In this work, the behavior of cerium, cobalt and manganese nitrates, and their mixtures as corrosion inhibitors for AA 2024-T3 aluminum alloy has been investigated by potentiodynamic polarization and electrochemical noise measurement. It was found that cerium nitrate provides the best inhibition performance, followed by cobalt nitrate, with manganese nitrate displaying little or no inhibiting properties. The concentration of the nitrate salt is critical in determining the inhibition performance; an excessive concentration of nitrate ions results in increase of the corrosion rate. Finally, a synergistic effect between different inhibitors was not observed, indicating that the best performing inhibitor, cerium nitrate, determines the overall anticorrosion behavior.

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Chromate surface treatments are often used for corrosion control of aluminum alloys (AA). However, much effort has been focused on the development of new treatments for the replacement of hexavalent chromium, since it is toxic and provokes cancer\(^1,2\) and environmental issues.

Cerium nitrate and several cerium based compounds are well known inhibitors and are promising candidates for the replacement of chromate compounds.\(^3,4\) The presence of cerium cations in proximity of the alloy surface results in the precipitation of insoluble deposits over the cathodic intermetallics, as a result of the local alkalinization due to the cathodic reaction.\(^9,10\) These deposits are formed by CeO\(_2\), Ce(OH)\(_4\) and Ce(OH)\(_3\).\(^11\)

Cobalt ions were previously reported as cathodic corrosion inhibitors for AA 2024-T3, since their presence decreased the oxygen reduction rate\(^8\) on the alloy. Cobalt sulfate was also found to suppress the cathodic reaction on copper electrodes by chemical precipitation of Co(OH)\(_2\) in alkaline solutions with a bulk pH close to 9.5.\(^13\) Cobalt ions were also found to be cathodic inhibitors for galvanized steel, due to the reduction of the cathodic reaction rate.\(^14\)

Manganese has been studied for anticorrosive properties due to its multiple oxidation states, a characteristic similar to chromium. Manganese-based conversion coatings were used on aluminum alloys and pure aluminum, providing corrosion protection by forming a protective layer.\(^15,16\)

Although studies on the inhibition performance of each of the above mentioned compounds are abundant in the literature, comparative studies are less common.\(^12\) Further, the techniques used for the assessment of the performance vary widely, ranging from potentiodynamic polarization\(^11,18\) to electrochemical impedance spectroscopy\(^17\) and salt spray testing\(^19\) which are generally performed in environments and with inhibitor concentrations that are not directly comparable. This work aims to illustrate the advantages in using image-assisted electrochemical noise analysis\(^20–22\) compared to more traditional approaches, such as potentiodynamic polarization, in order to comparatively evaluate the effectiveness of corrosion inhibitors. Additionally, in this study, corrosion testing was systematically conducted in environments containing relatively high amounts of chlorides (3.5 wt%) and low concentrations of inhibitors (mM) in order to evaluate the performance under demanding conditions.

In order to obtain information on the longer-term behavior of the candidate inhibitors, image assisted electrochemical noise analysis was employed.\(^3,20\) The technique is based on recording the potential and the coupling current of two nominally identical electrodes immersed in an aggressive environment in the presence and absence of the candidate corrosion inhibitor. Simultaneously, images of the surface are acquired at a fixed time interval, revealing the progress of corrosion on the surface. Finally, the electrochemical noise data are analyzed to obtain the time evolution of the low-frequency value of the noise impedance modulus, which can be used to qualitatively compare the inhibitor anticorrosion performance of the inhibitors. The advantage of this technique is that information on the effectiveness of the candidate inhibitor can be obtained without introducing any perturbation to the corroding surface.

**Experimental**

*Materials and reagents.*— Aluminum alloy AA 2024-T3 (nominal composition in wt%: Al 90.7–94.7, Si <0.5, Fe <0.5, Cu 3.8–4.9, Mn 0.3–0.9, Mg 1.2–1.8, Cr <0.1, Zn <0.25, Ti <0.15) electrodes obtained from 1.6 mm thick sheets were used for all the experiments. All chemicals were of analytical reagent grade. Cobalt nitrate, Co(NO\(_3\))\(_2\), cerium nitrate, Ce(NO\(_3\))\(_3\), manganese nitrate, Mn(NO\(_3\))\(_2\) were sourced from Sigma-Aldrich, St. Louis, USA.

*Specimen preparation and testing.*— In order to remove residual oxides and oil contamination from the production process, the AA 2024-T3 specimens were pre-treated by etching and desmutting. Etching involved initial immersion in 10% w/v NaOH for 30 seconds at 60°C. Subsequently, the specimens were rinsed with de-ionized water and desmutted by immersion in 30 vol% HNO\(_3\) for 30 seconds at room temperature. Finally, the specimens were rinsed with deionized water and dried in a cool air stream.

