Research Article

Effect of Plasma Surface Pretreatment on Ce^{3+} -Doped GPTMS- ZrO_2 Self-Healing Coatings on Aluminum Alloy

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A hybrid sol synthesized from an acid-catalyzed hydrolysis and condensation reaction of 3-glycidoxypolytrimethoxysilane (GPTMS) and zirconium n-propoxide was used as a matrix nanocomposite sol. To this sol, 0.01 M Ce^{3+} was added as an inhibitor to provide a self-healing coating system. The effect of an atmospheric air plasma surface pretreatment of aluminum alloy substrates prior to coating deposition of Ce^{3+} -doped/undoped GPTMS- ZrO_2 sol was studied with respect to corrosion protection. Coatings were generated by a dip coating technique employing a withdrawal speed of 5 mm/s and thermally cured at 130° C for 1 h. The coated Al surfaces were characterized using potentiodynamic polarization studies and electrochemical impedance spectroscopy. They were also subjected to accelerated corrosion testing using neutral salt spray test with 5% NaCl solution after creating an artificial scratch for more than 200 hours to assess the self-healing ability of coatings. It was observed that cerium (III) doping was effective for corrosion protection during long-term exposure to the electrolyte solution, and a plasma surface pretreatment of substrates prior to coating deposition of Ce^{3+} -doped coatings improved the adhesion of coatings that provides enhanced corrosion protection along with self-healing ability exhibited in case of damages/scratches caused in the coating.

1. Introduction

Aluminum and Al alloys are widely used in structural applications mainly in aircraft and automobile industries due to their light weight and high strength properties [1]. Aluminum alloys are very sensitive to corrosion when exposed to a chloride containing atmosphere. Although there are several surface engineering treatments available to prevent corrosion on Al/Al alloys, surface treatments that require low temperatures for post-treatment processing are recommended to prevent a deterioration of mechanical strength that occurs by dissolution of intermetallic particles during high temperature post-treatment [2]. Hybrid sol-gel coatings are the best alternatives as low temperature curable coatings that offer a barrier-type protection [3]. However, sol-gel coatings contain micropores, cracks and areas of low cross-link densities that provide pathways for diffusion of corrosive species to the coating metal interface [3]. In order

to overcome these problems, the use of inhibitors in the coating is usually resorted to. Such coatings may not also be able to provide continued corrosion protection in the event of development of a crack in the coating. Hence, instead of providing a metal with just a sol-gel barrier or inhibitor-doped coating for corrosion protection, which may lead to initiation of corrosion when the coating develops a crack or a damage, it is desirable to provide a coating that can self-heal when subjected to cracking and can still maintain the protection of the substrate from the surrounding environment under normal operating conditions. The self-healing mechanism can prolong the life of the object without removing the same from site for maintenance or repair, and this depends on the coating system used; in some cases, the inhibitor itself works as self-healer, and in some cases, an encapsulated self-healer (organic/inorganic inhibitor or polymer) is embedded in a sol-gel matrix, which releases the inhibitor/polymer during onset of the formation of the

cracks and fills the crack by the polymerization product or by forming a passivating layer. In most cases, the self-healing agents are encapsulated in a hybrid sol-gel matrix. Hexavalent chromium is the best inhibitor known so far and a self-healing agent that was widely used in the industry for corrosion protection of aluminum [4]. However, since hexavalent chromium has been proved to be carcinogenic [5, 6], the rare earth element cerium is being studied extensively [7–24] as a substitute to chromium since it also provides a good inhibition effect in addition to being environmentally friendly and having a self-healing ability. It blocks the pores and prevents corrosion even on scratched areas during long-term exposure. Cerium-doped hybrid sol-gel coatings have also attracted a lot of attention in the recent past [7–9, 11, 12, 17, 20, 23, 24].

