ZrO$_2$ sol–gel pre-treatments doped with cerium nitrate for the corrosion protection of AA6060

L. Paussa$^{a, *}$, N.C. Rosero Navarro$^{b}$, D. Bravin$^{a}$, F. Andreatta$^{a}$, A. Lanzutti$^{a}$, M. Aparicio$^{b}$, A. Durán$^{b}$, L. Fedrizzi$^{a}$

$^a$ University of Udine, Department of Chemistry, Physics, and Environment, Via del Cotonificio 108, 33100 Udine, Italy
$^b$ Instituto de Cerámica y Vidrio (CSIC), c/ Kelsen 5, Campus de Cantoblanco, 28049, Madrid, Spain

**A R T I C L E   I N   F O R M E D**

**Article history:**
Received 9 June 2011
Received in revised form 1 August 2011
Accepted 19 August 2011
Available online xxx

**Keywords:**
Sol–gel
ZrO$_2$
Ceramic conversion coatings
AA6060
Inhibition
Cerium

**A B S T R A C T**

Sol–gel coatings represent an alternative corrosion protection method to the chromate based systems which must be replaced. Recently, it was shown that ZrO$_2$ based sol–gel coatings deposited on AA6060 can provide a good corrosion protection to AA6060. However, ZrO$_2$ based sol–gel systems are not able to provide the self-healing effect which is instead the peculiar property of chrome conversion coatings. The structure of the ZrO$_2$ based sol–gel systems does not contain species able to restore the barrier properties when defects or damages impair the coating protection.

In this work, ZrO$_2$ based sol–gel coatings containing cerium nitrate were deposited on AA6060 aluminum alloy in order to evaluate the corrosion inhibition provided by the incorporated cerium ions. The cerium nitrate was added to the starting sol based on zirconium alkoxide precursors. Three types of samples were produced: a non inhibited type consisting of 3 layers of ZrO$_2$, an inhibited system consisting of two layers of ZrO$_2$ with an intermediate layer doped with cerium nitrate and an inhibited system consisting of two layers containing cerium nitrate with a top layer of ZrO$_2$.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Aluminum alloys are usually protected with a paint system consisting of a conversion layer, a primer, and a top coat. Chromium-based pre-treatments are extensively employed as conversion coatings because they provide very good adhesion for primers and top coats associated with good barrier properties [1]. Chrome conversion coatings also exhibit self-healing abilities [1]. However, the use of chrome conversion coatings is restricted and alternative pre-treatments should be employed for the corrosion protection of aluminum alloys [1–4]. Coatings obtained with sol–gel techniques are a possible replacement for chrome conversion coatings [5]. In previous works, our research group followed the strategy of developing thin sol–gel coatings for the corrosion protection of different aluminum alloys [6,7]. Thin ZrO$_2$ amorphous films (100–200 nm) deposited on AA1050 with the dip-coating technique [6], improved the adhesion of organic coatings to the metal substrate. ZrO$_2$ sol–gel films were further deposited on AA6060 [7]. Barrier properties of sol–gel coated AA6060 were similar to those of chrome conversion coated AA6060 when a continuous layer was deposited on the surface through successive dipping steps in the sol–gel solution [7]. Moreover, ZrO$_2$ films deposited with the sol–gel technique improved the corrosion resistance of AA2024 [5].

Several studies proved that cerium and rare-earth salts are able to inhibit the corrosion behavior of aluminum alloys in aqueous solutions containing chlorides [8–10]. The addition of cerium ions as chloride compounds to the electrolytic solution promoted the formation of a compact film of cerium hydroxide/oxide on the metal surface [11–14]. Several works [15–20] considered the sol–gel deposition of cerium containing layers for the replacement of chrome based conversion coatings. In our recent works [21,22], interesting results were obtained adding cerium nitrate to organic–inorganic hybrid sol–gel systems deposited on AA2024 aluminum alloy. AA2024 coated with hybrid coatings containing cerium evidenced corrosion rates lower than those detected for coatings without cerium. Cerium ions embedded in the coating structure were probably involved in the overall corrosion processes occurring at the metal surface providing an additional protection.

In this work, ZrO$_2$ sol–gel coatings containing cerium were studied in order to combine barrier properties, previously observed for ZrO$_2$ based systems on the same substrate [7], with the additional protection guaranteed by cerium species introduced in the coating structure [22]. The inhibited system has been developed as an alternative system for replacing chrome based conversion
coatings. Therefore, in order to completely evaluate the inhibition effect related to the cerium ions embedded in the sol–gel coating, the system should be characterized after the application of a top coat. This paper does not consider this aspect but it takes into account only the ability of cerium-containing zirconia-based sol–gel layers to provide inhibition effect when water penetrates into the coatings.

