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Short Communication

Evaluation and Characterization of Thin Films on AISI 9840 by Electrochemical Noise

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Recently researches have been focusing on thin films by sputtering processes deposited on different substrates. Metallic thin films may be formed by a single nanolayer, bilayers or multilayers structures to combine properties of different materials, also to create specific properties of the structure, especially when it has nanometer scale dimensions. The objective of this study was to optimize the deposition conditions and the characterization of bilayers of Al/Cr, Cr/Al, on substrates of steel alloys, in order to evaluate their performance under corrosive conditions. Two configurations were designed for Al and Cr, deposited by a sputtering system V3 with a magnetron, used a pulsed DC source on AISI 9840 steel substrates, the power was 50W, to constant temperature 150 ° C, with Argon flow of 5.8 sccm, deposition time was 15 minutes for each layer. Microstructural characterization of the bilayers was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Electrochemical potential noise was evaluated by potentiostat Solartron 1285, programmed data processor CorrWare. The bilayers were adherents and the configuration Al/Cr was more resistant to corrosion.

Keywords: Thin films, AISI 9840, Aluminum, Chromium, Sputtering, electrochemical noise, bilayer, TEM, SEM, AFM.

1. INTRODUCTION

Nanostructured materials are those in which the main structural dimensions vary on the nanometer scale, the typical dimensions of interest are between 1 and 100 nm [1].

In recent years, the number of components used in the process of wear resistance has increased considerably, which is the reason that the hard coatings play an important role at the industry, the coatings increase the life time of the tool and in many cases, properties typically achieved can not be obtained by bulk such as: high hardness, low friction, wear resistance and high corrosion resistance. [2] A wide variety of materials can be applied by sputtering, this technique need to cover almost any coating. Aluminum and chromium are among the materials most widely used at deposition and are gradually replacing cadmium in corrosion applications [3-5]. The mechanical characteristics of the Al layer can be strengthened by the addition of transition metals such as chromium. [6]

Aluminum is an important metal in the industry due to their excellent electrical and thermal conductivity properties, low density, high ductility and corrosion resistance. It is widely used as material for the automotive, aviation, household appliances, packaging and electronic devices [7]. The use of thin films of chromium has been a major engineering practice for years in the automotive, aerospace and decorative industry. Thin films are used as corrosion resistant, wear layers for shiny surfaces without luster, and layers of high temperature [8]. It is known that surface contamination plays a major role in the mobility and stability in metallic films, as well as roughness, electrical and mechanical characteristics. It is not known the precise reason for these phenomena for many materials occurred. In the case of aluminum, the main difference is the presence of oxygen, oxidation-inducing surface creating a passivation layer as soon as exposed to the atmosphere. [9]

Sputtering involves the transport from source material (target) to a substrate by bombardment it with argon gas ions that have been accelerated by a high voltage applied to the magnetron [3]. The electrochemical noise is one of the techniques for evaluating the performance of the coatings against corrosion. All corrosion processes, specifically general corrosion, localized corrosion such as pitting and stress corrosion cracking (SCC), and the passive film formation to cause spontaneous fluctuations in the amount of electrical, it is known as Electrochemical Noise (EN). These fluctuations are manifested as noise current signals and in different corrosion processes appear to be related to local variations in the speed of the anodic and cathodic reactions, as a result of stochastic processes (decomposition and repassivation of the passive film) and deterministic processes (film formation and propagation of pitting) [10,11].

2. EXPERIMENTAL PROCEDURE

2.1. Deposition by sputtering.

AISI 9840 steel was used as substrate, the surface preparation was realized by an abrasive sanding (SiC, number 1000), prior to the deposition; to major adhesion of the films on it, after the substrates were cleaned in soap, water, acetone and introduced in an ultrasonic bath with isopropanol to remove contaminants. The films were deposited using a sputtering system assisted by magnetron Intercovamex, model V3. Two configurations were designed for each substrate. In the first configuration the first layer deposited was aluminum, and then the chromium layer; in the second configuration chromium layer was deposited first followed the aluminum layer. Targets of Al and Cr are 99.99% purity (3 inches diameter x 0.125 inches thick). Table no. 1 shown the nomenclature as samples deposited on the substrates. Pressure base was $1.6X10^{-5}$ Torr, the pressure work was $6.5X10^{-3}$ Torr

