Avaliação da resistência à corrosão em chapas de aço-carbono protegidas por revestimentos nanocerâmicos a base de zircônio e titânio

Corrosion resistance evaluation of carbon steel plates protected by zirconium and titanium nanoceramic coatings

Evaluación de resistencia a la corrosión de placas de acero al carbono protegidas con recubrimientos nanocerámicos de circonio y titánio

Recebido: 03/02/2020 | Revisado: 15/02/2020 | Aceito: 20/02/2020 | Publicado: 10/03/2020

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Resumo

O pré-tratamento de superfícies metálicas é um processo conhecido e utilizado com o intuito de aumentar o desempenho contra a corrosão, bem como melhorar a aderência entre o substrato e a camada de tinta. O presente trabalho avaliou a resistência a corrosão do aço carbono antes e após o tratamento com revestimentos nanocerâmicos. A comparação foi entre um composto nanocerâmico de zircônio (Bonderite NT-1) puro, este com a adição de um dispersante (ácido poliacrílico) e um outro revestimento nanocerâmico desenvolvido a partir do óxido de titânio. Adicionalmente, foram realizados testes de névoa salina, potencial de circuito aberto (OCP), polarização e impedância para obter uma metodologia para avaliar quantitativamente a qualidade da proteção. O revestimento de zircônia apresentou melhor proteção a corrosão em relação ao revestimento de titânio e aço carbono sem revestimento. O potencial de corrosão deste revestimento foi cerca de duas vezes menor que o aço carbono sem revestimento, enquanto para o revestimento de titânio foi cerca de 1,5 vezes menor. A adição de dispersante não produziu melhorias significativas na resistência a corrosão e se mostrou semelhante ao aço carbono sem revestimento, possivelmente pela alta concentração utilizada.

Palavras-chave: Zircônio; Titânio; Revestimentos; Nanocerâmicos.

Abstract

Metal surface pre-treatment is a known process and is used to increase corrosion performance as well as improve adhesion between the substrate and the paint layer. The present paper evaluated the corrosion resistance of carbon steel before and after treatment with nanoceramic coatings. The comparison was between a pure zirconia nanoceramic compound (Bonderite NT-1), with the addition of a dispersant (polyacrylic acid) and another nanoceramic coating developed from titanium oxide. Additionally, salt spray, open circuit potential (OCP), polarization and impedance tests were performed to obtain a methodology to quantitatively assess the quality of protection. The zirconia coating presented better corrosion protection than the titanium coating and carbon steel without coating. The corrosion potential of this coating was about twice as low as carbon steel without coating, while for the titanium coating it was about 1.5 times less. The addition of dispersant produced no significant improvements.
in corrosion resistance and was similar to uncoated carbon steel, possibly due to the high concentration used.

**Keywords:** Zirconia; Titanium; Coatings; Nanoceramics.

**Resumen**

El pretratamiento de la superficie metálica es un proceso conocido y se utiliza para aumentar el rendimiento de corrosión y mejorar la adhesión entre el sustrato y la capa de pintura. El presente trabajo evaluó la resistencia a la corrosión del acero al carbono antes y después del tratamiento con recubrimientos nanocerámicos. La comparación fue entre un compuesto nanocerámico de circonio puro (Bonderite NT-1), con la adición de un dispersante (ácido poliácrylic) y otro recubrimiento nanocerámico desarrollado a partir de óxido de titanio. Además, se realizaron pruebas de niebla salina, potencial de circuito abierto (OCP), polarización e impedancia para obtener una metodología para evaluar cuantitativamente la calidad de la protección. El recubrimiento de circonio presenta una mejor protección contra la corrosión que el recubrimiento de titanio y acero al carbono sin recubrimiento. El potencial de corrosión de este recubrimiento era aproximadamente el doble que el acero al carbono sin recubrimiento, mientras que para el recubrimiento de titanio era aproximadamente 1.5 veces menor. La adición de dispersante no produjo mejoras significativas en la resistencia a la corrosión y fue similar al acero al carbono sin recubrimiento, posiblemente debido a la alta concentración utilizada.

**Palabras clave:** Circonio; Titanio; Recubrimientos; Nanocerámicos.

**1. Introduction**

Metals are fundamentals compounds for infrastructure development and daily life products. Therefore, it is of great relevance to the technological progress aiming to obtain greater resistance to aggressive conditions, expanding the range of these compounds applications (Gentil, 2011).

The carbon steel excels at industrials applications by its mechanical properties. However, it is unavoidable the occurrence of corrosion on harsh surroundings and means (Guo, Kaya, Obot, Zheng, & Qiang, 2017). This iron alloy has between 0.05 and 2.0 % per carbon mass besides small quantities of others compounds and it receives considerable attention for the solutions of problems involving corrosion (Bossardi, 2007; Guo et al., 2017). The pre-treatments of the metallic surfaces are presented as a mean to improve the
performance against corrosion, besides, to enhance the adherence of the substrate and the paint layer (Ramanauskas, Girčienė, Gudavičiūtė, & Selskis, 2015; Sugiarti et al., 2015).

