Sn (curve 1) is 50% greater than that of a battery with a tin-free alloy (curve 2). The cycle life increases with tin content, i.e., 0.01 wt.% (curve 4) < 0.2 wt.% (curve 1) < 0.5 wt.% (curve 3).

In lead-calcium multi-element alloys, the addition of tin is designed to improve the chemistry of the grid/active-material interface. Without the presence of tin, passivating layers of $PbSO_4$ or $CaSO_4$ develop at the grid/active-material interface. This lowers the ability of the plates to recover from deep discharge and, thus, shortens dramatically the life of the battery. In the presence of tin, however, this process is retarded and battery cycle life is extended.

Role of aluminium in lead-calcium multi-element alloys

It is known that calcium is easily oxidized to form an oxide and a dross that is suspended throughout the molten metal. These oxide and dross inclusions are responsible for reduced productivity in grid casting. Formation of calcium oxide inclusion within (or on) the cast grid surface, or the capture and entrapment of air by these same oxide particles within the grid, result in deep corrosion penetration at the grain boundaries. These problems are avoided by adding aluminium to lead-calcium alloys. For example, calcium oxidation losses have been almost eliminated for lead-calcium-tin alloys (Fig. 5). Aluminium concentrations as low as 0.015 wt.% are considered sufficient to ensure maintenance of calcium levels in both the pot and the grid.

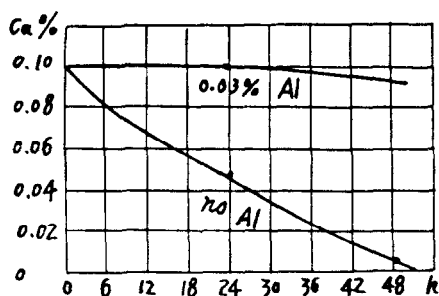


Fig. 5. Effect of aluminium addition on the rate of calcium oxidation.

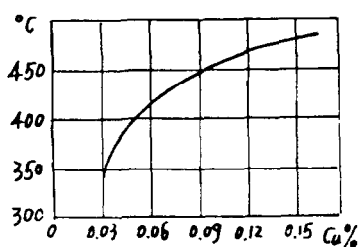


Fig. 6. Solubility of copper in lead.

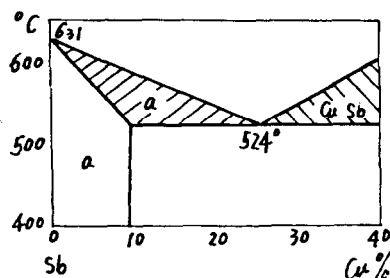


Fig. 7. Freezing-point curve for copper-antimony alloys.

Preparation of master alloys

Copper-antimony

The melting point of copper is 1084 °C. Its solubility in lead is small, as shown in Fig. 6. Therefore, copper is added to lead with difficulty. Copper easily forms an alloy with antimony. The freezing-point curve for copper-antimony alloys is given in Fig. 7. At 524 °C, a eutectic mixture of solid solution α and copper antimonide, Cu_2Sb is formed. The eutectic alloy reaches a mixture with the lowest freezing point and 25 wt.% Cu [8].

The authors prepared copper-antimony alloys in a crucible furnace. The method of operation was as follows. Add 75 parts of antimony to a graphite crucible and heat to over 700 °C. After the antimony has been melted, add 25 parts of copper and stir. The copper is quickly dissolved. After a homogeneous mixture is formed, cast into alloy ingots. The alloy is very brittle. The melted temperature is between 520 and 530 °C. The resulting low-antimony alloy is suitable as a master alloy.

Arsenic-antimony master alloy

Arsenic cannot be melted, but is sublimated at 633 °C when heated under atmospheric pressure. Arsenic is easily oxidized to form As_2O_3 or As_2O_5 . The As_2O_3 is hypertoxic. For this reason, the addition of arsenic to melted lead is hazardous.

The freezing-point curve for arsenic-antimony alloys is shown in Fig. 8. A eutectic mixture is formed at 612 °C with 17.5 wt.% As [9]. At a high temperatures, the alloys have a gel-like structure which is retained when the alloys are cooled rapidly. With slower cooling, crystals of one or both metals are formed. Arsenic-antimony alloys

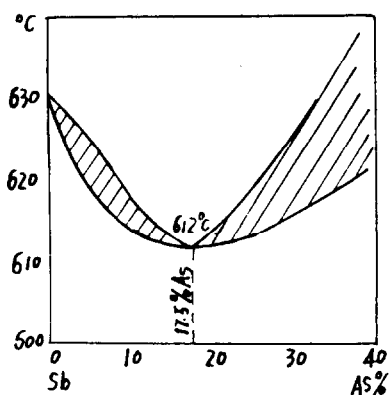


Fig. 8. Freezing-point curve of arsenic-antimony alloys.