2. Experimental

The substrate for the deposition of ZrO₂ pre-treatments was AA6060 aluminum alloy. Before deposition, the metal substrate underwent pickling procedure consisting of an alkaline etching followed by an acid etching. Sol–gel solutions were prepared using a metal-organic precursor of zirconium (0.1 M Zr(OPr⁴)) in anhydrous ethanol. Cerium species were introduced directly in the metal-organic solution precursor as cerium nitrate with an [Zr]/[Ce] molar ratio equal to 70/30. Acetic acid was added to the starting precursor as chelating agent. The initial precursors were mixed together for 1 h prior to the coating deposition. Sol viscosity was measured by using a HAAKE, model RS 50 RheoStress. Coatings were produced by means of dip-coating technique with 5 cm min⁻¹ and 22 cm min⁻¹ withdrawal rates. In this work, three different ceria-based coatings have been considered. The coating systems were produced as the combination between layers deposited with solutions containing the zirconium precursor and solutions where, in addition to the zirconium precursors, cerium nitrate was added. The sol–gel coatings were produced applying three layers by dipping. For the first sample, the three layers were deposited from the zirconium precursor solution not containing cerium nitrate (sample A). For the second sample, the intermediate layer was deposited starting from the precursor solution containing cerium nitrate while the other two layers were produced from the undoped solution (sample C). In the case of the third sample, the two layers near the metal substrate were produced with the zirconium precursor solution containing cerium species, while the top layer was produced with the zirconium precursor solution not containing cerium nitrate (sample B). The deposited sol–gel layers underwent thermal treatment in order to promote the formation of a cross-linking network. Thermal treatment was carried out at 250 °C employing two different drying times. For a first group of samples, each layer was held at 250 °C for 5 min (samples A–C). For a second group of samples, the sintering time was increased to 10 min for the first two layers and to 20 min for the top layer (sample D).

Table 1 shows the list of the sol–gel systems and the related thermal treatment times applied to produce them. In order to evaluate the redox ratio of Ce³⁺ to Ce⁴⁺ within zirconia based sol–gel films, Zr–Ce coatings were deposited on SiO₂ substrates on which UV–vis spectra were collected. The SiO₂ samples were treated in similar conditions to those of metals (AA6060, 10 min at 250 °C). Spectra were recorded in direct transmission between 190 nm and 1000 nm using an UV–PerkinElmer, Lambda 950 UV/VIS Spectrometer.

Sol–gel coated AA6060 samples produced in this work were characterized by Scanning Electron Microscopy in order to investigate the morphology of the sol–gel pre-treatment. Film thickness and composition were evaluated by means of Glow Discharge Optical Emission Spectroscopy (GDOES). The GDOES technique was also employed to acquire composition profiles in order to follow the coating evolution as a function of immersion time. All samples were analyzed with RI-GDOES using a JY RF-GD PROFILER instrument, manufactured by Horiba Jobin-Yvon, Longjumeau, France. The instrument was equipped with a standard 4 mm diameter anode, a polychromator with 28 acquiring channels, an RF-generator (13.6 MHz) and a Quantum XP software. The source conditions, employed for the analysis, were Ar pressure of 650 Pa and applied power of 25 W. The polychromator was a 0.5 m Paschen Runge with nitrogen purged optical path. The calibration was performed with 28 samples selected among SUS (Setting Up Samples) and CRMs (Certified Reference Materials), grinded and polished before the use. The electrochemical behavior of AA6060 sol–gel samples was studied by means of potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) in diluted Harrison solution (0.05 wt% NaCl, 0.35 wt% (NH₄)₂SO₄). A standard three-electrode setup was used. A platinum wire was employed as counter electrode; a stable Ag/AgCl electrode was used as reference while the working area exposed to the electrolyte was 3.2 cm². The scan rate used for polarization curves was 0.2 mV/s. Potentiodynamic polarization curves were carried out after 30 min of immersion in the electrolyte. Impedance measurements were carried out at open circuit potential with AC voltage amplitude of 10 mV and frequency range from 10 mHz to 100 kHz.

3. Results and discussion

Fig. 1 shows the viscosities curves obtained for both the zirconium sol (solid line) and the zirconium sol doped with cerium (dashed line) just immediately before the coating deposition. Apart from the behavior at low shear stress, it is possible to observe that the viscosity for the doped sol is almost 3 times higher than for the undoped one. This behavior is likely due to the addition of cerium nitrate to the initial sol. Cerium nitrate salts probably promote an increasing in the hydrolysis-condensation kinetics which are directly related to the viscosity of sols. From an industrial point of view, a low sol viscosity is preferred for spraying techniques because higher sol viscosity does not allow to easily performing the coating depositions. However, the viscosity of the doped and undoped zirconium sols is not far from typical values of aqueous solutions (1 mPa s) and it remains stable for a length of time long enough to allow the deposition on the metal substrate.

