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The corrosion resistance of 316L stainless steel coated with a silane hybrid nanocomposite coating

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ABSTRACT

The present work aims at evaluating the corrosion resistance of 316L stainless steel pre-treated with an organic–inorganic silane hybrid coating. The latter was prepared via a sol–gel process using 3-glycidoxypropyl-trimethoxysilane as a precursor and bisphenol A as a cross-linking agent. The corrosion resistance of the pre-treated substrates was evaluated by neutral salt spray tests, linear sweep voltammetry and electrochemical impedance spectroscopy techniques during immersion in a 3.5% NaCl solution. In addition, the effect of the drying method as an effective parameter on the microscopic features of the hybrid coatings was studied using Fourier transform infrared spectroscopy and scanning electron microscopy. Results show that the silane hybrid coatings provide a good coverage and an additional corrosion protection of the 316L substrate.

1. Introduction

One of the most effective metal corrosion control techniques consists of the electrical isolation of the anode from the cathode [1,2]. A chromium oxide (Cr_2O_3) passivation layer formed on the surface of stainless steel in oxidizing environments is a typical example of this and guarantees the durability and the corrosion resistance of this particular metal [2–4]. However, chromates are now heavily restricted in corrosion control procedures due to the Cr(VI) toxicity and their carcinogenic nature [5]. For this reason, a number of promising candidates, so called “green inhibitors”, have been explored with the hope of replacing chromates. Among them, silanes, a group of silicon based organic–inorganic chemicals, have emerged as a very promising alternative [6].

Silane films not only ensure the adhesion between metal substrates and organic coatings but they also provide a thin, but efficient, barrier against oxygen diffusion to the metal interface [7,8]. Recently, silane coatings have attracted the attention of the nanotechnology industry because they provide a highly uniform, robust and reliable coating with lateral resolution on the nanometer scale [9]. A general silane structure is $(XO)_3Si(CH_2)_nY$, where XO is a hydrolysable alkoxy group, which can be methoxy (OCH_3), ethoxy (OC_2H_5) or acetoxy ($OCOCH_3$). Y is an organofunctional group such as epoxy, vinyl (C=C) or amino (NH_2) which is responsible for a good adhesion of a silane treated metal surface [6,10].

3-Glycidoxypropyl-trimethoxysilane (GPTMS) is one of the organofunctional silane molecules that have been used as an effective coupling agent or adhesion promoter in glass/mineral-reinforced polymeric composites for decades [6,11–13]. Also it has been used in transparent abrasion-resistant hybrid coatings for polymers [14–17], metals [18–20] and for gas separation membranes [21,22].

GPTMS can undergo a variety of reactions during the preparation of a hybrid by a sol–gel route. Hydrolysis of the methoxy groups gives silanol groups, which can subsequently condense to form the silane network. The silicon atom in GPTMS is tri-functional in terms of the reactive methoxy groups and is therefore able to form a three-dimensional branched siloxane silane network with a nominal stoichiometry $SiO_{1.5}$. The epoxy rings can be opened and polymerised to form a linear poly(ethylene oxide) organic network [22,23].

Cross-links between the two networks arise either from the pre-existing link in the GPTMS molecule, by direct reaction of silanols with epoxy rings, or by condensation of silanols with hydroxyl of the opened epoxy rings. The uncatalysed ring opening reaction occurs at a useful rate only at elevated temperature and so thermal curing is required [22,23].

The use of the sol–gel process to prepare highly intermingled inorganic–organic hybrid polymer networks is of current scientific interest since it offers the possibility of tailoring the material properties by variation of the relative composition of the inorganic and organic phases. With such systems, the inorganic and organic

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networks are formed together (often simultaneously) to achieve homogeneous phase morphologies, which are impossible to produce by the other routes [22].

The microscopic features of the hybrid coatings obtained with sol–gel process depend on those hydrolysis and condensation reactions that are generally controlled by the pH of the solution [24,25]. In the acid catalyzed reaction, the hydrolysis step is faster than the condensation step, resulting in a more extended and less branched network structure. In the base catalyzed reaction, condensation is faster than hydrolysis, resulting in highly condensed species that may agglomerate into fine particles [24,26–28]. Furthermore, the sol–gel process includes a very complex reaction involving many variables such as pH, type and amount of solvent, water/alkoxide ratio [28,29], concentrations of organic [26] and inorganic [23] reactants, aging [30], cross-linking agent/alkoxide ratio, and drying methods. We investigated some of these factors in previous studies on a 1050 aluminium alloy [23,26,28,29,31].

