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Hybrid sol-gel coatings containing clay nanoparticles for corrosion protection of mild steel

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ABSTRACT

The development of a new environment-friendly anticorrosive coating for mild steel substrate is afforded in this work. The combined use of cerium, as a self-healing agent, and clay nanoparticles, as improvers of the barrier properties, was considered to the development of new anticorrosive sol-gel coatings. Nanostructured hybrid films were synthesized by the sol–gel route from tetraethoxysilane (TEOS) and 3-glicidoxipropyl-trimetoxisilano (GPTMS) using laminar nanoclays (Laponite $Na^{+}_{0.7}[Si_8Mg_{5.5}Li_{0.3}H_4O_{24}]^{-}_{0.7}$) to improve mechanical and barrier properties, and $Ce(NO_3)_3 \bullet 6H_2O$ as a supplier of Ce(III) to provide an inhibiting effect in the event of coating failure. Carbon steel plates, AISI 1010, were used as substrates. Prior to the application of the coating, samples were treated with a phosphoric acid 2% v/v in order to improve coating adherence.

In order to evaluate cerium effect, electrochemical behaviour of films containing Laponite and cerium salts (TGL-Ce) were compared with films containing only Laponite (TGL) by means of potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) measurements using a 0.35 wt% NaCl solution. Microstructural characterization and surface analysis of substrates and sol-gel coatings were performed by optical microscopy and by XPS techniques. The use of nanoclays allowed to achieve a significant improvement of the anticorrosive behaviour of the cerium doped coating at the same time that enhances the physical integrity of the coatings under immersion tests.

1. Introduction

Since the adoption of new regulations towards protection of the environment, in the field of the industrial anticorrosive products, the use of chromate based coatings is highly limited, being, at the moment, only permitted for the aeronautical industry, were the high performance of the chromate conversion coatings (CCC) is, at the moment, the only that provides the necessary safety criteria. So, the development of new environment-friendly high performance anticorrosive coatings is a hot topic for the scientific researchers due to the increasing demand from the industrial field. Is in this framework were the called self-healing coatings take wide importance thanks to their possibility of present a long-term anticorrosive protection with the use of safer compounds as the based on lanthanides elements like Ce and La [1,2].

The sol-gel science is a very promising alternative to allow us to reach a functional material coating that fulfills the high demands of the industrial field, as it is the high physicochemical and thermal stability and its possibility to incorporate almost any kind of functional additives as organic compounds and ionic salts [3,4]. Furthermore, sol-gel coatings are compatible with a variety of substrates and can be applied as very thin coatings. The development of a three-dimensional silica network as the main component of the coating structure can offer a well densified material with extremely good barrier properties [5–9]. For this reason, the research in the sol-gel field for anticorrosive coatings is worldwide extended. Nevertheless, the addition of ionic salts, behind conferring the desired functionality, usually carries to a detrimental of the barrier properties by its function as network modifiers. Then, to produce a Ce-functionalized self-healing coating, the use of multilayer coatings is a common strategy in order to reach both the barrier and self-healing properties. The barrier properties of sol-gel coatings can be substantially improved by controlling the crosslinking density of its structure or by incorporation of denser nanoparticles that, at the same time, work as mechanical reinforcement. Even so, the structural modification

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introduced by lanthanide compounds on the silica network leaves an open path to the water diffusion through the coating [10].

In the recent years, the development of new nanocomposites was highly explored by the use of nano-clays thanks to its highly availability and economical convenience. Those nanoparticles are highly employed as rheological modifiers in the industry of cosmetic and paints and, at the same time, their use as load for composite materials can improve both the mechanical and barrier properties[11–13]. However, the use of clay nanoparticles in the field of sol-gel thin coatings is an area that has not been extendedly analyzed[14–16]. The synthesis of a sol with an appropriated load of well exfoliated clay nanoparticles, and its deposition as a coating by the dip-coating process, could carry to the development of a high performance sol-gel material. This combination of material and deposition process is able to produce a matrix were the clay particles remain perfectly aligned with the substrate increasing the diffusive pathway for the corrosion process and a direct diffusive pathway for the active Ce ions towards the presence of an occasional defect or damage in the coating to confer the desired self-healing property.

