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EFFECT OF ZINC ADDITION ON THE PROPERTIES OF WASTE ACID BATTERY LEAD ELECTRODE (Pb-Sb ALLOY)

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ABSTRACT

In this research, an attempt has been made to improve the mechanical properties; tensile strength, impact energy, hardness values and corrosion behavior of Pb-Sb-Zn alloy system (waste lead electrode from lead acid battery) by alloying with zinc (Zn) (2-10%) using sand and metal mould casting techniques. The alloy was formed through casting by simultaneous addition of Zn. The mechanical properties of the alloys were determined using standard techniques while corrosion rates were determined by immersing the specimen in 0.5M of Sulphuric acid (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 tensile strength of the cast Pb-Sb-Zn alloy increased as a result of Zn addition (up to 6%) due to decrease in the grain size of the Pb-Sb-Zn alloy occasioned by increased uniform distribution of the Zn within the Pb-Sb matrix. The hardness values and corrosion resistance of the alloys increased as the percentage of zinc increased. The alloys cast in metal mould had the best properties. This work has established that the corrosion resistance and hardness values of waste lead electrode can be enhanced by alloying with zinc.

1. INTRODUCTION

Lead based alloys are the largest proportions of Non-ferrous alloys used in the production of automotive components like batteries, bearings/coatings and linings as they are characterized by high density, softness, malleability, low melting points, low strengths and high corrosion resistance (Ghosh et al., 2004). The high malleability of lead-based alloys enables them to be rolled, extruded, drawn, cast and stamped. They are applied as coating on other metals by hot-dipping, electroplating or spraying. The solid solubility of antimony in lead decreases with decreasing temperature below the eutectic temperature and this is responsible for age hardening of rapidly cooled lead-antimony and lead-antimony-tin alloys (Metals handbook, 2004).

Lead forms alloys easily with many metals including antimony, bismuth, arsenic, copper, cadmium and zinc (Robert, 1980; Okorajor, 1987). The alloys form soft matrix, which support the hard inter-metallic compounds thereby increasing the strength and hardness of the resulting alloys (Smith 1983; Rajan and Sharma, 1988). Metallic parts used in car batteries, such as grid, connectors and terminals, are made of 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 (Al-Ganainy et al., 2004). In order to fulfill all these properties, lead-acid batteries manufacturers have focused on modifications of production processes and on the alloys' chemical analysis (Ghasemi and Tizpar, 2007). Typical chemical compositions for lead-acid batteries parts are: (i) low antimony alloys (0.8%−3% Sb), with small additions of As, Sn, Zn etc; (ii) high antimony alloys (3%−11% Sb), containing low amounts of As, Sn, Zn etc; and (iii) Pb-Ca-Sn alloys (Ghasemi and Tizpar, 2007). Hence, the main alloying system used in batteries is lead-antimony.

Albert et al. (1997) investigated the effect of addition of Sn (up to 1.2 wt. %) and addition of Ag (up to 0.1 wt. %) to a Pb-0.08 wt. % Ca-0.6 wt. % Sn reference alloy in order to evaluate passivation, corrosion resistance of the grids of lead acid batteries. Next, they used that reference alloy in the processing of fully operative batteries that was tested under cycling conditions. Tizpar and Ghasemi (2006) investigated the effect of addition of Ag on the corrosion resistance and hydrogen-oxygen evolution of Pb-Sb-As-Se alloys used as positive grids. Their studies showed that hydrogen evolution rates are inhibited whereas oxygen evolution rates are enhanced by the addition of different concentration of Ag to Pb-Sb-As-Se alloy. Guo et al. (2009) investigated how the addition of various contents of Te (0.01-1.0 wt. %) affects corrosion and oxygen evolution phenomena. They reported that the penetrable corrosion of positive grid alloys might be lessened and also oxygen evolution might be increased by the use of Te. Another experiment carried out by Li et al. (2007) involved the effects of Ce addition on corrosion behavior of Valve Regulated Lead Acid batteries. According to the experiment results, the corrosion resistance of Pb-Ca-Sn alloy in Sulphuric acid (H_2SO_4) solution can be improved by the addition of Ce. For the improvement of the corrosion resistance and creeping of strength of maintenance-free electrode, Ag and/or Bi were added to the Pb-Ca-Sn ternary alloy. It's electrochemical and mechanical properties were improved by addition of Ag.

The original antimony alloy concentrations are in the range of 8%−12%. Nowadays, the content is reduced to 3%−6%, in order to contrast the adverse effect of antimony without decreasing its advantageous role. 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).

In this work, the performances of Pb-4%Sb alloyed with Zinc were investigated in order to obtain car battery parts characterized by improved mechanical properties. In particular, improvements in the mechanical properties allow the reduction of the net section area and consequently of the weight, i.e. consumption, of lead which is carcinogenic.

