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Dynamic Study of Current Fluctuations of Nanostructured Films

C. López-Meléndez[1,2], E. M Garcia-Ochoa[3], M.I. Flores-Zamora[4], , R.G. Bautista-Margulis[5], C. Carreño-Gallardo[1], C.P. Castillo Morquecho[1] , J.G. Chacon-Nava[1], A. Martínez-Villafañe[1].*

[1] Centro de Investigación en Materiales Avanzados, S.C. Miguel de Cervantes 120, Complejo Industrial Chihuahua C.P. 31109 Chihuahua, Chih. México
[2] Universidad La Salle Chihuahua. Prolongación Lomas de Majalca No. 11201 Col. Labor de Terrazas C.P. 31020 Chihuahua, Chih. México.
[3] Centro de Investigación en Corrosión (CICORR), Universidad Autónoma de Campeche, Av. A. Melgar s/n, Col. Buenavista, C.P. 24030 Campeche, Cam, Mexico.
[4] Universidad Autónoma de Chihuahua, Facultad de Ingeniería. Chihuahua, Chih., México.
[5] Universidad Juárez Autónoma de Tabasco, División Académica de Ciencias Biológicas, Villahermosa, Tab., 86040, México.
[*]E-mail: martinez.villafane@cimav.edu.mx

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The objective of the current research work is to study the polarization curves and electrochemical noise, the performance and nonlinear dynamic of corrosion protection of a nanostructured thin film of AISI 304 stainless steel on a AISI 304 substrate applied by magnetron sputtering technique. The graphical analysis of recurrence (recurrence plot) and the determination of the fractal dimension of the current time series were obtained from the nonlinear analysis techniques used.

Keywords: Recurrence Plot, Fractal, Electrochemical Noise, Stainless Steel, Nanostructure.

1. INTRODUCTION

The importance of the development of resistant materials to aggressive media is of vital importance in the industry. Today there are new materials and metals as nanostructured thin films. These materials have been shown a greater resistance to chemical attack than the base materials from which they were obtained, showing that the structure plays a fundamental role of resistance to corrosion. Corrosion is a heterogeneous process involving reactions between a metal and its environment. As corrosion reactions involve the transfer of electrons, corrosion is an electrochemical process of oxidation and reduction reactions. Electrochemical measurements are now widely used in most fields of corrosion research. Detailed reviews are available on the application of electrochemical techniques such as polarization curves (Tafel slopes) [1,2] and electrochemical noise (EN) [3-6]. Electrochemical Noise is a nondestructive technique [6] to reflect the individual sum of random events of potential fluctuations and / or current of a material [5,6] subjected to corrosive conditions and the value of the Root Mean Square (RMS) of amplitude of these events or standard deviation has been providing the fingerprint of the amount of dissolved metal, depending on the metal-environment combination [13]. Electrochemical noise is the only technique that does not cause any disturbance of the system studied, since it is the simple collection of fluctuations between current and potential, the details of this technique have been reported by Cottis and Turgoose [7]. In this context, there are two relevant parameters to be considered, 1) the noise resistance (Rn) in which its value is inversely proportional to the corrosion rate of the material and is the ratio of the standard deviations of potential and current fluctuations, as stated below:

$$Rn = \frac{\sigma V}{\sigma i}$$

Where σV is the standard deviation of the potential noise, and σi is the standard deviation of the current noise; and 2) the Localized Index (LI), proposed by Eden [7] which is based on statistical information of the electrochemical noise signal in the current. Likewise, it is the relationship between the standard deviation of the current noise and the mean square deviation (RMS), as expressed in the next equation:

$$IL = \frac{\sigma_i}{I_{RMS}}$$

$$I_{RMS} = \sqrt{\sigma_i^2 + \langle I \rangle^2}$$

Where <I> is the average value of the current fluctuations. The LI falls in the range of 0.0 to 1 values of the order of 0.001, indicating that uniform general corrosion is the predominant mechanism, whereas values approaching 1 indicate the predominance of a localized mechanism [Ref 32, 33]. The LI was found to differentiate between low-corrosion passive behavior and localized corrosion in this environment. It is clear that current fluctuations contain information about the dynamics of corrosion phenomenon that occurs on the surface of the sample. An approach for the treatment of electrochemical current and potential fluctuations occurring in the phenomenon of corrosion is the chaos theory, which started from the phenomena that are apparently random in nature, but are governed by deterministic laws. Hence mathematical tools should be employed for non-linear information dynamics of the process, one of these tools are recursive graphs (recurrence plots) [8,9,10].

