Novel Approach for Surface Roughness Quantification and Optimization of Cast-on-strap Lead-antimony Alloy via Two-point Statistical Correlation Function

by

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ABSTRACT

Surface roughness has a negative impact on several failures of materials medium. It can accelerate the pitting corrosion, increase effective heat transfer and increase the rate of effective charge loss. However, controlled surface roughness maybe desirable in many situations. The automotive lead-acid battery is very sensitive to such effects. The cast-on-strap machine has the largest effect on the surface roughness of the lead-antimony alloy in our case study. The two-point correlation function is an efficient characterization tool for two-phase heterogeneous materials. Considering the nature that the two-point correlation function is a spatial statistical function, it cannot distinguish between a two-phase material or materials with surfaces containing protrusion of distinct heights. A case study to examine its capability in quantifying surface roughness is introduced. The possibility of applying a simulated annealing procedure to optimize using information obtained from the two-point correlation function is investigated. Outcomes show a successful surface representation, as well as optimization, that agrees with the initially proposed hypothesis.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>iv</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION AND OVERVIEW</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Lead-acid Battery Materials</td>
<td>4</td>
</tr>
<tr>
<td>1.1.1 Alloying Materials Properties</td>
<td>4</td>
</tr>
<tr>
<td>1.1.2 Lead-Antimony Alloys</td>
<td>4</td>
</tr>
<tr>
<td>1.1.2.1 Microstructure of Pb-sb alloys</td>
<td>5</td>
</tr>
<tr>
<td>1.1.3 Lead-calcium-tin Alloys</td>
<td>6</td>
</tr>
<tr>
<td>1.1.3.1 Microstructure of Lead-calcium-tin Alloys</td>
<td>7</td>
</tr>
<tr>
<td>1.2 Lead-acid Battery Components</td>
<td>9</td>
</tr>
<tr>
<td>1.2.1 Positive Electrode</td>
<td>11</td>
</tr>
<tr>
<td>1.2.2 Negative Electrode</td>
<td>13</td>
</tr>
<tr>
<td>1.2.3 Separators, Poles, and Straps</td>
<td>14</td>
</tr>
<tr>
<td>1.3 General Failures of Lead-acid Batteries</td>
<td>15</td>
</tr>
<tr>
<td>1.3.1 Positive Plate Expansion</td>
<td>15</td>
</tr>
<tr>
<td>1.3.2 Positive Plate Corrosion</td>
<td>15</td>
</tr>
<tr>
<td>1.3.3 Negative Plate Sulfation</td>
<td>15</td>
</tr>
<tr>
<td>1.3.4 Water Loss</td>
<td>15</td>
</tr>
<tr>
<td>1.3.5 Acid Stratification</td>
<td>16</td>
</tr>
<tr>
<td>1.3.6 Extent of Fusion Between Plates and Strap</td>
<td>16</td>
</tr>
<tr>
<td>1.3.7 Open &amp; Closed Shrinkages in Poles and Straps</td>
<td>16</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Comparison of the Different Battery Technologies in Terms of Volumetric and Gravimetric Energy Density.</td>
<td>2</td>
</tr>
<tr>
<td>1.2. (A) Electrochemical Process of Lead-acid Battery. (B) Current-potential Representation of Positive and Negative Electrodes.</td>
<td>3</td>
</tr>
<tr>
<td>1.3. Pb-sb Phase Diagram</td>
<td>5</td>
</tr>
<tr>
<td>1.4. Microstructure of (a) 2 wt% Sb (b) 12 wt% Sb (c) 17 wt% Sb</td>
<td>6</td>
</tr>
<tr>
<td>1.5. Pb-ca Alloy Phase Diagram</td>
<td>8</td>
</tr>
<tr>
<td>1.6. Changes in (a) Yield Strength, (B) Ultimate Tensile Strength, (C) Creep Resistance According to Ca%sn% Content</td>
<td>8</td>
</tr>
<tr>
<td>1.7. Maintenance-free Lead-acid Battery</td>
<td>9</td>
</tr>
<tr>
<td>1.8. Lead-acid Battery Expanded the Grid and Pasted the Expanded Grid</td>
<td>12</td>
</tr>
<tr>
<td>1.9. Lead-acid Battery Poles and Strap</td>
<td>15</td>
</tr>
<tr>
<td>1.10. Corroded Lead-acid Battery Pole Operated for 8 Months</td>
<td>18</td>
</tr>
<tr>
<td>2.1. Materials Tetrahedron</td>
<td>19</td>
</tr>
<tr>
<td>2.2. Schematic of Random Two-phase Material</td>
<td>20</td>
</tr>
<tr>
<td>2.3. Design Domain for Two-phase Material Each Cube Represents a Finite Element of One Phase</td>
<td>21</td>
</tr>
<tr>
<td>2.4. Different Correlation Functions Representation in a Two-phase Material</td>
<td>27</td>
</tr>
<tr>
<td>3.1. Schematic Illustration of General Steps of Materials Quantifications</td>
<td>29</td>
</tr>
<tr>
<td>3.2. Schematic Illustration of Atomic Force Microscopy Technique</td>
<td>30</td>
</tr>
<tr>
<td>3.3. AFM Results Recorded of Surface Topography of Pb-sb Sample at 100 nm</td>
<td>31</td>
</tr>
</tbody>
</table>
3.4. Binary Image of Surface Topography of Pb-sb Sample with $\phi_i=0.038$ ..................32

3.5. Data Collected for the Two-point Correlation Function and Lineal-path Function for Surface Topography of Pb-sb Sample with Approximate $\phi_i=0.038$ .................................................................33

4.1. Visual Representation of Pixel Swapping or Exchange Procedure to Generate New Microstructure from Old One. .................................................................35

4.2. Visual Representation of Simulated Annealing Optimization Procedure. The Acceptance of Energy-increasing Trial Microstructure Allows the System to Escape from Local Energy Minima and Thus, Increases the Probability of Convergence to the Global Minimum........................................36

4.3. Reconstruction Results Using Two-point Correlation Function..........................37

4.4. Optimized 3-D Surface Reconstruction and 2d Surface Slices along with Main Directions for Pb-sb Sample ........................................................................37
CHAPTER 1
INTRODUCTION AND OVERVIEW

Energy is the main issue that is limiting our future technologies. Almost all industries experience this limitation, especially with the upcoming huge, estimated use due to climate change. So, our modern societies are undergoing an increasing and continuous demand for energy. Consequently, energy storage devices will be the key factor in this journey. In recent years, the urge for energy storage products is growing exponentially. There would be no interest in producing more energy unless it can be stored. The fact that energy can be transformed from one form to another, allows it to be stored in different forms. Electrical energy which is leading this energy revolution is produced by both fossil energy and clean renewable energy.

In this dissertation, I will use a novel technique of a microstructure quantification method to quantify the alloy used for battery connectors or as we call them “straps” and poles. Even more, I used the technique to find the optimal design for such an alloy. As a start, I will give a detailed idea about the widely used automotive batteries and the statistical correlation functions. This case study may be considered a step forward to implement a machine-learning in the lead-acid batteries industry.

As we know, the main concept of batteries is that they can store electrical energy in a form of electrochemical one and convert it to electrical when it is needed. We shall say that batteries are the correlative inseparable factor to energy production. The fact depending on this principle allowed the batteries to be a secondary source of energy and is being used in daily life in the automotive industry and allowed electric vehicles to exist.
as they may fully or partially be powered by batteries. However, a short introduction about lead-acid batteries is included (not a detailed one) just to give a hint about the application that we have used correlation functions to interpret.

Lead-acid batteries have the largest global market share, this outstanding secondary power source has a wide range of applications in automotive, wind energy storage, and solar energy storage. Despite its low energy and power density compared to other various types of batteries, as shown in Fig. 1.1., it has a low-cost and secure large-scale recycling system.

