**Probing the degradation mechanism of a Cr(VI) coating/aluminum alloy 2024-T3 system
based on dynamic mechanisms and a 2D deterministic-probabilistic approach**

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Abstract

Electrochemical impedance spectroscopy (EIS) has been experimentally used to characterize the degradation mechanisms of a multilayered Cr(VI) coating/aluminum alloy 2024-T3 substrate system in 3.5% NaCl solution at low pH. A 2D damage evolution model is proposed to understand the influence of defined elements into the multilayered coating/substrate degradation process. The model was developed assuming steady state conditions, while discretization of the model included multilayered stacks such as a topcoat, a primer, and a chromate conversion layer as a pretreatment on an aluminum substrate. The modeling technique was deterministic-stochastic in nature. The deterministic approach was based on a transmission line model that was developed to represent the local impedance for small segments of the system to characterize physicochemical properties inherent to the organic coatings and the transport mechanisms. The randomly generated structures including coating pore distributions are illustrated by stochastic modeling with probability density functions. The quantitative understanding of the degradation mechanism from this 2D model is achieved, and the 2D analysis shows consistent results with experimental conditions over various immersion times.

The degradation mechanism for the multilayered coating system at low pH can be described as follows: intact condition, electrolyte uptake, lixiviation of Cr(VI) ions/diffusion, and self-healing process that provide repassivation of the Cr(III) oxide layer.

Keywords: Aluminum; Metal matrix composites; EIS; Self-healing coatings, Hybrid coatings.

1. Introduction

Aluminum alloy 2024-T3 (AA2024-T3) is commonly used in aeronautical applications [1, 2]. It contains intermetallic compound phases (IMC) containing Cu, Mg, or Fe that provide excellent strength and fatigue resistance [3]. Nevertheless, the presence of IMC phases in aluminum substrates reduce the corrosion resistance of the material due to creation of galvanic couples between the different IMC phases and the AA2024-T3 matrix, which leads to localized corrosion and stress corrosion cracking, especially in the presence of chloride ions [4-6].

Organic and composite coatings have been proposed in order to control or mitigate the corrosion processes in aluminum alloys. Cr(VI) coating is a conventional aircraft coating composed of a chromate conversion layer, primer, and topcoat. The chromium conversion coating (CCC) acts as a corrosion protection layer as well as an adhesion promoter between the aluminum substrate and the primer. It has been reported that CCC provides the following benefits: 1) self-healing protection, 2) barrier protection due to the presence of a hydrophobic Cr(III) oxide layer, and 3) inhibition of the oxygen reduction reaction at the aluminum substrate [7, 8]. The primer usually corresponds to an epoxy polyamide coating containing chromate pigments (such as strontium chromate (SrCrO_4)) in order to provide active corrosion inhibition to the metallic substrate, in combination with other compounds such as fillers that can enhance the barrier properties of the epoxy coating and additives such as coloring agents [9, 10]. The

strontium chromate has low solubility in water; thus, when there is a damage in the coating, the dissolved Cr(VI) ions migrate to the affected area and inhibit additional deterioration of the metal surface. [10, 11]. Kendig et al. [7] reported that the corrosion inhibition afforded by SrCrO_4 was related to the following: 1) passivation of active intermetallic phases by the Cr(VI) ions, 2) electrochemical reactions between Cr(VI) ions and the aluminum substrate that inhibit cathodic reactions, such as oxygen reduction reaction and hydrogen evolution reaction, and 3) decrease in the zeta potential of the aluminum substrate by the presence of Cr(VI) ions leading to repulsion of aggressive ionic species, such as chloride ions. In addition, due to the low solubility of Cr(VI) ions, the epoxy coating can provide long-term protection since there is a good balance between ionic transportation for active inhibition and loss of Cr(VI) ions in the binder that increases the porosity of the primer and therefore the permeability of electrolyte. Finally, the topcoat is a polyurethane coating that confers excellent flexibility, UV protection, and chemical resistance to the multilayer system.

Despite of the excellent corrosion resistance of this multilayer system, there is great concern about the toxicity of Cr(VI) ions [7, 12]. Therefore, numerous studies have proposed alternatives to Cr(VI) chromium coatings [13-16]. The corrosion protection mechanisms of chromated coatings can lead to understanding the performance with time and serve as the benchmark for new, chromate-free coating developments. Damage evolution modeling of this coating can be approached by deterministic-probabilistic fundamentals, which represents a new direction in the assessment of corrosion control since several chromate-free coating systems attempt to mimic the inhibition properties of the Cr(VI) ions [9, 17-19].

