EFFECT OF ANTIMONY ADDITION RELATIVE TO MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CONTINUOUS CAST LEAD ALLOY

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Abstract

It is well documented that the addition of antimony in pure lead increases tensile strength and reduced elongation. The goal of the present work is to identify the cause of these phenomena by investigation of the effects of the addition of Sb (1.25 wt.%) on the structure of pure continuously cast lead and lead alloy rods. The microstructure and morphology of both pure lead and lead with 1.25 wt.% antimony were examined by digital optical microscope and scanning electron microscope respectively. Energy Dispersive X-ray Spectroscopy (EDX) was used to identify alloying elements. The results showed that the effect of additions of antimony on mechanical properties of lead-antimony alloys is mainly due to the solid solubility of the antimony. Distribution of the antimony results in a decrease in the grain size of the pure lead. These smaller grains mean higher strength so long as there is a homogeneous grain structure

Keywords: Continuous casting, lead, lead-antimony alloy, oscillation mark, metallography, SEM/EDX

1. INTRODUCTION

Pb-Sb alloys are frequently used in numerous industrial applications, such as cable sheaths, anti-friction bearings, solders and battery grids. This is due to their beneficial characteristics, such as the precipitation hardening effect, as well as their microstructural and mechanical properties [1-3]. Pb-Sb alloys can be produced by continuous and gravity casting processes [4] or Equal-Channel Angular Pressing (ECAP) [5]. The physical and mechanical properties of lead-antimony depend on the chemical composition of the alloy [6]. Previous works has shown that (compared with other metals) lead has much lower strength. [6]. Thus pure lead is unsuitable for many applications that require even significant strength. Small alloying additions significantly increase its strength. Bismuth, tin and antimony are the most common alloying elements of lead. For examples, addition of 20 wt.% Bi and 5 wt.% Sn can increase the strength of lead [7]. The addition of antimony in lead can enhance on mechanical properties, but higher content of antimony is avoided because of negative impact on electrochemical properties. So, lead-antimony alloys for battery grids in automotive applications are produced only with 1-3 wt.% Sb [8, 9]. The main goal of this study has been to contribute to a better understanding of the effect alloying elements on the physical, structural and mechanical properties of continuously cast lead alloys.

2. EXPERIMENT

2.1. Material Preparation and Casting Procedure

The trials were carried out on the model RS080 vertically upwards-continuous casting machine at Rautomead's premises in Dundee, UK. This report covers sample A, which produced 8 mm diameter rod in soft lead, and sample B, which produced 8 mm rod in lead 1.25 wt.% antimony. The chemical composition of the cast alloy was then tested using an AMETEK spectrometer. Tensile test, metallography and SEM/EDX were used to investigate the relationship between the microstructure and mechanical properties of continuous casting fabricated Pb and Pb-Sb rod. The representative samples analyzed in this work and their corresponding parameters are listed in **Table 1**.

Table 1 The lead samples tested in this research and their casting servo parameters

Sample	Alloy	Pull distance (mm)	Pull dwell (s)	Acceleration (s)	Deceleration (s)	Speed (mm/min)
A	Pb	20	0.027	0.025	0.025	7000
B	Pb-1.25 wt.%Sb	20	0.027	0.025	0.025	7000

2.2. Tensile Testing

To evaluate the mechanical properties of samples, the uniaxial tensile test was used. The test specimens were prepared according to ASTM E8 / E8M - 13a (Standard test methods for tension testing of metallic materials) and for each cast, three samples were selected and an average taken [10].

2.3. Metallography

Samples for microstructural observations were cut with a clean sharp hacksaw. Sectioning of the test samples was performed carefully to avoid destroying the structure of the material. The samples were sectioned to a convenient size, then ground by using alumina grinding paper and polished. The polished samples were etched according to the ASTM E407-07 (Standard practice for micro-etching metals and alloys) in a solution of 75 ml glacial acetic acid ($C_2H_4O_2$), 25 ml of 30% concentrated hydrogen peroxide (H_2O_2) and 15 ml glycerol ($C_3H_8O_3$) for 10-30 min (depending on the depth of the distributed layer). Then samples were then dried and cleaned with 70% concentrated nitric acid to appear the crystals [11, 12].

