STUDY OF ANODIZING TIME EFFECT ON THE CORROSION BEHAVIOR OF ZIRCALOY-4

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Abstract*. In this study, the effect of anodizing time on the corrosion behavior of Zircaloy-4 alloy was studied in 3.5 wt.% NaCl solution at room temperature. The anodizing bath consisted of a HF solution and the process was achieved by applying a fixed potential of 20 V to Zircaloy-4 specimens. The corrosion behavior was evaluated by electrochemical impedance spectroscopy and potentiodynamic polarization. The tests were conducted over seven days of immersion. The anodized layer morphology was examined by scanning electron microscopy and the chemical composition was evaluated by X-ray photoelectron spectroscopy (XPS). By increasing the anodizing time, the corrosion resistance was improved. This behavior was related to the compactness of the anodized layer, which was dependent on the processing time.*

Keywords*: Zircaloy-4, anodizing, corrosion, potentiodynamic polarization*

1. INTRODUCTION

Zirconium-based alloys are mainly used in nuclear power plants as cladding materials of nuclear fuels and structural components materials because of their low thermal absortion, high stability against corrosion, and adequate ductility. In early 1950s, zirconium alloys were developed for use as cladding materials. Since this period, many studies have been done due to corrosion mechanisms, both out- and in-reactor (Cox, 2005). Zircaloy refers to a group of zirconium alloys. Wettability control is a way of obtaining good surface performance in this kind of heater. Anodic oxidation (or anodization) is a fabrication technique, which can be utilized for hydrophilic surface modification and has several advantages.

Coatings obtained by electrochemical techniques have several more advantages than the conventional ones, as glazers, porcelains, nitride, boride. The thickness and morphology of the films can be controlled by electrochemical parameters (Li et al. 2006). The anodization technique produces roughness on the surface as well as an oxidized metal layer in a one-step fabrication (Ali et al, 2006). Moreover, anodization is easy to apply to a non-flat surface and to expand to a large surface (Lee et al., 2012).

In this paper, we use the fabrication process (via anodization) of anodic cristalline film on Zircaloy-4 surfaces using HF solution as the electrolyte. Different treatment times were employed to obtain the anodized layer. Its morphology and chemical composition characteristics were studied by SEM and XPS. In addition, the electrochemical corrosion behavior was investigated to evaluate its corrosion resistance.

2. EXPERIMENTAL

2.1. Material

The specimens were cut from a cilindrical tube of Zircaloy-4 kindly provided by INB (Indústrias Nucleares do Brasil). The nominal chemical composition of the alloy (wt.%) was 1.3% Sn, 0.20% Fe, 0.11% Cr, 0.11% O, 0.01% Si as Cox, 2006 provided. Specimens for anodizing were employed in the as-received state. The working electrodes for the electrochemical tests were prepared by encapsulating the specimens into cold cure epoxy resin. Surface preparation consisted of grinding in sanding paper in the following order (220, 600, 800, 1200 and 2400), and an area of 0.4 cm^2 were exposed to solution.

2.2. Anodizing

The anodizing bath consisted of a 5wt.% HF solution at room temperature. The procedure was carried out electrolytically at constant voltage of 20 V for different times, 1, 2 and 3 minutes. The anodizing potential was provided by a variable power supply. The cathode was a stainless steel bar and the Zircaloy-4 samples were the anodes. After anodizing the specimens were washed in deionized water and dried in air.

2.2. Microstructural characterization and surface analysis

The effect of anodization was evaluated through scanning electronical microscopy (SEM). Both as-cast and anodized specimens morphology surface were observed in MEV – FEI Quanta 250.

XPS analyses were carried out in K-alpha ThermoFisher Scientific instrument operating with Al-kα radiation source. The anodized layer was subjected to point analysis. Survey spectra were acquired with X-ray spot radius of 400 μm. The binding energies were calibrated with respect to the reference C1s peak at 284.6 eV.