Fig. 1.1. Comparison of the different battery technologies in terms of volumetric and gravimetric energy density. [1]
In 1850 LAB was first introduced by Gaston Planété, it was made of two electrodes (positive and negative) separated by an electrolyte, the electrochemical reaction occurs at the two interfaces of the electrodes and then the difference in potential between the positive and the negative electrodes creates Electro-Motive Force. By applying a load between the two electrodes, electric current flows through the load. Lead showed the highest cell voltage in an aqueous electrolyte (H$_2$SO$_4$), the positive electrode of the LAB is lead dioxide (PbO$_2$) and the negative electrode is sponge lead (Pb). During the discharge, the molecules of the diluted H$_2$SO$_4$ split into SO$_4^{2-}$ and 2H$^+$, in the negative electrode the SO$_4^{2-}$ loses 2e$^-$ and becomes radical, then reacts with the sponge lead Pb and forms the lead sulfate PbSO$_4$. In the positive electrode interface the 2H$^+$ attracts 2e$^-$ from PbO$_2$ to become an H$_2$ molecule, then reacts with PbO$_2$ and forms lead sulfate PbSO$_4$ and water H$_2$O. The reaction is reversed during charging as shown in schematic Fig. 1.2 (A). By charging the PbSO$_4$ will be converted back into Pb and PbO$_2$, higher current will give increase the hydrogen and oxygen gassing and a continuous loss in water from the electrolyte as in Fig. 1.2 (B). [2] The schematic shows the possibility of oxygen and hydrogen overpotentials increasing with increasing current, the high oxygen overpotential influence the conversion of PbSO$_4$ to PbO$_2$ before the appropriate evolution of oxygen. [2]
1.1 Lead-acid Battery Materials

1.1.1 Alloying Materials Properties

Lead alloy is the main component used in the LABs grids, straps, and battery connectors. The battery grid plays an important role in battery operation, it works as a carrier for the plate’s active materials and distributes the electric current to every point of the plate.
Required properties of LABs grids:

1. Mechanical properties: the positive plates function at high potentials and experience a volume expansion, part of the lead remains unoxidized. Corrosion layer formed on the positive plate, the volume expansion differs between the oxidized and unoxidized lead i.e., the corrosion layer from oxidized lead is (22% - 23%) larger than that from the unoxidized lead. Grids should have sufficient hardness and tensile strength to accommodate the stresses caused by different volume expansions of the corrosion layer and the thermal and mechanical strains that occur during the manufacturing process by the volume change in the discharge and recharge cycles without permanent deformation. [3]

2. Electrical properties: grids function similar to the blood system of the human body, it distributes the current to every part of the plate paste. So, they must have high electric conductivity to minimize possible voltage losses. [3]

3. Chemical properties: good chemical resistance is a demand for LABs grids as they are in direct contact with sulfuric acid. Many elements are added to alloys before casting grids to enhance their properties, Se, Ni, Te, and Mn in the negative plate alloy reduce the overpotential of the hydrogen evolution. While Bi, Ag, and Zn restrict the hydrogen evolution, Bi delays the oxygen evolution on the positive plate as well. [3]
1.1.2 Lead-Antimony Alloys

Antimony is a substantial alloying element used in lead-acid battery components including grids, straps (connectors), poles, and terminals. It is added to support and hardens grids and to grant desirable castability and mechanical properties for the cast-on-strap process. Antimony was used in the range of 0% to 12% in different battery components. Earlier 1880s, lead-antimony alloys occupied an outstanding role in the lead-acid battery industry due to their freezing range and good castability. The addition of antimony to lead stiffens the alloy, adds some rigidity to it, and makes the alloy bearable to process using novel cast-on-strap machinery.

Depending on properties lead-antimony alloys can be separated into:

1. **High-antimony alloys 9%-11% Sb.** Higher antimony relates to better casting properties and better conservation of positive active materials during cycling which are directly related to enhanced lifecycle and larger production rates. Therefore, high antimony alloys were used in long spine and tubular battery grids. Also enhances the creep strength properties of the grids. [3]

2. **Medium-antimony alloys 4%-7% Sb.** Used in balanced high capacity and lifespan traction batteries that only require low maintenance. Relatively good castability leads to higher productivity of casting machines.

3. **Cast-on-strap alloys 2.9%-4% Sb.** Used in battery terminals and straps connecting positive plates and negative plates. These alloys need additives such as copper, arsenic, tin, sulfur, and selenium. Fluidity and easily welding are required for these alloys.
4. **Low-antimony alloys 0.5%-2.7% Sb.** Used in continuous casting grids.

1.1.2.1 Microstructure of Pb-sb Alloys

According to the Pb-Sb phase diagram, eutectic phase starts at 11.1% Sb at an eutectic temperature of 252.2 °C which is not required in battery manufacturing. Battery industry only uses Sb content below this ratio in the pre-eutectic phase. The α-Pb phase is dependent on Sb% and temperature. As the temperature of the Pb-Sb melt decreases, α-Pb grains form first, then Sb grains enhance the alloy. On cooling below eutectic temperature, solubility of Sb in α-Pb decreases and coarse grains of β-Sb begin to appear until a solubility limit of 0.03 % is reached at 25 °C compared to 3.5 % at the eutectic temperature. \(^{[3]}\) Tendency to coarse grains solidification in low antimony content (lower than 5 %) gives rise to hot cracks and brittleness of the casted products. Selenium and sulfur were investigated as grain refiners for such antimony alloys.

![Fig. 1.3. Pb-Sb Phase Diagram](image-url)
Fig. 1.4. Shows the microstructure of different Sb wt%, the white dendrites are the α-Pb and the darker regions represent the eutectic phase. High Sb content increases β-Sb grains, these grains increase the hardness and castability of grids. At 2 wt% Sb, fast cooling shows a change in concentration of Sb to reach equilibrium, β-Sb increases, and white dendrites are formed along the cooling direction. With the increase of Sb content to reach mostly eutectic phase at (b) by cooling the alloy showed different mechanical properties, higher hardness, and better castability.

However, it was empirically observed that all of yield strength, ultimate tensile strength, creep resistance, and corrosion resistance of casted grids are enhanced as we go up with the Sb% to 11%.

Fig. 1.4. Microstructure of (a) 2 wt% Sb (b) 12 wt% Sb (c) 17 wt% Sb. [4]
On the other side, as we go up with Sb wt% there will be a low overpotential on the negative electrode which results in extreme self-discharge in negative active material causing early battery failure.

1.1.3 Lead-calcium-tin Alloys

A major drawback of using Pb-Sb alloys in battery current collectors is Sb has a low overpotential for hydrogen gassing as antimony particles leave a positive grid by corrosion and go through negative active material lowering its hydrogen overpotential. This is not environmentally friendly because we need thicker plate grids which contribute to the toxicity of lead and affects the lifespan of lead batteries negatively by high water consumption of the electrolyte. Pb-Ca-Sn alloys were introduced to solve this problem, and the use of such alloys introduced better and thinner plates for lead-acid batteries. On the other side, those alloys allowed a new concept of grid manufacturing other than gravity casting. Pb-Ca-Sn alloys opened the engineers’ eyes to continuous casting methods. Continuous casting methods such as expanded, rotary expanded, and con-casting technologies use a much lower amount of lead due to thinner plates and don’t consume the electrolyte like Pb-Sb alloy grids allowing the production of maintenance-free batteries.