As a follow-up of these results, the present work aims at evaluating the structure and corrosion protection performance of silane sol–gel hybrid coatings deposited on austenitic 316L stainless steel. This steel combines properties such as acceptable biocompatibility and excellent mechanical resistance with easy fabrication at low cost, which permits its use in many industrial applications, consumer products and temporary orthopedic devices [32,33]. In general 316L stainless steel presents good anticorrosion properties, however its corrosion resistance is weakened when it is subjected to a medium containing chloride or moisture environment [34,35], with a tendency to suffer localized corrosion (e.g. pitting corrosion). The corrosion may result in the loss of aesthetic appearance and structural integrity [36], and can be accompanied by the release of potentially toxic ions, which can be reduced by protective coatings [37–39]. Furthermore, the corrosion of stainless steel welds and joints occurs in the transpassive potential region in highly oxidizing environments of many industrial processes, especially in sulfuric acid media releasing Cr(VI) ions [40]. To resolve all these problems, the application of hybrid coatings has been increasingly investigated in the last years [38,41–43].

Sol–gel coatings were prepared from hydrolysis and condensation of 3-glycidoxypropyl-trimethoxysilane (GPTMS) as the precursor and bisphenol A (BPA) as the cross-linking agent in acid catalyzed condition. The effect of the drying method as an effective parameter on the microscopic features and morphology of the silane hybrid coating was examined using Fourier transform infrared spectroscopy (FTIR). In order to study the corrosion protection efficiency, the coated and uncoated steel samples were investigated using potentiodynamic polarization curves, neutral salt spray tests and electrochemical impedance spectroscopy. In addition, scanning electron microscopy (SEM) analysis was performed to visualize the surface.

The results show that pre-treatments based on silane hybrid solutions present improved corrosion resistance for the 316L substrates. Furthermore, the methodology proposed in this work is simple to apply and it is compatible with actual environmental concerns.

2. Experimental

2.1. Materials

All chemicals and reagents used were purchased from Merck, including 3-glicidoxypropyl-trimethoxysilane (GPTMS), bisphenol A (BPA), hydrochloric acid, sodium chloride and 1-methylimidazol (MI).

2.2. Preparation of the sol

The sol was prepared by adding stoichiometric amounts of the silane precursor (GPTMS) and the organic cross-linking agent (BPA) into HCl-acidified water (pH = 2). The H_2O/Si molar ratio was chosen to be 0.5, relying on results of a previous study [26]. The solution was stirred at ambient temperature for 80 min at a rate of 240 rpm. Then MI was added to accelerate the condensation reaction after hydrolysis. The MI/Si molar ratio was 0.01. The solution was stirred again for 10 min at ambient temperature. The result was a clear and colourless homogenous solution.

2.3. Substrate preparation and coating deposition

The substrate material used for the present investigation was 316L stainless steel alloy, purchased from Watrin-sprl CO. Plates (7 cm × 15 cm × 0.1 cm) were used for the salt spray tests, while coupons (4.98 cm^2 area and 0.1 cm thickness) were used for all other experiments. The substrates were initially degreased with detergent and then polished with 600 and 1200 grit sand papers. The polished samples were rinsed with distilled water and degreased with 1 M NaOH solution at 50 °C. Consequently the substrates were neutralized with 0.01 M HCl solution to remove excess of NaOH solution. As a last step, the substrates were cleaned with acetone to remove all dirt and grease and were then air-dried.

The cleaned substrates were dipped into the sol for a duration of 5–10 s. In order to study the effect of drying method on the microscopic features and morphology of the hybrid coatings, a series of the silane-treated substrates was dried at the ambient temperature for 2 weeks, denoted as air dried silica hybrid coating (A-SHC), while another series was dried at ambient temperature for 24 h and placed in a furnace to cure at temperatures ranging from ambient (25 °C) to 130 °C for 90 min to extensively crosslink the silane films. This series of the coatings is denoted as thermal cured silica hybrid coating (T-SHC).

2.4. Characterization techniques

2.4.1. FTIR measurements

FTIR measurements were carried out using a Bio-Rad 575C spectrophotometer in the mid-IR range from 4000 to 400 cm^{-1}. All spectra were obtained at an incident angle of 45° normal to the surface of the specimen, with a spectral resolution of 4 cm^{-1}. For each measurement 64 scans were collected.

2.4.2. Scanning electron microscopy

Scanning electron microscopy (SEM) measurements were performed on the surface of coated substrates to characterize the surface morphology with a XL30 SEM microscope. Secondary and backscattered electron images were collected at 15 kV.

2.5. Corrosion tests

2.5.1. Anodic and cathodic polarization tests

Anodic and cathodic polarization tests were carried out on 316L stainless steel substrates with and without the silane treatments at 25 °C in a neutral 3.5% NaCl solution. Prior to the measurements, in order to reach a steady potential, the silane treated samples were kept in the working solution for at least 3 h. An Ag/AgCl electrode and a platinum mesh were used as the reference and counter electrodes, respectively. The potentiodynamic measurements were taken within the range of −1500 to 1000 mV versus Ag/AgCl at a rate of 1 mV/s.