EFFECTS OF COMPOSITION AND COOLING RATE ON MECHANICAL PROPERTIES OF Pb–Sb–Sn–As GRID ALLOYS

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Abstract. The effects of chemical composition and cooling rate on the mechanical properties of Pb–Sb–Sn–As grid alloys for lead-acid batteries were investigated. Mechanical properties were characterized in terms of ultimate tensile strength and elongation at room temperature. Composition and cooling rate of the studied alloys should ensure the increase in the amount of Sn soluble in α-Pb and the decrease in the amount of brittle arsenic precipitates or eutectic β-Sb phase in the structure.

Key words: Pb–Sb–Sn–As grid alloys, ultimate tensile strength, elongation.

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1. INTRODUCTION

Lead-based alloys are widely used for the preparation of lead-acid battery grids [1, 2]. Pure lead is suited to the electrochemistry and corrosion requirements of the battery but does not have the mechanical strength. Lead is therefore strengthened by addition of alloying elements such as antimony [3]. Alloying by antimony increases lead’s hardness and its resistance to mechanical damages without appreciably reducing its corrosion resistance [4–11]. Such enhancement in the mechanical properties is due to some significant segregation of Sb at grain boundaries [12–15]. Today the more common concentration levels in batteries using lead-antimony alloys are in the 6–12 wt.% range [16]. But for the lower-maintenance battery technologies, these alloys are not suitable due to the high Sb content [17]. Although the addition of antimony to lead can enhance mechanical properties, higher antimony is avoided because of negative impact on electrochemical properties [4, 18]. The major problem in the use of high-antimony alloys is the transfer of antimony from the positive to the negative plate during cycling. Antimony reduces the hydrogen evaluation voltage and causes the generation of hydrogen gas and water loss during charging. Researchers are therefore concerned with lowering the Sb content to 2–5 wt.% while maintaining necessary properties [19–23]. However, these alloys have lower mechanical properties and are more difficult to process than the...
traditional high-antimony alloys. They become brittle and tend to crack because of their dendritic structure [24–32]. The main difficulty with casting low-antimony alloys is that the decrease in antimony content is accompanied by the appearance of hot cracks, so that additions of other alloying elements for improvement of castability become necessary [33–37]. Tin and arsenic are usually added to confer properties such as fluidity, grain refinement, and age-hardening characteristics to the grids. Tin also modifies the (grid/active material) interface and improves corrosion resistance and conductivity [38–49].

Considering that the battery grids must be dimensionally stable and must have sufficient mechanical properties to resist the stresses of the charge/discharge reactions without warping, bending, or stretching, tensile test is used to learn about the strength properties of grid alloys. It is used to check the results of technological processes or to verify that material meets its specifications [50–56]. Unfortunately, information regarding the tensile strength and elongation of Pb–Sb–Sn–As grid alloys is incomplete and, at times, contradictive. Therefore, the main goal of this study has been to contribute to a better understanding of the effects that Sn and As alloying elements and cooling rate have on ultimate tensile strength and elongation of as-cast Pb–Sb grid alloys containing 3.07–4.75 wt.% Sb.

2. EXPERIMENTAL

Preparation of the Pb–Sb–Sn–As grid alloys used in this study was carried out in the C.O.S. melting pot of production line for lead-acid batteries of BM Company (Austria) at Westa ISIC (City of Dnipro, Ukraine). The temperature of molten metal in the pot was in the range of 350–460°C. The chemical composition of the cast alloys was determined using an ARL 3460 optical emission spectrometer. The lead-based grid alloys tested were broken into three series whose chemical composition is shown in Table 1. Antimony content in the studied alloys was analyzed to be in the range of 3.07–4.75 wt.%, tin content – in the range of 0.0003–1.21 wt.%, arsenic content – in the range of 0.11–0.25 wt.%. Major impurities consisted of Cu (≤ 0.019 wt.%), Bi (≤ 0.012 wt.%), Ag (≤ 0.0023 wt.%), S (≤ 0.0016 wt.%), and Ni (≤ 0.0011 wt.%). Trace amounts of Fe, Se, Cd, and Zn (in a descending order) were detected as well, with all impurities amounting to ≤ 0.062 wt.%. To evaluate the mechanical properties of as-cast Pb–Sb–Sn–As grid alloys, the uniaxial tensile test up to rupture was used. The test was carried out at room temperature on a R-0.5 tensile testing machine powered electromagnetically. The test specimens designed to be used with serrated grips were prepared according to GOST 11701-84. They had a total length of 6.0 cm, a gage length of 4.5 cm, and a thickness of 0.3 cm. For tensile test, the samples of series no. 1 and 2 were cast at temperatures of 440–460°C and those of series no. 3 – at temperatures of 350–370°C. For each cast, six samples were selected, and an average taken to reduce experimental
error. Mechanical properties were assessed in terms of ultimate tensile strength ($\sigma_U$) and elongation ($\gamma$). The results were represented with their corresponding standard error not exceeding 6% on average.

