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Optimized Pulsed Anodization for Corrosion Protection of Aluminum Silicon Alloys

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ABSTRACT

The manuscript investigates new waveforms for pulsed anodization of Aluminum Silicon alloys (AlSi_x) and demonstrates: 1) an effective reduction of the anodic layers porosity degree; 2) an enhancement of the thickness homogeneity; and 3) a boost of the corrosion protection capability; of the obtained coatings.

The interplay between process parameters (e.g. current/potential waveforms), oxide layer morphology and corrosion resistance is investigated by means of several techniques. In particular, metallography, voltammetry and contact angle methods are used in order to correlate the electrochemical figures of merit (corrosion potential, corrosion current, breakdown potential and polarization resistance) with the layer morphological features.

It is concluded that the careful optimization of the anodization process can lead to the development of oxide layers with an enhanced corrosion resistance. In particular, the following level of performance on anodized AlSi₇ is achieved: corrosion potential (E_{corr}) = -285mV vs. SCE, corrosion current (I_{corr}) = 0.08nA·cm⁻², breakdown potential (E_{bp}) = +778mV vs. SCE and polarization resistance (R_p) = 215MΩ·cm⁻².

Key words: Aluminum-Silicon Alloy, Pulsed Anodization, Brake Caliper, Corrosion Protection, Anodic Layer.

1) INTRODUCTION

Brake efforts in new electric vehicles are strongly reduced due to the progressive evolution of regenerative braking.¹ As a consequence, the development of braking systems with a corrosion resistance as long as the vehicle life is a primary point among brake system producers.^{2,3,4,5}

At this regard, brake calipers for high-end cars, which are typically realized using Aluminum-Silicon alloys, can face severe corrosive phenomena in Chloride-rich environments and anodization of these components is often necessary.^{2,6} In spite of this, anodization of Aluminum alloys comprising a high Silicon content can be a particularly challenging task due to the presence of eutectic Silicon dendrites with poor electric conductivity and sluggish oxidation kinetic.⁷ As a results, anodic layers obtained under uncontrolled conditions can result in: a) poor thickness homogeneity; and b) presence of porosity and surface cracks; which render the coated parts unable to withstand to galvanic couplings and atmospheric corrosion events.⁴

As a consequence, the development of tailored current/potential waveforms plays a pivotal role in obtaining anodic layers with improved thickness homogeneity and corrosion protection capability.^{6,8,9} As an example, pulsed anodization waveforms, used in Aluminum treatment, can result in high performing oxides whose achievements can be found in recent publications.^{8,10} Nevertheless, when considering Aluminum-Silicon alloys the existing literature on pulsed anodization is limited and regards only few, case-specific, publications.^{11,12} It appears clear that a systematic investigation of the effects of anodization parameters on the oxidation results, such as those proposed in this work, is essentially missing.

Aiming at filling this gap, the manuscript investigates the interplay between pulse shape parameters, oxide layer morphology and corrosion resistance of anodized AlSi₇ alloys. The work: a) demonstrates how to obtain coatings with an improved corrosion protection capability on challenging substrates; and b) proposes an effective method in order to extend the corrosion resistance of brake calipers thus fulfilling the requirements of new electric vehicles applications. On a broader perspective, the results will allow to design future anodization processes capable to enhance the corrosion resistance of a next generation of AlSi₇ brake calipers.

2) EXPERIMENTAL PROCEDURE

2.1 Materials and Preparation of the Specimens

Aluminum-Silicon Alloys (AlSi₇) used in the anodization experiments are obtained from Brembo S.p.A. prototype calipers. Specimens have a surface of at least 30cm² and undergo to the following procedure before anodization: 1) grinding with SiC sandpaper up to 1000 grit; 2) washing with commercial soap; and 3) sonicating in ethanol for 5 minutes.

2.2 Anodization Setup and Parameters

Anodization is performed using a Biologic VMP-300 potentiostat/galvanostat coupled with a HCV-3048 booster. A two-electrode configuration is used with the AlSi₇ substrate as working electrode (WE) and graphite rods as counter electrodes (CE). The area of the CE is at least double than that of the WE. Experiments are performed in a stirred 2M H₂SO₄ solution at 17±0.2°C. The same anodization time is used in each treatment. Finally the specimens are sealed in boiling water for 30 minutes.¹³

2.3 Metallographic Analysis

In order to evaluate the morphology and measure the thickness of the oxide layers, anodized samples are: a) cut along the cross-section; b) mounted in a thermosetting phenolic resin; c) grinded with SiC papers (up to 4000-grit); and d) polished using a 1µm diamond suspensions. A Leica DM6 optical

microscope coupled with LASX software (version 3.0.11.20652) is used for the acquisition and analysis of the metallographic images.