2.4. SEM/EDX

In order to observe the morphology of lead-antimony, the etched samples were put onto the stage/holder, mounted on carbon sticks, and then placed into the vacuum chamber for examination by the Scanning Electron Microscopy (SEM) as well as Energy Dispersive X-ray Spectroscopy (EDX) - model JEOL JSM7400F.

3. RESULTS AND DISCUSSION

Small amount of alloying elements are often added to metals to improve their physical and mechanical properties. The objective of this study was to investigate the relationship between the microstructure and mechanical properties of continuous cast lead alloy.

3.1. Tensile Testing

In this work, mechanical properties were monitored by tensile test. **Table 2** shows the average elongation and tensile strength of the continuous cast Pb and Pb-1.25 wt.% Sb rod samples respectively. It can be seen that sample A (pure Pb) has higher elongation and lower tensile strength compared to the sample B (Pb-1.25 wt.% Sb). The addition of antimony increase the tensile strength of lead casting and, on the other hand, decrease the elongation percentage of lead casting as would be expected for an alloying elements. Lead unit cell structures are described as face centered cubic (FCC) and antimony is body centered cubic (BCC). Dislocations in BCC structure like antimony are no longer mobile making it brittle. However, dislocations in FCC alloys like lead can still move very quickly making it ductile. **Figure 1** shows the photographs of fracture surfaces. Results showed that the fracture of lead was ductile with necking. The Pb-1.25 wt.% Sb is still ductile, just less so than the pure Pb [13].

Table 2 Tensile test and elongation percentage results

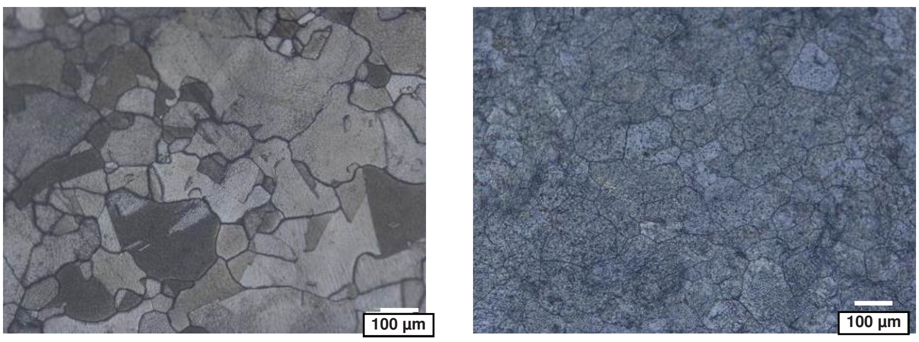
Sample	Sample No	Tensile strength (MPa)	Average tensile strength (MPa)	Initial length (mm)	Final length (mm)	Elongation percentage (%)	Average elongation percentage (%)
A (Lead)	1	17	17	100	143	43	41.3
	2	18		100	139	39	
	3	16		100	142	42	
B (Lead-Antimony)	1	30	29.7	100	112	12	14.3
	2	29		100	113	13	
	3	30		100	118	18	

