

Investigation of the effects of heat treatment on the microstructure and mechanical properties of Pb-Sb alloy used in fabrication of anode spines for high-capacity lead-acid batteries

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ABSTRACT

The as-cast Pb-Sb alloy typically exhibits a heterogeneous microstructure and significant residual stress, rendering it susceptible to structural failure under external mechanical loads. This study demonstrates that heat treatment effectively homogenizes the microstructure, eliminates residual stress, and enhances the alloy's suitability for subsequent processing stages in the fabrication of anode electrodes for high-capacity lead-acid batteries. Post-heat treatment, the Pb-Sb alloy achieves an average hardness of 13.4 HV, a tensile strength of 31.67 MPa, and an equiaxed grain structure with an average grain size of 0.0164 mm.

Keywords: Lead-acid battery; Anode spine; Pb-Sb alloy.

1. INTRODUCTION

Currently, approximately 70–80% of global lead production is utilized in the battery and accumulator manufacturing sector. Despite the emergence of advanced battery technologies, lead-acid batteries remain prevalent due to their straightforward production process, abundant raw material availability, cost-effectiveness, and adaptability in manufacturing [1, 2]. Within high-capacity lead-acid batteries, the anode spine serves as a critical structural component, providing mechanical support to the active electrode material while functioning as a conduit for uniform current distribution across the electrode. In practical applications, the anode spine is typically fabricated from lead alloys, as pure lead exhibits low hardness, excessive ductility, and insufficient strength. Lead alloys employed for anode fabrication must possess not only favorable electrochemical properties but also adequate hardness and durability to resist mechanical and thermal stresses encountered during production and operation.

Table 1. Chemical composition of the Indian anode spine.

Composition, %	Sn	Sb	Bi	Cu	As	Se	S	Pb
Anode spine	0.2184	2.3369	0.0035	0.0315	0.1866	0.0570	0.0047	The rest

Lead-antimony (Pb-Sb) alloys, with antimony content ranging from 1–12%, are widely adopted as anode spine materials in various lead-acid battery types, including those used in automotive, stationary uninterruptible power supply (UPS), marine, forklift, and mining applications [1, 5, 6]. In military contexts, high-capacity lead-acid batteries are integral to naval vessels, with countries such as the Russian Federation and India producing batteries exceeding 18,000 Ah in capacity. Achieving such high capacities necessitates proportionally large anode spines, which must exhibit exceptional durability to support both their own mass and the substantial volume of active electrode material. Additionally, during operation, the anode spine is exposed to a highly corrosive

acidic environment, requiring a stable and homogeneous microstructure to mitigate localized corrosion and prevent structural degradation. Consequently, heat treatment studies on anode spines tailored to specific battery types have garnered significant attention from manufacturers worldwide, with findings being actively integrated into production processes [2].

This study presents the outcomes of heat treatment investigations on Pb-Sb alloys designed for the anode spines of high-capacity lead-acid batteries. Furthermore, the results are benchmarked against comparable samples from India to provide a comprehensive evaluation.

2. EXPERIMENTS AND RESEARCH METHODS

2.1. Research equipment and supplies

The experimental setup included the following: a Leiton 1400 °C furnace (Germany), a heating oven (Vietnam), an analytical balance (Japan), a metal cutting machine (Netherlands), an IR-AHS0 remote temperature measuring device (Vietnam), a two-part mold with an integrated heating element for continuous casting, and a grinding and polishing machine (Netherlands).

The experiments utilized the following materials: Pb-Sb alloy ingots (Vietnam) with an antimony content of 2–4%; pure lead ingots (Vietnam) with a purity of Pb \geq 99.95%; pure tin ingots (Vietnam) with a purity of Sn \geq 99.75%; acetic acid (C₂H₄O₂, pro analysis [PA], Germany); hydrogen peroxide (H₂O₂, PA, Germany); glycerol (C₃H₈O₃, PA, Germany); and nitric acid (HNO₃, PA, Germany).

2.2. Experiment

According to the results presented in table 1, the chemical composition of the anode spine corresponds closely to the U.S. lead-antimony alloy standard UNS L52710. The typical composition of UNS L52710 is as follows: Sb 2.0%, Sn approximately 0.3%, As approximately 0.15%, with trace impurities constituting the remainder, and the balance being Pb. Based on this target composition, raw materials were selected and calculated for smelting, including a lead-antimony alloy with an Sb content of 2–4% (average 3%, containing 0.2% As), pure lead (Pb \geq 99.95%), and pure tin (Sn \geq 99.75%). Empirical burn-off rates during smelting were estimated at approximately 1.5% for Pb, 1% for Sb, 1% for Sn, and 1% for As.

