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Effects of ceria nanoparticle concentrations on the morphology and corrosion resistance of cerium–silane hybrid coatings on electro-galvanized steel substrates

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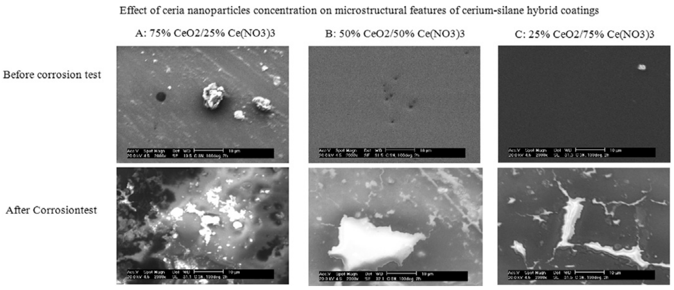
HIGHLIGHTS

- We investigate the effect of ceria content on corrosion resistance of silane coating.
- Microscopic images explain longer durability of the coating contain the lowest ceria.
- The EIS results confirm the lower ceria content results in better barrier properties.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigates the effect of the ceria nanoparticle concentration on the morphology and electrochemical behavior of cerium–silane hybrid coatings deposited on electro-galvanized steel substrates. The substrates were pre-treated with 3-glycidoxypropyl-trimethoxysilane and bisphenol A, modified with cerium ion-activated CeO_2 nanoparticles. The morphology of the coating before and after corrosion tests was examined using atomic force microscopy and scanning electron microscopy. The results indicate the formation of nanostructured surfaces with relatively uniform thicknesses and nanoparticle distribution. Microscopic observations explain the increased durability of the silane coating doped with the lowest content of activated ceria nanoparticles after short-term corrosion tests (456 h). The corrosion behavior of the sol–gel coatings was also investigated using natural salt spray tests, electrochemical impedance spectroscopy, and potentiodynamic polarization tests. The results show that the concentration of nanoparticles has a significant impact on the barrier properties of the silane films, which are improved for films with lower nanoparticle contents.

1. Introduction

Electroplated zinc coatings are employed as active galvanic protection for steel. However, zinc is highly reactive, and high corrosion rates of this coating are observed when exposed, both indoors and out. Therefore, a post-treatment is required to increase the lifetime of zinc coatings [1]. In current industrial practice, particularly in the automotive industry, this treatment consists of immersion in a chemical bath containing hexavalent chromium salts, forming an anti-corrosive layer over plated zinc. However, this type of anti-corrosive system presents a serious drawback due to the high toxicity of hexavalent chromium salts [2]. As a

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consequence, the European Community decided to ban the use of Cr(VI) in the car industry from July 1st 2007 on, to avoid environmental contamination either during the processing, use or recycling of coated sheets [3].

The need to replace the chromate-based surface treatments promoted the investigation of several classes of new pre-treatment systems. Among these, pre-treatments based on organosilanes attracted considerable interest, as they provide the formation of a thin organic coating that confers surface functionalization [4,5]. The silane pre-treatment creates a dense, oxygen-rich coating that generates a protective physical barrier [5]. The major drawback of silane pre-treatments is their inert character with respect to corrosion. The silane coating alone does not provide any active protection when aggressive species reach the metallic surface and initiate corrosion [4,6,7].

To overcome this limitation, a new challenge is to modify the bulk properties of silane coatings by adding “active” anti-corrosion species. These modifications should further improve the corrosion resistance of the layer, or introduce a self-healing capability in the silane coating [4,8,9].

Among the most effective anti-corrosion species, rare-earth salts offer good corrosion inhibition properties in addition to environmental friendliness [10]. Cerium nitrate has been successfully tested for corrosion protection of galvanized steel substrates, either as a conversion film [11–13] or as a corrosion inhibitor through addition to the silane formulation [10,14–16]. The results revealed improved corrosion protection of galvanized steel substrates.

Another approach to improve the corrosion protection of silane coatings is based on the addition of oxide nanoparticles. Van Ooij et al. [17] reported that bis-sulfur silane films could be thickened and strengthened by loading them with silica particles. However, when the bis-sulfur silane film was heavily modified with silica, it tended to form a porous film, which promoted electrolyte intrusion and premature film delamination.

