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The effects of tertiary dendrite arm spacing and segregation on the corrosion behavior of a Pb–Sb alloy for lead-acid battery components

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ABSTRACT

The aim of this study is to evaluate the effects of segregation and of the presence of tertiary dendrite arms in the microstructural arrangement of a Pb–Sb alloy on its resultant corrosion behavior. In this context, a water-cooled unidirectional solidification system was used to obtain alloy samples having different dendritic patterns. Electrochemical impedance spectroscopy and potentiodynamic polarization curves were used to analyze the corrosion resistance in a 0.5 M H_2SO_4 solution at 25 °C. Three different dendritic arrays were investigated as a function of the cooling rate and antimony macrosegregation profile. It was found that the tertiary dendritic arms associated with the antimony segregation have an important role on the resulting corrosion response. It is shown that the sample with a well defined tertiary dendritic array provide a more homogeneously distributed interdendritic eutectic mixture exhibiting better corrosion protection.

1. Introduction

It is well-known that Pb–Sb alloys are commonly used in the production of positive and negative grids, connectors and other components of both VRLA-valve-regulated lead acid and SLI-starting, lighting and ignition batteries [1–3]. There exists a number of manufacturing process generally used to produce these aforementioned components which generates different resulting microstructures [1,2]. It is also known that the antimony content of a Pb–Sb electrode affects the mechanical properties, the microstructure, the electrochemical behavior of active materials and corrosion layers on the electrode [1–6].

The cellular and dendritic arm spacings are important microstructural parameters affecting the segregation and mechanical properties. In particular the scale of cellular and secondary dendritic spacings was shown to strongly influence the overall surface corrosion resistance of binary lead-base alloys [7–15].

In a recent article, it was shown that coarser cellular structures tend to yield higher corrosion resistance than finer cellular structures for a dilute Pb–0.85 wt.% Sb alloy [7]. Such tendency was associated with the reduction of cellular boundaries when compared with finer cells, since the boundary has proved to be more susceptible to corrosion. It is known that antimony, which is segregated toward the cell boundaries and interdendritic regions during solidification of Pb–Sb alloys, has an important role on the corrosion behavior [7,8]. It was also concluded that finer dendritic arrays of Pb–Sb alloys tend to yield higher corrosion resistances than coarser dendritic structures [7]. The dendritic array morphology has the antimony-rich regions located in the lamellar eutectic mixture. The Sb-rich lamellae will envelope the Pb-rich phase more efficiently when the microstructure is characterized by finer dendritic spacings, due to the more extensive distribution of the eutectic mixture, and thus contributing to the protection of the Pb-rich matrix against the corrosion action [7]. Previous studies [7–15] evidenced that coarse cellular samples were associated with better corrosion resistance than fine cellular samples when considering experimental studies with Pb-based alloys subjected to corrosion tests in a sulfuric acid (H_2SO_4) solution. In another recent article [13], it was found that the experimental current density increased with the increase in both the Sb content and dendritic spacing, when the dendritic morphological arrays of Pb–2.2 and 6.6 wt.% Sb alloys were compared. It was concluded that independently of the micromorphological array, the Pb–2.2 wt.% Sb alloy sample has better corrosion resistance than both Pb–1 and 6.6 wt.% Sb alloys [13].

Mechanical strength and ductility are influenced by the dimensions and continuity of the primary dendritic branches. Campbell [16] stated that dendrite arm spacing (DAS) usually refers to the spacing between the secondary arms of dendrites. However, if tertiary arms were present at a smaller spacing, then it would refer

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to this. The availability of studies on tertiary dendrite arms is very restricted. As mentioned, in Pb–Sb components smaller DAS yield higher corrosion resistance than coarser dendritic structures. In this context, tertiary dendrite arms may contribute with a more homogeneous distribution of the anodic Pb-rich phase.

The aim of this study was to examine the effect of the presence of tertiary dendrite arms on the microstructural arrangement of Pb–Sb alloys on the resultant electrochemical corrosion behavior. For this purpose, a Pb–3.5 wt.% Sb alloy and a water cooled unidirectional solidification system were used were used to provide different dendrite patterns. Corrosion tests were performed with samples of different dendrite arm spacings in a 0.5 M H_2SO_4 solution at 25 °C, and the corrosion rate was correlated with both the resulting microstructure and the Sb segregation profile along the casting length.

2. Experimental procedure

A Pb–3.5 wt.% Sb alloy was prepared from commercially pure (c.p.) metals: Pb (99.97 wt.%) and Sb (99.99 wt.%). The mean impurities detected were: Fe (0.12 wt.%), Si (0.05 wt.%), Cu (0.015 wt.%), besides other elements with concentration less than 50 ppm.

A water-cooled unidirectional solidification system was used in the experiments. The solidification set-up was designed in such way that heat was extracted only through the water-cooled bottom, promoting vertical upward directional solidification, as shown in Fig. 1. The temperatures were monitored during solidification using a bank of type J thermocouples accurately located along the casting length at six different positions with respect to the metal/mold interface: 4, 12, 22, 38, 54 and 68 mm, at the center of the casting. The stainless steel mold had an internal diameter of 50 mm, a height of 110 mm and a wall thickness of 3 mm. The side walls were covered with a layer of insulating alumina to minimize radial heat losses. The bottom part of the mold was closed with a thin (3 mm thick) stainless steel sheet, which physically separates the metal from the cooling fluid.

