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Corrosion protection of carbon steel by silica-based hybrid coatings containing cerium salts: Effect of silica nanoparticle content



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ABSTRACT

One strategy for minimising corrosive attack on carbon steel involves the application of hybrid coatings rich in rare earths, on the basis of their low toxicity and environmental sustainability. Tetraethoxysilane (TEOS) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) were each used here as precursors, together with various quantities of colloidal silica suspension, to improve barrier properties of the coatings. Ce(NO₃)₃·6H₂O was added as a source of Ce(III) for further inhibition of corrosion. The corrosion resistance of each kind of sample was evaluated using potentiodynamic polarisation measurements and electrochemical impedance spectroscopy (EIS) in 0.35 wt.% NaCl solution. The effect of silica nanoparticle loading on corrosion. Additional testing was performed under harsh conditions of salt spray chamber. The microstructure and composition of sol–gel coatings were characterised by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS), focused-ion beam SEM/EDS analysis, X-ray photoelectron spectroscopy and confocal microscopy.

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1. Introduction

Mild steel is one of the most widely used materials is industry, but is readily corroded in many environments. The best known industrial system used to improve corrosion resistance of metals has been established on chromate based coatings. However, hexavalent chromium is carcinogenic, so much research is directed to replacing it by green alternatives.

Organic–inorganic sol–gel coating offers a promising alternative to chromate treatment. The process can be tailored to incorporate particles, salts and/or different types of precursor (leading to different amounts of organic content in the layer) to achieve the goal of enhanced resistance to corrosion. This technology can be applied on a range of substrates at lower temperatures (120–350 °C) than those required in the traditional ceramic processing methods. Silane based sol–gel coatings have been applied on a variety of metals, achieving good adhesion between the surface and the coating due to the formation of oxygen bridges between the Si and the metal, forming metallo-siloxane bonds [1–8]. In the case of mild steel, adhesion of the coating can be enhanced by treatment with phosphoric acid prior to sol–gel deposition [9]. Silica based sol–gel coatings are produced as thin films that range from

less than one to a few micrometres. The network that is formed in the coating is very stable, due to the covalent bonds in its structure. However, small defects or voids always remain after evaporation of volatiles during sol deposition. These can be partly overcome by using a more organic precursor and/or the application of multilayers [10–13]. Additionally the barrier effect can be enhanced by the addition of silica nanoparticles or clusters of metal oxides [14–17] that can increase the coating thickness and act as a reinforcement in the layer.

A rare earth incorporated in the sol could act as a corrosion inhibitor that could act in the event of a defect in the coating. Much research has been devoted to studying the addition of cerium salts (acetates, nitrates, chlorides) and cerium oxides to the sol to improve corrosion resistance, mainly of aluminium [18–27]. In this respect, Hinton [28,29] reported a series of rare earth compounds such as cerium nitrate, together with sodium vanadate, sodium molybdate and lanthanum 4-hydroxycinnamate, that improved the corrosion resistance of mild steel and aluminum alloys. It has been proposed that cerium ions in aqueous solution react and form an insoluble layer of cerium oxide on the surface, reducing the cathodic reaction and thus the overall corrosion rate [30–32].

With the aim to enhance the corrosion resistance of carbon steel in chloride solution we report a study of hybrid sol–gel coatings, using tetraethoxysilane (TEOS) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) as precursors, and containing various amounts of silica nanoparticles to improve the barrier effect of the coatings. The effect of adding Ce(NO₃)₃·6H₂O to the sol, as a source of Ce(III) for inhibitory purposes, has also been evaluated, together with the synergistic effect

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Fig. 1. The preparation of single- and two-layer sol-gel coatings.

of added cerium and silica nanoparticles. The coating is intended to supply chromate conversion coating treatments and should provide early protection being a primer for further coating processes

2. Experimental

Sheets of AISI 1010 mild steel (C 0.08–0.13%; Mn 0.3–0.6%; P 0.04% Max; S 0.05% Max; Fe balance) from Timar SRL, Argentina, cut in samples of 85 mm \times 50 mm \times 2 mm were abraded with emery paper up to grade 400, with water as lubricant, cleaned with detergent, rinsed with distilled water and ethanol, and dried at room temperature.

All samples were immersed in a solution of phosphoric acid, 2% v/v, for 10 min at room temperature (20 ± 1 °C), in order to enhance coating adhesion [9]. Samples were then placed in ethanol for 30 min to hydroxylate the surface and improve adhesion of the coating.