In this work, we present a novel strategy to provide a single-layer sol-gel coating with improved barrier and self-healing properties through the nano-structuring of its organic-inorganic hybrid matrix with the use of exfoliated synthetic nano-clays as potential prime coatings.

2. Experimental

2.1. Synthesis and deposition

Three different sols were synthesized in order to analyse the anticorrosive behaviour of cerium-doped coatings with a stratified laminar structure: an epoxy-silica hybrid sol (TG), a hybrid sol loaded with laminar nanoparticles (TGL) and a hybrid sol with laminar nanoparticles and cerium dopping (TGL-Ce). Hybrid sols were synthesized from the hydrolytic condensation of tetraethoxysilane (TEOS, Aldrich 99%) and glycidoxypropil-trimetoxysilane (GPTMS, Aldrich 98%) in acidic media using concentrated HNO_3 as catalyser. In order to incorporate the laminar nanoparticles in the precursor solution, hydrolysis of TGL sol was performed in presence of an aqueous suspension of a synthetic exfoliated clay nanoparticles (Laponite S482 ®, Rockwood Specialties, Inc.). $CeNO_3$ was used as supplier of cerium. In every case, TEOS/GPTMS molar ratio was kept to 60/40, Laponite was incorporated at a 0.5 wt % in respect to condensed silica and Ce(III) was added, from cerium nitrate, to attain a Ce/alkoxides molar ratio of 5/95.

Precursor sols were deposited by the dip coating process on AISI 1010 mild steel plates previously degreased and treated with phosphoric acid following a reported procedure [17][in order to improve the coating adhesion. After deposition, coated substrates were thermally treated at 120 °C in air atmosphere during 2 hours. Fig. 1 shows a schematic representation of the samples preparation.

2.2. Coatings Characterization

Morphology of the obtained coatings was analyzed through optical microscopy (Olympus, PMG3, Japan) in reflectance mode. Coating thickness was determined by mechanical profilometry (KLA Tecnor™ D-100) on samples with a slope performed on the film by scratching immediately after deposition and before the thermal treatment. Every measurement was performed at five different points for every sample composition.

Coatings wettability was analyzed through contact angle measurements performed with a contact angle goniometer (Ramé Hart model 500) with DropImage Advanced Software. A 5 μL drop of bi-distilled water was applied on coatings at 20 °C and a waiting time of 60 s was employed for every measurement. The process was repeated 4 times for every sample.

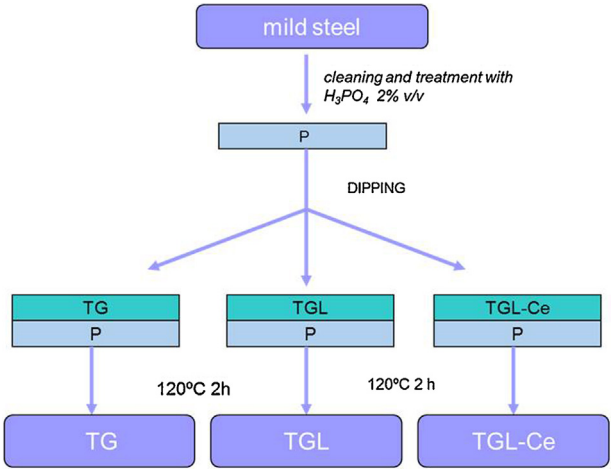

Fig. 1. Schematic representation of samples preparation of TG, TGL and TGL-Ce coatings.

X-ray photoelectron spectroscopy (XPS) was performed with a TFA Physical Electronics Inc. spectrometer using non- and monochromatised Al Kα radiation (1486.6 eV) and a hemispherical analyzer. 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.

2.3. Electrochemical behavior

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 MΩ cm). All measurements were carried out at room temperature (20 ± 1 °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 cm^2. 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 [18]. 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).

3. Results and Discussion

Transparent and colorless sols were obtained after the hydrolytic condensation. The dip coating process carried out to