



Electrochemical and chemical characterization of electrodeposited zinc surface exposed to new surface treatments



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ABSTRACT

A new environmentally friendly passivation treatment for electrogalvanized steel has been investigated in this study. The passivation treatments consisted of immersion in solutions containing hexahydrated cerium nitrate and organic additive. The effect of citric acid as an additive into the treatment solution has also been evaluated. For comparison reasons, the electrogalvanized steel was passivated in a commercial chromating and the corrosion performance of the new treatments compared to this last one. The effect of the proposed treatments on the corrosion resistance of the surface was investigated by electrochemical impedance spectroscopy (EIS) in sodium chloride solution. The morphology of the treated surface was investigated by field emission gun scanning electron microscopy (SEM-FEG). The treated surfaces were chemically characterized by X-ray Photoelectron Spectroscopy (XPS). The electrochemical results showed higher impedances along the time of exposure to the electrolyte for one of the new proposed treatments compared to the surface passivated in the chromating solution. XPS results suggested that the new treatments resulted in the formation of an organic film on the electrogalvanized steel surface. The cerium ions showed a synergistic effect with the organic film formed resulting in long-term protection of the metallic substrate in the corrosive electrolyte. The layer formed apparently acted as anchoring sites for inhibiting corrosion products leading to prolonged protection of the surface film formed.

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1. Introduction

Conversion coatings prepared by immersion in solutions containing salts of rare earths such as Ce, La, Pr, Nb and Y have been shown as one of the promising alternatives to toxic chromate conversion coating on various metals and alloys for provide exceptional resistance to localized corrosion through the formation of insoluble hydroxide/oxide layers [1–4]. One of the most investigated rare-earth (RE) for corrosion protection has been cerium and it has been applied on zinc and galvanized steels [5]. Rare-earth-based conversion coatings present some important advantages such as competitive price, low environmental impact, excellent corrosion resistance and compatibility with a wide range of inorganic and organic interfaces [6–8].

The pioneering studies in the field are those of Hinton [1]. Those works report the use of cerium chloride for corrosion inhibition on zinc and propose a cathodic mechanism to explain the formation of the RE oxide coating. According to that mechanism, the cathodic reactions generate an alkaline environment that leads to localized precipitation of RE oxides and thus to the formation of the surface coating.

Montemor et al. [8] complemented the mechanism with the view of a two-stage growth process with the formation of the conversion layer involving an oxidation process of Ce(III) to Ce(IV).

Recent studies have shown that layers with organometallic bonds obtained by treatments in solutions of carboxylic acids present significant corrosion resistance [6,9–14]. The inhibition of corrosion by carboxylic acid is due to the formation of a chemisorbed film on the steel surface, revealed by presence of a protective surface layer over the metal exposed to organics acid or when it is associated with the rare-earth salts [6,9].

Among the most investigated compounds used as potential replacements for hexavalent chromium conversion there are the oxyanions such as tungstates [15], molybdates [16], silicates [17–19], silanes [20, 21], and trivalent chromium [22–25]. However, the methods of preparation and the corrosion resistance associated to these coatings are not clear and their practical usage is still uncertain.

Surface films containing cerium might be produced by immersion in cerium salts solutions [26–31], electrodeposition from solutions with cerium ions [11,32–34], or by sol-gel processes [26,27].

Since the first studies carried out by Hinton [1,35] to investigate the effect of surface treatments with cerium compounds until now, the protection mechanisms propose the oxidation of trivalent cerium to tetravalent cerium [5,8,28].

According to Aldykiewicz Jr [36], oxygen acts as the oxidant agent that is consumed at the electrode vicinity. The cathodic reactions result

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in local pH increase leading to rare earth oxide/hydroxide precipitation and formation of a protective layer on the surface.

Aramaki [37] proposed a modification in the Ce₂O₃ film by introducing H₂O₂ as oxidant agent. The surface treatment was carried out in two steps. The first step consisted of immersion in a 10⁻³ mol/L Ce(NO₃)₃ solution at 30 °C for 30 min, and the second comprised exposure to a 10⁻² mol/L H₂O₂ solution. The results showed that the surface layer formed was highly resistant to 0.5 mol/L NaCl solution. XPS analysis of the surface showed a thin film (thickness inferior to 50 nm) with few quantities of Ce⁴⁺ due to the oxidation of Ce³⁺ supported by H₂O₂. The presence of Ce⁴⁺ together with Ce³⁺ in the film was further investigated by Aramaki [38].

Scholes [39] investigated the role of H₂O₂ in the surface treatments with cerium and showed that complexes such as Ce(H₂O₂)³⁺ are initially formed and this is followed by deprotonation, oxidation and precipitation processes, leading to Ce(IV)(O₂)(OH)₂ formation. They found a dependence on the peroxide content and the Ce(IV)(O₂)(OH)₂ crystal size. The crystal size decreased as the peroxide concentration increased.

Hamlaoui and Pedraza [12] investigated the effect of polyethylene glycol (PEG) on the composition and morphology of the cerium oxide film deposited on electrogalvanized steel. They found that the addition of PEG in the cerium nitrate solution decreased the cracks in the film and consequently hindered the hydrogen evolution reaction and the dissolution of the metallic substrate. The addition of organic compounds to cerium containing solutions has been investigated and it has been associated to an even surface where the defects in the conversion film were shielded.

In the present study, the effect of new surface treatments in solutions containing cerium nitrate and an organic compound, specifically 2 butyne-1,4 diol propoxylate, on the corrosion resistance of electrogalvanized steel has been investigated. The influence of citric acid as additive in the treatment solution has also been evaluated. The corrosion resistance of the surfaces after the treatments was compared with that of a surface passivated in hexavalent chromium containing solution.