Table 1. Nomenclature of the samples

Substrate	Bilayer	Nomenclature
AISI 9840	Aluminum/ chromium	9840 Al/Cr
	chromium /Aluminio	9840 Cr/Al

2.2. Samples characterization.

The superficial nanostructure were characterized by scanning electron microscope (SEM) JSM-5800 LV and atomic force microscope (AFM) VEECO SPM MultiMode (Tapping); the film thickness were characterized by Transmission electron microscope (TEM), JEM-2200FS; transversal sections were prepared with focus ion beam microscope JEM-9320FIB JEOL, before cutting, the bilayer were cover with an Au layer and other of carbon to protect the coating during the cut and be observed in TEM. The crystal structure were characterized by X-ray diffraction, Panalytical, X´pert PRO: MPO model, the parameters for the target were with an X´Celerator detector, 2θ angle from 20 to 140°, a step of 0.05, 30 seconds by step. For the thin films a PW3011/20 detector was used, with a step of 0.05, scanning range 2θ from 20 to 140°, grazing incident angle of 0.5° with 4 seconds by step.

2.3. Electrochemical Noise Parameters.

Each substrate bilayers with different tests were performed electrochemical potential noise and current, the tests were run under ASTM G199 [12]. The measurements were performed in a potentiostat Solartron 1285, programmed data processor CorrWare. The parameters for the measurement of current and potential noise were at an interval of 1 data point per second with 1024 points. As experimental arrangement a working electrode which is coated with the sample, the reference electrode saturated calomel 1 (SCE), and the auxiliary electrode of platinum.

2.3.1. Statistical analyzes

With electrochemical noise measurements were determined electrochemical noise resistance (Rn) and the equivalent of the polarization resistance (Rp), the result of dividing the standard deviation of the potential shown by the area between the standard deviation current to get a parameter units resistance multiplied by the area, [12] was also determined according to ASTM G102-89 [13] the rate of corrosion in terms of corrosion current density (icorr) using equation Stern - Geary [14]:

2.4. Solution

Sea water is a complex mixture of inorganic salts, dissolved gases, suspended solids, organic matter and microorganisms; it is used to evaluate corrosion process. It is also known that a solution with a high concentration of NaCl (3.5% NaCl) simulates sea water environment, [7]

3. RESULTS AND DISCUSSION.

3.1 Structural morphology by SEM.

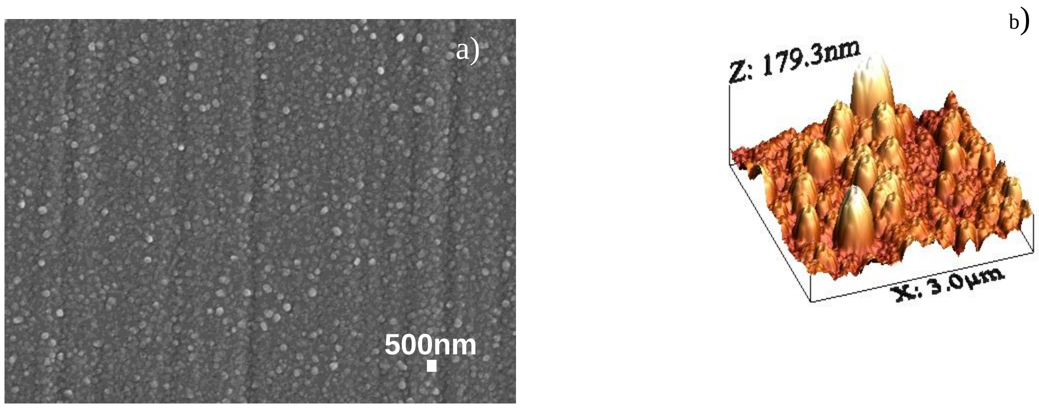

Figure 1. Bilayer surface morphology of the Al/Cr a) SEM at 5,000 X and b) AFM to 3µm x 3µm on steel 9840.