![Image](https://example.com/fig1.png)
The oxidation state of cerium ions in nitrate compounds is Ce³⁺ but during the sol–gel synthesis and heat treatment of the coatings [17], the cerium oxidation state can change. Therefore, it is possible that Ce³⁺ partially oxidizes to Ce⁴⁺ during the synthesis of zirconia doped coatings. Both oxidation states can be involved in the chemical precipitation of cerium oxide/hydroxide following the mechanisms described in literature [23]. Another fact is that the oxidation reaction involving Ce³⁺ to form Ce⁴⁺ is a competitive reaction of the aluminum dissolution reaction. Therefore, Ce³⁺ added to zirconia sol–gel coatings can be oxidized to Ce⁴⁺ rather than the aluminum substrate starts to dissolve. On the contrary, Ce⁴⁺ cannot be further oxidized but it can only be reduced, being a non competitive reaction with the aluminum dissolution. This aspect has to be taken into account because Ce⁴⁺ oxidation can act as an additional protection of the metal substrate. The determination of the Ce³⁺/Ce⁴⁺ ratio inside zirconia sol–gel coatings can be useful to understand how cerium can heal the metal substrate when corroded. As just observed, cerium ions can chemically precipitate on the corroding substrate without the change of their oxidation state (Ce³⁺, Ce⁴⁺) or can electrochemically precipitate changing the oxidation state (Ce²⁺ is oxidized to Ce⁴⁺). In order to study the redox ratio Ce³⁺/Ce⁴⁺, UV–vis spectra were recorded between 190 and 1000 nm on Zr–Ce coatings deposited on SiO₂ substrates and treated in conditions similar to those of metals (AA6060, 10 min at 250 °C). Fig. 2(a) shows the absorption spectra of Zr–Ce thin coatings with a 70/30 Zr/Ce molar ratio deposited on SiO₂ substrates from 0.1 M (Zr) (long-dashed line) and 0.4 M (Zr) (short-dashed line) precursor solutions compared to the spectrum of pure ZrO₂ coatings (solid line). Two main bands appear in both spectra acquired on the inhibited coatings (0.1 M and 0.4 M), one centered on 200 nm, assigned to Ce⁴⁺ charge transfer, and another wider band around 260 nm. The latter can be resolved in two bands, at 260 and 310 nm associated to Ce³⁺. This evidence is most clear in the spectrum relative to the sol–gel coating deposited from the solution 0.4 M (Zr) which contains a higher amount of cerium (Fig. 2(b)). The deconvolution of this spectrum confirms the visual approach exhibiting three bands centered at 193 nm, 257 nm, and 306 nm (Fig. 2(b)). For the calculation of the Ce⁴⁺/Ce³⁺ redox ratio the molar absorptivity (e) corresponding to the different observed transitions is required. Ce⁴⁺ is a 4f⁰ system and cannot present f→f transitions; the color of Ce⁴⁺ salts arises from the tail of a strong charge transfer band in the UV, centered on 200 nm. On the other hand Ce³⁺ has a 4f⁰ ground electronic configuration with a first excited configuration being 5d; the optical spectra of Ce³⁺ consists of one f→f transition in the near IR, that is Laporte forbidden, with very low molar absorptivity and two f→f transitions that are Laporte allowed in the UV. The wavelength of these transitions mainly depends on the neighbor ligands, being situated at 262 nm, 298 nm, and 328 nm in the ethanol solvent, similar to those appearing in the sol–gel coatings. Thus, it is reasonable to assign the molar absorptivity corresponding to these bands (480 and 150 L mol⁻¹ cm⁻¹) to perform the semi-quantitative calculation of the Ce³⁺ concentration. From these data, the redox ratio has been calculated leading to Ce⁴⁺/Ce³⁺ ≈ 10/90. Paul et al. [24] performed UV–vis measurements on sodium-silicate glasses containing cerium. The comparison of spectra shown by Fig. 2 with those obtained by Paul et al. [24], demonstrates that cerium in the inhibited zirconia coatings is present in ionic state (Ce⁴⁺ and Ce³⁺) with geometry coordinates similar to those appearing in glasses. In the conditions applied to produce zirconia coatings doped with cerium, the redox equilibrium is shifted to reducing conditions with more than 90% of Ce³⁺. Thus, the diffusion of Ce³⁺ ions will be much easier and faster than that occurring in the case of crystalline CeO₂, like in conversion coatings or CeO₂ nanoparticles added to the coatings.

