Analysis of the Formation of a Vinyltrimethoxysilane film on 1010 Carbon Steel Using Electrochemical Techniques

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Introduction

The need for surface protection of metallic materials aimed at improving the corrosion resistance is a market demand since it leads to products of higher value and extends the operational life of the painted surface. In most cases the presence of natural oxides on the metal surface is responsible for the low corrosion resistance and reduced adherence and durability of the paint layer [1, 2]. In this context, the pretreatment is of fundamental importance since, besides improving several characteristics of the metal, it aids the adherence of the paint layers providing the required visual and protector effects [3]. The objective of this study was to analyze variables in the formation of a vinyltrimethoxysilane (VTMOS) silane film on carbon steel applying electrochemical techniques.

Experimental

The formation of a VTMOS layer occurred on substrates of 1010 carbon steel. The specimens were grounded with grit emery paper, pickled in a solution of deionized water (DI) and concentrated HCl (7% v/v) for 5 min and degreased in a solution of DI and concentrated Saloclean 619 (5% v/v) in which they remained until silanization. This treatment of the substrate was also applied to steel samples which were not coated with the silane.

Solutions of the VTMOS and solvent (different ratios of DI water/ethanol) were hydrolyzed under stirring. The silanization was then carried out by dip coating process using manual immersion with controlled velocity in the previously hydrolyzed solution. The dip coated specimens were then submitted to curing in an oven at different temperatures.

The specimens were developed from three 2^3 factorial designs as shown in Tables 1, 2 and 3.

aDIG	the 1. Matrix of experiments and speciments codes developed for the first factorial design										
	Variables	P1N1	P1N2	P1N3	P1N4	P1N5	P1N6	P1N7	P1N8		
_	Ratio of DI water/ethanol	1:2	2:1	1:2	2:1	1:2	2:1	1:2	2:1		
	Concentration of silane	6 %	6 %	2 %	2 %	6 %	6 %	2 %	2 %		
_	Hydrolysis time	48 h	48 h	48 h	48 h	2 h	2 h	2 h	2 h		

 Table 1. Matrix of experiments and specimens codes developed for the first factorial design

Fable 2. Matrix of experiments	and specimens co	odes developed for th	e second factorial design
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Variables	P2N1	P2N2	P2N3	P2N4	P2N5	P2N6	P2N7	P2N8
Grit of emery paper	2500	400	2500	400	2500	400	2500	400
Hydrolysis temperature	90 °C	90 °C	30 °C	30 °C	90 °C	90 °C	30 °C	30 °C
Cure temperature	200 °C	200 °C	200 °C	200 °C	100 °C	100 °C	100 °C	100 °C

Table 3.	. Matrix	of ex	periments	and s	pecimens	codes	develop	oed for	the	third	factorial	desig	r
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Variables	P3N1	P3N2	P3N3	P3N4	P3N5	P3N6	P3N7	P3N8	
Immersion time	30 min	2 min	30 min	2 min	30 min	2 min	30 min	2 min	
Immersion velocity	1,6	1,6	25	25	1,6	1,6 mm	25	25	
	mm s ⁻¹	$mm s^{-1}$	$mm s^{-1}$	mm s ⁻¹	mm s ⁻¹	s^{-1}	$mm s^{-1}$	$mm s^{-1}$	
Cure time	60 min	60 min	60 min	60 min	20 min	20 min	20 min	20 min	

All of the experiments were conducted in non-stirred media at ambient temperature in a threeelectrode cell for flat samples. The electrochemical cell used comprised an Ag/AgCl/KCl reference electrode, a platinum foil as counter electrode, and coated or uncoated steel samples as the working electrode, with an exposed area of 1 cm^2 in a 0.1 mol L⁻¹ NaCl solution as the electrolyte. An EG&G/PAR potentiostat-galvanostat (model 273A), coupled to a Solartron frequency analyzer (model 1255B), was used.

Firstly, the open-circuit potential (*E*oc vs. time) was measured, where the immersion and stabilization time of the *E*oc was 1 h. After, the EIS was performed. The impedance diagrams were obtained within the frequency range of 50 kHz to 5 mHz, with 10 readings being carried out per logarithmic decade, with potential disturbance of 10 mV rms against *E*oc.

Results and Discussion

Figure 1a shows the Nyquist diagrams for the specimens of Design 1. It can be noted that sample P1N1 presented a larger capacitive arc than the other samples. Also, all of the samples coated with silane had higher real impedance than the uncoated carbon steel at 0.04 Hz frequency (represented by the point circled). Figure 1b shows the Bode diagrams, where the samples coated present a single time constant shifted to the medium and low frequency.



Figure 1. EIS diagrams in 0.1 mol L^{-1} NaCl for carbon steel coated with monolayers of VTMOS for the first factorial design and the uncoated specimen, (a) Nyquist diagrams and (b) Bode diagrams.

Figure 2a shows the Nyquist diagrams for the specimens of Design 2. It can be observed that the sample P2N7 presented a much larger capacitive arc than the other samples. However, for all other specimens the protection index was close to that of the uncoated carbon steel, and for P2N2 and P2N8 it was lower. Figure 2b shows the Bode diagrams, where the samples treated with VTMOS present a single time constant, shifted to the medium and low frequency region.



Figure 2. EIS diagrams in 0.1 mol L^{-1} NaCl for carbon steel coated with monolayers of VTMOS for the second factorial design and the uncoated specimen, (a) Nyquist diagrams and (b) Bode diagrams.

Figure 3a shows the Nyquist diagrams for the specimens of Design 3. It can be observed that the sample P3N3 presented a larger capacitive arc compared to other samples. All of the coated samples had a higher real impedance at 0.04 Hz than the uncoated carbon steel, except sample P3N8. Figure 3b shows the Bode diagrams, where all of the samples treated with VTMOS present a single time constant, shifted to the medium and low frequency region.



Figure 3. EIS diagrams in 0.1 mol L^{-1} NaCl for carbon steel coated with monolayers of VTMOS for the third factorial design and the uncoated specimen, (a) Nyquist diagrams and (b) Bode diagrams.

Equivalent circuit used to fit the experimental impedance data is presented in Figure 4, where R_s is the resistance of the electrolyte, R_f is the resistance of the film, CPE is the constant phase element representing the double electric layer and n is the value of exponent. The nonideal behavior of the capacitive element that represents the silane film was also observed by other authors [4-6].



Figure 4. Equivalent circuit used to fit the experimental impedance data.

Conclusions

It was concluded that a monolayer of the vinyltrimethoxysilane silane on 1010 carbon steel provided better properties of protection against corrosion, due to the larger capacitive arc and the real impedance value at 0.04 Hz, being higher than the uncoated sample. Thus, represents a promising alternative for the gradual replacement of treatments such as phosphatization and chromatization, representing an excellent approach considering its suitability from the environmental point of view. The lower impedance observed for three coated samples can be explained by the probable appearance of defects in the film which adversely affected the tests, reducing the protection effect.

Acknowledgements

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