2.3. Electrochemical tests

All the electrochemical measurements were performed with Autolab M101 potentiostat/galvanostat. The electrolyte employed for the measurements was a 3.5 wt.% NaCl at room temperature. This electrolyte traditionally employed for investigating the corrosion resistance of metallic materials. A conventional three-electrode cell was used for all the electrochemical tests with a platinum wire as the counter-electrode, Ag/AgCl as the reference and anodized Zircaloy-4 specimens as the working electrodes. As-received specimens were also tested for comparison. All the electrochemical tests were conducted in triplicate to examine the reproducibility of the results.

2.3.1. Electrochemical impedance spectroscopy (EIS)

To ensure a stable electrochemical condition, the open circuit potential was monitored for 1 h before the experiments. EIS measurements were performed over the frequency range from 100 kHz to 10 mHz, with an acquisition of 10 point per decade of frequency, at the open circuit potential (OCP), and an amplitude of the perturbation signal of 10 mV(rms). The measurements were carried out after 7 days of immersion in the electrolyte. The results are given as Nyquist plots.

2.3.2. Potenciodynamic polarization curves

Potentiodynamic polarization curves were obtained right after the EIS measurements using a scanning rate of $1mVs^{-1}$. The potential was swept from –0.3V versus the OCP up to +1.0 $V_{Ag/AgCl}$. A set of three different specimens was polarized at each anodization condition.

3. RESULTS AND DISCUSSION

3.1. Microstructural analysis

SEM micrographs of the bare Zircaloy-4 surface and anodized for 1 minute are shown in Fig. 1a and b, respectively. The anodized film was compact and uniformly covered the specimen. The surface is apparently smooth and has few defects.

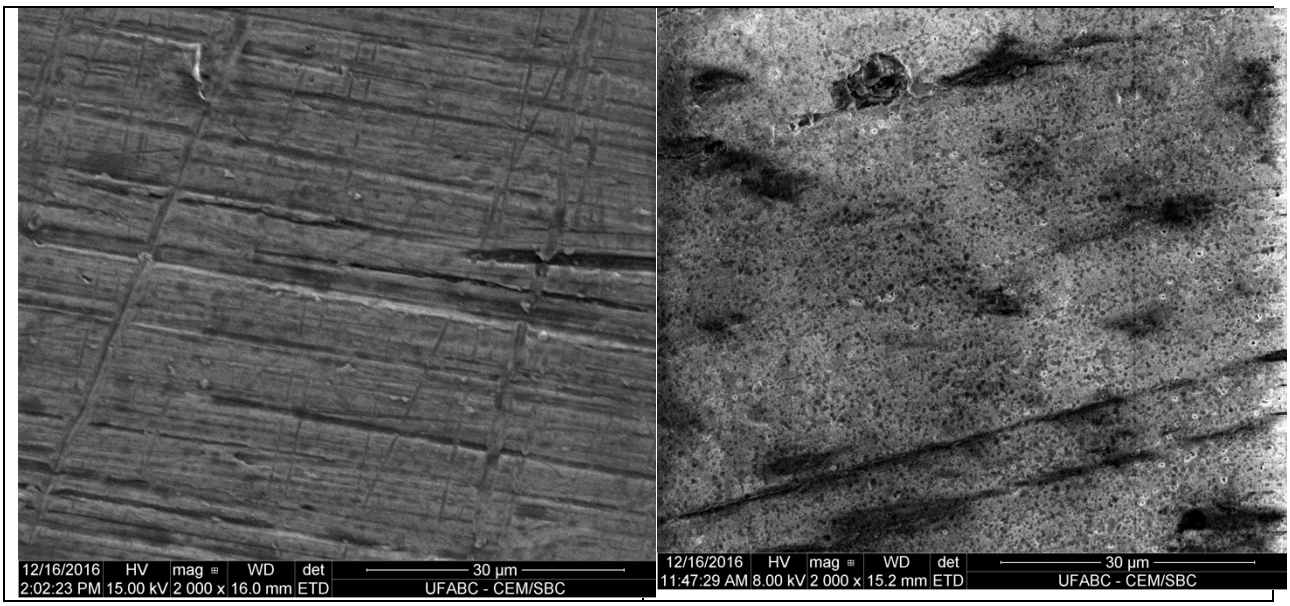

Figure 1. SEM micrographs of the surfaces of the Zircaloy-4: a) without anodizing; b) anodized for 1 min.