To investigate the effect of cooling rate on mechanical properties of the Pb–Sb–Sn–As grid alloys, the molten metal was poured into a casting mold heated in the temperature range between 40°C and 170°C. Temperature was monitored by chromel-alumel thermocouple. Six as-cast samples per tensile test were used and the results were averaged.

3. RESULTS AND DISCUSSION

The studied hypoeutectic Pb–Sb–Sn–As alloys are composed of dendritic $\alpha$-Pb crystals alloyed by tin and lamellar eutectics in the interdendritic regions constituted of Pb-rich $\alpha$-phase and Sb-rich $\beta$-phase [12]. According to the phase diagram Pb–Sb, the eutectic fraction increases with the antimony content in the alloys increasing [1]. The alloys also undergo precipitation processes due to other minor alloying elements, particularly arsenic, forming second-phase particles in the interdendritic regions and within the dendrites of the lead-rich phase [14, 16].

The composition of the tested samples and the results obtained in the ultimate tensile strength and elongation determinations are presented in Table 1. Comparing the data of tensile tests for the samples of series no. 1 and no. 2, it can be concluded that at almost the same average level of antimony in the alloys tensile strength increases with increasing tin content. There is an 11% difference between the low- and high-tin alloys. Higher tin concentrations soluble in $\alpha$-Pb produce finer microstructure of lead-based alloys and they therefore become stronger [57]. The decrease in an arsenic average content can also enhance tensile strength since smaller amount of brittle arsenic precipitates forms in the structure [16]. As would be expected, elongation of the alloys decreases as tensile strength increases.

With increase in the antimony average content of the samples of series no. 3 compared with that of the samples of series no. 1, the average value of ultimate tensile strength increases but that of elongation decreases, which may be explained by higher content of ($\alpha + \beta$) eutectics in the alloys with higher Sb content [1]. Despite the increase in the antimony average content of the samples of series no. 3 compared with that of the samples of series no. 2, the lower average content of tin leads to the decrease in both the ultimate tensile strength and the elongation (Table 1).

At any antimony content, higher tin additions to the alloys produce higher values of ultimate tensile strength. Elongation data exhibit more variations than appear in the tensile strength data. The first effect of the addition of up to 0.074 wt.% Sn is to decrease the average value of elongation (series no. 1 and no. 3), but as the tin is increased up to 0.45 wt.%, the elongation rises above the initial average value by
19% (series no. 2 and no. 3). This means that such amount of tin soluble in Pb-rich phases has positive effect on ductility of the alloys.

Besides, elongation results are also susceptible to average content of impurities, even at trace levels, that is the highest in the samples of series no. 3. As the number of segregated phases formed by impurities is increased, the alloys tend to become more brittle, as shown by their decreased elongation. The average values of tensile strength decrease with increasing impurities content as well. The mechanical properties are affected by impurities that have been segregated because they inhibit dislocation and grain boundary movement and decrease ability to deformation [58–60]. The exception is the samples of series no. 2, the negative effect of impurities for which is compensated by the increased tin content.