The phosphating and chromatization are common processes used as this purpose, however, it may present various environmental concerns and problems with the low surface cover (Popić et al., 2011; Ramanauskas et al., 2015). While the phosphating needs heating, resulting in an energetic cost, the chromate is known for being a toxic and carcinogenic compound (Milošev & Frankel, 2018). Insight of the need to use sustainable process, the technology of nanoceramics surfaces coatings is proposed and applied to reduce the environmental impacts caused by conventional treatments.

The main advantages of this new process encompass the high reactivity of the nanostructured compounds, the better utilization as well as the minor residues generation. The high reactivity makes possible the greater processing reduction time on the cold or room temperature processes. While the small residues generation solves one of the serious problems of phosphating. These two advantages together lead to an economy of water and energy (Adhikari et al., 2011).

The nanoceramics coatings have been presenting efficiency not only in carbon steel applications but also with others metals. The Roman and contributors (2011) study accomplished the coating of titanium surfaces on the search for biological applications. Given the titanium biocompatibility with the human body only occurred with the absence of corrosion. Costa and contributors (2015) used zinc as a substrate and they evidenced the great formation of the zirconium coating. The created protection was similar to the obtained by chromatization.

Roman and contributors (2011) performed a comparative study about the temperature variation used during the formation stage of a thin nanofilm and the obtained corrosion resistance. Regarding the temperature, it was verified that the major the variable is, the major will be the obtained corrosion resistance. However, the room temperature bath presented satisfactory quality, a fact of great importance for industrial applications due to is charge generated by having an energy supply.

Ramanathan and Balasubramanian (2016) studied the mechanism of nanoceramics coatings of low carbon steels. The researchers found a deposition of hydrated nano zirconia under the carbon steel surface. The formation of this thin and uniform layer of oxide gives the same special properties after the coating of the paint layer, comparing to the process involving phosphate and zinc.

According to Droniou and Fristad (2005), the high spontaneity of the process results
in a prompt deposition of the oxide metallic nanoparticles, between 20 to 30 seconds. Hence, there is a formation of an irregular coating layer. Therefore, the addition of a dispersant compound to decrease the deposition velocity is suggested. The compound forms a colloidal mixture through Brownian motion, charges repulsion and solvation. Among the dispersants, the polyacrylic acid shows interesting for being a compound with high molecular mass and it can decelerate the deposition. However, its addition must be with small concentrations, about 0.025 %m, aiming to maintain the process viable (Ramanathan & Balasubramanian, 2016).

The recent studies emphasized the possibility to apply nanoceramics titanium coatings (Zhang et al., 2019), due to is chemical and reactional similarity compared to the zirconium. Thence, this study proposes a new side for the bath immersion produced from the titanium oxide, similar to the methodology used by Ramanathan and Balasubramanian (2016) for the zirconium oxide.

The purpose of this study is to evaluate the corrosion resistance of carbon steel after application of the protective coatings. The layers were of three species: zirconia nanoceramics coatings with or without dispersant addition and titanium nanoceramics coatings. To measure the best coating, it was accomplished saline mist tests, Open Circuit Potential (OCP), polarization and impedance, analyzing the protection efficiency qualitatively and quantitative.

2. Materials and methods

2.1 Plates Cuttings, Pickling, Rinse and Degreaser

It was obtained 18 cold-rolled carbon steel plates with dimensions of 15 x 18 cm and, 10 plates of the same material, with dimensions of 10 x 10 cm. The plates with dimensions 15 x 18 cm were utilized on the Salt Spray tests, while the plates of 10 x 10 were cut in sheets of 2.5 x 2.5 cm for the impedance tests and the polarization curve accomplishment.

After the cut, the plates went to a degreaser process aiming to remove the mineral oil layer that is applied by the industry to protect the sheets during transportation and storage. The degreaser was performed with the assistance of an appropriate solvent (thinner) and a cotton waste. In sequence, it was performed the rinse of the samples to remove the solvent excess.

With the clean sheets, it was affected the pickling process aiming to remove the possible points of oxidation that may be formed on the metallic surface. This procedure was
accomplished from a concentrated solution of chloride acid (0.1 M) and a 3M-grain sandpaper 50.