Recurrence plots (RP) are graphical tools elaborated by Eckmann et al. (1987) based on Phase Space Reconstruction [11]. The method of RPs was introduced to visualize the time dependent behavior of the dynamics of systems, which can be pictured as a trajectory in the phase space [12, 13] and representing the recurrence of the m-dimensional phase space trajectory $\vec{x}_i$. They are a graphical representation of the N · N-matrix:

$$R_{i,j} = \Theta(\varepsilon - \|\vec{x}_i - \vec{x}_j\|), \quad i,\ j = 1,2,3,\ldots,N,$$

Where $\vec{x}_i \in R^d$ stands for the point in phase space at which the system is situated at time i, ε is a state dependent cut-off distance (a predefined threshold), ||. || is the norm of vectors, $\theta(.)$ is the Heaviside function and N is the number of states.

Recurrence plots contain subtle patterns that are not easily ascertained by qualitative visual inspection. Zbilut and Webber have presented the recurrence quantification analysis (RQA) to quantify RPs [12, 14, and 15]. RQA variables are usually examined: percent recurrence (%R), quantifies a percentage of the plot occupied by recurrent points, the number of time instants characterized by a recurrence in the signals interaction: the more periodic the signal dynamics, the higher the %R value; Percent determinism (%D), quantifies a percentage between the recurrent points that form upward diagonal line segments and the entire set of recurrence points.

The diagonal line consists of two or more points that are diagonally adjacent with no intervening white space. This parameter contains the information about the duration of a stable interaction: the longer the interactions, the higher the %D value. LM Maxima which corresponds to the largest diagonal in the recursive graph is inversely proportional to the coefficient most positive of Lyapunov; this parameter informs about the system sensibility to initial conditions, indicating that this sensibility is smaller as the size of such line increases. Recurrence plot analysis has been successfully used in different scientific disciplines such as medicine [16, 17], chemistry [18], physics [19] and electrochemical corrosion [20,21,22].

EN signal can be represented by its geometry [23,24] and, therefore, a fractal dimension can be assigned. This value is of upmost importance when characterizing corrosion phenomena. Roughness-length method was used to determine Hurst (H) and the corresponding fractal dimension for every time series. In the roughness-length relationship method, the standard deviation, or root-mean-square (RMS) roughness of the data, is taken in windows of size w, rather than the vertical range. For a self-affine trace, the RMS roughness S (w), (where s = standard deviation), measured in a window of size w, is related to the Hurst exponent as [25,26]:

$$S\ (W) = c\ W^H$$

Plotting log W versus log S (W) you will find that the slope is the Hurst coefficient, related to the fractal dimension of the time series (Df) by the following expression:

$$Df = 2\text{-}H$$

A very important approach to the evaluation of the protective degree of a coating, using fractal geometry of EN time series for polymeric coatings, was made my Skerry [27]. Hurst coefficient value was associated in the following way:

0 – 0.25	good corrosion protection
0.25 – 0.75	medium corrosion protection
0.75 – 1.0	low corrosion protection

The same criterion has been applied for water based coatings friendly to the environment [28].

The aim of this research is to study polarization curves, electrochemical noise performance and dynamic nonlinear corrosion protection of a nanostructured film AISI 304 stainless steel on a stainless steel substrate applied by magnetron sputtering technique, which is a process of physical vapor deposition. The graphical analysis of recurrence (recurrence plot) and the determination of the fractal dimension of the current time series were obtained from the nonlinear analysis techniques used.

2. EXPERIMENTAL

The nanostructured films were generated by magnetron sputtering in a sputtering system INTERCOVAMEX V3 with a source of pulsed direct current. The nanostructured deposit temperatures were subjected at 25,100 and 200°C. The target, obtained from the atoms eroded and the substrate, is an AISI 304 stainless steel. The chemical composition of 17.75 wt.%Cr, 7.77 wt.%Ni, 1.37 wt.%Mn, 0.370 wt.%Si, 0026 wt.%C. The balance Fe total dimensions white is 76mm in diameter and 1.6 mm thickness and dimensions for the specimens which were deposited films are 25 mm X20X1.5 pre-deposit preparation was grinding to 1000 SiC grit is degreased with acetone. The parameters for the deposit appear in table 2. In this experiment the variable of interest was the temperature of deposit at three different temperatures 25, 10 and 200°C (three specimens were made for each temperature of deposit). After each deposit the films were characterized by X-ray diffraction (DRX) employing a diffractometer model Panalytical X'Pert Pro with detector X'Celerator using a Cu Kα lamp. The difractogrameters were obtained using the following conditions: 30 to 120 degrees with a step of 0.05 degrees, 5 s/step and power 0.5 W to determinate the phase formed in each film. With the field emission scanning electron microscope model JSM-7401F (FESEM), the elementary composition and morphology was observed.

