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Corrosion Protection of Stainless Steel by Triethoxyoctylsilane and Tetraethoxysilane

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Different methods of silane coating deposition on the surface of 304 stainless steel were studied. Deposition was performed in different solutions with a variety of pH values. Three types of solutions were prepared i.e. neutral, containing only methanol with triethoxyoctylsilane and two acidic consisting of methanol, triethoxyoctylsilane, tetraethoxysilane and hydrochloric acid which was used to establish pH values equal to 1 and 3.5. Surface electrochemical analysis carried out using a 3.5 wt% NaCl solution and several common techniques including corrosion potential monitoring at open circuit conditions, linear polarization and electrochemical impedance spectroscopy tests showed that the way in which silane solution is prepared and silane coating is deposited is heavily influencing on the type of corrosion inhibition. Additionally, spectroscopic methods were employed. Due to oxide passive film on the steel surface, metal-O-Si bonds are formed, thus creating an intermediate layer between the oxide layer and the outermost siloxane layer (Si-O-Si). Furthermore, a long aliphatic chain of triethoxyoctylsilane compound increases steel surface hydrophobicity.

Keywords: Corrosion protection, Linear polarization, Organosilicon coatings, Stainless steel

1. INTRODUCTION

Until recently, corrosion protection was mainly ensured by adding heavy metals as corrosion process inhibitors to metalworking and coatings. Unfortunately, most heavy metals are toxic, including the compounds of Cr(VI) that were widely employed. Currently, chromate coatings are being phased out because of their carcinogenic and toxic properties [1-3]. They could be replaced with organofunctional silanes. Due to their structure, they are organic-inorganic hybrids that combine

features of both organic and inorganic compounds, which makes them capable of forming covalent bonds with inorganic substrates such as glass or metal, and with organic polymers [4-24].

Research on anti-corrosion silane coatings dates back to the early 1990s. For instance, organosilane was used as an adhesion promoter owing to its special chemical structure. It serve as a bridge between stainless steel and the anti-corrosion coating [5, 15, 19, 21, 23]. Silane was also successfully self-assembled on the thin anchoring layer of SiO₂ prepared on the surface of stainless steel, serving as a protection film [16]. Also, Xu et al. [17] obtained thin films of not more than 0.5 μ m in thickness from different silanes and their mixtures. These coatings are anti-corrosive and can successfully replace chromium. This method is effective in protecting metals such as aluminum or iron, wherein the siloxane coating is attached to the substrate through covalent bonds (Si-O-Al, Si-O-Fe).

In this study we present a new approach to silane coatings deposited on the surface of stainless steel 304. It contains a large amount of chromium and nickel components and due to an oxide passive film on its surface composed of chromium and iron oxides, it is possible to form metal-O-Si covalent bonds between the substrate and coating. The study is also aimed at showing the influence of different deposition methods on coating appearance and functionality. Anti-corrosive properties of triethoxyoctylsilane $CH_3(CH_2)_7Si(OC_2H_5)_3$ and tetraethoxysilane $Si(OC_2H_5)_4$ were examined using surface analysis as well as electrochemical and spectroscopic methods.

2. EXPERIMENTAL

2.1 Preparation of specimens

At first, discs made of stainless steel 304 (2.79 cm in diameter) were degreased using acetone and dried. Then a hot (85 °C) 10% KOH solution was prepared and the degreased steel was immersed in it for 15 minutes. Afterwards, the discs were washed twice with hot distilled water (90 °C, 3 min.) and once with cold distilled water (25 °C, 3 min.), in both cases in an ultrasonic bath. Purified samples were dried at 80 °C for 30 min.

2.2 Silane surface treatment

All chemicals were purchased from Sigma Aldrich and were used as received without any further purification. A 5% triethoxyoctylsilane solution in methanol was prepared by adding 5 ml of silane to 95 ml of methanol. This solution was stirred for 30 minutes. Then a stainless steel 304 disc, labelled as 1K, was immersed in a vessel with the above solution and then placed in an ultrasonic bath for 15 minutes (1K). Afterwards, another purified stainless steel disc labelled as 2K was immersed in the silane solution for 5 minutes, the liquid excess was removed and the disc was dried in air (5 min.). This was repeated three times. After the deposition process, the samples 1K and 2K, were cured at 80 °C for 1 hour.

