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Electrochemical Characterization of Copper Coatings on Low Carbon Steel from Industrial Waste

W. Aperador[1,*], *E. Delgado*[1], *A. Mejía*[2]

[1]Departamento de Ingeniería, Universidad Militar Nueva Granada, Carrera 11 No. 101-80, Fax:+57(1) 6343200, Bogotá, Colombia.
[2]Escuela Colombiana de Ingeniería – Julio Garavito, Bogotá, Colombia.
[*]E-mail: g.ing.materiales@gmail.com

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In the present investigation was obtained electro-copper coating on steel AISI SAE 1020, electrolyte was used as an industrial waste obtained from the stripping of copper. The current densities were 2.5 A/dm^2, 5 A/dm^2 y 7.5 A/dm^2 and concentration of 222 g / l of copper sulfate ($CuSO_4$). The corrosion behavior of the substrate and the coatings obtained were studied by electrochemical impedance spectroscopy and potentiodynamic polarization curves. Additionally, we examined the surfaces of the coatings by scanning electron microscopy (SEM). The study shows that these coatings comply with the standards for use as ground poles.

Keywords: industrial waste, electro-copper coating, corrosion.

1. INTRODUCTION

The copper and its alloys are used in a wide variety of systems and applications such as: industrial equipments, heat exchangers, bearings, connectors, transport, etc., [1-4] applications based on the beneficial effect of highly thermal and electrical conductivity, corrosion resistance, mechanical resistance and the wear [5-7]. In the construction industry; plumbing, wires, heating, air conditioning systems, in covers and facades of buildings [8, 6]. In electricity and electronics fields (printed circuits, which the selected elimination of the copper oxides formed instantly by air exposition is not resolved), semiconductor packaging [9, 10]. Like coins and ornamental elements, due to its excellent resistance to corrosion, extraordinary foundry (for example, bells and statues) and color variety. The copper compounds are used in biomedical applications as well, agriculture, water treatments, energy as in fuel cells, the solid oxide, etc.

The scaling in sulfuric and hydrochloric acid is the method more habitual to eliminate the formed oxides over the copper-based materials during the grinding process and fabrication operations. The organic acids such as the citric acid, presents advantages over the mineral acids of be less aggressive, easier to handle and do not present hazard for the health and the environment. This kind of scaling is adequate to eliminate the copper oxides and the spots (fogging) originated during the exposition of the copper to the atmosphere without attacking the copper substrate [7, 11, 12].

The copper processing industry is a productive activity that generates waste, as an example in the scaling process, which uses concentrated sulfuric acid (H_2SO_4) with the purpose to separate the oxide layers or the protective thin films of the metal [13], thus as all chemical compound adhered to the substrate surface. As a result of this procedure is obtained a solution compounded by copper sulphate ($CuSO_45H_2O$), sulfuric acid (H_2SO_4) and contaminants [14-16].

The electrodeposition technique is a process widely employed in the protection against corrosion of different types of parts and is based on the alteration of the superficial characteristics of coated materials improving the wear resistance and the obtaining of metallic surfaces with specific finished [17]. Within the electro-coatings gamma, the copper is constituted in one of the most widely applied in the coating of steel, due to its excellent protection against the corrosion. It is used as the first layer for decorative applications as well as for electric conduction applications [18].

In this work is shown the results about the study, applying the electrodeposition technique of produce a copper coating from the industrial residues in the scaling process of the same material. Substrates of low carbon steel were coated for grounding connection and it was evaluated the electrochemical response.

2. MATERIALS AND METHODS

2.1 Materials

The used specimens were (AISI 1020) low carbon steel sheets of 5 cm x 5 cm. The table 1 relates the chemical composition of the steel substrate. The used anode was lead in the same dimensions.

Table 1. Chemical composition of the steel substrate.

Carbon	Manganese	Silicon	Phosphorus	Sulfide
0.17	0.05	0.08	0.04	0.04

The chemical composition was evaluated by X ray fluorescence (FRX) of dispersive energies using a spectrometer Philips PW-1480 model, Sc/Mo anode generator tension of 80 kV and current of 35 mA. To determinate the concentration of sulfuric acid and copper sulfate presented in the solution was applied the titration method by precipitation.

The electro-coatings were obtained in a dynamic way in a cell with 8 liters of capacity, continuos current source of 15 Amperes and 30 volts. Three current density values were used: 2,5 A/dm^2; 5 A/dm^2 y 7,5 A/dm^2. It was configured as cathodes AISI 1020 steel sheet and as anode lead sheets.

