Evaluation of a Sulfursilane Anticorrosive Pre-treatment on Galvannealed Steel Compared to Phosphate under Waterborne Epoxy Coating

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Introduction

One of the metallic materials most used by the industry is the galvanized steel, produced from carbon steel or cast iron after immersion in a melt bath where metallic zinc is deposited in its surface. Galvanized steel can still be further treated under a thermal process called annealing, during which there is diffusion of iron ions into zinc layer, improving mechanical properties and corrosion resistance[1] and forming the galvannealed steel. Because of its inherent performance characteristics, this kind of steel is often used by automotive industry[2,3]. Despite of the excellent properties offered by galvannealed steel in terms of corrosion resistance, other surface pre-treatments are also used such as chromatation and phosphatation in order to guarantee the adhesion of anti-corrosive paints to be applied afterwards and thus the long term performance of the metal. These pre-treatments are widely used due to their functional advantages; however they produce toxic waste during their processes being harmful to human health and the environment. Thus studies about less aggressive alternatives have been conducted and one of these alternatives is pre-treatment based on silanes.

The objective of this study was to evaluate the use of silane-siloxane thin film as surface pre-treatment for galvannealed steel, analyzing its behavior after being submitted to this process followed by anti-corrosive paint application. Capelossi[4] studied and developed a methodology for sulfurssilane film application on galvannealed steel and this was reproduced in this study as well, before the application of the waterborne epoxy primer. Silane film was compared to one of the most common surface pre-treatment processes – phosphatation. Pre-treatments and waterborne epoxy primer combined form the corrosion protection system and will be assessed by electrochemical impedance spectroscopy (EIS) technique, which has been widely used for this purpose[5]. Other tests were performed to evaluate the coating scheme such as salt spray cabinet, adhesion and flexibility measurements

Experimental

Preparation of specimens

Specimens used in this study were made of galvannealed steel, zinc coating of 120 g/m^2, with dimensions of 100mm x 150mm x 1mm. Substrates were cleaned with ethanol and acetone. After that, the panels were immersed in acetone and sonicated for 5 minutes for a more effective cleaning. Second step was a degrease process using a commercial alkaline degreasing solution (produced by Itamarati Metal Química) 5% weight and was just applied to the specimens intended to be coated with silane film. Specimens were immersed in the degreasing solution heated up to 70°C for 10 minutes and then washed with distilled water and dried with a hot air flow. Using the conditions previously determined and already optimized[4] for obtaining a 5% bis-1,2-[triethoxysilylpropyl] tetrasulfide (BTESPT) solution in a 50/50 w/w water/ethanol solvent at pH 4 hydrolyzed in the presence of 50 ppm Ce (IV) ions for 135 minutes, the silane solution was applied on galvannealed steel samples by dip coating process with samples remaining immersed for 15 minutes before being withdrawn and cured for 40 minutes at 150°C. The phosphatated samples were prepared in an industrial facility using a cationic bath of undisclosed composition. The epoxy coating was applied with a brush to reach a 60 ± 6 µm dry film thickness. Dry film thickness was measured after 15 days drying at room temperature at 55% relative humidity. The samples were produced in triplicate for each test to ensure statically significant results after a careful screening for eventual defects.

Electrochemical measurements and salt spray chamber

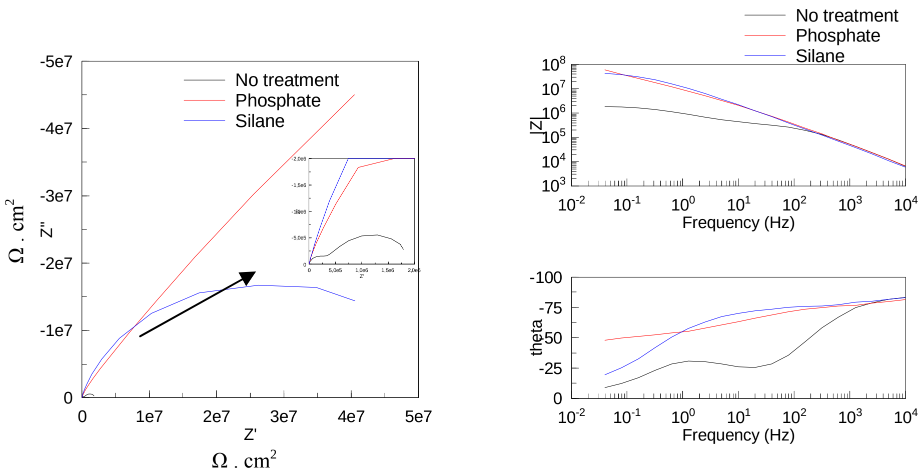
Electrochemical impedance spectroscopy measurements were performed in a three electrode cell where the working electrode was the coated sample with exposed area of 20 cm^2; Ag|AgCl|KClsat was used as reference electrode and a platinum foil with exposed area of about 10 cm^2 as counter electrode. Measurements were made after different immersion periods – 3h, 25h, 95h, 264h and 530h – using a frequency range from 50 kHz to 5 mHz and disturbance in the potential of 20 mV rms. The electrolyte was a 3.5% w/w NaCl solution at room temperature.

Coated specimens were scratched and put into a salt spray cabinet according to ASTM B-117. Deterioration of the systems were evaluated regarding level of blistering in the film, either near the incision or in the field, according to ASTM D-714 and also based on rust creepage reported in mm of rust.