Next, a solution containing 20 ml of triethoxyoctylsilane, 33 ml of methanol and 11 ml of tetraethoxysilane was prepared. The pH of the solution was lowered to 1 by adding 1 M HCl solution

and then stirred for 72 hours. Afterwards coatings were applied on steel discs by using an ultrasonic cleaner (3K) and by immersion technique (5K), exactly as in the case of samples 1K and 2K, and cured (80 °C, 1 hour).

Finally, a solution containing 20 ml of triethoxyoctylsilane, 33 ml of methanol and 11 ml of tetraethoxysilane was prepared. The pH of the solution was lowered to 3.5 by adding 0.1 M HCl solution. The coating was then applied on the steel discs by using an ultrasonic bath (4K) and by immersion technique (6K). Finally, the samples were cured at 80 °C for 1 hour.

2.3 Surface morphology analysis

FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases 16 scans at the resolution of 2 cm⁻¹ were collected for a spectrum. Microstructural characterization of sol–gel coatings was performed by scanning electron microscopy (SEM/EDS, Hitachi, SU3500).

2.4 Water contact angle measurements

Static water contact angle (WCA) was measured with a Krüss GmbH instrument model DSA 100 Expert. The measurement method was based on the analysis of drop shape and it enables performing measurements with the rate of up to 2000 f/s. The instrument was equipped with a fully automatic dosing system. Three regions of each specimen were selected randomly for the measurements and the average value of received results was considered.

2.5 Electrochemical measurements

Electrochemical studies were carried out in a Plexiglas[®] electrochemical cell using a threeelectrode system. The working electrode was a stainless steel disc or a stainless steel disc with deposited silane films. A platinum disc, previously degreased with acetone, served as the counter electrode. A saturated calomel electrode (SCE) was used for reference. All tests were performed in a 3.5% NaCl solution. In the beginning, (potential vs. time) method was applied. The potential (*E*) of the samples was monitored for two hours under open circuit conditions.

Then in order to determine the corrosion potential (E_{corr}) and current densities (*j*) values from Tafel extrapolation method, the linear polarization (LP) measurements were carried out. The test sample was polarized firstly cathodically and then anodically. The scan rate value was 0.2 mV s⁻¹.

Since the above experiment changed equilibrium potential significantly, a new sample was tested in order to stabilize the open circuit potential (OCP) and after that the electrochemical impedance spectroscopy (EIS) measurements were made. The test was conducted in the frequency (f) range from 100 kHz to 10 mHz, with the amplitude of ±10 mV.

All the electrochemical tests were carried out at ambient temperature on an electrochemical workstation (VMP3 Biologic, France).

3. RESULTS AND DISCUSSION

3.1 Surface morphology analysis



Figure 1. (a-b) SEM images of bare stainless steel 304, (c-d) SEM images of the sample 1K, (e-f) SEM images of sample 2K.





Figure 2. (a-b) SEM images of sample 3K, (c-d) SEM images of sample 4K, (e-f) SEM images of sample 5K.

Fig. 1(a-f), 2(a-f) and 3(a-b) show SEM images of stainless steel 304 surfaces and samples with silane coatings in two different magnifications. The obtained pictures make it impossible to assess the thickness of the deposited silane coatings. Stainless steel 304 contains visible grains on its surface (Fig. 1(a-b)). Among them there are crevices depicted by the dark areas. The surfaces of stainless steel 304

