

CORROSION BEHAVIOR OF A CONVERSION COATING BASED ON ZIRCONIUM AND COLORANTS ON GALVANIZED STEEL BY ELECTRODEPOSITION

Josiane Soares Costa ¹

Raquel Dei Agnoli ¹

Jane Zoppas Ferreira ²

Abstract

Corrosion performance of Zr-based coating on substrates obtained by zinc electrodeposition in an alkaline bath is compared to chromate coatings (Cr III and Cr VI). The “nano Zr” is a conversion coating formed by immersion in a hexafluorozirconic acid solution. Since the “nano Zr” coating is transparent, the addition of a colorant provides color to the surface. In this case, the colorant, when applied after the conversion coating, conferred the yellow color to the surface. The coating produced improves the corrosion protection of the substrate. For this study the samples were analyzed by electrochemical impedance spectroscopy (EIS) and accelerated corrosion test in a humidity chamber. The results showed similar behaviors between the “nano Zr”, colorant and the chromate (Cr III) coating. Therefore this kind of conversion coating is a promising substitute for chromate coatings.

Keywords: Nano Zr; Immersion process; Electrodeposited zinc; Hexafluorozirconic alkaline solution.

COMPORTAMENTO DA CORROSÃO DE UM REVESTIMENTO DE CONVERSÃO À BASE DE ZIRCÔNIO E CORANTES NO AÇO ZINCADO POR ELETRODEPOSIÇÃO

Resumo

No presente estudo, avaliou-se o desempenho de revestimentos à base de zircônio e corante sobre substratos de zinco obtidos por eletrodeposição em meio alcalino, em relação aos revestimentos de cromato (CrIII e CrVI). O revestimento “nano Zr” é obtido através da imersão em solução de conversão à base de ácido hexafluorzircônio. Uma vez que o revestimento “nano Zr” é transparente, a adição de um corante proporciona cor à superfície. Neste caso, o corante, quando aplicado depois do revestimento de conversão, confere cor amarela à superfície. O revestimento produzido melhora a proteção contra a corrosão do substrato. Para este estudo ensaios de espectroscopia de impedância eletroquímica (EIS) e testes em câmara úmida foram feitos. Os resultados mostraram comportamentos semelhantes entre o “Zr nano” e corante e o revestimento cromato (CrIII). Por conseguinte, este tipo de revestimento de conversão é um promissor substituto para os revestimentos de cromatização.

Palavras-chave: Nano Zr; Processo de imersão; Zinco eletrodepositado; Solução ácida de hexafluorzircônio.

I INTRODUCTION

Zinc electroplated coatings are employed as a galvanic protection for steel. However, zinc is very reactive, and high corrosion rates of this coating are observed in indoor and outdoor exposures [1,2]. Therefore, a post treatment is necessary to prevent the previous white corrosion. Well-known coatings based in chromium (VI) have been used for a long time and now they are being prohibited

because of their toxicity [3-5]. The trivalent chrome coating came up as an environmentally friendly solution but this coat does not confer the yellow color like the hexavalent chrome coating does [6].

New technologies have been proposed in order to prevent corrosion in metals; one example is nanoceramic coatings formed by immersion [7-9]. This conversion coating

¹Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais - PPG3M, Universidade Federal do Rio Grande do Sul - UFRGS, Porto Alegre, RS, Brazil. E-mail: josisc_25@hotmail.com

²Universidade Federal do Rio Grande do Sul - UFRGS, Porto Alegre, RS, Brazil.

can be zirconium and/or titanium-based and produces a nanostructured layer on the metal substrate. The advantage of these nanoceramic coatings is being toxic metals and organic compounds free [10,11]. On zinc substrates, the conversion layer produced by nanoceramic coating has no color, unlike the hexavalent chromium one, that confers a range of colors from yellow to black.

To provide colour, it can be used an organic colorant or a natural one, as compounds based in tannin.

Tannins are natural compounds usually extracted from the bark of some trees and used in some applications such as water treatment or as organic inhibitors in electrolytes for iron corrosion control and as iron rust converters [12-15]. Tannins can form complexes (tannates) with iron oxides/hydroxides produced during the corrosion process and these complexes could form crossed layers [12-14].

Since tannins are natural compounds, they are environmentally friendly and a good alternative for inhibitors currently used.

In this work, the nanoceramic zirconium-based coating behavior on zinc substrates was studied. Two colorants were applied over the nanoceramic layer: a yellow organic colorant and a brown natural colorant (tannin).

The samples were evaluated by electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM). The results were compared to hexavalent chromium and trivalent chromium conversion coatings.

2 MATERIALS AND METHODS

Samples of AISI 1010 steel (100mm × 34mm × 1mm) were cleaned in a commercial alkaline degreaser solution for 10 minutes at 60°C and then rinsed in cold deionized water (DI). The electrodeposition experiments were performed in a tank containing a zinc alkaline solution, according to Figure 1.

Under these conditions electrodeposits have about 12 μm thickness. After the zinc deposition, the samples were cleaned with DI and air dried.

