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Oxide nanoparticle reservoirs for storage and prolonged release of the corrosion inhibitors

Mikhail L. Zheludkevich [a,*], Ricardo Serra [a], M. Fatima Montemor [b], Mário G.S. Ferreira [a,b]

[a] *University of Aveiro, Department of Ceramics and Glass Engineering, 3810-193 Aveiro, Portugal*
[b] *Instituto Superior Técnico, ICEMS, Department of Chemical Engineering, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

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Abstract

The hybrid sol–gel-based films are promising pre-treatments for metallic substrates. Unfortunately, those films cannot obtain the effective self-healing effect when coating is partially destroyed. Present work demonstrates the possibility to use the zirconia nanoparticles as a reservoir for the storage and prolonged release of the corrosion inhibitor. The nanoparticles not only reinforce the hybrid matrix but also absorb inhibitors ions releasing them during contact with moisture offering the effective self-healing properties. The prolonged release of inhibitor provides long term corrosion protection of the aluminium alloy 2024 compared to the case when the inhibitor is added to the sol–gel matrix.

Keywords: Nanoreservoir; Sol–gel; Corrosion; Inhibitor; Coating

1. Introduction

Metallic substrates are pre-treated before application of an organic paint in order to improve adhesion between the polymer and the metal and to provide additional long term corrosion protection. So far, the mostly used pre-treatments contain chromates as active agents [1]. However, chromate compounds are strongly carcinogenic due to their high potential to oxidise the organic molecules. In order to avoid this drawback the new environmental-friendly pre-treatments have been actively developed in the recent decade [1–3]. Most of them provide an additional barrier to the corrosive species impairing the corrosion processes. An effective pre-treatment could be the hybrid silica-based sol–gel coatings, which combine flexibility and good compatibility with the paint systems due to the organic component and good mechanical properties and adhesion to the metallic substrate conferred by the inorganic compound [4]. In spite of good barrier properties several cracks and pores can appear in the hybrid films originating sites for starting the corrosion processes. Introduction of oxide nanoparticles into the hybrid matrix leads to formation of crack-free films and can enhance mechanical durability of the films improving corrosion protection [5,6]. Even so nanocomposite hybrid films cannot provide an effective long term corrosion protection due to the absence of self-healing effect as in the case of chromates. One way to improve the self-repair properties of the hybrid pre-treatments is the addition of a corrosion inhibitor, which can suppress corrosion initiated at the coating defects [7]. However, the inhibitors can also have a negative effect in the sol–gel film properties, decreasing the stability and consequently the barrier properties of the film [8]. Additionally, the release of inhibitors from coatings is relatively fast and not

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[*] Corresponding author. Tel./fax: +351 234 378146.
E-mail address: mzheludkevich@cv.ua.pt (M.L. Zheludkevich).

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controllable. Introduction of β-cyclodextrin, for example, provides a prolonged release of the mercaptobenzimidazole inhibitor due to complex formation, improving the corrosion protection conferred by the hybrid sol–gel system [9].

Several attempts were recently taken to obtain "intelligent" active corrosion protection systems introducing an ion-exchange pigment to the coating system. Dispersions of silica and bentonite-based Ce^{3+} cation-exchangers in the polymer coatings enable direct release of the inhibitor into the electrolyte in blisters and significantly retard coating delamination [10]. The active corrosion protection effect was also revealed in the case of the ion-exchanged hydrotalcite pigments doped with Ce^{4+} or organic inhibitors [11,12].

The idea of present work is to use oxide nanoparticles as a reinforcement of the hybrid sol–gel matrix and also as a reservoir for corrosion inhibitors. The nanoparticles can absorb the inhibitor ions during the preparation procedure and then slowly release them in contact with moisture. This way can provide an additional reinforcement of the hybrid matrix by the oxide nanoparticles, prolonged release of the inhibitors and also decrease the negative effect of the inhibitor ions on the hybrid film stability. In present work cerium nitrate was used as inhibitor, since it reveals an effective inhibiting effect on the corrosion processes on aluminium alloys, suppressing the cathodic reactions [13–15].