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique used to characterize the electrochemical performance of corrosion protection coatings [12, 20]. It is a

reliable technique because it can provide detailed electrochemical information of the interfacial reactions with a small excitation permitting the system to remain in steady state conditions [20-22]. Equivalent electrical circuits (EECs) underscore the advantage of using linear theory and consider the circuits as a viable option to interpret EIS data [23, 24] by associating interfacial processes with electrical analogs. However, one of the major weaknesses of this analytical approach arises in how to select the corresponding EECs that not only fit the values but also provide a physical interpretation of the studied interface with quantitative parameters, especially when several layers are present in the system. One-dimensional transmission line modeling (TLM) has been used to investigate porous electrodes, iron oxide layers, evolution of magnesium-rich primers, and zinc-rich powder coatings by partitioning and characterizing an electrochemical interface into sub-elements of defined scale as corrosion cells [25-29]. A one-dimensional TLM approach can define the relationship between the resistance, driving potential, and corrosion rate of a degradation system based on the electrical balance of each element of the electrical circuit network [30]. However, it is difficult for this approach to take into account geometrical effects of the corroding systems such as shape and localized pore distribution of coating layers, which have an impact on the corrosion rate [31].

In this study, the electrochemical behavior of a multilayer Cr(VI) coating/ AA2024-T3 substrate system immersed for 260 days in a 3.5% NaCl solution at a pH of 4 has been investigated using an EIS technique as well as morphology analysis. In addition, changes in the electrochemical impedance response over a long-term immersion have been estimated by using a deterministic and probabilistic 2D damage propagation model. This model is based on TLM and is proposed to understand the influence of heterogeneity in material properties and pore distributions of the corroding system by unifying the probability density function of the required

property within the integrated multilayer coating. Probability density function can describe physical distribution in percolation networks [32, 33], such as the electrolyte percolation length within the coating...The degradation mechanism from the 2D modeling is explained by using sensitivity analysis, and the validation of the modeling is considered by using experimental results.

2. Experimental procedure

2.1. Materials and Sample Preparation

The epoxy primer Deft 02-Y-40 (Strontium chromate-based primer) was prepared by mixing its respective resin [Bisphenol-A-(epichlorhydrin) epoxy resin based] and cross-linker for one minute in a Flacktek Speedmixer at 1700 rpm. The Cr(VI) -free polyurethane topcoat (Deft 99GY010) was prepared similarly. An induction time of 20-30 minutes was given to each coating. AA2024-T3 panels (76.2 mm x 152.4 mm x 0.762 mm) with a chemical composition (based on ASM material data sheet) of 0.1 wt% Cr; 0.15 wt% Ti; 0.25 wt% Zn; 0.5 wt% Fe; 0.5 wt% Si; 0.3–0.9 wt.% Mn; 1.2–1.8 wt% Mg; 3.8–4.9 wt% Cu; others 0.15 wt%; Al balance were cleaned with acetone and then mounted vertically on cardboard. Prior to the coating application, the prepared panels were pretreated with Alodine 1600 (Sodium Bichromate-based material). The epoxy primer was applied onto the aluminum panels with the help of a high volume low pressure (HVLP) spray gun to obtain a dry film thickness of approximately 30 μm . A similar procedure was followed for the application of the topcoat. The topcoat dry film thickness was about 40 μm . Finally, the panels were air cured for a week.

2.2. Electrochemical techniques

A glass electrochemical cell (25 mm Inner Diameter, 30 mm Outer Diameter, 76.2 mm length) was sealed onto the coated panel by using an O-ring and a metallic clamp. Approximately 25 ml of 3.5 wt% NaCl solution adjusted to a pH of 4 with a sodium acetate/acetic acid buffer was poured into the cell glass container.

A three-electrode system was used to perform open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) measurements. The coated panel was used as the working electrode; a saturated calomel electrode was used as the reference electrode; and a Pt/Nb mesh electrode of 2 cm diameter was used as the counter electrode. The electrochemical measurements were performed using Gamry potentiostat/galvanostat/ZRA Reference 600TM and a Faraday cage to avoid electromagnetic interferences. The EIS data were collected over a frequency range from 10 mHz to 20 kHz at open circuit potential with a sinusoidal AC perturbation of 10 mV rms. The data acquisition was controlled by Gamry Framework Version 5.8/EIS 300 software. All the measurements were performed in duplicates at room temperature for 260 days.

3. Two dimensional damage propagation model

3.1. Proposal of 2D substrate/coating model

A multilayered system of coatings was designed for studying the electrochemical activities on porous surfaces by including the transport mechanisms based on 2D deterministic and probabilistic approach to account for spatial distribution within solid state of a known commercial coating system. One coating layer is certainly a simple and initial point to understand the transport and mechanistic analysis of different species. However, this work considered a well-known commercial integrated system formed by a multi-layer. The mechanistic analysis with this developed tool as a further work will be considered in the future.

