SVET and SIET Studies on 7081-T73511 Aluminium Alloy

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Pure aluminium has a high resistance to corrosion in many environments as a result of a protective film rapidly formed on its surface when exposed to air or in neutral aqueous solutions, which may resist to long periods of immersion in acid and alkaline media [1]. With the main objective of increasing the mechanical properties of aluminium, alloying additions of Cu and Zn have been made, resulting in the 2000 and 7000 series of aluminium alloys. As the solubility in aluminium of both these elements is limited, second phase particles are formed, which are responsible for the enhancement of the mechanical performance that is characteristic of duraluminium. However, the formation of these precipitates has a deleterious effect on the corrosion resistance of the alloys, due to the galvanic coupling between the precipitates and the matrix. Aluminium alloys are more likely to undergo localised corrosion, as a result of defects on the passive protective film occurring near secondary phase particles.

Corrosion on aluminium alloys is essentially a microgalvanic process between its intermetallics and the matrix [2]. Pitting, a highly localised type of corrosion in the presence of aggressive chloride ions, is the most common form of corrosive attack in aluminium alloys. Corrosion pits are initiated at the oxide layer in sites weakened by chloride attack, normally chemical or physical heterogeneities at the surface, such as inclusions, second-phase particles, flaws, mechanical damage or dislocations [2,3]. Once the pit is formed, corrosion will progress due to the potential difference between the anodic area inside the pit – which often contains acidic, hydrolyzed salts – and the surrounding cathodic area and will be enhanced by the disadvantageous ratio between anodic and cathodic areas.

Due to the above mentioned microgalvanic nature of the processes taking place, a fundamental study of the corrosion of aluminium alloys should involve the use of techniques that allow the assessment of the localised characteristics of a corroding specimen, such as the SVET (Scanning Vibrating Electrode Technique) and the SIET (Scanning Ion-sensitive Electrode Technique) [4]. In fact, metallic corrosion is associated with anodic oxidation (metal oxidation followed by hydrolysis of the formed cation, with production of H^+) and cathodic reduction (water and oxygen reduction with production of OH^-). Thus, the combination of SVET (measuring the localised anodic and cathodic currents produced in the corrosion process) and SIET (probing the changes in local pH due to anodic acidification or cathodic alkalinisation) is a powerful tool for the assessment of the nature and evolution of the microgalvanic corrosion of Al alloys.

The results of local current and pH measurements on samples of 7081-T73511 aluminium alloys (developed for aeronautic applications, such as wing components or fuselage frames) in 0.05 M NaCl solution will be presented and related with the presence of precipitates.

Experimental

Samples of aluminium alloy 7081-T73511 were used as received, after ultrasonic cleaning in acetone. The wt% compositions of the major elements in this alloy are presented in Table 1.

Table 1 - Composition of the AA 7081-T73511 (wt%)

Elements	Zn	Cu	Si	Fe	Mg	Al
wt %	7.24	1.69	0.02	0.04	1.94	bal.

The sampling area of each specimen was defined by a mask of beeswax. Then, in order to assess the microstructure of the alloy and to locate the existing second phase particles, the specimens were observed in JEOL-JSM7001F field emission gun scanning electron microscope (FEG-SEM) equipped with EDX analysis.

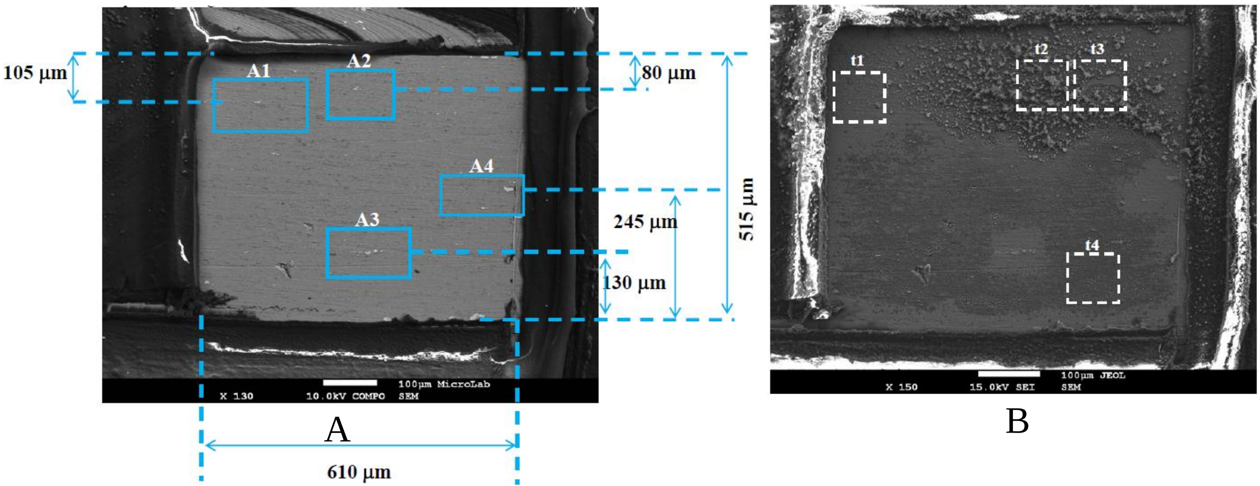
The evolution of the corrosion activity on the samples in 0.05M NaCl solution was studied by SVET and SIET. A commercial system from Applicable Electronics, controlled by the ASET software (Sciencewares), was used to perform these measurements. The total area exposed to the electrolyte was approximately 0.3-0.4 mm^2 for different samples. Measurements were performed in a 26 x 26 grid generating 676 data points, and the resulting measuring step depended of the size of the surface exposed to solution. An insulated Pt-Ir probe with platinum black deposited on a spherical tip of 18 µm diameter was used as vibrating electrode for the SVET measurements. The probe was placed 100 µm above the surface, vibrating in the planes perpendicular (Z) and parallel (X) to the sample's surface. The vibration frequencies of the probe were 124 Hz (Z) and 325 Hz (X). The localized pH measurements (pH-SIET) were carried out using pH-selective glass-capillary microelectrodes. Silanized glass micropipettes were back-filled with the inner filling solution and tip-filled with the H^+-selective ionophore-based membrane. The diameter of the tip of the glass-capillary microelectrodes was 1.5 µm. The pH-selective microelectrodes were calibrated using commercially available pH buffers in a range from pH = 2 to 10.5. The local activity of H^+ was detected 50 µm above the surface. The visual appearance of the tested areas was following during the SVET and SIET measurements, using a microscopic video system with 140 times magnification.