A further increase in the anodizing time influenced the surface appearance. This change is shown in Fig. 2, which shows the anodized films obtained at 2 and 3 minutes. The color of the anodized film is light gray and characterized by numerous pores and cracks.

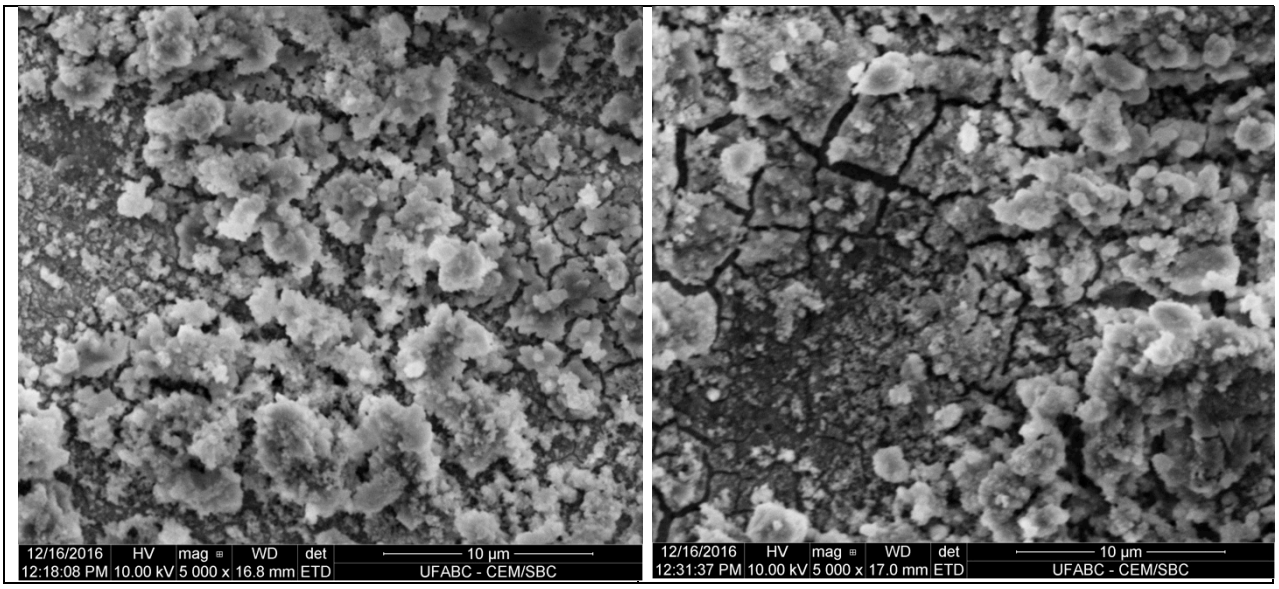

Figure 2. SEM micrographs of the surfaces of the Zircaloy anodized; (a) anodized for 2 minutes; (b) anodized for 3 minutes.

