Silica-based hybrid coatings for corrosion protection of carbon steel. Part I: Effect of pretreatment with phosphoric acid

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ABSTRACT

This work studies the synthesis and characterization of hybrid organic–inorganic coatings based on silica to improve the corrosion resistance of carbon steel. Hybrid organic–inorganic silica sol–gel coatings were obtained by dipping in an organically modified silica sol synthesized through hydrolysis and condensation of 3-glicidoxipropyl-trimetoxisilano (GPTMS) and tetraethoxysilane (TEOS) in acidic catalysis. The coatings were doped with a cerium salt ($Ce(NO_3)_3 \cdot 6H_2O$) and loaded with silica nanoparticles in order to improve both barrier effect and the anticorrosive behavior of the coatings by the inhibitory effect of cerium. Prior to the application of the coating, some samples were treated with a phosphoric acid 2% v/v in order to improve coating adherence. A two layered coating was applied onto AISI 1010 carbon steel, the outer containing with a cerium salt and the inner one with silica nanoparticles without the cerium salt, producing homogeneous and cracks-free films. Raman spectroscopy was used to characterize the compounds present in the surface of steel after pretreatment with phosphoric acid. Microstructural characterization of coatings was performed by means of scanning electron microscopy (SEM).
The evolution with time of the protective properties of films was studied by electrochemical impedance spectroscopy (EIS), providing quantitative information of the role of the pre-treatment. Electrochemical behavior in each stage of the corrosion processes was modeled by equivalent circuits. Additionally, films adhesion was evaluated by nano-scratch demonstrating that the phosphate treatment improves adhesion of the hybrid coating.

1. Introduction

One of the most common problems in industry related to materials is the damage that they suffer due to corrosion processes. Carbon steel is widely used in industry; however its susceptibility to corrosion in many environments limits its applications. For many years, chromate conversion coatings have been widely applied for corrosion protection of metals. However, the carcinogenic effect of chromate has generated serious environmental and health problems, for that reason its use is prohibited [1]. The application of hybrid organic–inorganic sol–gel coatings on different substrates has been thoroughly investigated in the last years [2–4]. Sol gel process is a chemical method that allows the synthesis of glassy and ceramic materials at lower temperatures than the conventional methods and can be used to obtain functionalized coatings. The corrosion behavior of sol–gel coatings has been extensively studied on various substrates, such as aluminum alloys [5–7], mild steel [8–11], stainless steel [12–14], galvanized steel [15,16] and others metals [2]. One strategy to minimize the corrosive

attack is the application of coatings containing rare earth (RE) salts due to their low toxicity and environmental feasibility [17,18]. Dip-coating process is one of the most used methods for deposition of sol–gel coatings; this consists in the immersion of the substrate in the sol with a subsequent withdrawal at a controlled rate. The fast solvent evaporation produced during drying leads to solidification of the thin film deposited on the substrate. The presence of organic components within the inorganic silica network increases the ductility and the critical thickness of coatings allowing an increment on their protective character [19].

Tetraethoxysilane (TEOS) is one of the most common precursors for sol–gel coatings, its hydrolytic condensation provides a 3D silica network which needs a thermal treatment upon 500 °C to reach an optimal densification. In order to achieve a crosslinked structure at lower temperatures and increase film plasticity, organic polymerization of a superimposed network should be performed. Glycidoxypropyl-trimethoxysilane (GPTMS) is an epoxy-functionalized alkoxyde able to promote both the hydrolytic condensation of a silica network and an organic polymerization of its epoxy rings producing a highly crosslinked hybrid network [20].

Addition of inhibitors into the sols has been widely studied being cerium salts one of the most documented [21–28]. Ce^{3+} and Ce^{4+}

contained in the coating have a high reactivity with oxygen, being the driving force for their migration through the coating and reaction with the groups OH^- present at defective areas or where the film was damaged. Cerium hydroxides/oxides precipitate on cathodic sites and provide a local and natural barrier to later corrosion processes constituting a phenomenon of self-healing [7,22,29] Additionally, in an effort to improve the corrosion resistance, the incorporation of SiO_2 nanoparticles to the films had been used in order to increase coating thickness and density [30–33].

One of the main problems when applying sol–gel coatings on iron based alloys is the lack of adherence of the film formed on a substrate that easily oxidizes forming bulky oxides as Fe_2O_3. The use of phosphate conversion treatments has been studied in the past years in order to improve coatings adhesion [34,35].

This work evaluates the effect of a pretreatment with phosphoric acid on the corrosion behavior of carbon steel coated by the sol–gel method. TEOS and GPTMS were used as precursors; hybrid sols were loaded with SiO_2 nanoparticles and doped with cerium salts. The effect of the phosphate treatment on the coating performance was studied using classical electrochemical techniques as polarization curves and EIS; additionally, coating adherence was evaluates by nano-scratch.