2. MATERIALS AND METHODS

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 100 ml capacity, a 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. Methods

2.2.1. Production of 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 (500 g) was placed on the crucible and then put inside the furnace. at 420ºC, the melt was de-slagged (since the whole constituent of the crucible had 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 were 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 to other 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 metal 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 metalsolidified 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, tensile strengths, impact energy and hardness values and corrosion of the alloys were determined using standard techniques.

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

2.2.2. Tensile test

This test was conducted by loading the specimen into a universal testing machine that can apply a load to the specimen at a specific rate. As the specimen was auxiliary loaded in tension, the distance between the gauge marks was monitored. The specimen was elongated by the moving crosshead, load cell and extensometer measure, respectively, the magnitude of the load and the elongation (see Figure 2). The tensile strengths of specimens and 0.2% strain yield strength were obtained from the stress-strain curves.

Figure 2: Schematic representation of the apparatus used to conduct tensile stress-strain test

2.2.3. Hardness values

The hardness values of the specimens were determined using the rockwell hardness tester on “b” scale with applied load of 100 kg and hardness value of 101.2 HRB as the standard block. before the test, the surface of each specimen was thoroughly prepared by removing scratches and oil. Three readings were taken for each specimen with the average value taken as the hardness value for each specimen.

2.2.4. Impact energy

The impact energy test of the polyester/carbonized banana peduncle particulate composite samples was carried out on the samples on charpy impact machine to determine the impact energy (see Figure 3). Samples were cut to 10mm×5mm×55mm dimensions using hack saw. A V-notch of 2mm deep was then cut on the narrow face which provides stress concentration during the impact test. The sample was then placed on the machine and the pendulum was raised and allowed to swing-fall under the gravity hitting the specimen. the impact energy was then read directly from the machine.

Figure 3: Diagram of impact testing machine

2.2.5. Corrosion rate

Lead alloy rods of various compositions were used for weight–losses measurements. before each experiment, the rods were washed, degreased with acetone, rinsed with double-distilled water, dried, weighted and introduced in 0.5 M of sulphuric acid (H_2SO_4) solution (Figure 4). The weight of each sample was measured after one day over a period of 7 days. From the data obtained, corrosion rate was determined. the weight loss was determined by finding the difference between the initial weight of the coupons and the new weight after using the relationship:

$$w = w_o - w_f \quad (1)$$

where w =weight loss, w_o = initial weight, w_f = final weight.

The corrosion rate was determined from standard expression for measurement of corrosion rate in mills per year (mpy).

$$MPY = \frac{534W}{\rho AT} \quad (2)$$

where w = weight loss (mg), d = density of material (g/cm^3), t = time of exposure (hours), a = total surface area (in^2).

Figure 4: Photograph of the corrosion experiment set-up

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties

3.1.1. Hardness values

Figure 5 shows the as-cast alloys hardness versus Zinc content. In Figure 5, it was observed that the hardness of Pb-Sb-Zn alloy increased with the amount of Zn added to the molten Pb-Sb alloy system. For example, the hardness values of the alloys increased from 4.31 HRB to 7.23 and 7.83HRB at 0 and 10wt% Zn for sand and metal casting respectively.

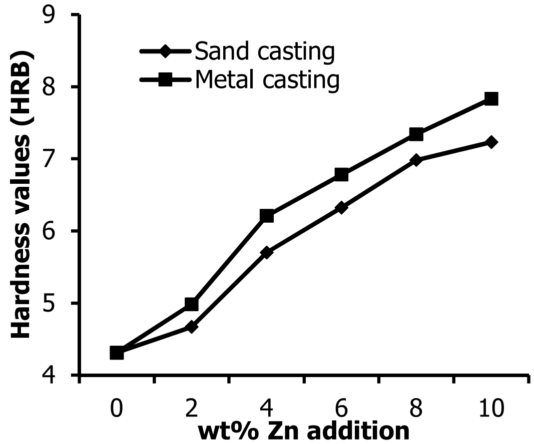

Figure 5: Graph of Hardness values with wt% Zn addition

3.1.2. Tensile properties

The series of stress-strain tensile test curves for Pb-Sb-Zn alloys are shown in Figures 6 and 7 to represent the general test results. The distribution of 0.2% strain yield stress and ultimate tensile strength as a function of alloy composition. From Figures 6 and 7 it was observed that the area under stress-strain curves increases as zinc content decreased in the alloys.