3.2 X-ray photoelectron spectroscopy (XPS)

XPS survey spectra of the untreated and anodized Zircaloy-4 specimens are shown in Fig. 3. Zirconium, oxygen and carbon were determined in the untreated surface. Carbon was ascribed to surface contamination (adventitious carbon), as frequently reported in the literature (Sánchez et al., 2011). Fluorine was incorporated into the anodic films after anodizing. Several authors have reported F^- incorportation into anodic films formed on zirconium-based alloys subjected to anodizing in fluorine-containing electrolytes (Romonti et al., 2016). Zirconium was detected as Zr 3d5/2 and Zr 3d3/2 peaks, denoting it is in the fully oxidized state as Zr^{4+} species (Wang and Luo, 2010). The concentration of Zr, F and O in the anodic films was determined from the XPS survey spectra. The results are shown in Fig. 4.

After anodizing the surface became enriched in zirconium and fluorine ions. Zr^{4+} enrichment has been reported for anodized zircaloy-2 (Satpati et al, 2005). Our results point to a similar behavior, in spite of the different electrolyte composition with respect to the work by Saptati et al. This effect has been ascribed to the high affinity of zirconium towards oxygen, leading to the forming of a thicker oxide layer. Notwithstanding, the zirconium atomic concentration did not present a clear direct correlation with the anodizing time, since it is lower for the 2 minutes-anodized surface than for the specimens anodized for 1 min.

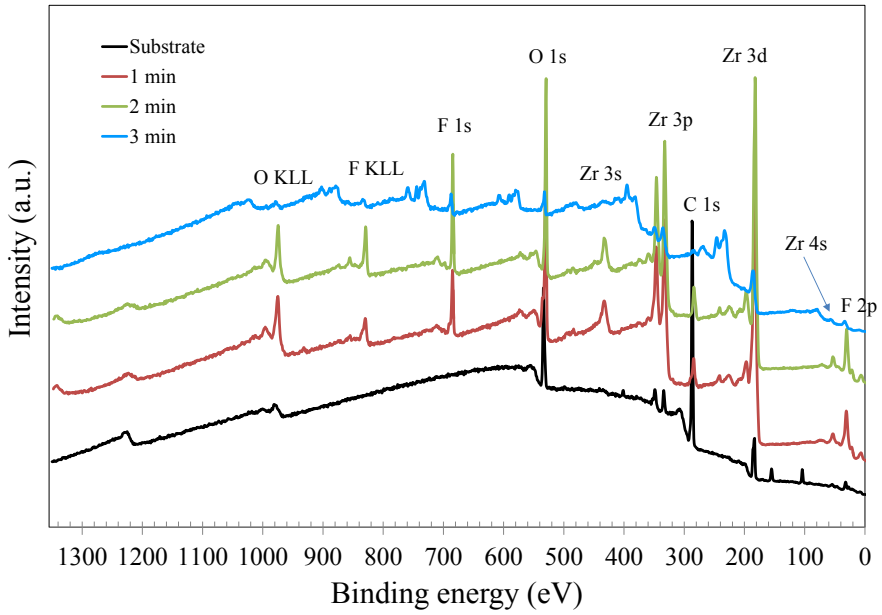

Figure 3. XPS survey spectra of the untreated and anodized Zircaloy-4 specimens.

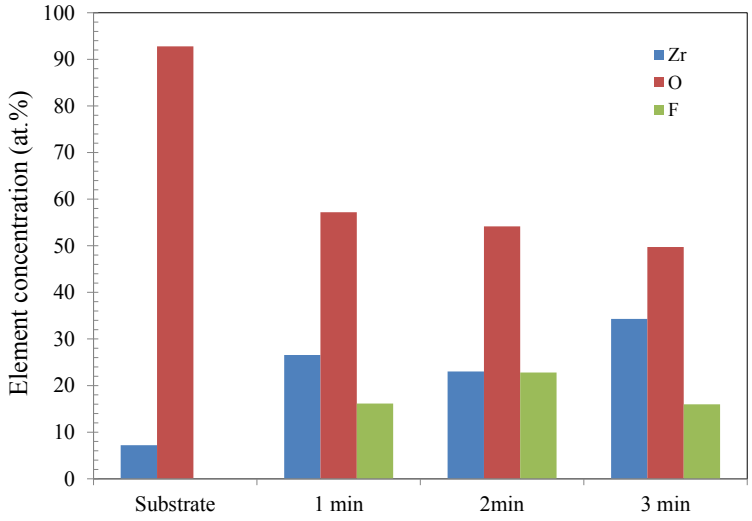

Figure 4. XPS atomic percentages of the untreated and anodized Zircaloy-4 surfaces.