2. Experimental

2.1. Samples preparation

AISI 1010 steel sheets (100 mm × 65 mm × 1 mm) were electrogalvanized using a cyanide-free alkaline bath containing Zn²⁺ (12.5 g/L), KOH (170 g/L), K₂CO₃ (50 g/L), additive (10 mL/L), brightening agents (1 mL/L), conditioner (10 mL/L). The following conditions were used: temperature (22 ± 2) °C and current density of 2 A/dm² for 45 min.

Prior to zinc electrodeposition, all the steel plates were degreased in a sodium silicate-based alkaline solution, at room temperature applying a current density of 2 A/dm² for 2 min for improving the surface wettability. The samples were rinsed in deionized water, activated in ammonia bifluoride 5% solution for 30 s, and rinsed again with deionized water.

Immediately after electrogalvanizing, the samples surface was activated in HNO₃ 1% solution (pH 1), for 10 s, and then, rinsed with deionized water. Subsequently, some of the electrogalvanized samples were passivated of the following conversion treatments: (i) immersion for 1, 3, 5, 7, and 9 min in the solution with cerium nitrate and 2-butyn-1,4 diol propoxylate. The solution composed of 0.04 mol·L⁻¹ NaNO₃, 0.04 mol·L⁻¹ Na₂SO₄, 0.04 mol·L⁻¹ of 2-butyn-1,4 diol propoxylate (organic additive) and 0.04 mol·L⁻¹ of Ce(NO₃)₃·6H₂O, (pH = 2.85); (ii) immersion for 1, 3, 5, 7, and 9 min in the previous solution modified by the addition of 0.05 mol·L⁻¹ of citric acid (pH = 1.73); (iii) immersion for 30 s in a commercial chromating solution with 2 g/L of Na₂CrO₇, sodium chloride as a conductive salt and diluted HCl solution for pH adjustment = 1.8. After the treatments, the treated surfaces were rinsed in distilled water and dried in an oven at 80 °C for 15 min (Table 1).

These treatments were exposed to the salt spray test for selection of the best results for electrochemical evaluation.

Table 1
Description of the surfaces evaluated in the present investigation.

Surfaces	Description
Zn	Electrogalvanized steel sheet without passivation
CeG5	Electrogalvanized steel passivated in solution containing cerium ions and organic additive (pH = 2.85) during 5 min with mechanical stirring.
CeG7	Electrogalvanized steel passivated in solution containing cerium ions and organic additive (pH = 2.85) during 7 min with mechanical stirring.
CeCiG5	Electrogalvanized steel passivated in solution containing cerium ions, organic additive and citric acid (pH = 1.73) during 5 min with mechanical stirring.
CeCiG7	Electrogalvanized steel passivated in solution containing cerium ions, organic additive and citric acid (pH = 1.73) during 7 min with mechanical stirring.
Cr VI	Zinc layer passivated in chromating solution with hexavalent chromium (pH 1.8) during 30 s with mechanical stirring.

Electrogalvanized samples without passivation treatment were also tested for comparison reasons.

2.2. Chemical and morphology analysis

Morphology evaluation of the surfaces after the passivation treatments investigated was carried out by Scanning Electron Microscope (LEO 1450VP SEM) using scattered electron detector and Scanning Electron Microscopy-Field Emission Gun (JEOL JSM-6330F FEG-SEM) with a Si detector and 20 keV energy.

The chemical composition of the surface after treatments was evaluated by X-ray Photoelectron Spectroscopy (XPS) carried out using a spectrometer Thermofisher Scientific Theta Probe. The XPS spectra acquired used X-ray source with monochromator Al K α ($h\nu = 1486.6$ eV). The analysis with X-ray spot radius of 300 μ m and high-resolution spectra were acquired at 50 eV for passage of the species of interest, such as carbon and cerium. The other spectra were acquired with steps of 30 eV, the case of carbon, zinc and oxygen. The values used for adjustments of C 1s elements, O 1s, Ce 3d and Zn 2p will be shown for comparison.

XPS analyses were performed at three different points (spots) per sample and the spectra are representative of surface discarding local variations. Quantitative surface chemical analyses were calculated from the high resolution core level spectra following the removal of a non-linear Shirley background.

2.3. Electrochemical behavior

The experimental set up used consisted of a three electrodes cell arrangement with an Ag/AgCl, KCl saturated electrode and a platinum wire used as reference and counter electrodes respectively. The working electrode was the samples with the various surface treatments tested exposing an area of 1 cm² to the electrolyte. The electrolyte used in the electrochemical tests was a 0.1 mol·L⁻¹ NaCl solution, quiescent and naturally aerated at (22 ± 3) °C. The evolution of the electrochemical behavior of the surfaces tested was monitored by electrochemical impedance spectroscopy (EIS) tests carried out in the frequency range from 100 kHz to 10 mHz, with a signal amplitude perturbation of 10 mV (rms), and data acquisition rate of 10 points per decade. EIS data was acquired in the potentiostatic mode at the open circuit potential (OCP), using a Gamry potentiostat controlled by Gamry Instruments software.

To evaluate the reproducibility and the reliability of the results, at least three tests were carried out for each condition tested.

The identification symbol and description of the investigated samples are summarized in Table 1.

3. Results and discussions

The researchers used 1, 3, 5, 7, and 9 min and selected the treatments that passed ASTM B117 salt spray test (168 h in the salt spray test) and selected the treatment times corresponding to 5 min and 7 min for electrochemical evaluation.

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