Based on the system comprising a top coat, a chromate-containing epoxy primer, CCC, and aluminum substrate, we considered a numerical element design by using a layer-by-layer composite coating strategy. Each segment in the designed domain has its own electrical properties including electrical resistivity and a dielectric constant, which can have different values based on the direction. The resistance $R_{(j,i)}$ and the capacitance $C_{(j,i)}$ of (j,i) element at each direction are defined as

$$R_{x(j,i)} = \rho_{x(j,i)} dx_i / dz_j \quad (1a)$$

$$R_{z(j,i)} = \rho_{z(j,i)} dz_j / dx_i \quad (1b)$$

$$C_{x(j,i)} = \epsilon_{x(j,i)} \epsilon_{0(j,i)} dz_j / dx_i \quad (1c)$$

$$C_{z(j,i)} = \epsilon_{z(j,i)} \epsilon_{0(j,i)} dx_i / dz_j \quad (1d)$$

where ρ denotes resistivity, ϵ is the dielectric constant, ϵ_0 is the permittivity of free space, and subscripts x and z explain x-direction and z-direction, respectively. In this model, the electrical properties of each segment are assumed to be isotropic. Each localized impedance is calculated with the help of an equivalent circuit analog at the elemental interface, which includes the electrical resistance and constant phase element (CPE) of the segments. The CPEs are used in this analysis instead of ideal capacitors due to the surface conditions or heterogeneous bulk properties of the composite coating systems[23, 34]. Fig. 1(a) describes the interfacial impedance between each segment as the physical degradation process of the coating system that is determined by the electrical materials' properties or the water-uptake process. The localized impedance at the interface of the segments is defined by the arithmetic averaged impedance at the cell interface, which is given by the following equation:

$$Z_{(j,i \leftrightarrow j,i+1)} = \frac{R_{x(j,i)}/2}{1 + (j\omega)^{\alpha_{x(j,i)}} C_{x(j,i)} R_{x(j,i)}} + \frac{R_{x(j,i+1)}/2}{1 + (j\omega)^{\alpha_{x(j,i+1)}} C_{x(j,i+1)} R_{x(j,i+1)}} \quad (2a)$$

$$Z_{(j,i \leftrightarrow j+1,i)} = \frac{R_{z(j,i)}/2}{1 + (j\omega)^{\alpha_{z(j,i)}} C_{z(j,i)} R_{z(j,i)}} + \frac{R_{z(j+1,i)}/2}{1 + (j\omega)^{\alpha_{z(j+1,i)}} C_{z(j+1,i)} R_{z(j+1,i)}} \quad (2b)$$

where $Z_{(j,i \leftrightarrow j,i+1)}$ and $Z_{(j,i \leftrightarrow j+1,i)}$ are localized impedances at the interface between the (j,i) and the (j,i+1) elements and at the interface between the (j,i) and (j+1,i) elements, respectively. ω denotes a perturbation frequency, and α is an empirical exponent of the CPE.

The interfacial impedance between segments that describes electrochemical reactions occurring at the interface is affected by non-faradaic impedance such as electrochemical double layer as well as faradaic impedance, which is composed of the charge transfer impedance induced from the kinetics of the charge transfer reaction and diffusion impedance. If electrochemical control processes such as charge transfer and diffusion phenomenon take place on the localized cell interface between the aluminum substrate and the CCC, impedance at the interface can be represented as shown in Fig. 1(b) and is defined by the following expressions.

$$Z_{(j,i \leftrightarrow j,i+1)} = \frac{R_{x(j,i)}/2}{1 + (j\omega)^{\alpha_{x(j,i)}} C_{x(j,i)} R_{x(j,i)}} + \frac{1}{(j\omega)^{\alpha_{x,int}} C_{x,dl} + \frac{1}{R_{ct,x,int} + Z_{diff,x,int}}} + \frac{R_{x(j,i+1)}/2}{1 + (j\omega)^{\alpha_{x(j,i+1)}} C_{x(j,i+1)} R_{x(j,i+1)}} \quad (3a)$$

$$Z_{(j,i \leftrightarrow j+1,i)} = \frac{R_{z(j,i)}/2}{1 + (j\omega)^{\alpha_{z(j,i)}} C_{z(j,i)} R_{z(j,i)}} + \frac{1}{(j\omega)^{\alpha_{z,int}} C_{z,dl} + \frac{1}{R_{ct,z,int} + Z_{diff,z,int}}} + \frac{R_{z(j+1,i)}/2}{1 + (j\omega)^{\alpha_{z(j+1,i)}} C_{z(j+1,i)} R_{z(j+1,i)}} \quad (3b)$$

where C_{dl} is the capacitance of the double layer, $R_{ct,int}$ is the charge transfer impedance, and $Z_{diff,int}$ is the diffusion impedance. In this work, we assume that the diffusion phenomenon is controlled in a thin layer, which has finite diffusion length of electroactive species from the

electrolyte solution to the metal surface. Thus, the impedance response of diffusion can be defined as a modified Warburg impedance, which is given by [35]