Hybrid films were synthesised under acid conditions by the solgel route from tetraethoxysilane (TEOS, Fulka, Germany) and 3glycidoxypropyl-trimethoxysilane (GPTMS, Dow Corning, USA). Colloidal silica suspension (Ludox AS-40, particle size 15 nm, Sigma Aldrich, USA) was present to improve mechanical and barrier properties, together with Ce(NO₃)₃·6H₂O (Sigma Aldrich) as a source of Ce(III). Sols were prepared in molar ratios of TEOS/GPTMS/SiO₂ = 42/18/40 (denoted as TGS40 sol), TEOS/GPTMS/SiO₂ = 56/24/20 (denoted as TGS20 sol) and TEOS/GPTMS/Ce = 66.5/28.5/5 (denoted as TGC sol). HNO₃ solution (0.1 mol dm⁻³) was used as both a source of water and a catalyst in both sols. The TGS sols were prepared by high speed stirring of a mixture of TEOS, GPTMS and silica nanoparticles (the latter either 20 or 40% in

Table 1

Contact angles for bare substrate (P) and coated with TGC, TGS20, TGS40, TGS20C, and TGS40C coatings.

Sample	Contact angle
Р	76.9 ± 2.6
TGC	75.3 ± 7.2
TGS40	77.8 ± 3.8
TGS20	68.4 ± 1.8
TGS40C	71.9 ± 1.9
TGS20C	71.3 ± 1.6

moles), to homogenise the immiscible phases resulting in a thin emulsion. 1 mL concentrated nitric acid was then added to catalyse the reactions. The system was stirred magnetically for 2 h at room temperature. The sols obtained were transparent and colorless. Cerium nitrate hexahydrate was dissolved in ethanol, then mixed with TEOS and GPTMS, resulting their molar concentration 5% in moles in the sol.

Substrates were prepared by phosphoric acid treatment, followed by heating at 120 °C for 30 min, and denoted as P (Fig. 1). Sol–gel coatings were then applied by two routes: single and two-layer. Single layers consisting of TG sol mixed with SiO₂ nanoparticles (TGS20 and TGS40) were applied by dipping at a withdrawal speed of 3 cm/min, and those mixed with cerium (TGC) at a withdrawal speed of 35 cm/min. After deposition, coatings were subjected to thermal treatment at 120 °C for 2 h. Double layers were produced by applying a second layer of TGC on top of the TGS20 and TGS40 first layers. Each deposition step was followed by heating in an atmosphere of air at 120 °C for 2 h.

2.1. Coating characterisation

The morphology and chemical composition of substrates and sol–gel coatings were analysed using an optical microscope (Olympus PMG3, Japan), scanning electron microscope (SEM) Jeol JSM-5800 and an energy dispersive X-ray spectrometer (EDS) (Oxford Instruments Link ISIS 300). Surface roughness and 3-D topography were analysed using a confocal microscope (Axio, CSM 700, Zeiss, Göttingen, Germany), with an objective of $10 \times$ magnification and Axio CSM 700 3-D software. The vertical

Table 2

Atomic compositions derived from the XPS survey spectra for prepared bare substrate (P) and coated with TGC, TGS20C and TGS40C coatings. Solvent contaminants are denoted italic.

Sample	Compos	ition/at.%					
	С	0	Fe	Ce	Si	Ca	Ν
Р	57.8	34.9	5.4	-	-	-	1.9
TGC	49.7	36.5	0.1	0.1	11.2	-	2.4
TGS20C	54.1	35.0	0.1	0.1	9.6	0.3	0.8
TGS40C	51.9	35.0	0.2	0.1	11.1	0.3	1.4



Fig. 2. XPS high resolution C 1s, O 1s, Si 2p, Fe 2p and Ce 3d spectra for carbon steel, bare (1) and modified by TGC (2), TGS20C3 (3) and TGS40C (4) coatings. Vertical dashed lines denote the positions of reference compounds as described in the text. In the Ce 3d spectra, dashed lines denote the Ce(III) species, and solid lines the Ce(IV) species.



Fig. 3. Polarisation curves for carbon steel coated with layers of TGS20 (○), TGS40 (▼), TGS(40, (■), TGS40C (●) and for the bare material (▲), (a) immediately following immersion and (b) 24 h after immersion. The arrow indicates the direction of polarisation.



Fig. 4. EIS curves for coated steel coated with TGS20C (\blacksquare), TGS40C (\blacklozenge) and the bare material (\blacktriangle), all immediately following immersion (t_0). The solid lines show fits according to the models presented in Fig 6.