The corrosion behavior of the coated and uncoated 304 SS was determined by potentiodynamic polarization curves and electrochemical noise measurements. A Solartron 1287 electrochemical interface using a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode consisted of base metal with the nanostructured coating at different deposition temperatures. The polarization curves were measured from the cathodic to anodic area with a potential sweep rate of 1mVs−1. The current noise and potential measurements were monitored simultaneously at a sampling interval of 1 s. Signals were collected over a period of 1024 s.

To carry out the electrochemical tests, a solution of NaCl 5% by weight was used as the corrosive medium.

3. RESULTS

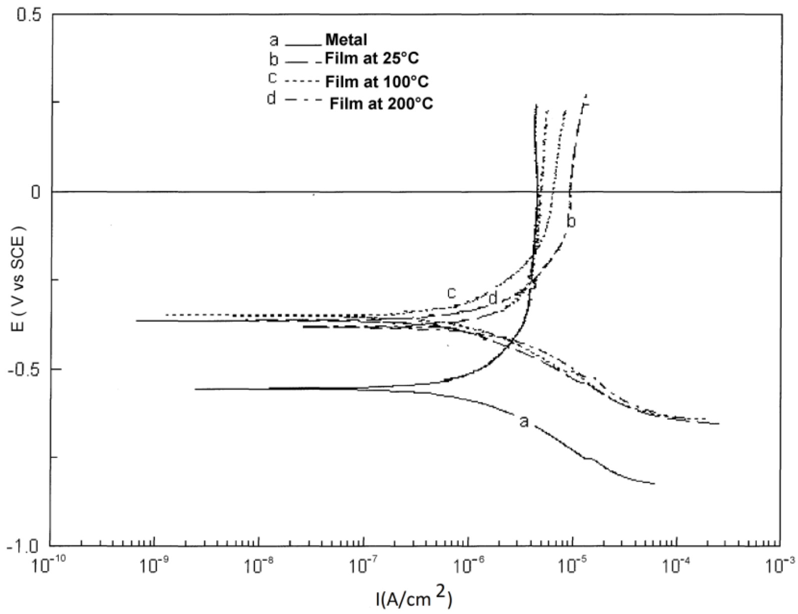

Figure 1. Polarization Curves

Table 1. Chemical Composition

	%Cr	%Ni	%Mn	%Si
Steel 304	17.75	7.77	1.37	0.37
25°C	17.86	6.65	1.62	0.26
100°C	16.78	6.91	2.56	0.61
200°C	17.38	7.40	1.08	0.84

Figure 1 shows the polarization curves both in the absence and presence of the coating at different deposition temperatures. It clearly shows that the corrosion potential value for the bare material was around -556 mV with respect to the saturated calomel electrode. In the presence of the coating the corrosion potential has a shift to more positive values of about -350 mV, suggesting that the chemical composition of the coating is different from the substrate. This does not happen as the nominal composition of the main alloying looks very similar to the base material, as shown in Table 1. However, the crystal structure changes from a face centered cubic (FCC) phase corresponding to a classical austenitic stainless steel, to a body centered cubic (BCC) structure which corresponds to a ferritic phase, explaining the change of corrosion potential, which remains in very similar values for the coating at different deposition temperatures. One would think that being a ferritic phase the coating does not confer protection but because it is a nanostructured surface substantially improves corrosion resistance, a fact which has been documented previously by some other researchers [1,29]