$$Z_{\text{diff,int}} = \frac{\sigma(1-j)}{\sqrt{\omega}} \left[\frac{\sinh \sqrt{\frac{\omega \delta^2}{2D}} \cosh \sqrt{\frac{\omega \delta^2}{2D}} - j \sin \sqrt{\frac{\omega \delta^2}{2D}} \cos \sqrt{\frac{\omega \delta^2}{2D}}}{\sinh^2 \sqrt{\frac{\omega \delta^2}{2D}} + \sin^2 \sqrt{\frac{\omega \delta^2}{2D}}} \right] \quad (4)$$

where σ is the Warburg coefficient, D is the diffusion coefficient, and δ is the thickness of the diffusion layer. δ^2/D is the characteristic diffusion time, which is assumed as 1 in order to reduce the number of calculation. The characteristic diffusion time value was enough for proposing qualitative variation of Warburg coefficient in this paper.

Based on the aforementioned local impedance at the interface of segments, the proposed composite coating system can be described as 2D networks of local electrochemical impedance elements, as shown in Fig. 2. The designed layer-by-layer composite coating system is divided into $n \times m$ segments. According to the local interfacial impedance of elements and Kirchhoff's law which is based on charge conservation ($\sum i_{\text{in}} = \sum i_{\text{out}}$) at a junction and energy conservation ($\sum \Delta V = 0$) for any closed path, the total impedance of the designed system can be specified as the following:

$$Z_{\text{total}}(\omega) = l_x \sum_{k=1}^{n-1} Z_{k,2} + l_x \sum_{l=2}^m Z_{n,l} + l_x Z_{1,1} + l_x Z_{n,m} - l_x \left(\sum_{k=1}^{n-1} Z_{k,2} \cdot i_{k,1}/i_b + \sum_{l=2}^m Z_{n,l} \cdot i_{n-1,l-1}/i_b \right) \quad (5)$$

where i is the electrical current of a closed path, and l_x is the length of the system in the x -direction.

3.2. Pore distribution of coated system

Previous works have used a probabilistic approach to describe water uptake within a barrier layer[21, 36, 37]. Orazem et al. developed the power-law CPE model, which can describe the insight into the distribution of electrolyte uptake and associated resistivity, and they considered the various volume fractions of electrolyte with respect to the coating thickness by using a power-law approach[37].

Water-uptake fields can also be considered as percolation clusters that are occupied by an electrolyte with a certain probability. If neighboring segments are occupied with an electrolyte, clusters are formed. The water-uptake in porous materials can be described as a random process of merging adjacent segments. Therefore, the number of electrolyte percolation lengths can be assumed to be inversely proportional to the water-uptake length because electrolyte has more possible regions to prevent penetration as the electrolyte propagates. This suggests that the log-normal probability density function(P) can be employed in order to define the distribution of the electrolyte percolation length, which is given by the following[32]:

$$P(z, \mu, \sigma) = 1/(z\sigma\sqrt{2\pi})\exp[-(\ln(z) - \mu)^2/(2\sigma^2)] \quad (6)$$

$$M = \exp(\mu + \sigma^2/2) \quad (7)$$

$$V = \exp(2\mu + \sigma^2)[\exp(\sigma^2) - 1] \quad (8)$$

where M is the mean of maximum percolation lengths of the electrolyte, and V is the variance of maximum electrolyte percolation lengths. The mean value M and the variance V can be calculated as functions of σ and μ which are the standard deviation and mean of the variable's natural logarithm, respectively, as shown in Equations (7) and (8). Fig. 3(a) demonstrates that the position distribution of various percolation lengths in the porous system can be generated by using the technique of a randomly structured model. This digitally stochastic model is coupled with specified statistical information such as the mean and variance of the maximum percolation

length for electrolyte uptake, as described in Fig.3(b). The mean M and the variance V values are 0.377 and 1.208 in this model, respectively.

3.3. The computation process of multilayer system

The first estimation of the material properties for the data analysis with 2d model and the experimental result at dry condition was done by sensitivity analysis. The sensitivity analysis was included to understand each independent parameter from variations in influencing the impedance of the system [38]. The detail process of calculation for the 2D model of distributed circuit elements is described in Fig. 4. The parameters obtained from the process describe the overall goodness of the fitting.

4. Results and discussion

Electrochemical impedance spectroscopy was used in order to characterize the interfacial mechanisms of a Cr(VI) coating/ AA2024-T3 substrate system immersed in 3.5 wt.% NaCl solution at a pH of 4.0 over 260 days. The experimental results were described quantitatively by the development of a 2D degradation model, which provides detailed interpretations of the existing mechanisms following exposure time. Different deterioration processes occurring at the multilayered coating composite system are quantified by integrating the localized transfer functions (impedance responses). The cross-section image of the layer-by-layer composite coating system is shown in Fig.5(a). There is a total of three different layers covering the aluminum substrate: two coating layers, including a polyurethane top coat with 40 μm and a chromate-containing epoxy primer with 30 μm ; also, a third layer (chromium conversion coating (CCC)) is formed on the aluminum substrate with a thickness between 10 nm to 50 nm, as illustrated in Fig.5(b). Based on the surface morphology of the Cr(VI) coating/ AA2024-T3 substrate system, a layer-by-layer composite coating system was designed for the 2D