At first, calcium was used in grid alloy manufacturing. It was a good solution for water consumption in the electrolyte and participated in a semi-maintenance-free battery, in the case of Pb-Sb batteries were needed to refill with water because of water loss problems. However, Pb-Ca alloy with 0.03% Ca showed poor mechanical properties
during casting, using Ca in the range of 0.03% to 0.15% has a good freezing range of 1–3
°C in contrast with 50–75 °C of Pb-Sb allowing for higher speed casting and continuous
casting technologies.[3] The main issue was the observation of large capacity loss only
after 30 to 40 battery cycles. Further investigations proposed that there was a side effect
at the grid interface with positive active material (PbO₂) creating a corrosion layer that
was rapidly growing in thickness and increasing ohmic resistance at the interface between
positive active material and grid. The addition of Sn was highly recommended then to
reduce this effect. [3]

1.1.3.1 Microstructure of Lead-calcium-tin Alloys

Pb-Ca phase diagram shows that near the melting point of Pb, there is a peritectic
reaction at low calcium content, and as the temperature is going down, the solubility of
Ca in α-Pb decreases reaching 0.01 wt% at room temperature. So, the possibility of
forming fine precipitation of Pb₃Ca compared to 0.1 wt% Ca before cooling and casting.
This causes large changes in microstructure and consequently mechanical properties of
such alloy. Increasing calcium content improved mechanical properties until it reached
0.07 wt% Ca which above it, the alloy suffered rapid corrosion rate because of the high
affinity to the oxygen of Ca. To reduce this effect Ca content was reduced to 0.06–0.08
wt% and Sn was used as an alloying element to improve the mechanical properties of the
alloy. Although the grain diameter decreases with increased Ca content, Sn addition
increases grain diameter. It was clear that the ratio between Ca wt% and Sn wt%
determines the mechanical properties of the alloy by changing grain sizes.
Sn addition to Pb-Ca alloy also decreased the corrosion layer thickness, making good contact between the grid and electrolyte. During oxygen evolution, it diffuses through the corrosion layer and oxidizes the grid. Sn increases the oxygen overpotential delaying the oxygen evolution and hence the corrosion of the grid. This increases the lifecycle of the positive plate. [3]
1.2 Lead-acid Battery Components

![Image of lead-acid battery components]

*Fig. 1.7. Maintenance-free lead-acid battery (Credits: German co. for manufacturing batteries)*

Lead-acid battery is an electrochemical system composed of a series of electrochemical cells with a nominal potential of 2.1 volts. Those 2.1-volt cells are connected in series, each cell contains a group of positive plates and negative plates which are separated by a micro-porous insulator such as polyethylene to avoid short-circuits between positive and negative electrodes, each group of positive plates is put
with a group of negative plates in the battery container and filled by an electrolyte of 5M H₂SO₄.

Lead-acid batteries are produced with different rated capacities depending on their applications. The utilization coefficient and mass of active material are the main factors that determine the battery capacity.

In discussing battery components, I will give a general idea of the manufacturing process of relatively new expanded plate technology as my focus is representing a case study of this type of battery. Battery manufacturing steps are included in the chart below.

![Battery Manufacturing Chart]

1.2.1 Positive Electrode

In expanded technology, current collectors (grids) are manufactured from the Pb-Ca-Sn alloy that was discussed earlier considering that positive plates have a thicker grid than negative to ensure proper battery life and reduce the effect of corrosion that correlated with high rates of oxygen evolution. Both positive and negatives electrodes
have the same grids alloy with different thicknesses and their active materials are first produced by pure lead ingots or cylinders oxidized with humid air in a ball mill (ball milling method) or pure lead melt in a presence of air (Barton-pot method) and turn to a mixture of PbO powder and Pb powder with a diameter of several microns. This powder then reacts with H₂SO₄ to be converted into lead oxide paste and forms tribasic lead sulfate (3PbO·PbSO₄·H₂O) and tetrabasic lead sulfate (4PbO·PbSO₄) phases. Tetrabasic-lead-sulfate or 4BS is the initial positive active material phase that converts to PbO₂ by charging. After pasting (coating) grids with PbO as shown in Fig. 8 plates are flash dried and then put into a curing chamber under certain humidity and temperatures to transform 3BS (initially formed in producing paste) into 4BS. The flash drier main function is to reduce the moisture content (9–11%) in the plate to the required content and dry the surface so that the plates do not stick to each other in the curing step. Residual moisture content is used in the curing step to oxidize the unreacted lead in the PbO paste. Depending on this moisture content and the curing program used, unoxidized lead (rest lead) can cause self-discharge to the battery if not talking into account in the charging step or even cracks may be initiated on the plates if the moisture content is not sufficient and cause early total battery failure.
After curing an adequate amount of 4BS and 3BS phases are formed, 4BS is a large needle shape crystal that improves the adhesion between the positive active material and the grid formed at an effective temperature > 80 °C and hence improves lifespan. However, 4BS crystals are more difficult and take a much higher time to fully convert into porous PbO$_2$ (positive active material). With the presence of the 3BS phase, there is a balance between cycling performance and a good formation of active materials.

By charging, the positive active material is highly porous PbO$_2$ to carry a portion of electrolyte inside its pores and allow moderate ions transport to and from the plate. It is highly recommended to have a good rate of PbSO$_4$ as it is needed in the reversible reaction of positive active material, so the formation process starts with a soaking step of 0.5–2 hours of battery with cured plates in dilute H$_2$SO$_4$ before applying computer charging program to transform 4BS and 3BS to lead sulfate.
The reactions that proceed during the positive active materials formation are represented by the following equations as proved in [3]

\[
PbO_2 + SO_4^{2-} + 4H^+ + 2e^- = PbSO_4 + 2H_2O \quad (1.1)
\]

\[
PbO_2 + HSO_4^- + 3H^+ + 2e^- = PbSO_4 + 2H_2O \quad (1.2)
\]

\[
2PbO_2 + SO_4^{2-} + 6H^+ + 4e^- = PbO.PbSO_4 + 3H_2O \quad (1.3)
\]

\[
4PbO_2 + SO_4^{2-} + 10H^+ + 8e^- = 3PbO.PbSO_4.H_2O + 2H_2O \quad (1.4)
\]

\[
3PbO_2 + 4H^+ + 4e^- = Pb_3O_4 + 2H_2O \quad (1.5)
\]

\[
PbO_2 + 2H^+ + 2e^- = PbO + H_2O \quad (1.6)
\]

\[
O_2 + 4H^+ + 4e^- = 2H_2O \quad (1.7)
\]

The formation process stabilizes amount of PbO₂ as an active material that totally transformed from cured Pb²⁺ compounds. During the battery processing (cycling), main reaction is 1.2. In case of battery discharge, PbO₂ dissolves into Pb⁴⁺ and Pb²⁺, Pb²⁺ ions react with HSO₄⁻ ions producing water, a side reaction of O₂ gas. In case of charging, the reaction in 1.2 is reversed, HSO₄⁻ ions dissolve, Pb²⁺ ions oxidize to Pb⁴⁺ and transformed to PbO₂.

\[
PbO_2 + HSO_4^- + 3H^+ + 2e^- \xrightarrow{(\text{Discharge})} PbSO_4 + 2H_2O \quad (1.8)
\]

1.2.2 Negative Electrode

Negative electrode active material is a highly porous, ductile, sponge-like lead. Fortunately, the negative plate production process is the same as the positive electrode production. It has a Pb-based alloy grid and PbO coating paste. Although positive and
negative electrodes have similar basic compounds, negative plate has different paste additives and a different curing program due to different PbSO₄ phases of interest.

i. Expander

Throughout the formation reaction of negative plate, an inevitable side reaction of continuously formed passivating PbSO₄ layer at the interface between negative plate and diluted sulfuric acid electrolyte. The passivating layer works as consumes charged ions preventing them from passing through to the high porous PbSO₄ in the bulk of the plate materials causing a substantial loss in battery capacity.