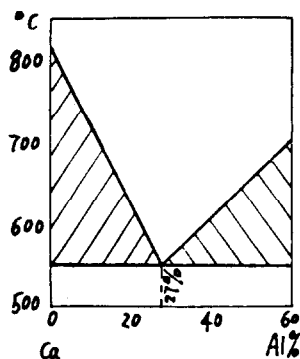


Fig. 9. Freezing point curve of calcium-aluminium alloys.

were made by adding arsenic to molten antimony. When arsenic is added to antimony it floats off due to its lower specific gravity, 5.7 versus 6.7. To prepare arsenic-antimony alloy, arsenic, in an amount calculated from the composition of the eutectic mixture, was put into a special container. The container was then immersed in molten antimony at about 700 °C and stirred vigorously. The alloys are formed at a lower temperature. After mixing thoroughly, the melt was poured into ingot moulds and cooled at a high speed. The alloy contained about 17 wt.% As.

Calcium-aluminium master alloys

Calcium has a low solubility in lead and a much higher melting point (814 °C). In addition, the specific gravity is smaller. It is easily oxidized to form CaO. The addition of pure calcium directly to lead is very difficult.

The freezing point curve for the calcium-aluminium alloys is shown in Fig. 9. At about 550 °C, the eutectic mixture contains 27 wt.% Al and 73 wt.% Ca [10]. The master alloy is formed when aluminium is introduced to molten calcium under argon atmosphere.

Preparation of low-antimony multi-element alloy

According to the authors' experience, the recommended alloy comprises: 1.5–2.0 wt.% Sb, 0.1–0.2 wt.% As, 0.005–0.02 wt.% Se, 0.05–0.2 wt.% Sn, 0.04–0.08 wt.% Cu, 0.004–0.007 wt.% S, the balance is lead, trace elements, known optional alloy ingredients and impurities.

The alloys are made from virgin lead (which typically comprises over 99.99 wt.% lead and traces of impurities) and Cu-Sb master alloy, As-Sb master alloy, antimony, selenium, tin and sulfur. The components are added at 550–600 °C. The mixture is stirred for 30 min at 550 °C. The alloy then is cast in moulds.

Preparation of lead-calcium multi-element alloy

The authors have prepared an alloy of composition: 0.06–0.12 wt.% Ca, 0.1–0.4 wt.% Sn, 0.02–0.05 wt.% Al, the balance is lead. A special sealed dissolution vessel

was used to make the alloy. The system offers particular advantages for use with allowing elements that have a lower specific gravity than lead so as to reduce segregation due to flotation, and with readily oxidizable metals to reduce dross in the furnace. The master alloy is best contained in a fine-mesh wire basket (or the like) which, like a filter, serves to prevent substantially any undissolved master alloy from escaping into the furnace.

Conclusions

The above-mentioned alloys have been used successfully in the production of grids for maintenance-free and sealed lead/acid batteries. When using low-antimony and lead-calcium multi-element alloys, great importance should be attached to the following three factors:

(i) Strict control of casting temperature. The recommended control temperature is shown in Table 2.

(ii) Strict control of calcium content. The lead-calcium alloy hardness is induced by an internal mechanism that involves grain-boundary migrations. There are very complex in nature. Initially, all calcium-alloy structures possess large as-cast grains. On solidification, the grain boundaries commence their migration. The rate of movement is dependent on the calcium content. At levels between 0.09 and 0.11 wt.%, there is an optimum in this movement that produces a desirable fine-grained structure. When these boundaries have moved throughout the metal, ageing is complete. It would appear that as an individual boundary moves, it redissolves any calcium phase material in its path and then reprecipitates it in its wake. As the rate of precipitation is dependent on calcium concentration, low concentrations of less than 0.09 wt.% will produce larger movements of the boundary and will cause a less coherent or regular structure. It is therefore critically important to control the calcium levels within the material.

Under conditions of normal grid casting, there are still calcium oxidation losses. When the grid surface is grey, or the grids are pliable, the calcium content is lower than 0.06 wt.%. The level should be increased by around 0.03 to 0.05 wt.% to make up for the loss.

(iii) Strengthen production management. From the phase diagram of the calcium-antimony alloy system it is found that a eutectic mixture is formed at 585 °C. At lower temperatures, calcium-antimony compound drosses float off. Therefore, alloys

TABLE 2
Casting temperature for alloys

	Pb-4.5wt.%Sb	Pb-1.8wt.%Sb multi-element	Pb-Ca-Sn-Al
Melting point (°C)	-296	-305	-327
Pot (°C)	450-470	470-490	490-510
Lead line (°C)	460-480	480-500	500-520
Ladle (°C)	470-490	490-510	510-530
Mold gate (°C)	140-160	160-180	180-200
Up mold (°C)	150-170	170-190	190-210
Down mold (°C)	160-180	180-200	200-215

containing antimony should never be mixed with lead–calcium alloys. Because the calcium content in lead–calcium alloys is small, a small amount of alloy containing antimony in a great quantity of lead–calcium alloy causes waste. The production management must be strengthened to minimize such losses.

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