Samples were cast using a two-part mold made of S45C steel, with dimensions of 8 mm in diameter and 250 mm in length. The as-cast sample, without heat treatment, was designated M0. Heat treatment was conducted at temperatures of 160 °C (sample M1), 180 °C (sample M2), and 200 °C (sample M3), each maintained for 1 hour. Subsequently, the samples underwent microstructural analysis, and their hardness and tensile strength were measured for comparative evaluation.

For benchmarking, Indian anode spine samples were similarly analyzed for microstructure and hardness.

2.3. Research methods

The study employed standard metallurgical research techniques, including the following: emission spectrum analysis using a Metal Lab 75/80J MVU-GNR device (Italy); Vickers hardness (HV) measurement conducted on a Duramin-4 device (Japan); tensile strength measurement performed on a WDW-100Y device (China); and metallographic analysis observed via an Axio Image A2M optical microscope (Germany).

The grain area and microstructure evaluation were determined through the Planimetric procedure. To perform this technique, a proper magnification was selected. A circle was drawn on the microscopic image, 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. In there: n_1 - Number of grains completely

inside the test circle; n_2 - Number of grains intercepting the circle. Number of particles: $NA = n_1 + (n_2/2)$. The area of the circle is A . The average grain area is $A/NA \text{ mm}^2$. The average grain size is determined by $d = (A)^{1/2}$.

3. RESULTS AND DISCUSSION

3.1. Results of microstructure and hardness analysis of Indian anode spine

The chemical composition analysis results for the anode spine of a high-capacity lead-acid battery from India are presented in table 1. Based on these findings, the chemical composition of the anode spine aligns closely with the U.S. lead-antimony alloy standard UNS L52710. The hardness and tensile strength of the anode spine were evaluated, with the results detailed in table 2.

Table 2. Hardness, tensile strength of the Indian anode spine.

Model name	Hardness (HV)			Medium hardness (HV)	Tensile strength (MPa)			Average tensile strength (MPa)
	L1	L2	L3		L1	L2	L3	
Anode spine	13.9	14.1	13.9	13.97	34	32	34	33.33

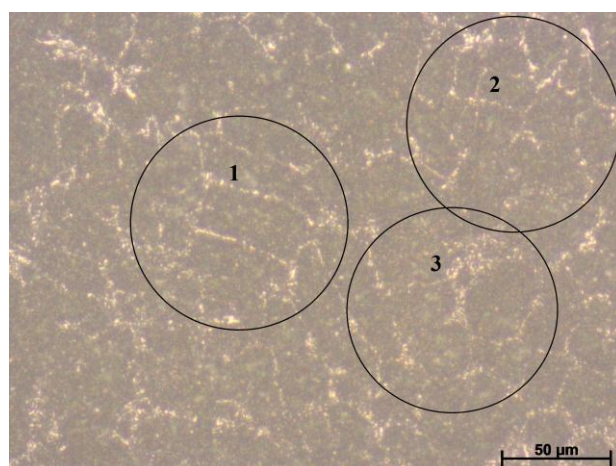


Figure 1. Microscopic image of Indian anode spine, 200x.

According to the results in table 2, the average hardness of the anode spine is 13.97 HV, and the average tensile strength is 33.33 MPa. Under operational conditions, the anode spine is continuously subjected to tensile stress and fatigue. Consequently, the material may undergo a degree of strain hardening, potentially resulting in a modest increase in hardness [3]. However, provided the material remains within its elastic limit, this increase is likely to be minimal. The microstructure of the anode spine sample is illustrated in figure 1. Microscopic examination reveals a uniform crystal grain structure with relatively fine grains. Smaller, finer grains increase the grain boundary area, which impedes dislocation movement during plastic deformation, thereby enhancing material toughness. Grain size was quantified using the Planimetric procedure (ASTM E-112) [1]. For this method, a suitable magnification (typically 200x) was selected, and a circle of a specified diameter was overlaid on the microscopic image. Grains entirely within the circle were assigned a weighting factor of 1, while those intersecting the circle's perimeter were assigned a factor of 0.5. The average grain size was then calculated. For the anode spine microstructure, draw 3 circles with a diameter of 50 μm on the microscopic image of figure 1, the number of counted crystal grains is 8, 8, 7, respectively. The calculated average grain area is 0.00026 mm^2 . So, the average grain size is 0,0161 mm.

