CHARACTERIZATION OF ZIRCONIUM–TITANIUM NANOCERAMIC COATING ON STEEL[1]

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Abstract

Conversion coatings enhance the adhesion of paint or lacquer and promote corrosion resistance on metals. Conventionally, conversion coatings have been developed based on phosphate and chromium elements. The phosphate ions eliminated in wastewater generated during such processes may cause eutrophication of surface waters. Similarly, hexavalent chromium is a toxic and carcinogenic substance. In the present study, a conversion solution based on hexafluozirconic/titanic acid was used on carbon steel 1006. The reaction time of the metal that is to be treated with the conversion solution strongly influences coating performance. The coating obtained is a thin layer of unevenly distributed zirconium (Zr)/titanium (Ti) oxide adherent to the steel surface. The performance of the treatment procedure was evaluated by electrochemical investigation, including open-circuit potential and electrochemical impedance spectroscopy. The electrochemical test indicates that the ability of the Zr/Ti coating to improve the corrosion resistance of steel is equivalent to that of the phosphate coating. However, the results of SST (salt spray test) show that the corrosion resistance of the Zr/Ti coating is less than that of the phosphate coating. The corrosion area in the Zr/Ti coating was less than 1% after 1032 h, whereas there was no area of corrosion observed in the phosphate coating at the same time point.

Key words: Pretreatment; Conversion coatings; Electrochemistry; Nanoceramics.

CARACTERIZAÇÃO DO REVESTIMENTO NANOCERÂMICO ZIRCÔNIO – TITÂNIO EM AÇO

Resumo

Os revestimentos de conversão melhoram a aderência da tinta ou verniz e promovem a resistência à corrosão em metais. Tradicionalmente, estes revestimentos de conversão foram à base de fosfato e cromo. Os íons fosfato geram efluente que podem causar a eutrofização das águas superficiais. O cromo hexavalente é tóxico e cancerígeno. Neste trabalho uma solução de conversão à base de ácido hexafluozircônio/titânio foi utilizado em aço carbono 1006. O tempo de reação do metal a ser tratado com a solução de conversão tem um forte impacto sobre o desempenho do revestimento. O revestimento obtido é uma fina camada de zircônio e óxido de titânio que adere ao metal e desigualmente distribuído sobre a superfície do aço. A eficácia do tratamento foi avaliada por investigação eletroquímica, incluindo o potencial de circuito aberto e impedância eletroquímica. O teste eletroquímico mostra que o revestimento de Zr/Ti melhora a resistência à corrosão do aço tanto quanto o revestimento do fosfato. Mas os resultados em Névoa salina mostram que a resistência à corrosão de Zr/Ti não é tão boa quanto o revestimento de fosfato. A área de corrosão é inferior a 1% após 1032 h, enquanto o revestimento de fosfato não havia área de corrosão.

Palavras-chave: Pré-tratamento; Revestimento de conversão; Nanocerâmicos; Eletroquímica.

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1 INTRODUCTION

Metallic structures receive an organic coating to improve their appearance and to protect against corrosion. The performance of such a coating is usually associated with the application of a pretreatment that modifies the surface of the metal and, thus, improves the adhesion of the subsequent coating and reduces the tendency for the occurrence of corrosion.(1,2)

Various efforts have been undertaken to reduce or abolish the use of chromium and phosphorus in manufacturing processes. However, phosphate has continued to be used in pre-coating of white lines, cars, office furniture, and the construction of electrical components.(3)

Environment-friendly processes began to be developed in the automotive industry; for example, several alternative processes that are free of chromium (chromium-free). Most of these processes are chemical conversion coatings that may incorporate an agent, such as molybdates, tannins, and rare metals, to promote adherence.(4)

The nanoceramic coating is a product developed from chemical compounds of hexafluorzirconic and/or hexafluortitanic acids for the pretreatment of metallic surfaces. A conversion reaction is assumed to be necessary for obtaining an oxide layer on the surface of the metallic substrate.