The treatment bath was prepared with hexafluorozirconic acid (Sigma Aldrich Chemical Co.). The Zr-based layers

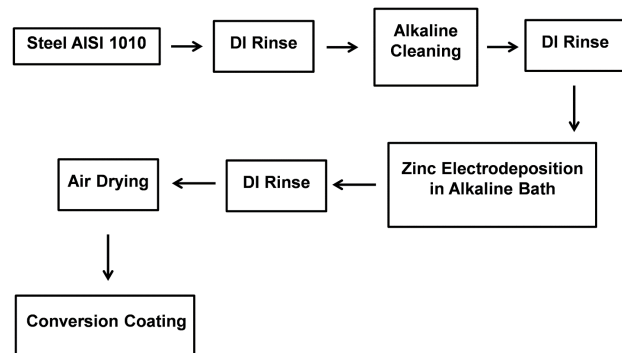


Figure 1. Experiment procedure used for the samples preparation.

were obtained by immersion in a 4.5vol% acid solution at pH 2.9 as used in previous works [16-18]. The immersion time was constant and equal to 2 or 5 minutes at room temperature.

Two colorants were used, the first one was an yellow organic colorant from Sinodal and a brown natural colorant tannins. Based the solutions concentration were 3 g/L and 2 g/L, respectively.

To the electrochemical impedance spectroscopy (EIS) it was used an AUTOLAB PGSTAT302 and the FRA software was used to analyze the data. A three electrode cell system was used, a platinum sheet served as the counter electrode and an electrode Ag/AgCl saturated served as the reference electrode. The measurements were made in the open circuit potential (OCP) and conducted in a NaCl 0,1M (pH 6.0) solution an area of (0.63 cm²) of the samples was exposed to the electrolyte. The system was at room temperature, the perturbation amplitude of the voltage was 10 mV and the scanning frequencies ranged from 10⁵ to 10⁻² Hz. Each sample was immersed in the NaCl solution for 24h and three replications were performed to ensure repeatability.

The humidity chamber essays were performed according to ASTM D-2247-11 with 100% of humidity and temperature of 40°C. The trial lasted 14 days (336 hours).

The microstructures of the samples before and after the EIS experiments were examined using a Dino Capture 2.0 optical microscope and a digital camera. The morphology and composition of the conversion coatings were investigated by a scanning electron microscope (SEM) and an energy dispersive X-ray spectrum (EDS).

3 RESULTS AND DISCUSSION

Figure 2 shows all the samples before the EIS measurements. The samples with only nano-Zr coating have no colour but with colorants they have an iridescent yellow color, similar to those with chromate.

Observing the micrographics in the Figure 3, it can be proposed that the conversion coating grew up without a preferential direction, once it basically has the same morphology as the substrate without coating. The EDS results (Figure 4) showed that the Zr was observed along the surface of the treated sample. Measurements in several surface regions showed the presence of Zr.

It is not possible to compare qualitatively the microstructure of the coatings due to the low signal of the Zr in the EDS spectrum. Moreover, the thickness of the nano-Zr film is on the nanometers order [19,20]. The immersion time is an important parameter that can modify the formation of the converted coating and its microstructure. Depending on the sample, the treatment time, the performance of the coating and its morphology changes, as well as the composition of the converted layer [8,21].

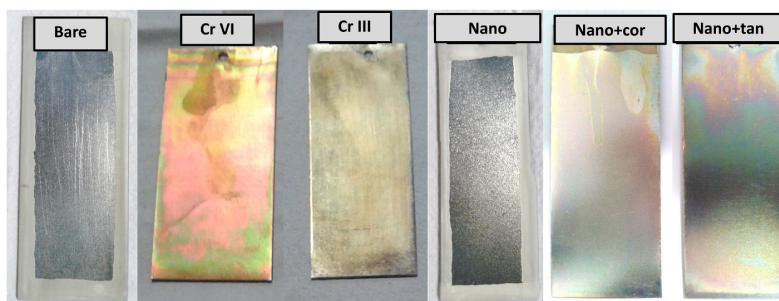


Figure 2. Samples of alkaline zinc (bare) with hexavalent chromate (Cr VI), trivalent chromate (Cr III), nanoceramic, nanoceramic and colorant (nano+cor) and nanoceramic whit brown colorant-based tannin (nano+tan) before the analysis.

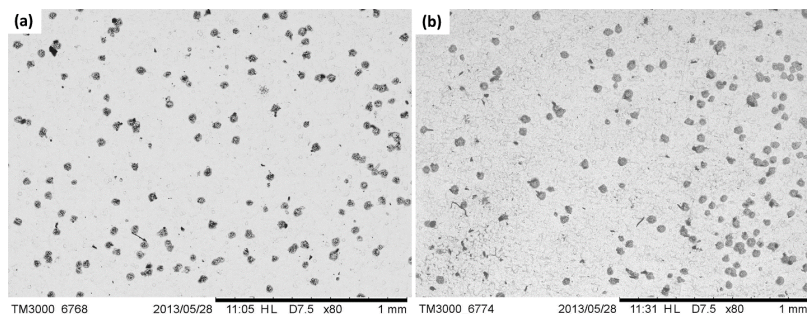


Figure 3. SEM micrographs of the sample: (a) alkaline zinc (bare) and nanoceramic coating (b).