Potentiodynamic polarization tests were performed at room temperature, using a three-electrode cell, consisting of the AA 2024-T3 working electrode (exposed area of \(\approx 2.25\) cm\(^2\)), a saturated calomel electrode (SCE) as the reference electrode, and a platinum electrode as the counter electrode.

The test environment was 3.5% NaCl with 0.15 mM concentration of each inhibitor. For anodic polarization, the potential was varied between –0.05 V vs open circuit potential (OCP) to –0.3 V vs SCE and for cathodic polarization, from the OCP to –1 V vs SCE. The scan rate was 0.10 mV/s. The measurements were undertaken after 1 hour of free corrosion at the OCP.

Electrochemical noise testing was performed by coupling two nominally identical electrodes by a 10 kohm resistor, using the method described in detail in.\(^20\) The potentials of each individual electrode with respect to a saturated calomel reference electrode were recorded by using a NI-USB6009 (National Instrument) analog to digital converter. The electrochemical noise signal was recorded using in-house developed software, acquiring 1023 Hz segments of 1000 points at each iteration. Between iterations, the 1000 values acquired were averaged to record a single value of potential. The final dataset comprised potential values spaced by \(\pm 0.05\) s in time. Under the assumption that the noise present above 1023 Hz is negligible compared with
the noise present below 0.5 Hz, this procedure enables an accurate recording of the potential noise in the frequencies of interest, avoiding aliasing of frequencies between 0.5 and 1023 Hz and minimizing the 50 Hz interference from the mains supply. The current exchanged between the two electrodes was calculated by taking the difference between the electrode potentials (equal to the potential difference across resistor used for the coupling) and dividing it by the value of the resistance used for the galvanic coupling. The advantages of the setup used and the detailed procedure enabled the value of noise resistance (or impedance) to be obtained, as described in detail in.20

In order to obtain the time-evolution of the low frequency value of the noise impedance, the following procedure was applied:20 1) from the complete potential and current dataset a segment of 8192 points (2 points equivalent to about 2.3 hours) was extracted; 2) linear trend removal and Hann windowing were applied to the extracted segment; 3) two potential (one for each electrode) and one current power spectral densities were calculated by fast Fourier transform; 4) the apparent noise impedance was calculated by taking the square root of the potential power spectral density of each electrode divided by the current power spectral density; 5) the average square of the noise impedance was calculated; 6) the positive solution of equation 1 was calculated to obtain the impedance spectrum20

\[ Z(f)_{1,2} = -R_m + \sqrt{4Z(f)^2_{\text{exv}} - R_m^2} \]  

7) the first 5 points from the low-frequency end of the impedance spectrum were averaged to obtain a value of low-frequency impedance; 8) the obtained value was assigned to the time corresponding to the first point of the segment used for the calculation; 9) a new segment was extracted 250 points after the previous segment; and 10) the described operations were repeated until the end of the dataset, obtaining the time evolution of the low frequency noise impedance. In equation 1, \( Z(f)_{1,2} \) is the noise impedance modulus of the electrodes (assumed identical), \( Z(f)^2_{\text{exv}} \) is the average of the squares of the apparent noise impedance modulus and \( R_m \) is the value of the resistor used for the galvanic coupling between the two nominally identical electrodes.

Image acquisition was performed by Maplin USB microscopes controlled by an in-house developed software based on the Labview programming language. Images were acquired every 10 minutes and saved as jpeg images. The reproducibility of the results and the reliability of the experimental setups were evaluated initially by repeating selected electrochemical noise and potentiodynamic polarization tests. For cathodic potentiodynamic polarization, the current response for tests conducted under nominally identical conditions was generally overlapping, whereas, for anodic polarizations, a maximum difference of ±15% in the current response was observed. The time evolution of the low-frequency values of the noise impedance generally displayed relatively large transient fluctuations but similar trends. Averaging the low-frequency noise impedance values for the entire duration of the experiment indicated maximum variations of ±10% for tests conducted in nominally identical conditions.

**Scanning electron microscopy (SEM).—** The specimens for SEM observation were mechanically polished to 1 a micron finish in order to generate a flat surface to facilitate identification of corrosion sites and inhibitor deposition. For SEM observation, the specimens were immersed in the 3.5% NaCl solution in the presence of inhibitors for 6 hours, then rinsed with distilled water and dried with a cool air stream. The surfaces of the specimens were examined in a ZEISS Ultra 55 field-emission gun scanning electron microscope. EDX (energy dispersive X-ray spectroscopy) was used to characterize the composition of the second phase particles present on the alloy surface.

