Assessment for corrosion resistance of electrodeposited silane films on mild steel by using electrochemical method

Mahmood Peikari[1]*, Sadeq Hooshmand Zaferani[1], Davood Zaarei[2], Iman Danaei[1], Mohmmad Javad Mostowfi Fakhraei[3]

[1]Technical Inspection Engineering Department, Petroleum University of Technology, Abadan, (IRAN)
[2]Technical Faculty, South Tehran Branch, Islamic Azad University, Tehran, (IRAN)
[3]East Oil & Gas Company, Khangiran, (IRAN)
E-mail : mahmoud.peikary@gmail.com

ABSTRACT

In this paper corrosion resistance of electrodeposited silane film (γ-glycidoxypropyl-trimethoxysilane (γ –GPS)) on mild steel substrate which prepared with various cathodic currents, was investigated by electrochemical methods. In comparison with conventional "dip-coated" silane films, electrodeposited films at cathodic currents exhibited obviously higher corrosion resistances.   © 2012 Trade Science Inc. - INDIA

INTRODUCTION

Silane films usually provide good adhesion between metal substrate and subsequent polymeric coating, so their main usage in the surface coating is adhesion promoter. In addition, they are environmental friendly; therefore they could be used as a substitute for toxic chromate metal pretreatments[1-4].

Silane films were usually prepared by conventional dip-coating method that is simply dipping metal substrates into pre-hydrolyzed silane/water/alcohol solutions then drying and curing at a certain high temperature. Recently, a new preparation technique, namely electro-assisted deposition, has been developed to facilitate the formation of sol–gel films on conductive substrates[5].
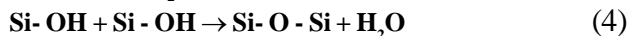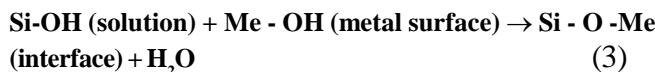
Woo, et al.[6], firstly, reported the electrodeposition of silane films but its purpose was to improve the adhesive performance. Lately et al[7] and Gandhi[8] applied this technique as an anti-corrosion treatment for metals and the results showed that silane films prepared at a certain cathodic potential present higher corrosion resistance than those obtained by conventional dip-coating method[9].

In electro-assisted deposition of silane particles, the main reactions, occurs at cathodicpotentials, are the reduction of oxygen and water as eq. (1) and (2)[10].

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (1)$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$
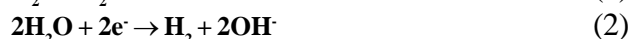
Both reactions produce OH^- ions near the metallic electrode surface. It was generally accepted that, hydroxyl ions OH^- could catalyze the reactions between silanol and metal as equations (3). Eq (4) shows the condensation reaction between silanol groups beneath the formation of silane films[10].

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Si-OH (solution) + Me - OH (metal surface) → Si - O -Me

(interface) + H₂O   (3)

Si- OH + Si - OH → Si- O - Si + H₂O   (4)

In eqs. (3) and (4), the silanol groups (Si - OH) come from the hydrolyze of silane agents. The catalysis of OH⁻ might be one of the reasons for higher uniformity of silane films prepared at cathodic potentials (more negative than corrosion potential)[10].

In this work, γ-glycidoxypropyl-trimethoxysilane (γ –GPS) was applied on steel substrate by electro- deposition process and the effect of various cathodic currents on film preparation has been investigated.

EXPERIMENTAL

Mild steel rods (with area 0.81cm²) with composition of (C: 0.16, Si: 0.23, Mn: 0.35, P: 0.03, S: 0.02, Fe: Balanced) embedded with epoxy/polymide resin were used as electrode samples. After polishing, the rods were thoroughly rinsed with acetone. After that the rods were washed with surfactant-based low alkaline cleaner, washed with deionized (DI) water and then being blow-dried with warm air. Silane monomer was γ-glycidoxypropyl-trimethoxysilane (γ –GPS) were purchased from Sigma Aldrich Co (Germany). The electrodeposition solutions used here consist of 5vol. % silane monomer dissolved in 90:10 volume ratio of ethanol/ DI water with adjusted pH in 4.5 by acetic acid. The electrodeposition process was performed by using three-electrode compartment. A saturated Ag/AgCl electrode was employed as reference electrode, and a platinum plate used as counter electrode. Apart from at the open- circuit potential (OCP), -0.65 V/SCE for these alloys in each silane solution, the electrodeposition process was mainly carried out at various cathodic currents (-0.03, -0.05,-0.07,-0.1A) for 1200 s. After that, samples were taken out from the solution and blow-dried. Finally, the silane films were oven cured at 100 °C for 15 min. For Tafel tests the scan rate was 0.5mV and for EIS tests, the measured frequency was from 100 kHz to 0.01 Hz, with AC excitation amplitude of 5 mV. The used electrolyte was 3.5 wt. % NaCl solution prepared by DI water. All of the electro deposition processes and electrochemical measurements were conducted using Auto lab PGSTAT 302N Potentiosat/ Galvanostat (Italy).