Fig. 5. EIS curves for coated steel coated with TGS20C (**•**), TGS40C (**•**) and the bare material (**▲**) following 24 h immersion in NaCl solution. The solid lines show the fits according to the models presented in Fig. 6.

resolution was 0.2 μ m, and the scanning range was 10 μ m. Coating thickness on glass samples was measured by means of a profilometer (Talystep, Taylor-Hobson, UK) on a scratch made immediately after deposition. Coating thickness was stated as the average of at least five independent measurements on each sample.

Contact angle measurements were carried out with a Ramé Hart model 500 advanced contact angle goniometer with DropImage Advanced Software. A 5 μ l drop of bi-distilled water was applied to substrates previously cleaned with absolute ethanol. All measurements were made 60 s after depositing the drop. Four measurements were performed on each sample and the mean values are given.

X-ray photoelectron spectroscopy (XPS) was performed with a TFA Physical Electronics Inc. spectrometer using non- and monochromatised Al K α radiation (1486.6 eV) and a hemispherical analyser. The monochromatised radiation used for high-resolution spectra yields a resolution of 0.6 eV, as measured on an Ag $3d_{5/2}$ peak. These spectra were used to differentiate the chemical environment of various species, whereas spectra obtained using the non-monochromatised variant were used for quantifying the chemical composition. A take-off angle (detection angle) of 45° with respect to the surface plane was used. The energy resolution was 0.5 eV. Survey scan spectra were recorded at a pass energy of 187.85 eV, and individual high-resolution spectra at a pass energy of 23.5 eV with an energy step of 0.1 eV. During the analysis a small shift was observed which was compensated by neutraliser. The values of binding energies were then aligned to carbon peak C 1s at 285.0 eV. The XPS measurements were repeated at several spots on the sample surface; the results were found to be similar. Representative measurements are reported.

Focused ion beam (FIB) cross sections were made under a Neon Zeiss 40 microscope equipped with an FE-SEM column (Germany), by milling with a Ga beam at 30 kV with decreasing current intensities up to a final polishing at 150 pA.

2.2. Electrochemical evaluation and salt spray testing

Corrosion resistance was evaluated by means of a potentiodynamic polarisation test and electrochemical impedance spectroscopy (EIS) measurements in 0.35 wt.% NaCl solution prepared from p.a. grade chemicals (Sigma-Aldrich) and bidistilled water (Millipore, 18.2 M Ω cm). All measurements were carried out at room temperature $(20 \pm 1 \text{°C})$ using a typical three-electrode configuration, with a saturated calomel electrode (SCE, Radiometer Analytical, France) as the reference electrode, a platinum wire of convenient area as counter electrode and the material to be tested as the working electrode. The latter was placed at the bottom of the cell, exposing an area of 3.54 cm². Electrochemical impedance spectroscopy (EIS) was performed at sweeping frequencies from 50,000 to 0.01 Hz and modulating 10 mV (rms) around the corrosion potential (E_{corr}). EIS fitting was performed using Zview software [33]. Potentiodynamic polarisation curves were scanned from -0.7 V to 1 V at a rate of 2 mV/s. All potentials in this work are referred to the saturated calomel electrode (0.241 vs Standard hydrogen electrode, SHE).

Corrosion resistance was measured in a salt spray chamber, capacity 0.17 m³ (ASCOTT, Staffs, Great Britain). Testing was carried out according to International Standard Organization (ISO) standard 9227-2006 "Corrosion tests in artificial atmosphere". The concentration of sodium chloride solution was 50 g/L. The pH of the NaCl solution was set



Fig. 6. Equivalent circuits used for modelling the experimental data corresponding to Figs. 4 and 5.