The corrosion protection efficiency of inhibitor (cerium)-doped sol-gel coatings depends upon the efficacy of inhibitor release from the applied coating system that enables active corrosion protection and self-healing. There are several reports on experimental studies on cerium-doped sol-gel coatings as self-healing coatings on Al/Al alloys. Effect of inhibitor (CeO_2) particle sizes [9], inhibitor concentrations [20], and the way in which the inhibitors are contained in the sol-gel matrix [7] have been studied and reported. According to Zheludkevich et al. [7], who studied on cerium ion doping in tetraethoxysilane, 3-Glycidoxypopyltrimethoxy silane (GPTMS), tetra-n-propoxyzirconium (TPOZ) hybrid sol-gel matrix, a higher corrosion protection was observed when the hybrid sol-gel films were prepared with cerium containing zirconia nanoparticles, compared to cerium ion doping directly into the sol-gel matrix. The reason attributed was that the nanostructured zirconia particles play the role of nanoreservoirs for storage and controllable release of the inhibitor, thereby providing a prolonged release of the cerium ions. They also reported that too high a concentration of cerium ions leads to degradation of barrier properties of the sol-gel matrix. This observation is also consistent with that reported by Schem et al. [20] and Paussa et al. [8]. There are only few reports on computational modeling of the inhibitor release from the sol-gel coating. Trenado et al. [22] studied the effect of porosity and viscosity on the release rate of the inhibitor. In their model, the inhibitors were considered as ions, immersed in sol-gel film, which are subjected to gradient of concentration and potential, where the capillary forces attributed to porous structures in the coating were taken into account.

Sol-gel coatings are inherently adherent to metallic substrate surfaces by forming covalent bonds. It is possible to further improve the adhesion of the sol-gel coatings through surface pretreatments. It has already been reported that an atmospheric air plasma surface pretreatment improves the adhesion of sol-gel coatings to aluminum and mild steel surfaces [25, 26]. Though there are several investigations reported on cerium ion-doped sol-gel coatings on aluminum alloys, there are no studies reported so far on the influence of a plasma surface pretreatment on corrosion protection of Ce^{3+} -based self-healing sol-gel coatings on aluminum alloys. Hence, the main aim of this study was to find out the effect of plasma surface treatment of Al alloy on the

corrosion inhibition and self-healing property of cerium (III) incorporated in a silica-zirconia hybrid sol-gel coating.

2. Experimental

2.1. Materials and Synthesis. 3-Glycidoxypopyltrimethoxysilane (GPTMS), zirconium n-propoxide from GELEST Inc., USA, methacrylic acid (ABCR GmbH, Germany), all of purity >97%, and high-purity solvent 2-butoxy-ethanol (LR) from SD Fine-Chem Ltd., Mumbai, India were used as-received. Cerous nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) 99.9% from Loba Chemie Pvt, Mumbai, India was used as source of Ce^{3+} . Aluminum substrates of dimensions $10\text{ cm} \times 10\text{ cm} \times 1\text{ mm}$ were used for the coating experiments. The chemical composition of the substrate as determined using X-ray fluorescence spectrometer (PANalytical model PW2400) was Al: 98.6%; Si: 0.4%; Mg: 0.5%; Fe: 0.3%; Na: 0.2%. The sol was synthesized in two parts. In the first part, 40.37 g of zirconium n-propoxide was diluted with 16.8 g butoxyethanol and complexed with 7.7 g of methacrylic acid under stirring in order to reduce the hydrolysis rate of zirconium n-propoxide. The second part was synthesized by adding acidified water (3.21 g) to 107.1 g of GPTMS, and after 20 minutes of stirring, the Zr-n-propoxide-MAA complex was added to part 2 under vigorous stirring, and the temperature was controlled using an ice bath. After stirring the mixture for 3–4 h, the sol was further diluted using 2-butoxy-ethanol, and cerous nitrate was added so that final concentration of Ce^{3+} in the sol would be 0.01 M. The silica-zirconia hybrid sol without any Ce^{3+} doping would henceforth be referred to as GPZ, and that with Ce^{3+} doping would be referred to as GPZ-Ce.