2.4 Contact Angle Measurements

Contact angle analyses are performed using a drop shape analyzer (KRÜSS, DSA100) in order to evaluate the wettability of the surface of anodized samples. Prior to measurements, samples are accurately cleaned according to the following procedure: 1) degreasing with commercial soap; 2) sonicating in ethanol for 4 minutes; and 3) sonicating in ultrapure water for 12 minutes. Specimens are rinsed with deionized water between each step. Tests are conducted in air at 22°C using a 2 μ L drop of water and ellipse (tangent-1) fitting equation. Five measurements are averaged for each specimen.

2.5 Linear Sweep Voltammetry and Corrosion Testing

Linear sweep voltammetry (LSV) experiments are performed in a three-electrode setup, where: a) the anodized specimen operates as working electrode (WE); b) a graphite rod is used as counter electrode (CE); and c) a saturated calomel electrode (SCE) is used as reference electrode (RE). Measurements are conducted at $30.0 \pm 0.1^\circ\text{C}$ in an aqueous solution containing 5%_{w/v} of NaCl. Data are acquired by means of a BioLogic VMP-300 potentiostat/gavanostat and low-current option. Experiments are performed: 1) between -150mV and +1500mV with respect to the OCV; 2) with a scan rate of 0.167 mV/s; and 3) only after the stabilization of open-circuit voltage (OCV) (fluctuation < 5mV/h). Polarization curves are analyzed using Tafel method,¹⁴ obtaining the: a) corrosion current (I_{corr}); b) corrosion potential (E_{corr}); c) polarization resistance (R_p); and d) anodic breakdown potential (E_{bd}).

3) RESULTS

Anodized specimens are characterized using a multi-technique approach. Results are discussed in terms of: a) oxide layer morphology (Paragraph 3.2 and 3.3); b) wettability of the anodized surface (Paragraph 3.4); c) corrosion resistance (Paragraph 3.5); and d) interplay between process parameters and anodization results (Paragraph 3.6).

3.1 Pulse Sequences, Anodization Parameters and Sample Labelling

All the investigated waveforms are square pulse current waves as schematically depicted in Figure 1.

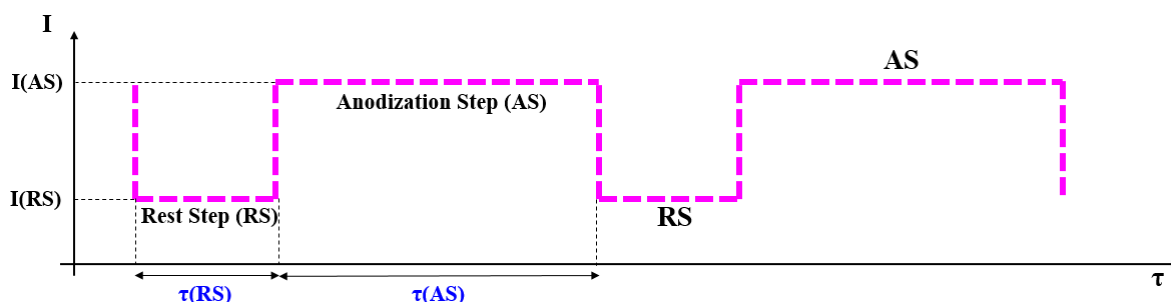


Figure 1: Schematic description of the waveform used in the anodization experiments. Anodization Step (AS) and Rest Step (RS) are described in terms of their: a) intensities $I(\text{AS})$ and $I(\text{RS})$; and b) lengths $\tau(\text{AS})$ and $\tau(\text{RS})$.

In detail, each waveform is composed of two steps, namely the: a) Anodization Step (AS); and b) Rest Step (RS). These steps are identified by two parameters, the intensity (I) and the length (τ). The anodization step has always a higher current density with respect to the rest step.

Nine waveforms are proposed along this manuscript and are summarized in Figure 2. The step intensity and length of all the modified pulse sequences are reported in percentage with respect to I and τ of the anodization step (AS)_s of a standard waveform (S) ($I(AS)_s$ and a $\tau(AS)_s$ are defined equals to 100%, see Figure 2a).