(a) Fracture of Pb (b) Fracture of Pb-1.25 wt.% Sb

Figure 1 Fracture of Pb and Pb-1.25 wt.% Sb

3.2. Microstructure evaluation and Average Grain Size Reading (Planimetric Method ASTM E-112)

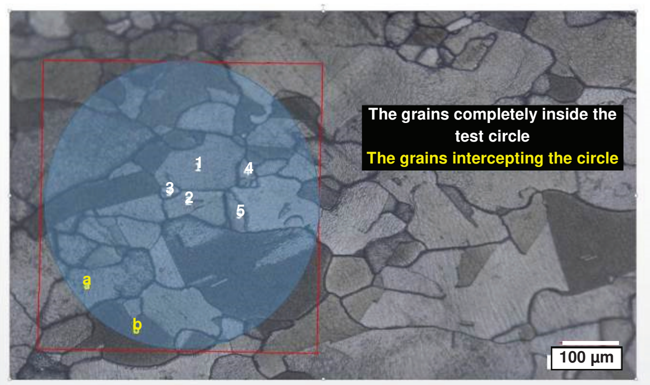
Figure 2a) shows the microstructure of the pure lead, **Figure 2b)** the grain structure of the alloy having lead 1.25 wt.% antimony continuous cast rod. These figures show clearly the precipitate distribution of the Pb-Sb alloy after adding antimony. As can be seen, in the antinomy added sample, there are many small dark spots with the reduced lead crystal grains. These dark spots are identified as a precipitated antimony rich particles. As will be demonstrated in the following section, in the high magnifications SEM image observations, the dispersion of antimony rich particles within the Pb grains can be seen clearly. The grain sizes of the homogenised, cast lead-antimony in **Figure 2** showed a strong influence of the alloy element additions on grain size, since the casting conditions were the same for both alloys. Additional alloying elements typically produce a fine and homogenize distribution of precipitation. Because of finer grain, there are more space precipitations. Thus, Pb-1.25 wt.% Sb exhibits higher tensile strength than pure lead. Sb additions in the Pb resulted in grain refinement. A possible grain refinement caused by increasing heating as melting temperature of pure lead was about 327°C and melting temperature of the Pb-Sb alloy was 380°C. So the grains within the structure recrystallize into many fine grains. This grain growth is also because the diffusion of the solute occurs. In general speaking, the smaller/finer grains, have the larger area of grain boundaries that inhibits dislocation motion and reducing the grain size therefore increases the available nucleation sites. Thus, grain-size reduction typically expands toughness due to the dislocations interacting with the grain boundary as in a larger grain there are more dislocations within the grain. There is a much greater chance for a dislocation to be stopped at a grain boundary in the smaller grains [13].



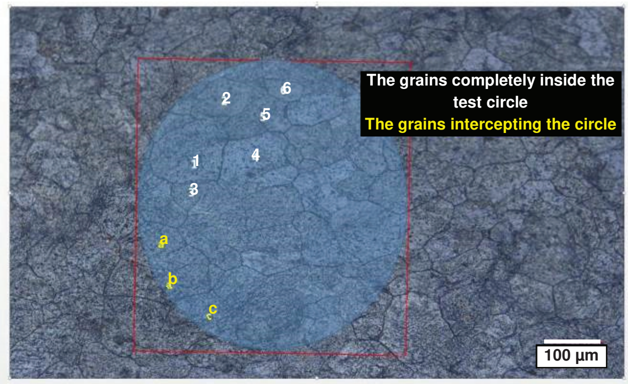
(a) Grain structure of pure Pb (b) Grain structure of Pb-1.25 wt.% Sb

Figure 2 Grain structure of Pb and Pb-1.25 wt.% Sb

The evaluation of grain size and microstructure was determined through planimetric procedure. To perform this technique, a proper magnification was selected. A circle was drawn on the image (**Figure 3**), the grains that were located entirely inside the circle were counted and then the grains intercepting the circle were counted separately and the average grain size was calculated by using the planimetric procedure. **Figure 4**, shows the analysis and quantification of grain size of lead and Pb-1.25 wt.% Sb by Jeffries method [14, 15].



(a) Pure Pb



(b) Pb-1.25 wt.% Sb

Figure 3 Average grain size measurement of Pb and Pb-1.25 wt.% Sb

Table 3 shows the average grain size of these two samples as discussed above which confirmed the average grain size of lead antimony sample is smaller. It has been shown that alloying elements have a significant influence on the refinement of the grains. Equiaxed grains were decreased by increasing amount of alloying element. Higher concentrations of Sb cause precipitation of finer equiaxed grains.

Table 3 comparison average grain size of sample A and B

Sample	**Alloy**	**Average Grain Size** (mm^2)	**The average grain per square** (mm)
A	Pb	0.0053	188
B	Pb-1.25 wt.% Sb	0.0045	223