3.3. Electrochemical tests

3.3.1. EIS measurements

First of all, the open circuit potential (OCP) was monitored for 1h in order to ensure a steady state condition for the EIS measurements. Figure 5 shows the plots of OCP versus time for the untreated Zircaloy-4 substrate and for the anodized surfaces obtained at 1, 2 and 3minutes. The tests were carried out in 3.5 wt.% NaCl at room temperature. The OCP of the substrate is more negative than the anodized specimens, suggesting that its surface is more prone to corrosion processes in comparison with the anodized layers(Oliveira, 2013). As observed in Fig. 5, a steady state condition was achieved after monitoring. The variation of the open circuit potential was found to be negligible for during the monitoring period, ensuring a stable condition for the EIS measurements. The noblest value of the OCP was achieved for the specimens treated for 1 minute. This result is likely to be related to the more compact surface morphology obtained at this anodizing condition, as shown in Fig. 1b.

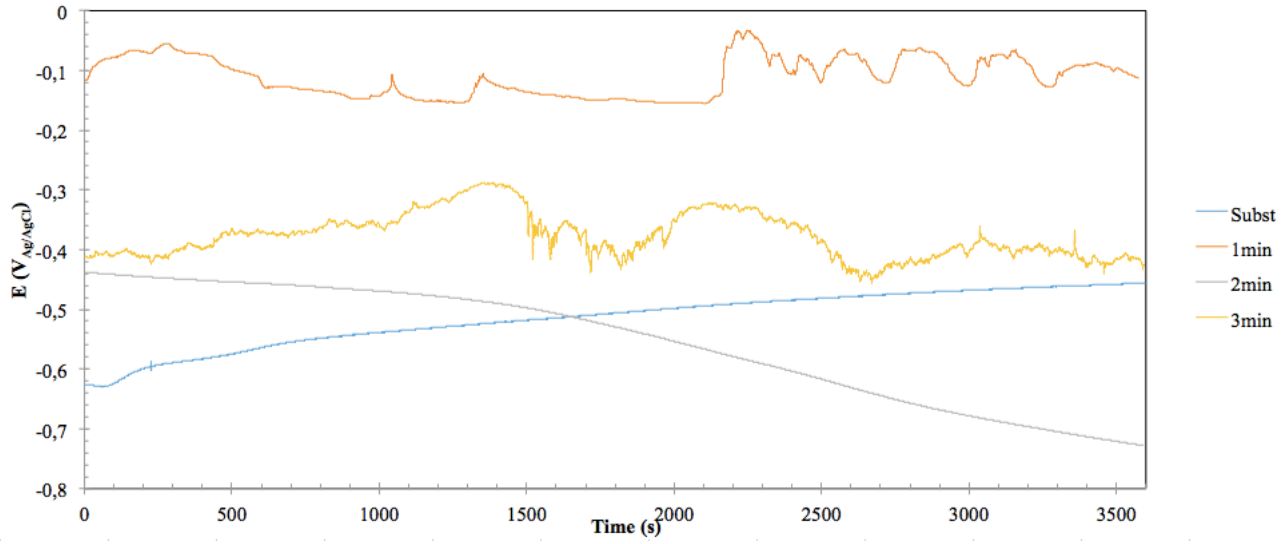

Figure 5. Open circuit potential versus time for the Zircaloy-4 specimens in the as-received condition and anodized for different times. Results obtained in 3.5 wt.% NaCl solution at room temperature.