3.2. Effect of heat treatment on the microstructure of Pb-Sb alloy

In this study, all Pb-Sb alloy samples were prepared from a single casting batch, ensuring a relatively uniform chemical composition across the samples. Consequently, chemical composition analysis was performed on only one representative sample. The composition of the as-cast Pb-Sb alloy is presented in table 3.

Table 3. Chemical composition of as-cast Pb-Sb alloy samples.

Composition, %	Sn	Sb	Bi	Cu	As	Se	S	Pb
Cast Pb-Sb alloy	0.2577	2.4895	0.0028	0.0249	0.1913	0.0487	0.0051	The rest

The chemical composition analysis revealed that the as-cast Pb-Sb alloy sample closely corresponds to the U.S. standard UNS L52710 [3].

To examine the microstructure, the samples were subjected to a sequence of preparation steps: coarse grinding, fine grinding, polishing, and etching in accordance with ASTM E407-07. The etching solution consisted of 75 mL of acetic acid ($C_2H_4O_2$), 25 mL of 30% hydrogen peroxide (H_2O_2), and 15 mL of glycerol ($C_3H_8O_3$), applied for 15 minutes. Subsequently, the samples were dried and cleaned using 70% nitric acid. Microstructure images of the alloy samples in various states are presented below.

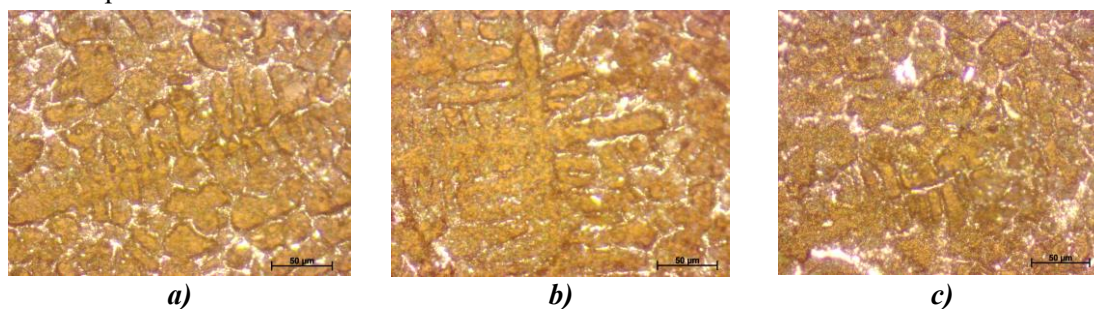


Figure 2. Metallographic micrograph of untreated Pb-Sb alloy M0, x200 (a, b, c are different positions on the cross-section of the sample, x200).

According to the results presented in figure 2, the microstructure of the untreated as-cast sample exhibits a dendritic morphology, resembling a tree branch or fishbone structure. This configuration is indicative of a heterogeneous microstructure, characterized by significant residual internal stress. During subsequent use, such castings are prone to failure under relatively low external loads, as the combination of external stress and pre-existing internal stress may exceed the strength threshold of the material [1]. In the dendritic regions formed during solidification from the liquid alloy, the primary branches are enriched with Pb, while the terminal branches exhibit a progressively lower Pb content [1]. The surrounding non-dendritic regions, which are Sb-rich, often transform into grain boundaries and phase boundaries following heat treatment. The spacing between dendritic branches, as observed in figures 2a, 2b, and 2c, predominantly falls within the range of $\leq 35 \mu\text{m}$ and appears relatively uniform. This inter-branch spacing and its uniformity influence the resulting crystal grain size during heat treatment. Smaller and more consistent spacing correlates with finer grain sizes, reducing the propensity for cracking and improving the physical and mechanical properties of the material.

The EDS analysis of the dendritic region and the surrounding region is shown in figure 3. Diagram 3a is the result of the analysis of the dendritic region, diagram 3b is the result of the analysis of the surrounding region. A small Sn peak is also observed in the diagram, indicating that there is a small amount of Sn in the alloy. This confirms that the precipitation of SbSn is likely to occur in the Pb-Sb alloy.