3.2.1. Lead-antimony phase diagram

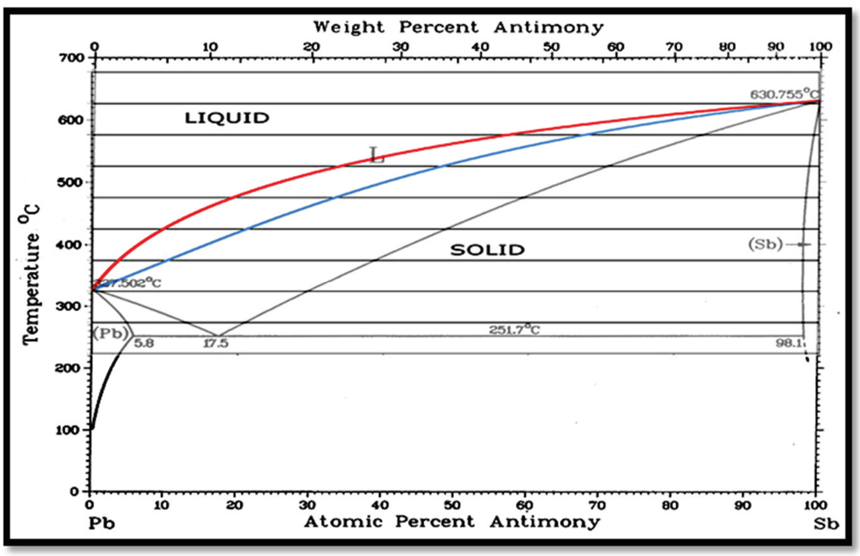
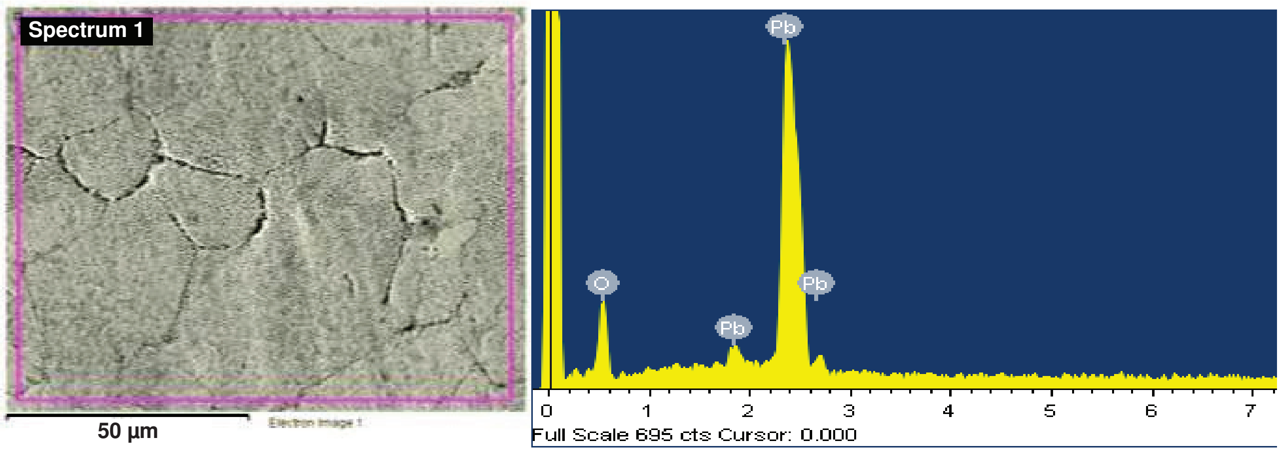


Figure 4 Phase binary diagram of Pb-Sb

According to the phase diagram of Pb-Sb (**Figure 4**), in a lead containing about 0.44 wt.% Sb the antimony is not dissolved until the temperature exceeds 100 °C. It will remain undissolved at temperatures up to and somewhat above 100 °C. Then, the grain growth and it can increase in grain size. The phase diagram of Pb-Sb shows, that Sb forms a eutectic phase with Pb. Lead-antimony system has a low-melting point binary eutectic. When a liquid of eutectic composition solidifies, a eutectic microstructure is formed with a layer of α and β phases. Sb rich grains are being formed when the Sb concentration in Pb-Sb alloy exceeds the solubility limit, which is only 0.44 wt.% at 100 °C. It is a result of segregation of Sb from the alloy at the mentioned state, here sample B at 382 °C with quantity of 1.25 wt.% Sb. So most Sb dissolves in Pb and Sb-rich grains segregate from the Pb-Sb solid solution [16].