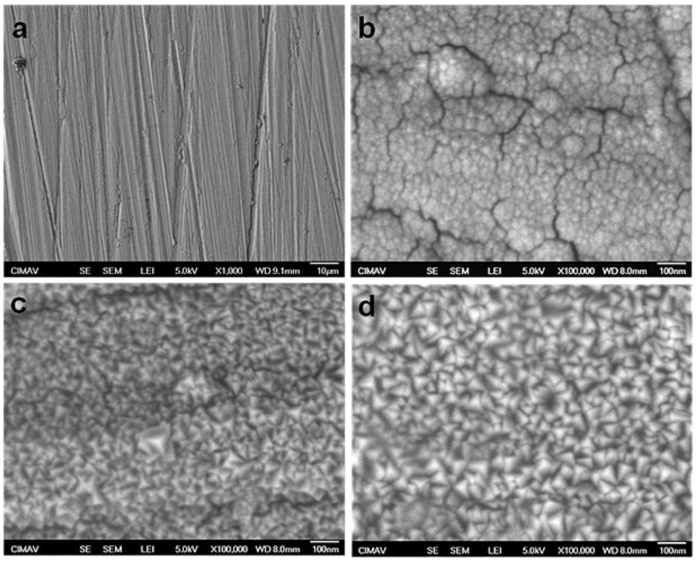

Figure 2. Surfaces a) Stainless Steel b),Thin Film at 25°C c),Thin Film at 100°C d),Thin Film at 200°C

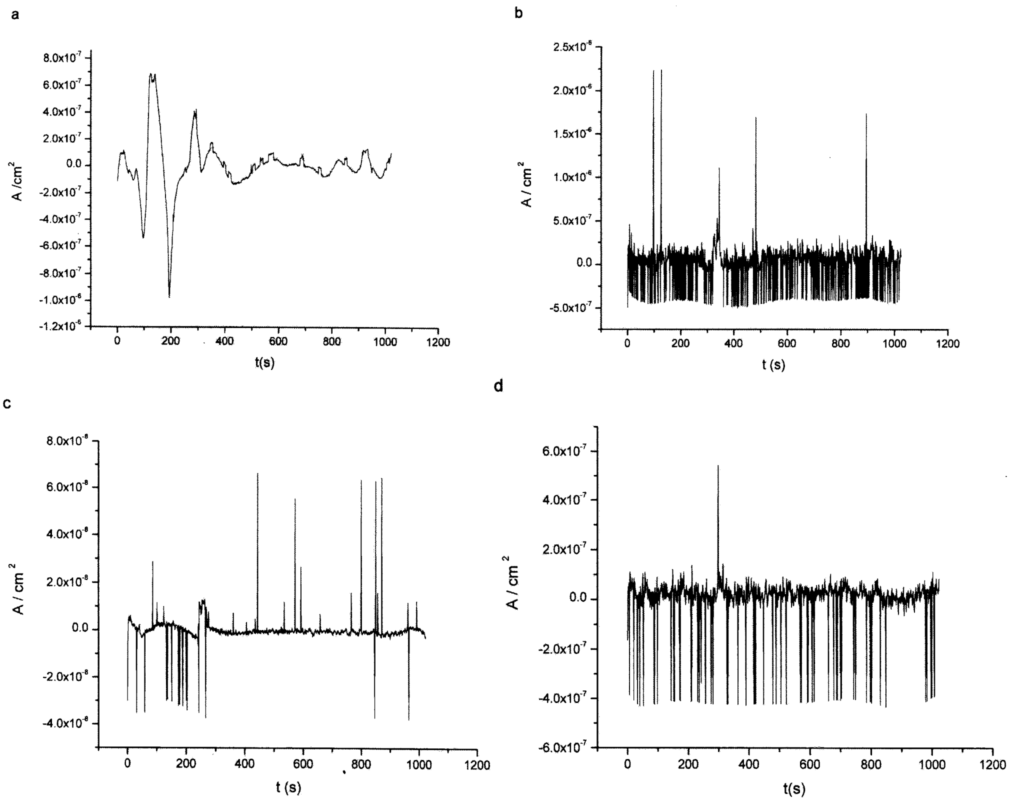

Figure 3. Time series a) Stainless Steel b),Thin Film at 25°C c) Thin Film at 100°C d), Thin Film at 200°C

Figure 2 shows the bare surface of stainless steel and nanostructured coatings at different temperatures. It shows very clearly that the deposition temperature definitely influences the morphology of this nanostructured film at 25 ° C where a surface is covered with hemispheres and the presence of some cracks. At temperature of 100°C, there is a radically different morphology showing a surface covered with a series of tetrahedral circumstances that significantly affected the degree of protection against corrosion of the deposited film. At 200°C, the same tetrahedral structure was present but more defined.