2.2. Pretreatment and Coating Deposition. The aluminum substrates were degreased using acetone and dried with hot air. Surface pretreatment of some of the substrates was carried out using atmospheric air plasma treatment equipment (Plasmatrete GmbH, Germany). The plasma produced using compressed air was used for activating the surface by inducing highly active species. A nozzle to substrate distance of 10 mm was used as the optimized parameter for the plasma treatment process [25], while the plasma exposure time was 10 seconds. Coatings were generated using dip coating technique on as-cleaned and plasma pretreated aluminum substrates by employing a withdrawal speed of 5 mm/s. GPZ coatings deposited on plasma-treated Al substrates would be referred to as GPZ-plasma, and GPZ-Ce coatings deposited on plasma-treated Al substrates would be referred to as GPZ-Ce-plasma.

2.3. Characterization. Thickness of coatings was measured using an optical thickness measurement equipment model F20 supplied by Filmetrics Inc., USA. Electrochemical tests were carried out using a Solartron electrochemical interface SI 1287 with Impedance Analyzer Solartron SI 1260. The corrosion test cell had the classic configuration of three electrodes (platinum as counter-electrode, a saturated calomel electrode as a reference electrode, and the uncoated/coated metallic sample as the working electrode). Polarization

studies of the coated/uncoated substrates were carried out at 25°C in a N₂ purged 3.5% NaCl solution with an exposure time of 1 h and 24 h. Potentiodynamic scans were recorded by applying potentials from -1.6 V to 0.0 V with a scan rate of 1 mV/s. The electrochemical impedance scan was carried out using an AC signal of 10 mV amplitude applied over a bandwidth from 100 kHz to 0.03 Hz. Five dip-coated samples, that is, 10 coated surfaces, for each set were used for corrosion testing to ascertain the reproducibility of the data. The results obtained were analyzed using Corrview2 and Zview2 software and compared with those obtained for bare Al substrates. Accelerated corrosion tests were carried out by ASTM B117 method with 5% NaCl solution at 35°C, using a salt spray chamber, where a scratch was artificially created on the uncoated and coated samples, before subjecting them to neutral salt spray test (SST).

3. Results and Discussion

In this study, effect of two factors on corrosion protection efficiency of the sol-gel coatings on Al was studied: (1) effect of direct incorporation of Ce³⁺ in silica-zirconia hybrid sol-gel coating matrix and (2) effect of plasma pretreatment on corrosion properties of substrates coated with and without Ce³⁺ doping in hybrid silica-zirconia matrix.

3.1. Potentiodynamic Polarization Studies. The data obtained from the potentiodynamic polarization studies are presented in Figures 1–4, and the results obtained after R_p fitting of the potentiodynamic polarization data after 1 h and 24 h exposure to 3.5% NaCl are presented in Table 1. It could be seen that all GPZ coatings, whether Ce³⁺-doped/undoped and deposited on untreated/plasma-treated substrates, provided a good barrier protection to the aluminum substrate, since the corrosion current density, i_{corr} , was lower by one order for all coatings when compared to that for the bare aluminum substrate.

In case of only the GPZ coating, after 1 h exposure, the i_{corr} values are two orders low in magnitude when compared to that for the bare substrate, which implies a very good barrier property due to very good densification of coating. However, after 24 h exposure to the electrolyte solution, the i_{corr} values increase by one order of magnitude, though the values are still lower than that of the bare substrate, as shown in Figure 1. The reason for the increase in i_{corr} values after long-term exposure there could be opening up of pores due to penetration of the electrolyte.

3.1.1. Effect of Plasma Pretreatment. Atmospheric air plasma surface pretreatment is expected to improve the adhesion of coating with the substrate, thereby increasing the corrosion resistance property [25, 26]. The corrosion current densities of GPZ and GPZ-plasma samples after 1 h and 24 h exposure time in 3.5% NaCl solution were seen to be nearly the same as seen from Table 1 and Figure 2. In case of GPZ coatings, the plasma pretreatment may not be seen as effective for short- and long-time exposure to electrolyte because the coating itself acts as a good barrier. Hence, in this case, the coating

FIGURE 1: Comparison of the potentiodynamic polarization data of the bare aluminum and Al coated with GPZ for 1 h exposure to 3.5% NaCl solution.

properties after plasma treatment are not much different from coatings deposited on an as-cleaned substrate.