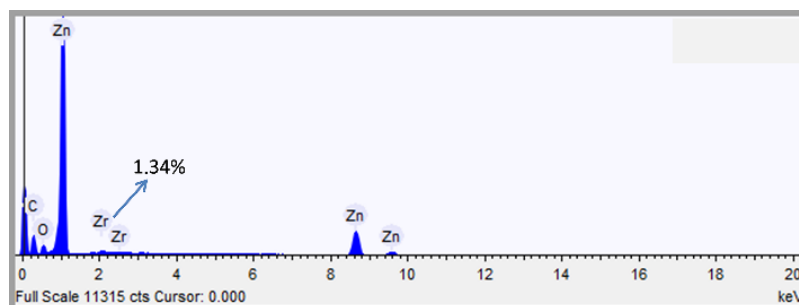


Figure 4. EDS analysis for the sample nanoceramic coating, showing the peak of Zr.

The immersion times in the hexafluorozirconic acid solution was then evaluated. The results of the EIS trial can be seen on Figure 5 that shows the Nyquist and Bode diagrams.

Although the Nyquist diagrams present a single semicircle for all samples (which is indicative of a reaction between the electrolyte and coatings), the Bode diagrams have at least two semicircles. It should be noted that although these curves appear to be similar in shape, they differ in size. This means that the same fundamental phenomenon may have occurred in all these coatings, but along a different effective area in each case. The appearance of these semicircles in the Bode diagrams of the coated samples showed that the corrosion process involves these coatings more than a time constant; this indicates that a double layer in the coating/electrolyte interface exists [3,7,8]. As it is known, each reaction or physical phenomenon presents one time constant [7].

In Bode diagrams, two time constants in the intermediated frequencies region are observed for the nano

(5 min) sample, that can be attributed to corrosion products due to the bad uniformity of the nano-Zr film [7,8]. The time constant appears in addition at lower frequencies, for the nano (2 min) sample and the bare sample, probably due to a diffusion process associated to localized corrosion [22]. To estimate the total resistance of the samples, an extrapolation was made on the circles. For the nano (5 min) and the nano (2 min) sample, the total resistance is approximately 8 K Ω and 4.5 K Ω respectively.

The 5 minute immersion time coating shows the largest semicircle; this shows that the coating has better anticorrosive performance in comparison with the other conversion coating.

The EIS measurements were made after 24 hours of immersion in NaCl 0.1M. As results, it is possible to affirm that the samples with coating had a superior behavior than the bare sample.

The best corrosion protection was conferred by the nano (5 min). So, the organic colorant application effects were evaluated with this sample (Figure 6).

After 24 hours of immersion in the NaCl 0.1M, it is possible to affirm that both colorants negatively influenced the corrosion protection since it reduced the resistances when compared to the sample covered with the nano-Zr coating only. Nevertheless, for the colorant tannin based one, the resistance reduction is very little. As *Mohammadloo* [7,8,23], the resistances are in the same order of magnitude, thus confirming that the nanoceramic coating and colorant tannin based is effective.

These results indicate that the yellow colorant conferred color to the nanoceramic coating but instead of improving the corrosion protection, this colorant reduced the resistance of the system. It happens due to the acid characteristic of the colorant that attacks the nanoceramic coating, reducing the layer. On the other hand, the tannin-

based colorant, besides the color conferred, protected the zinc substrate even reducing the resistance.

In Figure 7, it can be observed damage on the protective layer (appearance of white corrosion) and the loss of the yellow coloration in localized areas. It is necessary to emphasize that this test is aggressive to the sample, due to the immersion in a solution that simulates a saline environment. Even though the sample lost its color, the coating protected the zinc substrate.

The behavior of the samples coated with nano-Zr and tannin based colorant were compared with samples made by the same substrate but coated with Cr III and Cr VI based coatings. The samples remained immersed for 24 hours in a NaCl 0.1M solution and EIS measurement were made. Figure 8 shows that the hexavalent chromate treatment confers a more effective protection to the zinc substrate. Furthermore, the chrome-based coating diffusive character indicates the self-healing behavior from de Cr VI ions [1,22,24]. However, the trivalent chrome-based coating