Table 2. Electrochemical and dynamical parameters.

	E_{corr} mV	I_{corr} A/cm^2	Rn Ohm.cm^2	IL	%R	%D	Hurst(H)	Df
Steel 304	-556	1.58x10^{-6}	2265	0.017	17.93	84.79	0.840	1.160
25°C	-363	8.82x10^{-7}	3371	0.358	19.91	0.035	0.230	1.770
100°C	-349	2.99x10^{-7}	13372	0.065	79.58	60.58	0.250	1.750
200°C	-380	5.79x10^{-7}	6453	0.217	51.63	17.69	0.091	1.909

This structural change is reflected very clearly in the electrochemical noise signal in the current, which shows a qualitative change in the type of oscillations that occur in the absence and presence of the nanostructured coating, as shown in Figure 3. Within the oscillatory dynamics of the electrochemical noise signal in current, is clearly observed that the intensity of the signal decreases significantly in the presence of the nanostructured coating since the fluctuations are smaller when investigating the coating at a deposition temperature of 100°C. A quantitative assessment of the decrease in corrosion rate due to the coating is clearly seen in Table 2. The highest Rn value reported was 13,372 ohms.cm^2 for the coating deposited at 100 ° C. The next value corresponds to the coating deposited at 200 °C with a value of 6453 ohm cm^2, following at 25 °C with a value of 3371 ohm.cm^2 and finally the steel without any coating with a value of 2265 ohm.cm^2. Circumstance entirely consistent with the values obtained from polarization curves, as shown in Table 2. Also the IL was significantly modified by the presence of the coating causing a very considerable increase in the rate of localization. The coating deposited at 100 °C showed a general attack on the surface, surpassed only by the bare material.

The fractal dimension of time series corresponds very well with the criteria established by Skerry [27] where a high antipersistence value of the Hurst coefficient between 0 to 0.25 correspond to a good coating, as shown in table 2.

Finally, to study the dynamics between microcells, which are formed during the electrochemical process from corrosion and their interactions, is achieved through recurrence graphs which, in turn, shows the system periodicity and duration of a stable interaction. Figure 4 shows the recurrence graphs for the bare material and various coatings. In this figure, highly significant changes can be observed in the structure of recursive graphs corresponding mainly to two types of structure of the bare material, which presents a lot of green and blue dots that correspond to higher relative distances, and low numbers of white and yellow dots corresponding to relatively small vector distances. This is a completely opposite situation for systems where there is a coating. Qualitatively speaking, this indicates that recurrence is significantly increased by the presence of the coating and completely clear. At a temperature of 100 °C, the coating showed a higher recurrence.