computational model, as shown in Figures 5 (c) and (d). The parameters for the 2D simulation are shown in Tables 1 and 2. The overall responses of the multilayered system are governed by material properties that are dependent on the localized structures and electrochemical properties influenced by electrochemical reactions of local interfaces between each segment. The electrical resistivities and CPEs of each segment in the designed domain represent the material properties that are affected by the electrolyte transport throughout the coating system. The properties for the dry condition and the water-uptake process of topcoat, primer, and CCC were obtained using experimental results from the 2D model. The electrical resistivity and permittivity for the dry condition of each coating material are in the range of $10^{11} \sim 10^{13} \Omega \cdot \text{cm}$ and $10^{-11} \sim 10^{-10} \text{F} \cdot \text{cm}^{-1}$, respectively. Following the water-uptake process of each coating segment, the magnitudes were modified to approximately $10^7 \Omega \cdot \text{cm}$ and $10^{-10} \sim 10^{-9} \text{F} \cdot \text{cm}^{-1}$. From these results, the influence of the electrolyte diffusion on the dielectric properties of the material is clearly shown; resistivity decreased due to the presence of ionic species that created ionic conductive pathways along the material, and permittivity increased as a result of water penetration, which has a large permittivity value ($\epsilon \sim 80$) compared to the corresponding values for polymeric materials ($\epsilon \approx 3 - 4$) [39-41].

The degradation stages with time for this Cr(VI) coating/ AA2024-T3 system at low pH are illustrated in Fig. 6. The mechanisms represented the following conditions: intact at stage I, electrolyte-uptake at stage II, lixiviation of Cr(VI) ions at stage III, and the repassivation of the Cr(III) oxide layer at stage IV. The initial degradation mechanism described in stages I and II is developed due to the electrolyte transport through pores and defects of the multilayered coating. The degradation process occurring during stage III is related to the lixiviation of Cr(VI) from the chromate-containing epoxy primer into the electrolyte solution [7, 10, 42-44]. Stage IV involves

the dynamic repairing of defects or newly created breaks in the CCC as the protective film.

During the fourth stage, the breakdown of the CCC passivate film can occur in the presence of chloride ions. Chromium oxide layer can be de-passivated from complex reactions, which are attributed to the penetration of chloride ions through the chromium oxide layer [8, 45].

However, these depassivated regions can be self-healed by the Cr(VI)ions that were dissolved in the electrolyte as a result of the lixiviation process. Cr(VI)ions diffused to the defect sites and reacted with the aluminum substrate in order to form $\text{Cr(OH)}_3\text{(s)}$ and $\text{Cr}_2\text{O}_3\text{(s)}$ [44].

4.1.Stage I and II Intact and water uptake conditions

The impedance response for the Cr(VI) coating/ AA2024-T3 substrate system at its initial stage when immersed in an acid electrolyte is shown in Fig.7. The impedance response of the coating/aluminum system exhibitsthe characteristic of a capacitive behavior at a large impedance modulus of 0.01 Hz and a phase angle close to -90° along the frequency range.Since the coated layer is considereddry, water uptake and any other subsisting free ions within the polyurethane topcoat is minimum or negligible. Thus, the topcoat, which has the distribution of high resistance segments of around 10^{13} ohm cm^2 , as indicated inFig.7,can electronically act as a goodinsulated layer. This high capacitive behavior considers the intact polymer layer influencing the space-charge-polarization region in the composite coating system[46].

With time, water uptake in the form of electrolyte transportation occurs through the topcoat and reaches the chromate-containing epoxy primer following the chromate conversion coating on the metal surface. This composite coating layer is not homogeneous due to pore distribution and different properties conferred to the material during synthesis, which produces

heterogeneous or random-uptake processes. Nyquist and Bode representations during the degradation mechanism between the 2nd and 35th immersion day are described in Fig.8. The presence or formation of pores in each layer gives rise to significant differences in the impedance response due to the electrical properties of the electrolyte solution that fills pores. Following the first day of exposure, Fig.8(a) shows that the magnitude of impedance decreases rapidly because the electrolyte effect through the outermost layer of the coating system, which is the polyurethane topcoat, is very rapid. Water-uptake is considered the dominant process for damage evolution of coating at initial immersion conditions. During this process, as illustrated in Figs.8(b) and (c), the insulating structure of the polymer composed of organic compounds is locally changed and modifies the characteristics of the overall impedance, which is considered as ionic transport and subsequent substrate activation [46]. The basic purpose of the polyurethane topcoat is functionally used for UV protection, in this system the polyurethane topcoat could not provide an effective barrier protection against solution [47]. Thus, the electrolyte penetrates quickly through the topcoat at the 2nd day of immersion, as shown in Figs. 8(b) and (c). At this time, the epoxy primer layer functions as an electrical insulating barrier of the composite coating system because electrolyte penetrates inside the topcoat. The highest resistivity segments for electrical insulating (about $10^{11} \Omega \cdot \text{cm}$ indicated in Fig.8(b)) are distributed in the epoxy primer layer, and the capacitive loop displayed in the complex format represents the combining effect of the resistance and CPE behavior. At longer exposure times, the radius of the capacitive loop in the complex representation is continuously decreasing due to higher penetration of water and ionic species along the composite coatings, and the total impedance decreases.