Before the copper bond, the steel cathodes were subjected by 10 minutes to cleaning process with ultrasonic followed by electrolytic degreasing in Kleanex bath using with the purpose to remove all kind of dirtiness including greases and finally rinsing with distilled water.

It is continued by 10 minutes, with chemical scaling composed by HCl at 50% which purpose was to remove all the oxide present on the metal surface. After scaling and rising, to the specimen is dynamically pretreatment on a cyanide bath for 15 minutes in order to ensure good adhesion of the coating. Finally, it was applied the coating by copperbond until obtaining thinness greater than 100µm (indicated thinness in the grounding standards) [19] Standar IEC, 2002 handling parameters such as: concentration conditions and current density. The permanence time on the bath was 2.5 hours.

2.2 Electrochemical Tests And Characterization

For the static corrosion resistance evaluation was used a potentiostat - galvanostat, brand Gamry model PCI-4; it is developed test at room temperature, of Electrochemical impedance spectroscopy (EIS) and Tafel polarization curves.

The specimens were placed under immersion in a solution of NaCl 0.5 M prepared with distilled water. The electrochemical cell was configured by a platinum counterelectrode, a reference electrode of Ag/AgCl and as a working electrode the AISI 1020 steel specimen coated with copper. The Nyquist diagrams were obtained by frequency sweeps in the range of 0.001 Hz to 100 kHz using a sinusoidal signal amplitude of 10 mV. The polarization curves were measure after one hour of immersion, with a scan rate of 1 mV/s, in a range of voltages from -200mV to +800 mV with respect to corrosion potential (Ecorr). The corrosion rate values (Vcorr) were calculated from the Tafel slopes and the corrosion current density value (Icorr) in the potential range of ±250 mV vs. Ecorr, from the anodic polarization curves.

The scanning electron microscopy was used with the purpose to evaluate the morphological details and thinness of the obtained coatings. For this type of analysis was used a Philips XL 30 FEG equipment, with a detector of X ray and Lithium Beryllium secondary electrons.

3. RESULTS

3.1 Characterization Of Industrial Waste Solution

In the figure 1 is shown the results of the qualitative analysis of the residue solution obtained by the X-Ray Fluorescence tests.

Through the titration by precipitation method, was evaluated the concentration of the copper sulphate and the sulfuric acid of the Colombian copper industrial solution, the results were: pH of 0.86 and concentration if $CuSO_4$ of 224.91 g/l.

Copperbond process were developed taking concentration ranges of 200 to 250 $CuSO_4$ (g/l) [20]. In the laboratory from 150 ml of the original solution is added 3 ml of H_2SO_4 and 9.26 g of $CuSO_4$. By titration is evaluated the above concentration obtaining a value of 222 $CuSO_4$ g/l.

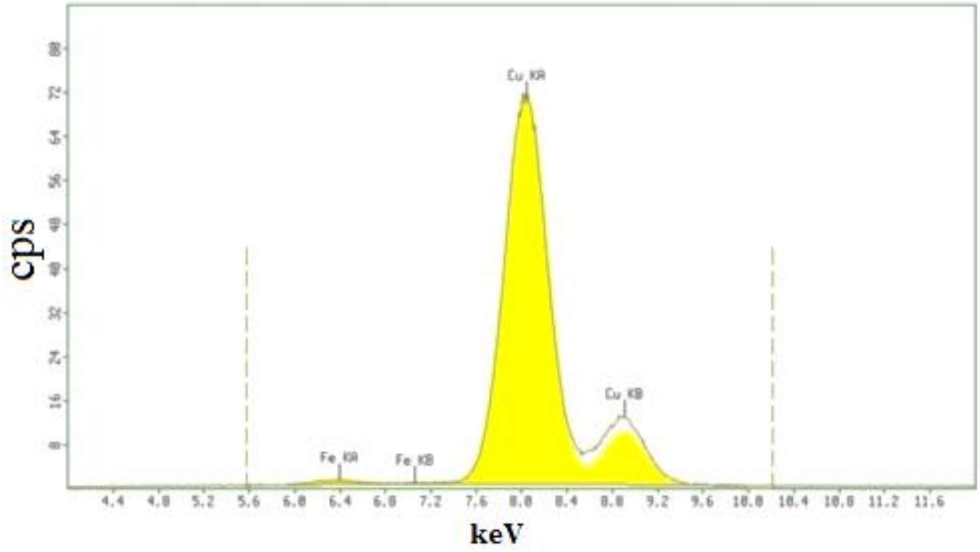
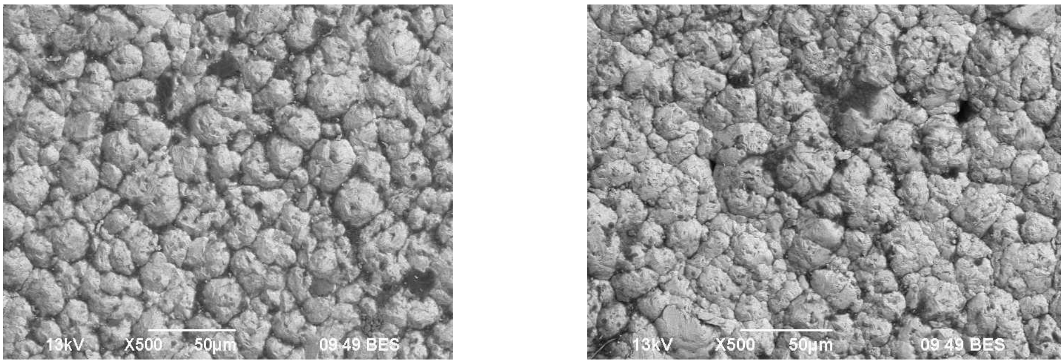


