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Effect of inhibition synergism of zinc chloride and 2-mercaptobenzoxzole on protective performance of an ecofriendly silane coating on mild steel

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ABSTRACT

This work aims to study the impact of zinc cation and 2-mercaptobenzoxzole (MBO) on the corrosion protection of a silane sol-gel coating on mild steel. First, effectiveness of the organic and inorganic inhibitors on the corrosion of bare mild steel in a NaCl solution was shown to be linked to formation of a surface film. Using electrochemical data as well as results of surface analysis, a sharp inhibition synergism was found when an equal mole percentage of $ZnCl_2$ and MBO was added to the NaCl solution. Finally, electrochemical data indicated superior performance of the coating with the combination of inhibitors.

Introduction

The silane sol-gel coatings, widely used as adhesion promoters, have been shown to enhance the corrosion resistance of metallic substrates [1–5]. However, the coatings reveal no active protection as the aggressive species access the substrate surface [6–10]. Addition of corrosion inhibitors to the sol-gel coating formulation has been reported as one of the most effective strategies to overcome the problem [11–16]. According to the literature, the use of inorganic inhibitors such as phosphates, vanadates and rare earth elements is a common way to improve the protective performance of hybrid coatings on aluminum alloys [17]. Palanivel et al. [18] showed that silane coatings with cerium nitrate, which provides corrosion protection to AA 2024-T3, are able to show self-healing properties.

The optimum concentration of cerium nitrate in the formulation of an eco-friendly silane sol-gel coating on pure Al was determined by Naderi et al. [19]. The enhanced corrosion protection in the presence of cerium component was suggested to be arised from deposition of an insoluble film on the cathodic sites. According to Zanotto et al. [20], the role of cerium ions in improvement of the protective performance of 3-mercapto-propyltrimethoxysilane film on AZ31 magnesium alloy was linked to lower porosity and defect and to self-healing ability. She et al. [21] showed that potassium permanganate can prolong the lifetime of silane films on AZ91D magnesium alloy through healing damages by formation of manganese oxide/hydroxide. Cerium nitrate was indicated to be more effective than zirconium nitrate on the corrosion protection of bis-[triethoxysilylpropyl] tetrasulfidesilane on galvanized steel, due to the accumulation of cerium dopant in the inner layers of the silane film [22]. Wang and Akid [23] showed that the release of encapsulated cerium inhibitor at defects of tetraethoxysilane (TEOS) coating on mild steel, which controls the cathodic reaction by precipitation of cerium hydroxide, can provide a long-term protection.

In addition to inorganic compounds, organic inhibitors have been also reported to enhance the protective performance of silane coatings [17]. Palanivel et al. [18] indicated that although addition of tolyltriazole to a water-based organofunctional silane coating could increase the corrosion resistance of AA2024-T3 alloy in 0.5 M NaCl solution, no self-healing effect was detected. 8-hydroxyquinolineas-doped silane coating composed of tetramethoxysilane (TMOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) was also reported to control the corrosion of AA2024-T3 in 0.005 M NaCl solution [24]. In this regard, the effective role of 8-hydroxyquinolineas in improvement of the resistance of the silane coating and the oxide film was shown. A protective silane film formulated with GPTMS and TEOS precursors on AA2024-T3 was shown to present desirable

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self-healing properties when 2-mercaptobenzothiazole and 2-mercaptobenzimidazole corrosion inhibitors are incorporated [14].

The present study intends to evaluate the effect of zinc chloride ($ZnCl_2$) and 2-mercaptobenzoxzole (MBO) on the protective performance of a water-based silane coating on mild steel. To top it off, it is aimed to examine the inhibition synergism of the organic and inorganic compounds in the hybrid coating composed of γ-glycidoxypropyltrimethoxysilane (γ-GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES). It is well-known that organic inhibitors with N, O and S heteroatoms increase the corrosion resistance of mild steel in acidic environment but they might reveal no significant inhibition in neutralized pHs [25]. However, the organic inhibitors have been reported to show a synergetic behavior in combination with some metal cations [26,27]. To provide an insight into the inhibition mechanism, the corrosion behavior of mild steel in the sodium chloride solutions with the organic and inorganic inhibitors was monitored through taking advantage of electrochemical methods and surface analysis.

Experimental

Materials

Mild steel panels with the chemical composition (wt.%: Fe: 97.7, C: 0.19, Si: 0.415, Mn: 1.39, P: <0.005, S: <0.005, Cr: 0.026, Mo: 0.018, Co: 0.0559, Cu: 0.0429, Nb: 0.0481) were cut down to dimensions of 3 cm × 6 cm. The specimen surface was abraded with abrasive papers, 400, 600, 800 and 1000 grit size, and degreased with acetone. In the next step, alkaline surface treatment was performed in 25 g/l NaOH solution at 55 °C for 7 min to facilitate an interaction between the metal surface and hydrolyzed silane molecules. The samples were then rinsed in distilled water and blow-dried with compressed air. The silane precursors in this research were tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and γ-glycidoxypropyltrimethoxysilane (γ-GPS), which were purchased from Aldrich. The coating solution was composed of 10% (w/w) of the silane mixture (TEOS/γ-GPS/MTES = 1/1/1 weight ratio) in DI water at pH = 3 adjusted by addition of acetic acid. Then, $ZnCl_2$ and MBO corrosion inhibitors, which were supplied by Merck, were added to the silane solutions. The mixture was magnetically stirred at a rate of 1000 rpm for 24 h at ambient temperature. The coating application was performed through immersion of the surface activated panel in the silane solution for 2 min. The coated sample was finally put in an oven at 150 °C for 30 min.

