Anti-corrosive characterization of silicon, titanium, and zirconium oxide coatings deposited on aeronautical aluminum substrates via sol-gel

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Abstract. Currently, aircraft wings made of AA2024 T3 aluminum are primed between the aluminum substrate and the outer layer of paint to improve the material’s adhesion and corrosion resistance. This type of primer contains chromates whose treatment generates highly toxic hexavalent chromium. This work studied the effect of applying dip-coating coatings of combined silicon, titanium, and zirconium oxides on AA2024 T3 aluminum substrates synthesized via sol-gel. The influence of the number of layers on the substrates anti-corrosive behavior in a 3% NaCl solution was studied using electrochemical impedance spectroscopy techniques and potentiodynamic polarization curves. The substrates corrosion resistance was found to improve substantially concerning the number of layers deposited.

1. Introduction
Since the beginning of the industrial revolution, metals are present in the essential equipment of most of the industrial support [1-3]. Within the sectors that use metals as infrastructure, the oil, chemical, automotive, food, construction, health, and air transport industries stand out. However, metals are susceptible to corrosive phenomena due to their nature due to chemical or electrochemical reactions, deteriorating their properties, limiting their useful life, and losing efficiency in the applications for which they are intended. These characteristics lead to an environmental, technological, and economic problem [4-8].

In the aeronautical industry, the most used material is aluminum due to its low density, high resistance to corrosion, and relatively low cost [9-12]. It is possible to increase its mechanical resistance through suitable alloys, but it leads to a decrease in its anti-corrosive properties. The most widely used alloy in aircraft structures is AA2024-T3. This alloy uses copper as the primary alloying element, has an excellent strength/weight ratio and good resistance to fatigue [13,14]. For an adequate anti-corrosive response of the alloy, chromium VI coatings are used [15]. The development of new effective methods of protection against corrosion on metallic substrates is of vital importance. In the case of aluminum, the elimination of hexavalent chromium from the industry due to its high environmental impact, by European and North American laws, generates the need to develop new materials that can replace chromium compounds [15-19]. One of the methods for the production of new materials is the Sol-gel synthesis [20,21]. This methodology involves processes at low temperatures with the corresponding energy savings. Also, the materials' high purity and homogeneity are attributable to the way they are
prepared in multi-component systems [22-25]. The Sol-gel process has allowed the design of new ceramic and composite systems with specific properties, such as anti-corrosive properties [26,27].

The sol-gel process involves forming a colloidal suspension (Sol), and its subsequent transformation to form a three-dimensional network immersed in a continuous liquid phase (gel). After going through the thermal drying and densification treatments, this gel gives rise to the formation of an oxidic material, either purely inorganic or with hybrid characteristics, organic-inorganic according to the material’s design be obtained [28].

Materials such as silicon oxide (SiO₂) can improve metals corrosion resistance under different temperatures due to their high thermal and chemical resistance [20,21]. On the other hand, zirconium oxide (ZrO₂) is characterized by a high coefficient of expansion, which can reduce cracks formation during the high-temperature curing process. This material also offers good chemical stability, high hardness, and good anti-corrosive and biological properties [29]. Titanium oxide (TiO₂) has excellent chemical stability, high mechanical strength, low electrical conductivity, biocompatibility, and good anti-corrosive properties [29]. Metal oxides such as SiO₂, ZrO₂, and TiO₂ all have been found to have excellent chemical stability and provide adequate protection to the metal substrate [6,20,21,29].

In the development of this research, ceramic coatings of the ternary type Silicon-Titanium-Zirconium were produced by the sol-gel methodology in the concentrations of the precursors [Si/Ti/Zr: 10/70/20] from tetraethyl orthosilicate, Titanium tetrabutoxide and zirconium tretabutoxide as precursors. Using the dip-coating technique, the shaped sols were deposited on AA 2024-T3 aluminum substrates. The anti-corrosive response was evaluated in a 3% NaCl solution, using potentiodynamic polarization curves (Tafel) and electrochemical impedance spectroscopy (EIS). It is concluded that all the coatings have an excellent anti-corrosive answer, especially the films with a higher concentration of titanium tetrabutoxide, for the uncoated samples. The results show that this type of coatings has excellent potential as an alternative for replacing hexavalent chromate.

2. Materials and methods

This section describes the characteristics of the coatings and their application on the substrate.

2.1. Sol preparation

The reagents used for the constitution of stable SiO₂-TiO₂-ZrO₂ sols are referenced in Table 1.

| Alkoxide                        | Purity/concentration | Molecular weight (g/mol) | Density (g/cm³) |
|---------------------------------|----------------------|--------------------------|-----------------|
| Tetraethyl orthosilicate Si (OC₂H₅)₄ | 98%                  | 208.33                   | 0.933           |
| Zirconium (IV) butoxide Zr (OC₃H₇)₄ | 80% solution in 1-butanol | 383.7                   | 1.049           |
| Titanium (IV) butoxide Ti (OBu)₄ | 97%                  | 340.36                   | 1               |

In the process of shaping the sols, the following relationships remain fixed:

- \( n(Zr+Ti)/n[Acomplexing]=1 \), where \( n \) is the number of moles
- \( nH₂O/n[Zr+Si+Ti] = 1.5 \), where \( n \) is the number of moles
- Total volume of the 100ml solution.
- Solution concentration: 50g/L.