2. Experimental

The nanostructured hybrid films were prepared using the controllable sol–gel route. The hybrid films were prepared by mixing two different sols. One sol contains zirconia nanoparticles and was synthesized hydrolysing the TPOZ (zirconium *n*-propoxide) precursor. The sol was prepared by the addition of ethylacetoacetate to the TPOZ, 70% in *n*-propanol, in a 1:1 volume ratio. This solution was stirred with synchronous ultrasonic agitation at room temperature during 80 min. Acidified water (pH ~ 1) or solution of $Ce(NO_3)_3 \cdot 6H_2O$ was added to the sol after 20 min of beginning the solution stirring. The hydrolysis and condensation reactions of TPOZ occur according to the following Eqs. (1)–(3).

Hydrolysis:

$$Zr(OPr)_4 + nH_2O \rightarrow Zr(OPr)_{4-n}(OH)_n + nPrOH \quad (1)$$

$$Zr(OPr)_{4-n}(OH)_n + (n-4)H_2O \rightarrow Zr(OH)_4 + (n-4)PrOH \quad (2)$$

Condensation:

$$mZr(OH)_4 \rightarrow HO-(Zr(OH)_2\text{–}O\text{–}Zr(OH)_2\text{–}O\text{–})_{m/2}H + (m-1)H_2O \quad (3)$$

The second organosiloxane sol was prepared by combining 3-glycidoxypropyltrimethoxysilane (GPTMS), tetraethylortosilicate (TEOS) and 2-propanol in a 1:1:2 volume ratio and then stirred for 30 min at room temperature. The cerium nitrate was added to TPOZ (Case A) or TEOS/GPTMS solution (Case B) in order to dope the zirconia nanoparticles or the hybrid matrix, respectively. The concentration of cerium in final sol–gel solution was 0.5 wt%. The aluminium alloy 2024-T3 (detailed composition is given in Table 1) was dipped in the final solution made of two sols and then cured in the oven. Coatings without addition of the cerium salt (Case C) and films containing only the second sol (i.e., without zirconia nanoparticles – Case D), were also prepared as references.

Electrochemical impedance spectroscopy (EIS) was used to study the corrosion protection performance of different hybrid sol–gel coatings on the AA2024-T3 during immersion in 0.005 M NaCl solution. A three-electrode arrangement was used, consisting of a saturated calomel reference electrode, a platinum foil as a counter electrode and the exposed sample ($3.4\ cm^2$) as a working electrode. The EIS measurements were performed using a Gamry FAS2 Femtostat with a PCI4 Controller. The impedance measurements were carried out at open circuit potential with applied 10 mV sinusoidal perturbation in a 100 kHz down to 10 mHz frequency range with 10 steps per decade at room temperature in a Faraday cage. At least two samples prepared at the same conditions were tested in order to ensure reproducibility of the results. The impedance plots were fitted using different equivalent circuits in order to simulate the different stages of the pre-treated system during immersion. The structure of the sol–gel coatings before and after immersion was studied by SEM (Hitachi S-4100 system with electron beam energy of 25 keV) and EDS (energy dispersive spectroscopy). The morphology of the sol–gel films was assessed by atomic force microscopy (AFM) using a Nanoscope Digital Instruments fitted with a NanoScope III controller.

Table 1
Composition of aluminium alloy 2024-T3

Element	Cu	Cr	Fe	Mg	Mn	Si	Ti	Zn	Other	Al
Concentration (wt%)	3.8–4.9	0.1	0.5	1.2–1.8	0.3–0.9	0.5	0.15	0.25	0.15	Balance