2.2 Zirconium Bath Immersion

The bath immersion has the purpose to create a protective layer of zirconium oxide over the substrate and it is prepared from the dilution on 50 mL of the commercial product Bonderite M-NT 1 on 950 mL of distilled water. Followed by the addition of the product Bonderite M-AD 700 until the bath reaches pH 4, according to the product instruction. Posteriorly, the plates were submerged on the bath for 60 seconds, the necessary time for the formation of the protective layer. There were also performed another zirconium bath similarly, diverging only for the addition of a dispersant compound (polyacrylic acid), to obtain a concentration of 0.025 %m.

2.3 Titanium Bath Immersion

Due to the absence of titanium commercial products, the study proposes the development of a methodology that searches for a bath formation that makes possible the application of this metal coating. The necessary reagents were the titanium oxide and the hydrofluoric acid 48 %v.

Primarily, it was dissolved 5 g of titanium oxide on 75 g of hydrofluoric acid on a reactor of Teflon, a material resistant to deterioration and recommended to experiments with hydrofluoric acid. The mixture passed by constant agitation at 40 °C for 12 hours to break the oxide bonds and to obtain a limpid solution and full of titanium ions.

The resulted supernatant solution went to centrifugation to remove possible colloidal oxides, and posteriorly, to an evaporation stage, obtaining solid crystals. On a volumetric flask of 1 L, it was added 500 mL of distilled water and it was dissolved one gram of the obtained solid of evaporation, then the flask had volume filled until its bounding mark.

The obtained solution passed by pH measurement and it was adjusted to 4 with a commercial neutralizer Bonderite M-AD 700. After these stages, it was performed the immersion of three steel plates on the solution for 60 seconds aiming at the coating.

2.4 Salt Spray Test
On this test, it was used steel sheet of 15 x 18 cm which was painted with black synthetic enamel and posteriorly it had coated edges with paraffin to prevent any interference of the test due to the difficulty to correct the coating on the piece ends.

Then, it was performed an “X” cut in the middle of the plates with the support of a stiletto to each line had 10 cm of length and it was distant by an angle of 30º, according to ISO 17872:2007. The pieces were placed on the interior of the chamber and the Salt Spray test was performed for 48 hours, by the standard ISO 9227:2012.

2.5 Electrochemical Tests

The twelve plates used on Open Circuit Potential (OCP), impedance and polarization curve tests obtained one of its faces and ends isolated by a polymeric resin (polymethylmethacrylate). This isolation aims to facilitate the exposed area quantification during the test, besides to avoid the influence of the corrosion in the ends.

The Open Circuit Potential (OCP) test was performed using the potentiostat Omnimetra PG-3906. The specific time was of 3600 seconds and a sampling of 5 seconds, resulting in 720 samples.

The impedance and the polarization curve tests were conducted by the software PG39M, being used as a potentiostat concerning an electrode of silver/silver chloride and an against electrode of platinum. All the tests were accomplished with NaCl 3.5% solutions.

On the impedance test was used a frequency variation between 10 mHz and 10 kHz, besides an excitation voltage of 10 mV. Then, it was performed the polarization essays using a scan rate of 1 mV/s, being applied between the limits of -0.5 and 1.5 V regarding the equilibrium potential obtained by the OCP test.

3. Results and Discussion

3.1 Salt Spray Test

After 48 hours of the Salt Spray test, it was verified that three coatings were sufficiently resistant to corrosion being possible to notice that the “X” cut has not increased in thickness and did not occur the casting phenomenon. Therefore, it is possible to classify the test as inconclusive, when it would be desirable to make official it there was an improvement.
of the deposition quality with the increase of the dispersant or with the use of the titanium coating. Thus, it becomes extremely relevant to the impedance and polarization curve tests analyses. The test was not followed up because the results of the impedance and polarization curve tests analyses show the difference in corrosion resistance between the coatings.

3.2 Open Circuit Potential (OCP) Test

The Open Circuit Potential (OCP) test has the purpose to express if the system analyzed is in equilibrium after one hour of metal excitation, which it searches for the dynamic equilibrium of the system (metal-solution) before the variation tests of current and potential start. Figure 1 presents the graphics of OCP for the unprotected carbon steel with the zirconia coating with or without dispersant addition and the titanium base.

Figure 1: Open Circuit Potential for the carbon steel with or without coatings.

Based on Figure 1, it is noticed that the potential reached the expected dynamic equilibrium. Since after the end of the 1h immersion, the potential did not present considerable variations. According to Wolynec (2003), for the unbalance or the passive layer break occur, it must have a variation superior to 0.5 V on the final 5 minutes of the test, which had not to happened on the performed tests.

It must be pointed out that the lower the Open Circuit Potential, the most active the material on the site and the lower the corrosion resistance (Hadinata et al., 2013).
it is noted corrosion potentials are similar among the coated steels and with superior values than the pure carbon steel. Consequently, the coated steels have presented more resistant to corrosion.