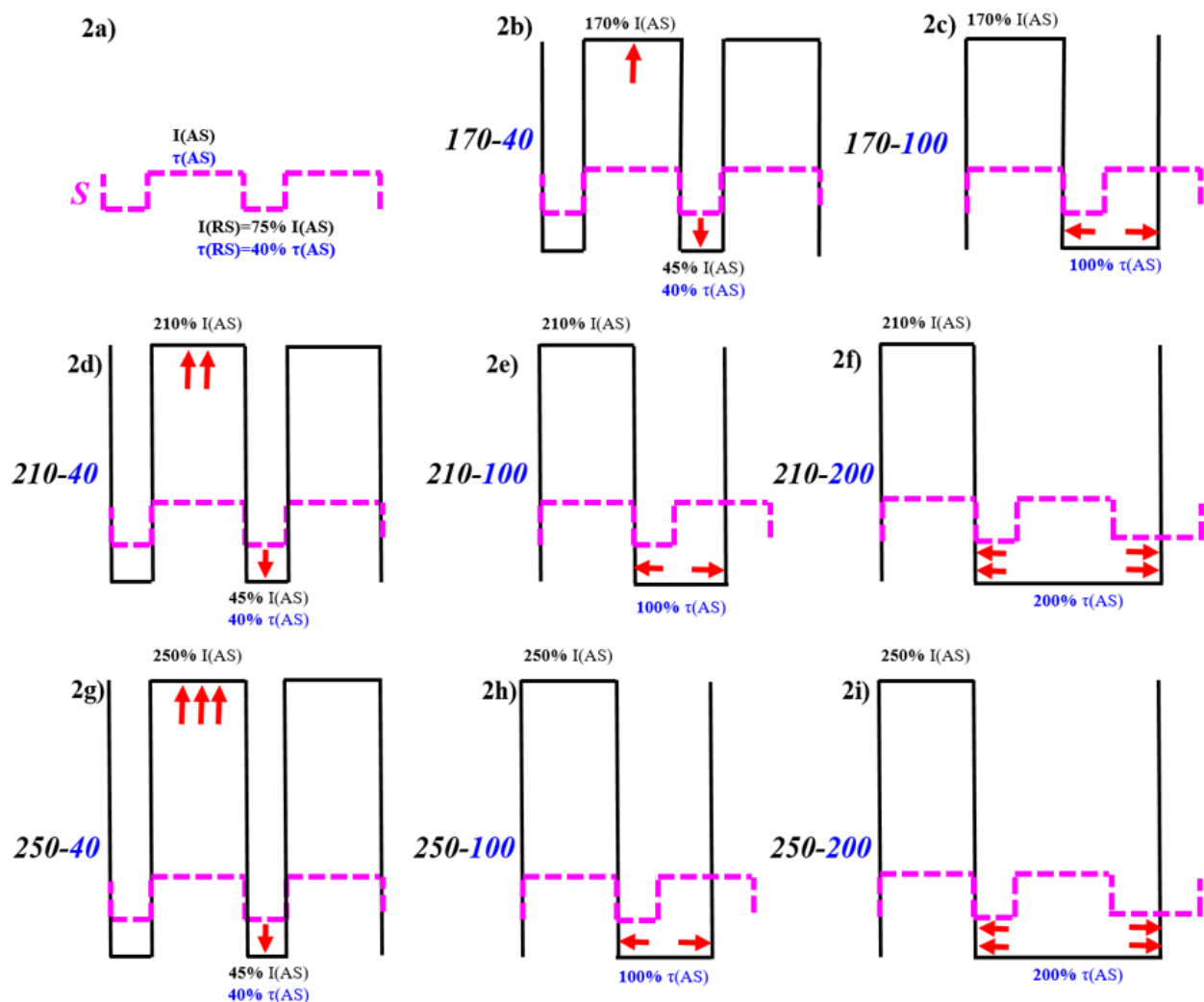


Figure 2: Investigated pulse sequences. Standard waveform (purple) is superimposed to the eight modified pulse sequences (black). Samples are labeled in agreement with the following nomenclature: 1) the first number is the relative intensity of the AS; and 2) the second number is the relative length of the RS.

The investigated waveforms are labeled following this nomenclature: 1) the first number refers to the intensity of the AS; and 2) the second number is the length of the RS. As an example, with respect to the standard waveform, “170-100” presents: a) $I(AS)_{170-100}=170\%I(AS)_s$; and b) $\tau(RS)_{170-100}=100\%\tau(AS)_s$.

Waveforms are divided into three families in agreement with the intensity of the anodization steps, namely: a) 170-x; b) 210-x; and c) 250-x.

The first pulse sequence of each family is generated by: a) decreasing the rest step intensity to 45% of $I(AS)$; and b) increasing the anodization step intensity (170% - 210% - 250% of $I(AS)$) (see Figure 2b-2d-2g).