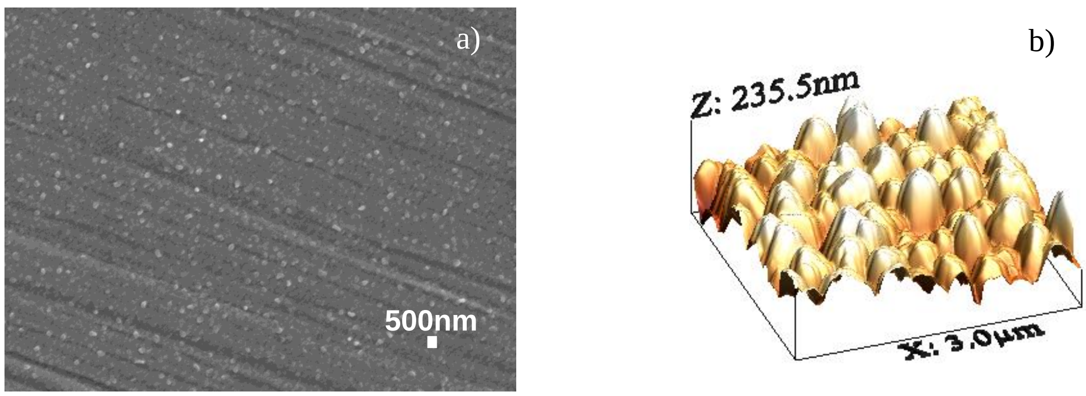

Figure 2. Bilayer surface morphology of the Cr/Al a) SEM at 5,000 X and b) AFM to 3µm x 3µm on steel 9840.

The Figures 1a) and 2a) show the SEM images, which can be observed uniformity and good adhesion of the films, in both bilayers Al/Cr and Cr/Al, deposited on 9840 steel substrates. In the images of atomic force Figures 1b) and 2b) respectively shows the morphology of the bilayers of Al/Cr, Cr/Al, each presents agglomerates whose particle size on the surface varies between 50 and 580 nm. The roughness of the films of Al/Cr varies for each substrate since 67nm to 23nm and films Cr/Al since 32 nm to 73 nm (not showed here). In the case of films Al/Cr a combined growth Stranki Krastanov in which the atoms have higher affinity between them and films of Cr/Al is observed more homogeneous growth rate, which has affinity for both the atoms as the substrate, this type of growth is known as Frank-van der Merwe.

In the bilayers Cr/Al onto 9840 steel substrates, no oxidations occur. All the samples have presenting good adherence. Two structures Al/Cr, Cr/Al, show homogenous thickness, this being between 120 and 140 nm with a columnar grow. This can be seen in Figures 3a and b.

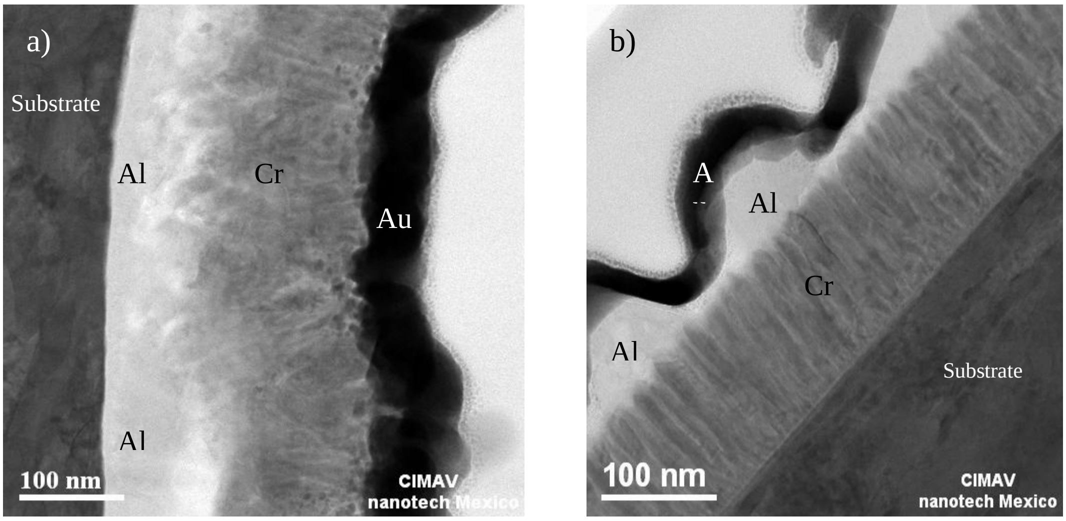

Figure 3. Image of thickness and columnar morphology by TEM of bilayers a) Al/Cr y b) Cr/Al on AISI 9840.

