Electrochemical evaluation of Zn-Fe coatings deposited with pulsed current

Evaluación electroquímica de Recubrimientos Zn-Fe depositados con corriente pulsante

Received: 20 - 11 - 2014 Accepted: 20-05-2015

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Abstract

This work presents the electrochemical characterization to evaluate the corrosion resistance of Zn-Fe metal coating electroplated foil substrates cold-rolled steel. The coating is deposited by a function generator, an oscilloscope and an electrolytic cell of 50 mL, provided with a soluble anode of pure zinc. The reagents used were analytical grade, and the tests were performed at a temperature of 25 ^{O}C. No complexing agents were used or polishes; so that the process is environmentally clean. The electrochemical characterization measurements made with open circuit potential, linear polarization resistance and electrochemical impedance spectroscopy show that within the range of duty cycle from 87.5 % to 97.5 %; and with varying frequencies between 40 Hz and 100 Hz, the effect of the reverse current pulse promotes corrosion resistance coating for frequencies of 100 Hz; the samples with higher corrosion resistance was obtained in 90 % duty cycle, and are shown in the content of this article.

Keywords: duty cycle; electroplating; LPR; pulsed current; reduction potential; Zn-Fe alloy.

Introduction

The electro-coating with reverse current pulse (PRC) is a technique in which a direct current (DC) is replaced with waves of currents of regular or irregular geometries. This technique has been recognized by a long time; the method of electro-covering using modulated currents it dates back of 1951, nevertheless the use of cathode simple pulses was studied strongly in the 70s; the technique (Electroplating) and its application for pulses enables the execution of top densities of plated by what refines the size of grain, improves the ductility and the conductivity of the warehouses, and removes incorporation of impurities (Silveston, 2013).

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Zn coating and its alloys on substrates of steel of low carbon, offer a variety of applications in the industry due to its moderate cost and its relative simplicity of obtaining. Additional, the corrosion of steel is a frequent reason of economic losses due to the fact that the material loses mechanical properties and of permanence affecting the safety of the persons due to the fault of structures and vehicles (Krugger, 2003).

Electrodeposited coatings from electrolyte that contained zinc and iron ions in solution were obtained, since the co-deposition of these two elements on the steel might improve the behavior opposite to the corrosion with regard to the pure zinc and other Zn's coverings with elements of alloy of the group of the iron (Carcel, 1990). Nevertheless, it is a topic of experimentation to find the parameters (Lodhi et al., 2007; Bajat et al., 2004) of frequency and cycle duty, in agreement with the covering that is wanted to obtain, since the changes in these variables are reflected in the type of obtained covering.

The electroplating by pulses was based on the application of different geometries of current both on the cathode pulses and on the anodic pulses. The introduction of the technology Pulsates Re-turn Current PRC reduces the use of additives, which limit the ductility and the electrical conductivity of the warehouses; modifying the parameters of the pulse wave changes are obtained in the composition, structure and porosity of the warehouses (Chandraseka, 2008).

Methodology

In the obtaining of the electro-coverings they were used: a volume of the electrolyte of 50 ml, reagents of analytical type, an acid electrolyte (pH=4.3) compound of $ZnSO_4$-$7H_2O$ 160 gm/l, $FeSO_4$-$7H_2O$ 16 gm/l, H_3BO_3 12 gm/l, Na_2SO_4 40 gm/l, and (Praveent, 2011), to a temperature of 25 °C, with a time of deposition of 5 minutes.

The tests of electroplating with reverse current pulse (PRC) carried out in a dynamic way; a cell was in use with capacity of 50 mL. Since cathodes in each of the processes used sheets of steel cold-rolled of 6 cm^2 and Zn's consumable anodes with a purity of 99 %. Before the process of deposition, the cathodes submerged in a solution of isopropyl alcohol for a process of cleanliness of degrease with help of ultrasound. For the ultrasound an equipment used Clean Ultrasonic, often of HF's delivery 35 kHz. After the ultrasound an electrolytic rinsing was realized by deionized water, and then (PRC) were covered with the technique of reverse current pulse.

They were realized electro depositions, with squared wave as 1 is observed in the Figure. The application of pulses of potential happened rapidly and alternative between two different values. The composition and thickness of the warehouse is possible to control them regulating the extent and width of pulse (Paunovic, 2010; Chandrasekar, 2008; Ravindra, 2008).

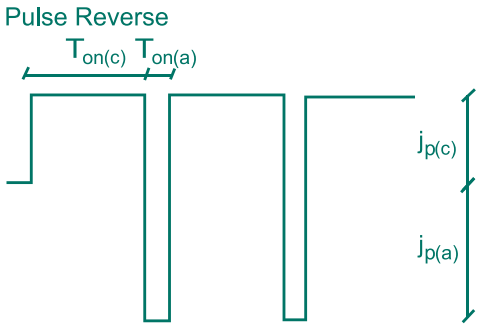

Figure 1. Square wave generated with reverse current pulsed. **Source:** (Silveston, 2013)

During each test the pH was checked and kept constant at a value of 4.3; the warehouses were realized without stir of the electrolyte on substrates of sheets of steel cold-rolled and with end of factory. It was worked with an effective dimension of the sample of 2 cm x 3 cm and thickness of 1mm.

