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Effect of Zinc Addition on the Microstructure of Waste Acid Battery Lead Electrode (Pb-Sb Alloy)

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ABSTRACT

In this research an attempt has been made to determine the microstructure of Pb-Sb alloy system (waste lead electrode from acid lead battery) by alloying with zinc using sand and metal mould casting techniques. Lead-antimony alloys having low Sb content provide the desired strength. However, batteries parts containing 1.5%−3.5% (mass fraction) antimony show brittle behaviour and tendency for cracking, apparently because of the coarse dendritic microstructure. The reduction of Sb content causes a decrease in mechanical properties and in castability of the alloys. This can be partly compensated by the introduction of other elements such as Se, As, Zn or Ag (Markandeya et al, 2004). The Pb-Sb-Zn alloy was formed through casting by simultaneous addition of zinc and pouring of the molten alloy by varying zinc from 2-10% with 2% interval. The microstructure of the alloys was determined using standard techniques. The alloys were immersed into 0.5M of H_2SO_4 solution and the weight loss was determined after one day over an interval of seven days. Results of this study show that increase in Zn addition (up to 6%) led to decrease in the grain size of Pb-Sb-Zn alloy occasioned by increased uniform distribution of the Zn within the Pb-Sb matrix. The alloys cast in metal mould have the best properties. Hence this work has established that in the microstructure of Pb-Sb-Zn alloy, the Zinc showed a uniform grain size up to a maximum level of 6%.

1. Introduction

Metallic parts used in car batteries, such as grid, connectors and terminals, are made in lead alloys. For these specific applications, lead alloys must guarantee some basic requirements as: (i) adequate hardness and strength, (ii) low mechanical and heat distortion, (iii) light intercrystalline corrosion and low corrosion rate, (iv) good casting properties, (v) good weldability, and (vi) low pollution and costs [1]. In order to fulfill all these properties, lead-acid batteries manufacturers have focused on modifications of production processes and on the alloys chemical analysis [2]. Typical chemical compositions for lead-acid batteries parts are: 1) low antimony alloys

(0.8%−3%Sb),with small additions of As, Sn, Zn etc. 2) high antimony alloys (3%−11% Sb), containing low amounts of As, Sn, Zn etc; and 3) Pb-Ca-Sn alloys[1]. Hence, the main alloying system used in batteries is lead-antimony alloys. This alloy family is characterized by a eutectic transformation at 251.5 °C and 11% (mass fraction) of Sb; it is easy to cast into complex shapes as those for grids, connectors and terminals that are commonly obtained by foundry casting. They are often cast in permanent moulds; hence, they are commonly characterized by dendritic microstructure surrounded by nobler Sb-rich segregations, which can reduce the mechanical properties and corrosion resistance. Furthermore, porosities related to the foundry process can negatively affect the mechanical properties of these castings [1].

Antimony is added to strengthen and harden lead as well as influence its conductive properties. It reduces corrosion resistance of the positive grid and, in high content in the negative plate, leads to the formation of stibin which is toxic [1]. The most critical non-active component in a lead-acid battery is the grid. This is used to support the positive and negative active materials, and also to provide a conductive path for the current to and from the plates during charge and discharge [3]. Lead as a malleable metal, is generally too soft to be used as a production grid material, except for a few battery types that utilize pure lead for high performance and life [3]. As a result of many investigations by battery workers by the end of the first half of the twentieth century, various lead alloys had become established. Numerous lead alloys have been tested for the manufacture of grids of pasted batteries especially Pb-Ca and Pb-Sb without or with other elements [3]. Although many lead alloys have desirable mechanical and casting properties, they suffer more or less from electrochemical corrosion, mostly due to overcharging and self-discharging. The main alloying system used in grids was lead-antimony [4]. This was usually based on the eutectic composition of about 11wt% antimony as such an alloy was easy to cast into the complex form required for battery grids [4]. Antimony is used to strengthen and harden the lead grids for improved handling and casting, as well as having good conductive properties. At one time almost all lead-acid batteries were made with lead-antimony grids, and the original antimony alloy concentrations were in 8-12% range (The more common concentration levels we see in batteries using lead-antimony alloys are in the 4-6% range) [4].