The Nyquist plots of the anodized films obtained after 7 days of immersion in 3.5 wt.% NaCl solution at room temperature are shown in Fig. 6. The plot obtained for the as-received Zircaloy-4 is also shown for comparison. The plots are characterized by one capacitive loop, independently of the anodizing time. The radii of the capacitive loops are much larger for the anodized material than for the substrate. Corrosion resistant surfaces are associated with high impedance values at low frequencies which correspond to less flattened capacitive loops with large radius (Pillis et al., 2016). The small capacitive loop of the substrate without anodization denotes its lower corrosion resistance when compared to the anodized samples.

The EIS response of the anodized and untreated substrates was also assessed by Bode phase angle plots (Fig. 6.b). The plots of the anodized samples have a wide plateau extending from approximately 100 Hz up to 0.01Hz. The plateau reaches -80^{o} at its maximum and then decreases to -70^{o} at the lowest frequencies. However, for the untreatedsubstrate, the phase plot is characterized by a plateau near -70^{o} and it is shorter than the plateau observed for anodized samples, beginning at approximately 10 kHz and extending up to 100 Hz. It is known from the literature that a phase angle of -90^{o} would be expected for a pure capacitive response of the electrode surface. The more the phase angle deviates from this value, the more imperfect is the capacitive behavior of the electrode surface (Liu et al., 2003). Drop off of the phase angle at low frequencies has been associated with decreased corrosion resistance due to charge transfer reactions at the electrode/electrolyte interface at the base of the defects of coated metals (Pillis et al. 2016). Bode plots showing the variation of the impedance modulus with frequency are also shown in Fig. 6b. The high impedance of the anodized specimens is clearly seen in comparison with the bare substrate.