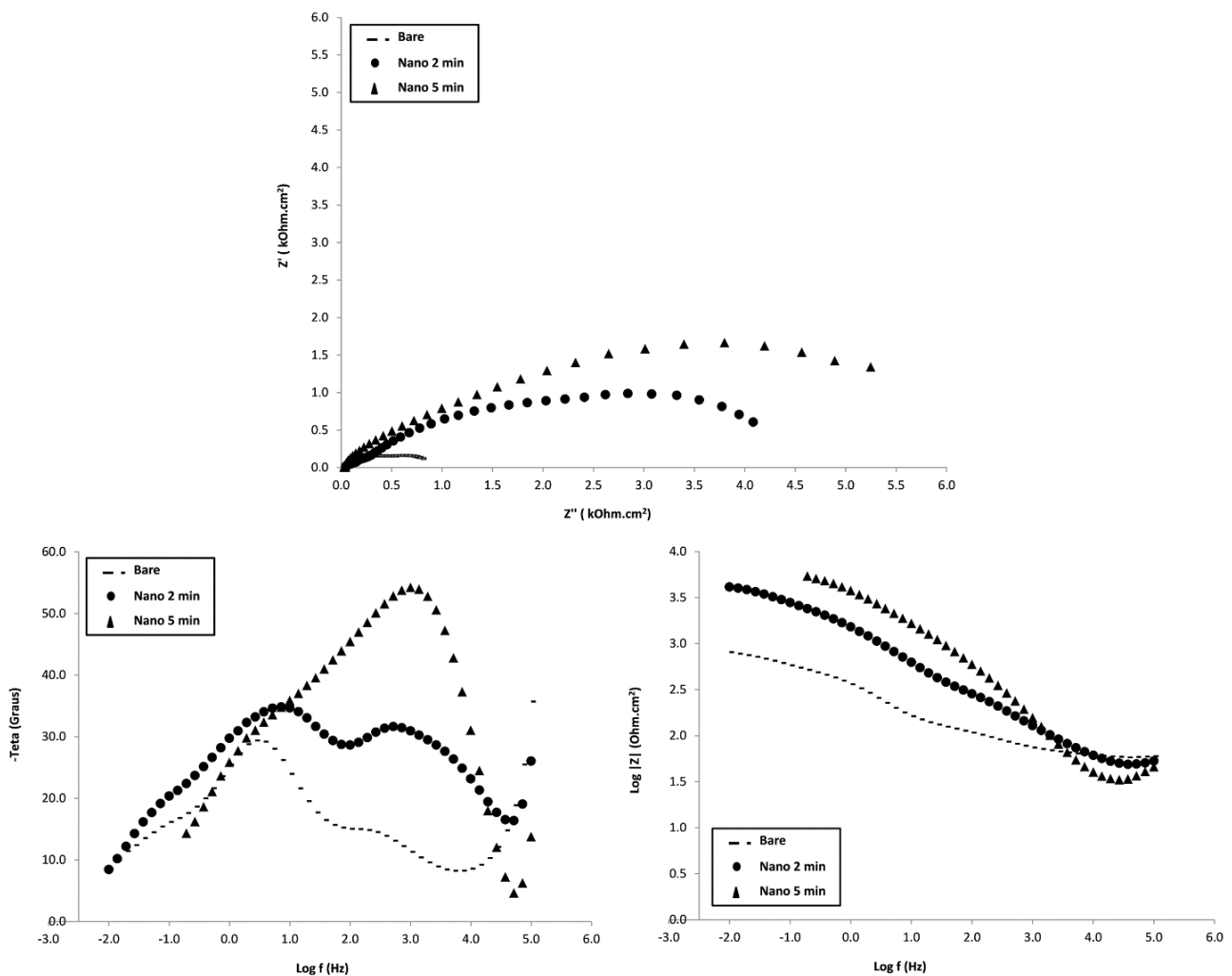


Figure 5. Nyquist and Bode diagrams for samples of alkaline zinc nanoceramic coated at different immersion times in the hexafluorozirconic solution after 24h immersion in NaCl 0.1 M.