tesults obtain	ained from fitting the ((t ₀) and 24 h after imr	experimental EIS data pre mersion (24 h) in 0.35% v	esented in Fig. wt. NaCl.	s. 4 and 5 fitted witt	the proposed ϵ	quivalent circuits shown i	in Fig. 6. Valu	es of C _{eff} calculated	l according to Eq. (5	() for TGS40C, TG	S20C and the	e bare metal in	ımediately after
	R_{e} (Ωcm^{2})	$Q_{coat}(s^{\alpha}\Omega^{-1}cm^{-2})$	$\stackrel{\rm C_{eff\ coat}}{(\rm F\ cm^{-2})}$	$\alpha_{\rm coat}$	$_{coat}$ (Ωcm^2)	$Q_{ox} \left(s^{\alpha} \Omega^{-1} cm^{-2} \right)$	$\stackrel{\rm C_{effox}}{(\rm Fcm^{-2})}$	α _{ox}	R_{ox} (Ωcm^2)	$\substack{ Q_{dl} \left(s^{\alpha} \\ \Omega^{-1} cm^{-2} \right) }$	$\stackrel{C_{eff \ dl}}{(F \ cm^{-2})}$	$\alpha_{\rm dl}$	$R_{ct}(\Omega cm^2)$
TGS20C t0	$2.6\ 10^2\pm 1.6$	$3.3 \ 10^{-9} \pm 3.5 \ 10^{-10}$	0 1.93 10 ⁻⁹	$0.96 \pm 1.3 \ 10^{-2}$	8.2 10 ²	$1.1\ 10^{-6}\pm 5.7\ 10^{-8}$	2.97 10 ⁻⁸	$0.41 \pm 9.6 \ 10^{-3}$	$2.7 \; 10^5 \pm 5.3 \; 10^3$				
TGS20C 24 h	50 ± 2.5	$1.310^{-6}\pm1.2\ 10^{-7}$	$9.4 10^{-9}$	$0.6\pm 8\;10^{-3}$	$4.40^{2} \pm 1.6$	$6.710^{-5} \pm 3.03 \ 10^{-6}$	$6.14 \ 10^{-5}$	0.79 ± 0.03	$1.110^4 \pm 1.5 \ 10^2$				
TGS40C t0	$1.09 \ 10^2 \pm 3.1$	$3.4\ 10^{-9}\pm 4.4\ 10^{-10}$	⁰ 2.02 10 ⁻⁹	$0.94 \pm 1 \ 10^{-2}$	$\begin{array}{c} 4.5 10^4 \pm 8.1 \\ 10^3 \end{array}$	$2.9\ 10^{-7}\pm 3.8\ 10^{-8}$	$1.81 \ 10^{-8}$	0.5 ± 0.03	$1.9\ 10^5 \pm 1.3\ 10^4$	$\frac{1.1\ 10^{-5}}{6.2\ 10^{-7}}$	$1.2 \ 10^{-5}$	$\begin{array}{c} 0.95 \pm 5 \\ 10^{-2} \end{array}$	$2.8\ 10^5\pm 2.9\ 10^4$
TGS40C 24 h	$2.1\ 10^2\pm 5.6\ 10^{-5}$	³ 2.2 $10^{-7} \pm 6.4 \ 10^{-12}$	² 1.25 10 ⁻⁸	$0.714 \pm 2.9 \ 10^{-6}$	$3.3 \ 10^3 \pm 9.6 \ 10^{-3}$	$2.02 10^{-4} \pm 6.1 10^{-10}$	$4.02 \ 10^{-4}$	$0.79 \pm 2 \ 10^{-6}$	7.2 $10^4 \pm 1.07$				
P t0	$1.24\ 10^2\pm 0.26$					$8.1 \ 10^{-5} \pm 3.2 \ 10^{-6}$	$2.13 \ 10^{-5}$	$0.74\pm5.9\ 10^{-3}$	$2.8 \ 10^2 \pm 4.4$	$3.8 \ 10^{-4} \pm 3.5 \ 10^{-6}$	3.910^{-4}	0.85 ± 3.5 10^{-3}	$3.1\ 10^3\pm 12.2$
P 24 h	$2.18\ 10^2\pm 3.09$					$1.1\ 10^{-4}\pm 3.3\ 10^{-5}$	$1.32 \ 10^{-5}$	$0.63 \pm 5 \ 10^{-2}$	$2.8\ 10^2\pm 30.4$	$4.9 \ 10^{-4} \pm$	$5.9 10^{-4}$	0.83 ± 2	$4.9 \ 10^{3} \pm$

 $4.9\ 10^3 \pm 1.36\ 10^2$

 $1.32 \ 10^{-5}$

 $1.1 \,\, 10^{-4} \pm 3.3 \,\, 10^{-5}$

 $3.5 \, 10^{-5}$

0

between 6.0 and 6.5 in order to obtain a pH between 6.5 and 7.2 after heating the solution to 35 °C. The temperature in the salt spray chamber was set to 35 $^{\circ}C \pm 2 ^{\circ}C$. The pH value was adjusted with 0.1 mol/L NaOH or HCl solutions. All chemicals were of p.a. quality and supplied by AppliChem (Darmstadt, Germany). The test lasted 24 h. Samples were taken from the chamber every 6 h and photographed (BX 51 Olympus optical microscope) in order to follow the progress of corrosion with time.