In order to solve this problem, “expander” materials shall be added to the component of PbO paste before coating the grids. Those expander materials basically contain [lignosulfonate + BaSO₄ + carbon black]. Lignosulfonate acts as a surfactant and inhibits passivating PbSO₄ crystals growth. BaSO₄ works as nucleation for PbSO₄ during discharge and helps make porous PbSO₄ uniformly distributed in the negative plate. Addition of carbon black increases surface area of the plate and hence the electrical conductivity and charge acceptance.

ii. Curing program

For 3BS pastes, the curing program does not require a high-temperature steaming step to convert 3BS to 4BS. Only we need steps for oxidation of residual free lead at a temperature below 70 and drying step to get rid of moisture content to avoid short-circuit failures.
iii. Negative active material

As mentioned above, negative active material is a high porous sponge Pb. Many reactions take place during the formation of negative plate as mentioned in [3]

\[ PbO + 2e^- = Pb + H_2O \] (1.9)

\[ 3PbO \cdot PbSO_4 \cdot H_2O + 8e^- + 8H^+ = 4Pb + H_2SO_4 + 4H_2O \] (1.10)

\[ PbO \cdot PbSO_4 + 4e^- + 4H^+ = 2Pb + H_2O + H_2SO_4 \] (1.11)

\[ PbSO_4 + 2e^- + 2H^+ = Pb + H_2SO_4 \] (1.12)

\[ PbSO_4 + 2e^- + 2H^+ = Pb + HSO_4^- + H^+ \] (1.13)

\[ 2H^+ + 2e^- = H_2 \] (1.14)

After formation under controlled temperature, electrolyte is replaced with more dense diluted sulfuric acid to reach specific gravity of 1.24 to 1.28. Equation 1.15 shows oxidation reaction occurs at the anode during discharge, sponge lead atoms are oxidized and reacts with sulfate ions forming PbSO₄ precipitation. At the charge state PbSO₄ dissolve into bivalent Pb and sulfate ions, as the battery has nearly fully charge, H₂ gas liberated during the reaction combining with O₂ from the cathode to form H₂O.

\[ Pb + HSO_4^- - 2e^- \rightarrow Pb^{2+} + SO_4^{2-} + H^+ \Leftrightarrow PbSO_4 \] (1.15)

\[ PbSO_4 \Leftrightarrow Pb^{2+} + SO_4^{2-} + H^+ + 2e^- \rightarrow Pb + HSO_4^- \] (1.16)

1.2.3 Separators, Poles, and Straps

A separator, from the name, it separates between positive and negative plates insides the galvanic cell. It is usually made of polymer (polyethylene) or glass fibres. Separator manufacturers must consider the following properties while designing new separator.
1. Insulator. [Should not conduct electricity, direct contact between opposite charged plates can cause short circuit or immediate high-rate self-discharge of the battery]

2. Porosity. [To allow the ionic transfer between plates]

3. Mechanical Resistance. [Volumetric expansion of active materials during charge-discharge cycles should be considered to avoid separator damage]

4. Chemical Resistance. [Battery cell is a serious corrosive media, separators shall have good corrosion resistance properties]

Poles and straps have the same alloy (our case-study). Poles are the terminals of the battery. Straps connect 2 V electrochemical cells to form 12 V battery and gather positive plates with each other and negative plates with each other in each single 2V battery cell.

Fig. 1.9. Lead-acid battery poles and strap. (Credits: German co. for manufacturing batteries)
1.3 General Failures of Lead-acid Battery

1.3.1 Positive Plate Expansion

PbSO$_4$ has a substantially larger volume than PbO$_2$ molecules, so as the battery is operating, continuous charge and discharge cycles produce excessive volumetric change. Positive plate expands with 92% of its original volume. Although, most of PbO$_2$ content is restored by recharging, the positive plate does not get back its original volume. Progressive expansion by cycling can initiate micro-cracks leading to total collapse at the end. At the anode, transforming Pb to PbSO$_4$, volume increases by 164%. However, tendency to expand has not been observed at the anode, sponge lead has better ability to sustain volumetric change than lead dioxide.

1.3.2 Positive Plate Corrosion

Accumulated corrosion of the positive grid occurs during oxygen gas evolution, some of oxygen atoms diffuse through PbO$_2$ and oxidize the grid to tet-PbO. Thickness of the corrosion layer is controlled by the electrical potential as it’s growing during oxygen gassing. Continuous growing in thickness also participates in plate volume expansion, loss in electrical conduction and hence lowers lifecycle numbers. Many factors affect the rate of corrosion such as, grid alloy composition, temperature during battery operation and the microstructure. Sn content is the key factor that enhances mechanical properties and corrosion resistance on the grid. Corrosion is known as a major failure resulting in decomposition of the positive plate.
1.3.3 Negative Plate Sulfation

When the battery is kept open circuit, partially or fully discharge, PbSO₄ formed during the discharge grow in size lowering the surface area of sulfate crystals. Charge acceptance and electrical conductivity are then decreased. Activation of the battery with high electric current is required to decompose those crystals and convert them partially to PbO₂. However, progressive sulfate crystal growth reduces battery capacity and volume expansion resulted from large crystals can mechanically deform the plate losing the adhesion between active material and negative grid.

1.3.4 Water Loss

Overcharge of the battery increases oxygen and hydrogen gassing rates at both plates. Excessive gassing rate causes water loss, electrolyte level lower and the surface of active material exposed to the electrolyte decreases and hence no chemical reaction. Water decomposition rate in influenced by the temperature (impurities of the electrolyte especially those which increase the internal resistance can increase the electrolyte temperature). Higher gas pressure inside the battery leads to battery explosion.

1.3.5 Acid Stratification

As the battery recharges, ions H⁺ and SO₄²⁻ recombine forming H₂SO₄. It is a fact that denser component of a solution goes down to the container. So, H₂SO₄ of higher relative density goes down lower density H₂SO₄ inside each cell leading to non-uniformity in reverse chemical reaction of active material and lead sulfate. As a consequence of this difference of density and rate of reaction between lower and higher
levels of electrolyte there would be nonuniform corrosion (accelerated and lower level of the plates) and nonuniform capacity.

1.3.6 Extent of Fusion Between Plates and Strap

Back to Fig.8. we can see how plates are welded together to the strap. Extent of fusion is how much the plates are immersed inside the strap. Poor of fusion in one or more than one plate with the strap results in poor current conductivity and influences fatigue initiation due to vibrations during battery operation.

1.3.7 Open & Closed Shrinkage in Poles and Straps

Poles and straps are made of lead-antimony alloy. Pb-Sb alloy has a wide freezing range, at the instant that the component is being solidified in the cast-on-strap machine, liquid phase of Pb-Sb alloy has lower density than solid phase. So, there is a shrinkage of the grain in solidification. Open shrinkage appears on the surface as pitting, it has an impact on the corrosion rate and current conduction. Upper open shrinkage that is connected to the car battery terminals loose connection and cause terminal fusion at high discharge currents. Lower open shrinkage on parts immersed in diluted H₂SO₄ or at the path of evolute hydrogen and oxygen gases can participate in initiation of stress corrosion cracking defect leading to fatigue fracture of pole or straps. Closed shrinkage appears as cavities which reduce the effective thermal and electrical conductivity or even fusion of battery poles and strap fracture in extreme conditions. Shrinkage can be controlled by operating conditions such as pouring temperature, mould temperature, water cooling temperature, cooling water flow rate, and design of risers and runners of the mould.
Positive plates corrosion, water loss and negative plate sulfation issues were investigated intensively in literature, many solutions recommended applying 2-D materials. Despite all those investigations, corrosion of straps wasn’t investigated that much this can be a common failure after enhancing battery life for more than one operational year using 2-D materials additives in modern automotive lead-acid battery. This type of corrosion cracks propagates under the stress of vibrations. Unfortunately, finding a surface analysis technique to image the highly rough surface is not an easy thing but I will attach images for corroded poles and will be on the future work.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sb</th>
<th>Sn</th>
<th>As</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>3.1</td>
<td>0.19</td>
<td>0.24</td>
<td>0.03</td>
<td>Bal</td>
</tr>
</tbody>
</table>

It is important to avoid any non-uniformity in spatial distribution of microstructures during solidification. This is usually related to mechanical properties. However, we infer that we can use statistical correlation functions and reconstruction data in finding optimum processing conditions. Two-point correlation and Lineal path functions were used in characterization of robust industrial samples, we find this is logical to directly apply the reconstruction data in optimizing surface roughness. This problem of interest is directly related to the mould design and processing parameters of the cast-on-strap machine. As of surface roughness has influence on pitting corrosion, this will be a challenge when producing longer lifespan batteries as the use of 2D materials found to enhance the lifecycle of the automotive lead acid battery. This thesis is a try motivated by our challenge when manufacturing 2- and 3-years warrantee batteries. Our next step is to manually apply the characterization and reconstruction data in finding
the optimal processing conditions or using new additive to solve the corrosion problem.