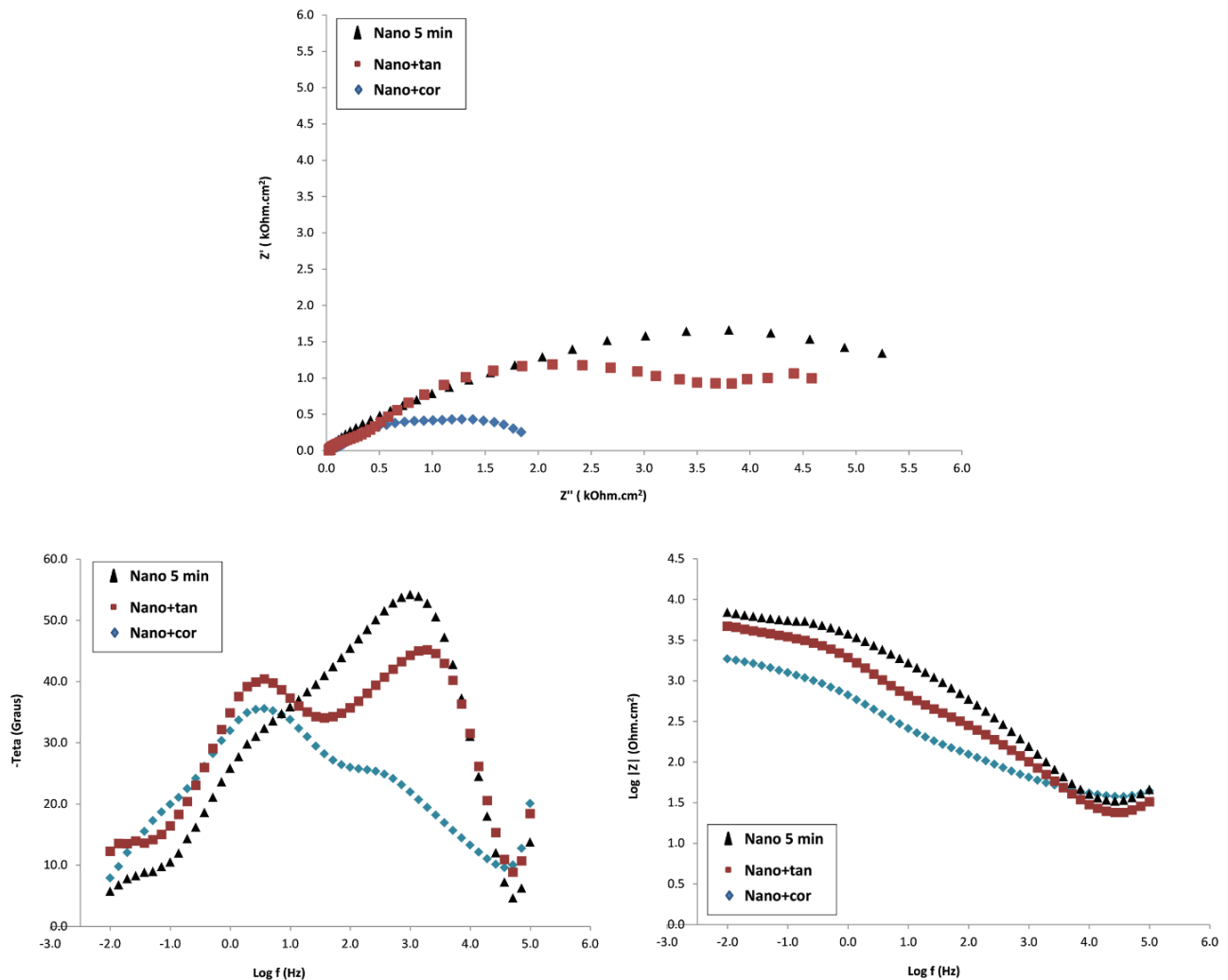


Figure 6. Nyquist and Bode diagrams for samples of alkaline zinc nanoceramic (5 min), nanoceramic coated and subsequent colorants after 24 h immersion in NaCl 0.1 M.

behavior is similar to the nanoceramic and tannin-based colorant coating, in terms of resistance.

It is important to notice that this study evaluated the coatings without a posterior organic paint layer. There are studies [23,25-28] where is shown that nano-Zr coatings are used as pre-treatments for organic paints. However, according to the purpose of this work, the nano-Zr and tannin based colorant can be used without the paint layer, whereas it had a similar corrosion protection to that of Cr III based coatings.

The performance of these coatings was evaluated for 336 hours in a humidity chamber [29]. The edges of the samples were isolated to avoid interferences. Table I describes the corrosion results.

At the end of the humidity chamber test, neither of the samples showed red corrosion, in other words, in none of them observed corrosion of the substrate. The codes B0,

B1, B2, B3, B4 and B5 are related to the corrosion from de zinc coating (white corrosion). The higher the number the greater the intensity of corrosion.

The Bare sample showed white corrosion since the first hours of the trial. Both of the chromate bases coatings were intact at the end of the test.

The sample coated with nano-Zr is sensitive to humidity therefore the white corrosion shows up quickly. Nevertheless, when a tannin-based colorant is deposited over this coating, a better protection is observed. The white corrosion points (B1) appearance observed since the beginning of the test can be explained by the coating heterogeneity. However, the sample showed no extra changes until the end of the test. This result confirms that the tannin-based colorant, besides conferring color, protected the zinc substrate against corrosion.

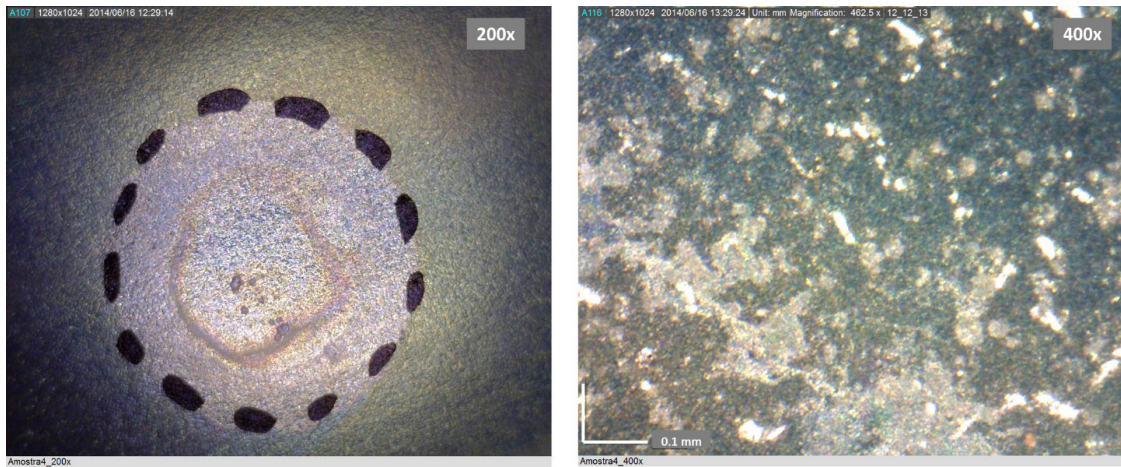


Figure 7. Optical microscope images at magnification 200x (left) and 400x (right) for the sample of alkaline zinc coated nanoceramic and later tannin based colorant after 24h test EIS.