3. Results and discussion

3.1. Thickness and composition of the coatings

Continuous and homogeneous coatings were obtained by the solgel technique. No cracking or discontinuities were observed after the thermal treatment. The thickness measured using a profilometer on glass samples for single layer coatings was 3.29 \pm 0.08 μ m for the TGS40, 1.01 \pm 0.05 µm for the TGS20 and 2.45 \pm 0.16 µm for the TGC. Loading samples with larger amounts of nanoparticles resulted in increased coating thickness. Contact angles are shown in Table 1. All angles reported are lower than 90°, indicating that wettability is high, with no marked differences between measurements.

XPS survey spectra are an important source of information concerning the general chemical composition of the metal surface modified with solgel coatings enriched with silica nanoparticles and cerium ions (Table 2). The composition of the bare alloy subjected to phosphoric acid is given for comparison (denoted as P). After acid pre-treatment the surface of carbon steel is composed mainly of iron and oxygen. Carbon is present as adventitious carbon (Table 2). Phosphoric acid pre-treatment promotes the formation of hematite and magnetite crystals on the steel surface and consequently improves the corrosion resistance [9]. Preparation of TEOS/GPTMS (TG) sol-gel coatings with the addition of $Ce(NO_3)_3$ as a source of cerium ions changed the surface composition significantly (sample TGC). The content of iron decreased to only 0.1 at.% and that of Si increased, indicating full coverage of the steel surface with silane coating. The concentration of cerium was about 0.1 at.%. Further modification of the surface included the addition of SiO₂ nanoparticles. Compared with silane coatings containing Ce ions (TGC), the addition of silica nanoparticles does not change the coating composition significantly. Other elements (Ca, N) were also detected, probably as contaminants arising from the solvents or during sample preparation.

High resolution spectra were analysed in order to reveal the oxidation state and chemical environment of individual elements (Fig. 2). Carbon spectra were centred at 285 eV, indicating that the main carbon bonding is C–C, C–H. An additional peak, observed in sol–gel coatings at higher binding energies, can be related to the presence of carbon bonded to oxygen at 286.0–286.2 eV (C-O), and carbon bonded to silicon (C-Si) [34]. For carbon steel pre-treated in acid two distinct peaks appeared in the O 1s spectrum at 530.3 eV and 531.6 eV related to the presence of iron oxide and hydroxide. The latter peak is more pronounced, related to the hydroxylation of the surface during the pre-treatment step. For sol-gel coatings a single O 1s peak appeared, centred at 531.2 eV. This may contain several contributions related to the bonding of oxygen with silicon (Si-O-Si bonds) at 532.6 eV [31] and with cerium. In Ce(III) compounds the oxygen peak is located at 531.5 eV, and at 529.8 eV in Ce(IV) [35]. The silicon 2p peak at 102.6–102.7 eV is a single peak that may be related to the presence of silicon bonded to carbon and/ or oxygen (Si-C, SiO₂-like), and silicon bonded to oxygen and silicon (Si-O-Si bond) at 103.8-103.9 eV [34]. The Si 2p peak, centred at 103.2–103.3 eV, indicates the formation of both species. Iron was present only on pre-treated steel samples not modified by coating. The position of the Fe 2p_{3/2} peak centred at 711.3 eV indicates the formation of mixed Fe(II) and Fe(III) oxides [36]. Two satellite peaks are characteristic of iron oxides-at ~715 eV for Fe(II) oxide and at ~721 eV for Fe(III) oxide [36]. Both peaks are observed in experimental spectra (Fig. 2). The peak



Fig. 7. SEM-EDS analysis of the surfaces of the TGC and TGS20C coatings after 24 h immersion in 0.35 % NaCl.

related to the Fe metal peak at 707.7 eV is absent, indicating full coverage of the metal surface by the oxide layer.

The XPS 3d spectra of cerium compounds are complex due to satellites related to energy-gain (the so-called "shake-down" states) [36]. The spectrum of CeO₂ is composed of six peaks corresponding to the pairs of spin-orbit doublets (at 882.7, 888.5, 898.3, 901.3, 907.3 and 916.7 eV). The Ce spectra for Ce(III) compounds are composed of two multiplets, corresponding to spin–orbit splitting; each is dominated by two features resulting in four peaks (at 880.9, 885.5, 899.1, 903.4 eV). The spectra for a sol–gel coating with added Ce(III) ions have features that can be identified with those of both Ce(III) and Ce(IV) species.