The sol characterization was followed by the evaluation of the properties of ZrO₂ sol–gel coatings deposited on the AA6060 aluminum alloy. Fig. 3 shows the morphology of the zirconia-based sol–gel coating deposited on the pickled AA6060 substrate. The image was acquired by means of scanning electron microscopy. The coating shown in Fig. 3 is composed of three layers of zirconia (sample A) deposited by dipping in a solution containing the metal-organic precursor without cerium nitrate. In the image, it is not
possible to clearly recognize the deposited sol–gel film. Since the zirconia-based sol–gel film deposited on the metal surface is very thin and defect-free, it is very difficult to recognize it on the pickled AA6060 surface. On the other hand, it is possible to observe the morphology of the metal substrate due to the pickling procedure carried out prior to deposition. The pickling procedure employed enables to remove the oxide layer and the intermetallic particles from the metal substrate. It is possible to recognize a selective attack at the grain boundaries (which are electrochemically more reactive than the center of the grains) producing a metallographic-like attack. The deep cavities are most probably generated by a localized attack due to the presence of intermetallics. The morphology of sol–gel systems constituted by the combination between layers deposited from solutions containing cerium nitrate and layers without the inhibitor (sample B, sample C and sample D) appears very similar to that observed in Fig. 3 for sample A.

In order to evaluate the composition and the thickness of the coatings, chemical compositional profiles were acquired by means of Glow Discharge Optical Emission Spectroscopy (GDOES). In particular, this technique was used to detect the profile of cerium contained in the inhibited system. Fig. 4 shows the chemical composition profiles acquired by means of GDOES on the coated systems listed in Table 1. Measurements were performed on coatings produced with 22 cm min\(^{-1}\) withdrawal rate. The profile displayed in Fig. 4(a) shows the composition in depth of the sol–gel coating not containing cerium layers. In this profile, the signals of zirconium, oxygen, carbon, and aluminum are visible. It can be observed that a not negligible amount of carbon was acquired. This is probably due to a fraction of organic compounds not eliminated during the thermal treatment. Indeed, the temperature of the drying step was 250 °C which was probably not high enough to allow the complete elimination of the organic fraction contained in the sol. Zirconium and oxygen signals are related to the presence of the ZrO\(_2\) based coating which was not clearly visible in Fig. 3. The thickness of the coating can be evaluated following a well known method suggested by Nélis et al. [26] for rough surface. This method has been explained in more detail in the section of this paper where cerium diffusion has been evaluated by GDOES measurements. According with this procedure, the thickness of sample A can be identified in the range of 120 nm. Fig. 4(b) shows the profile of the sol–gel system composed of two doped inner layers and a top layer without cerium (sample B). In this case, the cerium signal was also detected in addition to carbon, zirconium, oxygen, and aluminum. The profile suggests that cerium is localized in the region at the interface with the metal substrate confirming that the top layer deposited using a cerium-free solution contains only zirconium, oxygen, and carbon. The thickness of sample B is in the range of 160 nm which is 40 nm thicker than that of sample A. This can be related to the different viscosity of the inhibited and non inhibited sols. Since the viscosity of the solution containing cerium is higher than the one not containing cerium, the inhibited layers are usually thicker than those produced without the inhibitor. Fig. 4(c) shows the compositional profile for the sol–gel system with the intermediate layer containing cerium (sample C). It is possible to recognize a smaller cerium amount compared to the one acquired for sample B which is instead composed of two inhibited layers. The thickness of sample C can be evaluated in the range of 140 nm which is lower than that measured for sample B while it is higher than the one evaluated for the sample A. These results confirm that systems containing inhibited layers are thicker than those not containing cerium. By comparing the acquired cerium profiles, it is possible to evidence that the largest cerium amount is localized in the middle of the coating for sample C while it is shifted toward the substrate for sample B. As expected, in sample B the cerium amount is located closer to the metal surface with respect to sample C. Since inhibition mechanisms related to cerium ions depend on their diffusion path, the inhibition phenomenon should be more effective for sample B rather than for sample C. Fig. 4(d) shows the compositional profile obtained on the sol–gel system with the same structure of sample B but subjected to a longer thermal treatment (as listed in Table 1). It is possible to compare the profiles of the two systems evidencing that in the case of the system treated for longer time (Fig. 4(d)), the intensity of the zirconium signal starts to decrease at erosion depths lower than those observed for the system of Fig. 4(b). The longer heat treatment employed enables to shrink the sol–gel structure reducing the coating thickness to about 60 nm. The thickness was therefore reduced more than 60% indicating that a significant amount of organic fraction is still contained into the coating subjected to the shorter thermal treatment. Table 2 shows the film thickness of sol–gel systems produced by dipping with two different withdrawal rate: 5 cm min\(^{-1}\) and 22 cm min\(^{-1}\) (sample A, sample B, sample C). In Table 2, the thickness of the sol–gel system containing two doped cerium layer treated at 250 °C for a longer time (sample D), with a withdrawal rate of 22 cm min\(^{-1}\), is also reported. In Table 2, it is possible to observe that the film thickness increases as the number of dipped layers increases. A higher sol viscosity (i.e. sol doped with cerium) strongly affects the thickness of sol–gel multi-layer systems. By considering a withdrawal rate of 5 cm min\(^{-1}\), sample B, which consists of two layers containing cerium and the undoped top layer, is two times thicker than the undoped system (sample A). Moreover, it is possible to observe in Table 2 that there is a strong influence of the withdrawal rate on the sol–gel thickness. Sample A produced with a withdrawal rate of 22 cm min\(^{-1}\) is two times thicker than the same sample system produced with a withdrawal rate of 5 cm min\(^{-1}\). This is due to the inertia related to the withdrawal of the aluminum sheet. The faster the withdrawal rate is, the higher the sol–gel thickness is. For withdrawal rates commonly used for the sol–gel deposition by dipping, shear stresses are directly dependent on the derivative of the withdrawal rate. For this reason, sols can be considered Newtonian fluids. In these conditions, the sol–gel thickness deposited by dip-coating technique can be approximately calculated by the Landau–Levich Equation, which also considers the sol viscosity, the force of gravity, and the withdrawal angle as important parameters. However, the withdrawal rate is one of the most influential parameters of the sol–gel process concerning the maximum thickness obtainable. The maximum thickness which is possible to deposit by means of sol–gel processes is basically limited by the defect formation. Cracking phenomena are more probable to occur in thick coatings where the sol–gel system shrinkage, due to the solvent evaporation, is more critical. It was found that zirconia based coatings with a thickness higher than 200 nm are widely defected [25]. It was further found that on sol–gel coatings thicker than 300 nm, delaminating and cracking can occur at the same time [25]. In order to minimize these drawbacks, in this work the deposition of the inhibited system was carried out limiting both the withdrawal rate (22 cm min\(^{-1}\)) and the concentration of the inhibitor ([Zr]/[Ce]=70/30). In this way, sol–gel multi-layer structures with a total thickness lower than 200 nm were produced, as already confirmed by GDOES profiles shown in Fig. 4.