Nordlien et al.(1) and Lunder et al.(2) demonstrated, in their studies, that conversion coatings obtained from Zr–Ti in AA6060 aluminum substrates are not uniform and are strongly affected by the presence of cathodic inter-metallic particles present in the league. During the formation of the film, the presence of free fluoride ions will cause dissolution of the natural oxide layer on the surface, and this is accompanied by an initial shift of corrosion potential toward the negative direction; thus, it causes the dissolution of metal complexes and facilitates the following reactions:

$$Al \rightarrow Al^{3+} + 3e^- \quad [1]$$
$$Al^{3+} + TiF^{2-}_6 \rightarrow AlF^{3-}_6 + Ti^{4+} \quad [2]$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad [3]$$
$$2H^+ + 2e^- \rightarrow H_2 \quad [4]$$
$$Ti^{4+} + 3H_2O \rightarrow TiO_2.H_2O + 4H^+ \quad [5]$$
$$Zi^{4+} + 3H_2O \rightarrow ZiO_2.H_2O + 4H^+ \quad [6]$$

According to both these authors,(1,2) the diffusion layers formed in the alkali adjacent to inter-metallic particles result in reactions [3] and [4], which favor the precipitation of the conversion medium containing zirconium oxide and titanium according to reactions [5] and [6].

The film demonstrates a progressive lateral growth in the region around the inter-metallic particle to eventually cover the entire surface.(5)

This article presents results of a study of a surface treatment of carbon steel SAE 1006 using a solution with a base of hexafluorzirconic and hexafluortitanic acids, and evaluation of the associated paint adhesion and corrosion protection. The conversion products obtained are known commercially as "nanoceramics".

The tests included basic studies of electrochemical impedance spectroscopy (EIS), open-circuit potential (OCP), and accelerated corrosion tests in salt spray to evaluate degree of rusting and blistering.

2 MATERIALS AND METHODS

Plates of carbon steel SAE 1006, with dimensions of 1 × 50 × 100 mm were used as samples.

Steps involved in the preparation of the sample are detailed as follows:

- the samples were washed with detergent by using a polyurethane sponge for removal of excess protective oil, steel and dirt particles;
- degreasing was carried out in an alkaline degreasing 4% (Parco Cleaner 651 B) medium at a temperature of 85 °C for 300 s;
- the samples were washed with deionized water jets; and
- this was followed by drying with compressed air at approximately 60 °C.

The treatment solution, developed based on hexafluorzirconic/hexafluortitanic acids, was diluted with deionized water and adjusted to a pH of 4.0 with an alkaline solution. To form the conversion coating, steel sheets were immersed in the conversion medium by the dip-coat method, using the equipment Deep Coating Lift Disc 765-MA Marconi, at a sink rate of 7 mm s^{-1}. After immersion, the plates remained in the solution for the specified time at room temperature and were removed at the same speed. Following removal, the plates were washed with deionized water and dried at 110 °C for 10 min.

For comparison, uncoated plates were prepared for conversion, and these were only subjected to degreasing. These were called white sheets and were treated with zinc phosphate, following the same cleaning procedure described for the test samples.

The electrochemical measurements were performed using potentiostat AUTOLAB PGSTAT 302 in a three-electrode electrochemical cell (one electrode of silver/silver chloride reference (Ag/AgCl), a platinum counter electrode, and a working electrode). The contact interface with the electrolyte of the sample was 1 cm in diameter.

The extent of OCP e EIE was recorded as a function of time with:

- the immersion of the sample in a solution for conversion; and
- the immersion of the sample in a solution of 0.1 M NaCl for 5 min, to stabilize the system, before taking measurements.

The salt spray test was carried out at the BASS mark to evaluate the protection provided to steel when coated by layers of conversion and subsequently painted with enamel paint. The tests were conducted in accordance with ASTM B 117 to determine rusting and blistering (Table 1).

Table 1: Degree of blistering and blistering, and their respective standards

Rusting	NBR 5770/84	Degree of blistering	F0 → F5
Blistering	NBR 5841/74	Bubble size	T0 → T5
		Bubble density	D0 → D5

3 RESULTS AND DISCUSSION

3.1 Measurement of the Open-circuit Potential

3.1.1 Solution in 0.1 M NaCl, with a top coat

The extent of OCP was recorded as a function of time in 0.1 M NaCl solution to assess the barrier properties of conversion coatings on steel. The OCP was recorded for an immersion time of 3600 s. The samples had a dye layer measuring approximately 40 µm.