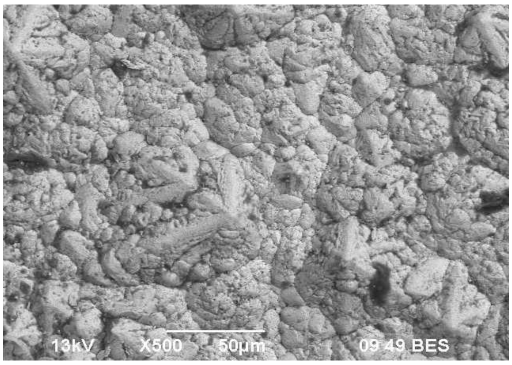
Figure 1. Qualitative analysis of waste solution

3.2 Microstructure

The figures 2a, 2b and 2c shown the surface micrographs, at 500X, of the electrolytes coatings obtained at different current densities of 2.5 A/dm^2, 5 A/dm^2, 7.5 A/dm^2 respectively. Comparing the micrographs in the figures a) and b) is observed that does not exist an appreciable difference in the grain size. However, the figure c) shows a diminution of the grain size in comparison with the micrograph a) and b) [6].



(a). **(b)**



(c)

Figure 2. Micrographs at 500X of the surface coatings at different current density. a) 2.5 A/dm^2, b) 5 A/dm^2 y c) 7.5 A/dm^2.

3.3 Electrochemical Evaluation

3.3.1 Electrochemical impedance spectroscopy

In the figure 3 is shown the Nyquist diagrams corresponding to the low carbon steel and copper coatings. According to the diagrams, the copper coatings applications with current density of 7.5 A/cm^2 have the best electrochemical behavior. This behavior is due to the high level of homogeneity on the film cause when it has smaller grains can be accommodate easily allowing a proper seal of the coating and preventing contact between the working solution and the substrate. This fact is evidenced by observing the micrograph of the figure 3 c).