3.2. Electrochemical measurements

The barrier effects achieved by hybrid coatings with various loadings of nanoparticles and cerium salt were compared with that of the uncoated metal pre-treated with phosphoric acid. Anodic polarisation curves were recorded 30 min after immersion (t₀) and after 24 h of immersion in 0.35% wt. NaCl (Fig. 3a). The bare steel shows active dissolution, while the lower current densities measured with the coated steel indicate protection conferred by the film. Single layers of TGC and TGS40 films exhibit a region of quasi constant current density up to approximately 0.1 V, at which value the current increases, evidencing rupture of the film. In contrast, a constant increase of current density with applied potential was observed from t₀ for a TGS20 film. The films have different thicknesses, those for TGC and TGS40 being more than twice the thickness of that for TGS20. The double layered films TGS20C and TGS40C show much lower current densities than do the bare material and the single layers, being smaller by around two orders of magnitude for TGS20C and three orders of magnitude for TGS40C. Moreover, in the case of TGS40C, a constant value of current density was observed, as pseudo passivity, over a wide range of potential (approximately 0.4 V). This is an indication that the coatings inhibit the anodic process, acting as an effective barrier to the electrolyte by obstructing its contact with the metal surface and thus reducing the active area.

After 24 h immersion the coatings exhibit some degradation, shown by the increased values of current densities (Fig. 3b). The single layers TGS20 and TGS40 show a progression of current density similar to that for the uncoated substrate, evidencing a high degree of deterioration of the film, as also observed, although less markedly so, for the TGS20C layer. However, a wide region of pseudopassivity is observed for the TGS40C and TGC coatings, with current densities around three orders of magnitude lower than those observed with bare steel after 24 h of immersion. A shift in the corrosion potential to more positive values is observed for the coated samples, being more notable for the TGS40C coating, suggesting that the coatings enhance the anticorrosion properties.

The EIS results for the coatings after 30 min of immersion in 0.35% wt. NaCl, shown in the Bode format, are compared with those for the bare material (Fig. 4). The system's response can be composed of two different contributions for the bare material: the one at higher frequencies could be associated with the oxide response resulting from penetration of the electrolyte through a porous film on the base material. The second one at low frequencies could be related to the metal response [34]. Coated samples present a different response in the Bode plots when compared with the bare material. It can be observed that in the high frequency region of the theta vs freq. plot a maximum can be associated with the coating; meanwhile in the low region frequency the presence of a maximum is associated to the defects in the coating [32,37,38]. The TGS40C coating presents a more capacitive behaviour, with angles close to 90° and an impedance modulus higher than that of the TGS20C coating. Both coatings present, in turn, a higher total impedance than that for the bare alloy. After 24 h immersion in NaCl, deterioration of the film is evidenced in the Bode plot (Fig. 5), in agreement with the observed polarisation curves (Fig. 3b). The total impedance of both coatings is reduced, reaching, especially in the case of TGS20C, values close to that of bare alloy. Although for the TGS40C coating a resistive

domain appeared at intermediate frequencies, associated with the presence of pores in the coating, values of impedance modulus remain high over the whole frequency range, showing a protective feature for the substrate (Fig. 5). The theta *vs* freq plot for the coated samples shows a decrease in angle in the high frequency region, together with an increase in the low frequency region, evidencing increased film porosity and, consequently, increased exposed area.

The electrochemical behaviour can be described in terms of an equivalent circuit in order to enable the most relevant parameters applicable to the corroding system to be obtained. Equivalent circuits used for fitting EIS data are shown in Fig. 6. A constant phase element (CPE) was used instead of an "ideal" capacitor, taking into account that the slopes of the curves in the log/Z/vs log f plot were not -1, the value expected for an ideal capacitor, and that a certain degree of inhomogeneity is observed in the surface.

The impedance of a constant phase element is given by the expression

where the parameter Q is independent of frequency [36]. When $\alpha = 1, Q$ represents the capacitance of the interface. When $\alpha < 1$, the system behaves in a manner that can be attributed to surface heterogeneity or to a distribution of time constants. Q has the units $s^{\alpha} \Omega^{-1} \text{ cm}^{-2}$ and α is a coefficient associated with system homogeneity [39,40].

In the equivalent circuits presented in Fig. 6, R_s represents the electrolyte resistance, R_{coat} is associated with the ionic resistance of the electrolyte in the coating pores, CPE_{coat} is the constant phase element ascribed to the sol–gel coating, CPE_{ox} is the constant phase element related to the oxide formed on the steel, R_{ox} corresponds to the oxide resistance, CPE_{dl} is the constant phase element associated with the electrochemical double layer capacitance, and R_{ct} is associated with the charge transfer resistance.