Indeed, it has already been demonstrated that the combination of a high density current during the AS and a low density current during the RS is capable of improving the anodization results on AlSi7

substrates.⁶ As a matter of fact, during the AS the coating grows faster due to a high current density while, in the RS, the heat produced during the AS is dissipated thus improving the compactness of the oxide.^{8,9}

It appears clear that the efficiency of the RS could be increased not only by decreasing its intensity, but also by increasing its length.

Following this, increasing $\tau(\text{RS})$ (40% - 100% - 200% of $\tau(\text{AS})$) are combined with three values of $I(\text{AS})$ (170% - 210% - 250% of $I(\text{AS})$) generating a nine pulse matrix.

This allows to investigate the combined effect of long rest steps and high anodization steps on the oxide layer morphology, wettability and corrosion resistance.

3.2 Morphologies of the Anodized Layers

Metallographic cross-sections of the coatings are: a) prepared in agreement with the procedure described in Paragraph 2.3; and b) reported in Figure 3.

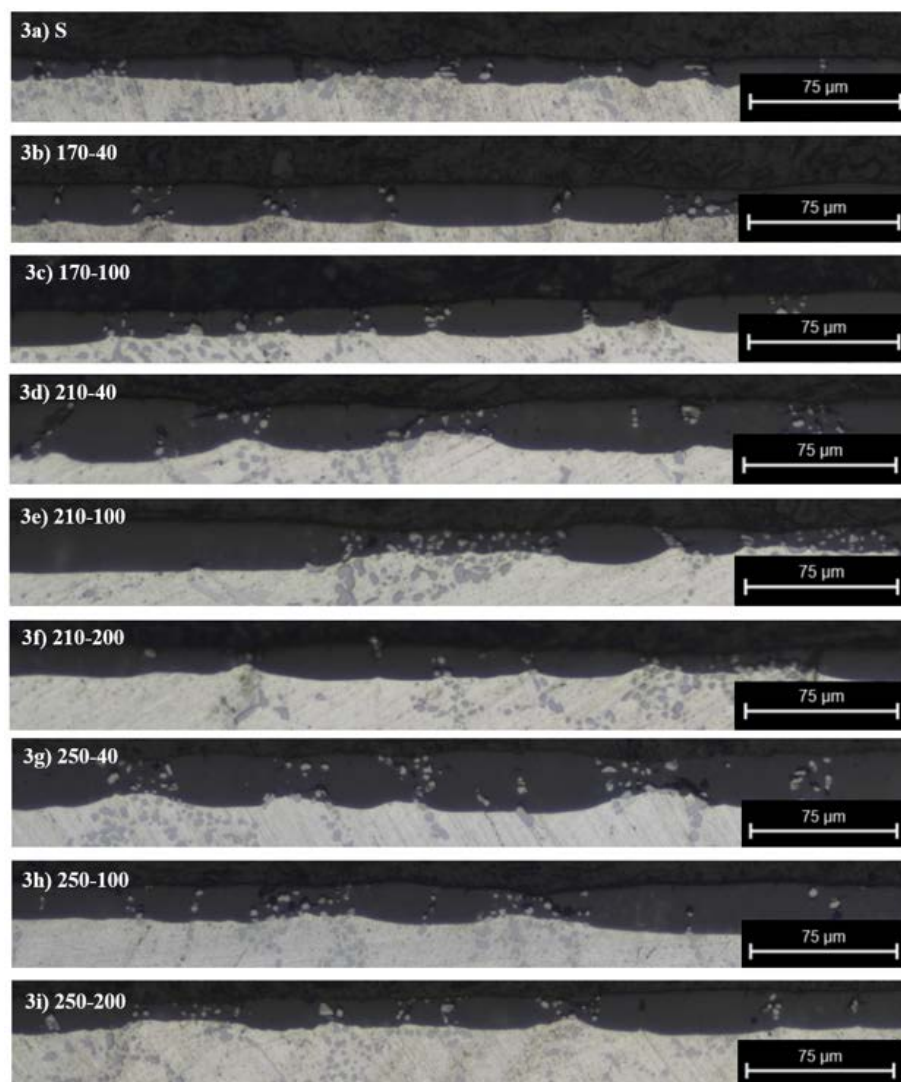


Figure 3: Metallographic cross-sections of the anodized specimens. Each image is labelled in agreement with the corresponding waveform.

The images show clear differences, in terms of micro porosity (voids in correspondence of Si particles), homogeneity and thickness, between the oxide layers. Maximum and minimum thicknesses of the coatings are reported in Table 1.