3.2 X-Ray Diffraction Analysis.

In the figures 4 a-c, are showed the XRD patterns of target and the configurations Al/Cr and Cr/Al respectively. Due to the small thickness of the film (approx. 140 nm) can be observed in all cases the main peak of Ni-Cr-Fe (110) and in the case of the peaks corresponding to double thin film last element aluminum or chrome deposited appears in major proportion. Samples in 9840 Al/Cr, peaks of Cr are observed because the Cr film located on the surface with a crystal structure of body-centered cubic (bcc) oriented in the planes (110) is very thin. In the case of 9840 structure Cr/Al it is similar to the spectra of the bilayer Al/Cr with less intensity, because the Al film is thinner and therefore the X-rays pass through the first layer. Aluminum has a structure face centered cubic (fcc) [15]. In 9840 steel shows characteristic peaks of some of the main alloying elements are the Ni-Cr-Fe.

In the X-ray diffraction pattern of the bilayer samples with Cr/Al were observed peaks corresponding to plane (200), with a higher intensity, and the plane (111) coinciding with the standard value (38.473 ° in 2θ) of Al, which in this case is not preferred. In patterns bilayers Al/Cr on each substrate, the strongest intensity peak of Cr is in the planes (110)

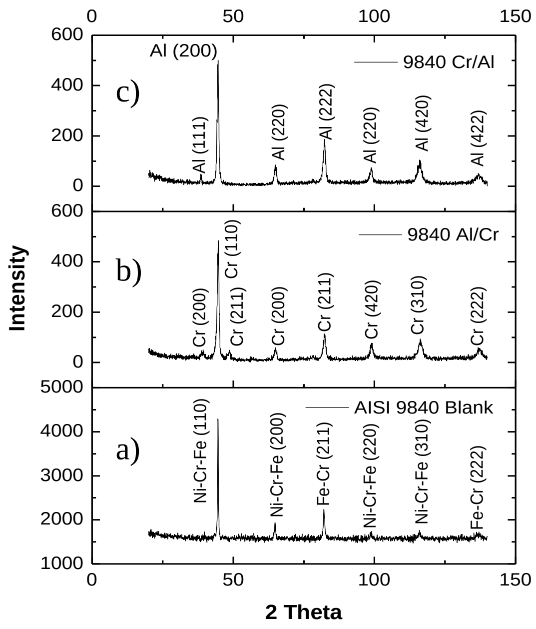

Figure 4. X ray Diffraction patterns a) substrate AISI 9840, b) bilayer Al/Cr and c) Cr/Al.

3.3. Electrochemical noise measurements.

In the case of Electrochemical Current Noise (ECN) signals, the target show transients in the signal of high amplitude (1e^{-5} A/cm^2), and developed a current and potential fluctuation both characteristic of pitting corrosion (see Figure 5). On other hand, both potential and current fluctuations in the sample 9840 Cr/Al of Figure 6, present smaller amplitude than the target showing not very noticeable pittings over time. While the structure Al/Cr has the lower frequency fluctuations during the time, localized corrosion observed in their home pinhole to -1.3885e^{-6} mA/cm^2, see Figure 7. Long-time changes in power can also be associated to the onset of localized corrosion, and the start of fissure corrosion usually causes the potential decay [16].

Table 2 shows the results of electrochemical noise measurement for each test in 3.5% NaCl as the electrolyte. In it table, is observed that the sample 9840 Al/Cr present the lower icorr (15.2438 µA-cm^2).

Table 2. Results of corrosion type by electrochemical noise.

Material		Open circuit (Volts)	Rn (Ω-cm^2)	Icorr (µA/cm^2)	Corrosion rate(mm/y)	IL	Corrosion type
9840	Target	-0.6116	323.9930	80.2486	0.8599	0.9999	Localized corrosion
	Al/Cr	-0.5381	1704.4907	15.2538	0.1202	0.9523	Localized corrosion
	Cr/Al	-0.5484	1088.9924	23.8753	0.26	0.9610	Localized corrosion