In the Figure 2 there appears the equipment of Generating laboratory of Functions AFG 2125 GW INSTEK, oscilloscope Gos 1152[a] Gw Instek, belonging to the Center of Technical Assistance to the Industry (ASTIN)-SENA.

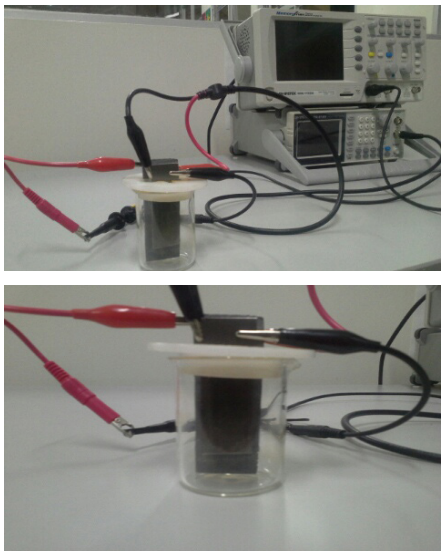

Figure 2. Image of the assembly used as unit of electro deposition for laboratory **Source:** The authors

To each of the coated samples there were realized tests of potential of opened circuit, resistance to the linear polarization and electrochemical impedance spectroscopy ; and diagrams obtained with graphs with an equipment brand GAMRY model PCI-4; belonging to the Pedagogic and Technological University of Colombia. The samples submitted to NaCl's solution to 1 %.

The results allowed to evaluate if the technology of pulsed current presented changes in the resistance to the corrosion of the coated material.

Outcomes

Potential of Balance

In the deposited coatings, the potential of balance was nearby to -1V, as are observed in the Figure 3. The warehouses realized with a duty cycle of 90 % and with a variation of the frequency they showed that for a value of 100 Hz, there was obtained a value of potential of more negative balance.

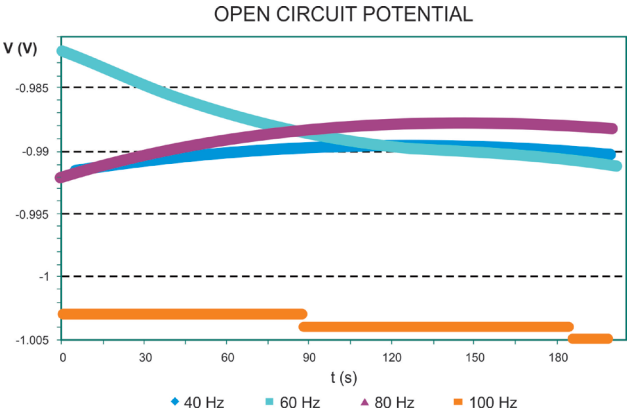

Figure 3. Curves of potential of circuit opened for coverings deposited with a duty cycle of 90 % and variation of the frequency. **Source:** The authors

Resistance to the Linear Polarization

In the figures 4 and 5 appear the curves of resistance to the linear polarization, realized to the coverings with a cycle Duty of 90 %; the major value was obtained for the covering realized with a frequency of 100 Hz.

The graphs obtained with the software Gamry Echem Analyst showed that as the frequency increased in the accomplishment of the warehouse, the curves presented an increase in the slope to a frequency of 100 Hz.

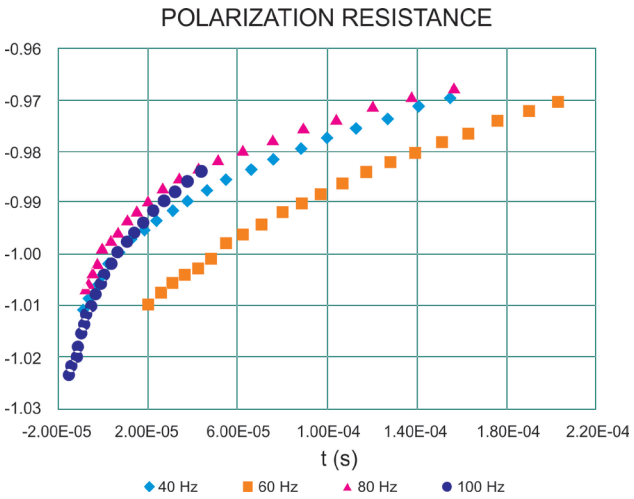

Figure 4. Graph of resistance to the polarization depending on the frequency. **Source:** The Authors.