Progressive corrosion on longer periods of time increases the risks of creep and fatigue. Fig. 9. clearly shows a real sample taken from car battery operated 7 months or approximately 17500 kilometres, the picture shows the real challenge for enhanced life automotive batteries in hot regions. Table 1. Shows the chemical composition of the pole alloy.

Fig. 1.10. Corroded Lead-acid battery pole operated for 8 months. (Credits: German co. for manufacturing batteries)
This was a very short introduction about the lead acid battery materials and manufacturing. On the second chapter we will discuss statistical correlation function and their application in calculating the microstructure properties of the materials.
CHAPTER 2  
MICROSTRUCTURAL DESCRIPTORS  

2.1 Introduction To Correlation Functions  

The crown jewel of materials science is the materials tetrahedron. Having knowledge of those important relations between its components is the key to design new materials with desired properties. Microstructure descriptors such as statistical correlation functions are considered as mirrors that contain data needed about those relations. In this chapter, I will introduce a general idea of correlation functions and quantification of microstructure using lower-order correlation functions.

In general, the most common structure representation is the standard $n$-point correlation function $S_n$ as ($n$ expands from 1 to $\infty$), it represents the probability of statistically finding events or points of interest in materials imaging to produce a quantitative microstructure of the material. This can be applied in different classes of materials including but not limited to random heterogeneous materials, polycrystalline materials, materials that have directional bonding and amorphous systems with spherically symmetric potentials.
Many materials can be considered as a random heterogeneous material including a polycrystal, materials composed of different phases, metallic alloys, granular media, composites, and ceramics. Thanks to correlation functions, in a heterogeneous material, we have the ability to predict the effective properties of interest. Microscopic length scale which defines the microstructure is the scale that any physical phenomenon can occur, and it is is much larger than the molecular dimensions but not as large as the characteristic length of the macroscopic scale, so it is recognized as a continuum on the microscopic scale, and macroscopic and determine the material’s effective properties. We can also use the data from statistical correlation functions to predict the microstructure from the effective properties inversely.\textsuperscript{[7]}

Consider a two-phase heterogeneous material (e.g., a binary alloy) consisting of a phase 1, a region $V_1$ of volume fraction $\phi_1$ with a general property coefficient $K_1$ and a
phase 2, a region $V_2$ of volume fraction $\phi_2 = (1 - \phi_1)$ with a general property coefficient $K_2$. Both phases are static and independent of time as we assume that $V_1 \cup V_2 = V$ and $V_1 \cap V_2 = 0$. Because properties depend on structure, $K_1$ and $K_2$ can be coefficients of any property (mechanical, chemical, electrical, …, etc.)

Let the probability of any point $x$ to lie in phase 1 is $I^{(1)}(x)$ so it is given by

$$I^{(1)}(x) = \begin{cases} 1, & x \in V_1 \\ 0, & x \in \text{otherwise} \end{cases}$$

(2.1)

$I^{(1)}(x)$ is called phase indicator. In other words, if we computationally throw an arbitrary point $I^{(1)}(x)$ will equal to 1 if it is located at phase 1 and 0 otherwise. Same for phase 2, $I^{(2)}(x)$ is the phase indicator of phase 2 and

$$I^{(2)}(x) = \begin{cases} 1, & x \in V_2 \\ 0, & x \in \text{otherwise} \end{cases}$$

(2.2)

Since phase 1 and phase 2 are independent of each other and complementary i.e. $\phi_2 = (1 - \phi_1)$ so

$$I^{(1)}(x) + I^{(2)}(x) = 1$$

(2.3)
In general, the phase indicator function is

\[ I^{(i)}(x) = \begin{cases} 1, & x \in V_i \\ 0, & x \in \text{otherwise} \end{cases} \]  

(2.4)

As we mentioned, phase \( i \) can be a solid, fluid, or void. The surface/interface indicator function is

\[ M(x) = |\nabla I^{(i)}(x)| = |\nabla I^{(2)}(x)| \]  

(2.5)

The whole idea for the probability functions in materials design is that for a given material domain distribution, periodic base cell can be represented as number of finite elements considering periodic boundary conditions. Statistical functions and reconstruction can find the effective and optimal distribution of those domains or phases (solids, liquids, voids) such that the objective function is minimized. As for the first step, we shall capture information about the microstructure using the correlation functions. Then we apply Monte Carlo to reconstruct domain and get the information of the reconstruction via correlation function. \(^{[8]}\)
Digitized image pixels an have various interpretations, it can reflect different properties such as distributions of electric or magnetic fields, variations in physical properties of the medium, structure geometry, velocity fields, temperature velocity and here we introduce that it represent surface deviations or irregularities from being a flat plane. (Surface roughness)

2.2 The Standard $n$-Point Correlation Function $S_n$

The $n$-point correlation function for a phase $i$ in multiphase material is defined as:

$$S_{n}^{(i)}(x_1, x_2, \ldots, x_n) = \langle I_{i}^{(x)}(x_1) I_{i}^{(x)}(x_2) \ldots I_{i}^{(x)}(x_n) \rangle$$  \hspace{1cm} (2.6)
Where the angular bracket $\langle \ldots \rangle$ is the ensemble averaging for independent observed distributions (realizations) of the system of interest.

In general, the $n$-point correlation function is a local position dependent function, it is the probability that $n$ points are on the absolute positions of $x_1, \ldots, x_n$. Hence, it can effectively provide a mathematical representation of the effective transport properties of the inhomogeneous media.

However, for statistically homogeneous and isotropic microstructures, the $n$-point correlation function does not depend on the absolute positions but their relative displacements i.e.,

$$S_n^{(i)}(x_1, x_2, \ldots, x_n) = S_n^{(i)}(x_{12}, x_{13}, \ldots, x_{1n})$$  \hspace{1cm} (2.7)

For instance, in a statically homogeneous material if $n = 1$ (i.e., one-point correlation function) $S_1^{(i)} = \phi_i$ which is constant everywhere and equals the volume fraction of each phase $i$ but contains no data for material’s structure. For $n \geq 3$, computations and storing probability distributions data encounter both analytical and numerical difficulties and require too much unreasonable computational power.

2.2.1 Two-Point Correlation Function $S_2$

The two-point correlation function is defined as

$$S_2^{(i)} = \langle I^{(i)}(x_1) I^{(i)}(x_2) \rangle$$  \hspace{1cm} (2.8)
It is one of the widely used statistical microstructure descriptors, it is the probability that two random points $x_1$ and $x_2$ are positioned in the same phase.

For statically homogeneous and isotropic media, two-point correlation functions depend only on the distance $r = |x_1 - x_2|$. When the two points coincide (i.e., $r = 0$), two-point correlation function is treated as one-point correlation function and is equal the volume fraction of phase $i \rightarrow S_2^{(i)}(0) = \phi_i$. In a two-phase material, the relation between two-point correlation of phases is defines as

$$S_2^{(2)} = S_2^{(1)}(r) - 2\phi_1 + 1 \quad (2.9)$$

The associated autocovariance function is defined as

$$\chi(r) = S_2^{(1)}(r) - \phi_1^2 = S_2^{(2)}(r) - \phi_1^2 \quad (2.10)$$

One crucial condition of $S_2^{(i)}$ for a two-phase homogeneous material with dimensions $d$ is that the $d$-dimensional Fourier transform of $\chi(r)$ shall be non-negative for all of the wave vectors $k$ i.e., the spectral function is positive semidefinite.

$$\tilde{\chi}(k) = \int \chi(r)e^{-ikr}dr \geq 0, \text{ for all } k \quad (2.11)$$

$\tilde{\chi}(k)$ is proportional to scattered radiation intensity.