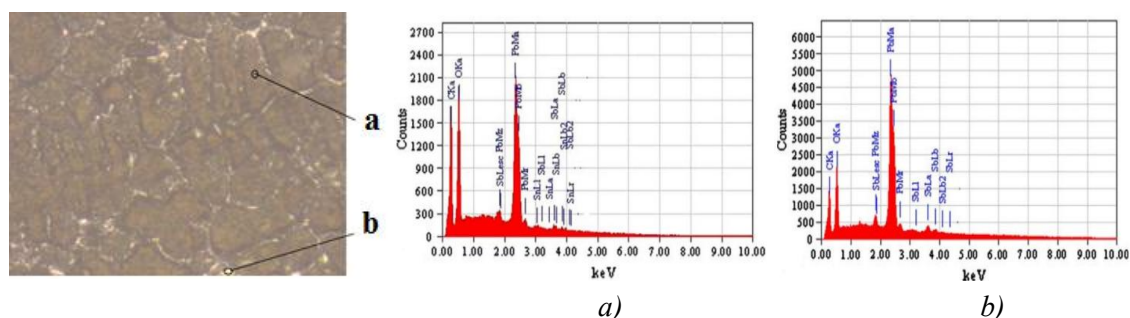


Figure 3. EDS diagram of the dendritic region (a-Pb rich) and surrounding region (b-Sb rich) of the untreated Pb-Sb alloy assemblies.

The microstructures of samples subjected to different heat treatment conditions are illustrated in figure 4. Following heat treatment at 160 °C, 180 °C, and 200 °C, the non-equilibrium dendritic crystal structure transforms into a uniform, fine-grained structure. This refined microstructure reflects characteristics of an equilibrium state, consistent with principles of physical metallurgy.

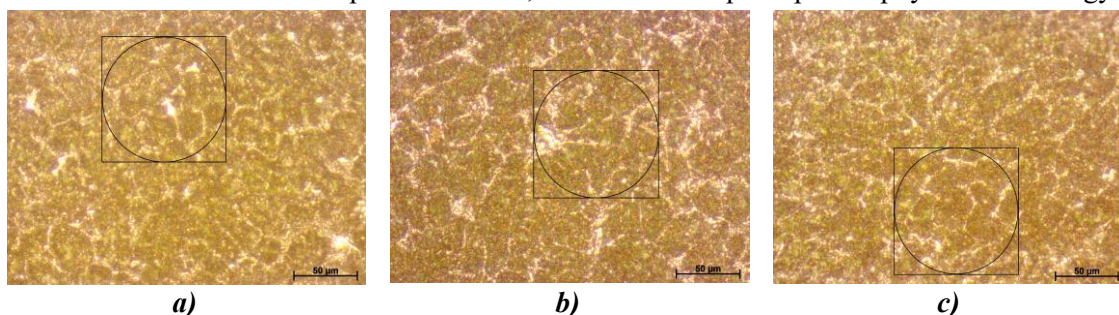


Figure 4. Metallographic micrographs of Pb-Sb alloy samples after heat treatment (a-temperature 160 °C, b-temperature 180 °C, c-temperature 200 °C, x200).

Evaluate the grain area according to the Planimetric procedure (ASTM E-112) by drawing 50 μm diameter circles on the images in figure 4. The average grain area is shown in table 4.

Table 4. Average grain size of Pb-Sb alloy samples treated at different temperatures.

Sample	Processing temperature (°C)	Average grain area (mm ²)	Average grain size (mm)
M1	160	0.000236	0,0154
M2	180	0.000268	0,0164
M3	200	0.000294	0,0171

According to the data in table 4, the average grain size increases with rising heat treatment temperature. Heat treatment at 160 °C yields the smallest average grain size of 0.0154 mm; however, examination of the entire cross-section of the sample reveals localized regions retaining dendritic crystals, indicating that the heat treatment at this temperature is incomplete. At 180 °C, the resulting grain structure consists entirely of regular, uniform, and fine grains, with no residual dendritic regions observed, the average grain size is 0,0164 mm. When the temperature is elevated to 200 °C, the grain structure remains regular, the average grain size is 0,0171 mm, but localized areas exhibit abnormally large grains. This phenomenon arises from the coalescence of adjacent grains sharing common boundaries, leading to the formation of larger grains - a process indicative of rapid grain growth driven by elevated temperature, commonly referred to as overheating. Such abnormal grain growth is detrimental to the microstructure and mechanical properties of the alloy and should be avoided during heat treatment. Consequently, heat treatment at 180 °C provides the optimal microstructural outcome for the Pb-Sb alloy.