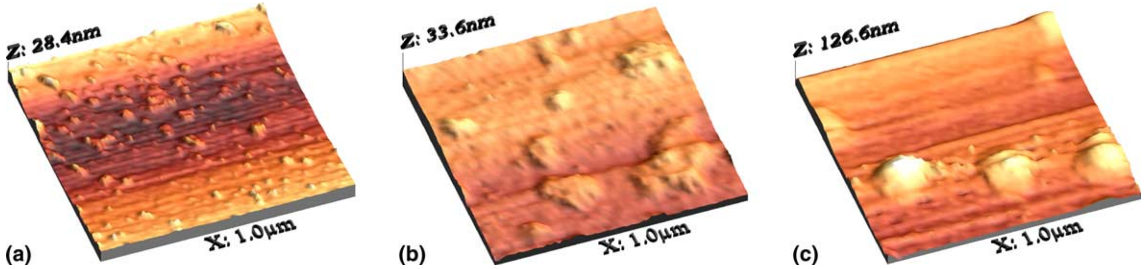

Fig. 1. Atomic force microscopy (AFM) scans of topography of the hybrid sol–gel films with zirconia nanoparticless: (a) with Ce-doped ZrO_2 nanoparticles; (b) with Ce-doped hybrid matrix; (c) undoped.

3. Results and discussion

3.1. Structure of films

The presence of nanoparticles and their distribution in the hybrid film are clearly shown in Fig. 1, for the different cases. The first AFM scan (Fig. 1(a)) presents the topography of the hybrid film with Ce-doped zirconia nanoparticles (Case A). The nanoparticles are about 50–100 nm in diameter and relatively uniformly distributed in the matrix when compared with Cases B and C. In the case of the coatings prepared without cerium addition (Case C, Fig. 1(c)) or those with the hybrid matrix doped (Case B, Fig. 1(b)) the agglomeration of the oxide nanoparticles occurs, leading to formation of large aggregates. These facts can be explained in terms of stabilisation of the zirconia particles by additional charge of the cerium ions, during the synthesis process. A hybrid sol–gel film containing the zirconia particles, acting as nanoreservoirs of corrosion inhibitor, is formed in this case. The nanoparticles can be chemically bounded to the matrix forming Zr–O–Si bonds after mixing the two sols.

3.2. Corrosion protection performance

Some details on the influence of the cerium inhibitor on the corrosion protection mechanism can be clarified analysing the hybrid coating surface after immersion in NaCl solution. Fig. 2 presents the typical defects in the hybrid films after two weeks of immersion. The undoped sol–gel film contains many cracks (about 400 per

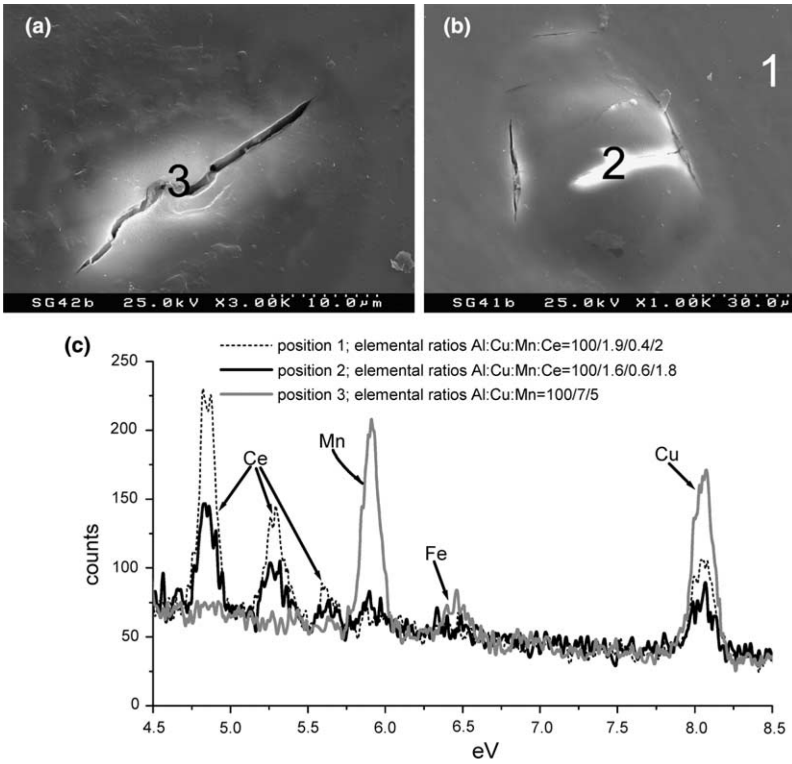

Fig. 2. SEM micrographs of the typical defects in the undoped hybrid coating (a) and in the film with Ce-doped zirconia nanoparticles (b) after two weeks of immersion in NaCl solution, (c) fragment of the EDS spectra in different zones of the hybrid films.