The cylindrical casting was sectioned on its midplane, ground, polished and etched with a solution to reveal the macrostructure. Transverse sections (perpendicular to the growth direction) extracted from the directionally solidified casting at 6 different positions along its length were polished and etched with a solution (37.5 mL of glacial acetic acid and 15 mL of H_2O_2, at 25 °C) for microscopy. Image processing systems Neophot 32 (Carl Zeiss, Esslingen, Germany) and Leica Quantimet 500 MC (Leica Imaging Systems Ltd, Cambridge, England) were used to measure the dendrite spacings. The λ_3 values were measured on the transverse section by averaging the distance between adjacent side branches. These measurements, about 20 values for each selected position from the metal/mold interface, were confirmed by comparison with values measured on longitudinal sections. The macrosegregation profile was determined by a scanning electron microscope (SEM, JMS T20 of Jeol Co., Japan) and an energy dispersive X-ray analyzer (EDAX, NORAN, System Six 1.5, USA).

In order to establish correlations between the corrosion resistance and the microstructural pattern, electrochemical impedance spectroscopy (EIS) and polarization tests were carried-out on samples collected at different positions along the casting length. The EIS tests were carried-out in a 500 cm^3 of sulfuric acid solution (0.5 mol L^{-1}) at 25 °C. Electrochemical corrosion tests were performed in a 1 cm^2 circular area of ground (600 and 1200 grit SiC finish) alloy samples. Electrochemical impedance spectroscopy (EIS) measurements began after an initial delay of 15 min for the samples to reach a steady-state condition. These tests were carried out in a stagnant and naturally aerated 500 cm^3 of a 0.5 M H_2SO_4 solution at 25 °C under a pH of about 0.86 (±0.14), used to simulate the battery electrolytic fluid. A potentiostat (EG & G Princeton Applied Research, model 273A) coupled to a frequency analyzer system (Solartron model 1250), a glass corrosion cell kit with a platinum counter-electrode and a saturated calomel reference electrode (SCE) were used to perform the EIS tests. The potential amplitude was set to 10 mV at open-circuit, peak-to-peak (AC signal), with 5 points per decade and the frequency range was set from 100 mHz to 100 kHz. Although the SCE electrode is not commonly used in lead-acid system studies, a SCE electrode can also be used as a reference electrode since the one inconvenient is the fact that chloride may contaminate the electrolyte, and other is to convert from SCE to MSE or other potential scales (ASTM G3).

Potentiodynamic measurements were also carried out in the aforementioned solution at 25 °C using a potentiostat at the same positions where the EIS tests were carried out. These tests were conducted by stepping the potential at a scan rate of 0.1667 mV s^{-1} from −0.75 V (SCE) to −0.35 V (SCE) at open-circuit. Using an automatic data acquisition system, the potentiodynamic polarization curves were plotted and both corrosion rate and potential were estimated by Tafel plots by using both anodic and cathodic branches at a scan rate of 0.1667 mV s^{-1} from −250 mV (SCE) to +250 mV (SCE) at open-circuit. This mentioned potentiodynamic range corresponds with −600 mV to −150 mV vs. MSE–Mercury/Mercurous Sulfate Electrode or Hg/Hg_2SO_4 electrode [17]. Duplicate tests for EIS and potentiodynamic polarization curves were carried out. In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (ZView version 2.1b) for equivalent circuit quantification has also been used.

3. Results and discussion

3.1. Macrostructure, microstructure and cooling rate

The macrostructure of the resulting directionally solidified Pb–3.5 wt.% Sb alloy casting is shown in Fig. 2(a). Columnar grains prevailed along the entire casting length, as previously obtained in other similar experiments using Pb-based alloys [7–15]. The positions in the casting from where the samples for microstructure characterization and corrosion tests were extracted are also indicated in Fig. 2(a). The following distances from the bottom of the casting (casting surface) were examined: P1 (8 mm), P2 (25 mm) and P3 (50 mm). Fig. 2(b) evidences the experimental results of the tip cooling rate during solidification as a function of position (distance) from the cooled bottom of the casting. It can be seen that the cooling rate is high for initial positions and that it decreases with the increase in distance from the bottom of the casting. The experimental Sb macrosegregation profile along the casting length is shown in Fig. 2(c).

The experimental evolution of the dendrite arm spacings (both primary, λ_1, and tertiary, λ_3) as a function of the resulting cooling rate is shown in Fig. 3. Points are experimental results and the line represents an empirical power function fit to the experimental points. Minimum and maximum measured dendrite spacings for each position are expressed by the error bars. As expected, the use of a water-cooled mould imposed higher values of tip cooling rates near the casting/chill surface and a decreasing profile along the casting length. This is correlated with the increase in the thermal resistance of the solidified shell with distance from the cooled surface. As a result, the dendritic array is fine close to the casting cooled surface and coarse far from it.

It is also interesting to observe in Fig. 3(a) that the experimental range of cooling rates varied from 6 to about 0.06 K s^{-1}, but the initial growth of tertiary dendrite arms was found to occur only for cooling rates lower than 0.4 K s^{-1}. It can be seen that the tertiary dendrite spacing is about 3.7 times lower than the primary dendrite