For all $r$ the two-point correlation function must satisfy that $0 \leq S_2^{(i)}(r) \leq \phi_i$ hence, the corresponding autocovariance function is given by

$$-\min(\phi_1^2, \phi_2^2) \leq \chi(r) \leq \phi_1\phi_2 \quad (2.12)$$
As for homogeneous and isotropic media (i.e., $S_2^{(i)}(r)$ depend on the relative distances), the derivative $r = 0$ must be negative for all $0 < \phi_i < 1$:

$$\frac{dS_2^{(i)}}{dr} \bigg|_{r=0} = \frac{dx}{dr} \bigg|_{r=0} < 0$$

(2.13)

One more condition for statistically homogeneous media is,

$$S_2^{(i)}(r) \geq S_2^{(j)}(s) + S_2^{(i)}(t) - \phi_i$$

(2.14)

Where $r = t - s$.

As we understand the nature of the two-point correlation function, we can obviously find out that the limits of $S_2$ can be shown as

$$\lim_{r \to 0} S_2(r) = \phi_1 \text{ and } \lim_{r \to \infty} S_2(r) = \phi_2^2$$

(2.15)

Generally, two-point correlation function is one of the most important and widely used probability functions to theoretically quantify morphological features of any material system. For homogeneous media, it can be acquired by randomly throwing line segments of length $r$ with a specific orientation and counting the fraction of times that $x_1$ and $x_2$ lie on the same phase.

2.3 Surface Correlation Functions

Surface correlation functions contain information about surface/interface characteristics, this information is beneficial in flow or trapping problems. Based on this, we can suppose that phase 1 maybe a fluid or void and phase 2 is a solid. This information for the interface indicator can be obtained by the gradient of the indicator function $\mathbf{M}(x) = \nabla I^{(i)}(x)$. function for inhomogeneous media, the trivial one-point surface correlation is the specific surface function $s(x)$. 

33
\[ S(x) = \langle \mathcal{M}(x) \rangle \]  
(2.16)

Two-point surface correlation functions are surface-surface function and surface-void function keeping in mind that \( I(x) \) is the indicator function for void phase.

\[ F_{ss}(x_1, x_2) = \langle \mathcal{M}(x_1) \mathcal{M}(x_2) \rangle \]  
(2.17)
\[ F_{sv}(x_1, x_2) = \langle \mathcal{M}(x_1) I(x_2) \rangle \]  
(2.18)

\( F_{ss} \) is the probability of finding \( x_1 \) and \( x_2 \) if an expanded interface region when the thickness is approximately zero.

\( F_{sv} \) is the probability of finding \( x_1 \) in an expanded region of a finite thickness interface and \( x_2 \) in the void phase. \(^8\)

For statistically homogeneous materials, \( F_{ss} \) and \( F_{sv} \) depend only on the displacement \( r = x_2 - x_1 \) and if the material is isotropic \( r \) becomes \( |r| \).

In systems that do not have long-range order but there are very large distances between each two points the surface-void and void-void correlation functions became as follow:

\[ F_{sv}(x_1, x_2) \rightarrow s(x_1) s_1(x_2) \]  
(2.19)
\[ F_{vu}(x_1, x_2) \rightarrow s(x_1) s(x_2) \]  
(2.20)

For homogeneous materials,

\[ F_{sv}(x_1, x_2) = s \phi_1 \]  
(2.21)
\[ F_{vu}(x_1, x_2) \rightarrow s^2 \]  
(2.22)

\( \phi = \langle I\rangle \) is the volume fraction of the void phase (i.e., porosity)

2.4 Lineal-Path Function \( L^{[\ell]}(r) \)

Lineal-path function is an appealing lower-order correlation function. For statistically homogeneous and isotropic media, it measures the probability that random
line segment of length \( r \) lies entirely on the same phase of interest \( i \) along \( r \) direction. \( L^{(i)}(r) \) contains information about linear partial topological connectedness of the material microstructure. As \( r = 0 \), the lineal-path function shrinks on itself and can be treated as a probability of finding only one-point on the phase of interest (i.e., \( L^{(i)}(0) = \phi_i \)) and for \( r \to \infty \) we have \( L^{(i)}(\infty) = 0 \). For homogeneous and anisotropic media, \( L^{(i)}(r) \) will only depend on the magnitude of vector \( r = x_2 - x_1 \) while it depends on the absolute positions \( x_1 \) and \( x_2 \) for inhomogeneous materials.

For a 3-D material structure, lineal-path function corresponds to the area fraction of phase \( i \) measured from the projected image of a 3-D slice of thickness \( r \) onto the plane so it is not effective in complex microstructures.

### 2.5 Chord-Length Density Function \( p^{(i)}(r) \)

For statistically isotropic material, chord-length density probability function is defined as the probability distribution of finding line segments lie between intersections of an infinitely long line with two-phase interface (i.e., between \( r \) and \( r + dr \) in phase \( i \)). Since it is a probability density function, \( p^{(i)}(r) \geq 0 \) for all \( r \) and it normalizes to unity. It is related to lineal-path function (special case) and [9] defined the relation between lineal-path function and chord-length density function as:

\[
L^{(i)}(r) = \frac{\phi_i \int_0^\infty (y-r) p^{(i)}(y) \delta(y-r) dy}{\int_0^\infty y p^{(i)}(y) dy} \tag{2.23}
\]

It is simple to assume that by integrating the probability of line segments are chords with length between \( y \) and \( y + dy \) for all \( y \) multiplied by the volume fraction of phase \( i \) will
give the probability of line segments lie entirely on phase \( i \). This is true only by considering the heaviest step function \( \Theta(x) = \begin{cases} 1, & x \geq 0 \\ 0, & x < 0 \end{cases} \)

By differentiating (2.23) we get

\[
\frac{dL^{(i)}(r)}{dr} = -\frac{\phi_i \int_0^\infty \gamma p^{(i)}(y) dy}{\int_0^\infty \gamma y p^{(i)}(y) dy}
\]

(2.24)

Where \( \int_0^\infty \gamma p^{(i)}(y) dy \) is the mean chord length and is denoted by \( \ell_c^{(i)} \). \[6\]

For isotropic media, the mean chord length \( \ell_c^{(1)} \) is relevant to the slope of the two-point correlation function at the origin via \[6\]

\[
\frac{d\gamma^{(3)}_S}{dr} \bigg|_{r=0} = -\frac{\phi_i}{\ell_c^{(i)}}
\]

(2.23) clearly shows that lineal-path function and chord-length density function are correlated to each other and have equal level of information about the microstructure.

2.6 Pore-Size Functions \( P(\delta) \)

Pore-size probability density function or pore-size distribution function is commonly used in voids or pores characterization in porous media. It is considered as the probability of finding a sphere of radius \( r \) lies entirely in the phase of interest. Usually involve information about permeability or coarse level connectedness of the microstructure phases. For isotropic materials, it is defined as \( P(\delta) d\delta \) which is the probability of randomly chosen point in phase 1 lies between \( \delta \) and \( \delta + d\delta \) from the nearest point on the pore-solid interface.\[6\] Since it is a probability density function, \( p^{(i)}(\delta) \geq 0 \) for all \( \delta \) and it normalizes to unity.

At the extreme values of \( P(\delta) \)
\[ P(0) = \frac{s}{\phi_1}, \quad P(\infty) = 0 \]  

(2.26)

\( \frac{s}{\phi_1} \) is the interfacial area per unit pore volume.

\( P(\delta) \) has a corresponding complementary nonincreasing distribution function which is the fraction of pore space that contain pores with \( \text{pore radius} > \delta \) and is defined as,

\[ F(\delta) = \int_0^\infty P(r) dr \]  

(2.27)

At the extreme values of \( F(\delta) \)

\[ F(0) = 1, \quad F(\infty) = 0 \]  

(2.28)

By definition, \( P(\delta) \) is an intrinsic 3-D microstructural descriptor and cannot be extracted from 2-D cross-section images of the material.