In the procedure developed for shaping the sols initially, two different solutions were prepared. The first of them contained half the volume of the solvent (EtOH), the total volume of the complexing agent (2,4 pentanediol), the total volume of titanium precursor (Ti(OBu)₄), and the total volume of zirconium precursor (Zr(OC₃H₇)₄). The reagents were mixed in the order they indicated above, considering alcohol as the precursors’ solvent. The second solution contained half the volume of ethanol, the total volume of the silicon precursor (Si(OC₂H₅)₄), and half the water volume. The reagents were mixed in the order
listed above. To obtain good miscibility of the precursors, and therefore good homogenization of the solutions, they were mixed using magnetic stirring at 300 rpm. Subsequently, the solutions were mixed, and the remaining water volume was added to promote the system’s hydrolysis. Magnetic stirring was maintained. Figure 1 indicates the process of shaping the sol for the ternary system, with the respective stages and times used in each one of them.

Figure 1. Process of conformation of the sol for the ternary system.

Table 2 indicates the amount of precursors Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, Ti(OBu)\textsubscript{4}, and Zr(OC\textsubscript{3}H\textsubscript{7})\textsubscript{4}. Also, the amounts of 2,4 petanodione and ethanol. These are the amounts used to obtain stable sols following the route in Figure 1. As shown in Table 2, 100 ml of solution was prepared to get stable sols in the concentration of the precursors [Si/Ti/Zr: 10/70/20]. 1.32 ml of Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, 14.19 ml of Ti(OBu)\textsubscript{4}, 5.27 ml of Zr(OC\textsubscript{3}H\textsubscript{7})\textsubscript{4}, 5.21 ml of 2,4 petanodione (ACAC), and 1.57 ml of water were added. To reach the total volume of 100 ml, 72.44 ml of ethanol (EtOH) were added.

Table 2. Composition of the sol.

| Si-Ti-Zr | TEOS (ml) | TBT (ml) | TBZ (ml) | ACAC (ml) | H\textsubscript{2}O (ml) | EtOH (ml) |
|---------|----------|---------|---------|-----------|-----------------|---------|
| 10-70-20 | 1.32     | 14.19   | 5.27    | 5.21      | 1.57            | 72.44   |

2.2. Substrates
The substrates used were AA2024-T3 aluminum sheets with dimensions 2.5 cm x 3 cm x 0.3 cm. The surfaces were first mechanically polished with 600 grit abrasive paper. Later the samples were polished by an electrolytic process at 12VDC, aluminum anode and copper cathode. Phosphoric acid 12% by volume was used as the electrolytic solution, with a time of nine minutes and a current of 2A.

2.3. Shaping and densification of coatings
The dip-coating technique was used to obtain the coatings at a constant speed of 0.23c m/s. The thin films’ sintering was carried out at a heating rate of 2 °C/min in a Ney Vulcan model 3-1750 muffle. The temperature rises from 20 °C to 150 °C, remaining constant for one hour. Finally, the coating substrate system is cooled to room temperature at the oven cooling rate.

2.4. Characterization
The Tafel polarization tests were carried out in a three-electrode cell: (i) Ag/AgCl reference electrode, (ii) platinum as a counter electrode, and (iii) sample as a working electrode. The analysis area was 1cm\textsuperscript{2}; the scan was 1mV/s in the 3% NaCl solution. The range of potential swept was from -200mV to 200mV.
concerning the corrosion potential (Ecorr). A Gamry instruments potentiostat-galvanostat 3000 was used. The equipment has a voltage resolution of 20V and a current of 1fA. The immersion time before testing was 45 minutes. For each coating, three potentiodynamic tests were carried out. Corrosion current density (i corr) and corrosion potential (E corr) values were determined by the Tafel extrapolation method using Gamry Echem Analyst 5.3 software.

The electrochemical impedance spectroscopy (EIS) tests made it possible to evaluate the coatings’ corrosion resistance as a function of time. They were developed in a three-electrode cell and under study of the same electrolyte solution carried out for the potentiodynamic polarization tests. Frequency is swept from 10^4 Hz to 0.01 Hz applying a voltage of 10 mV and ten points per decade. The tests were carried out under the ASTM G3-14 standard in a Gamry instruments 3000 potentiostat-galvanostat.

3. Results and discussion

Figures 2 show the EIS analysis results for the coatings [Si/Ti/Zr: 10/70/20] in monolayer and bilayer, and the substrate AA2024-T3. At frequencies from 0.01 Hz to 104 Hz, the EIS curves’ behaviors can show the region controlled by charge transfer or the region controlled by diffusion. In Figure 2, can see the linear part corresponding to the diffusion control indicated by the unit slope; the EIS analysis focuses mainly on the values of resistance to polarization, Rp. Rp is the resistance that the coating opposes to the passage of ions from the substrate's solution, preventing it from corroding. In general, terms, when a layer registers a high value of resistance to polarization, it can be concluded that it is an excellent anti-corrosive protector.