1 mm^2) of different lengths. All these cracks (Fig. 2(a)) appear in the places of the Al (Cu, Fe, Mn) intermetallic particles as shown in the EDS spectra (Fig. 2(c)). These places can act as effective cathodes initiating pitting corrosion [16,17]. In the case of the Ce-doped hybrid films no cracks are present in the coating. Only several small blister-like defects (Fig. 2(b)) were revealed on the surface area about 1 cm^2. These blisters are not formed in the places of the intermetallics showing that cerium ions can effectively block the cathodic Al (Cu, Fe, Mn) intermetallic particles and prevent film damage in these places.

The EIS was used in order to estimate corrosion protection of the different coatings. The low frequency impedance is dependent on the coating and on the immersion time. During the initial stage of immersion all the coatings showed identical impedance values. However, the impedance decreases with time. The smallest changes were revealed for the coating with Ce-doped nanoparticles. Fig. 3(a) presents EIS spectra of these coatings after 250 h of continuous immersion in 0.005 M NaCl solution. The impedance of the aluminium alloy coated with hybrid film with inhibitor-containing zirconia nanoparticles shows still high impedance value (above 10^6 $\Omega\,cm^2$) at low frequencies. Such high impedance values show a good corrosion protection when compared with similar hybrid sol–gel pretreatments [18]. Two maxima (two time constants) one at 5×10^4 Hz and another at 1 Hz are present in the phase angle plot, which can be ascribed to the sol–gel film and an intermediate mixed oxide layer formed on the alloy/film interface by –Si–O–Al– bonds, respectively [5]. Contrasting to this behaviour the coating without cerium shows impedance values at a frequency of 10^{-2} Hz about one order of magnitude lower. The impedance of the film with the Ce-doped matrix shows, at the same frequency, intermediate values of impedance. Additionally, the last two films depict a third time constant due to start of corrosion. These results show that the hybrid sol–gel films prepared with Ce-doped zirconia nanoparticles confer higher corrosion protection than the undoped ones or the films with doped hybrid matrix.

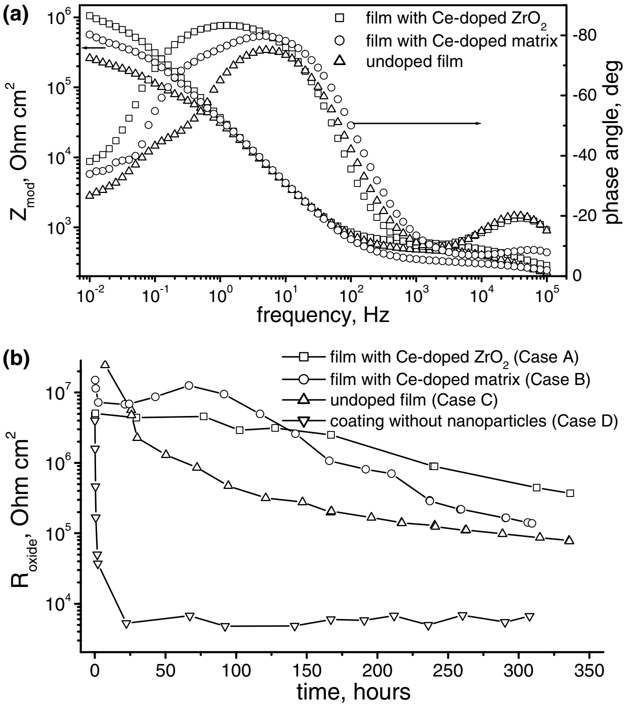

Fig. 3. (a) Electrochemical impedance spectra of the AA2024 covered with different hybrid films after 250 h of immersion in NaCl solution. (b) Evolution of the pore resistance of the intermediate oxide layer during immersion.