Methods

A three electrode cell including Ag/AgCl reference electrode, graphite counter electrode and the working electrode with an exposure area of 1.0 cm^2 was connected to the terminals of an IviumCompactstat instrument to perform EIS measurements. The impedance spectra were obtained within the frequency range of 10 kHz–10 mHz at open circuit potential (OCP) with 10 mV perturbations. The EIS tests for silanized plates were performed after 2, 4 and 6 h of immersion in 0.1 M NaCl solution. In solution phase study, EIS measurements were carried out on bare metals, which were immersed in 0.1 M NaCl solutions with different concentrations of $ZnCl_2$ and MBO. ZSimpwin software was used to analyze the impedance spectra. The polarization measurements were performed on bare mild steels after 4 h of immersion in 0.1 M NaCl solutions without and with the optimum concentration of inhibitors. Moreover, the test was also carried out on steel samples coated by silane without and with $ZnCl_2$/MBO corrosion inhibitor after 4 h of exposure to 0.1 M sodium chloride solution. The polarization curves were obtained at a scan rate of 1 mV/s from −250 mV to +250 mV of OCP by Autolab instrument model PGstat 302N. In addition to the working electrode with an exposure area of 1.0 cm^2, a platinum counter electrode and a saturated Ag/AgCl reference electrode were used for the polarization test.

The surface analysis of the bare metals after 4 h of immersion in the inhibited and uninhibited solutions was performed using AFM model Veeco operating in non-contact mode, FESEM/EDX model ZEISS σIGMA VP and Specs EA 10 Plus XPS equipped with a concentric hemispherical analyzer (CHA). An Al Kα radiation source at a pressure of 10^{-9} mbar was used in the XPS analysis chamber. The shift of binding energies (BE) was calibrated with respect to the reference peak of C 1s at binding energy of 285 eV. In the case of coated samples, a FESEM model ZEISS σIGMA VP was employed to study the effect of inhibitors on the film thickness and surface morphology. To measure the contact angle of water droplets (4 μl) on the surface of silane films without and with inhibitors, an OCA 15 contact angle tool was employed.

Results and discussion

Bare metal

The effect of concentration of $ZnCl_2$ and MBO on the impedance spectra of bare mild steels in 0.1 M NaCl solution is illustrated in Fig. 1.

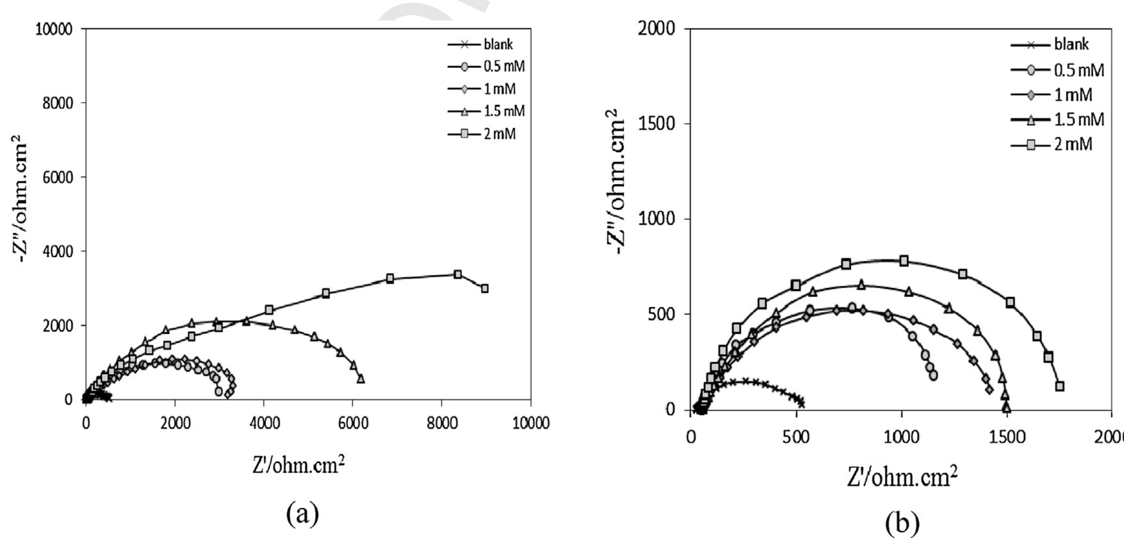

Fig. 1. AC impedance spectra of mild steel plates after 4 h of exposure to the NaCl solutions containing (a) $ZnCl_2$ and (b) MBO.

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