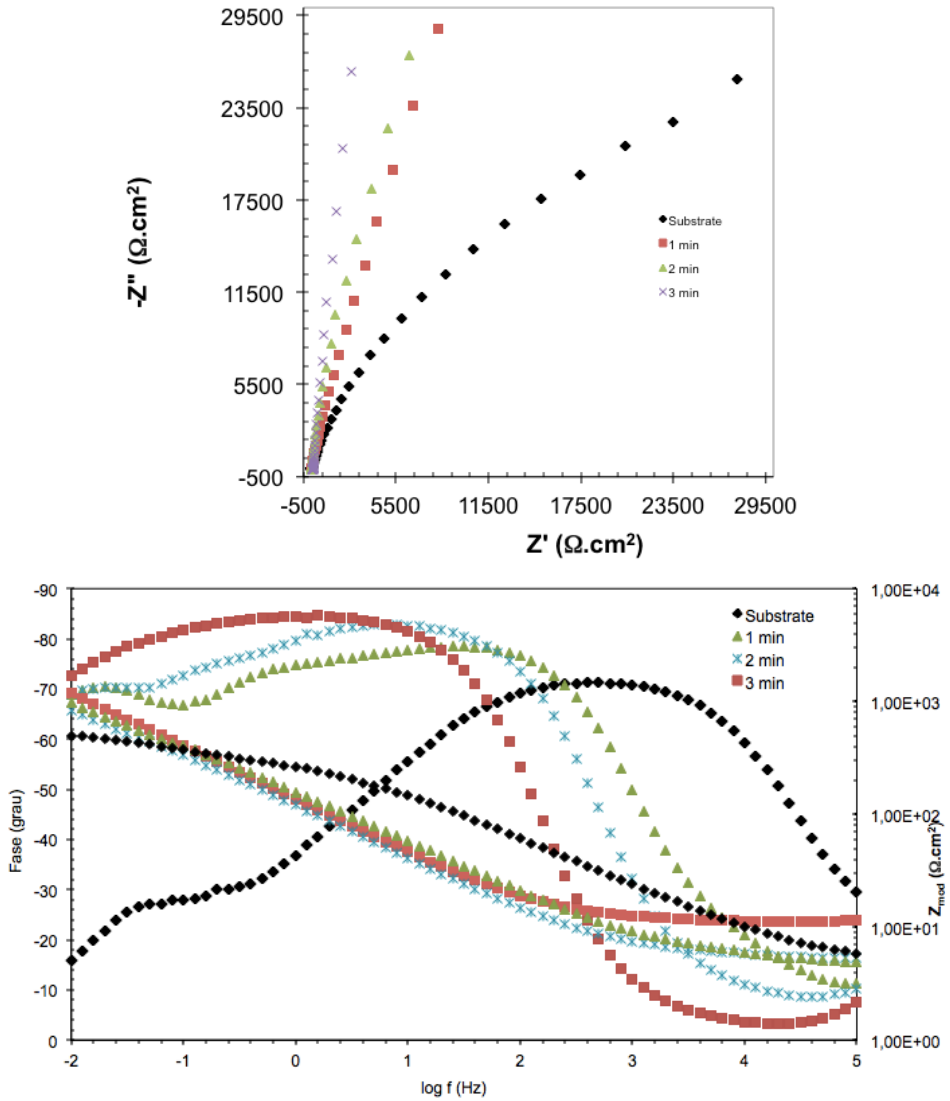

Figure 6. (A) Nyquist and (B) phase and Z_{mod} plots of the Zircaloy anodized and without anodization substrates obtained after 7 days of immersion 3.5 wt.% NaCl solution at room temperature.

3.3.2. Potentiodynamic polarization curves

The electrochemical behavior of the anodized Zircaloy-4 surfaces was further assessed using potentiodynamic polarization curves. The results are shown in Fig. 7. The values of corrosion potential (E_{corr}) and corrosion current density (i_{corr}) obtained from these curves are displayed in Tab. 1. The values of i_{corr} were obtained using the Tafel extrapolation method, considering only cathodic branch of the polarization curve. It was adopted based on the fact that the passive region in the polarization curves makes difficult to accurately determine the anodic Tafel slope (Quartarone et al., 2003).

From Fig. 7, it can be said that the anodizing treatment can improve the electrochemical corrosion resistance of Zircaloy-4 at least one condition, anodizing for 1 minute. The i_{corr} of the as-received Zircaloy-4 sample was about 0,40 $\mu A.cm^{-2}$ while that of the anodic oxid filme was reduced to 0,02 $\mu A.cm^{-2}$. Similar results were observed by Lii et al., 2006.