Considering a resistive-capacitive parallel circuit (ZR//CPE), and using a CPE, the impedance for each node of the circuit arrangement is given by Eq. (2):

$$Z_{CPE} = 1/Q(j\omega)^{\alpha}$$
(1) $Z_{R//CPE} = \frac{K}{1 + QR(j\omega)^{\alpha}}$ (2)



Fig. 8. SEM-FIB analysis of the TGC40C (a) and TGC20C (b) coatings following 24 h immersion in NaCl, together with the atom percentage from the EDS. The arrows indicate the points at which the spectra were taken.





Fig. 9. SEM-FIB examination of a failure in the TGS40C coating and EDS spectra showing the atom percentage in the marked region analysed.

where R is the resistance in parallel with the CPE, and where Q and α have the meaning as in Eq. (1). For a symmetrical distribution of relaxation times, the Cole–Cole [41] model gives a depressed semicircle in the Nyquist plot, and its impedance response is given in Eq. (3)

$$Z_{\text{R//CPE}} = \frac{R}{1 + (j\omega R C_{\text{eff}})^{\alpha}}$$
(3)

where C_{eff} is the effective capacitance associated with the impedance response. Equating Eqs. (2) and (3), Eq. (4) is obtained and the expression for the effective capacitance as a function of *R* and Z_{CPE} is attained (Eq. (5)).

$$QR(j\omega)^{\alpha} = \left(j\omega RC_{eff}\right)^{\alpha} \tag{4}$$

$$C_{eff} = \frac{(QR)^{1/\alpha}}{R}$$
(5)

The results obtained from fitting to experimental EIS data with the proposed equivalent circuits shown in Fig. 6, together with the calculation of C_{eff} according to Eq. (5), are presented in Table 3. The values of the coating corresponding to C_{eff} are similar for the two types of coating at the beginning of immersion, and correspond to values of protective coatings. However, following immersion, there is a marked increase in the capacitance value that cannot correspond just to water uptake by the film and can more probably be attributed to failure or degradation of the sol–gel layer [32,41]. Accordingly, R_{coat} and R_{ox} decrease in time

for both coatings evidencing the ingress of the electrolyte in the coating through defects.

3.3. The role of cerium in the coating-FIB/SEM/EDS analyses

The effect of cerium in the coating has still not been completely clarified. The results of Hinton [28,42] lead to the suggestion that cerium oxides precipitate on cathodic sites (i.e. on generation of an alkaline environment due to the oxygen reduction reaction) creating a barrier that inhibits oxygen reduction, thus acting as a cathodic inhibitor. However it has been claimed that cerium ions behave as anodic or mixed inhibitors, affecting both types of reaction [43–47]. The incorporation of silica nanoparticles into the silane film to enhance barrier protection has been reported for thicker-and presumably more compact-films [17,47]. In this work a shift to more positive potentials was observed with increasing time of immersion (Fig. 3), suggesting that the cerium ions act as a mixed inhibitor. This effect was more noticeable for the thicker TGS40C films that remained less damaged than the TGS20C, in which the defect area appeared to be larger and the quantity of cerium in the film was presumably not sufficient to cover the failures.

The formation of Ce(III) oxides follows the following reaction [48,49]:

$$Ce^{3+} + 3OH^{-} \rightarrow Ce(OH)_{3} \downarrow \tag{6}$$

The conversion from Ce(III) to Ce(IV) can occur during the course of coating preparation, due to the acidic conditions, leading to formation of $Ce(OH)_2^{2+}$ as the only stable form of Ce(IV) at lower pH [45,46]. The

oxidation may also be induced by oxygen during air exposure or during polarisation in aerated NaCl solution (the pH at which oxidation by O_2 takes place is between 4.3 and 6.3) [45,46]. The mechanism of oxidation of Ce(III) to Ce(IV) can proceed via two alternative paths. Thus, O_2 can act as oxidant and Ce(III) as a reductant [50]:

$$4Ce^{3+}(aq) + O_2(aq) + 4OH^{-}(aq) + 2H_2O \rightarrow 4Ce(OH)_2^{2+}(aq)$$
(7)

or may be reduced at cathodic sites, generating H_2O_2 which can then oxidise Ce(III) to Ce(IV):

$$2Ce^{3+}(aq) + H_2O_2(aq) + 2OH^{-}(aq) \rightarrow 2Ce(OH)_2^{2+}(aq)$$
(8)