3.1.2. Effect of Ce³⁺ Inhibitor. The GPZ coating when doped with Ce³⁺ does not provide a protective behavior against corrosion as seen from the potentiodynamic polarization results. The same observation was reported by [7–9]. This is due to more water uptake by the Ce³⁺ ions in the coating. When cerium ions are directly introduced into the hybrid silica-zirconia sol, it is probable that the cerium ions decrease the stability of the hybrid film leading to faster hydrolytic destruction in aqueous solutions [7]. After 1 h exposure to electrolyte, as shown in Figure 3(a), the corrosion current continues to increase in the GPZ-Ce coating with values close to that shown by the bare Al substrate but at one point stops and forms a passive region because of the pH increase in vicinity of the coating, which leads to precipitation of Ce(OH)₃ that closes the pores. The coating with the Ce³⁺ (GPZ-Ce) adds to the barrier properties and prevents the penetration of electrolyte during long-term exposure to the electrolyte. After 24 h exposure, the corrosion current continues to increase more rapidly with increasing potential, as shown in Figure 3(b). The GPZ-Ce coating exhibits more corrosion resistance compared to GPZ for 24 h exposure, because during long-time immersion, the Ce³⁺ ions slowly form Ce(OH)₃ precipitates that plug the pores, thereby forming a barrier to reduce electrochemical reactions. Hence, it is clear that the Ce³⁺ inhibition effect can be seen only during long-time exposure. This observation was also confirmed by the neutral salt spray test, as described later in Section 3.3.

3.1.3. Effect of Ce³⁺ Doping along with Plasma Pretreatment. The effect of plasma pretreatment on Ce³⁺-doped GPZ coatings can be seen from the R_p fitting of the data, though

TABLE 1: R_p fit data for the results obtained from potentiodynamic polarization measurements.

Sample	E_{corr} (volts)	I_{corr} (A/cm ²)	R_p (ohms/cm ²)
Bare Al-1 h	-0.772	$6.079E-6$	4291.2
Bare Al-24 h	-0.788	$4.728E-6$	5517.4
Al-GPZ-1 h	-0.838	$1.828E-8$	1.426E6
Al-GPZ-24 h	-0.781	$2.741E-7$	95159
Al-GPZ-Ce-1 h	-0.824	$1.758E-7$	1.483E5
Al-GPZ-Ce-24 h	-0.818	$2.655E-7$	98225
Al-GPZ-plasma-1 h	-0.819	$3.950E-8$	6.603E5
Al-GPZ-plasma-24 h	-0.754	$4.413E-7$	59109
Al-GPZ-Ce-plasma-1 h	-0.802	$6.499E-7$	40135
Al-GPZ-Ce-plasma-24 h	-0.761	$2.390E-7$	1.091E5

FIGURE 2: Potentiodynamic polarization data obtained for the GPZ and GPZ-plasma for (a) 1 h and (b) 24 h exposure to 3.5% NaCl solution.

not very clearly evident from Figure 4(b). The i_{corr} values are lower in the case of Ce^{3+} -doped GPZ coatings, which implies that a plasma pretreatment improves adhesion of Ce^{3+} -doped GPZ coatings and improves the corrosion resistance. The effect of plasma pretreatment can be better understood from electrochemical impedance spectroscopic analysis. Since it was seen that the effect of Ce^{3+} can be realized after long-term exposure to the electrolyte solution, impedance analysis was carried out only on coated samples after 24 h exposure to 3.5% NaCl solution.

3.2. Electrochemical Impedance Spectroscopy (EIS). EIS is a nondestructive testing technique for evaluation of the barrier properties of the coatings and adhesion to the substrate. The obtained EIS data for the coated substrates are shown as Nyquist plots in Figure 5 and were fitted using the equivalent circuit given by two time constants also shown in Figure 5.