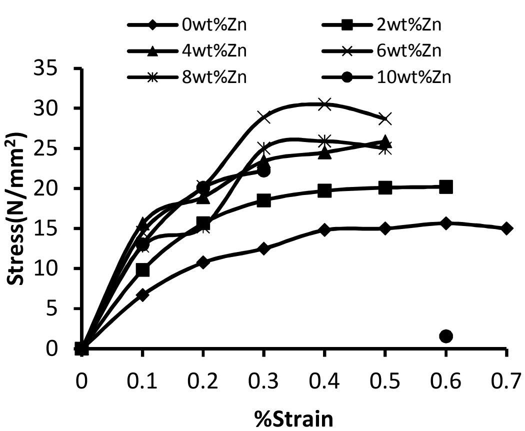

Figure 6: Stress-Strain curve of the alloys for sand casting

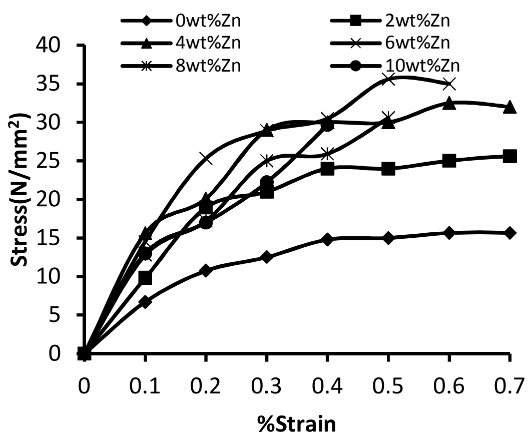

Figure 7: Stress-Strain curve of the alloys for metal casting

The yield and the tensile strength increased up to 6% Zn addition to Pb-Sb alloy (Figure 8). It is believed that the increase in tensile strength of Pb-Sb-Zn alloy is attributed to a decrease in the grain size of Pb-Sb-Zn alloy formed occasioned by increased uniform distribution of the Zn within the Pb-Sb matrix. This also agrees with past studies where decrease in the grain size of alloys resulted to increased yield and tensile strength (Pola et al., 2010). For example, the 0.2% strain yield stress was 20.23 and 25.31N/mm^2 at 6%Zn it decreased to 13.45 and 17.00N/mm^2 at 10%Zn for sand and metal casting respectively. The maximum ultimate tensile stress was 30.50 and 35.60N/mm^2 at 6% Zn decreased to 22.23 and 29.65N/mm^2 at 10% Zn for sand and metal casting respectively (Figure 9). The most important aspect of these results is that, the

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mechanical properties (Hardness and tensile strength) of the produced alloys are comparable to the mechanical properties of alloys with similar nominal chemical compositions (Salkind et al., 2002).

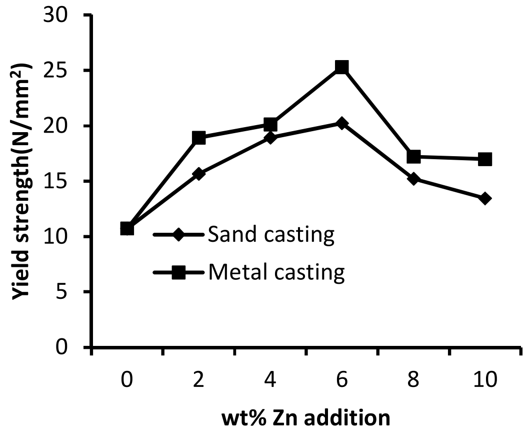

Figure 8: Graph of yield strength with wt% Zn addition

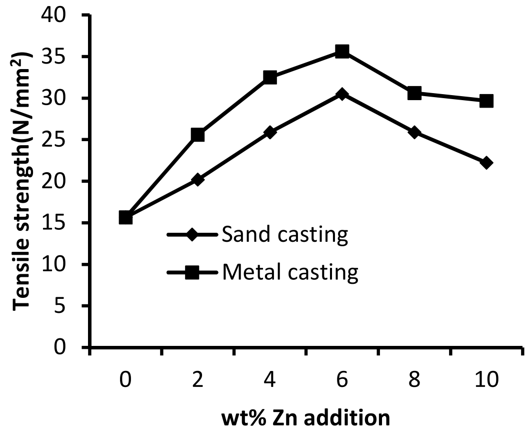

Figure 9: Graph of Tensile Strength with wt% Zn addition

3.1.3. Impact energy and percentage elongation

The results of impact energy and % elongation carried out on Pb-Sb-Zn alloys shows that the impact energy and % elongation of the alloys showed a decrease as the percentage zinc was increased in the Pb-Sb alloy system (Figures 10 and 11).