**Results**

**Corrosion tests.—** Polarization curves.— The anodic polarization curves for the various nitrate salts after 1 hour of exposure in the corrosive environment presented similar behavior to that of the specimen immersed in the solution without inhibitor (Figure 1). For all the nitrates, the anodic current density was similar to that revealed in the absence of inhibitor. Unreported anodic polarization experiments conducted in deaerated conditions showed similar behavior, i.e. little or no changes in the shape of the anodic polarization curves as a result of inhibitor addition. Only during cathodic polarization in aerated electrolyte, a slightly decreased current density was observed for the electrode immersed in the presence of cerium nitrate.

**Image assisted electrochemical noise.—** In order to evaluate the anticorrosion performance of each inhibitor, image assisted electrochemical noise measurements were undertaken. Figure 2a shows the evolution of the low frequency noise impedance as a function of time in 3.5% NaCl with addition of Ce(NO₃)₃ at three different concentrations. The low concentration (0.15 mM) of Ce(NO₃)₃ had a beneficial effect, as the impedance was four to five times higher than the impedance measured for the specimen immersed in the absence of the inhibitor at the end of the 40 hours test. The specimen immersed in the presence of the inhibitor in concentration of 1.5 mM displayed an impedance modulus higher compared to the specimen immersed in the environment without inhibitor, but lower than the impedance of the specimen immersed in the presence of the low concentration of inhibitor. High concentration (15 mM of cerium nitrate) resulted in the reduction of the impedance by almost one order of magnitude compared to the uninhibited case. The optical images obtained during the experiment corroborate the results of the electrochemical noise analysis (Figure 2b); the surface of the alloy immersed in the environment with low concentration of Ce(NO₃)₃ appeared less corroded than in the absence of the inhibitor or in the presence of higher inhibitor concentration. Importantly, the surface of the alloy immersed in the environment with the higher inhibitor concentration appeared more corroded that the surface of the alloy immersed in the environment without the inhibitor. The addition of Co(NO₃)₃ to the 3.5% NaCl environment had an effect similar to that revealed for Ce(NO₃)₃. The specimens immersed in the environment with a low concentration of inhibitor presented impedance values significantly higher than the specimen immersed in the absence of the inhibitor. It is worth noticing that potentiodynamic polarization tests did not provide any evidence of anodic or cathodic inhibition for cobalt nitrate, but the inhibiting effect was evident from the electrochemical noise analysis. Similarly to what had been observed for cerium nitrate, increasing the concentration of Co(NO₃)₃ resulted in a reduction in the noise impedance (Figure 3a). The optical images recorded during exposure indicated that corrosion progressed less in the presence of low
Figure 2. a) Variation of noise impedance with time, b) optical images during EN measurement for AA 2024-T3 1) without inhibitor, with 2) 0.15 mM Ce(NO₃)₃, 3) 1.5 mM Ce(NO₃)₃ and 4) 15 mM Ce(NO₃)₃ in 3.5% NaCl solution.

and medium concentrations of inhibitor compared to high concentration of inhibitor. For the high concentration of inhibitor, the surface of the alloy appeared more severely corroded with evidence of copper deposits in proximity of pits (Figure 3b). Addition of Mn(NO₃)₂ in low and medium concentrations resulted in a value of noise impedance similar to that observed in the absence of inhibitor (Figure 4a). As in all the previous cases, high concentration of Mn(NO₃)₂ resulted in reduction of the noise impedance to a value below that estimated for the specimen immersed in the absence of inhibitor. From the optical images, it appears that corrosion propagated from the early hours of exposure for all conditions (Figure 4b).

As a control test, nitric acid neutralized with NaOH to pH 7.00 (NaNO₃) was added to the 3.5% NaCl electrolyte in a similar set of experiments. The presence of low and medium concentrations of NaNO₃ into the NaCl solution resulted in values of noise impedance similar to those revealed in its absence, while addition of a high concentration of NaNO₃ (15 mM), resulted in a significant reduction in the noise impedance (Figure 5a). From the optical images, it is evident that the extent of corrosion was similar for the alloy immersed in the absence and in the presence of low and medium concentration of sodium nitrate. As in all the previous cases, higher concentration of nitrate ions resulted in increased corrosion, with the surface displaying several large pits surrounded by dark copper deposits (Figure 5b).

Surface morphology.— The surface morphology of AA 2024-T3 after 6 hours exposure to 3.5% NaCl solution with and without inhibitors was examined by SEM. Figures 6a, 6b present the alloy surface after corrosion in the absence of inhibitors. Trenching is evident in the proximity second-phase particles and abundant corrosion products are observed. Unreported backscattered electron images reveal that little or no copper has re-deposited after 6 hours of exposure.