Table 1
Chemical composition, ultimate tensile strength (σu) and elongation (δ) of Pb–Sb–Sn–As alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition, wt.%</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sb</td>
<td>Sn</td>
</tr>
<tr>
<td>Sample series no. 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>3.07</td>
<td>0.0003</td>
</tr>
<tr>
<td>1.2</td>
<td>3.39</td>
<td>0.0003</td>
</tr>
<tr>
<td>1.3</td>
<td>3.34</td>
<td>0.0005</td>
</tr>
<tr>
<td>1.4</td>
<td>3.69</td>
<td>0.0003</td>
</tr>
<tr>
<td>average</td>
<td>3.37</td>
<td>0.0004</td>
</tr>
<tr>
<td>Sample series no. 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>3.27</td>
<td>0.43</td>
</tr>
<tr>
<td>2.2</td>
<td>3.33</td>
<td>0.51</td>
</tr>
<tr>
<td>2.3</td>
<td>3.46</td>
<td>0.43</td>
</tr>
<tr>
<td>2.4</td>
<td>3.51</td>
<td>0.44</td>
</tr>
<tr>
<td>2.5</td>
<td>3.51</td>
<td>0.42</td>
</tr>
<tr>
<td>2.6</td>
<td>3.62</td>
<td>0.45</td>
</tr>
<tr>
<td>average</td>
<td>3.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Sample series no. 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>4.5</td>
<td>0.076</td>
</tr>
<tr>
<td>3.2</td>
<td>4.64</td>
<td>0.069</td>
</tr>
<tr>
<td>3.3</td>
<td>4.65</td>
<td>0.069</td>
</tr>
<tr>
<td>3.4</td>
<td>4.71</td>
<td>0.069</td>
</tr>
<tr>
<td>3.5</td>
<td>4.75</td>
<td>0.087</td>
</tr>
<tr>
<td>average</td>
<td>4.65</td>
<td>0.074</td>
</tr>
</tbody>
</table>

To investigate the influence of tin in more detail, additions of up to 1.21 wt.% Sn were made to the samples of series no. 2. The effects of these additions are shown in Fig. 1. The ultimate tensile strength results are quite irregular, but in general slightly decrease (by 1–2%) with changing compositions (Fig. 1a). The elongation tends to decrease steadily throughout this range of composition reaching the value
that is by 26% lower than initial value (Fig. 1b). That is why, the alloys with a tin average content higher than 0.45 wt.% Sn were not used in further studies.

The sensible influence on the mechanical properties can be as a cooling rate of the alloys is reduced from 100 to 50 K/s, which corresponds to the increase in a heating temperature of casting mold from 40°C to 170°C [61]. As seen in Fig. 2, increasing temperature of casting mold decreases the mechanical properties of the samples of series no. 1. In the temperature range between 60°C and 170°C average values of ultimate tensile strength decrease by 12% with gradient of 0.033 MPa per 1°C of increasing temperature (Fig. 2a) and those of elongation decrease by 15% with gradient of 0.0085% per 1°C (Fig. 2b). The highest mechanical properties are achieved at heating temperature of casting mold that is not higher than 50°C since at

Fig. 1 – Effect of the tin content in the samples of series no. 2 on average values of ultimate tensile strength (a) and elongation (b).
higher temperatures cooling rate of the alloys decreases and more brittle arsenic precipitates can form in the structure.

Figure 2 – Effect of a temperature of casting mold on average values of ultimate tensile strength (a) and elongation (b) of the samples of series no. 1.

Figure 3 summarizes the influence of a heating temperature of casting mold on the mechanical properties of the samples of series no. 2. With temperature increasing from 75°C to 170°C, the average values of the ultimate tensile strength decrease by 4% with gradient of 0.015 MPa per 1°C (Fig. 3a), but those of elongation slightly increase by 2% with gradient of 0.002% per 1°C (Fig. 3b). It can be assumed that the obtained results relate to the lower arsenic content of this series of the Pb–Sb–Sn–As alloys as compared with series no. 1. As known, arsenic precipitates are mainly localized at the grain boundaries causing embrittlement of the alloys [16]. Considering the
The effect of the cooling rate on the mechanical properties of the samples of series no. 2, the temperature of casting mold can be maintained within the range of 165–185°C. In this case, higher heating temperatures of casting mold and, correspondingly, lower cooling rates (as compared with series no. 1) contribute to a more uniform distribution of tin in the Pb-rich phases [62, 63].