By the end of the measurements and after removal of the testing solution, the samples were again characterized in the FEG-SEM, in order to assess the morphological changes and, in particular, to detect modifications on the surface composition.

Results and Discussion

The FEG-SEM micrographs of one of the specimens, before and after the SVET measurements, are presented in Figures 1a and 1b, respectively. Delimited zones were the near-surface composition was determined by EDX are shown.

Typical SVET and SIET maps obtained in this work are depicted in Figures 2a and 2b, respectively.



A B

Figure 1 – Appearance of the sampling area of the specimens, before (a) and after (b) the SVET measurements. The dimensions of this area are depicted in (a).

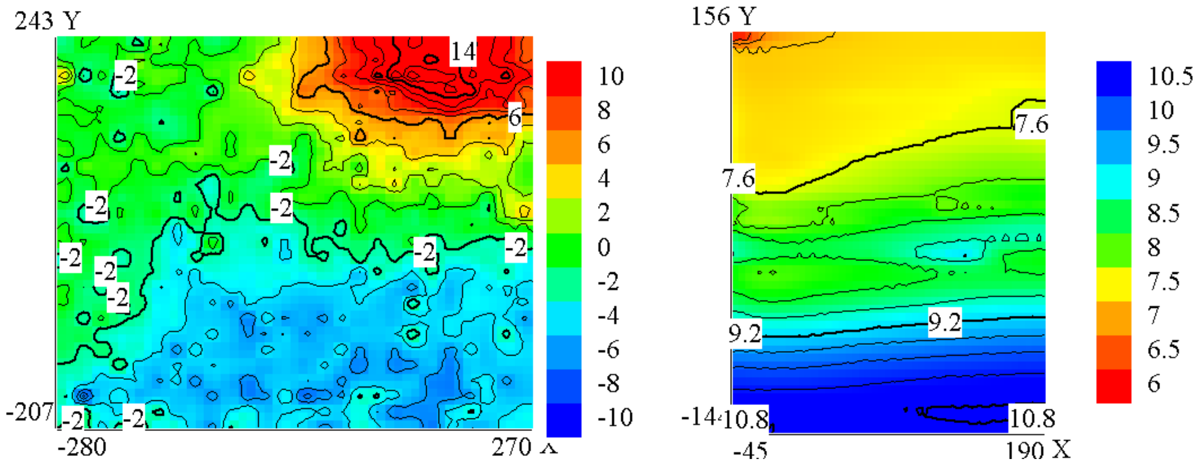


Figure 2 – Typical SVET (a) and SIET (b) maps for AA7081-T73511 samples after approximately 24h of testing in 0.05M NaCl.

The results of the SVET measurements in the AA7081-T73511 can be characterized by rather low activity during the first hour of immersion and formation of anodically active area in the upper central-right area of the sample (Figure 2a). This anodic activity remains stable throughout all 24 hours of immersion. No passivation due to formation of precipitation products is observed. Stable cathodic activity is detected at all lower part of the sample after 2 h of immersion. This activity intensifies after 9 h of immersion and remains stable until the end of the test at 24 hours of immersion.

The results of the pH-microscopy (pH-SIET) can be characterized by slight acidification (pH 5.3 to 5.6), suggesting anodic activity, in the left upper corner of the sample and cathodic activity (alkalinisation, pH 6 to 7.3) in the lower central and right part of the sample. This activity pattern develops from the first minutes of immersion. As immersion continues, acidic anodic activity keeps being stable in the right upper corner, while alkaline cathodic activity spreads to a bigger area. Additionally, a new site of acidification develops in the left lower corner after 12 hours of immersion, pH 6.1- 5.8. This anodic activity ceases after 16 hours of immersion. Anodic activity at the left upper corner proceeds until the end of immersion at 24 hours with pH ca.6.3 (Figure 2b), whereas the cathodic activity with alkalinisation (pH's higher than 9) at the lower part of the specimen remains stable until the end of the test.

SEM/EDS performed on the sample analysed by SVET in the anodic areas suggests dissolution of Al matrix and precipitation of amorphous $Al(OH)_3$ and, eventually, $Al(OH)_2Cl$ at the same sites that correlate well with the pH of formation of said corrosion products and pH measured in anodic sites by pH-SIET. Apparently Al is the only material dissolved there as relative amounts (at%) of Mg, Zn and Cu remain similar to those values in the matrix before immersion.

These and other results will be presented and discussed in more detail during the symposium, leading to the main conclusion that the SVET and pH-SIET are valuable techniques for the assessment of fundamental knowledge on the onset and evolution of the corrosion processes occurring on the inhomogeneous surfaces of aluminium alloys.

References

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