The effect of zinc cation on the anticorrosion behavior of an eco-friendly silane sol–gel coating applied on mild steel

S. Alinejad [a], R. Naderi [a,*], M. Mahdavian [b]

[a] School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran
[b] Surface Coatings and Corrosion Department, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

A B S T R A C T

To provide active protection of mild steel, an eco-friendly silane sol-gel coating with $ZnCl_2$ as zinc cation source was used. The optimal concentration of zinc cation was found using electrochemical impedance spectroscopy (EIS) and surface analysis. Evaluation of EIS data indicated that the superiority of doped-silane is mainly attributed to the corrosion inhibitive function of zinc cation at interface. Zinc cation showed no effect on the thickness and hydrophobicity of coatings which were evaluated by FESEM and water contact angle, indicating no influence on condensation reactions. Using electrochemical techniques and surface analysis, an insight into the zinc cation inhibition mechanism was obtained in the absence of silane coating. In the presence of zinc cation, FESEM/EDS indicated precipitation of a layer composed of zinc hydroxide and/or oxide on the mild steel surface.

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1. Introduction

It is frequently reported that silane sol-gel coatings functioning as adhesion promoters can increase corrosion resistance of metallic substrates [1–5]. However, the sol-gel films could not provide active protection when the aggressive species penetrate to the metal surface [6–10]. In other words, crosslinking of silanol groups during the curing process leads to the formation of a siloxane network, ensuring an effective temporary barrier against water and oxygen diffusion to the coating/metal interface. Hence, many efforts have been made to enhance protective performance of silane coatings [11–16]. According to the literature, one of the effective approaches is to incorporate corrosion inhibitors into the sol-gel coatings. For instance, the use of inorganic inhibitors, such as phosphates, vanadates and rare earth elements, and organic molecules, such as triazole and thiazole derivatives has been frequently reported to enhance the protective performance of hybrid coatings on aluminum alloys [17]. Palanivel et al. [18] suggested the incorporation of organic inhibitors, tolyltriazole and benzotriazole, and an inorganic cerium salt into a hybrid silane coating as an effective approach to enhance the corrosion resistance of AA2024-T3 in a sodium chloride solution. Moreover, an examination on the scratched silane film revealed its self-healing ability. The corrosion of AA2024-T3 in 0.005 M NaCl solution was also reported to be controlled by the application of 8-hydroxyquinolineas-doped silane coating composed of tetramethoxysilane (TMOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) [19]. The behavior was connected to the role of inhibitor in enhancement of the resistance of the hybrid coating and the oxide film. Naderi et al. [20] determined the optimum concentration of cerium nitrate in the formulation of an eco-friendly silane sol-gel coating applied on pure Al. In the presence of cerium component, the enhanced corrosion protection was suggested to be associated with the deposition of an insoluble film on the cathodic sites. Zanotto et al. [21] indicated that the Ce^{3+} ions can improve the corrosion protection of 3-mercapto-propyltrimethoxysilane coating formed on AZ31 magnesium alloy in a sodium chloride solution through decreasing film porosity and developing self-healing ability. Potassium permanganate ($KMnO_4$) was also introduced as a promising inhibitor healing a damaged hybrid silane coating on AZ91D magnesium alloy by formation of manganese oxide/hydroxide when corrosion happened [22]. In the case of bis-[triethoxysilylpropyl] tetrasulfide silane pretreatment on galvanised steel, Trabelsi et al. [23] compared the inhibitive function of cerium nitrate and zirconium nitrate. They found that the accumulation of cerium mainly in the inner layers of the silane coating may make the dopant more efficient than zirconium releasing during exposure to the electrolyte. As an environmentally-friendly alternative for toxic pretreatments based on chromium, Wang and Akid [24] introduced a tetraethoxysilane coating formulated with cerium ions for mild steel substrates.

* Corresponding author.
E-mail address: rezanaderi@ut.ac.ir (R. Naderi).

It was shown that a long-term corrosion protection was provided as a result of the release of the encapsulated rare earth inhibitor at the coating defects limiting the cathodic reaction by deposition of cerium hydroxide. In order to control the mild steel corrosion in a NaCl solution, Lian-Kui Wu et al. [25] electrodeposited a zinc-doped silane coating on the metallic substrates. In addition to the barrier properties of the reticulated silane film, the cathodic protection of the zinc arising from sacrificial dissolution was suggested to make a major contribution to the protective performance of the composite.

After evaluation of the influence of various parameters, such as the sol pH, immersion time in the silane solution, heat treatment, coating composition and nanoparticles [26–28] on the performance of an eco-friendly silane sol-gel film composed of γ-glycidoxypropyltrimethoxysilane (γ-GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) on mild steel, this research intends to determine the optimum concentration of zinc cation as corrosion inhibitor in the coating formulation. The protective behavior of the inhibitor doped coatings was studied using electrochemical methods as well as surface analysis. Through taking advantage of electrochemical impedance spectroscopy (EIS), polarization curves, field emission scanning electron microscopy-energy dispersive spectroscopy (FESEM/EDS) and atomic force microscopy (AFM), it was tried to obtain an insight into the inhibitive function of zinc cation in the solution phase.