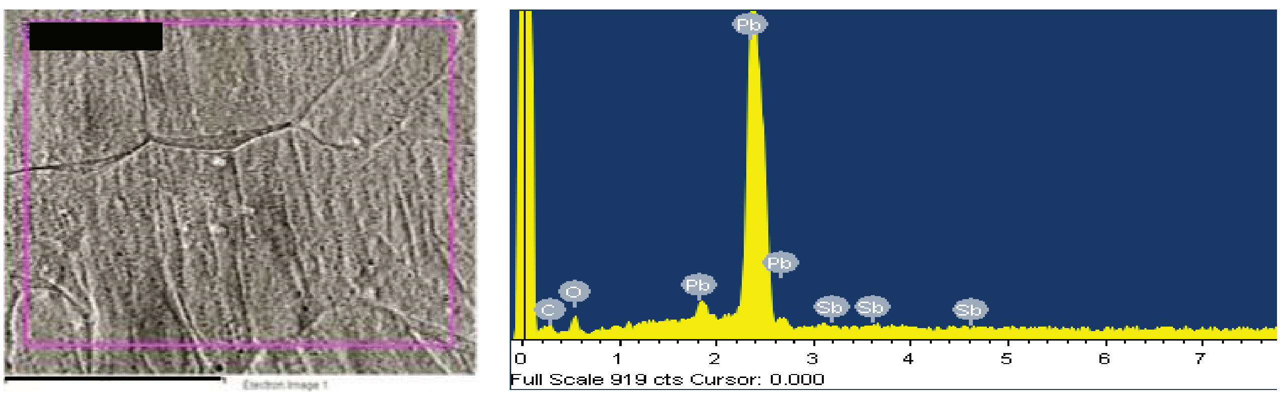
3.3. SEM image observation and EDX analysis

A JEOL JSM7400F field emission Scanning Electron Microscope (SEM) was used for microstructural analysis. Energy Dispersive X-ray Spectroscopy (EDX) was performed to analyse the chemical composition of the alloys. **Figures 5** and **6** show the electron image (an enlarged view) of the both pure lead and lead-antimony alloy in the as-cast condition, whereas presents the similar image of the optical microscope. The darker regions in which are seen in more detail around the precipitates in the second figure is antimony rich regions, which is not observed in the as-cast pure lead structure. It can be clearly seen that the bright grey phase is lead.

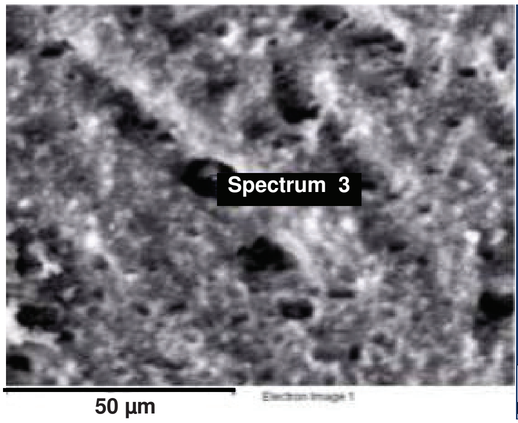


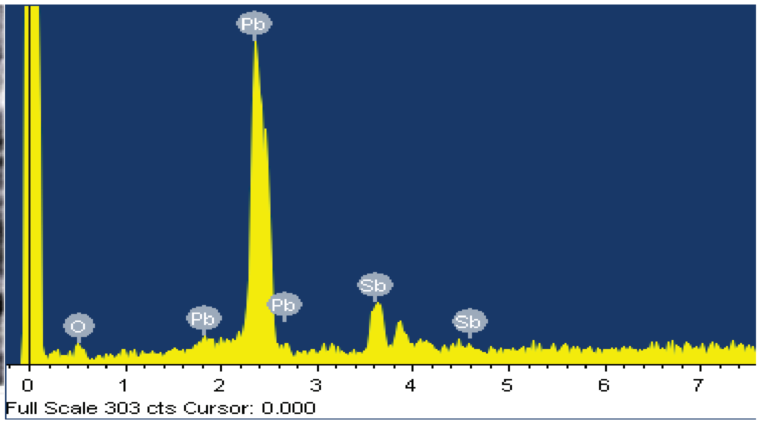
a) SEM of pure lead (b) EDX of pure lead