A constant phase element (CPE) was used instead of an “ideal capacitor” to explain the deviations from ideal behavior. The possible reasons for a nonideal behavior could be due to surface roughness, inhomogeneous reaction rates on the surface, or varying thickness or composition of a coating [27–29]. The impedance of a CPE, that is, Z_{CPE} , could be defined as $Z_{\text{CPE}} = 1/Y(j\omega)^n$, where ω is the angular frequency in $\text{rad}\cdot\text{s}^{-1}$, Y is the pseudocapacitance, and n is called the CPE exponent, which is associated with the system inhomogeneity. When $n = 1$, the system behaves like a pure capacitor and $Y = C$. When CPE is used to fit the experimental data, $n < 1$. R_s is the resistance of the electrolyte, R_{pore} is the resistance to charge transfer through pores, Y_{coat} is the pseudocapacitance of coating, and Y_{dl} is pseudocapacitance associated with the double layer formed at the metal-electrolyte interface in parallel with charge transfer resistance R_{ct} describing the corrosion of the metal substrate. Table 2 presents the fitting parameters for the

FIGURE 3: Potentiodynamic polarization data of GPZ- and GPZ-Ce-coated Al substrates for (a) 1 h and (b) 24 h exposure to 3.5% NaCl solution.

FIGURE 4: Potentiodynamic polarization curves of aluminum coated with GPZ and GPZ-Ce with and without plasma pretreatment for (a) 1 h and (b) 24 h exposure to 3.5% NaCl solution.

coated samples exposed to 3.5% NaCl for 24 h obtained from the impedance data using the equivalent circuit as previously explained. The time constant at high frequencies is related to the properties of coating.

3.2.1. Effect of Plasma Pretreatment. After 24 h exposure, the pore resistance and R_{ct} values for GPZ coating after plasma pretreatment are higher when compared to those for GPZ coating on an untreated substrate, which implies that plasma pretreatment prior to coating deposition is very effective in

sustaining the corrosion resistance due to improved adhesion of the coating.

3.2.2. Effect of Ce^{3+} Doping. The R_{pore} is less in Ce^{3+} -doped coating compared to that without cerium due to water uptake and presence of Ce^{3+} which does not allow formation of a dense cross-linked structure which is able to protect the metal substrate [7–9]. Since cerium (III) is very reactive, it immediately reacts with water from the electrolyte, forming the $Ce(III)$ hydroxide that subsequently

FIGURE 5: (a) Nyquist plots of coated Al under different conditions after 24 h exposure to 3.5% NaCl solution; (b) equivalent circuit used for fitting the EIS data.

TABLE 2: Fitting parameters of the EIS data obtained for the coated substrates after 24 h exposure to 3.5% NaCl.

Sample after 24 h exposure	R_s ($\Omega \cdot \text{cm}^2$)	Y_{coat} ($\text{Ss}''\text{cm}^{-2}$)	n_{coat}	R_{pore} ($\Omega \cdot \text{cm}^2$)	Y_{dl} ($\text{Ss}''\text{cm}^{-2}$)	n_{dl}	R_{ct} ($\Omega \cdot \text{cm}^2$)	χ^2
Al-GPZ	37.32	$3.53E-6$	0.98	3884	$6.42E-7$	0.98	$5.23E4$	0.0045
Al-GPZ-Ce	31.79	$5.15E-6$	0.96	812.5	$3.58E-7$	0.94	$1.07E5$	0.00003
Al-GPZ-plasma	37.82	$4.28E-6$	0.95	$4.72E4$	$2.17E-7$	0.97	$4.92E5$	0.00066
Al-GPZ-Ce-plasma	32.53	$3.36E-6$	0.97	5163	$5.32E-7$	0.98	$1.00E5$	0.0055

gets converted to Ce(IV) hydroxide [30]. When exposed to electrolytes for longer time, the conversion of Ce(III) to Ce(IV) is less because the upper layer of coating containing Ce(IV) opposes the electrolyte to penetrate into the coating, due to which the R_{ct} for Ce^{3+} -doped coating is higher than the GPZ coating. Hence, the cerium effect is evident only during long-time exposure.