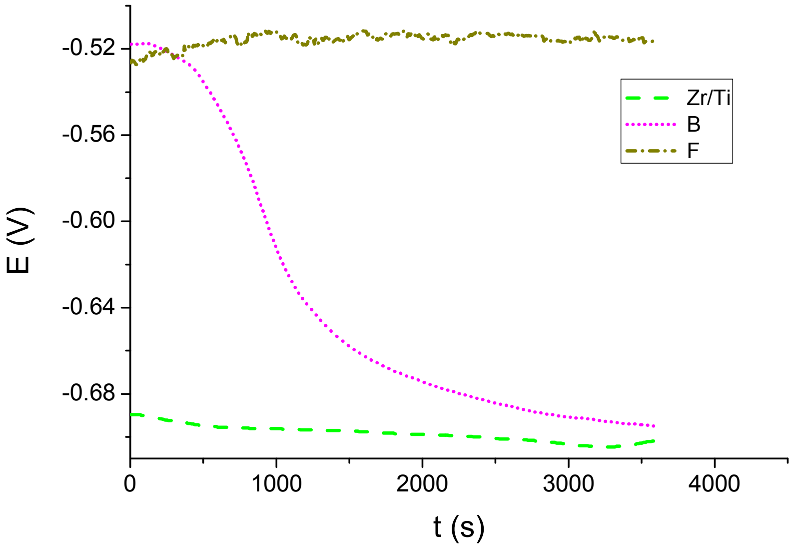

Figure 1 - Variation of open-circuit potential in 0.1 M NaCl plates of SAE 1006 steel conversion coating based on Zr/Ti treated for 60s and painted with acrylic paint and for comparison, the phosphated steel (F) and without pretreatment (B).

The curve representing the sample without pretreatment (B) showed an inclination between the first and second plateau, with a potential difference over time; however, the curve of potential change of the coating based on Zr/Ti was equally stable as the coating obtained by phosphating, although with a lower potential. This can be attributed to the presence of fluoride in the substrate^{2} or in the porous layer obtained by the conversion.$^{(6)}$

3.1.2 In the conversion solution, without a top coat

To verify the influence of time of conversion on the barrier properties of the nanoceramic coating formed, became the measure of using OCP as the electrolyte solution itself conversion.

The extent of OCP was recorded as a function of time for dipping of sample in a solution constituted based on hexafluorzirconic/hexafluortitanic acid in order to monitor the rate of deposition of the conversion layer. The OCP was recorded for an immersion time of 2100 s.

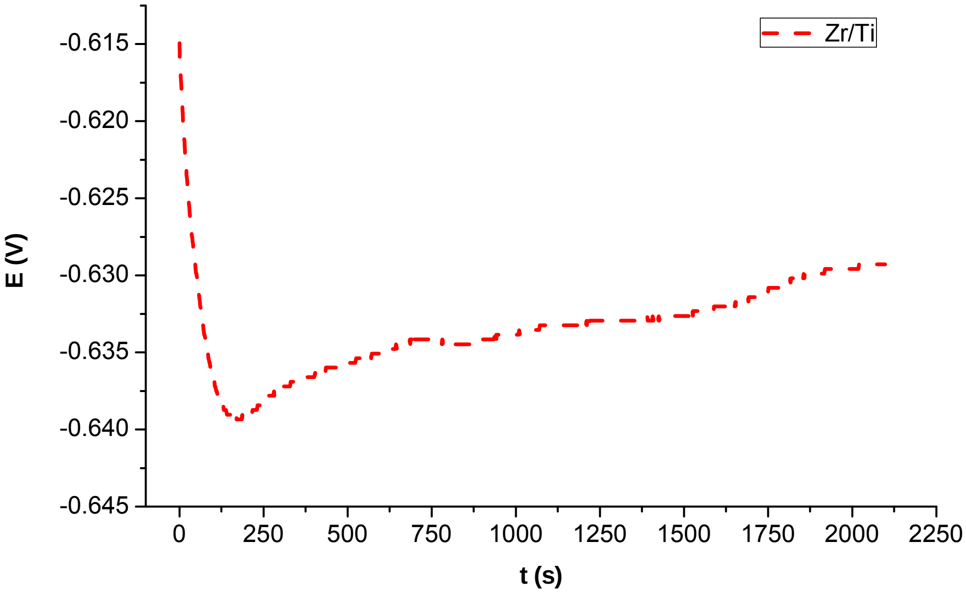

Figure 2 - Variation of OCP of steel during the pretreatment solution hexafluorzirconium / titanium based during 3600s.

The results showed that the conversion solution, in the initial period of 180 s of immersion, promotes an attack on metal surface by activating the metallic surface and consequentially reducing its potential. Thereafter, the area undergoing deposition is larger than that subjected to dissolution; consequently, there is an increased potential, which, over time, remains stable but with a tendency to increase. According to Nordlien et al.,(1) this can be attributed to the constant deposition of zirconium and titanium oxides on the metallic surface as well as to prolonged contact with the conversion solution, which tends to increase the potential over time.(2)

3.2 Measurement of the Potentiodynamic Polarization

In order to evaluate the corrosion current density (icorr), samples with conversion coatings subjected to different durations of conversion, the respective polarization curves were considered. Measurements were performed in 0.1-M NaCl solution in an electrochemical cell comprising three electrodes, and the scan rate was 2 mV/s. The samples were conditioned in the electrolyte for 5 min before polarization.
The icorr is depicted in Figure 3.