Antimony additive has some advantages and some disadvantages. On the one hand antimony stabilizes the active material of the positive electrode, the cycle life of the battery is improved and passivation effects disturbing mainly the discharge are not observed when alloys with high antimony content are used for positive grids [5]. On the other hand, antimony migrates to the negative plate where it is precipitated and reduces the hydrogen over voltage. This leads to lower charge voltage, increased self-discharge and therefore increased water loss of the battery. The main difficulty with casting low antimony alloys is that the decrease of antimony content is accompanied by the appearance of hot cracks, if no special precautions are taken [6]. The development of low-maintenance and maintenance free batteries and the move towards purer systems, with no poisoning of the negative plate, has resulted in the use of binary lead calcium grids in the negative plates of hybrid batteries [6]. For improving the cast ability of low-antimony alloys, some alloying additives are used, one of these main additives is Zinc [7]. The formation of dendrites, which disturbs the feeding capacity of the mould during casting and leads to casting defaults, is almost fully suppressed.

In this work, the performances of Pb-4%Sb alloyed with Zinc were investigated in order to determine the microstructure of the alloy.

2. Materials and Method

2.1 Materials

The commercial Pb-4%Sb alloy electrode specific for the production of car batteries parts was used for the research. Zinc ingot was obtained in Jos, Nigeria.

The equipment used in this work includes: measuring cylinder of 100ml capacity, a 500kg digital weighing balance, crucible furnace, molding (casting) boxes, hacksaw, file, universal strength testing machine, a digital Rockwell Hardness machine and Charpy Impact machine.

2.2 Method

2.2.1 Production of the test samples

Samples of Pb-Sb-Zn alloys were produced from the Pb-Sb scraps by addition of several percentages of Zn, the added Zn were measured to produce alloys with Zn at 2, 4, 6, 8 and 10% wt. a weighed quantity of lead-antimony alloy (500g) was placed on the crucible and then put inside the furnace. At 420^0C, the melt was slagged (since the whole constituent of the crucible have melted). Various quantities of Zinc were added simultaneously with pouring of molten Pb-Sb into the mould. A total of six melts were produced. The compositions of each melt are given in Table 1.

Table 1. Alloys composition in weight percent

Heat	**%Zn**
A1	0
A2	2
A3	4
A4	6
A5	8
A6	10

Sand and metal mould was used for the casting of the alloys. The metal mould was prepared by cutting a long steel pipe of diameter 20mm x 250mm length with the help of hack-saw for each mould. The pipes were then split vertically into two parts for easy removal of the cast samples and finally held together using copper wires. When the melting was completed, the crucible was left in the furnace for about 10 minutes during which the mould were thoroughly dried and preheated. After that, the furnace was turned off and the molten alloys were stirred for few seconds with a steel rod and the molten metal was poured from the crucible pot into the moulds. after the molten metal solidified inside the mould, it was left to cool at ambient temperature, after which the alloy was removed from the moulds (see Figure 1). After casting the microstructure of the alloys were determined using standard techniques.

Figure 1. Photograph of the cast Pb-Sb-Zn alloys

2.2.5 Sample Preparation

For the metallographic study of the samples which is the microscopic study of the characteristics of the alloys. The following operations were carried out as follows:

Grinding: The samples were cut, faced and grinded using fairly coarse file. Intermediately, a fine grinding was carried out using four grades of energy paper (silicon carbide water proofed paper) in the order of 240, 230. 400 and 600 grits respectively. Afterwards, the samples were washed to remove chips.

Polishing: The well ground specimens with fine scratches were taken to a polishing machine to remove the fine surface scratches (i.e. to mirror finished). Aluminum oxide (Al_2O_3) which is a polishing powder was used as the lubricant. After polishing the specimens were rinsed with water and finally dried.

Etching: As the specimens were removed from the fine polishing machine they were immersed in a soap solution after which they were washed on a tap water. After that the specimens were immersed again in a mixture of dilute hydrochloric acid (1cm^3) and methylated spirit (99 cm^3) for about 2 minutes after which they were washed again in a tap water for final cleansing.