3.2.3. Effect of Ce^{3+} Doping along with Plasma Pretreatment.

The R_{pore} for the GPZ-Ce coatings after plasma pretreatment was seen to have increased when compared to coatings without plasma treatment, though the R_{ct} values remained the same for both coatings. This is due to the fact that the plasma treatment enables increased adhesion of coatings to substrate. Due to introduction of Ce^{3+} in the coatings, there is less formation of inorganic network in the coatings and possibly more organic polymerization (cationic polymerization of epoxy groups from the GPTMS precursor catalyzed by Zr^{4+} [26] and additionally by Ce^{4+}). This possibility has been stated since the viscosity of the GPZ sol with Ce^{3+} was observed to increase more rapidly with time than the sol without Ce^{3+} . The increase in viscosity could be attributed to increased organic polymerization in the sol that is catalyzed by Ce^{3+} in addition to Zr^{4+} . In spite of the above, the surface pretreatment provides an increased

R_{pore} due to increased adhesion, which provides long-term corrosion protection. Zheludkevich et al. [7] reported that in the case of direct doping of Ce^{3+} in the hybrid sol-gel matrix, the pore resistance of the sol-gel film dropped down very fast due to the formation of a fragile film with poor barrier properties. In the present case, though Ce^{3+} was added directly to the silica-zirconia hybrid sol-gel matrix, the pore resistance increased when the coatings were deposited on a plasma pretreated substrate.

3.3. Neutral Salt Spray Tests. The photographs of coated and uncoated substrates with an artificial scratch after salt spray testing for 208 h are shown in Figure 6. The uncoated Al substrate exhibited corrosion within 24 h of exposure to salt spray, which was visible even with naked eyes, whereas in case of the GPZ coatings, initiation of corrosion was observed after 48 h. The scratched area of GPZ coated substrate was seen to be corroded and filled with the corrosion product by 208 h. However, no sign of corrosion was found either on the surface or on the scratched areas in case of GPZ-Ce coatings up to 120 h. After that, corrosion was seen to have initiated on the surface. It can be concluded that, in case of GPZ-Ce coatings, the Ce(III) moves towards the damaged part and inhibits the corrosion of substrate by two mechanisms; one is by forming an insoluble hydroxide on the surface,

FIGURE 6: Photographs of samples after 208 h of salt spray tests: (a) bare aluminum; (b) GPZ; (c) GPZ-plasma; (d) GPZ-Ce; (e) GPZ-Ce-plasma.

and the other is by catalyzing the epoxide polymerization of the epoxy group from the GPTMS precursor, which fills the scratched area thereby forming a barrier layer between the electrolyte and the substrate.

The plasma-treated GPZ-Ce substrates showed still better corrosion properties when compared to other samples as seen from Figure 6(e). Here, it can be confirmed that the Ce^{3+} inhibits the corrosion process, and the plasma treatment improves the adhesion of coatings and, hence, provides an added improvement to the corrosion resistance. It can be observed that there are absolutely no signs of

corrosion near the scratch which is an evidence for the self-healing properties that confirm that the Ce^{3+} present in the sol-gel coating have a greater inhibitive activity in the damaged areas. The corrosion is inhibited by migration of the Ce(III) ions through the coating or a defect in the coating to the site of the attack [7, 23, 24].

4. Conclusion

The effect of direct doping of Ce^{3+} in the silica-zirconia hybrid sol-gel matrix and effect of plasma pretreatment

prior to sol-gel coating deposition was studied in terms of corrosion inhibition and self-healing ability under conditions of external damages caused to the coating. It was found that the Ce^{3+} is effective in providing self-healing corrosion protection whenever a scratch/damage was caused to the coating. In addition, plasma pretreatment prior to deposition of Ce^{3+} -doped silica-zirconia nanocomposite sol-gel coating improved the adhesion of coatings to the substrate. Ce^{3+} provided self-healing activity in two ways; one by inhibiting the corrosion reactions on the surface by forming insoluble hydroxides and another by catalyzing a polymerization reaction of the epoxy group present in the hybrid coating along with Zr^{4+} , thereby forming a dense barrier layer and resisting corrosion. It could be concluded that a combination of the Ce^{3+} doping in the hybrid sol-gel matrix containing a polymerizable organic group along with plasma pretreatment of substrate prior to the coating deposition of the self-healing coating composition provided a long-lasting corrosion protection to Al substrates. The highlighted success of the present work is the development of a process to yield chromate-free eco-friendly self-healing coatings for improved and long-term corrosion protection of aluminum and its alloys.