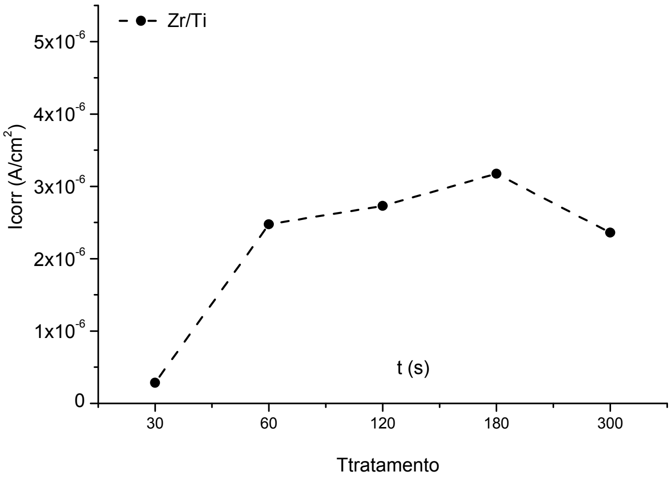

Figure 3 - Nyquist diagram for carbon steel with conversion coating based on hexafluorzirconium / titanium with different treatment times of 30s to 300s, and blank samples and phosphate, with top coat, in 5% NaCl for 96 hours in electrolyte.

Treatment with 30 s of immersion in the conversion medium resulted in lower icorr, indicating the presence of a greater barrier capacity of this substrate; in addition, at the specified time, there was greater current flow, which may have been caused by increase in the porosity of the layer with increasing time of conversion(7) and the resultant increase in irregular thickness.

3.3 Measurement by Electrochemical Impedance Spectroscopy

Samples treated with conversion solution for periods of 30, 60, 120, and 180 s were painted and analyzed by electrochemical impedance spectroscopy.

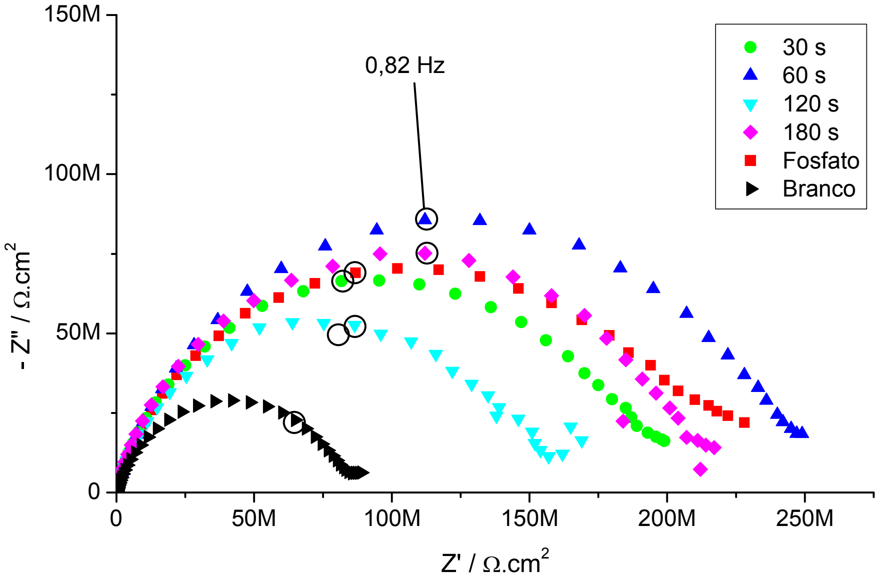

Figure 4 - Nyquist diagram for carbon steel with conversion coating based on hexafluorzirconium / titanium with different treatment times of 30s to 600s, and blank samples and phosphate, with top coat, in 5% NaCl for 96 hours in electrolyte.