The thickness of sol–gel systems, determined by GDOES analyses, can give only rough information about their corrosion behavior because it does not take into account local defects and/or the physical barrier properties. It is possible that thick sol–gel coatings can be not as protective as thin systems. In order to evaluate how the withdrawal rate and the film thickness affect the sol–gel barrier property, potentiodynamic polarization curves were performed on systems produced with different withdrawal rates. Fig. 5 shows the potentiodynamic polarization curves in the diluted Harrison solution for the undoped zirconia sol–gel system produced with 5 cm min\(^{-1}\) (dashed line) and 22 cm min\(^{-1}\) (dashed-dotted line).

The potentiodynamic polarization curve for bare AA6060 is also reported as reference (solid line). By comparing the electrochemical behavior of sol–gel coatings produced with 5 cm min\(^{-1}\) withdrawal rate to that of the bare AA6060, it is possible to point out that the sol–gel coating is able to reduce the corrosion current density of more than one order of magnitude. For the system produced with 5 cm min\(^{-1}\) withdrawal rate, the anodic current densities are shifted to lower values with respect to the bare AA6060. Moreover, a passive behavior (50 mV wide) is exhibited by the sol–gel system produced by using 5 cm min\(^{-1}\) withdrawal rate. However, the protection provided by this system is not good because the coating thickness is very limited (as seen in Table 2). The electrochemical behavior of undoped sol–gel coatings produced by dipping with 22 cm min\(^{-1}\) withdrawal rate is better than that of the sol–gel coatings produced with a lower withdrawal rate (Fig. 5). The corrosion protection guaranteed by thick sol–gel coatings is due to the higher amount of sol deposited on the metal substrate which subsequently is dried to form the protective coating. By considering the sol–gel coating as the insulating material of parallel plate capacitors, it is possible to estimate the influence of the sol–gel thickness on the barrier properties provided. The lower the sol–gel coating capacitance is, the higher the insulating ability is. Therefore, thicker sol–gel systems are able to provide better insulating properties against the attack of aggressive species.

Fig. 6 shows the potentiodynamic polarization curves in diluted Harrison solution for the sol–gel systems of Table 1 produced with 22 cm min\(^{-1}\) withdrawal rate. The potentiodynamic polarization curve for bare AA6060 is also reported as reference. The barrier property provided by the sol–gel coatings is strongly influenced by the number of layers deposited with the solution containing cerium. Sample A (consisting of three layers without cerium)
evidences a corrosion current density almost 3 orders of magnitude lower than that observed for bare AA6060. It also displays a wide passive region ranging from the corrosion potential to 0 V vs Ag/AgCl. Sample C (an intermediate layer containing cerium) evidences lower barrier properties than those evidenced by sample A. Hence, the corrosion current density is higher than the one for sample A. In addition, the passive current densities displayed by sample C are higher than those shown by sample A. In the case of sample C, the breakdown potential is 100 mV more negative than that observed for sample A. Furthermore, the barrier property evidenced by sample B (2 layers containing cerium and one top layer without cerium) is lower than that exhibited by sample C. The barrier property of the sol–gel systems is therefore strongly influenced by the number of the inhibited layers. For the inhibited systems, the network developed during the heat treatment is most probably influenced by the presence of cerium ions which does not allow the formation of a dense cross-linked structure able to protect the metal substrate. In order to improve the cross-linking, sample D underwent thermal treatment for an extended time (see Table 1). A longer thermal treatment enables to obtain a denser structure because the further elimination of organic compounds allows the formation of a more compact structure. Sample D evidences a better electrochemical behavior than the one observed for the same system treated at 250 °C for a shorter time (sample B). Although sample D consists of 2 layers containing cerium and a top layer without cerium, its barrier properties are better than those evidenced by sample C which contains only one cerium layer. The improvement of the barrier properties related to the densification of the sol–gel coating is therefore due to the formation of a denser sol–gel structure.