3. Results

3.1 Microstructure

The microstructures of Pb-Sb-Zn alloys with different concentrations of Zinc were investigated to determine the effect of the sand casting and metal casting on the grain size and grain boundaries of the alloys. Figure 2 shows the cast structure of Pb-Sb grids containing different concentrations of Zinc. It can be seen that with increasing Zinc concentrations grain size reduces up to 6%Zn at higher addition of Zn (8-10%) structure changes to round and globulitic form (see Figure 7 - Figure 8). This solidification takes place in a coarse dendritic structure containing cracks along grain boundaries. This is one of the main reasons why lead-antimony alloys were formerly not used on a large scale in the industry because the zinc have a limit solubility in lead (Pb) due to the large difference in their atomic radius which is greater than 15% this make the Pb-Sb-Zn alloy to form hard intermetallic phases rather than a solid solution phases these structure obtained are in par with the work of [6].

During the solidification of cast Pb-Sb-Zn alloy some Zn is displaced from the solidifying grain front to the remaining liquid. Zn is highly segregated at the interdentritic and grain boundaries. As a result of this, the alloy may exhibit different corrosion and mechanical characteristics. The alloys cast in metal mould offer a more homogeneous microstructure, almost free from porosity and lightly coarse phases than the sand cast alloys these can be attributed to the chilling effect of the metal mould as a result of quicker solidification. The slower the rate of solidification of the alloy of the sand casting, the higher is the amount of segregation of Zn to the interdentritic sub-boundaries and grain boundaries. The solidification time in sand casting is always greater than the solidification time in metal casting. The major difference here is that the metal mould has a much larger thermal conductivity than sand, and so the solidification will be much more rapid. In metal mould the rate limiting step is at the interface between the metal and mould, where heat is transferred between the solidifying metal and the metal mould.

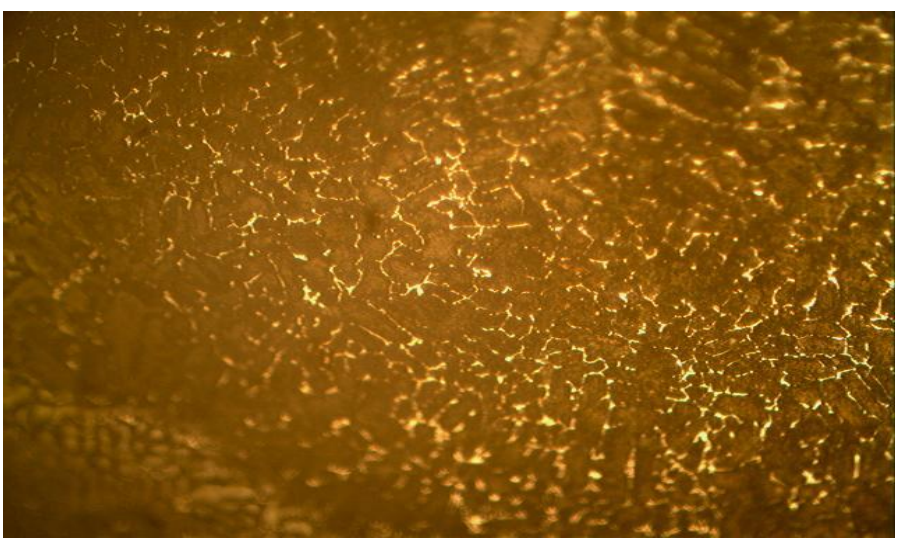

Figure 2: Microstructure of Pb-Sb alloy(x200)