After 96 h in contact with saline (NaCl 0.1 M), it was observed that the resistance of the 60-s sample was larger than that of samples treated for 30, 120, and 180 s.
This impedance value was greater than the value obtained for the substrate phosphate, and also for a period of 180 s of treatment. This could potentially be attributed to the production of corrosive products in the porosity of the layer obtained in the presence of paint and the increased protective barrier to current flow that increase the value of real impedance.(8)

3.4 Measurement by Salt Spray

The salt spray test was conducted with solution treatment times in the conversion solution of 30, 60, 120, 180, and 300 s, and the results were compared for samples without pre-coating (B) and with phosphating as a pretreatment (F). The samples were painted with enamel paint to a thickness of approximately 40 µm.

Table 5: Results of tests of blistering and rusting for samples treated with acid hexafluorzircônio / titanium resin and painted with synthetic enamel

Degree of rusting and Degree of Blistering									
Samples		**96h**		**600h**		**624h**		**1032h**	
Zr/Ti	30	F0	T0 D0	F0	T0 D0	F0	T0 D0	F0	T0 D0
Zr/Ti	60	F0	T0 D0	F1	T0 D0	F1	T2 D2	F1	T2 D2
Zr/Ti	120	F0	T0 D0	F1	T0 D0	F1	T0 D0	F1	T0 D0
Zr/Ti	180	F0	T0 D0	F1	T0 D0	F1	T0 D0	F1	T0 D0
Zr/Ti	300	F0	T0 D0	F0	T0 D0	F0	T0 D0	F0	T0 D0
	F	F0	T0 D0	F0	T0 D0	F0	T0 D0	F0	T0 D0
	B	F1	T3 D3						

A sample with treatment time of 30 s endured a period of 1032 h of salt spray, which is in agreement with the polarization test; similar results were obtained for the sample treated for a period of 300 s. It appears that the polarization for this period of treatment resulted in a decrease in the icorr, and this implies the presence of a greater barrier layer. However, for samples with immersion periods of 60, 120, and 180 s, the salt spray time endured was less than that of those with the phosphate.

4 CONCLUSION

For a coating, ascertaining the stability of its behavior by OCP and its behavior through deposition of PCO conversion solution makes it is possible to evaluate the expected period of a plateau when the coating will demonstrate peak performance. It was possible to define the attributes of the sample following the 300-s treatment in conversion solution. However, a behavior that was not expected for samples in the early periods of deposition, such as in the case of treatment with 30-s immersion in the conversion solution, and which may have occurred due to the dissolution of corrosive products associated with painting promoted the barrier layer.

This novel pretreatment developed based on Zr–Ti has significant potential for application in of the substitution of phosphates in industrial processes.

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REFERENCES

1 NORDLIEN, J.H., WALMSLEY, J.C., ØSTERBERG, H., NISANCIOGLU, K. Formation of a zirconium-titanium based conversion layer on AA 6060 Aluminium. Surface and Coatings Technology. v.153, p.72–78.2002.
2 LUNDER, O., SIMENSEN, C., YU, Y., NISANCIOGLU, K. Formation and characterization of Ti–Zr based conversion layers on AA6060 Aluminium. Surface and Coatings Technology. v.184, p. 278–29, 2004.
3 ZHELUDKEVICH, M. L., SERRA, R., M. MONTEMOR, F., FERREIRA, M. G.S. Oxide nanoparticle reservoirs for storage and prolonged release of the corrosion inhibitors. Electrochemistry Communications v.7, p. 836–840, 2005.
4 MENEZES, T. L., Desenvolvimento e caracterização de revestimentos híbridonano estruturados para a proteção contra a corrosão de substratos metálicos. INTERCORR 2010, Fortaleza/CE maio de 2010.
5 ANDREATTA F., TURCO A., GRAEVE I., TERRYN H., FEDRIZZI L. SKPFM and SEM study of the deposition mechanism of Zr/Ti based pre-treatment on AA6016 aluminum alloy. Surface & Coatings Technology v: 201, p. 7668–7685. 2007.
6 FEDRIZZI, L., DEFLORIAN F., BONORA. L., Corrosion behaviour of fluotitanate pretreated and painted aluminium sheets. Electrochimica Acta, v. 42, No. 6, pp. 969-978, 1997.
7 WANG S.H., LIU C.S. SHAN F.J., Structural investigation of the zirconium-titanium based amino trimethylene phosphonate hybrid coating on aluminum alloy. Acta Metall. Sin.(Engl. Lett.) v. 22 n.3 p. 161-166, 2009.
8 MORAES, J. A., Estudo do Comportamento do Revestimento de Conversão à base de Zircônio e Zircônio/Titânio Sobre Aço Carbono. Dissertação - Mestre em Engenharia. PPGEM – UFRGS, Porto Alegre, 2010.