![Figure 2](image1.png)

**Figure 2.** Comparison of Nyquist plots (a) monolayer coatings and substrate, (b) bilayer coatings.

Figure 2, the same behavior of the Nyquist diagrams is observed. That is, all the graphs are open. This type of behavior shows the existence of high values in resistance to polarization and, therefore, low corrosion rates. Figure 2(a) presents the Nyquist diagrams for monolayer coatings. An open behavior is observed, more significant than that registered for the substrate. The same trend is observed in Figure 2(b) for bilayer coatings. These behaviors allow us to infer that films [Si/Ti/Zr: 10/70/20] deposited on AA2024-T3 aluminum substrates act as a protective barrier when they are in contact with the 3% NaCl solution, giving the bilayer greater efficiency. According to these results and correlating with the values of resistance to polarization recorded in Table 3, it is possible to affirm that the increases in layers densify the final coating, improving its performance as an anti-corrosive barrier.

In corrosion studies using the EIS technique, the impedance spectra obtained are usually analyzed using electrical circuits, made up of components such as resistances, capacitances, and inductances combined in such a way as to reproduce the measured impedance spectra. The behaviors described in Figures 2(a) and Figure 2(b) are modeled with the equivalent circuit of Figure 3. This circuit is related to a metallic substrate covered with layers of ceramic material. It is composed of the following elements: Rs, dissolution resistance, corresponds to the resistance offered by the working solution, in this case,
3\% NaCl solution. Rp, resistance to polarization and Cd, constant phase element of the coating or porous outer layer.

![Equivalent electrical circuit](image)

**Figure 3.** Equivalent electrical circuit.

The values of parameters or constituent elements of the equivalent circuit for the coatings studied are recorded in Table 3. The work resistance value is 120 \( \Omega \). The Rp value for the substrate was 67 k\( \Omega \).

**Table 3.** Equivalent circuit parameter values for thin films [Si/Ti/Zr: 10/70/20].

| Parameter   | Monolayer | Bilayer |
|-------------|-----------|---------|
| R_s (\( \Omega \) cm\(^{-2} \)) | 117.21 | 122.08 |
| R_p (k\( \Omega \) cm\(^{-2} \)) | 154.33 | 753.20 |
| Cd (10\(^{-6} \) F cm\(^{-2} \)) | 21.41 | 108.58 |

To determine the kinetic parameters of Table 4 experimentally (anodic slope and cathodic slope, potential corrosion, corrosion current, and corrosion rate), a graphical representation is necessary for which the current density is on a logarithmic scale, since this shows the linear relationship between the log \( i \) and the overpotential, especially when the latter, in absolute value, has considerable value as shown in Figure 4. When charged species take part in the reaction, the energy barrier that must be overcome in the charge transfer is affected by the electric field and can be demonstrated from the electrochemical theory kinetics than the partial processes’ current densities. The Tafel extrapolation method's corrosion rate calculation is based on the extrapolation of the linear zone in an experimental E vs. log \( i \). According to this method, the corrosion current can be obtained without extrapolating any of the Tafel lines to the potential corrosion value, as represented in Figure 4.

Figure 4 shows the Tafel diagrams for the coatings [Si/Ti/Zr: 10/70/20] in monolayer and bilayer and the substrate AA2024T3. The figure shows the variation of the ceramic films’ corrosion potentials for the substrate's corrosion potential. In general, the corrosion potential tends to take on more positive values as the number of layers increases. Concerning Figure 4, it is possible to affirm: that to the corrosion potentials, the most positive potential is presented by the bilayer, followed by the monolayer. It is emphasized that all films indicate a corrosion potential more significant than the value found for the substrate. With regard to corrosion currents, it is indicated that these values are lower with respect to the information found for the uncoated substrate. The corrosion potentials' values and the corrosion currents for the coatings [Si/Ti/Zr: 10/70/20] as a function of the number of layers applied to the substrate is recorded in Table 4.
From the information recorded in Table 4, it is evidenced that the lowest corrosion rate value is for the bilayer with 53.81x10⁻³ mpy (milli-inch per year) and the monolayer with 120.40x10⁻³ mpy. This value indicates that the bilayer's anti-corrosive effectiveness for the substrate and the monolayers is higher. It is possible that when applying a second coating, the cracks and pores of the first layer are homogenized, and therefore, a denser coating is consolidated that prevents the working electrolyte from reaching the substrate. Corrosion current values and corrosion potentials corroborate the results. In general, good anti-corrosive behavior is established with low corrosion rates, more positive corrosion potentials, and low corrosion currents. These characteristics are observed for two-layer coatings.

4. Conclusions

From the research results, it is possible to conclude that bilayer coatings improve the anti-corrosive response of the aluminum substrate. The bilayer films showed low corrosion rates, more positive corrosion potentials, and low corrosion currents.

Based on the results obtained, it is possible to infer that the number of coatings deposited on the A2024T3 aluminum substrate allows the previous layers to be densified, reducing the presence of pores and cracks. This behavior enables the coatings to function as an anti-corrosive barrier between the substrate and the working electrolyte solution.

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