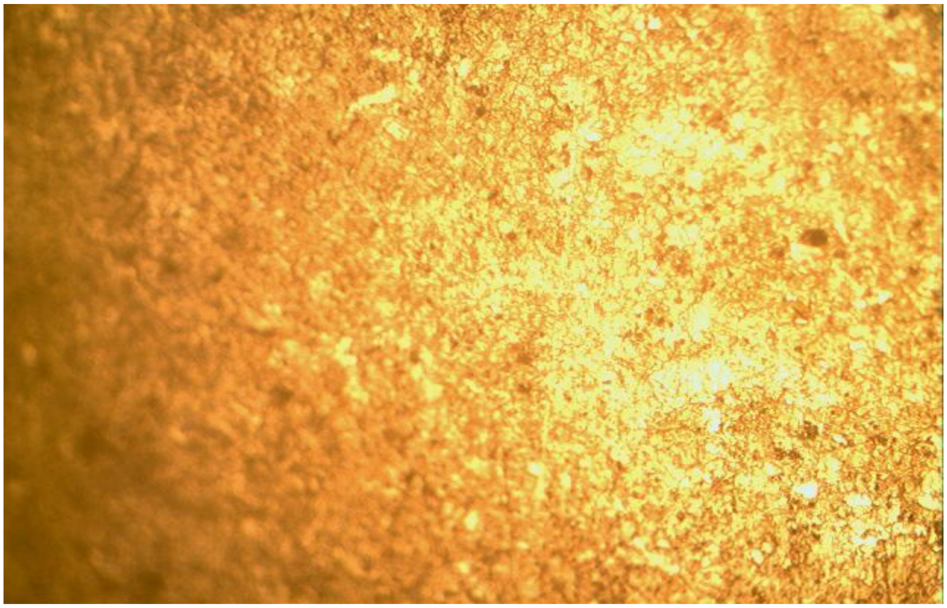

Figure 3: Microstructure of Pb-Sb-4%Zn alloy(x200) cast in metal mould

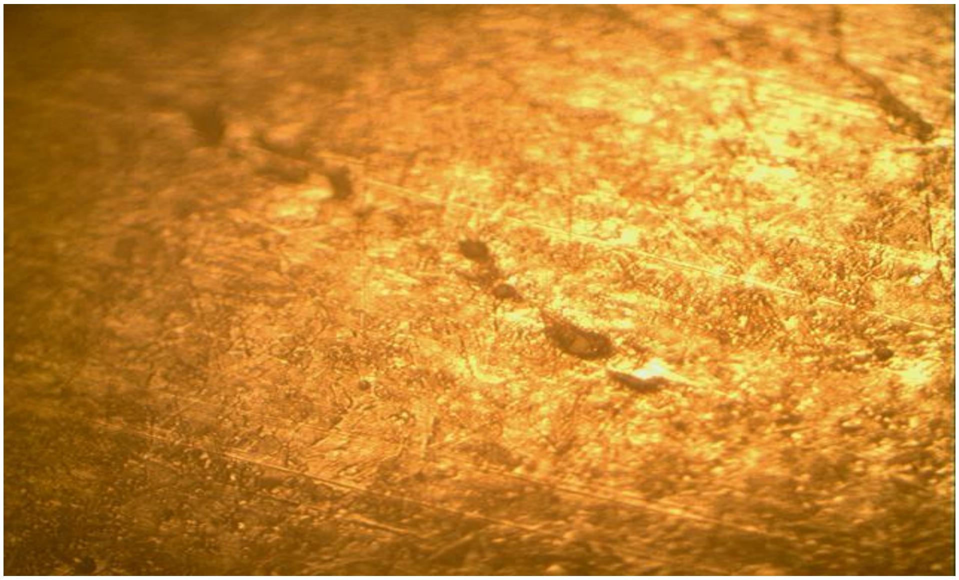

Figure 4: Microstructure of Pb-Sb-4%Zn alloy(x200) cast in sand mould

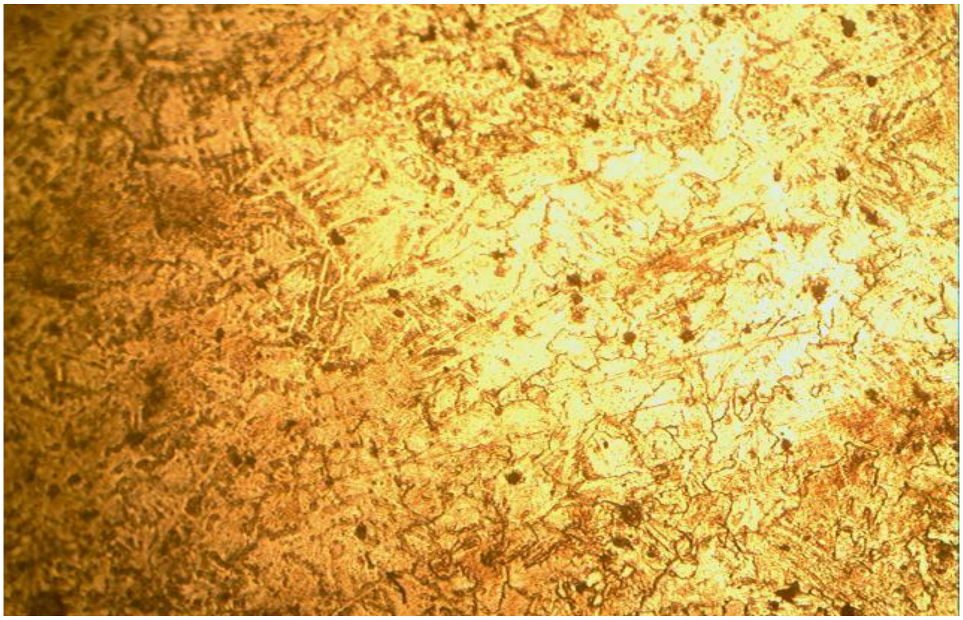

Figure 5: Microstructure of Pb-Sb-6%Zn alloy(x200) cast in metal mould

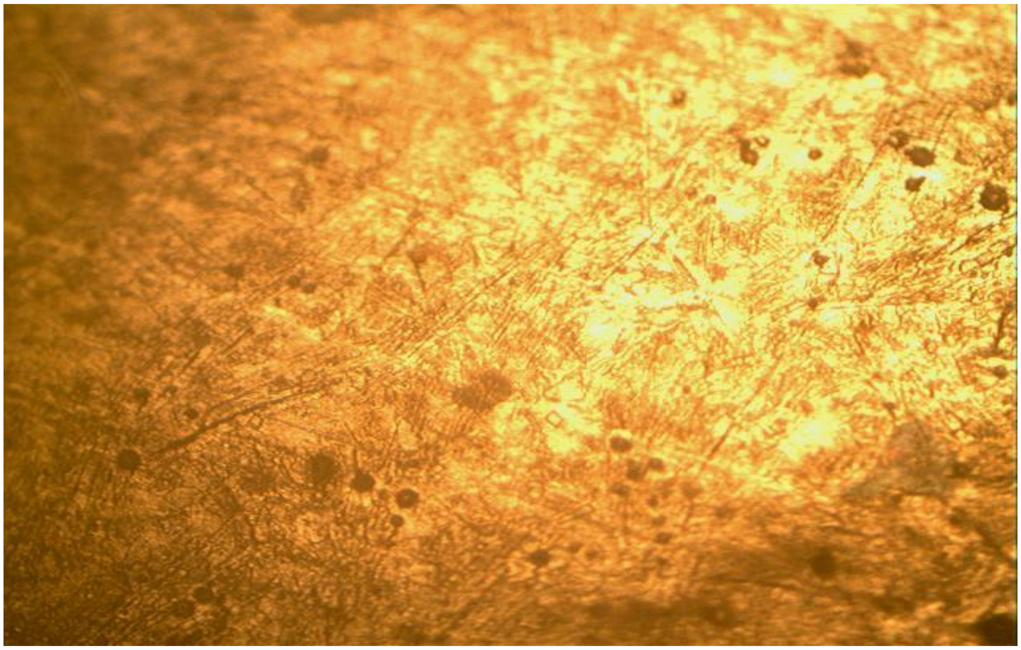