2.7 Percolation and Cluster Function \( C_2(x_1, x_2) \)

The macroscopic properties are extremely affected by the presence of clusters in the heterogeneous materials. A point in phase \( i \) can be connected to a cluster on the same phase without passing through other phases of the material. Two-point cluster function \( C_2^{(i)}(x_1, x_2) \) is slightly different from ordinary two-point correlation function that it is the probability of finding the two points lie in the same cluster in the phase of interest. Unlike \( S_2^{(i)}(x_1, x_2) \) is an intrinsic 3-D microstructural function that contain non-trivial information about the microstructure.

For statistically isotropic materials, two-point cluster function depend on the separation distance \( r = |x_2 - x_1| \) (i.e., \( C_2^{(i)}(x_1, x_2) \equiv C_2^{(i)}(r) \)). At the origin, extreme values of \( C_2^{(i)}(r) \)
\[ c_2^{(i)}(0) = \phi_v, \quad c_2^{(i)}(\infty) = 0 \] (2.29)

Fig. 2.4. Different correlation functions representation in a two-phase material.

2.8 Conclusion

In this chapter, we have discussed a group of several types of lower-order statistical correlation functions. They are very beneficial in quantifying microstructures of different material systems, they can be used in extracting important microstructural information from digital images of the microstructure via different imaging techniques such as X-ray tomography, Atomic force Microscope (AFM) and Scanning Electron Microscope (SEM). In general, those simple statistical functions are the backbone to
design super-efficient material with desired properties. Other types of statistical descriptors for particle system have been widely investigated in Ref. [6].
CHAPTER 3
METHODS AND MATERIALS QUANTIFICATION

3.1 Methodology

In this chapter we will discuss in detail the method we have used on our approach as well as sample preparation and the results for quantification the Pb-Sb cast-on-strap alloy as our system of interest. We will present our recent developments in modelling Pb-Sb alloy via lower-order correlation functions. As a first step of our case-study based research, we directly get our samples from a robust battery large scale assembly line. Large scale samples are not ideal samples, processing can extremely alter the materials properties. Many problems in most of materials produced in industrial scale have not been investigated much in literature, this is just because in labs we use the ideal conditions just to eliminate the undesired problem to keep focus on the main ideal properties. On the other hand, researchers may just stop at this point and do not give attention to the actual problems that may appear during manufacturing.

As mentioned before, our system of interest (Pb-Sb alloy) forms a critical part in lead-acid battery, it is used in the connection or straps which connect galvanic cells in series together to connect electric current, it is also used in poles and terminals which delivers electric current to and from the battery. The sample was collected from the furnace of the cast-on-strap machine, simulated to reach the same conditions of the COS.

As to illustrate the processing conditions at the COS. COS machine has automated functioning main parts. A furnace at temperature 470 °C to melt the alloy of Table 1.1., the melted alloy is pumped through pipes to the main mould with specific
speed and being poured to the mould cavities with for 2.2 seconds or depending on the design of each battery type. The mould has a water-cooling system with constant flow rate and constant water temperature not reaching 120 °C but in most cases, the cooling temperature is 110 °C for 8 seconds. The sample was taken from the furnace, quenched in water for 8 seconds and is cut into pieces, then its surface was polished to be prepared for imaging.

![Schematic illustration of general steps of materials quantifications.](image)

In general, X-ray tomography technique is widely used in microstructure imaging, it is exceptionally effective, low-cost, and non-destructive technique for producing 3-D images from 2-D images at different angles to generate grayscale images of the microstructure. However, due to the interested features of my case-study I have used Atomic Force Microscopy (AFM) technique to determine surface roughness and small
surface defects present as active sites influencing corrosion because AFM is more reliable for surface representation. AFM is a topographical imaging technique that is very sufficient on the microscale and nanoscale, as illustrate on Fig. 3.1., its operation depends on a cantilever with a flexible sharp tip that scan all over the sample surface, attraction and repulsion between surface and tip (swinging) represent the roughness of the surface. As the cantilever deflects towards and from the surface, a laser beam is used to detect those deflections and reflected to a screen forming an image of surface topography. AFM is considered as the most precise tool for representing surface topography for most of solid samples and is indispensable technique for characterization of corrosion of metallic alloys.

**Atomic Force Microscopy (AFM) : General Components and Their Functions**

![Schematic illustration of Atomic Force Microscopy technique. (Credits: Lurie Nanofabrication Facility (LNF), University of Michigan)](image)

**Fig. 3.2. Schematic illustration of Atomic Force Microscopy technique. (Credits: Lurie Nanofabrication Facility (LNF), University of Michigan)**
Before going through the data collected, it is important to invoke that we are quantifying surface and its probable influence on surface issues as well as the interconnection between poles and terminals as well as the effective conductivity loss at the boundaries. It is proven that there is a loss in effective electrical conductivity and heat transfer [10, 11] which extremely affect the battery performance. While many studies highlighted Pb-Sb system alloy corrosion on strap and pole due to hydrogen evolution as the battery is operating. [12] Fig.1.10 is a real image representing corrosion of pole due to gas evolution influenced by surface defects. To have a clear representation for surface defects and normal roughness, the sample was polished to remove any macrosegregations appear on the surface by solidification or surface coarsening that have low contribution in battery system failures and can affect the quantification of the Pb-Sb system. Fig. 3.3. shows the surface roughness analysis for the sample.

3.2 Quantification Results

The next step for material’s surface quantification is that the acquired AFM surface imaging data is then converted into greyscale binary image using MATLAB. Once we covert the AFM results into binary images, we process them via in-house C++ code to extract the data from the binary images and produce probability maps for the structure. On the programming code, we set the black pixels as the feature data of interest and white pixels represent the matrix data.
Fig. 3.3. AFM results recorded of surface topography of Pb-Sb sample at 100 nm.

The characterization of the structure computed using a combination of two-point correlation function $S_2(r)$ and lineal-path function $L(r)$ discussed on chapter 2. A surface image of a slice of Pb-Sb cast-on-strap sample is shown in Fig. 3.4. (b) in which the black areas are higher surface toughness spots which is the phase of interest, and the white areas are the equal roughness heights solid phase.
Fig. 3.4. Binary image of surface topography of Pb-Sb sample with $\phi = 0.038$.

For simplification, only square binary images of length MAXX were used in characterization, MAXX must be an even number. As discussed in chapter 2, two-point correlation function for statistically homogeneous medium can be interpreted as the total length of line segment as well as its both ends lie completely on the same phase. In sampling $S_2$, we compute the probability of the fraction of times that distances between a black pixel $i$ and all other surrounding pixels $j$ of black pixels successfully separated with distances $r$ such that the end point are located at pixels centers to the total number of throwing line segments trials. Sampling the two-point correlation function only along the principal directions of hypercubic lattice, mainly in rows or columns in 2-D. Hence, $S_2$ is a linear function of distances between adjacent pixels. $^6$

$$S_2[r] = (1 - f)S_2(i) + fS_2(i + 1) ; i \leq r < i + 1,$$

(3.1)

Where $f$ is the fractional part of $i$.

Lineal-path function $L(r)$ present the probability of finding an entire line segment of length $r$ at the phase of interest. Sampling $L(r)$ is straightforward, we detect a point A at an oriented line at orthogonal direction and move A along this line until we encounter
other phases at point B. Calculate the ratio between lines of lengths equal distance between A-B and total number all inserted lines with all lengths. Consider line segments lengths at orthogonal directions are stored in an array counter $L[r]$ while $r \leq r_i$ an integer value increasing by 1 and $r_i$ is the length of $i_{th}$ line.

$$L(r) = \frac{L[r]}{\text{lines with all possible lengths}}$$  \hspace{1cm} (3.2)

By applying the code to the digitized image at Fig. 3.4, we obtain the surface structure probability functions. The information contained in $S_2(r)$ and $L(r)$ was similar showing the volume fraction higher roughened part of the sample slice $\phi_1 = 0.03836$ and the smooth surface with volume fraction $\phi_2 = 0.96164$.