Fig. 7 shows the Nyquist plot of the electrochemical impedance measurements carried out in diluted Harrison solution on the undoped sol–gel system (sample A). For each spectrum, the lowest frequency point was acquired at 10 mHz. During the first 7 h of immersion, the evolution described by the spectra evidences that the barrier property tends to be reduced as a function of the immersion time. After 7 h of immersion, the semi-circle size described by the impedance spectrum is quite different if compared to the one related to the spectrum acquired immediately after immersion. For longer immersion time, the electrochemical behavior is further modified. After 23 h of immersion, the barrier property of the undoped coating is strongly reduced. By comparing the Nyquist plot acquired immediately after immersion and the one detected after 47 h, it is possible to observe that the real part of impedance (X-axis) at low frequency is strongly reduced. Since the real part of impedance at low frequency can be considered equal to the resistance correlated to the Faradic processes, its strong reduction suggests that corrosion processes occur at the metal substrate. Therefore, impedance measurements carried out on sol–gel systems without layers containing cerium evidence a gradual deterioration of the coating properties due to the progressive loss of the initial barrier.

Fig. 8 shows the Nyquist plot of the electrochemical impedance measurements carried out in diluted Harrison solution on the sol–gel system composed of two layers with cerium and one top layer without cerium (sample D). For each spectrum, the lowest frequency point was acquired at 10 mHz. In the first hours of immersion, the coating displays a gradual degradation due to water penetration, as seen for sample A. The impedance data acquired immediately after immersion (0 h) exhibits lower barrier properties if compared to the ones evidenced by sample A. Immediately after immersion, sample D is not able to guarantee the same
protection of sample A, as it has already been shown by the polarization curves. After 2 h of immersion, the impedance spectrum for sample D is very similar to that detected after 47 h of immersion on sample A. The following measurements carried out on sample D evidence a different evolution. After 3 h, the impedance modulus tends to increase rather than to decrease. Moreover, after 9 h of immersion, the magnitude of the impedance spectrum is similar to that of the spectrum acquired immediately after immersion (0 h). The corrosion resistance tends to be improved as a function of immersion time. The maximum of the impedance modulus is reached after 47 h of immersion. This behavior can be associated to the interaction between the metal substrate and cerium ions contained in the coating. The improvement of the corrosion behavior of system D can occur probably because cerium ions diffuse toward the metal substrate. The inhibition provided by cerium species can be supported by the comparison between the electrochemical impedance behavior of the inhibited (D) and the non-inhibited (A) samples. No recovery of the electrochemical behavior has been seen for the system without cerium which is in contrast with the trend observed for the inhibited system. Impedance measurements carried out on the other two types of inhibited samples (B and C) did not evidence a clear recovery of the initial electrochemical properties. In these two cases, the inhibition action due to cerium ions is probably limited by the larger open-structure of the sol–gel coatings. Indeed, samples B and C underwent shorter thermal treatment than sample D which has been instead treated for longer time. Hence, in order to achieve an effective inhibition action, the inhibited systems have to be subjected to thermal treatments able to produce a dense sol–gel structure in which cerium ions can be suitably incorporated. Otherwise, an open sol–gel structure is less able to avoid the leaching of cerium ions toward the electrolytic solution subtracting part of the active protection of the embedded inhibitor.