Figure 6: Microstructure of Pb-Sb-6%Zn alloy(x200) cast in sand mould

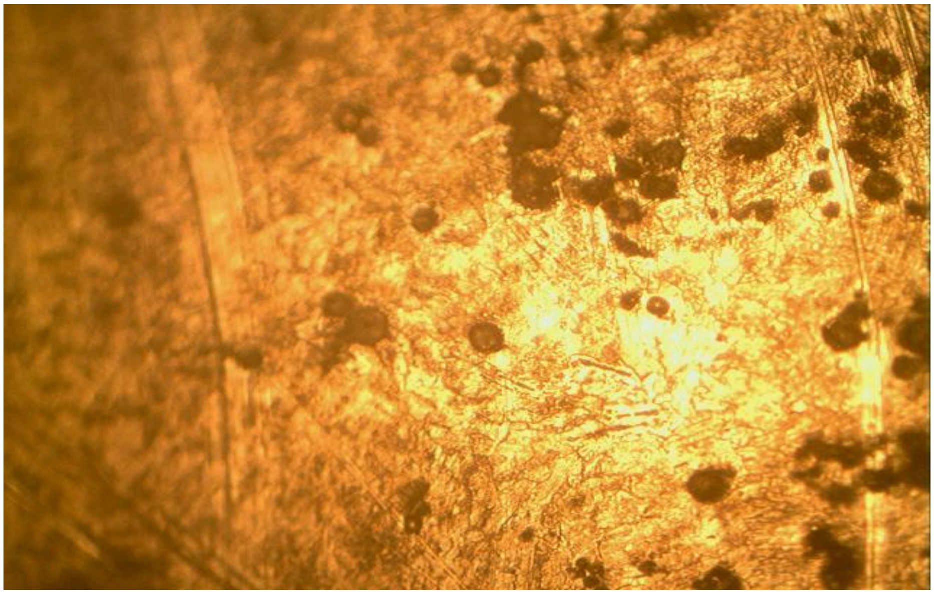

Figure 7: Microstructure of Pb-Sb-10%Zn alloy(x200) cast in metal mould

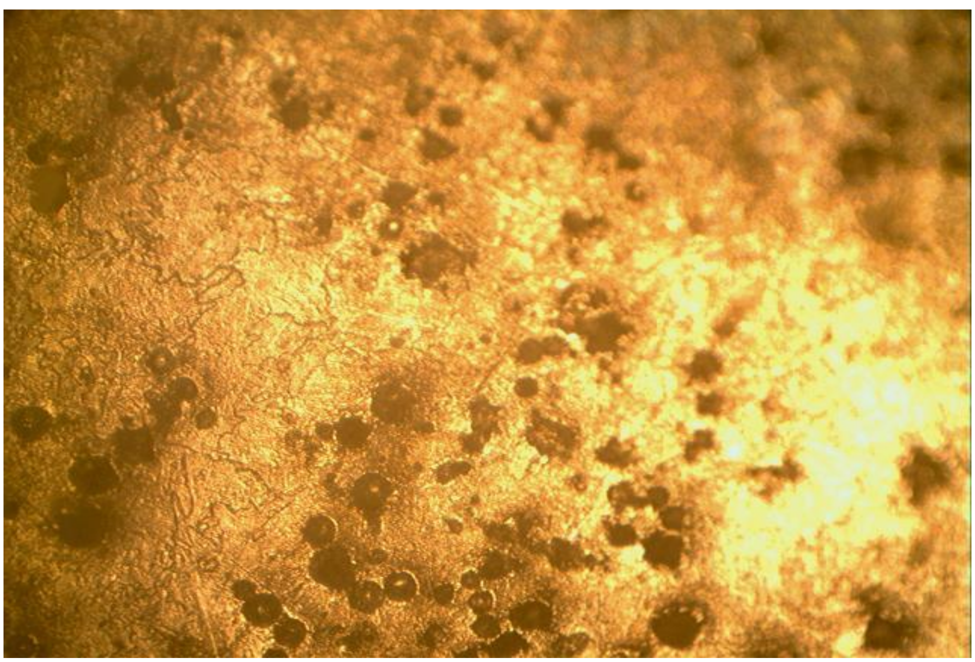

Figure 8: Microstructure of Pb-Sb-10%Zn alloy(x200) cast in sand mould

4. Conclusion

The Pb-Sb-Zn alloys was successfully produced through sand and metal casting and in the microstructure of Pb-Sb-Zn alloy, the Zinc showed a uniform grain size up to a maximum level of 6%.The alloys cast in the metal mould have better properties than the alloys in sand casting, because solidification rate of Pb-Sb-Zn alloys in sand casting is greater than the solidification of Pb-Sb-Zn alloys in metal casting.

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