Evaluation of the electrical conductivity and corrosion resistance for layers deposited via sputtering on stainless steel

J Blanco¹, Y Salas², C Jiménez³, Y Pineda¹ and A Bustamante²
¹ Universidad INCCA, Bogotá, Colombia
² Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia
³ Pontificia Universidad Javeriana, Bogotá, Colombia

E-mail: juan.blanco@uptc.edu.co

Abstract. In some Engineering fields, we need that conductive materials have a mechanic performance and specific electrical for that they maintain conditions or corrosive attack if they are in the environment or if they are closed structure. The stainless steels have an inert film on their surface and it has the function to act in contrast to external agents who generates the corrosion, especially for stings, spoiling the film until to fail. We found a solution taking into account the electrical performance and the anticorrosive; into the process we put recovering of specific oxides on, stainless steel using the method of sputtering with Unbalanced Magnetron, (UBM) varying the oxygen in the reactive environment. The coating obtained had a thickness one micron approximately and we saw on serious structural uniformity [1]. The corrosion resistance was evaluated through the potentiodynamics polarization and electrochemical spectroscopy impedance in NACL according to the standard. The cathode protection is the most important method employed for the corrosion prevention of metallic structures in the soil or immersed on the water. The electrical resistivity was evaluated with the four points methods and it showed a behaviour of diode type in some substrates with a threshold potential in several volts. We noticed a simple resistance solution when it was analysed in the Nyquist graphics whith the Electrochemical Impedance Spectroscopy technique. With on equivalent circuit, for this reason we determinate a variation in the corrosion speed in almost two orders of magnitude when we analysed the potentiodynamics curve by Tafel approximation. The data obtained and analysed show that this type of surface modification maintains the conductivity condition at the interface, improving the resistance in relation whit the corrosion of these elements where the recovering allowed the ionic flow wished for overcoming threshold voltage, acting as an insulator in different cases.

1. Introduction

The growth of electrical systems, causes a greater number of failures and accidents of electrical origin, so that the issue of quality and safety in facilities should be a priority in the development of any territory, promoting the construction of facilities Safe and reliable. [2]

The development of the project seeks to evaluate the electrical performance and corrosion behaviour of stainless steel rods of a grounding system, seeking the protection of electromagnetic compatibility and the safety of people, as well as reducing the risks and problems caused by corrosion. [3]. Oxides are binary compounds in which oxygen has an oxidation state of -2. One of the techniques in which samples of stoichiometrically very precise oxides are obtained is the deposition of thin films by reactive sputtering. Controlled manipulation of the gases in the sputtering process can cause
variations in the crystal structure of the oxide. It has been noted that the relative size between the atomic motifs of the crystal lattice in the substrate and the molecules formed by oxidation of the target material in the deposition affects the adhesion of these oxides. It is also known the extraordinary property of titanium oxide when connecting with the metallic crystalline networks. This work explores the management of these oxides, creating vacancy defects or excess free electrons in this crystal lattice to provide semiconductor properties, taking advantage of the ability to generate both types of semiconductors, whether type P or type N. The manipulation is intended to provide desirable electrical properties at grounding electrodes, as this buried structure, in addition to the typical corrosion and corrosion performance properties, also requires an electrical performance determined by the function for which Design in a complex electrical system. Have been developed some series materials intended to mitigate the effect of corrosion, among which stand out the coatings, especially those deposited in the form of thin film. With the investigations that have been undertaken were discovered other properties of thin films. In the case of niobium, in addition to its superconducting properties, identified characteristics such as hardness, resistance to wear and corrosion [4].

Work on barriers against corrosion is generally oriented to provide the substrate coating system with mechanical properties, thermal and anti-degradation, but rarely considered elements such as grounding systems, which require a specific electrical performance [5]. The multicomponent coatings are developed as multi-tier heterostructures in order to improve the wear resistance and the oxidation of coated components.

The improvements occur in alternating deposition of two (or more) chemical and / or mechanically different layers, so that the stress concentration and conditions for the propagation of nano cracks can be controlled. Therefore, the multi-layered structure can act as an inhibitor of nano cracks and increase the resistance to fracture [6]. In addition to the characterization of the behaviour against corrosion, an evaluation of its performance against minimum working voltages of the coating scheme was done. The thermal performance produced by Joule effect was guaranteed when using oxides that supported high working temperatures.

2. Methodology technological product
Within the technological product development process, it must be taken into account that the coating to be deposited on the stainless steel substrate has a physical, chemical and ecological performance, being able to maintain electrical levels of transmission in case of failure, and Insulation otherwise; It must also be a corrosion protection agent. It must not harm the environment causing consumption of non-renewable materials and sterilizing the sectors where it is installed.

The techniques to take into account to make the deposition of thin films and manufacture of nano structures Top Dow, are: Spray thermal, sol gel and plasma. For the work done, the Sputtering Plasma technique was used, which guarantees homogeneity in the coating and adhesion when exchanging electrons between the surface and the target (coating), being films of the order of nanometres become susceptible to abrasion.