Addition of Ce(NO₃)₃ into the aggressive environment resulted in effective corrosion inhibition, with the alloy matrix appearing relatively smooth and cerium deposits evident over the second phase particles (Figure 7). This is due to the well-known cathodic inhibition effect associated with cerium ions, which form insoluble compounds in the proximity of cathodic sites due to the pH increase. In the presence of Co(NO₃)₂, a surface modification is observed as the topography is rougher (Figure 8). The exact nature of the observed morphology of the corrosion product is unclear, but it is possible that it might be due to a variation in pH due to the presence of cobalt nitrate. In the presence of Mn(NO₃)₂, the morphology of the substrate is similar to the substrate without inhibitor, with large corrosion sites in the vicinity of second phase particles, which are abundantly covered by corrosion products (Figure 9). The micrographs of the specimens immersed in
Figure 4. a) Variation of noise impedance with time, b) optical images during EN measurement for AA 2024-T3, 1) without inhibitor, with 2) 0.15 mM Mn(NO₃)₂, 3) 1.5 mM Mn(NO₃)₂ and 4) 15 mM Mn(NO₃)₂ in 3.5% NaCl solution.

Figure 5. a) Variation of noise impedance with time, b) Optical images during EN measurement for AA 2024-T3 without inhibitor, with 2) 0.15 mM NaNO₃, 3) 1.5 mM NaNO₃ and 4) 15 mM NaNO₃ in 3.5% NaCl solution.

Discussion

The evaluation of the performance of inhibitors by electrochemical methods is a non trivial task since, depending on the technique used, different outcomes are obtained. In the case of potentiodynamic polarization, for the high-chloride, low-inhibitor concentration inspected, only weak evidence of corrosion inhibition is revealed for cerium nitrate. In particular, it appears that cerium nitrate acts as a cathodic inhibitor.

However, based on the image-assisted electrochemical noise analysis, it is apparent that cobalt nitrate also provides some degree of corrosion inhibition at long exposure times, although to a lesser extent than cerium nitrate. Importantly, when the concentration of the corrosion inhibitor is excessive, the corrosion process is intensified. The results of the control experiment performed with sodium nitrate suggest that such an effect is attributed to the high concentration of nitrate ions. Specifically, below 1.5 mM, the nitrates have no significant effect on the corrosion behavior but, at a concentration of 15 mM, the corrosion process is accelerated, as suggested by the lower noise impedance and worse surface appearance. For pure aluminum, nitrate ions act effectively as anodic inhibitors by increasing the pitting potential. However, for AA 2024-T3, it has been reported that adding low concentration of nitrate ions (0.005–0.01 M) in an environment with high concentration of chlorides (1 M) results in a significant increase in the corrosion rate.
It is experimentally observed from all the electrochemical noise tests that increasing the concentration of nitrates, generally results in a more severe corrosion, evident as decrease in values of noise impedance and more extensive corrosion in the images. Additionally, from the optical images of the corroding surface, it is revealed that in all cases, the presence of a high concentration of nitrate ions resulted in the formation of dark regions in proximity of the corrosion sites. This could be due to increased copper redeposition in proximity of the cathodic sites associated to the presence of nitrate ions. The occurrence of such re-deposition is supported by the optical images of recorded during the electrochemical noise measurements and by observation of...
copper nanoparticles on the surface of the specimen immersed in the presence of sodium nitrate by scanning electron microscopy.

Based on the experimental evidence gathered, it can be concluded that both cerium and cobalt nitrate display corrosion inhibition properties at low concentration. Manganese nitrate displays behavior closely similar to that observed for sodium nitrate, suggesting that the composition provides little or no corrosion inhibition at the same concentration. In the light of these considerations, it is important to notice that mixtures of the inhibitors do not appear to display a synergistic effect. This can be rationalized by considering that the most effective inhibition mechanism, in this case provided by cerium nitrate, determines the rate-determining step in the corrosion process and, therefore, addition of another, less effective inhibitor, does not produce any beneficial effect.

Conclusions

A comparative study on the effectiveness of the corrosion inhibition of selected nitrate salts for AA 2024-T3 was undertaken. It was found that cerium nitrate offers the better inhibition performance, followed by cobalt nitrate. However, the inhibitor concentration must be kept at a relatively low level, otherwise the corrosion attack is intensified. The deterioration of the inhibiting properties at high concentrations is attributed to the presence of the nitrates ions that promotes the redeposition of copper at cathodic sites. Comparison between potentiodynamic polarization results and image-assisted electrochemical noise analysis reveals that the latter provides a reliable tool for the long-term evaluation of inhibitor performance, with values of low frequency noise impedance well correlated with the surface appearance of the corroding specimens. Due to the absence of electrical perturbation to the corroding system, the method is intrinsically representative of the real-life behavior.

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