Montemor et al. [8,18] reported a new approach, consisting of the modification of bis {triethoxysilylpropyl} tetrasulfide silane (BTESPT) with nanoparticles, such as CeO_2, SiO_2 or CeO_2–ZrO_2. In some cases, to obtain a synergistic effect and improved corrosion resistance, the nanoparticles were initially activated with cerium nitrate. Results demonstrated that the ceria nanoparticles are a very effective filler, leading to both improved barrier properties of the silane coatings and improved corrosion resistance. Furthermore, the protective behavior depends on the concentration of nanoparticles, and the activation of the nanoparticles with cerium ions leads to the formation of thicker and more protective silane films.

A number of studies have examined the effect of cerium nitrate concentration on the properties of coatings [6,14,19,20]. However, information concerning the influence of the CeO_2 nanoparticle concentration on the morphology, microstructure, and anti-corrosion performance is still limited in the literature, and hence requires further investigation.

Our previous work [15] has reported and discussed the anti-corrosion behavior of 3-glycidoxypropyltrimethoxy silane (GPTMS) modified with CeO_2 nanoparticles. The nanoparticles were activated with cerium nitrate to improve the corrosion resistance of the galvanized steel substrates. Based on the corrosion test results, the effect of the nanoparticles on the barrier properties of the silane films immersed in NaCl solution are ranked as follows: $CeO_2+Ce(NO_3)_3 > Ce\ (NO_3)_3 > CeO_2 >$ blank silane film. These results demonstrate that the cerium activated nanoparticles strongly improve the barrier properties of the silane coatings, and present a better anti-corrosion performance when compared with other coatings.

The objective of this work was to investigate the effect of the CeO_2 nanoparticle concentration on the morphology, microstructure, and anti-corrosion performance of the silane coatings modified with activated CeO_2 nanoparticles on an electro-galvanized steel substrate. The morphological and microstructural features of the coated substrates were evaluated before and after corrosion tests using atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. The corrosion behavior of the sol–gel coatings was investigated using natural salt spray tests, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization tests.

2. Experimental procedure

2.1. Sample preparation

Ceria nanoparticles (10 wt% in water, particle size <25 nm, Sigma Aldrich, St. Louis, USA) were activated by ultrasonic dispersion in an aqueous solution of cerium nitrate (Fluka, Buchs, Switzerland). Three sets of aqueous solutions with different molar ratios of $CeO_2/Ce(NO_3)_3$ were prepared, which were then used to prepare the silane solutions marked as (A), (B), and (C) (Table 1).

The silane solution was prepared by adding 4.084 mL of 3-glycidoxypropyl-trimethoxy silane or GPTMS (Merck, New Jersey, USA) to 0.5 mL of HCl-acidified water (pH = 2) (H_2O/Si mole ratio = 0.5 [21]). The solution was placed in a sealed beaker and stirred at room temperature for 20 min at a rate of 240 rpm to hydrolyze and condensate the silane precursors. The aqueous dispersion of ceria nanoparticles was added at the end of this synthesis step, followed by stirring for 10 min. The total Ce/Si mole ratio was 0.05 [14]. In the next step, 2.111 g of bisphenol A (BPA) (Merck) was added to the solution as a cross-linking agent (BPA/Si mole ratio = 0.5). The latter has been shown to realize a significant effect on the morphology and improvement of the corrosion resistance of coatings [22]. The BPA was dissolved by mixing the solution for 80 min. To accelerate the condensation reaction, 0.0152 mL of 1-methylimidazol (MI) (Merck) (MI/Si mole ratio = 0.01) was added to the solution, which was followed by stirring for 5 min. The result was a clear, colorless, homogenous solution.

The metallic substrate consisted of electro-galvanized steel coupons (4.98 cm^2 area and 0.1 cm thickness for the AFM, SEM, and electrochemical tests) and plates (7 × 15 × 0.1 cm for the salt spray tests). The zinc coating had a weight of approximately 112 g m^{-2}, and a thickness of approximately 8 μm. The galvanized steel specimens were degreased using an alkaline cleaner. After cleaning, the substrates were washed with distilled water, dried in air, and immersed in the silane solution for 60 s. The coated specimens were dried at room temperature for 24 h, and subsequently submitted to a 25–130 °C curing process for 90 min, to initiate extensive cross-linking in the hybrid films [23]. The coating thickness was measured by profilometry (Check line 3000 pro, Germany). A schematic flow chart diagram of the synthesis of Ce-modified silane coatings is shown in Fig. 1.

Table 1
Molar ratio (mol%) of CeO_2 nanoparticles and cerium nitrate in the aqueous dispersion of activated ceria nanoparticles.

Set	Molar ratio (mol%)	
	CeO_2 nanoparticles	$Ce\ (NO_3)_3 \cdot 6H_2O$
A	0.0375	0.0125
B	0.0250	0.0250
C	0.0125	0.0375