The impedance plots were fitted using different equivalent circuits described elsewhere [5]. The evolution of the resistance of the intermediate oxide layer (taken from fitting results) for the different coatings is presented in Fig. 3(b). In the case of the hybrid film prepared without addition of cerium and zirconium compounds (Case D) the resistance decreases three orders of magnitude during the first 25 h of the immersion test showing poor corrosion protection. The resistance of the hybrid film with zirconia nanoparticles without inhibitor (Case C) shows much slower decrease and reaches values around 10^5 $\Omega\,cm^2$ after two weeks of immersion. This difference in corrosion protection shows significant enhancement of the barrier properties of the sol–gel film due to introduction of the zirconia nanoparticles. The resistance of intermediate layer in the coating system with doped hybrid matrix (Case B) shows very stable values during 100 h and then a relatively fast decrease of the resistance occurs. The stable behaviour during the initial stage of immersion can be caused by action of cerium ions that are fast released from the hybrid matrix inhibiting the corrosion processes. The fast decrease of resistance occurs when cerium is completely released from the sol–gel film ceasing the inhibiting action. For the coating with cerium-doped zirconia nanoparticles (Case A) the pore resistance is evenly decreasing during all the period of immersion. After 300 h of immersion this coating shows resistances about 5 times higher than the other nanocomposite films. This behaviour can be explained in terms of the slower release of the cerium ions from the zirconia nanoparticles. This prolonged release of inhibitor from oxide nanoreservoirs confers longer protection to the metallic substrate.

EDS analysis was used to provide semiquantitative estimation of the variation of the relative concentration of cerium in the sol–gel films during the immersion tests and to confirm the prolonged release of inhibitor. It was observed that the difference in relative concentration of cerium before and after two weeks of immersion in the NaCl solution is about 2.3 times for the hybrid film with doped zirconia nanoparticles. In the case of the sol–gel coating with cerium-doped hybrid matrix the cerium concentration decreases for more than 3 times after the same period of time. This difference between the two coatings can evidence once again that zirconia nanoparticles act as nanostructured cerium reservoirs and can provide prolonged release of the inhibitor ions. Additionally, doped sol–gel films contain the nitrate anions which can be released inhibiting the corrosion. However, the inhibiting effect of nitrate is lower than that of the cerium ions [19].

The mechanism of cerium ions storage in the hybrid matrix and in the oxide nanoparticles is still an open question. In the case of the inhibitor storage in the sol–gel matrix the cerium cations are most probably physically entrapped or they have weak electrostatic bonds with silica network since the release of inhibitor is fast. In the case of nanoreservoirs the cerium ions have stronger bonds with oxide providing slower release. The preliminary XPS results show remarkable shift of the $Zr3d_{5/2}$ peak when the cerium ions are incorporated into ZrO_2 nanoparticles in comparison with the case of the doped sol–gel matrix. The Ce^{3+} ions can be chemisorbed on oxide surface and/or incorporated into zirconia structure. However, the additional experiments are necessary to provide reliable information on mechanism of storage and release of the cerium inhibitor in the nanostructured sol–gel coatings. This will be an objective of future work.

4. Conclusions

Herein, we have demonstrated the possibility to use the oxide nanoparticles as a reservoir for the storage and prolonged release of the corrosion inhibitor. The zirconia nanoparticles not only reinforce the hybrid matrix but also absorb cerium ions releasing them during contact with moisture. This prolonged release provides long term corrosion protection of the metallic substrate compared to the case when the inhibitor is added to the sol–gel matrix. Detailed investigation on the inhibitor release kinetics from the oxide nanoreservoirs and also details on the mechanism of corrosion protection are under further investigations.

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