The evaluation of the electrochemical behavior of the inhibited and the non-inhibited systems can be studied thoroughly by fitting EIS data. The sol–gel coatings investigated in this paper were modeled with an equivalent circuit consisting of two RC meshes and well known in literature. In the equivalent circuit employed, the constant phase element (CPE) was used instead of an ideal capacitor to explain the deviations from the ideal behavior. The circuit used is shown in Fig. 9 where \( R_{\text{sol}} \) is the solution resistance, \( R_{\text{coat}} \) is the sol–gel coating resistance, \( R_{\text{d}} \) is the charge transfer resistance, CPEcoat is the sol–gel coating capacitance and CPE\(_{\text{el}}\) is the double layer capacitance. Fig. 10 reports the trends of the sol–gel coating resistance (\( R_{\text{coat}} \)), for the inhibited (sample D – long dashed line) and the non inhibited (sample A – solid line) systems as a function of immersion time. The error bars have also been reported in order to evaluate the accuracy of the fitting procedure. Immediately after immersion, for the inhibited and the non inhibited systems, the \( R_{\text{coat}} \) does not take on the same value. The \( R_{\text{coat}} \) is higher for the non inhibited system because it is probably denser than the inhibited one. After the first hours, for the non-inhibited system, the \( R_{\text{coat}} \) trend exhibits a fast decrease which is probably related to the progressive water diffusion into the coating. The \( R_{\text{coat}} \) trend for the inhibited system shows instead a more uniform behavior. Indeed, the initial value is held constant for the entire test. This value is equal to the one observed for the non-inhibited system after 1 day. From these results, it might be possible to hypothesize that the inhibited sol–gel system is not able to provide an effective physical barrier since immediately after immersion. This was expected because the inhibited sol–gel coatings are not as dense as the non-inhibited ones. Dense sol–gel structures are required to provide good barrier properties but are not required for the development of porous systems where embedded chemical species have to be able to diffuse. This is exactly the case of this work (cerium ions embedded in zirconia sol–gel coatings) because its target was to develop thin ceramic films as a pre-treatment providing self-healing abilities. The cerium inhibition effect (self-healing ability) on the corrosion behavior of AA6060 can be therefore evaluated by considering the charge transfer resistance trends shown in Fig. 11. Immediately after immersion, the non-inhibited system shows a \( R_{\text{ct}} \) which is almost 10 times higher than that exhibited by the inhibited sol–gel coating. Since the corrosion rate of AA6060 aluminum alloy is the same for both, in the case of the doped system, the area exposed to the electrolyte is 10 times larger due to the addition of cerium to the initial sol which does not allow the formation of a dense cross-linked sol–gel structure. The higher porosity of doped systems has been also confirmed by the \( R_{\text{coat}} \) trend (Fig. 10) which shows lower barrier properties for the inhibited coating. For longer immersion time, the trends of the charge transfer resistance (\( R_{\text{ct}} \)) are substantially different. In the case of the non-inhibited system, the \( R_{\text{ct}} \) continuously tends to decrease due to the progressive increase of the substrate areas involved in the corrosion processes. After 2 days of immersion, the \( R_{\text{ct}} \) is very close to that of bare AA6060 aluminum alloy shown in our previous works [7]. The
behavior exhibited by the inhibited system follows a different evolution. Immediately after immersion, the $R_{ct}$ values are very similar to the ones estimated for the non-inhibited system after 2 days. In the first hours of immersion, for the inhibited system, the $R_{ct}$ starts to decrease to a minimum corresponding to the impedance spectrum acquired after 2 h (Fig. 8). From this point, $R_{ct}$ starts to increase exceeding the $R_{ct}$ value of the non-inhibited system, after 20 h of immersion. In correspondence with this point, the corrosion rates for the inhibited and the non-inhibited systems can be considered identical. For longer immersion time, the $R_{ct}$ of the inhibited system continues to increase reaching $6 \times 10^6 \ \Omega \cdot \text{cm}^2$ after 48 h. This value is 3 times higher than the corresponding one estimated immediately after immersion. The improvement in the corrosion behavior of AA6060 aluminum alloy depicted by the $R_{ct}$ trend can be likely related to the diffusion of cerium-free ions toward the substrate. Once cerium ions reach the metal, the corrosion inhibition starts following the mechanisms proposed in literature [8–10]. As can be seen in Fig. 11, the full additional protection related to cerium precipitation needs several hours to occur due to the fact that the cerium diffusion is slow. The diffusion rate of cerium ions depends on the compactness of the sol–gel structure. Dense ZrO$_2$ sol–gel coatings developed in this work (not shown in this paper) did not evidence the increase in $R_{ct}$ probably because a compact sol–gel structure hindered the cerium diffusion. However, dense sol–gel coatings are able to provide a better physical barrier against the diffusion of water and aggressive ions. The additional protection provided by cerium precipitation is however limited by the amount of inhibitors embedded in the coating. Since cerium leaching occurs in the direction of the solution test, a not negligible amount of cerium ions cannot diffuse toward the metal substrate for the improvement of the AA6060 corrosion behavior.