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References

- [1] J. D. Minford, *Handbook of Aluminum Bonding Technology and Data*, Marcel Dekker, New York, NY, USA, 1993.
- [2] A. Wittmar, M. Wittmar, A. Ulrich, H. Caparrotti, and M. Veith, "Hybrid sol-gel coatings doped with transition metal ions for the protection of AA, 2024-T3," *Journal of Sol-Gel Science and Technology*, vol. 61, pp. 600–612, 2012.
- [3] T. L. Metroke, R. L. Parkhill, and E. T. Knobbe, "Passivation of metal alloys using sol-gel-derived materials—a review," *Progress in Organic Coatings*, vol. 41, no. 4, pp. 233–238, 2001.
- [4] S. A. Kulinich and A. S. Akhtar, "On conversion coating treatments to replace chromating for Al alloys: recent developments and possible future directions," *Russian Journal of Non-Ferrous Metals*, vol. 53, no. 2, pp. 176–203, 2012.
- [5] J. H. Duffus, "Chemical speciation terminology: chromium chemistry and cancer," *Mineralogical Magazine*, vol. 69, no. 5, pp. 557–562, 2005.
- [6] A. Caglieri, M. Goldoni, O. Acampa et al., "The effect of inhaled chromium on different exhaled breath condensate biomarkers among chrome-plating workers," *Environmental Health Perspectives*, vol. 114, no. 4, pp. 542–546, 2006.
- [7] M. L. Zheludkevich, R. Serra, M. F. Montemor, K. A. Yasakau, I. M. M. Salvado, and M. G. S. Ferreira, "Nanostructured sol-gel coatings doped with cerium nitrate as pre-treatments for AA2024-T3 Corrosion protection performance," *Electrochimica Acta*, vol. 51, no. 2, pp. 208–217, 2005.
- [8] L. Paussa, N. C. Rosero-Navarro, D. Bravin et al., "ZrO₂ sol-gel pre-treatments doped with cerium nitrate for the corrosion protection of AA6060," *Progress in Organic Coatings*, vol. 74, pp. 311–319, 2012.
- [9] A. Wittmar, M. Wittmar, H. Caparrotti, and M. Veith, "The influence of the inhibitor particles particles sizes to the corrosion properties of hybrid sol-gel coatings," *Journal of Sol-Gel Science and Technology*, vol. 59, pp. 621–628, 2011.
- [10] J. Carneiro, J. Tedim, S. C. M. Fernandes et al., "Chitosan-based self healing protective coatings doped with cerium nitrate for corrosion protection of aluminum alloy 2024," *Progress in Organic Coatings*, vol. 75, pp. 8–13, 2012.
- [11] N. C. Rosero-Navarro, M. Curioni, Y. Castro, M. Aparicio, G. E. Thompson, and A. Durán, "Glass like Ce_xO_y sol-gel coatings for corrosion protection of aluminum and Magnesium alloys," *Surface and Coatings Technology*, vol. 206, pp. 257–264, 2011.
- [12] L. S. Kasten, J. T. Grant, N. Grebasch, N. Voevodin, F. E. Arnold, and M. S. Donley, "An XPS study of cerium dopants in sol-gel coatings for aluminum 2024-T3," *Surface and Coatings Technology*, vol. 140, no. 1, pp. 11–15, 2001.
- [13] A. K. Mishra and R. Balasubramaniam, "Corrosion inhibition of aluminum alloy AA 2014 by rare earth chlorides," *Corrosion Science*, vol. 49, no. 3, pp. 1027–1044, 2007.
- [14] B. R. W. Hinton, "Corrosion inhibition with rare earth metal salts," *Journal of Alloys and Compounds*, vol. 180, no. 1-2, pp. 15–25, 1992.
- [15] W. Pinc, S. Geng, M. O'Keefe, W. Fahrenholtz, and T. O'Keefe, "Effects of acid and alkaline based surface preparations on spray deposited cerium based conversion coatings on Al 2024-T3," *Applied Surface Science*, vol. 255, no. 7, pp. 4061–4065, 2009.
- [16] P. Campestri, H. Terryn, A. Hovestad, and J. H. W. de Wit, "Formation of a cerium-based conversion coating on AA2024: relationship with the microstructure," *Surface and Coatings Technology*, vol. 176, no. 3, pp. 365–381, 2003.
- [17] N. N. Voevodin, N. T. Grebasch, W. S. Soto, F. E. Arnold, and M. S. Donley, "Potentiodynamic evaluation of sol-gel coatings with inorganic inhibitors," *Surface and Coatings Technology*, vol. 140, no. 1, pp. 24–28, 2001.
- [18] M. Misevicius, O. Scit, I. Grigoraviciute-Puroniene, G. Degutis, I. Bogdanoviciene, and A. Kareive, "Sol-gel synthesis and investigation of un-doped and Ce-doped strontium aluminates," *Ceramics International*, vol. 38, pp. 5915–5924, 2012.
- [19] A. J. Davenport, H. S. Isaacs, and M. W. Kendig, "XANES investigation of the role of cerium compounds as corrosion inhibitors for aluminum," *Corrosion Science*, vol. 32, no. 5-6, pp. 653–663, 1991.
- [20] M. Schem, T. Schmidt, J. Gerwahn et al., "CeO₂-filled sol-gel coatings for corrosion protection of AA2024-T3 aluminium alloy," *Corrosion Science*, vol. 51, no. 10, pp. 2304–2315, 2009.
- [21] F. J. Presuel-Moreno, H. Wang, M. A. Jakab, R. G. Kelly, and J. R. Scully, "Computational modeling of active corrosion inhibitor release from an Al-Co-Ce metallic coating," *Journal of the Electrochemical Society*, vol. 153, no. 11, Article ID 002611JES, pp. B486–B498, 2006.
- [22] C. Trenado, M. Wittmar, M. Veith et al., "Multiscale numerical modeling of Ce^{3+} -inhibitor release from novel corrosion protection coatings," *Modelling and Simulation in Materials Science and Engineering*, vol. 19, pp. 025009–025017, 2011.
- [23] A. Pepe, M. Aparicio, A. Durán, and S. Ceré, "Cerium hybrid silica coatings on stainless steel AISI 304 substrate," *Journal of Sol-Gel Science and Technology*, vol. 39, no. 2, pp. 131–138, 2006.
- [24] A. Pepe, M. Aparicio, S. Ceré, and A. Durán, "Preparation and characterization of cerium doped silica sol-gel coatings

