Using LEIS to evaluate the local electrochemical activity of Al 7475 T761/Cu model electrodes

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Introduction

Interpretation of classical EIS diagrams of passive metals undergoing localized corrosion may be complicated since the diagrams can present coupled responses associated both with localized corrosion sites and with the surrounding passive matrix^[1]. High strength Al alloys are particularly prone to this type of corrosion due to the presence of intermetallics (IMs) in their microstructures^[2].

Local Electrochemical Impedance Spectroscopy (LEIS) was initially developed in the beginning of the 90's by Lillard et al.^[3] aiming to study local reactivity in heterogeneous electrodes. The technique is based on the same principles of EIS but with higher spatial resolution, which is a characteristic of techniques that use microprobes positioned near the electrode surface in order to acquire electrical signals from electrochemical reactions. In this technique local ac potential difference is obtained by a bi-microelectrode, and the local current is calculated with the Ohm law's using equation (1):

$$i_{loc}(\omega) = \frac{\Delta V_{microref}(\omega)\kappa}{d}$$
 (1)

Where $\Delta V_{microref}(\omega)$ (V) is the ac potential difference between the two microreference electrodes and κ is the electrolyte specific conductivity (Ω^{-1} cm⁻¹). The dimensional analysis shows that a local current density (A cm⁻²) is calculated, even though the spatial resolution of the measuring probe is not exactly known. From this pioneering work LEIS has been used to investigate the local electrochemical activity of different systems.

In the present work LEIS was used to investigate the electrochemical behavior of Al 7475 T761/Cu model electrodes in sulfate solution. This same approach has already been employed in the literature for different metals ^[4]; however, in the present study a commercial Al alloy was used to build the galvanic couple. Throughout this abstract, definition of local impedances will be used according to the notation defined by Huang et al.^[5], which are represented with low-case letter (z) for local impedance and with high-case (Z) for classical EIS measurements.

Experimental

The model electrodes were constructed by mechanically forcing cylinders of pure copper (5 mm or 11 mm diameter) into circular Al 7475-T761 samples (20 mm diameter) into which a central circular hole with the same diameter of the copper cylinders had been previously drilled. These electrodes were embedded with epoxy resin and ground to obtain a uniform and smooth surface. Before LEIS experiments the model electrodes were mechanically grounded with SiC emery paper up to 4000 grade and then polished with diamond paste down to 1 μ m, followed by rinsing with distilled water and alcohol. Optical microscopy observation revealed that the model electrodes presented no crevice in the junction of the two metals.

The bi-microelectrode (probe) was fabricated with two Ag wires of 160 μ m diameter, which were covered by an AgCl deposit forming a bi-microreference electrode. The experiments were performed with a five electrode system: the three electrodes usually used to perform

global EIS measurement (namely, the working electrode (WE), a large Pt grid as counterelectrode and a sulfate reference electrode (K_2SO_4 saturated) - SSE), and the bimicroelectrode. The scheme of this setup has already been presented elsewhere^[6].

LEIS diagrams were acquired in the frequency range from 63 kHz to 1 Hz, with perturbation amplitude of 50 mV (rms) and 8 points per decade of frequency. It is worth to emphasize that the low frequency limit of the diagrams was limited by the noise in the acquisition of the local potential difference. Experiments were performed in 10 mM Na₂SO₄ solutions, prepared with analytical grade reagent and bi-distilled water. The conductivity of the solution was $2.1 \ 10^{-3} \ \Omega^{-1} \ cm^{-1}$.

Data acquisition was carried out using a Solartron (1254) four-channel frequency response analyzer (FRA), coupled to a high impedance potentiostat (home-made). This setup enables concomitant registration of global (Z) and local (z) impedance diagrams.

Results and Discussion

Figure 1 shows Nyquist diagrams obtained with the model electrodes with Cu core of 11 mm (a-b), and 5 mm (c-d). The z diagrams, Figures 1 (b) and (d), were acquired when the probe was positioned above the WE (the distance from the lower tip to the WE surface was about 160 μ m) and by displacing it from the center (above the Cu core) to the periphery of the WE (*i.e.* at the AA 7475/resin interface). On the other the hand the various Z diagrams were acquired simultaneously with each local measurement. These latter diagrams present only slight variations during the whole experiment duration indicating that the system was at steady state.

The overall analysis of the diagrams presented in Figure 1 demonstrates that, for each electrode and in the same frequency range, the magnitudes of Z and z are similar showing that the local measurements reproduce adequately the global results. However the local impedance presents variations according to the positioning of the probe, showing that it is sensitive to local changes in the electrochemical activity.

Initially local impedance magnitudes were lower when the probe was positioned above the Cu core than when it was placed above the Al alloy. This can be likely ascribed to the increased area for the oxygen reduction reaction in the former situation. As already stated, the electrochemical behavior of high strength Al alloys is mostly governed by the electrochemical activity between the IMs and the matrix ^[7]. The Z diagrams presented in Figures 1(a) and 1(c) indicate a diffusion controlled process in the low frequency domain pointing that the oxygen reduction reaction must be the rate determining step for the overall corrosion process. Therefore, increasing the area of the cathodic site (Cu) diminishes the local impedance response as oxygen can be reduced in greater quantity.

Figures 1(b) and 1(d) also show that, for both model electrodes, the lowest impedance values were obtained when the probe was positioned at the Al 7475-T761/Cu interface. In this particular region the proximity between the Cu core (cathode) and the Al alloy (anode) enhances the electrochemical activity reducing the impedance. Indeed optical microscopy observation of this region showed the deposition of Cu on the Al surface, and also increased corrosion process with the formation of microscopic pits.

The overall analysis of the local diagrams obtained above the Al alloy shows that when the probe is displaced towards the electrode/resin interface z increases again. Due to easier access of the electrolyte to the border of the electrode, it is expected that local impedances would be smaller at the electrode border^[8], deviations from this expected behavior has been ascribed to geometry induced potential distribution^[5]. However, in the present study, the observed response cannot be ascribed solely to geometric features. Indeed, the z values obtained when the probe was positioned above the Al alloy were higher when the ratio Al 7475-T761/Cu was higher, *i.e.* when the Cu core was smaller. This indicates that galvanic effects play a role in the local impedances acquired above Al alloy, otherwise the local diagrams should be of the same order of magnitude.



Figure 1 – Global (a) and (c) and local (b) and (d) Nyquist diagrams for Al 7475-T761/Cu model-electrode with Cu core of 11 mm (a) and (b) and 5 mm (c) and (d) after 2 hours immersion in Na_2SO_4 10 mM.

Conclusions

LEIS measurements were sensitive to local electrochemical phenomena developed in the different regions of the model electrodes.

The results also evidence that the galvanic activity developed between the Al matrix and the Cu core influences the local measurements. In this way lower z values were obtained when the probe was positioned at the Al 7475-T761/Cu interface and higher z values were acquired when the probe was positioned above the Al alloy when the Cu core was smaller.

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