RESULTS

Polarization

The results of polarization test were shown as Tafel diagrams (Figure 1) and their parameters were calculated and reported as TABLE 1. Figure 1 shows the effect of varied applied cathodic currents on prepared film. The corrosion current density (i_{corr}) was determined through superimposing a straight line along the linear portion of the anodic curve and extrapolating it through E_{ocp}. The polarization resistance (R_p) was also evaluated from Tafel plots according to Stern-Geary equation[11]:

$$Rp = \frac{\beta_\alpha . \beta_c}{2.303 i_{corr} (\beta_\alpha + \beta_c)}$$
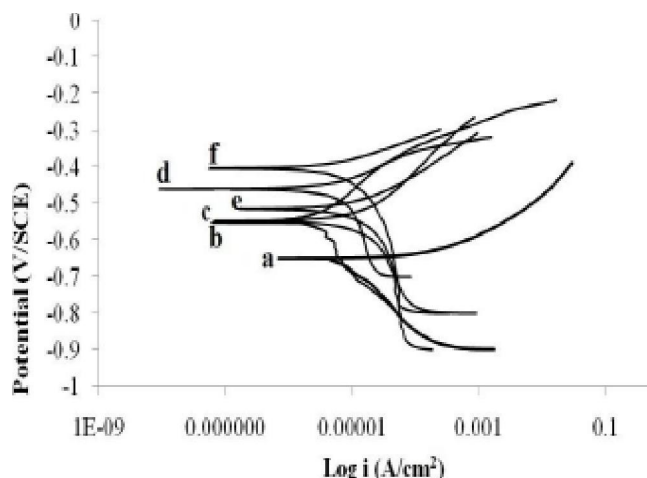

Figure 1 : Tafel diagrams of various cathodic currents in film formation (25 °C). a. Bare sample, b. Prepared sample with dipping method, c.-0.03 A, d.-0.05 A, e.0.07 A, f 0.1A

TABLE 1 : Polarization parameters for various applied cathodic currents (25 °C).

Sample	Applied current (A)	I_{corr} (A/cm²)	β_c(v/dec)	β_a(v/dec)	$R_p(\Omega)$	E_{corr} (V)
a	0.0	6.476E-5	0.184	0.123	3.021E+2	-0.626
b	0.0	8.352E-6	0.077	0.145	1.133E+3	-0.524
c	0.03	1.965e-5	0.088	0.189	6.375E+2	-.513
d	0.05	1.729E-5	0.093	0.307	7.023E+3	-0.457
e	0.07	1.458E-5	0.166	0.164	7.605E+2	-0.564
f	0.1	1.418E-5	0.057	0.232	8.136E+2	-0.391

where i$_{corr}$, β_a and β_c are the corrosion current density, anodic Tafel slope and cathodic Tafel slope, respectively.

The obtained values for polarization resistance confirm the corrosion resistance of produced coatings. These values increase as applied cathodic currents increases and oppositely the current densities decreased. This means that electrodeposition at cathodic currents facilitates the silane films formation by producing OH$^-$ ions and thereby enhances their protective properties[1].