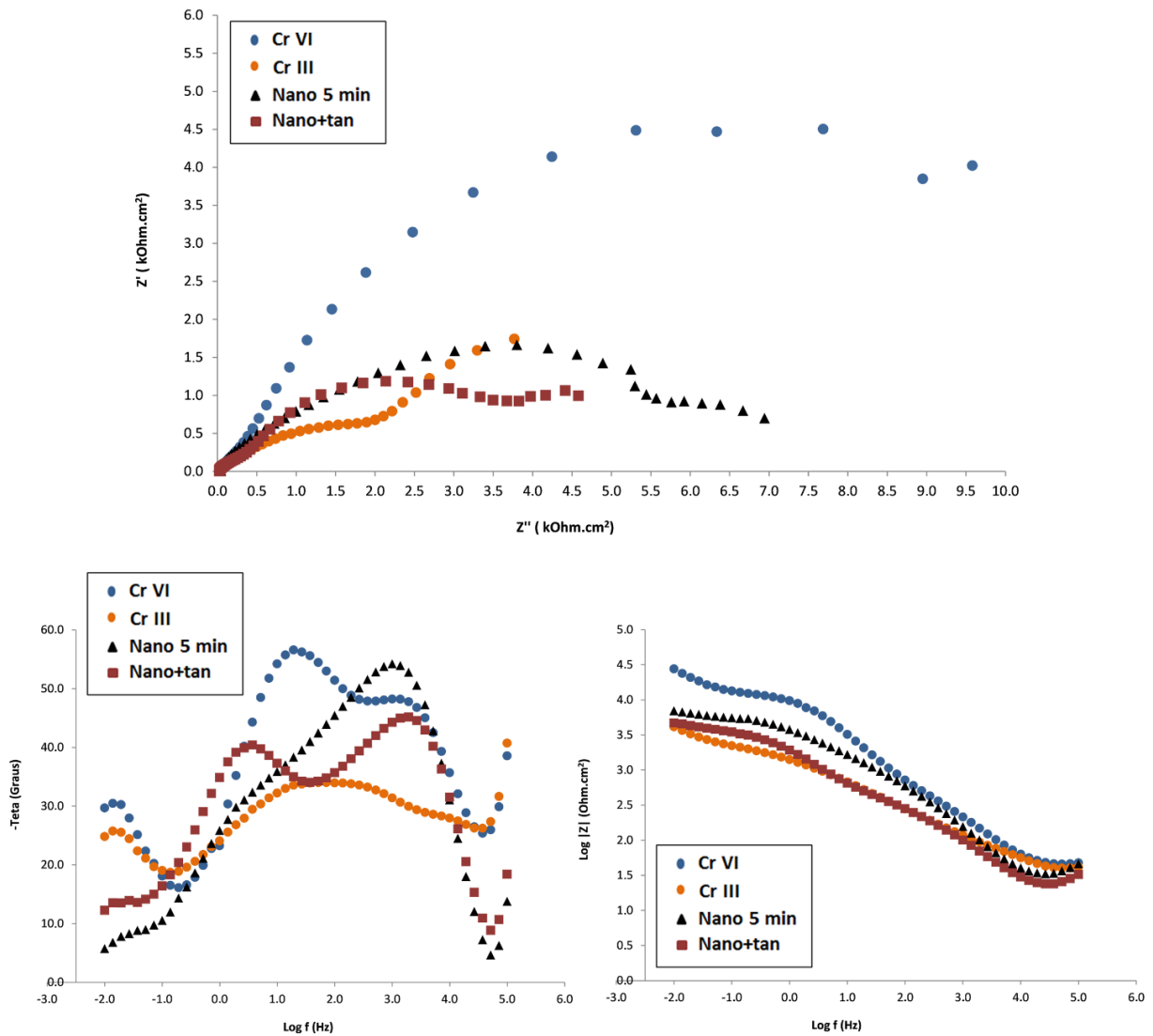


Figure 8. Nyquist and Bode diagrams for samples of alkaline zinc nanoceramic coated and later brown colorant-based tannin, hexavalent chromate and trivalent chromate, after immersion in NaCl 0.1 M to 24h.

Table 1. Samples with different coatings, exposed in a humidity chamber, during 336h

Time / Samples	Bare	Nano 5 min	Nano+cor	Nano=tan	Cr VI	Cr III
24h	B5	B1	B3	B1	B0	B0
48h	B5	B2	B4	B1	B0	B0
72h	B5	B2	B4	B1	B0	B0
168h	B5	B2	B5	B1	B0	B0
192h	B5	B2	B5	B1	B0	B0
216h	B5	B4	B5	B1	B0	B0
240h	B5	B4	B5	B1	B0	B0
264h	B5	B4	B5	B1	B0	B0
336h	B5	B4	B5	B1	B0	B0

Aspect or finishing (V-red, B-white). Corrosion degrees (0-perfect; 1-points in localized areas; 2-points in general; 3- localized areas; 4-partial; 5-total).