Figure 5 SEM and EDX analyses of pure lead

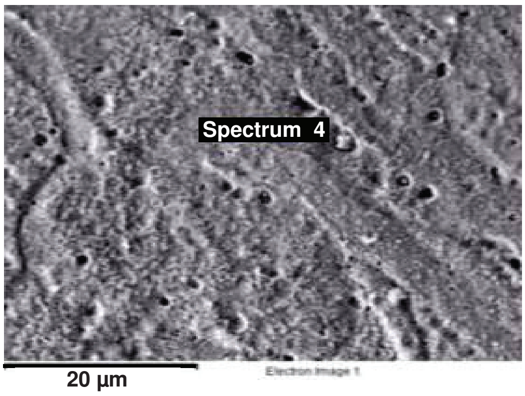


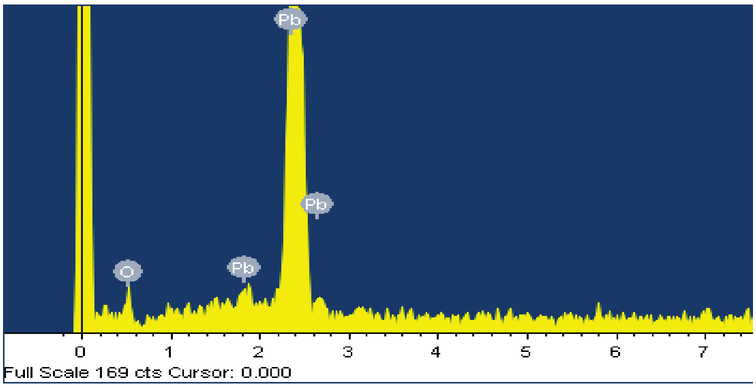
(a) SEM of Pb-1.25 wt.% Sb (b) EDX Pb-1.25 wt.% Sb





(a) SEM of Pb-1.25 wt.% Sb - selected point (b) EDX of Pb-1.25 wt.% Sb - selected point





a) SEM of Pb-1.25 wt.% Sb - selected point - matrix (b) EDX of Pb-1.25 wt.% Sb - selected point - matrix

Figure 6 SEM and EDX of Pb-1.25 wt.% Sb alloy

Further investigations by EDX revealed that the darker spots in the above figures are rich of antimony element while the matrix is lead. The elemental analysis was carried out in different representative area. The difference on atomic number between Pb and Sb gives a sharp contrast between the Pb matrix and solid solution of Sb in SEM images. According to the phase diagram Pb-Sb system and EDS results, the dark spot corresponds to the antimony solid solution with the composition of 1.25 wt.% and the bright matrix phase corresponds the lead. **Figure 6** shows the existence of antimony in the bright grey phase, which illustrates the precipitation of antimony in matrix of lead. These SEM/EDX observation and analysis was useful to understand the solidification process of Pb-1.25 wt.% Sb alloys and explore the relationship between the tensile strength of Pb-Sb alloy with the structure.

4. CONCLUSIONS AND FUTURE WORK

In this study, the influence of an alloying element on the microstructure and mechanical properties of lead 1.25 wt.% antimony alloys were investigated.

From the experimental results and their analysis, the following conclusions can be drawn:

- The addition of antimony as an alloying elements improve the tensile strength of the continuous cast lead alloy. The tensile strength increases from 17 MPa for pure lead to 29 MPa when 1.25 wt.% Sb was added to the lead. This improvement was a consequence of the observed Pb precipitated antinomy rich particles in the microstructure of lead using OM and SEM/EDX tools.
- The addition of antimony results in a decreases in the elongation percentage. It was found that the addition of 1.25 wt.% antimony into the pure lead reduces its elongation from 41% to 14%.

- The effect of addition of antimony on mechanical properties of lead-antimony alloys is mainly due to the solid solubility of the antimony.
- The fracture of lead was ductile with necking. The Pb-1.25 wt.% Sb is still ductile, but less so than the pure Pb.
- The average grain size analysis using Jeffries planimetric method shows the grain size of the pure lead alloy is reduced by adding the antimony. Grain-size reduction is mainly due to solid-solution alloying.
- As for future work, this research can be extended by investigation into the influence of alloying elements on electrical conductivity (EC) of continuous cast lead alloy.

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