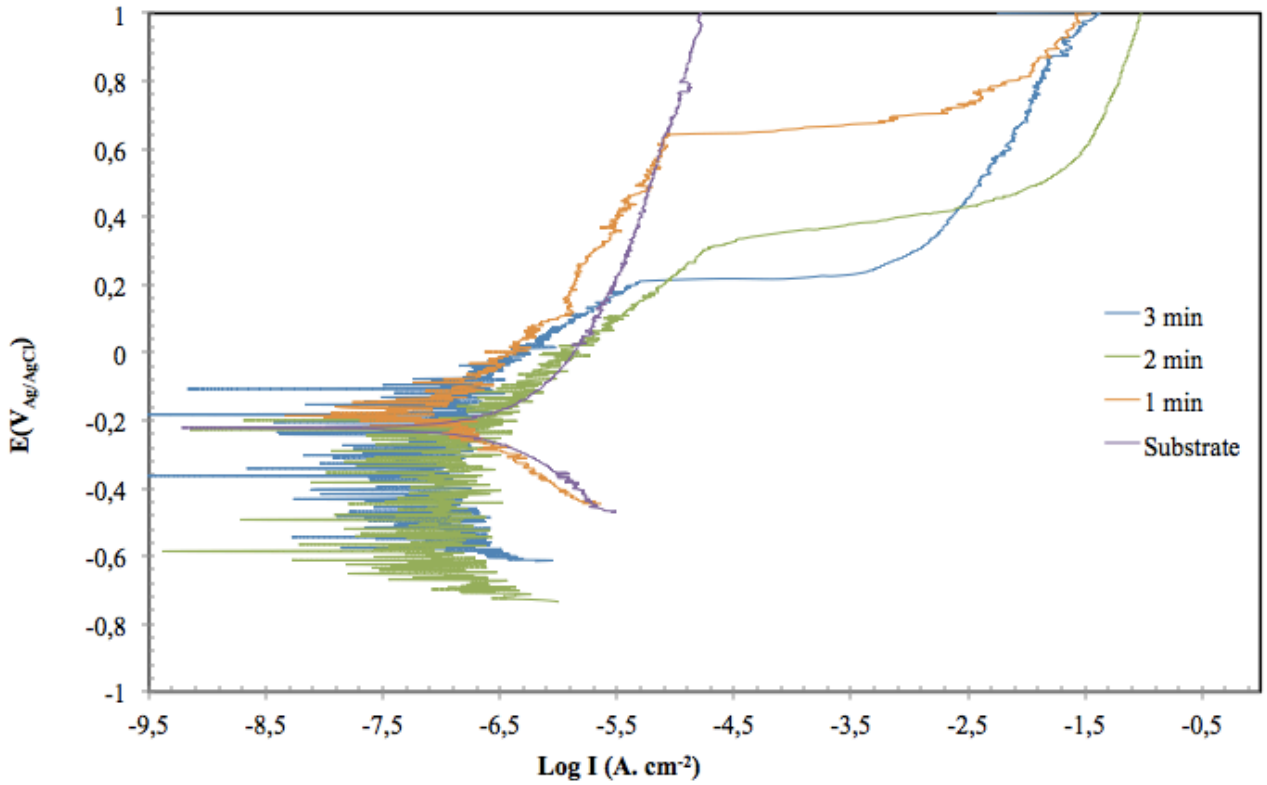

Figure 7. Potentiodynamic polarization curves of untreated and anodized Zircaloy-4 specimens obtained after 7 days of immersion 3.5 wt.% NaCl solution at room temperature.

Table 1. Eletrochemical parameters of the bare Zircaloy substrate and anodized samples.

Condição	$E_{corr}(V_{Ag/AgCl})$	I_{corr} ($\mu A.cm^{-2}$)	b_c (V/decade)
3 min	-0,29	0,10	-0,41
2 min	-0,3	0,08	-0,21
1 min	-0,19	0,02	-0,20
Substrate	-0,22	0,40	-0,20

In general the polarization curves show a typical passive region. The polarization curve of anodized Zircaloy is typical of passive surfaces. This can be realized by the presence of an approximately constant current density region in the anodic branches of the curves. It is also considerable that the passive behavior of the anodized samples is more stable than that of the sample without anodization, since the current density in the passive region is clearly lower than that in the polarization curve of the bare sample, as shown in Tab. 1, also corresponding for I_{corr}. The values of b_c for the anodized samples are similar to that for the bare substrate, indicating that the cathodic reactions were slightly affected by the presence of the anodized film. For samples in condition of 1 minute anodizing, the corrosion current density has been the lowest values between others conditions, what corresponds to better corrosion resistance.

4. Conclusions

The effect of the anodizing time on the surface morphology, chemical composition and corrosion behavior of Zircaloy-4 specimens has been evaluated. Several cracks were formed for anodizing at 2 and 3 minutes whereas 1 minute-treatment yielded the most compact and homogeneous anodized layer. Surface chemical composition was altered by anodizing. Fluorine ions were incorporated into the anodic films. Zirconium ions enrichment was also observed. The corrosion behavior could be associated rather with surface morphology than with the chemical composition of the anodized layers. The anodic films obtained at the 1 minute-treatment were the most corrosion resistant. This effect was likely due to the compact and homogeneous film formed at this condition.

5. ACKNOWLEDGEMENTS

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