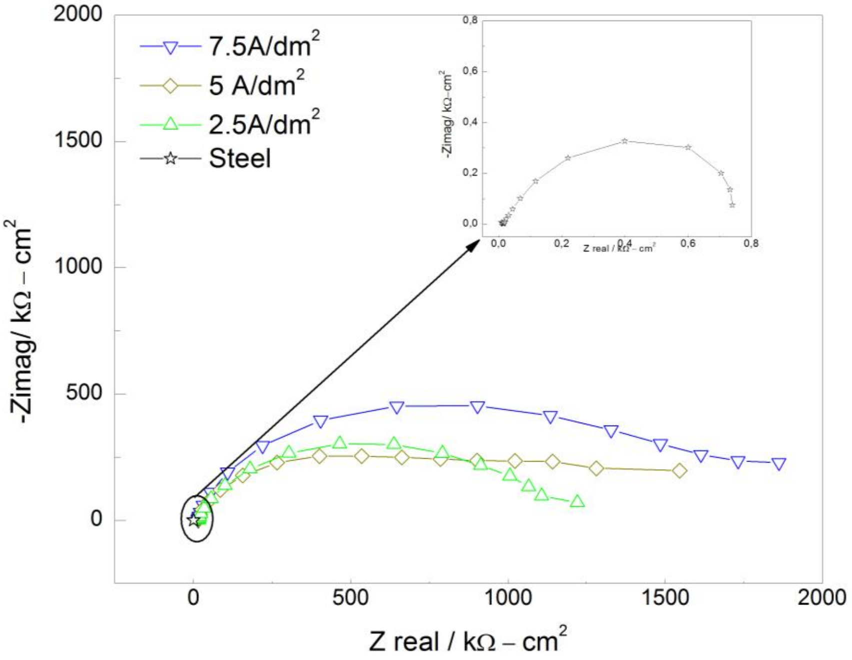


Figure 3. Nyquist Diagram of the substrate and the copper coatings for different current densities

With the purpose to evaluate the process that occur during the electrochemical test on the substrate-coatings system, was used the electrochemical impedance microscopy technique (EIS). This technique allows the homologation of the electrochemical response of the studied system behavior with interconnected physics elements [15], as it is observed in the figure 4 and 5, resulting of the study of the figure 3.

In the figure 4 for the steel specimen, is obtained a small semicircle insignificant in comparison with the coatings. The model of equivalent circuit that provided the best fit is presented in figure 3, in this equivalent circuit is observed a time constant in parallel with the charge transference resistance, and in series with the solution resistance.

For the coatings were observed two semicircles, which are modeled by the equivalent circuit of the figure 5. Due to this behavior was configured a equivalent circuit with two constant phase elements (CP_1 and CP_2), the elements CP_1-R_1, are represented at high frequencies and are associated to the reactions that occur around the passivant surface oxide layer. A second set of elements composed by CP_2-R_2, found at very low frequency (1 mHz) is due to charge transfer and represent the response of the obtained process that occur in the system, which are slow in the obtained coatings. In the figure 3 is observed a total impedance value of 0.78kΩ, corresponding to the substrate, this value increases as the used current density for the copperbond process is amplified, and it is obtained a maximum impedance value of 2600 kΩ for the system when is used the 7.5A/cm^2, this value widely increases due to formation of reduced grain size and the achieved homogeneity of the coating [16-17].

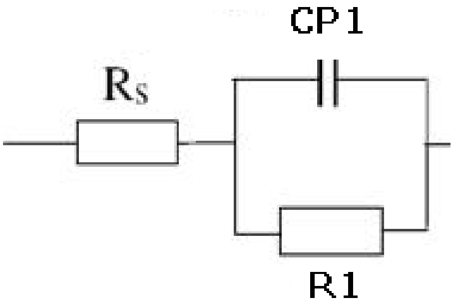


Figure 4. Equivalent circuit used to model the impedance behavior in the substrate.

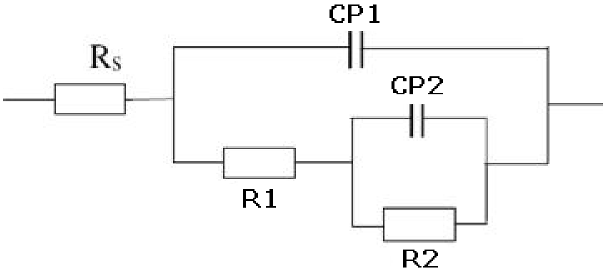


Figure 5. Equivalent circuit used to model the impedance behavior in the coatings for three current densities.

3.3.2 Anodic polarization curves

In the figure 6 is shown the anodic polarization curves for both, the steel substrate and the copper coatings in function of the used current densities are observed that the potential more active correspond to the substrate (-557mV vs Ag/AgCl). For the films have seen a displacement of the curves toward passive zones, passing from the -350mV for 2.5A/cm^2 to the -162mV for 7.5A/cm^2. Therefore, the relation of cathodic/anodic areas in the coatings matrix increases proportionally to the used current density in the electrodeposition process.