2. Experimental

2.1. 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 abraded with abrasive papers of 400, 600, 800 and 1000 grit size, and degreased with acetone. The samples were then dipped in 25 g/l NaOH solution at 55 °C for 7 min. After the alkaline surface activation, the samples were rinsed in distilled water and blow-dried with compressed air. The alkaline etching may result in the formation of hydroxyl groups, which are responsible for the interaction between the metal surface and the hydrolyzed silane molecules. The three silane precursors, γ-glycidoxypropyltrimethoxysilane (γ-GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) were products of Aldrich. By dissolving 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, the coating solution was prepared. After addition of different concentrations 0, 0.5, 1, 2 and 4 mM of $ZnCl_2$ (purchased from Merck), the mixture was stirred at ambient temperature for 24 h. The hybrid sol-gel coating was applied by immersion of the pretreated sample in the silane solution for 120 s at ambient temperature. The withdrawal rate was 0.3 m/min. According to some studies on the optimization of the curing conditions of analogous materials [26,29], the samples were put in an oven at 150 °C for 30 min for curing process.

2.2. Methods

In order to perform EIS test, a three electrode cell including the working electrode with an exposure area of 1.0 cm^2, Ag/AgCl (3 M KCl) reference electrode and graphite counter electrode was connected to the terminals of an Ivium Compactstat instrument. The impedance spectra within the frequency range of 10 kHz to 10 mHz were obtained at open circuit potential using a sine wave of 10 mV amplitude peak to peak. In the case of coated samples, EIS tests were carried out after 2, 4 and 6 h of immersion in 0.1 M NaCl solution. To acquire EIS data in solution phase study, bare metals were immersed in 0.1 M NaCl solutions with different concentrations 0, 0.5, 1, 1.5 and 2 mM of $ZnCl_2$. The EIS data was analyzed using ZSimpwin software. The polarization measurements on bare mild steels after 6-h immersion in the test solutions were carried out at a scan rate of 1 mV/s from −250 mV to +250 mV of OCP by Ivium Compactstat instrument. To provide polarization curves, the exposure area was 1.0 cm^2. The 3-electrode cell for polarization test was the same as the one used for EIS measurements.

The surface roughness of the bare samples exposed to the sodium chloride solutions without and with 2 mM $ZnCl_2$ for 6 h was studied using AFM model Veeco operating in non-contact mode. The effect of zinc cation on the surface morphology and thickness of the hybrid sol-gel coating was evaluated employing a FESEM model ZEISS ΣIGMA VP. Moreover, the surface of bare mild steels after 6-h dipping in 0.1 M NaCl solutions without and with 2 mM of the inhibitor, was analyzed using FESEM/EDS. A Perkin-Elmer Spectrum One spectrometer was employed to obtain FTIR spectra of silane coatings incorporated with and without 4 mM of $ZnCl_2$. For this test, the powder sample was prepared through dropping silane solution on a Teflon sheet. After curing at 150C for 30 min, the dried flakes were milled to provide fine powder.

3. Results and discussion

Typical Nyquist and Bode diagrams of mild steel substrates coated by silane sol-gel films with different formulations after 6 h of exposure to 0.1 M NaCl solution is shown in Fig. 1. From the impedance spectra, significant influence of the zinc cation concentration on the anticorrosion performance of silane coatings is observed. According to the values of low frequency impedance ($|Z|_{0.01Hz}$) as the sum of all resistances in the system, the inhibitor concentration providing the most effective protection was 2 mM. In addition to impedance at low frequencies, the phase angle at high frequency (θ_{10kHz}), which can be considered as an indication of the corrosion resistance of system under study [26], revealed that further increase in the inhibitor concentration had a negative effect on the protective performance. From the two parameters, addition of 4 mM of $ZnCl_2$ to the hybrid coating formulation provided the worst protection. The anticorrosion behavior of neat silane was more effective than that of silane film with 4 mM of $ZnCl_2$. Furthermore, the noticeable impact of the inhibitor content on the coating performance was also observed from the diameter of semicircles in the Nyquist diagrams. In the AC impedance spectra, the time constant at high frequencies might be associated with the hybrid film and the response of coating/metal interface can be monitored from low frequency time constant [30].

Due to the presence of two time constants in the plots, the equivalent circuit in Fig. 2 was selected to model EIS data, where R_s, R_f, CPE_f, R_{ct}, and CPE_{dl} represent the solution resistance, film resistance, constant phase element of silane film, charge transfer resistance, and constant phase element of double layer, respectively. A typical impedance diagram fitted with the equivalent circuit is illustrated in Fig. 3. Table 1 shows the evolution of some parameters obtained from modeling of the impedance spectra during 6 h of immersion in the sodium chloride solution. In Table 1, the double layer capacitance was calculated using Eq. 1 [31]:

$$C = (Y_0.R^{1-n})^{1/n} \tag{1}$$

where, Y_0 and n represent the admittance and exponent of constant phase element, respectively.

As a striking feature, the parameters all were significantly affected by the concentration of zinc cation. Moreover, a failure was observed in the performance of systems under study with increasing the immersion time, probably due to increased permeation of the electrolyte as well as progress of underfilm corrosion. To top