The impedance response of the porous composite coating system and the effect of electrolyte penetration ratio can be useful to understand the barrier protection behavior of the

system. The length ratio of electrolyte penetration, which is defined as the ratio of the maximum uptake length in a direction perpendicular to the sample surface to the length of the multilayers of the coating, is estimated by immersion time, as illustrated in Fig.9. The trend of electrolyte penetration ratio versus immersion time is assumed to demonstrate approximately square-root behavior, which means the primer layer is a better protection barrier for electrolyte uptake than the topcoat. As shown in Fig. 10, the epoxy primer is a heterogeneous material comprising a number of inorganic phases such as titanium dioxide (TiO_2), strontium chromate (SrCrO_4), and barite (BaSO_4) incorporated into the organic matrix [10]. These pigments in the primer would reduce the existence of pores and improve the barrier protection for electrolyte penetration as well as provide active corrosion protection to the metallic substrate.

4.2.Stage III Lixiviation stage

Following 45 days of immersion, the electrolyte reaches the surface of the aluminum substrate through the pores of the primer and inert CCC, as illustrated in Fig.11(c-d). From this stage III, the electrochemical behavior of the whole system is affected by not only local physical degradation such as electrolyte-uptake but also localized electrochemical processes such as charge transfer and diffusion. At the substrate/electrolyte interface, mass and charge transfer influence appears in parameters illustrated in Table 2. As shown in Fig.11(a), diffusion characteristic behavior at low frequency regime is detected in complex impedance plane, but this behavior does not obey linear Warburg behavior, which considers an ideal infinite-length diffusion from the electrolyte to the metal surface [46]. This is because local aluminum elements for the dissolution and diffusion as the anodic reaction from the local pores of CCC occupied with electrolyte are finite in dimensions, so modified Warburg behaviors, which describe the proper finite-length diffusion processes, are observed.

The equivalent area of the electrolyte-uptake primer (about $10^7 \Omega \cdot \text{cm}$ resistivity) at day 60 is extended more than the area at day 45, as described in Fig.11(c). This area increase can be attributed to the delamination of the paint film, but the visual inspection performed following the samples exposure revealed no indication of any delamination processes. Thus, to explain and describe the higher equivalent area of the electrolyte uptake primer, the most important phenomenon for designing a simple model was only considered by using chromate pigments. The chromium species added in the epoxy primer are electrolyte-soluble, so the SrCrO_4 compound could be leached into the bulk solution when it is exposed to the electrolyte solution [48]. The dissolution of SrCrO_4 modifies pores in the epoxy primer, and these modified pores are filled with the electrolyte. The more areas of the electrolyte-uptake epoxy primer create more conducting paths, as shown in Fig.11(c). This latter can be followed by the smaller radius evolution of the semi-circle of impedance response in the complex plane of Fig.11(a). At day 60, the behavior of the charge transfer phenomenon is more predominant than at day 45 because the area of the electrolyte-uptake epoxy primer increases at day 60, the primer has higher possibilities to create connected paths of pores within the primer and the pores in CCC, and the electroactive surface area between aluminum substrate and electrolyte is increased.

4.3. Stage IV Self-healing/Stable Cr(III) oxide layer

Following 100 days of immersion, the impedance plot showed a significant change in the electrochemical mechanism, as described in Fig.12. This time period demonstrates the influence of stage IV in the damage evolution. From the Nyquist diagram, the presence of two impedance loops from high to intermediate frequencies and a quasi-vertical straight line at the low frequency range are shown. The capacitive loop at the high frequency regime represents the electrical resistance of the composite coatings, which are mainly affected by the electrolyte-