and samples 1K and 2K do not differ in terms of appearance, unlike the coatings deposited from aqueous solutions (3K, 4K, 5K and 6K) (Fig. 2(a-f) and Fig. 3(a-b)). A large number of dark areas can be observed on the surface of those samples. They are probably aggregates of silane compounds with Si-O-Si covalent bonds which were embedded within the crevices. Additionally, samples 3K, 4K, 5K and 6K have bubbles on its surface that look like dots. There are two explanations of this phenomenon. Firstly, those may be colloids particles from the silane sol-gel solutions or pores in the silane coating structure which resulted from the solvent evaporating during curing. Hydrolysis and subsequent condensation reaction rates are higher in the case of solutions with pH equal to 1 and 3.5 rather than anhydrous ones (1K and 2K). Thus, creation of well developed, cross-linked structures is favoured in aqueous solutions (3K, 4K, 5K and 6K). This aggregates are characterized by a greater molecular weight and greater porosity when compared to samples 1K and 2K. They consist of long polymeric chains created by Si-O-Si covalent bonds [25-27]. This is also caused by the addition of tetraethoxysilane.



Figure 3. (a-b) SEM images of sample 6K.

Fig. 4 presents FT-IR spectra. The broad peak between 3100 cm⁻¹ and 3500 cm⁻¹ corresponding to OH vibrations is the highest for the samples 3K, 4K, 5K and 6K [28-30]. This peak is virtually absent in the spectra of the samples 1K and 2K. Those observations are consistent with the previous assumptions. The higher rate of hydrolysis reaction and a tetraethoxysilane compound added create a greater number of Si-OH moieties. Moreover, the peaks that originated from -CH₃ asymmetric stretching (2957 cm⁻¹), -CH₂- asymmetric stretching (2922 cm⁻¹), -CH₃ symmetric stretching (2853 cm⁻¹), -CH₂- bending (1464 cm⁻¹) vibrations are the highest for the coatings deposited from aqueous solutions [28-32]. This is also a result a tetraethoxysilane having been added to the modifying silane solution. Bands at 1267 cm⁻¹ and 1053 cm⁻¹ are assigned to the Si-C (symmetric bending) and Si-O-Si (asymmetric stretching) vibrations, respectively [28, 30-33]. Intensities of those peaks confirm that there is a well developed, cross-linked structure in the case of coatings deposited from aqueous

solutions which contain uncondensed (Si-OH, 895 cm⁻¹) and unhydrolyzed (Si-O-CH₂CH₃, 799 cm⁻¹) groups within the structure [32, 34]. The results presented in the Fig. 4 suggest that 3K, 4K, 5K and 6K samples coatings are much thicker.



Figure 4. FTIR spectra of bare stainless steel 304 and samples 1K, 2K, 3K, 4K, 5K and 6K.

Fig. 5(a-c) show the EDS spectra of bare steel and samples 1K and 5K, respectively. It can be noticed that the intensities of the peaks indicating the content of the Si and C elements are the greatest for the sample 5K. It can also be seen that for the coated samples, peaks intensities of Fe and Cr elements decreased in comparison with the bare stainless steel 304.



Figure 5. (a) EDS spectra of bare stainless steel 304, (b) EDS spectra of sample 1K, (c) EDS spectra of sample 5K.

3.2 Water contact angle measurements

Table 1 presents results of static water contact angle (WCA) measurements. The surface of stainless steel 304 is hydrophilic. Its WCA is equal to 70.1°. Furthermore, it can be seen that silane solution treatment of every single specimen in this research enhanced the hydrophobicity of bare steel. However, only 1K and 2K indicate hydrophobic properties. WCA is equal to 98° and 97.3° respectively. The surfaces of samples 3K, 4K, 5K and 6K are hydrophilic. Their WCA is lower than 90°.

Sample	WCA (deg.)		
Stainless steel 304	70.1		
1K	98.0		
2K	97.3		
3K	85.3		
4K	81.0		
5K	87.1		
6K	78.8		

Table 1. Water contact angle values of bare stainless steel 304 and samples 1K, 2K, 3K, 4K, 5K and
6K.