In order to prove cerium migration through the ZrO$_2$ coatings, the samples A, B, and C were immersed in diluted Harrisson solution in order to analyze the electrolyte ingress in the sol–gel coating. Each sample was analyzed by GDOES after an immersion time of 0.1, 2, 3, 4, 5, 6, 7, 8, 24, 30 and 48 h. The coating thickness and the Ce peak position were measured by means of Quantum XP software in order to evaluate the electrolyte ingress and Ce migration. The coating thickness was calculated as the average value between three points: the intersection between the Zr signal and the Al one, the sputtering depth corresponding to an Al content in the coating equal to 2 wt% and the sputtering depth at which the Zr content is 2 wt% in the substrate. This method, already employed to estimate the thickness related to the profiles of Fig. 4, was previously used in order to reduce the roughness effect on GDOES analyses [26]. Fig. 12 shows the signals of Al, Zr and S acquired by GDOES as a function of immersion time for sample B. It is possible to observe that there is an evolution of these signals as a function of immersion time. In the case of the Zr and Al signals, this trend might suggest that there should be a coating swelling due to electrolyte absorption. As a consequence, the coating thickness increases with immersion time. This is confirmed by the trend of the S signal, which is mainly due to the ammonium sulphate in the electrolyte. Therefore, the S signal can be considered as a marker to evaluate electrolyte penetration in the sol–gel coating. Moreover, in Fig. 12 it can be observed that the S signal is higher on the coating surface than in the sol–gel layer itself. This is an indication that a smut nanometric layer containing sulphates is formed on the coating surface.

Fig. 13 shows the coating thickness as a function of immersion time for samples A, B and C. The coating thickness has been evaluated not considering the contribution of the smut nanometric layer containing sulphates on the coating top surface. The sample A exhibits a progressive increase of the coating thickness with immersion time. The thickness of the sol–gel film is about 160 nm after 48 h in the electrolyte. As discussed above, this is most probably due to coating swelling. The coating thickness after 48 h immersion in the electrolyte is 240 nm for sample C and 255 nm for sample B. This indicates that the increase of coating thickness is more marked for samples containing Ce inhibitor. This behavior is probably due to the different structure of the layers containing Ce than the ZrO$_2$ layer.

Fig. 14(a) exhibits the position of the Ce peak in the coating as a function of immersion time for sample B. An example of cerium distribution in the coating as a function of immersion time is given in Fig. 14(b). It can be seen that the depth of the Ce peak progressively increases with the immersion time. This behavior might be attributed to Ce migration in the coating. However, it should be taken into account that the coating is also subjected to swelling due to electrolyte absorption.

Fig. 15 shows the difference between the sputtering depth corresponding to the Ce peak and the thickness of the conversion layer as a function of immersion time for sample B. Sample B exhibits a marked decrease of the difference between the sputtering depth corresponding to the Ce peak and the coating thickness. The Ce peak is at about 80 nm from the sample surface before immersion while it is at 25 nm from the sample surface after 48 h immersion. This is a clear indication that Ce migrates through the sol–gel film and this phenomenon is more relevant than coating swelling. Further investigations are still now in progress in order to better clarify the migration phenomenon involving cerium ions embedded in zirconia-based sol–gel coatings.

Please cite this article in press as: L. Paussa et al., ZrO$_2$ sol–gel pre-treatments doped with cerium nitrate for the corrosion protection of AA6060, Prog. Org. Coat. (2012), doi:10.1016/j.porgcoat.2011.08.017
4. Conclusions

Sol–gel coatings produced by dip-coating have been considered for the corrosion protection of aluminum alloy AA6060. ZrO₂ based sol–gel coatings were deposited from a solution containing a metal-organic precursor of zirconium. In order to produce a protective system with self-healing ability, cerium nitrate was added to the sol. Sol–gel ZrO₂ based coatings deposited on AA6060 are uniform and defect-free. The deposited film appears colorless and covers the entire metal surface. Critical areas for the sol–gel deposition, like cavities produced by the pickling procedure, are also coated. The coating consisting of layers containing cerium shows a very similar surface morphology to that of the non-inhibited system. Since the addition of cerium nitrate to the starting solution increases the sol viscosity, the inhibited layers are thicker than the non-inhibited ones. The UV–vis analysis confirmed that cerium is present in ionic state with a redox ratio Ce⁴⁺/Ce³⁺ ≈ 10/90. The GDOES results provide information on chemical composition of the coating for all samples considered. In particular it is observed that all coatings are subjected to swelling during immersion and that this phenomenon is more intense in Ce containing coatings. It is also proved that Ce tends to move toward the aluminum surface. The undoped systems display a strong barrier effect, as indicated by the passive behavior of AA6060 aluminum alloy coated with three layers of ZrO₂. The barrier property associated to the sol–gel systems is strongly influenced by the inhibited layers. Inhibited systems are generally not able to guarantee the same barrier protection evidenced by sol–gel systems without cerium. Nevertheless, electrochemical impedance measurements indicate that the gradual decrease of the corrosion behavior of ZrO₂ coated aluminum alloys can be recovered only if cerium nitrate is added to the starting sol. An improvement of the corrosion behavior of coated AA6060 is due to the beneficial action of cerium ions moving toward the metal substrate as proved by GDOES measurements.

Acknowledgement

The authors are grateful to Patrick Chapon (R&D Jobin Yvonne Division) for the valuable and useful contributions on the discussion of GDOES analyses.

References