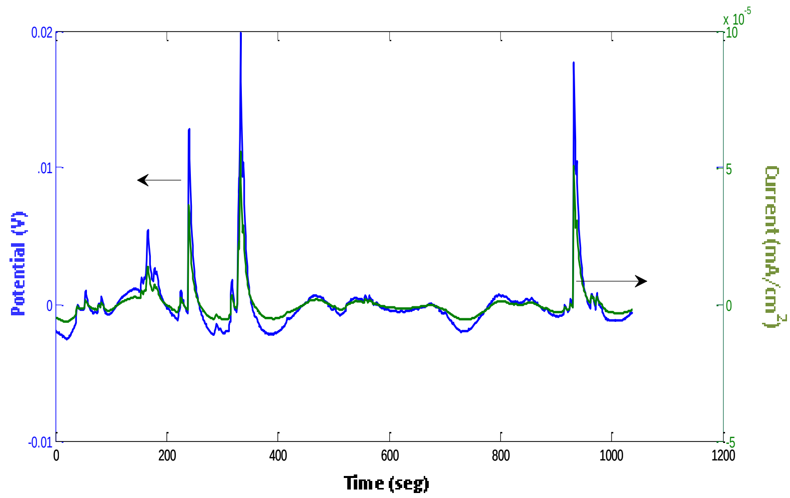

Figure 5. Electrochemical noise curve of AISI 9840 target evaluated on 3.5%wt NaCl.

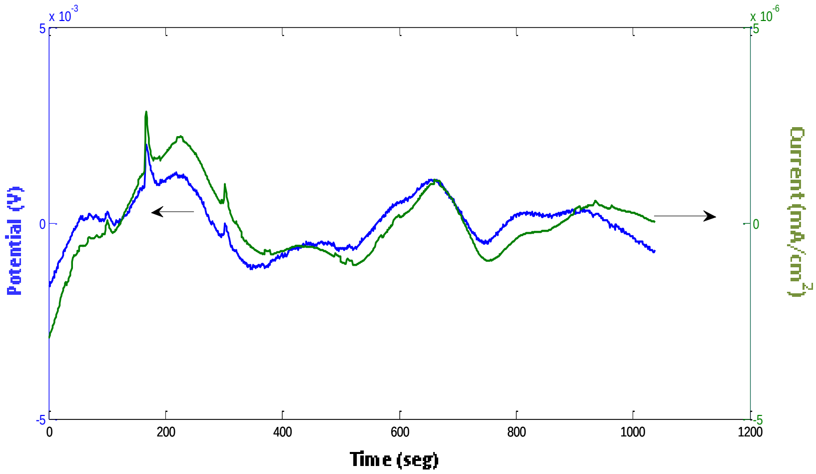

Figure 6. Electrochemical noise curve of bilayer Cr/Al evaluated on 3.5%wt NaCl.

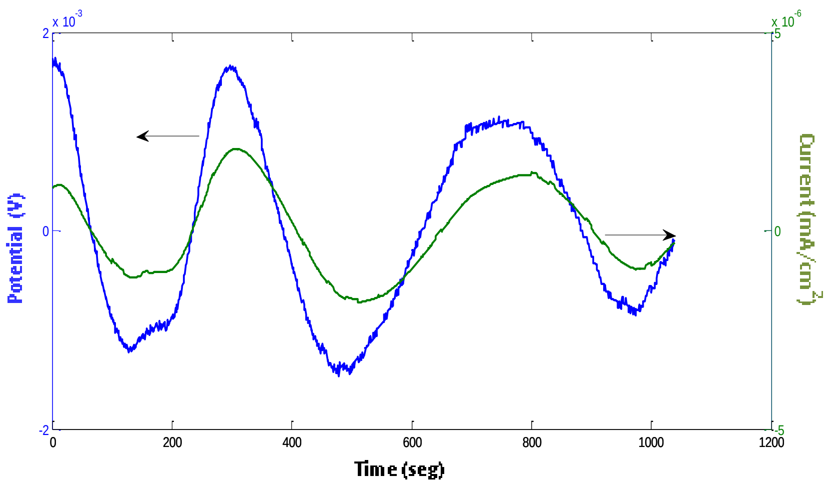

Figure 7. Electrochemical noise curve of bilayer Al/Cr evaluated on 3.5%wt NaCl.

4. CONCLUSIONS

In the evaluation electrochemical noise, the thin films show localized corrosion generating galvanic couples because different nature between the two films, so being the same thin films, they will behave differently according to substrate conditions. In the case of bilayer Al/Cr, it is the best bilayer, because it protects most the substrate, due to the first layer of Al as a material more active than the Cr and the substrate.

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