2. Experimental

2.1. Materials and samples preparation

Nanostructured hybrid films were synthesized by the sol–gel route from TEOS (Fulka, Germany) and GPTMS (Dow Corning, USA) using a colloidal silica suspension (Ludox AS-40, Sigma Aldrich, USA) to improve mechanical and barrier properties, and $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich) as a supplier of Ce(III). Sols were prepared keeping molar ratios of TEOS/GPTMS/SiO2 = 42/18/40 (for so-called TGS sol) and TEOS/GPTMS/Ce = 66.5/28.5/5 (for the TGC sol), both in acidic conditions. Cerium nitrate hexahydrate was dissolved in ethanol and then mixed with TEOS and GPTMS keeping the relationship of 5% in moles in the sol stated above for the sol containing Ce (TGC). $0.1\,mol\,dm^{-3}$ HNO3 solution was used both as a water source and catalyzer in the TGC sol. The system was magnetically stirred for 2 h at room temperature. The TGS sol was prepared by high speed stirring of TEOS, GPTMS and silica nanoparticles, to promote the homogenization of the immiscible phases producing a thin emulsion prior the addition of concentrated nitric acid to catalyze the reactions. A transparent and colorless sol was obtained. The sol was also stirred for 2 h at room temperature.

Carbon steel plates, AISI 1010, (Timar SRL, Argentina) previously polished with emery paper up to grade 400, degreased with ethanol and rinsed with distilled water, were used as substrates. Table 1 shows the chemical composition of substrates analyzed by spark emission spectroscopy (BAIRD DV6 with MC20 processor, Baird Corporation, 1996, USA).

In order to study the influence of phosphoric acid pretreatment on the corrosion resistance and film adherence on the coated samples, half of the samples were immersed in a solution of phosphoric acid 2% v/v for 10 min at room temperature (20 ± 1 °C). With the aim of clarity, samples with phosphoric treatment are named as "P" meanwhile the ones without phosphoric treatment are referred as "B" along this work. Sol–gel coatings were applied by dipping using a withdrawal speed of $3\,cm\,min^{-1}$ for the first layer (TGS) and $35\,cm\,min^{-1}$ for
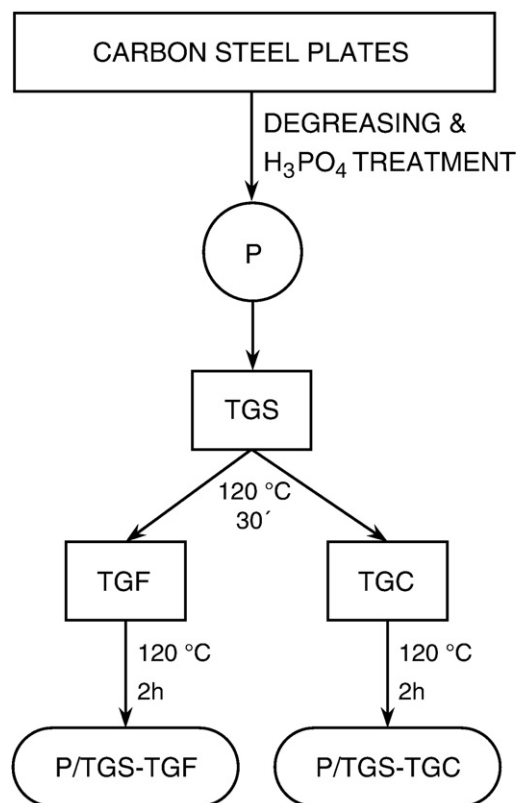

Fig. 1. Sketch of deposition procedure for steel plates.

the second layer (TGC). Glass slides were also coated with single layers of both sols for thickness measurement.

Deposition procedure for steel plates is sketched in Fig. 1.

2.2. Surface characterization and electrochemical measurement

Microstructural characterization of substrates and sol–gel coatings was performed by optical microscopy (Olympus PMG3, Japan) and scanning electron microscopy (SEM/EDS, Jeol 6460, Japan).

Roughness was measured on substrates and coated samples using a profilometer (Surtronic 3^+, Taylor-Hobson, UK) with a vertical resolution of 0.02 μm. Data were processed with Taly Profile Gold software. A cut-off of 0.8 mm and a measurement length of 4 mm were used. Four independent measurements were performed on each sample.

The crystalline phases present in the surface compounds on the steel, with and without pretreatment, were determined by Raman spectroscopy using an Invia Reflex confocal Raman microscope (Renishaw, UK) in order to determine surface composition and to establish if any compounds coming from the bath are incorporated to the final structure of the film. The Raman spectra were obtained using an argon laser of 514 nm (25 mW) in backscattering mode with a laser spot of 10 μm. An exposure time of 20 s and 3 accumulations were used, with $50\times$ objective. No thermal effects were observed on the samples during these measurements.

Table 1
Chemical composition (wt.%) of mild steel obtained by spark emission spectroscopy.

Element	Fe	C	S	P	Mn	Si	Mo
wt.%	Balance	0.003 ± 0.0002	0.009 ± 0.002	0.015 ± 0.0003	0.153 ± 0.006	0.0014 ± 0.0003	0.006 ± 0.002