uptake in the topcoat and primer regions with a magnitude about $10^7(\Omega \cdot \text{cm})$. As shown in Fig.12 (b), the time constant at intermediate frequencies describes electrical resistance of Cr(III) oxide layer and the charge transfer process between the aluminum substrate/oxide layer and the electrolyte (i.e., anodic dissolution of the aluminum substrate and reduction reaction of the Cr(VI) ions to form insoluble hydrated chromium oxide) [44]. The quasi-vertical straight line at low frequency region can be attributed to the presence of a diffusion phenomenon due to the reactions occurring at the metal surface [49]. Furthermore, the magnitude at high frequencies remained nearly constant; this indicates that the organic layer was completely saturated with the electrolyte after 100 days of immersion. In contrast, the capacitive loop formed at medium frequencies, and the charge transfer mechanism was favored due to the self-healing process provided by the Cr(VI) ions, assuming that these ions were previously dissolved in the electrolyte solution during the lixiviation process taking place in stage II. The self-healing process is observed due to the leaching of Cr(VI) ions from the epoxy primer into the electrolyte solution that is subsequently transported to the aluminum substrate leading to repassivation of the chromium oxide layer on the active sites [10, 50]. According with the chromium oxide layer, which is formed at the aluminum surface, several steps are involved in the corrosion protection mechanism of this thin oxide layer; this explains its excellent performance in the protection of the metal substrate during Stage IV [7, 51-53]. The first step is where the aluminum surface is oxidized:

Meanwhile the chromium conversion coating is formed due to electrochemical reactions at the AA2024-T3 substrate where the Cr(VI) is reduced to Cr(III) [7]:

This Cr(III) oxide layer provides good barrier protection due to its hydrophobic nature, good adhesion, and inhibition of the oxygen reduction reaction and metal dissolution [7]. In addition, the residual Cr(VI) ions can also provide self-healing to the damage areas and repassivation of the oxide layer similar to the chromate pigments in the epoxy primer by leaching from the CCC and transport to the corrosion sites by diffusion and/or migration processes [51].

During the self-healing process, the rate of electrochemical interfacial reaction controls the growth of the Cr(III) oxide layer. As shown in Fig.12 (c), the Cr(III) oxide layer grows over longer immersion times. Also, Fig.13 experimentally shows the thickness change of the Cr(III) oxide layer. The thickness of the CCC before exposure is in the range of 10 nm to 50 nm. However, after 260 days of immersion, the average thickness (over 50 nm) of CCC increases (shown in Fig.13[d]). This growth of the Cr(III) oxide layer results in the increase of the capacitive loop formed at medium frequencies, as described in Fig.s12 (a) and (b). This is due to the fact that the formation of the Cr(III) oxide layer can play a role in the insulator and decrease charge transfer areas.

The Warburg coefficient, which expresses a mass transfer process including ionic diffusion [54], can also be used to explain the degradation mechanism based on the activation process occurring at the interface. As shown in Fig. 14, the Warburg coefficient based on the activation process was shown to increase up to $35000 \Omega \cdot \text{cm}^2 \cdot \text{s}^{-1/2}$ at stage III as an activation period, but a constant value ($11000 \Omega \cdot \text{cm}^2 \cdot \text{s}^{-1/2}$) was obtained at stage IV due to forming the stable oxide layer through the self-healing process. This explains that the Cr(III) oxide layer can play a role as a barrier to delay corrosion phenomenon in the multilayered composite system.

5. Conclusions

- In this work, the degradation mechanism of a composite Cr(VI) coating/aluminum alloy 2024-T3 system was studied by EIS in 3.5% NaCl solution at low pH. Following exposure for 260 days in 3.5 NaCl, the composite coating shows four different stages marked as 1) intact coating, 2) water-uptake, 3) lixiviation of Cr^{6+} , and 4) the self-healing.
- A 2D damage propagation model is proposed to characterize and quantify each stage in the degradation mechanism of a multilayered coating/aluminum substrate system. The 2D damage evolution technique is assumed to be based on a deterministic approach and stochastic modeling for coating pore distributions. The physical (electrolyte-uptake) and electrochemical degradation processes are explained by using the spatial distribution of electrical material properties such as electrical resistivity and permittivity as well as the interfacial distribution for electrochemical properties including diffusion and charge transfer parameters.
- To quantitatively understand the mechanism of physical degradation through electrolyte-uptake, the 2D model was developed by distributing and integrating electrical resistivity ($10^6 \sim 10^{10} \Omega \cdot \text{cm}$) and permittivity ($10^{-10} \sim 10^{-7} \text{F} \cdot \text{cm}^{-1}$) of each segment based on composite coating materials and water-uptake processes over various immersion times at stages I and II. The computational results showed that the overall magnitude of impedance response at 0.01 Hz decreases from around $10^{10} \Omega \cdot \text{cm}^2$ to $10^7 \Omega \cdot \text{cm}^2$, which represents compatible results with experimental condition.
- By using the integration of local electrochemical impedances at each segment interface, the electrochemical behaviors of a self-healing process provided by the chromium (VI) dissolved in the electrolyte solution are validated with experimental results. A stable Warburg coefficient magnitude at stage IV can be obtained through the self-healing process.

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Fig. 1. The schematic of 2D finite volume grid a) Impedance of interfacial elements as physical degradation process. b) Impedance as electrochemical process at interface between the aluminum substrate and the CCC.

