



## 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-glycidioxypropyl-trimethoxysilane (GPTMS) were each used here as precursors, together with various quantities of colloidal silica suspension, to improve barrier properties of the coatings.  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  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 electrochemical behaviour at various immersion times was modelled by equivalent circuits to demonstrate 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 in 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 aluminium 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-glycidioxypropyl-trimethoxysilane (GPTMS) as precursors, and containing various amounts of silica nanoparticles to improve the barrier effect of the coatings. The effect of adding  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  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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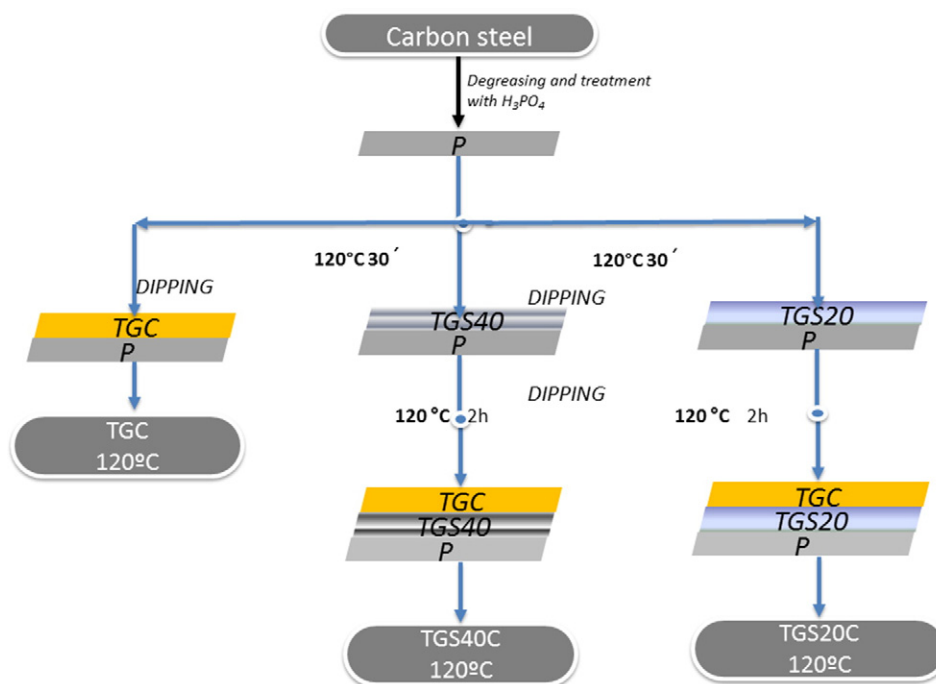


Fig. 1. The preparation of single- and two-layer sol-gel coatings.

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 × 50 mm × 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 ( $20 \pm 1^\circ\text{C}$ ), 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 sol-gel route from tetraethoxysilane (TEOS, Fulka, Germany) and 3-glycidoxypropyl-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  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma Aldrich) as a source of Ce(III). Sols were prepared in molar ratios of  $\text{TEOS}/\text{GPTMS}/\text{SiO}_2 = 42/18/40$  (denoted as TGS40 sol),  $\text{TEOS}/\text{GPTMS}/\text{SiO}_2 = 56/24/20$  (denoted as TGS20 sol) and  $\text{TEOS}/\text{GPTMS}/\text{Ce} = 66.5/28.5/5$  (denoted as TGC sol).  $\text{HNO}_3$  solution ( $0.1 \text{ mol dm}^{-3}$ ) 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

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  $120^\circ\text{C}$  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  $\text{SiO}_2$  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  $120^\circ\text{C}$  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  $120^\circ\text{C}$  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 1

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

Sample	Contact angle
P	$76.9 \pm 2.6$
TGC	$75.3 \pm 7.2$
TGS40	$77.8 \pm 3.8$
TGS20	$68.4 \pm 1.8$
TGS40C	$71.9 \pm 1.9$
TGS20C	$71.3 \pm 1.6$

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	Composition/at.%						
	C	O	Fe	Ce	Si	Ca	N
P	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

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