- on glass and aluminum substrates,” *Journal of Non-Crystalline Solids*, vol. 348, pp. 162–171, 2004.
- [25] R. Subasri, A. Jyothirmayi, and D. S. Reddy, “Effect of plasma surface treatment and heat treatment ambience on mechanical and corrosion protection properties of hybrid sol-gel coatings on aluminum,” *Surface and Coatings Technology*, vol. 205, no. 3, pp. 806–813, 2010.
- [26] P. Kiruthika, R. Subasri, A. Jyothirmayi, K. Sarvani, and N. Y. Hebalkar, “Effect of plasma surface treatment on mechanical and corrosion protection properties of UV-curable sol-gel based GPTS-ZrO₂ coatings on mild steel,” *Surface and Coatings Technology*, vol. 204, no. 8, pp. 1270–1276, 2010.
- [27] J. Vogelsang and W. Strunz, “The evaluation of experimental dielectric data of barrier coatings by means of different models,” *Electrochimica Acta*, vol. 46, no. 24-25, pp. 3619–3625, 2001.
- [28] W. H. Mulder, J. H. Sluyters, T. Pajkossy, and L. Nyikos, “Tafel current at fractal electrodes. Connection with admittance spectra,” *Journal of Electroanalytical Chemistry*, vol. 285, no. 1-2, pp. 103–115, 1990.
- [29] C. H. Kim, S. I. Pyun, and J. H. Kim, “An investigation of the capacitance dispersion on the fractal carbon electrode with edge and basal orientations,” *Electrochimica Acta*, vol. 48, no. 23, pp. 3455–3463, 2003.
- [30] S. Böhm, R. Greef, H. N. McMurray, S. M. Powell, and D. A. Worsley, “Kinetic and mechanistic studies of rare earth-rich protective film formation using in situ ellipsometry,” *Journal of the Electrochemical Society*, vol. 147, no. 9, pp. 3286–3293, 2000.