The process of sputtering-Sputtering is mainly a process of ionic bombardment, which obtains the deposition in vapor phase, on a substrate of the bombarded material. In this technique, the ions formed in the plasma are accelerated towards the material to be deposited, through an electric field. The plasma is made up of process gases, in this case argon and oxygen, ionized by the strong electric field [7]. Under defined experimental parameters, the water spray technique can ensure a good anchoring surface between the coating and the substrate. This method extracts atoms on the surface of a negatively polarized called White electrode, the electrode eroded by the action of ions and atoms of high-energy contained in the Argon (Ar), from the formation of the plasma that bombards the atoms of the surface of the white. If it generates enough kinetic energy the atoms or molecules of the white they are torn [8].

In order to apply the sputtering technique, it is necessary to prepare the substrates for the most homogeneous surface polishing possible by removing scratches, holes or pores leaving a surface metallography to mirror brightness as seen in Figure 1, this will facilitate and optimize the deposition
of the Thin films, maintaining a flat and homogeneous surface without concentrations where failures may occur.

![Image](image_url)

Figure 1. Microstructure stainless steel at (a) 700 X y (b) 1400 X.

The targets to be considered are binary oxides that are stable in their free energies of Gibbs which reacted with the use of titanium, zinc and copper targets, the results showed purity of 99.99999%.

The production of titanium, zinc and copper oxide coatings on stainless steel specimens is performed by dc reactive Sputtering in argon and magnetron assisted oxygen [9], whites are 3 inches in diameter in the configuration of parallel and coaxial flat electrodes, In a high vacuum chamber of approximately 0.023m³ and final vacuum 4mPa. Luminescent discharge is obtained with pressures ranging from 0.3 to 3Pa, voltages between 150 and 350V, voltage between 0.1 and 1A, distance between electrodes of 3 and 4.5cm, concentration of oxygen between 10 and 30%, substrate temperature and test specimens between 370 and 520K. With deposition times of 20 minutes, the yield on the substrate varies between 30 and 50nm/min. The possible species in the plasma are monitored through a NUV spectrometer VIS NIR with FO; the morphology, structure and stoichiometry of the coating, will be determined mainly by the stoichiometry of the surface of the white, the reactions of the material pulverized in its transit to the substrate and by the absorption and adsorption of oxygen of the coating of the substrate in the presence of the plasma in the luminescent zone. The absorption and adsorption of oxygen from the surface and the balance between the spray yields of the oxidized surface area and the non-oxidized zone of the target will determine the control of the oxidation state of this surface. If spraying is maintained under this yield competition regime, the type of pulverized species passing through the substrate will be controlled.

The morphology and structure of the coating is balanced between the amorphous and/or polycrystalline state of the oxides and it can be indirectly controlled and assisted with the balance between the anneals due to the substrate temperature and the temperature of the reactive plasma on the substrate [10]. The matrix can be amorphous with embedded polycrystalline, which determines the possible compromises between hardness and corrosion resistance. The substrate temperature is assisted and measured with thermocoax and Pt100 and thermocouple. The monitoring and controlling of the growth of parameters were assisted with NI and LabVIEW cards. Post-deposition should be kept empty for 2 hours to avoid any thermal shock. Post-deposition should be kept empty for 2 hours to avoid any thermal shock.

3. Discussion and results
Oxides that occurred during the deposition reaction in the sputtering in its atmosphere with 16% oxygen and 84% argon were polar covalent bonds that generated elements as: $\text{TiO}_2$, $\text{ZnO}$, $\text{TiN}$ y $\text{CuO}$, With a percentage ionic character, according to the mathematical relationship of paulling of link with
an ionic character of 25%, average for the 4 elements and in the same form of a 75% of polar covalent bond.

In Table 1 is reported the chemical composition obtain the characterization of stainless steel substrate before and after treating, where it shows the small proportions that reflect the additional compositions that generate the thin film, in the face of two techniques to quantitative and with other quantitative results may vary with respect to each other, for this reason, it makes for a single sample.

**Table 1.** Results chemical composition of stainless steel 304 (%) determined from the techniques of atomic emission spectroscopy without surface treatment and X-ray fluorescence technique with surface treatment.

|                  | The composition of the surface without treatment (%) |                  | The composition of the surface with treatment (%) |
|------------------|-----------------------------------------------------|------------------|--------------------------------------------------|
|                  | C          | Mn       | P        | S        | Si       | Cr       | Mo       | Ni       | Al       | Co       | Mg  | Al  | Si  | Ti  | Cr  | Mn  | Fe  | Co  | Ni  | Zn  |
|                  | 0.049      | 1.530    | 0.0249   | ~0.020   | 1.19     | 18.04    | 0.154    | 10.26    | 0.171    | 0.171    | 3.8 | 0.6 | 0.2 | 4.01| 11.1| 0.76| 46.6| 0.1 | 6.01| 26.8|

The deposition on the substrates of 304 stainless steel with coatings ZnO and TiN and ZnO and uncle, evidence the homogeneity that generates the technique of sputtering, as seen in the images obtained by optical microscopy in Figure 2. By having an area of uniform appearance with small inclusions, at the rate of a pore or impurity in the preparation of the substrate. Usually when there is a presence of corrosive media, stainless steels and TiN ceramic layers formed on its surface a protective oxide layer. However, when the aggressive substance contains hard particles, these layers of oxides are seriously damaged due to the large number of shocks on its surface, a fact which implies a new formation of the oxide layer [11].