Results and Discussion

Electrochemical impedance spectroscopy (EIS)

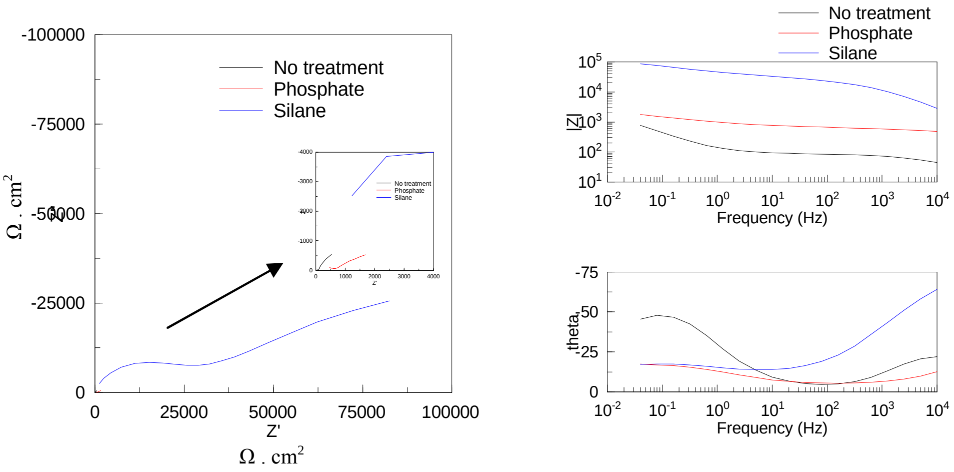
Results for EIS measurements after 3 hours of immersion are presented in Figure 1. Initial values of impedance modulus already showed marked difference between the system with no pretreatment and the other two surface pretreatments. Impedance modulus for phosphate and silane systems was around 6,0 x 10^8 **Ω**, while the untreated system was around 1,0 x 10^6 **Ω**, presenting two orders of magnitude lower impedance modulus values. It is probably due to the thin film of organic coating applied that was not able to offer a good protection to the galvannealed steel even with short immersion time. The type of the coating can also be taken into account, considering that it is a waterborne coating therefore its formulation carries additives and components that are soluble in water and thus might help the electrolyte harm the film faster and penetrate reaching the steel.



A) B)

Figure 1 – Electrochemical impedance diagrams A) Nyquist and B) Bode for specimens coated with waterborne epoxy primer with different pretreatments after 3 hours of immersion in 3.5% w/w NaCl solution

After 530 hours (approximately 22 days) of immersion, the three systems presented distinct behaviors, highlighting the performance difference among the pretreatments applied before the organic coating. The impedance diagrams are presented in Figure 2. Analyzing Bode diagrams it is possible to notice a second time constant for the system without pretreatment, evidenced mainly by Bode diagram of phase angle x log f. It is because the electrolyte penetrated through the organic coating film and probably has reached the substrate, behavior already observed after 3 hours of immersion, starting the water uptake process. Impedance modulus also substantially decreased, being three orders of magnitude below initial values.



A) **B)**

Figure 2 - Electrochemical impedance diagrams A) Nyquist and B) Bode for specimens coated with waterborne epoxy primer with different pretreatments after 530 hours of immersion in 3.5% w NaCl solution

Bode Diagrams related to phosphate and silane systems also evidence the appearance of a second time constant, however both present a less distinct change in the behavior compared to the untreated system. This second time constant for phosphate and silane systems can be associated to diffusion processes, considering that the electrolyte – after penetrating through the organic coating film – reached the pretreatment layer and is spreading through the pores of this pretreatment. Impedance modulus dropped for both pretreated systems, decreasing three orders of magnitude for the silane system and five orders for the phosphate, demonstrating silane film's superior performance in corrosion protection to the substrate.

Accelerated test – salt spray chamber

Corrosion resistance test in salt spray chamber is a reference for organic coatings evaluation in the coating industry and thus was included in this study. Partial evaluations were performed and after 60 hours it was possible to notice blistering and corrosion in the cut for the untreated and the phosphate treated system. The silane system remained free of blistering and corrosion for at least 168 hours.

Conclusions

- Electrochemical tests proven the superior performance of the sulfurssilane thin film with smaller decrease of impedance modulus among the three systems.
- Application tests also proved the excellent performance of the silane film pretreatment, standing out in the salt spray test
- Although phosphate is a thicker layer, it presented inferior performance compared to the silane in all corrosion resistance tests.

References

1. Arcelor Mittal. Aço *Galvannealed*. Acessed on February 22nd, 2012, available at http://www.vegadosul.com.br/produtos_mercados/galvanizados/galvanizados_galvannealed/galvanizados_galvannealed.asp

2. Queiroz, F. M., Costa, I. (2002). Avaliação do comportamento de corrosão de um aço "galvannealed" comercial por espectroscopia de impedância eletroquímica. **22º CONBRASCORR – Congresso Brasileiro de Corrosão**.

3. Santos, D., Raminhos, H., Costa, M., Diamantino, T., Goodwin, F.. (2008). Performance of conductive pre-primers applied on galvanized steel sheets for automotive bodies. **Corros. Prot. Mater.** vol. 27**,** 15-21.

4. Capelossi, V. R. (2011). Filmes finos à base de polissilanos aditivados com nanopartículas de sílica e/ou cério (IV) ou cério (III) como pré-tratamentos protetores contra corrosão de aço *galvannealed*.. São Paulo:Tese. Universidade de São Paulo.

5. Bonora, P. L., Deflorian, F., & Fedrizzi, L. (1996). Electrochemical impedance spectroscopy as a tool for investigating underpaint corrosion. **Electrochimica Acta**, Vol. 41 , 1073-1082.