Fig.2.The schematic of 2D networks of electrochemical impedance elements for layer-by-layer composite coating system based on charge and energy conservation.

Fig.3. Pore distribution of coated system. a) The pore position distribution based on randomly structured model. b) Log-normal probability density function for the distribution of maximum electrolyte percolation length.

Fig. 4.Flow diagram for obtaining parameters and characterization of the multilayer system.

Fig.5. Surface morphology of Cr(VI) full military coating/AA2024-T3 substrate system before immersing in 3.5 wt.% NaCl solution under pH =4.0. a) Cross-section image of the coating system. b) Magnified view of image (a) close to the CCC layer between primer layer and metal substrate. c) Numerical design of layer-by-layer composite coating. d) Magnified view of image (c) close to the CCC layer between primer layer and metal substrate.

Fig.6. Schematic illustration diagrams of degradation mechanism of Cr(VI) Coating/ AA2024-T3 System– Stage I: intact, Stage II: electrolyte uptake, Stage III: lixiviation of Cr(VI), Stage IV: self-healing/stable Cr(III) oxide layer.

Fig.7. Impedance Spectra of experiment and 2D modeling for Cr(VI) Coating/AA2024-T3 System immersed in 3.5 wt.% NaCl solution under pH =4.0 in the first day of immersion. a) Nyquist diagram. b) Bode diagram. c) Resistivity plot. d) Permittivity plot.

Fig.8.Effect of electrolyte penetration on the impedance response ofCr(VI) Coating/ AA2024-T3System immersed in 3.5 wt.% NaCl solution under pH =4.0 between the 2nd and 35th immersion day; a) Nyquist diagram and b) Bode diagram with experimental and 2D modeling results.The distributions of c) electrical resistivities and d) permittivities of each segment dependent on electrolyte penetration process for damage evolution mechanism of the multilayered coating system with various time periods.

Fig.9.The electrolyte penetration ratio of the maximum penetration length of electrolyte to the length of coating layers dependent on immersion time.

Fig. 10. EDS mapping of Cr(VI) Coating/ AA2024-T3System immersed in 3.5 wt.% NaCl solution under pH =4.0over 260 days.

Fig.11.Effect of electrolyte penetration on the impedance response of Cr(VI) Coating/AA2024-T3 System immersed in 3.5 wt.% NaCl solution under pH =4.0 at the 45th and 60th day of immersion; a) Nyquist diagram with experimental and 2D modeling results. b) Bode diagram. c) electrical resistivities and d) permittivities of each segment due to Lixiviation process for damage evolution mechanism of the multilayered coating system with various time periods.

Fig.12.Effect of electrolyte penetration on the impedance response of Cr(VI) Coating/AA2024-T3 system immersed in 3.5 wt.% NaCl solution under pH =4.0 at the 100th, 125th, and 160th day of immersion; a) Nyquist diagram with experimental and 2D modeling results. b) Bode diagram. c) Self-healing process of the multilayered coating system with various time periods.

Fig. 13. SEM morphology of CCC in the interface of primer/substrate before (a-b) and after (c-d) exposure for 260 days.

Fig.14. Degradation mechanism of Cr(VI) Coating/ AA2024-T3 System based on Warburg constant for diffusion phenomenon.

Table 1. Material properties for 2D multilayered microstructure.

	Designed	Electrical	$\epsilon_{(j,i)} \epsilon_{0(j,i)}$	
	Thickness	Resistivity	Permittivity	n-value
Materials	(μm)	($\Omega \cdot \text{cm}$)	($\text{F} \cdot \text{cm}^{-1}$)	for CPE
Electrolyte	N/A	20	0	1
Topcoat	40	1.3E13	1.4E-11	0.91
Primer	30.11	2.4E11	2.0E-11	0.75
CCC	0.034	1.0E11	5.0E-11	0.78
Aluminum	N/A	2.75E-6	0	1
Water-uptake Topcoat	N/A	3.0E7	5.0E-10	0.78
Water-uptake Primer	N/A	2.0E7	1.0E-9	0.78
Water-uptake CCC/ Water-uptake Cr(III) oxide layer	N/A	2.0E7	1.0E-9	0.78

Table 2.Electrochemical properties for 2D multilayered microstructure.

Materials	Diffusion	Charge		n-value for CPE
	Coefficient	Transfer	Double layer	
	Factor	Resistance	Capacitator	
	$(\Omega \cdot \text{cm}^2 \cdot \text{s}^{-1/2})$	$(\Omega \cdot \text{cm}^2)$	$(\text{F} \cdot \text{cm}^{-2})$	
45 days of immersion	30000	18E6	3E-8	0.7
60days of immersion	35000	8.5E6	6E-8	0.7
100days of immersion	12000	3.5E5	1.2E-6	0.7
125days of immersion	12000	6.5E5	1.1E-6	0.7
160days of immersion	12000	8.5E5	1.0E-6	0.7