The soluble Ce(IV) species then precipitate as insoluble CeO_2 due to the local rise in pH caused by the production of OH^- ions:

$$Ce(OH)_{2}^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ce(OH)_{4}(s) \rightarrow CeO_{2}(s) + 2H_{2}O$$
(9)

The composition of cerium at the surface, following 24-hour immersion in NaCl solution, and its self-healing ability were followed by SEM-EDS and FIB-SEM-EDS analyses. The former, presented for the TGC and TGS20C samples (Fig. 7), was carried out at a spot sized approximately 50 μ m \times 50 μ m. Cerium is shown by EDS analysis to be present at the surface, even after immersion for 24 h. The iron content is higher in the TGC coating than the TGS20C and TGS40C coatings, confirming the electrochemical results (Fig. 3b). Partial degradation of the TGC coating allows iron to reach the coating substrate. Loading coatings with silica nanoparticles achieved better barrier protection, preventing iron ions from the substrate from passing through the coating.

SEM-FIB analysis of TGS20S and TGS40C samples after 24 h immersion in NaCl is shown in Fig. 8, together with the atom percentages obtained by the EDS. Cerium is shown to be present in the top layers of each coating and, although Fe is observed in that layer in both samples after 24 h of immersion, the atom percentage is lower for TGS40C, in good agreement with the results shown in Figs. 3 and 7.

The coatings were dense and homogeneous (Fig. 8). The thickness of the coatings estimated by this technique is in good agreement with the results of profilometry. Individual defects/cracks were located randomly at the surface and it was difficult to find them using FIB. Whenever a failure in the coating was detected (Fig. 9), cerium was found to be present in the defect. Thus cerium is able to move within the coating and migrate to defective zones.

3.4. Salt spray testing

The deposited coatings were tested under standardised corrosion testing conditions in a harsh atmosphere (5% NaCl) in the salt spray chamber. Images and topography of the bare substrate and TGS20C and TGS40C coated samples after 1 h and 20 h exposure in the salt spray chamber are presented in Figs. 10 and 11. For poorly resistant materials as carbon steel this period of time was sufficient to evaluate the effect of the coating compared to bare substrate [51,52]. Bare pre-treated substrate was already corroded after 1 h, while coated samples remained grey and without visible signs of corrosion (Fig. 10). After 20 h exposure the coatings began to exhibit signs of deterioration, especially TGS20C, but remained attached to the surface. In contrast, bulky corrosion products were observed on the uncoated substrate. The significant differences in topography observed between bare



Fig. 10. Surfaces of the bare substrate (P) and of substrates coated with TGS20C and TGS40C photographed after 1 h and 20 h exposure in the salt spray chamber. Size of the samples 1 cm × 1 cm.



Fig. 11. 3D topography images of the bare substrate (a,b) and substrates coated with TGS20C (c,d) and TGS40C (e,f), before (a,c,e) and after 20 h (b,d,f) exposure in the salt spray chamber.

and coated steel were confirmed by confocal microscopy (Fig. 11). In agreement with the electrochemical measurements, the TGS40C sample performed better than TGS20C after exposure to the salt spray test.

4. Conclusions

Hybrid coatings prepared from TEOS and GPTMS, using a sol-gel procedure, were modified by including silica nanoparticles and cerium ions. This has been shown to markedly increase corrosion protection of carbon steel in 0.35% NaCl. Continuous and homogeneous singleand two-layer coatings were prepared. XPS confirmed the silane composition of the coatings and the presence of cerium has been demonstrated in oxidation states Ce(III) and Ce(IV).

The corrosion resistance of single layer coatings is higher at higher contents of nanoparticles, indicating their barrier effect due to increased thickness. Single layer coatings containing cerium offer a similar enhanced degree of protection. Combining both effects in two-layer coatings resulted in a further increase in corrosion resistance. A coating formulated with a higher content of nanoparticles and consequently thicker film in the bottom layer and cerium in the top layer offered the best protection with the establishment of a pseudo-passivity region. This coating remained protective even after 24 h immersion in chloride solution. The presence of cerium was after immersion was demonstrated at the surface by SEM-EDS and FIB-SEM-EDS analysis. Moreover, it was

concentrated at local defects, indicating the self-healing ability of the coating at failure sites. The rapid deterioration of the bare substrate under harsh testing conditions in a salt spray chamber was slowed down significantly by the presence of these coatings. Hybrid coatings modified with nanoparticles and cerium ions thus offer good protection against corrosion of the otherwise poorly resistant carbon steel in chloride environments.

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