3.3. Effect of heat treatment on the mechanical properties of Pb-Sb alloy

The hardness and tensile strength test results for the samples, both before and after heat treatment, are presented in table 5. Measurements were conducted at three distinct locations on each sample, and the average values were calculated. The hardness of the as-cast M0 sample, prior to heat treatment, was notably high at 22 HV. This elevated hardness corresponds to the heterogeneous dendritic microstructure and significant residual internal stress observed in the untreated state.

Table 5. Hardness and tensile strength of Pb-Sb alloy samples before and after heat treatment.

Sample	Hardness (HV)			Medium hardness (HV)	Tensile strength (MPa)			Average tensile strength (MPa)
	L1	L2	L3		L1	L2	L3	
M0	22.1	23.0	22.0	22,3	30	29	29	29.33
M1(160,1h)	14.2	14.0	13.1	13.8	33	32	32	32.33
M2(180,1h)	13.2	13.0	14.1	13.4	32	32	31	31.67
M3(200,1h)	12.2	12.9	12.0	12.3	30	31	30	30.33

Sample M1, heat-treated at 160 °C for 1 hour, exhibited an average hardness of 13.8 HV. Under identical treatment durations of 1 hour, samples heat-treated at 180 °C and 200 °C yielded hardness values of 13.4 HV and 12.3 HV, respectively. Evidently, heat treatment significantly reduced the hardness of the Pb-Sb alloy samples. This reduction is attributed to the transformation of the heterogeneous dendritic microstructure and substantial residual internal stress into a uniform, equilibrium grain structure, effectively eliminating residual stress. The decrease in hardness from 22.3 HV to 13.8 HV at 160 °C indicates a pronounced transition from a dendritic to a regular grain structure at this temperature. However, as the heat treatment temperature increased from 160 °C to 180 °C and 200 °C, the hardness exhibited only a slight further decline. This suggests that at temperatures between 180 °C and 200 °C for 1 hour, the microstructure no longer undergoes a significant transformation from dendritic to regular grains; rather, the existing regular grains undergo growth. These findings align with the microstructural analysis presented in section 3.2.

Regarding tensile strength, the as-cast M0 sample, without heat treatment, displayed the lowest value of 29.33 MPa, reflecting the presence of significant residual stresses that rendered the material susceptible to failure under reduced external loads. Post-heat treatment, tensile strength increased, reaching a maximum of 32.33 MPa at 160 °C, followed by 31.67 MPa at 180 °C, and 30.33 MPa at 200 °C. The difference in tensile strength between the 160 °C and 180 °C treatments was minimal. Consequently, heat treatment at 180 °C is identified as yielding the most favorable overall mechanical properties for the alloy.

4. CONCLUSIONS

Following heat treatment, the quality of the castings was markedly enhanced. The initial heterogeneous dendritic microstructure, characterized by substantial residual internal stress, was transformed into a uniform, equilibrium, and fine-grained structure. This resulted in a hardness of 13.4 HV, a tensile strength of 31.67 MPa, and an average grain size of 0.0164 mm. The refined microstructure of the Pb-Sb alloy not only improved the overall physical and mechanical properties of the material but also established a stable structure, mitigating the risk of corrosion when the anode spine is exposed to the electrolyte solution during subsequent use.

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TÓM TẮT

Nghiên cứu ảnh hưởng của quá trình xử lý nhiệt đến tổ chức tế vi và cơ lý tính của hợp kim Pb-Sb dùng cho chế tạo sườn cực dương ắc quy chì-axit dung lượng lớn

Hợp kim Pb-Sb sau khi đúc thường có tổ chức tế vi không cân bằng, ứng suất dư lớn, dễ gây ra phá hủy kết cấu khi chịu tác động của ngoại lực. Kết quả nghiên cứu cho thấy quá trình xử lý nhiệt đã tạo ra được tổ chức cân bằng, khử bỏ ứng suất dư, thuận lợi cho các nguyên công tiếp theo trong tiến trình chế tạo điện cực dương ắc quy chì-axit dung lượng lớn. Hợp kim Pb-Sb sau khi xử lý nhiệt có độ cứng trung bình 13.4 HV, độ bền kéo 31.67 MPa, tổ chức hạt tinh thể đều trực có kích thước trung bình 0.0164 mm.

Keywords: Ắc quy chì-axit; Sườn cực dương; Hợp kim Pb-Sb.