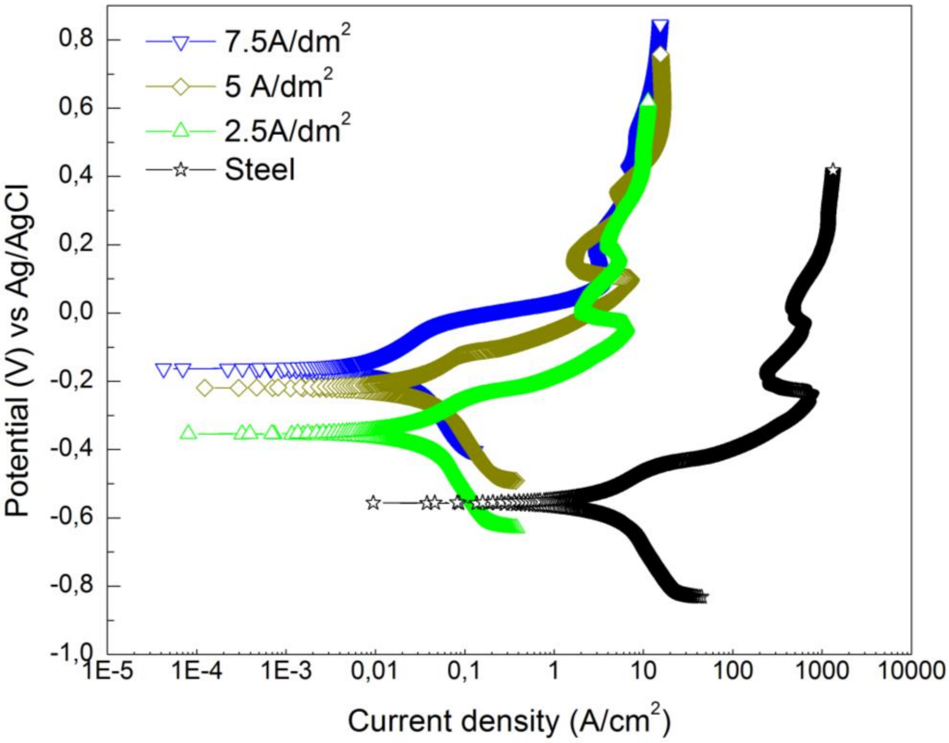


Figure 6. Anodic polarization curves for the steel substrate, and the coatings with the variations of the solutions and current densities.

In all cases, the polarization curves generate a repassivation behavior, in which the anodic branch describes the tendency to keep or reduce the current flow as the potential increase. For the substrate case, it is due to the oxide layer formed spontaneously.

The polarization resistance values, calculated by EIS, vary in relation with different corrosion current values. The corrosion rate is calculated with the corrosion current values due to the directly proportional relationship among these quantities, so the polarization resistance values are inversely proportional to the corrosion rate values [16].

The table 2 has the corrosion potential values Ecorr, corrosion current Icorr and corrosion rate Vcorr for the substrate and the electrodeposited coatings at different current densities. The results show that the current density has a strong influence in the corrosion rate due to the high current density to obtain coatings with fine grain size and low porosity.

The current density and corrosion rate values show copper coatings with a passivating oxide layer. Nevertheless, this passivating layer is not stable as follows of the anodic polarization curves, when it partially diluted up to the decomposition zone of the H_2O.

Table 2. Corrosion potential parameters, corrosion density and corrosion rate for the steel substrate and the coatings in function of the current density variation in the electrodeposition.

Material	Ecorr (mV)	Icorr (A/cm^2)	Vcorr (µmy)
Substrate	-557	6.65	87.92
2.5A/cm^2	-350	0.047	0.047
5 A/cm^2	-213	0.030	0.041
7.5A/cm^2	-162	0.020	0.026

Source: Presentation by the authors.

4. CONCLUSIONS

From the industrial waste, in concentration of 222 g/l de $CuSO_4$, pickling product copper was possible to obtain electrodeposited coatings at current densities of 2.5 A/dm^2, 5 A/dm^2 and 7.5 A/dm^2.

The best electrochemical performances were the copper coatings applications with current density of 7.5 A/cm^2. This behavior is due to high degree of homogeneity of the film cause the smaller grains can be accommodate more easily, allowing proper sealing of the coating and preventing contact between the working solution and the substrate. Situation verifiable with the micrograph of scanning electron microscopy.

According to the Tafel diagrams, for the films have seen a displacement of curves toward passive zones, passing from the -350mV for 2.5A/cm^2 to the -162mV for 7.5A/cm^2. Therefore, the relation cathodic/anodic areas in the coatings matrix increases proportionally to the used current density in the electrodeposition process.

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