EIS measurements

To confirm the results of polarization methods and also Tafel diagrams, EIS method was used. Figure 2 shows the effect of applied currents, in electrodeposition process, on electrochemical properties of resultant coating films. As depicted in Figure 2.a, increase of
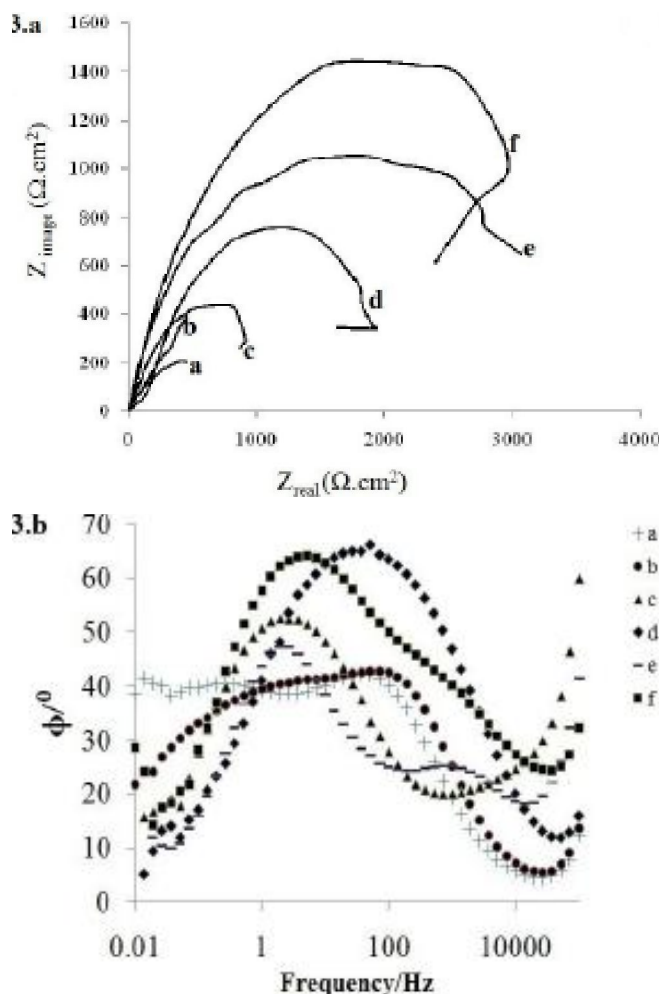

applied currents leads to increment of radius of capacitive loop. On the other hand, the radius of capacitive loop of electrical applied films is greater than that of dipped samples; this process confirmed the polarization resistances which obtained from Tafel diagrams. Figure 2.b shows the phase angle plots. Based on this Figure, it can be seen that the presence of an additional relaxation process in high-frequency region for the silane-treated samples, which is associated with the existence of protective silane film[12].

More detailed interpretation of the EIS results can be made by using equivalent circuit (Figure 3) and their fitted data have been shown as TABLE 2. There are two time constants observed from the phase angle plots (Figure 2(b)) for the silane- treated samples: one in high-frequency domain, which is associated with the existence of protective silane film; another one in low frequency domain, which is associated with the corrosion onset of steel substrate[12]. As observe in TABLE 2 the sample which prepared with -0.1A applied cathodic current. This means that the local alkalization near the cathode surface may improve the condensation rate and film preparation[13].
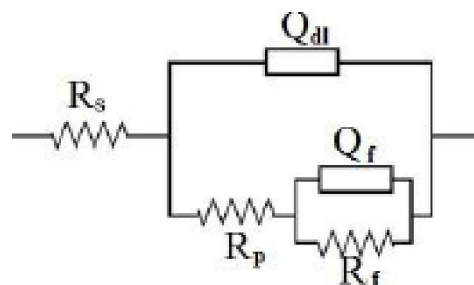

Figure 3 : Equivalent electrical circuits of a coated metal.

TABLE 2 : EIS parameters for electrodeposited silane films in various applied cathodic currents (25 °C).

Sample	Applied currents (A)	Rs(Ω)	R$_p$(Ω)	Q$_{dl}$ (Ω.S^{-n})	n$_1$	R$_f$(Ω)	Q$_f$ (Ω.S^{-n})	n$_2$
a	0.0	4.1	57	0.004	0.72	819	0.01	0.55
b	0.0	4.5	80	0.006	0.67	1842	0.019	0.58
c	0.03	6.5	31	0.006	0.6	1482	0.003	0.79
d	0.05	5.6	73	0.0003	0.95	3368	0.0011	0.7
e	0.07	33	163	0.0005	0.64	1991	0.001	0.85
f	0.1	4.3	40	0.0007	0.77	3957	0.008	0.8

Figure 2 : Nyquest (2.a) and phase diagrams (2.b) of various applied currents. a.Bare sample, b. Prepared sample with dipping method, c.-0.03 A, d.-0.05 A, e.0.07 A, f 0.1 A.

Experimental results showed that negative deposition currents facilitate the formation of silane films and thereby enhance their corrosion inhibition properties.

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Cathodic current (CC), has been used for the present investigation system, at which silane films prepared exhibit higher compactness and uniformity and thereby the best barrier properties in comparison of dipped sample. This behavior is interpreted by that at CC the significant amount of condensation catalysts, OH⁻ ions, is generated, accompanying with the negligible evolution of hydrogen that is supported by the cathodic voltammetry measurements[14].

CONCLUSIONS

Electrodeposited silane films showed better corrosion inhibition properties than dip coated films. Amount applied currents in electrodeposion process was very important. This current facilitated the formation of silane films and thereby enhances their corrosion inhibition properties.

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