3.3 Electrochemical measurements

Fig. 6 shows potential changes of samples in an aerated 3.5% NaCl solution under open circuit conditions. After two hours, potentials of deposited silane film samples and bare steel stabilized. However, in the beginning the potentials of coated silane samples decreased noticeably. This means that the equilibrium potential (*E*) shifts towards more active values. Probably the porous structure of each coating was soaked with water during the experiment [18, 35]. Fig. 6 shows that potentials of samples 1K and 2K stabilized faster than those of samples 3K, 4K, 5K and 6K. Most likely, this phenomenon indicates a lower coating thickness of samples 1K and 2K. By contrast, bare stainless steel behaves differently and its potential is more or less constant. This is due to the presence of a passive oxide layer formed on the surface of the stainless steel 304 before being placed in the cell [2, 3].



Figure 6. Open circuit potential of bare stainless steel 304 and samples 1K, 2K, 3K, 4K, 5K and 6K.

Fig. 7 shows polarization curves of the tested samples. The inhibition of the corrosion process was observed for samples 1K, 2K, 3K and 5K. The values of the cathode and anode current densities of these samples were much lower compared to bare steel. In addition, the corrosion potentials (E_{corr}) were shifted towards more positive values. Table 2 presents the calculated corrosion potentials, corrosion current densities (*i*) and also anodic (β_a) and cathodic (β_c) Tafel slopes of all tested samples. As previously mentioned, the treatment of stainless steel samples consisted in the immersion of the steel in the acidic solution containing Cl⁻ ions (3K, 4K, 5K, 6K) or the immersion in a neutral solution containing methanol (1K, 2K). The oxide film was destroyed due to the reaction with HCl. This created pits on the oxide surface. Consequently, there were considerably fewer metal-OH bonds, which makes it impossible to form a large number of metal-O-Si bonds. These bonds resulted from the condensation reaction [1, 4-34]. Pits had already been created before the specimens were immersed in a testing 3.5% NaCl solution. Because of this, accumulation of corrosion products formed underneath the silane coating caused tensile stresses which subsequently resulted in the coating delamination around the pits. Thus, the anodic Tafel slopes (β_a) are greater for samples 3K, 4K, 5K, and 6K than for samples 1K and 2K due to diffusion polarization caused by corrosion products. Additionally, as has been mentioned, silane films deposited from aqueous solutions were cross-linked and well developed due to the large number of Si-O-Si bonds [30, 31, 33]. They were also thick and porous, as discussed in the surface morphology analysis section (Fig. 2(a-f), Fig. 3(a-b) and Fig. 4). Due to the higher porosity, the amount of water absorbed by the coating is greater. This caused the silane film to crack. Delamination and film cracking as well as their impact on the deposited silane coatings were clearly described by Zhu et al. [18]. In the case of samples 1K and 2K, pretreated stainless steel was immersed in a neutral anhydrous solution.



Figure 7. Linear polarization (LP) curves of bare stainless steel 304 and samples 1K, 2K, 3K, 4K, 5K and 6K.

Thus more active metal-OH sites on the surface of the steel were "filled" because of the condensation reaction between triethoxyoctylsilane and the metal-OH moieties (Fig. 8). All the electrochemical results and considerations presented above are consistent with the static WCA measurements (Table 1). In summary, coatings 1K and 2K control the corrosion of steel kinetically, blocking the cathodic area on the steel surface, while coatings 3K, 4K, 5K and 6K impede molecular oxygen diffusing into the steel surface. Fig. 6 shows that the *E* of sample 3K is smaller and that of 5K is equal to the *E* of bare stainless steel. However, it can be inferred from Fig. 7 that for both the above samples E_{corr} is greater than that of bare stainless steel. As already mentioned, this is due to diffusion polarization. Table 2 presents that slope of the cathodic branch (β_c) for samples 3K and 5K is greater than in case of 1K and 2K and 6K, the applied pH equal to 3.5 was too high to form a sufficiently thick coating.. Moreover, Cl⁻ ions make it impossible to establish a sufficient number of metal-O-Si bonds. Thus, samples 4K and 6K are characterized by the lowest and the highest values of corrosion potentials and corrosion current densities, respectively.

Table 2. Corrosion potentials, corrosion current densities and Tafel slopes of bare stainless steel 304 and samples 1K, 2K, 3K, 4K, 5K and 6K.