![Fig. 3.5. Data collected for the two-point correlation function and lineal-path function for surface topography of Pb-Sb sample with approximate $\phi_1 = 0.038$.](image)

In the data collected from $S_2$, the first portion of data exhibits almost no fluctuations representing that for line segments with length, almost all line segments are at distances as $r \leq 23$ pixels and as the $S_2(0)$ connection 2 points within the same phase and $L(0)$ is the line within the same phase as the spatial distribution $S_2(0)$ at small $r$ values may equal to the line pathways $L(0)$ as they are not highly convoluted at small $r$. 

46
and highly convoluted for large $r$. Considering the binary image at Fig 3.3. $\phi_i = 0.038$ is very reasonable meaning that our approach in characterization of surface roughness of such alloy via correlation functions is successful.
CHAPTER 4

MATERIAL’S RECONSTRUCTION USING SIMULATED ANNEALING METHOD

Reconstruction of materials microstructure has a great practical significance even from poor satisfying information obtained from lower-order correlation functions. There are many different structure reconstruction methods such as Gaussian random field method, phase recovery method and raster path methods. The Gaussian field method postulate that we need only the volume fraction and two-point correlation function $S_2(r)$ to find a sufficient description for spatial statistics of a two-phase media. Phase recovery algorithm is limited to $S_2(r)$ although it is very effective for certain microstructures. On Raster-path algorithm, it is not possible to regenerate the discontinuities in constructed paths.

Rintoul & Torquato and Yeong & Torquato [12, 13] stated that the reconstruction can be posed as optimization problem. Initially, target correlation functions are recommended by theoretical models or experiments data. As the problem is an optimization problem, the aim is to find the best approximation to target functions. We start by some initial realizations and based on target functions, the method starts to compute the correlation functions by minimizing the error based upon the distance between calculated and target correlation. [17]

For statistically isotropic two-phase medium, consider a single two-point level correlation function $f_2(r)$ and $\hat{f}_2(r)$ is the reconstructed corresponding function at some time step. With initial realizations, we try to evolve the microstructure to reach $f_2(r)$. Assume energy $E$ at any distinct stage, the aim of reconstruction is to minimize $E$. (i.e., $E \to 0$).
\[ E = \sum r \left[ f_2'(r) - f_2(r) \right]^2 \]  \hspace{1cm} (4.1)

where the summation is over all discrete values of \( r \).

\( E \) is a function of states (microstructures).

Two-point level correlation functions could be: standard two-point probability function \( S_2(r) \), the lineal-path function \( L(r) \), the surface-surface correlation function \( F_{ss}(r) \), the surface-void correlation function \( F_{sv}(r) \), the chord-length density function \( p(r) \), the pore-size function \( F(r) \), and the two-point cluster function \( C_2(r) \).

However, conventional mathematical programming techniques are fruitless for such complex problems, correlation functions contain large and complex microstructural information resulting in very difficult optimization problem to solve. Simulated annealing technique is usually employed to solve such large-scale optimization problems, it can be used to switch digitized image pixels to find the optimum microstructure. The superiority of the simulated annealing technique has been clear because of its simplicity in that it does not need special complex setups, inexpensive and in its capability to escape local minima via accepting locally unfavorable configurations. One can predict the lowest possible energy state via simulated annealing based on the fact that: when a system is heated to high temperature \( T \) (excitation energy state), by slowly cooling down the system to temperatures near to and equal to absolute zero, it samples all different energy states until equilibrium at the ground energy state (minimum stable energy state). For canonical ensemble, at a temperature \( T \), the probability for the system to be at energy state \( E \) is a Boltzmann distribution

\[ P(E) = \text{Const} \times e^{-\frac{E}{T}} \]  \hspace{1cm} (4.2)
For each annealing step $t = k$, the system samples and reaches equilibrium temperature $T_k$. The temperature is then lowered for each annealing step $T(t)$ until it approximates the ground energy level. Meaning that, in the simplest form starting with given microstructures, states of two arbitrary pixels of different phases are swapped, conserving the volume fraction of both phases.\textsuperscript{[7]}

![Visual representation of pixel swapping or exchange procedure to generate new microstructure from old one.]

Change in energy between two successive states is calculated by

$$\Delta E = E' - E$$  \hspace{1cm} (4.3)

Whether the new energy state is accepted as the next energy state or not is determined by the acceptance probability which is given by

$$p(\Delta E) = \begin{cases} 
1, & \Delta E \leq 0, \\
\frac{1}{e^{\frac{\Delta E}{T}}}, & \Delta E > 0,
\end{cases}$$  \hspace{1cm} (4.4)

Where $T$ is a hypothetical high initial temperature.

Although, ideal annealing to reach the ground state, is to decrease temperature steps according to $T(k) \sim \frac{1}{\ln(k)}$, it may cause very slow energy convergence. Hence, we use faster annealing schedule of
\[ \frac{\tau(\lambda)}{\tau(0)} = \lambda^k ; \quad \lambda \to 1 \] (4.5)

Where \( \lambda \) is the annealing rate.

Although, the modified annealing schedule has faster energy convergence, it puts the system at the risk of being trapped in local minima and optimum annealing is not guaranteed anymore.

![Simulation diagram](image)

Fig. 4.2. Visual representation of simulated annealing optimization procedure. The acceptance of energy-increasing trial microstructure allows the system to escape from local energy minima and thus, increases the probability of convergence to the global minimum. \([14]\)

Unfortunately, quantification of surface roughness via correlation function is not a popular case of study. We could not find any literature in such topic. There was no need to examine other surface-surface \( F_{ss} \) or surface-void \( F_{sv} \) functions as two-point correlation function \( S_2 \) was efficient. Actually, representing surface roughness need to be studied equal or higher than some distinct height we see it has higher impact on corrosion or effective general conductivity.

We expect that roughness cannot be studied as void-surface unless the void phase is taken as our matrix phase. This is why we \( S_2 \) was our first choice to investigate the capability of roughness quantifications via statistical spatial correlation functions. On the
following lines, we introduce the reconstruction results using $S_2(r)$ of construction results on the previous chapter as our target function.

As shown in Fig. 4.3, the representation of surface roughness using the reconstruction of data obtained by two-point correlation function, the optimization results in minimization of lengths of line segments of $S_2(r)$. As we take images for the surface at distinct heights (approximated to 100 nm), line segments lengths are extremely decreased (average $r \approx 0.001475$), meaning that there is a propagation growth for the surface at horizontal directions eliminating the surface roughness. Which concludes that optimization $S_2(r)$ is extremely efficient in smoothing the surface with very low rough lengths for such system.

![Graph showing reconstruction results using two-point correlation function.](image)

Fig. 4.3. Reconstruction results using two-point correlation function.
Fig. 4.4. Optimized 3-D surface reconstruction and 2D surface slices along main directions for Pb-Sb sample.
CHAPTER 5

CONCLUSION AND FUTURE WORK

In this project, we examined the possibility for quantifying surface roughness using lower-order spatial correlation functions, both two-point correlation function \( S_2(r) \) lineal-path function \( L(r) \) were used in quantifying Pb-Sb surface which is very important in enhancing battery performance. We introduced surface issues in the battery industry and how they will be forming serious issues in longer life batteries. Our study solves the postulated problems that will be present by involving 2-D materials in lead-acid batteries as a consequence of longer life or terminals melt at high discharge rate caused by poor heat transfer in the inner surface due to large roughness degree. Results mentioned in chapter 4 are realistic and serve the aim of the study. The over-all idea we found is that we can use such functions for enhancing surface properties of any alloy by identifying certain roughness heights as the phase of interest. We conclude that this technique can be applied also in metals polishing industry or as data map for Pb-Sb alloy in batteries industry for machine learning implementation.

For future work, we will execute this technique in different materials systems used in automotive battery industry and we will try to experimentally reach the optimized surface images from reconstruction. It was initially reached by increasing the percentage of Sn in the alloy but needs further investigations. The reconstruction results are very important in our future work as we are currently working on designing new automotive battery alloy system.
REFERENCES