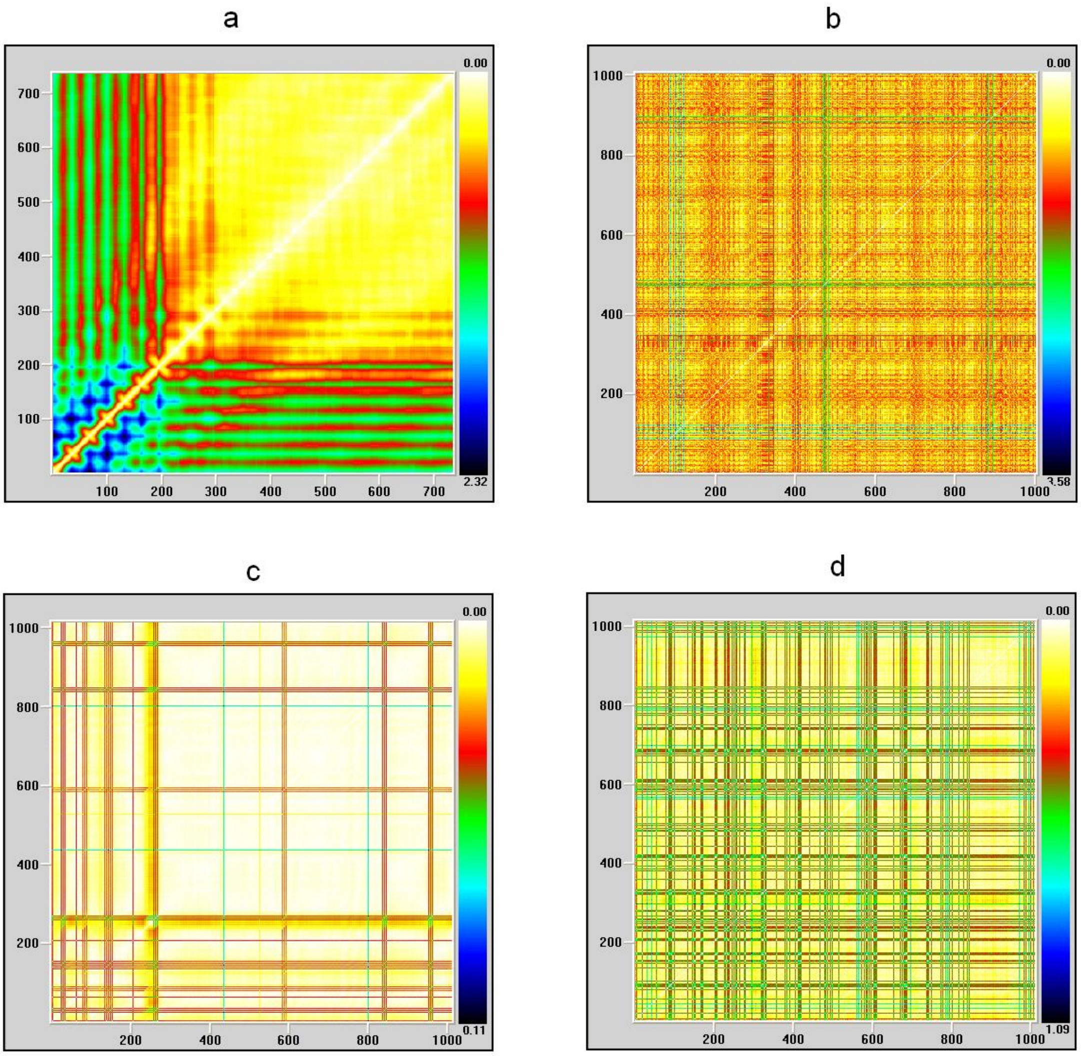

Figure 4. Recurrence Plot a) Stainless Steel b),Thin Film at 25°C c),Thin Film at 100°C d),Thin Film at 200°C.

At his point, the dynamics of microcells using recurrence graphs have been qualitatively determined. In Table 2, however, a quantitative RQA analysis proposed by Zbilut and Webber was also reported with % R and % D. From these results, it can be appreciated that the bare material has the lowest degree of % R with a value of 17.93% while the coating at 100°C reported the highest value of recurrence with % R 79.58, showing that the microstructure formed by the coating generates a microcell interaction with more periodicity. In the case of the % D, a stable interaction between microcells was clearly observed. At these conditions and despite having very little periodic behavior, the bare material manifested the greatest value of this parameter (84.79% D), as shown in Table 2, followed by the coating deposited at 100 °C (60.58% D). From the experimental results, it may be indicated that the more synchronized the electrochemical microcells the lesser probability of the attack on the surface. This synchronization could be related to the two parameters of recurrence mentioned above. In such a case, a more frequent process aids at improving the protection of the coating, having more stable interactions. This behavior is entirely consistent with the results observed from the polarization curves for the coating deposited at 100 °C. Hence a greater synchronization may take place since both% R and% D are higher, following the coating at 200 °C, continuing at 25 °C and ending with the bare material.

From the aforementioned, it may be stated that the formation and interaction of microcells on the nanostructured coatings are reflected in the dynamics of the corrosion process which, in turn, setup a direct relationship with the faradic transformation of the material under study and also with the nanostructure of the coating.

4. CONCLUSIONS

1.) The film with the best characteristics of corrosion protection in the medium studied was deposited at a temperature of 100°C.

2.) Deposition temperature is critical in the morphology of the nanostructure coating.

3.) Fractal analysis of the current noise signal was a good tool to determine if the thin film is a good for protection against corrosion.

4.) The recurrence plot is a tool to analyze the dynamics of the corrosion process in the coating and the interaction of the electrochemical microcells that are formed.

5.) The nanostructure defines the interaction of the microcells, the more synchronized the smaller the faradic effect and, consequently, the greater the degree of protection conferred.