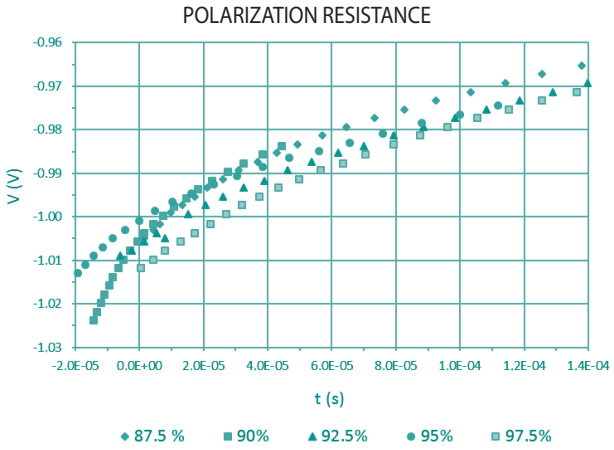

Figure 5. Graph of resistance to the polarization depending on the duty cycle. **Source:** The Authors

In the Figure 6 it is observed as the slope of the curve of linear polarization, it allowed to calculate the speed of corrosion, using the software Gamry Echem Analyst and selecting two points on the curve with values of more or less 10 mV above and below of the potential of balance and planning a straight line between them; the speed value of corrosion was calculated in thousandth of inch for year (mpy) obtaining a value of 968 mpy.

The pulsed current with greater anodic times of 90 % from the duty cycle, presented the coating with the minor speed of corrosion with regard to other coatings, for presenting the major slope of the curve of linear polarization; likewise the speed of corrosion diminished. In the Figure 7 the Bode diagram is observed where the values of impedance of the electrolytic solution remained nearby for each of the depositions, reflecting the stability of the electrolyte; likewise there

was confirmed the major resistance of polarization of the coating represented by the line plotted in the top left part, which value approaches to 1 KOhm.

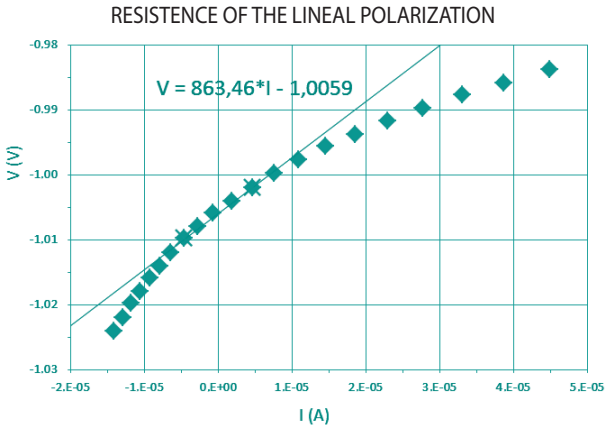

Figure 6. Graph of resistance to the linear polarization; for the coating realized to a frequency of 100 Hz.
Source: The Authors

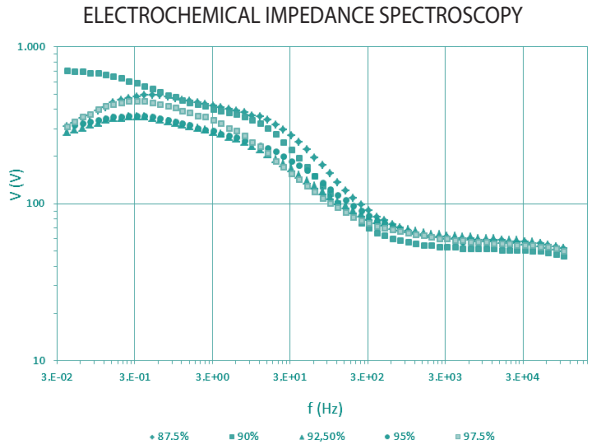

Figure 7. Bode Diagram.
Souerce: The Authors.

In the Image 1 is observed the superficial condition of five samples coated by means of the mentioned technique, which allowed to check how the coated region remained protected before the corrosive assault of the environment.

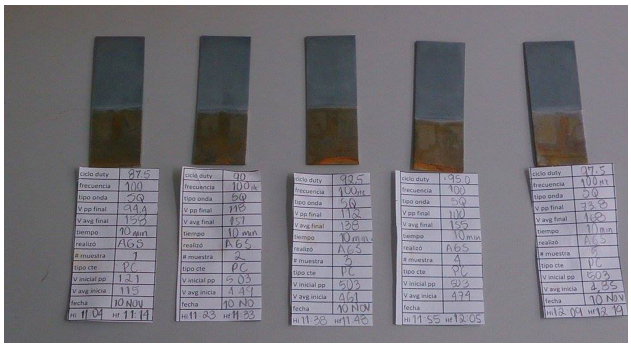

Image 1. Natural evolution of the phenomenon of the corrosion and the protective effect of the deposited coated.
Source: The Authors.

Conclusions

To low frequencies of deposition, the coating samples prove minor slopes in the curve of linear polarization. In this way the speed values of corrosion increase, indicating that the coatings will have major trend to deliver its electrons to the surrounding way of agreement with the reaction of oxidation.

An increase in the value of resistance to the linear polarization, reflects a minor speed of corrosion of the coating. This agrees with the indication of which the technology of electrolytic deposition pulsed current sources and it improves the refinement of the size of grain of the warehouses; the size of grain of the coating obtained with a frequency of 100 Hz will be minor that the obtained ones with lower values of frequency.

Independently of the technique of deposition with current DC, it allowed to observe changes in the speed of corrosion of the deposited coating. The neat registry of these physicochemical changes allows to fit new warehouses to environmental specific conditions of agreement with the applications of profiles, panels and elements for the self-propelling industry.

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