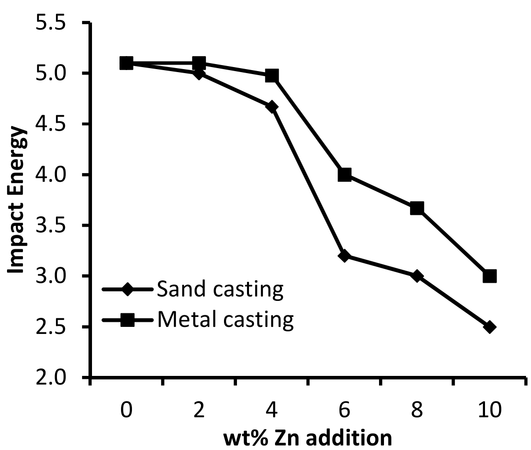

Figure 10: Graph of impact energy with wt% Zn addition

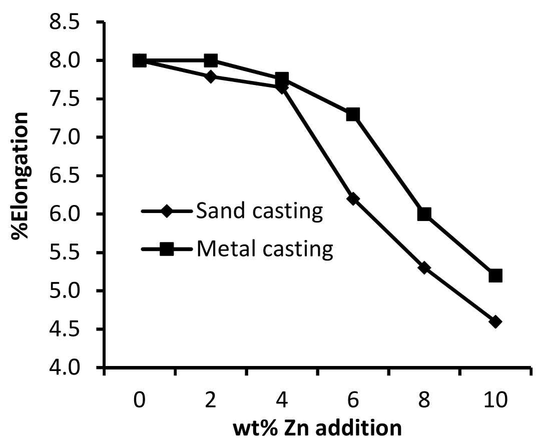

Figure 11: Graph of %Elongation with wt% Zn addition

It is believed that increased uniform distribution of the zinc resulted to the decrease in the grain size of the Pb-Sb-Zn alloy which resulted in increment of impact energy at this low percentage of zinc addition. As the wt% of Zn increased, the hard intermetallic phases formed hardening the alloys which lower the impact energy, this observation can be seen in the stress-strain curves at Figures 5 and 6 increase in the area under the stress-strain curves leads to increase in the impact energy and % elongation.

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3.2. Corrosion Rate

From the results obtained (Figures 12 and 13), it could be observed that, addition of Zinc to the alloy system imparted the highest corrosion resistance to the alloy due to the formation of inter-metallic and complex compounds, this formed hard and passive phases once the alloy starts corroding and these phases served as strong protective barriers to further corrosion attacked as depicted in Figures 12 and 13. It can be seen that, the rate of corrosion of the alloys in the medium decreased with increase in the number of days of exposure. Also, from the results obtained in this work it is clear, that the control coupons (0%Zn) had the highest corrosion rate compared to those with zinc addition.

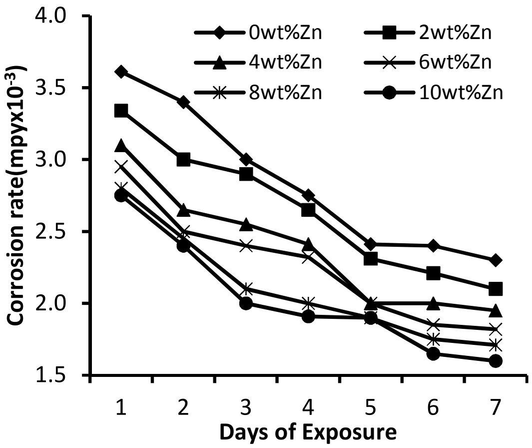

Figure 12: Graph of Corrosion rate with days of exposure for sand casted alloys

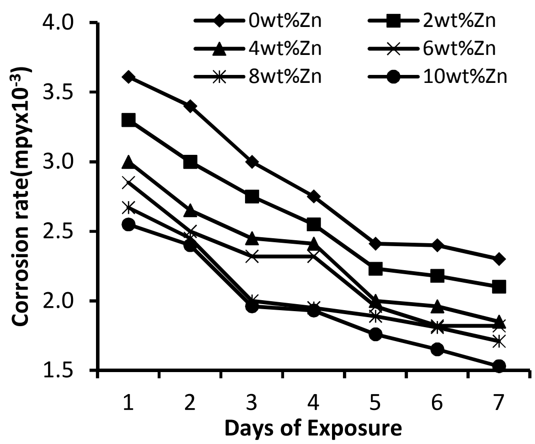

Figure 13: Graph of Corrosion rate with days of exposure for metal casted alloys

4. CONCLUSION

Based on the results, the following conclusions were made:

1. The Pb-Sb-Zn alloys was successfully produced through sand and metal casting
2. The alloys cast in the metal mould have better properties than the alloys in sand casting
3. The corrosion products resulting from the corrosion of the formed alloy after the addition of zinc have some shielding effect and helped to retard further corrosion attack.
4. The addition of zinc to the alloy system (Pb-Sb) significantly improves the corrosion resistance and hardness value of the resulting alloy.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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