4 CONCLUSIONS

The conversion coating from the hexafluorozirconic acid solution (5 minutes immersion) as a pre-treatment is efficient because there is a film formation that protects the substrate against the corrosion. To confer color to the sample, the most efficient colorant was the tannin based one. This combination of nano-Zr coating and tannin based colorant proved to be efficient against corrosion, protecting the samples in both tests (EIS and humidity chamber).

Therefore, the nanoceramic zirconium based coating is a potential substitute for the chromate-based coating. Besides conferring color and protections against corrosion, this conversion coating is environmental friendly.

Acknowledgments

The authors thank CAPES, CNPq and FAPERGS – Brazil for financial support.

REFERENCES

- Hosseini M, Ashassi-Sorkhabi H, Ghasvand HAY. Corrosion protection of electro-galvanized steel by green conversion coatings. *Journal of Rare Earths*. 2007;25(5):537-543. [http://dx.doi.org/10.1016/S1002-0721\(07\)60558-4](http://dx.doi.org/10.1016/S1002-0721(07)60558-4).
- Almeida E, Fedrizzi L, Diamantino TC. Oxidising alternative species to chromium VI in zinc-galvanized steel surface treatment. Part 2 - an electrochemical study. *Surface and Coatings Technology*. 1998;105(1-2):97-101. [http://dx.doi.org/10.1016/S0257-8972\(98\)00476-9](http://dx.doi.org/10.1016/S0257-8972(98)00476-9).
- Yu S-X, Zhang R-J, Tang Y-F, Ma Y-I, Du W-C. Composition and performance of nanostructured zirconium titanium conversion coating on aluminum-magnesium alloys. *Journal of Nanomaterials*. 2013;2013:1-8. <http://dx.doi.org/10.1155/2013/594273>.
- Wang SH, Liu CS, Shan FJ. Corrosion behavior of a zirconium-titanium based phosphonic acid conversion coating on AA6061 aluminium alloy. *Acta Metallurgica Sinica. English Letters*. 2008;21(4):269-274. [http://dx.doi.org/10.1016/S1006-7191\(08\)60048-4](http://dx.doi.org/10.1016/S1006-7191(08)60048-4).
- Ghanbari A, Attar MM. Surface free energy characterization and adhesion performance of mild steel treated based on zirconium conversion coating: a comparative study. *Surface and Coatings Technology*. 2014;246:26-33. <http://dx.doi.org/10.1016/j.surfcoat.2014.02.057>.
- Bustamante G, Fabri-Miranda FJ, Margarit ICP, Mattos OR. Influence of prephosphating on painted electrogalvanized steel. *Progress in Organic Coatings*. 2003;46(2):84-90. [http://dx.doi.org/10.1016/S0300-9440\(02\)00214-X](http://dx.doi.org/10.1016/S0300-9440(02)00214-X).
- Mohammadloo HE, Sarabi AA, Alvani AAS, Salimi R, Sameie H. The effect of solution temperature and pH on corrosion performance and morphology of nanoceramic-based conversion thin film. *Materials and Corrosion*. 2013;64(6):535-543. <http://dx.doi.org/10.1002/maco.201106384>.
- Eivaz Mohammadloo H, Sarabi AA, Sabbagh Alvani AA, Sameie H, Salimi R. Nano-ceramic hexafluorozirconic acid based conversion thin film: surface characterization and electrochemical study. *Surface and Coatings Technology*. 2012;206(19-20):4132-4139. <http://dx.doi.org/10.1016/j.surfcoat.2012.04.009>.
- Bibber JW. Non-chrome-containing conversion coatings for zinc and zinc alloys: environmentally friendly alternatives provide equal or better adhesion and corrosion resistance as conventional methods. *Metal Finishing*. 2008;106(4):41-46. [http://dx.doi.org/10.1016/S0026-0576\(08\)80091-8](http://dx.doi.org/10.1016/S0026-0576(08)80091-8).