In spite of the steel with zirconia coating and titanium coating presenting a similar behavior, the Open Circuit Potential the zirconia coating was greater at the end of the test. Therefore, this coating has a better resistance to corrosion in relation to the titanium coating.

The Open Circuit Potential of the zirconia coating with dispersant addition had decreased with time and it reached the value of the uncovered carbon steel corrosion potential. This behavior is due to the addition of the dispersant that had produced a very thin coating that did not resist for a long time to corrosion and eventually it left the steel uncovered.

3.3 Linear Polarization Tests

For the polarization analyses, it was performed the arithmetic mean of the data relative to the triplicate of each coating. Figure 2 resumes the results of the polarization obtained for the carbon steel without coating, with zirconia coating, with zirconia coating and dispersant and with titanium coating. The current density is represented on the graphic abscissa.

Figure 2: Polarization curves for carbon steel with or without coating.

Source: Authors.
The carbon steel without coating, with nanoceramic zirconia coating and dispersant and with titanium coating have corrosion potential raised in the module, around 0.89 V, -0.88 V and -0.75 V, respectively. The carbon steel with nanoceramic zirconia coating was the one that presented major corrosion resistance with a corrosion potential of -0.47V. The minor titanium performance is because the literature presents that the TiCl₄ baths produce more uniforms layers than the ones produced by the H₂TiF₆ baths (Milošev & Frankel, 2018), consequently, these layers are more resistant to corrosion.

The carbon steel without coating presented high current density and therefore, greater corrosion rates (Behzadnasab, Mirabedini, & Esfandeh, 2013; Ramanathan & Balasubramanian, 2016). It is noticed that the corrosion potential indicated by the polarization curves shows that the carbon steel with titanium coating presented lower current density, while the carbon steel with nano-ceramic coating and dispersant presented a greater density, thus, it is verified that the dispersion acted negatively on the substrate protection. It was not observed the presence of “current shots”, which indicated the absence of local corrosion on the samples analyzed.

Similarly, to Ramanathan and Balasubramanian (2016), the carbon steel with nanoceramic zirconia coating presented a small corrosion potential and inferiors current densities when compared to the steel without coating, being this one the coating with the greater performance on the tests accomplished at this article.

### 3.4 Impedance Tests

Figures 3 and 4 exhibits the tests results for the impedance test through the Nyquist and Bode graphics, respectively.

Figure 3: Nyquist curves representation for the carbon steel with and without coating.
According to Figure 3, Nyquist graphic, it is noticed the increase of the corrosion resistance with the coatings. On the analyzed frequencies, the coatings supported the entrance of corrosives species, however, there is not the protection of the corrosive raw metal during the time and with the increase of the excitation frequency. The distortions indicate the number of attempts on the entrance of the corrosives species on the coating, showing a greater tendency to corrosion with the increase of the excitation. It must be accentuated that the pure
steel behavior is entirely different, having a small resistance module due to the imaginary axis contribution, indicating to be more prone to the attack of corrosives species (Behzadnasab et al., 2013; Ramanathan & Balasubramanian, 2016).

By Figure 4, Bode graphic, it is noticed the decrease of the log | Z | values as the increase of frequency is created, which was expected. The log | Z | value for the pure carbon steel was 1.75 kΩ and for the coated carbon steel was 2.00 kΩ. According to the literature, the greater the log | Z | value, the greater the corrosion resistance (Ramanathan & Balasubramanian, 2016). Therefore, all the coatings presented performance superior to pure carbon steel.

4. Final considerations

The commercial nanoceramic coating presented efficiency to increase the corrosion resistance of the carbon steel but the dispersant addition, even at small quantities, made the deposition process unavailable, possibly dispersing the coating and causing the unprotection at certain regions. This result was corroborated by the polarization and impedance tests, in which the commercial coating presented better results when compared to the one that was added the dispersant. It was noted for the titanium coating that it did not show efficient as the zirconium coating, which does not discard its application on the metal protection, expanding the possibility of the investigation of new methodologies for this bath preparation. Among the alterations that can be accomplished, there is the possibility to use hydrochloric acid on titanium oxide dilution. The attitude that would lead the TiCl₄ formation instead of H₂TiF₆.

Acknowledgments

The authors thank the support of the Federal University of São João Del-rei (UFSJ), Federal University of Viçosa (UFV) and Federal University of Itajubá (UNIFEI). Especially to the Department of Chemical Engineering (UFSJ), Department of Chemistry (UFV) and Institute of Integrated Engineering (UNIFEI). This paper was carried out with the support of the Higher Education Personnel Improvement Coordination - Brazil (CAPES) – Financing Code 001, Minas Gerais State Research Support Foundation (FAPEMIG) and Arthur Bernardes Foundation (FUNARBE). The authors also thank Henkel for making a sample of their products available for the development of research.
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