**Figure 2.** Stainless steel with ZnO coatings (a) and (b) TiN and ZnO and TiO with an increase of 1400X.

A cross section of the substrate was cut to observe the interfaces of the coatings, determining that they have a uniform bilayer with values of approximately 200 and 450 nanometres, respectively, as can be seen in the images obtained by electron microscopy in the Figure 3. Cutting the cross section to observe the interfaces should be very careful because the coatings can be detached as shown in Figure 4.
Figure 3. Stainless steel with ZnO and TiN and ZnO and TiO 500X

Figure 4. Stainless Steel with Coatings ZnO and TiN, ZnO and TiO 500X.

Surface properties, the microhardness of the surface treatments was determined and a comparison was made with a pattern that for this case would be the substrates without coating obtaining the following results (see Table 2).

| Measurement Register | TiN+ZnO  | ZNO+TiO2 | Substrate |
|----------------------|----------|----------|-----------|
| Load Duration        | 100 gf   | 200 gf   | 1000 gf   |
| Standard Deviation   | 25 seconds | 25 seconds | 25 seconds |

Table 2. Microhardness of 304 stainless steel substrates with thin films and without them.

The standard deviation is within the range of the microhardness of the substrate, the characteristics that are allowable for the surface that was drawn up in order to be buried in its use the grounding system. With these tests elaborated topographic graphs observing the depth and the traces that were obtained with the test of microhardness; Taking into account the referent of the substrate, the actual notions of hardness in the coatings were obtained, as shown in Figure 5.

Figure 5. Topography for the coatings (a) ZnO+TiO and (b) ZnO+TiN.
The electrical performance was evaluated by the 4-point method, which intends to see the curve of the diode in the coating in the form of bilayers simulating an active element, where one layer works as Type P and the other N, in the results obtained not all the configurations made with the coatings worked with the electrical purpose we intended as can be seen in Figure 6.

![Figure 6](image1)

**Figure 6.** Diode curve where it behaves as a resistive element, where is observed the behaviour of current in function of tension. (a) ZnO+TiO and (b) ZnO+TiN.

The configuration that finally solved the problem and generated the expected electrical performance, consists of a layer of copper oxide that served as a P-type semiconductor; And then a slightly thicker layer of titanium oxide was deposited, which served as n-type material, resulting in the curve of the diode shown in Figure 7.

![Figure 7](image2)

**Figure 7.** Diode curve where the device is activated at 7V.

Electrochemical impedance spectroscopy, the conditions of the scans in frequency for all experimental units were made with an initial frequency of 100KHz up to 0.2Hz; 10 points per decade were determined for an exposed area of 2.41 cm² electrode, in aqueous NaCl solution. The experimental data obtained by means of IS-dynamic tests are see Table 3.

The corrosion rate and the polarization resistance, as a function of the number of bilayers, can clearly be seen that the lower value of the resistance to effect corrosive occurs in the substrate, which generates the highest speed value to corrosion, as the number of bilayers increases, an increase in polarization resistance is generated, indicating a significant decrease in the corrosion rate. See diagrams of Figures 8 and 9. This implies that the energy required for the solutions to migrate freely from the surface to the film / substrate interface, is greater with the increase in the number of bilayers. [12].
Table 3. Electrochemical impedance spectroscopy on the surface of 304 stainless steel substrates with thin films and without these.

| Parameter     | Value without treatment | Value with treatment |
|---------------|-------------------------|----------------------|
| lower Fit Limit | -87.18mV vs. Ref. (Pt#0) | -557.9mV vs. Ref. (Pt#0) |
| Upper Fit Limit | -67.22mV vs. Ref. (Pt#0) | -517.9mV vs. Ref. (Pt#0) |
| Beta A        | 455.8e-3V/decade        | 120.0e-3 V/decade    |
| Beta C        | 116.8e-3V/decade        | 120.0e-3 V/decade    |
| Icorr         | 285.3nA                 | 5.168nA              |
| Ecorr         | -83.21mV                | -537.9mV             |
| Rp            | 141.5Kohms              | 5.041Mohms           |
| Corrosion Rate | 84.61e-3mpy             | 8.272e-3mpy          |

Figure 8. Bode diagram.

Figure 9. Nyquist diagram.

4. Conclusions
The behaviour of the semiconductor is acceptable for the purpose of earthing system with an excitation voltage of 7V.
The behaviour against corrosion for stainless steel with surface treatment improved by an order of magnitude, compared to the characterization tests performed in previous sequential projects that do not have surface treatment.

The preparation of the substrates for the application of the coatings may be different, depending on the characteristics of the coating to be deposited.

The electrical and corrosion-resistance characteristics of the coatings are defined by their deposition settings.

Surface treatments in the form of bilayer are a successful solution to maintain levels of conductivity and corrosion resistance.

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