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References

1. Wei Ye, Ying Li, Fuhui Wang. *Electrochim. Acta*, 51 (2006) 4426.
2. C.D. Arrieta-González, J. Porcayo-Calderon , V.M. Salinas-Bravo, J.G. Chacon-Nava , A. Martinez-Villafañe, J.G. Gonzalez-Rodriguez. *Int. J. Electrochem. Sci.*, 6 (2011) 3644.
3. M. G. Pujar, T. Anita, H. Shaikh, R. K. Dayal and H. S. Khatak. *Int. J. Electrochem. Sci*., 2 (2007**)** 301.
4. E. Sarmiento, J. G. González-Rodriguez, J. Uruchurtu, O.Sarmiento, M. Menchaca. *Int. J. Electrochem. Sci*., 4 **(**2009**)** 144.
5. X.Y. Wang, D.Y. Li. *Electrochim. Acta*, 47 (2002) 3939.

6. Konstantinas Leinartas, Meilute Samuleviciene, Audrius Bagdonas, Remigijus, Juskenas, Eimutis Juzeliunas. *Surf. Coat. Tech.* 168 (2003) 70.
7. Electrochemical Impedance and Noise. Robert Cottis, Stephen Turgoose . *NACE International* 1999.
8. E. García, M.A. Hernández, F.J. Rodríguez, J. Genescá, and F.J. Boerio. *Corros. 59* (2003)50.
9. Michael Pagitsas , Aggeliki Diamantopoulou, Dimitra Sazou Chaos, *Solitons and Fractals*, 17 (2003) 263.
10. Dimitra Sazou , Aggeliki Diamantopoulou, Michael Pagitsas. *J. Electroanal. Chem.*, 489 (2000) 1.
11. J.P. Eckmann,S.Oliffson Kamphost,D. Ruelle. *Euro Phys. Lett*. 4 (1987) 973.
12. J. P. Zbilut, C. L. Webber, *Phys Lett. A*, 171 (1992) 199.
13. G. McGuire, N.B. Azar, M. Shelhamer, *Phys. Lett. A.* 237 (1997) 43.
14. Webber, Jr. C.L., Zbilut, J.P., *J. Appl. Physiol*., 76 (1994) 965.
15. Trulla, L.L., Giuliani, A., Zbilut, J. P., Webber, Jr. C. L., *Phys. Lett. A*, 223 (1996) 255.
16. Claire Morana, Sofiane Ramdani, Stéphane Perrey, Alain Varray, *J. Neurosci. Meth.* 177 (2009) 73.
17. F. Censi, V. Barbaro, P. Bartolini, G. Calcagnini, A. Michelucci, G. F. Gensini, and S. Cerutti, *Ann. Biomed. Eng*. 28 (2000) 61.
18. Mauro Colafranceschi, Alfredo Colosimo, Joseph P. Zbilut, Vladimir N. Uversky, Alessandro Giuliani, *J. Chem. Inf. Model*. 45 (2005**)** 183.
19. Norbert Marwan, M. Carmen Romano, Marco Thiel, Jürgen Kurths, *Physics Reports*, 438 (2007) 237.
20. E. Cazares-Ibáñez , G.A. Vázquez-Coutiño , E. Garcia-Ochoa, *J. Electroanal. Chem*. 583 (2005) 17.
21. E.Garcia-Ochoa, J. Gonzalez-Sanchez , N. Acuña, J. Euan, *J Appl Electrochem*, 39 (2009) 637.
22. Yang, Tao Zhang , Yawei Shao, Guozhe Meng, Fuhui Wang, *Corros. Sci*. 52 (2010) 2697.
23. Á. Horváth , R. Schiller, Corros Sci 45 (2003) 597.
24. Nikita Zaveri, Rongtao Sun, Nephi Zufelt, Anhong Zhou, YangQuan Chen. *Electrochim Acta*, 52 (2007) 5795.
25. J. Wawszcak, *Research Materials Science-Poland*, 23 (2005) 585.
26. J. C. Gallant, I. D. Moore, M. F. Hutchinson, P. Gessler, *Mathematical Geology*, 26 (1944) 455.
27. M. Moon, B. Skerry, *J. Coat. Technol*. Vol 67 No 843 (1995) 35.
28. M.Hernández, J.Genescá, J. Uruchurtu, A. Barba, *Corros. Sci*. 51 (2009) 499.
29. Rama B Inturi, Z Szklarska-Smialowska. *Corros. Sci.*, 34 (1993) 1973.

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