- 10 Droniou P, Fristad WE, Liang J-L. Nanoceramic-based conversion coating: Ecological and economic benefits position process as a viable alternative to phosphating systems. *Metal Finishing*. 2005;103(12):41-43. [http://dx.doi.org/10.1016/S0026-0576\(05\)80849-9](http://dx.doi.org/10.1016/S0026-0576(05)80849-9).
- 11 Xia X, Zhitomirsky I, McDermid JR. Electrodeposition of zinc and composite zinc–yttria stabilized zirconia coatings. *Journal of Materials Processing Technology*. 2009;209(5):2632-2640. <http://dx.doi.org/10.1016/j.jmatprotec.2008.06.031>.
- 12 Rahim AA, Rocca E, Steinmetz J, Kassim MJ, Adnan R, Sani Ibrahim M. Mangrove tannins and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium. *Corrosion Science*. 2007;49(2):402-417. <http://dx.doi.org/10.1016/j.corsci.2006.04.013>.
- 13 Qian B, Hou B, Zheng M. The inhibition effect of tannic acid on mild steel corrosion in seawater wet/dry cyclic conditions. *Corrosion Science*. 2013;72:1-9. <http://dx.doi.org/10.1016/j.corsci.2013.01.040>.
- 14 Ross TK, Francis RA. The treatment of rusted steel with mimosa tannin. *Corrosion Science*. 1978;18(4):351-361. [http://dx.doi.org/10.1016/S0010-938X\(78\)80049-3](http://dx.doi.org/10.1016/S0010-938X(78)80049-3).
- 15 Matamala G, Smeltzer W, Droguett G. Comparison of steel anticorrosive protection formulated with natural tannins extracted from acacia and from pine bark. *Corrosion Science*. 2000;42(8):1351-1362. [http://dx.doi.org/10.1016/S0010-938X\(99\)00137-7](http://dx.doi.org/10.1016/S0010-938X(99)00137-7).
- 16 Moraes JA. Estudo do revestimento nanocerâmico zircônio/titânio em aço carbono na proteção contra corrosão. Fortaleza: INTERCORR; 2010.
- 17 Costa JS. Influência da adição de corante nos revestimentos de conversão à base de zircônio em peças de aço zincado por eletrodeposição. Fortaleza: INTERCORR; 2014.
- 18 Costa JS. Avaliação do revestimento de conversão à base de zircônio e tanino sobre aço zincado por eletrodeposição. Porto Alegre: UFRGS; 2014.
- 19 Gusmano G, Montesperelli G, Rapone M, Padeletti G, Cusmà A, Kaciulis S, et al. Zirconia primers for corrosion resistant coatings. *Surface and Coatings Technology*. 2007;201(12):5822-5828. <http://dx.doi.org/10.1016/j.surfcoat.2006.10.036>.
- 20 Fedrizzi L, Rodriguez FJ, Rossi S, Deflorian F, Di Maggio R. The use of electrochemical techniques to study the corrosion behaviour of organic coatings on steel pretreated with sol–gel zirconia films. *Electrochimica Acta*. 2001;46(24-25):3715-3724. [http://dx.doi.org/10.1016/S0013-4686\(01\)00653-3](http://dx.doi.org/10.1016/S0013-4686(01)00653-3).
- 21 Andreatta F, Turco A, de Graeve I, Terryn H, de Wit JHW, Fedrizzi L. SKPFM and SEM study of the deposition mechanism of Zr/Ti based pre-treatment on AA6016 aluminum alloy. *Surface and Coatings Technology*. 2007;201(18):7668-7685. <http://dx.doi.org/10.1016/j.surfcoat.2007.02.039>.
- 22 Duarte RG, Bastos AC, Castela AS, Ferreira MGS. A comparative study between Cr(VI)-containing and Cr-free films for coil coating systems. *Progress in Organic Coatings*. 2005;52(4):320-327. <http://dx.doi.org/10.1016/j.porgcoat.2004.05.011>.
- 23 Eivaz Mohammadloo H, Sarabi AA, Mohammad Hosseini R, Sarayloo M, Sameie H, Salimi R. A comprehensive study of the green hexafluorozirconic acid-based conversion coating. *Progress in Organic Coatings*. 2014;77(2):322-330. <http://dx.doi.org/10.1016/j.porgcoat.2013.10.006>.
- 24 Ramezanzadeh B, Attar MM, Farzam M. Corrosion performance of a hot-dip galvanized steel treated by different kinds of conversion coatings. *Surface and Coatings Technology*. 2010;205(3):874-884. <http://dx.doi.org/10.1016/j.surfcoat.2010.08.028>.
- 25 López Ibáñez R, Martín F, Ramos-Barrado JR, Leinen D. Large area zirconia coatings on galvanized steel sheet. *Surface and Coatings Technology*. 2008;202(11):2408-2412. <http://dx.doi.org/10.1016/j.surfcoat.2007.09.016>.
- 26 Vermoyal JJ, Frichet A, Dessemond L, Hammou A. AC impedance study of corrosion films formed on zirconium based alloys. *Electrochimica Acta*. 1999;45(7):1039-1048. [http://dx.doi.org/10.1016/S0013-4686\(99\)00307-2](http://dx.doi.org/10.1016/S0013-4686(99)00307-2).
- 27 Cerezo J, Vandendael I, Posner R, Lill K, de Wit JHW, Mol JMC, et al. Initiation and growth of modified Zr-based conversion coatings on multi-metal surfaces. *Surface and Coatings Technology*. 2013;236(0):284-289. <http://dx.doi.org/10.1016/j.surfcoat.2013.09.059>.

- 28 Verdier S, van der Laak N, Dalard F, Metson J, Delalande S. An electrochemical and SEM study of the mechanism of formation, morphology, and composition of titanium or zirconium fluoride-based coatings. *Surface and Coatings Technology*. 2006;200(9):2955-2964. <http://dx.doi.org/10.1016/j.surfcoat.2004.10.139>.
- 29 ASTM International. D2247: standard practice for testing water resistance of coatings in 100% relative humidity. West Conshohocken, PA: ASTM International; 2011. <http://dx.doi.org/10.1520/D2247-11>.

Received: 12 Dec. 2014

Accepted: 25 May 2015