Sample	$E_{\rm corr}$ (mV vs SCE)	$j_{\rm corr}$ (nA cm ⁻²)	$\beta_{a} (mV)$	$\beta_{\rm c} ({\rm mV})$
Stainless steel 304	-106	2.87	289	54
1K	-90	1.59	130	40
2K	-77	1.27	122	40
3К	-102	3.50	254	84
4K	-121	6.05	377	64
5K	-91	0.96	131	65
6K	-155	3.19	150	46



Figure 8. Scheme of stainless steel 304 surface after deposition of triethoxyoctylsilane.

All of the above results are supported by EIS measurements. Fig. 9 shows the Bode plots for all samples. In the high frequency range, sample 5K has a maximum phase angle (θ) value, which confirms that the coating is the thickest, followed by 3K [35, 36]. Both of these films were deposited at pH 1. Samples 1K and 2K have the smallest thickness. According to Ref. [18], the outermost layer that contains Si-O-Si bonds acts as a physical barrier, whereas the intermediate layer, located between the outermost silane film and the oxide film that contains metal-O-Si bonds, makes a chemical barrier. At the frequency (f) of 1 Hz, phase angle (θ) values of samples 3K, 4K, 5K and 6K, modified with hydrochloric acid, become less than 45°, which makes it possible to estimate f_b (breaking point frequency), where $\theta = 45^{\circ}$. This point specifies the change in the character of the sample system from the capacitive to resistive behaviour [35, 36]. Thus, in the case of samples treated in the acidic solution, silane coatings are so thick that it is possible to distinguish two time constants, one assigned to both outermost and intermediate layer (first loop) and the other to passive oxide film (tail in the low frequency range). As has been mentioned, pH equal to 3.5 is not high enough to create as thick outermost layer as it is in the case of samples 5K and 3K. However it is low enough to create thicker film than for samples 1K and 2K. It is apparent in the high frequency range region. Bode plots of samples 1K and 2K show a negligible thickness of the outermost layer consisting of Si-O-Si bonds. By this fact, two time constants are poorly separated. It is impossible to estimate f_b because the phase angle is greater than 45° at f_{min} . The lowest point in the Bode plots for sample 2K in the low frequency range corresponds to 55° [35].

It can also be noticed from the Bode plots that the samples on which silane films were deposited using ultrasonication indicate a much thinner layer. The sample 2K coating was thicker than that of 1K. The same conclusions could be drawn for coatings 3K, 5K and 4K, 6K. The shakes created by the ultrasonic bath may not promote the formation of Si-O-Si bonds.



Figure 9. Electrochemical impedance spectroscopy (EIS) Bode plots of bare stainless steel 304 and samples 1K, 2K, 3K, 4K, 5K and 6K.

4. CONCLUSIONS

The obtained results allow drawing the conclusion that conditions of silane coating deposition process have a major impact on the subsequent anti-corrosion properties of these coatings. Two major aspects were considered, namely solution and the deposition method. Firstly, it was shown that samples with coatings deposited from solutions with a lower pH are characterized by well developed, thick, porous and cross-linked structures consisting of Si-O-Si covalent bonds (physical barrier). It is associated with the higher rates of hydrolysis and condensation reactions. Thus, amongst aqueous solutions, the best anti-corrosive properties are indicated by samples starting with 5K, 3K, 4K, and ending up with 6K.

The samples 2K and 1K are characterized by the highest corrosion potentials. Coatings deposited on the steel surface from anhydrous solutions inhibit corrosion to the greatest extent. The presence of hydrochloric acid as a catalyst is undesirable and detrimental. Cl⁻ ions initiate pits formations underneath silane film. Thank to this, it was possible to create more metal-O-Si bonds (chemical barrier) between stainless steel 304 and the silane coating for samples 1K and 2K rather than 3K, 4K, 5K and 6K.

Considering the second aspect i.e. deposition method, it is evident that films deposited in an ultrasonic bath indicate lower thicknesses when compared to the immersion technique. This conclusion is drawn based on EIS results of three different pairs of samples with coatings deposited from three different solutions (1K-2K; 3K-5K; 4K-6K).

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