![Graph](image_url)

Fig. 3 – Effect of a temperature of casting mold on average values of ultimate tensile strength (a) and elongation (b) of the samples of series no. 2.

The decline in mechanical properties of the samples of series no. 3 as a function of temperature of casting mold is shown in Fig. 4. With temperature increasing from 100°C to 170°C, the average values of ultimate tensile strength and elongation go down by 16% and 3.5% correspondingly. The tensile strength decreases with gradient that equals to 0.08 MPa per 1°C of increasing temperature. The reduction
in the elongation values is much less than that found for the samples of series no. 1, which indirectly confirms the positive effect of lowering arsenic content in the studied Pb–Sb–Sn–As alloys. Besides, the alloys of series no. 3, containing the highest antimony content among other alloys, are most fragile due to the increase in an amount of brittle eutectic $\beta$-Sn phase in the structure. To ensure higher mechanical properties of the samples of series no. 3, the heating temperature of casting mold should not exceed 110°C.

![Graph](image)

Fig. 4 – Effect of a temperature of casting mold on average values of ultimate tensile strength (a) and elongation (b) of the samples of series no. 3.

Thus, the determined ranges of heating temperature of casting mold relate to the phase structure of the investigated Pb–Sb–Sn–As alloys. For the samples of series no. 1 containing up to 0.25 wt.% As, cooling rate should be high enough to
Effects of composition and cooling rate on mechanical properties

prevent precipitation of brittle arsenic phases in the interdendritic regions and within the α-Pb dendrites. Cooling of the samples of series no. 2 can be slowed due to the decreased content of As (less than 0.17 wt.%) and increased content of Sn (greater than 0.42 wt.%) that dissolves in Pb-rich phases enhancing their mechanical properties. The samples of series no. 3 can be cooled with intermediate rate since the average content of antimony is raised from 3.4 wt.% to 4.65 wt.%, which increases an amount of brittle eutectic β-Sb phase in the structure.

4. CONCLUSIONS

In this study, the influence of chemical composition and cooling rate on the mechanical properties of the hypoeutectic Pb–Sb–Sn–As alloys was investigated. From the experimental results and their analysis, the following conclusions can be made. The addition of up to 4.75 wt.% antimony enhances the ultimate tensile strength but reduces elongation of the studied alloys. These mechanical properties can be higher as an average amount of tin is increased up to 0.45 wt.%. Further increase in the tin content up to 1.21 wt.% slightly improves ultimate tensile strength but significantly lowers elongation. The effect of addition of tin on the mechanical properties of the studied alloys is mainly due to the solid solubility of this element in the Pb-rich phases. The ultimate tensile strength and elongation depend on the level of precipitated arsenic particles, reaching higher values as the arsenic content does not exceed 0.13–0.15 wt.%. The mechanical properties of the investigated grid alloys have also a correlation with the number of segregated phases formed by impurities. Both the ultimate tensile strength and the elongation decrease as the amount of such embrittling phases is increased by higher impurities content.

The mechanical properties of the Pb–Sb–Sn–As alloys can be additionally improved by controlling their cooling rate through heating casting mold to the defined temperature. To enhance ultimate tensile strength and elongation, cooling rate should ensure decrease in the amount of brittle arsenic precipitates and eutectic β-Sb phase in the structure. The series of lead-based alloys with the average content of 3.45 wt.% Sb, 0.45 wt.% Sn, and 0.15 wt.% As exhibits the highest elongation in combination with the highest ultimate tensile strength provided that the heating temperature of casting mold is maintained within the range of 165–185°C. These alloys are valuable for specific applications such as structural grid components that experience high dynamic loads. The use of the recommended low antimonious, tin, and arsenic Pb-based grid alloys for lead-acid batteries proves to be beneficial in producing new generation of rechargeable batteries that strictly meets the stringent requirements of the market and guarantees excellent performance.
REFERENCES